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Theoretical Investigations of the Electronic Structure and Optical Properties of Metallic Nanoshells

by

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ABSTRACT

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The electronic structure and optical properties of metallic nanoshells are theoretically investigated. An efficient implementation of the Time Dependent Local Density Approximation creates the possibility of applying ab initio calculations to real size metallic nanoshells for which experimental data are available. It is proven that, when the dielectric effects of the core, embedding medium and d-electrons are taken into account, the ab initio calculations reproduce the experimentally measured photo-absorption cross section of these unique nanoparticles.
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This thesis is a discussion and extension of the following publications.


E. Prodan and P. Nordlander, On the Kohn-Sham Equations with Periodic Back-
Chapter 1

Introduction and Outline

In the last few years, a considerable amount of research has been devoted to the optical properties of nanoparticles.\[1\] Semiconductor nanocrystals, or quantum dots, have received extensive attention due to the dramatic effects of confinement on electron-hole pair excitations within the particle due primarily to particle size. By contrast, the optical response of metallic nanoparticles has been thought to span a continuum from a regime where quantum effects dominate (for nanoparticles nominally \(< 100\) atoms) to a classical regime, where the optical response is determined by the properties of the nanoparticle plasmon. The plasmon response in this regime has typically been assumed to be classical and has been interpreted using Mie scattering theory.\[2\]

A particularly interesting and possibly very useful new type of nanoparticle is the metallic nanoshell.\[3\] The particles consist of a thin gold or silver shell around a dielectric core.\[4, 5, 6, 7\] Mie scattering theory predicts that by varying the ratio of the shell thickness with respect to the overall diameter of the particle, the plasmon frequencies of the nanoshells can be placed at arbitrary wavelengths between the mid infrared and the UV region of the optical spectrum.\[8, 9, 10\] The structural tunability of the plasmon frequencies of these unique nanoparticles has been experimentally verified in a series of studies where monodisperse nanoshells of
different shell thickness and core sizes have been fabricated and characterized with optical measurements.[11] This tunable plasmon resonance is not only of fundamental interest for nanocavity physics,[12] but also makes these nanoparticles particularly attractive for applications such as resonant photo-oxidation inhibitors[13] and optical triggers for opto-mechanical materials,[14] drug delivery implants,[15] environmental sensors,[16] and Raman sensors.[17]

In this thesis, the electronic structure and optical properties of these unique nanoparticles are investigated from first principles. Chapter 2 presents a simple formalism, based on an incompressible fluid model of the conduction electrons, which explains very intuitively why particles with more than one surface exhibit, in general, geometry dependent plasmon resonances. Within this formalism, the quasi-statical Mie results are reproduced. The formalism is also applied to multi-concentric metallic nanoshells and explicit equations for the plasmon resonances are derived. The full quantum analysis begins in Chapter 3, where the many-body effects are investigated. Chapters 4 and 5 present the implementation of the Time Dependent Local Density Approximation to real size nanoshells. Structural tunability is validated from first principles. Chapter 6 and 7 presents a rigorous method of including dielectric effects in the TDLDA formalism. Chapter 7 in particular considers the effects of the dielectric core, dielectric embedding medium and d-electrons and shows that the theory can reproduce the experiment almost perfectly.
Chapter 2

Plasmonics of the Single and Multi-Concentric

Metallic Nanoshells

2.1 Introduction

It is known that the optical response of the metallic particles is dominated by the plasmon resonances which can be defined as collective motions of the conduction electrons. These resonances occur at particular frequencies, which depend in general on the density of the conduction electrons and geometry of the particles. At these frequencies, the electromagnetic radiation is strongly absorbed by the metallic particles. Plasmons can appear in the bulk of the metal or at the surface. As it will follow, the optical response of the metallic nanoshells are determined by the surface plasmons.

It should be mentioned from the very beginning that, although the geometry of the metallic shells is quite simple, the presence of two distinct surfaces has a fundamental impact on the plasmonics of these particles. Because there are two surfaces, one can naturally assume that there are two plasmon modes, one for each surface. This remark is true up to a point because the two plasmon modes cannot live independently, they interact with each other. If the two surfaces are separated by a large distance, then one can indeed assign one plasmon mode to each surface. As the separation between
the surfaces becomes smaller, the two surface plasmons interact stronger and the result is a hybridization between the two. These hybridized plasmons live on both surfaces.

The picture of interacting surface plasmons is very intuitive and it will be used many times to interpret the positions and shifts of the plasmon resonances seen in our numerical simulations. It will become even more important, if not essential, when the plasmonics of more complex metallic particles needs to be interpreted. As one knows, the plasmons can be found by looking for the complex poles of the absorption cross section. This cross section can be calculated within the classical electrodynamics formalism. However, its expression can be very complex even for relative simple systems and it is not always easy to give simple physical reasons for why a particular pole appears at a particular frequency.

This chapter presents the theory of the interacting plasmons for single and multi-metallic shells. It will follow that this framework is not only very intuitive, thus useful for physical interpretations and for the design of new nanoparticles, but it also predicts the plasmon frequencies as accurately as the quasi-static Mie theory.

2.2 The Incompressible Fluid Model

Within this framework, the conduction electrons are modeled as an incompressible, irrotational charged fluid sitting on top of a uniform positive background charge distribution, \( \rho_0 \), representing the ion cores. The positive background charge extends
Figure 2.1  A possible configuration of the incompressible fluid of electrons (gray color).

Around the edges, the electrons can spill in or out, leading to surface charges.
only over the shell and the entire system is considered charge neutral. The general equations that describe an incompressible, irrotational fluid are the continuity equation,

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0 \tag{2.1}
\]

and a second equation which says that no vortices are present

\[
\vec{\nabla} \times \vec{j} = 0. \tag{2.2}
\]

The charge density is constant and equal to \( ne \) inside the boundaries of the fluid. The current is related to the density through \( \vec{j} = \rho \vec{v} \), where \( \vec{v} \) is the velocity of the fluid at a given position. It follows from the above equations that there must be a scalar function \( \eta \) such that \( \vec{v} = \vec{\nabla} \eta \) \( (\vec{j} = ne \vec{\nabla} \eta) \). Moreover, the scalar function \( \eta \) must satisfy the Laplace equation, \( \vec{\nabla}^2 \eta = 0 \). When the system is excited by an electromagnetic wave, the boundaries of the incompressible fluid will change, leading to a spill out charge, \( \rho - \rho_0 \), as it is illustrated in Fig. 2.1. In the limit of infinite small excitation fields (linear response), when the boundaries of the incompressible fluid remain close to the particle's boundaries, one can view the spill out charge as a superficial charge. Indeed, with the notations from Fig. 2.2, one can define the superficial charge as:

\[
\sigma = \lim_{\delta S \to 0} \frac{1}{\delta S} \int_{\delta V} \rho dV. \tag{2.3}
\]

From the continuity equation written over the volume \( \delta V \),

\[
\frac{d}{dt} \int \rho dV + \int \vec{j} d\vec{S} = 0, \tag{2.4}
\]
Figure 2.2  A small region around the surface of the shell. The gray color represents the incompressible fluid of electrons. The charge inside the volume $\delta V$ can be regarded as a superficial charge.
one can immediately find the surface charge and current relation. Because there is no current flow through the boundary of the incompressible fluid, the above equation reduces to:

$$\frac{\partial \sigma}{\partial t} + \vec{n} \cdot \vec{j} = 0 \Leftrightarrow \partial_t \sigma = -ne \frac{\partial n}{\partial n},$$  \hspace{1cm} (2.5)

when $\delta S$ goes to zero. Up to this point, the analysis applies to any geometry of the metallic phase. In the following however, the spherical symmetry of the problem will be taken into account. Before considering the shell geometry, it is important to investigate two simple systems, a cavity inside a bulk metal and a spherical metallic particle. Suppose the metallic phase is described by a Drude dielectric function:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2},$$ \hspace{1cm} (2.6)

where $\omega_p$ is the bulk plasmon frequency:

$$\omega_p = \sqrt{4\pi e^2 n/m}.\hspace{1cm} (2.7)$$

Then the classical Mie theory predicts the following plasmon frequency for the cavity:

$$\omega_c = \omega_p \sqrt{\frac{l + 1}{2l + 1}} \hspace{1cm} (2.8)$$

and for the solid sphere:

$$\omega_s = \omega_p \sqrt{\frac{l}{2l + 1}}. \hspace{1cm} (2.9)$$

As it was discussed in the introduction, it is the interaction of these two plasmon modes that determines the plasmonics of the metallic nanoshells.
2.3 Plasmonics of the Cavity and Solid Sphere

In the case of a cavity of radius $a$, the solution of the Laplace equation can be written as a sum of spherical multipoles:

$$ \eta_{lm} (r, \Omega) = \hat{x}_{lm}^c (t) r^{-l-1} Y_{lm} (\Omega), $$  \hspace{1cm} (2.10)

where the time dependent coefficient $x_{lm}^c$ will represent our new degree of freedom.

In terms of the new variable, the expression of the current becomes

$$ \vec{J}_{lm} (t; r, \Omega) = ne\hat{x}_{lm}^c (t) \vec{\nabla} \left( r^{-l-1} Y_{lm} (\Omega) \right) $$  \hspace{1cm} (2.11)

and the surface charge,

$$ \sigma_c (t, \Omega) = -ne (l + 1) a^{-l-2} x_{lm}^c (t) Y_{lm} (\Omega). $$  \hspace{1cm} (2.12)

The kinetic energy of the incompressible fluid is given by

$$ T = \frac{1}{2} \int \left( \frac{n m}{2} \int (\vec{\nabla} \eta)^2 \right) d\Omega $$

$$ = \frac{nm}{2} \int \vec{\nabla} \left( \eta \vec{\nabla} \eta \right) d\Omega = \frac{nm}{2} \int \eta \vec{\nabla} \eta d\tilde{S} $$

$$ = -\frac{nm}{2} \int a^2 \eta \partial_r \eta |_{r=a} d\Omega. $$  \hspace{1cm} (2.13)

Using the multipole expression for $\eta$, one can readily find

$$ T_{lm} = \frac{nm l + 1}{2} a^{2l+1} (\hat{x}_{lm}^c)^2. $$  \hspace{1cm} (2.14)

The electrostatic energy of the system will be calculated next. The electric field is generated only by spill out charges. The contributions from bulk electrons are
neutralized by the positive background charge. The electric potential generated by
the multipole of Eq. (2.10) is
\[ \Phi_{lm} (\rho, \Omega) = \frac{4\pi}{2l+1} a^2 v_l (r, a) \sigma_c (\Omega), \tag{2.15} \]
where \( v_l (r, r') = r^l / r'^{l+1} \). The electrostatic potential energy of the system is given by
\[
V_{lm} = \frac{1}{2} \int \rho \Phi_{lm} d\mathbf{r} = \frac{1}{2} \int (\rho - \rho_0) \Phi_{lm} dS \tag{2.16}
\]
\[ = \frac{1}{2} \int \sigma \Phi_{lm} dS = \frac{1}{2} a^2 \sigma_c \Phi_{lm} (a). \]
The fact that we subtracted \( \rho_0 \) above has no influence if \( l \) is different from zero. The
final expression of the electrostatic potential is
\[ V_{lm} = \frac{nm (l + 1)}{2 a^{2l+1}} \omega_c^2 (x_{lm}^c)^2. \tag{2.17} \]
The Lagrangian of the system is then
\[ L' = \frac{nm l + 1}{2 a^{2l+1}} [(\dot{x}_{lm}^c)^2 - \omega_c^2 (x_{lm}^c)^2], \tag{2.18} \]
which leads correctly to an oscillator frequency equal to \( \omega_c \), as predicted by the
classical Mie theory.

One can repeat the same steps for a solid metallic sphere of radius \( b \). The difference
is that, inside the sphere, the solution of the Laplace equation is a sum of multipoles
of the form:
\[ \eta_{lm} (r, \Omega) = \dot{x}_{lm}^g (t) r^l Y_{lm} (\Omega). \tag{2.19} \]
The expressions of the current and surface charge become

$$ j_{lm} = ne \vec{\nabla} (\dot{x}_{im}^e (t) r^l Y_{lm} (\Omega)) $$

$$ \sigma_s (t, \Omega) = -nelb^{l-1} x_{im}^e (t) Y_{lm} (\Omega) . $$

The kinetic and electrostatic energy of the system can be calculated in the same way,

$$ T = \frac{nm}{2} lb^{2l+1} (\dot{x}_{im}^s)^2 $$

$$ V_{lm} = \frac{nm}{2} l \omega_s^2 b^{2l+1} (x_{im}^e)^2 . $$

This leads to the following Lagrangian

$$ L^s = \frac{nm}{2} lb^{2l+1} \left[ (\dot{x}_{im}^e)^2 - \omega_s^2 (x_{im}^e)^2 \right] , $$

which, again, reduces the problem to an oscillator with oscillating frequency equal to exactly the plasmon frequency predicted by the classical Mie theory.

### 2.4 Plasmonics of the Metallic Shell

The following calculations refers to a metallic shell of inner radius $a$ and outer radius $b$. The ratio between the inner and outer radius will be referred as the aspect ratio of the shell, $x \equiv a/b$. For a shell, the general solution for $\eta$ is of the form,

$$ \eta_{lm} (r, \Omega) = (\dot{x}_{im}^e (t) r^{-l-1} + \dot{x}_{im}^e (t) r^l) Y_{lm} (\Omega) , $$

which leads to the following expression for the surface charges on the inner respectively outer surfaces:

$$ \sigma_c (t, \Omega) = ne \left[ l a^{l-1} x_{im}^e (t) - (l + 1) a^{-l-2} x_{im}^e \right] Y_{lm} (\Omega) $$
\[
\sigma_s(t, \Omega) = -ne \left[ b^{l-1} x_m(t) - (l + 1) b^{-l-2} x_m(t) \right] Y_{lm}(\Omega). \tag{2.25}
\]

The kinetic energy of the incompressible fluid can be found by following the same steps as in Eq. (2.13),

\[
T = \frac{1}{2} \int n m v^2 d\tau = \frac{nm}{2} \int \left[ b^2 \eta \partial_r \eta |_{r=b} - a^2 \eta \partial_r \eta |_{r=a} \right] d\Omega. \tag{2.26}
\]

Using the multipole expression for \( \eta \), one can readily find

\[
T_{im} = \frac{nm}{2} \left( 1 - x^{2l+1} \right) \left[ lb^{2l+1} (\dot{x}_m^e)^2 + \frac{l+1}{a^{2l+1}} (\dot{x}_m^c)^2 \right]. \tag{2.27}
\]

As one can see, the kinetic energy is not simply the sum of the kinetic energies for a cavity and a solid sphere, which is true only when the aspect ratio goes to zero. The electrostatic energy of the system will be calculated next. Starting from the multipole expansion of the electric potential,

\[
\Phi(r, \Omega) = \sum_{l,m} \frac{4\pi}{2l+1} Y_{lm}(\Omega) \int_{r_L}^{r_U} Y_{lm}^*(\Omega') \sigma(\Omega') r'^2 d\tau' d\Omega', \tag{2.28}
\]

by remembering that only the spill out charges have a contribution to the potential, one finds

\[
\Phi_{lm}(r, \Omega) = \frac{4\pi}{2l+1} \left[ a^2 v_l(r, a) \sigma_c(\Omega) + b^2 v_l(r, b) \sigma_s(\Omega) \right], \tag{2.29}
\]

where \( v_l(r, r') = r_L^{l+1} / r_U^{l+1} \). A very useful observation, which follows directly from Eqs. (2.24) and (2.25) of the inner and outer surface charge, is

\[
\Phi_{lm} = -\frac{4\pi ne}{2l+1} \left( 1 - x^{2l+1} \right) Y_{lm}(\Omega) \begin{cases} 
\frac{(l+1)r^l}{a^{2l+1}} x_m^e, & r \leq a \\
\frac{lb^{2l+1}}{r^{l+1}} x_m^c, & r \geq b.
\end{cases} \tag{2.30}
\]
The electrostatic potential energy is given by:

\[
V_{lm} = \frac{1}{2} \int (\rho - \rho_0) \Phi_{lm} d\tau = \frac{1}{2} \int \sigma \Phi_{lm} dS
\]

\[
= \frac{1}{2} \left[ a^2 \sigma_c \Phi_{lm} (a) + b^2 \sigma_s \Phi_{lm} (b) \right],
\]

which leads to:

\[
V_{lm} = -\frac{nm}{2ne} \left( 1 - x^{2l+1} \right) \left[ \omega_c^2 a^{-l+1} x_{lm}^c \sigma_c + \omega_s^2 b^{l+1} x_{lm}^s \sigma_s \right].
\]

Plugging in the expressions of the surface charges Eqs. (2.24) and (2.25), one obtains

\[
V_{lm} = \frac{nm}{2} \left( 1 - x^{2l+1} \right) \left[ \frac{\omega_c^2 l + 1}{a^{-2l+1}} (x_{lm}^c)^2 - 2l (l + 1) \omega_s \omega_c x_{lm}^c x_{lm}^s + b^{2l+1} \omega_s^2 (x_{lm}^s)^2 \right].
\]

The second term of the above equation represents the interaction between the cavity and sphere plasmons. The equations of motion can be easily obtained now,

\[
\ddot{x}_{lm}^c = -\omega_c^2 x_{lm}^c + a^{2l+1} \omega_s^2 x_{lm}^s
\]

\[
\ddot{x}_{lm}^s = -\omega_s^2 x_{lm}^s + b^{-2l-1} \omega_c^2 x_{lm}^c.
\]

The system exhibits two fundamental frequencies,

\[
\omega_{\pm} = \frac{\omega_b}{2} \left[ 1 \pm \frac{1}{2l+1} \sqrt{1 + 4l (l + 1) x^{2l+1}} \right],
\]

as predicted by the classical Mie theory. The lower energy mode corresponds to a symmetric coupling between the cavity and sphere plasmons while the higher energy mode corresponds to an antisymmetric coupling.
2.5 Dielectric Effects

In this section, a dielectric core $\varepsilon_c$ and a dielectric medium $\varepsilon_o$ will be introduce in the formalism. Due to the polarization of the dielectrics, there will be a net surface charge given by the sum of the spill out charge and the polarization charges. The net charge $\sigma^t$ can be related to the real charge (spill out charge $\sigma$) through a linear combination of the form

$$
\sigma_i^t = \chi_{ii}\sigma_i + \chi_{io}\sigma_o
$$

$$
\sigma_o^t = \chi_{oi}\sigma_i + \chi_{oo}\sigma_o.
$$

The $\chi$ matrix is calculated by solving the Poisson equation with the appropriate boundary conditions. This step will be discussed in detail when the dielectric effects on the multi-concentric metallic shells will be investigated. For a given angular number $l$, the matrix $\chi$ takes the following form:

$$
\chi = \frac{1}{\Delta} \begin{pmatrix}
(l + 1)\varepsilon_o + l & - (\varepsilon_o - 1)(l + 1)x^{l+2} \\
-(\varepsilon_c - 1)lx^{l-1} & l\varepsilon_c + l + 1
\end{pmatrix},
$$

where

$$
\Delta = \frac{(l\varepsilon_c + l + 1)((l + 1)\varepsilon_o + l) - (\varepsilon_c - 1)(\varepsilon_o - 1)l(l + 1)x^{2l+1}}{2l + 1}.
$$

The electric potential is given now by the net surface charge,

$$
\Phi_{lm}(r, \Omega) = \frac{4\pi}{2l + 1} \left[ a^2v_l(r, a)\sigma_i^t(\Omega) + b^2v_l(r, b)\sigma_o^t(\Omega) \right].
$$
The kinetic energy of the fluid remains the same while the electrostatic energy changes according to

\[
V_{lm} = \frac{1}{8\pi} \int \vec{D} \vec{E} d\vec{r} = -\frac{1}{8\pi} \int \vec{D} \vec{\nabla} \Phi_{lm} d\vec{r} = \frac{1}{8\pi} \int \vec{\nabla} \left( \Phi_{lm} \vec{D} \right) d\vec{r} + \frac{1}{8\pi} \int \vec{\nabla} \vec{D} \Phi_{lm} d\vec{r} = \frac{1}{2} \int \sigma \Phi_{lm} d\vec{r},
\]

(2.40)

where \( \sigma \) is the real charge (spill out charge). It will be very convenient to make one step further, by noticing that \( \sigma = -\frac{1}{4\pi} \vec{\nabla}^2 \tilde{\Phi} \), where \( \tilde{\Phi} \) is the electric potential generated by the spill out charge. Replacing \( \sigma \) by this expression and integrating by parts two times, we can conclude:

\[
V_{lm} = \frac{1}{2} \int \tilde{\Phi}_{lm} \left( -\frac{1}{4\pi} \vec{\nabla}^2 \tilde{\Phi}_{lm} \right) d\vec{r} = \frac{1}{2} \int \sigma^t \tilde{\Phi}_{lm} d\vec{r}.
\]

(2.41)

The reason for this step is the fact that \( \tilde{\Phi}_{lm} \) has been already computed in Eq. (2.30).

One can now simply say that, when the dielectrics are present, the spill out charge \( \sigma \) has to be replaced by the total charge \( \sigma^t \) in the expression Eq. (2.32) of \( V_{lm} \):

\[
V_{lm} = -\frac{nm}{2ne} (1 - x^{2l+1}) \left[ \omega_c^2 a^{-l+1} x_{lm}^c \sigma_i^l + \omega_s^2 b^{l+2} x_{lm}^s \sigma_o^l \right].
\]

(2.42)

The equations of motions can be readily found,

\[
\ddot{x}_{lm}^c = -\omega_c^2 \left( \chi_{ii} - x^{l+2} \chi_{io} \right) x_{lm}^c
\]

(2.43)

\[
+ a^{2l+1} \omega_s^2 \left( \frac{\chi_{ii} + \chi_{oo}}{2} - \frac{\chi_{oi} + x^3 \chi_{io} x^{-l-2}}{2} \right) x_{lm}^s
\]

\[
\ddot{x}_{lm}^s = -\omega_s^2 \left( \chi_{oo} - x^{l-1} \chi_{oi} \right) x_{lm}^s
\]

(2.43)

\[
+ b^{-2l-1} \omega_c^2 \left( \frac{\chi_{ii} + \chi_{oo}}{2} - \frac{\chi_{oi} + x^3 \chi_{io} x^{-l-2}}{2} \right) x_{lm}^c,
\]
which again lead to exactly the plasmon frequencies predicted by the Mie theory.

2.6 Plasmonics of the Multi-Concentric Metallic Shells

This section investigates a system of $N$ concentric metallic shells of inner radius $a_j$ and outer radius $b_j$. The analysis of the incompressible fluid can be applied independently for each shell. The spill out charge for an individual shell $(j)$ will be given by the same equations:

\[
\sigma_{cj}(t, \Omega) = ne \left[ l a_j^{l-1} x_{lm}^{cj}(t) - (l + 1) a_j^{-l-2} x_{lm}^{cj} \right] Y_{lm}(\Omega) \tag{2.44}
\]

\[
\sigma_{sj}(t, \Omega) = -ne \left[ l b_j^{l-1} x_{lm}^{sj}(t) - (l + 1) b_j^{-l-2} x_{lm}^{sj} \right] Y_{lm}(\Omega).
\]

The electric field produced by the spill out electrons is the sum of the electric fields $\Phi_j$ produced by the individual shells. The electric potentials $\Phi_j$ will have the same expression as for a single shell:

\[
\Phi_j = \frac{4\pi}{2l + 1} \left[ a_j^2 v_i(r, a_j) \sigma_{cj} + b_j^2 v_i(r, b_j) \sigma_{sj} \right]. \tag{2.45}
\]

Because the surface charges are defined by the same algebraic expressions as in the case of the single shell, one can also conclude:

\[
\Phi_{lm}^j = -\frac{4\pi ne}{2l + 1} \left( 1 - x_j^{2l+1} \right) Y_{lm}(\Omega) \begin{cases} 
\frac{(l + 1) r^l}{a_j^{2l+1}} x_{lm}^e, & r \leq a_j \\
\frac{lb_j^{2l+1}}{r^{l+1}} x_{lm}^s, & r \geq b_j. \end{cases} \tag{2.46}
\]

The electrostatic energy of the system is calculated again from $V = \frac{1}{2} \int \sigma \Phi d\tilde{r}$,

\[
V_{lm} = \frac{1}{2} \sum_{i,j} \left[ a_i^2 \sigma_{ci} \Phi_{lm}^j (a_i) + b_i^2 \sigma_{si} \Phi_{lm}^j (b_i) \right]. \tag{2.47}
\]
Plugging in the above expression of the $\Phi_{lm}^{ij}$ calculated above, one can conclude that

$$V_{lm} = \Sigma_{i,j} V_{lm}^{ij},$$

where

$$V_{lm}^{ij} = \frac{-nm}{2ne} \left( 1 - x_j^{2l+1} \right) \left\{ \begin{array}{ll}
\omega_c^2 a_j^{-2l-1} x_{lm}^{ci} [a_i^{l+2} \sigma_{ci} + b_i^{l+2} \sigma_{si}] , & \text{for } i < j \\
\omega_c^2 a_i^{-l+1} x_{lm}^{ci} \sigma_{ci} + \omega_s^2 b_i^{l+2} x_{lm}^{si} \sigma_{si} , & \text{for } i = j \\
\omega_s^2 b_j^{2l+1} x_{lm}^{sj} [a_i^{-l+1} \sigma_{ci} + b_i^{-l+1} \sigma_{si}] , & \text{for } i > j.
\end{array} \right. \quad (2.48)$$

The extension to the case when dielectrics are present is straightforward. As in the case of the single shell, we have to replace the spill out charge by the net charge at the surface, $\sigma_{ci}, \sigma_{si} \rightarrow \sigma_{ci}^t, \sigma_{si}^t$. There will be again a linear relation between $\{\sigma_{ci}^t, \sigma_{si}^t\}$ and $\{\sigma_{ci}, \sigma_{si}\}$ which will be investigated in detail in the following. Below are the notations used in these calculations,

$$\hat{x}_{lm} \equiv \left( \begin{array}{c}
x_{lm}^{ci} \\
x_{lm}^{ci}
\end{array} \right), \quad \hat{\sigma} = \left( \begin{array}{c}
\sigma_{ci} \\
\sigma_{si}
\end{array} \right). \quad (2.49)$$

Also, we will use $r_{2j-1} = a_j$ and $r_{2j} = b_j$ to specify the geometry of the shells. In these notations, $j$ goes from 1 to $N$, the number of concentric shells. In the presence of dielectrics, the electric potential of the multi-concentric metallic shell system is given by:

$$\Phi(r, \Omega) = \frac{4\pi}{2l+1} \sum_j r_j^2 \varphi_l (r, r_j) \sigma_j^t (\Omega), \quad (2.50)$$
where the net charge $\sigma^t$ includes the polarization charges. This net charge is yet unknown but can be found from the usual boundary conditions:

$$\varepsilon_i \frac{\partial \Phi}{\partial r} \bigg|_{r_i^+} - \varepsilon_i \frac{\partial \Phi}{\partial r} \bigg|_{r_i^-} = -4\pi \sigma_i. \quad (2.51)$$

Using the above expression of the potential we can continue:

$$-(2l + 1) \sigma_i = \varepsilon_{i+1} \left( \sum_{j \leq i} (l + 1) \left( \frac{r_j}{r_i} \right)^{l+2} \sigma_j^t + \sum_{j > i} l \left( \frac{r_i}{r_j} \right)^{l-1} \sigma_j^t \right) \quad (2.52)$$

$$-\varepsilon_i \left( \sum_{j < i} (l + 1) \left( \frac{r_j}{r_i} \right)^{l+2} \sigma_j^t + \sum_{j \geq i} l \left( \frac{r_i}{r_j} \right)^{l-1} \sigma_j^t \right).$$

This leads to a linear relation between $\sigma^t$ and $\sigma$, $\sigma^t = \hat{E} \sigma$, where:

$$\hat{E}_{ij} = \frac{1}{2l + 1} \begin{cases} 
(\varepsilon_i - \varepsilon_{i+1}) l \left( \frac{r_i}{r_j} \right)^{l-1}, & \text{for } i < j \\
(l + 1) \varepsilon_{i+1} + l \varepsilon_i, & \text{for } i = j \\
(\varepsilon_{i+1} - \varepsilon_i) (l + 1) \left( \frac{r_j}{r_i} \right)^{l+2}, & \text{for } i > j.
\end{cases} \quad (2.53)$$

The matrix $\hat{\chi}$ is just the inverse of the matrix $\hat{E}$ defined above.

The next goal is to find the quadratic form of the kinetic energy,

$$T_{lm} = \frac{nm}{2} (\hat{x}_{lm})^T \hat{T} \hat{x}_{lm} \quad (2.54)$$

and of the electrostatic potential,

$$V_{lm} = \frac{nm}{2} (\hat{x}_{lm})^T \hat{V} \hat{x}_{lm} \quad (2.55)$$

and derive the general equation for the plasmon frequencies. For this we remember that the electrostatic energy was explicitly written in the form

$$V_{lm} = -\frac{nm}{2ne} (\hat{x}_{lm})^T \hat{A} \hat{\sigma}^t, \quad (2.56)$$
where the elements of the matrix $\hat{A}$ are given in Eq. (2.48). We continue by relating the net surface charge $\hat{\sigma}^t$ to the spill out charge $\hat{\sigma}$ through the matrix $\hat{\chi}$ and finally by relating the spill out charge to our variables, $\hat{\sigma} = \hat{B} \hat{x}_{lm}$, where $\hat{B}$ is the block diagonal matrix

$$\hat{B} = \begin{pmatrix} \hat{B}_1 & 0 \\ \vdots & \ddots \\ 0 & \hat{B}_N \end{pmatrix}, \quad \hat{B}_j = \begin{pmatrix} - (l + 1) a_j^{l-2} & la_j^{l-1} \\ (l + 1) b_j^{l-2} & -lb_j^{l-1} \end{pmatrix}. \quad (2.57)$$

We can conclude:

$$V_{lm} = \frac{nm}{2} (\hat{x}_{im})^T \hat{A} \hat{x}_{im} \Rightarrow \hat{V} = \hat{A} \hat{x}. \quad (2.58)$$

The kinetic energy can be expressed as:

$$T_{lm} = \frac{nm}{2} \left( \frac{d\hat{x}_{lm}}{dt} \right)^T \hat{T} \frac{d\hat{x}_{lm}}{dt}, \quad (2.59)$$

where $\hat{T}$ is the block diagonal matrix defined below:

$$\hat{T} = \begin{pmatrix} \hat{T}_1 & 0 \\ \vdots & \ddots \\ 0 & \hat{T}_N \end{pmatrix}, \quad (2.60)$$

where

$$\hat{T}_i = (1 - x_i^{2l+1}) \begin{pmatrix} (l + 1) a_i^{2l-1} & 0 \\ 0 & b_i^{2l+1} \end{pmatrix}. \quad (2.61)$$

The equations of motion lead to the following equation for the plasmon frequencies:

$$\det \left[ \omega^2 \hat{T} - \frac{1}{2} (\hat{V} + \hat{V}^T) \right] = 0. \quad (2.62)$$
2.7 Discussion and Summary

The picture of interacting surface plasmons allows us to map the plasmonics of the nanoshell into a two energy level system. The unperturbed system consists of the cavity and sphere plasmons, which, when combined in a shell, start to interact with each other leading to shifts of the energy levels and hybridization between the two plasmon modes. It is important to mention that the only assumption made is that the electron gas behaves as an incompressible fluid. Starting from this assumption alone, one can calculate the two level Hamiltonian without making any other assumptions or approximations. This Hamiltonian leads to the correct dynamics of the plasmons. The system of $N$ concentric metallic shells can be also mapped into a $2N$ energy level system. In this case, the unperturbed system consists of the cavity and sphere plasmons located on the surfaces of each individual nanoshell. The interaction between the surface plasmons can be calculated again without any supplementary assumptions of approximations. The shifts and splittings of the plasmon resonances observed in the classical Mie simulations for these complex particles can be now understood as the perturbation of a $2N$ energy level system.
Chapter 3

Many Body Effects in Metallic Nanoshells

3.1 Introduction

The full many body investigation of the electronic structure and optical properties of the metallic nanoshells starts in this chapter. For a microscopic understanding of the electronic and optical properties of metallic nanoshells, it is necessary to develop a method capable of calculating the electronic structure and polarizabilities of metallic nanoshells in vacuum, on surfaces and when interacting with chemisorbed impurities. This chapter investigates how large are the correlation between the electrons in these relatively small systems. By correlation one should understand all the effects due to electron-electron interaction that cannot be accounted by the Hartree-Fock approximation. Determining the strength of the correlations is important for the following reason. It is known that for small molecules, the correlation effects are relatively small and the Hartree-Fock approximation gives relatively good results. As the size of the system increases, the correlation effects become more important. For mesoscopic metallic particles, the neglect of the correlation effects can lead to errors as large as 100%.[18] It will be important then to investigate this problem for nanoscale metallic system, because these systems are situated exactly in between the two limits mentioned above.
A comparison between the Hartree (H), Hartree-Fock (HF) and local density (LDA) approximations is presented. The results show that, even for very small metallic nanoparticles, the differences between these three approximations are similar to the differences seen for bulk electrons in metals,[18] where the HF approximation is known to overestimate the bandwidths and the screening lengths. The results show that the correlation terms are important even for very small nanoparticles and suggest that the LDA is an appropriate approach for the electronic structure of nanoshells.

3.2 Jellium Model for Metallic Nanoshells

A metallic nanoshell is composed of a metallic layer (the shell) grown over a spherical dielectric core.[3, 4] Since the optical properties are determined by the conduction electrons of the shell, we expect a jellium model to provide an accurate model. Previously, jellium models of shell structures have been successfully used for the investigation of the electronic structure of C$_{60}$ and endohedral fullerene systems with impurity atoms trapped inside the cage.[19] Also, jellium models have been used to model small spherical metallic clusters. [20, 21]

We will denote the interior radius of the shell by $a$ and the exterior radius by $b$. In the jellium approximation, the positive charge of the ion cores is approximated by a uniformly distributed positive charge $n_0$ over the shell. We model the gold shells using jellium with a free electron radius $r_\alpha = 3$ (a.u.). The effect of the dielectric phase and the multipole interaction between the conduction electrons and ion cores
are taken into account by introducing a background potential:

\[
V_{\text{ext}}(r) = \begin{cases} 
V_i, & r < a \\
V_s, & a < r < b \\
0, & b < r
\end{cases}
\] (3.1)

The value of the potential in the dielectric core is kept the same for all three approximations, \(V_i=0.07 \text{ Hartree}\). The value of the background potential inside the shell has to be adjusted such that the calculated Fermi energy describes correctly the ionization potential of the metal. For gold, the ionization potential is 5.4 eV.

To avoid the problem associated with partial filling of degenerate electronic levels, the calculations were performed at finite temperature. The temperature was chosen smaller than the lowest excitation energy of the shells.

All three approximations consist of solving self-consistently a set of equations of the form:

\[
\left( -\frac{1}{2} \Delta + V_{\text{ext}} + \Sigma \right) \phi_i = \varepsilon_i \phi_i 
\] (3.2)

\[
n(\vec{x}) = \sum_i \left( 1 + e^{\beta(\varepsilon_i - \mu)} \right)^{-1} |\phi_i(\vec{x})|^2.
\]

The chemical potential \(\mu\) is determined from:

\[
N = \sum_i \left( 1 + e^{\beta(\varepsilon_i - \mu)} \right)^{-1},
\] (3.3)

\(N\) being the number of conduction electrons. The term \(\Sigma\) represents the self-energy.

The self-energy depends only on the density of electrons for Hartree and LDA, while
it depends on all orbitals \( \{ \phi_i \} \) for the Hartree-Fock approximation:

\[
\Sigma_H (\vec{x}, \vec{y}) = \delta (\vec{x} - \vec{y}) \int \frac{n (\vec{x}')}{|\vec{x} - \vec{x}'|} d\vec{x}' \tag{3.4}
\]

\[
\Sigma_{HF} (\vec{x}, \vec{y}) = \Sigma_H (\vec{x}, \vec{y}) - \sum_j f_{PD} (\varepsilon_j - \mu) \frac{\phi_j (\vec{x}) \phi_j (\vec{y})^*}{|\vec{x} - \vec{y}|}
\]

\[
\Sigma_{LDA} (\vec{x}, \vec{y}) = \Sigma_H (\vec{x}, \vec{y}) + \delta (\vec{x} - \vec{y}) v_{xc} (n (\vec{x})).
\]

The exchange correlation potential \( v_{xc} \) used in the present calculations was taken from Ref. [22]. For a local potential such as Hartree or LDA, the most suitable approach for solving the Schroedinger equation would be direct integration. Unfortunately, the Hartree-Fock potential is non-local and, consequently, such methods cannot be applied. To compare the results of the three approximations, we therefore developed a method that is based on the expansion of the electron wavefunctions in a fixed basis set. As usual, we will solve the self-consistent equations by an iterative process. At every step of iterations, we use the same orthonormal basis to calculate the matrix elements of the self-energy. This basis set can be chosen as:

\[
\phi_{k\ell m}^0 (r, \Omega) = r^{-1/2} g_k^0 (r) Y_{\ell m} (\Omega),
\]

where \( \{ g_k^0 \}_k \) is a complete set of orthonormal functions defined on the positive real axis. Suppose the spherical symmetry is preserved after the \( n \)-th iteration. In this case, the eigenvectors of \( H^{(n)} = -\frac{1}{2} \Delta + V_{ext} + \Sigma^{(n)} \) can be expressed as \( r^{-1} g_{k\ell}^{(n)} (r) Y_{\ell m} (\Omega) \), where \( \Sigma^{(n)} \) is the self-energy after \( n \) iterations, calculated in any of the three approximations. Let \( \varepsilon_{k\ell}^{(n)} \) be the corresponding eigenvalues and let \( \mu^{(n)} \) be the Fermi energy after the \( n \)-th iteration. We will use the notation \( \xi_{k\ell}^{(n)} \) for \( \varepsilon_{k\ell}^{(n)} - \mu^{(n)} \). The density of
electrons, \( n^{(n)}(r) \) after the \( n \)-th step of the iteration is given by:

\[
n^{(n)}(r) = \frac{2s + 1}{r^2} \sum_{k,l} (2l + 1) (1 + e^{\beta \xi_{kl}})^{-1} |g_{kl}^{(n)}(r)|^2.
\] (3.6)

For two positions \( r \) and \( r' \), the minimum and maximum between \( r \) and \( r' \) will be denoted by \( r_\ast \) and \( r_\ast' \), respectively. Then, for the \( (n + 1) \)-th iteration, the Hartree term of the self-energy is given by:

\[
\langle \phi^0_{km}, \Sigma_H^{(n+1)} \phi^0_{k'l'm'} \rangle = \delta_{lm,l'm'} \int r'^2 g_k^0(r) g_k^0(r) \frac{n^{(n)}(r') - n_0(r')}{r_\ast'} dr dr'.
\] (3.7)

The matrix elements of the Fock term are given by:

\[
\langle \phi^0_{km}, \Sigma_F^{(n+1)} \phi^0_{k'l'm'} \rangle = -\delta_{lml'm'} \sum_{j_1,l_2} \frac{2l_2 + 1}{1 + e^{\beta \xi_{kjl_1}}} jjj \left( l_1 l_2 l \right)^2 \times
\]

\[
\int g_k^0(r) g_{j_1 l_1}^{(n)}(r) g_{j_2 l_2}^{(n)}(r') g_k^0(r') dr dr',
\] (3.8)

where \( jjj \) denotes the three j's symbols. For LDA, the exchange-correlation part of the self-energy is given by:

\[
\langle \phi^0_{km}, \Sigma_{xc}^{(n+1)} \phi^0_{k'l'm'} \rangle = \delta_{lml'm'} \int g_k^0(r) \nu_{xc}(n^{(n)}(r)) g_k^0(r) dr.
\] (3.9)

The main advantage of the present basis set is that the matrix elements in Eqs. (3.7) and (3.9) do not depend on the angular quantum numbers. The exchange part of the self-energy in the HF approximation given in Eq. (3.8) depends however on the angular quantum number \( l \) which is the main source of CPU cycles in the numerical calculations. Equations (3.7), (3.8) and (3.9) show that, if the spherical symmetry
is preserved after the $n$-th iteration, the self-energy at the $(n+1)$-th iteration is
diagonal with respect to the angular quantum numbers $l$ and $m$. This shows that the
spherical symmetry is also preserved after the $(n+1)$-th iteration and thus at any
iteration, for all three approximations. The final result of the iterative process will be
a set of orbitals of the form $r^{-1} g_{kl}(r) Y_{lm}(\Omega)$. The corresponding eigenvalues depend
only on the radial quantum number $k$ and angular quantum number $l$. Each of the
eigenvalues has a $2(2l + 1)$-fold degeneracy.

3.3 Electronic Structure

In this section, the electronic structure of two different gold nanoshells are cal-
culated using Hartree, HF and the LDA. The first nanoshell has the interior radius
$a = 10$ a.u. and exterior radius $b = 20$ a.u. and contains 259 conduction electrons.
The second nanoshell has the interior radius $a = 10$ a.u. and exterior radius $b = 25$
and contains 542 conduction electrons. The parameter $V_{\alpha}$ used in the calculations are
as follows: $-0.45$ Ha for the Hartree approximation, $-0.30$ for Hartree-Fock approx-
imation and $-0.18$ for LDA. This values provide the same ionization potential (5.4
eV) for all three approximations. In the numerical implementation of our method,
the nanoshell was considered in a finite volume, a sphere of radius $R >> b$. The
following functions were chosen as the radial basis set:

$$g^0_n(r) = \sqrt{\frac{2}{R}} \sin \left( n \pi \frac{r}{R} \right).$$  (3.10)
In the present calculations, $R = 50$ a.u. and the expansion of the wavefunction includes all such radial wavefunctions up to $n = 30$ and all spherical harmonics up to the angular quantum number $l = 15$. The results do not change for larger values of these parameters.

The major differences in the electronic structure calculated using the three approximations appears when the density of states is compared. Qualitatively, all calculated densities of states show a few common features, like the dependence on the radial and angular quantum numbers as shown in Fig. 3.1. The electronic structure is analogous to the result that was obtained by Puska and Nieminen in their application to $C_{60}$. [19]

For each radial quantum number $k$, the eigenstates with different angular momentum $l=0, \ldots, \infty$ generates a branch of the DOS. The five branches that show up in Fig. 3.1 correspond to different radial quantum numbers, $k=0, \ldots, 4$. Quantitatively, there is a major difference between HF and the other two approximations. For both nanoshells, the bandwidth is much larger in the first case. The Hartree and LDA approximations predicts the same bandwidths of 0.175 Ha for the small nanoshell and 0.187 Ha for the large nanoshell. Within the Hartree Fock approximation, the bandwidth is 0.283 for the small nanoshell and 0.323 for the large nanoshell, which means an increase by a factor of 1.62 and 1.71 respectively. For homogeneous electron gas, with the same $r_s = 3$ a.u. as in our simulations, the HF approximation is also known to overestimate the bandwidth by around a factor of two.

The electron densities, calculated using the three approximations, are shown in
Figure 3.1  The density of states calculated using the LDA approximation for the shell of inner radius 10 a.u. and outer radius 25 a.u.. The highest occupied orbital is drawn with the dashed line.
Fig. 3.2, for the two nanoshells under study. The calculated charge densities were found to be similar in all three many-body descriptions. In all three cases, one can observe that the electrons spread well over the edges of the shell, while the general features in the middle of the shells are preserved. The oscillations of the density of the electrons inside the shell are caused by the nodes of the radial wavefunctions. For the smaller shell, the $k = 0$ and $k = 1$ states with zero and one node respectively are populated and cause the two maxima in the density distribution. For the larger shell, also the $k = 2$ state with two nodes contributes to the charge density giving rise to the three maxima. Figure 3.2 shows that the electronic charge calculated using HF and LDA shows a slightly larger electron spill out into the dielectric core and the vacuum regions than is calculated with the Hartree approximation. This is caused by the attractive exchange interaction. Although a weak phenomenon, the effect is strongest for the HF approximation. While this effect is barely visible in the density of electrons, it has a major effect on the Coulomb potential, as it can be seen in Fig. 3.3. Since the nanoshell is assumed neutral, the Coulomb potential vanishes to zero outside the shell and at $R$. However for the HF approximation, the Coulomb potential becomes positive inside the dielectric core. As we already discussed, this is due to the asymmetry of the electron charge relative to the shell. The non-localized, attractive nature of the exchange interaction in the HF approximation forces the electrons to spill out more into the dielectric core. Figure 3.3 also illustrates how unstable this problem can be. Small deviations of the electron charge produce large
Figure 3.2  The density of electrons in the three approximations: Hartree (solid), HF (dotted) and LDA (dashed), for the two nanoshells, 10-20 a.u. (panel a) and 10-25 a.u. (panel b).
Figure 3.3  The Coulomb potential for the 10-25 a.u. nanoshell, in the three approximations: Hartree (solid), HF (dotted) and LDA (dashed).
deviations in the effective potential.

3.4 Screening Charge

Another relevant comparison between the three approximations is provided by the linear response of the electrons to an external perturbation. In general, the linear response calculations must include the continuum spectrum, especially for high frequencies and when the external perturbation is not spatially localized. The approach presented in the previous section provides an accurate description of the bound states but a relatively poor description of the scattering states. For this reason, when comparing the screening properties, we should restrict ourselves to static and spatially localized perturbations. An interesting and also relevant application that fulfills these two criteria is the calculation of the screening charge due to an impurity point-charge, located in the middle of the metallic shell.

Within linear response theory, the screening charge is given by

$$\delta n(\vec{r}) = - \int \Pi(\vec{r}, \vec{r}'; \vec{r}^\prime) \frac{Z}{|\vec{r}^\prime - \vec{r}_0|} d\vec{r}^\prime,$$

(3.11)

where \(\vec{r}_0\) denotes the position of the impurity (of charge \(Z\)) and \(\Pi\) is the trace over the spin degrees of freedom of the polarization function. The polarization function will be computed using two different approximations: the independent electron approximation (Lindhart), \(\Pi^0\) and the random phase approximation (RPA), \(\Pi^{RPA}\). The evaluation of the polarizability function is based on the electronic structure calculated in the previous section using the Hartree, HF and LDA approaches.
The expression of the Lindhart polarization function[23] at zero temperature can be easily generalized for finite temperatures,

\[
\Pi^0(\vec{r}, \vec{r}') = (2s + 1) \sum_{ij} e_i(\vec{r})^* e_j(\vec{r}) \frac{f(\xi_i) - f(\xi_j)}{\xi_i - \xi_j + i\delta} e_i(\vec{r}') e_j(\vec{r}')^*,
\]

(3.12)

where \(e_j\) are the orbitals calculated in the previous section and \(f\) is the Fermi-Dirac distribution. The second approximation for the polarization function is given by the well known RPA expression:[24]

\[
\Pi^{RPA}(\vec{r}, \vec{r}') = \Pi^0(1 - V\Pi^0)^{-1}(\vec{r}, \vec{r}').
\]

(3.13)

This expression takes into account the screening by the electrons. For the Hartree and Hartree-Fock models, \(V\) represents the Coulomb interaction between electrons. For LDA, the term

\[
\delta v_{xc} = \frac{dv_{xc}}{dn}(n(\vec{r})) \delta(\vec{r} - \vec{r}')
\]

(3.14)

has to be also included.[25] Since Eq. (3.13) involves a matrix inversion, we decided to expand all the functions in the basis \(\{r^{-1}g_k(\vec{r})Y_{lm}(\Omega)\}_{klm}\) discussed in the previous section. In this case, Eq. (3.13) is reduced to a simple algebraic calculation. The expression of the polarization function in the independent electrons approximation can be found from Eq. (3.12) if one plugs in the orbitals \(\{r^{-1}g_{kl}(\vec{r})Y_{lm}(\Omega)\}_{klm}:\)

\[
\Pi^0(r, \Omega; r', \Omega') = \frac{2}{r^2 r'^2} \sum_{l_1, k_1, m_1} \frac{f(\xi_{k_1l_1}) - f(\xi_{k_2l_2})}{\xi_{k_1l_1} - \xi_{k_2l_2} + i\delta} g_{k_1l_1}(r) g_{k_2l_2}(r) \times
\]

(3.15)

\[g_{k_1l_1}(r')g_{k_2l_2}(r')Y_{l_1m_1}(\Omega)Y_{l_2m_2}^*(\Omega')Y_{l_1m_1}^*(\Omega')Y_{l_2m_2}(\Omega').\]
One can simplify the above expression by using the identity

$$
\sum_{l_1, l_2, m_{1,2}} F_{l_1 l_2} Y_{l_1 m_1} (\Omega) Y_{l_2 m_2}^* (\Omega') Y_{l_1 m_1}^* (\Omega) Y_{l_2 m_2} (\Omega')
$$

$$
= \sum_{l, m} \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi} F_{l_1 l_2} \sum_{j, j', \ell} \delta_{j j'} (\ell_{l_1 l_2})^2 Y_{lm} (\Omega) Y_{lm}^* (\Omega').
$$

(3.16)

With this simplification, the matrix elements of the polarization function in the independent electron approximation become

$$
\langle \phi_{klm}^0 | \Pi | \phi_{k'l'm'}^0 \rangle
$$

$$
= \delta_{l, l'} \delta_{m, m'} \sum_{l_1, l_2} \frac{(2l_1 + 1)(2l_2 + 1)}{2\pi} \frac{f(\xi_{k_1 l_1}) - f(\xi_{k_2 l_2})}{\xi_{k_1 l_1} - \xi_{k_2 l_2} + i\delta} \delta_{j j'} (\ell_{l_1 l_2})^2 \int \frac{dr}{r} g_k^0 (r) g_{k_1 l_1} (r) g_{k_2 l_2} (r) \int \frac{dr'}{r'} g_{k'}^0 (r') g_{k_1 l_1} (r') g_{k_2 l_2} (r').
$$

(3.17)

From the above, it follows that the polarization function is diagonal with respect to the quantum numbers $l$ and $m$ and is independent of $m$. For both, the independent electron and RPA polarization functions, one can therefore use the notation:

$$
\langle \phi_{klm}^0 | \Pi | \phi_{k'l'm'}^0 \rangle \equiv \delta_{ll'} \delta_{mm'} \Pi_{kk'}^{(0)}.
$$

(3.18)

For an impurity of unit charge located at $r_0 = \frac{1}{2}(a + b)$ and $\theta = 0$ (in the middle of the shell), the expression for the screening charge at some position $(r, \theta)$ reduces to:

$$
\delta n (r, \theta) = - \sum_l P_l (\cos \theta) \sum_{kk'} r^{-1} g_k^0 (r) \Pi_{kk'}^{(0)} \int dr' g_{k'}^0 (r') \frac{r_{<}}{r_{>}}.
$$

(3.19)

The symbols $r_{<}$ and $r_{>}$ denote the maximum and minimum of $r$ and $r_0$.

Qualitatively, the screening charge shows similar features in all three models. In Fig. 3.4 and 3.5, examples of the spatial dependence of the calculated screening
Figure 3.4  The screening charge induced by an impurity placed in the middle of the 10-25 a.u. nanoshell within Lindhart (panel a) and RPA (panel b) approximations. The center of the nanoshell is placed at the origin of the coordinate system. The impurity is placed at (0,0,12.5) a.u. The screening charge is shown as a function of $x$ and $z$ in the plane $y=0$. The electronic structure of the shell was calculated using LDA.
Figure 3.5  Comparison of the radial dependence of the screening charge calculated using the RPA approach Eq. (3.13) using Hartree (solid line), HF (dotted line) and LDA (dashed line) models for the electronic structure. Panel a) shows the result for the 10-20 a.u. shell and panel b) shows the result for the 10-25 a.u. shell. The insets show the screening charge on a finer scale.
charges are shown. The induced charge is very large around the impurity and decays as the distance to the impurity is increased. At the inner and outer surfaces of the nanoshell, a strong spatial dependence of $\delta n$ is induced. These surface effects are large in the independent electron approximation while they are almost negligible for RPA. This is because, in the latter case, the screening charge is confined within a volume of a radius approximately equal to the Thomas-Fermi screening length, which is smaller than the distance from the impurity to the shell surface. A quantitative comparison of the results from the different approximations is shown in Fig. 3.5. The insets show charge density oscillations similar to Friedel oscillations in bulk systems. As can be seen, the Hartree and LDA lead to similar screening charges, while the HF model leads to a very different result. A similar behavior can be observed for the homogeneous electron gas and in small atoms.[25]

3.5 Discussion and Summary

Our numerical results show that correlation effects are still strong even for very small metallic nanoshells. The neglect of correlation corrections in the HF approximation has the same effects as for the bulk electrons: an unphysical increase of the conduction electron bandwidth and inefficient screening of an impurity charge. The correlation correction in LDA makes the results more similar to the Hartree approximation, as for bulk metals. For larger nanoshells, we expect the analogy, from this point of view, between nanoshells and infinite metallic phases to be even stronger, a
fact that favors the LDA among the three approximations considered here.

As it is pointed out in Ref. [26], the finite metallic clusters, besides the metal surfaces, present a crucial test for the Local Density Approximation. Lang and Kohn have shown that the surface energies and work functions of the metal surfaces can be accurately reproduced by LDA for metals with \( r_s > 4 \) while the approximation may totally break down for \( r_s < 2.3 \).[27, 28] These type of calculations depend with some degree on what exchange-correlation potential is used. The new exchange-correlation potentials developed by Vosko, Wilk and Nusair [29], Perdew and Zunger [22] or Perdew and Wang [30] may extend these limits.

Studies that focus on the comparison between the Hartree-Fock and LDA are quite abundant. The main problem addressed in these studies was how good is the local approximation of the exchange in the LDA compared with the exact Hartree-Fock exchange. All these studies have been extensively discussed in the reviews of Ref. [26] and Ref. [31] and all of them concluded that LDA performs remarkably well even for small metallic clusters. We will mentioned here in particular the study carried by Hansen and Nishioka [32], which also found that the Hartree-Fock leads to stronger bounding of the lowest energy states, i.e. larger bandwidths. The effects were less stronger than in our case, given the fact that their study considered alkali metal clusters with up to 58 atoms.

The computational method used to investigate the electronic structure is not very efficient. For this reason, the simulations presented in this chapter were limited to
very small nanoshells. This approach was enforced by the non-locality of the Hartree-Fock term. It became clear to us that such a method cannot be implemented to real size metallic nanoshells. The results of this chapter and the existing simulations for small metallic clusters indicate that LDA is more suitable for describing the electronic properties of the metallic nanoshells. Within the LDA approximation, the exchange-correlation is local. Therefore one can find the orbitals by a direct integration of the Schroedinger equation. Such an approach can be implemented to real size metallic nanoshells, as will be shown in the next chapter.
Chapter 4

Electronic Structure of Metallic Nanoshells

4.1 Introduction

This chapter presents an efficient implementation of the Local Density Approximation (LDA) to metallic nanoshells. The goal is to simulate real size nanoshells, i.e. nanoshells of sizes that can be fabricated experimentally. Even the smallest nanoshells that can be fabricated with the existent experimental techniques will contain a number of conduction electrons of order $10^6$. From a computational point of view, implementing LDA to such large systems can be very challenging. There are two major difficulties that need to be overcome. The first one is of course related with reducing the CPU cycles as much as possible. As it will follow, any particularity of the system must be exploited to maximum for these large simulations to succeed. The second problem is the convergence of iterative process. As it was observed after running many simulations, the larger the nanoparticle gets the more difficult is to make the iterative process converge. This observation and attempts of solving this problem have triggered our interest for a rigorous analysis of the Kohn-Sham equations. The question we tried to answer was the existence and uniqueness for these equations. These results will be presented in the first section of this chapter. They will be stated without the proofs which are too technical for the present context. However, it was
this study that clearly identified the cause of the slow convergency and this was a
decisive step for overcoming the problem of slow convergence.[33, 34, 35]

The LDA will be implemented to three small nanoshells, which were characterized
by optical experiments. The experimental data were obtained as snapshots during
the growing process of a complete nanoshell. At the intermediate times when the
snapshots were taken, the nanoshells were not fully completed. At these stages,
the nanoshells have a rugged surface. In a first approximation however, they can
be modeled as perfect shells and from classical Mie simulations, one can determine
their geometry. Complete shells of sizes considered in this section have not been yet
fabricated experimentally. However, the experimentally measured optical absorption
of these incomplete nanoshells will provide a test for our theoretical predictions.

4.2 A Short Overview of the Density Functional Theory

We start this chapter with a short overview of the Density Functional Theory.
The foundations of the Density Functional Theory are contained in two theorems,
which were both proved by Hohenberg and Kohn in 1964.[36] Very formally, these
theorems can be stated as follows.

1. The electron density \( n(\vec{r}) \) in the ground state is in one to one relation with the
   background potential.

2. There exists a universal functional \( F_{HK} \) depending only on the particle density,
   i.e. independent of the background potential \( u \), such that the ground state
energy is given by

\[ E_g = \inf_n \{ F_{HK} [n] + \int nud\bar{r} \}. \]  \hspace{1cm} (4.1)

The Hohenberg-Kohn functional can be defined as it follows. The ground state energy of a \( N \) body system,

\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \vec{\nabla}_{i}^2 + \sum_{i=1}^{N} u(\bar{r}_i) + \frac{1}{2} \sum_{i \neq j}^{N} v(\bar{r}_i - \bar{r}_j), \]  \hspace{1cm} (4.2)

is defined by

\[ E [u] = \inf\{ \langle \Psi | \hat{H} | \Psi \rangle, \Psi \in W_N \} \]  \hspace{1cm} (4.3)

\[ W_N = \{ \Psi, \text{antisymmetric}, \langle \Psi | \Psi \rangle = 1, \langle \nabla_i \Psi | \nabla_i \Psi \rangle < \infty \}. \]

The ground energy is a functional of the background potential \( u \), i.e. there is a one to one relation between the two. Then one can use the first theorem to transfer the functional dependence of \( E [u] \) on \( u \) into a functional dependence on \( n \) by substituting \( u [n] \). The Hohenberg-Kohn functional is defined by:

\[ F_{HK} = E [u [n]] - \int n u [n] \, d\bar{r}. \]  \hspace{1cm} (4.4)

At this stage, the theorems make no clear steps towards solving for the ground state of the many body system. This is because finding the Hohenberg-Kohn functional will require first to calculate the ground state of the system. However, the Hohenberg-Kohn theorems contain the key for further developments. Let us explain why these theorems are so important. Before DFT has been invented, scientists relayed on
the Hartree-Fock approximation for their electronic structure calculations. In the Hartree-Fock approximation, the ground state wave function is approximated by a Slater determinant. This is an approximation because an antisymmetric function \( \Psi(\vec{r}_1, ..., \vec{r}_N) \) cannot be always written as a Slater determinant. The key observation now is that, while an antisymmetric wave function cannot be always written as a Slater determinant, the density corresponding to an antisymmetric wave function can be written as a density coming from one or a combination of Slater determinants.[37, 38, 39] At this point, the Hohenberg-Kohn theorems become relevant. Because the variational statement of Eq. (4.1) depends only on the density, it is irrelevant how we expressed the density as long as we sweep the entire set of densities. This fact has been exploited by Kohn and Sham, who in 1965 were able to write the Euler Lagrange equations corresponding to the Hohenberg-Kohn functional.[40]

\[
\left( -\frac{1}{2} \nabla^2 + u + v_{eff} [n] \right) \phi_i = \varepsilon_i \phi_i \tag{4.5}
\]

\[
n(\vec{x}) = \sum_{i=1}^{N} |\phi_i (\vec{x})|^2.
\]

The equations look like the Hartree-Fock equations. There are two major differences however. The Hartree-Fock method cannot be improved and all one can hope is that the answers it provides are closed to reality. The Kohn-Sham equations on the other hand, will lead to the exact density if the effective potential is known. This means that better and better approximations of the effective potential will lead to better and better results. The second difference is that the effective potential now may have
a complicated functional dependence on the density. To find good approximations for the effective potential, one has to use all the information available, including analytical or computer assisted calculations (especially the Quantum Monte Carlo simulations) and the available experimental data. The Local Density Approximation is the most popular approximation because of its simplicity. In general, the effective potential is divided in a Hartree term and another term called the exchange-correlation potential, that contains all the effects beyond the mean field approximation,

\[ v_{\text{eff}} [n] = \int v(\vec{r} - \vec{r}') n(\vec{r}') \, d\vec{r}' + v_{xc} [n]. \tag{4.6} \]

In LDA, the exchange-correlation potential becomes a function instead of a functional of \( n \). The value of \( v_{xc} (n) \) is parametrized such that LDA correctly describes the ground state energy of the homogeneous electron gas.

Finally, it should be mentioned that the zero temperature formalism can be extended to finite temperatures as it was proven in the same year by Mermin.\[41\] In this case, one has to replace the ground state energy with the grand canonical potential which becomes a functional of the density of particles. The Euler Lagrange equations for this functional have a similar form,

\[ \left(-\frac{1}{2} \vec{\nabla}^2 + u + v_{\text{eff}} [n]\right) \phi_i = \epsilon_i \phi_i, \tag{4.7} \]

where the effective potential is now temperature dependent. The density of particles is given by

\[ n(\vec{r}) = \sum_i \left(1 + e^{\beta(\epsilon_i - \mu)}\right)^{-1} |\phi_i(\vec{r})|^2. \tag{4.8} \]
The chemical potential $\mu$ has to be adjusted such that the number of particles remains fixed,

$$ N = \sum_i \left( 1 + e^{\beta(\varepsilon_i - \mu)} \right)^{-1}. $$

(4.9)

As one can see, the finite temperature formalism involves an infinite set of orbitals. In practice however, only the states with energy less than approximately $\mu + kT$ has to be considered. The rest of the orbitals have a negligible contribution to the density of particles. In our simulations for example, all the bound states are included in $n(\vec{r})$ and the continuum states are neglected. This is totally justified because metals have a large ionization potential, which means that the continuum states are far above the Fermi energy.

4.3 Existence, Uniqueness and Thermodynamic Limit for Kohn-Sham Equations

While most of the work on the Kohn-Sham formalism has been focused on finding better and better approximations of the exchange-correlation potential or implementing the formalism to different physical systems, very little it is known (on a rigorous ground) about the solutions of these equations. While for an exact exchange-correlation potential the equations are expected to have a unique solution if we are far from a phase transition, the uniqueness is not obvious at all for the approximations used in the practical calculations. It should be pointed that, at the time when this
study has been initiated, the question of uniqueness and the thermodynamic limit was still open even for Hartree or Hartree-Fock equations. The results for finite volume and finite temperature are stated below.

**Theorem 1.** Suppose the following conditions are satisfied.

C1) The Kohn-Sham Hamiltonian is self-adjoint for all densities with \( N \) particles.

C2) For \( n \) and \( n' \) two arbitrary densities with \( N \) particles, the effective potential satisfies

\[
\int_{V} |v_{\text{eff}}[n](\vec{r}) - v_{\text{eff}}[n'](\vec{r})| \, d\vec{r} < L \int_{V} |n(\vec{r}) - n'(\vec{r})| \, d\vec{r}, \tag{4.10}
\]

for some positive and finite constant \( L \).

Then the Kohn-Sham equations have a unique solution at finite temperatures, provided the coupling constant is smaller than a critical value. This critical value depends on the constant \( L \) of Eq. (4.10) and temperature.

Also, it follows that, if C1) and C2) are satisfied, than the usual iterative process used for solving the Kohn-Sham equations converges to a unique solution, independent of the starting point. The interesting part comes when the thermodynamic limit is considered, i.e. the number of particles and the volume of the system is increased to infinity. To properly talk about the thermodynamic limit, we need to know how the background potential behaves as the volume become larger and larger. A common assumption is that the background potential is periodic. The same assumption has been made in our study. If \( N_0 \) denotes the number of particles in the primitive cell \( \Omega \),
the thermodynamic limit consists of taking the number of primitive cells to infinity while keeping the number of particles per unit cell constant to \( N_0 \).[35]

**Theorem 2.** Suppose the following conditions are satisfied.

T1) The Kohn-Sham Hamiltonian is self-adjoint for all periodic densities with \( N_0 \) particles in the primitive cell.

T2) For \( n \) and \( n' \) two periodic, but otherwise arbitrary densities, the effective potential satisfies

\[
\int_\Omega |v_{eff}^n (\vec{r}) - v_{eff}^{n'} (\vec{r})| \, d\vec{r} < L \int_\Omega |n (\vec{r}) - n' (\vec{r})| \, d\vec{r}.
\]  \( (4.11) \)

T3) The effective potential converges in the following way,

\[
\int_\Omega |v_{eff}^{K+1} [n] (\vec{r}) - v_{eff}^K [n] (\vec{r})| \, d\vec{r} \rightarrow 0,
\]  \( (4.12) \)

as the number of primitive cells is increased from \( K^3 \) to \((K+1)^3\) and \( K \) goes to infinity.

Then the Kohn-Sham equations have a unique solution for all volumes provided the coupling constant is smaller than a critical constant, which is independent of volume. The sequence of finite volume solutions of the Kohn-Sham equations converges as the volume goes to infinity.

The conditions T1)-T3) represents the most general conditions we could find on the effective potential for the thermodynamic limit to be well defined. These conditions are not yet optimal and can be improved. Regarding the Local Density Approximation we were able to prove the following.[35]
**Theorem 3.** Suppose the following conditions are satisfied.

L1) The singularity of the two-body interaction is at least $L^2$ integrable, i.e.

$$\int |v((|\vec{r} - \vec{r}'|)|^2 d\vec{r}' < \infty, \quad (4.13)$$

where the integration is over any finite vicinity of $\vec{r}$.

L2) The two-body interaction decays at least as $r^{-2}$ asymptotically, i.e.

$$v(\vec{r}) \sim r^{-a} \text{ as } r \to \infty, \quad a > 2. \quad (4.14)$$

L3) The exchange-correlation potential is differentiable and there exists $p \geq 1$ such that

$$v_{xc}(n)/n^{1/p} < \infty, \quad n^{1-1/p} \frac{dv_{xc}(n)}{dn} < \infty \quad (4.15)$$

for all $n \in (0, \infty]$.

Then, the effective potential satisfies the conditions T1)-T3).

Condition L3) is satisfied by the local density approximation used in our simulations for gold nanoshells. Condition L1) is also satisfied by the Coulomb interaction but the condition L2) it is not. We believe that our methods can be improved and, at the end, the thermodynamic limit can be proven also for long range interactions such as the Coulomb force. Examining the proof of these results, it is easy to identify that it is in fact the Hartree term that limits our results to short range interactions.

This actually prompted us to study first the Hartree approximation where our first results were valid only for interactions that decays at least as $v \sim r^{-3}$. [33, 34] The
charge neutrality however proved to be essential when longer range interactions are considered and it helped us to extend the results to longer range interactions as it was stated in the third Theorem of this section.

At the end of this section we want to mention that, at zero temperature, we were able to prove that the Kohn-Sham equations do not have, in general, a unique solution. The full proof has been given only for Hartree model, but the methods can be easily extended to the Kohn-Sham equations.[43] These bifurcations occur when there is an incomplete last occupied energy level. For this reason, our calculations are carried at finite temperatures.

4.4 LDA Implementation to Metallic Nanoshells

The electronic structure of the metallic nanoshells will be determined by solving self consistently the Kohn-Sham equations

\[
\left(-\frac{1}{2}\Delta + V_{\text{ext}} + v_H + v_{\text{zc}} [n]\right) \phi_i = \varepsilon_i \phi_i
\]

\[
n(\vec{x}) = \sum_i (1 + e^{\beta(\varepsilon_i - \mu)})^{-1} |\phi_i(\vec{x})|^2.
\]

The chemical potential is fixed by the condition:

\[
N = \sum_i (1 + e^{\beta(\varepsilon_i - \mu)})^{-1},
\]

\(N\) being the number of conduction electrons. The external potential \(V_{\text{ext}}\) represents the interaction of the conduction electrons with the positively charged ion cores. As in the previous chapter, a jellium approximation will be used, defined by the following
parameters:

\[
V_{\text{ext}}(\vec{r}) = \begin{cases} 
0.02 \text{ Ha}, & \text{for } r < a \\
-0.16 \text{ Ha}, & \text{for } a < r < b \\
0 \text{ Ha}, & \text{for } b < r.
\end{cases} \tag{4.18}
\]

This background potential leads to an ionization potential of approximately 5.4 eV for a density of electrons corresponding to \( r_s = 3 \) a.u., appropriate for gold. The local density approximation of the exchange correlation potential was taken from Ref. [30].

Because the system is spherically symmetric, the Kohn-Sham orbitals must be of the form, \( r^{-1}u_{lk}(r)Y_{lm}(\hat{r}) \), in which case the Kohn-Sham equations can be reduced to a set of coupled radial Schroedinger equations:

\[
\left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_{\text{eff}}[n] \right) u_{lk}(r) = \varepsilon_{lk} u_{lk}(r), \tag{4.19}
\]

where

\[
n(r) = \frac{2s+1}{r^2} \sum_{l,k} \frac{2l+1}{1 + e^{\beta(\varepsilon_{lk} - \mu)}} |u_{lk}(r)|^2. \tag{4.20}
\]

In the largest simulation performed so far, the angular quantum number \( l \) was as high as 300 and the radial quantum number \( k \) of the discrete states was as high as 18. Thus, even with the spherical symmetry, one still needs to compute around 3000 orbitals each iteration. In consequence, the success of this program depends on how fast can one perform each iteration.

The Kohn-Sham orbitals are found by direct integration of the radial Schroedinger equations. We start the iteration process with \( n = n_0 \), the density of the positive
background charges, and suppose we know the density and the effective potential after $k$ iterations. At this moment, we pick an arbitrary energy, between the lowest value of the effective potential and zero, and the radial Schroedinger equation,

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_{\text{eff}}(r) - E\right) u_{l,E}^{1,2} = 0,$$

(4.21)

is directly integrated using a 4-th order Runge-Kutta algorithm. $u_{l,E}^1$ corresponds to the boundary conditions

$$u_{l,E}^1(r) \approx r^{l+1}, \quad \frac{d u_{l,E}^1(r)}{dr} \approx (l+1) r^l \quad \text{for} \ r \to 0,$$

(4.22)

and $u_{l,E}^2$ to the boundary conditions

$$u_{l,E}^2(r) \approx e^{-\sqrt{2|E|}}, \quad \frac{d u_{l,E}^2(r)}{dr} \approx -\sqrt{2|E|} e^{-r\sqrt{2|E|}} \quad \text{for} \ r \to \infty.$$  

(4.23)

The eigenvalues correspond to those particular values of the energy $E$ for which the two solutions become linear dependent, i.e. the Wronskian,

$$W(E) = u_{l,E}^1(r_0) \frac{d u_{l,E}^2(r_0)}{dr} - u_{l,E}^2(r_0) \frac{d u_{l,E}^1(r_0)}{dr},$$

(4.24)

cancels out. It is more practical to use this condition in the following form:

$$\frac{1}{u_{l,E}^1(r_0)} \frac{d u_{l,E}^1(r_0)}{dr} - \frac{1}{u_{l,E}^2(r_0)} \frac{d u_{l,E}^2(r_0)}{dr} = 0.$$ 

(4.25)

This condition should be independent of where $r_0$ is located. In the above form however, $r_0$ must not coincide (or be close) with a node of the two solutions. In the present calculations, $r_0$ will be always located at a local maximum or minimum of the wave function $u_{l,E}^1$. The local maxima and minima can be easily found during
the process of direct integration. To find all the eigenvalues, one has to sweep the value of energy $E$ from the bottom of the effective potential $v_{eff}(r)$ up to zero and count the points where the Wronskian changes its sign. We remember that, for each $E$, one has to solve the differential equation Eq. (4.21) with the boundary conditions Eqs. (4.22) and (4.23) and the process has to be repeated for each $l$. Typically, one needs an accuracy of at least four decimals for the eigenvalues. This requires a large number of grid points which in the present calculations is 33,000. In consequence, one can easily see why computing the eigenvalues is the most time consuming step of our program. This is why the following observation is crucial. The eigenvalues have a certain structure, given by the fact that, for two consecutive angular quantum numbers, $l$ and $l + 1$, the corresponding eigenvalues $\varepsilon_{lk}$ and $\varepsilon_{l+1,k}$ are very close and $\varepsilon_{l+1,k}$ is always above $\varepsilon_{lk}$. Moreover, as the size of the nanoparticle increases, the eigenvalues come closer and closer to each other. In consequence, the energy $E$ must be swept over a large interval only for $l = 0$. Once the eigenvalues for $l = 0$ are found, the eigenvalues for $l = 1$ are found by searching in a vicinity of the $\{\varepsilon_{l=0,k}\}_k$. The same argument applies for $l = 2$ and so on. Once all the eigenvalues are found, we use a 4-th order Runge-Kutta to compute the normalized eigenvectors.

The second difficult problem is the convergence of the iterative process. It was already pointed out in the literature that iterative methods,[44] which work just fine for small systems, will diverge for large many-body systems. The analysis presented in the previous section becomes very important at this point. When the thermo-
dynamic limit of the Kohn-Sham equations was investigated, it became clear that interactions with long range, such as the Coulomb interaction, can rise difficult problems. Moreover, it was proven that it is the Hartree term that is responsible for these convergency problems. But once the cause of the problem has been identified, it is easy to find a solution. One has to replace the Coulomb interaction with a screened Coulomb interaction in the Hartree potential:

$$ v_H \rightarrow \int \frac{e^{-|\vec{x} - \vec{y}|/\lambda}}{|\vec{x} - \vec{y}|} n(\vec{y}) d\vec{y}. $$

(4.26)

In this case, the iteration converges and suppose the result is $n_\lambda$. The next step is to increase the screening length $\lambda$ by a finite amount and start again the iteration process with $n_\lambda$ as the initial density. This step has to be repeated until the results stabilizes. In the present calculations, the screening length was increased by 2 a.u. and, for each $\lambda$, 8 iterations were needed to achieve the convergence. The first four decimals of the eigenvalues become independent of $\lambda$ for $\lambda \gtrsim 40$ a.u..

The above implementation is applied in the following to three gold nanoshells which were fabricated and characterized by optical measurements.[3] The first nanoshell has an inner radius of 4.1 nm (77.47 a.u.) and outer radius of 5.1 nm (96.37 a.u.) and contains around $1.6 \times 10^4$ conduction electrons. The second nanoshell has an inner radius of 8.6 nm (162.05 a.u.) and outer radius of 9.9 nm (187.07 a.u.) and contains around $8.4 \times 10^4$ conduction electrons. The third nanoshell has an inner radius of 13.1 nm (247.54 a.u.) and outer radius of 15.1 nm (285.33 a.u.) and contains around $3 \times 10^5$ conduction electrons. Figure 4.1 shows the density of states of the
Figure 4.1  The calculated density of states for the 4.1-5.1 nm nanoshell. The plot represents the eigenvalues and the corresponding degeneracy.
smallest nanoshell. The density of states displays a set of branches that correspond to different radial quantum numbers $k$. Each branch starts from $\varepsilon_{l=0,k}$ and contains all the eigenvalues $\varepsilon_{lk}$, $l = 0, 1, \ldots$. The figure also illustrates the fact that $\varepsilon_{kl}$ are very close for consecutive angular quantum numbers, as it was pointed above. These DOS are typical for spherically symmetric systems and similar results were found for solid metallic particles or the C$_{60}$ molecule. Figures 4.2, 4.3 and 4.4 present the calculated electron density distribution and the effective potential after the convergence have been achieved for the three nanoshells under study. The oscillations inside the shell are due to the nodes of the occupied eigenstates as explained in the previous chapter. The sharp oscillations near the inner and outer surface of the shell are Friedel oscillations and have a wavelength of $\pi/k_F$. The Friedel oscillations will have an important effect on the optical properties of the nanoshells. For the effective potentials, it should be noted the dipole potential induced at the nanoshell surfaces. Such surface effects were also found in the case of the semi-infinite homogeneous electron gas.
Figure 4.2  The calculated electron density (panel a) and the effective potential (panel b) for the 4.1-5.1 nm nanoshell. The dashed line in panel a) represents the positive background charge.
**Figure 4.3** The calculated electron density (panel a) and the effective potential (panel b) for the 8.6-9.9 nm nanoshell. The dashed line in panel a) represents the positive background charge.
Figure 4.4  The calculated electron density (panel a) and the effective potential (panel b) for the 13.1-15.1 nm nanoshell. The dashed line in panel a) represents the positive background charge.
Chapter 5

Optical Properties of Metallic Nanoshells

5.1 Introduction

The optical response of the metallic nanoshells has been studied in a series of experiments where monodispersive nanoshells of different shell thickness and core sizes have been fabricated and characterized by optical measurements. The agreement between the classical Mie theory and the experiment is quite amazing. In fact, using the measured optical absorption spectrum and the classical Mie theory, it was possible to predict, thus control, the geometry of the nanoshells during the chemical reaction used to fabricate these nanoparticles. This chapter will be devoted to the calculation of the optical absorption spectrum of the metallic nanoshells, but this time from the first principles. Even though the classical Mie theory explains so well the optical response of these nanoparticles, a first principle calculation will be important for the following reasons. First, it will provide the dielectric function of the metallic phase. This is a critical input in the classical Mie simulations. The dielectric function assumed in the classical simulations is that of the bulk metal. Corrections that account for surface scatterings (finite size) have been also considered and shown to improve the results. Second, a full quantum description can incorporate effects that cannot be treated classically, such as molecules chemically binding to the nanoshell
surface or the presence of bias magnetic or electric fields. The frequency dependence of the polarizability has been theoretically investigated for another nanoscale system with a shell geometry: the $C_{60}$ molecule.[45, 46, 47, 48, 49, 50, 51, 52, 53] There are two major differences between this system and the nanoshells of our study. A gold nanoshell has a lower electron density, i.e. larger $r_s$, resulting in a lower plasmon energy than the $C_{60}$ molecule. The second difference is a larger ionization potential for the gold nanoshells. As a consequence, discrete-discrete excitations will contribute in the frequency range around the collective plasmon excitations. For this reason, the contribution of the discrete states to the response functions must be evaluated carefully. The method we present below for the calculation of the polarizability is based on the theoretical approach by Zangwill and Soven which is known as the Time Dependent Local Density Approximation (TDLDA).[23] Although the LDA describes, in principle, only the ground state properties of the electronic systems, its implementation within RPA is known to often provide realistic description of the optical response of real systems such as atoms,[23, 25] large molecules,[51, 46] or clusters of atoms.[54]
5.2 TDLDA Implementation

The dipole moment induced by a time varying electric field, $\vec{E} = \vec{E}_0 e^{i\omega t}$, is defined by

$$\vec{P}(\omega) = \int d^3 \vec{r} \delta n(\vec{r}, \omega) \vec{r}, \quad (5.1)$$

where $\delta n(\vec{r}, \omega)$ is the induced screening charge. Within the linear response theory,[24] the screening charge is given by

$$\delta n(\vec{r}, \omega) = - \int \Pi(\vec{r}, \vec{r}'; \omega) \left( \vec{E}_0 \vec{r}' \right) d^3 \vec{r}', \quad (5.2)$$

where $\Pi$ is the response function, summed over the spin degrees of freedom, which has been already introduced in Chapter 3. Due to the spherical symmetry of the system, $\Pi$ can be factorized like

$$\Pi(\vec{r}, \vec{r}'; \omega) = \sum_{l,m} \Pi_l (r, r'; \omega) Y_{lm} (\hat{r}) Y_{lm}^* (\hat{r}'). \quad (5.3)$$

With this expression, the induced dipole moment can be written as

$$\vec{P}(\omega) = -\vec{E}_0 \frac{4\pi}{3} \int r^3 \Pi_{l=1} (r, r'; \omega) r' d\omega dr dr', \quad (5.4)$$

which leads to the following expression for the polarizability:

$$\alpha(\omega) = -\frac{4\pi}{3} \int r \vec{\Pi}_{l=1} (r, r'; \omega) r' d\omega dr dr', \quad (5.5)$$

where we use the more convenient function:

$$\vec{\Pi}_{l=1} (r, r'; \omega) = r^2 \Pi_{l=1} (r, r'; \omega) r'^2. \quad (5.6)$$
The photoabsorption cross section is directly related to the polarizability through

\[ \sigma_{abs} (\omega) = \frac{2\pi}{c} \omega \Im \alpha (\omega). \] (5.7)

We will compute the response function in the random phase approximation, defined by the integral equation:

\[ \Pi^{\text{RPA}} (\vec{r}, \vec{r}'; \omega) = \Pi^0 (\vec{r}, \vec{r}'; \omega) + \int d^3 r_1 \int d^3 r_2 \Pi^0 (\vec{r}, \vec{r}_1; \omega) \times \left[ \frac{1}{|\vec{r}_1 - \vec{r}_2|} + \frac{\delta^2 E_{xc}}{\delta n (\vec{r}_1) \delta n (\vec{r}_2)} \right] \Pi^{\text{RPA}} (\vec{r}_2, \vec{r}'; \omega), \] (5.8)

where \( \Pi^0 \) is the response function for the independent electrons. In the local density approximation,

\[ \frac{\delta^2 E_{xc}}{\delta n (\vec{r}_1) \delta n (\vec{r}_2)} = \delta (\vec{r}_1 - \vec{r}_2) \left. \frac{d v_{xc} (n)}{dn} \right|_{n=n(\vec{r}_1)}. \] (5.9)

For the component we are interested in, \( l = 1 \), the RPA approximation reads:

\[ \tilde{\Pi}^{\text{RPA}}_{l=1} (r, r'; \omega) = \tilde{\Pi}^0_{l=1} (r, r'; \omega) + \int dr_1 \int dr_2 \tilde{\Pi}^0_{l=1} (r, r_1; \omega) \times \left[ \frac{4\pi}{3} \frac{r_1^2}{r_2^2} + \delta (r_1 - r_2) v_{xc} (n (r_1)) / r_2 \right] \tilde{\Pi}^{\text{RPA}}_{l=1} (r_2, r'; \omega), \] (5.10)

where \( r_1 \) and \( r_2 \) represents the maximum and minimum of \( r_1 \) and \( r_2 \) respectively.

This equation can be solved first and then plugged into Eq. (5.5) to calculate the polarizability.[44, 19] However, a more efficient approach is outlined below. The first step is to define the induced dipole-moment density:

\[ \alpha (r, \omega) = -\int \tilde{\Pi}_{l=1} (r, r'; \omega) r'dr'. \] (5.11)
Multiplying Eq. (5.11) by \( r' \) and integrating over \( r' \), we obtain the equation

\[
\alpha^{RPA} (r, \omega) = \alpha^0 (r, \omega) + \int dr_1 \int dr_2 \Pi_{i=1}^0 (r, r_1; \omega) \times \left[ \frac{4\pi}{3} \frac{\tau_s}{r_2^3} + \delta (r_1 - r_2) v_{sc} (n (r_1)) / r_1^2 \right] \alpha^{RPA} (r_2, \omega).
\]  

(5.12)

Once this equation is solved, the polarizability follows from

\[
\alpha (\omega) = \frac{4\pi}{3} \int dr \frac{r \alpha (r, \omega)}{r}.
\]

(5.13)

The response function for the independent electrons can be computed with arbitrary accuracy. It can be expressed in terms of Green functions.\[23\] For \( l = 1 \), the expression takes the form,\[44\]

\[
\Pi_{i=1}^0 (r, r'; \omega) = \sum_{l_1, l_2, k} \frac{(l_1 + l_2 + 1)}{4\pi} f_\beta (\varepsilon_{kl_1}) u_{kl_1} (r) u_{kl_1} (r') \times [G_{l_1} (r, r'; \varepsilon_{kl_1} + \omega + i\delta) + G_{l_2} (r, r'; \varepsilon_{kl_1} - \omega - i\delta)],
\]

(5.14)

where \( G_l, l = 0, 1, \ldots, \) represent the radial Green functions:

\[
\left( \frac{1}{2} \frac{d^2}{dr^2} - \frac{l (l + 1)}{2r^2} - v_{\text{eff}} (r) + E + i\delta \right) G_l (r, r'; E + i\delta) = \delta_{rr'},
\]

(5.15)

and \( u_{kl} \) are the orbitals calculated in the previous section. Thus, all the contributions from the continuum spectrum have been incorporated in the Green function. These contributions are essential in our calculations because the energy of the antisymmetric plasmon mode already discussed in Chapter 2 is larger than ionization potential. The advantage of the above expression of the response function is that the Green function
can be computed virtually with infinite accuracy, using the Sturm-Liouville formula,

\[ G_l (r, r'; E + i\delta) = \frac{u_{l,E}^1 (r<) u_{l,E}^2 (r>)}{W(E)}, \]  

(5.16)

where \( W(E) \) is the Wronskian. Also, \( u_{l,E}^{1,2} \) are the solutions of the radial equation Eq. (5.15) with the boundary conditions

\[ u_{l,E}^1 (r) \approx r^{l+1}, \quad \frac{d u_{l,E}^1 (r)}{d r} \approx (l + 1) r^l \]  

(5.17)

for \( r \to 0 \), and

\[ u_{l,E}^2 (r) \approx e^{-r\sqrt{2(E+i\delta)}}, \quad \frac{d u_{l,E}^2 (r)}{d r} \approx i\sqrt{E+i\delta} e^{-r\sqrt{2(E+i\delta)}} \]  

(5.18)

for \( r \to \infty \). The square root is given by

\[ i\sqrt{E+i\delta} = (\cos \phi - i \sin \phi) \sqrt{E^2 + \delta^2} \]  

(5.19)

\[ \tan \phi = \frac{\delta}{\sqrt{E^2 + \delta^2} - E}. \]

This expression works for positive as well negative \( \delta \) as it is required in Eq. (7.13).

The value of the broadening parameter \( \delta \) was chosen at \( 10^{-3} \) Hartree. Some authors have argued that an \( \omega \) dependent \( \delta \) should be more appropriate.[45] For example, since the relative rather than the absolute error in the energy resolution in a measurement typically is constant, a linear dependence of \( \delta \) on \( \omega \) could be used.[46]

In the present calculations, these solutions of the radial equation have been calculated by using the 4-th order Runge-Kutta algorithm on the same grid points used in the electronic structure calculations. We found that it is paramount to calculate
the Green's function exactly in the same manner as we calculated the Kohn-Sham orbitals. The response function was recorded on a smaller grid. Only one in ten points of the electronic structure grid has been used for solving the RPA equation. Figure 5.1 illustrates the calculated frequency dependence of $\alpha(\omega)$ for a test nanoshell of inner radius $a = 76.5$ a.u. and outer radius $b = 127.5$ a.u. (aspect ratio 0.6). The curve looks very different from what would be expected from bulk jellium. As it was discussed in the first chapter, the classical approaches predict a symmetric and an antisymmetric plasmon oscillation mode for each angular momentum. Also, as it will be discussed later, the semiclassical limit of the RPA approximation predicts the same plasmon frequencies.[55] The energies of these plasmons are:

$$\omega_{l \pm}^2 = \omega_s^2 [1 \pm \frac{1}{2l + 1} \sqrt{1 + 4l(l + 1)x^{2l+1}}],$$

(5.20)

where $\omega_s = \sqrt{2\pi e^2 n_0 / m}$ is the flat surface plasmon energy, and $x$ depend on the shell geometry, $x = a/b$. The TDLDA prediction is in excellent agreement with the classical approach. It will be shown in the next section that this agreement is valid for a wide range of values of the aspect ratio.

5.3 Structural Tunability of the Plasmon Resonances

In this section, the time dependent local density approximation will be applied to a set of nanoshells in order to investigate the structural tunability of metallic nanoshells. This will prove that, indeed, the plasmon energies depend on the aspect ratio of the nanoshell in a manner similar to what has been predicted by the classical
Figure 5.1  The imaginary part of the calculated polarizability for a nanoshell of inner radius 76.5 a.u. and outer radius 127.5 a.u.. The arrows indicate the prediction of the classical Mie calculations for the plasmon frequencies. The inset shows the same results in a logarithimic scale.
Mie theory and the semiclassical approaches. The size of the nanoshells will be kept much smaller than the wavelength of the photons so that retardation effects can be neglected.[2] Figure 5.2 presents the calculated frequency dependence of $Im[\alpha(\omega)]$ for nine nanoshells with a thickness of 17 a.u. but with varying overall size. The calculated spectra are shown on a logarithmic scale in order to enhance the details.

The dominant features in each spectra are two prominent peaks corresponding to the symmetric shell plasmon mode $\omega_{1-}$ and the anti-symmetric $\omega_{1+}$ mode. Single particle excitations show up as narrow spikes in the low energy region (below the ionization potential 5.4 eV) and are strongest for the smallest nanoshells. The curves also display several collective features around the bulk plasmon mode at an energy $\omega_p = 9$ eV which will be further discussed below. For the largest nanoshell, which contains around $2 \times 10^5$ electrons, the single electron levels start to approach a continuum. Consequently the curves are relatively smooth and the optical response is dominated by collective excitations. The figure clearly shows that the energies of the dipolar plasmon resonances depend on the aspect ratio of the nanoshell. Figure 5.3 shows a comparison of the energies of the two dipolar plasmon resonances calculated using TDLDA and Eq. (5.20) as a function of the aspect ratio $x = a/b$ of the nanoshell. For the three largest nanoshells, the $\omega_+$ resonance lies very close to the aforementioned collective modes near the bulk plasmon frequency and it is difficult to assign a precise value. Our procedure for determining the $\omega_+$ value here is to fit a Lorentzian to the multiple peak structure and let its center be identified as the energy of the $\omega_+$. 
Figure 5.2  The imaginary part of the calculated optical absorption as a function of photon energy for several nanoshells of thickness 17 a.u. and varying sizes. The optical absorption spectra for each nanoshell has been offset for clarity. The plots are in a logarithmic scale. In order from the bottom, the nanoshells are of sizes 25.5-42.5, 31.6-58.6, 39.7-58.7, 51.0-68.0, 68.0-85.0, 96.3-113.3, 153.0-170.0, 209.7-226.7 and 323.0-340.0 a.u., respectively.
Figure 5.3  Comparison of calculated symmetric \( \omega_- \) and anti-symmetric \( \omega_+ \) plasmon resonances (open circles) for the nanoshells in Fig. 5.2 as a function of their aspect ratio \( x = a/b \) with the result from the classical Mie approximation (solid line).
mode. It can be seen that the calculated plasmon energies follow the predictions of
the classical Mie theory Eq. (5.20) when the aspect ratio of the nanoshell is varied
over a wide range of values.

The physical feature that makes the nanoshells attractive for practical applica-
tions is that there is only one parameter which controls the position of the absorption
peaks. Classical models show that the energy of the plasmon modes depend only on
the aspect ratio of the shell and it is independent of the overall size of the particle.
In the following, we apply TDLDA to a series of nanoshells with the same aspect
ratio but different overall size. In the upper panel of Fig. 5.4 we show the calculated
(TDLDA) optical absorption spectra $\text{Im}[\alpha(\omega)]$ for three different nanoshells. The
calculated plasmon energies show only a weak size dependence with a slight red shift
of the plasmon energies with increasing size of the shell. Such a size dependent shift
is absent for the simple expression of the plasmon energies Eq. (5.20) of a uniform
nanoshell but could be caused by a size dependent change in the electron density
distribution.[56] To investigate this effect, we apply the so called semi classical ap-
proach (SCA) to the electronic density profiles calculated for each nanoshell using
our LDA method.[55] The SCA is obtained from RPA in the limit where the energy
of quantum excitations is much smaller than the external excitation frequency. In
this limit, the response function depends only on the density of electrons. Therefore
SCA provides a convenient way of investigating the effects of the density profile. For
a uniform distribution of electronos, the SCA predicts the same plasmon energies as
Figure 5.4  The imaginary part of the calculated optical absorption as a function of photon energy for three nanoshells with the same aspect ratio, x=0.6, 25.5-42.5 a.u. (solid line), 51-85 a.u. (dashed line), and 76.5-127.5 a.u (dotted line). Panel a) shows the TDLDA results and panel b) shows the SCA results when the real electron density profiles are used. The inset shows the calculated $n(r)$ for the 76.5-127.5 a.u. nanoshell.
the classical Mie theory Eq. (5.20). The equation for the local polarizability, written in atomic units, becomes:

\[
\alpha(r, \omega) = -\frac{4\pi}{3(\omega^2 - \omega_{pl}^2(r))} \frac{dn}{dr} \left[ 1 - \int_0^\infty dr' G(r, r') \alpha(r', \omega) \right],
\]

(5.21)

where

\[
G(r, r') = 2\theta(r - r')(r'/r)^3 - \theta(r' - r).
\]

(5.22)

The local plasmon energy \(\omega_{pl}(r)\) is linked to the local density of electrons \(n(r)\) through \(\omega_{pl}^2(r) = 4\pi n(r)\). Equation (5.21) has been discretized using the same grid as in the TDLDA calculations. The resulting algebraic equation was solved using conventional methods. The results are shown in Fig. 5.4. It can be seen that the plasmon resonances obtained using Eq. (5.21) are much broader than the TDLDA results in panel a) of Fig. 5.4. This is caused by the SCA sampling of a charge density that varies between the bulk value in the center of the shell and zero outside its surfaces. The SCA calculations display a relatively strong absorption peak around 5 eV which is not seen in the quantum mechanical calculations. This feature is an artificial surface plasmon located in the region of reduced charge density in the surface region of the shell. The figure shows that the inclusion of a realistic electron density distribution rather than a simple step charge density model accounts for the weak red shift of the \(\omega_+\) mode observed in the TDLDA calculations. The TDLDA calculations in Fig. 5.4 show a small size dependence of the \(\omega_-\) resonant mode. For the smallest nanoshell, this resonant mode is slightly blue shifted with respect to the energy predicted by
Eq. (5.20). As the size of the nanoshell is increased, the $\omega_-$ resonant mode redshifts continuously until it reaches the value given by Eq. (5.20). This effect is absent in the SCA results which indicates that the SCA may break down for very small nanoshells where quantum size effects are expected to be strong.[57]

The data in Fig. 5.2 shows that for the largest nanoshells, several peaks at energies around the bulk plasmon frequency are observed. These features can be qualitatively understood from a simple step model of the surface charge density profile of the nanoshells. When the density of electrons is approximated by step functions, the integral equation Eq. (5.21) reduces to a set of linear equations.[56] When the surface charge is modeled as in the inset of Fig. 5.5, Eq. (5.21) reduces to a set of four linear equations and, consequently, four plasmon modes are expected. The curves in Fig. 5.5 show the energies of these plasmon resonances as a function of the ratio between the surface charge density and interior charge density $n_o/n_i$. For small $n_o$ there is very little coupling between the plasmon modes associated with the inner charge density $n_i$ and the surface charge density $n_o$. The energies of the two dipolar plasmon resonances associated with each charge density distribution are essentially given by the SCA result, Eq. (5.20) with $\omega_s$ evaluated for the two charge densities $n_o$ and $n_i$ and a geometry (78.5,125.5) a.u.. As $n_o$ increases, the plasmon modes interact resulting in more complicated, hybridized plasmon modes. For $n_o = n_i$, the physical situation is a homogeneous nanoshell of a (74.5,129.5) geometry. For this $n_o$, only three different plasmon energies are present. The two with the lowest energy are the
Figure 5.5  Calculated plasmon energies $\omega^i_+ \text{ and } \omega^0_+$ for nanoshells with a simple stepped surface charge electron density. The plasmon energies are calculated as a function of $n_o/n_i$, where $n_o$ is the surface charge density and $n_i$ is the interior electron density. The charge density model is schematically indicated in the inset.
two dipolar plasmon resonances for a nanoshell of geometry (74.5,129.5). The high energy modes collapse into a degenerate mode located exactly at the bulk plasmon energy and their spectral weights go to zero. If we further increase $n_o$, the degeneracy of the two high energy modes is lifted and their spectral weights become finite. From Fig. 5.5 it can be seen that a ratio of about 1.1 between $n_o$ and $n_i$ most suitably fits the TDLDA calculations for the (76.5,127.5) a.u. nanoshell. For this ratio, the step model predicts an energy of 4.25 and 8 eV for the lower energy modes and an energy of about 9.5 eV for the higher energy modes, in qualitative agreement with the results of Fig. 5.4. Such an $n_o \neq n_i$ ratio is in reasonable agreement with the charge density profile shown in the inset of Fig. 5.4, which includes strong Friedel oscillations near the surfaces.

5.4 Discussion and Summary

Summarizing, we have shown that the optical properties of real size metallic nanoshells can be modeled using a jellium model and TDLDA. We have implemented the TDLDA to a series of nanoshells with an overall diameter ranging from 4 nm up to 36 nm. For all nanoshells considered in this chapter, we found that the optical response is dominated by two collective resonant plasmon modes. The energy of the plasmon modes vary with the ratio of shell thickness to particle radius in a manner similar to what has been predicted earlier using classical Mie scattering and a semi-classical model applied to a nanoshell with uniform electron density. The strong
Friedel oscillations near the surfaces of the shell were found to induce additional collective modes at energies comparable with the bulk plasmon energy.
Chapter 6

The Effect of a Dielectric Core or Embedding Medium

6.1 Introduction

Prior to metallic nanoshells, the traditional approach for tuning the plasmon resonances of nanoparticles was by modifying the embedding medium of solid metal nanoparticles. The effect of dielectric coatings and embedding media on the optical properties of nanoparticles is an interesting and technologically important topic and has been the subject of many investigations in the past. Classical Mie scattering theory has been applied to metal-coated dielectric particles, oxide-coated metallic particles and metallic particles in dielectric solutions,[9, 58, 59, 60, 61] and found to well explain experimentally observed dependencies of optical properties of nanoparticles in dielectric media. In nanoshells, the possibilities to independently vary the dielectric properties of either the core or the embedding medium, in addition to the core and shell dimensions, provides several parallel strategies for the systematic control and modification of the optical resonances of this nanostructure.

First principles investigations on the effects of dielectric embedding media on the optical properties of nanoparticles have been relatively scarce. The systems of interest typically contain several thousands of atoms and rigorous quantum chemical
approaches cannot be applied. An \textit{ab initio} jellium on jellium approach for the calculation of the electronic structure and optical polarizability of a metallic cluster covered by a metallic layer has been developed and applied to small clusters in the size range of up to 100 atoms.[62] An extension of the jellium model has been also developed to include the effects of a dielectric embedding medium on the electronic structure and consequently on the optical properties of spherical metallic particles.[20] These studies have reported substantial deviations between the quantum mechanical and classical Mie calculations.

The purpose of this chapter is to include the effects of a dielectric core or embedding medium into the time dependent density functional theory (TDLDA) method. We will show that the presence of a dielectric medium has only a very small influence on the electronic structure of the nanoshell. The large effect of a dielectric core or embedding medium on the optical properties of nanoshells is due to the polarization of the dielectric. These polarizations need to be included self-consistently in the equations for the polarizability.

\section{6.2 Theory}

The TDLDA approach for calculating the polarizability of nanoparticles amounts to first calculating the electronic structure of the system and then self-consistently calculating the polarizability within the random phase approximation (RPA). The electronic structure of the nanoshell is calculated using a jellium model combined
with the local density approximation as was presented in Chapter 4. The effect of a dielectric phase on the electronic structure is included by modifying the Hartree potential so that it satisfies Poisson's equation and the boundary conditions at the interface between the metal and the dielectric.[20] In Fig. 6.1 we show a comparison of the electronic structure for the 40-80 a.u. nanoshell with a vacuum core in vacuum, a nanoshell with a dielectric core placed in vacuum and a nanoshell with a vacuum core placed in a uniform dielectric embedding medium. The density of states has been convoluted with a Gaussian of width 0.007 Ha. The figure clearly shows that the effect of the dielectric on the electronic structure is very small. The effect is largest when the nanoshell is embedded in a dielectric medium, resulting in an almost uniform shift of the electrostatic potential and the associated density of states. We will show below that the effects of the dielectric media on the electronic structure alone cannot account for the experimentally observed large effects of a dielectric core or embedding medium on the optical properties of metallic nanoshells.

The dominant effect of the dielectric media on the polarizability of the nanoshell comes from the induced screening charges at the boundary between the nanoshell and the dielectric. When the nanoshell is placed in a time dependent external field, $\vec{E}_0 \exp \imath \omega t$, the dielectrics will polarize and produce an additional component to the excitation field across the nanoshell. The electrons will not only screen the original excitation field, but also the field produced by the dielectric. In the following we will show how this effect can be included self-consistently in the RPA equation for the
Figure 6.1  The electronic structure of the 40-80 a.u. nanoshell with vacuum core placed in vacuum (solid), with dielectric core ($\epsilon_C = 4$) placed in vacuum (dotted) and with vacuum core placed in a dielectric medium ($\epsilon_E = 4$) (dashed). The figure illustrates the density of states in units of $10^5$ (panel a), electron density (panel b) and effective potential (panel c).
polarizability.

The two situations when a metallic shell with a dielectric core is placed in vacuum and when a metallic shell with no dielectric core is placed in dielectric medium can be treated within the same formalism. Let us consider a heterogeneous dielectric medium,

\[
\varepsilon = \begin{cases} 
\varepsilon_i \text{ for } r < r_0 \\
\varepsilon_o \text{ for } r > r_0.
\end{cases}
\]  

(6.1)

For \(\varepsilon_i = \varepsilon_C\), \(\varepsilon_o = 1\) and \(r_0 = a\), Eq. (6.1) will refer to the dielectric core with a dielectric constant \(\varepsilon_C\). For \(\varepsilon_i = 1\), \(\varepsilon_o = \varepsilon_E\) and \(r_0 = b\), Eq. (6.1) refers to the embedding medium with a dielectric constant \(\varepsilon_E\).

According to the linear response theory, the screening charge in the nanoshell is given by

\[
\delta n (\vec{r}, \omega) = \int \Pi^{(0)} (\vec{r}, \vec{r}'; \omega) [\delta v_{xc} (\vec{r}', \omega) + \phi (\vec{r}', \omega)] d\vec{r}',
\]

(6.2)

where \(\delta v_{xc}\) is the exchange-correlation contribution to the screening potential as it was already discussed. The potential \(\phi (\vec{r}, \omega)\) is the electric potential when the system is placed in the homogeneous electric field \(\vec{E}_0 \exp i\omega t\). If we have a composite dielectric medium, then the potential must satisfy Maxwell’s equations together with the appropriate boundary conditions. As it has been previously argued, one can consider the quasi-static limit of the Maxwell equations since for small nanoshells, the retardation effects are very small. [2] In this limit, the electric potential \(\phi\) must satisfy the
Poisson equation together with the boundary conditions at the dielectric interfaces:

\[
\begin{align*}
\vec{\nabla}^2 \phi (\vec{r}, \omega) &= -\frac{4\pi}{\varepsilon} \delta n (\vec{r}, \omega), \text{ for } \vec{r} \notin S_{r_0} \\
\varepsilon_i \frac{\partial \phi}{\partial n} |_{S_{r_0}^-} &= \varepsilon_o \frac{\partial \phi}{\partial n} |_{S_{r_0}^+},
\end{align*}
\]  

(6.3)

where \( S_{r_0} \) is the sphere of radius \( r_0 \). Due to the symmetry of the problem, we can write the screening charge in the following form:

\[
\delta n (\vec{r}, \omega) = E_0 \delta n (r, \omega) \cos \theta,
\]

(6.4)

where the OZ axis is oriented along the electric field \( \vec{E}_0 \). Using the notation \( v (r, r') = r_2 / r_2' \), the solution of Poisson’s equation Eq. (6.3) with the appropriate boundary conditions is given by:

\[
\phi (r, \theta) = -E_0 \cos \theta \left[ r + \frac{\varepsilon_o - \varepsilon_i}{\varepsilon_i + 2\varepsilon_o} r_0^2 v (r_0, r) \right] + \frac{4\pi}{3} E_0 \cos \theta \int v (r, r') \frac{\delta n (r', \omega)}{\varepsilon (r')} r'^2 dr' + \frac{4\pi}{3} E_0 \cos \theta \frac{\varepsilon_o - \varepsilon_i}{\varepsilon_i + 2\varepsilon_o} r_0^2 v (r_0, r) \times \int \frac{dv (r, r')}{dr} \left|_{r=r_0} \frac{\delta n (r', \omega)}{\varepsilon (r')} r'^2 dr'.
\]

(6.5)

Let us define the local polarizability as

\[
\alpha (r, \omega) = r^2 \delta n (r, \omega).
\]

(6.6)

The polarizability is then given by \( \alpha (\omega) = \frac{4\pi}{3} \int r \alpha (r, \omega) dr \). Using the decomposition:

\[
\Pi^{(0)} (\vec{r}, \vec{r}'; \omega) = \sum_{l,m} \Pi_{l}^{(0)} (r, r'; \omega) Y_{lm} (\hat{r}) Y_{lm}^* (\hat{r}'),
\]

(6.7)
the self-consistent equation for the local polarizability follows immediately from Eqs. (6.2) and (6.6):

\[
\alpha (r, \omega) = \int dr' \tilde{\Pi}_1^{(0)} (r, r'; \omega) r'^{-2} v_{xc} (r') \alpha (r', \omega)
\]

\[
-\frac{4\pi}{3} \int dr' \int dr'' \tilde{\Pi}_1^{(0)} (r, r'; \omega) \frac{v (r', r'')}{\varepsilon (r'')} \alpha (r''; \omega)
\]

\[
-\frac{4\pi}{3} X (r, \omega) \int dr' \frac{dv (r, r')}{dr} \frac{\alpha (r', \omega)}{\varepsilon (r')}
\]

\[=
-\int \tilde{\Pi}_1^{(0)} (r, r'; \omega) r' dr' - X (r, \omega),
\]

where

\[
X (r, \omega) = \frac{\varepsilon_o - \varepsilon_i}{\varepsilon_i + 2\varepsilon_o} r_0^2 \int \tilde{\Pi}_1^{(0)} (r, r'; \omega) v (r_0, r') dr',
\]

and

\[
\tilde{\Pi}_1^{(0)} (r, r'; \omega) \equiv r^2 \Pi_1^{(0)} (r, r'; \omega) r'^2.
\]

The independent electron response function \(\tilde{\Pi}_1^{(0)}\) is calculated directly from the electronic structure of the nanoshell using the approach described in the previous chapter.[63]

To demonstrate the importance of including the polarizability of the dielectric medium when calculating \(\alpha (\omega)\), we show in Fig. 6.2 the polarizability for a nanoshell with a vacuum core placed in a uniform dielectric embedding medium with \(\varepsilon_E = 4\) calculated with and without the \(X (r, \omega)\) term. For comparison we include the results for a nanoshell with a vacuum core placed in vacuum. Each optical absorption spectra is characterized by two dipolar plasmon resonances.[55, 63] The peak at the
Figure 6.2  The effect of the embedding dielectric medium ($\varepsilon_E = 4$) on the optical absorption of the 40-80 a.u. nanoshell. The dashed line includes only the change in the electronic structure and the dotted line includes both, the change in electronic structure and the term $X(r, \omega)$ is included in Eq. (6.9). For comparison we show the optical absorption for a nanoshell with a vacuum core placed in vacuum (solid line).
lower energy $\omega_-$ corresponds to symmetric coupling between surface charge oscillations on the inner and outer surface of the nanoshell. The peak at higher energies $\omega_+$ corresponds to anti-symmetric coupling. It can be seen the effects on the optical polarizability caused by the change in electronic structure are very minor. Only the symmetric mode $\omega_-$ shows a shift. As it will be discussed in the results section, the symmetric mode $\omega_-$ is dominated by the contribution from the plasmon resonance on the outer surface of the nanoshell. The anti-symmetric plasmon mode $\omega_+$ gets its dominant contribution from the (cavity) plasmon on the inner surface. The presence of a dielectric embedding medium will only influence the electronic structure on the outer surface and therefore leave $\omega_+$ relatively unaffected. In contrast, when the dielectric polarization term is included, a strong shift of $\omega_+$ to lower energies is induced. Also the anti-symmetric plasmon resonance $\omega_+$ is shifted to lower energies. The shifts caused by the polarization term will be further discussed and explained in the next section. The figure clearly demonstrates the importance of including the polarization of the dielectric medium $X(\tau, \omega)$ when calculating $\alpha(\omega)$.

6.3 Numerical results

We now apply the method presented in the previous section to calculate the frequency dependent polarizability of a gold nanoshell with inner radius $a = 40$ a.u. and outer radius $b = 80$ a.u.. We will investigate the effects of a dielectric core and embedding medium effects separately. The situation of both a dielectric core and a dielectric
embedding medium requires significant modifications of Eqs. (6.9) and (6.9) and it will be developed in the next chapter.

The upper panel in Fig. 6.3 shows the polarizability of the gold nanoshell for four different core dielectric constants when the nanoshell is placed in vacuum. The overall effect of the dielectric core is a shift of the dipolar plasmon energies to lower values. The effect is strongest for the anti-symmetric plasmon modes. Also, the relative amplitude of the symmetric and anti-symmetric resonances change with $\varepsilon_C$. The weight of the symmetric dipolar plasmon resonance decreases and the weight of the anti-symmetric mode increases as the dielectric constant increases.

For comparison, we also calculated the polarizability of the gold nanoshell using the extension of classical Mie scattering theory to coated spheres. [64] The nanoshell is here modeled using a Drude dielectric function:

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma},$$

(6.11)

where the bulk plasmon frequency $\omega_p = 9.07$ eV corresponds to the free electrons radius $r_s = 3.0$ we used to model the metallic phase in the TDLDA calculations. The damping parameter has been fixed to $\gamma = 0.132$ eV so that the plasmon widths in the classical and TDLDA calculations are similar. The lower panel in Fig. 6.3 shows the Mie calculations of the polarizabilities for the same dielectric constants as used in the TDLDA calculations. The energies and the shifts of the plasmon modes agree remarkably well in the two calculations. Also, both approaches predict a similar dependence of the weights of the two dipolar plasmon resonances with dielectric
Figure 6.3  The calculated optical absorption of the 40-80 a.u. nanoshell as a function of photon energy for 4 different core dielectric constants of 1 (solid), 2 (dashed), 3 (dotted) and 4 (dash-dotted). Panel a) shows the TDLDA results and panel b) shows the classical Mie theory results.
constant $\varepsilon_C$.

In Fig. 6.4 we show the TDLDA and the classical Mie scattering theory calculations of the frequency dependent polarizability of the same gold nanoshell with a vacuum core and embedded in a medium with different dielectric constants $\varepsilon_K$. The dielectric medium has the same overall effect of shifting the energies of the dipolar plasmon resonances to lower values as in the case of a dielectric core. However, the effect is much stronger for the symmetric dipolar plasmon resonance than for the antisymmetric mode. In contrast to the situation with a dielectric core, the weights of the symmetric dipolar plasmon resonance increase with the dielectric constant of the medium while the amplitude of the antisymmetric mode remains relatively constant.

The general finding that the presence of a dielectric core or embedding medium induces a redshift of the plasmon resonances is not surprising. We can interpret the shifts of the plasmon resonances using the results from Chapter 2. Quasistatically, the plasmon resonances of this system can be thought of in terms of a homogenous electron gas oscillating over a fixed positive background, with induced surface charges providing the restoring force. When the surrounding medium is a dielectric, it polarizes in response to the resulting field, effectively reducing the strength of the surface charge and leading to a decreased restoring force and, consequently, lowering the plasmon energies. A qualitative understanding of the shifts and changes of the weights of the dipolar plasmon peaks can be obtained by regarding the two dipolar plasmon resonances of a nanoshell as resulting from the interaction of a "bare" dipolar cavity
Figure 6.4  The calculated optical absorption of the 40-80 a.u. nanoshell as a function of photon energy for 4 different medium dielectric constants of 1 (solid), 2 (dashed), 3 (dotted) and 4 (dash-dotted). Panel a) shows the TDLDA results and panel b) shows the classical Mie theory results.
plasmon $|C^0>$ on the inner surface with an energy $\omega_C^0 = \sqrt{\frac{2}{3}} \omega_p$ and a "bare" surface plasmon on the surface of a solid sphere $|S^0>$ with an energy $\omega_S^0 = \frac{1}{\sqrt{3}} \omega_p$. With finite shell thickness, these plasmons interact and form a symmetric mode $|-->$ with energy $\omega_-$ and an anti-symmetric mode $|+>$ with energy $\omega_+$. The lower energy $\omega_-$ mode has a stronger admixture of $|S^0>$ and the higher energy $\omega_+$ mode has a stronger admixture of the $|C^0>$ mode. The coupling to incident electromagnetic light occurs predominantly through the outer component $|S^0>$.

We first consider the effect of a dielectric core on the optical absorption of the nanoshell. The presence of the dielectric core lowers the plasmon energy $\omega_C^0$. As this happens, both $\omega_+$ and $\omega_-$ will shift to lower energies. The effect is most pronounced for the $|+>$ mode since this mode contains a stronger admixture of the $|C^0>$ mode. As $\omega_C^0$ becomes more resonant with the surface plasmon $\omega_S^0$, the $|+>$ mode will contain a larger admixture of the $|S^0>$ plasmon and therefore couple stronger to light, resulting in an increased spectral weight in the absorption spectrum. This increase in spectral weight comes at the expense of a reduced admixture of $|S^0>$ in the $|-->$ mode and consequently a reduced spectral weight of the $\omega_-$ plasmon peak in the absorption spectrum.

When the nanoshell is embedded in a dielectric medium, the energy of the surface plasmon $\omega_S^0$ is lowered. This increases the energy difference between the bare modes $\omega_C^0$ and $\omega_S^0$. This results in an increased admixture of the $|S^0>$ component in the $|-->$ mode leading to a strong redshift of $\omega_-$ and an increased spectral weight in
the absorption spectrum. The lowering of $\omega^0_S$ with increased dielectric constant $\varepsilon_E$ slightly decreases the energy of the $\omega_+$ mode. Also the admixture of $|S^0>$ in the $|+>$ mode should decrease slightly. The expected decrease of the spectral weight of the $|+>$ mode shows up in the lower panel of Fig 6.4 but cannot really be seen in the upper panel of Fig. 6.4. Clearly, our qualitative conceptual "two-level" model for the nanoshell plasmons has its limitations.

6.4 Discussion and Summary

We have shown how to incorporate the effects of a dielectric core or a dielectric medium into the TDLD$\Delta$A self-consistent equations. We found that the presence of a dielectric core or a dielectric embedding medium have different and important effects on the optical properties of gold nanoshells. We demonstrated that the results obtained using classical Mie scattering theory are in good agreement with the fully quantum mechanical TDLD$\Delta$A results. The numerical implementation of the new self-consistent RPA equations can be done very efficiently. Because the most time consuming part of the polarizability calculations is when the free electron response function is calculated, the new RPA algorithms run practically at the same speed as the old ones. As we will see in the next chapter, the new algorithms can be applied to real size metallic nanoparticles. We should mention at the end that such extensions of the RPA equations have been considered in the past. These studies were primarily concerned with the effect of the highly polarizable ion cores of noble metals. The
method was pioneered by Liebsch, [65] who treated the ion cores as a background
dielectric medium. His results showed a major improvement in the flat surface plas-
mons calculations of Ag. His approach was later applied to spherical Ag clusters in
Ref. [66].
Chapter 7

Comparison with Experiment

7.1 Introduction

In the present chapter, we consider the more complicated but experimentally relevant situation where both a dielectric core and a dielectric embedding medium are present. In this case, there will be induced bound charges at the surfaces of both dielectrics. These surface charges will interact with each other resulting in a relatively complicated response of the system when externally excited. We show how the TDLDA equations can be extended to describe this more complex situation. We investigate the combined effects of dielectric cores and embedding media and show that the interaction of the screening charges at the dielectric interfaces plays a crucial role in determining the energies of the plasmon resonances. We find that the effect of the dielectric core on the plasmon resonances can be reduced or enhanced by the presence of a dielectric embedding medium and vice versa. The calculated dependence of the plasmon resonances on the dielectric constants of core and embedding media are found to be in good agreement with results from classical Mie scattering theory.

The theoretical extension presented in this chapter allows the first application of the TDLDA method to an experimentally available nanoshell system: a gold nanoshell with a gold sulfide core in an aqueous solution. [3] The optical absorption spectra
are calculated for nanoshells of three different sizes. The calculated plasmon energies are found to be in relative good agreement with the experimental results. In all three cases however, the calculated plasmon resonances are blue shifted relative to the experimental values. This clearly indicates that the polarization of the d-electrons must be taken into account. The inclusion of the d-electron effects brings the theoretically calculated plasmon frequencies in perfect agreement with the experimental values.

### 7.2 Theory

We start again from the TDLDA expression of the screening charge induced by an external electric field $E_0 e^{-i\omega t}$,

$$
\delta n(\vec{r}) = \int d\vec{r}' \Pi^{(0)}(\vec{r}, \vec{r}'; \omega) \left[ \delta v_{xc}(\vec{r}', \omega) + \phi_C(\vec{r}', \omega) \right],
$$

(7.1)

where $\Pi^{(0)}$ represents the response function of the independent electrons. $\delta v_{xc}$ represents the variation of the exchange-correlation potential due to the screening charge. The second term in Eq. (7.1) is the electric potential generated by the screening charge itself. This screening charge consists of induced charge densities both from the metallic shell and from the surfaces of the dielectric media. It is these latter contributions as well as their interactions that represent the new physics presented in this paper.

In the quasistatic limit,[67] the electric potential $\phi_C$ must satisfy the Poisson equation with the appropriate boundary conditions. We consider the following background
dielectric function:

\[
\varepsilon (r) = \begin{cases} 
\varepsilon_1 = \varepsilon_C & \text{for } r < r_1 \\
\varepsilon_2 = \varepsilon_S & \text{for } r_1 < r < r_2 \\
\varepsilon_3 = \varepsilon_E & \text{for } r_2 < r,
\end{cases}
\]

(7.2)

which accounts for the presence of the dielectric core, embedding medium and the d-electrons. Poisson’s equation for the electric potential then takes the form:

\[
\begin{align*}
\varepsilon_i \nabla^2 \phi_C (\vec{r}, \omega) &= -4\pi \delta n (\vec{r}, \omega) \\
\varepsilon_i \frac{\partial \phi_C}{\partial n} \bigg|_{r = r_i} &= \varepsilon_{i+1} \frac{\partial \phi_C}{\partial n} \bigg|_{r = r_i^+} \\
\phi_C (\vec{r}, \omega) &\rightarrow -\vec{r} \vec{E}_0 \text{ for } |\vec{r}| \rightarrow \infty.
\end{align*}
\]

(7.3)

The solution of the Poisson equation can be expressed as:

\[
\phi_C (\vec{r}, \omega) = -\vec{r} \vec{E}_0 + \int_{\mathbb{R}^3} \frac{\delta n (\vec{r}', \omega)}{\varepsilon (\vec{r}')} \frac{d \vec{r}'}{|\vec{r} - \vec{r}'|} + \sum_{i=1,2} \int_{S_i} \sigma^{(i)} (\vec{r}') dS',
\]

(7.4)

where \(\sigma^{(i)} (r)\) represent the bound surface charges distributed over the interfaces of the dielectrics \(S_i\). Because of the symmetry of the problem, \(\phi_C\) contains only dipolar terms. Then, we can assume

\[
\delta n (\vec{r}, \omega) = E_0 \delta n (r, \omega) \cos \theta,
\]

(7.5)

and Eq. (7.4) reduces to:

\[
\phi_C (\vec{r}, \omega) = \left( -r + \phi_V (r) + \sum_{i=1,2} r_i^2 \sigma^{(i)} v_1 (r, r_i) \right) E_0 \cos \theta.
\]

(7.6)

In this expression we have used the following notations:

\[
\phi_V (r) = \frac{4\pi}{3} \int \frac{v_1 (r, r')}{\varepsilon (r')} \delta n (r', \omega) r' d\vec{r}',
\]

(7.7)
and \( v_1 (r, r') = r_\lt / r_\gt^2 \), where \( r_\lt \) and \( r_\gt \) denotes the maximum and minimum respectively between \( r \) and \( r' \). The coefficients \( \sigma^{(i)} \) in Eq. (7.6) are found from the boundary conditions Eq. (7.3). A part of these coefficients will be independent of the screening charge and it is therefore appropriate to rewrite the coefficients as \( \sigma_0^{(i)} + \sigma^{(i)} \). From the boundary conditions:

\[
\sigma_0^{(1)} = \frac{1}{\xi_\varepsilon} \frac{\varepsilon_C - \varepsilon_S}{\varepsilon_C + 2\varepsilon_S \varepsilon_S + 2\varepsilon_E} \frac{3\varepsilon_E}{\xi_\varepsilon} 
\]

\[
\sigma_0^{(2)} = 1 - \frac{3\varepsilon_E}{\xi_\varepsilon \varepsilon_S + 2\varepsilon_E} 
\] (7.8)

and

\[
\sigma^{(1)} = -\frac{1}{\xi_\varepsilon} \frac{\varepsilon_C - \varepsilon_S}{\varepsilon_C + 2\varepsilon_S} \frac{\partial \phi_V}{\partial r} (r_1) + \frac{\xi_\varepsilon - 1}{2\xi_\varepsilon} \left( \frac{r_2}{r_1} \right)^3 \frac{\partial \phi_V}{\partial r} (r_2) 
\]

\[
\sigma^{(2)} = -\frac{\xi_\varepsilon - 1}{\xi_\varepsilon} \frac{\partial \phi_V}{\partial r} (r_1) + \frac{1}{\xi_\varepsilon} \frac{\varepsilon_E - \varepsilon_S}{\varepsilon_S + 2\varepsilon_E} \frac{\partial \phi_V}{\partial r} (r_2), 
\] (7.9)

where \( \xi_\varepsilon \) is a dielectric factor given by:

\[
\xi_\varepsilon = 1 - 2 \frac{\varepsilon_C - \varepsilon_S \varepsilon_E - \varepsilon_S}{\varepsilon_C + 2\varepsilon_S \varepsilon_S + 2\varepsilon_E} \left( \frac{r_1}{r_2} \right)^3. 
\] (7.10)

We can also divide the electric potential in two terms, \( \phi_C^0 + \phi_C \). The first term is the electric potential in the absence of the screening charge \( \delta n (\vec{r}, \omega) \), i.e. the response of the composite dielectric medium Eq. (7.2) when it is excited with the electric field \( \vec{E}_0 e^{-i\omega t} \). The expression for this term is given by:

\[
\phi_C^0 (\vec{r}) = (-r + \sum_{i=1,2} r_i^2 \sigma_0^{(i)} v_1 (r, r_i)) E_0 \cos \theta. 
\] (7.11)

The second term represents the screening of the above electric potential:

\[
\phi_C (\vec{r}, \omega) = (\phi_V + \sum_{i=1,2} r_i^2 \sigma^{(i)} (\omega) v_1 (r, r_i)) E_0 \cos \theta. 
\] (7.12)
Retaining only the dipolar terms in Eq. (7.1), and defining the local polarizability as
\( \alpha(r, \omega) \equiv r^2 \delta n(r, \omega) \) and \( \Pi_1^{(0)}(r, r'; \omega) = r^2 r'^2 \Pi_1^{(0)}(r, r'; \omega) \), the self-consistent equation reduces to:

\[
\alpha(r, \omega) = \int dr' \Pi_1^{(0)}(r, r'; \omega) \phi_C^0(r') \\
+ \int dr' \Pi_1^{(0)}(r, r'; \omega) r'^{-2} v'_{xc}(r') \alpha(r', \omega) \\
+ \frac{4\pi}{3} \int dr' \int dr'' \Pi_1^{(0)}(r, r'; \omega) \frac{v_1(r', r'')}{\varepsilon(r'')} \alpha(r'', \omega) \\
+ \sum_{i=1,2} r_i^2 \sigma^{(i)} \int dr' \Pi_1^{(0)}(r, r'; \omega) v_1(r', r_i).
\]

(7.13)

This expression can be simplified by introducing two quantities, which are independent of the screening charge:

\[
X_i(r, \omega) = r_i^2 \int dr' \Pi_1^{(0)}(r, r'; \omega) v_1(r', r_i).
\]

(7.14)

We now introduce the explicit expressions for \( \sigma^{(i)} \) in Eq. (7.13) and we factorize out terms like

\[
\frac{\partial \phi}{\partial r}(r_i) = \frac{4\pi}{3} \int dr' \frac{v_2(r_i, r')}{\varepsilon(r')} \alpha(r', \omega),
\]

(7.15)

where \( v_2(r, r') = dv_1(r, r')/dr \). The final integral equation for the local polarizability is:

\[
\alpha(r, \omega) = \int dr' \Pi_1^{(0)}(r, r'; \omega) r'^{-2} v'_{xc}(n(r')) \alpha(r', \omega) \\
- \frac{4\pi}{3} \int dr' \int dr'' \Pi_1^{(0)}(r, r'; \omega) \frac{v_1(r', r'')}{\varepsilon(r'')} \alpha(r'', \omega) \\
- \frac{4\pi}{3} \sum_{i=1,2} X^{(i)}(r, \omega) \int \frac{v_2(r_i, r')}{\varepsilon(r')} \alpha(r', \omega) dr' \\
= \int dr' \Pi_1^{(0)}(r, r'; \omega) \phi_C^0(r'),
\]

(7.16)
where
\[ X^{(1)} (r, \omega) = \frac{1}{\xi_c \xi \varepsilon_C + 2 \varepsilon_S} X_1 (r, \omega) - \frac{\xi_c - 1}{\xi_c} X_2 (r, \omega) \]  
(7.17)
\[ X^{(2)} (r, \omega) = \frac{\xi_c - 1}{2 \xi_c} \left( \frac{r_2}{r_1} \right)^3 X_1 (r, \omega) + \frac{1}{\xi_c \xi \varepsilon_C + 2 \varepsilon_E} X_2 (r, \omega). \]

The results can be checked by considering the following limits: \( \varepsilon_C, \varepsilon_S \to 1, \varepsilon_E, \varepsilon_S \to 1 \), or \( r_1 \to r_2 \). For these three cases, the above results should converge (and they do) to the results derived previously for the polarizability of a nanoshell with a dielectric core placed in vacuum, and a nanoshell with a vacuum core placed in a dielectric embedding medium.[67] Equation (7.18) explicitly illustrates the presence of an interaction between the screening charges on the two dielectric/metal surfaces and will be discussed in the following section.

### 7.3 TDLDA versus Mie Theory

In this section, the notation a-b will be used for a nanoshell of inner radius a and outer radius b. We investigate first the effects of the dielectric core and dielectric embedding medium. Thus, the background dielectric constant within the shell is fixed to \( \varepsilon_S = 1 \) in this section. In Fig. 7.1, the calculated optical absorption \( \text{Im}[\alpha] \) as a function of photon energy is shown for a test nanoshell (60-90 a.u.) with different dielectric cores and embedding media. For comparison the figure also includes the data for a nanoshell with a vacuum core in vacuum. Panel a) shows the effect on the optical absorption caused by a dielectric core. The dominant effect is a redshift \( \Delta \omega^C_+ = 1.0 \text{ eV} \) of the \( \omega_+ \) mode. The redshift of the \( \omega_- \) mode is smaller, \( \Delta \omega^C_- = 0.7 \text{ eV} \) as
Figure 7.1  The calculated optical absorption as a function of frequency for the 60-90 a.u. nanoshell with different dielectric cores $\varepsilon_C$ and embedding media $\varepsilon_E$. Panel (a) is for $\varepsilon_C = 4$ and $\varepsilon_E = 1$. Panel (b) is for $\varepsilon_1 = 4$ and $\varepsilon_E = 4$. Panel (c) is for $\varepsilon_C = 4$ and $\varepsilon_E = 4$. For comparison we also included the case $\varepsilon_C = 1$ and $\varepsilon_E = 1$ (dashed line)
discussed previously. [67] Panel b) shows the effect of a dielectric embedding medium on the two modes. Using a similar notation as above, we find for the redshifts of the plasmon peaks $\Delta \omega^E_0 = 0.2 \text{ eV}$ and $\Delta \omega^E_1 = 1.5 \text{ eV}$. Panel (c) shows the combined effect of the two dielectric media. The figure clearly shows that the shifts of the plasmon modes when both a dielectric core and embedding medium is present are different than the sum of the shifts induced by the individual dielectric media. The combined shift of the $\omega_+$ mode $\Delta \omega^{CE}_+ = 1.5 \text{ eV}$ which is larger than $\Delta \omega^C_+ + \Delta \omega^E_+$. The figure also shows that $\Delta \omega^{CE}_- = 1.5 \text{ eV}$ which is smaller than $\Delta \omega^C_- + \Delta \omega^E_-$. The nonadditivity of the influences of the dielectric core and dielectric embedding medium is caused by the interaction of the surface charges on the two dielectric surfaces described by Eq. (7.18).

In Fig. 7.2 we show how the TDLDA energies of the nanoshell plasmon resonances depend on the dielectric constant of the core $\epsilon_C$ for embedding media with different dielectric constants $\epsilon_E$. The figure shows that the energies of both plasmon resonances depend strongly on $\epsilon_C$. The $\omega_+$ mode exhibit the strongest $\epsilon_C$ dependence because it has the largest admixture of the cavity plasmon which depends very sensitively on $\epsilon_C$. It is interesting to note that the dependence of $\omega_+$ on $\epsilon_C$ is strongest for a large $\epsilon_E$ while the $\epsilon_C$-dependence of $\omega_-$ is strongest for the smallest $\epsilon_E$. This finding can be qualitatively understood from the simple two-level model proposed in Chapter 2.

[67] When the embedding medium has a large dielectric constant, the $\omega_-$ mode has only a very small cavity plasmon content and will not depend strongly on $\epsilon_C$. The
Figure 7.2  The calculated plasmon energies as a function of core dielectric constant $\varepsilon_C$ for the 60-90 a.u. nanoshells in embedding media of different dielectric constants $\varepsilon_E$. The circles represents the TDLDA calculations and the solid lines represents the classical Mie calculations using a bulk Drude dielectric function.
contribution of the cavity plasmon to the $\omega_+$ mode increases with increasing dielectric constant of embedding medium. Consequently, the strongest $\epsilon_C$ dependence for the $\omega_+$ mode is expected for the largest $\epsilon_E$. The solid lines in Fig. 7.2 represents the dependence of the plasmon energies on the dielectric functions, but calculated using classical Mie scattering and a bulk Drude dielectric function. The results from the Mie scattering calculation agree remarkably with the TDLDA results.

7.4 TDLDA versus Experiment

The extension of the TDLDA formalism to the case of a nanoshell with a dielectric core embedded in a dielectric medium enables the first direct comparisons of our theoretical model of nanoshells with experimental data. In this application, for simplicity, we will use the established bulk value $r_s=3$ for gold although in principle there is no reason to expect that this electron density would be appropriate for a nanoparticle. In Figs. 7.3, 7.4 and 7.5 we show a comparison of the calculated and measured optical absorption spectra for the three nanoshells analysed in Chapter 4. These nanoshells have a $\text{Au}_2\text{S}$ core ($\epsilon_C = 5.4$) and they were suspended in an aqueous solution ($\epsilon_E = 1.78$) during the experimental measurements. [3] The dielectric constant for $\text{Au}_2\text{S}$ was obtained from theoretical calculations and the dielectric constant of 1.78 for water is the one appropriate for water at optical frequencies (index of refraction of water is $n=1.33$ and $\epsilon = n^2$ for lossless media). [3] The experimental curves are composed of two structures. The feature around 520 nm is the optical absorp-
Figure 7.3  Comparison of the calculated optical absorption spectra (circles) with measured spectra (solid line) for the 4.1-5.1 nm nanoshell. The nanoshells have a gold sulfide core, $\epsilon_C = 5.4$ and were suspended in an aqueous solution $\epsilon_E = 1.78$. The dotted line is the absorption spectra for solid gold colloidal nanoparticles also present in the solution calculated using classical Mie scattering theory.
Figure 7.4  Comparison of the calculated optical absorption spectra (circles) with measured spectra (solid line) for the 8.6-9.9 nm nanoshell. The nanoshells have a gold sulfide core, $\varepsilon_C = 5.4$ and were suspended in an aqueous solution $\varepsilon_E = 1.78$. The dotted line is the absorption spectra for solid gold colloidal nanoparticles also present in the solution calculated using classical Mie scattering theory.
Figure 7.5  Comparison of the calculated optical absorption spectra (circles) with measured spectra (solid line) for the 13.1-14.8 nm nanoshell. The nanoshells have a gold sulfide core, $\epsilon_C = 5.4$ and were suspended in an aqueous solution $\epsilon_E = 1.78$. 
tion from solid gold colloid which is present as a background. The feature at higher wavelengths is the $\omega_-$ resonance of the nanoshell. To make it easier to distinguish the nanoshell resonances, we include in the first two figures the optical absorption from the solid gold nanoparticles as calculated using classical Mie scattering. These results clearly show that the calculated energies of the nanoshell plasmons are systematically blueshifted relative to the experimental value. This is a consequence of neglecting the polarizability of the gold ion cores in the TDLDA calculations. We should underline that the classical Mie calculations agree with the experimental results only when the experimentally measured dielectric function for gold is used. If a pure Drude dielectric function is used,

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2},$$ (7.18)

then the Mie theory predicts the values indicated by arrows in Figs. 7.3, 7.4 and 7.5 which are also blue shifted and very close to the TDLDA predictions. The gold dielectric function is Drude like in the range of frequencies where the plasmon resonances are observed.[68] However a fit will show that, in this range of frequencies, the dielectric function should rather be written as

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2},$$ (7.19)

with $\varepsilon_\infty$ close to 7. As it is well known, this $\varepsilon_\infty$ is due to the polarization of the ion cores. Unlike the alkali metals where the polarization of the cores can be neglected, the ion cores of the noble metals are highly polarizable due to the d-band electrons.
With a value, $\varepsilon_\infty = 7$, the classical Mie calculations predicts the correct value of the plasmon frequencies. In Figs. 7.6, and 7.7, we show the TDLDA calculated polarizabilities for the 4.1-5.1 nm and 8.6-9.9 nm nanoshells when the shell dielectric function has been fixed to $\varepsilon_S = 7$. These results prove that the TDLDA is able to correctly predict the values of the plasmon frequencies for gold nanoshells.

There is however a notable difference between the calculated plasmon peaks and the experiments. The calculated spectrum is considerably narrower than the measurement. We believe that this discrepancy is due to the fact that the experimental nanoshells have a finite size distribution. The experimental estimate of the size distribution is a 11% standard deviation. The neglect of size averaging can be the major reason for the disagreement between the TDLDA and the experiments. We should also not exclude the possibility that better exchange-correlation potentials can improve the results. A gradient correction can be easily implemented in our numerical algorithms. However, it is doubtful that a local correction can improve the widths of the plasmon resonances.

A study of the plasmon widths has been conducted in Ref. [69]. At a classical level, this study found that the major contributions to the plasmon lineshape come from phase retardation effects and electron-interface scattering. According to this study, these two broadening mechanisms are much stronger than the broadening due to the size variation. In our calculations however, the broadening of the plasmon lineshapes due to the size averaging is expected to be much larger due to the fact
Figure 7.6  Comparison of the calculated optical absorption spectra (circles) with measured spectra (solid line) for the 4.1-5.1 nm nanoshell when the d-electrons are taken into account. The nanoshells have a gold sulfide core, $\epsilon_C = 5.4$ and were suspended in an aqueous solution $\epsilon_E = 1.78$. The dotted line is the absorption spectra for solid gold colloidal nanoparticles also present in the solution calculated using classical Mie scattering theory.
Figure 7.7  Comparison of the calculated optical absorption spectra (circles) with measured spectra (solid line) for the 8.6-9.9 nm nanoshell when the d-electrons are taken into account. The nanoshells have a gold sulfide core, $\varepsilon_C = 5.4$ and were suspended in an aqueous solution $\varepsilon_E = 1.78$. The dotted line is the absorption spectra for solid gold colloidal nanoparticles also present in the solution calculated using classical Mie scattering theory.
that the plasmon resonances are situated in an energy range where strong single excitations are also present. The interaction of the collective mode with these single excitations can lead to a pronounced broadening. This mechanism known as Landau damping has been investigated in a series of studies by Yannouleas and co-workers for alkali clusters and proven to have an important role.[70, 71, 72, 73, 74] The RPA prediction for the plasmon’s life time has been proven to agree quite well with the experimental measurements for small silver particles.[75] It is interesting to remark that our plasmon widths are in agreement with these RPA predictions.
Chapter 8

Conclusions

The simulations presented in this thesis prove that the \textit{ab initio} calculations can be pushed to a limit where real size metallic nanoparticles can be investigated. The present study ends by proving that TDLDA is capable of predicting the energies of the plasmon resonances of metallic nanoshells. We always view this not as an end point, but rather as a starting point for further investigations of the physical properties of metallic nanoshells. Because the method has been proven reliable and because now we can make contact with the experiment, one can investigate and understand physical situations that cannot be treated classically. Such situations will include molecules chemically binding to the nanoshell surface, nanoshells placed in bias magnetic and electric fields or to a nearby surface. From this point of view, the present study represents only the first step towards a thorough microscopic understanding of the structure and properties of these novel nanoparticles.

The width problem has not yet been solved and more investigations are needed in this direction. As we already argued, the size averaging and the Landau damping can be the explanation for the broad plasmon lineshape observed experimentally. Better density functionals may also improve the theoretical predictions of the plasmon widths.

We have reached a limit in our calculations where the phase retardation effects can be observed. For example, we have calculated the polarizability of a series of
nanoshells for which the classical Mie theory indicates appreciable retardation effects. Our first attempt of including such retardation effects in the TDLDA by simply replacing the Poison equation with a Helmholtz wave equation for the Coulomb potential failed. This lead us to conclude that, for phase retardation effects, one needs to consider the full current-density functional theory. The metallic nanoshells are a perfect benchmark for this newly developed theory because, compared with a solid metal sphere of the same overall diameter, a metal nanoshell has far less conduction electrons which makes the \textit{ab initio} calculations much easier.
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