Quantum corrections in nanoplasmonics & Deep neural network training with reverse supervision

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Abstract

This thesis presents the work done by the author in Prof. Soljačić’s group, in the Department of Physics of the Massachusetts Institute of Technology. Two projects have been developed simultaneously and therefore the content is divided into two parts.

In the first part, we develop analytical and numerical tools that provide a quantum description of nanoplasmonics. First, we review the classical theory and its failure when predicting the behavior of nanostructures smaller than \( \sim 30 \) nm. Then, we present Feibelman’s perturbative theory as a solution to this problem. We apply this theory to extract analytical expressions for the cross sections and resonances of single and coupled particles, and we implement boundary element method tools in order to solve more complex geometries. This project was done under the supervision of Dr. Thomas Christensen. A publication about the results obtained and the numerical tools developed is currently being prepared.

The second part is focused on deep neural networks training supervision. Since paired input and output data are the only resource for training deep networks, supervision by connecting hidden layers to additional output layers has been a practical solution. Here, we propose a different approach: we supervise learning by connecting hidden layers to a small reconstruction network that regenerates the input data. We provide a theoretical justification of our technique evaluating the mutual information path between hidden layers and input or output layers. In addition, we show that our technique improved the results of ResNet on CIFAR-10 image recognition. This work was done in collaboration with PhD candidate Li Jing, and a publication is currently under development.
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### Acronyms

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<td>Boundary element method</td>
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<td>FEM</td>
<td>Finite element method</td>
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<td>HDM</td>
<td>Hydrodynamic model</td>
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<td>HEG</td>
<td>Homogeneous electron gas</td>
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<td>LRA</td>
<td>Local response approximation</td>
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<td>ML</td>
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<td>NBIE</td>
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<td>NN</td>
<td>Neural network</td>
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<td>PTT</td>
<td>Photothermal therapy</td>
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<tr>
<td>QBEM</td>
<td>Quantum boundary element method (MATLAB toolbox)</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SERS</td>
<td>Surface-enhanced Raman spectroscopy</td>
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<tr>
<td>SP</td>
<td>Surface plasmon</td>
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<tr>
<td>SPP</td>
<td>Surface plasmon polariton</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TDDFT</td>
<td>Time-dependent density functional theory</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse electric</td>
</tr>
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<td>TM</td>
<td>Transverse magnetic</td>
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We are not to tell nature what she’s gotta be …
She’s always got better imagination than we have.
— Richard Feynman (1918-1988)
1 | Introduction

In the recent years, we have witnessed a notorious progress in the understanding and control of light, which is mainly due to improvements in computational tools and more refined experimental techniques. In particular, plasmonics is a flourishing field of science and technology that has unveiled new promising features such as extreme optical field confinement [1] and subwavelength light-concentration beyond the diffraction limit [2], both in the subbranch of nanoplasmonics.

Plasmons are collective free-electron excitations in conductive materials that can be considered as quasi-particles. In this project we focus on surface plasmons (SPs), which are the kind of plasmons existing in the interface between materials where there is a sign change in the real part of the dielectric function (e.g. metal-dielectric interfaces). On the other hand, a polariton is a quasi-particle resulting from the combination of an external electromagnetic field and the electric and magnetic polarizations induced in the material. In most cases, a polariton is employed to excite the SP, and experts usually refer to this phenomenon as surface plasmon polariton (SPP), although others use SP and SPP with no distinction [3].

Metallic nanoparticles exhibit characteristic properties, which emerge from this ability to support collective electron excitations, that are continuously giving rise to new lines of technological research, such as photothermal therapy (PTT), which is a non-invasive cancer treatment technique [4], photocatalytic purification of water [5], and the field of plasmonic colors generation, which includes applications like transparent displays, subwavelength-resolution printing, and dynamically reconfigurable colors [6,7].

Nevertheless, we are interested in the subfield of nanoplasmonics, where geometric length scales are below ∼30 nm. Two of the most promising applications in this subfield are plasmonic nanoantennas and surface-enhanced Raman spectroscopy. Plasmonic nanoantennas operate at optical frequencies and allow us to explore new possibilities in nanoelectronics by providing a strong coupling between far-field radiation and localized nanoscale sources (see Fig. 1.1) [8]. Raman spectroscopy has a broad range of applications in fields like solid-state physics, nanotechnology, chemistry, and molecular biology. The main drawback of this technique relies on the low intensity of Raman scattering compared to the intense Rayleigh scattering. Surface-enhanced Raman spectroscopy constitutes a solid technique that can increase the effect of Raman scattering in factors up to $10^{10}$ [9].

The development of these cutting-edge technologies requires a complete and accurate description of every phenomenon involved. Classical plasmonics theory fails when applied at the nanoscale. As an example, see Figure 1.2. It shows the plasmonic
resonance energy of a silver nanosphere over 3 nm carbon films [11]. The classical prediction is independent of the radius and it fails dramatically when decreasing the diameter of the particle below 20 nm. Therefore, we face a need for new theories where quantum effects are not neglected.

In this thesis we focus on Feibelman’s $d$-parameters theory. First introduced by Feibelman in 1982 [12], his theory allows to add first-order quantum corrections to the classical results. Several quantum effects are simultaneously overcame: nonlocality, spill-in or spill-out of the electronic wave function and incomplete accounting of internal electron dynamics, especially surface-enhanced Landau damping. This perturbative theory separates the influence of shape, scale and material in different factors such that they can be analyzed independently. The goal of this project is to extend the work of Christensen et al. in Ref. [13], where they studied single nanoparticles with Feibelman’s theory, to coupled structures. First, we study single particles to give evidence that it is a general theory that can reproduce the results from other models, such as the hydrodynamic model (HDM) or the time-dependent density functional theory (TDDFT). Then, we derive new analytical expressions for
the parameters involved in Feibelman’s theory for a system composed by coupled cylinders. Finally, we obtain numerical results for a system of coupled spheres.

1.1 State of the art

As discussed before, nanostructures of very precise shapes can be fabricated (see Fig. 1.3), and the classical description of the behavior of this systems is not valid, so a quantum theory is required. Researchers have used different approaches to the quantum effects that govern nanoplasmonics. For instance, in Ref. [14], Christensen et al. study the response of graphene disks introducing edge states and nonlocal response in their model via a modified conductivity (edge-state conductivity) and the HDM, respectively.

A popular state-of-the-art \textit{ab initio} approach is the TDDFT [15,16], whose results are more rigorous and accurate since it performs a fully quantum treatment of the problem. However, this quantum treatment of the optical properties of large plasmonic systems is very demanding in terms of computational cost, due to the large number of atoms and electrons involved. Thus, TDDFT is limited to small systems. Moreover, it is an intrinsically computational technique and it does not allow the study of the model parameters in absence of simulations.

Figure 1.3. (a) Scanning transmission electron microscopy (STEM) image of a gold nanorod dimer. Each rod has a diameter of \textasciitilde 30 nm and length of \textasciitilde 65 nm. (b) Zoom to the gap as indicated with the red dotted lines that shows the atomic structure of the left nanorod. The average gap width is 1.3 nm. Original figure from [17].

1.2 Outline

In the first chapter, \textit{Fundamentals of nanoplasmonics}, we provide a theoretical background of classical and nonclassical plasmonics. A brief introduction to the techniques we use in our work is also given.

Then, in \textit{Quantum corrections to classical nanoplasmonics}, we present the results of our work. First, Section 3.1 provides a summary of the numerical tools developed for this project. Then, we study different geometries. In Section 3.2 we analyze the single sphere analytically, and provide evidence of the generality of Feibelman’s theory. In Sections 3.3 and 3.4 we review the case of a cylinder and twin cylinders,
respectively, deriving new analytical expressions for the coupled cylinders system using transformation optics (TO). Finally, in Section 3.5 we obtain numerical results for two coupled nanospheres.

Final remarks and a summary of the results can be found in Conclusions. The derivations and intermediate results that are not fundamental for the understanding of this thesis are discussed in Appendices A-B.
2 | Fundamentals of nanoplasmonics

Surface plasmons (SPs) are collective oscillations of electromagnetic fields and electrons in a dielectric-metal interface. Here, we focus on nanoplasmonics, which studies plasmons at the nanoscale (<100 nm). One of the most attractive features of SPs is their ability to enhance fields and concentrate light below the limit of diffraction [18].

Nanofabrication is currently pushing the limits of plasmonics towards smaller scales, below \( \sim 30 \) nm, where the classical theory is no longer accurate enough. Hence, it is usual to rely in a fully quantum model or in a semi-classical model to describe nanoplasmonics when the classical framework fails. The most accurate approach is the time-dependent density functional theory (TDDFT), which evaluates the properties of many-body systems under time-dependent potentials and fields [15,16]. Nevertheless, TDDFT is a highly time-consuming computational technique and does not provide analytical results. On the other hand, semi-classical models provide faster computational tools and analytical expressions for particular geometries, which allow to study the relation between the plasmonic variables.

In Section 2.1, we describe the basics of electromagnetism and establish the notation we will employ. Then, we review the fundamentals of plasmonics in Section 2.2, going into details about the case of a single sphere. Next, in Section 2.4, we present the quantum aspects that must be included in the description of nanoplasmonics. We discuss the main ideas of the hydrodynamic model (HDM) in Subsection 2.4.1 and, in Subsection 2.4.2, we present Feibelman’s theory, which is the core of our project. Finally, we give some notions about transformation optics (TO) in Section 2.5, since results derived using this technique are employed in the next chapter.

2.1 Basics of electromagnetism

Maxwell’s equations are the fundamental laws that describe the electromagnetic nature of a system. They can be written in differential form as [19]:

\[
\nabla \times \mathbf{E}(\mathbf{r}, t) = -\partial_t \mathbf{B}(\mathbf{r}, t), \tag{2.1a}
\]

\[
\nabla \times \mathbf{H}(\mathbf{r}, t) = \mathbf{J}_f(\mathbf{r}, t) + \partial_t \mathbf{D}(\mathbf{r}, t), \tag{2.1b}
\]

\[
\nabla \cdot \mathbf{D}(\mathbf{r}, t) = \rho_f(\mathbf{r}, t), \tag{2.1c}
\]

\[
\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0, \tag{2.1d}
\]
where \( E, B, D, \) and \( H \) stand for the electric, magnetic, displacement, and induction fields, respectively. \( J_f \) and \( \rho_f \) are the free charge currents and densities, respectively. In addition, currents and charge densities are related by the continuity equation:
\[
\nabla \cdot J_f(r, t) + \partial_t \rho_f(r, t) = 0.
\]

(2.2)

A natural way to decompose free currents and densities is into external (the ones that generate the external fields) and induced (originated as a response to external fields) charges: \( J_f = J_{ext} + J_{ind} \) and \( \rho_f = \rho_{ext} + \rho_{ind} \). Both external and induced charge currents and densities fulfill the continuity equation (see Eq. 2.2) independently. By adopting this convention, it is possible to group all the induced effects, i.e. polarization and induced currents, in a total dielectric function \( \varepsilon(r, r'; \omega) \) [19].

For linear media, the bound-response dielectric function \( \varepsilon_B(r, r'; \omega) \) and the free-carrier conductivity \( \sigma(r, r'; \omega) \) relate \( D \) and \( J_f \) to \( E \), respectively. In Fourier domain this reads as:
\[
D(r, \omega) = \varepsilon_0 \int_{\mathbb{R}^3} \varepsilon_B(r, r'; \omega) E(r', \omega) \, dr',
\]
\[
J_{ind}(r, \omega) = \int_{\mathbb{R}^3} \sigma(r, r'; \omega) E(r', \omega) \, dr'
\]
where \( \varepsilon_0 \) is the vacuum permittivity. The induced variables can be combined in a modified displacement field \( \tilde{D}(r, \omega) = D(r, \omega) + \frac{i\sigma}{\varepsilon_0} J_{ind}(r, \omega) \) which can also be written in terms of the electric field as:
\[
\tilde{D}(r, \omega) = \varepsilon_0 \int_{\mathbb{R}^3} \varepsilon(r, r'; \omega) E(r', \omega) \, dr',
\]
where the total dielectric function \( \varepsilon(r, r'; \omega) \) is:
\[
\varepsilon(r, r'; \omega) = \varepsilon_B(r, r'; \omega) + \frac{i\sigma(r, r'; \omega)}{\varepsilon_0 \omega}.
\]

(2.5)

All the relevant magnitudes that are studied in plasmonics rely directly on the dielectric function \( \varepsilon(r, r'; \omega) \). Both its spatial- and frequency-dependence are hard to evaluate theoretically and experimentally. However, this issue has been overcome with different approximations that give successful results in the classical framework. The problem of nonlocality of can be solved with the local response approximation (LRA), which leads to [19]:
\[
\tilde{D}(r, \omega) \equiv \varepsilon_{LRA}(r, \omega) E(r, \omega),
\]
where
\[
\varepsilon_{LRA}(r, \omega) \equiv \int \varepsilon(r, r'; \omega) \, dr'.
\]

(2.7)

On the other hand, there are several models that deal with the spectral behavior of \( \varepsilon \). The Drude model, which is based on the jellium ansatz (free-electron gas in a background of fixed ions), yields the following frequency dependence for the conductivity [20]:
\[
\sigma_{\text{Drude}}(\omega) = \frac{i \varepsilon_0 \omega_p^2}{\omega + i\gamma},
\]

(2.8)
where the plasma frequency and is a phenomenological damping that includes a restoring force in the model. The plasma frequency is defined as:

\[ \omega_p^2 = \frac{n e^2}{\varepsilon_0 m_{\text{eff}}} \]  

(2.9)

where is the electron density, and and are the charge and effective mass of the electron in the ionic background, respectively. This definition does not take into account the ionic background in the metal. For that purpose, some authors use the screened plasma frequency, defined as \( \omega_{\text{p screened}}^2 = \omega_p^2 / \sqrt{\varepsilon_B} \). We will refer to \( \omega_p \) unless otherwise specified.

Nonlocality is not considered in the Drude mode, therefore the LRA approximation for the dielectric function can be applied. Its frequency-dependence is derived by inserting Eq. (2.8) into (2.5):

\[ \varepsilon_{\text{Drude}}(\omega) = \varepsilon_B(\omega) - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}. \]  

(2.10)

The frequency-dependence of the bound-response dielectric function \( \varepsilon_B(\omega) \) can be generally estimated at low frequencies as a constant that represents the ionic background of the metal. Near an interband transition, it is well represented by a lorentzian. In this project we will employ a constant \( \varepsilon_B \) unless otherwise specified. Therefore, at higher frequencies, above \( \omega_{\text{p screened}} \), Eq. (2.8) and (2.10) are no longer valid since different phenomena related to the atomic structure of the metal –predominantly interband transitions- arise, and they should be considered via an energy-dependent \( \varepsilon_B \). Fig. 2.1 shows a comparison between experimental and Drude dielectric functions. It can be seen that the validity of the model is limited to energies below \( \sim 3 \) eV and \( \sim 4 \) eV for gold and silver, respectively, due to interband transitions. The screened plasma frequency plays an important role in a lossless metal (\( \gamma = 0 \)) since it also corresponds to the bulk plasmon frequency: \( \varepsilon_{\text{Drude}}(\omega_{\text{p screened}}) = 0 \). Bulk plasmons originate at this particular frequency inside the metal and correspond to longitudinal excitations of the plasma.

2.2 Classical plasmonics

Let us take a planar surface located at \( z = 0 \) separating a dielectric medium with real and positive dielectric function \( (\varepsilon_d > 0, \text{constant for simplicity}) \), such as air, and an unknown material described by \( \varepsilon_m(\omega) \) (see Fig. 2.2a). We will assume (i) local dielectric functions \( (\varepsilon(r) = \varepsilon) \), since the characteristic electronic length scale in our materials is much smaller than the wavelength of the incoming radiation \( (r \ll \lambda) \), and (ii) absence of external charge and current densities. The fields propagate in the \( xz \)-plane and exhibit harmonic time-dependence: \( E(r, t) = E(r)e^{-i\omega t} \), with \( E(r) = E_0 e^{-k_d z} e^{i k_1 x} \) in the dielectric and \( E(r) = E_0 e^{k_m z} e^{i k_1 x} \) in the second material. \( k_\parallel \) is the component of the wave vector parallel to the surface, and \( k_d \) and \( k_m \) are the perpendicular components in the dielectric and the second material, respectively.

Under these assumptions, it is possible to reduce Eqs. (2.3) to the Helmholtz equation with \( x \)-propagating fields [22]:

\[ \frac{\partial^2 E(z)}{\partial z^2} + (k_0^2 \varepsilon - k_1^2) E = 0, \]  

(2.11)
Figure 2.1. Dielectric function $\varepsilon(\hbar \omega)$ of gold and silver as a function of the energy. Experimental values and Drude parameters (gold: $\varepsilon_B = 9.5$, $\hbar \omega_p = 8.95$ eV, $\gamma = 69$ meV; silver: $\varepsilon_B = 3.3$, $\hbar \omega_p = 9.01$ eV, $\gamma = 22$ meV) from [21]. (a) Negative real part of the dielectric function. The experimental values for silver between 3.8 and 4.7 eV are positive so they are not displayed in this visualization. Same for the Drude model values after 2.9 eV (4.9 eV) for gold (silver). (b) Imaginary part of the dielectric function.

where $k_0 = \omega/c$ is the wave number in vacuum and $\mathbf{E}(z) = \mathbf{E}(r)e^{-ik_0 x}$. This equation can be similarly written for the magnetic field.

Eq. (2.11) yields two types of solutions: TE and TM modes. By applying boundary conditions, one finds that TE modes cannot be confined to the surface, while TM modes require the following condition to be fulfilled [22]:

\[
\frac{k_m}{k_d} = -\frac{\varepsilon_m(\omega)}{\varepsilon_d},
\]

(2.12)

with $k_d^2 = k_\parallel^2 - k_0^2 \varepsilon_d$ and $k_m^2 = k_\parallel^2 - k_0^2 \varepsilon_m(\omega)$.

Re($k_d$) and Re($k_m$) should be both positive in order to have evanescent fields in the $z$-direction and confine the charges to the surface (see Fig. 2.2). A first condition arises by imposing this in Eq. (2.12):

\[
\varepsilon_m^\bot(\omega)\varepsilon_d^\bot < 0.
\]

(2.13)

This condition forces the dielectric function of the second material to have negative real part, i.e. to be a conductor. Therefore, the SP is generated at a dielectric-metal interface, although the condition is only met below the screened plasma frequency in Drude metals (see Eq. 2.10). A different interpretation of this condition can be found by examining the conservation of the normal component of $\mathbf{D}$ across the surface:

\[
\tilde{D}_d^\bot = \tilde{D}_m^\bot,
\]

\[
\varepsilon_\bot^d E_d^\bot = \varepsilon_\bot^m(\omega) E_m^\bot,
\]

\[
E_d^\bot E_m^\bot < 0,
\]
Figure 2.2. (a) Sketch of the electric and magnetic fields in a SPP. The electric field only has $x$ and $z$ components and it is represented by the solid red lines. The magnetic field is oriented along the $y$ axis due to the transverse magnetic nature of the SPP. (b) The electric field normal to the surface is enhanced near the interface and decays rapidly away from it. The decay length in the dielectric ($\delta_d$) is usually larger than in the metal ($\delta_m$).

Figure 2.3 shows the dispersion relation from Eq. (2.14). In a lossless metal ($\gamma = 0$), a SPP is generated if the frequency is below the surface plasma frequency $\omega_{sp} = \omega_p/\sqrt{\varepsilon_n + \varepsilon_d}$, which corresponds to the frequency of the SPP in a quasistatic large-$k_\parallel$ limit. For an homogeneous electron gas (HEG — $\varepsilon_n = 1$) next to vacuum ($\varepsilon_d = 1$) the value of the surface plasma frequency is $\omega_{sp} = \omega_p/\sqrt{2}$. Propagation is forbidden between $\omega = \omega_{sp}$ and $\omega = \omega_p$, since $k_\parallel$ becomes purely imaginary, while radiative modes, known as Brewster modes, appear above $\omega_p$ [19]. These limits are no longer valid if a lossy metal is considered. However, if the losses are small enough, $\omega_{sp}$ and $\omega_p$ can still be used as reference values (see Fig. 2.3b).

Finally, there is a clear discrepancy between the relation dispersions of the plasmon and the light traveling in the dielectric medium (dielectric light lines in Fig. 2.3).
Figure 2.3. SPP dispersion relation (see Eq. (2.14)). (a) Lossless homogeneous electron gas (HEG) adjacent to vacuum ($\varepsilon_d = \varepsilon_b = 1$ and $\gamma = 0$). There are no bound modes above the surface plasma frequency ($\omega_{sp} = \omega_p/\sqrt{2}$): propagation is forbidden between $\omega = \omega_{sp}$ and $\omega = \omega_p$, and radiative modes appear above $\omega_p$. (b) Lossy HEG ($\gamma = \omega_p/50$). Losses appear in the SPP region and $\omega_{sp}$ shifts, so the lossless value is only useful as a reference value if the losses are small.

As a result, it is not trivial to experimentally generate a SPP. The most simple technique to couple electromagnetic fields and SPs consists in surface modulations, such as gratings, although more advanced geometries (e.g. conical structures) and techniques are also employed [22,24]. However, this drawback does not affect finite particles, where the momentum coupling is provided by the geometry.

### 2.2.1 Single sphere

The classical behavior of a plane wave incident on a metallic sphere of radius $R$ has been studied by many authors since Mie described this system in 1908 [25]. In the quasistatic limit ($R \ll \lambda$), the dipolar polarizability relates the induced dipole moment to the constant external field $E_0$: $p = \varepsilon_0 \varepsilon_d \alpha E_0$. For a sphere, it is given by [20]:

$$\alpha(\omega) = \frac{4\pi}{3} R^3 \frac{3(\varepsilon_m(\omega) - \varepsilon_d)}{\varepsilon_m(\omega) + 2\varepsilon_d},$$

(2.16)

where $\varepsilon_m(\omega)$ and $\varepsilon_d$ are the dielectric functions of the metal and the external dielectric medium, respectively. The scattering and absorption cross sections, whose sum constitutes the extinction cross section, can be obtained by dividing the re-radiated power and the absorbed power by the intensity of the incident wave, respectively. These cross sections can be written as [20]:

$$\sigma_{sca} = \frac{k^4}{6\pi\varepsilon_0^2} |\alpha(\omega)|^2,$$

(2.17a)

$$\sigma_{abs} = \frac{k}{\varepsilon_0} \text{Im}\{\alpha(\omega)\},$$

(2.17b)
where \( k = \sqrt{\varepsilon_d \omega/c} \) is the wave number in the dielectric medium. Note that \( \sigma_{\text{scat}} \sim R^6 \) and \( \sigma_{\text{abs}} \sim R^3 \). Consequently, the extinction mechanism is different depending on the size of the particle. For small spheres absorption dominates, whereas for bigger particles incoming radiation is scattered. The physical mechanism behind this phenomenon is the ability of the particle to radiate like an antenna. Very small spheres \((R \ll \lambda)\) cannot scatter incoming fields, since the wavelength of light radiated by an antenna will be of the same order of magnitude than its characteristic length. As we increase the size of the sphere, the radius gets closer to the incoming wavelength, so the scattering at that particular frequency will be stronger.

A resonant enhancement of the interaction of the sphere with incoming light will appear at the poles of \( \alpha(\omega) \), i.e. when the Fröhlich condition is fulfilled:

\[
\text{Re}\{\varepsilon_m\} = -2\varepsilon_d.
\]  

For a lossless Drude metal, this condition can be combined with Eq. 2.10 \((\varepsilon_B = 1, \gamma = 0)\) to yield the classical resonance frequency for the dipolar mode of a metallic nanosphere in vacuum:

\[
\omega_{l=1} = \frac{\omega_p}{\sqrt{3}}.
\]  

More generally, the multipolar resonance frequency is given by [26]:

\[
\omega_l = \omega_p \sqrt{\frac{l}{2l+1}}.
\]  

### 2.3 Nonretarded boundary integral equation

The nonretarded boundary integral equation (NBIE) is a fundamental building block in our project. Therefore, as an intermediate step between the classical and quantum theories, we provide a simple derivation of the NBIE for an interface between a metal and a dielectric with dielectric functions \( \varepsilon_m = \varepsilon_B - \frac{\omega_p^2}{\omega^2} \) and \( \varepsilon_d \), respectively. In Subsection 2.4.2, we will include quantum corrections to the NBIE, and, in Section 3.1, we discuss the numerical tools we employ, which are based on the resolution of the NBIE.

Electric and magnetic fields can be written in terms of the scalar potential \( \phi \) and the vector potential \( A \) as [20]:

\[
\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t},
\]  

\[
\mathbf{B} = \nabla \times \mathbf{A}.
\]

In addition, both potentials are related by the Lorentz gauge condition: \( \nabla \cdot \mathbf{A} + c^2 \partial_t \phi = 0 \), where \( c \) is the speed of light in the medium.

Our work can be performed under a quasistatic approximation \((\partial_t = 0)\), since the geometrical characteristic length of the particles studied \((< 50 \text{ nm})\) is much smaller than the wavelength of incoming radiation \((\text{visible region, } \sim 500 \text{ nm})\). Hence, we are only interested in solving Poisson’s equation, which can be derived by substituting
$E = -\nabla \phi$ in Gauss’ law (Eq. 2.1d): $\nabla^2 \phi = -\rho/\varepsilon_B$. The solution can be conveniently written in terms of the electrostatic Green function $g(\mathbf{r}, \mathbf{r}')$ [27], defined as

$$g(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi |\mathbf{r} - \mathbf{r}'|}. \quad (2.22)$$

Then, the general form of the solution is [27]:

$$\phi(\mathbf{r}) = \phi_{\text{ext}}(\mathbf{r}) + \frac{1}{2\varepsilon_0} \int_{\partial \Omega} g(\mathbf{r}, \mathbf{r}') \sigma(\mathbf{r}') \, d^2 \mathbf{r}', \quad (2.23)$$

where $\phi_{\text{ext}}(\mathbf{r})$ is the external potential, $\partial \Omega$ is the union of all boundaries—in our case, between metallic particles and dielectric medium—and $\sigma(\mathbf{r})$ is the surface charge distribution at those boundaries. One then applies boundary conditions to find $\sigma(\mathbf{r})$. Continuity of the component of the electric field parallel to the surface has no significant impact in the calculations, since it implies that $\sigma(\mathbf{r})$ should be the same inside and outside the surface. However, continuity of the normal component of the displacement field yields the classical NBIE [13]:

$$\Lambda \sigma(\mathbf{r}) = 2\varepsilon_0 \frac{\partial \phi_{\text{ext}}(\mathbf{r})}{\partial z} + \int_{\partial \Omega} \frac{\partial g(\mathbf{r}, \mathbf{r}')}{\partial z} \sigma(\mathbf{r}') \, d^2 \mathbf{r}', \quad (2.24)$$

where $z$ is the normal direction to the surface (outwards, from the metal to the dielectric) and

$$\Lambda \equiv \frac{\varepsilon_d + \varepsilon_m}{\varepsilon_d - \varepsilon_m}. \quad (2.25)$$

The external potential can be omitted to write the NBIE as an eigenproblem:

$$\Lambda_n^{(0)} |\sigma_n^{(0)}\rangle = K |\sigma_n^{(0)}\rangle, \quad (2.26)$$

where the eigenvector $|\sigma_n^{(0)}\rangle$ corresponds to the state $\sigma_n^{(0)}(\mathbf{r}) \equiv \langle \mathbf{r} |\sigma_n^{(0)}\rangle$, i.e., to the charge distribution of the mode $n$, the eigenvalue of the mode $n$ is $\Lambda_n^{(0)}$, and $^{(0)}$ identifies the classical magnitudes. The interest in the eigenvectors is obvious, since we can compute the potentials and fields with them. Regarding the eigenvalues, they provide useful spectral information. In particular, they are related to the resonance frequency by the following expression:

$$\omega_n^{(0)} = \omega_p \sqrt{\frac{1 + \Lambda_n^{(0)}}{\varepsilon_d + \varepsilon_B - (\varepsilon_d - \varepsilon_B)\Lambda_n^{(0)}},}$$

which can be easily derived by imposing $\Lambda = \Lambda_n^{(0)}$.

### 2.4 Nonclassical nanoplasmonics

The classical theory described in the previous sections does not reproduce the quantum effects that emerge at characteristic geometric scales smaller than $L \sim 30$ nm. This failure comes from neglecting three main effects: electronic wave function spill-in or spill-out beyond the boundaries of the materials [28] (see Fig. 2.4),
nonlocality [26] and inaccurate description of internal electron dynamics, such as Landau damping [29].

The hydrodynamic model (HDM) solves the problem of nonlocality, while Feibelman’s $d$-parameters theory overcomes all three issues simultaneously [12]. In this section we will briefly review the HDM, which will serve to validate some of the $d$-parameters results, and then we discuss Feibelman’s theory.

![Figure 2.4](image)

**Figure 2.4.** Electron equilibrium density $n_0$ relative to the ionic density $n_{\text{ion}}$ as a function of the position $x$ relative to the surface of a metal ($x = 0$) normalized to the Fermi wavelength $\lambda_F = h v_F / E_F$, where $h$ is Planck’s constant, $v_F$ is the Fermi velocity and $E_F$ is the Fermi energy. Electron densities in red, blue, and green computed in the jellium approximation of density functional theory (DFT) with Wigner’s xc-potential by Lang and Kohn [30] for different Wigner-Seitz radius $r_s$ in units of Bohr radius $a_0$. In a classical framework, $n_0 = n_{\text{ion}}$, which originates a sudden drop of electron density at the boundary of the material. However, quantum effects like spill-out for $x > 0$ and Friedel oscillations for $x < 0$ should be taken into account when working at the nanoscale. Figure from [19].

### 2.4.1 Hydrodynamic model

The HDM provides nonlocal corrections for a variety of results. Most of them are out of the scope of this project, so here we will focus on the general idea behind the model.

The HDM can be derived from different perspectives, ranging from the classical Hamiltonian including quantum functional energy to quantum many-body Schrödinger equations [31]. A starting point can also be the Boltzmann equation which, after some labor, yields [19]:

\[ \partial_t n + \nabla \cdot (n \mathbf{v}) = 0, \quad (2.27a) \]

\[ m_{\text{eff}} n [\partial_t + (\mathbf{v} \cdot \nabla)] \mathbf{v} = -en \mathbf{E} - \nabla \cdot \mathbf{P}, \quad (2.27b) \]

where $n(\mathbf{r}, t)$ is the density of particles, $\mathbf{v}(\mathbf{r}, t)$ is the field of velocities, $m_{\text{eff}}$ is the effective mass of the conduction electrons in the ionic background of the metal, $e$ is the electron charge, $\mathbf{E}(\mathbf{r}, t)$ is the electric field and $\mathbf{P}(\mathbf{r}, t)$ is the pressure tensor. Eqs. (2.27) correspond to the continuity and momentum equations in Navier-Stokes
equations, in the field of fluid dynamics. Therefore, the HDM assumes that the flow of electrons inside the metal can be compared to a fluid whose motion is determined by these equations.

The high nonlinearity of Navier-Stokes equations makes them hard to manipulate. Therefore, it is usual to linearize them in order to extract useful information in a cleaner way. Luckily, the plasmonic behavior relies in a regime that can be linearized [19], so we can rewrite the variables of the problem in terms of equilibrium and induced quantities: \( n = n_0 + n_{\text{ind}} \), \( \mathbf{v} = \mathbf{v}_0 + \mathbf{v}_{\text{ind}} \). Moreover, the system is initially at rest (\( \mathbf{v} = 0 \)), so the electric field acts as a first-order magnitude. Regarding the pressure tensor, the HDM in nanoplasmonics is based on the ansatz that \( \mathbf{P} \) is diagonal [19], since we assume that the perturbed quantities are much smaller than those at equilibrium. The value of \( \mathbf{P} \) arises from Pauli’s exclusion principle:

\[
\mathbf{P} = \frac{\sqrt{3} \pi^2}{6 \hbar^2 n_0^5} \mathbf{I},
\]

where \( \mathbf{I} \) is the identity matrix. Under these assumptions and keeping only first-order terms, Eqs. (2.27) can be simplified to:

\[
\partial_t \rho_{\text{ind}} + \nabla \cdot \mathbf{J}_{\text{ind}} = 0, \tag{2.28a}
\]

\[
\partial_t \mathbf{J}_{\text{ind}} = \varepsilon_0 \omega_p^2 \mathbf{E} - \beta^2 \nabla \rho_{\text{ind}}, \tag{2.28b}
\]

where \( \rho_{\text{ind}} \equiv -e n_{\text{ind}} \) is the charge density, \( \mathbf{J}_{\text{ind}} \equiv -e n_0 \mathbf{v}_{\text{ind}} \) is the charge current and \( \omega_p \) is the plasma frequency. It is usual to introduce here the hydrodynamic parameter \( \beta \), which is proportional to the Fermi velocity, \( v_F = \sqrt{3} \pi^2 n_0 / m_{\text{eff}} \). Following our derivation, we find that \( \beta^2 \equiv \frac{1}{3} v_F^2 \). However, the ansatz for the pressure tensor is not completely valid, since it assumes an equilibrium where decay rates are much larger than oscillations, and that is not the case of plasmonics. A frequency-dependent \( \beta \) should be introduced as a correction, although many authors often use the constant value that we will employ in this project: \( \beta^2 = \frac{3}{5} v_F^2 \) [19,32].

Note that the HDM successfully predicts some experimental results, e.g. the blueshift of the surface plasmon resonance that Ag nanoparticles experience when decreasing its size [11].

### 2.4.2 Feibelman \( d \)-parameters theory

In 1982, Feibelman published a perturbative approach to quantum plasmonics that provides first-order corrections [12]. Originally, this idea was employed for very simple geometries—concretely, for a planar interface by Feibelman, and for a sphere by Apell and Ljungbert [33]. Christensen et al. have applied the same treatment to more complex geometries [13]. As a result, Feibelman’s theory has led to analytical expressions for spectral properties, i.e. resonance frequencies, of several geometries: a metallic half-space, a slab, a sphere and a cylinder. The content presented in this subsection is based on Ref. [13].

As stated previously, Feibelman’s \( d \)-parameters theory allow to extend the classical NBIE (see Eq. (2.24)) to a quantum-corrected equation. In the nonclassical framework, charges and currents are not restricted to the boundary and nonsingular charge distributions with spill-in or spill-out originate in the direction perpendicular to the surface (see Fig. 2.5). Therefore, if we allow induced charges to have a distribution in the perpendicular direction to the interface instead of being attached to it, a
first-order corrected eigenproblem emerges naturally when deriving the NBIE [13]:

\[ \Lambda \sigma(r) = \mathcal{P} \int_{\partial \Omega} [\hat{n} \cdot \nabla g(r, r')] \sigma(r') \, d^2r' + d_1 \lim_{\delta \to 0^+} \int_{\partial \Omega} [\hat{n} \cdot \nabla \nabla' g(r + \delta \hat{n}, r') \cdot \hat{n}] \sigma(r') \, d^2r' - d_\parallel \int_{\partial \Omega} \nabla_\parallel^2 g(r, r') \sigma(r') \, d^2r', \]  

(2.29)

where \( \mathcal{P} \) stands for Cauchy principal value, \( g(r, r') \equiv 1/(2\pi|\mathbf{r} - \mathbf{r}'|) \) is the scalar Coulomb interaction, \( \sigma(r) \) is the surface charge distribution, \( \nabla_\parallel \) is the surface Laplacian, \( d_1 \) and \( d_\parallel \) are the perpendicular and parallel \( d \)-parameters, and \( \Lambda \equiv \frac{\varepsilon_{\alpha}^m}{\varepsilon_{\alpha}^m - \varepsilon_{m}^\infty} \) is the eigenvalue, as defined in Section 2.3. The frequency dependence is implicit for \( \Lambda, \sigma(r), d_1, \) and \( d_\parallel \).

![Electronic distributions at the boundary of a metal \( \partial \Omega \). The horizontal axis, \( \mathbf{r}_\parallel \), represents the direction perpendicular to the surface (see inset). The electron equilibrium density \( n(r) \) exhibits spill-out and Friedel oscillations as explained in Fig. 2.4. The induced charge \( \rho(r) \) is not tied to the surface: its centroid, \( d_1 \), is located outside from the metal due to electronic spill-out. This is one of the important nanoplasmonic features that is considered in Feibelman’s theory. Figure from [13].](image)

**Feibelman’s \( d \)-parameters.** At this point, Feibelman’s \( d \)-parameters are introduced [12]:

\[ d_1 = \frac{\int_{-\infty}^{\infty} x \rho(x) \, dx}{\int_{-\infty}^{\infty} \rho(x) \, dx}, \]

(2.30a)

\[ d_\parallel = \frac{\int_{-\infty}^{\infty} x \partial_x J_y(x) \, dx}{\int_{-\infty}^{\infty} \partial_x J_y(x) \, dx}, \]

(2.30b)

where \( x \) is the direction perpendicular to the surface, \( \rho(x) \) is the induced charge and \( J_y(x) \) is the induced current tangential to the surface. These expressions for the \( d \)-parameters are derived assuming an external potential \( \phi^{\text{ext}}(r) = e^{ik_y x + k_x y} \) that leads to the microscopic quantities \( \rho(r) = \rho(x) e^{ik_y y} \) and \( \mathbf{J}(r) = e^{ik_y y} \).

The physical meaning of the \( d \)-parameters, which are only material-dependent, becomes apparent from the definitions above: \( d_1 \) corresponds to the centroid of the induced charge, while \( d_\parallel \) is the normal derivative of the tangential current. Both \( d_1 \) and \( d_\parallel \) can be complex numbers, and are implicit functions of frequency \( \omega \) and
momentum $k$, although the $k$-dependence contributes as a second order effect [33]. This is an important remark, as it allows the extension of the local $d$-parameters ($k \to 0$) of a planar interface to arbitrary geometries. In addition, these are model-dependent parameters. They will exhibit a different $\omega$-dependence if the HDM is assumed or if the TDDFT is employed to compute $d_\perp$ and $d_\parallel$. Nonlocality is also present in the $d$-parameters: they can be rewritten in terms of derivatives of moments of the nonlocal dielectric tensor $\varepsilon(r, r')$ [13].

An analytical form of the $d$-parameters can be derived within the HDM [13]:

$$d_{\parallel}^{\text{HDM}} = \frac{-\beta}{\sqrt{\omega_p^2 - \omega^2}}, \quad (2.31a)$$

$$d_{\perp}^{\text{HDM}} = 0, \quad (2.31b)$$

where $\beta$ is the hydrodynamic velocity and $\omega_p$ is the plasma frequency. Two relevant remarks about these expressions are: (i) the metal is assumed to be an homogeneous electron gas (HEG – $\varepsilon_n = 1$) adjacent to vacuum ($\varepsilon_d = 1$), and (ii) they cannot be employed at frequencies above $\omega_p$.

In the next chapter we will also employ $d$-parameters numerically computed via TDDFT. Additionally, if their frequency-dependence is not very strong, they can even be linearized for a particular range of frequencies.

**Perturbed eigenvalues.** The eigenproblem from Eq. (2.29) can be written in operator form as:

$$\Lambda |\sigma\rangle = (K + d_\alpha V_\alpha)|\sigma\rangle,$$

with operators $K$ and $d_\alpha V_\alpha$ (implicitly summed over $\alpha = \{\perp, \parallel\}$) and $|\sigma\rangle$ corresponding to the state $\sigma(r) \equiv \langle r |\sigma\rangle$.

The $d$-parameters theory calculates deviations from the classical predictions under a first-order approach. Therefore, it is possible to apply perturbation theory to solve Eq. (2.32). The zeroth-order eigenproblem corresponds to the classical one: $\Lambda_n(0)|\sigma_n(0)\rangle = K|\sigma_n(0)\rangle$. Then, the first-order perturbed eigenvalue around the classical value can be written as:

$$\Lambda_n = \Lambda_n(0) + \Lambda_{\alpha,n}^{(1)} d_\alpha + O(d_\alpha^2), \quad (2.33)$$

with perturbation factors $\Lambda_{\alpha,n}^{(1)} \equiv \langle \phi_n(0)|V_\alpha|\sigma_n(0)\rangle / \langle \phi_n(0)|\sigma_n(0)\rangle$, where $|\phi_n(0)\rangle \equiv (2\varepsilon_0)^{-1}g|\sigma_n(0)\rangle$ are the associated surface potentials that form a biorthogonal basis over the surface, i.e. $\langle \phi_n(0)|\sigma_n(0)\rangle \propto \delta_{nn'}$, and $\langle r |g| r'\rangle \equiv g(r, r')$. These factors can be simplified to [13]:

$$\Lambda_{\perp,n}^{(1)} = \frac{\Lambda_n(0)}{2\varepsilon_0} - 1 \frac{\langle \phi_n(0)|\sigma_n(0)\rangle}{\langle \phi_n(0)|\sigma_n(0)\rangle}, \quad (2.34a)$$

$$\Lambda_{\perp,n}^{(1)} = 2\varepsilon_0 \frac{\langle \nabla_{\perp} \phi_n(0) | \nabla_{\parallel} \phi_n(0) \rangle}{\langle \phi_n(0)|\sigma_n(0)\rangle}, \quad (2.34b)$$

although they can be reduced to simpler forms for several particular geometries, e.g. spherical and cylindrical (see Table 2.1).
Table 2.1. Analytical eigenvalues \( \Lambda \equiv \Lambda^{(0)} + d_\perp \Lambda^{(1)} + d_\parallel \Lambda^{(1)} \) of Eq. (2.29) valid to all orders in \( d_\alpha \) [13]. The eigenindices correspond to the polar and azimuthal angular momenta, \( l \) and \( m \), respectively. \( R \) is the radius of the sphere and the cylinder, and \( \bar{k} \equiv kR \), where \( k \) is the axial wave number. \( K_m \) and \( I_m \) are the modified Bessel functions.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>( \Lambda^{(0)} )</th>
<th>( \Lambda^{(1)}_\perp )</th>
<th>( \Lambda^{(1)}_\parallel )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>(-\frac{1}{2l+1})</td>
<td>(\frac{2(l+1)}{(2l+1)R} )</td>
<td>(\frac{2(l+1)}{(2l+1)R} )</td>
</tr>
<tr>
<td>Cylinder</td>
<td>( \bar{k} \frac{\partial}{\partial \bar{k}} { K_m(\bar{k}) I_m(\bar{k}) } )</td>
<td>( \frac{(\Lambda^{(0)})^2-1}{2K_m(\bar{k}) I_m(\bar{k}) R} )</td>
<td>( 2K_m(\bar{k}) I_m(\bar{k}) \frac{m^2+\bar{k}^2}{R} )</td>
</tr>
</tbody>
</table>

An important property of the eigenvalues is their shape- and scale-dependence. \( \Lambda^{(0)} \) is only shape-dependent, while \( \Lambda^{(1)}_\perp \) and \( \Lambda^{(1)}_\parallel \) are also scale-dependent, since \( V_\alpha \sim 1/L \), and they have units of \( 1/L \). Moreover, \( \Lambda^{(1)}_\perp < 0 \) and \( \Lambda^{(1)}_\parallel > 0 \).

A great advantage of Feibelman’s approach is that the information about the materials is contained in \( d_\alpha \), while the geometry only affects \( \Lambda^{(0)} \) and \( \Lambda^{(1)}_\alpha \), so their influence can be studied independently.

**Spectral corrections.** Feibelman’s theory provides spectral corrections to the classical plasmonic resonances \( \omega_{\alpha}^{(0)} \) that shift to \( \omega_{\alpha}^{(0)} + \omega_{\alpha}^{(1)} \). The general expressions for both values are [13]:

\[
\omega^{(0)} = \omega_p \sqrt{\frac{1 + \Lambda^{(0)}}{(\varepsilon_d + \varepsilon_b) - (\varepsilon_d - \varepsilon_b)\Lambda^{(0)}}},
\]

\[
\omega^{(1)} = \frac{\Lambda^{(1)}_\alpha d_\alpha(\omega^{(0)})}{\left[ \frac{\partial}{\partial \omega}(\Lambda - \Lambda^{(1)}_\alpha d_\alpha) \right]_{\omega=\omega^{(0)}}},
\]

where the eigenindices \( n \) have been omitted for clarity.

This result can be particularized for the lossless (\( \gamma = 0 \)) HEG next to vacuum, yielding:

\[
\omega^{(0)} = \omega_p \sqrt{\frac{1 + \Lambda^{(0)}}{2}},
\]

\[
\omega^{(1)} = \frac{1}{4} \Lambda^{(1)}_\alpha d_\alpha(\omega^{(0)}) \frac{\omega_p^2}{\omega^{(0)2}}.
\]

Note from this expression that \( d_\perp < 0 \) (\( >0 \)) causes a blueshift (redshift) since \( \Lambda^{(1)}_\parallel < 0 \). Then, the \( d \)-parameters from the HDM (Eq. 2.31) agree with the blueshift that the HDM generates in spectral predictions, since \( d_\perp^{\text{HDM}} < 0 \).

**Polarizability.** The polarizability of a system of particles will be studied in the next chapter, and it can be written in terms of its \( d \)-parameters as [13]:

\[
\alpha_d = 2 \sum_n \frac{\alpha^{(0)}_\alpha + \alpha^{(1)}_{\alpha,n} d_\alpha}{\Lambda^{(0)}_n + \Lambda^{(1)}_{\alpha,n} d_\alpha - \Lambda} + O(d^2_\alpha),
\]

(2.37)
where

\begin{align}
\alpha_n^{(0)} & \equiv \frac{\langle \phi_n^{(0)} | \hat{n} \cdot \hat{j} | r \cdot \hat{i} | \sigma_n^{(0)} \rangle}{\langle \phi_n^{(0)} | \sigma_n^{(0)} \rangle}, \quad (2.38a) \\
\alpha_n^{(1)} & \equiv \frac{\langle \phi_n^{(0)} | V_n \Phi_n \hat{n} \cdot \hat{j} | r \cdot \hat{i} | \sigma_n^{(0)} \rangle}{\langle \phi_n^{(0)} | \sigma_n^{(0)} \rangle}, \quad (2.38b) \\
\end{align}

and \( P_n \equiv \sum_{n' \neq n} \frac{1}{\Lambda - \Lambda_n} \frac{|\phi_n^{(0)}\rangle \langle \phi_n^{(0)}|}{\langle \phi_n^{(0)} | \sigma_n^{(0)} \rangle} \) is the weighted projection operator. The dipole is perturbed along \( \hat{j} \) and induced along \( \hat{i} \).

### 2.5 Transformation Optics

Transformation optics (TO) is a mathematical tool commonly used for the design of metamaterials, which control the behavior of electromagnetic waves to create particular effects, like invisibility [34].

Fermat’s principle, formulated in 1662 by Pierre de Fermat, states that light rays traveling from point A to B will choose the shortest optical path, which is defined as the integral of the refractive index \( n(r) \) along the path: \( s = \int_A^B n(r) \, dl \) [35]. Hence, for light, the shortest path is generally not a straight line, and it depends on the medium. Fig. 2.6 represents light rays traveling in straight lines (left), as they do in vacuum, and curved optical paths (right) due to a material with a particular refractive index \( n(r) \). Filling the vacuum with this material corresponds mathematically to a geometrical conformal transformation: the geometry is transformed while respecting Fermat’s principle [35]. This idea has been employed in general relativity to develop the mathematical theory of TO [36], and it has spread to other fields, such as plasmonics.

We do not make explicit use of TO in this project, but we employ results that have been derived from this theory. It is not possible to derive analytical expressions for cross sections and resonances for any arbitrary geometrical shape. However, it is possible to do so for a cylindrical dimer by using TO (see Section 3.4) [32]. For further information about TO, see Ref. [35].
Figure 5: Optical conformal mapping [72]. Suppose that an optical medium performs a coordinate transformation from a straight Cartesian grid (left) to curved coordinates in physical space (right). The trajectories of light rays follow the curved coordinates, but this apparent curvature is an illusion and may be used to create optical illusions, for example in invisibility.

\( n_0 = 1 \) intact, they correspond to materials with an isotropic refractive index profile. If \( n_0 \) the transformed space is empty; light would propagate along a straight line there: the refractive-index profile acts as a transformation medium.

So far we have discussed light rays. How does the conformal transformation (2.4) act on light waves? Suppose that both amplitudes of the optical polarization satisfy the Helmholtz equation

\[
\nabla^2 + \frac{\omega^2}{c^2 n^2} = 0
\]

where \( \omega \) denotes the frequency and \( c \) the speed of light in vacuum. It is convenient to write the Laplacian

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial}{\partial x} + i \frac{\partial}{\partial y}
\]

(2.7)

We obtain from the differential equations (2.4) of the conformal map the transformation

\[
\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} = \left( \frac{\partial}{\partial x_0} + i \frac{\partial}{\partial y_0} \right) \frac{\partial}{\partial x} + \left( \frac{\partial}{\partial x_0} + i \frac{\partial}{\partial y_0} \right) \frac{\partial}{\partial y}
\]

(2.8)

\( 8 \)

Figure 2.6. (Left) Light rays in vacuum propagate in straight lines. (Right) If the space is filled with a material that bends optical paths as shown, light rays traveling in the horizontal direction will not be able to detect an object in the central region. Figure from [35].
3 | Quantum corrections to classical nanoplasmonics

The behavior of metallic nanoparticles interacting with light, as seen in the previous chapter, is relatively well understood even including quantum corrections. However, the major interest of nanoparticles regarding its applications relies in the behavior of coupled structures. These structures have also been studied by many researchers in classical [37,38] and quantum [39] frameworks. TDDFT simulations provide a complete quantum description of these systems but it is an extremely demanding computational tool and it cannot be used to study the relationship between variables in an analytical way.

In this chapter, we develop both analytical and numerical tools to evaluate the quantum effects over coupled plasmonic nanostructures.

First, in Section 3.1, we review the numerical tools that we have developed for this project (QBEM) in order to obtain numerical quantum-corrected results. In Section 3.2, we derive an analytical expression for the polarizability of the single sphere, based on the $d$-parameters theory. We use this result to check the performance of QBEM. Then, in Section 3.3, we show that Feibelman’s theory is a general approach that can be particularized to obtain results from a particular model, concretely the HDM, by studying a single cylinder.

In Section 3.4, we develop new analytical expressions for the perturbed eigenvalues of twin cylinders, making indirect use of transformation optics. Finally, in Section 3.5, we use our computational tools to analyze coupled spheres.

3.1 QBEM

Finite elements method (FEM) and finite differences method are commonly used in engineering to solve a wide variety of problems, from fluid dynamics to electromagnetism [40]. A powerful alternative in some cases is the boundary element method (BEM), which reduces the dimension of the problem by 1, since it only requires a discretization of the boundaries [41]. BEM is particularly useful in problems with infinite domains. Most of the nanoplasmonic systems are composed by semi-infinite materials or particles embedded in a infinite medium. Hence, BEM constitutes a solid method to solve the problems we will propose in this chapter.

A potential-based BEM approach is numerically favorable, since it involves the computation of the potentials and their first-order derivatives, when applying the
boundary conditions. Conversely, solving Maxwell’s equations for the fields translates into poor convergence as they invoke second derivatives of the potentials, which have larger gradients and require a finer mesh to obtain a similar accuracy. Therefore, we employ the BEM to solve the classical NBIE. The discretization of Eq. (2.24) reads:

$$\Lambda \sigma_i = 2\varepsilon_0 \left( \frac{\partial \phi_{\text{ext}}}{\partial n} \right)_i + \sum_j \left( \frac{\partial g}{\partial n} \right)_{ij} \sigma_j$$  \hspace{1cm} (3.1)$$

for the boundary elements $i$ and $j$.

MNPBEM (Metallic NanoParticles Boundary Element Method) is a MATLAB toolbox aimed at solving the NBIE for systems of particles embedded in a dielectric environment with homogeneous and isotropic dielectric functions. The main features include geometry and mesh design, BEM eigenmodes solver, and solver under different excitations ($\phi_{\text{ext}}$). The codes can be found in http://physik.uni-graz.at/mnpbem/. For further information about MNPBEM, see Ref. [42].

Nevertheless, the numerical treatment discussed in this section is not valid for the purpose of this project, and a numerical implementation of Feibelman’s theory was needed. Based on MNPBEM, we have developed QBEM (Quantum Boundary Element Method), a complementary toolbox that solves the NBIE including first-order $d$-parameters terms, in order to take into account nonlocality, spill-out and Landau damping. The main functions in QBEM compute the eigenvalues ($\Lambda^{(0)}$, $\Lambda^{(1)}_\perp$ and $\Lambda^{(1)}_\parallel$), polarizability and resonance frequency for a system of metallic nanoparticles. This has been done by discretizing the brackets involved in Eqs. (2.34) and (2.37) as:

$$\langle \varphi | \psi \rangle = \sum_i \varphi_i A_i \psi_i,$$  \hspace{1cm} (3.2)$$

where $A_i$ is the area of the $i$-th boundary element. Shape functions, which depend on the type of boundary element employed (triangular or quadrilateral), are used to compute the derivatives required for $\nabla \parallel \phi$. The codes can be found at https://github.com/AlvaroGI/QBEM, as well as a README file with further information. Moreover, the codes have been validated by reproducing the results from Ref. [13], where Christensen et al. computed $\Lambda^{(0)}$, $\Lambda^{(1)}_\perp$ and $\Lambda^{(1)}_\parallel$ as a function of the aspect ratio for a nanocube, a nanorod, a nanospheroid and a nanotriangle.

All the numerical results shown in this thesis have been obtained via QBEM, unless otherwise specified.

### 3.2 Single sphere

The classical polarizability of the sphere is given by Eq. (2.16), while Eq. (2.37) determines the polarizability for an arbitrary geometry in a quantum framework using the Feibelman $d$-parameters. If the geometry exhibits spherical symmetry, then the eigenfunctions that are solution to Maxwell’s equations, i.e. to the eigenproblem from Eq. (2.29), are also spherically symmetric. Therefore, the induced charge over the surface of the sphere for each classical eigensolution $\{\Lambda^{(0)}_n, |\sigma^{(0)}_n\rangle\}$ can be written in terms of a spherical harmonic:

$$\sigma^{(0)}_{lm}(r) = \sigma(r) Y^m_l(\theta, \varphi),$$  \hspace{1cm} (3.3)$$
where $\sigma(r)$ is a radial function and $Y^m_l(\theta, \phi)$ is the spherical harmonic for the quantum numbers $l$ and $m$. This allows us to particularize Eq. (2.37) for the single sphere (see Appendix A for further details), yielding a polarizability in terms of the $d$-parameters:

$$\alpha_d = \frac{4\pi}{3} R^3 \left( -\frac{2}{3} - \frac{4\pi}{3\pi} d - \Lambda \right).$$

(3.4)

The contribution from $d_\parallel$ is negligible in the cases we will study, so we neglected it in the derivation of the previous expression. In addition, $d_\parallel = 0$ for the HDM and also for the numerical values obtained via TDDFT that we will use.

The polarizability from Eq. (3.4) has been compared to simulations from QBEM. Figures 3.1 and 3.2 show the accuracy of the numerical calculations and the convergence towards the analytical expression. The mean error is smaller than 0.5% even for the smallest number of elements available in QBEM (508). Moreover, the main discrepancies are located around the resonant frequency and the plasma frequency.

![Figure 3.1](image_url) Error computed as $\epsilon_{\text{Re}} = \frac{|\text{Re}(\alpha_Q) - \text{Re}(\alpha_d)|}{\text{Re}(\alpha_d)} \cdot 100$ and $\epsilon_{\text{Im}} = \frac{|\text{Im}(\alpha_Q) - \text{Im}(\alpha_d)|}{\text{Im}(\alpha_d)} \cdot 100$, where $\alpha_d$ is the analytical polarizability from Eq. (3.4) and $\alpha_Q$ is the numerical polarizability. 964 boundary elements were used for this simulation, and the model employed for the $d$-parameters was the HDM.

![Figure 3.2](image_url) Mean error in the polarizability of a single sphere between Eq. (3.4) and QBEM calculations. Error computed as $\epsilon_{\text{Re}} = \frac{|\text{Re}(\alpha_Q) - \text{Re}(\alpha_d)|}{\text{Re}(\alpha_d)} \cdot 100$ and $\epsilon_{\text{Im}} = \frac{|\text{Im}(\alpha_Q) - \text{Im}(\alpha_d)|}{\text{Im}(\alpha_d)} \cdot 100$, where $\alpha_Q$ is the numerical polarizability. The average is performed over the interval $\omega/\omega_p = [0.2, 0.999]$. 964 boundary elements were used for this simulation, and the model employed for the $d$-parameters was the HDM.

A similar expression to Eq. (3.4) was derived by Apell and Ljungberg in 1982 [33]:

$$\alpha_{\text{Apell}} = \frac{4\pi}{3} R^3 \frac{2}{3} \cdot \left( 1 + \frac{d_\parallel}{R} \right) - \frac{4\pi}{3\pi} d_\perp - \Lambda.$$  

(3.5)
Note that it matches our expression except for an extra term in the numerator, which is not relevant since generally \(\frac{d}{R} \ll 1\). This discrepancy is due to a different derivation of the expression (see Ref. [33]). It is important to remark that the denominators agree, since the position of the resonance will be given by the poles of the polarizability.

In addition, the HDM provides an analytical expression for the multipolar polarizability of a single sphere [43]:

\[
\alpha_l^{\text{HDM}}(\omega) = \frac{4\pi}{3} R^{2l+1} \frac{3l(\varepsilon_m - (1 + \delta_l) \varepsilon_d)}{l\varepsilon_m + (l + 1)(1 + \delta_l)\varepsilon_d},
\]

with \(\delta_l = \Delta_t/[j_l(x_M)(l+1)]\) and \(\Delta_t = l(l+1)j_l(x_M)\varepsilon_m^{-l}d_{l}^{N}j_l(x_M)\), where \(x_M = k_M R\) and \(x_{NL} = k_{NL} R\) are dimensionless parameters in terms of the radius \(R\) and the transverse and longitudinal wavenumbers in the metal \((k_M^2 = k_0^2 \varepsilon_m\) and \(k_{NL}^2 = (\omega_p/\beta)^2 \varepsilon_m/[\varepsilon_d(\varepsilon_d - \varepsilon_m)]\), respectively, where \(k_0\) is the vacuum wavenumber, and \(j_l(x)\) is the spherical Bessel function. Note that Eq. (3.6) reduces to Eq. (2.16) in a classical dipolar framework \((l = 1\) and \(\beta = 0\)).

Figure 3.3 displays the polarizability spectrum computed via the different analytical expressions discussed so far and QBEM. Eq. (3.6) has been evaluated at \(l = 1\) to consider the dipolar mode. The three quantum-corrected curves show a good agreement, except for the region near \(\omega = \omega_p\), as expected. Moreover, the mean relative error between our numerical calculations and Apell’s polarizability is about 5% over the interval of interest, \(\omega/\omega_p = [0.2, 0.9]\). It can be reduced by increasing the number of boundary elements.

![Figure 3.3](image)

Figure 3.3. (a) Real and (b) imaginary parts of the polarizability of a single sphere \((R = 20 \text{ nm and 964 boundary elements in QBEM})\). It has been computed using classical (Eq. (2.16), green line), Apell’s (Eq. (3.5), dotted blue line), and HDM (Eq. (3.6), dashed red line) expressions and numerical simulations (black line). Error estimated as \(\varepsilon_{\text{re}} = |\text{Re}(\alpha_q) - \text{Re}(\alpha_{\text{Apell}})|/\text{Re}(\alpha_{\text{Apell}}) \cdot 100\) and \(\varepsilon_{\text{im}} = |\text{Im}(\alpha_q) - \text{Im}(\alpha_{\text{Apell}})|/\text{Im}(\alpha_{\text{Apell}}) \cdot 100\), where \(\alpha_q\) and \(\alpha_{\text{Apell}}\) are the numerical and Apell’s polarizabilities, respectively.

Likewise, the resonances of a single sphere derived in Section 2.2.1 are no longer valid in the nanoscale. Feibelman \(d\)-parameters also constitute a powerful tool to study the first-order quantum corrections to the eigenfrequency, as stated in Section
2.4.2. Let us consider the material of the sphere as a lossless HEG embedded in vacuum ($\varepsilon_d = \varepsilon_B = 1$) for simplicity. Due to the spherical symmetry of the problem, the classical and perturbed eigenvalues feature a simple $l$-dependence (see Table 2.1). Moreover, the HDM provides easy to handle expressions for the $d$-parameters. We also assume $d_\perp = d_\perp^{\text{HDM}}$ and $d_\parallel = d_\parallel^{\text{HDM}}$. The, the HEG and HDM hypotheses yield an explicit form of the resonance from Eq. (2.36) in terms of the polar quantum number $l$ and the ratio $\beta/R$:

$$\omega_{\text{HDM,sphere}}^{(0)}(0) = \omega_p \sqrt{\frac{l}{2l+1}},$$

(3.7a)

$$\omega_{\text{HDM,sphere}}^{(1)}(1) = \frac{\sqrt{l(l+1)}}{2} \frac{\beta}{R}.$$

(3.7b)

This result is particularly elucidating as it has been derived by other authors from a hydrodynamic approach [26]. This constitutes a first proof of the generality of the $d$-parameters theory since hydrodynamic results have been obtained as a particularization of this theory. If the HEG assumption is not made, the following values are obtained:

$$\omega_{\text{HDM,sphere}}^{(0)}(0) = \omega_p \sqrt{\frac{l}{\varepsilon_d(l+1) + \varepsilon_B l}},$$

(3.8a)

$$\omega_{\text{HDM,sphere}}^{(1)}(1) = \frac{1}{2} \sqrt{\frac{l(l+1)}{\varepsilon_d} \frac{\beta}{\varepsilon_B R}}.$$

(3.8b)

To conclude, we analyze experimental measurements from [11] in Fig. 3.4a. The experiment was performed using electron energy loss spectroscopy (EELS) over a silver nanoparticle deposited on ultrathin (3 nm) carbon films. The green dots are the experimental points, while the blue dashed line corresponds to the classical resonance $\omega^{(0)}$. The absorption efficiency, which corresponds to the absorption cross section normalized by the cross sectional area of the sphere, has been calculated combining Eqs. (2.17b) and (3.4). As an example of the versatility of the $d$-parameters, we do not use $d_\alpha^{\text{HDM}}$. Instead, we employ constant values that successfully fit this system in the range of energies analyzed: $d_\perp = -0.18$ nm and $d_\parallel = 0$.

The agreement between the resonance in the absorption efficiency and the experiments shows that Feibelman’s theory can successfully predict the blueshift in Ag nanoparticles. Silver is a special material that exhibits blueshifts, which correspond to $d_\perp < 0$, so its behavior can be also modeled by the HDM, as mentioned in Section 2.4.1.

In addition, the absorption cross section takes values above 100 in the resonance, which means that the sphere absorbs the energy that flows over more than 100 cross sectional areas. This fact suggests that nanoplasmics can effectively achieve extreme light-matter interaction.

We also show the resonance shifts for higher order modes in Fig. 3.4b.
Figure 3.4. (a) Absorption efficiency for a single sphere of radius $R$. Experimental values from Ref. [11] as red dots. The blue dashed line corresponds to $\omega^{(0)}$. The inset shows a representation of the charge distribution of the dipolar mode — positive (negative) charge in red (blue). (b) Classical (dotted lines) and quantum-corrected (solid lines) resonances, based on the HDM, for the dipolar mode ($l = 1$) and two higher order modes ($l = 2, 3$). The inset shows a representation of the charge distribution of $l = 2$ mode — positive (negative) charge in red (blue). (a-b) The values of the parameters involved in the calculations are: $\hbar \omega_p = 9.01$ eV (silver) [21], $\varepsilon_d = 3.2$, and $\varepsilon_B = 1.53$. The system is composed by silver nanospheres over 3 nm carbon films, and both dielectric constants have been found by fitting to the experimental results [11].

### 3.3 Single cylinder

The case of a single cylinder is similar to the sphere. Again, let us assume the lossless HEG adjacent to vacuum hypothesis ($\varepsilon_d = \varepsilon_u = 1$) for simplicity. Then, the resonant frequency can be found by combining the general resonant frequency for an HEG (Eqs. (2.36)) and the HDM form of the $d$-parameters (Eq. (2.31)), and replacing the classical and quantum first-order eigenvalues by their corresponding expressions for a single cylinder (see Table 2.1). After simplifying the results, one finds that:

$$\omega_{cyl}^{(0)} = \omega_p \sqrt{1 + \frac{k \partial}{\partial k} \left( \frac{1}{2} K_m(k)I_m(k) \right)} \quad \text{(3.9a)}$$

$$\omega_{cyl}^{(1)} = \frac{1}{2} Z_m(\tilde{k}) \frac{\beta}{R} \quad \text{(3.9b)}$$

where

$$Z_m(\tilde{k}) = \frac{1 - \left[ \frac{k \partial}{\partial k} \left( \frac{K_m(k)I_m(k)}{2K_m(k)I_m(k)} \right) \right]^2}{2K_m(k)I_m(k) \sqrt{1 - \frac{k \partial}{\partial k} \left( \frac{1}{2} K_m(k)I_m(k) \right)}} \quad \text{(3.10)}$$

The expressions above are particularly simple in the local case ($\tilde{k} \to 0$). The classical local theory yields an infinitely degenerate unique resonance $\omega_{cyl, local}^{(0)} = \omega_{cyl}^{(0)}(k = 0)$,
which is corrected by an \( m \)-dependent first order term:

\[
\omega_{\text{cyl,local}}^{(0)} = \omega_p \frac{1}{\sqrt{2}}, \tag{3.11a}
\]

\[
\omega_{\text{cyl,local}}^{(1)} = \frac{1}{2} m \frac{\beta}{R}. \tag{3.11b}
\]

These results can also be derived from the local theory based on the HDM \[44\], so we face a new proof of generality of the \( d \)-parameters theory.

Finally, Fig. 3.5 shows classical and first-order corrected resonances under the local approximation. For large diameters (\( > 80 \) nm), the shift is not relevant. However, it should be taken into account for smaller sizes. Note also that \( \omega_{\text{cyl,local}}^{(1)} > 0 \), i.e. there is a blueshift, as a result of using HDM-based \( d \)-parameters.

![Figure 3.5. Resonance energy (\( \hbar \omega \)) of a single cylinder of radius \( R \) (local approximation). Classical prediction as a dashed black line. Linear approximation based on the HDM for the dipolar and two higher order (\( m = 2, 3 \)) modes in blue, green and red, respectively.](image)

### 3.4 Twin cylinders

In this section, we study a system composed by two metallic nanocylinders of radius \( R \) separated by a gap \( g \). This particular geometry can be analyzed under a transformation optics (TO) treatment including nonlocal effects, i.e. assuming a HDM. We will compare the HDM results to Feibelman’s theory with hydrodynamic \( d \)-parameters in order to infer explicit expressions for the classical and first-order-corrected eigenvalues \( \Lambda^{(0)}, \Lambda^{(1)}_\perp, \) and \( \Lambda^{(1)}_\parallel \). Recall that \( d^{\text{HDM}}_\perp = -\beta / \sqrt{\omega_p^2 - \omega^2} \) and \( d^{\text{HDM}}_\parallel = 0 \) implicitly assume that the metal is a lossless HEG next to vacuum, so we are forced to work under this assumption. The advantage of the method we will
follow is that the eigenvalues are not material-dependent, so this strong hypothesis will not affect the results.

Fernández-Domínguez et al. studied the cylindrical dimer by applying TO [32]. With this technique, a system of twin parallel cylinders embedded in vacuum can be transformed into a vacuum gap between two semi-infinite metallic spaces. The original excitation, a plane wave, is converted into a collection of dipoles placed inside the gap under this conformal transformation. After obtaining the fields and potentials in the transformed space within the HDM, the transformation is inverted. Then, the absorption cross section of the dimer can be expressed as:

\[
\sigma_{\text{abs}} = \frac{(8R)^2 \pi \omega}{\eta^2 c} \rho'(1 + \rho') \text{Im} \left\{ \sum_{n=1}^{\infty} \xi_n \right\},
\]

(3.12)

where

\[
\xi_n = \frac{n e^{\alpha_n}}{(\sqrt{\rho'} + \sqrt{\rho' + 1})^{4n} - e^{\alpha_n}},
\]

(3.13)

\[
\alpha_n = \ln \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) \gamma_n(\omega) + 1},
\]

(3.14)

\[
\gamma_n = \sqrt{1 + \left(\frac{2R}{\beta} \right)^2 \omega_p^2 - \omega^2 \rho'(\rho' + 1) \frac{n^2}{(2\rho' + 1 - 2/\pi)^2}}.
\]

(3.15)

The geometrical parameter \(\rho' = \rho + \rho_0\) is dependent on the relative gap size \(\rho = \frac{\phi}{4R}\) and the phenomenological term \(\rho_0 = \frac{g_0}{4R}\). The parameter \(g_0\) is introduced to recover the nonlocal predictions for touching nanocylinders. It is calculated by matching the first resonant condition \((n = 1)\) in Eq. (3.12) and in the touching case [45]. However, \(g_0 \approx \frac{2\beta}{\omega_p}\) for realistic values of \(\beta\) (around \(10^6\) m/s) [32]. Our goal is to achieve an explicit analytical solution that does not require any iterative process to be solved, therefore, we make use of this approximation, yielding \(\rho_0 = \frac{\beta}{2\omega_p R}\).

The resonances of this system appear at the poles of (3.13). Hence, the resonance condition can be written as:

\[
C^{4n} - \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) \gamma_n(\omega) + 1} = 0,
\]

(3.16)

where \(C' = \sqrt{\rho'} + \sqrt{\rho' + 1} > 1\).

By expanding the solution of Eq. (3.16) around \(\beta = 0\) it is possible to compute the classical resonance frequency and the first-order nonlocal correction:

\[
\omega_n^{(0)} = \omega_p \sqrt{\frac{C^{4n} - 1}{2C^{4n}}},
\]

(3.17a)

\[
\omega_n^{(1)} = \frac{1}{2\sqrt{(C^{4n} - 1)\rho(\rho + 1)}} \left[ \frac{C^{1-3n}}{\sqrt{2}} + (\rho + \frac{1}{2} - \frac{1}{\pi}) \sqrt{(C^{4n} + 1)} \right] n \frac{\beta}{R},
\]

(3.17b)

where \(C = \sqrt{\rho'} + \sqrt{\rho' + 1} > 1\) (\(\omega_n^{(0)}\) and \(\omega_n^{(1)}\) exist for any \(\rho > 0\)). These resonances are explicit functions of the geometrical parameters of the model (\(R\) and \(\rho\)) and the hydrodynamic parameter \(\beta\), as expected. They allow us to extend the \(d\)-parameters
Figure 3.6. Absorption efficiency for a cylinder dimer of radius $R$ and $\rho = 0.25$ (left) and $\rho = 0.025$ (right), computed via Eq. (3.12). Frequency is normalized by the surface plasma frequency $\omega_{\text{sp}}$. Black/blue/green lines correspond to the position of the classical/HDM/d-parameters position of the resonance. The HDM form of the $d$-parameters is employed. We use the same parameters as in Ref. [32]: $\varepsilon_d = \varepsilon_B = 1$, $\omega_p = 2.2 \cdot 10^{15}\text{rad/s}$, $\gamma = 1.8 \cdot 10^{13}\text{rad/s}$, and $\beta = 10^6\text{m/s}$.

theory to coupled nanowires, i.e. to find an expression for $\Lambda^{(0)}$ and $\Lambda^{(1)}_\parallel$. One can do that by comparing Eqs. (3.17) and (2.36), which yield:

$$\omega^{(0)} : \omega_p \sqrt{\frac{1 + \Lambda^{(0)}_\parallel}{2}} = \omega_p \sqrt{\frac{C^{4n} - 1}{2C^{4n}}}, \quad (3.18a)$$

$$\omega^{(1)} : \frac{1}{4} \Lambda^{(1)}_\perp d_\perp (\omega^{(0)}_n) \frac{\omega_p^2}{\omega^{(0)}_n} = Z(\rho, n, \beta, R), \quad (3.18b)$$

where $Z(\rho, n, \beta, R)$ corresponds to the right-hand side of Eq. (3.17b), and $d^{\text{HDM}}_\parallel(\omega^{(0)}_n) = -\beta / \sqrt{\omega_p^2 - (\omega^{(0)}_n)^2}$. It becomes apparent that it is not possible to find the value of $\Lambda^{(1)}_\parallel$ since $d_\parallel = 0$. After some algebra, one can solve Eqs. (3.18) for $\Lambda^{(0)}_n$ and $\Lambda^{(1)}_{1,n}$:

$$\Lambda^{(0)}_n = -C^{-4n}, \quad (3.19a)$$

$$\Lambda^{(1)}_{1,n} = -\frac{\sqrt{C^{4n} + 1}}{C^{4n} \sqrt{\rho (\rho + 1)}} \left[ C^{1-3n} \sqrt{\frac{1}{2}} + (\rho + \frac{1}{2} - \frac{1}{\pi}) \sqrt{(C^{4n} + 1)} \right] \frac{n}{R}. \quad (3.19b)$$

Recall that we validated the $d$-parameters approach in the previous sections by proving that it is a general theory that recovers first-order perturbation results from the HDM when $d_\perp = d^{\text{HDM}}_\perp$ and $d_\parallel = d^{\text{HDM}}_\parallel$. In Figures 3.6 and 3.7, we check that the agreement between the full HDM approach and the first-order perturbative solution is good. They display the absorption cross section from Eq. (3.12) as a function of $R$, $\rho$ and $\omega$. Fig. 3.6 shows the absorption efficiency versus radius for two different values of $\rho$: $\rho = 0.25$ (left) and $\rho = 0.025$ (right). Black lines indicate the position of the classical resonance ($\omega^{(0)}$). Blue lines correspond to the exact value of the poles of Eq. (3.12), i.e. the resonances under a full hydrodynamic treatment. Finally,
Figure 3.7. Absorption efficiency for a cylinder dimer of radius $R = 10$ nm and gap $d = 4R\rho$, computed via Eq. (3.12). Frequency is normalized by the surface plasma frequency $\omega_{sp}$. Black/blue/green lines correspond to the position of the resonance under a classical/HDM/$d$-parameters approach. The HDM form of the $d$-parameters is employed. We use the same parameters as in Ref. [32]: $\varepsilon_d = \varepsilon_0 = 1$, $\omega_p = 2.2 \cdot 10^{15}$ rad/s, and $\gamma = 1.8 \cdot 10^{13}$ rad/s. (Top, left) $\beta = 0$ (classical approach). (Top, right) $\beta = 10^5$ m/s. (Bottom) $\beta = 10^6$ m/s.

green lines indicate the linear approximation to the poles of Eq. (3.12), $\omega^{(0)} + \omega^{(1)}$, i.e. the position of the resonance under a $d$-parameters approach. Remarkably, the classical predictions fail even for large radius. However, the $d$-parameters results are almost in perfect agreement for $\rho = 0.25$ and slightly deviate for small radii and $\rho = 0.025$. Fig. 3.7 focuses on the gap-dependence. First, it is worth noting that the parameters of the model employed to compute the $d$-parameters have a strong impact on the results. As an example, the top-left, top-right and bottom plots are computed with $\beta = 0$, $10^5$ and $10^6$ m/s, respectively. For the first two of them, the linearized resonances agree with the full HDM, and the classical predictions already deviate for $\beta = 10^6$ m/s. For $\beta = 10^6$ m/s, there is perfect agreement up to 4 nm gaps.
3.5 Twin spheres

TO constitutes a very useful resource only for some geometries, and it is particularly non-trivial to apply in closed non-infinite particles. A system composed by two spherical particles has been solved by TO only for touching spheres [46], to the best of our knowledge. Due to this drawback, we cannot derive analytical expressions for twin spheres separated by a gap.

In any case, we are interested in studying the effect of the gap, since most practical applications of nanoplasmonics are based on spilling metallic nanospheres in an embedding medium, e.g. photothermal therapy [4] and plasmonic screens [7]. Therefore, we will compute quantum corrections to plasmonic resonances and cross sections via QBEM. The numerical eigenvalues $\Lambda^{(0)}$, $\Lambda^{(1)}$ and $\Lambda^{(2)}$ for the twin spheres can be found in Appendix B.

The energy of the dipolar mode of a single sphere features triple degeneracy, so it is independent of the direction of the total induced dipole. When two excited spheres are brought closer, the induced charge distributions over both of them interact. As a result, an energy splitting of the dipolar mode arises: bonding (lower energy) and anti-bonding (higher energy) plasmonic hybridization modes appear depending on the direction of the dipoles (see Fig. 3.8a). We will refer to each of the modes by a pair of arrows representing the direction of the total dipole moment of each sphere. Under this notation, the bonding modes are $\rightarrow\rightarrow$ and $\uparrow\downarrow$, and the anti-bonding modes are $\uparrow\uparrow$ and $\rightarrow\leftarrow$, ordered from lower to higher energy. Fig. 3.8b shows the evolution of the modes when the gap is closed. The bonding modes are reinforced as the surface charges of both spheres couple. Conversely, the charge distributions of the spheres repel each other in the anti-bonding modes and they become even less energetically favorable.

The energy of each mode can be computed via Eqs. (2.35) or (2.36). To study the energy splitting, we use sodium (Na), a metal that can be reasonably well described by the HEG approach. The plasma frequency is determined via Eq. (2.9), with electron density $n = 3/(4\pi r_s^3 a_0^3)$, where $r_s = 4$ is the Wigner-Seitz radius for Na and $a_0$...
is the Bohr radius \[13\]. In this section, every time we refer to \(d\)-parameters computed via TDDFT, we implicitly assume that we are using the values obtained for \(r_s = 4\) from Ref. \[13\].

Fig. 3.9 shows the energy splitting for a sodium spherical dimer \((R = 10 \text{ nm})\). Solid lines represent the energies calculated in a classical framework \(\omega^{(0)}\), while dashed (Fig. 3.9a) and dash-dotted lines (Fig. 3.9b) are first-order corrected results \(\omega^{(0)} + \omega^{(1)}\) with \(d\)-parameters from the HDM (Eqs. 2.31) and TDDFT calculations, respectively. The grey region displays an energy splitting diagram, where the \(x\)-axis is not respected. Black lines are used as a reference, and they correspond to the energy of a single sphere dipolar mode. The white panel respects the \(x\)-axis and shows the evolution of the resonance energy as the particles are brought closer. Red, blue, purple and green correspond to each of the modes of the dimer, ordered from lowest to highest energy: \(\rightarrow\rightarrow\), \(\uparrow\downarrow\), \(\uparrow\uparrow\), and \(\rightarrow\leftarrow\), respectively.

Figure 3.9. Energy splitting in a spheres dimer \((R = 10 \text{ nm})\). Solid lines represent the energies calculated in a classical framework, while dashed (a) and dash-dotted (b) lines are first-order corrected results with \(d\)-parameters from the HDM and TDDFT calculations \[13\], respectively. Black lines correspond to the energy of a single sphere dipolar mode. Red/blue/purple/green correspond to each mode of the dimer (\(\rightarrow\rightarrow\)/\(\uparrow\downarrow\)/\(\uparrow\uparrow\)/\(\rightarrow\leftarrow\)). The grey region displays an energy splitting diagram. Only the white panel respects the \(x\)-axis (logarithmic scale).

The first remarkable comment is that the HDM model predicts blueshifts with respect to the classical values, since \(d_{\text{HDM}} < 0\), while TDDFT calculations present a redshift in all cases. As the gap decreases, it becomes apparent that the energies of the bonding modes dramatically decrease, both in the classical and the quantum frameworks, while the anti-bonding modes slowly increase their energy of resonance. Therefore, the bonding modes are more easily excited when the spheres are closer.

It is not easy to graphically evaluate the influence of the gap in Fig. 3.9, since the shifts produced are a combined effect of the size of the particles and the separation between them. Figure 3.10 shows the difference between the classical and the quantum-corrected (via TDDFT) resonances as a percentage. The color code is the same as before: red, blue, purple and green for \(\rightarrow\rightarrow\), \(\uparrow\downarrow\), \(\uparrow\uparrow\), and \(\rightarrow\leftarrow\), respectively. The shift for large gaps is about 1.2\%, and it is due to the size of the spheres. This
deviation increases when closing the gap for all the modes, although the slope of the energy of anti-bonding modes is almost flat. A relevant finding is that the quantum correction due to the gap is larger for lower energy modes. In fact, this spectral shift goes up to a 12% for the →→ mode when the gap is ~0.3 nm.

Figure 3.11 shows the marginalized effect of radius and gap. The values displayed correspond to the lowest energy mode (→→), which exhibits the strongest sensitivity to quantum corrections. For large gaps, the deviation with respect to the classical prediction is caused by the effect of small radii. If the gap closes, there is a combined effect of gap and radius that yields different outcomes depending on the model employed for the $d$-parameters.

On the other hand, an interesting feature of this nanoplasmonic system is the amount of energy it interacts with. Figure 3.12 shows the absorption efficiency, $\sigma_{\text{abs}}/(\pi R^2)$, of the dimer as a function of the gap and the energy of the excitation ($\hbar \omega$), computed with QBEM. The external electric field propagates in the perpendicular direction to the axis that connects both spheres, and it is polarized in the direction of that axis (see sketch in the Figure). From top to bottom, the radius of the spheres

---

Figure 3.10. Percentage of spectral correction ($-\omega^{(1)}/\omega^{(0)} \cdot 100$) versus gap for a 10 nm radius spherical dimer. Red/blue/purple/green correspond to each mode of the dimer (→↑/↑↓/↑↑/→←).

Figure 3.11. Resonance energy of the lowest energy mode (→→). From left to right, different models for the $d$-parameters are employed: classical, HDM, and TDDFT (numerical calculations from Ref. [13] for $r_s = 4$).
used are 30, 15 and 5 nm. From left to right, we employ different models for the $d$-parameters: classical, HDM and TDDFT.

Spectral properties become apparent when analyzing the absorption efficiency. The main resonance in all cases corresponds to the $\rightarrow \rightarrow$ mode, as expected, and it is indicated with a black dash-dotted (orange solid) line for the classical (quantum-corrected) case. However, several higher-order modes with nonzero total dipole moment are excited when decreasing the gap. The common behavior of the resonances is to redshift, as predicted in Fig. 3.9 for the bonding modes. These shifts do not have a quantum origin since they are also observed in the classical framework as a result of the coupling between the charge distributions of both particles. Again, the HDM predicts a blueshift with respect to the classical values, and the TDDFT calculations produce a redshift that is more pronounced as the spheres are brought closer. These shifts cannot be neglected when the gap is very small, e.g. below 1 nm for a 15 nm radius. Moreover, we find that the smaller the spheres are, the larger is the shift due to the gap, showing that the effect of both variables should not be studied independently.

The different deviations produced by the HDM and the TDDFT constitute another proof of the model-dependency of Feibelman’s theory. As discussed in Fig. 3.4, the correct model for $d_\alpha$, that can even a constant value if the window of frequencies is small, should be fitted from experimental values for each combination of materials.

Note also that the absorption efficiency takes large values at the resonances, from 10 to 100. This means that the energy absorbed by the dimer corresponds to the energy that flows over the cross sectional area of 10 to 100 spheres.
Figure 3.12. Numerical computation of the absorption cross section for a spherical dimer via QBEM. (Top/Middle/Bottom) Spheres of 30/15/5 nm radius. (Left) $d$-parameters are set to 0 to reproduce classical results. (Center) The HDM expression for the $d$-parameters is employed, with $\beta = 10^6$ m/s, which is a common value for most metals. (Right) Numerical $d$-parameters computed via TDDFT, taken from Ref. [13] ($r_s = 4$). Black dash-dotted lines correspond to the classical resonance $\omega^{(0)}$ from Eq. (2.36a), computed using numerical eigenvalues (see Appendix B) and $d_i = d_\parallel = 0$. (Center/Right) Orange lines correspond to the first-order corrected resonance $\omega^{(0)} + \omega^{(1)}$ from Eqs. (2.36), computed with the same numerical eigenvalues but $d$-parameters under a HDM/TDFFT framework. The sketch in the left-down corner shows the direction of propagation (red) and polarization (black) of the external electric field $\mathbf{E}(\mathbf{r})$, as well as the charge distribution of the main mode that is excited (→→). The noise present in some of the subfigures corresponds to numerical noise.
Conclusions

Nanofabrication is pushing the limits of plasmonics towards smaller scales, with applications like surface-enhanced Raman spectroscopy and nanoantennas. Quantum effects arise when the characteristic geometric length of the system is reduced over 30 nm [11]. It is natural then to seek for a quantum theory or quantum corrections to the classical approach in order to describe the behavior of nanoplasmomics.

We have presented Feibelman’s theory, a perturbative approach that corrects the classical predictions including quantum effects like electronic spill-in or spill-out of the wave function, nonlocality, and surface-enhanced Landau damping. This theory is not as accurate as the TDDFT, which solves a many-body Schrödinger’s equation. In exchange, several advantages make Feibelman’s $d$-parameters approach more appealing for some applications. It provides analytical results for planar, spherical and cylindrical geometries that allow us to explore the relation between variables without the need of carrying out numerical simulations. Moreover, we have implemented Feibelman’s results numerically through a BEM approach (QBEM), based on the MNPBEM MATLAB toolbox. This method is tremendously less computationally demanding than TDDFT and it can be employed to extract spectral information and cross sections, amongst other features. Feibelman’s theory also makes a distinction between material and geometrical parameters: the $d$-parameters only depend on the materials of the system, while the classical and perturbed eigenvalues ($\Lambda_0$, $\Lambda_1^{(1)}$ and $\Lambda_\parallel^{(1)}$) are only shape and size dependent.

We have given evidence that the $d$-parameters approach is a general theory that recovers results from other models, e.g. the HDM, when we employ $d$-parameters calculated within that model. In particular, we have worked with a single sphere and a single cylinder. In addition, in Section 3.2, we also validated the $d$-parameters approach by predicting EELS experimental results.

We also showed that it is possible to infer analytical expressions for the eigenvalues using results from other models. We used the absorption cross section of a cylinder dimer, which was derived via TO, to obtain the analytical form of $\Lambda_0$ and $\Lambda_1^{(1)}$.

The last system we studied was composed by two coupled spheres. Using QBEM we computed the resonances and the absorption efficiency of the system for bonding and anti-bonding modes. There are two main remarks regarding this system: ($i$) the anti-bonding modes are not very sensitive to small gaps, while the lowest energy modes suffer a great energy shift when the gap closes, and ($ii$) there is a combined effect of radius and gap that should not be studied marginally.

Future research in this subfield can employ the analytical and numerical tools we have developed, which are mainly relevant when predicting spectral properties.
PART II

DEEP NEURAL NETWORK TRAINING WITH REVERSE SUPERVISION

What I cannot create, I do not understand.
— RICHARD FEYNMAN (1918-1988)
1 Introduction

Neural networks (NNs) are a particular set of algorithms englobed in machine learning (ML), which is a subfield of artificial intelligence [47].

ML has been probably the hottest topic in computer science in the last few years, driven by its revolutionary applications, ranging from self-driving cars [48] to early cancer detection [49]. Generally, there are two types of ML: supervised and unsupervised learning. An example of supervised learning is image classification through a NN. The input of the algorithm is an image and the output is a category. Using labeled data, we can train the network: after classifying a training image, it will compare the output with the correct label and it will update the parameters in the model. When the training is finished, the network has learned how to map from the space of images to the space of categories. Therefore, supervised tasks consist in training the algorithm with labeled data such that it learns the rules to classify new samples. On the other hand, unsupervised learning uses unlabeled data, so that the machine extracts information from the training data, e.g. it can discover hidden patterns [50].

This part of the thesis is dedicated to the research of the author on supervised learning with NNs. Originally, this project was focused on studying the interpretability of NNs, i.e. to explain how the knowledge was organized inside the network. With that purpose, we created a small reconstruction network that took the activations from a hidden layer of a main network as inputs, and tries to reconstruct the input of the main network. We realized that, when trained simultaneously to the main network, it improved the results on image recognition.

A publication is currently being developed and will be submitted soon, and this part of the thesis is an extended version of the first draft of the publication. However, the reader of this thesis is not expected to be familiar with this topic. Therefore, we review the most fundamental concepts of NNs in Chapter 2 to provide the reader with the basic ideas to interpret and understand our work and results. Some of the concepts will not be explained due to the limited space of this thesis, but we give references so that the reader can look up any term that has not been discussed in detail here.
2 | Fundamentals of neural networks

The goal of this chapter is to provide the reader with the minimum background required to understand the basics of our project, and then discuss related work that has been done previously.

2.1 Basics of neural networks

The basic unit of a neural network is a neuron. It is characterized by several weights and a bias. The neuron takes a multidimensional input $x$ and weights each of the components: $x^T w$. Then, it adds a bias $b$. Finally, the output of the neuron is given by an activation function $f(x^T w + b)$ (see Table 2.1).

As an example, take a simple case of weather forecast. Assume that we want to predict whether it will rain tomorrow. The inputs for our toy model could be the speed of the wind today, $x_1 \in [0, \infty)$, and a binary input $x_2$ that takes value 0 if it rained today and 1 if it did not. Then, we can build a small network with two inputs and only one output neuron with weights $w = [w_1, w_2]^T$ and bias $b$ (see Fig. 2.1).

![Figure 2.1. Sketch of a very simple neural network, composed by two input neurons and one output neuron.](image)

If we employ a Heaviside function as activation, we will get binary outputs ($0 = \text{it will rain}$, $1 = \text{it will not rain}$). However, a sigmoid activation function outputs a probability of rain between 0 and 1. The last step is to train the network with data from previous days. These data is labeled, i.e. it is composed by pairs $\{x, y\}$, where $x = [x_1, x_2]^T$ is the input and $y$ is the output. The training procedure consists in 3 steps that should be repeated until a proper performance of the network is achieved, i.e. until obtaining a small enough error in the predictions:

1. Give an input data point $x$ to the network and compute the output $y'$.
2. Calculate the value of a loss function that compares \( y' \) to the desired output \( y \), e.g. \( \mathcal{L} = (y - y')^2 \).

3. Update the weights and bias aiming for the global minimum of \( \mathcal{L} \):

\[
w_{i}^\text{NEW} = w_i - \eta \frac{\partial \mathcal{L}}{\partial w_i}
\]

\[
b_{\text{NEW}} = b - \eta \frac{\partial \mathcal{L}}{\partial b}
\]

where \( \eta \) is the learning rate, whose value is defined by the user.

After the training and the test, which consists in measuring the error percentage over a test dataset, the network is ready to work.

This toy network serves to explain the basic ideas, but every functional network employs a particular number of hidden layers, which are groups of neurons whose inputs come from a previous layer and whose outputs are the inputs for the next layer (see Fig. 2.2). When using a large number of layers, we refer to it as a deep neural network. Moreover, there are different types of networks depending on its architecture, i.e. the number of layers and neurons and the connections between them.

The most popular types of layers are fully connected and convolutional layers. Fully connected layers take all the outputs from the previous one as inputs for all its neurons, as in Fig. 2.2. Convolutional layers are three-dimensional, and they apply convolutions to the outputs from the previous layer instead of directly weighting all of them (see Ref. [50] for further details).

In any network with hidden layers, the step 3 of the training should be performed backwards, since the derivative of the loss function with respect to any weight or bias depends on the updated value of weights and biases of the deeper layers. Hence, this step is known as backpropagation. Some additional techniques, such as dropout and regularization, are employed to speed up the convergence of the algorithm and avoid overfitting and convergence to local minima [47].

![Figure 2.2](https://www.digitaltrends.com/cool-tech/what-is-an-artificial-neural-network/)

Another important remark is the distinction between variables (or parameters) and hyper-parameters. Variables correspond to those parameters that change its value during training, basically weights and biases. On the other hand, hyper-parameters are tuned before training and then generally remain constant: architecture (number of hidden layers and connections between them), learning rate, etc.

The field of deep neural networks is extremely wide, and it has been growing extremely rapidly in the last years. Due to the restricted number of pages for this
thesis, it is left to the reader to get more insight into the concepts that we use later and have not been discussed here. As a general reference on deep learning, we strongly encourage the reader to go through Ref. [50].

2.2 Related work

Since AlexNet won ImageNet competition in 2012 with a deep convolutional neural network [51], deeper and deeper networks have been developed and dominated computer vision in varieties of applications, such as object detection, segmentation, and video classification. However, training deep neural networks is hard and very easily fails due to convergence of the loss function to a local minimum. Many strategies have been developed to help training neural networks within the scope of tuning hyper-parameters.

Our idea is inspired by Ref. [52]. In this paper, Schwatz-Ziv and Tishby show that the learning behavior of hidden layers does not simply consist in becoming closer to the output but show a learning and forgetting path compared to the input layer. The information shared between a hidden layer and the input or the output can be measured via the mutual information, defined as [52]:

$$I(X;Y) = D_{KL}[p(x,y)||p(x)p(y)] = \sum_{x \in X, y \in Y} p(x,y) \log \left( \frac{p(x,y)}{p(x)p(y)} \right)$$

$$= \sum_{x \in X, y \in Y} p(x,y) \log \left( \frac{p(x|y)}{p(x)} \right) = H(X) - H(X|Y),$$

(2.1)

where $X$ and $Y$ are two random variables with a joint distribution $p(x,y)$, $D_{KL}[p||q]$ is the Kullback-Liebler divergence of the distributions $p$ and $q$, and $H(X)$ and $H(X|Y)$ are the entropy and conditional entropy of $X$ and $Y$, respectively. We will refer to the outputs from a hidden layer as $T$, while the input and output data are drawn from spaces $X$ and $Y$, respectively.

This definition of mutual information is useful to study the information stored inside the network. As they show in their paper, the hidden layer first acquires information about the inputs and outputs, i.e. $I(X;T)$ and $I(Y;T)$ increase, and then keeps the useful features from the input and forgets the rest ($I(X;T)$ decreases) so that it learns more about the desired output, i.e. $I(Y;T)$ keeps increasing (see Fig. 3.1). This behavior is strictly corresponding to the gradient descent algorithm. The information is a balanced path from both input data flow and backward gradient flow, and the mutual information map ($I(X;T)$ vs $I(Y;T)$) gives a finer tuning solution to understand how to balance these two flows. We will employ these ideas in Section 3.2 to support the training technique that we present in this project.

Supervision by connecting hidden layers to additional output layers has been a practical solution, since the only resource for the training is the paired input and output data. Deep supervision connects certain hidden layers to the label data and generate a new regularization (see Fig. 2.3a). This regularization consists in adding a second loss $L_2$ to the loss of the original network $L_1$ and try to achieve the global minimum of $L = L_1 + L_2$. This can help to change the behavior of information flow.
of hidden states during training so that the model will not get stuck in local minima of $L_1$ so easily.

![Diagram of neural network architectures](image)

Figure 2.3. (a) Arbitrary architecture of a neural network (in blue and green) and secondary path (in orange and yellow) whose output serves to compute the regularization loss $L_2$ (see main text). (b) Mirror reconstruction architecture used in [53] and [54]. The original network is composed by the layers in green and blue, while the reconstruction path is in orange and yellow. The connections between hidden layers from the main network and the reconstruction path can change (see Ref. [53] for further details). (c) Our approach: a small reconstruction network (RecNet) is attached to a main network and one of the hidden layers serves as input map.

On the other hand, some authors have employed a similar idea to the algorithm we have developed [53,54]. Zhang et al. focus on image recognition in Ref. [53]. In particular, they show that their method improves the accuracy on ImageNet ILSVRC-2012 validation dataset based on 16-layer VGGNet. They propose a reconstruction path that mirrors the main network: they add an additional network to original one that is trained to reconstruct the input data, and they supervise the learning of the main network by minimizing the addition of both losses, as explained before. The difference with the previous approach is that $L_2$ is now a loss function between the input and the reconstructed input: $L = L_1(y, y') + L_2(x, x')$, where $x$, $x'$, $y$, and $y'$ are the input, the reconstructed input, the label data, and the output, respectively. The architecture of the reconstruction path mimics the main network (see Fig. 2.3c). Then, they tune the connections between layers, so that the input to the reconstruction path are one or more hidden layers. Regarding training, the algorithm is complex and demanding: they combine different connection schemes between the reconstruction layers and alternate between them after some epochs. In addition, a pretraining is required.

Huang et al. [54] propose a strategy to enhance the SAR target classification with limited labeled data. They also create a mirror network that is trained to reconstruct input data. In this case, they pretrain both networks with unlabeled data, and claim that the reconstruction path transfers knowledge to the main network. Then, they train with labeled data.

These reconstruction techniques have improved the results of the networks they
were tested on. Nevertheless, they are not scalable, in the sense that they nearly double the number of parameters of the original algorithms. The networks they used (less than 17 layers) have been surpassed by new architectures that involve a much higher number of layers. Conversely, the approach we present here is friendlier with current deep neural networks, which range from dozens to hundreds of hidden layers, and does not significantly increase the computational cost of the algorithm. We created a finer supervision strategy that not only connects hidden layers to labels but also to input data, as in Refs. [53,54], but using a simpler and scalable algorithm. Moreover, the regularizer starts to perform only after certain training steps.
Table 2.1. Examples of activation functions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>fully connected</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heaviside</td>
<td>$f(x) = \begin{cases} 0, &amp; \text{if } x &lt; 0 \ 1, &amp; \text{if } x \geq 0 \end{cases}$</td>
<td><img src="image" alt="Plot" /></td>
</tr>
<tr>
<td>Rectified linear unit (ReLU)</td>
<td>$f(x) = \begin{cases} 0, &amp; \text{if } x &lt; 0 \ x, &amp; \text{if } x \geq 0 \end{cases}$</td>
<td><img src="image" alt="Plot" /></td>
</tr>
<tr>
<td>Tanh</td>
<td>$f(x) = \tanh(x)$</td>
<td><img src="image" alt="Plot" /></td>
</tr>
<tr>
<td>Sigmoid / Logistic</td>
<td>$f(x) = \sigma(x) = \frac{1}{1+e^{-x}}$</td>
<td><img src="image" alt="Plot" /></td>
</tr>
</tbody>
</table>
3 Supervision through reconstruction network

In this chapter, we present our training technique, which is based on backward supervision. As a proof of concept, we follow Ref. [52]'s setting and show that the extra backward supervision can generally improve the performance of learning process by showing the trajectory of a hidden layer mutual information. Then, we demonstrate the performance of our backward supervision on CIFAR-10 dataset with many existing deep convolutional neural networks. We show that by simply applying backward supervision network, the final performance can generally increase.

3.1 Training algorithm

The starting point of our algorithm is an arbitrary network. We take one of its hidden layers as input for an additional small reconstruction network that we call RecNet, see Fig. 2.3c. This second network generates data trying to reconstruct the input of the main network. The technique we present here consists in training both networks simultaneously, with a total loss function formed by the addition of the losses of each network:

\[ \mathcal{L} = \mathcal{L}_1 + \lambda_r \mathcal{L}_2, \]  

where \( \mathcal{L}_1 \) is the loss function of the main network, \( \mathcal{L}_2 \) is the loss function of RecNet and \( \lambda_r \) is the reconstruction factor. The hyper-parameter \( \lambda_r \) constitutes an essential factor that must be tuned to compensate the difference in orders of magnitude between \( \mathcal{L}_1 \) and \( \mathcal{L}_2 \). If \( \lambda_r \) is too large, the backpropagation along the main network will focus on improving the reconstruction instead of the main output, therefore it will penalize the training of the main network. Conversely, if \( \lambda_r \) is too small, the regularization term will not play a crucial role so we will recover the same results as if the main network was trained alone.

We also introduce another two hyper-parameters: the transition step \( s_{tr} \) and the number of the layer that serves as input for RecNet, \( N_r \). For the first epochs of training, we only use the original network, i.e. \( \mathcal{L} = \mathcal{L}_1 \), and we add RecNet after \( s_{tr} \) steps.

Note that this technique can be combined with any other methods, e.g. dropout and weight decay, to improve the performance of a network.
3.2 Proof of concept with mutual information

As a proof of concept, we performed the same toy experiment as in Ref. [52]. We employ a network of 7 fully connected layers with decreasing size: 12, 10, 7, 5, 4, 3, and 2 neurons. The activation is tanh, except for the last layer, where we use a sigmoid function. In this experiment, both loss functions, $L_1$ and $L_2$ are computed through a softmax cross-entropy between the predicted and the actual inputs and labels [50,55].

Each pair of data corresponds to a 12-component binary input $\mathbf{x}$ and a single binary label $y$. The labels are generated through a spherically symmetric real valued function $f(\mathbf{x})$, which is compared to a threshold $\theta$. Then, a step function $\Theta$ is applied: $y(\mathbf{x}) = \Theta(f(\mathbf{x}) - \theta) \in \{0, 1\}$. Finally, we force $p(y = 1) \approx 0.5$ by applying a stochastic rule through a standard sigmoidal function. See Ref. [52] for further details about the generation of the data for the toy task.

The probability distributions needed to compute the mutual information (see Eq. (2.1)) between the input or the output layer and a hidden layer, $I(X;T)$ and $I(Y;T)$, respectively, are obtained by discretizing the space $T$ and using a numerical quadrature.

The structure of the RecNet employed in this experiment consists in a single fully connected output layer with sigmoid activation. The hyper parameters are: $\lambda_R = 10^{-5}$, $s_r = 100$ and $N_r = 6$ (RecNet attached to the penultimate layer).

Figure 3.1 shows the information plane for the last layer. The transparent lines are different realizations of the experiment, while the solid lines are the mean values. Blue is used for the original network and red corresponds to the original network with RecNet.

The information path has two parts, as discussed in Section 2.2. It starts near the position $(0,0)$, since the network is randomly initialized and it does not have information about the data. Then, the hidden layer starts storing information about the input ($I(X;T)$ increases) at the same time that it extracts information about the labels ($I(Y;T)$ also increases). After some steps, a maximum value of $I(X;T)$ is reached. At this point, the network starts learning the useful features from the input that are needed to improve the predictions. Therefore, $I(X;T)$ decreases but $I(Y;T)$ keeps increasing until it reaches a maximum value before overfitting.

The maximum value of $I(Y;T)$ obtained with RecNet is higher than the original one. This suggests that our technique helps the main network to extract knowledge from the data in a more efficient way, which will translate into higher accuracy, as we will check in the next section.

\footnote{The TensorFlow codes for this experiment can be found in: \url{https://github.com/AlvaroGI/NANet_Mutual_Info}.}
3.3 Experiment on CIFAR-10

We conducted an experiment on the CIFAR-10 dataset classification task. This dataset consists of 50k training images and 10k test images, which are classified in 10 different categories (airplane, automobile, bird, cat, deer, dog, frog, horse, ship, and truck). The size of each sample is 32x32x3, since they are RGB images.

We do a preprocessing of the images to enhance training. First, we add 2 layers of zero padding at each side of the image and then we randomly crop them to the original size. A horizontal flip is also applied randomly to 50% of the samples. Finally, a whitening transformation is applied.

The network used for this experiment takes a ResNet [56] as a main network, with a small RecNet attached to the penultimate layer. The inputs are the CIFAR-10 images after preprocessing. The first layer is a 3x3 convolutional layer and the next 6n layers consist in 3 groups of 2n layers with feature maps of sizes \{32, 16, 8\} and \{16, 32, 64\} filters, respectively. At the last layer of the first 2 groups, we perform a downsizing using a stride of 2. The output layer is a global pooling layer with 10 outputs. Hence, the total number of layers is 6n + 2. Here we analyze ResNet20, 32, 44, 56 and 110 (n = 3, 5, 7, 9, and 18, respectively). Moreover, the activation function applied to the output of every layer is relu. The reconstruction path is much simpler: it is composed by 3 fully connected layers of sizes \{1536, 3072, 3072\} (the total number of pixels in the original images is 32x32x3=3072). In this case, we employ tanh as activation function for the first 2 layers and sigmoid for the last one. The justification behind this choice is that relu would omit part of the information.

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2CIFAR-10 dataset can be downloaded here: [https://www.cs.toronto.edu/~kriz/cifar.html](https://www.cs.toronto.edu/~kriz/cifar.html)

3The TensorFlow codes for this experiment can be found in: [https://github.com/AlvaroGI/NANet_cifar10](https://github.com/AlvaroGI/NANet_cifar10)
since it maps negative values to 0. Regarding the loss functions, $\mathcal{L}_1$ is a softmax cross-entropy between the predicted and the actual labels, and $\mathcal{L}_2$ is computed as a mean squared error between the values of the pixels of the original and reconstructed images [50,55].

A hyper-parameter search was performed before running the experiment. The learning rate was tuned by studying its influence on the error of the original ResNet. We start with an initial learning rate of 0.1 and then divide it by 10 at 50k and 60k steps, similarly to what He et al. did in Ref. [56]. Each training batch is composed by 128 samples. The hyper-parameters that define this RecNet are: $\lambda_R = 10$, $s_r = 5000$ and $N_R = 6n$. The optimal values for $\lambda_R$, $s_r$ are found to be a local minimum, while $N_R$ is inversely proportional to the minimum error, so we pick the largest possible value (see Fig. 3.2). The tuning of these three parameters was performed for ResNet56, so they might not be the optimal values for other sizes or architectures of the main network. Additionally, a weight decay of 0.0002 and momentum of 0.9 are employed.

![Figure 3.2](image_url)

**Figure 3.2.** ResNet + RecNet minimum error versus the feature map used as input for RecNet ($N_R$). The values in this Figure correspond to a single realization of the experiment for each $N_R$. The linear fitting shows a tendency to smaller error for deeper feature maps.

Table 3.1 compares the results from the original ResNet [56] to those from the ResNet combined with RecNet. It shows the minimum error $\varepsilon_{\text{best}}$ as a percentage, and the mean value $\mu$ and standard deviation $\sigma$ after 5 trainings, in the format $\varepsilon_{\text{best}} (\mu \pm \sigma)$. He et al. only provide the best value for ResNet20, 32, 44, and 56 in Ref. [56]. We also trained 5 times the original ResNet56 to check that the model we built gives similar results to those from He et al., and we obtained 6.58 (6.72±0.23), which is slightly smaller than their value due to a different hyper-parameter selection. This value and the best error provided by He et al. (6.97%) improve when adding the RecNet: the best error and the mean value decrease to 6.30% and 6.54%, respectively, while the standard deviation remains almost unchanged. The performance of ResNet20, 32, 44 and 110 is also improved when adding RecNet to the original architecture (see Table 3.1).

For a better visualization of the results, Fig. 3.3 shows the values from Table 3.1.
Table 3.1. Top-1 error in the classification task on CIFAR-10. The experiments were reproduced for different number of layers. ResNet values (second column) taken from [1]. Results presented in the form $\varepsilon_{\text{best}}(\mu \pm \sigma)$, where $\varepsilon_{\text{best}}$ is the minimum error as a percentage, $\mu$ is the mean value and $\sigma$ is the standard deviation, computed after 5 trainings. He et al. only provide the best value for ResNet20, 32, 44, and 56.

<table>
<thead>
<tr>
<th>Number of layers</th>
<th>ResNet$^4$</th>
<th>NANet</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>8.75</td>
<td>8.37 (8.47±0.08)</td>
</tr>
<tr>
<td>32</td>
<td>7.51</td>
<td>7.29 (7.58±0.22)</td>
</tr>
<tr>
<td>44</td>
<td>7.17</td>
<td>6.80 (7.08±0.26)</td>
</tr>
<tr>
<td>56</td>
<td>6.97</td>
<td>6.30 (6.54±0.22)</td>
</tr>
<tr>
<td>110</td>
<td>6.43 (6.61±0.16)</td>
<td>6.11 (6.50±0.25)</td>
</tr>
</tbody>
</table>

It can be easily seen that our technique enhances the accuracy of ResNet in all of the cases. The improvement is greater for ResNet56 since the hyper-parameter search was performed on that network.

To conclude, we also provide the evolution of the error versus the training step for different number of layers in Fig. 3.4.

![Figure 3.3. Minimum error (crosses) and mean value (dots) with error bars (1 standard deviation) after 5 trainings on ResNet (blue) and ResNet + RecNet (red). The number of layers correspond only to the size of ResNet.](image)
Figure 3.4. ResNet + RecNet error versus training step for different number of layers.
In this project we have developed a supervised learning technique that can be implemented with a very small computational cost in deep NNs. We have provided a theoretical justification for our technique in terms of the mutual information. Additionally, the experiments we ran on the CIFAR-10 dataset were successful: we achieved an improvement of $\sim 0.5\%$ in the test error.

This project is still under research as we want to extend the mutual information theory and compare the evolution of the path in mutual information plane between different supervision techniques (forward, backward and combined supervision). Moreover, current image classification efforts are mostly focused on ImageNet, a much more complex database with millions of images$^1$. We are developing an image classification experiment on the ImageNet dataset to compare with ResNet results on the same dataset.

$^1$The ImageNet database can be found in: http://www.image-net.org.
Part III

Appendices
A | Polarizability of a single sphere

The general expression for the polarizability can be particularized for the case of a single spherical particle. Its general form (Eq. (2.37)) reads:

$$\alpha_d = 2 \sum_{l'=l}^{\infty} \sum_{m'=-l'}^{l'} \frac{\alpha_{lm}^{(0)} + \alpha_{lm}^{(1)} d_a}{\Lambda_{lm}^{(0)} + \Lambda_{lm}^{(1)} d_a - \Lambda} + O(d_a^2), \quad (A.1)$$

where

$$\alpha_{lm}^{(0)} = \frac{\langle \phi_{lm}^{(0)} | \hat{n} \cdot \hat{j} \rangle \langle \mathbf{r} \cdot \hat{i} | \sigma_{lm}^{(0)} \rangle}{\langle \phi_{lm}^{(0)} | \sigma_{lm}^{(0)} \rangle}, \quad (A.2a)$$

$$\alpha_{lm}^{(1)} = \frac{\langle \phi_{lm}^{(0)} | V \mathbf{P}_{lm} | \hat{n} \cdot \hat{j} \rangle \langle \mathbf{r} \cdot \hat{i} | \sigma_{lm}^{(0)} \rangle}{\langle \phi_{lm}^{(0)} | \sigma_{lm}^{(0)} \rangle}, \quad (A.2b)$$

$$\mathbf{P}_{lm} = \sum_{l' \neq l \text{ or } m' \neq m} \frac{\langle \phi_{lm}^{(0)} | \sigma_{lm}^{(0)} \rangle}{\Lambda - \Lambda_{lm}^{(0)} - \Lambda_{lm}^{(1)} d_a - \Lambda} \langle \phi_{lm}^{(0)} | \sigma_{lm}^{(0)} \rangle$$

is the weighted projection operator. The dipole is perturbed along $\hat{j}$ and induced along $\hat{i}$. Each mode $n$ from Eq. (2.37) corresponds to a particular combination $l$ and $m$ in Eq. (A.1).

As explained in the main text (Section 3.2), the induced charge over the surface for each classical eigensolution $\Lambda_{lm}^{(0)}, |\sigma_{lm}^{(0)}\rangle$ can be written in terms of a spherical harmonic:

$$\sigma_{lm}^{(0)}(\mathbf{r}) = \sigma(\mathbf{r}) Y_l^m(\theta, \phi), \quad (A.3)$$

where $\sigma(\mathbf{r})$ is a radial function and $Y_l^m(\theta, \phi)$ is the spherical harmonic for the quantum numbers $l$ and $m$.

The associated surface potentials are given by $|\phi_{lm}^{(0)}\rangle \equiv (2\varepsilon_0)^{-1} g |\sigma_{lm}^{(0)}\rangle$, with $\langle \mathbf{r} | g | \mathbf{r}' \rangle \equiv$
\(g(\mathbf{r}, \mathbf{r}')\) [13]. Hence:

\[
\phi^{(0)}_{lm} = \langle \mathbf{r} | \phi^{(0)}_{lm} \rangle = \int_{\Omega} \frac{1}{2\varepsilon_0} g(\mathbf{r}, \mathbf{r}') \sigma^{(0)}_{lm}(\mathbf{r}') d^2 \mathbf{r}'
\]

\[
= \frac{1}{2\varepsilon_0} \int_{\Omega} \sum_{l'=-\infty}^{\infty} \sum_{m'=-l'}^{l'} \frac{1}{2l'+1} Y_{l'm'}^*(\theta', \varphi') Y_{lm}^m(\theta, \varphi) g_{lm}^{(0)}(\mathbf{r}) d^2 \mathbf{r}'
\]

\[
= \int_{\Omega} \sigma(r) \sum_{l'=-\infty}^{\infty} \sum_{m'=-l'}^{l'} \frac{1}{2l'+1} Y_{l'm'}(\theta', \varphi') \int_{\Omega} Y_{lm}^*(\theta', \varphi') Y_{l'm}^m(\theta, \varphi') d^2 \mathbf{r}' \quad (A.4)
\]

\[
= \int_{\Omega} \sigma(r) \frac{1}{\varepsilon_0} \frac{1}{2l+1} Y_{lm}^m(\theta, \varphi)
\]

with the following steps:

(a) The representation of the Coulomb interaction \(g(\mathbf{r}, \mathbf{r}')\) in spherical coordinates

\(g(\mathbf{r}, \mathbf{r}') = 2\sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} Y_{lm}^m(\theta', \varphi') Y_{lm}^m(\theta, \varphi) r_{\ast} r_{\ast}' [13]\), where \(r_{\ast} = \min(|\mathbf{r}|, |\mathbf{r}'|)\) and \(r_{p} = \max(|\mathbf{r}|, |\mathbf{r}'|)\), is introduced.

(b) Substitution of \(\sigma^{(0)}_{lm}(\mathbf{r}) = \sigma(r) Y_{lm}^m(\theta, \varphi)\) and rearrangement of terms.

(c) Application of the orthogonality of the spherical harmonics:

\[\int_{\Omega} Y_{l'm'}(\theta', \varphi') Y_{lm}^m(\theta, \varphi') \sin \theta d\theta d\varphi = \delta_{l'l} \delta_{mm'}\]. Recall that \(d^2 \mathbf{r} = R^2 \sin \theta d\theta d\varphi\).

(d) Reduction of the sums via \(\delta_{l'l} \delta_{mm'}\).

The polarizability can be particularized for the case of a single sphere by inserting these eigensolutions into Eq. (2.37). The value of each factor is derived here:

\[
\langle \phi^{(0)}_{lm} | \sigma^{(0)}_{lm} \rangle = \int_{\Omega} \frac{R}{2\varepsilon_0} \frac{1}{2l+1} \sigma(r) \sigma(r) Y_{lm}^m(\theta, \varphi) Y_{lm}^m(\theta, \varphi) d^2 \mathbf{r} = \frac{\sigma(r) \sigma(r) R^3}{\varepsilon_0 (2l+1)}, \quad (A.5)
\]

\[
\langle \phi^{(0)}_{lm} | \hat{n} \cdot \hat{j} \rangle \overset{a}{=} \int_{\Omega} \frac{R}{2\varepsilon_0 (2l+1)} \sigma(r) Y_{lm}^m(\theta, \varphi) \cos \theta d^2 \mathbf{r}
\]

\[
\overset{b}{=} \frac{R^3 \sigma(r)}{\varepsilon_0 (2l+1)} \int_{\Omega} Y_{lm}^m(\theta, \varphi) \cos \theta \sin \theta d\theta d\varphi \quad (A.6)
\]

\[
\overset{c}{=} \frac{R^3 \sigma(r)}{\varepsilon_0 (2l+1)^2} \sqrt{\frac{\pi}{3}} \delta_{l0} \delta_{mm'},
\]

with the following steps:

(a) In a sphere, \(\hat{n} = \hat{r}\). Moreover, due to the spherical symmetry of the problem, there is no preferred direction for the excitation of a dipolar mode. Therefore we can assume \(\hat{j} = \hat{z}\). Under this assumption, \(\hat{n} \cdot \hat{j} = \cos \theta\).

(b) Substitution of the differential element of surface \(d^2 \mathbf{r} = R^2 \sin \theta d\theta d\varphi\).
Reformulation of $\cos \theta$ in terms of the spherical harmonic with $l = 1$ and $m = 0$: $\cos \theta = 2\sqrt{\frac{3}{\pi}} Y_1^0(\theta, \varphi)$. Then, application of the orthogonality of the spherical harmonics.

\[
\langle \mathbf{r} \cdot \mathbf{i} | \sigma_{lm}^{(0)} \rangle = \frac{b}{2} \sqrt{\frac{\pi}{3}} R^3 \sigma(\theta) \cos \theta \int_{\partial \Omega} \overline{Y_1^0(\theta, \varphi)} Y_1^0(\theta, \varphi) \sin \theta d\theta d\varphi
\]

with the following steps:

(a) Over a spherical surface, $\hat{\mathbf{r}} = R \hat{\mathbf{r}}$. As stated before, due to the spherical symmetry of the problem, there is no preferred direction for the excitation of a dipolar mode. Hence, we can assume $\hat{\mathbf{i}} = \hat{\mathbf{z}}$. Under this assumption, $\hat{\mathbf{r}} \cdot \hat{\mathbf{i}} = R \cos \theta$.

(b) Substitution the differential element of surface $d^2 r = R^2 \sin \theta d\theta d\varphi$ and reformulation of $\cos \theta$ in terms of the spherical harmonic with $l = 1$ and $m = 0$: $\cos \theta = \cos \theta = 2\sqrt{\frac{3}{\pi}} Y_1^0(\theta, \varphi)$.

(c) Application of the orthogonality of the spherical harmonics.

Substituting all these brackets in the definition of $\alpha_{lm}^{(0)}$ (Eq. (A.2a)) yields:

\[
\alpha_{lm}^{(0)} = \frac{4\pi}{3} R^3 \delta_{ll} \delta_{mm}.
\]

Next we simplify one of the brackets involved in the calculation of $\alpha_{lm}^{(1)}$:

\[
\langle \phi_{lm'}^0 | V_t | \sigma_{lm}^{(0)} \rangle = \frac{(\Lambda_{lm'}^{(0)})^2 - 1}{2\varepsilon_0} \int_{\partial \Omega} \sigma_{lm'}^{(0)}(\mathbf{r}) \sigma_{lm}^{(0)}(\mathbf{r}) d^2 r
\]

with the following steps:

(a) Similar derivation as the one used in [13] to derive their Eq. (3b). A coordinate transformation, divergence theorem and other mathematical relations are employed in this step. See Eq. (S29) in the Supplemental Material from [13] for further details.

(b) Substitution the differential element of surface $d^2 r = R^2 \sin \theta d\theta d\varphi$ and $\sigma_{lm}^{(0)}(\mathbf{r}) = \sigma(\mathbf{r}) Y_l^m(\theta, \varphi)$.

(c) Application of the orthogonality of the spherical harmonics.
Finally, the value of $\alpha^{(1)}_{lm}$ is:

$$
\alpha^{(1)}_{lm} \equiv \frac{\langle \mathbf{r} \cdot \hat{i} | \sigma^{(0)}_{lm} \rangle}{\langle \phi^{(0)}_{lm} | \sigma^{(0)}_{lm} \rangle} \sum_{l' \neq l, m' \neq m} \frac{1}{\Lambda - \Lambda^{(0)}_{lm'}} \frac{\langle \phi^{(0)}_{lm'} | V_{lm'} \sigma^{(0)}_{lm'} \rangle}{\langle \phi^{(0)}_{lm} | \sigma^{(0)}_{lm'} \rangle},
$$

(A.10)

with the following steps:

(a) Substitute the expression for the weighted projection operator.

(b) Replace the bracket $\langle \phi^{(0)}_{lm} | V_{lm'} \sigma^{(0)}_{lm'} \rangle$ by the expression from Eq. (A.9).

(c) The result is 0 since $l \neq l'$ and $m \neq m'$, and the bracket in the denominator is a finite value different from zero (see Eq. (A.5)).

Combining Eqs. (A.1), (A.8), and (A.10) one gets the final expression for the polarizability of a single sphere:

$$
\alpha_d = \frac{4\pi}{3} R^3 \frac{2}{\Lambda^{(0)}_{dip} + \Lambda^{(1)}_{dip} d_{\parallel} - \Lambda},
$$

(A.11)

where the subscript “dip” stands for “dipolar mode”. In a sphere, the dipolar mode corresponds to $l = 1$ and any $m$. The contribution from $d_{\parallel}$ is negligible in the cases we will study, and even $d_{\parallel} = 0$ in the HDM, so we neglected its term in the denominator. Moreover, for a sphere, $\Lambda^{(0)}_{dip} = -\frac{1}{3}$ and $\Lambda^{(1)}_{dip} = \frac{4}{3\hbar}$.
The classical and first-order quantum eigenvalues ($\Lambda^{(0)}$, $\Lambda^{(1)}_\perp$, and $\Lambda^{(1)}_\parallel$) for a system composed of two identical spheres are particularly important, since the resonance frequency depends on them (see Subsection 2.4.2). Here, we show the results as a function of the ratio between gap and diameter ($g/D$). The number of elements used was 964 for each sphere.

Note that we recover the eigenvalues of the single sphere in the limit $g \gg D$: $\Lambda^{(0)} = -1/3$, $\Lambda^{(1)}_\perp = -4/(3R)$, and $\Lambda^{(1)}_\parallel = 4/(3R)$. These values are indicated as dashed lines in the plots. The small discrepancies with the single sphere eigenvalues observed for $g \gg D$ in the anti-bonding modes ($\uparrow\uparrow$ and $\rightarrow\leftarrow$) are due to the mesh size: a higher number of elements provides more accurate results.

Figure B.1. Classical eigenvalue ($\rightarrow\rightarrow$ mode). See main text for details.
Figure B.2. Classical eigenvalue (↑↓ mode). See main text for details.

Figure B.3. Classical eigenvalue (↑↑ mode). See main text for details.
Figure B.4. Classical eigenvalue (→← mode). See main text for details.

Figure B.5. First-order quantum eigenvalues (→→ mode). See main text for details.
Figure B.6. First-order quantum eigenvalues (↑↓ mode). See main text for details.

Figure B.7. First-order quantum eigenvalues (↑↑ mode). See main text for details.
Figure B.8. First-order quantum eigenvalues (→← mode). See main text for details.
Bibliography


