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Strong coupling between a metallic nanoparticle and a single molecule

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1. Introduction

Mankind in the 21st century is surrounded by a world of material objects. More than ever our lives are influenced by the things and applications around us and it is materials that give substance to everything we see and touch [1].

Since the first scientific works in ancient times, the human race endeavours to increase the perception of the world around us and to make our life easier by inventing technical applications. These efforts are still going hand in hand with a better understanding of the fundamental physical properties of solid bodies and with the insight in physical processes. The enormous technical progress in the last one hundred years led to more scientific mile stones than ever before. Especially the progress in science and research during the last decade formed a new keyword: nanotechnology. Today it is possible, for example, to work with objects one thousand times smaller than the diameter of a human hair, see Fig. 1.1. In the human body – to mention only one of the relevant fields of application – the majority of vital biological processes like cell separation, reproduction or metabolism happens on this tiny length scale. For instance, direct drug delivery into cells may be a possible candidate to cure cancer.

But to focus on the topic of this diploma thesis, what exactly are nanoparticles and what can we do with them?

1.1. What is a nanoparticle?

Nanoparticles are small clusters with a diameter of about 10 to 100 nanometers and they consist of several million atoms. There exists no rigorous definition at which point one has to call an entity a nanoparticle, but a good guiding value is if the length scale in at least one dimension is less than 100 nanometres. Examples for such
1. Introduction

Figure 1.1.: The left hand side shows the size of micro cog-wheels compared to a mite (courtesy of Sandia National Laboratories, SUMMiT(TM) Technologies, www.mems.sandia.gov). On the right you see a nerve cell on carbon nano wires (with friendly permission from W. Hällström).

objects are carbon nanotubes, fullerenes, semiconducting fluorophores, and so on. Although Richard Feynman had already realized and mentioned the great potential of nanoscale physics almost 50 years ago, mainly the rapid advance of nanoscience and nanotechnology in the last years led to an increase of research activities and inspired many scientists and research groups to explore the physics near or beyond the diffraction limit of light.

The combination of inorganic nanostructures and organic molecules, which is the subject of this diploma thesis, constitutes a particularly powerful route for creating novel functional devices with synergetic properties found in neither of the constituents [2, 3]. The improvement of nanofabrication methods and the involved advancement in controlling the shape and arrangement pattern of nanoparticles [4] opens a wide range of unexplored physical properties. The field of application is widespread, ranging from quantum optics, surface technology, and biochemistry, to also less obvious areas like nutrition science or medicine. Nowadays the use of nanoparticles even in the everyday life is not so far off, because they are already employed in suntan lotions, catalysers for cars, self-cleaning surfaces or bactericidal wall coatings for hospital rooms for instance.
1.2. Formalism

Since we now know the considered length dimensions and some of the possible applications, the question for the mathematical formalism and the underlying physical theory arises. In this work, we investigate the interaction between a metallic nanoparticle and a single fluorescent molecule, whose most important intrinsic property is the existence of an electric dipole moment, see Fig. 1.2 for a typical setup in experiments. The interaction of metals with electromagnetic radiation is largely dictated by the free conduction electrons in the metal [2, 5]. Noble metal nanoparticles can interact with visible light due to the resonant excitation of surface plasmon modes (explained in Chap. 2.1). These modes give rise to an enhancement of the local field with respect to the exciting light field [8]. Applications which are based on this effect are, for instance, surface–enhanced Raman scattering [9, 10, 11, 12] or optical addressing of subwavelength volumes [13]. Anger et al. [14] recently investigated the fluorescence of a single molecule close to a single spherical gold nanoparticle, and demonstrated the continuous transition from fluorescence enhancement to fluorescence quenching.

\footnote{This fact leads to a huge fluorescence increase in the molecule’s spectrum, which makes biochemical detection possible. See e.g. [6] and [7].}

Figure 1.2.: Schematic diagram of a typical experimental setup. Gold nanoparticles are located on a transparent glass layer and molecules are randomly distributed around them (they can also lie on them).
1. Introduction

by varying the distance between molecule and nanoparticle.
As we are working with electromagnetic fields in the presence of dielectric media
and structures and excitations at very small length scales, the task is to combine
Maxwell’s theory\(^2\) with quantum mechanics. The aim of this diploma thesis is a
quantum mechanical description of the above-mentioned electromagnetic interac-
tion. The considered energies are in the area of some electronvolt. Since the thermal
energy at room temperature corresponds to a few tens of meV, thermal influences
can be neglected. Additionally, we compare our results with published calculations
within Mie theory\(^8\) and a numerical simulation of the discussed problem has also
been developed.

\(^2\)Some mathematical properties of Maxwell’s equations for macroscopic dielectrics can be found in
the paper of A. Tip\(^15\). There one can also find a rigorous decomposition into independent
equations for longitudinal and transverse fields, which is important for this work.
2. Basics

Metals have many remarkable qualities, like good conduction of heat and electricity, their elastic properties, or the possibility to compound alloys. The challenge to explain these properties initiated the development of modern solid state physics [16]. In the course of time, many physicists tried to develop simple models for the quantitative and qualitative understanding of metallic states.

One century ago, P. Drude [17] made a very important and successful contribution. Three years after Thompson had detected the electron, Drude transferred the kinetic gas theory to metals and treated them as electron gases [16]. In the simplest version of the Drude model, electrons are moving around inside a solid body, and heavy immobile ions, with a positive electric charge, compensate the contribution of the negative charged particles. Although nowadays we have much more insight to the quantum structure of solid bodies, this simplified description is still very important and can be applied in many cases.

However, if one is working with materials of nanometer lengthscales, a priori it is not quite clear if a description of metals within the Drude model is still valid. For example, is the continuum form of Ohm’s Law, \( j = \sigma E \), where the current density \( j \) is proportional to the electric field \( E \), still valid for nanostructures? One possible approach to such problems is given by semiclassical approximations, where quantum–mechanical calculations are obtained by considering small perturbations given by a classical field. As already mentioned at the beginning, the task of this diploma thesis is a quantum mechanical framework for the physics concerning the interaction of nanoparticles with molecules. Before we outline the theory and mathematical aspects of the quantum mechanical formulation in Chap. 3, we start with an introduction of the concepts of how to describe the properties of a metallic particle in general. We begin with the explanation of the term \textit{plasmon}, which yields a very important
2. Basics

concept for the intrinsic properties of the nanoparticle. In Chap. 2.2 we discuss the
dielectric function of a material and derive a simple Drude–form for the semiclassical
description.

Throughout this thesis all calculations and formulas are given in atomic units, see
Appendix A.1.

2.1. Plasmons

2.1.1. Plasma oscillations

A plasma is an ionised gas and it is treated as a distinct state of matter. Usually it
contains free electric charges which are responsible for the electric conductivity. We
assume that a plasma consists of identical point–like charged particles embedded in
an uniform background of charge (Drude [16] or jellium model – will be elucidated
in Chap. 2.2.3), and that the unbound electrons in a noble metal nanoparticle cor-
respond to this scenario. The long–range nature of the Coulomb interaction of these
free electrons leads to the phenomena of screening and plasma oscillations in the
nanoparticle or in charged fluids and gases in general (see [18]). Each electron in the
plasma interacts not just with a limited number of neighbours, but with all the other
electrons. As a consequence, the plasma exhibits a strong collective behaviour in the
long wavelength regime (i.e. where the wave vector $k \rightarrow 0$).

The restoring force in such collective oscillation modes is provided by the mean field
produced by all the electrons moving ’in concert’ [18]. If we restrict ourselves to slow
variations in space, we may take the force on an electron as given by charge times
the electric field $E(r, t)$. At a semiclassical point of view, the velocity of an electron
$\dot{r}(t)$ is equal to the current density $j(r, t)$ divided by the electron density $n$. In this
case Newton’s law for the electrons yields

$$\frac{\partial^2 r}{\partial t^2} = \frac{1}{n} \frac{\partial j(t)}{\partial t} = E(r, t). \quad (2.1)$$

The continuity equation

$$\frac{\partial \rho(r, t)}{\partial t} + \nabla \cdot j(r, t) = 0, \quad (2.2)$$

10
2.1. Plasmons

together with Poisson’s equation [see also Eq. (2.7)]

$$\nabla \cdot \mathbf{E}(\mathbf{r}, t) = 4\pi \varrho(\mathbf{r}, t),$$

(2.3)

leads to a wave equation for the charge density:

$$\frac{\partial^2 \varrho}{\partial t^2} = -4\pi n \varrho = -\omega_p^2 \varrho.$$  

(2.4)

From this equation we see that the plasma performs collective oscillations with the plasma frequency \(\omega_p\), which is proportional only to the square root of the electron density \(n\):

$$\omega_p = \sqrt{4\pi n}.$$  

(2.5)

In plasma physics these longitudinal oscillations are known as Langmuir waves\(^1\). A more detailed derivation of plasma oscillations can be found in [20], for instance. These collective electron excitations can be treated as quantum mechanical quasiparticles, called plasmons (see next chapter). The existence of plasmons has a great influence on the optical properties of the considered material. If the frequency \(\omega\) of the incident light is below the plasma frequency \(\omega_p\), the electrons screen the electromagnetic field. On the other hand, if the light frequency is above \(\omega_p\), the electrons cannot respond fast enough, and the light gets transmitted. But what happens if \(\omega = \omega_p\)? We spend special attention to this interesting case, because under this circumstances optical excitations of plasmons and energy transfers are possible.

2.1.2. Quasiparticles

If an electromagnetic field impinges on a solid body, this process gives rise to elementary excitations in the considered material due to the underlying physical phenomena of absorption, reflection and dispersion of the electromagnetic radiation. These elementary excitations (one can visualise them as low–lying excited states close to the ground state of the system) can be described and understood as so called quasiparticles\(^2\) which are quantised vibration modes for example.

\(^1\)In [19] one finds a snapshot of these waves as a capture of laser wakefields. 

\(^2\)The idea of quasiparticles originates in the theory of Fermi liquids of the Russian physicist Lev Landau [21, 22]. A Fermi gas is a system of noninteracting fermions and a Fermi liquid is basically the same system with interactions [23].
2. Basics

Quasiparticles are applicable to an extremely wide range of many–body systems and the quasiparticle concept is very important in condensed matter physics. Phonons, for instance, are quantised modes of lattice vibrations and they are the primary mechanism for heat conduction, propagation of sound in solids and so on. Other possible quasiparticles are, e.g., excitons (Coulomb–correlated electron–hole pairs), cooper–pairs (two correlated electrons, responsible for superconductivity) or plasmons (quantum of a collective oscillation of the Fermi gas as introduced in the previous chapter). Because the interaction of plasmons is one of the main parts of this work, we will go a little bit more into detail about them in the next subsection.

2.1.3. Surface plasmons

One process for plasmon detection is the bombardment with electrons, as illustrated in Fig. 2.1. Since a plasmon is nothing more than a quantised collective vibration of the free electron gas in a solid body with frequency $\omega_p$, the electron charge interacts with fluctuations of the electromagnetic plasmon fields [23]. Although many of the important properties of plasmons can be derived from Maxwell’s equations, they are quantum mechanical entities. But one should keep in mind, that in this collective oscillation of the Fermi gas a huge amount of electrons are involved, i.e., we work
2.1. Plasmons

with macroscopic quantum states! This fact leads to a very short plasmon lifetime due to fast dephasing and decay processes. A typical decay time is less than 10 fs and corresponds to Landau damping. This type of damping describes the exponential decrease of longitudinal waves in a plasma (or similar environments) due to the energy exchange between the wave and particles or impurities in the plasma. In our case, as a typical process the plasmon decays in an electron–hole–pair, see Fig. 2.2.

Figure 2.2.: Typical plasmon decay process: After 10 fs the plasmon $p$ decomposes in an electron $e^-$ and an electron–hole $h^+$.

If the plasmons are confined to a surface they are called surface plasmons. This confinement occurs at the interface of materials where the real part of the dielectric function is positive on one side and negative on the other, which is a typical scenario for the interface between metals and air. This restriction yields longitudinal surface waves (Langmuir waves) as solutions of the electromagnetic equations [20]. The energy of these surface plasmon modes is different from the energy of bulk plasmons, and hence they can be treated separately. The bulk modes correspond to electron density oscillations within the volume of the particle, thus they are oscillating with the plasma frequency $\omega_p$. The energy of surface plasmons will be discussed in Chap. 3.1.3. The numerical value for $\omega_p$ using the parameters of gold is about 9 eV (see Tab. 2.1), and we will see that the surface plasmon energies of spherical gold nanoparticles are around 2.5 eV. In [25] it is shown, how to separate the volume and surface plasmons by splitting the charge density $\rho$ into a surface charge density and a volume part.

These surface plasmons are involved in many surface effects and play an important role in the task of building two-dimensional structures in quantum optics or nanotechnology.
2. Basics

2.2. Dielectric function of the electron gas

To gain insight into the considered problem, we now derive a simple model for the dielectric description of a metal. One of the essential characteristics of Maxwell’s equations is the existence of propagating electromagnetic waves [26]. If no dispersion is present, these waves propagate undisturbed in space. But in reality, only in vacuum or in small frequency domains the propagation velocity can be considered as frequency independent, and almost all media show some kind of dispersion. Therefore, the dielectric function of a material is not a constant in general but rather depends on the wave vector \( \mathbf{k} \) and the frequency \( \omega \).

This distinct frequency and wave vector dependence of \( \varepsilon(\omega, \mathbf{k}) \) of an electron gas is a characteristic result of the physical properties of a solid body. In one limiting case \( \varepsilon(\omega, 0) \) describes the collective excitations of the Fermi gas (these are the volume and surface plasmons respectively), and on the other hand \( \varepsilon(0, \mathbf{k}) \) describes the electrostatic screening of the electron interaction.

In this section a simple oscillator model of \( \varepsilon(\omega, \mathbf{k}) \) is derived, and a general introduction of the dielectric function is given. The following definitions and calculations are based on [23] and [26].

2.2.1. Definition of the dielectric function

The dielectric constant\(^3\) \( \varepsilon \) in electrostatics is defined through the ratio of the electric field \( \mathbf{E} \) and the dielectric displacement \( \mathbf{D} \),

\[
\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} = \varepsilon \mathbf{E},
\]

where \( \mathbf{P} \) is the polarisation vector. The introduction of the dielectric displacement comes with the macroscopic Maxwell equations, see Eq. (2.9). With \( \mathbf{D} \), Poisson’s equation looks the same in the micro- and macroscopic regime:

\[
\nabla \cdot \mathbf{D} = \nabla \cdot (\varepsilon \mathbf{E}) = 4\pi \varrho_{\text{ext}}, \quad \quad (2.7)
\]

\[
\nabla \cdot \mathbf{E} = 4\pi \varrho = 4\pi (\varrho_{\text{ext}} + \varrho_{\text{ind}}). \quad \quad (2.8)
\]

The charge density \( \varrho_{\text{ext}} \) induces the density \( \varrho_{\text{ind}} \) in the system.

\(^3\)In the literature \( \varepsilon \) is also sometimes called the relative permeability [20].
2.2. Dielectric function of the electron gas

2.2.2. Dispersion relation

The macroscopic Maxwell equations in atomic units read as follows [26]

\[ \nabla \cdot \mathbf{D}(r, t) = 4\pi \varrho_f(r, t), \quad \text{(Gauss’s Law)} \tag{2.9a} \]

\[ \nabla \cdot \mathbf{B}(r, t) = 0, \quad \text{(magnetic analogon)} \tag{2.9b} \]

\[ \nabla \times \mathbf{H}(r, t) = \frac{4\pi}{c} \mathbf{j} + \frac{1}{c} \frac{\partial \mathbf{D}(r, t)}{\partial t}, \quad \text{(Ampère’s Circuital Law)} \tag{2.9c} \]

\[ \nabla \times \mathbf{E}(r, t) + \frac{1}{c} \frac{\partial \mathbf{B}(r, t)}{\partial t} = 0. \quad \text{(Faraday’s Induction Law)} \tag{2.9d} \]

Here \( \mathbf{B} = \mu \mathbf{H} \) is the magnetic field (magnetic permeability \( \mu = 1 \) throughout), \( \varrho_f \) the free charge density, \( c \) the speed of light, and \( \mathbf{j} \) the current density. If no sources are present these equations reduce to

\[ \nabla \cdot \mathbf{D} = 0, \quad \nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = 0, \tag{2.10a} \]

\[ \nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0, \tag{2.10b} \]

and the combination of (2.10) yields the wave equation of Helmholtz form:

\[ \left( \nabla^2 + \frac{\varepsilon \omega^2}{c^2} \right) \begin{bmatrix} \mathbf{E} \\ \mathbf{B} \end{bmatrix} = 0. \tag{2.11} \]

As possible solution we can write down a plane wave propagating in \( \mathbf{e}_r \)-direction: \( \exp(i \mathbf{k} \cdot \mathbf{r} - i \omega t) \), with \( \mathbf{k} = k \mathbf{e}_k \). From Eq. (2.11) then follows the dispersion relation for the wave number \( k \):

\[ k = \sqrt{\varepsilon \frac{\omega}{c}}. \tag{2.12} \]

2.2.3. Drude form

To get a feeling for the underlying physics, we now discuss the dielectric function of Drude form. Within this Drude framework it is possible to establish a microscopic description of the electron dynamics in the metal, and to obtain an equation of motion for the nanoparticle charge excitations [8], see Appendix A.3.

If we consider the case of long wavelength\(^4\) \((k \to 0)\), the dielectric function of an

\[^4\text{This assumption is valid for nanoparticles due to their small diameter compared to optical wavelengths.}\]
2. Basics

electron gas \varepsilon(\omega, 0) = \varepsilon(\omega) can be derived from the motion of a free electron with charge \(-1\) in an electric field \(\mathbf{E}(\mathbf{r}, t)\). If the electron is bound by a harmonic force \(\mathbf{F}(\mathbf{r}, t) = -\omega_0 \mathbf{r}(t)\) with an additional phenomenological damping constant\[\gamma\], the equation of motion reads

\[
\ddot{\mathbf{r}}(t) + \gamma \dot{\mathbf{r}}(t) + \omega_0^2 \mathbf{r}(t) = -\mathbf{E}(\mathbf{r}, t).
\] (2.13)

Following [26], we assume a harmonic time dependence \(e^{-i\omega t}\) for \(\mathbf{r}(t)\) and the field \(\mathbf{E}(\mathbf{r}, t)\). If the oscillation amplitude of the electron is very small (so that the electric field can be computed at the averaged position of the electron, \(\mathbf{E}(\mathbf{r}, t) \approx \mathbf{E}(t) = \mathbf{E} e^{-i\omega t}\)), the solution of the above equation is given by

\[
\mathbf{r} = -\frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma} \mathbf{E}.
\] (2.14)

The dipole moment of one electron is defined as charge times distance, and therefore we get

\[
\mathbf{d} = -\mathbf{r} = \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma} \mathbf{E}.
\] (2.15)

The electric polarisation \(\mathbf{P}\) is defined as dipole moment over volume and with the electron density \(n\), we derive

\[
\mathbf{P} = -n \mathbf{r} = \frac{n}{\omega_0^2 - \omega^2 - i\omega\gamma} \mathbf{E}.
\] (2.16)

The electric susceptibility \(\chi_e\) is defined with the relation \(\chi_e = 4\pi \mathbf{P}/\mathbf{E}\) and the final solution for the oscillator model of the dielectric function is

\[
\varepsilon_D(\omega) \equiv \frac{\mathbf{D}(\omega)}{\mathbf{E}(\omega)} = 1 + \chi_e = 1 + \frac{4\pi n}{\omega_0^2 - \omega^2 - i\omega\gamma}.
\] (2.17)

(The subscript \(D\) stands for the appellation 'Drude form'.) Considering an electron density \(n_0\) to contain only free electrons \((\omega_0 = 0)\) with the relaxation rate \(\gamma_0\), one can split these unbound electrons off and derive

\[
\varepsilon_D(\omega) = \varepsilon_0 - \frac{\omega_p^2}{\omega(\omega + i\gamma_0)}.
\] (2.18)

with the plasma frequency \(\omega_p = \sqrt{4\pi n_0}\), and with \(\varepsilon_0\) as a static dielectric background constant accounting for the contribution of the bound electrons to the polarisability.

\[\text{This damping constant also includes all possible electron collision effects.}\]
2.2. Dielectric function of the electron gas

\( n_0 \) is given by \( \frac{3}{4 \pi r_s^3} \), where \( r_s \) is the electron gas parameter (see Table 2.1).

It is important to distinguish \( \varepsilon_0 \) in Eq. (2.18) from the background dielectric function of the surrounding medium, which we introduce as \( \varepsilon_b \). Throughout this work, \( \varepsilon_0 \) corresponds to the positive ion background inside our nanoparticle and \( \varepsilon_b \) refers to the outside homogeneous dielectric matrix, in which the particle and molecule are embedded (see Fig. 3.1). Both quantities hold \( \varepsilon_0, \varepsilon_b \in \mathbb{R} \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background dielectric constant</td>
<td>( \varepsilon_0 )</td>
<td>10</td>
</tr>
<tr>
<td>Dielectric background matrix (glass)</td>
<td>( \varepsilon_b )</td>
<td>2.25</td>
</tr>
<tr>
<td>Electron-gas parameter</td>
<td>( r_s )</td>
<td>3</td>
</tr>
<tr>
<td>Metal electron density</td>
<td>( n_0 )</td>
<td>( 8.84 \cdot 10^{-3} \text{ a.u.} )</td>
</tr>
<tr>
<td>Inverse relaxation rate</td>
<td>( \gamma_0^{-1} )</td>
<td>10 fs</td>
</tr>
<tr>
<td>Plasma frequency</td>
<td>( \omega_p )</td>
<td>9.07 eV</td>
</tr>
</tbody>
</table>

Table 2.1.: Parameters used for the calculations of the Drude dielectric function (2.18) for gold [8] and other common values in the considered system.

The relatively large value of \( \varepsilon_0 \) is due to the pronounced \( d \)-band density of states close to the Fermi energy [27].

A word of caution should be given at this point, because the plasmon energies are above the threshold for \( d \)-band transitions in gold. The \( d \)-band density of states for gold has a relatively large value, which leads to an increased screening [27] that is not included in this simplified Drude framework. Nevertheless, we can still use the Drude dielectric function for a semiclassical approximation, but we have to be careful when comparing to experimental data. In Chap. 4, Fig. 4.1 and Fig. 4.2 show the comparison of \( \varepsilon_D \) with experimental results and one can see, that for a frequency dependent damping \( \gamma(\omega) \) the convergence remains tolerable.

By following [8], we can also describe the metal in terms of a jellium model [28], instead of using the Drude form directly (see Appendix A.3). In this model, free electrons are moving in a material with dielectric constant \( \varepsilon_0 \).
3. Theory

The last chapter was meant to illustrate the collective behaviour of electrons within a metallic nanoparticle, following the usual textbook contents.

We now change to a more technical description of the quantum mechanical processes in the considered system, see Fig. 3.1. Although the well developed mathematical formalisms in quantum optics will lead us to the desired results, our approach is different to those which can be found in the literature. We start with the introduction of the involved energies and Hamilton operators of the system, where we also present one of the crucial points of this work: The quantisation of the surface plasmon modes. As far as we know, most authors start with classical or semiclassical equations of motion and quantise the electromagnetic fields later on. Opposed to

Figure 3.1.: The nanoparticle and the molecule are lying on a transparent glass matrix, described by a constant dielectric function $\varepsilon_b$. 
3. Theory

this concept, we derive the dynamics of our system from the time evolution of the
density operator, i.e., by the appliance of intrinsic fundamental quantum mechanical
concepts. We compare our results to a semiclassical method in the literature [8],
where the starting point is given by the Boltzmann equation for the motion of the
electrons. In this paper, the assumption of a dielectric function of Drude form (2.18)
and the combination with Maxwell’s equations (2.9) yields a microscopic description
of the electron dynamics in the metal. An equation of motion for the nanoparticle
charge excitations is obtained, whose solutions can be interpreted in simple physical
terms. In this sense, we compare two different approaches in this diploma thesis. In
the calculations published in [8], the behaviour of the electrons is dominated by the
Drude dielectric function with the background $\varepsilon_0$ of the positive ions in the metal-
lic nanoparticle. In our work, we incorporate the electron dynamics explicitly and
introduce a phenomenological damping constant to maintain the electron relaxation
processes. Some of the advantages of our method are the simple to handle expan-
sion to a system consisting of more particles and many molecules, the possibility
to consider strong or nonlinear coupling, or the elegant way how all the important
and needed information is contained in only one operator (see Chap. 3.2.1), whose
eigensystem allows us to calculate the presented results.
3.1. Description of the system

As outlined before, the main idea behind this diploma thesis is the quantised description of surface plasmon modes, and the interaction between a nanoparticle and a single molecule. In this chapter we derive the Hamilton operator of the considered problem and calculate the interaction between the nanoparticle and the molecule. To determine the time–evolution of this system and to include dissipative effects, we consider a composite regime $S \otimes R$, where a subsystem $S$ interacts with an open reservoir $R$. A reduced formalism, where the contribution of the reservoir has been integrated out, is derived in Chap. 3.2.

3.1.1. Complete Hamilton operator

The constituents of our system are embedded in a dielectric medium. The molecule gets optically pumped by a strong monochromatic laser beam which is treated as a classical field. The open reservoir $R$ corresponds to a vacuum photon field, which interacts with the subsystem $S$ consisting of the nanoparticle and the molecule.

The complete Hamilton operator of this system reads as follows

$$H = H_{\text{mol}} + H_{\text{pl}} + H_{\text{pl-mol}} + H_{\text{ph}} + H_{\text{rad}} + H_{\text{int}},$$

(3.1)

with the notation:

- $H_{\text{mol}}$ ... Hamilton of the molecule,
- $H_{\text{pl}}$ ... Hamilton of plasmons (nanoparticle),
- $H_{\text{pl-mol}}$ ... Interaction between plasmon modes and molecule,
- $H_{\text{ph}}$ ... Hamilton of photon field (open reservoir),
- $H_{\text{rad}}$ ... Hamilton of laser beam (classical field),
- $H_{\text{int}}$ ... Interaction of system with radiation field (see Chap. 3.2).

1. In experiments this is realised by a transparent glass layer with dielectric constant $\varepsilon_b = 2.25$, see Fig. 3.1.
2. To be consistent with other chapters in this thesis, we always use the calligraphic symbol $\mathcal{H}$ to distinguish a Hamilton operator from its representation in the interaction picture, which we denote by the normal letter $H$. See Chap. 3.2 and Appendix A.6.
3. Theory

In this section the first three parts of Eq. (3.1) are derived and discussed.

3.1.2. Hamilton operator of the molecule

The complete set of energy eigenstates of the molecule is given by \( \{ |i\rangle, i = 1, \ldots, n \} \). If we consider only the first two energy states with the approximation that the energy gap between the next states is much bigger than between these two, we derive a simple two–level–system \[30\], with the groundstate \( |0\rangle \) and the excited state \( |1\rangle \). The applied strong monochromatic laser beam is tuned to the atomic transition in the molecule and hence excites an electron from the ground state \( |0\rangle \) to \( |1\rangle \). The *Rabi–frequency* \[30\ [31\] describes the strength of the laser–matter coupling. The energy of the groundstate is put to zero and

\[
|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad E_1 = \omega_1, \\
|0\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad E_0 = \omega_0 = 0. \tag{3.2}\tag{3.3}
\]

A two–state system can be described in terms of the Pauli spin operators \[32\]. Let us briefly review some of their properties. The three Pauli matrices \( \sigma_1, \sigma_2, \sigma_3 \) and the unity \( \sigma_0 \) are given by \[29\]

\[
\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{3.4}
\]

with the well–known properties \( (i, j = 1, 2, 3) \)

\[
\{ \sigma_i, \sigma_j \} = 2\delta_{ij}, \quad \sigma_i^2 = 1, \quad \det \{ \sigma_i \} = -1, \\
[\sigma_i, \sigma_j] = 2i\varepsilon_{ijk}\sigma_k, \quad \sigma_i^\dagger = \sigma_i, \quad \tr \{ \sigma_i \} = 0.
\]

This yields the following representation

\[
\mathcal{H}_{\text{mol}} = \omega_1 |1\rangle\langle 1| = \begin{pmatrix} \omega_1 & 0 \\ 0 & 0 \end{pmatrix} = \frac{1}{2} (\sigma_0 + \sigma_3) \omega_1. \tag{3.5}
\]

In our calculations we additionally include a simple expansion of this equation to a three level system, where we allow transitions from upper states to the lowest excited
3.1. Description of the system

Figure 3.2.: A laser beam excites the molecule from the groundstate $|0\rangle$ to an upper state $|2\rangle$, and after some ps the electron falls down to the lowest excited state, where the interaction with the plasmons take place. The inset shows a schematic picture of the gold particle and the molecule.

state in the molecule (see Fig. 3.2). The laser field excites the molecule from the ground state $|0\rangle$ to some upper level $|2\rangle$. After some time the excited electron falls back to a lower excited state $|1\rangle$, where the interaction with the plasmon modes takes place. This de-excitation from $|2\rangle$ to $|1\rangle$ is a phononic process and happens at a picosecond-timescale ($\sim 10^{-12}$ sec.), which is three orders of magnitude slower then the typical femtosecond-processes of plasmons.

Dipole moment of the molecule

The transition between $|0\rangle$ to $|1\rangle$ and vice versa can be described with the two lowering and raising operators (see e.g. [30, 31, 32])

$$
\sigma_+ \equiv |0\rangle\langle 1| = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \sigma_- \equiv |1\rangle\langle 0| = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad \sigma_\pm = \frac{1}{2}(\sigma_1 \pm i\sigma_2). \quad (3.6)
$$
The action of these transition operators is given by

\[ \sigma_+ |0\rangle = |1\rangle, \quad \sigma_+ |1\rangle \equiv 0, \quad (3.7) \]
\[ \sigma_- |1\rangle = |0\rangle, \quad \sigma_- |0\rangle \equiv 0. \quad (3.8) \]

The dipole moment \([30]\) of the molecule (charge times distance) reads as follows\(3\)

\[ \mathbf{p} = q \mathbf{r} = \sum_{i,j} q |i\rangle \langle i| \mathbf{r} |j\rangle \langle j| = q (|0\rangle \langle 0| |1\rangle \langle 1| + |1\rangle \langle 1| |0\rangle \langle 0|). \quad (3.9) \]

Although we are working with atomic units, the electric charge of the molecule has not been set to 1 in this equation for better comprehension. \(\mathbf{r}\) is the coordinate operator for the charge. Defining the electric dipole transition matrix element as

\[ d \equiv q |0\rangle \langle 1|, \quad d^* \equiv q |1\rangle \langle 0|. \quad (3.10) \]

yields together with \((3.6)\) and the assumption \(d = d^*\) the final result for the quantum mechanical dipole moment operator of the molecule:

\[ \mathbf{p} = d (\sigma_+ + \sigma_-). \quad (3.11) \]

### 3.1.3. Hamilton operator of the nanoparticle

In Appendix [A.3] we derive an equation of motion for the surface charge density of the nanoparticle, see Eq. \((A.29)\). We solve this equation by computing the eigensystem of the matrix \(M\) through Eq. \((A.30)\),

\[ M u_\lambda = \omega_\lambda u_\lambda. \]

In the case of spherical symmetry, the expansion in spherical harmonics \(Y_{lm}\) leads to the identification of \(u_\lambda\) with \(Y_{lm}\) (see Appendix [A.2]). This means that we can write down an eigenvalue equation for the Hamiltonian \(\mathcal{H}_{pl}\) of the form

\[ \mathcal{H}_{pl} |u_\lambda\rangle = E_\lambda |u_\lambda\rangle, \quad (3.12) \]

\(3\)If one is working with a representation in terms of a complete set of states \(\{|i\rangle\}\), any operator \(A\) can be expanded as \(A = \sum_{i,j} \langle i|A|j\rangle |i\rangle \langle j|\) by multiplying the identity operator on the left and right.

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and identify the eigenfunctions as spherical harmonics and the eigenvalues as the corresponding energies:

\[ u_\lambda(\mathbf{r}) \rightarrow Y_{lm}(\theta, \varphi), \quad |u_\lambda\rangle \rightarrow |lm\rangle, \quad E_\lambda \rightarrow \omega_l. \]

The eigenmodes are degenerate, for every energy \( \omega_l \) exist \( 2l + 1 \) eigenfunctions \( Y_{lm}(\theta, \varphi) \). The eigenenergies can also be calculated from Eq. (A.30). We obtain

\[ \omega_l = \sqrt{\frac{l}{\varepsilon_b(l+1)}} \omega_p, \quad (3.13) \]

with the bulk plasma frequency \( \omega_p = \sqrt{4\pi n_0} \) of Eq. (2.18), \( \varepsilon_0 \) the background dielectric constant of the metallic nanoparticle, and \( \varepsilon_b \) the outside dielectric background. The limit \( \varepsilon_b = \varepsilon_0 = 1 \) yields the classical Mie energy [33] of the surface plasmon \( \omega_l = \sqrt{l/(2l+1)} \omega_p \) [34].

Let us now describe the formalism for quantised surface plasmons in a metallic sphere in more detail. By following [35, 36, 37], we introduce a velocity–potential function \( \Psi(\mathbf{r}, t) \) so that

\[ \mathbf{v}(\mathbf{r}, t) = -\nabla \Psi(\mathbf{r}, t). \quad (3.14) \]

The Hamilton operator can be written in the form

\[ \mathcal{H}_{pl} = \frac{1}{2} \int d^3r \left\{ n_0 |\nabla \Psi(\mathbf{r}, t)|^2 + \varrho_s \Phi_s \right\}, \quad (3.15) \]

where \( \varrho_s = -n_s \) is the induced charge density, \( n_0 \) is the electron density of the metal and \( \Phi_s \) is the scalar potential at the surface. The scalar potential expanded in spherical harmonics inside and outside the sphere is given by [26]

\[ \Phi_{in}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} b_{lm} r^l Y_{lm}(\theta, \varphi), \quad (3.16) \]

\[ \Phi_{out}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} c_{lm} r^{-l-1} Y_{lm}(\theta, \varphi), \quad (3.17) \]

\[^4\text{We are only considering the surface plasmon modes. Normally the eigenfunctions of the Hamiltonian also include the bulk modes, but for the derivation of Eq. (A.30) we have already neglected the contribution of the volume oscillation terms.}\]
3. Theory

where we temporarily have neglected the dipole potential of the molecule. The surface electron density can be written as

\[ n_s(r, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} n_{lm}(t) Y_{lm}(\theta, \varphi) \delta(r - a), \tag{3.18} \]

and the radial component of the electric field reads

\[ \begin{align*}
(E_{in})_r &= -\frac{\partial \Phi_{in}}{\partial r} = -\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l + 1} b_{lm} l^{l-1} Y_{lm}(\theta, \varphi), \tag{3.19} \\
(E_{out})_r &= -\frac{\partial \Phi_{out}}{\partial r} = c_{lm} (l + 1) r^{-(l+2)} Y_{lm}(\theta, \varphi). \tag{3.20}
\end{align*} \]

The boundary conditions are discussed in Appendix A.4 and for a sphere with radius \( a \) in a dielectric medium we can write

\[ \begin{align*}
\varepsilon_b (E_{out})_r - \varepsilon_0 (E_{in})_r &= -4\pi \sigma, \tag{3.21} \\
\varepsilon_b (E_{out})_r - \varepsilon(\omega) (E_{in})_r &= 0, \tag{3.22}
\end{align*} \]

where we distinguish two cases. In the first expression \( \varepsilon_0 \) is the static ion background in the metallic particle and \( \sigma \) is the the surface charge density \( n_s = \sigma \delta(r - a) \). Looking at Eq. (3.18) leads to

\[ \sigma = \sigma(\theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} n_{lm}(t) Y_{lm}(\theta, \varphi). \tag{3.23} \]

In the second equation (3.22) the electron dynamic is lumped into the frequency dependent dielectric function \( \varepsilon(\omega) \), which can be approximated with the Drude form, for example.

Using the inner–region \( r < a \) expansion in spherical harmonics for the velocity potential \( \Psi(r, t) \) yields

\[ \Psi(r, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l + 1} \psi_{lm}(t) r^l Y_{lm}(\theta, \varphi). \tag{3.24} \]

The continuity equation

\[ \frac{\partial n_s}{\partial t} = -n_0 \nabla v = n_0 \nabla^2 \Psi \tag{3.25} \]
3.1. Description of the system

together with Green’s theorem

\[
\frac{\partial \Psi}{\partial r} \bigg|_{r=a} = \frac{\dot{\sigma}}{n_0} \bigg|_{r=a}
\]

(3.26)
yields a relation between the coefficients \(\psi_{lm}\) and \(n_{lm}\):

\[
\psi_{lm} = \frac{2l + 1}{4\pi n_0 a^{l-1}} \dot{n}_{lm}.
\]

(3.27)
The boundary condition \(\Phi_{in}(r)|_{r=a} = \Phi_{out}(r)|_{r=a}\) results in

\[
c_{lm} = \frac{a^{2l+1}}{2l + 1} b_{lm},
\]

(3.28)
and from Eq. (3.21) we find

\[
\Phi_{out}(\theta, \varphi) = -\sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{\varepsilon_b(l+1) + \varepsilon_0 l} n_{lm} Y_{lm}(\theta, \varphi).
\]

(3.29)
Now we are able to calculate the Hamiltonian in terms of \(n_{lm}\) and \(\dot{n}_{lm}\). Writing the potential energy part as

\[
H_{pl}^{pot} = -\frac{1}{2} \int d^3 r \ n_s \Phi_s,
\]

(3.30)
and the kinetic term as

\[
H_{pl}^{kin} = \frac{1}{2} \int d^3 r \left[ \nabla^2 \Psi(r, t) \right],
\]

(3.31)
yields

\[
H_{pl} = H_{pl}^{pot} + H_{pl}^{kin} = \frac{a^3}{2n_0} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{l} \left( \dot{n}_{lm} \dot{n}_{lm}^* + \omega_l^2 n_{lm} n_{lm}^* \right).
\]

(3.32)
Luckily the result for the surface plasmon energy

\[
\omega_l^2 = \frac{l}{\varepsilon_b(l+1) + \varepsilon_0 l} \omega_p^2
\]

(3.33)
is the same than in Eq. (3.13).
The final step to a quantised operator is given by the second quantisation of Eq. (3.32). We can introduce coefficients \(b_{lm}\) and \(b_{lm}^*\) so that

\[
n_{lm} = \frac{\gamma_l}{2\omega_l} (b_{lm} + b_{l-m}^*), \quad n_{lm}^* = \frac{\gamma_l}{2\omega_l} (b_{lm}^* + b_{l-m}),
\]

\[
\dot{n}_{lm} = -i \frac{\gamma_l}{2} (b_{lm} - b_{l-m}^*), \quad \dot{n}_{lm}^* = i \frac{\gamma_l}{2} (b_{lm}^* - b_{l-m}).
\]
where $\gamma_l = (2n_0\omega_l/a^3)^{1/2}$. Inserting this in Eq. (3.32) and identifying $b_{lm}$ and $b_{lm}^*$ with plasmon annihilation and creation operators respectively yields

$$H_{pl} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \omega_l \left( b_{lm}^\dagger b_{lm} + \frac{1}{2} \right).$$  (3.34)

### 3.1.4. Interaction between molecule and nanoparticle

The physical essence of this subsection is the dipole interaction [38] of the molecular dipole, defined by the two-state system approach above, with the different plasmon modes, see Fig. 3.3. We have seen in the previous chapter, that for the description of surface plasmon modes the expansion in spherical harmonics (Appendix A.2) is needed. To determine the interaction Hamiltonian also the dipole potential $\Phi_{dp}$ has to be expressed within an expansion in these functions.

In the next subsections we derive the basic ingredients needed for the interaction, and finally the main result for $H_{pl-mol}$ is presented.

---

Figure 3.3.: The excited molecule interacts with the different plasmon modes of the nanoparticle. The plasmon energies show a square root dependence: $\omega_l = \sqrt{l/(\varepsilon \cdot l + \varepsilon_b(l+1))} \omega_p$, see Eq. (3.13). $l$ corresponds to the particular surface mode.
3.1 Description of the system

Dipole potential

Following [26], the general formula for the scalar potential $\Phi_{\text{dip}}$ of a dipole expressed within the expansion in spherical harmonics reads as follows

$$\Phi_{\text{dip}}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} a_{lm} r^l Y_{lm}(\theta, \varphi).$$

(3.35)

The dipole is located at the position $r' = r' \cdot e_{r'}$, i.e. a distance $r'$ away from the origin of the coordinate system. $e_{r'}$ is the unit vector pointing in the $r'$-direction. This fact is included in the expansion coefficients $a_{lm}$ which are now going to be derived.

The dipole moment is calculated by charge times distance:

$$d = \int_V r' \rho(r') \, d^3 x'.$$

(3.36)

The charge density $\rho(r')$ of a point-like dipole can be expressed by taking the limit of two infinitesimal separated point charges $\pm q$:

$$\rho(r') = \lim_{\delta \to 0} \frac{1}{\delta} \left[ \rho(r') - \rho(r' + \delta d) \right].$$

(3.37)

The same procedure can be applied to the potentials of the two point charges to derive the potential of the dipole:

$$\Phi_{\text{dip}}(r) = \lim_{\delta \to 0} \frac{1}{\delta} \left[ \frac{1}{|r - r'|} - \frac{1}{|r - r' - \delta d|} \right].$$

(3.38)

A second order Taylor expansion of the last term in this formula cancels the first term on the right hand side, and after taking the limit the solution is given by

$$\Phi_{\text{dip}}(r) = d \cdot \nabla' \frac{1}{|r - r'|}.$$  

(3.39)

To determine the dipole expansion coefficients $a_{lm}$, and the expanded scalar potential $\Phi_{\text{dip}}$, another contrary way to calculate the dipole potential is an expansion in spherical harmonics about a displaced centre. This was our first approach, but it becomes intricate and lengthy. Literature to this topic is for example [39] and [40].
3. Theory

harmonics. The potential of a point charge at place \( r' \) in spherical harmonics is given by \([26]\)

\[
\frac{1}{|r-r'|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} r \frac{r'^{l}}{r'^{l+1}} Y_{lm}^{*}(\theta', \varphi') Y_{lm}(\theta, \varphi). \tag{3.40}
\]

If \( r' > r \) is assumed (i.e. \( r \) ranges between the coordinate origin to the molecule position \( r' \)), this leads to

\[
\Phi_{dip}(r) = d' \cdot \nabla' \left( 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} r \frac{r'^{l}}{r'^{l+1}} Y_{lm}^{*}(\theta', \varphi') Y_{lm}(\theta, \varphi) \right). \tag{3.41}
\]

The calculation of Eq. (3.41) is a little bit lengthy but with a simple manipulation of the nabla operator known from Mie theory and the use of vector spherical harmonics\([6, 41]\) the solution is quickly derived.

The angular momentum operator in quantum mechanics \([29]\) is defined as

\[
L \equiv r \times p \equiv \frac{1}{i} (r \times \nabla), \tag{3.42}
\]

and using the formula \( e \times (e \times \nabla) = e \cdot (e \cdot \nabla) - \nabla \), where \( e \) is an arbitrary unit vector, leads to the following expression with \( e = e_r \),

\[
\nabla = e_r \cdot (e_r \cdot \nabla) - i \frac{e_r \times L}{r} \implies d \cdot \nabla' = (e_r' \cdot d) \frac{\partial}{\partial r'} + \frac{i}{r'} (e_r' \times d) \cdot L. \tag{3.43}
\]

Because the derivative \( \nabla' \) in Eq. (3.41) is acting only on the variables \( (r', \theta', \varphi') \) of the dipole position \( r' \), the solution of the scalar potential reads as follows:

\[
\Phi_{dip}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} r^{l+1} Y_{lm}(\theta, \varphi) \left[ d \cdot \nabla' \left( Y_{lm}^{*}(\theta', \varphi') \frac{r^{l}}{r'^{l+1}} \right) \right], \tag{3.44}
\]

with the expansion coefficients

\[
a_{lm} = d \cdot \nabla' \left( \frac{Y_{lm}^{*}(\theta', \varphi')}{r'^{l+1}} \right). \tag{3.45}
\]

Using the definition of vector spherical harmonics \([26, 41]\),

\[
X_{lm}(\theta, \varphi) \equiv \frac{1}{\sqrt{l(l+1)}} L Y_{lm}(\theta, \varphi), \tag{3.46}
\]

\( ^{6}\)These functions occur in the multipole expansion of electromagnetic fields for example, see \([26]\).
3.1. Description of the system

Eq. (3.45) can be calculated. The final result is

\[ \Phi_{\text{dip}}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} a_{lm} r^l Y_{lm}(\theta, \varphi), \quad (3.47) \]

\[ a_{lm} = -\frac{1}{r^{l+2}} \left[ (l+1)(e_r \cdot \mathbf{d}) Y_{lm}^{*}(\theta', \varphi') + i\sqrt{l(l+1)}(e_r \times \mathbf{d}) X_{lm}^{*}(\theta', \varphi') \right]. \quad (3.48) \]

**Boundary conditions**

We recall the scalar potential inside and outside the sphere (now with \( \Phi_{\text{dip}} \))

\[ \Phi_{\text{in}}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} b_{lm} r^l Y_{lm}(\theta, \varphi), \]

\[ \Phi_{\text{out}}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} c_{lm} r^{-(l+1)} Y_{lm}(\theta, \varphi) + \Phi_{\text{dip}}(r), \]

together with the boundary conditions

\[ \Phi_{\text{in}}(r)|_{r=a} = \Phi_{\text{out}}(r)|_{r=a}, \quad (3.49) \]

\[ \varepsilon_0 \Phi_{\text{in}}'(r)|_{r=a} = \varepsilon_b \Phi_{\text{out}}'(r)|_{r=a}. \quad (3.50) \]

The continuity of the potential shown in condition (3.49) now leads to \( b_{lm} = a^{-(2l+1)} c_{lm} + a_{lm} \) and inserting this solution into (3.50), together with the ratio of the dielectric functions \( \varepsilon = \varepsilon_0/\varepsilon_b \), yields the *static Mie coefficients*

\[ c_{lm} = \frac{(1-\varepsilon) a^{2l+1}}{(1+\varepsilon) l + 1} a_{lm}. \quad (3.51) \]

**Interaction**

To calculate the interaction with an external probe we again follow [37]. In electrostatics the interaction of a charge distribution \( \varrho_s(r) \) with a potential \( \Phi_{\text{out}}(r) \) in a dielectric medium is given by [26]

\[ W = \int d^3r \varrho_s(r) \Phi_{\text{out}}(r), \quad (3.52) \]
where the potential $\Phi_{\text{out}}$ in our case is given by the previous calculations:

$$
\Phi_{\text{out}}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l+1} \frac{4\pi}{2l+1} c_{lm} r^{-(l+1)} Y_{lm}(\theta, \varphi) + \Phi_{\text{dip}}(r). \tag{3.53}
$$

$\Phi_{\text{dip}}$ is the result for the dipole potential (3.47), where $a_{lm}$ are the Mie coefficients of Eq. (3.48) and $c_{lm}$ is given by Eq. (3.51). The calculation of Eq. (3.52) with $\rho_s = -\sigma \delta(r-a)$ and $\sigma$ given by (3.23), yields the coupling constant

$$
\lambda_{lm} = \sqrt{\omega \frac{3}{2l+1} a_{lm}}. \tag{3.54}
$$

From Eq. (3.47) and Eq. (3.48) we know the solution of the dipole potential in spherical harmonics. If we insert the dipole operator $p = d (\sigma_+ + \sigma_-)$ of Eq. (3.11) in (3.39), we derive the quantised version of $\Phi_{\text{dip}}$:

$$
\Phi_{\text{dip}} = \left( \nabla \frac{1}{|r-r'|} \right) p = \left( \nabla \frac{1}{|r-r'|} \right) d (\sigma_+ + \sigma_-). \tag{3.55}
$$

The calculation of $\nabla [1/|r-r'|]$ by using Eq. (3.40) is simply the same procedure as outlined before. From this it follows that the change from the scalar dipole potential to a quantum mechanical operator is performed by means of

$$
a_{lm} \rightarrow a_{lm} \left( \sigma_+ + \sigma_- \right). \tag{3.56}
$$

We have seen that the potential $\Phi_{\text{out}}$ consists of two parts: The outside term of a general potential expanded in spherical harmonics and the dipole potential. With the result of the boundary conditions given by Eq. (3.51) we know the outside potential in dependence of the dipole expansion coefficients $a_{lm}$, and because of Eq. (3.56) we know the quantum mechanical expression of $\Phi_{\text{out}}$.

Inserting the substitution (3.56) in Eq. (3.52) and using the orthogonality relation of spherical harmonics [see Eq. (A.12)] yields

$$
\mathcal{H}_{pl-mol} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left[ \lambda_{lm} b_{lm} \sigma_+ + \lambda_{lm}^* b_{lm}^\dagger \sigma_- \right], \tag{3.57}
$$

with the above defined coupling constant $\lambda_{lm}$.

In last expression we have applied the rotating wave approximation [30, 42] and therefore have neglected the terms $b_{lm}^\dagger \sigma_+$ and $b_{lm} \sigma_-$, where, respectively, the creation
or annihilation of a plasmon is linked to the transition in the upper or lower energy level of the molecule. If we transform the operators $\sigma_\pm$ and $b_{lm}^{(1)}$ into the interaction picture (see next chapter), we get

$$
\sigma_+ \rightarrow \sigma_+ e^{i\omega_1 t}, \quad b_{lm} \rightarrow b_{lm} e^{-i\omega_1 t},
$$

(3.58a)

$$
\sigma_- \rightarrow \sigma_- e^{-i\omega_1 t}, \quad b_{lm}^\dagger \rightarrow b_{lm}^\dagger e^{i\omega_1 t}.
$$

(3.58b)

Hence, the terms $b_{lm}^\dagger \sigma_+$ and $b_{lm} \sigma_-$ are rotating rapidly with frequencies $\omega_l + \omega_1$ and are neglected, while terms oscillating with $\omega_l - \omega_1$ are kept.
3. Theory

3.2. Master equation

Now we want to derive an equation for the time–evolution of the system’s density operator (see Appendix A.5 for a short overview of the concept of the density operator). This type of equation is called master equation\(^7\) and good introductions to this formalism can be found in the books of Carmichael \[32\] or Gardiner and Zoller \[44\], for example. In this section we are following the latter one.

In reality no quantum system is isolated, there are always interactions with the environment. The strength of these is responsible for decoherence and the loss of the quantum nature of the considered processes. Therefore a mathematical framework to include this effect is needed, and we should now develop such an approach in terms of a quantum master equation. These equations remain an important tool for predicting the quantum mechanical dynamics of small subsystems interacting with open reservoirs \[45\]. In our case, the subsystem consisting of the nanoparticle and the molecule interacts with a vacuum photon field \(R\), which represents the influence of the environment. Since we are only interested in the dynamics and properties of the subsystem \(S\) without requiring detailed information about the composite system \(S \otimes R\), a reduced formalism is of big advantage. Let \(\chi(t)\) be the density operator for the composite system and define the reduced density operator as

\[
\rho(t) \equiv \text{tr}_R \{\chi(t)\},
\]

where the trace is taken over the reservoir states \[32\]. If we only have the knowledge of \(\rho(t)\) and not know the full \(\chi(t)\), the average of an operator \(A\) in the Hilbert space of \(S\) can be calculated in the Schrödinger picture:

\[
\langle A \rangle = \text{tr}_{S \otimes R} \{A \chi(t)\} = \text{tr}_S \{A \text{tr}_R \{\chi(t)\}\} = \text{tr}_S \{A \rho(t)\}.
\]

In Appendix A.6 the derivation of an equation for \(\rho(t)\) with the properties of the reservoir only entering as parameters is given (master equation in the Born–Markov approximation).

\(^7\)The master equation approach was first developed in a quantum optical context by Louisell \[43\]. It is the quantum mechanical analog of the Fokker–Planck equation.
3.2. Master equation

3.2.1. Lindblad Form

Abstractly viewed, the master equation of either kind can be written in the form

\[
\frac{d\rho(t)}{dt} = \dot{\rho}(t) = L(t)\rho(t),
\]

(3.61)

where \( L(t) \) is a linear operator whose form depends on the particular case and it may or may not have an explicit time dependence. \( L \) is called a 'superoperator' (in the language of the Brussells–Austin group \[46\]), because it acts on the operators of the system rather than on the states. Superoperators are only acting on the right and only on each other and the density matrix, their action on a wavefunction being undefined \[47\]. The solution of Eq. (3.61) is given in terms of the evolution operator \( V(t,t_0) \) or the time–ordered product

\[
\rho(t) = T \exp \left[ \int_{t_0}^{t} dt' L(t') \right] \rho(t_0) = V(t,t_0)\rho(t_0).
\]

(3.62)

Since the evolution operator \( V(t,t_0) \) satisfies the same Eq. (3.61) as \( \rho(t) \), it follows that \( V(t,t_1)V(t_1,t_0) = V(t,t_0) \), which is known as the semigroup property of the evolution operator \[48\].

The existence of a time evolution equation for the density operator (or the conditional probability) is the physical essence of the Markov property \[8\]. The problem is, that not every such equation will fulfil the properties required for a density operator (see Appendix A.5.1), like positive probabilities or positive semidefiniteness \[9\]. The issue of positivity is so important, because matrix elements like \( \langle \phi | \rho(t) | \phi \rangle \) of the subsystem density \( \rho(t) \) are occupation probabilities and they should be positive for any state \( \phi \). If the quantum master equation is of the so called Lindblad form \[49, 51\], the positivity of the density operator is guaranteed for it (see \[44\]):

\[
\dot{\rho} = L\rho = -i[H,\rho] + \sum_{J} \left[ 2A_{J}\rho A_{J}^{\dagger} - \rho A_{J}^{\dagger}A_{J} - A_{J}^{\dagger}A_{J}\rho \right].
\]

(3.63)

\[8\] Markov idea: One only needs to know the density matrix \( \rho \) at time \( t \) to predict it for all future times \[44\]. The past of the system is irrelevant. E.g., Hamilton’s equations of motion in classical mechanics are Markovian.

\[9\] The only master equations which are known \[45\] to produce positive \( \rho(t) \) for all \( \rho(0) \) are of the completely positive dynamical semigroup (CPDS) form \[49, 50, 51\].
3. Theory

Here \( H \) is some self adjoint operator and the \( A_J \) are arbitrary\(^{10} \). Because the Lindblad form is the quantum mechanical analog of the Liouville equation in classical mechanics, \( L \) is called \textit{Liouville operator}. It has been shown \cite{48}, that \( L \) must be of this Lindblad form for the case of a quantum Markov process. If a master equation cannot be written in the form of (3.63), like the one for the quantum Brownian motion for example, unphysical solutions are included \cite{52}.

3.2.2. Quantum Schrödinger equation

One important thing to notice is that within this master equation formalism the knowledge of the matrix elements of the Liouville superoperator allows us to calculate the time evolution of the density matrix. In the previous formula we have introduced operators labelled by \( A_J \) without explaining their sense. The derivation of (3.63) gives us the physical meaning of these operators. Since this derivation produces some lengthy expressions, by following \cite{47} we only present the main idea of this calculation. We start with the master equation in the Born–Markov approximation \cite{A.63}, deduced in Appendix A.6.

\[
\dot{\rho}(t) = -\int_0^\infty d\tau \text{ tr}_B \{ [H_{\text{int}}(t), [H_{\text{int}}(t-\tau), \rho(t) \otimes \rho_B] ] \},
\]

where the transformed interaction Hamiltonian \cite{A.52} enters,

\[
H_{\text{int}}(t) = e^{i(H_{\text{sys}}+H_B)t} H_{\text{int}} e^{-i(H_{\text{sys}}+H_B)t}.
\]

As can be seen by this equation, the transformation of an operator \( \mathcal{O} \) into the interaction picture \cite{29}

\[
O(t) = U(t, 0) \mathcal{O} U^\dagger(t, 0),
\]

is maintained by the operator

\[
U(t, 0) = e^{i(H_{\text{sys}}+H_B)t}.
\]

Using the Baker–Campbell–Hausdorff formula \cite{29},

\[
e^{\alpha A} B e^{-\alpha A} = B + \alpha [A, B] + \frac{\alpha^2}{2!} [A, [A, B]] + \ldots,
\]

\(^{10}\)The rigorous proofs actually require bounded operators for the \( A_J \).
yields the transformation of $H_{\text{int}} \to H_{\text{int}}$ in the interaction picture. For example, if we consider the interaction between the nanoparticle and the molecule (3.57)

$$H_{\text{pl-mol}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \left[ \lambda_{lm} b_{lm} \sigma_+ + \lambda_{lm}^* b_{lm}^\dagger \sigma_- \right],$$

this transformation is done by the replacements (3.58)

$$\sigma_+ \longrightarrow \sigma_+ e^{i\omega_1 t}, \quad b_{lm} \longrightarrow b_{lm} e^{-i\omega_l t},$$

$$\sigma_- \longrightarrow \sigma_- e^{-i\omega_1 t}, \quad b_{lm}^\dagger \longrightarrow b_{lm}^\dagger e^{i\omega_l t}.$$ 

Expanding the commutators in the master equation (A.63) gives 16 terms, each of which contains a product of two system operators, $\rho(t)$, two bath operators, and $\rho_B$. The trace over the bath variables in this decorrelated form acts only on the bath operators and $\rho_B$. Using the cyclic property of the trace operation gives

$$\text{tr}_B \left\{ b_{lm} \rho_B b_{lm}^\dagger \right\} = \text{tr}_B \left\{ b_{lm}^\dagger b_{lm} \rho_B \right\} = \langle b_{lm} b_{lm}^\dagger \rangle = \delta_{l'l} \delta_{m'm}.$$ (3.67)

Since correlation functions of the form $\langle b_{lm} b_{m'}^{\dagger} \rangle$ and $\langle b_{lm}^\dagger b_{m'}^{\dagger} \rangle$ vanish in general, after some straight forward calculations, we get an equation of the Lindblad form (3.63) where the operators $A_j$ correspond to $\sigma_-$ for the molecule decay channel or to $b_{lm}^\dagger$ for the plasmon decay for instance.

Thus, the master equation for $N_c$ output channels with the damping constants $\gamma_j$ for each decay channel is given by

$$\dot{\rho}(t) = -i[H, \rho] + \sum_{j=1}^{N_c} \frac{1}{2} \gamma_j \left[ 2c_j \rho c_j^\dagger - \rho c_j^\dagger c_j - c_j^\dagger c_j \rho \right]$$ (3.68)

$$\equiv -i \left( H_{\text{eff}} \rho - \rho H_{\text{eff}}^\dagger \right) + \sum_{j=1}^{N_c} J_j \rho \equiv L \rho,$$ (3.69)

where the Hermitian operators $c_j$ mediate interactions of the subsystem with the reservoir and the effective subsystem Hamiltonian\textsuperscript{11} in Eq. (3.69) is

$$H_{\text{eff}} = H - \frac{i}{2} \sum_j \gamma_j c_j^\dagger c_j.$$ (3.70)

\textsuperscript{11}This operator is non-Hermitian. Therefore the appellation 'Hamiltonian' is merely conventional and probably misleading.
The equivalence of Eq. (3.69) and Eq. (3.68) clearly follows straightforwardly by inserting $H_{\text{eff}}$ in (3.69). In (3.69) $J_j$ is the recycling operator:

$$J_j \rho = \gamma_j c_j \rho c_j^\dagger.$$  \hspace{1cm} (3.71)

We use the symbol $\mathcal{L}$ to refer to the Liouville superoperator of the form of Eq. (3.69), and the superoperator signed as $L$ for the form of Eq. (3.63).

Now we have the mathematical equipment to calculate the evolution of our system. The Lindblad operators $c_j$ correspond to the decay of each plasmon state, the decay of the excited molecular state, and to an optical decay process. The damping factors $\gamma_j$ in (3.68) are different for each decay process. They correspond to $\gamma_0/2$ in the Drude framework. We will discuss this fact in Chap. 4, where we present our numerical results.

The determination of the eigensystem of the superoperator $\mathcal{L}$ solves the equation

$$\dot{\rho} = \mathcal{L} \rho.$$  \hspace{1cm} (3.72)

As $\mathcal{L}$ must not be a normal matrix, we have to distinguish left and right eigenvectors. Writing all right eigenvectors in a matrix $v_r$, the left ones in a matrix $v_l$, and introducing a diagonal matrix $\mu$ containing all eigenvalues leads to

$$\mathcal{L} v_r = v_r \mu,$$  \hspace{1cm} (3.73a)

$$v_l \mathcal{L} = \mu v_l.$$  \hspace{1cm} (3.73b)

---

12 A matrix is called normal, if it commutes with its Hermitian conjugate, $A \cdot A^\dagger = A^\dagger \cdot A$. The eigenvectors of a normal matrix with distinct eigenvalues are complete and orthogonal, spanning the $N$-dimensional vector space. 

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3.3. Optical spectrum

After this rather technical chapter, it is only fair to earn some benefits of the presented description. As we have seen, the superoperator $L$ generates the time evolution of our system and the eigensystem of $L$ constitutes a simple way to calculate physical results. Thus, let us determine observable properties, so that we can check the accuracy of our derivations. One way to get some measurable information out of the considered problem is the observation of the fluorescence spectrum.

In quantum mechanics, the calculation of optical spectra accompanies two–time correlation functions \[30, 32, 44, 47\] of the form

$$ G^{(1)}(t + \tau, t) \propto \langle a^\dagger(t + \tau)a(t) \rangle. \quad (3.74) $$

3.3.1. Resonance fluorescence spectrum

In practice, the investigation of atomic spectra is carried out by shining light onto atoms and observing the emitted radiation. If we introduce the quantities $c_{\text{in}}$ and $c_{\text{out}}$ as inputs and outputs of the system, the spectrum of fluorescent light is given by the Fourier transformation of the correlation function $\langle c_{\text{out}}(t')c_{\text{out}}(t) \rangle$, with $t' \geq t$. In our case, these output–operators correspond to the $c_j$ of the Liouville superoperator $L$ in Eq. (3.68) and (3.69). The Fourier transformation of a quantity $f$ and its inverse are given by \[54\]

$$ F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} f(t) e^{i\omega t}, \quad (3.75a) $$

$$ f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega F(\omega) e^{i\omega t}. \quad (3.75b) $$

Since we are interested in the steady state solution, we let the system propagate a very long time $t$ (ideally $t \to \infty$ for a steady state). Then, by following \[47\], the fluorescence spectrum (only for one operator $c$ at the moment) is given by

$$ S(\omega) = \lim_{T \to \infty} \lim_{t \to \infty} \left( \int_{-T}^{T} d\tau \langle c^\dagger(t + \tau)c(t) \rangle e^{-i\omega \tau} \right), \quad (3.76) $$
where the first limit for \( t \) denotes the propagation to the steady state, and the second one for \( T \) formally omits initial transients. In the last equation, it is convenient to split the integration over \( \tau \) into two parts
\[
\int_{-T}^{T} d\tau \langle c^\dagger(t + \tau)c(t)\rangle e^{i\omega \tau} + \int_{-T}^{0} d\tau \langle c^\dagger(t + \tau)c(t)\rangle e^{i\omega \tau}.
\]

Assuming that in a steady state the correlation function depends only on \( \tau \), we can rewrite the correlation function in the second integral as
\[
\langle c^\dagger(t)\rangle e^{-i\omega \tau}.
\]
We change the variable of integration in this integral from \( \tau \) to \( -\tau \), and since
\[
\langle c^\dagger(t)\rangle e^{-i\omega \tau}
\]
is the complex conjugate of \( \langle c^\dagger(t + \tau)c(t)\rangle e^{i\omega \tau} \), we get the result
\[
S(\omega) = \lim_{T \to \infty} \lim_{t \to \infty} 2 \Re \left[ \int_{0}^{T} d\tau \langle c^\dagger(t + \tau)c(t)\rangle e^{i\omega \tau} \right],
\]
where \( \Re \) denotes the real part. It is worthwhile noting that in this form \( S(\omega) \) is formally the real part of the Laplace transform of \( \lim_{t \to \infty} [2\langle c^\dagger(t + \tau)c(t)\rangle] \) evaluated at \( s = -i\omega \). The two–time expectation value in (3.77) can be obtained from the quantum regression theorem \[32, 44, 47\]. Using the time evolution \( \dot{\rho} = \mathcal{L}\rho \) with the Liouville superoperator \( \mathcal{L} \), leads to the general result for two arbitrary operators of the system \( S \) with \( \tau \geq 0 \) \[32\]:
\[
\langle O_1(t)O_2(t + \tau) \rangle = \text{tr}_{S}\{ O_2(0)e^{\mathcal{L}\tau}[\rho(t)O_1(0)] \},
\]
\[
\langle O_1(t + \tau)O_2(t) \rangle = \text{tr}_{S}\{ O_1(0)e^{\mathcal{L}\tau}[O_2(0)\rho(t)] \}.
\]

The square brackets on the right hand side should highlight the fact that the time evolution \( e^{\mathcal{L}\tau} \) only acts on the expression inside these brackets. Inserting (3.78b) in the spectrum (3.77) and considering again \( N_c \) decay channels yields
\[
S(\omega) = \sum_{j=1}^{N_c} \left\{ \lim_{T \to \infty} \lim_{t \to \infty} 2 \Re \left[ \int_{0}^{T} d\tau e^{i\omega \tau} \text{tr}_{S}\{ c_j^\dagger(0)e^{\mathcal{L}\tau}[c_j(0)\rho(t)] \} \right] \right\}.
\]

---

\[13\] \( \mathcal{L}[f(t)](s) = \int_{0}^{\infty} dt f(t)e^{-st} \) with \( s \in \mathbb{C} \) and \( f(t) \) defined for \( t \geq 0 \) \[55\].
4. Results

In this chapter we present the calculated results, starting with the comparison to
the published data [8]. Although in Tab. 2.1 we have already given a listing of the
parameters used for our calculations, we recall the most important in Tab. 4.1. We

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background dielectric constant</td>
<td>ε₀</td>
<td>10</td>
</tr>
<tr>
<td>Dielectric background matrix</td>
<td>ε_b</td>
<td>2.25</td>
</tr>
<tr>
<td>(glass)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inverse relaxation rate</td>
<td>γ₀⁻¹</td>
<td>10 fs</td>
</tr>
<tr>
<td>Plasma frequency</td>
<td>ω_p</td>
<td>9.07 eV</td>
</tr>
</tbody>
</table>

Table 4.1.: Recap of the parameters of a gold nanoparticle used in our calculations.

investigate a gold nanoparticle with a diameter of 10 nm. As mentioned previously,
the only property of the molecule entering our calculations is the dipole moment. For
rhodamine 6G, an organic molecule used as a dye, we choose 6.4 a.u. as numerical
value. The excited molecule energy ω₁ is tuned to 2.38 eV – the frequency of the
plasmon dipole mode – by the laser field.

We begin with different plots of the dielectric function for the nanoparticle and show
the agreement of our description with experimental data. After that, we demonstrate
the decay rates in our system for two different approaches. In the end, we show some
plots of the surface and flux lines of the nanoparticle and present the calculated
resonance fluorescence spectrum.
4. Results

4.1. Dielectric function

At the beginning we have introduced the Drude dielectric function (2.18) as a possible semiclassical description of metals and mentioned the problem due to the pronounced $d$-band density of states for gold. Fig. 4.1 and Fig. 4.2 show the comparison between experimental results from Johnson and Christy [56] and the dielectric function of Drude form $\varepsilon_D$.

Figure 4.1.: Comparison between the real part of the experimental measured dielectric function [56] and the Drude form. The red line corresponds to a frequency dependent damping $\gamma(\omega)$, the dotted line to a fixed $\gamma$–value, and the blue line to the experimental results. The inset shows the zoomed area, where the energies of two plasmon modes are marked.
4.1. Dielectric function

Figure 4.2.: The same as in Fig. 4.1, but now for the imaginary part of the dielectric function. The inset shows again the zoomed area with the two plasmon energies.

One can see that at least for photon energies below 2.5 eV $\varepsilon_D$ is a very good approximation. We have calculated the frequency dependent damping $\gamma(\omega)$ through a fit to the experimental data of the dielectric function. If we insert the plasmon frequencies $\omega_l$, we get the damping constant for each plasmon mode.

In Fig. 4.3, the inverse relaxation rate $\gamma(\omega)^{-1}$ is shown. We have introduced the value $\gamma_0^{-1} = 10$ fs in our calculations and one can see that for low photon energies the frequency dependent damping more or less reproduces this value. Fig. 4.4 again shows the comparison of the dielectric functions, but now for the case of a silver nanoparticle. There the Drude approximation also holds for larger photon energies.
4. Results

![Inverse relaxation rate graph](image)

**Figure 4.3.** Inverse of the frequency dependent damping $\gamma(\omega)$.

![Real and imaginary part of dielectric function](image)

**Figure 4.4.** Real and imaginary part of the dielectric functions for a silver nanoparticle. For the real part, the lines for the Drude approximation with fixed and frequency dependent damping is one upon the other.
4.2. Decay rates

The radiative lifetime \[24\] for a two level atom in vacuum is given by \( \Gamma_0 \), which can be calculated by the Wigner–Weisskopf formula\[1\]. Since our nanoparticle and our molecule are embedded in a dielectric medium, we have to include the outside dielectric constant \( \varepsilon_b \). From this follows the Wigner–Weisskopf decay rate in the following form:

\[
\Gamma_0 = \frac{4}{3} \sqrt{\varepsilon_b} |d|^2 \left( \frac{\omega}{c} \right)^3 ,
\]

(4.1)

where \( d \) is the dipole moment of the molecule, \( c \) the speed of light, and \( \omega \) the frequency.

To calculate the decay constant \( \Gamma \) in our system, we only have to consider the occupation probabilities of the different states at a time \( t \) and \( t + \delta t \). At the beginning we have mentioned the Landau damping of longitudinal plasma waves as an exponentially decreasing process, see Fig. 4.5. \( \Gamma \) describes the damping constant of this

![Figure 4.5.](image)

Figure 4.5.: Excitation probability of the molecule and the plasmon respectively. The linear plot on the left shows the decay in time for two fixed molecule distances. The dotted lines correspond to a distance of 2 nm and the continuous lines to 0.01 nm. On the right hand side the same lines are given in a semilogarithmic plot. The \( x \)-axis is scaled by \( \Gamma_0 \) and therefore dimensionless.

\[1\]This formula can be obtained by Fermi’s Golden Rule, see e.g. [30, 47].
4. Results

decay. A simple approximation leads to the result shown in Fig. 4.6. The blue lines

![Graph showing decay rate](image_url)

Figure 4.6.: Decay constant $\Gamma$ in dependence of the distance between the molecule and the nanoparticle divided by the vacuum value $\Gamma_0$. The molecular dipole moment is pointing in $z$-direction.

correspond to the jellium model description with the experimental measured dielectric function (continuous line with dots) and the Drude approximation (dotted line). The red lines show the decay in the quantum mechanical framework of this diploma thesis with a fixed value for $\gamma$ (dotted line) and for the fitted frequency dependent $\gamma(\omega)$ (continuous line with dots), respectively. As one can see, the agreement between the two approaches with a fixed $\gamma$ (dotted lines) fits well. The match of the jellium model description with the experimental detected $\varepsilon$ (instead of the Drude form) and the explicit dynamic with $\gamma(\omega)$ is also excellent. Especially for small distances it is important to consider a large number of plasmon modes, since the coupling to higher modes increases with a smaller distance. For Fig. 4.6 we have taken into account the first 30 modes.
4.3. Nanoparticle

In this section we present some plots of the spherical nanoparticle. In Fig. 4.7 the spherical harmonics $Y_{lm}(\theta, \varphi)$ as eigensolutions are evaluated on the particle surface.

![Spherical Harmonics](image)

Figure 4.7.: Surface plasmon eigenmodes for a spherical 10 nm nanoparticle [8]. One can see the eigenfunctions exhibit the expected $s,p$ and $d$–like symmetries. The energies of the one–, three–, and fivefold degenerate state are $0 \text{ eV} \ (l = 0)$, $2.38 \text{ eV} \ (l = 1)$ and $2.48 \text{ eV} \ (l = 2)$.

Fig. 4.8 shows the electric flux lines of the dipole and quadrupole mode.

![Electric Flux Lines](image)

Figure 4.8.: Electric flux lines of the nanoparticle. On the surface the eigensolutions are plotted, on the left hand side for the dipole mode $l = 1$, and on the right for the quadrupole mode $l = 2$. The arrow above refers to the molecule.
4. Results

The energy levels of the first 50 plasmon modes are plotted in Fig. 4.9, evaluated using Eq. (3.13),

$$\omega_l = \sqrt{\frac{l}{\varepsilon_0 l + \varepsilon_b (l + 1)}} \omega_p.$$ 

Figure 4.9.: Energy of the first 50 plasmon modes. The inset shows the induced surface charge as expectation value of the plasmon density operator.
4.4. Resonance fluorescence spectrum

In Chap. 3.3 we have obtained Eq. (3.79) for the fluorescence spectrum of our system,

\[ S(\omega) = \sum_{j=1}^{N_c} \left\{ \lim_{T \to \infty} \lim_{t \to \infty} 2 \Re \left[ \int_0^T d\tau e^{i\omega \tau} \text{tr}_S \left\{ c_j^\dagger(0)e^{L\tau} [c_j(0)\rho(t)] \right\} \right] \right\}. \]

In Fig. 4.10 the results for different molecule distances are shown. Due to the coupling between the molecule and the nanoparticle the molecular fluorescence line becomes broadened and we see the expected appearance of sidebands.

Figure 4.10.: Resonance fluorescence intensity for different molecule distances ranging from 2 to 4.4 nm (stepwidth 0.4 nm). We have considered 30 plasmon modes for this plot and a sphere with a diameter of 20 nm.
4. Results

4.5. Conclusion and outlook

In this thesis we have investigated the interaction between a spherical gold nanoparticle and a fluorescent molecule. Contrary to the discussed semiclassical approach, where all details of the material response are described by the dielectric function, we presented a suitable quantisation framework for the surface plasmons. We have developed an elegant formalism how to describe the dynamics of a reduced system, where the contribution of the environment – described as an open reservoir – has been integrated out.

The decay rates show the expected behaviour for the coupling, and the eigensolutions of the nanoparticle can be described by spherical harmonics. We have seen that with decreasing molecule–particle distance the molecular fluorescence line becomes broadened and eventually split. The result for the fluorescence spectrum will soon be verified by experiments.\(^2\)

The investigation of interactions at small length scales is an emerging new field of study, and a variety of applications are based on this effects. A better theoretical understanding of the fundamental physical properties of nanoparticles goes hand in hand with the application–oriented research in nanotechnology. There are many open questions to explore and an obvious continuation of the presented work is to ascertain the interaction of many particles with many molecules or the possible collective behaviour of such a system [57, 58, 59].

\(^2\)Measurements are done by the 'Nano–Optics/Optics and Laser Science' groups at our institute.
Acknowledgements

First of all I want to thank my parents and my family for their ongoing support and love, for giving me the opportunity to study one of the most interesting fields in science, and besides, for the constant refilling of my refrigerator.

With Univ. Prof. Dr. Ulrich Hohenester I had the luck of working with a really great supervisor and physicist and I want to express my gratitude for his guidance and for conveying the enjoyment for his work. Furthermore special thanks also go to the 'Nano–Optics/Optics and Laser Science’ groups of Univ. Prof. Dr. Joachim Krenn and Univ. Prof. Dr. Alfred Leitner at the department for experimental physics in Graz for their collaboration.

Last but not least I am indebted to all my friends for their encouragement and amity. They always had coffee and time for me, and especially I want to mention Julia Danzer and Markus Huber for reading and correcting my typing.
A. Appendix

A.1. Atomic units

In 1959 H. Shull and G. G. Hall wrote a paper [60] with the suggestion of a new unit system to be used for quantum mechanical calculations:

*It seems to us that the time is ripe for some standardisation in the use of units, for some agreed notations for the most common units and for a general agreement to specify units so carefully in writing papers that future scientific generations may be spared [the] difficulties [caused by conversion factors which depend on the currently accepted best values of \( \hbar, m, e, c, N, \text{etc.} \)].*

They suggested the use of atomic units (a.u.) which nowadays are convenient for many different disciplines in physics, e.g. atomic physics, condensed-matter physics, electromagnetism or quantum electrodynamics. Like the Planck units the atomic unit system is derived from certain fundamental physical properties and it is free of anthropocentric considerations [60]. For these fundamental properties the electron attributes of a hydrogen atom are used. Therefore it follows that, for example, a binding energy calculated in a.u. has the unit Hartree\(^1\) (double Rydberg) which is the primary result of the calculation.

As a very useful simplification, the numerical values of six physical constants are all unity by definition of the atomic unit system:

\(^1\)The Hartree energy is equal to the absolute value of the electric potential energy of the hydrogen atom in its ground state.
A. Appendix

Electron mass \( m = 1 \) Bohr radius \( a_0 = 1 \)

Electron charge \( e = 1 \) Hartree energy \( H = 1 \)

Dirac’s constant \( \hbar = 1 \) Coulomb constant \( k_c = 1 \)

(These six constants are not independent, it suffices to normalise any four of them; further reading again in [60].) The unity of the Coulomb constant \( k_c = 1/(4\pi\varepsilon_0) \) comes with the use of Gaussian units, where \( \varepsilon_0 = 1/4\pi \). The fundamental units are also given by the six constants above, see Table A.1.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit name</th>
<th>Symbol</th>
<th>SI value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>Bohr radius</td>
<td>( a_0 )</td>
<td>( 5.292 \times 10^{-11} ) m</td>
</tr>
<tr>
<td>Charge</td>
<td>Elementary charge</td>
<td>( e )</td>
<td>( 1.602 \times 10^{-19} ) C</td>
</tr>
<tr>
<td>Mass</td>
<td>Electron mass</td>
<td>( m_e )</td>
<td>( 9.109 \times 10^{-31} ) kg</td>
</tr>
<tr>
<td>Energy</td>
<td>Hartree energy</td>
<td>( H )</td>
<td>( 4.360 \times 10^{-18} ) J</td>
</tr>
<tr>
<td>Angular momentum</td>
<td>Dirac’s constant</td>
<td>( \hbar )</td>
<td>( 1.055 \times 10^{-34} ) Js</td>
</tr>
<tr>
<td>Electrostatic force constant</td>
<td>Coulomb’s constant</td>
<td>( k_c )</td>
<td>( 8.988 \times 10^9 ) N m^2/C^2</td>
</tr>
</tbody>
</table>

Table A.1.: Atomic units and corresponding SI values, taken from 'CODATA', provided by the National Institute of Standards and Technology, [http://physics.nist.gov/cuu/Constants/index.html](http://physics.nist.gov/cuu/Constants/index.html).

Another advantage of atomic units is the simplification of various equations. For example the Maxwell equations take the elegant form of \( \text{(2.9)} \) or the Hamiltonian of the hydrogen atom transforms from \( H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} \) in SI units to \( H = -\frac{1}{2} \nabla^2 - \frac{1}{r} \).

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A.2. Spherical harmonics

Many problems in physics lead to equations containing the Laplace operator $\Delta$, e.g. the wave or the Poisson equation. Depending on the symmetry of the considered problem one will try to solve the equations in an adequate set of variables. If spherical symmetry is present, one will choose the spherical coordinates $(r, \theta, \varphi)$. For example the Laplace equation

$$\triangle f(r, \theta, \varphi) = 0 \quad (A.1)$$

can be solved by the ansatz $f(r, \theta, \varphi) = R(r)S(\theta)T(\phi)$ (see e.g. [61]). The Laplace operator in this coordinate system reads

$$\Delta \equiv \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right], \quad (A.2)$$

and the above product ansatz allows us to separate Eq. (A.1) into three parts. The expression for $\varphi$ yields a wave equation with the solution \{e$^{im\varphi}$, e$^{-im\varphi}$\}, and the one for the variable $\theta$ has the form of an associated Legendre differential equation with the associated Legendre polynomials $P^m_l(\cos \theta)$ [55] as solution. Therefore the angular part of the complete solution is given by

$$T(\varphi)S(\theta) = e^{\pm im\varphi}P^m_l(\cos \theta). \quad (A.3)$$

This leads to the definition of an orthogonal system of functions and together with a normalisation factor\(^2\) the spherical harmonics $Y^l_m(\theta, \varphi)$ are derived\(^3\)

$$Y^l_m(\theta, \varphi) = \sqrt{\frac{(2l + 1)(l - m)!}{4\pi (l + m)!}} P^m_l(\cos \theta)e^{im\varphi} \quad (A.4)$$

A detailed explanation and rigorous definition of these functions can be found in the book of Varshalovich et al. [41], which we will follow from here on.

In Eq. (A.4) we see that a spherical harmonic $Y^l_m(\theta, \varphi)$ is a single–valued, continuous,

\(^2\)Unfortunately also different normalisation factors and signs can be found in the literature. We will stick to the definition (A.4).

\(^3\)Another less obvious but more elegant way is the definition of spherical harmonics as components of some irreducible tensor of rank $l$ with the commutation relations $[L_\mu, Y^l_m(\theta, \varphi)] = \sqrt{l(l + 1)}C^l_{l-m-\mu}Y^l_{m+\mu}(\theta, \varphi)$ where $L_\mu(\theta, \varphi)$ is a spherical component of the operator $L$. See [41] for further details.
bounded complex function of two real arguments $\theta, \varphi$ with $0 \leq \theta \leq \pi$ and $0 \leq \phi < 2\pi$.
For a given $l$ there exist $(2l + 1)$ functions corresponding to different $m$’s.
These functions are eigenfunctions of the orbital angular momentum operator in quantum mechanics which is defined as

$$L \equiv \mathbf{r} \times \mathbf{p} = \frac{1}{i} (\mathbf{r} \times \nabla). \quad (A.5)$$

The eigenvalue equations read

$$L^2 Y_{lm}(\theta, \varphi) = l(l + 1) Y_{lm}(\theta, \varphi), \quad (A.6)$$
$$L_z Y_{lm}(\theta, \varphi) = m Y_{lm}(\theta, \varphi), \quad (A.7)$$

or in expanded form

$$\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + l(l + 1) \right] Y_{lm}(\theta, \varphi) = 0, \quad (A.8)$$
$$\left[ i \frac{\partial}{\partial \varphi} + m \right] Y_{lm}(\theta, \varphi) = 0. \quad (A.9)$$

In Eq. (A.6) one can see that $l$ specifies the absolute value of orbital angular momentum (because $l(l + 1)$ is the eigenvalue of $L^2$) and $m$ in Eq. (A.7) is the eigenvalue of $L_z$, which is the projection of the orbital angular momentum operator on the quantisation axis.

Equation (A.8) has two linearly independent solutions for fixed $l$ and $m$, but only one of them is regular (i.e. satisfies the condition $|Y_{lm}(\theta, \varphi)|^2 < \infty$) while the other is singular at $\theta = 0$ and $\theta = \pi$. In quantum mechanics and electrodynamics the regular solution is of major interest. The homogeneous boundary conditions

$$Y_{lm}(\theta, \varphi \pm 2\pi n) = Y_{lm}(\theta, \varphi), \quad (A.10)$$
$$\frac{\partial}{\partial \varphi} Y_{lm}(\theta, \varphi)|_{\theta=0,\pi} = 0, \quad (A.11)$$

lead to integer values of $l$ and $m$ (with $|m| \leq l$). Since the differential equations (A.8) and (A.9) and the boundary conditions determine the spherical harmonics only up to some arbitrary complex factor a normalisation of the functions is needed.
A.2. Spherical harmonics

A.2.1. Completeness and normalisation

The normalisation and orthogonality relation of spherical harmonics [55] is given by

\[ 2\pi \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta Y^*_{lm}(\theta, \varphi)Y_{l'm'}(\theta, \varphi) = \delta_{ll'}\delta_{mm'}, \quad (A.12) \]

and the completeness relation reads as follows:

\[ \sum_{l=0}^\infty \sum_{m=-l}^l Y^*_{lm}(\theta, \varphi)Y_{lm}(\theta', \varphi') = \delta(\varphi - \varphi')\delta(\cos \theta - \cos \theta'). \quad (A.13) \]

A detailed list of symmetry properties can again be found in [41]. Here we only mention the complex conjugation

\[ Y^*_{lm}(\theta, \varphi) = Y_{lm}(\theta, -\varphi) = (-1)^m Y_{l-m}(\theta, \varphi). \quad (A.14) \]

A.2.2. Expansions in series of the spherical harmonics

An arbitrary function \( f(\theta, \varphi) \) which is defined in the interval \( 0 \leq \theta \leq \pi, 0 \leq \varphi < 2\pi \) and satisfies the condition

\[ 2\pi \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta |f(\theta, \varphi)|^2 < \infty, \quad (A.15) \]

can be expanded into a series of spherical harmonics as

\[ f(\theta, \varphi) = \sum_{l=0}^\infty \sum_{m=-l}^l a_{lm}Y_{lm}(\theta, \varphi), \quad (A.16) \]

with the expansion coefficients \( a_{lm} \) given by

\[ a_{lm} = \frac{2\pi}{2\pi} \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta Y^*_{lm}(\theta, \varphi)f(\theta, \varphi). \quad (A.17) \]
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This last relation may be treated as an integral transformation of \( f(\theta, \varphi) \) from the continuous variables \( \theta, \varphi \) to the discrete variables \( l, m \). The transformation matrix in this case is given by \( Y_{lm}(\theta, \varphi) \equiv \langle \theta, \varphi | lm \rangle \).

\[
\langle lm | f \rangle = \langle lm | \theta, \varphi \rangle \langle \theta, \varphi | f \rangle ,
\]
where

\[
\langle lm | f \rangle \equiv a_{lm}, \quad \langle lm | \theta, \varphi \rangle \equiv Y^*_{lm}(\theta, \varphi), \quad \langle \theta, \varphi | f \rangle \equiv f(\theta, \varphi).
\]

The expansion (A.16) is widely used in different branches of physics. It is called the multipole expansion and \( a_{lm} \) are the multipole moments (e.g. see [26]). The transformations (A.17) and (A.18), respectively, are unitary

\[
\langle f | lm \rangle \langle lm | f \rangle = \langle f | \theta, \varphi \rangle \langle \theta, \varphi | f \rangle ,
\]
and the expansion coefficients \( a_{lm} \) satisfy the Parseval condition (see [55] or [61])

\[
\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} |a_{lm}|^2 = \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta |f(\theta, \varphi)|^2.
\]

\(^4\text{Summation or integration is assumed over all variables which are repeated twice.}\)
A.3. Equation of motion for the surface charge

By following [8] fairly closely, we will derive an expression for the motion of the surface charge density. In this simple model there are free electrons moving around inside the particle, whereas the other ones are bounded and result in a positive background dielectric function (jellium or hydrodynamic model [20, 62]). The Boltzmann equation with the electron distribution function \( f = f(r, v, t) \) describes the dynamics of the electron gas:

\[
\frac{\partial f}{\partial t} + v \cdot \nabla f + F \cdot \nabla v f = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}. 
\]  
(A.22)

The electron velocity is given by \( v \), and the Lorentz force \( F \) is acting on the particles. The left–hand side accounts for the drift and force contributions, and the right–hand side for electron collisions. A more simplified description scheme can be obtained by introducing the moments of \( f \) through

\[
\begin{align*}
n(r, t) &= -\int d v\ f(r, v, t), \quad \text{(charge density)} \quad \text{(A.23a)} \\
j(r, t) &= -\int d v\ v f(r, v, t). \quad \text{(current density)} \quad \text{(A.23b)}
\end{align*}
\]

The minus sign accounts for the negative electron charge. Higher moments, such as the kinetic stress tensor, will be neglected. Performing this moment expansion in Eq. (A.22) and truncating at the level of \( n \) and \( j \) readily yields

\[
\begin{align*}
\frac{\partial n}{\partial t} + \nabla j &= 0, \quad \text{(continuity equation)} \quad \text{(A.24a)} \\
\frac{\partial j}{\partial t} + E n + j c \times B &= \left( \frac{\partial j}{\partial t} \right)_{\text{coll}}. \quad \text{(force equation)} \quad \text{(A.24b)}
\end{align*}
\]

The collision term in (A.24b) again corresponds to scattering processes. If the metal nanoparticle is in the equilibrium state, we deal with a constant electron density \( n_0 \) (also see Chap. 2.2.3). The field produced by \( n_0 \) is precisely cancelled by that of the positive jellium background. If an external perturbation is applied, this density will be modified

\[
n = n_0 + \delta n,
\]
and a current \( \mathbf{j} \) will be induced (for simplicity we use the same symbol \( n \) for the modified density). We now expand the force equation (A.24b) in terms of this modified density, the induced current, and the electric field \( \mathbf{E} \). The field \( \mathbf{E} \) is the sum of the external and induced electric field, \( \mathbf{E}_{\text{ext}} \) and \( \mathbf{E}_{\text{ind}} \) respectively. The latter is the solution of the Poisson equation for the induced charge \( n \). Using the continuity equation (A.24a) and keeping only lowest order terms yields

\[
\frac{\partial^2 n}{\partial t^2} - n_0 (\nabla \cdot \mathbf{E}) - \mathbf{E} \cdot (\nabla n_0) + \nabla \left( \frac{\partial \mathbf{j}}{\partial t} \right)_{\text{coll}} = 0.
\]

(A.25)

In [25] it is shown, how to separate the density \( n \) into a volume and a surface part. Further on, we label the volume term with \( \nu \) and the surface term with \( \sigma \). Introducing the outer surface normal as \( \mathbf{n} \), we obtain

\[
\nabla n_0 = -n_0 \mathbf{n}.
\]

(A.26)

Inserting \( n = \nu + \sigma \) in (A.25), and performing a Fourier transform in time leads to the following separation

\[
\omega (\nu) - n_0 \nabla \cdot \mathbf{E} = 0,
\]

(A.27)

\[
\omega (\sigma) + n_0 \mathbf{n} \cdot \mathbf{E} = 0.
\]

(A.28)

Here all collision effects have been lumped into the relaxation rate \( \gamma_0 \). For simplicity we shall neglect below the volume part \( \nu \) [25].

The use of the boundary integral method presented in [8] results in the equation of motion for the surface charge in linear response for an external excitation \( \mathbf{E}_{\text{ext}} \) with frequency \( \omega \):

\[
\omega (\omega + i\gamma_0)\sigma - M\sigma = -n_0 \mathbf{n} \cdot \mathbf{E}_{\text{ext}}.
\]

(A.29)

The Hermitian matrix \( M \) accounts for the mediation of the force exerted by the complete surface charge distribution. A convenient way to solve the last equation is by computing the eigenvalues and eigenvectors of the matrix \( M \) through

\[
Mu_\lambda = \omega_\lambda u_\lambda.
\]

(A.30)

The eigenmodes \( u_\lambda \) form a complete set and we can thus expand \( \sigma \) in terms of the \( u_\lambda \). Multiplying Eq. (A.29) from left and right with \( u_\lambda \), and using (A.30), we obtain

\[
\sigma = -n_0 \sum_\lambda \frac{u_\lambda (\mathbf{n} \cdot \mathbf{E}_{\text{ext}})}{\omega (\omega + i\gamma_0) - \omega_\lambda} u_\lambda.
\]

(A.31)
It is important to realise that the complete spectrum of surface charge excitations is obtained through a single diagonalisation of $M$, and that the eigenvalues $\omega_\lambda$ and eigenmodes $u_\lambda$ describe the genuine excitations of metal nanoparticles [8].
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A.4. Boundary conditions at different media

Maxwell’s equations (2.9) are local differential equations for every spacetime point \((x, t)\). By using the relations of Stokes and Gauss \[55\] they can be transformed into integrals. Following \[26\], let \(V\) be a finite space volume bordered by the surface area \(S\), and let \(\mathbf{n}\) be the unit vector in outside direction of the surface element \(da\) (see Fig. A.1).

![Figure A.1: Schematic diagram of the interface between two different dielectric media 1 and 2. The small cylinder of height \(h\) is given by the volume \(V\) and surface \(S\). The cylinder’s lower and upper top surface area is labeled by \(\Delta a\). The normal vector \(\mathbf{n}\) points in outside direction (from medium 1 to medium 2). The vector \(\mathbf{t}\) is tangential to the surface \(\Sigma\). The surface spanned by the rectangular kink \(C\) is perpendicular to the interface, i.e., \(\mathbf{t}\) is perpendicular to the kink. At the interface \(\Sigma\) exists an idealised surface charge \(\sigma\).]
A.4. Boundary conditions at different media

\[ \oint_S \mathbf{D} \cdot \mathbf{n} \, da = 4\pi \int_V \rho \, d^3x, \]  
(Gauss’s Law) \hspace{1cm} (A.32a)

\[ \oint_S \mathbf{B} \cdot \mathbf{n} \, da = 0, \]  
(magnetic analogon) \hspace{1cm} (A.32b)

\[ \oint_C \mathbf{H} \cdot d\mathbf{l} = \int_S \left[ \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \right] \cdot \mathbf{n}' \, da, \]  
(Ampère’s Circuital Law) \hspace{1cm} (A.32c)

\[ \oint_C \mathbf{E} \cdot d\mathbf{l} = -\int_S \frac{\partial \mathbf{B}}{\partial t} \cdot \mathbf{n}' \, da. \]  
(Faraday’s Induction Law) \hspace{1cm} (A.32d)

This well–known form of Maxwell’s equations lead to the boundary conditions of electromagnetic fields and potentials at the interface of two different media. At first we apply Eq. (A.32a) and Eq. (A.32b) to the volume of the small cylinder in Fig. A.1. In the limit of infinitesimal height \((h \to 0)\) only the lower and upper top surface area are non–zero. Let us assume that this surface has the value \(\Delta a\). It follows that

\[ \oint_S \mathbf{D} \cdot \mathbf{n} \, da = (\mathbf{D}_2 - \mathbf{D}_1) \cdot \mathbf{n} \, \Delta a, \]  
(A.33)

\[ \oint_S \mathbf{B} \cdot \mathbf{n} \, da = (\mathbf{B}_2 - \mathbf{B}_1) \cdot \mathbf{n} \, \Delta a. \]  
(A.34)

If the charge density \(\rho\) at the surface \(\Sigma\) is singular and forms an idealised surface charge density \(\sigma\), the right hand side of Eq. (A.32a) yields

\[ 4\pi \int_V \rho \, d^3x = 4\pi \sigma \, \Delta a. \]  
(A.35)

From these equations follow the boundary conditions for the normal components of \(\mathbf{D}\) and \(\mathbf{B}\):

\[ (\mathbf{D}_2 - \mathbf{D}_1) \cdot \mathbf{n} = 4\pi \sigma, \]  
(A.36)

\[ (\mathbf{B}_2 - \mathbf{B}_1) \cdot \mathbf{n} = 0. \]  
(A.37)

Applying the same procedure to the rectangular kink \(C\) with (A.32c) and (A.32d), yields the boundary conditions for the tangential field components:

\[ \mathbf{n} \times (\mathbf{E}_2 - \mathbf{E}_1) = 0, \]  
(A.38)

\[ \mathbf{n} \times (\mathbf{H}_2 - \mathbf{H}_1) = \mathbf{K}, \]  
(A.39)

\footnote{Remarks to the idealisations in electrodynamics can again be found in the fabulous book of Jackson [26].}
where $\mathbf{K}$ is an idealised surface current density.

The scalar potential $\Phi$ obeys analogous conditions, which are quickly derived by using the relations

$$
\mathbf{D}_1 = \varepsilon_1 \mathbf{E}_1 = -\varepsilon_1 \nabla \Phi_1, \quad \mathbf{D}_2 = \varepsilon_2 \mathbf{E}_2 = -\varepsilon_2 \nabla \Phi_2.
$$

(A.40)

Inserting this in Eq. (A.36) leads to

$$
\varepsilon_1 \Phi'_1 \bigg|_{\text{surf}} = \varepsilon_2 \Phi'_2 \bigg|_{\text{surf}},
$$

(A.41)

where the apostrophe $'$ denotes the normal derivative, i.e. perpendicular to the surface. Eq. (A.38) shows, that the tangential components of $\mathbf{E}$ are continuous at the interface and therefore the derivation of the potential in tangential direction is also continuous.

Using spherical coordinates and considering a sphere with radius $a$ and surface charge density $\sigma$ in a dielectric medium yields

$$
\varepsilon_{\text{in}} \frac{\partial \Phi_{\text{in}}}{\partial r} \bigg|_a - \varepsilon_{\text{out}} \frac{\partial \Phi_{\text{out}}}{\partial r} \bigg|_a = 4\pi \sigma 
$$

(A.42a)

$$
\frac{\partial \Phi_{\text{in}}}{\partial \theta} \bigg|_a - \frac{\partial \Phi_{\text{out}}}{\partial \theta} \bigg|_a = 0
$$

(A.42b)
A.5. Density operator

The following statements can be found in various books about quantum mechanics. For this short overview we have again used the book of Gardiner and Zoller [44].

The density operator was introduced by von Neumann in order to treat situations where there is a statistical element to the physics other than that which arises directly from quantum mechanics. It is possible to define the density operator of a pure system by the outer product of the system’s state vector $|\Psi,t\rangle$ (in the Schrödinger picture)

$$\rho(t) \equiv |\Psi,t\rangle\langle\Psi,t|.$$  \hspace{1cm} (A.43)

All measurable information in the wavefunction is contained in the density operator. With $\rho(t)$ one can calculate the expectation value of an operator $A$:

$$\langle A \rangle = \langle \Psi, t | A | \Psi, t \rangle = \text{tr} \{ A \rho(t) \}.$$  \hspace{1cm} (A.44)

A more general formulation of $\rho$ for the case that the state of the system is not known with the precision implicit in the specification of a state vector $|\Psi,t\rangle$ is also possible. If the system is prepared with probabilities $P(a)$ in various states $|\Psi_a\rangle$, the new definition of $\rho$ reads

$$\rho \equiv \sum_a P(a) |\Psi_a\rangle\langle\Psi_a|,$$  \hspace{1cm} (A.45)

and the formula for the mean of an operator $A$ is then again

$$\langle A \rangle = \sum_a P(a) \langle \Psi_a | A | \Psi_a \rangle = \text{tr} \{ A \rho \}$$  \hspace{1cm} (A.46)

The density operator in the form of Eq. (A.45) contains both the statistical and quantum mechanical information about the system.

A.5.1. Properties

- **Semidefiniteness**
  
  $\rho$ is positive semidefinite. For any state $|A\rangle$ it holds the relation $\langle A|\rho|A\rangle = \sum_a P_a |\langle A|\Psi_a\rangle|^2 \geq 0$.  

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- Pure state
  \( \rho = |\Psi_a\rangle\langle \Psi_a| \) is said to be a pure state, since the system is always in the state \( |\Psi_a\rangle \). Then \( \rho \) is idempotent: \( \rho^2 = \rho \).
  Conversely, if \( \rho^2 = \rho \), we can write \( \rho \) as a pure state. Since \( \rho \) is Hermitian, we can write a spectral representation \( \rho = \sum \lambda_i |i\rangle\langle i| \) with the eigenvalues \( \lambda_i = 0, 1 \).
  Because of tr \( \{\rho\} = 1 \), only one \( \lambda_i \) is 1 (let’s say for \( i = m \)), and therefore \( \rho = |m\rangle\langle m| \).

- Trace
  The trace of \( \rho \) is equal to 1 and tr \( \{\rho^2\} \leq 1 \), the equality only applying to pure states.
A.6. Master equation in Born–Markov approximation

The idea of the physics behind the master equation and its derivation will be presented here. The philosophy is to model environmental interactions by coupling a system \( S \) to a reservoir \( R \) \[32\]. Following \[44\] fairly closely once again, we consider a system described by a Hamiltonian of the form

\[
H = H_{\text{sys}} + H_B + H_{\text{int}},
\]

where the constituent Hamiltonians correspond, respectively, to the system, a reservoir (heat bath), and the interaction between them. The bath is only of indirect interest, and its properties need only to be specified in very general terms. The total density operator for the composite system is called \( \chi(t) \). In the Schrödinger picture it satisfies the von-Neumann equation

\[
\dot{\chi}(t) = -i[H, \chi(t)] = -i [H_{\text{sys}} + H_B + H_{\text{int}}, \chi(t)] .
\]

This expression is obtained directly from the Schrödinger equation for the time development of the state vector \( \mathcal{H}[\psi] = i \frac{d}{dt} |\psi\rangle \). Writing the density operator as \( \chi = |\psi\rangle\langle\psi| \) and using \( \dot{\chi} = |\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}| \) yields Eq. (A.48).

The definition of the reduced density operator, where the contribution of the bath states is traced out, leads to the desired description of the subsystem \( H_{\text{sys}} \),

\[
\tilde{\rho}(t) = \text{tr}_B \{ \chi(t) \} .
\]

The next step is the transformation of the equation of motion (A.48) into the interaction picture, defined by setting

\[
\chi_I(t) = e^{i(H_{\text{sys}}+H_B)t} \chi(t) e^{-i(H_{\text{sys}}+H_B)t} .
\]

In physical terms, we separate the rapid motion generated by \( H_{\text{sys}} + H_B \) from the slow motion generated by the interaction \( H_{\text{int}} \). The von-Neumann equation does not change its form after this transformation

\[
\dot{\chi}_I(t) = -i [H_{\text{int}}(t), \chi_I(t)] ,
\]

\( ^6 \)This equation differs in sign from the Heisenberg equation of motion for dynamical operators (in the Heisenberg picture) \( \dot{A}(t) = i[H, A(t)] \).
which follows straight forward. The explicitly time–dependent operator $H_{int}$ is given
by
\[ H_{int}(t) = e^{i(H_{sys} + H_{B})t} H_{int} e^{-i(H_{sys} + H_{B})t}. \]  
(A.52)
Writing $\chi(t)$ as the inverse transformation of $\chi_I(t)$ and inserting this in the expression
for the reduced density operator (A.49) yields
\[ \tilde{\rho}(t) = \text{tr}_B \left\{ e^{-i(H_{sys} + H_{B})t} \chi_I(t) e^{i(H_{sys} + H_{B})t} \right\}. \]  
(A.53)
Since $H_B$ is a function only of bath variables, the appliance of the cyclic property of
the trace cancels the factors involving $H_B$ and we get
\[ \tilde{\rho}(t) = \text{tr}_B \left\{ e^{-iH_{sys}t} \rho(t) e^{iH_{sys}t} \right\}, \]  
(A.54)
with the reduced density operator in the interaction picture
\[ \rho(t) \equiv \text{tr}_B \{ \chi_I(t) \}. \]  
(A.55)

A.6.1. Initial condition

Initially the system and the environment are assumed to be uncorrelated. The total
density operator then factorises into a direct product
\[ \chi(0) = \tilde{\rho}(0) \otimes \rho_B. \]  
(A.56)
Additionally, we assume that the reservoir should be so large that its statistical
properties are unaffected by the weak coupling to the system. The bath always stays
in the vacuum state or thermal equilibrium.

A.6.2. Perturbation series

If we integrate Eq. (A.51) from 0 to $t$ and consider the initial condition (A.56), we
obtain a power series in the perturbation $H_{int}$ by an iteration procedure. After two
iterations we derive
\[ \chi_I(t) = \chi_I(0) - i \int_0^t dt' \ [H_{int}(t'), \chi_I(0)] - \int_0^t dt' \ \int_0^{t'} dt'' \ [H_{int}(t'), [H_{int}(t''), \chi_I(t'')]]. \]
The differentiation of this result with respect to $t$ yields an integro–differential equation for $\chi_I(t)$

$$\dot{\chi}_I(t) = -i [H_{int}(t), \chi_I(0)] - \int_0^t dt' [H_{int}(t), [H_{int}(t'), \chi_I(t')]].$$

(A.57)

But why do we need a second order expansion? As will we see in the next equation, the first expression on the right hand side in (A.57) leads to terms which are proportional to $\langle H_{int} \rangle$ and therefore are zero! Thus, the first non–vanishing term is given by the second order term. Using the reduced density operator (A.55) and tracing both sides of (A.57) over the bath variables yields

$$\dot{\chi}_I(t) = -\int_0^t dt' \text{tr}_B \{ [H_{int}(t), [H_{int}(t'), \chi_I(t')]] \},$$

(A.58)

where we have used the following two assumptions

$$\text{tr}_B \{ H_{int}(t) \chi_I(0) \} \rightarrow \langle H_{int} \rangle = 0,$$

(A.59)

$$\chi_I(0) = \chi(0) = \tilde{\rho}(0) \otimes \rho_B.$$

(A.60)

A.6.3. Born approximation

We now want to replace $\chi_I(t')$ in (A.58) by a factorised approximation

$$\chi_I(t') \approx \rho(t') \otimes \rho_B,$$

(A.61)

where the direct product is given by the reduced density operator at $t'$ multiplied with the bath density operator. This replacement of the density matrix of the composed system by a product of the two components is called Born approximation. This means that the reservoir density operator $\rho_B$ and the bath correlation functions are not significantly affected by the interaction. The assumption is justified for the case of a

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7We have assumed that the density operator may be written approximately as a direct product. In practice the interaction can be written as a sum of terms like $X_{sys} Y_B$, where both operators act only in the system and bath spaces respectively. Therefore all we really need, is that approximations like $\text{tr}_B \{ [Y_B(t), [Y_B(t'), \chi_I(t')]] \} \approx \rho(t') \otimes \text{tr}_B \{ [Y_B(t), [Y_B(t'), \rho_B]] \}$ are valid.
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weak system–bath coupling \[63\]. Because the bath is much bigger than the system, and therefore the interaction affects the system much more than the bath, the system density operator is allowed to change.

A.6.4. Markov approximation

Inserting (A.61) in Eq. (A.58) yields an integro–differential equation for the reduced density operator in the interaction picture

\[
\dot{\rho}(t) = -\int_0^t dt' \text{tr}_B \left\{ \left[ H_{\text{int}}(t), \left[ H_{\text{int}}(t'), \rho(t') \otimes \rho_B \right] \right] \right\} .
\] (A.62)

To get the final result, the Markov approximation \( \rho(t') \approx \rho(t) \) is needed. The meaning of it is that \( \rho(t') \) changes insignificantly over the time taken in the last equation. Since the interaction is assumed to be weak, the rate of change of the interaction picture system density operator will be quite slow compared to that of the bath operators. If \( t \) is much bigger than the thermal correlation time, we can let the lower limit of the time integral go to \(-\infty\), and finally deduce the master equation

\[
\dot{\rho}(t) = -\int_0^\infty d\tau \text{tr}_B \left\{ \left[ H_{\text{int}}(t), [H_{\text{int}}(t-\tau), \rho(t) \otimes \rho_B] \right] \right\} .
\] (A.63)

Since the Markov approximation appears as an additional assumption besides the Born approximation, one is tempted to believe that the master equation (A.62) is more accurate than (A.63). In \[63\] it is shown, that both approximations are only valid to second order in the coupling strength and are hence equally accurate.

Markovian behaviour seems reasonable on physical grounds, see \[32\] for instance: If we make our model a little more specific by writing \( H_{\text{int}} \propto \sum_i s_i r_i \), where \( s_i \) are operators in the Hilbert space of \( S \) and the \( r_i \) are reservoir operators, then the expansion of the commutators in (A.63) leads to correlation functions of the form

\[
\text{tr}_B \{ \rho_B r_i(t) r_j(t') \} = \langle r_i(t) r_j(t') \rangle_B ,
\] (A.64a)

\[
\text{tr}_B \{ \rho_B r_j(t') r_i(t) \} = \langle r_j(t') r_i(t) \rangle_B .
\] (A.64b)
The properties of the reservoir enter the master equation through these two correlation functions. The Markov approximation is justified, if \( \rho(t) \) decays very rapidly on the timescale on which \( \rho(t) \) varies. Ideally, the correlations are proportional to \( \delta(t - t') \), because then the approximation relies on the existence of two widely separated time scales. A slow time scale for the dynamics of \( S \), and a fast scale characterising the decay of reservoir correlation functions.

As alluded at the beginning of this section, we were following [44] for the derivation of (A.63), and we also end this chapter with their words:

*The Markov property is a highly desirable property from a mathematical point of view, because a whole structure of measurement theory can be built around it in a compact and self-contained way. The elegance of this structure leads to the formulation in the abstract of the concept of the quantum Markov process as a branch of mathematics. Nevertheless, it is important to remember that it is an assumption, based on the existence of short correlation times in the heat bath, and the use of perturbation theory.*
Bibliography


Bibliography


