

Light-matter interactions in lossy and lossless media.

Report submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy

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DECLARATION

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ABSTRACT

Light-matter interactions lie at the core of modern technologies. Different decay channels get activated depending on the structure of matter used and on the properties of the exciting light. In particular, nano-antennas are used as the quintessential object to redistribute the energy of single-photon emitters in the nano-scale or of free-electrons oscillations in metals. Two different kind of nano-antennas are studied: metallic (lossy) and dielectric (lossless). Metallic nano-antennas are shown to be applicable to technologies benefiting from enhancement of both radiative and non-radiative properties. In stark contrast, certain dielectric nano-antennas are essentially lossless in the visible regime, which benefits their coupling to far-field modes.

The metallic nano-antennas used in this work are either asymmetric nano-cavities or the ubiquitous bow-tie antenna. With the former we show enhancement of the radiative rate of single photon emitters located in the neighbourhood of the strongly modified electromagnetic environment. Here, two competing processes collude to either enhance or quench the coupling to the far-field. As will be shown via simulations, these two scenarios are strongly wavelength dependent and two very differentiated regions can be recognised where one overwhelms the other. Contrariwise, the bow-tie antennas are used to enhance the opposite effect: non-radiative channels exclusively. Here it is experimentally demonstrated that surface plasmon polaritons excited in the nano-structure can decay into hot carriers, instead of far-field radiation. A sub-diffraction mapping of the rate of hot electron generation is traced by depositing nano-particles and analysing many scanning electron micrographs.

In order to show that nano-photonics also has the potential to get rid of losses, we investigated the possibility of applying gallium phosphide nano-antennas as efficient far-field out-couplers. A comparison between metallic and dielectric nano-antennas is carried out using a unified theory and finally experimental results corroborate the large enhancement predicted by the theory of the fluorescence rate of single-photon emitters located around the scatterers

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- **Cambiasso, J.**, Grinblat, G., Li, Y., Rakovich, A., Cortés, E., Maier, S. A., "Bridging the gap between dielectric nanophotonics and the visible regime with effectively lossless gallium phosphide antennas", Nano Lett., **2017**, 17(2), 1219-1225
- Cortés, E., Xie, W., **Cambiasso, J.**, Jermyn, A. S., Sundararaman, R., Narang, P., Schlücker, S., Maier, S. A., "Plasmonic hot electron transport drives nano-localized chemistry", Nature Comm., **2017**, 8, 14880.

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1

INTRODUCTION TO LIGHT-MATTER INTERACTIONS

This thesis is about the physics of interactions between light and matter, or, in order to tickle the ears of quantum field theorists, the interaction between bosons and fermions [1]. The fuel for this work, was the exciting developments in nanotechnology and computation capabilities of the last decades. Counting with top-notch fabrication facilities allows to fabricate state-of-the-art nano-objects, that can be tailored to different applications like on-demand single photon emitters [2] and realisation of quantum gates [3]. This thesis was aimed at the development of technologies that could facilitate the communication between the far-field realm and near-field phenomena. As will be seen in the following chapters, this not only includes interrogating nano-scale objects with a far-field source efficiently and equivalently measuring their response in the far-field, but also using the far-field to drive nano-scale reactions in confined spaces. Notwithstanding, all of these phenomena require the understanding of the physics of the interaction of light with matter, and that is what this chapter is devoted to.

1.1 EMITTERS IN ELECTROMAGNETIC ENVIRONMENTS

The story of light absorption and emission by atoms was initially studied by Dirac exactly 90 years ago [4]. There, it was shown that certain transitions could take place radiatively, while others could occur without the need of photons being generated at all. Later on, Purcell showed that both mechanisms were not an intrinsic property of the atom but could be tuned by modifying the electromagnetic environment [5]. Most strikingly, these modifications had an impact in the demeanour of the emitter, even without exciting electromagnetic fields. This process is called spontaneous emission, and lies at the heart of quantum electrodynamics [1, 6].

Real emitters are very complicated quantum objects. We could think of the hydrogen atom as the simplest of them all, but even this one has a very intricate energy level structure that presents difficulties in calcu-

lations [7]. Even more complicated systems involving large numbers of atoms include molecules and quantum dots. However, when observing the absorption spectra of all these species, one finds that a reasonable approximation lies in assuming a two-level system [6, 8–11]. In the following, I shall adopt the so-called dipole approximation (or minimal coupling [1]) between the electromagnetic field and an arbitrary charge/current¹ distribution $\rho(\mathbf{r}, t)$. This distribution can be understood either classically or quantum mechanically. In the first case, it is simply a continuous field, that integrated over a certain region of spaces is equal to the charge or current contained in that region. Quantum mechanically it is just the probability density/current given by the wave functions multiplied by the total charge/current.

Figure 1.1 shows other examples of modern single-photon emitters. Colloidal and Stranski-Krastanov quantum dots in figure 1.1(a) and (b) are further studied in chapter 3. Their optical properties arise from the confinement of electrons in a potential well. They are efficient transducers of electromagnetic energy into far-field radiation and lack blinking [13]. Colour centres in diamond, schematised in figure 1.1(c), also lack blinking but have a broad vibrational structure that pollutes the emission properties [14]. Finally, figure 1.1(d) shows two notable examples of fluorescent molecules, including anthracene [15] and terrylene [16].

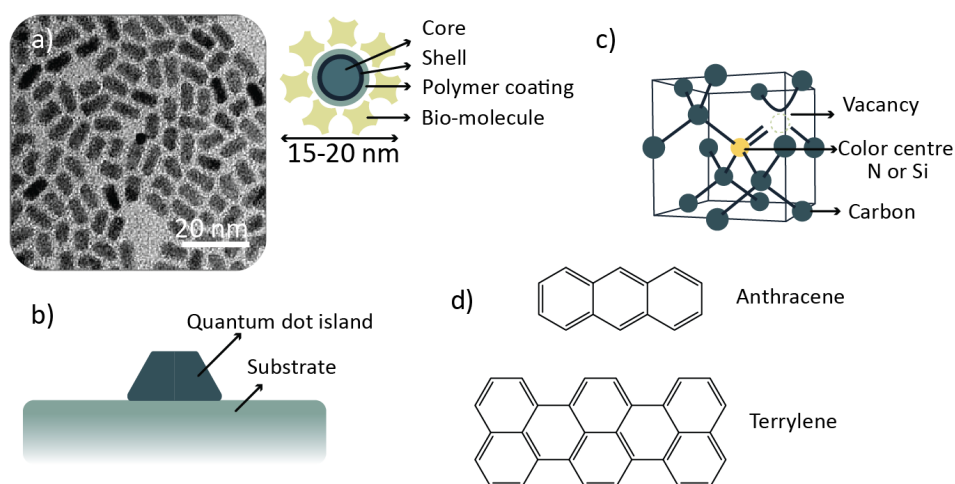


Figure 1.1 Single photon emitters. (a) Colloidal nano-crystal quantum dots. (b) Stranski-Krastanov grown quantum dot. Colour centres in diamond. (d) Fluorescent dyes.

The minimal coupling approximation consists in assuming that the charge/current density distribution is strongly localised, with respect to

¹I refer to charge/current rather than just charge or current because both of them are intrinsically connected via conservation of charge [12].

the space variations of the electromagnetic field. It must be noted that in certain asymmetric quantum dots this condition is not satisfied, because the wave functions of their excitations are spread out over several nanometers [17–19].

Let us start, however, by examining the coupling of a classical charge/-current distribution with the electromagnetic field.

1.1.1 Classical picture

Poynting's theorem [12, 13] quantifies the amount of power radiated by any charge/current distribution as:

$$\frac{dU}{dt} = -\frac{1}{2} \int_{\mathbb{R}^3} \text{Re} [\mathbf{j}^*(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t)] d^3\mathbf{r}, \quad (1-1)$$

where dU/dt is the energy modification due to the presence of the current/charge density, $\mathbf{j}(\mathbf{r}, t)$ is the spatially-localised current density and $\mathbf{E}(\mathbf{r}, t)$ is the total electric field.

Expanding the current density to lowest order [20]:

$$\frac{dU}{dt} = -\frac{1}{2} \text{Re} [\dot{\mathbf{p}}^*(t) \cdot \mathbf{E}(\mathbf{r}_0, t)], \quad (1-2)$$

where $\mathbf{p}$ is the dipole moment and $\mathbf{r}_0$ the position of the dipole. For harmonic oscillations of both electric field and dipolar moment we obtain the textbook relationship [13]:

$$\frac{dU}{dt} = \frac{\omega}{2} \text{Im} [\mathbf{p}^* \cdot \mathbf{E}(\mathbf{r}_0)]. \quad (1-3)$$

This is exactly the minimal coupling Hamiltonian, also known as the dipole approximation Hamiltonian. The electric field is just the electric field produced by the dipole $\mathbf{p}$ located at position $\mathbf{r}_0$ and can be found by solving Maxwell's equations.

To obtain the final expression of the dissipated power, we must replace the electric field $\mathbf{E}(\mathbf{r}_0)$ with the solution given by Maxwell's equations. In general, the field $\mathbf{E}(\mathbf{r}, t)$ from equation 1-1 refers to the *total* electric field given by an exciting source $\mathbf{E}_0(\mathbf{r}, t)$ and the scattered field $\mathbf{E}_{\text{scat}}(\mathbf{r}, t)$ [21]. Assuming there is no exciting field, the scattered field can be replaced with its expression in terms of the Green dyad $\mathbb{G}(\mathbf{r}, \mathbf{r}'; \omega)$ of a dipole located at $\mathbf{r}'$ in the specific geometry considered:

$$\frac{dU}{dt} = \frac{\omega^3 \|\mathbf{p}\|^2}{2c^2 \epsilon_0} \hat{\mathbf{n}}^T \cdot \text{Im} \mathbb{G}(\mathbf{r}_0, \mathbf{r}_0; \omega) \cdot \hat{\mathbf{n}}, \quad (1-4)$$

where we have extracted the dipolar moment amplitude from the brackets. It must be emphasised that $\hat{\mathbf{n}}$ is *not* an operator in the quantum mechanical sense, it is a vector of unit norm (*i.e.* a versor). Moreover, $\hat{\mathbf{n}}^T$ is the transpose of the column versor. This expression is of utmost importance, as the mere knowledge of the Green function suffices to calculate the dissipated power by the emitter.

We can readily obtain an expression for the energy dissipation of a dipole in vacuum by replacing the corresponding Green function and choosing an arbitrary orientation for the dipole moment. Choosing $\hat{\mathbf{n}} = \hat{\mathbf{z}}$ we obtain that:

$$\frac{dU_0}{dt} = \frac{\|\mathbf{p}\|^2}{12\pi} \frac{\omega}{\epsilon_0} k^3, \quad (1-5)$$

where $k = \omega/c = 2\pi/\lambda$. It is worth noting that the emitter has to be located in an index with unit relative permittivity, but this expression is easily generalisable to a medium of arbitrary positive permittivity.

This expression helps normalise the power dissipated by the dipole for other more complicated geometries. Calculating the ratio between equation 1-4 and 1-5 we obtain:

$$\frac{dU/dt}{dU_0/d} = \frac{6\pi}{k} \hat{\mathbf{n}}^T \cdot \text{Im}\mathbf{G}(\mathbf{r}_0, \mathbf{r}_0; \omega) \cdot \hat{\mathbf{n}} \quad (1-6)$$

This expression is going to prove useful to predict quantum properties of the two-level system in the next subsection.

1.1.2 Quantum picture in the weak-coupling regime

The quantum dynamics of an emitter-field system are ruled by the joint Hamiltonian of a two-level emitter and the second quantised electromagnetic field. Solving the full problem consists also in introducing the interaction term in the Hamiltonian. Depending on the limiting values of the strength of the coupling we can distinguish between two different behaviours [13, 22, 23]. Strong-coupling [6, 22] can be pictorially understood as having an interaction between the objects that is stronger than the interaction to losses in the environment.

However, throughout this thesis I concerned myself with the study of the weak-coupling, where the interaction can be treated as a perturbation in the decoupled Hamiltonian. Not only is this simplification beneficial enough to use first order time dependent perturbation theory, but it also lets itself to be interpreted classically. A parallel between quantum and classical magnitudes can also be obtained. It will be shown that equation

1–6 is equal to the ratio of decay rates, obtained via Fermi-golden rule. This has the paramount advantage that no quantum mechanical calculations have to be performed to predict the behaviour of nature. Solving Maxwell equations using numerical routines suffices to understand the quantum mechanics of the problem. Experimentally, it allows to relate a directly measurable quantity with the inner quantum mechanical structure of an emitter.

We start by recalling Fermi's golden rule for the decay rate γ from an initial excited state $|i\rangle$ to a set of final states $\{|f\rangle\}$:

$$\gamma = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f | \hat{\mathcal{H}}_{\text{int}} | i \rangle \right|^2 \delta(\omega_i - \omega_f), \quad (1-7)$$

where $\hat{\mathcal{H}}_{\text{int}}$ is the interaction Hamiltonian given by the minimum coupling approximation ²:

$$\hat{\mathcal{H}}_{\text{int}} = -\hat{\mathbf{p}} \cdot \hat{\mathbf{E}}(\mathbf{r}_0), \quad (1-8)$$

with both dipole and electric field operators. Note that $\mathbf{r}_0$ is not an operator but, mathematically, just a parameter of the electric field operator specifically evaluated at the emitter's position. Saying that the position of the emitter is fixed implies that we are dealing with an approximation where the wavefunction of the electrons involved in creating the dipole moment are centred at $\mathbf{r}_0$ with a very small dispersion. Small is, of course, measured relative to the spatial variations of the electric field. In other words, this approximation would fail for very short wavelengths. This is just synonymous to say that this formula works for low photon energies. Furthermore, the amplitude squared of the field also needs to be small, so that the interaction term can indeed be considered a perturbation to the de-coupled Hamiltonian.

Figure 1.2 shows a schematic picture of the decay from an excited species with no photons, labelled with the state $|e\rangle \otimes |0\rangle \stackrel{\text{def}}{=} |e, 0\rangle$, to a set of final states $|g\rangle \otimes |n_l = 1\rangle \stackrel{\text{def}}{=} |g, n_l = 1\rangle$. Here $\otimes$ represents the tensor product between an emitter ket state and a photon ket state. The vacuum photon state $|0\rangle$ gets excited via the emission of a photon into a mode labelled with the letter l . This mode can be free-space modes, $l = \mathbf{k}, \omega$ or resonant eigenmodes of the specific geometry in which the emitter is enclosed. Just as an example, figure 1.2 shows decay into free-space modes

²An equal interaction is given by the $\hat{\mathbf{p}} \cdot \hat{\mathbf{A}}(\mathbf{r}_0)$ interaction, which takes into account the momentum $\hat{\mathbf{p}}$, not the dipole moment, and the electromagnetic potential $\hat{\mathbf{A}}(\mathbf{r}_0)$ at the position of the emitter. Note that conservation of energy is obtained from the delta function $\delta(\omega_i - \omega_f)$. This formulation is equivalent to the one used in the main text when dealing with long wavelengths [6, 24, 25]

for simplicity, but there is no theoretical nor experimental reason why a photon should be considered as a free-propagating wave [6].

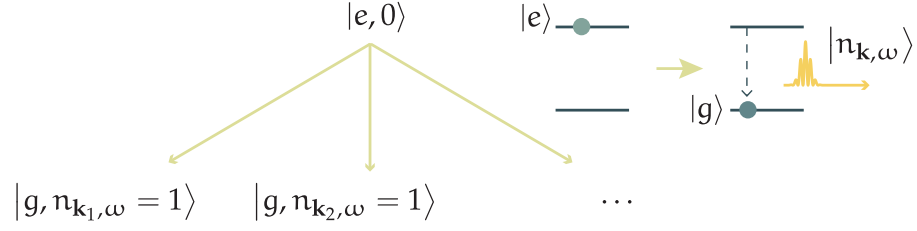


Figure 1.2 Transitions from initial states of an excited emitter with no photons in the background $|e, 0\rangle$ to a set of final states $|g, n_{\mathbf{k}, \omega_0} = 1\rangle$, where $n_{\mathbf{k}, \omega_0}$ is the number of photons with energy $\hbar\omega_0$ and momentum $\mathbf{k}$. In this example, just for simplicity, the coupling is assumed to freely propagating photons, however, other decay modes can exist, such as resonating eigenmodes in nanostructures.

Second quantised electric field

In order to calculate the matrix elements from Fermi's golden rule equation 1-7 we need to express the electric field in its second quantised form and the electric dipole in operator form. No derivation is given here for the expression of the electric field as it can be found in many textbooks [1, 6-11, 13, 26, 27]. The electric field can be expanded in a set of properly normalised eigenmodes and creation/annihilation operators $\hat{a}_l^\dagger/\hat{a}_l$ for each mode l :

$$\hat{\mathbf{E}}(\mathbf{r}) = \sum_l \sqrt{\frac{\hbar\omega_l}{2\epsilon_0}} \mathbf{u}_l(\mathbf{r}) \hat{a}_l + \text{h.c.}, \quad (1-9)$$

where $\mathbf{u}_l(\mathbf{r})$ are the eigenmodes of the whole system solved via Maxwell equations and h.c. simply means hermitian conjugate.

Dipole operator

The dipole operator can be inspired by classical electromagnetism, where it is defined as the mean value of the position operator given a charge density:

$$\mathbf{p}(t) = \int_V \mathbf{r} \rho(\mathbf{r}, t) d^3\mathbf{r}. \quad (1-10)$$

Now, starting with this equation, we can write the charge density in quantum mechanics as follows:

$$\rho(\mathbf{r}, t) = q|\psi(\mathbf{r}, t)|^2, \quad (1-11)$$

where q is the charge of an electron in the emitter and $\psi(\mathbf{r}, t)$ its complex wavefunction, found using the non-interacting Hamiltonian for the emitter. Rewriting the dipole moment we obtain:

$$\mathbf{p}(t) = \int_V \psi^*(\mathbf{r}, t) q\mathbf{r} \psi(\mathbf{r}, t) d^3\mathbf{r} = \langle \psi | q\hat{\mathbf{r}} | \psi \rangle. \quad (1-12)$$

From here we can define the intuition of a dipole moment operator as $\hat{\mathbf{p}} = q\hat{\mathbf{r}}$ and its associated observable $\mathbf{p}(t)$. Notice that in this case all the time dependence is hidden in the wave-functions so this is then the operator written out in a Schrödinger picture.

We can decompose this dipole operator in a set of orthonormal eigenstates of the emitter de-coupled from the electromagnetic environment. In this case we can write quite generally for an N level atom:

$$\hat{\mathbf{p}}(t) = q \sum_{i,j=1}^N \mathbf{r}_{ij} |i\rangle \langle j|, \quad (1-13)$$

where $\mathbf{r}_{ij} = \langle i | \hat{\mathbf{r}} | j \rangle$ is the matrix element of the position operator. For the case of a 2 level emitter this sum contains only 4 terms, however the diagonal terms of the matrix elements are usually assumed to be zero. This can, again, be proved in general if we assume that the states $|i\rangle$ have a specific parity such that they are eigenvalues of the parity operator (as it happens with the hydrogen atom):

$$\hat{P} |i\rangle = (-1)^p |i\rangle, \quad (1-14)$$

with $\hat{P}$ the parity operator and $p = 0, 1$ depending on the parity of the state. Now, from the definition of parity, we obtain that $\hat{P}\hat{\mathbf{r}}\hat{P}^\dagger = -\mathbf{r}$ so that:

$$\begin{aligned} \mathbf{r}_{ii} &= \langle i | \hat{\mathbf{r}} | i \rangle = \langle i | \hat{P}^\dagger \hat{P} \hat{\mathbf{r}} \hat{P}^\dagger \hat{P} | i \rangle \\ &= -\mathbf{r}_{ii} \quad \Rightarrow \quad \mathbf{r}_{ii} = \mathbf{0}, \end{aligned} \quad (1-15)$$

if and only if the states $|i\rangle$ of the emitter have a specified parity.

This means that for our 2-level emitter we can write (using the notation g for the ground and e for the excited state):

$$\hat{\mathbf{p}}(t) = \mathbf{p}_{eg}(t) |e\rangle \langle g| + \underbrace{\mathbf{p}_{ge}(t)}_{=\mathbf{p}_{eg}^*(t)} |g\rangle \langle e|. \quad (1-16)$$

We can further assume that $\mathbf{p}_{eg} \in \mathbb{R}$ and write the operators in terms of the convenient Pauli matrices $\hat{\sigma}_+$ and $\hat{\sigma}_-$ to describe fermionic excitation and de-excitation:

$$\hat{\mathbf{p}}(t) = \mathbf{p}(t) (\hat{\sigma}_+ + \hat{\sigma}_-). \quad (1-17)$$

Finally, note that the energy difference between the ground and excited states is defined as $\hbar\omega_0$.

Interaction

With all this artillery we can finally write down the total decay rate as:

$$\begin{aligned} \gamma &= \frac{2\pi}{\hbar^2} \sum_l \langle g, n_l = 1 | \hat{\mathcal{H}}_{\text{int}} | e, 0 \rangle|^2 \delta(\omega_0 - \omega_l) \\ &= \frac{\pi}{\epsilon_0 \hbar} \sum_l \omega_l |\mathbf{p} \cdot \mathbf{u}_l^*(\mathbf{r}_0)|^2 \delta(\omega_0 - \omega_l) \end{aligned} \quad (1-18)$$

The delta function just sums the contributions from all those modes that have the correct energies to produce the excitation. It is interesting to note that we can write the modulus square as the matrix product between vectors expressed as column matrices:

$$|\mathbf{p} \cdot \mathbf{u}_l^*(\mathbf{r}_0)|^2 = \mathbf{p}^T \cdot \mathbf{u}_l^*(\mathbf{r}_0) \mathbf{u}_l^T(\mathbf{r}_0) \cdot \mathbf{p}, \quad (1-19)$$

where $\mathbf{u}_l^*(\mathbf{r}_0) \mathbf{u}_l^T(\mathbf{r}_0)$ is a 3×3 matrix. Now, it can be shown [13, 28–30] that the Green dyad of a system can be decomposed in terms of its orthonormal eigenmodes as:

$$\mathbb{G}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_l c^2 \frac{\mathbf{u}_l^*(\mathbf{r}') \mathbf{u}_l(\mathbf{r})^T}{\omega_l^2 - \omega^2}. \quad (1-20)$$

We would like to somehow input the information of the geometry of the system via the Green function in the expression for the decay rate. For that purpose, Appendix A provides a proof of the following identity:

$$\text{Im} \left[\frac{1}{\omega_l^2 - \omega^2} \right] = \frac{\pi}{2\omega_l} [\delta(\omega - \omega_l) - \delta(\omega + \omega_l)] \quad (1-21)$$

With this result, we can rewrite the imaginary part of the Green dyad as:

$$\text{Im} [\mathbf{G}(\mathbf{r}, \mathbf{r}'; \omega)] = \frac{\pi c^2}{2\omega} \sum_l \mathbf{u}_l^*(\mathbf{r}') \mathbf{u}_l^T(\mathbf{r}) \delta(\omega_0 - \omega_l), \quad (1-22)$$

where we dropped the $\delta(\omega_0 + \omega_l)$ because we will only evaluate the Green dyad in the positive part of the spectrum, so this delta is always equivalent to zero. Furthermore, we have evaluated all the ω_l to ω because of the delta constraint.

Finally, the expression for the decay rate can be summarised as:

$$\begin{aligned} \gamma &= \frac{2\omega^2/c^2}{\epsilon_0 \hbar} \mathbf{p}^T \cdot \text{Im} [\mathbf{G}(\mathbf{r}_0, \mathbf{r}_0; \omega_0)] \cdot \mathbf{p} \\ &= \frac{2\omega^2 \|\mathbf{p}\|^2}{c^2 \epsilon_0 \hbar} \hat{\mathbf{n}}^T \cdot \text{Im} \mathbf{G}(\mathbf{r}_0, \mathbf{r}_0; \omega_0) \cdot \hat{\mathbf{n}}, \end{aligned} \quad (1-23)$$

where, as before, $\hat{\mathbf{n}}$ just represents the orientation of the dipole moment operator observable. This expression is very similar to equation 1-4. By normalising it with the decay rate in vacuum:

$$\gamma_0 = \frac{\omega_0^3 \|\mathbf{p}\|^2}{3\pi \epsilon_0 \hbar c^3}, \quad (1-24)$$

and comparing with equation 1-6 we can obtain the final result of this section:

$$\frac{\gamma}{\gamma_0} = \frac{dU/dt}{dU_0/dt'} \quad (1-25)$$

which simply states that a classical description suffices to understand the quantum behaviour. Figure 1.3 shows a protocol to find the change in decay rate of an emitter in a specific nano-structure environment by calculating classical quantities. Once a specific nano-structure is chosen, the only parameters left to study the frequency behaviour of the emitter are the position $\mathbf{r}_0$ and its dipole orientation. Once they are fixed, we just need to calculate the power coming out of a box containing both structure and emitter and normalise it to the power emitted by the same structure in vacuum.

Local density of optical states

The quantity:

$$\hat{\mathbf{n}}^T \cdot \text{Im} \mathbf{G}(\mathbf{r}_0, \mathbf{r}_0; \omega_0) \cdot \hat{\mathbf{n}} \quad (1-26)$$

from equation 1-23 can be interpreted as a local density of optical states (LDOS). It is local because it is evaluated at the position of the emitter $\mathbf{r}_0$

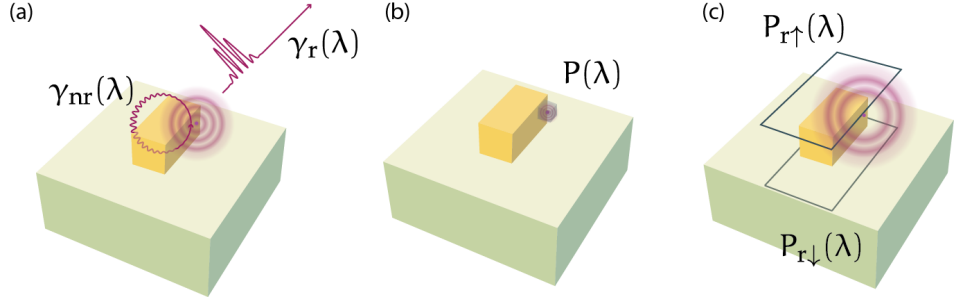


Figure 1.3 Protocol for finding the decay rate from simulations. (a) We are interested in calculating the radiative, non-radiative and the total decay rates. (b) First we evaluate the energy coming out of a monitor surrounding the emitter, this is proportional to the total decay rate. (c) Finally we calculate the power radiated upwards $P_{r\uparrow}(\lambda)$ and/or downwards $P_{r\downarrow}(\lambda)$. We can use the free-space decay rate to normalise and obtain $\gamma/\gamma_0 = P/P_0$ from equation 1–25 and similarly for the radiative rate. For the non-radiative rate we just evaluate $\gamma/\gamma_0 - \gamma_r/\gamma_0$, which technically defines non-radiative as processes we do not want to happen.

and it depends on its dipole orientation. It is a density of states because it contains the delta function $\delta(\omega - \omega_l)$ which can define the density of states with energies between ω_1 and ω_2 as [29]:

$$\int_{\omega_1}^{\omega_2} \text{DOS}(\omega) d\omega = N_{\omega_2, \omega_1}, \quad \text{DOS}(\omega) = \sum_l \delta(\omega - \omega_l) \quad (1-27)$$

where $\text{DOS}(\omega)$ is the density of states and N_{ω_2, ω_1} is the number of states with energies in the interval $[\omega_1, \omega_2]$.

The relationship between the LDOS and the DOS is:

$$\int_0^\pi \int_0^{2\pi} \int_{\mathbb{R}^3} \text{LDOS}[\mathbf{r}, \hat{\mathbf{n}}(\theta, \phi); \omega] \sin \theta d\theta d\phi d^3\mathbf{r} = \text{DOS}(\omega), \quad (1-28)$$

where the local integration is done over all solid angles for the orientation of the dipole emitter and over all position vectors in space. This relabelling only gives us a re-interpretation of the decay rate. It can be said that the decay rate is proportional to the local density of optical states, which is a measure of the number of states that a dipole located at $\mathbf{r}_0$ with orientation $\hat{\mathbf{n}}$ and with transition energy $\hbar\omega_0$ can couple to. So, it filters out all the possible electromagnetic states that do not have the necessary strength at $\mathbf{r}_0$, or the appropriate polarisation to couple to $\hat{\mathbf{n}}$ or the necessary energy $\hbar\omega$ to conserve. The equivalence between the decay rates, a property that was initially presumed to be an intrinsic property

of the emitter, and the local density of electromagnetic modes is what is called the Purcell effect [5].

Notably, out of all these states we can recognise radiative and non-radiative modes of the system. To see this, note that the Green dyad can be decomposed into radiative and non-radiative parts by a simple inspection of the eigenmodes of the system, therefore allowing the definition of radiative and non-radiative decay channels. In particular, we are interested in radiative modes in chapter 3 and 6. However, 4 deals with non-radiative channels, in particular, to those related to the generation of hot electrons ³.

Conclusions

All the previous derivations were based in the decomposition of the Green dyad in eigenmodes. It is not at all clear that a dissipative system such as that of plasmonics exhibits a spectral decomposition as that proposed in equation 1–9. A complete base might not exist. However several methods exist [31] to expand the field in eigenmodes, even in an approximated matter. Furthermore, it must be noted that it has also been shown that the final result, the one just involving the Green function, is still valid to calculate the rate of decay [32].

Finally, all these results were developed with view in spectroscopy, which used to be the buzz word from early to mid 20th century. Nowadays, as we approach the second quantum revolution, we find that other kind of emitters or systems can be treated equally well with this formalism. This, in turn, inspired a plethora of applications ranging from biology to fundamental physics. To mention a few, the advent of quantum computation and communications would require fully studied platforms that can be integrated in photonic chips. These platforms include single-photon emitters in cavities or nano-antennas that tailor light matter interaction in the nano-scale [3, 33]. Enhancing light-matter interactions can also find applications in biology and chemistry, for example, for Raman enhanced scattering [34, 35], super-resolution microscopy [36, 37] or enhanced photocurrent generation [38], among others.

³In that chapter we can model surface plasmon polaritons, as discussed in chapter 2, as decaying non-radiatively into hot electrons. In this case a surface plasmon polariton can be thought of as a two level system where the ground state is the non existence of an oscillation and the excited state is one quanta of oscillation. However, a less eyebrow raising theory shall be developed in that respective chapter.

1.2 OUTLINE OF THE THESIS

This introductory chapter was aimed at discussing the physics of electromagnetic interactions with matter, specifically with dipole emitters. As is seen later in the thesis, these interactions do not only need to be radiative in character, as other nano-scale phenomena can be interesting for specific technological applications. Nano-antennas appear ubiquitously in this thesis in both flavours: metallic and dielectric. The first part of this thesis is dedicated to the understanding of collective oscillations of charge in metals and how they can be used to modify the interactions of light with matter.

Chapter 2 introduces the main concepts of surface plasmon polaritons both in unbounded and bounded media. There, a description of the interaction between electrons and light is sketched, which gives rise to the phenomena described in the two subsequent chapters.

Chapter 3 builds on this and describes the behaviour of a very specific kind of single photon emitter (the colloidal quantum dot) and also the concept of a nano-antenna. The latter, is the interacting object *par-excellance* in nano-photonics applications. In this chapter, however, I concentrate on the radiative properties of matter. In particular a non-concentric ring-disk cavity made out of gold is used to test light-matter interactions with colloidal quantum dots.

Chapter 4 generalises the understanding of nano-antennas. Indeed, it is explained here how non-radiative couplings can be obtained in the nano-scale to drive chemical reactions. Furthermore, this reactivity intensity could be mapped experimentally; a missing gem in the development of reactive plasmonics. More precisely, a chemical reaction is driven from the generation of hot-electrons generated from a surface plasmon polariton decay.

Part one, therefore, serves as a display of technologies that can be exploited with metallic nano-antennas. Here two opposing views of one very same phenomenon (the interaction of light with matter) is presented.

Following the motivation of metallic nanostructures, part two specialises in dielectric materials, as promising candidates to remove losses and only retain the lossless nature of the nano-antennas for radiative applications.

To this end, chapter 5 introduces the theoretical background of multipole expansion of the electromagnetic field, giving a physical meaning into the several orders that can appear in dielectric structure.

Chapter 6 is the result of several efforts to fabricate essentially lossless nano-antennas that operate in the visible regime. Here it is shown how a simple gallium phosphide dimer antenna of gallium phosphide can be used to enhance the fluorescence rate of molecules located nearby. This phenomenon, yet again, is just a consequence of the modified local density of optical states described previously.

The final chapter is a brief conclusion of the thesis, where a perspective on future work is outlined to help understand the footpath on where we stand.

Part I

METALS ON THE NANOSCALE

2 | SURFACE PLASMON POLARITONS

Many different expressions appear in this context, among them: plasmon, surface plasmon-polariton, localised surface plasmon-polariton, propagating surface plasmon, and in many cases arbitrary combinations of the aforementioned. — Le Ru and Etchegoin in Ref. [39]

This chapter sets up the basic theory to understand the concept of plasmons and surface plasmon polaritons [13, 39, 40]. I have separated the approaches to the field in two complementing viewpoints, as illustrated in figure 2.1.

The first one, the macroscopic approach of section 2.1, assumes the existence of an electric permittivity and a magnetic permeability function describe all the optical properties of the material dependent on the relevant parameters. The second one, gives a microscopic model for this permittivity. Furthermore, there is a clear operational distinction: the macroscopic viewpoint allows us to calculate the properties of the light. It suffices to solve the macroscopic Maxwell equations¹. These equations are the same ones solved by numerical packages (e.g. COMSOL Multiphysics and Lumerical FDTD) using measured data for the permittivity or some reasonable functional dependence based on physical principles. Conversely, the microscopic approach does not usually act as a tool for calculating the behaviour of the electromagnetic field as a response to the interaction with matter, but rather the response of a medium as it interacts with an electromagnetic field.

In summary a microscopic understanding of the materials facilitates the identification of the measured electromagnetic field's behaviour with solid-state phenomena occurring in the nanoscale.

Section 2.1 describes the macroscopic formalism necessary to understand the phenomena observed in plasmonics. It is furthermore separated into two subsections with two quintessential examples: two homogeneous half-spaces one of which is a metal (section 2.1.1) and a small metallic sphere in a homogeneous dielectric medium (section 2.1.2).

¹The proper definition of a *macroscopic* Maxwell equation is in itself a laborious theoretical endeavour. I will use the easier phenomenological approach applied by Jackson [12]. However, Chō [41] shows a more intricate reconstruction from first principles that is completely beyond the relevance of this thesis.

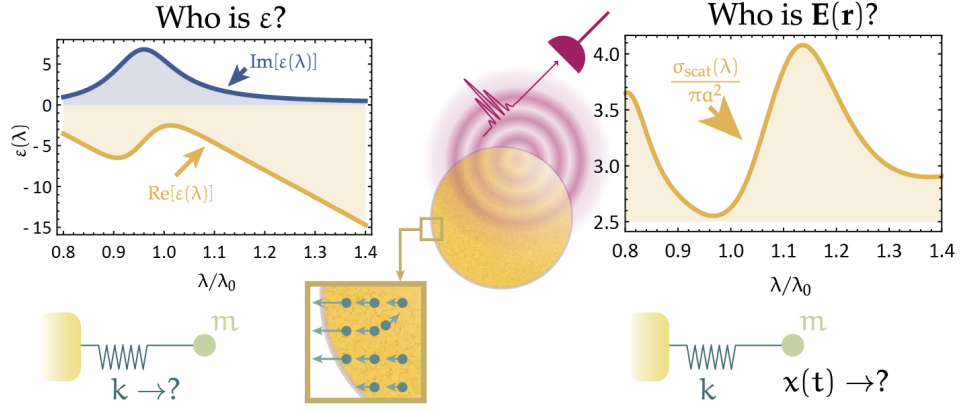


Figure 2.1 The macroscopic theory requires the electrical permittivity and magnetic permeability of a material to describe the interaction of matter with light. This information can be provided either via indirect experimental measurements (e.g. ellipsometry) or via a careful model of the microscopic phenomena. The two points of view are akin to either modelling the spring constant from a microscopic theory of matter (left), or either modelling the macroscopic dynamics of the system (right).

Section 2.2 describes a semi-classical approach to the definition of an electrical permittivity. Here it will be shown how the constraints obtained in section 2.1, necessary to obtain resonances, are related to the microscopic concept of plasmons.

Finally, section 2.3 gives a brief discussion of cross-sections. These are the measurable quantities *par excellence* and provide information about the modes excited in plasmonic nanostructures.

2.1 MACROSCOPIC THEORY

Below, I will first find the modes that appear at a metal-dielectric interface by solving the macroscopic Maxwell equations in SI units [12, 13]:

$$\nabla \cdot \mathbf{D}(\mathbf{t}, \mathbf{r}) = \rho(\mathbf{t}, \mathbf{r}), \quad (2-1a)$$

$$\nabla \times \mathbf{E}(\mathbf{t}, \mathbf{r}) = -\frac{\partial \mathbf{B}(\mathbf{t}, \mathbf{r})}{\partial t}, \quad (2-1b)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (2-1c)$$

$$\nabla \times \mathbf{H}(\mathbf{t}, \mathbf{r}) = \mathbf{j}(\mathbf{t}, \mathbf{r}) + \frac{\partial \mathbf{D}(\mathbf{t}, \mathbf{r})}{\partial t}. \quad (2-1d)$$

Here, $\mathbf{r} = (x, y, z) \in \mathbb{R}^3$ is the observation point and $t \in \mathbb{R}$ the observation time. $\mathbf{E}$ and $\mathbf{H}$ the electric and magnetic fields, respectively. $\mathbf{D}$ the electric displacement and $\mathbf{B}$ the magnetic induction field. Finally, $\mathbf{j}$ and ρ are the free current and free charge densities. Some previous knowledge has to be had with regards to the dependence of the displacement and induction fields with respect to the electric and magnetic fields. It is customary to assume a linear, isotropic, spacially-local and dispersive relationship between them parametrised by the position/frequency-dependent electric permittivity and magnetic permeability, which in the frequency space reads as:

$$\mathbf{D}(\omega, \mathbf{r}) = \varepsilon_0 \varepsilon(\omega, \mathbf{r}) \mathbf{E}(\omega, \mathbf{r}), \quad (2-2a)$$

$$\mathbf{B}(\omega, \mathbf{r}) = \mu_0 \mu(\omega, \mathbf{r}) \mathbf{H}(\omega, \mathbf{r}), \quad (2-2b)$$

where ε_0 and μ_0 are the electric permittivity and magnetic permeability of free space. Conversely, $\varepsilon(\omega, \mathbf{r})$ and $\mu(\omega, \mathbf{r})$ are the linear isotropic spatially-local dispersive electric permittivity and magnetic permeability².

In what follows we will assume that $\mu(\omega, \mathbf{r}) = 1$ (no magnetic response) and furthermore that $\varepsilon(\omega, \mathbf{r}) = \varepsilon(\omega)$ in each of the regions into which our geometry is divided. It will also be assumed that the problem is source-free. However, this might not be the case for metals as we would expect currents arising from Ohm's law: $\mathbf{j} = \sigma(\omega) \mathbf{E}$, where $\sigma(\omega)$ is the conductivity of the metal. It can easily be shown [12] that this

²A more general still linear relationship would be a convolution taking into account non-local effects both in time and space. Furthermore, anisotropy can be modelled by proposing a tensorial linearity as follows:

$$\mathbf{D}(t, \mathbf{r}) = \iint_{\mathbb{R}^4} \varepsilon_0 \underbrace{\mathbb{E}(t, u; \mathbf{r}, \mathbf{s})}_{\text{Tensorial permittivity}} \cdot \mathbf{E}(u, \mathbf{s}) \, du d\mathbf{s}$$

Non-local spatial effects *are* necessary to be taken into account in some examples where the size of the studied structures is of the order of the electron mean free path [13], but otherwise they can be safely neglected. Temporal dispersion, however, must be taken into account as it is widely established to make a difference. In other words, it is usually clearer that my past affects my present but not that a demonstration in Jaipur affects my commute to Imperial College. The main point here is that I can be considered as a point particle, however in quantum mechanics electrons have wave-like extensions and this makes them interact [42]. If temporal invariance can be assumed then the permittivity's time dependence can be replaced with $t - u$. Similarly if space invariance can be assumed the permittivity can be replaced with $\mathbf{r} - \mathbf{s}$. For the system treated in the main text we have a temporally and spatially invariant isotropic dispersive local permittivity described by: $\mathbb{E}(t, u; \mathbf{r}, \mathbf{s}) = \varepsilon(t - u, \mathbf{r}) \delta(\mathbf{r} - \mathbf{s}) \mathbb{1}$.

corresponds to adding conductivity to the permittivity. Therefore, the permittivity will be considered in general a complex number:

$$\begin{aligned} \text{Description in terms of } \varepsilon(\omega), \sigma(\omega) &\longrightarrow \\ \varepsilon'(\omega) &= \varepsilon(\omega) + i\sigma(\omega)/\omega \end{aligned} \quad (2-3)$$

2.1.1 Two media: cartesian discontinuity

The main purpose of this subsection is to find surface modes. A surface mode is simply a mode confined to the boundaries of our geometry. In this case let us assume that our geometry consists of two media of indices ε_1 (dispersionless) and $\varepsilon_2(\omega)$ (dispersive) as shown in figure 2.2. From this we can define the term *confined* more rigorously by assuming that the functional dependence in the z direction has to be a decaying exponential to *both sides*. Inspired by this, let us write the field by a functional dependence $e^{-i(k_{x,1}x + k_{z,1}z)} e^{i\omega_1 t}$, which simply means that we are finding eigenmodes of a fixed frequency that solve our superficial problem in each subregion $l = 1, 2$ ³.

Using these assumptions alone together with Maxwell equations 2-1 we note that the values of k_x , k_z and ω cannot be independent and have to be related to each other in each subregion as follows:

$$\begin{aligned} k_{x,1}^2 + k_{z,1}^2 &= \varepsilon_1 \omega_1^2 / c^2, \\ k_{x,2}^2 + k_{z,2}^2 &= \varepsilon_2(\omega_2) \omega_2^2 / c^2, \end{aligned} \quad (2-4)$$

where the sub-index indicates the region 1 ($z > 0$) or 2 ($z < 0$) and $c = 1/\sqrt{\varepsilon_0 \mu_0}$ is just the speed of light in vacuum. Furthermore, using the boundary condition on the surface, which must be valid $\forall x, t \in \mathbb{R}$ and $z = 0$:

$$\hat{\mathbf{z}} \cdot \left[\varepsilon_1 \mathbf{E}_1 e^{i(\omega_1 t - k_{x,1} x)} - \varepsilon_2(\omega_2) \mathbf{E}_2 e^{i(\omega_2 t - k_{x,2} x)} \right] = 0, \quad (2-5)$$

we obtain $\omega_1 = \omega_2$ and $k_{x,1} = k_{x,2}$ just by integrating over both sides over the whole x, t region after multiplying by $e^{-i\omega_1 t + ik_{x,1} x}$. This implies that the only parameter that is not continuous throughout the surface is k_z . Returning to the dispersion relation we can find that:

$$k_{z,2}^2 - k_{z,1}^2 = (\varepsilon_2(\omega) - \varepsilon_1) \omega^2 / c^2. \quad (2-6)$$

³I have left no y dependence for symmetry reasons.

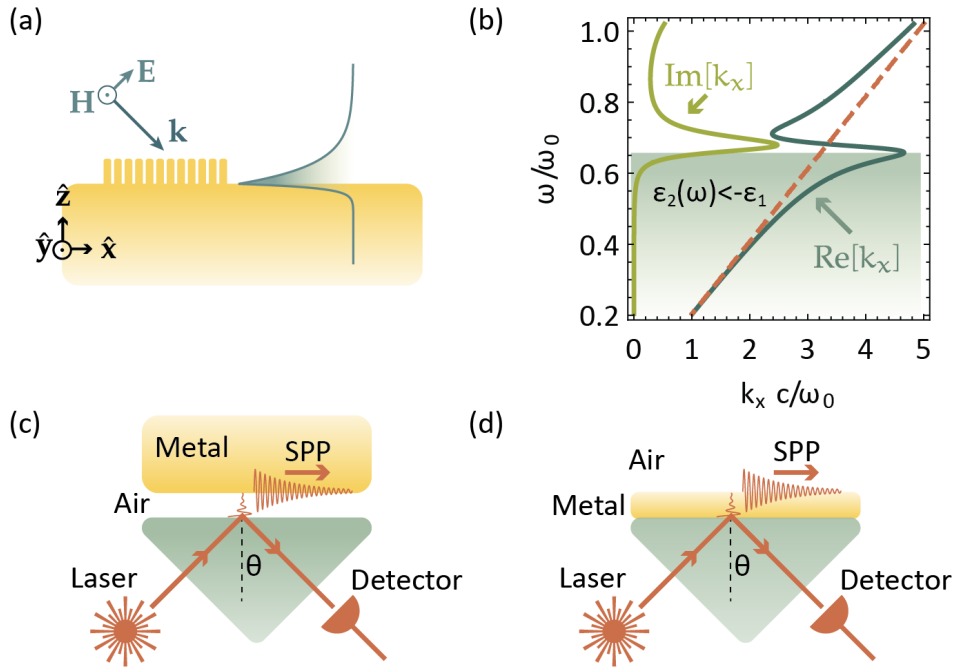


Figure 2.2 (a) Geometry for the existence of superficial modes at a plane interface (also known as surface plasmon polaritons) (b) Dispersion relation of surface plasmon polaritons on silver calculated from a modified equation similar to equation 2-14 (below) and the phenomenological complex permittivity from reference [43]. Both the real and imaginary part k_x are shown, representing dispersion and dissipation. The dashed line represents the light line $k_x = \omega/c$. In this plot $\omega_0 = 8.729$ eV and is used in equation 2-38 to describe the restoring force between the free electrons and the atoms in the crystal. (c) Otto and (d) Kretschmann configurations for excitation of the superficial modes.

Now that we have exhausted the study of the dispersion relation, let us go back to the continuity equation 2-5. Here we have two vectorial entities $\mathbf{E}_{1,2}$ that depend on $k_{z,1,2}$. The dependence can be seen if we firstly note that Maxwell equation 2-1(a) suggests that for this field the $\mathbf{k}_l = (k_x, 0, k_{z,l})$ vector has to be perpendicular to the electromagnetic field. In other words $\mathbf{E}_l \perp \mathbf{k}_l$. We, thus, need to decompose our field into two components that are orthogonal to $\mathbf{k}_l$ and also to themselves.

Clearly, $\hat{\mathbf{y}}$ is one possibility for $\hat{\mathbf{y}} \cdot \mathbf{k}_l = 0$ ⁴. Literature refers to this polarisation as the s-polarisation, we will therefore call the electric field produced from this polarisation $\mathbf{E}_s = E_s \hat{\mathbf{y}}$. The other possibility to decompose the electric field is usually called p-polarisation ($\mathbf{E}_p$) and is just given by that vector (which I shall call $\hat{\mathbf{p}}$) perpendicular both to $\hat{\mathbf{y}}$ and $\hat{\mathbf{k}}_l$ ⁵. This vector is just, in a three-dimensional space, the vector product

$$\begin{aligned} \hat{\mathbf{p}}_l &= \hat{\mathbf{y}} \times \hat{\mathbf{k}}_l \\ &= \frac{-k_{z,l} \hat{\mathbf{x}} + k_x \hat{\mathbf{z}}}{\sqrt{k_x^2 + k_{z,l}^2}} \\ &= \frac{-k_{z,l} \hat{\mathbf{x}} + k_x \hat{\mathbf{z}}}{\sqrt{\epsilon_l} \omega / c} \end{aligned} \quad (2-7)$$

for each subspace $l = 1, 2$.

This allows us to define the electric and magnetic fields we need to input into the boundary conditions to find further conditions between our $k_{z,l}$:

$$\begin{aligned} \mathbf{E}_l &= \left\{ E_{s,l} \hat{\mathbf{y}} + \frac{-k_{z,l} \hat{\mathbf{x}} + k_x \hat{\mathbf{z}}}{\sqrt{\epsilon_l} \omega / c} E_{p,l} \right\} e^{-i(k_x x + k_{z,l} z - \omega t)}, \\ \mathbf{H}_l &= \frac{\sqrt{\epsilon_l}}{\mu_0} \hat{\mathbf{k}} \times \mathbf{E}_l. \end{aligned} \quad (2-8)$$

⁴It is of utmost importance to realise that I am defining orthogonality between two possibly complex vectors as $\mathbf{a} \cdot \mathbf{b}$ without taking any complex conjugate on either of both as is the usual costume. That is because the condition that has to be satisfied is given by the Maxwell equation $\nabla \cdot \mathbf{D} = 0$, from where it follows $\mathbf{k} \cdot \mathbf{E} = 0$ without any complex conjugate. It is this equation that is important in the definition of what I am calling orthogonal and not an ulterior mathematical definition.

⁵Note that, in my notation, all the vectors that have a hat on top are normalised to unity. For example: $\hat{\mathbf{k}} = \frac{\mathbf{k}}{\sqrt{\mathbf{k} \cdot \mathbf{k}}}$ but *not* $\hat{\mathbf{k}} = \frac{\mathbf{k}}{\sqrt{\mathbf{k}^* \cdot \mathbf{k}}}$.

The boundary conditions define linear equations between $E_{s,1}$, $E_{s,2}$, $E_{p,1}$, $E_{p,2}$, $k_{z,1}$ and $k_{z,2}$:

$$(\mathbf{D}_2 - \mathbf{D}_1) \cdot \hat{\mathbf{z}} = 0 \Rightarrow \frac{\varepsilon_2 E_{p,2}}{k_x^2 + k_{z,2}^2} = \frac{\varepsilon_1 E_{p,1}}{k_x^2 + k_{z,1}^2}. \quad (2-9a)$$

$$(\mathbf{E}_2 - \mathbf{E}_1) \times \hat{\mathbf{z}} = \mathbf{0} \Rightarrow E_{s,1} = E_{s,2}, \quad (2-9b)$$

$$\frac{k_{z,2} E_{p,2}}{k_x^2 + k_{z,2}^2} = \frac{k_{z,1} E_{p,1}}{k_x^2 + k_{z,1}^2}. \quad (2-9c)$$

$$(\mathbf{H}_2 - \mathbf{H}_1) \cdot \hat{\mathbf{z}} = 0 \Rightarrow E_{s,2} = E_{s,1}. \quad (2-9d)$$

$$(\mathbf{H}_2 - \mathbf{H}_1) \times \hat{\mathbf{z}} = \mathbf{0} \Rightarrow E_{s,2} k_{z,2} = E_{s,1} k_{z,1}, \quad (2-9e)$$

$$\sqrt{\varepsilon_2} E_{p,2} = \sqrt{\varepsilon_1} E_{p,1} \quad (2-9f)$$

As can be seen from equations 2-9(b) and (e), and requiring that $k_{z,1} \neq k_{z,2}$ we obtain that $E_{s,1} = 0$. In other words, there cannot be any modes with s-polarisation. From equation 2-9(a) and (c) we obtain a homogeneous set of equations that can be solved non trivially by imposing that the charactersitic polynomial of the system be equal to zero:

$$\begin{aligned} \det \begin{vmatrix} \varepsilon_1 & -\varepsilon_2(\omega) \\ k_{z,1} & -k_{z,2} \end{vmatrix} &= -\varepsilon_1 k_{z,2} + \varepsilon_2(\omega) k_{z,1} \\ &= 0 \Leftrightarrow \\ k_{z,2} &= \frac{\varepsilon_2(\omega)}{\varepsilon_1} k_{z,1}. \end{aligned} \quad (2-10)$$

This allows us to rewrite the final expression for the dispersion relationship from equation 2-6:

$$k_{z,1}^2 = \frac{\varepsilon_1}{1 + \varepsilon_2(\omega)/\varepsilon_1} \omega^2/c^2 = \left[\frac{\varepsilon_2(\omega)}{\varepsilon_1} \right]^2 k_{z,2}^2 \quad (2-11)$$

Moreover, the full solution of the problem is found with equation 2-9(f) from where we obtain that $E_{p,2} = \sqrt{\varepsilon_2/\varepsilon_1} E_{p,1}$.

The induced surface charge $\sigma(t, x, z)$ is given by the boundary condition:

$$\begin{aligned} (\mathbf{E}_2 - \mathbf{E}_1) \cdot \hat{\mathbf{z}} &= \sigma(t, x, z)/\varepsilon_0 \\ &= \frac{k_x}{\sqrt{\varepsilon_1} \omega/c} \left\{ \frac{\varepsilon_1}{\varepsilon_2(\omega)} e^{-ik_{z,2}z} - e^{-ik_{z,1}z} \right\} E_{p,1} e^{i(\omega t - k_x x)}. \end{aligned} \quad (2-12)$$

So far we have seen that we can get p-polarised modes with a dispersion relation given by 2-11. Let us note the following cases:

Propagating surface waves

Assume $\varepsilon_2(\omega) \in \mathbb{R}$. In this case, if we want to impose the surface wave condition (in other words that the mode be localised on the boundary), we should require that the denominator in equation 2-11 be negative, so that both $k_{z,1}$ and $k_{z,2}$ become purely imaginary. This condition is translated into the celebrated negativity of the refractive index found in metals [13, 40]:

$$\varepsilon_2(\omega) < -\varepsilon_1. \quad (2-13)$$

In this case the oscillating z exponentials become decaying z exponentials.

Another equation that we have to take into consideration is that defining k_x (obtained from equations 2-4 and 2-11):

$$k_x^2 = \frac{\varepsilon_2(\omega)}{1 + \varepsilon_2(\omega)/\varepsilon_1} \omega^2/c^2, \quad (2-14)$$

this is the dispersion relation plotted in figure 2.2(b). In order to do that plot, we need to establish a functional dependence for $\varepsilon_2(\omega)$. It is exactly here where the macroscopic model needs to be fed from the microscopic model to continue doing predictions. As will be seen in section 2.2.1 the Drude-Lorentz model describes a reasonable semi-classical dependence in terms of microscopic parameters. This dependence is far from the trivial free-space linear relationship. Note that two branches appear. The upper one gives a complex k_z which would define propagation plus attenuation in the metal and is thus not a true surface wave. For this reason it has to be discarded as characterising a surface mode [13]. This topic will be reintroduced once a microscopic model for the metal has been developed in section 2.2.1.

From the relationship 2-14 we see that if $\varepsilon_1 > 0$ (which is usually the case as in many examples it chiefly represents air or any non metallic environment), then we obtain that k_x is going to be always real ($k_x^2 \geq 0$).

It is clear then that a real k_x and a purely imaginary $k_{z,1}$ are obtained just by requiring $\varepsilon_2(\omega) < -\varepsilon_1 < 0$. This defines a propagating ($k_x \in \mathbb{R}$) surface ($k_z \in \mathbb{I}$) wave. Also known as propagating surface plasmon polaritons (PSPPs) because of the microscopic nature of the negativity in the electric permittivity. The word plasmon has to do with oscillating free electrons which are coupled to polaritons, coupled oscillations in matter. A quantised version of the theory that takes into account all these phenomena is briefed in section 2.2.2 to understand the choice of these ominous names.

Localised surface waves

In order to obtain waves that are not only localised in the z direction but also in the x direction we need to assume a general complex dependence for $\varepsilon_2 \in \mathbb{C}$. Inserting this intrinsic absorption we can obtain surface modes that can be localised in space. These modes are usually called localised surface plasmon polaritons (LSSPs) and they arise in a more natural fashion when studying a metallic spherical particle surrounded by a homogenous environment.

Excitation configurations

As can be seen from equation 2-14 these modes have $k_x > \sqrt{\varepsilon_1}\omega/c$, *i.e.* they have a larger momentum than in the homogeneous surrounding space. In other words, the only thing we could get by impinging with photons onto the surface would be the ubiquitous reflection and transmission phenomena [39]. This causes troubles to observe them as they cannot be excited from normal far-field illumination. The main trick that near-field optics has taught us is that we can obtain higher momentum than in free-space by patterning near-field objects which provide the necessary kick in momentum via evanescent waves [13]. The configurations used by Otto and by Kretschmann shown in figure 2.2 exploit the evanescent fields produced at the interface of a prism to excite the SPPs. In the Otto configuration a SPP is launched with an evanescent field obtained via total internal reflection on a metallic surface separated a small distance from the prism. In the Kretschmann configuration, the careful positioning of the metallic surface above the prism is resolved by firstly depositing a thin layer of the chosen metal [13, 39, 40].

In the next section I show how a localised surface wave can be excited from the far-field using a nanoscale object, namely a metallic nanosphere.

2.1.2 Two media: spherical discontinuity (quasistatic approach)

In this example, I will introduce the concept of a localised surface wave in a nano-scale object. In other words I will model the interaction of a metallic nanosphere with an external driving field as shown in figure 2.3(a). Furthermore, I am going to make a strong assumption that is going to simplify the calculations [13, 40]: the radius a of the sphere is much smaller than the wavelength of the exciting light λ . However, in chapter 5 I will not take this approximation and a full solution of the problem will be obtained using the Mie scattering formalism [44, 45].

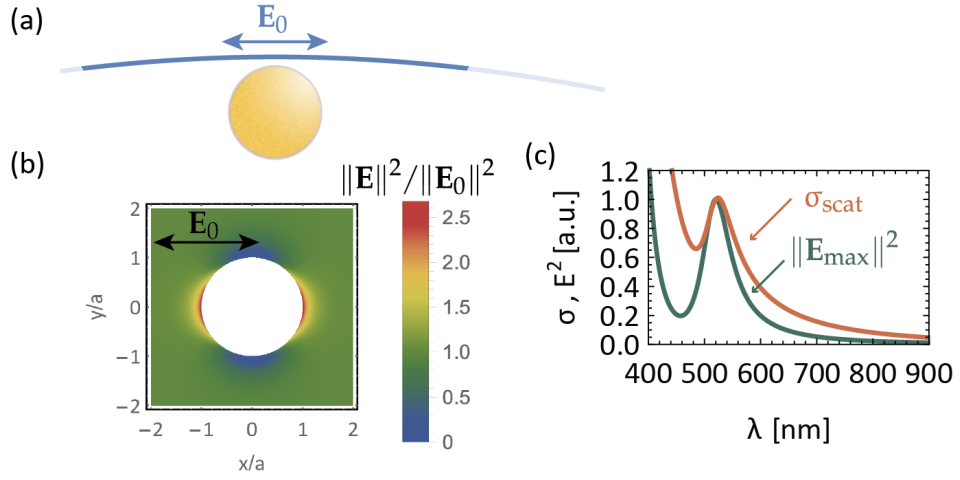


Figure 2.3 (a) Geometry of excitation of a surface mode on a nanosphere. The dimensions of the sphere are much smaller than the wavelength of the excitation light, validating the quasi-static approximation. (b) Ratio of near-field and excitation field magnitude, showing a clear enhancement of the electric component in the vicinity of the nanosphere at the resonant wavelength for a subwavelength gold nano-particle. (c) Scattering cross-section of the nanosphere. The refractive index of the nano-sphere was modelled via a Drude-Lorentz phenomenological permittivity given in [43].

The following calculations are based on the electrostatic solution provided by Jackson [12]. In this approximation, the electric field can be thought of as coming from an electrostatic potential $\Phi(r, \theta, \phi)$ such that $-\nabla\Phi = \mathbf{E}$, which in spherical coordinates can be expanded as:

$$\Phi(r, \theta, \phi) = \sum_{l=0}^{+\infty} \sum_{m=-l}^l f_{lm}(r) y_{lm}(\theta, \phi), \quad (2-15)$$

where $y_{lm}(\theta, \phi)$ are the spherical harmonics of order l, m and $f_{lm}(r)$ are just functions that will depend on the exact nature of the differential equation that has to be solved. This equation has to be the source-free Laplace equation both inside and outside the sphere:

$$\nabla^2 \Phi_j(r, \theta, \phi) = 0, \text{ for } j = 1, 2, \quad (2-16)$$

together with the Dirichlet boundary condition at the interface of the sphere:

$$\hat{\mathbf{r}} \cdot \left[\overbrace{\varepsilon_2(\omega) \mathbf{E}_2}^{\mathbf{D}_2} - \overbrace{\varepsilon_1 \mathbf{E}_1}^{\mathbf{D}_1} \right] = 0 \Leftrightarrow \quad (2-17)$$

$$\varepsilon_2(\omega) \frac{\partial \Phi_2(\mathbf{a}, \theta, \phi)}{\partial r} - \varepsilon_1 \frac{\partial \Phi_1(\mathbf{a}, \theta, \phi)}{\partial r} = 0, \quad \forall \theta \in [0, \pi], \phi \in [0, 2\pi]$$

the continuity of the tangential component:

$$\hat{\mathbf{r}} \times [\mathbf{E}_2 - \mathbf{E}_1] = 0 \Leftrightarrow$$

$$\frac{\partial}{\partial \theta} [\Phi_2(\mathbf{a}, \theta, \phi) - \Phi_1(\mathbf{a}, \theta, \phi)] = 0 \quad (2-18)$$

$$\frac{\partial}{\partial \phi} [\Phi_2(\mathbf{a}, \theta, \phi) - \Phi_1(\mathbf{a}, \theta, \phi)] = 0$$

and these two asymptotic equations:

$$\lim_{r \rightarrow +\infty} \frac{\Phi_2(r, \theta, \phi)}{\Phi_0(r)} = 1 \text{ far-field asymptote: } -\nabla \Phi_0 = E_0 \hat{\mathbf{z}}, \quad (2-19a)$$

$$\lim_{r \rightarrow 0} \Phi_1(r, \theta, \phi) < \infty \text{ finite at } r \rightarrow 0. \quad (2-19b)$$

The first simplification is given by the far-field asymptote which has to be equal to $\Phi_0(r) = -E_0 z = -E_0 r \cos \theta$. This can be rewritten using spherical harmonics as follows [12]:

$$\Phi_0(r) = -E_0 x = -E_0 \sqrt{\frac{4\pi}{3}} r y_{10}(\theta, \phi), \quad (2-20)$$

which indicates that (using equation 2-19a):

$$y_{10}(\theta, \phi) = \sum_{l=0}^{+\infty} \sum_{m=-l}^l \left[\lim_{r \rightarrow +\infty} \frac{f_{lm,2}(r)}{-E_0 \sqrt{4\pi/3} r} \right] y_{lm}(\theta, \phi). \quad (2-21)$$

After multiplying by $y_{10}^*(\theta, \phi)$ and integrating over all solid angle we obtain:

$$\lim_{r \rightarrow +\infty} \frac{f_{lm,2}(r)}{r} = -E_0 \sqrt{\frac{4\pi}{3}} \delta_{l1} \delta_{m0}, \quad (2-22)$$

which simply implies that

$$\Phi_2(r, \theta, \phi) = -E_0 \sqrt{\frac{4\pi}{3}} f_{10,2}(r) y_{10}(\theta, \phi). \quad (2-23)$$

Note that even though the dependence in ϕ is explicated, there is no real dependence in this parameter. The azimuthal symmetry has been granted by the azimuthal symmetry of the excitation field.

We cannot continue further if we do not solve the Laplace equation first, which states that:

$$f_{lm,j}(r) = A_{lm,j}r^l + B_{lm,j}r^{-(l+1)}. \quad (2-24)$$

The limit equation 2-22 is automatically satisfied when we plug this information together with equation 2-23. This yields:

$$\Phi_2(r, \theta, \phi) = -E_0 \sqrt{\frac{4\pi}{3}} \left[r + \frac{B_{10,2}}{r^2} \right] y_{10}(\theta, \phi). \quad (2-25)$$

Similarly, imposing the limit boundary condition at $r \rightarrow 0$ of equation 2-19(b) implies that $B_{lm,1} = 0$, so that, in principle the most general expression for the potential inside the sphere is:

$$\Phi_1(r, \theta, \phi) = \sum_{l=0}^{+\infty} \sum_{m=-l}^l A_{lm,1} r^l y_{lm}(\theta, \phi). \quad (2-26)$$

On a parallel level, the Dirichlet boundary condition 2-17 can be multiplied by $y_{l'm'}(\theta, \phi)$ and integrated over all solid angles to yield:

$$\frac{df_{lm,2}(a)}{dr} = \frac{\varepsilon_1}{\varepsilon_2(\omega)} \frac{df_{lm,1}(a)}{dr}. \quad (2-27)$$

This general equation can be recast into:

$$A_{lm,1} l a^{l-1} = -\frac{\varepsilon_1}{\varepsilon_2(\omega)} E_0 \sqrt{\frac{4\pi}{3}} \left(1 - 2 \frac{B_{10,2}}{a^3} \right) \delta_{l1} \delta_{m0} \quad (2-28)$$

so that the only non-zero $A_{lm,1}$ are for $l = 1, m = 0$:

$$A_{10,1} = -\frac{\varepsilon_1}{\varepsilon_2(\omega)} E_0 \sqrt{\frac{4\pi}{3}} \left(1 - 2 \frac{B_{10,2}}{a^3} \right). \quad (2-29)$$

The continuity of the tangential component of the electric field of equation 2-18 solves for $B_{10,2}$ which finishes the calculations to yield (replacing all the spherical harmonics with their more familiar trigonometric expressions):

$$\Phi_1(r \leq a, \theta) = -\frac{2}{2 + \varepsilon_2(\omega)/\varepsilon_1} E_0 r \cos \theta, \quad (2-30a)$$

$$\Phi_2(r \geq a, \theta) = \underbrace{-E_0 r \cos \theta}_{\text{Far-field asymptote}} + \frac{\varepsilon_2(\omega)/\varepsilon_1 - 1}{\varepsilon_2(\omega)/\varepsilon_1 + 2} E_0 a \left(\frac{a}{r}\right)^2 \cos \theta. \quad (2-30b)$$

Induced dipole moment

The potential outside of the nanosphere is just that of an external excitation constant field plus that of a dipole with moment:

$$\mathbf{d}_{\text{induced}} = 4\pi\varepsilon_0\varepsilon_1 \underbrace{\frac{\varepsilon_2(\omega)/\varepsilon_1 - 1}{\varepsilon_2(\omega)/\varepsilon_1 + 2}}_{\text{Polarisability } \alpha(\omega)} \mathbf{E}_0. \quad (2-31)$$

The polarizability $\alpha(\omega)$ is the proportionality factor between the applied electric field and the dipole induced in the sphere. In the next section we shall see how this polarisability arises in dielectrics from a microscopic point of view. Furthermore, this polarisability implies that, as long as the permittivity does not depend on the electric field [46], the induced dipole moment is proportional to the exciting electric field. This polarisability achieves a maximum whenever:

$$\text{Re}[\varepsilon_2(\omega)] = -2\varepsilon_1, \quad (2-32)$$

where we have assumed $\varepsilon_2(\omega) \in \mathbb{C}$ for generality.

Localised surface mode

Figure 2.3(b) shows the near-field distribution of the electric field for a gold nanosphere at the wavelength where the polarisability, depicted in 2.3(c), obtains a maximum. We can also observe, that the maximum field enhancement correlates with the position of the maximum polarisability. The field is highly confined to the nanostructure, and as a consequence thereof, it shall be called a localised surface mode. Note that we could obtain this mode only if the permittivity becomes negative, which can only be attained for metals with free charges as we shall see in the next section. Again, we reach that moment when the macroscopic theory can only continue if we feed it with the necessary data (if measurements are available) or models of the structure of matter.

Quantum mechanics in Maxwell's equations

The quasi-static approximation is founded in the assumption that the nano-object has dimensions much smaller than the wavelength of the driving field. Although mathematically speaking we can make this object arbitrarily small, physics prohibits such a miniaturisation. The smaller the object gets the more quantum effects will start influencing the results. Another implicit assumption in the whole development of this classical theory was that we could use the local dielectric function $\epsilon_2(\omega)$ as the constitutive parameter of our system. This function can acquire non-local effects when the size of the nanoparticle is comparable to the electron mean-free path [13] as previously mentioned. Furthermore, the electrons cannot be considered to have a continuous spectrum of energies any more and they will start behaving as a particle in a confined potential, defined by the nanoparticle [42, 47]. The macroscopic theory is still valid, as long as the correct dielectric function is utilised. This brings us directly to the next section, where we study different proposals for dielectric functions.

2.2 MICROSCOPIC THEORY

Figure 2.4 shows examples of measured refractive indices of different materials using ellipsometry [44]. The refractive index is simply:

$$n(\omega) + i\kappa(\omega) = \sqrt{\epsilon(\omega)\mu(\omega)}, \quad (2-33)$$

and is usually a complex magnitude. The magnetic permeability is generally unity at optical frequencies [13, 40]. Its real part is related to dispersion as it appears in an oscillating exponential $e^{-in(\omega)k_0x}$, with $k_0 = \omega/c$. This will give rise to the complex dispersive behaviour when a non-monochromatic field impinges on the material. The second parameter is related to absorption, as it appears in a decaying exponential $e^{-\kappa(\omega)k_0x}$.

Before proceeding a useful relationship between the real and imaginary parts of the refractive index and the electrical permittivity can be written just by squaring equation 2-33:

$$\text{Re}\{\epsilon\} = n^2 - \kappa^2, \quad (2-34a)$$

$$\text{Im}\{\epsilon\} = 2n\kappa. \quad (2-34b)$$

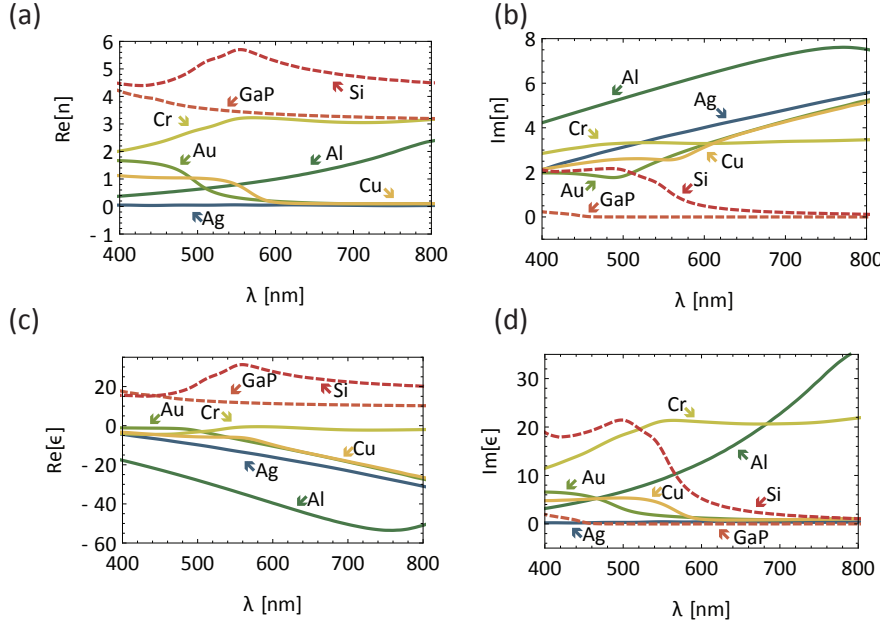


Figure 2.4 (a) Real and (b) imaginary part of the experimentally measured refractive index. (c) Real and (b) imaginary part of the relative permittivities calculated as $\epsilon = n^2$ from the experimental data for n . All the refractive indices measured with ellipsometry. Ag and Cr from [48], Al, Au and Cu from [49] and Si and GaP from [50].

From here we can already see why metals are good candidates for surface modes: they have large losses that can yield large negative $\text{Re}\{\epsilon\}$.

In order to try to understand the spectral dependence of these parameters I resort in section 2.2.1 to first analyse the problem of an electron forced by a classical field. This is a fully-classical approach as the electron will be simply modelled as a harmonic oscillator forced by an external agent. Assuming non-interacting electrons, this formalism gives rise to the description of plasmons: collective oscillations of charges. However, in section 2.2.2 a partially quantised proposal to model plasmons in matter is sketched. No full details will be given as the quantisation procedure is rather involved [51].

2.2.1 Classical: Drude-Sommerfeld model

I will start by assuming that our metal is composed of atoms which contain electrons that can be modelled as a harmonic oscillator bound to their nucleus as shown in Figure 2.5. This approximation is clearly valid when we are interested in analysing the behaviour of an electron close to the minimum of the effective potential defined by the central

potential to the nucleus. Furthermore, I will not assume any interaction between electrons, besides instantaneous collisions. These collisions can be treated as mere fluctuations, if Einstein's hypothesis are correct and a specific dependence is chosen for the correlation of the velocities of the electrons, and will be henceforth buried under the dissipation constant as an effective under-the-hood interaction [13]. An external time-dependent electric field is applied to the electrons, which gives rise to an electric force. The magnetic Lorentz force [12] will not be taken into account as the electron will be considered to be always contained within the non-relativistic regime. In other words, we must require the driving field not to be *too large* so as to make all these approximations valid. This last insight already reveals the final nature of the solution: the motion is going to be proportional to the applied external field. This should not be a surprise, as all the approximations taken in the beginning are practically imposing this linearity.

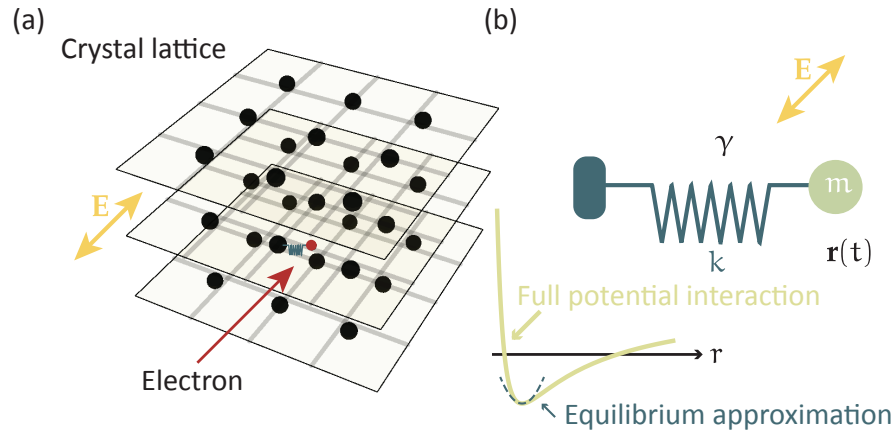


Figure 2.5 Classical model of an electron interacting with an electric field. (a) The electrons are located in the vicinity of the atomic nuclei forming the crystal lattice and an external arbitrarily polarised electromagnetic field excites their dynamics. (b) The considered system is much simpler. The full interaction is modelled close to the equilibrium position using a quadratic approximation.

Writing down Newton's equations for the electron we obtain:

$$\frac{d^2 \mathbf{r}}{dt^2} + \gamma \frac{d\mathbf{r}}{dt} + \overbrace{\frac{k}{m}}^{\omega_0^2} \mathbf{r} = -\frac{|e|\hbar}{m} \mathbf{E}_0 e^{i\omega t}, \quad (2-35)$$

where $\mathbf{r}$ is the displacement vector of the electron from its equilibrium position in the atom, γ its collision induced dissipation, k the restoring

force per unit length to the nucleus⁶, m the mass of the electron⁷, $-|e|$ the charge of the electron, $\mathbf{E}_0$ the external exciting electric field and ω its angular frequency.

We can easily solve this equation and find:

$$\begin{aligned}\mathbf{r}(t) &= \alpha(\omega)\mathbf{E}(t) \\ &= -\frac{|e|\hbar}{m(\omega_0^2 - \omega^2) + i\gamma\omega}\mathbf{E}(t).\end{aligned}\quad (2-36)$$

The amplitude $\alpha(\omega)$ is known as the induced polarisability. This solution allows us to rewrite the dipole moment [12] as follows:

$$\begin{aligned}\mathbf{p}(t) &\stackrel{\text{def}}{=} \int \mathbf{r}' \overbrace{(-|e|\delta[\mathbf{r}' - \mathbf{r}(t)])}^{\text{Charge density}} d\mathbf{r}' = \\ &= -|e|\mathbf{r}(t) = -|e|\alpha(\omega)\mathbf{E}(t).\end{aligned}\quad (2-37)$$

The important parameter to finally derive the electric permittivity is the polarisability vector density $\mathbf{P}$ defined as the sum of dipole moments of all the electrons in the material per unit volume, so that $\mathbf{P} = \rho_e \mathbf{p}(t)$, with ρ_e the density of electrons per unit volume. Furthermore, the connection with the permittivity is given by $\mathbf{P} = \epsilon_0 \mathbf{E} - \mathbf{D} = \epsilon_0(1 - \epsilon(\omega))\mathbf{E}$. From these equations we can find:

$$\begin{aligned}\epsilon(\omega) &= 1 - \frac{\rho_e |e| \alpha(\omega)}{\epsilon_0} \\ &= 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 + i\gamma\omega}, \quad \omega_p^2 = \frac{\rho_e |e|^2 \hbar^2}{m\epsilon_0},\end{aligned}\quad (2-38)$$

with ω_p defined as the plasmon angular frequency. Figure 2.6 shows both the real and imaginary part of the refractive index obtained from this purely classical model. This formula is the main result of the Drude-Sommerfeld model of matter. The regions where the permittivity less than -1 are highlighted. In this frequency ranges, the toy-model material behaves effectively as a metal. This can clearly happen for not so large electron-electron scattering (γ/ω_p not large) and also for electrons bounded very feebly to their atomic nuclei (ω_0/ω_p not large). We can see the influence of these parameters in the real part of the permittivity in figures 2.6(a) and (c). Conversely, figure 2.6(b)-(d) imaginary part is

⁶This can be obtained from the central potential $V(r)$ by expanding to second order and evaluating in the equilibrium position: $k = V''(r_0)$.

⁷The mass can be corrected to take into account the lattice interaction. Again, we can bury all the details of the lattice in the effective mass of the electron [24, 30, 52].

negative below the plasma frequency ω_p . The experimental data of figure 2.4 is plotted above the plasma frequency, therefore this behaviour is not observed there.

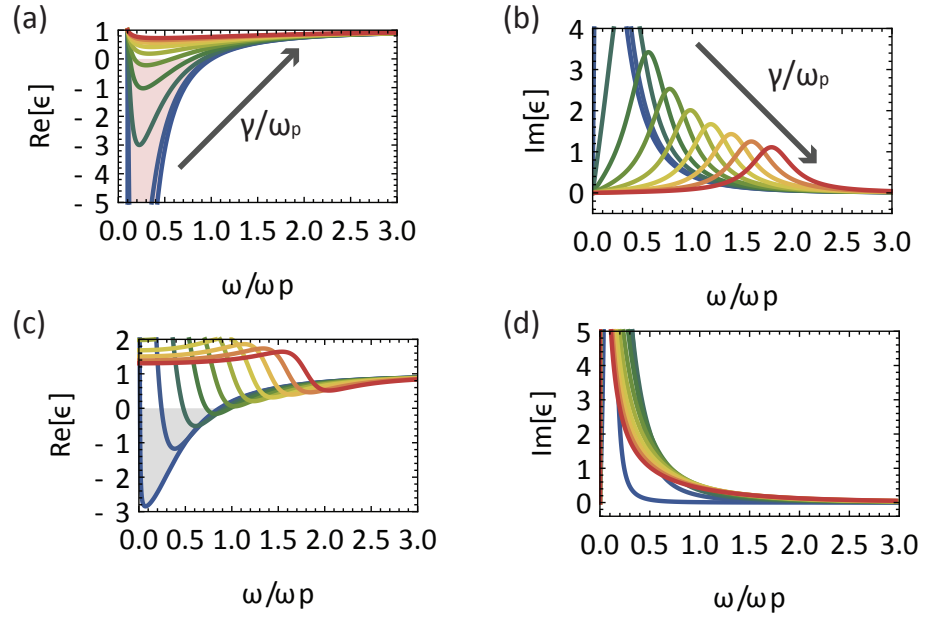


Figure 2.6 Permittivity from a material modelled as continuous homogeneous distribution of non-interacting classical electrons close to equilibrium. (a)–(c) Real part of the permittivity and (b)–(d) imaginary part of the permittivity. In (a)–(b) the dissipation is increased (so a stronger electron–electron scattering, or electron–phonon coupling) while keeping $\omega_0/\omega_p = 0.1$. Contrariwise, in (c)–(d) the coupling constant ω_0 is tuned from dark colours to bright colours while keeping $\gamma/\omega_p = 0.5$. In this case, ω_0 quantifies how strongly bounded an electron is to the atomic nucleus. In the case of semiconductors, this value is large, but for metals it should be close to zero.

We can also use this model as a basis to build more complicated models. For example, the dispersion relation shown in figure 2.2 uses three different Drude-Lorentz contributions to describe the measured refractive index. Here, we can see that the dispersion relation varies from that of free-space $k_x = \omega/c$. In particular, when $\omega \sim \omega_p$ the straight line dispersion starts bending around the light-line. Surface plasmon can only exist when $\varepsilon_2(\omega) < -\varepsilon_1$ as shown in equation 2–13. The region where this happens is shaded in figure 2.2(b). Above this line we do not have true SPPs as these modes are not confined.

To final notes, firstly this model is implying that all the electrons move in consonance to each other, this collective oscillation is what is called

a plasmon, and when a macroscopic description implies that the fields are confined to the surface, we shall refer to them as surface plasmons. Secondly, this model can be extended to the study of bulk plasmons by making the electrons free ($\omega_0 = 0$), which ends up adding two different contributions to the total dielectric function: from the free-electron gas background and from the electrons bounded to the atoms. A model including only the former describes pure metals, one including solely the latter describes dielectrics. All materials can be described quite generally as a mixture of both.

2.2.2 Quantum

A full quantum treatment will not be sketched here. I will just mention a modification induced into the electrical permittivity due to first quantisation of the electron.

The first modification to the Drude-Sommerfeld model of equation 2-38 is that the plasmon frequency ω_p is replaced with what is known as the oscillator strength [24, 53]:

$$\omega_p^2 \longrightarrow f_{ij} = \frac{2\rho_e|\omega_{ij}|}{\hbar} \left| \langle j | \hat{\mathcal{H}}_{\text{dip}} | i \rangle \right|^2, \quad (2-39)$$

where $\hbar$ is Planck's reduce constant, $\hbar\omega_{ij}$ the energy difference between the initial state i and the final state j . This transition has to be dipole allowed⁸, which means that the matrix element of the interaction Hamiltonian $\hat{\mathcal{H}}_{\text{dip}}$ with the electric field is not zero. Assuming the initial state is the ground state ($i \rightarrow 0$), we can sum over all the final states and re-write the permittivity as:

$$\begin{aligned} \varepsilon(\omega) &= 1 - \frac{\rho_e|e|\alpha(\omega)}{\varepsilon_0} \\ &= 1 + \sum_j \frac{f_{0j}}{\omega_{0j}^2 - \omega^2 + i\gamma_{0j}\omega}. \end{aligned} \quad (2-40)$$

This is the so-called Helmholtz-Ketteler or Kramers-Heisenberg dielectric function [53], which takes into account the quantised nature of the electron and the classical nature of the electromagnetic field. This expression can take into account the finer structure of the material. It is a relief for the experimentalist, as it has more parameters to adjust to the data.

⁸An exactly mathematically similar approach is sketched in chapter 1.

2.3 THE EXPERIMENTS: CROSS-SECTIONS

Finally, let us concentrate on an experimentally accessible quantity that is of great utility for nano-optics: the scattering cross-section. Throughout the whole thesis we are concerned with localised surface plasmon polaritons, arising from local oscillations of matter in nanostructures, as previewed in section 2.1.2.

We are interested in the far-field properties of our nano-antenna⁹. They should be efficient scatterers [54] in a specific wavelength range. The most standardised measure of this is the scattering cross-section defined as:

$$\sigma_{\text{scat}}(\omega) = \frac{P_{\text{rad}}(\omega)}{I_{\text{exc}}(\omega)}, \quad (2-41)$$

where $P_{\text{rad}}(\omega)$ is the far-field irradiated power and $I_{\text{exc}}(\omega)$ is the excitation intensity at frequency ω . This quantity has units of area and is usually normalised by the geometric cross-section of the object (its transversal area)¹⁰. It is also generally found out that the scattering cross-section is larger than its area, meaning that light interacts with the nanoparticle for extensions larger than its geometrical one.

The scattering problem is usually very difficult to solve analytically so numerical simulations have to be done. The calculated power is just the flow of the poynting vector $\mathbf{S} = \text{Re}\{\mathbf{E} \times \mathbf{B}\}$ out of the antenna that reaches the far-field. Numerically speaking, it suffices to locate the power monitors far away from the nanostructure. Mathematically speaking we are just interested in radiative terms, that is, terms that scale as $1/r$, where r is the distance from the scattering object to the observation point in the far-field [12].

Clearly, the Fourier-transform of the scattering cross-section multiplied by the incident irradiance gives the response of the system to this external excitation:

$$P_{\text{rad}}(t) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \sigma_{\text{scat}}(\omega) I_{\text{exc}}(\omega) e^{+i\omega t} d\omega. \quad (2-42)$$

We can assume the scattering cross-section to be a Lorentzian (this is just an *ad hoc* assumption, which arises from the fact that they generally look like resonance functions):

$$\sigma_{\text{rad}}(\omega) \propto \frac{\zeta/2}{(\omega - \omega_0)^2 + (\zeta/2)^2}, \quad (2-43)$$

⁹The full concept of a nano-antenna is developed in chapter 3.

¹⁰For example, for a sphere of radius a the geometric cross-section is just πa^2 .

where ζ is the full-width half-maximum (due to losses) and ω_0 is the position of the peak of the Lorentzian. Moreover, assuming that the excitation intensity is fairly constant throughout the full width-half maximum of the cross-section (*i.e.* $I_{\text{scat}}(\omega) = I_0$), we can easily integrate this equation to obtain:

$$P_{\text{rad}}(t) \propto e^{-\zeta\pi|t|}, \quad (2-44)$$

In other words the inverse of the full-width half-maximum $1/(\pi\zeta)$ is a characteristic time that relates to how fast the emitted intensity dissipates. In the literature people refer to broad modes as super-radiant and narrower modes as sub-radiant [55, 56]. This is terminology borrowed from atomic physics [57], where a collection of dipoles can collectively interact to produce an increase in the emitted intensity in a burst of short duration or, conversely, in a total or partial cancellation of it in a prolonged time [6].

It must be noted that even though I used a Lorentzian above to derive the expression for the scattered power, the general result is not dependent on the particular functional dependence of the scattering cross-section on frequency. The only requisite is, as always, that it is a function that falls off sufficiently fast¹¹.

Another related quantity is the differential scattering cross-section for a specific excitation polarisation $\hat{n}$ as a function of spherical angles (θ, ϕ) [12]:

$$\sigma_{\text{scat}, \hat{n}}(\omega; \theta, \phi) = \frac{P_{\text{rad}, \hat{n}}(\omega; \theta, \phi)}{I_{\text{exc}}(\omega)}, \quad (2-45)$$

This is sometimes written as $d\sigma/d\Omega$, however this is not a true derivative: it is just a function that gives a normalised version of the total radiated power at a specific angle. Angle-resolved and polarisation-resolved scattering cross-section is a more descriptive (more verbose too!) name.

By its definition, the differential scattering cross-section is related to the polarisation-resolved scattering cross-section as follows:

$$\sigma_{\text{scat}, \hat{n}}(\omega) = \int_0^\pi \int_0^{2\pi} \sigma_{\text{scat}, \hat{n}}(\omega; \theta, \phi) \overbrace{\sin\theta d\theta d\phi}^{d\Omega} \quad (2-46)$$

¹¹It would be good to justify the integration on frequencies over the whole real line. We are assuming that the resonance frequency is far away from the DC limit ($\omega = 0$), and that the width is sufficiently narrow so that at close to zero frequency the signal is basically zero. In this case, including the negative frequencies does not create any physical inconsistencies but it facilitates the mathematical manipulation of the integral.

A related quantity can be obtained experimentally via a technique known as dark-field microscopy [40]. In the next chapters, I show the scattering cross-section of specific nano-antennas designed throughout my thesis. Figure 2.7 shows the experimental set-up used to measure the scattering cross-section.

Measured scattering cross-section

The truly measured quantity, however, is equation 2-46 but integrated over $0 \leq \theta \leq \sin \text{NA} = \theta_0 \leq \pi/2$, where NA is the numerical aperture of the objective as illustrated in figure 2.7:

$$\sigma_{\text{scat}, \hat{\mathbf{n}}}(\omega; \theta_0) = \int_0^{\theta_0} \int_0^{2\pi} \sigma_{\text{scat}, \hat{\mathbf{n}}}(\omega; \theta, \phi) \sin \theta d\theta d\phi, \quad \sin \theta_0 = \text{NA}, \quad (2-47)$$

the condition $\theta_0 \leq \pi/2$ indicates that we are only collecting light from the top, and not from all the directions. Moreover, the polarisation $\hat{\mathbf{n}}$ of excitation can be controlled by modifying the orientation of a polariser.

In real samples, nano-antennas are located on top of substrates. These substrates give a reflection contribution that needs to be removed for proper analysis of the antennas. A solution to this problem is to illuminate from the side. However, this also modifies the spectrum, as light can excite modes in the vertical direction of the antennas as shown in figure 2.7 which can give rise to new peaks. For this reason, interest in developing dark-field microscopy from a near-normal incidence have been part of research [58]. In this thesis, all the spectra taken from experiments are done at an angle.

The mechanism of inferring the scattering cross-section is as follows. An extended white source passes through a converging lens placed closed to an aperture that only allows a ring of light to transmit. A condenser is placed after the focal plane of the lens to form image of the source onto the sample containing the nano-antennas. This arrangement has the advantage that it allows to blur out the spatial irregularities in the brightness distribution. This illumination method is a combination of what is called Köhler illumination [44] and a centrally-blocked aperture. As the nano-antenna interacts with the light it scatters photons that can be detected in the far field coupled into a fibre.

These scattered counts $N_{\text{scat}}(\omega)$ have to be corrected due to the dark-counts of the cooled coupled-charge device (CCD), $N_{\text{dark}}(\omega)$. The dark-counts corrected background signal arising from scattering imperfections

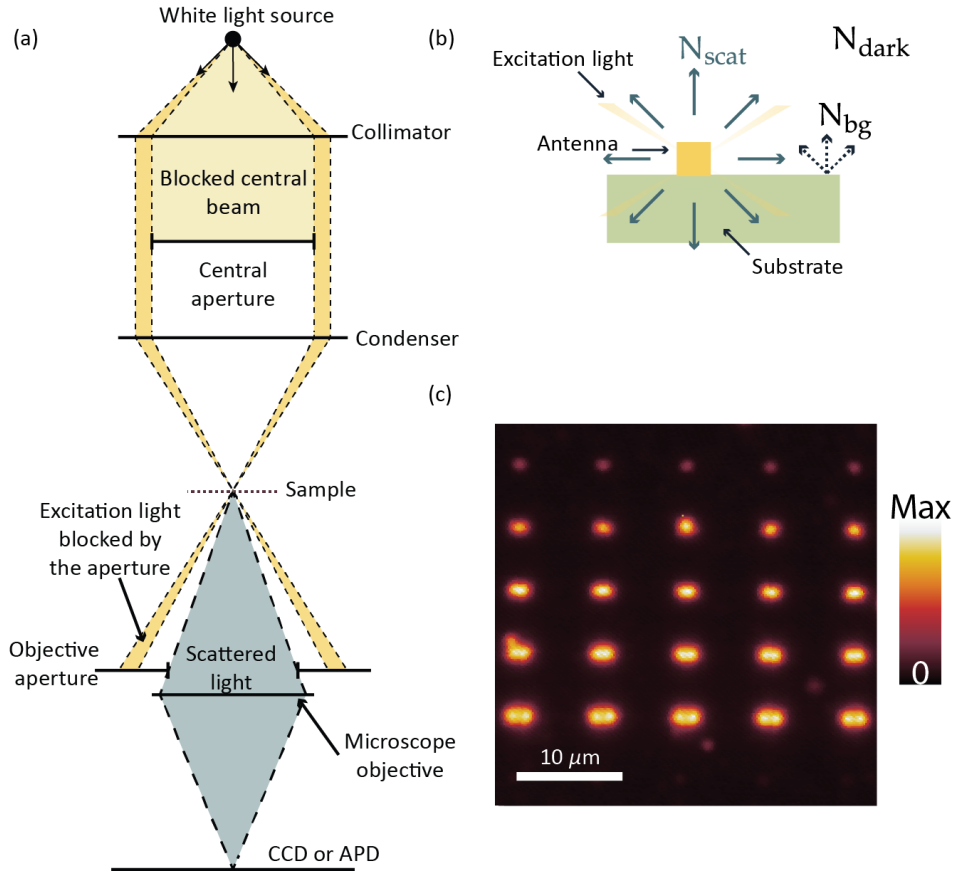


Figure 2.7 (a) Dark-field microscopy set-up. APD stands for avalanche photo-diode and CCD for charge-coupled device. (b) The background and scattered counts are dark-count corrected. The efficiency of the set-up as a function of wavelength is also taken into account, as it modifies the output signal from the system. Equation 2-48 is proportional to the scattering cross-section by a constant independent of wavelength. (c) Experimental confocal counts map of a sample illuminated with dark field microscopy. We can easily observe a variation in the total counts in each antenna. This qualitatively defines which of them are stronger scatterers. In this particular sample, gallium phosphide dimer antennas increase in size from the top to the bottom, being the bottommost the largest ones. More information on these antennas in chapter 6.

in the substrate $N_{bg}(\omega)$ also needs to be removed to obtain the contribution of the nano-antenna. Furthermore, the spectrum of a perfectly white scatterer has to be obtained to characterise the frequency dependent transmission of the system (which contains its quantum efficiency at specific frequencies) but also the frequency dependency of the illuminating lamp. This spectrum is called $N_{ref}(\omega)$. In summary:

$$\sigma_{scat, \hat{n}}(\omega, \theta_0) \propto \frac{N_{scat, \hat{n}}(\omega, \theta_0) - N_{bg, \hat{n}}(\omega, \theta_0)}{N_{white, \hat{n}}(\omega, \theta_0) - N_{dark, \hat{n}}(\omega, \theta_0)}, \quad (2-48)$$

where the proportionality constant has the units of area and does not depend on frequency.

It must be noted that a fully-vectorial theoretical treatment of a partially-coherent white source imaged with a condenser onto a sample is far from trivial [44, 59]. The numerical simulations are carried out by creating an annular monochromatic source that excites a nano-antenna by adding two out-of-phase gaussians so that the field in the inner region is cancelled out. Finally, the far-field radiation is integrated over the solid-angles defined by the numerical aperture.

Absorption cross-section

Just as we can define the scattering cross-section as a measure of the incident energy coupled to the far-field, we can define the absorption cross-section as a measure of the energy that remains in the near-field. The sum of both absorption and scattering cross-sections is called extinction and it is related to the imaginary part of the scattered field via the optical theorem [12, 44]. The extinction is usually measured via transmission measurements and is based on the assumption that the substrate is thin enough to actually detect something on the other side.

Absorption has contributions from all those modes that lose their energy in the near field. As I tried to emphasise throughout this whole chapter, macroscopically all of them arise from the same complex permittivity $\epsilon(\omega)$. Microscopically, they can be understood as whole zoo of processes [60, 61] that contribute to dissipating energy in the near-field as shown in figure 2.8(a)-(d). In particular, (a)-(d) can be found in metals, while for a very good insulator the processes in (d) are the most prominent. Furthermore, other non-radiating processes like the existence of localised non-radiating modes of figure 2.8(e) contribute to decreasing the overall far-field properties of the nano-object.

In general, absorption increase at energies above the band-gap of the material given that the energy can be used to excite electrons to the con-

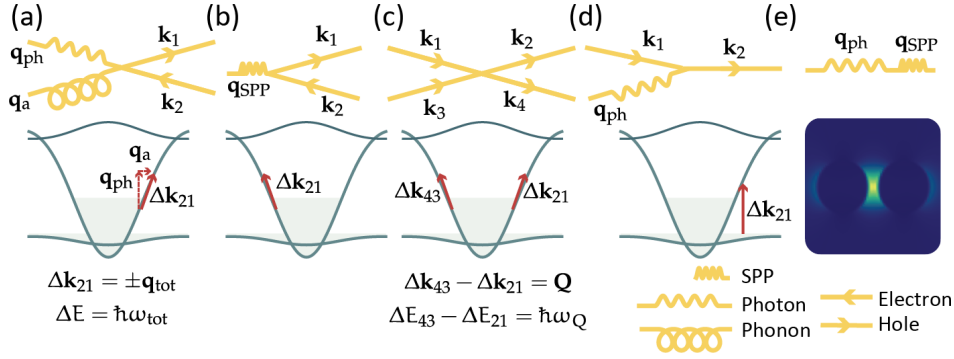


Figure 2.8 Different processes that contribute to increase the absorption cross-section. (a) Phonon assisted absorption: a phonon provides the necessary momentum matching together with a photon to produce an electron-hole transition. (b) Landau damping: an SPP with the matching momentum and energy decays into an electron-hole pair. (c) Umklapp process: electron-electron scattering. This scattering is essentially coulombic, but can be easily pictured as an elastic scattering between classical point-like particles. (d) Direct band transition by a photon from the exciting source with matching momentum and energy. (e) Near-field non-radiating electromagnetic modes that contribute to the decrease in the far-field properties of the antenna. Note: $\mathbf{q}_{\text{ph}}$ is the momentum of a photon, $\mathbf{q}_{\text{a}}$ the momentum of an acoustic phonon, $\mathbf{q}_{\text{tot}} = \mathbf{q}_{\text{a}} + \mathbf{q}_{\text{ph}}$, $\hbar \omega_{\text{tot}}$ the sum of the energies of the photon and assisting phonon, $\mathbf{Q}$ is a vector in the reciprocal lattice of the crystal, $\hbar \omega_{\mathbf{Q}}$ the energy associated to that momentum via the dispersion relation of the crystal.

duction band [24, 61]. Certain processes are beneficial for near-field applications as is shown in chapter 4 where hot-electrons are used to drive chemical reactions in the nano-scale. However if low-losses are desired, then metals, having an intrinsically small band-gap, should be replaced with larger gap semiconductors. Chapter 5 deals with low-loss dielectrics and how they can be exploited for nanophotonic applications.

2.4 CONCLUSIONS

In this chapter I presented both a macroscopic and a microscopic description of surface plasmon polaritons. Macroscopically they can be understood as modes localised to the surface of metallic boundaries or nano-objects. It was pointed out that the only parameter that linked this electromagnetic modes with the inner structure of the metals was the dispersive dielectric permittivity $\epsilon(\omega)$. This function can be modelled microscopically in many ways and I have just sketched a classical derivation based on the Drude-Sommerfeld model of matter. A related quantum mechanical description takes into account all the possible transitions of an electron in its surrounding environment. This description is still incomplete as it does not account for electron-electron interactions, nor does it take into account Fermi exclusion principle, electron-phonon scattering, a crystalline lattice, etc. The same way that the macroscopic theory buries all the intricacies of the specific materials in the electrical permittivity, the classical and semi-classical descriptions briefed above bury a plethora of interactions with the environment in effective parameters or effective Hamiltonian terms. The theory is far from complete but it gives us a glimpse into why the vocabulary is shifted from “electromagnetic modes” into “surface plasmon polaritons”. It tries to convince that naming these light modes in matter as quasi-particles is not (just) a caprice of the modern-scientist seeking buzz words.

Finally, cross-sections were defined as these quantities are ubiquitously found throughout this thesis. They give us a measure of the fraction of energy of an exciting source that interacts with a nano-antenna that either returns to the far-field or stays in the near-field.

3

NON-CONCENTRIC RING DISK CAVITIES FOR RADIATIVE RATE ENHANCEMENTS

Metallic optical nano-antennas [13, 54] are the quintessential plasmonic elements. Their main goal is to enhance light-matter interactions in the nano-scale and out-couple the near-field energy to a detectable far-field. In other words, one would like the antennas to have a strong coupling to far-field modes, so that it can be both excited and detected from the far-field. Both the geometry and the material directly influence the properties of the nano-antenna.

The experimental study of light-matter interactions with plasmonic nano-antennas is not new [47, 62]. Several works have utilised metallic nano-spheres to couple to fluorescent molecules [62–66] or quantum dots [67–69]. The basic theory of dipolar like single-photon emitters and the electromagnetic field is laid out in the introduction. In this chapter, we shall concentrate ourselves with the main advantage of using nano-antennas to out-couple light into the far-field.

In this chapter, I present a theoretical introduction to the concept of nano-antennas coupled to single-photon emitters. The theory laid out here is not only applicable to metallic nano-antennas, but can also be utilised to understand the phenomena of chapters 5 and 6. Firstly, in section 3.1, I describe the single-photon emitters used: colloidal nano-crystals. There, their advantages are laid out and some of their properties mentioned. Furthermore, several experiments are presented that back the widely known theoretical results. Secondly, I describe the properties of isolated nano-antennas: what makes them efficient scatterers and which parameters quantify the performance of a nano-antenna. Furthermore, I introduce the non-concentric disk-ring cavity (NCRDC): the antenna that is used throughout this chapter to modify light-matter interactions. Section 3.3 is solely dedicated to the fabrication and optical characterisation of the NCRDC. I finish this chapter with section 3.4 where the coupling between both objects is explained. Theoretical predictions for emitters in the vicinity of these nano-antennas are presented and several experiments proposed to corroborate them.

3.1 COLLOIDAL NANOCRYSTALS

The oil crisis in the late 1970s fuelled research directions into other kinds of energy harvesting. Among them, exploiting solar energy via several photochemical process started to seem appealing not only to researchers but also to politicians. In the early 1980s, CdS and TiO₂ colloidal nano-particles were being routinely synthesised. This, together with the discovery of quantum-size effects in nanometer sized semiconductors [70, 71], triggered the development of several techniques to fabricate many other species of colloidal quantum dots. Colloidal nano-crystals

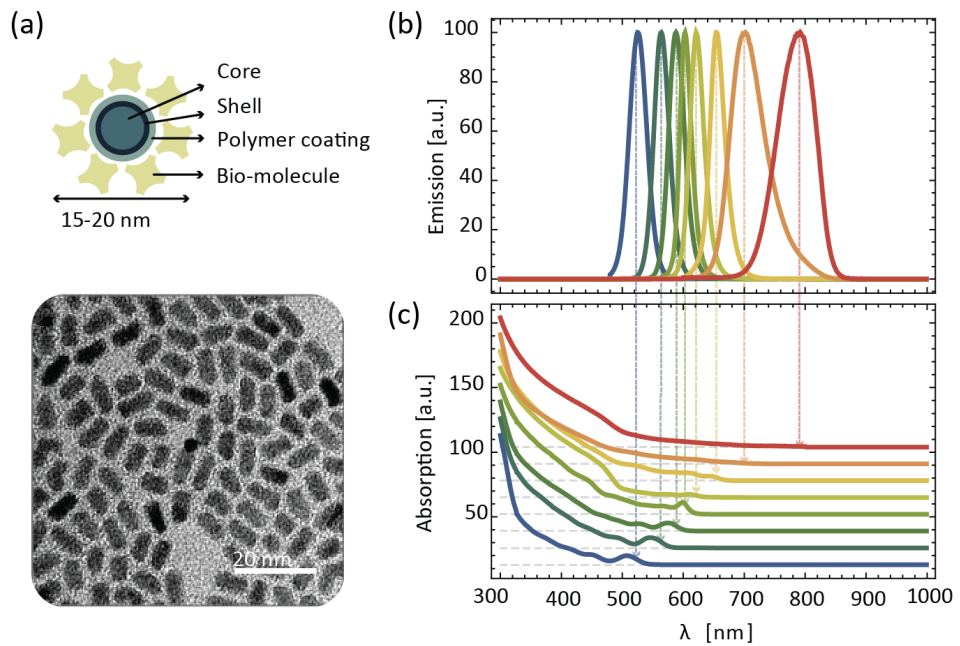


Figure 3.1 (a) Scheme of a generic colloidal nano-crystal and a transmission electron micrograph of several CdSe/CdS nano-crystals taken from the manufacturer (ThermoFisher). (b) Representative photoluminescence spectra of several colloidal nano-crystals. (c) Representative absorption spectra of the quantum dots in (b). They have all been shifted upwards for clarity. However, the zero absorption lines have been highlighted with dashed grey lines. The quantum dots with resonances between 525 nm – 655 nm have a core:shell composition of CdSe/ZnS. The quantum dots with emission peaks at 705 nm and 800 nm are composed of a CdSeTe core and a ZnS shell. All spectra and TEM from [72].

(also known as colloidal quantum dots) are mesoscopic objects capable of absorbing and emitting light at wavelengths defined chiefly by the size of the structure [73–75]. Their importance lies in that they can emulate the quantised behaviour of fluorophores or other single-photon emitting nano-objects, but on a more controllable scale. The quantisation of their

spectra arises as a consequence of electron confinement. Figure 3.1(a) shows a scheme of an epitomical nanocrystal together with a transmission electron micrograph. The easiest model for these objects is a spherically symmetric core of a specific semiconductor, covered by a thicker shell of another semiconductor. Quantum dots come in many flavours [76], among them, ZnSe/ZnS [77], CdSe/CdS [78], CdTe/CdS [79, 80], CdHgTe/CdS [81] and HgTe/CdS [82]. As can be seen, the usual shape of the nano-crystals is far from spherical. However, this does not hinder the quantisation of the energy spectrum, as the system is still confined within the boundaries of the shell. This asymmetry clearly modifies the induced transition dipole moment that couples to the electromagnetic field, being, in the case of colloidal nano-crystals, degenerate along the short transversal axis and of smaller magnitude for the vertical longitudinal axis.

Figure 3.1(b) shows a representative image of the absorption and emission spectra of several quantum dots that can readily be purchased from international vendors. The spectra depend strongly on the environment in which they are immersed, be it a solvent or a rigid polymeric matrix.

In sub-section 3.1.1 I present a brief theory of how the quantised energy levels appear in a very simple model of a quantum dot. However, it must be stressed out that colloidal nano-crystals are not only likeable because of their quantum but also their chemical properties. Their surfaces are easy to functionalise with organic ligands [74], a property that is exploited in sub-section 3.1.2 to efficiently deposit quantum dots on quartz.

3.1.1 Quantised spectrum

There are many phenomena conspiring for the specific look of the spectrum of a colloidal nano-crystal. Firstly, the crystal structure of the semiconductors has to be taken into account, which complicates the simple treatment of a free electron, producing bands. Secondly, quantum confinement modifies the spectrum of the electrons by quantising their energy levels. Thirdly, electrons excited from the Fermi level can interact with the positive hole left behind to form excitons, adding a Coulombic central potential to the already complicated problem.

All of these effects can be understood by applying several approximations. First, we can bury the complex structure of the Bloch bands in the mass of the electron if we assume the electron has an energy and momentum close to a band extrema, be it a maximum or a minimum. We

must also assume that the properties of an unbounded crystal also hold for the semiconductor in the core of the quantum dot. In this case, the intrinsically complicated dispersion relation can be approximated with:

$$E_k = \frac{\hbar^2 k^2 f(k)}{2m_0} \approx \frac{\hbar^2 k^2}{2m_0} \left[\underbrace{f(k_0)}_{\text{Constant}} + \underbrace{f'(k_0)}_{=0} (k - k_0) + \frac{1}{2} f''(k_0) (k - k_0)^2 \right] \\ = \frac{\hbar^2 k_0^2}{2m^*}, \quad (3-1)$$

where k is the absolute value of the wavevector, $\hbar$ is Planck's constant and $f(k)$ is a complicated function that depends on the specific form of the crystal. The effective mass $m^* = 2m_0/f''(k_0)$ is a modified effective mass for an electron in an extremum of the band. This re-interpretation of mass as essentially the radius of curvature of the energy is useful for the theoretical simplicity that follows, and, in fact, is not unique to condensed matter physics as it can also be used to understand why the Higgs boson field gives mass to the elementary particles [26].

Secondly, we need to take into account the material change at radius a . This is just textbook quantum confinement [6, 24], which revolves around an electron in a box, *i.e.* a particle inside a potential well. In the case of a colloidal nano-crystal, we work with spherical coordinates to define the well. The solution which is analytically solvable is that of an infinite well of radius a , so that the potential, in spherical coordinates, ends up being:

$$V(r) = \begin{cases} 0 & \text{if } r \leq a, \\ +\infty & \text{if } r > a. \end{cases} \quad (3-2)$$

By using this potential, and applying the necessary boundary conditions, we can find that the energies are given by the eigenvalues of Schrödinger equation:

$$E_{nl} = \frac{\hbar^2 \chi_{nl}^2}{2ma^2}, \quad (3-3)$$

where χ_{nl} are the roots of the spherical Bessel function, which naturally appear as a basis when solving the wave equation in spherical coordinates. In this notation $n \in \mathbb{Z}$ labels the roots of the l -th spherical Bessel $j_l(x)$. In other words:

$$j_l(\chi_{nl}) = 0. \quad (3-4)$$

Taking into account both approximations, we can obtain the spectrum of an electron close to the extremum of a band in a spherical potential by simply modifying the mass. Finally, we must take into account the

Coulombic interaction that appears between an electron and a hole, called an exciton. Solving this textbook problem we find that the energies must be of the form:

$$E = E_g - \frac{\frac{m_e^* m_h^*}{m_e^* + m_h^*} \frac{|e|^4}{2\epsilon^2 \hbar^2}}{\tilde{n}^2} = E_g - \frac{R}{\tilde{n}^2}, \quad (3-5)$$

where E_g is the energy gap between valence and conduction bands of the core semiconductor, $-|e|$ is the charge of the electron, $m_{e/h}^*$ the Bloch band structure modified mass of the electron/hole, ϵ is the refractive index of the core semiconductor¹ and, most importantly, $\tilde{n} \in \mathbb{N}_{\geq 1}$ is the Coulomb energy level index.

When the radius of the core semiconductor is just a few times larger than the electron-hole mean distance, then we can simply write the whole energy spectrum of the quantum dot as [73]:

$$E_{nl,\tilde{n}} = E_g - \frac{R}{\tilde{n}^2} + \frac{\hbar^2}{2(m_e^* + m_h^*)a^2} \chi_{nl}^2, \quad (3-6)$$

which can be understood as basically an exciton in a well. The first two terms contain information about internal structure of the electron-hole interaction and the third term has the information of the centre-of-mass electron-hole as a unity, in the presence of a potential well. Dephasing could be used to understand the appearance of surface modes or the coupling to other environmental modes. This would provide a certain width to the otherwise discreet delta-like spectrum. This phenomenon is referred to as homogeneous broadening. These other coupling mechanisms are usually undesired as they diminish the overall intrinsic quantum yield q_i of the emitter, defined as the ratio between emitted photons to absorbed photons [13]. Similarly, a large mismatch between the crystal structures of the core-shell layers can lead to blinking [83], an undesired effect for efficient on-demand single photon sources.

It must finally be mentioned that real samples contain a dispersion in the actual size of colloidal nano-crystals. This causes the actual measured absorption spectrum to be broader than would have been expected, even at low temperatures. Experimental spectra seen in figure 3.1(b) show broad resonances. This phenomenon is known as homogeneous broadening.

¹How could this macroscopic electromagnetic property filter into the equations of motion of quantum mechanics? Simply, the Coulomb interaction is a manifestation of an electromagnetic interaction between two charged particles. Of course, the simplest answer is however: that it is simply Coulomb's law.

Colloidal nano-crystals are therefore a suitable platform to study light-matter interactions with emitters whose energy levels are quantised. Their main benefit lies in the fact that quantum confinement discretises the energy levels, which in turn, contribute to emitting single photons. Their purity is ultimately defined by their intrinsic quantum yield and whether they blink. Inhomogeneous broadening will almost certainly occur in all chemically fabricated colloidal nano-crystals.

In the next sub-section, I show how to covalently bind colloidal nano-crystals to quartz substrates, exploiting their surface functionalisation.

3.1.2 Activation and deposition

Figure 3.2 shows the scheme of colloidal nano-crystal deposition. A thin layer of poly(methyl methacrylate) (PMMA) is spun coat onto a quartz substrate (with or without nano-antennas, more details in the next two sections) and holes of <50 nm in diameter are patterned with electron beam lithography. The whole patterning process is described in more detail in section 3.3 and, specifically, in figure 3.7. The PMMA-exposed quartz is functionalised with silane-PEG-biotin monolayer, shown in figure 3.2(a). CdSe/ZnS colloidal nano-crystals are purchased covalently functionalised to streptavidin (STV), a biotin binding molecule, which can covalently bind to the silane-PEG-biotin monolayer previously deposited on the coverslip.

In particular, 5 mg of silane-PEG-biotin powder are dissolved in 0.5 ml of ethanol by sonicating a plastic vial for 2 min at high power. The solution is deposited on top of the patterned coverslip for 30 min to form the monolayer. After this, the sample is cleaned with ethanol and water and dried with a nitrogen gun. While waiting for the monolayer formation to occur, 5 μ l of colloidal quantum dots are dissolved in 0.5 ml of phosphate saline buffer (PBS). The quantum dot solution is centrifuged at 3000 rpm for 1 min and around 100 μ l of the supernatant are separated from the rest of the solution. The patterned sample is dipped in PBS buffer and immediately after a droplet of ~ 100 μ l of quantum dot solution is carefully deposited with a pipette on top of a specially designed holder that allows the sample to be facing down. This step is crucial, as otherwise large numbers of non-specific quantum dot binding could occur. The sample is left to react for 12 h, after which careful rinsing with water and PBS follows. This configuration is schematised in figure 3.2(b). Finally, the PMMA is lifted-off with acetone for 12 h and the sample is ready to be imaged. Figure 3.2(c) shows a photoluminescence map of the desired

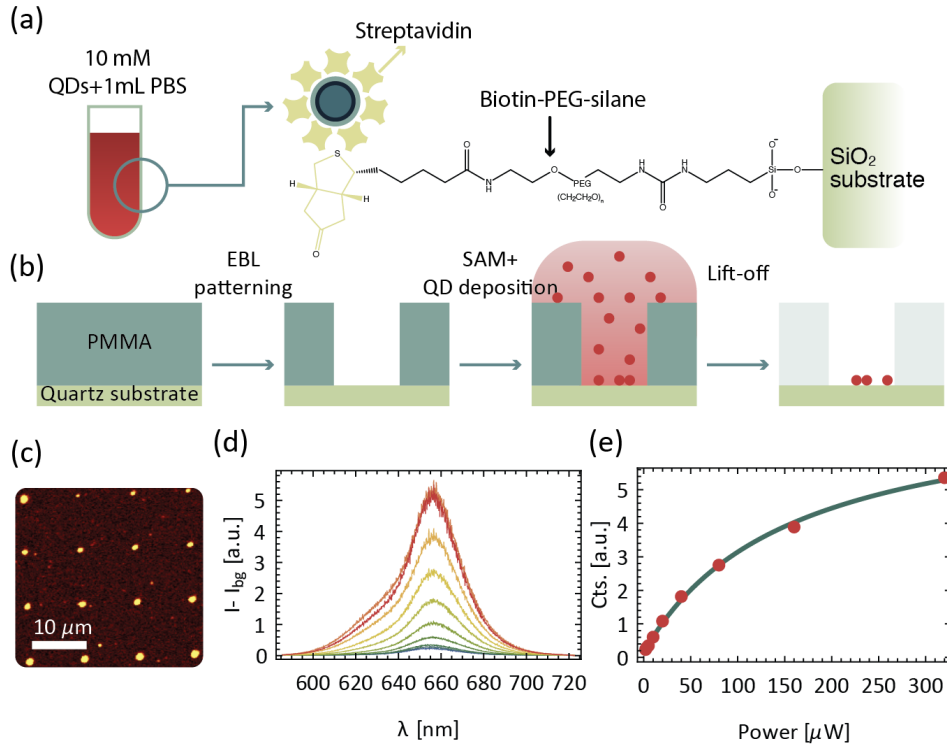


Figure 3.2 Scheme of a colloidal nano-crystal deposition on quartz. (a) The STV-QDs are suspended in a PBS buffer and (b) a droplet is deposited onto the patterned and properly functionalised substrate for 12 h. After lift-off of the PMMA resist, the quantum dots are deposited only in the regions of interest. (c) Photoluminescence map of a successful deposition of quantum dots in a periodic array. (d) Emission spectrum and (e) saturation curve of the deposited quantum dots. The saturation power is 155 μW . The saturation intensity can be calculated knowing the numerical aperture of the objective used to excite the QDs. In particular $I = P/[\pi(\lambda/2\text{NA})^2] = 56\ \text{kW cm}^{-2}$, where $\lambda = 533\ \text{nm}$.

final arrangement of quantum dots, located solely in the electron-beam exposed regions.

This protocol is the same, whether the substrate was originally patterned with nano-antennas or not. Several control experiments can be performed to understand the photoluminescence of this CdSe/ZnS nano-crystals. For example, in figure 3.2(c) we can observe a confocal map of a successful deposition of nano-crystals on a patterned sample. The excitation laser was focused with a NA=0.9 objective and the wavelength chosen was 533 nm. In figure 3.2(d) we can see the intensity plots of a selection of quantum dots as the intensity increases. The curves were fitted with gaussians, from where the maximum counts value and the width could be obtained. Figure 3.2(e) shows the saturation curve of maximum counts as a function of intensity, displaying a typical saturation curve. It is worth mentioning that the quantum dots showed no photobleaching throughout the whole experiment, therefore rendering them stable.

3.2 NANO-ANTENNAS

3.2.1 General introduction

Commercial antennas work in the radio and microwave part of the spectrum. The mesoscopic analogue is the optical antenna, which enhances the local light-matter interactions [13], as schematised in figure 3.3. Radio-engineers quantify the appeal of a certain antenna by defining quantities such as directivity and gain. The quality of an antenna is therefore directly related to its ability to communicate with the far-field and transduce a near-field signal into a detectable region, and conversely to the capability of the far-field to efficiently interrogate the near-field state of a nano-object via the antenna mediator. In radio- and microwave engineering, the antennas are fed with AC currents. The textbook example is a centre-fed antenna [12].

As discussed in section 2.3, we have to be careful in defining the parameters of interest. Similar to the definition of scattering cross-section, we just need to define the radiated power of an antenna and compare it to a magnitude which represents the whole interaction of the antenna with light. In fact, the scattering cross-section compared to the extinction cross-section is one of the parameters of interest in the characterisation of the antenna, and is called efficiency of radiation at a specific polarisation of excitation:

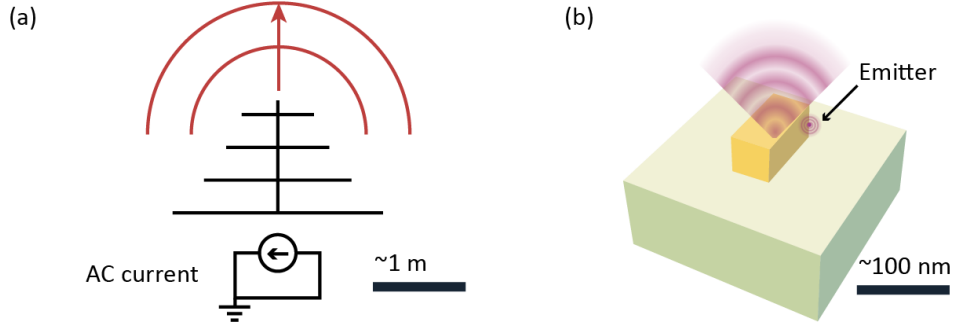


Figure 3.3 Scheme of a conventional (a) and an optical antenna (b).

$$\eta_{\text{rad},\hat{n}}(\lambda) = \frac{\sigma_{\text{scat},\hat{n}}(\lambda)}{\sigma_{\text{ext},\hat{n}}(\lambda)} = \frac{P_{\text{rad},\hat{n}}(\lambda)}{P_{\hat{n}}(\lambda)} \quad (3-7)$$

where $P_{\hat{n}}(\lambda) = P_{\text{rad},\hat{n}}(\lambda) + P_{\text{loss},\hat{n}}(\lambda)$ is the sum of both total radiated $P_{\text{rad},\hat{n}}$ and dissipated power $P_{\text{loss},\hat{n}}(\lambda)$.

In complete analogy to the angular distribution of scattering cross-section, another more primitive parameter is an effective radiated power per solid angle, which receives the name of directivity $D(\theta, \phi)$ and provides information about the directionality of the radiation pattern:

$$D_{\hat{n}}(\theta, \phi; \lambda) = 4\pi \frac{p_{\text{rad},\hat{n}}(\theta, \phi; \lambda)}{P_{\text{rad},\hat{n}}(\lambda)}, \quad P_{\text{rad},\hat{n}}(\lambda) = \iint p_{\text{rad},\hat{n}}(\theta, \phi; \lambda) d\Omega, \quad (3-8)$$

where $p_{\text{rad},\hat{n}}(\theta, \phi; \lambda)$ is the radiation pattern as a function of spherical angles when excited with light polarised in the $\hat{n}$ polarisation.

As has been already explained, the importance of an antenna is its coupling to nano-emitters: they are near to far-field transducers, and *vice versa*. All the properties previously mentioned can be studied either with an emitter in the vicinity of the antenna or with a plane wave illuminating from infinity. The latter is equivalent to placing a dipole at an infinite distance from the antenna. The technological importance of nano-antennas thus lies in the fact that they can control the radiative properties of single-photon emitters [84]. For example, for surface enhanced fluorescence [62, 64, 85, 86], spontaneous emission engineering [17, 18, 87], strong coupling [22, 88], surface enhanced Raman scattering [34, 35, 89] and for energy extraction in solar cells [90].

The main concerns when fabricating nano-antennas are the losses. It is important to understand the origin of losses and how it relates to photonics. Every mechanism that is non-radiative is defined as a loss, *i.e.* electromagnetic modes that are non-detectable in the far-field. Examples of losses include Ohmic heating in metals due to the material's intrinsic properties. These intrinsic losses are buried in the imaginary part of the refractive index of the materials, as is described in section 2.2. However the geometry can also play a role in that it can support localised SPPs that cannot couple to the far-field.

It is interesting to realise that in the language of photonic microresonators [19, 91], as schematised in figure 3.4, the coupling to the far-field is considered as a loss and near-field modes are the desired effects. However, losses due to dissipation are still considered detrimental. In short, cavities and antennas are completely different objects.

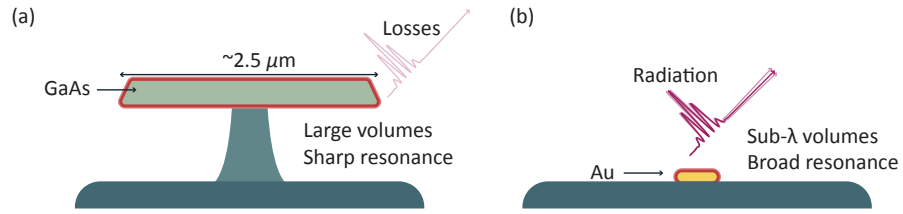


Figure 3.4 (a) A GaAs micro-resonator vs. (b) a gold optical nano-antenna.

Another differing point is that the resonances in the micro-resonators are very sharp, quantified with what is called the Q-value:

$$Q = \frac{\omega_0}{\delta\omega}, \quad (3-9)$$

where ω_0 is the resonant frequency and $\delta\omega$ some characteristic measure of the width of the resonance. In comparison to micro-resonators and photonic cavities ($Q \sim 10^3 - 10^{10}$ [91, 92]), metallic nano-structures have lower Q-values: $Q \sim 3 - 30$ [93]. The interpretation is similar though: low Q-values imply that the energy cannot be localised in the near-field for too long before it's radiated or lost.

In summary, photonic micro-cavities are characterised by high Q-values, narrow bandwidths, very slow response and largely extended modal volumes. In contrast to this, optical nano-antennas are characterised by small Q-values, very broad bandwidths, fast response and highly confined modal volumes.

Figure 3.5 shows various examples of nano-antennas fabricated via top-down fabrication techniques [13, 54]. More examples can be found in

the remaining of this thesis. In what follows, I present the theoretical optical properties of the nano-antenna to be used in this chapter: the non-concentric ring disk cavity [55, 56].

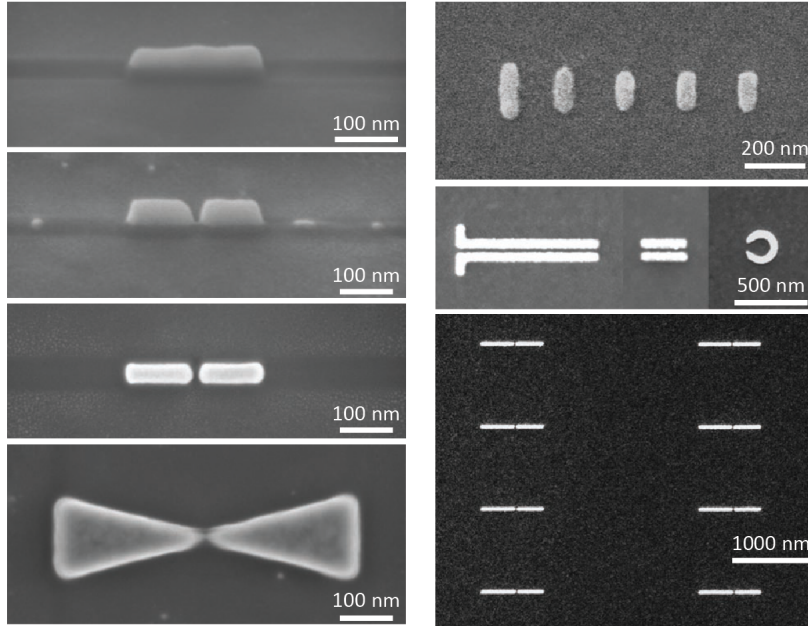


Figure 3.5 (a)–(c) Dimers with various gap sizes of around 10 nm fabricated with focus ion beam milling. (d) Bow-tie antenna fabricated with focus ion beam milling. (e) Yagi-Uda antenna, (f) gap antennas and (g) plasmonic waveguides and a split ring resonator, all fabricated with electron beam lithography. All examples taken from reference [54].

3.2.2 Non-concentric ring-disk cavities

Most of the simplest nano-antenna configurations present strong dipolar resonances [55] in their scattering cross-sections. This is also revisited in chapter 5 section 5.2. This means that the antenna can be effectively described as an induced radiating dipole, like the sphere case of section 2.1.2. Literature usually assigns the labelling of radiative mode to bright modes and non-radiative modes to dark modes, even if they are only negligibly radiative. Ways of coupling these non-radiative modes to the far field consist in breaking the symmetry. Symmetry can be broken in various ways: by anisotropic materials, asymmetric geometries or non-normal excitation light. The latter is one of the reasons as to why the scattering spectrum measured in a dark-field spectra can differ from a theoretical normal incident plane electromagnetic wave. This was briefly

mentioned in section 2.3. In this work we studied the breaking of symmetry of the geometry of a specific nano-antenna.

Figure 3.6(a) shows the experimental scheme that we wish to achieve in these studies. A non-concentric ring-disk cavity (NCRDC) interacting with colloidal nano-crystals for enhanced radiative rate generation. To analyse the properties of the nano-antennas, figure 3.6(b) shows the cross-sections normalised to the geometric cross-section of gold NCRDCs with varying gap size. Gold was chosen for being relatively easy to deposit [49] and because it is amenable to surface functionalisation [69, 94]. This simulated quantity does not necessarily need to correlate with the measured quantity of the next section, as here it represents the total scattered field integrated, not just the field detected in the far-field. Higher-order resonances can couple to the incident electromagnetic field and made to couple in such asymmetric structures to give a much richer spectrum. The interaction between a sharp non-radiating mode and a broad far-field mode is called a Fano resonance. This phenomenon is not new to wave mechanics, as it can happen in strongly coupled systems [95, 96].

In view of this, the spectral response can be understood as the hybridisation of two dipolar modes: one of the disk and the other of the ring [55, 97]. Figure 3.6 shows the simulated spectra of a ring and a disk. The Fano resonances arise as destructive interaction between the radiating dipolar mode of the disk at around 600 nm and the dark tail of the dipolar resonance of the ring. The community likes using words lent from quantum chemistry, where, when studying the interaction between orbitals in a Hartree-Fock approximation, different combinations arise as a solution to the molecular problem. Some of these solutions are anti-bonding, indicating that the energy of the molecule is higher than the energy of its separated species. Another interaction is bonding, and in this case the electron density is nearly evenly spread out in-between the molecules forming the bond.

Bonding and anti-bonding interactions do not, however, need to be mystified with the *deus ex machina* invocation of molecular chemistry to explain what is actually happening in the plasmonic nano-antenna. They can also be easily understood as two interacting springs [23]. As we can all very easily verify, the eigenmodes of two coupled springs of masses m_1 , m_2 with coupling κ and frequencies ω_1 and ω_2 get modified into two new modes:

$$\omega_{\pm}^2 = \frac{1}{2} \left[\omega_1^2 + \omega_2^2 \pm \sqrt{(\omega_1^2 - \omega_2^2)^2 + 4 \frac{\kappa^2}{m_1 m_2}} \right], \quad (3-10)$$

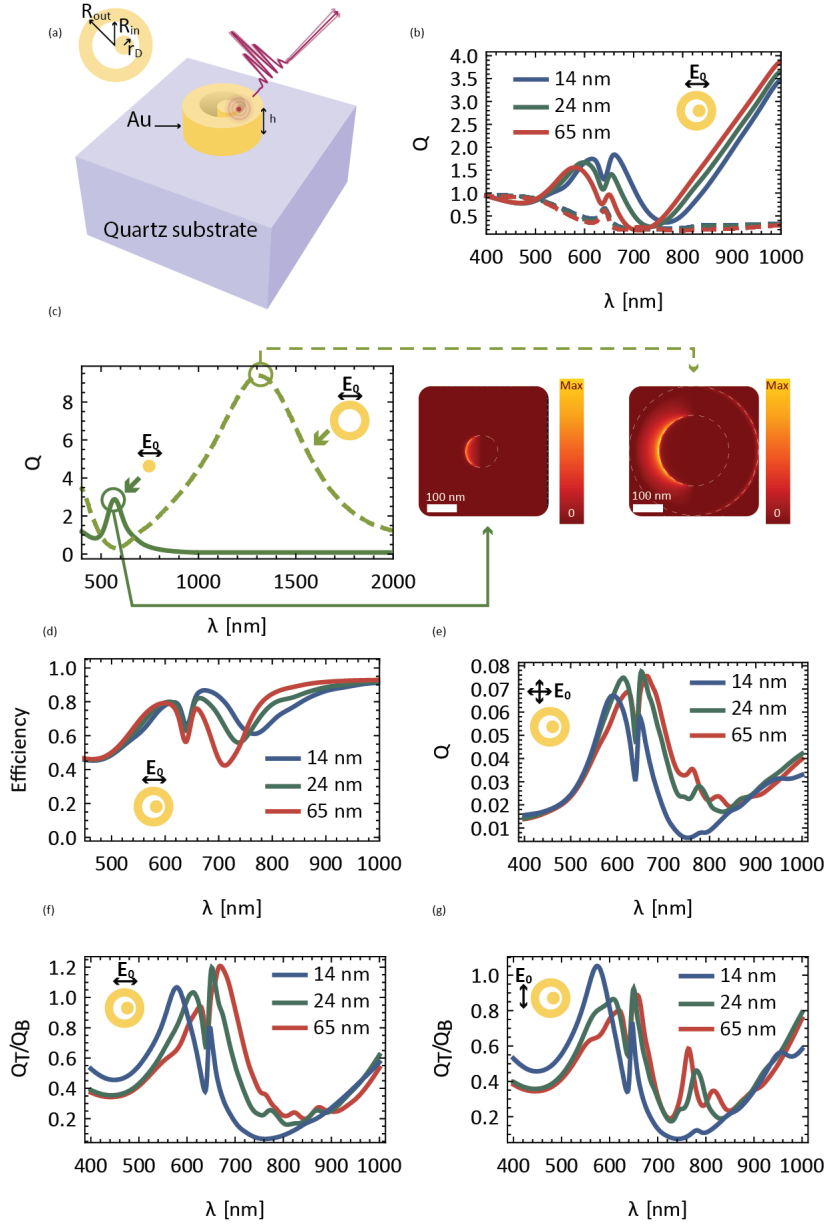


Figure 3.6 (a) Scheme of a NCRDC interacting with a colloidal nano-crystal. Throughout this whole chapter: $h=60$ nm, $R_{out} = 220$ nm, $R_{in} = 120$ nm, $r_D = 55$ nm. (b) Simulated scattering (bold lines) and absorption (dashed lines) cross-sections for NCRDCs of various gap sizes. The simulated excitation light is a plane wave. (c) Origin of Fano resonance. Hybridisation model of two interacting resonances. The right side shows the charge distribution on the structures calculated as $(\mathbf{E}_{out} - \mathbf{E}_{in}) \cdot \hat{\mathbf{z}} = \sigma/\epsilon_0$ evaluated at $h = 60$ nm, *i.e.* the top surface of the antenna. (d) Simulated efficiency of scattering for plane-wave illumination. (e) Simulated dark-field spectra of unpolarised excitation light for NCRDCs of various gaps. (f)–(g) Directionality into the detection objective as a function of wavelength for horizontal (f) and vertical (g) polarisations.

where clearly the strength of the interaction κ determines how far the new modes are from the original two modes. The higher frequency (energy) mode is usually called anti-bonding in chemistry and the lower energy one is called bonding. In our case, this interaction will be parametrised with the gap size between the ring and the disk.

In particular, the broad resonance observed around 590 nm in figure 3.6(b) is mainly a bonding combination of the anti-bonding ring dipole and the disk dipole. The lower energy (higher wavelength) resonance corresponds to a bonding combination of the disk dipole and bonding-type ring dipole². The resonance that got activated due to the geometry breaking is, as can be seen from the modulation in the gap, the high energy anti-bonding ring dipole, due to the presence of the disk.

These antennas can have a strongly wavelength dependent scattering efficiency as shown in figure 3.6(d). We can clearly observe the footprints of the interaction between the displaced disk and the ring. For example, at around 620 nm we get a sharp decrease in the far-field coupling efficiency, given by an increase in absorption as demonstrated by the dash lines in figure 3.6(a).

All these considerations notwithstanding, our experimental set-up consists of a dark-field microscope which excites the antenna in a completely different way as that of a plane wave. Figures 3.6(e)-(g) take this detail into consideration to help compare the measured spectra with the scattering cross-section of the nano-antennas. The far-field power was integrated over the solid angle defined by the numerical aperture $\theta = \arcsin \text{NA}$ as mentioned in section 2.3 and the results of two simulations with perpendicular polarisation were summed up to emulate the behaviour of the unpolarised light source in our set-up. We can see a similar Fano dip at around 620 nm, but more spectral structure starts appearing around the IR due to coupling to higher order modes by breaking the symmetry of the illumination.

Finally, we need to calculate how much power gets scattered into the objective relative to how much power is forward-scattered into the quartz substrate. This is just a measure of directionality:

$$\frac{Q_T}{Q_B} = \frac{\int_0^\pi \int_0^{2\pi} D_{\hat{n}}(\theta, \phi; \lambda) \sin \theta d\theta d\phi}{\int_\pi^{2\pi} \int_0^{2\pi} D_{\hat{n}}(\theta, \phi; \lambda) \sin \theta d\theta d\phi}, \quad (3-11)$$

²Note that in the case of the disk I am only talking about the dipole mode and not the bonding or anti-bonding dipole as this structure has only one mode. However, when talking about the ring, we can obtain different charge distributions for higher and lower energies. Inspired by the quantum chemistry, we adopt the plasmonic community convention of calling the higher energy mode the anti-bonding and the lower energy mode the bonding.

assuming the detector is at $\theta = 0$.

Figures 3.6(f)-(g) show the relevant spectra for two orthogonal illumination polarisations. As we can observe, the back-scattered light is usually dominant, except in a very limited wavelength range around 680 nm for large gaps for horizontally polarised excitation light. In other words, as is to be expected, most of the power gets sucked up by the quartz substrate, reducing the effective scattering cross-section of the nano-antenna.

Despite this directional drawback, as will be seen in section 3.4 small-gap NCRDCs can enhance the radiative rate of single photon emitters located in the gap up to around 200 times. The next section, describes the fabrication and characterisation protocols to pattern Au NCRDCs on quartz substrates.

3.3 FABRICATION AND CHARACTERISATION

Non-concentric ring-disk cavity nano-antennas were fabricated following a two-step electron beam patterning protocol. Figure 3.7 shows the basic protocol at each step. The first step consisted in patterning the ring and the second step the disk. Structures with varying gaps were fabricated and also single disks and single rings to make comparisons with the primitive structures.

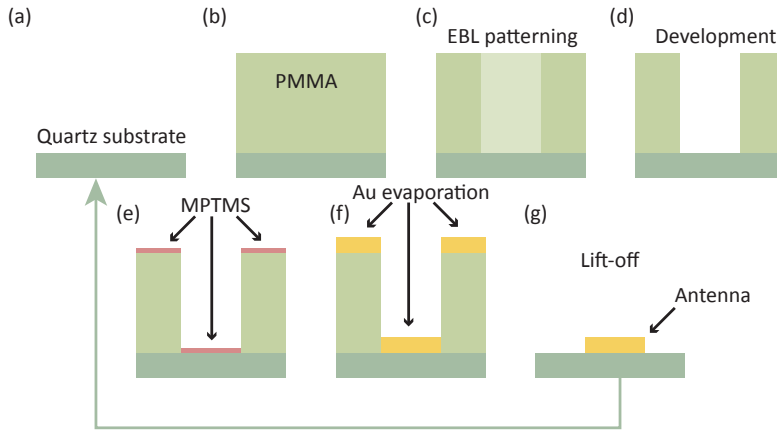


Figure 3.7 Fabrication procedure of one step of the NCRDC. The second step follows a similar recipe.

The fabrication protocol is described in what follows. A quartz coverslip is thoroughly cleaned in water, acetone and isopropyl alcohol (IPA) by immersing in each solution for 3 min and sonicating at maximum power. Poly(methyl methacrylate) (PMMA) is spun coat on the sample at 3500

rpm for 1 min, after which it is baked for 1 min in a hot plate at 180°C. This baking step is of utmost importance to guarantee homogeneity in the deposited PMMA. The final thickness of the PMMA 950k A4 spun coat under this conditions is 200 nm. To finish preparing the sample to be patterned, a thin layer of 2 nm of a conductive polymer (Showa Denko's ESpacer 300Z) is deposited to prevent charging effects [98]. Figure 3.7(b) shows a scheme of the layer of PMMA on top of the quartz substrate.

The PMMA is patterned with a 20 kV, 10 μm aperture, 10 mm working distance electron beam, as schematised in figure 3.7(c). After exposure, the sample is developed in a solution of 3:1 methyl isobutyl ketone : IPA for 30 s and cleaned for 30 s in IPA to stop the development process. Figure 3.7(d) shows the patterned PMMA after development.

In order to ensure good adhesion of gold to the quartz substrate a self-assembled monolayer is deposited prior to the evaporation of the metal. Figure 3.7(e) shows a scheme of (3-Mercaptopropyl)trimethoxysilane (MPTMS), which is deposited by mixing it with ethanol in a 5% solution and baked for 15 min at 90°C. Following that, gold is thermally evaporated at a rate of 2 $\text{\AA s}^{-1}$ to a final thickness of 60 nm at 10^{-6} Torr. This recipe produces highly homogeneous golden films [49]. The evaporated golden layer can be observed in figure 3.7(f). Finally, the sample is lifted-off by immersing in acetone for 12 h and rinsing at the end with acetone and IPA to eliminate any remanent debris of PMMA. The final structures appears in the scheme of figure 3.7(g).

After this final step, a new electron beam patterning protocol can be done to define the inner disks of the NCRDC. The quantum dot deposition can be done after this step or, indistinctly the study of its optical properties by dark-field microscopy.

Figure 3.8 shows scanning electron micrographs of typical NCRDCs together with their respective scattering spectra measured with dark-field microscopy as explained in section 2.3. The comparison with theoretical values is also shown. The theoretical calculations for the scattering cross-sections had into account that the illumination was annular and that the collection was limited to a numerical aperture of $\text{NA}=0.7$. However, the Fano dip is not resolved in our current experimental set-up, probably given to surface roughness that increases the effective losses of the antenna. The SEM show homogeneity in fabrication, even for gaps smaller than 20 nm.

In what follows, I will theoretically analyse the spectral dependence of an emitter interacting with this kind of nano-antennas via simulations. It will be shown that the scattering cross-section maximum is strongly

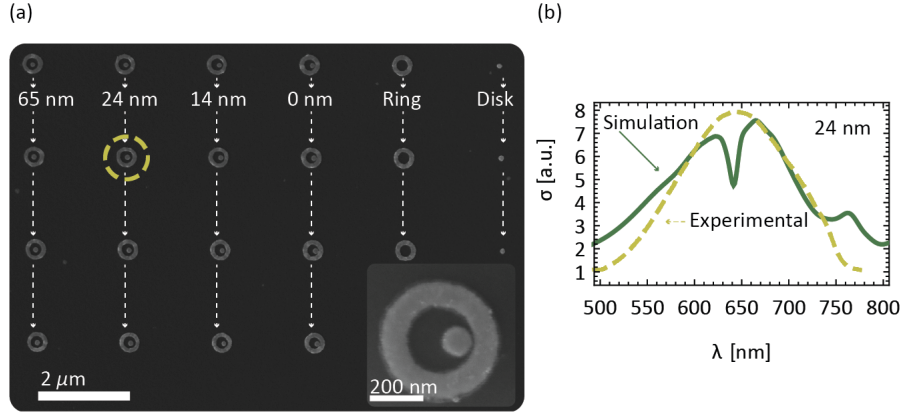


Figure 3.8 (a) Scanning electron micrographs of some NCRDCs. The encircled antenna is the one whose dark-field is shown in (b). The inset shows a $\lesssim 14$ nm. (b) Dark-field measured and simulated scattering cross section of NCRDCs.

correlated, as should be expected, to the region of highest radiative rate enhancement.

3.4 RADIATIVE RATE MODIFICATIONS

As was discussed in the introduction, several channels can be activated in the near-field of a resonating antenna. An emitter located in the vicinity of such a modified electromagnetic environment can decay into either radiative or non-radiative channels. The former are of paramount importance for quantum computation and spectroscopic applications [19, 32, 93].

In particular, figure 3.9(a) shows both the radiative and non-radiative rate enhancement for a 20 nm gap NCRDC, a ring and a disk. In all cases the emitter is located 12 nm away from the ring (inside) and disk, and inside the gap for the NCRDC, 12 nm away from both the disk and the ring. The simulations were performed following the protocol of figure 1.3. The other parameters are exactly the same as in figure 3.6(a). A nearly 150 fold enhancement of the radiative rate can be expected at around 650 nm and up to 200-fold increase for 800 nm single-photon emitters. However, this parameter alone is not sufficient to quantify the performance of an antenna. The quantum efficiency, defined as radiative rate over total rate, is shown in figure 3.9(b) proves that above 650 nm only 60% of light is radiatively coupled to the far-field, while the rest is lost in non-radiating

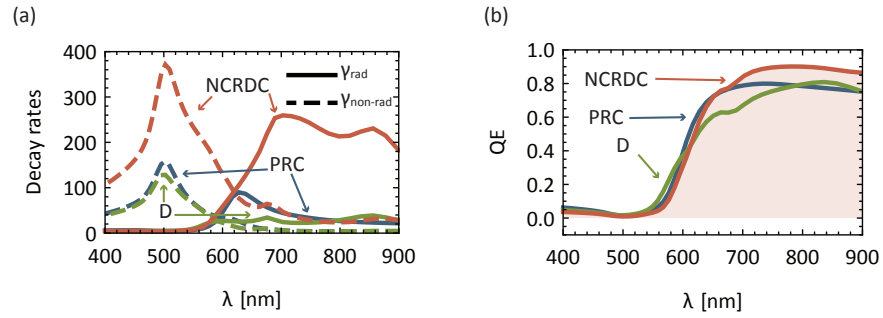


Figure 3.9 (a) Simulated decay rate enhancements and (b) quantum efficiency of emitters inside the gap and half the gap distance away from the ring in NCRDCs gap, half the gap away from the plasmonic ring cavities (PRCs) and half the gap distance away from the disks (Ds).

channels. As will be shown in chapter 5, the intrinsic losses of metals hamper their excellent performance. However, metals provide sufficiently tight electromagnetic volumes and extremely large field enhancements that can aid, under certain circumstances, to increase the radiative rate without losing too much efficiency.

To conclude, non-concentric ring-disk cavities were fabricated and their isolated optical properties studied. Moreover, colloidal quantum dots were deterministically positioned on quartz and their saturation curve measured. This gives us information about the saturation intensity. As is shown in chapter 5 the fluorescence rate enhancement is intensity dependent and two different regimes can be obtained to describe the behaviour of single-photon emitters. Therefore, knowing the saturation curve immediately inspires the realisation of experiments in two limiting cases. Finally, simulations were done to show convincing data that justifies carrying out the experimental measurement of the fluorescence lifetime.

The main challenge is depositing the colloidal quantum dots in the very small gaps of the NCRDC to do fluorescence lifetime imaging microscopy. This is clearly the next step that is currently being carried out to prove interaction of matter with plasmonic nano-structures.

4

BOW-TIE ANTENNAS
FOR THE EXPLOITATION
OF NON-RADIATIVE
PROPERTIES

In the previous chapter I presented a platform for enhancing the radiative properties of single-photon emitters. In that case it was desired that the number of non-radiative channels was diminished, so that the far-field coupling could be optimum. However, given the constraints introduced in plasmonics, losses cannot be fully extinguished. In chapter 6 I show a proposal to get rid of these intrinsic losses to optimise the far-field radiation. In spite of this, losses can be beneficial if the right application can be found. And in fact, losses have been exploited in useful ways [38, 99–101], for example by localising heating in the nano-scale with photo-thermal effects [102], by utilising the generated hot-electrons to induce highly localised photocurrents [103] or to drive chemical reactions at desired nanoscale regions [89, 100, 101, 104, 105], among others. In other words, the term *loss* needs to be understood as something beneficial in these applications, meaning that radiative properties are detrimental. In this scenario, we should call far-field coupling as a radiative loss and we state the scope of the problem as a study of non-radiative decay channels.

The interaction of light with matter is not only limited to the study of light with single-photon emitters as discussed in the previous chapter and in chapter 6. This has already been exemplified in the introductory chapter 2, section 2.2, where free electrons were made to interact with an electromagnetic field, from where a simple model for the dielectric function of a metal was found.

In this chapter, we deal with a very specific kind of non-radiative decay channels: that of hot electron generation. The mechanism can be easily understood as the decay of a surface plasmon polariton into a hot electron-hole pair. It is, indeed, akin to an electron-positron decay from a photon in the context of quantum electrodynamics in vacuum. The whole rate dynamics can be understood with a simple time dependent first order perturbation expression that takes into account the interaction Hamiltonian between non-interacting Bloch electrons (electrons in

the metallic lattice) and the electromagnetic field [89, 106, 107]. The interaction is of the form

$$\hat{\mathcal{H}}_{\text{int}}(t) = \frac{-|e|\hbar}{2m_e} \sum_{\sigma} \int_{\mathbb{R}^3} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}, t) \hat{\mathbf{A}}(\mathbf{r}, t) \cdot \hat{\mathbf{p}} \hat{\psi}_{\sigma}(\mathbf{r}, t) d^3\mathbf{r} + \text{h.c.}, \quad (4-1)$$

where $-|e|\hbar$ is the electron's charge, m_e its mass, $\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}, t)$ the creation operator for an electron with spin σ at position $\mathbf{r}$, $\hat{\mathbf{A}}(\mathbf{r}, t)$ the time-position dependent electromagnetic field and $\hat{\mathbf{p}}$ the momentum operator of the second quantised electron field. Henceforth we skip the addition of the hermitian conjugate as it just represents the inverse process.

The creation operator for an electron in the band n with wavevector $\mathbf{q}$ is $\hat{c}_{n,\mathbf{q}}^{\dagger}$. Therefore a hole-electron state plus a modified Fermi sea can be described as:

$$|\mathbf{q}'n', \mathbf{q}n, \tilde{F}\rangle = \frac{\hat{c}_{\mathbf{q}n}^{\dagger} \hat{c}_{\mathbf{q}'n'}}{\sqrt{(1 - f_{\mathbf{q}'n'}) f_{\mathbf{q}n}}} |F\rangle, \quad (4-2)$$

where $|F\rangle$ is the unperturbed initial Fermi sea state and the normalisation constant $f_{\mathbf{q}n}$ is its population in the state $\mathbf{q}n$ and $\tilde{F}$ is the modified Fermi sea where an electron was added into the $\mathbf{q}n$ state and one hole into the $\mathbf{q}'n'$ state. It is important to note the relationship between the field operator $\hat{\psi}_{\sigma}(\mathbf{r}, t)$ and the Bloch creation operators:

$$\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}, t) = \sum_{\mathbf{q}n} \underbrace{\psi_{\mathbf{q}n,\sigma}(\mathbf{r})}_{\text{Bloch function}} e^{-iE_{\mathbf{q}n}t/\hbar} \hat{c}_{\mathbf{q}n}^{\dagger}. \quad (4-3)$$

Similarly, a bosonic creation operator for the plasmonic field with momentum $\mathbf{k}$ and energy $\hbar\omega$ can be defined such that

$$|\mathbf{k}, \omega\rangle = \hat{a}_{\mathbf{k}\omega}^{\dagger} |0\rangle, \quad (4-4)$$

from where we can expand the electromagnetic field as follows:

$$\hat{\mathbf{A}}(\mathbf{r}, t) = \sum_{\mathbf{k}\omega} A_{\mathbf{k}\omega} \mathbf{u}_{\mathbf{k}\omega}(\mathbf{r}, t) \hat{a}_{\mathbf{k}\omega}, \quad (4-5)$$

where $A_{\mathbf{k}\omega}$ is an expansion coefficient and $\mathbf{u}_{\mathbf{k}\omega}(\mathbf{r}, t)$ is an eigenmode of Maxwell's equations with the appropriate boundary conditions and properly normalised. Note that for strong illumination the requirement of a quantised electromagnetic field is unnecessary, in that case we could just deal with the easier problem of a classical field.

Using this notation, we can write the rate of hot carrier generation to a first order approximation using Fermi golden rule summing over all

possible final states (hot holes with energy $E_{q'n'}$ and hot electrons with energy E_{qn}) as [106, 107]:

$$\gamma = \frac{2\pi}{\hbar} \sum_{q'n', qn} \underbrace{\delta(E_{q'n'} - E_{qn} - \hbar\omega)}_{\text{Energy conservation}} \left| \langle q'n', qn, \tilde{F}, 0 | \hat{\mathcal{H}}_{\text{int}} | 0, 0, F, k\omega \rangle \right|^2 \quad (4-6)$$

where the notation implies: |hole, electron, Fermi sea, SPP>. From this equation all the rates can be calculated if the band structure of the material is known and Maxwell's equations have been previously solved for the case geometry of interest. Note that all the time dependences vanish due to the Dirac delta.

This formalism clarifies the origin of the hot-electron generation in solids. If electron-electron or electron-phonon scatterings are taken into account, then equation 4-3 is modified appropriately by solving the full Hamiltonian that takes into account this interactions. If these interactions are weak we could calculate the corrections to the wavefunctions and then replace those solutions in equation 4-3.

These equations give us a theoretical means of finding the total rate of hot-electron rate density. The distribution of energetic electrons gives us tremendous insight into where in a nano-structure we can find electrons to drive chemical reactions. As can be seen from the equations above, the theoretical calculations are abhorrently [106, 107] involved because they take the whole crystalline structure of the material into account. Experimental mapping of this hot-carrier generation density is tricky and is currently missing from literature. Our work tried to shed some light into this matter of utmost importance for nano-scale localised chemistry.

4.1 OUTLINE OF EXPERIMENT

Essentially, we fabricated bow-tie nano-structures that allowed for the generation of hot-electrons in the tips. In order to corroborate this, we coated the antennas with a monolayer composed of a molecule which just for brevity I shall label A. When exciting the coated antenna with polarised light, we measured the Raman signal and observed a modification in the spectrum. This indicates that the molecule A transformed into molecule B. This transformation, as will be explained below, can only occur if at least one high energy electron is present. Therefore, the regions where hot electrons got generated are highly correlated to the

areas where the molecule A was transformed into molecule B. However, given that the antenna is sub-diffraction, a simple Raman map cannot give local information about the distribution of molecule B on the surface of the nano-antenna. In order to map this, we deposited properly functionalised Au nanoparticles that could only bind covalently with the molecule B but not with molecule A.

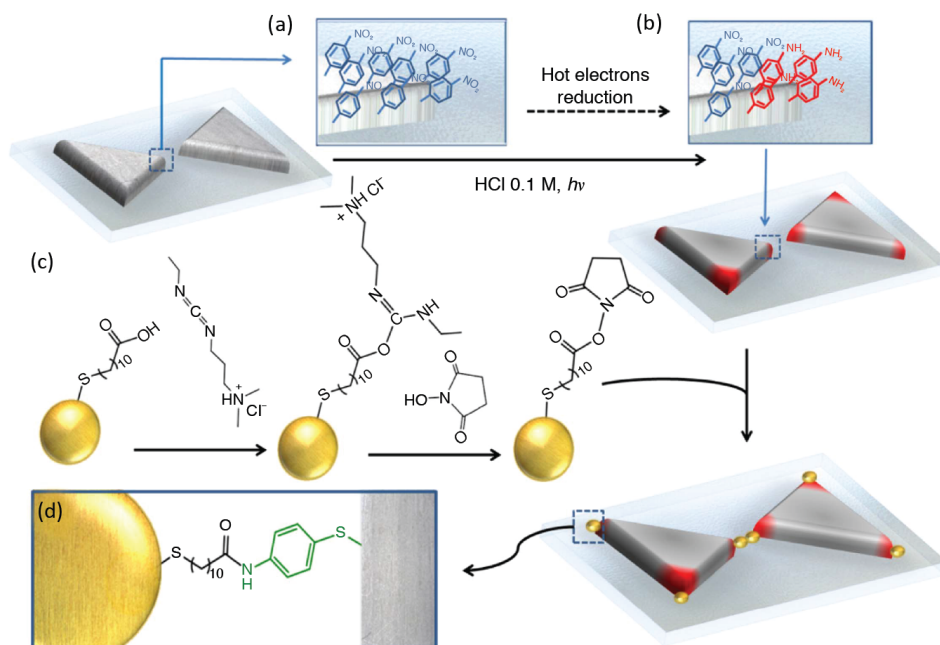


Figure 4.1 (a) Ag nano-antennas overnight modification with 1 mM ethanolic solution of 4-nitrothiophenol (4-NTP), molecule A. (b) The coated antennas are immerse in 0.1 M hydrochloric acid solution and illuminated for different times at their plasmon resonant wavelength (~ 633 nm) with a power density of 1 W cm^{-2} . This reduces de 4-NTP molecule to 4-aminothiophenol (4-ATP), molecule B. After rinsing with water the samples are immersed in a solution of activated gold nanoparticles. (c) The gold nanoparticles of 15 nm in diameter are coated with 11-mercaptoundecanoic acid (MUA) as a capping layer. This nanoparticles can only bind to the 4-ATP. (d) The activated nanoparticles are left to react with the hot-electron-converted silver antennas for a whole night. After several steps of washing with water a 2 nm layer of Pt was sputtered and the sample imaged. Adapted from ref. [89].

Several scanning electron micrographs revealed the positions of the nanoparticles to statistically appear in the gap region. Given that the positioning of the nanoparticles is highly correlated with the location of the molecule B, and that the molecule B could only have appeared in the regions where hot electrons were generated, we concluded that knowing the distribution of nanoparticles maps out the locations of the high dens-

ity of hot electron generation. With this technique we achieved around 15 nm resolution (the size of the nanoparticles). Figure 4.1 shows the scheme of our experimental conditions, including further details of what has just been described.

In section 4.2 I describe the fabrication, simulation and characterisation details of the nano-antennas. The fabrication is essentially the same as that for the non-concentric ring-disk cavities of section 3. Following that I show the optical properties of the nano-antennas, which should be such that they absorb in the wavelength range of interest (to have the hot carrier generation non-radiative decay channel), but also, as is therein described, that they scatter appreciably into the far-field (to detect the Raman signal of the molecule B). Finally, I present the location of the nanoparticles, which represents a sub-diffraction mapping of hot electrons in the nano-antennas.

4.2 FABRICATION, SIMULATION AND CHARACTERISATION

Light incident on metallic nano-antennas can excite surface plasmon polaritons which may decay into hot carriers through several mechanisms [60, 61], including direct interband transitions, phonon-assisted intraband transitions and geometry-assisted transitions. All of these channels are usually called Landau damping [38, 61, 105, 107]. The possibility to obtain these transitions in metals was initially seen as a universal drawback, but that was basically because most efforts were concentrated into having far-field radiation. Now, exciting opportunities are arising for energy conversion, photodetection, photochemistry and photocatalysis [99–101].

The package Lumerical FDTD was used to simulate the scattering behaviour of both bow-tie and dimer antennas. The details are very similar to those mentioned in section 3.2. The antennas were simulated with a complex phenomenological dielectric function measured by McPeack et al. [49]. Their height was $h = 60$ nm and they lied above a quartz substrate. The dielectric function for the quartz was that of SiO_2 [108]. Given that the experiments are performed in a halide solution (hydrochloric acid, as shown in figure 4.1) the simulations were done both in air (refractive index 1 [109]) and in a medium of index 1.324 [110]. The simulations in air were done to compare with the experimental results of dark field microscopy and the ones in water to simulate the experimental situation where

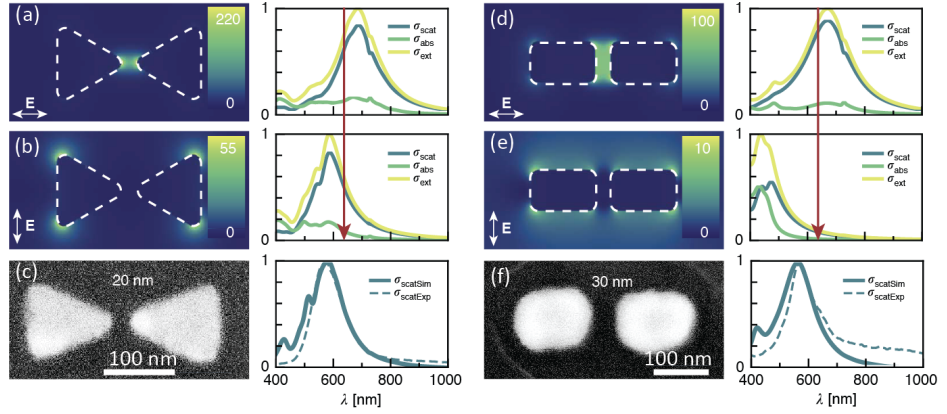


Figure 4.2 (a,b) FDTD simulations of a bow-tie antenna excited with horizontal (a) and vertical (b) polarisation. On the left the field enhancement distribution on a plane at half the height of the nano-antenna (*i.e.* $\|\mathbf{E}(x, y, h/2; \lambda)\|^2 / \|\mathbf{E}_0\|^2$, where h is the height of the nano-antenna and $\lambda = 633$ nm). On the right, the scattering, absorption and extinction cross-sections for each illumination condition. These simulations were done with the antennas in a homogeneous medium similar HCl. (c) Scanning electron micrograph of one of the fabricated bow-ties with a gap size of 20 nm. Scale bar: 100 nm. To the right, the experimental dark-field spectrum together with the simulated scattering cross-section. Both this simulation and the dark-field measurement were done in air. (d,e) Same as (a,b) but for a dimer. (f) Same as (c) but for a dimer of gap 30 nm. Scale bar: 100 nm. Adapted from ref. [89].

the capping molecule A (4-NTP) is transformed into molecule B (4-ATP) as schematised in figure 4.1(b).

Figure 4.2 contains all the optical-information of the nano-antennas. It shows both the simulated near field and the simulated cross-sections of the nano-antennas. It also contains a comparison between the experimental dark-field spectra and the simulated scattering spectrum in air. Furthermore, we can clearly see a red-shift in the scattering cross-section of the antennas that are immersed in the liquid solution of HCl. The wavelength of the laser light used to excite the surface plasmons is also highlighted in the figure. As is to be expected, a larger field enhancement is observed in the gap of the bow-tie antennas when excited horizontally than when exciting a dimer under the same illumination conditions. This is due to the sharper corner in the bow-tie. The edges were rounded and simulated with an 8 nm radius of curvature so as to resemble the experimental conditions.

4.3 HOT-ELECTRON MAPPING

After fabrication and characterisation of the nano-antennas, we performed the conversion experiments as described in figure 4.1. A series of control experiments needed to be done however, to show that:

- the reaction takes place, and that
- the Au nano-particles only bind to 4-ATP (and not 4-NTP).

We performed single-antenna surface enhanced Raman spectroscopy (SERS) to detect the conversion from 4-NTP to 4-ATP (as shown in figure 4.3). The strong electromagnetic confinement in the gap of the nano-antennas allowed label-free monitoring of this reaction by *in situ* SERS. The 4-NTP coated Ag antennas in the presence of 0.1 M HCl and by using a 10 μ W diffraction-limited spot at $\lambda = 633$ nm (at the plasmon resonance of our antennas), the C–C and C–H stretching bands of 4-ATP appeared at ~ 1590 and ~ 1180 cm^{-1} , respectively, as shown in figure 4.3. Concomitantly, the 4-NTP peaks decreased.

Following that, we tested the surface chemistry reactions. A negative control experiment showed that Au nano-particles cannot bind to a 4-NTP coated sample. This is shown in figure 4.3(b) for both the case of a silver film and a nano-antenna (inset). However, when the same experiment was repeated in a 4-ATP coated sample, we observed that the activated

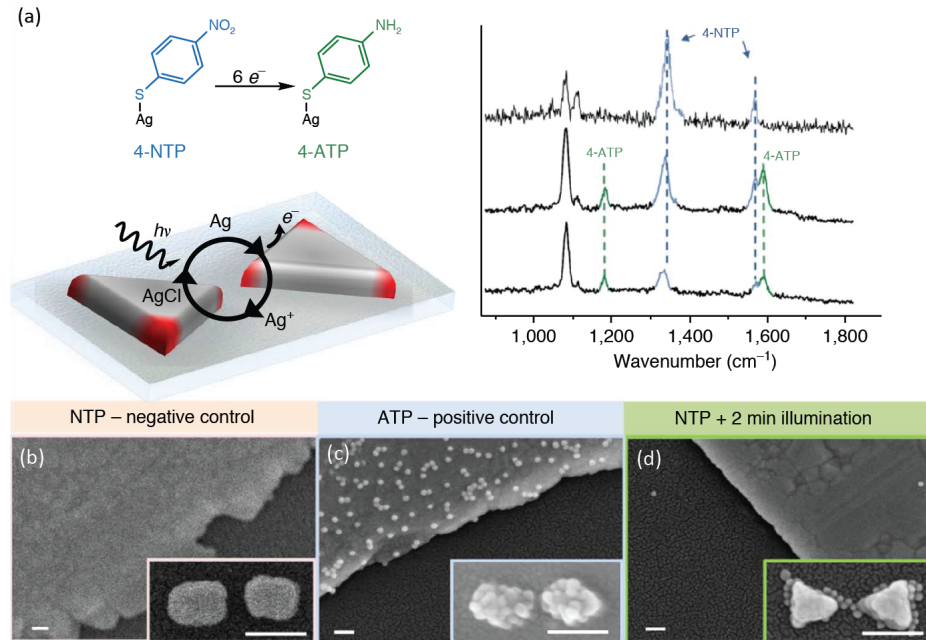


Figure 4.3 (a) 4-NTP to 4-ATP conversion scheme, together with the proposed mechanism of hot electron extraction. The sample is immersed in 0.1 M HCl and the illumination wavelength is 633 nm. To the right, the Raman spectra proving the success of the conversion. Integration time 5 s. (b) Scanning electron micrographs of a negative test control experiment. A sample of silver nano-antennas and thin films was coated with 4-NTP and left to react with Au nanoparticles. After several rinsing steps, no Au nano-particles were found in either the film or the nano-antenna. Scale bars: 100 nm. (c) Same experiment, but coating the sample with 4-ATP. The Au nano-particles are located in both films and nano-antennas, but not on the substrate. Scale bars: 100 nm. (d) Same as in (b) but here the sample was illuminated for 2 min in a 0.1 M HCl at a power density of 1 mW cm^{-2} . The Au nano-particles were solely found in the nano-antenna. Scale bars: 100 nm. Adapted from ref. [89].

Au nano-particles could efficiently bind to both the film and the nano-antenna (inset). In neither case were Au nano-particles found on the quartz substrate. The clear results can be seen in figure 4.3(c).

These two control experiments indicate that the reaction is highly specific to the presence of 4-ATP and that the amide-bond between the Au nano-particle and the 4-ATP capped nano-antenna is formed at a high yield.

Finally, a conversion experiment on an array of nano-antennas was performed. For these experiments, the laser spot was expanded to a diameter of 0.5 mm and the power was set up at 1 W and the sample was immersed in HCl acid. The sample was illuminated for 2 min. After this, immersion in the activated gold nano-particles solution and scanning electron micrographs taken. As can be seen from figure 4.3(d), Au nano-particles were only found in the vicinity of the antenna and not in the silver film. Given that hot electrons cannot be generated by interband transition in Ag at this wavelength (633 nm), we have to conclude that the only non-radiative decay mechanism that could generate the necessary electrons to produce the reaction are those generated by SPP decay.

Having analysed around 100 nano-antennas we mapped the statistical positioning of the nano-particles. Figure 4.4 shows the near-field distribution of both bow-tie and dimer antennas, in order to correlate the positioning of Au reporters to these regions. Furthermore, examples of SEM images of Ag nano-antennas/Au reporters can be found. We can clearly see that in the case of the bow-tie antennas, the reactivity increases with the illumination time, 1 min for figure 4.4(a) and 2 min for 4.4(b). In both cases, the polarisation of the excitation field is horizontal, *i.e.* parallel to the bow-tie preferential axis. The progression of the reaction can be deduced from these images: the reaction starts occurring close to the tips of the Ag nano-antennas, where more and more Au reporters appear. After some time, however, the surface starts to be more and more populated. The statistical analysis from the last panel also confirms this.

For our Ag bow-ties, the results imply that the reactivity is highest at sharp tips and lowest on flat planar surfaces. In particular, the mean free path of ~ 10 nm for electrons with energies above 2 eV above the Fermi level in Ag correlates to the ~ 8 -10 nm radius of curvature of our sharp tips. This allows us to correlate the sharpness of the features to high hot carrier generation densities. In our experiments, the reaction is temporally limited by the amount of hot carriers that reach the surface with the necessary energy to react with 4-NTP.

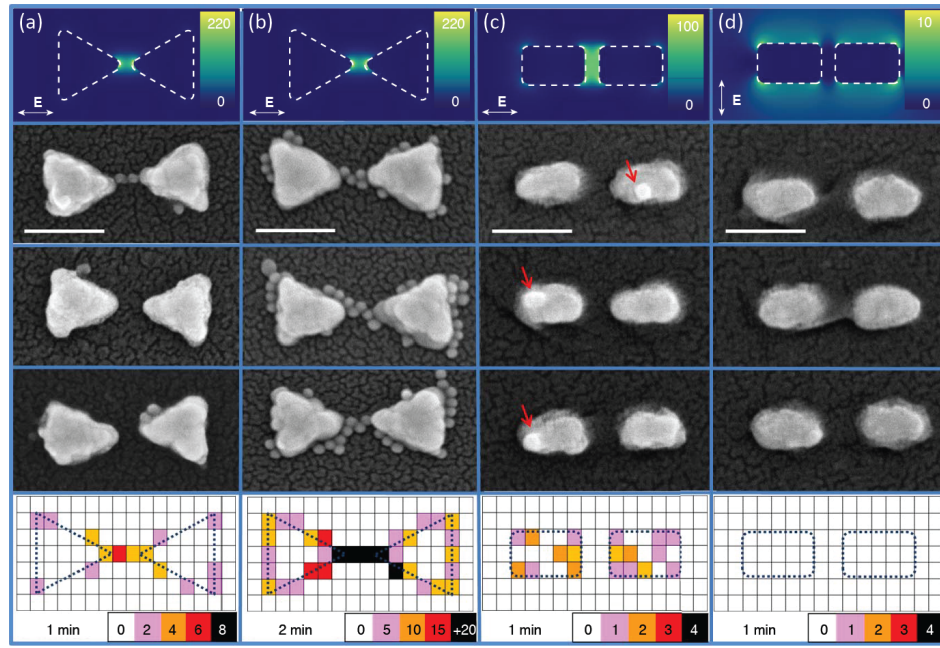


Figure 4.4 Au reporter nano-particles binding to 4-NTP-coated Ag bow-ties after (a) 1 min and (b) 2 min illumination with parallel polarisation at 633 nm in 0.1 M HCl. Au reporter particle binding to 4-NTP coated Ag dimers conversion after 1 min of (c) parallel polarised illumination and (d) perpendicular polarised illumination at 633 nm in 0.1 M HCl. The top panels show the near-field distribution of the field enhancement and the polarisation direction of the incident electric field. The three middle panels show the SEM images of different examples of nano-antennas after illumination and Au nano-particle deposition. The bottommost panels show the statistical maps with a spacing of 15 nm (the Au reporters size). The colour bar indicates the frequency of appearance of Au nano-particles localised in each pixel after performing the statistical analysis. Adapted from ref. [89].

It is interesting to compare these results with those of Ag dimers from figures 4.4(c)-(d). In these cases, either the Au nano-particles were found covering the whole nano-antenna, figure 4.4(c), or nowhere at all, figure 4.4(d). This supports our hypothesis that sharp corners have a higher rate of hot electron extraction than blunt regions. Furthermore, this density is clearly polarisation dependent, proving the involvement of the plasmons in the process of generating hot electrons.

Our results establish that site-selective extraction of hot-carriers is the most important aspect to assess the reactivity of a nano-antenna. It does not suffice to calculate the generation rate of hot-carriers as they can be generated inside the bulk of the nano-antenna, but never reach the surface with enough energy to drive the reaction. Through careful design of the antennas with sharp tips, this method could be used to deliver nano-objects to high electromagnetic field intensity regions†[111]. For example, small catalytic particles, which by themselves do not have a significant far-field cross-section, can be incorporated to larger size structures that possess higher electric dipole moments to perform as nano-antennas [112–114]. Furthermore, photo-polymerisation [115], three-photon absorption of disulphuric species [116] or local solvent heating strategy [117], among others, have been recently employed for high electromagnetic field hot-spots modification.

Finally, our easy, fast and cheap strategy could serve as a selective and large-scale method of positioning molecules/nano-materials in a variety of plasmonic nano-antenna reactive spots or hot spots.

Part II

DIELECTRICS ON THE NANOSCALE

5

INTRODUCTION: MIE RESONANCES IN DIELECTRICS

Metallic nanostructures have been used in nanophotonic devices operating in the visible regime for several decades [118]. However the initial excitement in them was later partially eclipsed, as losses were then realised to play an important role in quenching radiative properties [54, 61, 119–121]. These losses do not hamper the development of technology as other applications can be found where it thrives, as described in chapter 4 and other examples mentioned therein.

In the urge to find devices that have reduced losses, dielectric nano-antennas emerge as complementary candidates to plasmonic systems. Nano-structured high-refractive index dielectrics can highly confine electric and magnetic fields at sub-wavelength volumes [122], while presenting ultra-low absorption –relative to metals– when the energy of the exciting photons lies below the energy of the material’s bandgap. Thus, they could be considered as an alternative to overcome the current limitations of plasmonic nano-antennas.

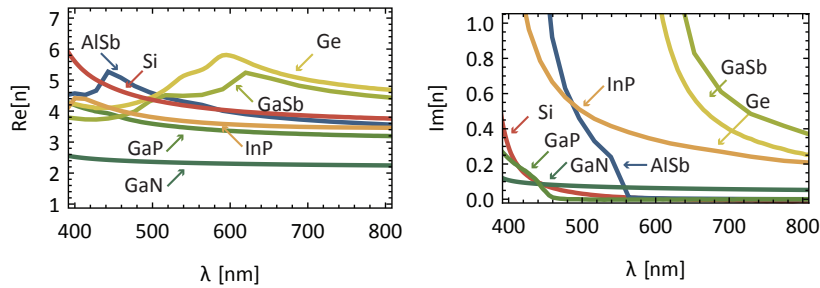


Figure 5.1 (a) Real part of the refractive index of several dielectrics. (b) Imaginary part of the refractive index of the same dielectrics. AlSb from [123], GaN from [124], GaP from [50], GaSb from [125], Ge and Si from [126], InP from [127]

It is important to shed light into the different underlying physical phenomena between the widely used dielectric microcavity and the novel concept of the dielectric nano-antenna. While micro-resonators use high Q-factors to generate field enhancements [128, 129], nano-antennas use

small modal volumes with low Q-factors, broadening the spectral range of operation, while reducing field-enhanced region volumes.

A wide variety of materials can be chosen. Figure 5.1 shows the real and imaginary part of a panoply of single and binary dielectric materials and table 1 lists the associated bandgap of these materials [91]. GaP, in particular, has an associated bandgap wavelength as small as 549 nm with a refractive index of ~ 3.3 , opening interesting opportunities for the realisation of low-loss nano-photonic antennas in the optical regime [130].

Table 1 Bandgap properties of several dielectrics [91].

Material	Bandgap type	Gap energy [eV]	Wavelength [μm]
AlN	Direct	6.20	0.200
AlP	Indirect	2.45	0.506
AlAs	Indirect	2.16	0.574
AlSb	Indirect	1.58	0.785
GaN	Direct	3.39	0.366
GaP	Indirect	2.26	0.549
GaAs	Direct	1.42	0.873
GaSb	Direct	0.73	1.700
Ge	Direct	0.66	1.880
InN	Direct	0.65	1.910
InP	Direct	1.35	0.919
InAs	Direct	0.36	3.44
InSb	Direct	0.17	7.29
Si	Direct	1.12	1.11

Recently, applications such as second or third harmonic generation as well as surface enhanced Raman or fluorescence spectroscopy were explored by exploiting the ability of high-refractive index nano-antennas to highly confine the electric field at sub-wavelength volumes [34, 86, 120, 122, 128, 131, 132]. Indeed, since the efficiency of nonlinear phenomena and the enhancement factors of surface-enhanced spectroscopies increase with the excitation density, locally enhancing the incident light intensity can significantly amplify these processes.

Given their intrinsically low absorption GaP nano-antenna could be considered as a potential alternative material to those found in plasmonic systems [133] for surface enhanced fluorescence (SEF), since all standard fluorophores absorb and emit in the visible range. Clearly, ohmic losses and quenching effects, typically present in metal structures, would be completely avoided in GaP nanoantennas for excitation wavelengths above their bandgap (*i.e.* $\lambda_{\text{exc}} > 549$ nm). Regarding reported research on dielectric nanoantennas for SEF, up to now, only Si dimers with nano-

scale gaps have been investigated for this purpose, reaching fluorescent enhancement values ranging from 250 to 2000 when placing the fluorescent molecules in their gaps [128, 132]. It is worth mentioning that even though Si does absorb light in the visible regime, its absorption coefficient is nearly two orders of magnitude lower than that of Au [134]. However, the remaining absorption of Si is still one order of magnitude larger than that of GaP [135] and therefore represents a limitation for fluorescent enhancement, with non-negligible non-radiative contributions [132]. GaP could, thus, boost radiative emission even more than Si.

In this chapter I trace the theory of dielectric nano-antennas, based in the multipolar decomposition of the solution of Maxwell equations using an approach similar to Mie's seminal work [45]. In chapter 6 I show experimental results that support the application of gallium phosphide for nanophotonics applications. There the properties of GaP nanoantennas as effectively lossless platforms at optical frequencies. In appendix ?? I present further experimental results that support the idea of using dielectric materials in nano-photonics. There, it is briefly shown that second harmonic light can be obtained from these nano-structured GaP materials with high conversion efficiencies.

5.1 MIE RESONANCES IN A SPHERE

In section 2.1.2 we studied the response of a small sphere to an external electromagnetic field in the quasi-static approximation. Here, we extend the analysis to take into account any sphere radius. This section is full of mathematical results and definitions. The physical insight is derived in section 5.2. A comparison between dielectrics and metals can also be found there.

Below, I start with a description of the problem including the geometry. Following that, I describe how to expand a plane wave into spherical waves. The final subsection shows the scattering solution. This description is based on ordinary textbook examples [44, 45, 114], however I use a different approach in which I assume all the knowledge that operator algebra has given us from quantum mechanics. Here, in contrast to other approaches, I make strong usage of angular momentum operators and their properties. This strongly simplifies the calculations (removes the large amount of integrals and buries all that dirt under the carpet of the algebra of operators).

5.1.1 Boundary conditions and geometry of the problem

We are interested in solving the problem of a linearly polarised, monochromatic plane wave from a sphere of radius a and complex, spatially-homogeneous but dispersive relative dielectric permittivity $\epsilon_{\text{in}}(\omega)$ and magnetic susceptibility $\mu_{\text{in}}(\omega)$. Figure 5.2 shows the geometry of the problem. The sphere is immersed in a medium with permittivity $\epsilon_{\text{out}}(\omega)$ and susceptibility $\mu_{\text{out}}(\omega)$, with probably frequency dependence too. All the frequency dependences will not be made explicit in the calculations below unless noted. Moreover, there are no real assumptions on either permittivities, besides that they satisfy Kramers-Kronig relations [53] individually, and they have all the hypothesis required there.

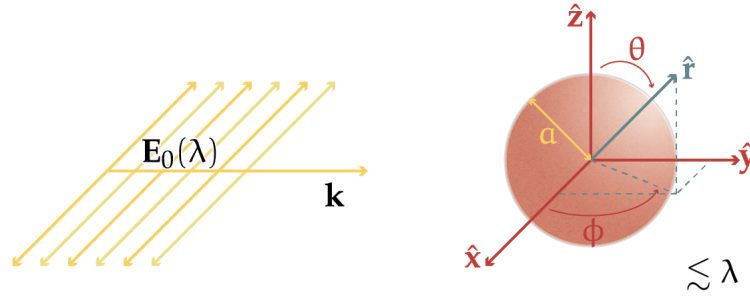


Figure 5.2 Geometry of the problem of a linearly polarised monochromatic light source scattering from a sphere of radius a .

We start by separating space into two regions, each with a constant dielectric permittivity. The time-harmonic Maxwell equations inside and outside the sphere thus reduce to:

$$\nabla \times \mathbf{H}_j(\mathbf{r}) = -ik_0 c \epsilon_j \mathbf{E}_j(\mathbf{r}), \quad j = \text{in, out} \quad (5-1a)$$

$$\nabla \times \mathbf{E}_j(\mathbf{r}) = ik_0 c \mu_j \mathbf{H}_j(\mathbf{r}), \quad j = \text{in, out} \quad (5-1b)$$

$$\nabla \cdot \mathbf{E}_j = 0, \quad j = \text{in, out} \quad (5-1c)$$

$$\nabla \cdot \mathbf{H}_j = 0, \quad j = \text{in, out} \quad (5-1d)$$

where $k_0 = \omega/c$ is the free-space wave-vector. The refractive index in each subspace is clearly: $n_i = \sqrt{\frac{\epsilon_i \mu_i}{\epsilon_0 \mu_0}}$, $i = \text{in, out}$. These equations could easily be recast in a vectorial wave equation by, for example, taking the curl of equation 5-1(b) and using equation 5-1(a):

$$\nabla^2 \mathbf{E}_j(\mathbf{r}) - k_0^2 n_j^2 \mathbf{E}_j(\mathbf{r}) = \mathbf{0}. \quad (5-2)$$

The incident electromagnetic field is:

$$\mathbf{E}_0(\mathbf{r}) = E_0 e^{ik_0 n_{\text{out}} z} \hat{\mathbf{x}}, \quad (5-3a)$$

$$\mathbf{H}_0(\mathbf{r}) = \frac{n_{\text{out}}}{c\mu_2} E_0 e^{ik_0 n_2 z} \hat{\mathbf{y}}. \quad (5-3b)$$

The boundary conditions on the surface of the sphere ($r = a$) are:

$$\mathbf{H}_{\text{out}} \times \hat{\mathbf{r}} = \mathbf{H}_{\text{in}} \times \hat{\mathbf{r}} \quad (5-4a)$$

$$\mathbf{E}_{\text{out}} \times \hat{\mathbf{r}} = \mathbf{E}_{\text{in}} \times \hat{\mathbf{r}}, \quad (5-4b)$$

$$\varepsilon_{\text{out}} \mathbf{E}_{\text{out}} \cdot \hat{\mathbf{r}} = \varepsilon_{\text{in}} \mathbf{E}_{\text{in}} \cdot \hat{\mathbf{r}} \quad (5-4c)$$

$$\mu_{\text{out}} \mathbf{H}_{\text{out}} \cdot \hat{\mathbf{r}} = \mu_{\text{in}} \mathbf{H}_{\text{in}} \cdot \hat{\mathbf{r}} \quad (5-4d)$$

where $\hat{\mathbf{r}}$ is the spherical radial versor and it depends on the azimuth and axial angles, θ and ϕ respectively. However, the first two boundary conditions already satisfy the last two [44].

5.1.2 Mathematical solution to the differential equations

The whole problem will be reduced to solving the scalar wave equation in spherical coordinates. To that end, let us start by observing that from $\nabla \cdot \mathbf{E}_j = 0$ it follows that the electric field has to be divergenless in each sub-region. We could propose the following clearly divergenless expression:

$$\mathbf{M}(\mathbf{r}) = \nabla \times [\mathbf{f}(\mathbf{r})], \quad (5-5)$$

so that, after manipulating the expressions, we obtain:

$$\nabla \times [\nabla^2 \mathbf{f}(\mathbf{r}) - k_0^2 n_i^2 \mathbf{f}(\mathbf{r})] = \mathbf{0}. \quad (5-6)$$

Because of spherical symmetry we would be tempted (or actually inspired by plenty of textbooks) to try $\mathbf{f}(\mathbf{r}) = \psi(\mathbf{r})\mathbf{r}$. In this case, we obtain:

$$\begin{aligned} \nabla \times \{ \mathbf{r} [\nabla^2 \psi(\mathbf{r}) - k_0^2 n_j^2 \psi(\mathbf{r})] + 2\nabla \psi(\mathbf{r}) \} = \\ \nabla \times \{ \mathbf{r} [\nabla^2 \psi(\mathbf{r}) - k_0^2 n_j^2 \psi(\mathbf{r})] \} = \mathbf{0} \end{aligned} \quad (5-7)$$

In other words, if $\psi(\mathbf{r})$ satisfies the scalar wave equation, then we can guarantee that $\mathbf{M}(\mathbf{r})$ also satisfies the vectorial wave equation.

This solution would help satisfy the divergenless aspect of the fields. However, it cannot help satisfy the coupling between them from equation 5-1(a)-(b). We can note that if we define:

$$\mathbf{N}(\mathbf{r}) = \frac{1}{k_0 n_i} \nabla \times \mathbf{M}(\mathbf{r}), \quad (5-8)$$

it will satisfy the wave equation and it will be coupled to $\mathbf{M}$ the same way that the electric displacement and magnetic fields are coupled, *i.e.* the curl of one is proportional to the other:

$$\nabla \times \varepsilon_j \mathbf{E}(\mathbf{r}) = k_0 n_j i \mathbf{H}(\mathbf{r}) \Leftrightarrow \nabla \times \mathbf{N}(\mathbf{r}) = k_0 n_j \mathbf{M}(\mathbf{r}). \quad (5-9)$$

Enough of mathematical identities. The general solutions for the scalar wave equation are:

$$\psi_{lm}(\mathbf{r}) = f_l(k_0 n_j r) y_{lm}(\theta, \phi), \quad (5-10)$$

where $f_l(k_0 n_j r)$ is one of the four spherical Bessel functions ($j_l(x)$, $y_l(x)$, $h_l^{(1)}(x) = j_l(x) + iy_l(x)$ or $h_l^{(2)}(x) = j_l(x) - iy_l(x)$) and $y_{lm}(\theta, \phi)$ is a spherical harmonic. However, if we want that at the origin $r = 0$ the solution does not blow up (implicit boundary condition), we would require to remove $y_n(x)$ from the expansion of the full solution inside the sphere. Outside the sphere, we'll require that at infinity, it reaches an asymptotic form similar to an outgoing spherical wave, in which case we'll end up having $h_n^{(1)}(x)$ as the radial function. Therefore:

$$f_l(k_0 n_j r) = \begin{cases} j_l(k_0 n_j r) & \text{if } r \leq a \\ h_l(k_0 n_j r) & \text{if } r > a. \end{cases} \quad (5-11)$$

Just to simplify notation, $k_0 n_j$ will be replaced with k_j from here onwards.

Usual textbooks proceed to finding through a lot of mathematical formulae, identities that relate to $\mathbf{M}$ and $\mathbf{N}$. I propose to use the knowledge we have about angular momentum in quantum mechanics. Let's notice that:

$$\begin{aligned} \mathbf{M}_{lm}(\mathbf{r}; k_j) &\stackrel{\text{def}}{=} \nabla \times [\mathbf{r} f_l(k_j r) y_{lm}(\theta, \phi)] \\ &= -\mathbf{r} \times \nabla [f_l(k_j r) y_{lm}(\theta, \phi)] \\ &\rightarrow \hat{\mathbf{L}} |k_j, lm\rangle. \end{aligned} \quad (5-12)$$

where $\hat{\mathbf{L}}$ is the angular momentum operator and $|k_j, lm\rangle$ is just a ket of the $\mathbf{r}$ -representation of $\psi_{lm}(\mathbf{r}; k_j) = \langle \mathbf{r} | k_j, lm \rangle$. Now, if we want to prove an orthogonality relationship between the $\mathbf{M}$'s it will be very easy:

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} \mathbf{M}_{lm}^*(\mathbf{r}; k_j) \cdot \mathbf{M}_{l'm'}(\mathbf{r}; k'_j) d\Omega &= \langle k_j, lm | \hat{\mathbf{L}}^\dagger \cdot \hat{\mathbf{L}} | k'_j, l'm' \rangle \\ &= \langle k_j, lm | L^2 | k'_j, l'm' \rangle \\ &= l(l+1) \langle k_j | k'_j \rangle \delta_{ll'} \delta_{mm'}, \end{aligned} \quad (5-13)$$

where $\langle k_j | k'_j \rangle$ is understood to be equal to $f_l^*(k_j r) \tilde{f}_l(k'_j r)$ with f and $\tilde{f}$ not necessarily the same spherical Bessel or Hankel function.

Similarly:

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} \mathbf{N}_{lm}^*(\mathbf{r}; k_j) \cdot \mathbf{N}_{l'm'}(\mathbf{r}; k'_j) d\Omega &= \frac{1}{k_j k'_j} \langle k_j, lm | (-\hat{\mathbf{p}} \times \hat{\mathbf{L}})^\dagger \cdot (-\hat{\mathbf{p}} \times \hat{\mathbf{L}}) | k'_j, l'm' \rangle \\ &= \frac{1}{k_j k'_j} \langle k_j, lm | \hat{\mathbf{p}}^2 \hat{\mathbf{L}}^2 | k'_j, l'm' \rangle \\ &= \frac{k_j'^2}{k_j k'_j} l(l+1) \langle k_j | k'_j \rangle \delta_{ll'} \delta_{mm'}, \end{aligned} \quad (5-14)$$

where I used the fact that $[\hat{L}_i, \hat{p}_j] = i\epsilon_{ijk} \hat{p}_k$, $(\hat{p}_i \hat{L}_j)^\dagger = \hat{L}_j \hat{p}_i$ and that $\hat{\mathbf{p}}^2 = \nabla^2$. Note that with this approach we did not have to explicitly use any of the complicated identities quoted in reference [114].

Finally:

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} \mathbf{M}_{lm}^*(\mathbf{r}; k_j) \cdot \mathbf{N}_{l'm'}(\mathbf{r}; k'_j) d\Omega &= \frac{1}{k'_j} \langle k_j, lm | \underbrace{\hat{\mathbf{L}}^\dagger \cdot (-\hat{\mathbf{p}} \times \hat{\mathbf{L}})}_{\perp \Rightarrow 0} | k'_j, l'm' \rangle \\ &= 0. \end{aligned} \quad (5-15)$$

$\mathbf{M}_{lm}(\mathbf{r}; k_j)$ and $\mathbf{N}_{lm}(\mathbf{r}; k_j)$ are the spherical harmonics and they represent a complete orthogonal set in each subspace. The choice of the radial function will depend on the subspace that we are working with. Finally, note that both $\mathbf{M}$ and $\mathbf{N}$ become zero when $l = 0$.

5.1.3 Expansion of the exciting plane wave

This is undoubtedly the result of the unwillingness of a plane wave to wear a guise in which it feels uncomfortable; expanding a plane wave in spherical wave functions is somewhat like trying to force a square peg into a round hole.

— Bohren and Huffman, from [114].

Any field, can be decomposed into the spherical vectors $\mathbf{N}$ and $\mathbf{M}$. In particular, we can expand the exciting plane wave in spherical vectors. Let us start by expressing it in the formalism developed above:

$$\begin{aligned}\mathbf{E}_0(\mathbf{r}) &= E_0 e^{ik_{\text{out}}z} \hat{\mathbf{x}} \stackrel{\text{def}}{=} |E_0(z)\rangle \hat{\mathbf{x}} \\ &= E_0 \sum_{l=1}^{+\infty} i^l \sqrt{4\pi(2l+1)} j_l(k_{\text{out}}r) |l0\rangle \hat{\mathbf{x}},\end{aligned}\quad (5-16)$$

where $e^{ik_{\text{out}}z} = e^{ik_{\text{out}} \cos \theta r}$ was projected into the spherical harmonics base $\mathcal{Y}_{lm}$, and the following identity was used:

$$j_l(x) = \frac{1}{2i^l} \int_0^\pi e^{ix \cos \theta} P_l(\cos \theta) \sin \theta, d\theta. \quad (5-17)$$

We now need to project $\mathbf{E}$ into both $\mathbf{M}$ and $\mathbf{N}$, and not forget to divide by the integral norm of both orthogonal but non-unitary spherical vectors. We have

$$\begin{aligned}& \frac{\int_0^\pi \int_0^{2\pi} \mathbf{M}_{lm}^*(\mathbf{r}; k_{\text{out}}) \cdot \mathbf{E}_0(\mathbf{r}) d\Omega}{\int_0^\pi \int_0^{2\pi} \|\mathbf{M}_{lm}(\mathbf{r}; k_{\text{out}})\|^2 d\Omega} = \\ &= \frac{E_0}{|f_l(k_{\text{out}}r)|^2} \sum_{l'=0}^{+\infty} i^{l'} \frac{\sqrt{4\pi(2l'+1)}}{l(l+1)} \langle k_{\text{out}}; lm | \overbrace{\hat{\mathbf{L}} \cdot \hat{\mathbf{x}}}^{\hat{L}_x} | k_{\text{out}}; l', 0 \rangle \\ &= E_0 \sum_{l'=0}^{+\infty} \frac{j_{l'}'(k_{\text{out}}r)}{f_{l'}(k_{\text{out}}r)} i^{l'} \frac{\sqrt{4\pi(2l'+1)}}{l(l+1)} \langle lm | \left[\frac{\hat{L}_+ + \hat{L}_-}{2} \right] | E_0(z) \rangle \\ &= 2i^l \sqrt{\frac{4\pi(2l+1)}{l(l+1)}} \frac{j_l(k_{\text{out}}r)}{f_l(k_{\text{out}}r)} \left[\frac{\delta_{m,+1} + \delta_{m,-1}}{2} \right]\end{aligned}\quad (5-18)$$

and for the projection onto $\mathbf{N}$:

$$\begin{aligned}& \frac{\int_0^\pi \int_0^{2\pi} \mathbf{N}_{lm}^*(\mathbf{r}; k_{\text{out}}) \cdot \mathbf{E}_0(\mathbf{r}) d\Omega}{\int_0^\pi \int_0^{2\pi} \|\mathbf{N}_{lm}(\mathbf{r}; k_{\text{out}})\|^2 d\Omega} = \\ &= \frac{1}{l(l+1)f_l(k_{\text{out}}r)} \langle k_{\text{out}}; lm | (-\hat{\mathbf{p}} \times \hat{\mathbf{L}})^\dagger \cdot \hat{\mathbf{x}} | E_0(z) \rangle \\ &= \frac{1}{l(l+1)f_l(k_{\text{out}}r)} \langle k_{\text{out}}; lm | [\hat{L}_z \hat{p}_y - \hat{L}_y \hat{p}_z] | E_0(z) \rangle \\ &= -\frac{1}{l(l+1)f_l(k_{\text{out}}r)} \langle k_{\text{out}}; lm | [\hat{L}_y \hat{p}_z] | E_0(z) \rangle \\ &= -\frac{ik_{\text{out}}}{l(l+1)f_l(k_{\text{out}}r)} \langle k_{\text{out}}; lm | \left[\frac{\hat{L}_+ - \hat{L}_-}{2i} \right] | E_0(z) \rangle \\ &= -2i^l \sqrt{\frac{4\pi(2l+1)}{l(l+1)}} \frac{j_l(k_{\text{out}}r)}{f_l(k_{\text{out}}r)} \left[\frac{\delta_{m,+1} - \delta_{m,-1}}{2i} \right]\end{aligned}\quad (5-19)$$

where we have used that $\hat{p}_y e^{ik_{\text{out}}z} = 0$ and $\hat{p}_z e^{ik_{\text{out}}z} = ik_{\text{out}} e^{ik_{\text{out}}z}$.

If we take $f_l(k_{\text{out}}r) = j_l(k_{\text{out}}r)$ we simplify the expressions and can finally write the expansion of the electric field in spherical vectors:

$$\frac{\mathbf{E}_0(\mathbf{r})}{E_0} = \sum_{l=1}^{+\infty} 2i^l \sqrt{\frac{4\pi(2l+1)}{l(l+1)}} \left[\frac{\mathbf{M}_{l,1}(\mathbf{r}; k_{\text{out}}) + \mathbf{M}_{l,-1}(\mathbf{r}; k_{\text{out}})}{2} - \frac{\mathbf{N}_{l,1}(\mathbf{r}; k_{\text{out}}) + \mathbf{N}_{l,-1}(\mathbf{r}; k_{\text{out}})}{2i} \right] \quad (5-20)$$

Usually, this expression appears in terms of even and odd functions. We can clearly see that, for example:

$$\begin{aligned} \mathbf{M}_{l,1} + \mathbf{M}_{l,-1} &= \hat{\mathbf{L}} \left[f_l(k_{\text{out}}r) (\mathcal{Y}_{l,1} + \overbrace{\mathcal{Y}_{l,-1}}^{-\mathcal{Y}_{l,1}^*}) \right] \\ &= \hat{\mathbf{L}} [f_l(k_{\text{out}}r) \mathcal{Y}_{o,l,1}] \\ &= \mathbf{M}_{o,l,1} \end{aligned} \quad (5-21)$$

where the subscript o means that it is an odd function in ϕ (*i.e.* $\propto \sin m\phi$). We can similarly define even and odd functions for $\mathbf{N}$ and the expression for $\mathbf{E}$ would somewhat simplify as seen in textbooks [44, 114].

To finalise this section, I would like to establish the following convention:

- If the radial function is $j_l(x)$ the harmonics will look like this: $\mathbf{M}$ and $\mathbf{N}$.
- If the radial function is $h_l^{(1)}(x)$: $\mathbf{M}^{(1)}$ and $\mathbf{N}^{(1)}$.

5.1.4 Solution of the problem

We now need to expand the electric field both inside and outside the sphere and satisfy the boundary conditions. Outside of the sphere, we shall propose an expansion in terms of $\mathbf{M}$'s and $\mathbf{N}$'s as any other radial functions would blow up at $r \rightarrow 0$. Outside of the sphere, the expansion will contain $\mathbf{M}^{(1)}$ and $\mathbf{N}^{(1)}$, because we would like to find solutions that in the far field $k_{\text{out}}r \rightarrow +\infty$ resemble an outgoing wave. $\mathbf{M}^{(2)}$ and $\mathbf{N}^{(2)}$ however present converging waves to the origin.

The field can be cast in the following form:

$$\mathbf{E}_{\text{in}}(\mathbf{r}) = \sum_{l=1}^{+\infty} \sum_{m=-l}^l \left[a_{lm}^{\text{in}} \mathbf{M}_{lm}(\mathbf{r}; k_{\text{in}}) + b_{lm}^{\text{in}} \mathbf{N}_{lm}(\mathbf{r}; k_{\text{in}}) \right], \quad (5-22a)$$

$$\mathbf{E}_{\text{out}}(\mathbf{r}) = \sum_{l=1}^{+\infty} \sum_{m=-l}^l \left[c_{lm}^{\text{in}} \mathbf{M}_{lm}^{(1)}(\mathbf{r}; k_{\text{out}}) + b_{lm}^{\text{out}} \mathbf{N}_{lm}^{(1)}(\mathbf{r}; k_{\text{out}}) \right] \quad (5-22b)$$

Again, note that neither of the expansions include terms with $l = 0$ as the spherical vectors vanish when the amplitude of the angular momentum is zero.

In order to apply the boundary conditions we would require to stop using this nice quantum mechanical formalism and move onto integrals and derivatives of spherical harmonics. Luckily, all this work has already been done in the past. The solutions for the coefficients are the well known [44, 114, 136]:

$$a_l^{\text{out}} = \frac{\nu \psi_l'(k_{\text{out}}a) \psi_l(k_{\text{in}}a) - \psi_l'(k_{\text{in}}a) \psi_l(k_{\text{out}}a)}{\psi_l'(k_{\text{in}}a) \xi_l(k_{\text{out}}a) - \nu \xi_l'(k_{\text{out}}a) \psi_l(k_{\text{in}}a)}, \quad \nu = \sqrt{\frac{\epsilon_{\text{out}} \mu_{\text{in}}}{\epsilon_{\text{in}} \mu_{\text{out}}}} \quad (5-23)$$

with $\psi_l(x) = x j_l(x)$ and $\xi_l(x) = x h_l^{(1)}(x)$ and $m = \pm 1$. Similarly:

$$b_l^{\text{out}} = \frac{\nu \psi_l'(k_{\text{in}}a) \psi_l(k_{\text{out}}a) - \psi_l'(k_{\text{out}}a) \psi_l(k_{\text{in}}a)}{\psi_l(k_{\text{in}}a) \xi_l'(k_{\text{out}}a) - \nu \xi_l(k_{\text{out}}a) \psi_l'(k_{\text{in}}a)}, \quad \nu = \sqrt{\frac{\epsilon_{\text{out}} \mu_{\text{in}}}{\epsilon_{\text{in}} \mu_{\text{out}}}}, \quad (5-24)$$

where it is understood that $m = \pm 1$ and cannot take any other value.

The road to this results has been very exhausting. However, now comes the interesting part. The calculation of the scattering cross-sections.

5.2 ELECTRIC AND MAGNETIC RESONANCES

We can prove that:

$$\sigma_{\text{scat}} = \frac{2\pi}{k_{\text{out}}^2} \sum_{l=1}^{+\infty} (2l+1) \{ \text{Re}[a_l] + \text{Re}[b_l] \}. \quad (5-25)$$

This is what is called a multipolar decomposition and the a_l terms are related to electric resonances while the b_l to magnetic resonances. That is because the former are constants multiplying the $\mathbf{M}$ fields, which act as an analogue of the electric field. Similarly, the latter multiply the $\mathbf{N}$ fields analogous to the magnetic field.

Figure 5.3 shows the scattering cross-sections as a function of wavelength for different materials and radii. The wavelength range shown lies in the visible and the surrounding medium is air. In 5.3(a) we can compare the influence of the refractive index in the overall scattering cross-section. As can be seen, the central wavelengths of the different resonances are shifted to the red. This implies that low-energy light can be more easily scattered from high index materials. In other words, less photon energy is required (they converge to the infra-red).

Figure 5.3(b) shows the total scattering spectra for GaP and Si as a function of radius. Given that whole radial dependence appears in the coefficients as $k_0 n_{\text{out}} a$, modifying the radius by a factor of η , has the same effect as increasing the refractive index (and the absorption!) or equivalently, contracting the wavelength range. It is under this last scenario that we can understand the shift in the resonances to the red.

It must also be noted that dielectric nano-antennas behave differently to its metallic counterparts, even though the theory is essentially the same. Figure 5.3(c) shows the scattering spectrum of a 90 nm radius Au sphere. Only the electrical component of the scattering cross-section is plotted, as the magnetic one was more than one order of magnitude smaller. This is the first key diverging point: metals cannot show magnetic resonances, therefore their application lies solely in the realm of electric active materials (both in linear and in non-linear optics). The second difference is the scattering intensity. This, as can be seen by comparing the density plots for Au with Si and GaP, is less strong, and in particular does not present the same rich structure found in dielectrics. This can be understood when taking into account the losses.

Qualitatively, losses indicate that more energy is going to be dissipated in the near field, and therefore will fall in the non-radiative buckets. However, more quantitatively, the sharp resonances arise from the zeros of the denominators in equations 5-23 and 5-24. These denominators are, essentially, a linear combination of spherical Bessel and Hankel functions. They have a real and imaginary part which prevents the resonances from blowing up to infinity. The origin of the imaginary parts comes from evaluating the spherical functions in arguments that are in general complex due to the complex refractive index. The imaginary part of this denominator dampens the total resonance and harmfully impacts the scattering cross-section of the nano-sphere.

Furthermore, from the density plots in figure 5.3(b) we observe that as the radius of the sphere increases, the resonances also shift. This is

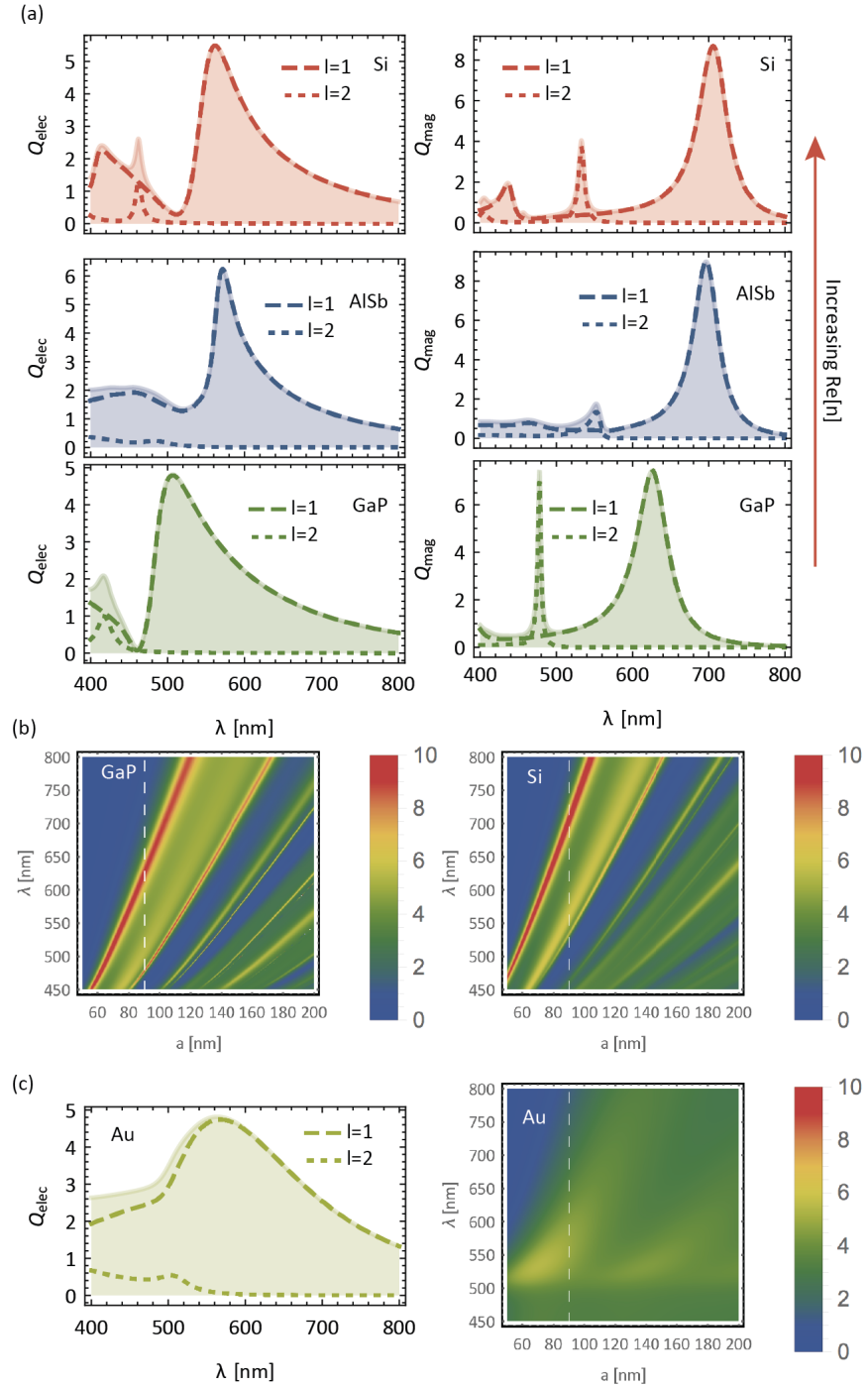


Figure 5.3 (a) Normalised scattering cross-sections of spheres of Si, GaP and AlSb calculated using 5–25. The radii of the spheres is 100 nm. The surrounding medium of the spheres is air. The left panels show the contribution of the electric field to the cross-section (the a_l 's) for two different orders $l = 1, 2$. Similarly, the right panels show the contribution of the magnetic field to the cross-section (the b_l 's). (b) Total scattering as a function of radius for GaP (left) and Si (right). They present a similar red-shifting behaviour of the main resonance, which is more steep in the case of the Si. The dashed white lines represent the radius ($a=90$ nm) at which the plots from (a) were calculated. (c) Similar results but for Au. To the right, the density plot of total scattering cross-section as a function of radius shows weaker scattering properties.

expected, given that, in general, the larger the structure, the less photon energy is required to excite it¹.

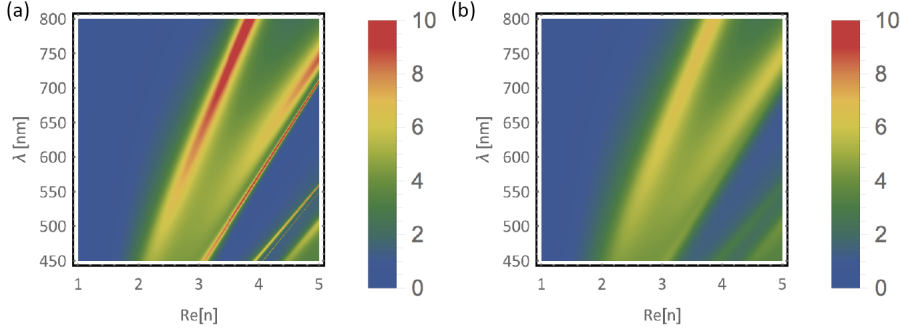


Figure 5.4 (a) Scattering cross-section as a function of real part of the refractive index with zero imaginary part for a sphere of radius $a = 100$ nm. (b) Same, but with a small $\kappa = 0.1$ imaginary contribution.

We can also observe the role played by the absorption in the scattering resonances. Figure 5.4 shows the scattering cross-section as a function of the real part of the refractive index. As described in section 2.3, the width is inversely proportional to the typical lifetime of a pulse exciting a structure. Therefore, the larger width we observe by increasing the losses (or, similarly, the radius) should inversely impact the decay time of the scattered light.

As can also be seen from figure 5.4(a), materials with refractive index between 1 and 2 do not present any resonances for a sphere of radius 100 nm. If the radius increases, this threshold decreases, which means that larger structures can hold modes more or less irrespective of the refractive index. However, the situation becomes critical when the radius gets smaller and smaller. More importantly, if a large number of devices are desired to be integrated in a photonic chip, the length-scales to work need to lie in the range of several 10s of nm. For example for a 50 nm radius sphere, the threshold increases to around $\text{Re}[n] = 4$ for the main dipolar resonance. This is a challenge that can only be overcome by developing high refractive index materials with low-losses.

Finally, the true strength of dielectrics comes in two flavours. Firstly, we can obtain stronger scattering cross-sections, due to the low losses, which enhance the efficiency of an antenna. Secondly, the lack of losses, together with high refractive indices, opens the possibilities of studying higher order modes, that would in metals remain dormant. In the next section,

¹In order to demystify electromagnetism, I propose the following easy-to-understand textbook example. The longer a rope is, the longer the wavelength of the fundamental mode is going to be. As wavelength is inversely proportional to frequency and frequency is proportional to energy, the previous assertion holds.

I perform a similar analysis but comparing radiative rates of emitters located in the vicinity of nano-spheres.

5.3 LIGHT-MATTER INTERACTIONS REVISITED

The main advantage of using dielectric materials is their low-losses, which help compete with metallic scattering efficiencies. Furthermore as is mentioned in the previous section, the possibility of exciting multipolar modes that are otherwise absent in metals is also a very attractive feature. In this section I show some results of multipolar analysis that help elucidate the interaction between light and matter in dielectrics.

We can obtain expressions for the radiative rate of emitters located in the vicinity of spheres with a similar mathematical juggling as the one painstakingly developed in the last pages. For the sake of keeping the reader, and the examiner, perusing this thesis until the end, I only quote the results for the radiative and total decay rates.

For far-field applications, radiative rate enhancement is a very important quantity. In particular, it can be cast in two different forms, depending on the orientation of the dipole moment. Figure 5.5(a) shows the geometry and orientation of the dipole with respect to the nano-sphere. For an electric dipole located at $z_0 > a$ from the sphere, the radiative rate enhancements are given by [136]:

$$\frac{\gamma_{\hat{x}}^r}{\gamma_0} = \frac{3}{4} \sum_{l=0}^{+\infty} (2l+1) \left[|j_l(k_{\text{out}}z_0) + b_l h_l^{(1)}(k_{\text{out}}z_0)|^2 + \left| \frac{\psi_l'(k_{\text{out}}z_0) + a_l \xi_l'(k_{\text{out}}z_0)}{k_{\text{out}}z_0} \right|^2 \right], \quad (5-26a)$$

$$\frac{\gamma_{\hat{z}}^r}{\gamma_0} = \frac{3}{2} \sum_{l=0}^{+\infty} (2l+1)l(l+1) \left| \frac{j_l(k_{\text{out}}z_0) + a_l(k_{\text{out}}z_0)}{k_{\text{out}}z_0} \right|^2. \quad (5-26b)$$

Similarly, the total decay rate is given by²:

$$\frac{\gamma_{\hat{x}}}{\gamma_0} = 1 + \frac{3}{4} \sum_{l=0}^{+\infty} (2l+1) \text{Re} \left\{ a_l \left[\frac{\xi_l'(k_{\text{out}}z_0)}{k_{\text{out}}z_0} \right]^2 + b_l \left[h_l^{(1)}(k_{\text{out}}z_0) \right]^2 \right\}, \quad (5-27a)$$

$$\frac{\gamma_{\hat{z}}}{\gamma_0} = 1 + \frac{3}{2} \sum_{l=0}^{+\infty} (2l+1)l(l+1) \text{Re} \left\{ a_l \left[\frac{h_l^{(1)}(k_{\text{out}}z_0)}{k_{\text{out}}z_0} \right]^2 \right\}. \quad (5-27b)$$

²The results in [136] can be obtained by replacing $a_l \rightarrow -a_l$ and $b_l \rightarrow -b_l$.

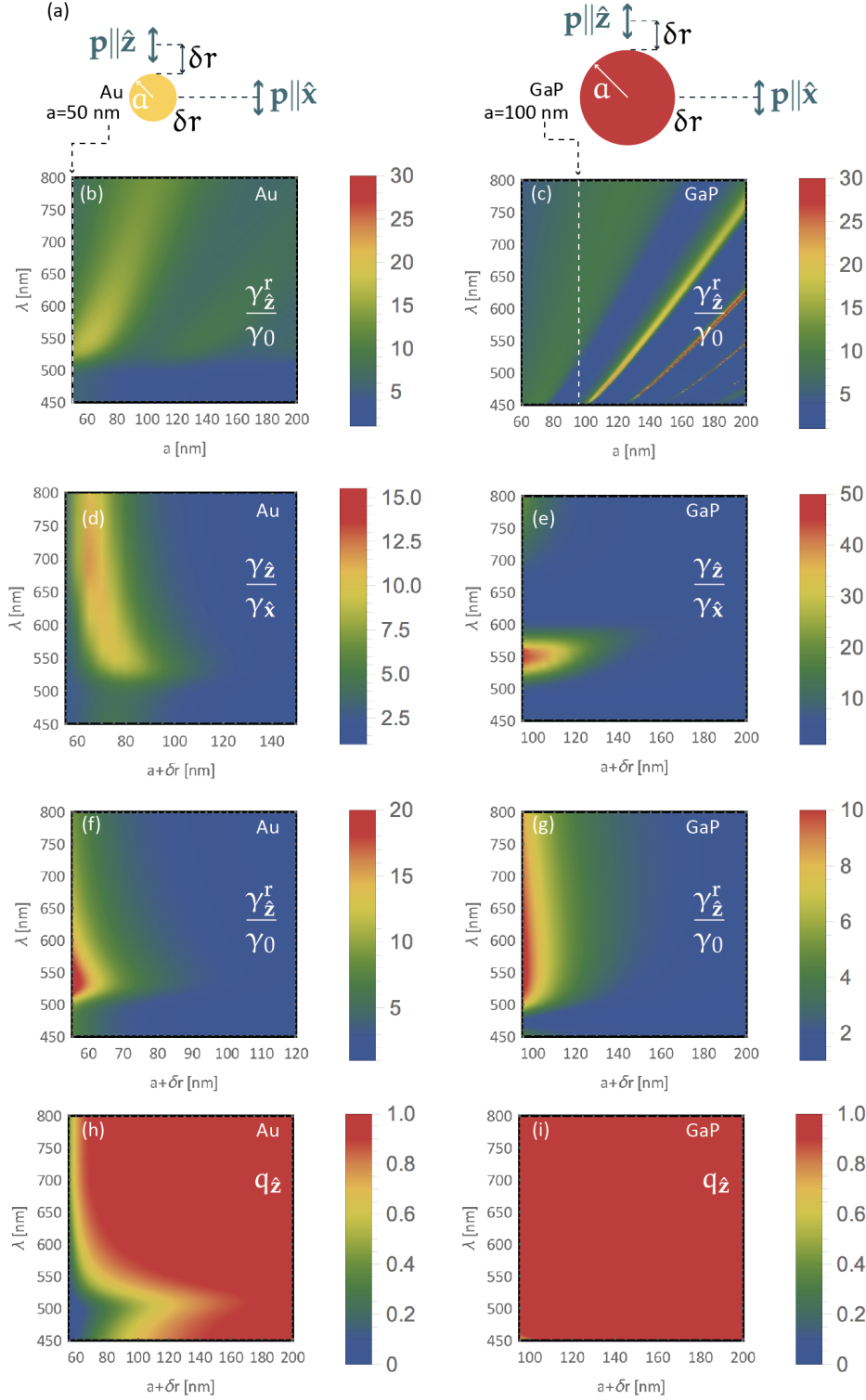


Figure 5.5 (a) Scheme of a Au and a GaP nano-sphere and two differently positioned dipoles. The radii quoted in the schemes refer to the dashed lines in (b)–(c) and are the radii used to evaluate (d)–(i). (b)–(c) Radiative rate enhancement with dipole parallel to the $\hat{z}$ direction for a Au (b) and for a GaP (c) nano-sphere of varying radius. δr is fixed at 10 nm. (d)–(e) Ratio of total rate enhancement between both dipole orientations for a Au (d) and for a GaP nano-sphere (e) as a function of δr . (f)–(g) Same parameters as in (d)–(e) but here the radiative rate is plotted as a function of emitter-sphere separation. (h)–(i) Quantum efficiency of radiation for a Au and a GaP nano-spheres, same parameters as before, as a function of emitter-sphere separation.

From these equations, we can also define the quantum efficiency of an emitter modified by its electromagnetic environment:

$$q(\lambda) = \frac{\gamma_r(\lambda)}{\gamma(\lambda)} = \frac{\gamma_r(\lambda)}{\gamma_{nr}(\lambda) + \gamma_r(\lambda)}. \quad (5-28)$$

The quantum efficiency tells us how much of the energy used by the emitter, in the vicinity of the nano-antenna, is actually coupled to far-field radiation. The radiative-rate enhancement tells us how much the rate of photons emitted to the far-field is enhanced by the proximity of the nano-antenna. Both quantities are of paramount importance, as having large quantum yield can only mean that no non-radiative channels are being activated but the radiative rate can stay the same. Similarly, large radiative rate enhancements can be accompanied by even larger non-radiative rate enhancements as is the case for metals, in which case the overall antenna is not suitable for far-field radiative rate enhancement.

We can plot the influence of the dipole orientation, separation from the sphere and sphere's radius on the decay rates and the quantum efficiency. Figure 5.5(a) shows a scheme a Au and a GaP nano-sphere interacting with a nearby dipole emitter. As was shown in figure 5.3, the radius of a sphere influences the amount and type of resonances to be supported by the structure. In other words, the size of the nano-structured material correlates to the number of optical states to which an emitter can couple. It can be compared in figure 5.5(b) how the addition of losses creates less sharp resonances in the far-field radiative rate γ_z^r . Conversely, figure 5.5(b) shows sharp stronger resonances, implying that emitters coupled to GaP spheres of radii greater than ~100 nm can enhance the radiative rate more than single gold nano-spheres.

The dipole orientation is of paramount importance, as can be seen in figures 5.5(d)-(e). Here the ratio between two orthogonal dipole orientations is plotted as a function of wavelength and sphere-emitter separation. It can be observed that the $\hat{z}$ dipole orientation provides larger decay rate enhancements as its perpendicular counterpart. This can be qualitatively understood as follows. In the near-field the electric field pattern for a dipole follows the orientation of the dipole moment's direction (in contrast to its far-field pattern which is perpendicular). Therefore, the $\hat{z}$ oriented dipole interacts more strongly in the near-field with the nano-sphere. As is expected, the farther apart (larger δr , in the figure's notation) the dipole is from the antenna, this ratio converges to one. For the lossy case, figure 5.5(d), we obtain highly damped resonances, whereas for a single-mode GaP nano-antenna (at a radius of 100 nm), the ratio of perpendicular

orientations achieves a 50-fold increase for a localised wavelength range around 550 nm and short sphere-emitter separations. This resonance coincides with the main electric dipolar resonance of figure 5.3(a) ($l = 1$), indicating that high scattering cross-sections expectedly label the appearance of efficient far-field out-coupled light from single photon emitters.

Figures 5.5(f)-(g) show the influence of the emitter-sphere separation on the radiative rate enhancement. As is to be expected, this is increased the stronger the emitter-sphere interaction is accomplished, which in turn is monotonically increasing with the emitter-sphere distance. Of course, there is a saturation to the amount of enhancement that can be achieved, as the closer the emitter is to the nano-structure, the easier it is to couple to near-field non-radiating modes (specially in metallic nano-particles [63, 64]). To try to quantify the phenomenon of quenching, we defined the quantum efficiency in equation 5-28. Figures 5.5(h)-(i) show the quantum efficiency as a function of wavelength and emitter-sphere separation. This efficiency converges to 1 for large separations (in the case of zero intrinsic non-radiative losses), because the total decay rate in the denominator and the radiative rate in the numerator converge to the same value. The interesting region is, however, the near-field quantum efficiency. For example, an emitter located only 5 nm from a 50 nm Au sphere would have a nearly zero quantum efficiency (yet a nearly 10-fold radiative rate enhancement), indicating that most of the energy is used for non-radiative processes. In stark contrast to this, an emitter arbitrarily close to a GaP nano-sphere has near unity quantum efficiency, implying that the emitter can hardly couple to the meagre amount of non-radiative channels that can be supported by the nano-sphere. It is interesting that this trend is widespread throughout the whole visible regime and only starts to kick-in around the UV, where absorptions in GaP are already established.

To sum up, in this chapter we studied the quintessential nano-photonics structure: a nano-sphere. I showed how an exact solution of Maxwell's equation can be found using the convoluted formalism of spherical vector harmonics and used these results to calculate empirically relevant magnitudes. Among them, the scattering cross-section was decomposed into its many modes and it was shown that dielectric nano-particles can support higher order multipolar resonances. This feature is not observed in simple metallic nano-spheres. Furthermore, a decomposition into electric and magnetic modes allows to study light-matter interactions outside the usual electric dipole approximation. However, in this chapter I only analysed electric dipolar emitters interacting with spherical nano-particles. Finally, I showed the influence of several parameters such as sphere's ra-

dius and emitter-sphere separation on the far-field coupling properties of the emitter. To sum up, Au nano-spheres can provide larger rate enhancements but in general the efficiencies of radiation are smaller than those provided by dielectric nano-antennas. Furthermore, dielectric nano-antennas provide a more broadband wavelength range than its metallic counterparts and are also less sensitive to emitter-sphere separation. Supporting higher-order modes that can efficiently couple to the far-field also provide these antennas with promising applications in yet only the negligibly explored field of light-matter interactions for other types of emitters [17–19].

The next chapter shows an application to a real-life situation of a GaP dimer interacting with fluorescent dyes. There it is shown how this interaction provides larger fluorescence rate enhancements in these emitters when comparing their behaviour close to a nano-structured dimer GaP nano-antenna and away from it.

6

GALLIUM PHOSPHIDE
DIMERS FOR
FLUORESCENCE RATE
ENHANCEMENT

In this chapter I show the modification of the radiative properties of emitters located in the neighbourhood of dimer gallium phosphide antennas. Section 6.1 theoretically deals with the modification of the rate of fluorescence of dyes located in the vicinity of any nano-antenna. Following that, I describe the properties of gallium phosphide nano-antennas in isolation in section 6.2. The next three sections refer to the actual experiments and give details of the dye that was used (section 6.3), the fabrication of the nano-antenna (section 6.4) and the optical properties of the specific antenna 6.5. I conclude this chapter in section 6.6 with the experimentally obtained fluorescence enhancement and modification of decay rates.

6.1 FLUORESCENCE ENHANCEMENT: A COMBINATION
OF EFFECTS

In order to understand the interaction of a fluorescent molecule with a nano-antenna we have to consider a more complicated emitter. A two-level emitter, as considered in chapter 1 cannot intrinsically suffice, because fluorescent molecules (and in fact, also colloidal nano-crystals) absorb light more strongly out of resonance. This simply means that the emission and absorption lines do not coincide. For example, most colloidal nano-crystals from figure 3.1 on page 44 present an emission shifted out from the faint emission peaks. Figure 6.1(a) shows a scheme of the three-level emitter to be analysed and figure 6.1(b) the spectral behaviour of a more realistic emitter. In the approximation below, we shall consider illumination at a shorter wavelength (around 633 or 640 nm in our case) and collection of emission at wavelengths above it (specifically, around 651 nm). These two resonance peaks correlate to the transition $|g\rangle \rightarrow |e_2\rangle$ for absorption and the $|e_1\rangle \rightarrow |g\rangle$ for emission. The different decay rates will suffer different modifications because they belong to sep-

arated wavelength ranges. For example the total decay rate of the bright transition can be decomposed into $\gamma_{10} = \gamma_r + \gamma_{nr}$. This total decay rate can be given by Fermi golden rule. The radiative and non-radiative components can be calculated as explained in figure 1.3 on page 10. Similarly, Ω is given by the stimulated transition rate of excitation, given by the square of the coupling constant:

$$\begin{aligned}\Omega = g^2 &= |\langle e_2 | -\mathbf{n} \cdot \mathbf{E}(\mathbf{r}_0; \lambda_{\text{abs}}) | g \rangle|^2, \\ &= |\hat{\mathbf{n}} \cdot \mathbf{E}(\mathbf{r}_0; \lambda_{\text{abs}})|^2,\end{aligned}\quad (6-1)$$

where $\hat{\mathbf{n}}$ is the orientation versor of the dipole and $\mathbf{E}(\mathbf{r}_0; \lambda_{\text{abs}})$ is the electric field at the position $\mathbf{r}_0$ of the dipole at the wavelength of absorption. Notice that this is the field squared obtained from far-field illumination.

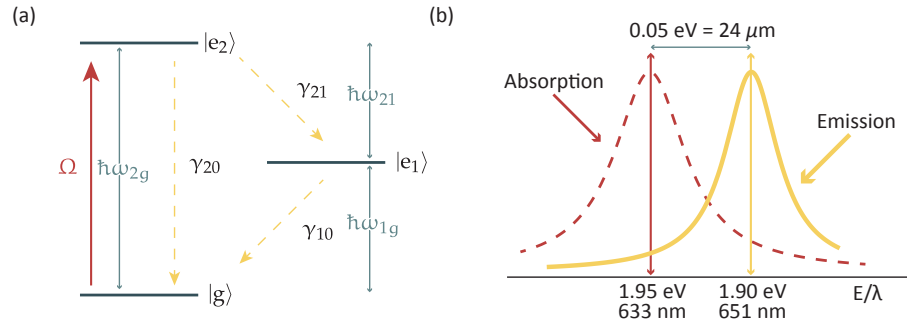


Figure 6.1 Scheme of fluorescent molecule as a 3 level emitter.

I will derive the solution quite generally, but at the end I will assume certain hypothesis that should hold for any reasonable system. We could start with a fully-quantum description, using Lindblad operators [8, 137] to describe the dynamics of the system. However, the final result coincides with this far easier approach, which is based on an intuitive rate equation description. The main discrepancies between the fully quantum and this simpler approach lies in the description of coherences between different energy levels. Given that we are not interested in calculating quantities that take into account off-diagonal elements of the density matrix describing the system, we shall continue our analysis, therefore, with the rate equation approach.

We begin by writing down the equations governing the probabilities $p_i(t)$ of finding the molecule in a specific energy level $i = g, 1$ and 2 as a function of time. As an example, I will derive the equations for $p_1(t)$ and then write down those for $p_2(t)$ and $p_g(t)$. The probability of finding the emitter in state 1 at $t + \delta t$ is given by $p_1(t + \delta t)$. Now, it can be in state 1 because:

- It decayed from state 2, having been there at time t , with probability $(\gamma_{21}\delta t) \times p_2(t)$. This is the product because the premise is *emitter decayed* AND *emitter was in 2*. Furthermore, we note that the probability that it was indeed in level 2 at time t is given by $p_2(t)$ and the probability of it actually decaying by $\gamma_{21}\delta t$. Note that γ_{21} is a probability per unit time (also known as a rate), therefore $\gamma_{21}\delta t$ is adimensional.
- It was already in state 1, with probability: $p_{\text{stay}}p_1(t)$. Now given that on this level it can either stay or decay, simple consistency of probabilities requires that: $p_{\text{stay}} + \gamma_{10}\delta t = 1$.

From these two considerations we obtain:

$$p_1(t + \delta t) = \overbrace{\gamma_{21}p_2(t)}^{\text{decays at } t \text{ AND is in 2 at } t} \underbrace{+}_{\text{XOR}} \overbrace{(1 - \delta t\gamma_{10})p_1(t)}^{\text{NOT decays at } t \text{ AND is in 1 at } t}, \quad (6-2)$$

which after reshuffling the terms around and taking the limit $\delta t \rightarrow 0$:

$$\dot{p}_1(t) = \gamma_{21}p_2(t) - \gamma_{10}p_1(t). \quad (6-3)$$

Similarly,

$$\dot{p}_g(t) = \gamma_{20}p_2(t) + \gamma_{10}p_1(t) - \Omega p_0(t), \quad (6-4a)$$

$$\dot{p}_2(t) = \Omega p_g(t) - (\gamma_{21} + \gamma_{20})p_2(t). \quad (6-4b)$$

We must not forget the normalisation condition:

$$p_g(t) + p_1(t) + p_2(t) = 1, \quad \forall t, \quad (6-5)$$

which basically states that in our model there is certainty that the system can be found in either of the three states in which we are describing it.

Given that fluorescence enhancement measurements are carried out with continuous wave excitation, we shall assume that the system has reached a stationary state, from where all the time derivatives are zero and the time dependence is ignored.

The quantity of interest is the rate of photon emission $\mathcal{R}$, which is the probability of finding the state in the excited level 1 times the probability that it actually decays into a radiative photon:

$$\mathcal{R} = \gamma_r p_1. \quad (6-6)$$

Solving the stationary equations ($d/dt = 0$) we find that, quite generally,;

$$\mathcal{R} = \gamma_r \frac{\gamma_{21}/\gamma_{10}}{1 + \frac{\gamma_{21} + \gamma_{20}}{\Omega} + \frac{\gamma_{21}}{\gamma_{10}}}. \quad (6-7)$$

The fluorescence enhancement parameter η is, therefore, the ratio between the rate of emission $\mathcal{R}$ in a specific environment and the rate of emission $\mathcal{R}_0$ in a different environment, usually vacuum but not necessarily. As shown in figure 6.1(b), the energy distance between the excited levels 2 and 1 is so small, that in order to be modified by an electromagnetic environment we would need to have a resonating structure at around 24 μm , far in the telecom regime. Given that we are only interested in optical resonances, we can consider that this rate remains unchanged in the presence of the nano-antenna. However, both the radiative and the total decay rates will suffer modifications. We can also assume that γ_{20} is negligible. This is reasonable because we rarely detect photons with the same wavelength as the excitation wavelength. This rate should be modified in the presence of the nano-antenna, however, we still consider this modification to be not significant enough to contribute to the description of the experiment. Beyond this reasonable assumptions, there is compelling experimental evidence in our work that justifies this. The general expression can be cast in the form:

$$\eta = \frac{\mathcal{R}}{\mathcal{R}_0} = \frac{q(\lambda_{10})}{q_0(\lambda_{10})} \frac{1 + \gamma_{21}^0 \left(\frac{1}{\Omega^0} + \frac{1}{\gamma_{10}^0} \right)}{1 + \gamma_{21}^0 \left(\frac{1}{\Omega} + \frac{1}{\gamma_{10}} \right)}, \quad (6-8)$$

where λ_{10} is the emission wavelength. Similarly λ_{20} is the absorption wavelength and q is the quantum yield at emission wavelength, defined as the ratio between the radiative rate and the total decay rate for this transition.

Two limiting values can be obtained, depending on the power of excitation, parametrised by Ω . In the first case, the rate of excitation is intrinsically low, where we obtain [37, 84]:

$$\eta = \frac{\mathcal{R}}{\mathcal{R}_0} = \frac{q(\lambda_{10})}{q_0(\lambda_{10})} \overbrace{\left| \frac{\hat{\mathbf{n}} \cdot \mathbf{E}(\mathbf{r}_0; \lambda_{20})}{\hat{\mathbf{n}} \cdot \mathbf{E}_0(\mathbf{r}_0; \lambda_{20})} \right|^2}^{\Omega/\Omega_0} \gamma_{21}^0 \gg \Omega, \Omega^0 \quad (6-9)$$

In other words, the fluorescence enhancement is given by the product of the change in efficiency of radiation at the emission wavelength and the change in efficiency of excitation [84].

The opposite limiting case is when the excitation power is too high. In this case, the system saturates to a power-independent enhancement:

$$\eta = \frac{\mathcal{R}}{\mathcal{R}_0} = \frac{\gamma_r(\lambda_{10})}{\gamma_r^0(\lambda_{10})} \quad \gamma_{21}^0 \ll \Omega, \Omega^0, \quad (6-10)$$

which implies that the absorption has saturated and the only mechanism contributing to the far-field radiation is the number of far-field optical modes to which the emitter can couple to.

6.2 GALLIUM PHOSPHIDE DIMERS, ULTRA-LOW LOSSES AND ULTRA-HIGH SCATTERING

We turn now our attention towards the experimental study of the fabricated GaP nano-antenna as a nano-photonic platform optimised for the enhancement of radiative properties of fluorescent molecules in the visible range (schematic in Figure 6.2). To that end, we fabricated GaP dimer-like nano-antennas with 35 nm gap size.

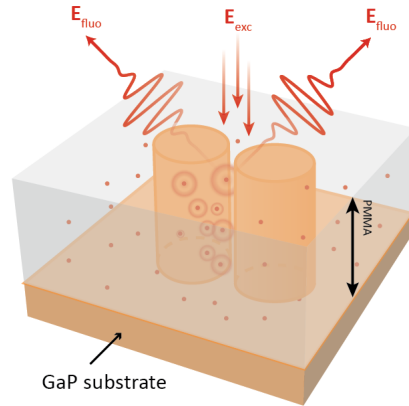


Figure 6.2 Scheme of gallium phosphide nano-antenna interacting with fluorescent dyes embedded in a polymeric matrix. Adapted from ref. [86].

To characterise the scattering resonances of the nano-antennas, we simulated and subsequently measured the scattering cross section of the different GaP dimers. In this section I describe the simulated behaviour of GaP monomers and dimers. Figure 6.3 shows the simulated optical properties of GaP nano-antennas. The radii of the structures were fixed at 50 nm and the height at 200 nm. This choice is related to the fabricated structures, as mentioned in section 6.4. Firstly, the response of GaP

monomers and dimers was studied in vacuum. Figure 6.3(a) shows the scattering cross-section of several GaP dimers and of a GaP monomer. We can observe a broadband response in the visible region with absolutely negligible losses from 450 nm to the red. In Particular, the single dipolar resonance at around 500 nm gets more and more pronounced the larger is the gap between the dimers.

In order to quantify the efficiency of an antenna, as mentioned in section 3.2 (and in particular in equation 3-7) we need to calculate the power coupled into the far-field over the total power consumption (given by both scattering and absorption). Figure 6.3(b) shows the sharp trend of the efficiency of these GaP nano-antennas, which after around 500 nm achieve near unity scattering. In other words, absorption is so negligible, that no near-field modes can be labelled as lossy. This proves that the GaP antenna, both monomer and dimers, act as very efficient far-field couplers in vacuum and therefore as promising candidates for coupling single-photon emitters to them. We can observe that this value highly contrasts with the maximum radiation efficiency of about 75% simulated for a Si Yagi-Uda antenna in this spectral range [120], anticipating the potential benefits of exploiting the close to zero absorption of GaP at visible wavelengths.

The coupling to an emitter at low excitation power is given by equation 6-9, which states that the near-field excitation enhancement plays a crucial role in enhancing the fluorescence rate of the emitters. In particular, the total field enhancement at the wavelength of absorption ($\lambda_{\text{abs}} = 633$ nm in our experiments) represents a paramount figure to describe the light-matter interactions in the nano-scale. Figures 6.3(c)-(f) show that we can expect, in vacuum, up to a 32-fold field enhancement in the gaps of very tightly packed GaP pillars. However, a more precise value is that of the $\hat{x}$ and $\hat{z}$ components of the electric field in the regions where the emitters are located.

As is explained in section 6.6, we compared the fluorescence rate of molecules immersed in a PMMA matrix in the vicinity of GaP dimer nano-antennas to that of molecules in the same PMMA matrix on top of the GaP substrate. Therefore we need to simulate the excitation enhancement for these two configurations. For this reason, in figures 6.3(g)-(h) the simulated set-up was closer to that in 6.2, in order to try to replicate our experimental conditions as close as possible. In this case, horizontally linearly polarised light was used and the absolute value squared of the $\hat{x}$, figure 6.3(g), and $\hat{z}$, figure 6.3(h), electric field components were calculated with and without the GaP dimer. The ratio between both situations

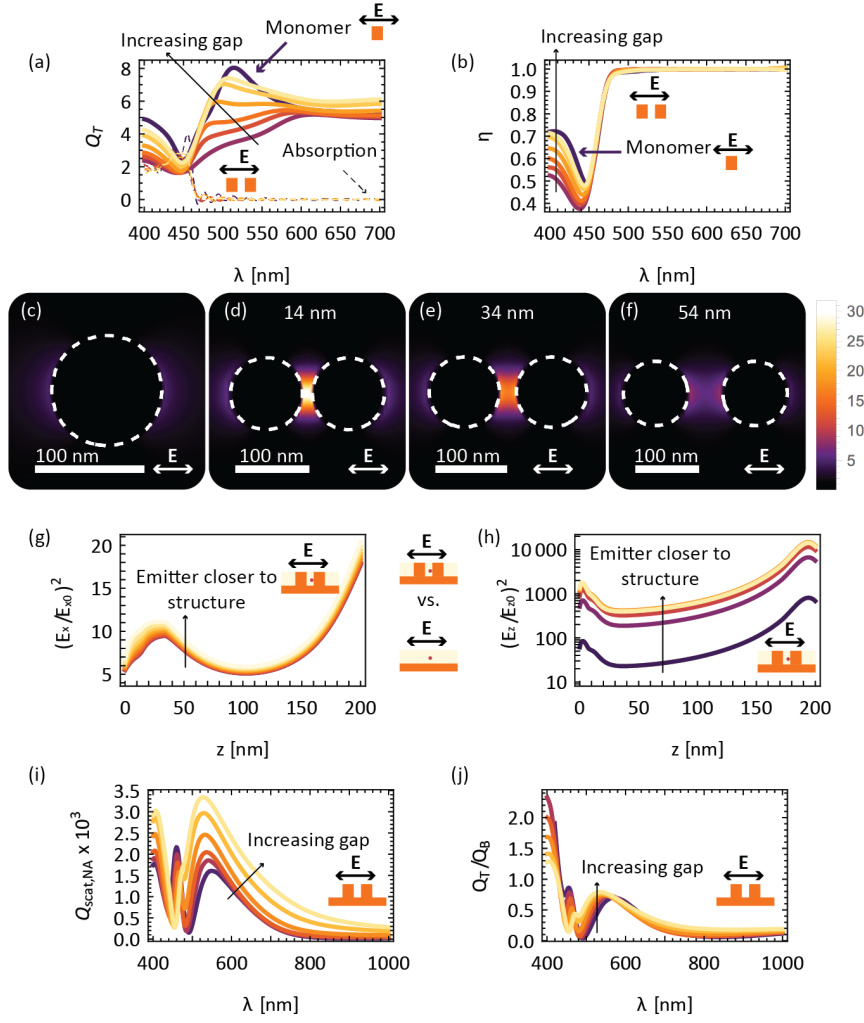


Figure 6.3 (a) Total scattering and absorption cross-section for a GaP monomer of radius 50 nm and height 200 nm and for several dimers of 50 nm radius and 200 nm height. All the structures are suspended in vacuum. (b) Scattering efficiency as a function of wavelength for GaP monomers and dimers. (c)–(f) Near-field maps of the field enhancement $\|\mathbf{E}(\mathbf{r}, \lambda_{\text{abs}})\|^2 / \|\mathbf{E}_0(\lambda_{\text{abs}})\|^2$ in the vicinity of a GaP monomer (c) or GaP dimers (d)–(f). All the structures are in vacuum. The size of the gaps appear in the title of the figures. The excitation polarisation is horizontal. (g)–(h) Excitation enhancement for single-photon emitters located in the gap of a GaP dimer, immersed in PMMA and on top of a GaP substrate. The inset inbetween (g) and (h) represents the situations to be compared: top emitters in the vicinity of GaP dimers immersed in PMMA vs. bottom, emitters in PMMA close to a GaP substrate. (i) Dark-field simulated scattering cross-section for horizontal polarisation for GaP dimers on a GaP substrate. (j) Forward-to-backward scattering ratio of GaP dimers on a GaP substrate. All the insets represent a side view of either the monomer or dimers, together with the excitation beam.

gives a relative excitation enhancement that is directly related to the measurement values. As we can clearly see, when the dipoles are oriented vertically we obtain large excitation enhancements. This is mainly due to the fact that the discontinuity of the refractive index on sub-wavelength scales in the case of a GaP dimer, provides the necessary $\mathbf{k}$ vectors to have non-negligible $\hat{\mathbf{z}}$ which would otherwise be nearly non-existent when exciting with horizontally polarised light. These simulations clearly indicate that large fluorescence enhancements are expected for properly placed single-photon emitters.

Finally, figure 6.3(i)-(j) quantify the properties of the GaP nano-antennas on a GaP substrate. The excitation light was simulated to closely resemble the dark-field illumination set-up, in order to properly compare with experimental measurements. In particular, figure 6.3(i) shows the scattering cross-section measured by an NA=0.7 objective (the one we use for dark-field measurements). As we can see, the resonances are much sharper than its plane-wave counterparts, implying that under this type of illumination only certain modes get excited, in particular, the dipolar modes close to 600 nm. A sharp magnetic resonance can also be seen at around 480 nm for the smallest gaps nano-antennas. Furthermore, figure 6.3(j) shows the forward to backward scattering cross-section under dark-field illumination. As we can see, more light gets scattered into the substrate as onto the objective located on top of the structures. However, at around 630 nm - 650 nm we can expect a nearly 50-50 partition of energy between the detection objective and the substrate.

In other words, even though this geometry is not directional, we can state that it is highly efficient in scattering electromagnetic radiation. This comes together with large near field and excitation enhancements, which, as will be empirically shown below, aid at obtaining large fluorescence enhancement factors. The problem of directionality can be optimised with other architectures as shown in references [138–140] for other materials. In the following section, I briefly introduce the molecule used in our experiments for probing fluorescence enhancement of GaP nano-antennas.

6.3 MOLECULES: FLUORESCENT PROBES

The fluorescent probe that was used in this work was Abberior STAR 635P, chosen due to its low photobleaching rate [141]. The concentrated powder was dissolved in poly(methyl methacrylate) (PMMA) to a 500 μM concentration. This concentration of molecules was chosen so as to yield

an average density of 50 molecules in a 35 nm gap. Figure 6.4(a) shows the chemical structure of the dye and 6.4(b) shows the absorption of the dye+PMMA matrix in solution measured in an UV-vis spectrometre. The marked wavelength represents the excitation wavelengths used in fluorescence and time resolved measurements (more information found in section 6.6). As can be observed the absorption is red shifted with respect to the one given by the manufacturer, which could be due to the different solvent used in our experiments.

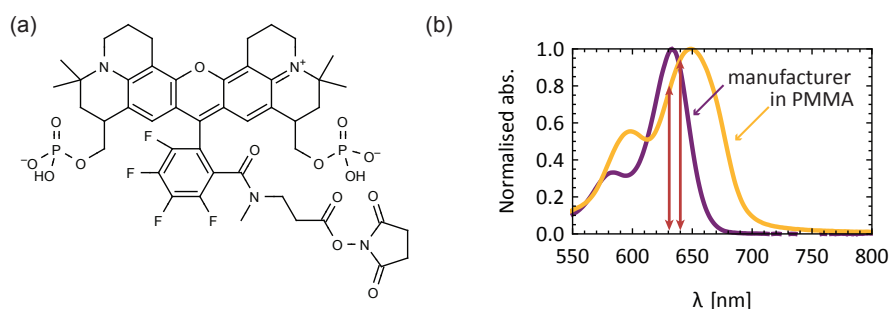


Figure 6.4 (a) Chemical structure of the fluorescent molecule used in the experiments. (b) Absorption of the molecule as provided by the manufacturer and as measured by us in a PMMA matrix. The molecule concentration in the PMMA is 10 μM . The red arrows mark the wavelengths used in the experiments (633 nm and 645 nm).

6.4 GALLIUM PHOSPHIDE DIMERS FABRICATION

Figure 6.5 shows the protocol for the fabrication of the nano-antennas. A pure undoped GaP(100) wafer was purchased from UniversityWafers. A layer of 40 nm of SiO_2 was sputtered at a rate of $0.2 \text{ \AA s}^{-1}$. This layer of SiO_2 acted as a mask for the GaP in later steps. Following this, PMMA was spin-coated at 3000 rpm for 1 min and E-beam patterned using a commercial Raith eLine system. The acceleration voltage was 20 kV, working distance 10 mm and aperture size 10 μm . The patterned sample was developed using standard MIBK:IPA 1:3 solution for 30 s followed by cleaning in a pure IPA solution. 40 nm of Au were subsequently evaporated at a rate of $2 \text{ \AA s}^{-1}$ at 10^{-6} Torr and the whole sample was immersed in acetone for lifting off the PMMA mask. After overnight immersion in acetone, the SiO_2 layer was etched with CHF_3 using a reactive ion etcher. This step left a ≤ 40 nm mask of SiO_2 which protected the underlying

GaP. Following this, Cl_2 based etching was used to remove 150 nm of GaP, except in those regions protected by the SiO_2 mask. Finally, remaining SiO_2 layer was fully removed with wet etching based on hydrofluoric acid (buffered oxide etch) immersion for 2 min and cleaned with several acetone and water steps.

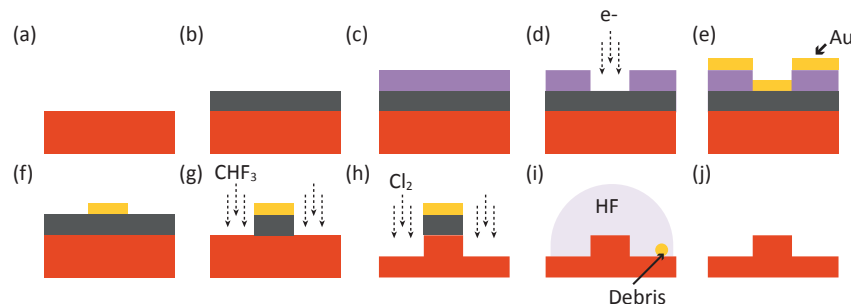


Figure 6.5 (a) GaP wafer. (b) Sputtering of SiO_2 at a rate of $0.2 \text{ \AA s}^{-1}$. (c) Spin coating of PMMA. (d) E-beam patterning of desired structures. (e) Au evaporation at a rate of $2 \text{ \AA s}^{-1}$. (f) PMMA lift-off. (g) SiO_2 inductively coupled reactive ion etching. (h) GaP chlorine reactive ion etching. (i) Hydrofluoric acid removal of SiO_2 mask and cleaning steps with acetone and water. (j) Final structure.

6.5 GALLIUM PHOSPHIDE DIMERS CHARACTERISATION

Figure 6.6(a) a scanning electron micrograph of the nano-antenna used in this work and figure 6.6(b) shows the theoretical and experimental scattering together with the theoretical absorption cross sections for the particular case of the 35 nm gap dimer. A single broad peak can be seen in the scattering cross sections in the selected spectral range, which would correspond to a dipolar mode, as deduced from integrating the current distribution on the nano-antenna†[20, 142, 143].

In figure 6.6(c)-(d) we can see the simulated electric field intensity distribution at resonance for both X and Y incident light polarization, *i.e.* parallel and perpendicular to the dimer orientation, respectively. As expected, the simulated patterns exhibit a dipolar behaviour, giving rise to a field intensity enhancement factor of up to >32 for the X polarisation. Conversely this enhancement is only 10 when considering the perpendicular direction. Therefore, when the excitation light is polarised parallel to the dimer orientation, the gap region provides a suitable location for placing fluorescent molecules, with highly localised and enhanced fields.

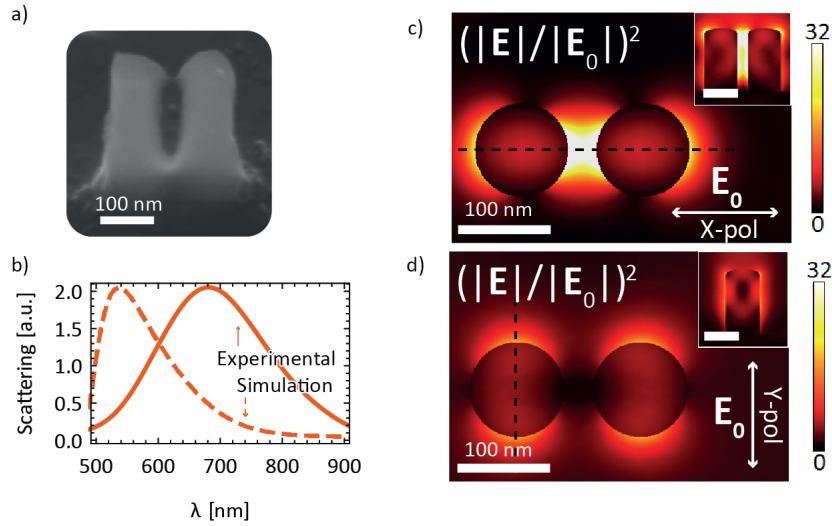


Figure 6.6 (a) Scanning electron micrograph of a 35 nm gap gallium phosphide nano-antenna. (b) Dark field spectra of GaP nano-antennas and simulated scattering cross-section. The collection angle in the simulation was set to $\arcsin \text{NA}$ (as mentioned in section 2.3), where NA is the numerical aperture of the dark-field objective. The absorption cross-section is also plotted. (c)-(d) Near-field distribution of the electric field, normalised to its excitation value. Adapted from ref. [86].

We shall exploit this properties of GaP nano-antennas in the next section to prove the enhancement of fluorescent dyes.

6.6 FLUORESCENCE ENHANCEMENT IN GALLIUM PHOSPHIDE DIMERS

To evaluate the experimental enhancement of fluorescence, the PMMA:dye coated nano-antenna was excited at resonance with linearly polarised 633 nm light at a power density of 2.5 MW cm^{-2} . The polarisation of the excitation laser was chosen to be either parallel or perpendicular with the dimer's main axis. The fluorescence was collected in a back-scattering configuration, using a long-pass filter to remove the laser's contribution to the spectrum.

In Figure 6.7(a) we plot the fluorescence spectra registered when exciting the coated nanoantenna with the two different polarisations, including, as reference, the result obtained when illuminating a bare PMMA:dye layer on the GaP substrate. We note that a bare PMMA film (*i.e.* containing no fluorescent dyes) on the GaP substrate produced only dark counts,

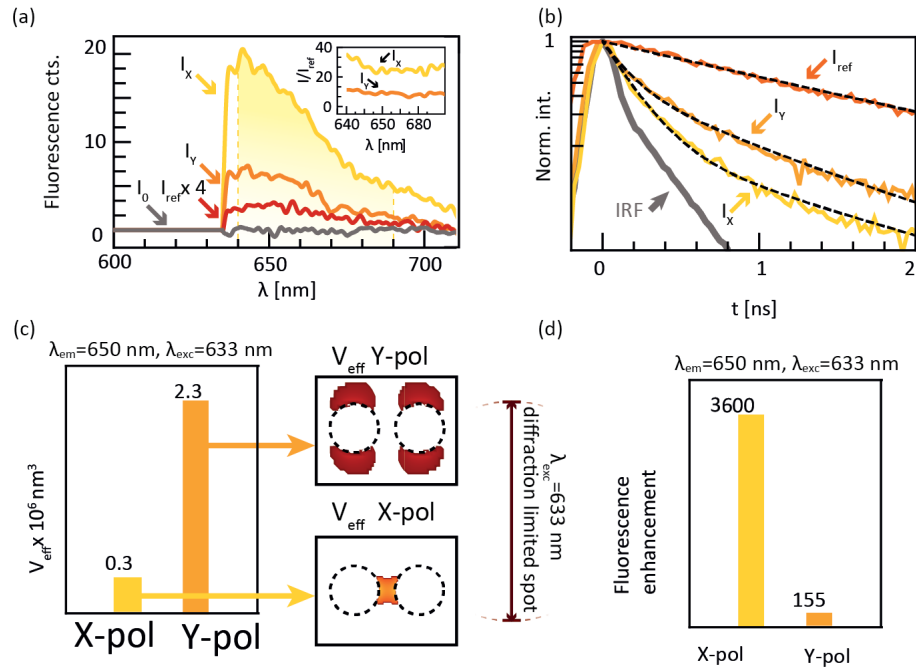


Figure 6.7 (a) Fluorescence spectra from the PMMA:dye coated 35 nm gap nanodimer excited at X and Y polarizations (I_X and I_Y , respectively), a region of molecules not interacting with the nanoantenna (I_{ref}) and bare PMMA/GaP (I_0), i.e. without the fluorescing molecule. The shaded area is inspected in the inset, where the counts are normalized to I_{ref} to obtain the increase in counts due to the presence of the nanoantenna for both polarization excitations. (b) Fluorescence emission decay rate curves together with the instrument response function (IRF). A bi-exponential model was used both for X and Y polarizations, however a single-exponential fit sufficed to describe the dynamics of the background. (c) Effective detection volumes used to calculate the enhancement factors in (b). The size of the used spot is also shown. The measured spot size coincided with the width of a focused gaussian spot (i.e. with an excitation spot radius of $\lambda/(\pi NA) = 230 \text{ nm}$, with NA the numerical aperture $NA = 0.9$). The volume of the spot interacting with the molecules is $(\lambda/(\pi NA))^2 \pi \times 200 \text{ nm} = 3 \times 10^7 \text{ nm}^3$. (d) Fluorescence enhancement factors, at 40 nm, calculated from Equation 6–13. Adapted from ref. [86].

indicating that the collected emission unequivocally corresponds to the STAR 635P molecules. The inset of Figure 6.7(a) shows the relative increase of counts due to the presence of the antenna under X polarisation (I_X/I_{ref}) and Y polarisation (I_Y/I_{ref}) excitation.

By analysing the measured spectra, a clear polarisation-dependent behaviour can be observed when exciting fluorophores in the vicinity of the antenna. More specifically, for polarisation parallel to the dimer's main axis, the emission intensity was found to be nearly four times that corresponding to the perpendicular polarisation, and approximately 20 times that of the bare PMMA:dye mixture, excited at any polarisation.

It is necessary to mention here that these effective fluorescence enhancement factors do not yet take into account differences in the amount of molecules contributing to the emission in each case. Indeed, as it has been recently shown by fluorescence correlation experiments [132], the effective detection volume (V_{eff}), when considering resonant dimers excited with X polarisation, corresponds to that defined by the gap size (V_{gap}), where the field is concentrated, whereas for measurements far from the antenna, V_{eff} is simply that of the diffraction-limited excitation spot (V_{spot}). A similar reasoning can be made for the Y polarisation, by considering the associated regions of enhanced fields. The calculation of the effective volume for each polarisation relies on the simulated near fields. Given a specific excitation polarisation $\hat{\mathbf{n}}$ we can define the wavelength-polarisation dependent effective volume as:

$$V_{\text{eff}}(\lambda_{\text{abs}}, \hat{\mathbf{n}}) = \iiint \Theta [\|\mathbf{E}(\mathbf{r}, \lambda_{\text{abs}})\|^2 / \|\mathbf{E}_0(\lambda_{\text{abs}})\hat{\mathbf{n}}\|^2 - \eta_{\text{th}}^2(\lambda_{\text{abs}})] d^3\mathbf{r}, \quad (6-11)$$

where $\Theta[x]$ is the Heaviside Theta function ($\Theta[x] = 1$ if $x \geq 0$ and 0 otherwise), $\mathbf{E}_0(\lambda)\hat{\mathbf{n}}$ is the excitation electric field polarised in the $\hat{\mathbf{n}}$ direction, $\mathbf{E}(\mathbf{r}, \lambda)$ the position and wavelength dependent electric near-field and η_{th}^2 a threshold value above which the effective volume is to be calculated. The threshold value is chosen as half the value of the maximum field enhancement, so that only those points where the electric field was above this threshold contributed to the calculation of the effective volume. The obtained values are:

$$V_{\text{eff},X}(\lambda_{\text{abs}} = 633 \text{ nm}) = V_{\text{gap}} = 2.97 \times 10^5 \text{ nm}^3 \quad (6-12a)$$

$$V_{\text{eff},Y}(\lambda_{\text{abs}} = 633 \text{ nm}) = 2.27 \times 10^6 \text{ nm}^3. \quad (6-12b)$$

Figure 6.7(b) shows the effective volumes predicted for our GaP dimer at each excitation polarisation. Under these considerations, when the

Table 2 Fitting parameters for the lifetime decay curves in Figure 6.7(d). τ_0 is the decay time of the slow component, τ_1 the decay time of the fast component and $\Delta\tau$ is the FWHM of the IRF.

	Background	Y-pol	X-pol	IRF
τ_0 [ns]	1.10 ± 0.01	1.10 ± 0.01	1.10 ± 0.01	-
τ_1 [ns]	-	0.12 ± 0.01	0.04 ± 0.01	-
$\Delta\tau$ [ns]	-	-	-	0.180

antenna is excited with polarisation X or Y, the fluorescence enhancement factor ($\mathcal{F}_{X,Y}$) can be calculated as:

$$\mathcal{F}_{X,Y} = \frac{V_{\text{spot}}}{V_{\text{eff}}} \frac{I_{X,Y}}{I_{\text{bg}}} \quad (6-13)$$

where $I_{X,Y}$ is the emission intensity measured when exciting at the antenna either parallel or perpendicularly, while I_{bg} corresponds to the signal registered when illuminating outside antenna regions. Remarkably, we obtain a value of $\mathcal{F}_X$ as large as 3600 (figure 6.7(c)). It is worth mentioning here that DNA origami approaches used to fine-tune the position of fluorophores in < 5 nm gaps between Au colloids led to $\mathcal{F}_X$ values of 5000, with associated lifetimes in the picosecond range [144, 145]. Noticeably, our approach provides comparable results, even though it uses considerably larger gap distances, demonstrating the advantage of employing an ultra-low loss dielectric nanoantenna. When switching to the perpendicular polarization the enhancement factor drops to $\mathcal{F}_Y = 86$, in accordance with the reduced field-confinement capabilities of the nanoantenna in this situation (figure 6.6(b)).

Regarding the decay rate of the fluorescence emission, it is intrinsically dependent on the localized density of optical states (LDOS). Qualitatively, the LDOS indicates the amount of states that can be excited by a local source at a given wavelength [13], including both non-radiative modes and radiative (scattering) excitations. In the traditional case of a metallic nanostructure, even though the LDOS is strongly enhanced at the plasmonic resonance, inherent losses of the metal can induce large lifetime reductions of nearby emitters via the usually undesired non-radiative channels [37, 63]. However, if the radiation efficiency of the nanoantenna is high, the reduction in the lifetime will be accompanied by an increase in the radiative rate of emission; a condition that can be met, in principle, with low-loss dielectrics. In this context, GaP presents as an excellent candidate in the visible range. We explore next the effect of the GaP dimer nanoantenna on the decay dynamics of the fluorescence probes.

Figure 6.7(d) shows time-resolved fluorescence measurements of the PMMA:dye coated nano-antenna at 640 nm excitation wavelength, for the two different polarisations: parallel and perpendicular to the main dimer's axis. The optical response from the bare PMMA:dye film on the GaP substrate is also included. As predicted, a much faster decay is observed for the molecules interacting with the antenna, when compared to the case of the bare layer of molecules. Furthermore, it can be seen that the fastest decay occurs when exciting the nano-antenna with the X polarisation. In order to extract lifetime values from the measurements, we fit exponential decay functions to the data, convoluted with the instrument response function (IRF). The characteristic time of the IRF, determined by its FWHM (full width half maximum), is 0.18 ns, allowing the determination of lifetime values of up to ~ 0.05 ns [132].

The fluorescence decay lifetimes obtained from the fittings are summarised in Table 2. A mono-exponential decay is observed for the bare dyes, yielding a total lifetime of 1.10 ns. Remarkably, in the presence of the GaP dimer, corresponding lifetime values are calculated to be as short as < 0.05 ns and 0.12 ns for X and Y excitation polarisations, respectively. In these two cases, the long lifetime component of 1.10 ns was also included in the fitting to account for background emission from dyes from outside enhanced-field regions. Indeed, for $t > 1$ ns in Figure 6.7(d), when fast processes vanish, the slopes of the decay curves are found to be nearly the same for all three considered situations.

It is important to remark that the shortest value of 0.04 ns in table 2 cannot be accurately determined, as it falls well below the IRF characteristic time of 0.18 ns, and it is consequently limited by the instrument itself. However, this provides us with a lower bound on the Purcell factor of $1.1 \text{ ns}/0.05 \text{ ns} \sim 22$ when the excitation of the nano-antenna is optimum. It must be noted here that Si dimer nano-antennas with similar gap sizes have been reported to produce considerably smaller fluorescence enhancement and lifetime reduction, highlighting the importance of effectively lossless GaP against Si for 633 nm [132].

In conclusion, I have shown the use of essentially lossless all-dielectric GaP nano-systems for a quintessential semiclassical quantum optics problem: that of fluorescence. In this published work, we have investigated the manipulation of Mie-resonant modes to highly confine the electric field at the surfaces of the dielectric structure, benefiting two ubiquitous nanophotonic applications in the visible light regime, namely SHG and surface fluorescence enhancement. However, in this chapter I only discussed the relevant part of this work to this thesis, namely that of the

interaction of light with matter. When exciting fluorescent dyes placed within a 35 nm gap of a GaP dimer nano-antenna, we have shown that a large fluorescence enhancement (3600) can be obtained. It is remarkable that this material shows such a strong enhancement at relatively large gaps. In comparison, enhancement values of around 100 were reported for 30 nm gap Si dimers [132]. We explained this achievement as a direct consequence of the negligible absorption of GaP, which prevents it from enhancing non-radiative decay paths. A nearly 20 times lifetime reduction (limited by the IRF) in the fluorophores is obtained, indicating a strong near-field light-matter interaction of the emitter with the localised density of optical states. Engineering smaller gap GaP nano-antennas, or even other ubiquitous geometries commonly used in plasmonics[146], might pave the way towards further improving field-confinement capabilities in the visible regime with practically lossless characteristics.

Part III

CONCLUSIONS

7 | CONCLUSIONS AND FUTURE OUTLOOK

In this thesis I explored the interactions of light with matter in different types of materials. I started the studies with metallic nano-antennas and showed how to exploit their radiative and non-radiative properties. All the experimental studies involved a large amount of fabrication and similar optical analysis. The theories behind them, laid out in chapters 1, 2 and 5 deal principally with understanding the electromagnetic field in nano-structured materials. The core experimental chapters 3, 4 and 6 dealt with applying these concepts to novel architectures. Furthermore, the applications can be decomposed in two different technologies. Those that exploit losses, as in chapter 4, and those that do not, as in chapters 3 and 6.

In particular, in chapter 3 I showed several results involving the fabrication and characterisation of gold non-concentric ring-disk cavities (NCRDC). Here the nature of the electromagnetic modes supported by the nano-structures was initially analysed from a theoretical point of view. Experimental measurement of dark-field spectra corroborated the working spectral range of the nano-antennas and motivates the study of future work in which colloidal quantum dots are actually embedded in them. The radiative properties of these nano-antennas were theoretically investigated and around 240-fold radiative rate enhancement together with a nearly theoretical 80% quantum efficiency at 633 nm inspires the application of similar antennas to single photon sources. Losses, however, seem to be limiting the overall quantum-efficiency in these architectures. Future challenges include, mastering the deterministic deposition of single colloidal quantum dots near the nano-antennas and measuring the fluorescence lifetime of reporters located in the vicinity of their vicinity.

As was mentioned in that chapter, losses in metals play an important role in incrementing the number of non-radiative modes to which an emitter can couple. However, other flavours of light-matter interactions can be studied where, what we understand as losses, are indeed the desired effect. Specifically, chapter 4 shows a possible application of the interaction of free-electron oscillations with light. Here, the collective charge oscillations of the excited surface-plasmons decay into the non-radiative channel of hot carrier generation. These carriers can usu-

ally be extracted for photovoltaic applications in diametrically different geometries. However, in this work we utilised these hot-carriers to drive chemical reactions in the nano-scale. By carefully fabricating Ag bow-tie antennas, we showed that we could selectively and locally transform molecules in the tips of the bow-tie. Probing this localisation could not be done with usual microscopy as the scales involved are sub-diffraction. To this end, properly functionalised gold nano particles were deposited on the nano-antenna bearing substrate. After several washing steps, the gold reporters were found with scanning electron microscopy and their locations statistically coincided with the tips of the bow-ties. Both in this chapter and in our published work [89] we show how these regions correlate to those with high hot electron generation rate. All in all, this geometry dependence makes absolute sense. All dipolar light-matter interactions have a weak-coupling transition rate given simply by Fermi golden rule, which is essentially proportional to the strength of the electric field. Therefore, plasmonics is exquisitely tailored to this end, due to its field confinement capabilities. Future work includes the study of drop-ties antennas, where the external tips of the bow-ties have been removed to concentrate all the hot-electron generation in the gap region.

The first part of the thesis therefore dealt with the study of light-matter interactions in metals (lossy materials) and how they can be used to enhance both radiative and non-radiative properties. This part just highlights the versatility of plasmonics for nano-photonic applications.

It must be noted that the possibility of studying materials with nearly zero losses in the visible is highly appealing for the photonics community. The second part of the thesis, therefore, dealt with this particular scenario, studying the properties of nano-structured dielectrics and in particular of gallium phosphide nano-antennas. In particular, chapter 6 showed the possibility of using gallium phosphide nano-antennas for fluorescence enhancement. This is far from a new concept [120], but our work [86] was one of the first experimental realisations of nearly lossless nano-photonics in the visible regime. By performing multiple molecule fluorescence we estimated the single-molecule fluorescence enhancement to be on the order of 3600 for the correct excitation polarisation. This opens the prospect for myriad of new experiments, including real single molecule fluorescence enhancement experiments. In these, the power dependence can be studied to analyse the saturation behaviour of the enhancement. Furthermore, wavelength-selective lifetime measurements can give information about the many decay rates that are actually measured in a single experiment.

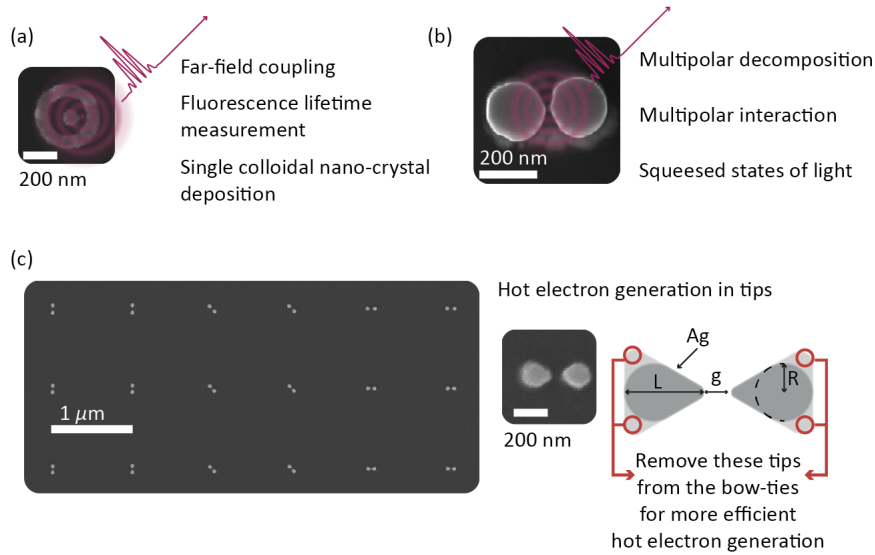


Figure 7.1 Future works and outlooks. (a) Non-concentric ring-disk cavities for coupling with single photon emitters and fluorescence lifetime measurements. SEM of fabricated nano-antennas. (b) Dielectric nano-antennas for fluorescence enhancement, squeezed states of light generation, multipolar interactions. SEM of fabricated Si nano-antennas. GaP examples are shown in chapter 6. (c) Silver drop-ties for local generation of hot electrons, by removing the extra tips of the bow-tie antenna. To the left, SEM of fabricated drop-ties.

Another future research topic involves the study of squeezed light states generation for continuous variable quantum optics [147]. Among the many applications of squeezed states, it is worth mentioning simple entanglement distillation by a beam-splitter [147] or accurate metrology [11]. It has been theoretically shown that plasmonic nano-spheres can be used to enhance the generation of squeezed states of light from a single-photon emitter [148]. It would be worth studying the possibility of generating squeezed states of light with dielectric nano-antennas, probing the effect of each multipole on the strength of squeezing and proving the stability of the squeezed state. The latter should be larger than that for metallic nano-particles due to the lack of losses that add the undesired decoherence to reduce the squeezed state into a true vacuum state.

Finally, a strong comparison between dielectric and metallic antennas has to be stressed, in order not to neglect the applicability of metallic nano-antennas in an area that might surpass the properties of dielectrics. To illustrate the future progresses and proposed work, figure 7.1 schematically shows possible venues of future work. For example, metallic and dielectric nano-antennas can be used together for the far-field enhance-

ment of radiation of single-photon emitters, while other re-engineered structures can be used to manipulate chemical reactions in the nano-scale. In other words, it is in those regions where losses become so important that they hamper the applications for far-field communication, we can manipulate them for our needs and apply them to scenarios where these near-field effects are desirable.

Part IV

APPENDIX AND BACKMATTER

We want to calculate the following integral:

$$\int_{\mathbb{R}} \frac{f(\omega)}{\omega_l^2 - \omega^2} d\omega, \quad (\text{A-1})$$

by the method of simple fractions we can rewrite

$$\frac{1}{\omega_l^2 - \omega^2} = \frac{1}{2\omega_l} \left(\frac{1}{\omega + \omega_l} - \frac{1}{\omega - \omega_l} \right). \quad (\text{A-2})$$

Now, the trick is to use complex contour integration to find the result of this integral. Assuming $f(z)$ (the analytic extension of the real valued function $f(\omega)$) does not have any poles, we can do contour integration to find (see figure A.1):

$$\int_{\mathbb{R}} \frac{f(\omega)}{\omega_l^2 - \omega^2} d\omega = \frac{i\pi}{2\omega_l} [f(\omega_l) - f(-\omega_l)], \quad (\text{A-3})$$

which simply states that we can define the delta distribution function from the denominator in equation A-1 as:

$$\text{Im} \left[\frac{1}{\omega_l^2 - \omega^2} \right] = \frac{\pi}{2\omega_l} [\delta(\omega - \omega_l) - \delta(\omega + \omega_l)], \quad (\text{A-4})$$

as long as all the necessary assumptions hold for $f(\omega)$ and its analytic continuation. Below are some details regarding the calculation.

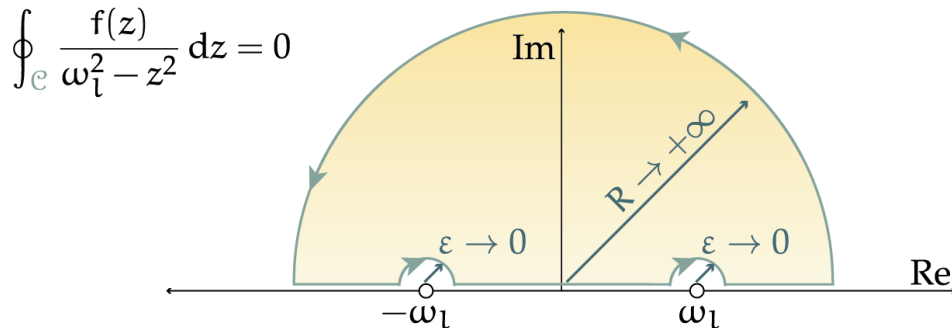


Figure A.1 Contour used for the evaluation of equation A-1.

1. The contour integral has to be recast into a sum of different curves:

$$\begin{aligned}
\mathcal{C}_R &= \{z \in \mathbb{C} : |z| = R, \operatorname{Im} z \geq 0\} \Rightarrow z = Re^{i\theta}, \theta \in [0, \pi], \\
\mathcal{C}_{\epsilon, \pm} &= \{z \in \mathbb{C} : |z \mp \omega_1| = \epsilon, \operatorname{Im} z \geq 0\} \Rightarrow z = \epsilon e^{i\theta}, \theta \in [0, \pi], \\
\mathcal{C}_1 &= \{z \in \mathbb{C} : \operatorname{Re} z \leq -(\omega_1 + \epsilon), \operatorname{Im} z \geq 0\}, \\
\mathcal{C}_2 &= \{z \in \mathbb{C} : -(\omega_1 - \epsilon) \leq \operatorname{Re} z \leq (\omega_1 - \epsilon), \operatorname{Im} z \geq 0\}, \\
\mathcal{C}_3 &= \{z \in \mathbb{C} : \operatorname{Re} z \geq (\omega_1 + \epsilon), \operatorname{Im} z \geq 0\},
\end{aligned} \tag{A-5}$$

so that the total curve can be decomposed into:

$$\mathcal{C} = \mathcal{C}_R^- \cup \mathcal{C}_1^+ \cup \mathcal{C}_{\epsilon,+}^+ \cup \mathcal{C}_2^+ \cup \mathcal{C}_{\epsilon,-}^+ \cup \mathcal{C}_3^+, \tag{A-6}$$

where the superscript means that the curve runs clockwise (+) or anti-clockwise (-). The total contour integral is therefore a sum of integrals for each curve. Furthermore, the desired integral is obtained when we let $\epsilon \rightarrow 0$ and $R \rightarrow +\infty$. It must be noted that the integral over this contour has to be zero because there are no singularities enclosed.

2. The integral involving $\mathcal{C}_R^-$ can be shown to be equal to zero by taking its absolute value and bounding it from above:

$$\begin{aligned}
\left| \int_{\mathcal{C}_R^-} \frac{f(z)}{\omega_1 - z} dz \right| &= \left| \int_0^\pi \frac{f(Re^{i\theta})}{\omega_1^2 - R^2 e^{2i\theta}} iRe^{i\theta} d\theta \right| \\
&\leq \max_{\alpha \in [0, \pi]} f(Re^{i\alpha}) \frac{\text{Constant}}{R} \\
&\xrightarrow{R \rightarrow +\infty} 0
\end{aligned} \tag{A-7}$$

provided f remains bounded as $R \rightarrow +\infty$.

3. The integrals involving ϵ can be easily solved by using a slight modification of the residue theorem. Let $H(z)$ have one pole in $z = \omega_1 \in \mathbb{R}$, then it can be recast in the following form:

$$H(z) = \frac{\alpha}{z - \omega_1} + g(z), \tag{A-8}$$

where $g(z)$ is holomorphic everywhere. Then the integral over $\mathcal{C}_{\varepsilon,+}$ becomes:

$$\int_{\mathcal{C}_{\varepsilon,+}} H(z) dz = - \int_0^\pi \frac{\alpha}{\varepsilon e^{i\theta}} i \varepsilon e^{i\theta} d\theta + G(\varepsilon) \quad (\text{A-9})$$

$$\xrightarrow{\varepsilon \rightarrow 0} -i\alpha\pi$$

where α is the definition of the residue of $H(z)$ and $G(\varepsilon)$ is a bounded function that goes to 0 when $\varepsilon \rightarrow 0$ because $g(z)$ is holomorphic and therefore bounded. Taking $H(z) = f(z)/(\omega_l^2 - z^2)$ and using this theorem in both $\pm\omega_l$ we obtain the desired result:

$$\int_{\mathcal{C}_{\varepsilon,\pm}} \frac{f(z)}{\omega_l^2 - z^2} dz = -i\pi [\pm f(\pm\omega_l)/2] \quad (\text{A-10})$$

4. The last three integrals can be recast into

$$\lim_{\varepsilon \rightarrow 0} \lim_{R \rightarrow +\infty} \int_{C_1^+ \cup C_2^+ \cup C_3^+} \frac{f(z)}{\omega_l^2 - z^2} dz = \int_{\mathbb{R}} \frac{f(\omega)}{\omega_l^2 - \omega^2} d\omega \quad (\text{A-11})$$

which is the original integral to be calculated.

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