Coupled Plasmon/Molecule Dynamics Near Core-Shell Nanoparticles: Synthesis, Ultrafast Characterization, and Quantum/Classical Modeling

Holden Tyler Smith
Louisiana State University and Agricultural and Mechanical College, avxseven@gmail.com

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COUPLED PLASMON/MOLECULE DYNAMICS NEAR CORE-SHELL NANOPARTICLES: SYNTHESIS, ULTRAFAST CHARACTERIZATION, AND QUANTUM/CLASSICAL MODELING

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Holden Tyler Smith
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All of the experience and knowledge that I have gained has made me into a better person, scientist, and learner, and has culminated in my decision to obtain my doctorate in chemistry. The desire to seek out knowledge has led to many extraordinary connections and opened many doors. Chemistry is the study of change, and with that change brings new possibilities and insight on the inner workings of the world around us. It is very humbling to know that something as simple as a question can spark an idea that has the potential to change how we view the universe itself.

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Abstract

In this dissertation, the resonance coupling of chromaphoric dyes adsorbed on the surface of plasmonic nanoparticles (NPs) are investigated using a combined theoretical and experimental approach. Colloidal gold, gold-silver core-shell, silver-gold core-shell, and gold-silver-gold core-shell-shell NPs are considered. These NPs are thiolated with mercaptosuccinic acid, and malachite green dyes are adsorbed to the surface of the nanoparticle (NP) via electrostatic interactions. Second harmonic generation is used to determine the surface to the isotherm of the molecular dyes to the colloidal nanoparticle surface. Adsorption isotherms show that the SHG intensity increases as the concentration of dye increases, reaching a plateau signal at saturation. These adsorption isotherms are fit with a modified Langmuir equation to determine the best fit parameters corresponding to the free energy and adsorbate population at the surface. However, the molecular orientation and separation from the NP surface is unknown experimentally.

Strong coupling at the NP-molecule interface results in a new quantum state called a polariton. Difference extinction measurements reveal these polaritonic states overlapped in a Fano-like resonance profile. A hybrid quantum/classical theoretical model is presented to model the plasmon-molecule interactions of adsorbed molecules at the surface of a mercaptosuccinic acid capped gold and silver-gold core-shell NP. This model employs classical electrodynamics using a finite-difference time-domain (FDTD) approach for the NP response and a 3-level quantum treatment for the molecules. The coupling at the surface is highly dependent on the adsorbate/NP separation distance and molecule transition dipole angle. Increasing the separation distance or transition dipole angle results in a weaker coupling between the NP and molecule, decreasing the splitting energy. This allows us to predict the most likely separation distance and transition dipole angle for a given dye, capping agent and NP composition.
In the second part of this dissertation, the synthesis and ultrafast characterization of novel gold-silver-gold core-shell-shell (CSS) nanoparticles are presented. These CSS NPs have highly tunable extinction peaks that can be controlled over the visible and near-infrared regions and exhibit an enhanced near field absorption and photothermal effect. Transient absorption measurements show that the phonon-phonon scattering lifetimes of the CSS NPs are much faster than that of colloidal gold nanospheres and gold nanorods, which contributes to the enhanced photothermal efficiency.
Plasmonics is the study of how electromagnetic waves interact with charges such as free electrons in a metal. On resonant frequencies, light can induce coherent oscillations of the electron density, resulting in classical plasma oscillations (Fig. 1.1). The frequency of this oscillation is the most important property of any plasma, and dictates the amount of light scattered and absorbed by the matter. In plasmons, this is typically referred to as the plasmon frequency. In general, when the frequency of light is below the plasma frequency, light is reflected or scattered from the plasma. Conversely, when the frequency of light is above the plasma frequency, light propagates through. By extension, plasmons are considered as quasiparticles as they arise from the quantization of these classical plasma oscillations, similar to phonons which are quantizations of mechanical vibrations.

In the context of metal nanoparticles (NPs), such as gold and silver, “surface plasmons” are confined to the surface of the nanoparticle (NP), due to a discontinuous change in the relative permittivity between the metal and the surrounding medium. More specifically,
Figure 1.2: FDTD calculated extinction spectra for gold of increasing diameters. As the diameter increases, the plasmon frequency red shifts towards longer wavelengths, and the magnitude of the extinction cross section increases.

these localized surface plasmon resonances (LSPRs) occur when the positive real part of the relative permittivity of a dielectric (e.g., vacuum, air, water, etc.) is interfaced with a negative real permittivity, such as a metal (Fig. 1.3). This sharp discontinuity in permittivity binds light to surface of the NP, creating an enhanced near-field absorption at the surface. The electrons travel parallel to this interface, and the electric fields decay exponentially away from this interface. Generally, by increasing the positive real part of the permittivity of the dielectric material (e.g., changing the material from water to quartz glass), the plasmonic resonance exhibits an increase in magnitude of the amount of light that is scattered and absorbed, as well as, a “red shift” towards longer wavelengths. Likewise, finite-difference time-domain (FDTD) calculated extinction spectra in Figure 1.2 show that as the diameter of the NP increases, a “red shift” in the plasmon frequency is observed.
Figure 1.3: Real part of the permittivity of water compared to the real part of the permittivity of gold over the visible region. The sharp change in the permittivity at the gold/water interface confines light to the surface, resulting in localized plasmon resonances.

Noble metal NPs possess unique chemical, electronic, and optical properties with important applications spanning molecular sensing, catalysis, metamaterials, and biologically-relevant technologies.¹⁻¹⁰ Many of these applications exploit the near field enhancements due to the localized surface plasmon resonances, which are coherent oscillations of the free electrons at the NPs surface.¹¹⁻¹⁴ Changing the composition, size, shape, and surrounding medium of the NP allows for highly tunable materials that are important for the development of molecular detectors, metamaterials, and novel dispersion properties.¹⁵ For example, silver has a longer plasmon lifetime, but is more chemically reactive than gold. Moreover, plasmonic gold and silver nanoparticles can be functionalized with biological molecules and polymers through thiolation for applications in biolabeling,¹⁶,¹⁷ drug delivery,¹¹,¹⁸ and pho-
Plasmon-enhanced absorption in the near-infrared region (650-1350 nm), which corresponds to wavelengths of light that have maximum penetration depth in tissue, is important for biological applications such as photothermal therapy and noninvasive bioimaging. Several types of plasmonic nanoparticles have been studied due to their potential application in photothermal cancer therapy, including gold nanorods, gold nanocages, silica–gold core–shell nanoparticles, hollow spherical nanoshells, and gold nanoparticles coated with reduced graphene oxide. When the NIR light is absorbed, these NPs convert this energy to heat through nonradiative processes, resulting in a localized photothermal effect which can be used for selectively killing cancer cells. Methods to increase the NIR photothermal efficiency of plasmonic nanoparticles can provide an alternative to harmful chemotherapy, radiation treatment, and invasive surgeries. For example, gold-silica-gold nanomatryoshkas were shown to be more efficient as photothermal transducers than gold–silica core-shell. Au@Ag/Au nanospheres composed of a gold nanorod core and a silver/
gold alloy shell demonstrated higher photothermal efficiencies and lower cytotoxities than gold nanorods. In Chapter 5, we discuss a new type called gold-silver-gold core-shell-shell nanoparticles that has an even higher photothermal efficiency compared to gold nanorods which are the current standard for photothermal cancer therapy. These NPs (patented by our group) provide a new direction for plasmonic engineering for highly efficient photothermal therapies at NIR wavelengths.

Nonlinear responses of plasmonic nanoparticles such as second harmonic generation (SHG) and sum frequency generation (SFG) can be significantly enhanced due to these plasmon resonances. The near-field dynamics and coupled dynamics of molecules, such as light harvesting dyes adsorbed to the surface of plasmonic nanostructures, show promise in the fields of photovoltaics, catalysis, and chemical sensing. For example, the strong electromagnetic fields near the surface of metal nanoparticles can boost the response of nearby adsorbates in low concentrations which is ideal for sensing applications such as surface enhanced Raman spectroscopy (SERS). Conversely, the optical responses of adsorbates at the surface of metallic nanostructures can induce plasmonic modes via surface-enhanced fluorescence.

Additionally, the interactions between plasmonic nanoparticles and chromaphoric dyes give rise to molecular and plasmonic resonance coupling, which can be measured via extinction spectroscopy. When the plasmon frequency is nearly on resonance with a molecular excitation, strong coupling can lead to the formation of hybrid states, resulting in exciton-polariton peaks separated by a splitting energy. This coupling results in a characteristic Fano-type resonances with corresponding plasmon and molecular spectral depletions.

There has been much recent progress towards modeling these molecule/plasmon systems. Some of the many approaches to model the dynamics between plasmons and molecules include point-plasmon/random phase approximation (RPA), a molecule treated with time-dependent Hartree Fock coupled to a continuous dielectric metal nanoparticle, resonant
energy transfer via quantum molecules embedded in a classical continuum background,\textsuperscript{50,51} coupled Liouville/Maxwell equations,\textsuperscript{52} electrodynamics coupled to a density matrix master equation,\textsuperscript{41} extended Mie Theory on plasmonic nanospheres coupled to a two-level quantum model,\textsuperscript{53} finite-difference time-domain/real time-TDDFT,\textsuperscript{54–57} and quantum electrodynamics coupled with time-dependent Hartree-Fock.\textsuperscript{40} In Chapter 3 a new method is presented that is suited to modeling thousands of quantum molecules adsorbed on the surface of a plasmonic NP. This hybrid approach uses classical electrodynamics to describe the plasmonic response with embedded 3-level quantum regions to describe the molecules.

1.2 Project Funding

The experimental work on the core-shell-shell NPs was supported by Louisiana State University, and the plasmon-molecule coupling was supported by the Board of Regents Research Competitiveness Subprogram under contract number LEQSF(2014-17)-RD-A-03 (PI: Lopata). The FDTD development was supported by the National Science Foundation under the NSF EPSCoR Cooperative Agreement No. EPS-1003897 (LaSiGMA project at LSU). Hardware used for computation was supported by the 2015 Ralph E. Powe Junior Faculty Enhancement Award from Oak Ridge Associated Universities (PI: Lopata).

1.3 Scope of Dissertation

This dissertation describes the combination of theoretical and experimental approaches to investigate the coupling dynamics between molecular adsorbates and plasmonic NPs. The surface properties of NPs with chromaphoric adsorbates are investigated experimentally using SHG and modeled using a hybrid quantum/classical approach. Additionally, the optical properties of core, core-shell (CS), and core-shell-shell (CSS) NPs are investigated. All of the structures are validated and characterized using a combination of transmission electron microscopy (TEM), extinction spectroscopy, ultrafast transient absorption and classical electrodynamics simulations (FDTD).
Chapter 2 presents the computational and experimental techniques used to study the optical properties, surface chemistry and ultrafast dynamics of colloidal noble metal nanoparticles. Additionally, the basic concepts behind second harmonic generation (SHG) and ultrafast transient absorption spectroscopy as well as the schematics of each optical setup is presented. Moreover, the basic principles of the finite-difference time-domain (FDTD) method are derived, encompassing key points necessary for developing the hybrid quantum/classical method derived in Chapter 3.

Chapter 3 describes a hybrid quantum/classical method derived from FDTD and is used to investigate the surface properties of chromaphoric dyes adsorbed to a NP surface. The computed results are compared to experimental SHG and difference extinction spectroscopic measurements. This work has culminated in a published manuscript.

Chapter 4 provides insight into the resonance coupling and surface properties of colloidal silver-gold core-shell nanoparticles with adsorbed malachite green dyes. The experimental results are compared to colloidal gold nanoparticles with the same dye and validated using the hybrid quantum/classical method derived in Chapter 3. This ongoing work is currently in preparation for a manuscript.

Finally, in Chapter 5, extinction spectroscopy, photothermal measurements, and ultrafast transient absorption are used to investigate and characterize our patented colloidal gold-silver-gold core-shell-shell nanoparticles which exhibit an enhanced photothermal effect and highly tunable optical properties. This work has resulted in a patent and published manuscript with several manuscripts in preparation.

As of October 25, 2017, these works have resulted in 2 publications, 1 patent, and 3 manuscripts in preparation.

1.4 References


Chapter 2: Computational and Experimental Methodologies

This dissertation focuses on a combined theoretical and experimental approach to investigate the optical properties, ultrafast dynamics, surface chemistry, and resonance coupling of colloidal nanoparticle systems. We employ several different optical techniques utilizing an ultrafast laser system and compare these results with theoretical models.

2.1 Second Harmonic Generation

Second harmonic generation (SHG) is a nonlinear optical process involving two photons of the same frequency that add coherently to generate a third photon at double the frequency $2\omega$ (Figure 2.1). This frequency doubling is typically forbidden in bulk media as it has inversion symmetry but allowed at surface, where the symmetry is broken. By measuring the intensity of this third photon generated, we can probe the surface properties of a material, such as the surface of a NP. For example, let’s consider the case of a perfect, spherical gold nanoparticle in water. Initially, this NP has an appreciable SHG signal due to the curvature, surrounding medium, and lack of inversion symmetry at the surface. Now, as we add an organic adsorbate to the surface of this NP, we observe an increase in SHG signal due to a change in the surface symmetry and surface second-order nonlinear optical susceptibility. This trend will continue until the NP is fully decorated with adsorbates, where the SHG signal will plateau. When using a strong electric field, such as an intense laser beam, a second-order nonlinear polarization $P^{(2)}$ is created and defined as

$$P^{(2)}(t) = 2\varepsilon_0\chi^{(2)}EE^* + (\varepsilon_0\chi^2E^2e^{-i2\omega t} + c.c.) \quad (2.1)$$

where $E$ is the optical electric field, $\chi^{(2)}$ is the second-order nonlinear optical susceptibility, and $\varepsilon_0$ is the vacuum permittivity. We see that the first term is the contribution at zero frequency, whereas the second term is the contribution at $2\omega$. The SHG signal intensity for
colloidal nanoparticles is given by the first term in Eq. 2.1 which contains a $2\omega$ frequency dependent term:

$$I_{2\omega}^{\text{total}} \propto \sum_{j=1}^{n} \sum_{k=1}^{n} E_{2\omega}^j E_{2\omega}^k e^{i(\phi_j - \phi_k)}$$

(2.2)

where $E_{2\omega}^j$ is the $j$’th electric field from the second harmonic, $\phi_j$ is the phase of the second harmonic electric field of the $j$’th particle, and $n$ is the density of particles. For a low density of nanoparticles, each nanoparticle is independent of other spheres, resulting in random phases. Therefore, since $j=k$, Eq. 2.2 becomes

$$I_{2\omega}^{\text{total}} \propto \sum_{j=1}^{n} (E_{2\omega}^j)^2 = n (E_{2\omega})^2 = n I_{2\omega}$$

(2.3)

where $I_{2\omega}$ is the SHG contribution from a single sphere and $n$ is the particle density.\textsuperscript{1} For this dissertation, SHG is used to examine the adsorption of chromophoric dyes onto the surface of colloidal nanoparticles and yield information such as site density and Gibbs free energy. By measuring the SHG signal of a nanoparticle sample as a function of adsorbate
concentration, we see that the total SHG signal is given by

\[ SHG_{total} = A \left( \frac{N}{N_{max}} \right)^2 + B + Ma \]  

(2.4)

where \( A \) is the SHG amplitude at the plateau, \( B \) is the offset due to the SHG signal from nanoparticles in water without the addition of dyes, \( M \) is the concentration of free dyes in solution, and \( a \) is the slope obtained by fitting the SHG signal of dye molecules in water versus dye concentration. The \( N N_{max} \) term is found via the modified Langmuir formula

\[
\frac{N}{N_{max}} = \frac{(C + N_{max} + \frac{55.5}{K}) - \sqrt{(C + N_{max} + \frac{55.5}{K})^2 - 4CN_{max}}}{2N_{max}}
\]  

(2.5)

where \( N \) is the adsorbate population on the nanoparticle surface, \( N_{max} \) is the maximum number of adsorbate sites on the nanoparticle surface multiplied by the concentration of nanoparticles in solution (determined via classical electrodynamics simulations), \( C \) is the adsorbate bulk concentration added to the nanoparticle sample, and \( K \) is the adsorption equilibrium constant. From this fit, we can determine the free energy of adsorption

\[ \Delta G = -RT \ln K \]  

(2.6)

as well as the adsorbate site density. Our second harmonic generation setup is composed of an ultrafast titanium:sapphire oscillator laser with an optical setup coupled to a high-sensitivity charged-coupled device (CCD) spectroscopy detector (Fig. 2.2). This Ti:sapphire laser produces 75 fs pulses centered at 800 nm with a repetition rate of 80 MHz and an average power of 2.7 W.
2.2 Transient Absorption Spectroscopy

Ultrafast spectroscopy can be used to probe the dynamics of light/matter interactions. However, these interactions are extremely fast and are difficult to measure experimentally. Advancements in ultrafast lasers have decreased the pulse duration below the time scale of interest (i.e., femtosecond time scale), allowing us to study the dynamics of these systems. Specifically, we use transient absorption spectroscopy wherein a resonant pump pulse excites the system, and the relaxation time back to ground state is measured by a delayed probe pulse.\textsuperscript{2,3}

Our transient absorption setup consists of an amplified titanium:sapphire oscillator laser coupled to an optical parametric oscillator (OPA), an optical setup, and a fiber optic spectrometer with a charge-coupled device detector. The laser is capable of producing 0.7 mJ, 75 fs pulses centered at 800 nm with a repetition rate of 10 kHz. A beamsplitter separates...
the pump and probe pulses. The pump pulses are directed to a retroreflector on a computer-controlled translation state which controls the pump-probe temporal delay by varying the optical path length difference between the pump and probe beams. The 800 nm probe beam is focused into a 1 cm fused quartz flow cell containing water to generate femtosecond white light pulses which are refocused to a spatial overlap with the pump pulse at the sample. The sample of interest is contained in a 2 mm fused quartz cell under constant stirring. Figure 2.3 is a schematic of the experimental setup. This setup is used in Chapter 5 to investigate the origins of an enhanced photothermal effect of novel gold-silver-gold core-shell-shell NPs by measuring the phonon-phonon and electron-phonon lifetimes.

2.3 Finite-Difference Time-Domain Techniques

The finite-difference time-domain (FDTD) is a computational method for solving a wide range of problems in electromagnetics. FDTD is an iterative approach that uses finite-differences to approximate the spatial and temporal derivatives of Maxwell’s equations (specifically Ampere’s and Faraday’s laws). FDTD is an iterative approach in which the electric and magnetic fields can be computed in both space and time via leapfrog manner:
the electric field vector components at one point in space are computed for a given point in time; then the magnetic field vector components are computed at the next point in time; and the process is repeated until the simulation is ended.\(^4\)

This dissertation will focus on modeling the optical properties of plasmonic nanoparticles (NPs), wherein the wavelength of light is much larger than the nanoparticle (NP) diameter. One of the difficulties, however, lies within modeling the motion of the electrons in the plasmon. Due to the large size of these nanoparticles (on the order of \(10^6\) atoms per NP), a quantum mechanical treatment to describe the NP is tractable as it would be extremely computationally expensive. Instead, we can use the bulk permittivity \(\varepsilon(\omega)\) response of the metal to mimic the electron motion in the FDTD method. In sections (2.3.1-2.3.5), a few of the modeling considerations will be discussed as well as some of the textbook techniques that go into the FDTD method. A full 1D-FDTD code is available in Appendix B.

For simplicity, consider the Taylor expansions of the function \(f(x)\) expanded about the
point \( x_0 \) with an offset of \( \pm \Delta \):

\[
\begin{align*}
f (x_0 + \Delta) &= f (x_0) + \Delta f' (x_0) + \frac{1}{2!} (\Delta)^2 f'' (x_0) + \frac{1}{3!} (\Delta)^3 f''' (x_0) + \ldots \tag{2.7a} \\
f (x_0 - \Delta) &= f (x_0) - \Delta f' (x_0) + \frac{1}{2!} (\Delta)^2 f'' (x_0) - \frac{1}{3!} (\Delta)^3 f''' (x_0) + \ldots \tag{2.7b}
\end{align*}
\]

where the primes indicate differentiation. Subtracting (2.7b) from (2.7a) and dividing by \( \Delta \) produces

\[
\frac{f (x_0 + \Delta) - f (x_0 - \Delta)}{\Delta} = f' (x_0) + \frac{1}{2!} (\Delta)^2 f'' (x_0) + \ldots \tag{2.8}
\]

Therefore, we find that the left part of the equation can be approximated as the derivative of the function at point \( x_0 \) plus a term that depends on \( (\Delta)^2 \) plus an infinite number of higher order terms (not shown). If we ignore all higher order terms and rearrange slightly, Eq. 2.8 becomes:

\[
\frac{df(x)}{dx} \bigg|_{x=x_0} = f(x_0 + \Delta) - f(x_0 - \Delta) + O(\Delta)^2 \tag{2.9}
\]

where the \( O \) symbol means “on the order of” and incorporates all of the higher order terms and the value \( (\Delta)^2 \) indicates the lowest order of these terms. When \( \Delta \) is small, we can approximate Eq. 2.9 as

\[
\frac{df(x)}{dx} \bigg|_{x=x_0} \approx \frac{f(x_0 + \Delta) - f(x_0 - \Delta)}{\Delta} \tag{2.10}
\]

It is important to note that although the derivative is approximated as a function at \( x_0 \), this value is not actually sampled here and depends on its neighboring values at \( x_0 + \Delta \) and \( x_0 - \Delta \). Because we ignore \( O(\Delta)^2 \), this central difference scheme is said to be second-order accurate. Thus, if you decrease \( \Delta \) by a factor of 10, the error will be reduced by a factor of about \( 10^2 \). In the limit as \( \Delta \) goes to zero, the central difference approximation becomes exact. However, as with all numerical methods, it hosts a range of numerical artifacts and the
accuracy of this method depends on the level of implementation and the temporal and spatial step size. The FDTD method can solve complicated problems, but is rather computationally expensive, as simulations require a large amount of memory and computation time.

### 2.3.1 Maxwell’s Equations in Three Dimensions

Consider a system that contains lossy and dispersive materials that absorb electric and magnetic field energy. In three dimensions, Maxwell’s equations are

\[
\begin{align*}
-\mu \frac{\partial \mathbf{H}}{\partial t} &= \nabla \times \mathbf{E} - \mathbf{M}_{\text{source}} \quad (2.11a) \\
\varepsilon \frac{\partial \mathbf{E}}{\partial t} &= \nabla \times \mathbf{H} - \mathbf{J}_{\text{source}} \quad (2.11b)
\end{align*}
\]

In three dimensions, we get 6 coupled partial differential equations that depend on both space and time from 2.11a and 2.11b. These form the basis of the FDTD method and allow for modeling the optical properties of materials. In Cartesian coordinates, the coupled scalar equations are:

\[
\begin{align*}
\frac{\partial H_x}{\partial t} &= \frac{1}{\mu} \left[ \frac{\partial E_y}{\partial z} - \frac{\partial E_z}{\partial y} - M_{\text{source}_x} \right] \quad (2.12a) \\
\frac{\partial H_y}{\partial t} &= \frac{1}{\mu} \left[ \frac{\partial E_z}{\partial x} - \frac{\partial E_x}{\partial z} - M_{\text{source}_y} \right] \quad (2.12b) \\
\frac{\partial H_z}{\partial t} &= \frac{1}{\mu} \left[ \frac{\partial E_x}{\partial y} - \frac{\partial E_y}{\partial x} - M_{\text{source}_z} \right] \quad (2.12c) \\
\frac{\partial E_x}{\partial t} &= \frac{1}{\varepsilon} \left[ \frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} - J_{\text{source}_x} \right] \quad (2.12d) \\
\frac{\partial E_y}{\partial t} &= \frac{1}{\varepsilon} \left[ \frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} - J_{\text{source}_y} \right] \quad (2.12e) \\
\frac{\partial E_z}{\partial t} &= \frac{1}{\varepsilon} \left[ \frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} - J_{\text{source}_z} \right] \quad (2.12f)
\end{align*}
\]

where $\mu$ is the frequency dependent permeability and $\varepsilon$ is the frequency dependent permittivity. This system of coupled partial differential equations forms the basis of the FDTD
algorithm to describe interactions between electromagnetic waves and materials. One caveat of FDTD, however, requires that the electric and magnetic fields be interlaced in both space and time to satisfy continuity. The accuracy and stability of this algorithm is primarily dictated by the temporal and spatial step size.

2.3.2 Reduction to One Dimension

At this point, it is useful to see the FDTD algorithms in 1D to help understand some of the complex machinery that will go into the FDTD simulations to yield more information on the system, increase accuracy and lower computational time. Consider the simplest one-dimensional case in a vacuum ($\varepsilon = \varepsilon_0, \mu = \mu_0$) where our system can only propagate in the x-direction. Since, our system only depends on $H_x$, $H_y$, and $E_z$, Eqs.(2.12a- 2.12f) reduce to

\[
\frac{\partial E_z}{\partial t} = \frac{1}{\varepsilon_0} \frac{\partial H_y}{\partial x} \tag{2.13a}
\]

\[
\frac{\partial H_y}{\partial t} = \frac{1}{\mu_0} \frac{\partial E_z}{\partial x} \tag{2.13b}
\]

which represents an x-directed, z-polarized transverse electromagnetic (TEM) plane wave in one dimension. Using the same the central difference approximation discussed in section 2.3, we can rewrite the spatial and temporal derivatives of Eq.(2.13a) as

\[
\frac{E_z^{n+1}(i) - E_z^n(i)}{\Delta t} = \frac{1}{\varepsilon_0} \frac{H_y^{n+\frac{1}{2}}(i + \frac{1}{2}) - H_y^{n+\frac{1}{2}}(i - \frac{1}{2})}{\Delta x} \tag{2.14}
\]

where the temporal derivative is replaced by a finite difference involving $E_z^{n+1}(i)$ and $E_z^n(i)$ (i.e., the electric field at a fixed location but two different times) while the spatial derivative is replaced by finite differences involving $H_y^{n+\frac{1}{2}}(i + \frac{1}{2})$ and $H_y^{n+\frac{1}{2}}(i - \frac{1}{2})$ (i.e., the magnetic field at a two different locations but one time). The temporal and spatial steps are denoted
by \( n \) and \( i \), respectively. Solving for \( E_{z}^{n+1}(i) \) yields

\[
E_{z}^{n+1}(i) = E_{z}^{n}(i) + \frac{\Delta t}{\varepsilon_{0} \Delta x} \left[ H_{y}^{n+\frac{1}{2}}(i + \frac{1}{2}) - H_{y}^{n+\frac{1}{2}}(i - \frac{1}{2}) \right]
\]  (2.15)

Similarly from Eq.(2.13b),

\[
H_{y}^{n+\frac{1}{2}}(i - \frac{1}{2}) = H_{y}^{n-\frac{1}{2}}(i - \frac{1}{2}) + \frac{\Delta t}{\mu_{0} \Delta x} \left[ E_{z}^{n}(i + 1) - E_{z}^{n}(i) \right]
\]  (2.16)

Hence, the electric and magnetic fields are computed in both space and time (see Fig. 2.5). It is important to note that the coefficients \( \Delta t/(\varepsilon_{0} \Delta x) \) and \( \Delta t/(\mu_{0} \Delta x) \) dictate how far energy can propagate in a single temporal step within a single spatial step. The maximum speed at which an electromagnetic wave can travel is the speed of light in a vacuum \( c = 1/\sqrt{\varepsilon_{0} \mu_{0}} \); therefore, the maximum distance energy can travel in one time step is \( c \Delta t \) (i.e., energy can travel one grid point per time step). The coefficient \( c \Delta t/\Delta x \) is referred to as the Courant Stability limit (i.e., the maximum allowed time is \( \Delta t_{\text{max}} = c \Delta x/\sqrt{3} \)) and limits the stability and accuracy of an FDTD simulation. Similarly, one can derive the other 1D electromagnetic
2.3.3 Total-Field / Scattered-Field Formulation

In order to observe the optical response of a scatterer, an incident source must be used to “excite” the system. Intuitively, one may naively create a point source near the surface of the nanoparticle by setting the value of an electric field component equal to some value and observing the resulting fields after propagation; however, this “hard source” introduces undesirable dispersion effects and most absorbing boundary conditions cannot handle this type of source. A more clever approach has been developed to handle long-duration pulsed illuminations in the form of plane-waves. The formulation is an attempt to resolve the problems experienced by introducing hard sources. This method assumes that the total electric and magnetic can be decomposed into incident and scattered fields:

\[
E_{total} = E_{scat} + E_{inc} \quad (2.17a)
\]

\[
H_{total} = H_{scat} + H_{inc} \quad (2.17b)
\]

where \( E_{inc} \) and \( H_{inc} \) are the values of the incident plane wave. The basic idea splits the FDTD grid into two regions: Region 1, which contains all stored values of the total field components, and Region 2, which contains all stored values of the scattered field components. The total-field scattered-field (TF/SF) method employs a nonphysical virtual surface connecting the two regions. Through this formulation, it is possible to use any arbitrary incident wave.

The virtual surface connecting Regions 1 and 2 requires consistency across the boundary. Consider the one–dimensional x-directed, z-polarized TEM in a vacuum example mentioned in Sec. 2.3.1:

\[
E_{z}^{n+1}(i) = E_{z}^{n}(i) + \frac{\Delta t}{\varepsilon_{0} \Delta x} \left[ H_{y}^{n+\frac{1}{2}}(i + \frac{1}{2}) - H_{y}^{n+\frac{1}{2}}(i - \frac{1}{2}) \right] \quad (2.18)
\]
Eq. (2.18) is only consistent if all three field components on the right hand side exist within the same grid region (total or scattered). First, let’s examine the total fields within Region 1:

\[ E_{z,total}^{n+1}(i) = E_{z,total}^{n}(i) + \frac{\Delta t}{\varepsilon_0 \Delta x} \left[ H_{y,total}^{n+\frac{1}{2}}(i + \frac{1}{2}) - H_{y,total}^{n+\frac{1}{2}}(i - \frac{1}{2}) \right] \]  

(2.19)

wherein \( E_z \) and \( H_y \) components are assumed to be stored in computer memory. Likewise, if the spatial positions \((i - 1/2), (i), \) and \((i + 1/2)\) are all in Region 2, we get the following scattered fields:

\[ E_{z,scattered}^{n+1}(i) = E_{z,scattered}^{n}(i) + \frac{\Delta t}{\varepsilon_0 \Delta x} \left[ H_{y,scattered}^{n+\frac{1}{2}}(i + \frac{1}{2}) - H_{y,scattered}^{n+\frac{1}{2}}(i - \frac{1}{2}) \right] \]  

(2.20)

Now consider the special spatial point at \( i_L \) which serves as the bridge between Regions 1 and 2,

\[ E_{z,total}^{n+1}(i_L) = E_{z,total}^{n}(i_L) + \frac{\Delta t}{\varepsilon_0 \Delta x} \left[ H_{y,total}^{n+\frac{1}{2}}(i_L + \frac{1}{2}) - H_{y,scattered}^{n+\frac{1}{2}}(i_L - \frac{1}{2}) \right] \]  

(2.21)

However, Eq. (2.21) is inconsistent as it subtracts field components in different regions. To make this consistent, one must apply a correction term

\[ E_{z,total}^{n+1}(i_L) = E_{z,total}^{n}(i_L) + \frac{\Delta t}{\varepsilon_0 \Delta x} \left[ H_{y,total}^{n+\frac{1}{2}}(i_L + \frac{1}{2}) - H_{y,scattered}^{n+\frac{1}{2}}(i_L - \frac{1}{2}) \right] - \frac{\Delta t}{\varepsilon_0 \Delta x} \left[ H_{y,inc}^{n+\frac{1}{2}}(i_L - \frac{1}{2}) \right] \]  

(2.22)

since

\[ -H_{y,scattered}^{n+\frac{1}{2}}(i_L - \frac{1}{2}) - H_{y,inc}^{n+\frac{1}{2}}(i_L - \frac{1}{2}) = -H_{y,total}^{n+\frac{1}{2}}(i_L - \frac{1}{2}) \]  

(2.23)

\( H_{y,inc}^{n+\frac{1}{2}} \) can take the form of any plane wave and can be introduced into the main FDTD
lattice through this correction term. By correcting the inconsistent points on the TF/SF boundary, the error associated with this point discontinuity is fixed. Figure 2.6 Within the context of plasmonics, this TF/SF boundary is a crucial tool for distinguishing between absorption and scattering. Once the 1D case is understood, it is straightforward to extend to 3D. The flexibility of this technique will help facilitate the implementation of a quantum-classical model (see Chapter 3) which serves as the basis of modeling the near field dynamics of organic dyes adsorbed to the surface of a nanoparticle in this dissertation.

2.3.4 Terminating the Grid: Absorbing Boundary Conditions

For real world applications, there exists large unbounded regions for the electromagnetic waves to propagate. The simulation box size must contain the structure of interest and
a boundary at the box edge to extrapolate the computational domain to infinity. As the propagation distance goes to infinity, the electromagnetic waves damp out to zero. Although

![Figure 2.7: Schematic of the FDTD simulation box with a TF/SF boundary (See Sec. 2.3.3) with an absorbing boundary condition terminating the simulation box.](image)

the boundary condition derived below is by no means state-of-the-art, e.g., perfectly matched layers (PML’s), it provides sufficient termination of the grid with reflections on the order of $10^{-4}$.

The wave equation for an electric field propagating in space and time through vacuum in one direction is

$$
\left( \frac{\partial^2}{\partial x^2} - \mu_0 \varepsilon_0 \frac{\partial^2}{\partial t^2} \right) E_z = 0 \quad (2.24)
$$

After factoring this operator into the product of two operators, Eq. 2.24 becomes

$$
\left( \frac{\partial}{\partial x} - \sqrt{\mu_0 \varepsilon_0} \frac{\partial}{\partial t} \right) \left( \frac{\partial}{\partial x} + \sqrt{\mu_0 \varepsilon_0} \frac{\partial}{\partial t} \right) E_z = 0 \quad (2.25)
$$

When one of these operators acts on the electric field and yields zero, this wave equation is
automatically satisfied. Therefore, an electric field $E_z$ that satisfies either of the following equations is a solution to the wave equation:

$$\left( \frac{\partial E_z}{\partial x} - \sqrt{\mu_0 \varepsilon_0} \frac{\partial E_z}{\partial t} \right) = 0 \quad (2.26)$$

$$\left( \frac{\partial E_z}{\partial x} + \sqrt{\mu_0 \varepsilon_0} \frac{\partial E_z}{\partial t} \right) = 0 \quad (2.27)$$

However, there is no solution that will satisfy both of these advection equations. Let’s consider an identical wave traveling in the opposite or negative $x$ direction, i.e., $E_z(t + \sqrt{\mu \varepsilon} x)$. Let’s validate this solution with $\chi = t + \sqrt{\mu \varepsilon}$. The temporal and spatial derivatives are given by

$$\frac{\partial \chi}{\partial t} = 1 \quad \text{and} \quad \frac{\partial \chi}{\partial x} = \sqrt{\mu \varepsilon} \quad (2.28)$$

After substitution into Eq. 2.26, we see that the partial derivatives become

$$\frac{\partial E_z}{\partial x} = \frac{\partial E_z}{\partial \chi} \frac{\partial \chi}{\partial x} = \sqrt{\mu \varepsilon} \frac{\partial E_z}{\partial \chi} \quad (2.29a)$$

$$\frac{\partial E_z}{\partial t} = \frac{\partial E_z}{\partial \chi} \frac{\partial \chi}{\partial t} = \frac{\partial E_z}{\partial \chi} \quad (2.29b)$$

Thus, by substituting the right hand sides of Eq. 2.29, this solution to the wave equation satisfies the advection equation.

Now, we need to use this solution to terminate our simulation box. However, due to the staggered nature of the electric and magnetic fields in space, there are electric field points at the box edge that are not updated. Therefore, we utilize these points to terminate our simulation. Let $E_z^{n+1}[1]$ be the boundary node. We can expand the advection equation around the spatial point $\Delta x/2$ and temporal point $(n + 1/2)dt$. However, since the FDTD grid points fall on whole integers, we will need to approximate this point by taking the
central difference in space and time. The resulting temporal derivative is:

\[ \sqrt{\mu \varepsilon} \frac{\partial E_z}{\partial t} \bigg|_{\Delta x/2, (n + 1/2)\Delta t} \approx \sqrt{\mu \varepsilon} \frac{E_z^{n+1}[1] + E_z^{n+1}[2] - E_z^n[1] + E_z^n[2]}{2 \Delta t} \]  

(2.30)

and the resulting spatial derivative is:

\[ \sqrt{\mu \varepsilon} \frac{\partial E_z}{\partial t} \bigg|_{\Delta x/2, (n+1/2)\Delta t} \approx \sqrt{\mu \varepsilon} \frac{E_z^{n+1}[1] + E_z^{n+1}[2] - E_z^n[1] + E_z^n[2]}{2 \Delta t} \]  

(2.31)

By combining Eq. 2.30 and 2.31, the finite-difference form of the equation is

\[ \sqrt{\mu \varepsilon} \frac{E_z^{n+1}[1] + E_z^{n+1}[2]}{2 \Delta t} - \sqrt{\mu \varepsilon} \frac{E_z^n[1] + E_z^n[2]}{2 \Delta t} = 0 \]  

(2.32)

Finally, by letting \( \sqrt{\mu \varepsilon} = \sqrt{\mu_r \varepsilon_r} / c \) and solving for \( E_z^{n+1}[0] \), Eq. 2.32 becomes

\[ E_z^{n+1}[1] = E_z^n[2] + \frac{S_c}{S_c \sqrt{\mu_r \varepsilon_r} + 1} \left( E_z^{n+1}[2] - E_z^n[1] \right) \]  

(2.33)

where \( S_c \) is the Courant number (i.e., \( c \Delta t / \Delta x \)). This is a first order absorbing boundary condition (ABC) for a one-dimensional FDTD grid. Similarly, a second-order ABC can easily be derived by taking the advection operator twice.\(^4\) This type of boundary works best for fields with a relatively narrow bandwidth. Figure 2.8 shows the electric field \( E_z \) in both space and time with the fields terminated with a second-order ABC at the nodes located at \( x = 1 \) and \( x = nx + 1 \).

### 2.3.5 Modeling Dispersive Media: Gold and Silver

Before Maxwell’s equations can be solved, we must first develop a way of describing the material properties. Since the large size of the nanoparticles precludes a quantum description, we can incorporate the measured bulk permittivity \( \varepsilon(\omega) \) into the FDTD update equations. This classical picture for the electron motion works very well for describing plasmons and
Figure 2.8: $E_z$ electric field intensity plotted in both space and time. This field is terminated using a second-order absorbing boundary condition at the box edge which prevents reflections from the simulation edge.

accurately captures the geometry effects at the surface. In this dissertation, gold and silver are the primary plasmonic materials and will be described using a sum of Lorentzian oscillators. Coomar et al. has fit the permittivity of gold and silver over a wide frequency range (0.6-6.7 eV), covering a large range of the bulk gold and silver data for Johnson and Christy. Figures 2.9 and 2.10 show excellent agreement between the experimental data and the fit for gold and silver over a large frequency range. The permittivity fit for gold uses an 8-pole Lorentzian with the parameters in Table 2.1, whereas the permittivity fit for silver uses a 9-pole Lorentzian with the parameters in Table 2.2.

These fitting parameters can be directly incorporated into FDTD using an auxiliary-
Table 2.1: Fitting parameters for the permittivity of gold taken from Coomar et al.\textsuperscript{5}

<table>
<thead>
<tr>
<th>$\omega_j$ (eV)</th>
<th>$\alpha_j$ (eV)</th>
<th>$\beta_j$ (eV\textsuperscript{2})</th>
</tr>
</thead>
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<td>0.2350</td>
<td>0.1551</td>
<td>95.62</td>
</tr>
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<td>0.4411</td>
<td>0.1480</td>
<td>-12.55</td>
</tr>
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<td>0.7603</td>
<td>1.946</td>
<td>-40.89</td>
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<tr>
<td>1.161</td>
<td>1.396</td>
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<tr>
<td>2.946</td>
<td>1.183</td>
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<td>4.161</td>
<td>1.964</td>
<td>36.63</td>
</tr>
<tr>
<td>5.747</td>
<td>1.958</td>
<td>22.55</td>
</tr>
<tr>
<td>7.912</td>
<td>1.361</td>
<td>81.04</td>
</tr>
</tbody>
</table>

Table 2.2: Fitting parameters for the permittivity of silver taken from Coomar et al.\textsuperscript{5}

<table>
<thead>
<tr>
<th>$\omega_j$ (eV)</th>
<th>$\alpha_j$ (eV)</th>
<th>$\beta_j$ (eV\textsuperscript{2})</th>
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</tr>
<tr>
<td>7.197</td>
<td>2.774</td>
<td>31.02</td>
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</tbody>
</table>

differential equation (ADE) method to model dispersive media.\textsuperscript{4} First, the frequency response of gold and silver can be represented as a sum of Lorentz oscillators

$$
\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_p\omega_p^2}{\omega_p^2 + 2i\omega\delta_p - \omega^2} \tag{2.34}
$$

where $P$ denotes the number of Lorentz pole pairs, $\Delta\varepsilon_p = \varepsilon_{s,p} - \varepsilon_{\infty,p}$ is the change in relative permittivity due to the $p$'th pair, $\omega_p$ is the undamped frequency of the $p$'th pole pair, and $\delta_p$ is its damping factor. Assuming a good $\varepsilon(\omega)$, this linear multi-pole Lorentz dielectric dispersion model accurately describes the intraband (free electrons) and interband (bound electrons) effects in metals, and can easily be implemented into Maxwell’s curl equations.
through the ADE method. From Eq. (2.34) each pole pair can be written as a phasor polarization current by

\[
\hat{J}_p = \varepsilon_0 \Delta \varepsilon_p \omega_p^2 \left( \frac{i\omega}{\omega_p^2 + 2i\omega \delta_p - \omega^2} \right) \hat{E}
\]  

(2.35)

Multiplying both sides of this equation by the denominator gives

\[
\omega_p^2 \hat{J}_p + 2i\omega \delta_p \hat{J}_p - \omega^2 \hat{J}_p = \varepsilon_0 \Delta \varepsilon_p \omega_p^2 i\omega \hat{E}
\]  

(2.36)

After the inverse Fourier transform of each term in Eq.(2.36), this becomes

\[
\omega_p^2 J_p + 2\delta_p \frac{\partial J_p}{\partial t} + \frac{\partial^2 J_p}{\partial t^2} = \varepsilon_0 \Delta \varepsilon_p \omega_p^2 \frac{\partial \mathbf{E}}{\partial t}
\]  

(2.37)

Following the central-difference approximation mentioned in Sec. 2.3.1 and solving for \( J_{p}^{n+1} \), we obtain

\[
J_{p}^{n+1} = \alpha_p J_{p}^{n} + \zeta_p J_{p}^{n-1} + \gamma_p \left( \frac{E_{n+1}^{n} - E_{n-1}^{n}}{2\Delta t} \right)
\]  

(2.38)

where

\[
\alpha_p = \frac{2 - \omega_p^2 (\Delta t)^2}{1 + \delta_p \Delta t}
\]  

(2.39a)

\[
\zeta_p = \frac{\delta_p \Delta t - 1}{\delta_p \Delta t + 1}
\]  

(2.39b)

\[
\gamma_p = \frac{\varepsilon_0 \Delta \varepsilon_p \omega_p^2 (\Delta t)^2}{1 + \delta_p \Delta t}
\]  

(2.39c)

Finally, after collection of terms, we obtain the following time-stepping relation for \( \mathbf{E} \)

\[
\mathbf{E}^{n+1} = C_1 \mathbf{E}^{n-1} + C_2 \mathbf{E}^{n} + C_3 \cdot \left[ \nabla \times \mathbf{H}^{n+1/2} - \frac{1}{2} \sum_{p=1}^{P} \left[ (1 + \alpha_p) J_{p}^{n} + \zeta_p J_{p}^{n-1} \right] \right]
\]  

(2.40)
Figure 2.9: Real (left panel) and imaginary (right panel) permittivity of gold measured by Johnson and Christy fit to 8-pole Lorentzian with parameters determined by Coomar et al.

where

\[ C_1 = \frac{1}{2} \sum_{p=1}^{P} \gamma_p } { 2\varepsilon_0 \varepsilon_\infty + \frac{1}{2} \sum_{p=1}^{P} \gamma_p } \]  

(2.41a)

\[ C_2 = \frac{2\varepsilon_0 \varepsilon_\infty} { 2\varepsilon_0 \varepsilon_\infty + \frac{1}{2} \sum_{p=1}^{P} \gamma_p } \]  

(2.41b)

\[ C_3 = \frac{2\Delta t} { 2\varepsilon_0 \varepsilon_\infty + \frac{1}{2} \sum_{p=1}^{P} \gamma_p } \]  

(2.41c)

Thus, the ADE-FDTD algorithm for modeling a dispersive medium with \( P \) Lorentz pole pairs is a three-step procedure. Since the values for \( \mathbf{E}^{n-1} \), \( \mathbf{E}^n \), \( \mathbf{J}^{p-1}_p \), \( \mathbf{J}^n_p \), and \( \mathbf{H}^{n+1/2} \) are stored, we first calculate the new \( \mathbf{E}^{n+1} \) using Eq. (2.40). Second, the \( \mathbf{J}^{p+1}_p \) components are calculated using Eq. (2.38) from the recently calculated \( \mathbf{E} \) components. Finally, the remaining \( \mathbf{H} \) components are calculated via the usual FDTD manner.\(^4\) Figures 2.9 and 2.10 show the real and imaginary parts of the permittivity from 0.6-6.7 eV using the fitting parameters determined by Coomar, et al.\(^5\)

32
Figure 2.10: Real (left panel) and imaginary (right panel) permittivity of silver measured by Johnson and Christy fit to 8-pole Lorentizian with parameters determined by Coomar et al.

2.3.6 Calculating Optical Cross Sections in FDTD

Consider a surface $A$ which encloses a volume $V$. A normal vector, $\hat{n}$, is chosen along every point of $A$ such that it has a positive magnitude facing outwards. The rate of electromagnetic energy that is transferred across $A$ is given by

$$W = -\oint_S \mathbf{S} \cdot \hat{n} dA$$  \hspace{1cm} (2.42)

where $\mathbf{S}$ is the time-average Poynting vector. $\mathbf{S}$ indicates the average rate of energy transferred per unit area and is given by

$$\mathbf{S} = \frac{1}{2} Re \left\{ \mathbf{E} \times \mathbf{H}^* \right\}$$  \hspace{1cm} (2.43)

with dimensions of power density (e.g. $W/m^2$).\(^7\) Negative values for $W$ corresponds to energy being transferred out of the surface and a positive values for $W$ corresponds to energy being transferred into the surface. Now consider an arbitrary scatterer (e.g., nanoparticle) enclosed by $A$ that is excited via light with a particular frequency and polarization. At every point
along $A$, the time-average Poynting vector is given by Eq. 2.43. Because the energy of the system is conserved, $S$ can also be written as a sum of three components,

$$S = S_{\text{inc}} + S_{\text{scat}} + S_{\text{ext}}$$ \hspace{1cm} (2.44)

where $S_{\text{inc}}$ is the time-averaged Poynting vector due to the incident light, $S_{\text{scat}}$ is the time-averaged Poynting vector due to the scattered light, and $S_{\text{ext}}$ is the time-averaged Poynting vector due to the interaction between the incident and scattered light. Each of these can be expressed in terms of incident and scattered electric and magnetic fields:

$$S_{\text{inc}} = \frac{1}{2} Re \left\{ E_{\text{inc}} \times H_{\text{inc}}^* \right\}$$ \hspace{1cm} (2.45a)

$$S_{\text{scat}} = \frac{1}{2} Re \left\{ E_{\text{scat}} \times H_{\text{scat}}^* \right\}$$ \hspace{1cm} (2.45b)

$$S_{\text{ext}} = \frac{1}{2} Re \left\{ E_{\text{inc}} \times H_{\text{scat}}^* + E_{\text{scat}} \times H_{\text{inc}}^* \right\}$$ \hspace{1cm} (2.45c)

Therefore, the rate of energy flow into the surface $A$ is given by

$$W_{\text{inc}} = -\int S_{\text{inc}} \cdot \hat{n} dA$$ \hspace{1cm} (2.46)

and the rate of energy that gets scattered and transferred out of $A$ is given by

$$W_{\text{scat}} = -\int S_{\text{scat}} \cdot \hat{n} dA$$ \hspace{1cm} (2.47)
The resulting time dependent electric and magnetic fields can readily Fourier transformed to obtain the corresponding frequency dependent quantities (i.e., \( E(\omega) \) and \( H(\omega) \)):

\[
E_z^q(i, j, k) = \mathcal{F}[E_z^q(i, j, k)] = \frac{1}{N_T} \sum_{it} E_z(i, j, k) e^{-i\omega t} \, dt
\]  \hspace{1cm} (2.48a)

If we assume the surface \( A \) completely encloses the scattering particle, the rate at which scattered energy \( (W_{scat}) \) is transferred out of this surface is given by the integral of the Poynting vector (units of \( W/m^2 \)) over the whole surface. This scattering power is defined as

\[
P_{scat}(\omega) = Re \left\{ \hat{n} \cdot \oint_{\text{monitors}} E_{scat}(\omega) \times H_{scat}^*(\omega) \right\}
\]  \hspace{1cm} (2.49)

where

\[
E_{scat}(\omega) = E_{total}(\omega) - E_{inc}(\omega)
\]  \hspace{1cm} (2.50)

Likewise, we can define an absorption power that indicates the rate of energy transferred into the entire surface:

\[
P_{abs}(\omega) = Re \left\{ \hat{n} \cdot \oint_{\text{monitors}} E_{total}(\omega) \times H_{total}^*(\omega) \right\}
\]  \hspace{1cm} (2.51)

Typically, the absorption and scattering quantities are expressed as cross sections. By normalizing the absorption and scattering powers by the incident field intensity \( (I_{inc}) \), we obtain the corresponding cross sections:

\[
\sigma_{abs}(\omega) = \frac{P_{abs}(\omega)}{I_{inc}(\omega)}
\]  \hspace{1cm} (2.52a)

\[
\sigma_{scat}(\omega) = \frac{P_{scat}(\omega)}{I_{inc}(\omega)}
\]  \hspace{1cm} (2.52b)
A cross section has units of area and is typically expressed in $m^2$.

To calculate cross sections in FDTD, we must construct 6 flux monitors within the main TF/SF boundary for the absorption cross section $\sigma_{abs}$ and 6 flux monitors outside the main TF/SF boundary for the scattering cross section $\sigma_{scat}$ (2D slice of setup is illustrated in Fig. 2.11). Total fields (scattering + incident) inside the total field region are collected on the absorption flux monitor (See Fig. 2.11 B). Outgoing (scattered) electric and magnetic fields are collected on the scattering flux monitor (See Fig. 2.11 C).

Basic FDTD requires the electric and magnetic fields to be offset by half-steps both spatially (i.e., $\Delta x/2$) and temporally (i.e., $\Delta t/2$). The staggered nature of the grid, however, poses difficulty in collating the electric and magnetic fields for coarse grid spacings. This problem can be mitigated by correcting for the spatial and temporal offsets of both the $E$ and $H$ fields. Additionally, the errors from calculating the near field scattering cross section can be minimized by using a near to far field (NTFF) transformation which extrapolates the scattered electric fields out to infinity by exploiting Green’s theorem.
Figure 2.11: Schematic of a typical FDTD setup (in 2 dimensions) with TF/SF boundary and flux monitors. Panel A shows both the absorption and scattering monitors, while panels B and C show only absorption flux monitors inside the TF/SF boundary with inward pointing normals and scattering flux monitors outside the TF/SF boundary with outward pointing normals, respectively. Absorption flux monitors are located inside the TF/SF and scattered flux monitors are located outside the TF/SF.
2.4 References


3.1 Introduction

Noble metal nanoparticles (NPs) possess unique chemical, electronic, and optical properties with important applications spanning molecular sensing, catalysis, metamaterials, and biologically-relevant technologies.\textsuperscript{1–10} Many of these applications exploit field enhancements due to localized surface plasmon resonances, which are coherent oscillations of the free electrons at the NPs surface.\textsuperscript{11–14} Changing the composition, size, shape, and surrounding medium allows for tunable optical properties of these plasmonic NPs. These broadly tunable NPs show promise for the molecular detection, metamaterials, and novel dispersion properties.\textsuperscript{15} Plasmonic gold and silver nanoparticles can be functionalized with biological molecules and polymers through thiolation for applications in biolabeling,\textsuperscript{16,17} drug delivery,\textsuperscript{11,18} and photothermal therapy.\textsuperscript{19–21}

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Nonlinear responses of plasmonic nanoparticles such as second harmonic generation (SHG) and sum frequency generation (SFG) can be significantly enhanced due to these plasmon resonances.\textsuperscript{22–29} Additionally, interactions between plasmonic nanoparticles and chromatic dyes give rise to molecular and plasmonic resonance coupling, which can be measured via extinction spectroscopy. When the plasmon frequency is in resonance with a molecular excitation, strong coupling can lead to the formation of hybrid states, resulting in exciton-polariton peaks separated by a splitting energy. Additionally, this coupling leads to characteristic Fano-type resonances with corresponding plasmon and molecular spectral depletions.\textsuperscript{30–32,32–38}

The near-field dynamics and coupled dynamics of molecules, such as light harvesting dyes adsorbed to the surface of plasmonic nanostructures\textsuperscript{11}, show promise in the fields of photovoltaics, catalysis, and chemical sensing. For example, the strong fields near the surface of metal nanoparticles can boost the response of nearby adsorbates in low concentrations which is ideal for sensing applications such as surface enhanced Raman spectroscopy (SERS), or conversely, the optical responses of molecules at the surface of metallic nanostructures can induce plasmonic modes via surface-enhanced fluorescence. There has been much recent progress towards modeling these hybrid molecular/plasmonic systems. Some of the many approaches to model the dynamics between plasmons and molecules include point-plasmon/random phase approximation (RPA),\textsuperscript{39,40} a molecule treated with time-dependent Hartree Fock coupled to a continuous dielectric metal nanoparticle,\textsuperscript{41} resonant energy transfer via quantum molecules embedded in a classical continuum background,\textsuperscript{42,43} coupled Liouville/Maxwell equations\textsuperscript{44}, electrodynamics coupled to a density matrix master equation,\textsuperscript{33} extended Mie Theory on plasmonic nanospheres coupled to a two-level quantum model,\textsuperscript{45} finite-difference time-domain/real time-TDDFT,\textsuperscript{46–49} and quantum electrodynamics coupled with time-dependent Hartree-Fock.\textsuperscript{32}

Quantum/classical approaches based on a finite-difference time-domain (FDTD) solu-
Figure 3.1: Schematic of the gold/dye interface. The cationic malachite green (MG) molecules are held at the surface via electrostatic interactions with the anionic mercaptosuccinic acid (MSA) with a small water solvation layer between the MG and MSA. The transition dipole moment for the brightest absorption is tilted with respect to the normal of the surface by angle $\eta$. Assuming roughly two water shells, the overall separation $\ell$ between the Au surface and the MG center of mass is roughly 25.4 Å. For simplicity, in this paper we approximate the molecular monolayer as two supermolecules with scaled oscillator strengths.

tion to Maxwell’s equations, with embedded quantum oscillators, are especially versatile as they can describe arbitrary geometries of nanostructures with a nearby quantum emitter (e.g., molecule or quantum dot), potentially with solvent effects included. Typically these approaches involve a single quantum point source, but in many real systems there is coupling between nanoparticles (NPs) and thousands of nearby dyes (e.g., adsorbed on the surface). This requires an extensible approach capable of describing an arbitrary number of quantum sub-regions within the FDTD main grid. In this paper, we present a method for modeling a monolayer of molecules on the surface of a spherical plasmonic nanoparticle using two “super molecules” and compare these results to experimental extinction measurements. The method can readily be extended to an arbitrary number of molecules. We use a phenomenological $N$-level Hamiltonian for each molecule, but this approach can be extended to accommodate any quantum description.
The remainder of the paper is structured as follows: In Sec. ??, we present expressions for the FDTD evolution of the electric fields, magnetic fields, currents and polarizations for a combined plasmon/molecule system, followed by an explanation of how to implement a combined FDTD/N–level approach. Sec. ?? presents validation simulations including: single gold NP extinction spectra, long-range resonant energy transfer (FRET) between two molecules, and finally difference extinction spectra for malachite green monolayers adsorbed on a Au NP (See Fig. 3.1). Comparison of these spectra with experiment allows us to extract approximate transition dipole angles and monolayer separation distances. Finally, conclusions and future extensions are presented in Sec. 3.8.

In this chapter, we outline an approach for coupling multiple quantum oscillators within a classical electrodynamics background described using FDTD. Broadly, this involves five components:

1. Describe the electric and magnetic fields in the vacuum (or background medium), and the fields and currents on the metal nanoparticle, using FDTD.

2. Partition an auxiliary FDTD subregion around each quantum oscillator (molecule) to remove spurious self-excitation of the molecules with their radiated fields. This uses a total-field/scattered-field (TF/SF) approach.

3. Propagate each quantum molecule in time under the influence of the external field from the FDTD. This can be done using any quantum method, but here we use phenomenological N-level molecules.

4. The quantum currents on each molecule act as source terms for the main FDTD grid via the TF/SF boundary around each molecular subregion.
3.2 Basic FDTD Considerations

In the finite-difference time-domain (FDTD) approach, the fields and currents are discretized on a grid and solved in time and space using a “leap-frog” integrator. The spatial and frequency-dependent permittivity \( \varepsilon(r) \) and permeability, \( \mu(r) \) are typically fit to experimental bulk values. Neglecting magnetization effects in the metal (i.e., \( \mu = \mu_0 \)), the Maxwell’s equations are:

\[
\varepsilon_{\text{eff}}(r) \frac{\partial}{\partial t} \mathbf{E}(r, t) = \nabla \times \mathbf{H}(r, t) - \mathbf{J}(r, t) \tag{3.1a}
\]

\[
\mu_0 \frac{\partial}{\partial t} \mathbf{H}(r, t) = -\nabla \times \mathbf{E}(r, t) \tag{3.1b}
\]

where \( \mathbf{E}(r, t) \) is the electric field, \( \mathbf{H}(r, t) \) is the magnetic field, and \( \mathbf{J}(r, t) \) is the electric current density. Note that in this paper, \( \mathbf{J} \) is only present on the metal nanostructure.

To avoid issues with “hard sources,” where propagated fields interact in non-physical ways with the source, we use a total-field scattered-field (TF/SF) approach. Here, an auxiliary 1D simulation with a specified pulse is propagated separately from the main 3D grid. To excite the system, the 1D incident field is projected to 3D and added uniformly to one side of the TF/SF boundary. The pulse is then subtracted out as it reaches the opposite side, resulting in purely scattered fields outside the TF/SF boundary. By subtracting the incident field, the resulting simulation outside the total-field region contains only scattered fields. This technique is commonly used to calculate the scattering cross sections of arbitrary objects via the outgoing flux (outside the TF/SF) along with a near-to-far-field (NTFF) transform. The corresponding absorption cross section can be computed inside the TF region using flux monitors, but this approach can be somewhat sensitive to monitor position and grid spacing. Details on calculating the absorption and scattering cross sections are outlined in the Section 2.3.6.
3.3 Coupling between Quantum Mechanics and FDTD

The electron dynamics in molecules must be described using quantum mechanics, which necessitates a multiscale coupling between the main FDTD grid and multiple quantum sub-regions. We assume that each molecule only occupies one FDTD grid point. This can be justified for both the absorption and emission of the molecule as follows: For absorption, when the wavelength of light is much greater than the size of the molecule, the applied field on a molecule is essentially constant. Thus, the coupling is dominated by dipolar coupling and the molecule can be treated as experiencing a uniform electric field with the value given by the FDTD field at a single point in space (at the center of mass of the molecule). For the molecular radiation, the fields near the molecule may not be dipolar (especially for long chromophores) but will become dipolar far enough away from the molecule. Given the relatively large distances between the NP and molecules (∼25 Å), this is also a reasonable approximation. Extensions to close molecule-molecule distances may require going beyond this dipolar emission approximation. This can be accomplished by solving the FDTD and QM on the same (or overlayed) grids. Thus, the FDTD electric field at that point acts as an external field on the molecule, and the molecular current acts as a source for the FDTD. Direct application of this, however, results in spurious self-excitation of the molecule, as the radiated field can immediately “re-excite” the emitting molecule. One way of overcoming this is to use a full auxiliary FDTD grid for each molecule, but this is not tractable for a large number of molecules. A better alternative is to instead partition a small FDTD region around each molecule using a TF/SF-like coupling, such as the approach developed by Seideman and coworkers. By propagating the fields in this small region using the analytical expression for a radiating dipole, the radiated fields from the molecule do not interact with the molecule itself, but are instead coupled back into the main grid some distance away using a “reverse” TF/SF boundary. In this paper we instead propagate using a FDTD with a point source, which is valid for any quantum emitter.
Figure 3.2: Schematic of the multiscale quantum/classical approach. A main finite-difference time-domain (FDTD) region contains the background and any potential metal nanostructures, while each quantum molecule is contained within its own FDTD subregion. These molecules are excited via the electric field in the main region, but emit into their own auxiliary sub-region to prevent self-excitation. These emitted fields are then introduced into the main region using reverse total-field/scattered-field (TF/SF)-like interfaces (arrows). This approach allows for an arbitrary number of quantum molecules treated using any quantum method.
Fig. 3.2 shows a schematic of the approach for the case of two molecules. The main FDTD has two regions: a total field (TF) region which contains all nanostructures and molecules, and a scattered field (SF) region which contains only the scattered fields (i.e., no incident pulse). The boundary of the main FDTD region was taken to be a second-order Mur absorbing boundary to remove non-physical reflections. The system is excited with a broadband pulse via the TF/SF interface, as described in the previous section. This electric field then acts as an external applied source for each quantum molecule in the region. Rather than radiate back into the TF region, which would allow the molecule to nonphysically excite itself, instead each molecule radiates into its own auxiliary FDTD region centered around the molecule (see Fig. 3.2). After propagating some distance from the molecule, this molecular field is then added back to the main FDTD grid via a “reverse” TF/SF boundary. These interfaces act as sources for the TF region. Finally, each molecular subregion has its own absorbing boundary to prevent reflections.

An approach based on point polarizable dipole molecules, parameterized to either experiment of QM calculations, would likely give a similar result for this application. Our embedded time-dependent quantum method, however, can be extended to other nontrivial cases. Because this method propagates the quantum molecules in the time domain, it can capture nonlinear responses such as strong field excitations (e.g., Rabi cycling, tunnel ionization, etc), and multiphoton processes (e.g., hyperpolarzabilities, high harmonic generation, etc.). Additionally, it allows for extension to molecular photochemistry under plasmonic fields via non-adiabatically (beyond Born-Openheimer) coupled electron/nuclear dynamics simulations (e.g., surface hopping).

This technique has three advantages: (1) It does not assume any analytic form for the molecular fields and is thus valid for any quantum point source (e.g., non-dipolar), (2) if the grid parameters are consistent between the main and molecular FDTD regions, artifacts from the interfaces will be minimal, and (3) it can be extended to a large number of molecules, as
the computational cost associated with each subregion is insignificant compared to the main grid, and each region can be computed in parallel.

3.4  \( N \)-Level System with Dephasing

The above-described embedding technique is valid for virtually any quantum treatment of the molecules (e.g., time-dependent Schrödinger equation, time-dependent density functional theory, etc). For simplicity, here we will use a phenomenological \( N \)-level picture for the quantum dynamics. In the density matrix representation, the equation of motion is governed by the von Neumann equation:

\[
\frac{i}{\hbar} \frac{\partial \rho(t)}{\partial t} = [\rho(t), H(t)]
\]  

(3.2)

where for a \( N \)-level system \( H \) and \( \rho \) are \( N \times N \) matrices. To incorporate dephasing, it is convenient to instead use a Liouville representation:

\[
\frac{i}{\hbar} \frac{\partial \|\rho(t)\\rangle\rangle}{\partial t} = \mathcal{L} \|\rho(t)\\rangle\rangle,
\]

(3.3)

where \( \|\rho(t)\\rangle\rangle \) is the density vector (length \( N^2 \)) and \( \mathcal{L} \) is the Liouville operator (matrix size \( N^2 \times N^2 \))

\[
\|\rho(t)\\rangle\rangle = \begin{pmatrix}
\rho_{11}(t) \\
\rho_{12}(t) \\
\vdots \\
\rho_{1N}(t) \\
\rho_{21}(t) \\
\vdots \\
\rho_{NN}(t)
\end{pmatrix}
\]

(3.4)
The Liouville operator can be constructed from the Hamiltonian by converting from 2–index to 4–index form:

\[ \mathcal{L}_{jklm} = H_{jl} \delta_{km} - H_{mk} \delta_{jl} \quad j, k, l, m \in [1, N] \]  

(3.5)

where, without dephasing, the Hamiltonian is given by

\[ \mathbf{H}(t) = \mathbf{H}^0 - \mu \cdot \mathbf{E}(t) \]  

(3.6)

and \( \mu \) is the transition dipole (tensor) operator, \( \mathbf{E}(t) \) is a time dependent electric field, and \( \mathbf{H}^0_{kl} = \varepsilon_k \delta_{kl} \). The transition dipole matrix elements in direction \( d \) are

\[ \mu^d_{kl} = - \langle k|d|l \rangle, \quad (d = \{x, y, z\}) \]  

(3.7)

The 4–index \( \mathcal{L}^0 \) operator \( (N \times N \times N \times N) \) is then reshaped to 2–index for \( (N^2 \times N^2) \). For example, if \( N = 2 \)

\[
\mathcal{L}^0 = \begin{pmatrix}
0 & \mu_{12} \cdot E & -\mu_{12} \cdot E & 0 \\
\mu_{12} \cdot E & -\Delta \varepsilon_{2-1} + \Delta \mu_{2-1} \cdot E & 0 & -\mu_{12} \cdot E \\
-\mu_{12} \cdot E & 0 & \Delta \varepsilon_{2-1} - \Delta \mu_{2-1} \cdot E & \mu_{12} \cdot E \\
0 & -\mu_{12} \cdot E & \mu_{12} \cdot E & 0
\end{pmatrix}
\]  

(3.8)

where the energy of the transition is defined as \( \Delta \varepsilon_{l-k} = \varepsilon_l - \varepsilon_k \) (e.g., \( \Delta \varepsilon_{2-1} = \varepsilon_2 - \varepsilon_1 \)), and the difference in static dipole moments is defined as \( \Delta \mu_{l-k} = \mu_l - \mu_k \). For a three level
system (N=3), we get

\[
\mathcal{L}^0 = \begin{pmatrix}
0 & \mu_{12} \cdot E & \mu_{13} \cdot E & -\mu_{12} \cdot E & 0 \\
\mu_{12} \cdot E & -\Delta \varepsilon_{2-1} + \Delta \mu_{2-1} \cdot E & \mu_{21} \cdot E & 0 & -\mu_{12} \cdot E \\
\mu_{13} \cdot E & \mu_{23} \cdot E & -\Delta \varepsilon_{3-1} + \Delta \mu_{3-1} \cdot E & 0 & 0 \\
-\mu_{12} \cdot E & 0 & 0 & \Delta \varepsilon_{2-1} - \Delta \mu_{2-1} \cdot E & \mu_{12} \cdot E \\
0 & -\mu_{12} \cdot E & 0 & \mu_{12} \cdot E & 0 \\
0 & 0 & -\mu_{12} \cdot E & \mu_{13} \cdot E & \mu_{23} \cdot E \\
-\mu_{13} \cdot E & 0 & 0 & -\mu_{23} \cdot E & 0 \\
0 & -\mu_{13} \cdot E & 0 & 0 & -\mu_{23} \cdot E \\
0 & 0 & -\mu_{13} \cdot E & 0 & 0
\end{pmatrix}
\]

(3.9)

Now if we want to introduce dephasing of the coherences (i.e., $T_2$ lifetimes) in a Redfield–like picture,\textsuperscript{58} we add an imaginary part to the Liouville operator

\[
\mathcal{L} = \mathcal{L}^0 + i\mathcal{L}^d
\]

(3.10)
In 4-index form:

\[ \mathcal{L}_{j,k,l,m}^d = \gamma_{jk} \delta_{jk,jk}, \quad j \neq k \]  
(3.11)

where \( \gamma_{jk} = \gamma_{kj} \) and the dephasing parameters are the inverse of the \( T_2 \) lifetimes:

\[ T_{2,jk} = \frac{1}{\gamma_{j,k}} \]  
(3.12)

Note that we have not included \( T_1 \) lifetimes here (energy loss/damping) although this is easily done. E.g. for \( N = 2 \)

\[ \gamma_{12} = \gamma_{21} = -\frac{i}{T_{2,12}} \]  
(3.13)

and zero for other terms.

For a three level system, the 4-index dephasing Liouvillian is:

\[ \mathcal{L}_{12,12}^d = \mathcal{L}_{21,21}^d = -i\gamma_{12} \]  
(3.14a)

\[ \mathcal{L}_{13,13}^d = \mathcal{L}_{31,31}^d = -i\gamma_{13} \]  
(3.14b)

\[ \mathcal{L}_{23,23}^d = \mathcal{L}_{32,32}^d = -i\gamma_{23} \]  
(3.14c)
(other terms are zero). In the 2–index form:

\[
\mathcal{L}^d = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -i\gamma_{12} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -i\gamma_{13} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -i\gamma_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i\gamma_{23} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i\gamma_{13} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i\gamma_{23} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

(3.15)

Now, if we assume the system starts purely in the ground state

\[
||\rho(0)|| = \begin{pmatrix}
1 \\
0 \\
\vdots \\
0
\end{pmatrix}
\]

(3.16)

we can propagate \(||\rho(t)||\) by integrating the equation of motion:

\[
||\rho(t + \Delta t)|| = \hat{U} ||\rho(t)||
\]

(3.17)

where the propagator \(\hat{U} \equiv e^{-i\mathcal{L}(t)\Delta t}\). In simple cases, the matrix exponentiation can be done using diagonalization, but other methods, such as power series expansion, can be used.\(^{59,60}\)

Now, the expectation value of the polarization can be computed from the density vector:

\[
\langle p^d(t) \rangle = p^d(t) = \langle \langle \mu^d | \rho(t) \rangle \rangle
\]

(3.18)
where $\mu^d$ is the dipole superoperator in the $d$-direction:

$$
\mu^d = \begin{pmatrix}
\mu^d_{11} \\
\mu^d_{12} \\
\mu^d_{13} \\
\vdots \\
\mu^d_{1N} \\
\vdots \\
\mu^d_{NN}
\end{pmatrix}
$$

(3.19)

Note, this includes on-diagonals $\mu_{kk}$ which represent static dipole moments of the ground and excited states. The time derivative of the polarization (Eq. 3.18) is required for coupling to the FDTD:

$$
\frac{d}{dt} \langle p(t) \rangle = \frac{d}{dt} \langle \langle \mu | \rho(t) \rangle \rangle 
$$

(3.20a)

$$
\frac{d}{dt} \langle p(t) \rangle = \langle \langle \mu | \frac{d\rho(t)}{dt} \rangle \rangle
$$

(3.20b)

Since

$$
\frac{d\rho(t)}{dt} = -i \mathcal{L} \rho(t)
$$

(3.21)

Eq. 3.20a becomes

$$
\frac{dp}{dt} = -i \langle \langle \mu | \mathcal{L} \rho \rangle \rangle
$$

(3.22)

This single molecule (microscopic) polarization is scaled by the volume of a simulation voxel ($\Delta V = \Delta x \times \Delta y \times \Delta z$) to obtain the macroscopic current density:

$$
\frac{dP}{dt} = \frac{dp}{dt} \Delta V = J(t)
$$

(3.23)
This becomes a current source term in Maxwell’s equations via Eq. 3.1a.

3.5 Validation of FDTD

Before discussing the coupled plasmon/molecule case, we validate the electrodynamics and FDTD/QM approaches separately. For the electrodynamics, we developed our own FDTD code to allow for ease of integration with the quantum code. For each simulation, the total volume was approximately $2281 \times 2281 \times 2281 \text{ nm}^3$. Convergence with grid spacing was testing for $\Delta x = \Delta y = \Delta z = 16, 12, 8 \text{ au} = 8.47, 6.35, 4.23 \text{ Å}$. For the finest grid, this corresponds to $539^3$ total grid points. The time step was taken to be $0.8$ times the Courant stability limit which corresponds to $0.036 \text{ a.u.} = 8.71 \times 10^{-4} \text{ fs}$. Each simulation was allowed to continue until the fields decayed to $0.1\%$ of the maximum intensity, corresponding to about $3500 \text{ au}$ of time. This required roughly $9.72 \times 10^4$ time steps, which took about 20 hours on 16 processors (OpenMP parallelized) and used approximately 160 GB of RAM.

For each simulation, the system was initialized using the TF/SF boundary with an $x$-directed, $z$-polarized broadband plane-wave excitation centered on the plasmon frequency. The pulse was chosen to be a discrete Ricker Wavelet to minimize grid artifacts:

$$f_r[q] = \left(1 - 2\pi^2 \left[\frac{S_c q}{N_p} - M_d\right]^2\right) \exp\left(-\pi^2 \left[\frac{S_c q}{N_p} - M_d\right]^2\right)$$

(3.24)

where $S_c$ is the Courant stability number, which is a dimensionless quantity representing the ratio of the chosen simulation time step to the largest stable time step. Here, $\Delta t_{max} = c\Delta x/\sqrt(3)$, is the Courant stability limit for a cubic 3D grid ($\Delta x = \Delta y = \Delta z$), i.e., the maximum possible time step for which the Yee FDTD propagation is stable. $N_p$ is the number of points per wavelength at the center frequency $\omega_0$ and is defined by

$$N_p = \frac{S_c}{\omega_0 \Delta t}$$

(3.25)
and the temporal delay $M_d$ is the delay multiple. This pulse contains no DC component, and its spectral content is set by a single parameter (i.e., $\omega_0$). After excitation, the energy flow into and out of the system is measured as a function of time via a scattering flux monitor located outside the total field region (in the scattering region) and an absorption flux monitor located inside the total field region. By collecting the outgoing electric and magnetic fields on these flux monitors, we can obtain extinction properties of the system (molecule, nanoparticle, combined, etc). See section 2.3.6 for details.

Before progressing to the coupled quantum/FDTD case, we first validate our FDTD implementation for a single gold nanoparticle. As is commonly done, the frequency-dependent permittivity of the metal is modeled as a sum of Lorentzians

$$\varepsilon(\omega) = \varepsilon_{\infty} + \varepsilon_0 + \sum_{j=1}^{N_L} \frac{\beta_j}{\omega_j^2 - i\alpha_j \omega - \omega^2}$$

where $\alpha_j$, $\omega_j$, and $\beta_j$ are real material-dependent parameters. These parameters can be directly incorporated through the auxiliary difference equation technique. For the parameters, we use the $N_L = 9$ Lorentzian fit to experimental bulk values obtained by Neuhauser et al. This fit is valid over the energy range between 0.6 – 6.7 eV.

For this validation we computed the extinction (absorption + scattering) of a single 80 nm diameter gold nanosphere in water with various grid spacings and compared it to the experimental extinction measured with a UV/Vis spectrophotometer. Additionally, we can change the background medium through $\varepsilon_{eff} = \varepsilon_0 \varepsilon_r$ in Eq. 1a. For these simulations, we used $\varepsilon_r = 1.782$, which corresponds to a water solvent. Fig. 3.3 shows the spectra for various grid spacings. Overall the spectrum is relatively insensitive to grid, and agrees well with experiment in the region of the plasmon resonance. Deviations at lower ($\sim 1.8$ eV) and higher ($\sim 2.5$ eV) are likely due to polydispersity in the experiment. Based on these results, we henceforth use a grid spacing of $\Delta x = 8$ au = 4.23 Å for subsequent calculations of this
Figure 3.3: Comparison of FDTD computed and experimentally measured extinction (absorption + scattering) for a 80 nm diameter gold nanoparticle. The computed spectra are insensitive to grid and are consistent with experiment.
size nanoparticles.

3.6 Energy Coupling Between Two Molecules

To validate our multi-molecule embedding scheme, we computed resonant energy transfer between a pair of spatially separated two-level molecules with aligned transition dipole moments. Here, to emphasize the effect, we chose each to have a non-physical transition dipole moment of $57 \text{ au} = 144 \text{ D}$. The frequency was chosen to be $0.073 \text{ au} = 2.0 \text{ eV}$. For this simulation, the subregion around each molecule was 30 au wide with an absorbing boundary beyond each TF/MF boundary. The left molecule was initialized via a delta kick excitation. The transfer was quantified by computing the maximum energy on the right molecule as a fraction of the maximum energy on the left molecule. Figure 3.4 shows this fractional energy transfer as a function of intermolecular separation $R$. The observed $1/R^6$ behavior is characteristic of a Förster-like resonance energy transfer (FRET) mechanism, which arises from long-range dipole-dipole interactions.$^{64-66}$ The energy transfer between the two embedded molecules is mediated by the propagation of the electric fields through the FDTD background. This yields the dipole-dipole coupling without additional distance-dependent terms in the Liouvillian (or corresponding operator for other QM methods). This type of interaction can be modeled using purely quantum approaches such as TDDFT transition-dipoles$^{67}$ or transition density cube methods.$^{68}$ Embedded QM schemes like previous work$^{40,44,47}$ and our approach here have a few advantages. Since the molecules and intermediate fields are propagated explicitly in time and space, these methods can be extended to FRET in environments with non-trivial frequency responses (e.g., near plasmons and surfaces, certain solvents, etc). Additionally, they open the door to resonant energy transfer under intense fields.
Figure 3.4: Computed resonant energy transfer between a pair of two-level chromophores as a function of separation ($R$). The transition dipole moments are shown with arrows. The fractional energy transfer from an excited (donor) molecule to the acceptor follows a $1/R^6$ trend, consistent with a Förster-like process (dipole-dipole coupling).
3.7 Plasmon/Molecule Coupling

Now we turn to the main topic of this paper, namely computing the coupled excitations of plasmons with multiple nearby chromophores. Here we study the system consisting of a 80 nm gold NP with a full monolayer of malachite green molecules adsorbed on the surface (See Fig. 3.1). Previous experimental studies on this system have exhibited strong coupling between the plasmons and excitations on the dyes, which can be observed via a difference UV-visible extinction spectrum. These systems have well-characterized nanoparticle sizes (via transmission electron microscopy) and known surface coverage (via second harmonic generation isotherms). Questions remain, however, about the physical origins of the observed features in the coupling spectra, as well as the orientation (transition dipole angle) and distance of the dye molecules from the NP surface. In this section, we present simulations for interpreting these difference spectra and approximating the geometries of the dyes with respect to the NP.

We model malachite green as a three-level molecule, focusing only on the transitions at 2.02 eV and 2.13 eV. The molecular parameters were determined by fitting the experimental spectrum to the sum of two Lorentzian functions, with the peak positions yielding $\Delta \varepsilon_{2-1} = 0.07423 \text{ au} = 2.020 \text{ eV}$ and $\Delta \varepsilon_{3-1} = 0.07822 \text{ au} = 2.129 \text{ eV}$, respectively. The oscillator strengths were found by integrating the extinction, which gives the transition dipole moments $\mu_{12} = 1.985 \text{ au} = 5.046 \text{ D}$ and $\mu_{13} = 1.575 \text{ au} = 4.003 \text{ D}$. Here, we are only interested in modeling the two lowest excitations of the malachite green molecule: $|1\rangle \rightarrow |2\rangle$ and $|1\rangle \rightarrow |3\rangle$. Since the $|2\rangle$ states will be negligibly populated (due to low field intensities), the $|2\rangle \rightarrow |3\rangle$ is not experimentally observable and can be neglected. We thus turn off the excited state absorption ($|2\rangle \rightarrow |3\rangle$) by setting $\mu_{23} = 0$. For the lifetimes, it is generally impossible to deconvolute an experimental absorption peak into $T_1$ (damping) and $T_2$ (dephasing) contributions. A more sophisticated approach would be to use time-resolved techniques, such as pump-probe transient absorption spectroscopy, to measure the $T_1$ and $T_2$ contributions.
For simplicity we assume only dephasing, with the corresponding lifetimes fit to the full
width half maximum of the experiment. Here, \( T_{12} = 481.4 \text{ au} = 11.65 \text{ fs and } T_{13} = 291.9 \text{ au} = 7.061 \text{ fs, corresponding to the dephasing times between states } |1\rangle \text{ and } |2\rangle \text{ and } |1\rangle \text{ and } |3\rangle, \) respectively.

Experimentally, we previously determined that each 80 nm Au NP had \( M \approx 9200 \) molecules adsorbed to the surface.\(^ {34} \) Although the formalism could be applied to directly
model this system, for simplicity we instead model the monolayer as two “super” molecules
with scaled-up transition dipole moments. This allows us to mimic the response of mala-
chite green covering the entire gold surface using only two quantum molecules. A super
molecule approach implicitly assumes a particular orientation of each molecule with respect
to the surface and neglects coupling between molecules. These super molecules then cou-
ple indirectly through the plasmonic fields. Additionally, we experimentally determined the
adsorption site area of malachite green to be approximately \( 2.19 \text{ nm}^2 \), where the average
molecule-molecule distance is \( 1.14 \text{ nm.} \) Although these molecules are potentially within the
strong coupling regime,\(^ {69} \) we believe the overall spectra are dominated by the plasmon/-
molecule coupling as evidenced by our good agreement with experiment. For smaller NP’s
(i.e., < 50 nm), higher site densities, or molecules with higher oscillator strengths, we suspect
that the molecule/molecule interaction will play a more important role in the coupling.

We determined the super molecule transition dipole moments such that the absorp-
tion of the pair matches the expected response of a fully covered nanoparticle. Neglecting
molecule/molecule coupling, the scaling factor can be approximated from the experimentally
measured surface coverage \( M \). Since absorption scales linearly with the number of molecules,
the total absorption of a collection of independent oscillators is given by:

\[
\tilde{\sigma} = \tilde{M} \sigma
\]  

(3.27)
Figure 3.5: Computed extinction spectra for a single malachite green molecule, modeled as a three-level system with parameters fit to match experiment.
where $\sigma$ is the absorption of a single molecule, $\tilde{\sigma}$ is the absorption of the collection of molecules, and $\tilde{M}$ is an effective number of molecules. For an isotropic arrangement, $\tilde{M}$ is simply the number of molecules in solution. For the case of molecules adsorbed to a spherical nanoparticle with a well-defined angle with respect to the normal, and for a particular light polarization (say $z$), this becomes an orientational average. This is a surface integral of the transition dipoles dotted into the normal, which accounts for alignment of the molecules with respect to the $z$-polarized light field:

$$\tilde{M} = M \int_0^\pi d\theta \sqrt{\frac{\langle \cos^2(\theta) \rangle}{\langle \cos^2(0) \rangle}} = M \frac{1}{\sqrt{2}} \quad (3.28)$$

Now, since absorption is directly proportional to the square of the transition dipole, $\tilde{\sigma} \propto \tilde{\mu}^2$, the effective “super” transition dipole moment is given by:

$$\tilde{\mu} = \sqrt{M \mu} \quad (3.29)$$

A single molecule is unable to capture molecule-plasmon-molecule polariton modes so we instead used two super dyes positioned at the $\theta = 0$ and $\theta = 180^\circ$ poles of the nanoparticle. Before proceeding to the nanoparticle case, we first validated the super molecule approach by comparing the $z$-polarized extinction of two dyes with purely $z$-oriented dipole moments against that of four dyes, each located at some angle $\theta$ with respect to the $z$-axis. For a pair, the transition dipole is scaled by an additional $\frac{1}{\sqrt{2}}$ such that the absorption cross section is the same (see Eq. 3.29). Fig. 3.6 shows the calculated extinction spectra for these two systems. Note here, for molecules the scattering is negligible so the extinction is predominantly absorption. The two are essentially identical, demonstrating that two super molecules can represent an arbitrary number of molecules, at least in the limit of no molecular coupling.
Figure 3.6: Computed $z$-polarized extinction of four molecules ($\theta = 30^\circ, 150^\circ, 210^\circ, \text{and } 330^\circ$) is captured correctly by two “super” molecules ($\theta = 0^\circ, 180^\circ$). Here, the long axis of the red ovals point along the direction of the transition dipole. This can be extended to modeling an arbitrary number of molecules using only two oscillators, at least in the limit of negligible molecule-molecule interactions.
Using this approach we now model the coupled plasmon-molecule polariton response of Au NP with malachite green adsorbed on the surface. This is a follow up on our previous experimental results.\textsuperscript{34} For these coupled nanoparticle/molecule simulations, we parameterized our grid using the best grid spacing from the convergence test of gold in Fig. 3.3 (i.e., $\Delta x = 8$ au). The malachite green monolayer was modeled using a pair of three-level super molecules, with the molecular parameters fit to experiment (See Sec. ??). For the surface coverage, we use our experimentally determined value of $M \approx 9200$, which was obtained using second harmonic generation (SHG) isotherm for a 80 nm gold nanoparticle.\textsuperscript{34}

The physical distance between the NP surface and dye monolayer ($\ell$), as well as the angle of the transition dipole with respect to the normal ($\eta$) both remain unknown. As a first approximation, we estimate the distance by measuring the length of mercaptosuccinic acid (MSA) (i.e., $9 - 12$ Å), the capping agent molecule, which is chemically bound to the surface of gold, and the length from the edge of the dye to its center (i.e., $7 - 10$ Å). Additionally, since these dyes are held at the surface via electrostatic interactions, we estimate that there are at least 1-2 water shells between the dye and MSA (i.e., $\sim 6$ Å). Therefore, we estimate the distance from the NP surface to the center of the dye to be $\sim 25$ Å (See Figure 3.1). For the angle, previous studies attribute observed results to a tilt angle of the dyes, but the angle remains unclear. Moreover, the molecular tilt angle is potentially different from the transition dipole angle. Thus for this paper, we compute the plasmon-molecule spectra for a range of separations ($\ell$) and transition dipole angles ($\eta$) to determine rough values.

First, we explore the effect of transition dipole angle on the coupling. To start, we pick the monolayer distance to be $\ell = 48$ au = 25.4 Å. This is consistent with approximately 1-2 shells of water between the surface and the center of the dye. Figure 3.7 shows resulting $z$-polarized coupling spectra for a range of transition dipole angles. As in experiment, this extinction spectrum was obtained by computing the spectrum of the NP+molecule system, then subtracting the extinction spectrum of the lone gold nanoparticle, as well as that of
a solution of $M$ molecules. For the molecule subtraction, to be consistent with experiment we used an ensemble average of molecular orientations, which corresponds to $\frac{1}{3}M$ for the $z$-polarization.

Figure 3.7 shows the difference in extinction as a result of the molecule-plasmon interactions, that is, in the absence of plasmon/molecule coupling, the difference extinction would be zero. In this case, the residuals reveal a Fano-like resonance centered at the molecular frequency $\Delta \varepsilon_{2-1}$, which results in two additional peaks. The lower energy peak corresponds to an in-phase coupled polaritonic mode $|P-\rangle$ involving the primary dye absorption ($|1\rangle \rightarrow |2\rangle$ transition) and the plasmon. This mode is significantly red-shifted from the uncoupled molecular mode. The complimentary out-of-phase polariton $|P+\rangle$ is blue-shifted and lower in magnitude. Additionally, there is a prominent negative feature at $\sim 2.02$ eV which corresponds to depletion of the main molecular mode at $\omega_m = \Delta \varepsilon_{2-1}$, i.e., energy transferred from the molecule to the plasmon, forming the polaritonic states $|P-\rangle$ and $|P+\rangle$. The corresponding plasmon depletion and second molecular mode (i.e., $\Delta \varepsilon_{3-1}$) overlap the $|P+\rangle$ polariton and are not clearly visible due to the small $\mu_{13}$ transition dipole for this molecular mode. These signals would likely be more prominent for the case of a smaller nanoparticle, where the cross section of the molecules would be closer in magnitude to that of the plasmon.

The effect of transition dipole angle $\eta$ on these polaritonic states is also shown in Figure 3.7. Regardless of angle, the frequency of the $|P+\rangle$ polariton is $\sim 2.14$ eV, while the magnitude decreases with increasing $\eta$. In contrast, the $|P-\rangle$ frequency blue-shifts and the magnitude decreases with increasing $\eta$. At a distance of $\ell = 25.4$ Å, for example, a transition dipole angle of $\eta = 60^\circ$ gives the best agreement with experiment, for both the frequency ($\sim 1.89$ eV) of the modes as well as the relative magnitudes. The energy difference between the two polariton peaks, $\Delta E_P$, corresponds to the splitting energy. This is a measure of the coupling strength between the molecular and plasmon excitations. Our model predicts an approximate splitting energy of $\Delta E_P = 263$ meV for malachite green and a 80 nm Au NP.
Figure 3.7: Comparison of FDTD computed and experimentally measured difference extinction spectra (coupled system pure Au NP dye solution) for a 80 nm diameter Au nanoparticle (NP) surrounded by malachite green molecules. The difference spectra reveals the coupling between the plasmon and molecular excitations. The system is modeled using two “super” dye molecules by fixing either the separation distance from the NP surface (Panel A) or transition dipole angle (Panel B) and varying the other (e.g., Panel A $\ell = 25.4$ Å and vary $\eta$). The residual Fano-type resonances correspond to an in-phase polariton $|P^-\rangle$ (lower energy) and an out-of-phase polariton $|P^+\rangle$ (higher energy). The depletion in the brightest molecular mode is visible at 2.02 eV ($\omega_m$). The corresponding plasmon depletion and second molecular mode overlap the $|P^+\rangle$ polariton and are not clearly visible.\textsuperscript{34}
This is in agreement with our experimental difference extinction measurements (Fig. 3.7C)\textsuperscript{34}.

Additionally, since the exact distance $\ell$ between the metal surface and the malachite green monolayer is not implicitly known, we also explored its effect on the splitting energy $\Delta E_P$. Figure 3.7B shows the difference spectra with a fixed transition dipole angle ($\theta = 60^\circ$) and various monolayer distances ($\ell = 48, 60, 80, 100$ au). The splitting energy decreases with increasing $\ell$, as evidenced by a blue-shifting $|P^-\rangle$ (in-phase) polariton frequency. The magnitude, on the other hand, is relatively insensitive to $\ell$. This is likely due to the relatively large separation from the surface, where the exponentially decaying electric field has a shallow gradient. The $|P^+\rangle$ (out-of-phase) polariton frequency and magnitude appears relatively insensitive with increasing $\ell$. From these results, however, it is clear that the splitting energy $\Delta E_P$ decreases with $\ell$.

Since both $\eta$ and $\ell$ affect the splitting energy, there is some ambiguity in using these simulations to determine the molecular geometry. Without some experimental measure of either of the parameters, it is difficult to conclusively approximate their values. In principle, a full 2D parameter scan might be illustrative, but choosing a “best” angle and distance by matching $\Delta E_P$ might still be ambiguous. Regardless, assuming $\ell = 25.4$ Å gives a transition dipole angle of $\eta = 60^\circ$ which is consistent with a tilted malachite green molecule. Future molecular simulation studies will give more insight into the geometry of malachite green adsorbed to the surface of Au NP.

3.8 Conclusions

In conclusion, we have presented a multiscale method for computing the coupled plasmon/molecule excitations for systems containing an arbitrary number of molecules on the surface of a metal. This uses finite-difference time-domain (FDTD) for the classical fields and quantum mechanical for the electron dynamics on each molecule. In this paper, we derive the expression for an $N$-level Hamiltonian with dephasing via a Redfield-like treatment, but this approach can also be extended to use any time-dependent quantum method.
We validated our results for the simple cases of a lone gold nanoparticle, as well as resonant energy transfer between two isolated molecules. The technique was then extended to model the extinction spectra of gold nanoparticles with an adsorbed monolayer of malachite green described using two “super molecules.” This was used to predict the orientation of the dye molecules (or at least that of their transition dipole), as well as the separation of the monolayer from the gold surface. Our results capture the experimentally observed polariton modes (coupled plasmon/molecule excitations) and agree with the observed experimental splitting energy of $\sim 263$ eV, with a “best guess” for the distance of $\ell \sim 25.4$ Å, and a transition dipole angle of $\eta \sim 60^\circ$.

Both quantities $\ell$ and $\eta$ are difficult to measure experimentally, but are crucial for interpreting spectra and for applications spanning molecular sensing, plasmonic photovoltaics, and near-field photocatalysis. As the coupling depends simultaneously on both transition dipole angle of the molecule, as well as the separation from the surface, it is difficult to conclusively assign their values from these simulations. Nevertheless, this ambiguity can be remedied if one parameter is known, either from experimental measurements, or computed using molecular simulations. In subsequent studies, to include potential molecule/molecule interactions, we will use a larger number of oscillators rather than two “super molecules”. The agreement of these results, however, with experiment suggests that primary mechanism of coupling is due to the interaction between the molecule and plasmon, rather than intermolecular effects. The role of molecule-molecule coupling on the spectra will be explored in future studies. Finally, this method can be extended beyond the simple $N$-level model using real-time quantum chemistry techniques such as time dependent Hartree-Fock, \cite{70-72} time-dependent density functional theory, \cite{60,73-76} configuration interaction, \cite{77,78} coupled cluster, \cite{79,80} and two-electron reduced density matrix methods. \cite{81} Moreover, to mitigate the computational cost of multiple molecules, the FDTD as well as each molecule can be computed in parallel, either using traditional MPI-like parallelization, or by using accelerator cards.
Finally, spectral acceleration techniques such as filter diagonalization\textsuperscript{82,83} or Padé approximants,\textsuperscript{84} can significantly decrease simulations times.

### 3.9 References


[60] K. Lopata and N. Govind, “Modeling fast electron dynamics with real-time time-


Chapter 4: Plasmon/Polariton Dynamics of Malachite Green at the Surface of Silver-Gold Core-shell Nanoparticles

4.1 Introduction

Gold and silver nanoparticles are particularly attractive for potential applications in molecular sensing, catalysis, photovoltaics and biologically relevant technologies due to their unique chemical, electronic and optical properties.\textsuperscript{1-10} These technologies exploit the localized surface plasmon resonances which lead to large optical field enhancements. At the nanoparticle/dielectric interface, coherent oscillations from free electrons lead to localized surface plasmon resonances which are heavily influenced by the nanoparticle composition, size, shape and surrounding medium, resulting in highly tunable optical properties. Additionally, these nanoparticles have been shown to greatly enhance nonlinear optical signals such as second harmonic generation (SHG) and sum frequency generation (SFG). Recently, there has been a great interest in the synthesis and characterization of core-shell nanoparticles, such as spherical silica-gold core-shell,\textsuperscript{11,12} spherical gold-silver-gold core-shell-shell,\textsuperscript{13} gold-silica core-shell,\textsuperscript{14} and graphene-coated gold nanoparticles.\textsuperscript{15} Unlike pure gold and silver nanoparticles, the relative size between the core and shell in core-shell nanoparticles allows for more control over the optical properties.\textsuperscript{13} However, more information on the surface properties of these core-shell nanoparticles and their interactions with different molecules is crucial for the development and optimization of these applications. Plasmonic gold and silver nanoparticles can be easily functionalized with a range of molecules through thiolation for applications in biolabeling, drug delivery,\textsuperscript{16,17} photothermal therapy,\textsuperscript{11,13,18,19} and chemical sensing.

Second harmonic generation (SHG) is a powerful tool used to study the adsorption properties of molecules to the surface of colloidal nanoparticles. SHG is nonlinear technique where two incident photons of frequency $\omega$ add coherently to scatter a photon of frequency
$2\omega$ (See Section 2.1). This frequency doubling is typically forbidden in bulk media with a center of inversion, making this a surface-specific technique ideal for the study of colloidal nanoparticle surfaces. Recent SHG research has studied TiO$_2$ microparticles, liposomes, and noble metal nanoparticles of gold, silver, and gold-silver alloys.

Furthermore, interactions between plasmonic nanoparticles and chromophoric dyes have been shown to give rise to molecular and plasmonic resonance coupling through polaritons, which can be measured by extinction spectroscopy and modeled via quantum/classical simulations. When the plasmon and molecular spectra overlap, a strong coupling is observed resulting in a new quantum mechanical state called a polariton. The coupling can be quantified by the splitting energy which is the difference between the in-phase and out-of-phase polaritonic modes. In Chapter 3, we report that 9180 malachite green molecules adsorbed on the surface of 80 nm gold nanoparticles have a measured splitting energy of $\sim 263$ eV, with a “best guess” based on the hybrid quantum/classical model for the adsorbate/NP separation of $\sim 25.4$ Å and a transition dipole angle of $\sim 60^\circ$ with respect to the surface normal. It was shown that the adsorption properties are governed by the adsorbate molecular structure and the nanoparticle environment.

In this chapter, SHG and extinction spectroscopy are used to monitor the adsorption isotherm of malachite green, a triphenylmethane dye, at the silver-gold core-shell nanoparticle surface. Additionally, the number of adsorbate sites per nanoparticle and the free energy of adsorption are determined by fitting the isotherm to a modified Langmuir model (See Sec. 2.1). Complementary linear absorption spectroscopy reveals plasmonic and molecular resonance coupling which lead to new polaritonic states overlapped in a Fano-type resonance profile. Hybrid quantum/classical modeling is used for validating the surface coverage and nanoparticle structure, as well as, giving insight into the transition dipole angle of malachite green adsorbed to the surface of the silver-gold core-shell nanoparticles.
4.2 Nanoparticle Synthesis and Characterization

Figure 4.1: Two steps involved in the synthesis of colloidal silver-gold core-shell nanoparticles.

The preparation of colloidal silver nanoparticles was carried out under reflux and vigorous stirring conditions. All chemicals were purchased from Alfa-Aesar and used without further purification in ultrapure water. For the preparation of incubation mixture, 250 µL of AgNO₃ (1 wt %), 1 mL of sodium citrate (1 wt %) and 30 µL of 98 µM potassium iodide were mixed in 1.25 mL of water and incubated for 5 minutes at room temperature. For the synthesis of colloidal silver core, 100 µL of 10 mM ascorbic acid was added to 47.5 mL of boiling water. After 1 minute, the incubation mixture was injected into the boiling ascorbic acid solution and refluxed for one hour. The colloidal solution was removed from heat and cooled to room temperature after 1 hour or when a pale yellow color was reached.

For the growth of the gold shell, 100 µL of silver nanoparticles were added to 10 mL of ultrapure water. The mixture was kept at room temperature under vigorous stirring with additions of 200 µL of gold chloride (1 wt %), 30 µL of 34 mM sodium citrate (1 wt %) and 100 µL of 30 mM hydroquinone. The size of the gold shell can be controlled by selecting the number of gold chloride, sodium citrate and hydroquinone sequential additions. The colloidal silver-gold core-shell samples were then dialyzed against a 22 mM aqueous solution of mercaptosuccinic acid for three consecutive days, followed by dialysis against ultrapure
water for another two additional days. Figure 4.2 a-b shows representative TEM images of the 64 nm colloidal silver nanoparticle sample with particle size distribution in Figure 4.2 c. Likewise, Figure 4.3 a-b shows representative TEM images of 64-15 nm silver-gold core-shell sample, respectively. After surveying over 500 particles from TEM, the core-shell nanoparticle diameter is determined to be 94.30 ± 4.7 nm, indicating a silver shell with thickness of ~15 nm.

4.3 Second Harmonic Generation

Our second harmonic generation setup is composed of an ultrafast titanium:sapphire oscillator laser with an optical setup coupled to a high-sensitivity charged-coupled device (CCD) spectroscopy detector (Fig. 2.2). This Ti:sapphire laser produces 75 fs pulses centered at 800 nm with a repetition rate of 80 MHz and an average power of 2.7 W. The laser beam is
Figure 4.3: Transmission electron microscopy images (a-b) of silver-gold core-shell nanoparticles on a carbon-coated copper grid. After analysis of over 500 particles, the distribution in the total diameter size is fit to a lognormal distribution (b) with the average diameter determined to be $94.3 \pm 4.7$ nm.

Focused on a 1 cm quartz cuvette containing the sample of $1.226 \times 10^{10}$ NPs/mL in water using a 20 mm focal length lens. An optical fiber is placed in front of the cuvette to remove any residual SHG light prior to the sample. Another filter is placed after the sample to remove the fundamental light while transmitting the SHG signal, which is collected in the forward direction and refocused to a monochromator connected to a high-sensitivity spectroscopy CCD. The dyes are added using a computer-controlled burette during automated stirring. Multiple spectra and background are acquired using a computer-controlled beam block. Several spectral scans are acquired for each addition of dye solution, and the isotherms are acquired several times for statistical analysis.
4.4 Theoretical Considerations

The coupled plasmon/molecule dynamics are modeled using a hybrid quantum/classical approach incorporating a classical electrodynamics treatment for the NP and an \( n \)-level quantum description for the molecules.\(^{25} \) We use our own FDTD code for the NP response which allows for ease of integration into an arbitrary quantum description for the molecule. The system utilizes an \( x \)-directed, \( z \)-polarized broadband plane-wave excitation centered at the plasmon frequency via injection at the TF/SF boundary (See Section 2.3.3). The pulse was chosen to be a discrete Ricker wavelet to minimize grid artifacts. The simulation box was terminated using a second order absorbing boundary condition (ABC) to prevent spurious reflections at the box edge (See section 2.3.4). Additionally, we use an auxiliary differential equation technique within the FDTD framework to incorporate the material parameters using the bulk permittivity values for gold and silver fit to a multi-pole Lorentzian model.\(^{26} \) These computational details are outlined in Section 2.3.5.

For each simulation, the total volume was approximately \( 2324 \times 2324 \times 2324 \) nm\(^3 \). Figure 4.4 shows the convergence of silver extinction cross section with grid spacing. For the finest grid, this corresponds to \( 549^3 \) total grid points. We chose our time step to be 0.8 times the Courant stability limit which corresponds to 0.036 au. The simulation is stopped after the electric field decays to 0.1% of the maximum intensity, which corresponds to about 3500 au of time. This requires approximately \( 9.72 \times 10^4 \) time steps, which took about 31 hours on 16 processors (OpenMP parallelized) and used approximately 94 GB of RAM.

4.5 Plasmonic Properties

FDTD is used to calculate the scattering, absorption and extinction cross sections while providing the local field enhancement at the resonant frequencies for a silver and silver-gold core-shell nanoparticle. For these simulations, we used \( \varepsilon_r = 1.335 \) which corresponds to a water solvent. Figure 4.4 shows the FDTD computed absorption, scattering and extinction cross sections for a 63 nm silver nanoparticle. Overall, the extinction cross section is insen-
sitive to grid spacing, and agrees well with experiment at the plasmon resonance. However, the experimental spectrum is much broader than the calculated spectra which is related to the high distribution of particle sizes. Figure 4.5 is the FDTD computed extinction cross section for silver-gold core-shell nanoparticles compared to extinction measurements. Good agreement with experiment indicates a core-shell structure. Deviations at lower wavelength, however, are likely due to polydispersity in the experiment.

4.6 Molecular Adsorption and Resonance Coupling

The SHG spectra at each concentration is used to determine the adsorption isotherm. Figure 4.6 shows the spectra for each concentration of malachite green. The signal at lower
wavelengths corresponds to the second harmonic generation, whereas, the rise at higher wavelengths corresponds to two photon fluorescence.\textsuperscript{22,27,28} As the concentration of dye increases, the resulting SHG signal increases until the adsorbates reach their saturation levels. The peak widths stay relatively constant within experimental uncertainty for all concentrations of dye added. For the SHG spectra of silver-gold core-shell alone in water without the addition of dye, an SHG peak is observed is primarily due to the nanoparticles themselves.

Figure 4.7 shows the adsorption isotherm from the SHG spectra from additions of malachite green to the colloidal silver-gold core-shell sample. Additionally, these data were corrected by subtracting out the hyper-Raleigh scattering of the free dye molecules in solution. The corrected experimental data are fit to a modified Langmuir adsorption model which includes the depletion of adsorbates form the bulk. The modified Langmuir equation is given
Figure 4.6: Spectra of silver-gold nanoparticle solutions at various malachite green concentrations. The SHG peak is detected near 400 nm.

by

$$\frac{N}{N_{\text{max}}} = \frac{(C + N_{\text{max}} + \frac{55.5}{K}) - \sqrt{(C + N_{\text{max}} + \frac{55.5}{K})^2 - 4CN_{\text{max}}}}{2N_{\text{max}}}$$

(4.1)

where $N$ is the number of adsorbates at the nanoparticle surface, $N_{\text{max}}$ is the maximum number of adsorbate sites on the nanoparticle surface multiplied by the concentration of nanoparticles in solution, $C$ is the adsorbate concentration added, and $K$ is the adsorption equilibrium constant. Using this fit, we find the best fit parameters for $K$ and $N_{\text{max}}$. Additionally, the free energy $\Delta G^\circ$ is obtained using the equation $\Delta G^\circ = -RT \ln K$.\(^{22,29}\)

The maximum number of adsorbate sites can easily be determined from $N_{\text{max}}$ and the nanoparticle concentration. However, the nanoparticle concentration is difficult to determine from these experimental conditions. To fit for an unknown nanoparticle concentration, we
need a combination of an experimentally measured extinction spectrum and a calculated extinction spectrum via FDTD simulations. From the Beer-Lambert law, we know that the optical absorbance (or optical extinction) is linearly proportional to the concentration:

$$A = \varepsilon \ l \ c$$  \hspace{1cm} (4.2)

where $A$ is the unitless absorbance, $\varepsilon$ is the “molar absorptivity” constant or the molar extinction coefficient, $l$ is the path length, and $c$ is the concentration. From FDTD, we can directly calculate $\varepsilon$ which is the extinction for one nanoparticle and has units of $m^2$ per NP. The path length $l$ of the quartz cuvette used to measure extinction is 0.01$m$. After
rearranging Eq.4.2 and solving for concentration, the Beer-Lambert Law becomes

\[ c = \frac{A}{\varepsilon l} \] (4.3)

After calculating the extinction cross section \( \sigma_{ext} \) (See Sec. 2.3.6) from FDTD, substitute the max intensity at the plasmon frequency for \( \varepsilon \). Then use the max value at the plasma frequency (unitless) which is obtained from the UV/Vis measurement. This results in a value for the concentration in units of NPs/mL. Finally, the number of molecules adsorbed to the surface \( N \) of a NP by can be determined by dividing \( N_{max} \) by the NP sample concentration. The best fits to adsorption isotherm is show as a red line in Figure 4.7. The free energy of adsorption obtained from the best fit of the modified Langmuir equation to the SHG adsorption isotherm is \(-11.08\) kcal/mol. Furthermore, the number of adsorption sites per core-shell nanoparticle for malachite green is determined to \(1.28 \times 10^4\) sites per particle. This value will be used to model the plasmon-polariton dynamics with the hybrid FDTD/quantum framework (See Section 3).

The SHG signal has been shown previously to depend on the tilt angle of the molecule and, by extension, the molecular dipole angle with respect to the surface. Previously, we have shown that the transition dipole angle and distance from the NP surface dictate the surface chemistry, including the electrostatic, hydrophilic and hydrophobic interactions, influences the molecular distance from the NP surface and the transition dipole angle, which dictates the splitting of new quantum states, called polaritons, from the interaction between the molecules and the near field enhancement at the plasmonic surface.\(^{22,25}\) These polaritonic states have a splitting energy that helps quantify how well the NP couples to the adsorbates. The general trend shows the splitting energy increases as the adsorbate gets closer to the surface (e.g., changing the capping agent or solvent) and decreases as the molecular dipole tilt angle increases. Figure 4.8 shows the extinction changes as the added dye concentration
increases. As the concentration of malachite green increases, a peak around the molecular frequency starts to become visible accompanied by a slight plasmon depletion. These features become more prominent in Figure 4.9 which is obtained after subtracting the extinction spectra of silver-gold core-shell nanoparticles and the dye alone in water from the spectra in Figure 4.8. The resulting spectra reveal coupling between the molecules and plasmon, including new polaritonic states embedded in a Fano-like profile with plasmon and molecular depletions. The enhanced near fields at the NP surface induce a splitting in the adsorbed dye modes, creating new polaritonic states separated by a splitting energy $\Delta E_p$. Using the FDTD/quantum embedding approach discussed in Chapter 3, we now model the coupled plasmon-molecule interactions between the silver-gold core-shell NP and malachite green
Figure 4.9: Measured difference extinction spectra obtained by subtracting silver-gold nanoparticles and dye extinction spectra alone in water from the coupled spectra measured from mixtures of both at the same concentrations for malachite green. Residuals reveal coupling between malachite green molecules and the plasmon, resulting in a polariton overlapped in a characteristic Fano-resonance profile.

dyes adsorbed to the surface. For these simulations, we parameterized our grid using the best grid spacing from the FDTD convergence test of silver-gold core-shell in Figure 4.5 (i.e., $\Delta x = 8$ au). The response of the malachite green monolayer is approximated as a pair of three-level “super” molecules with scaled oscillator strengths. We have previously shown that this approach is valid for gold and triphenylmethane systems (See Chapter 3). We parameterize our dyes using experimental extinction measurements of malachite green in water fit to two lorentzians to obtain the dephasing lifetimes and oscillator strengths for a single malachite green molecule in water (Figure 3.5). See Section 3.7 for details. However, the physical distance between the NP surface and dye monolayer is still unknown.
Figure 4.10: Comparison of FDTD computed and experimentally measured difference extinction spectra (coupled system – pure Ag-Au CS NP – dye solution) for a 64-15 nm silver-gold core-shell nanoparticle (NP) surrounded by malachite green molecules. The difference spectra reveals the coupling between the plasmon and molecular excitations. The system is modeled using two “super” dye molecules by fixing either the separation distance from the NP surface (Panel A) or transition dipole angle (Panel B) and varying the other (e.g., Panel A $\ell = 25.4$ Å and vary $\eta$). The residual Fano-type resonances correspond to an in-phase polariton $|P-\rangle$ (lower energy) and an out-of-phase polariton $|P+\rangle$ (higher energy). The depletion in the brightest molecular mode is visible at 2.02 eV ($\omega_m$). The corresponding plasmon depletion and second molecular mode overlap the $|P+\rangle$ polariton and are not clearly visible.\textsuperscript{22}
Figure 4.10 shows the difference in extinction as a result of the molecule-plasmon interactions, that is, in the absence of plasmon/molecule coupling, the difference extinction would be zero. Similar to previous studies of malachite green adsorbed to a gold surface, we see residuals that reveal a Fano-like resonance centered at the molecular frequency which results in two additional peaks. The mode at lower energy is designated as the in-phase polaritonic mode $|P-\rangle$ which is significantly red-shifted from the uncoupled molecular mode. The complimentary out-of-phase polariton $|P+\rangle$ is blue shifted and lower in magnitude. Additionally, another feature is observed at $\sim 2.02$ eV which corresponds to the depletion of the molecular mode, i.e., energy transferred from the molecule to the plasmon, resulting in the polaritonic states $|P-\rangle$ and $|P+\rangle$.

The effect of transition dipole angle $\eta$ on these polaritonic states is also shown in Figure 4.10. Regardless of the angle, the frequency of the $|P+\rangle$ is $\sim 1.899$ eV, while the magnitude decreases with increasing $\eta$. However, the $|P-\rangle$ frequency is relatively unchanged for all angles and decreases in magnitude with increasing $\eta$. At a distance of $\ell = 25.4$ Å, for example, a transition dipole angle of $\eta = 70^\circ$ gives the best agreement with experiment, for both the frequency ($\sim 1.899$ eV) of the modes as well as the splitting energy. The splitting energy, $\Delta E_P$ is defined as the energy difference between the two polaritonic modes. Our model predicts an approximate splitting energy of $\Delta E_P = 264$ meV for malachite green adsorbed to a 64-15 nm silver-gold core-shell NP. This result, however, is slightly different from the experimentally determined splitting energy of $\Delta E_P = 288$ meV.

This difference appears to be consistently related to the $|P-\rangle$ polariton. Discrepancies at this polaritonic mode are most likely due to a polydispersed core-shell nanoparticle sample. Since the system is modeled using the mean values from the lognormal distribution of the silver core and gold shell widths, the calculated extinction could be shifted as the mean size is not representative of the entire sample. Small deviations in the extinction spectrum towards lower energies will lead to a higher coupling with the molecules as it is more on resonance
with the molecular modes. By extension, the molecular distance to the nanoparticle surface and the transition dipole angle with respect to the surface are likely distributions rather than fixed values. Additionally, a sample with high polydispersity could lead to an overestimate in the number of adsorbates determined from by fitting the adsorption isotherm with the modified Langmuir.

4.7 Conclusion

Second harmonic generation is used to study the adsorption properties of malachite green to the surface of 64-15 nm silver-gold core-shell nanoparticles capped with mercaptosuccinic acid in aqueous colloidal suspension. The SHG results are analyzed and fit to a modified Langmuir model to determine the free energy of adsorption and the adsorbate site densities at the NP surface. These results are in agreement with previous SHG measurements of malachite green on the surface of 80 nm gold NPs. Furthermore, extinction spectroscopy measurements show plasmonic and molecular resonance coupling, resulting in hybrid polaritonic modes overlapped by a Fano-like resonance profile, separated by a splitting energy $\Delta E_P$. Complimentary calculations using a hybrid quantum/classical model derived in Chapter 3 further suggest that the coupling strength is highly dependent upon the angle of the transition dipole as well as the separation distance of the adsorbates from the outer gold shell surface. Our “best guess” of a separation distance of $\ell = 25.4$ Å gives a transition dipole angle of $\eta = 70^\circ$. Further improvement of the synthesis will allow for more precise calculations when determining the transition dipole angle and separation distance.
4.8 References


Chapter 5: Enhanced Photothermal Effects and Excited-State Dynamics of Plasmonic Size-Controlled Gold-Silver-Gold Core-Shell-Shell Nanoparticles

5.1 Introduction

Metallic nanoparticles composed of gold and silver possess unique chemical, electronic, and optical properties that are useful for applications in the fields of molecular sensing, catalysis, and biologically relevant technologies.\(^1\)–\(^10\) Localized surface plasmon resonances, characterized by the coherent oscillations of free electrons at the nanoparticles surface,\(^11\)–\(^13\) are highly dependent on the nanoparticle composition, size, shape, and surrounding medium. Plasmonic gold and silver nanoparticles can be functionalized with biological molecules and polymers through thiolation for applications in biolabeling,\(^14\),\(^15\) drug delivery,\(^16\),\(^17\) and photothermal therapy.\(^18\)–\(^20\) Plasmon-enhanced absorption in the near-infrared (NIR) photon energies, corresponding to the optical window in biological tissues, is advantageous for biological applications such as photothermal therapy and noninvasive bioimaging.\(^6\)

Several different types of plasmonic nanoparticles have been extensively studied due to their potential use in photothermal therapy including gold nanorods,\(^18\),\(^21\) gold nanocages,\(^22\) silica-gold core-shell nanoparticles,\(^20\),\(^21\) hollow spherical nanoshells,\(^23\),\(^24\) and gold nanoparticles coated with reduced graphene oxide.\(^25\) These nanoparticles can absorb light in the NIR wavelengths and convert it to heat through nonradiative processes, leading to a localized photothermal effect that can be used for selective killing of cancer cells. Methods to increase the NIR photothermal efficiency of plasmonic nanoparticles can provide more effective photothermal cancer therapies.\(^10\),\(^26\) For example, gold-silica-gold nanomatrioshkas were shown to be more efficient as photothermal transducers than gold-silica core-shell.\(^26\) Au@Ag/Au
nanospheres composed of a gold nanorod core and a silver/gold alloy shell demonstrated higher photothermal efficiencies and lower cytotoxities than gold nanorods.\textsuperscript{27} Another type of nanoparticle called gold-silver-gold core-shell-shell nanoparticles has been studied for potential applications in sensing and labeling,\textsuperscript{28} and represents a new direction for plasmonic engineering for highly efficient photothermal therapies at NIR wavelengths.

In this paper, we describe the synthesis, characterization, photothermal measurements, and transient absorption investigations of colloidal gold-silver-gold core-shell-shell nanoparticles. These nanoparticles exhibit plasmonic enhancement and controllable extinction spectra extending from the ultraviolet (UV) to the NIR wavelengths. The ratio of the outer gold shell thickness to the overall particle size shows a linear dependence with the position of the plasmon extinction peak wavelength. Temperature measurements after laser irradiation demonstrate that the colloidal gold-silver-gold core-shell-shell nanoparticles have a higher photothermal effect compared to colloidal gold nanospheres and gold nanorods. The excited-state dynamics of these plasmonic nanoparticles are studied using pump-probe transient absorption spectroscopy. The lifetime associated with phonon-phonon scattering is shown to be remarkably faster in core-shell-shell nanoparticles than in gold nanospheres and nanorods, which is an important contributing factor leading to their higher photothermal efficiencies. In addition, the synthesis of extended core-shell architectures with alternating gold/ silver shells and controllable core and shell dimensions is reported for advanced plasmonic engineering.

5.2 Synthesis

For the nanoparticle syntheses, all chemicals are purchased from Sigma-Aldrich and used without further purification in ultrapure water. For the synthesis of 12 nm gold nanoparticle seeds for the gold core, 30 mL of 290 M gold chloride in water is brought to reflux under vigorous stirring conditions, followed by the addition of 900 L of 34 mM sodium citrate. The colloidal solution undergoes a color change from pale yellow to bright red after 20 min
and is removed from heat and cooled to room temperature. For the growth of the first silver shell, 300 L of the gold seeds is added to 10 mL of ultrapure water. The mixture is kept at room temperature under vigorous stirring with additions of 60 L of 100 mM ascorbic acid, 15 L of 100 mM silver nitrate, and 75 L of 100 mM sodium hydroxide. Ascorbic acid is a mild reducing agent that reduces Ag\(^{+}\) onto the gold core under basic conditions.\(^{29}\) The size of the silver shell can be controlled by selecting the number of ascorbic acid, silver nitrate, and sodium hydroxide sequential additions. The gold-silver core-shell colloidal nanoparticles are centrifuged at 2400 rpm for 20 min and redispersed in 10 mL of ultrapure water. Different sizes of outer gold shells are then grown by adding 100, 200, or 300 L of 29 mM gold chloride, followed by the addition of 25 L of 34 mM sodium citrate and 100 L of 0.03 M hydroquinone under vigorous stirring at room temperature for 60 min. These gold-silver-gold core-shell-shell nanoparticles can be easily thiolated and functionalized for potential biochemical applications. The three steps involved in the synthesis are depicted in Scheme 5.1. All samples are centrifuged and washed with ultrapure water twice before optical measurements to remove excess salts and reactants from the solution. Spherical gold nanoparticles and gold nanorods are used for comparison studies of the photothermal effects of the colloidal core-shell-shell nanoparticles. The gold nanospheres of diameter 54 ± 6 nm are prepared using a seeding growth technique reported previously.\(^{33-36}\) Here, 250 L of the 12 nm seed solution, 100 L of 0.03 M hydroquinone, and 22 L of 34 mM sodium citrate are added consecutively to 10.0 mL of 2.9 mM gold chloride solution. The solution is left at room temperature and under vigorous stirring conditions for 60 min. The gold nanorod sample is purchased from Nanopartz, has a 10 ± 1 nm width, a 35 ± 6 nm length, and is capped with CTAB in aqueous colloidal suspension. All gold nanosphere and gold nanorod studies reported here use these samples with 54 nm diameter nanospheres and 10 nm width, 35 nm length gold nanorods, respectively.
Figure 5.1: Three Steps Involved in the Synthesis of Colloidal Gold-Silver-Gold Core-Shell-Shell Nanoparticles

5.3 Characterization

High-resolution transmission electron microscopy (HR-TEM), extinction spectroscopy, emission spectroscopy, energy dispersive X-ray spectroscopy (EDS), and photothermal measurements are used to characterize the nanoparticles. The average sizes and size distributions are determined using greater than 100 HR-TEM images for each sample. HR-TEM images and extinction spectra of the gold core and gold-silver core-shell nanoparticles are shown in Appendix A. The EDS results, shown in Appendix A, verify that both gold and silver are present in significant quantities in the final gold-silver-gold core-shell-shell nanoparticles. The core-shell-shell nanoparticle concentrations are determined with inductively coupled plasma optical emission spectroscopy (ICP-OES) using both gold and silver atomic emission measurements, where the relative gold to silver concentration is in agreement with the TEM results.
5.4 Photothermal Analysis

The photothermal performance of 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles at a concentration of $3.6 \times 10^{10}$ nanoparticles/mL is studied in solution under NIR light. A 0.8 mL volume of the colloidal sample is placed in a 1.0 mm path-length quartz cuvette and irradiated with a laser beam centered at 800 nm with an average power of 1.7 W, a beam size of $1.2 \pm 0.2$ mm, a pulse width of 75 fs, and a repetition rate of 80 MHz. The temperature change is measured using a K type thermocouple connected to a computer using a data acquisition card. The results are compared to an ultrapure water sample, the colloidal gold nanosphere sample in water, and the colloidal gold nanorod sample in water. The gold nanosphere concentration determined using ICP-OES and Mie theory is $3.1 \times 10^{10}$ and $2.9 \times 10^{10}$ nanoparticles/mL, respectively. The concentration of the gold nanorod samples determined using ICP-OES is $2.7 \times 10^{11}$ nanoparticles/mL. The optical density (OD = 0.26) of the plasmon peak of the colloidal gold nanospheres at 540 nm is equal to the optical density of the plasmon peak of the gold-silver-gold core-shell-shell nanoparticle sample at 800 nm as well as the gold nanorod sample at 800 nm for a quantitative comparison of the photothermal effects of the different nanoparticle samples.

5.5 Transient Absorption Setup

The transient absorption setup consists of an amplified titanium:sapphire laser system, an optical parametric amplifier (OPA), an optical setup, and a fiber optic spectrometer with a charge-coupled device detector. The laser produces 0.7 mJ, 75 fs pulses centered at 800 nm with a repetition rate of 10 kHz. The fundamental beam is split using a beam splitter to separate the pump and probe pulses. The pump pulses are passed through an OPA to generate 400 nm, 5 µJ pump pulses that are reflected by a retroreflector on a computer-controlled translation stage to control the pump-probe temporal delay. The probe beam is focused into a 1 cm fused quartz flow cell containing water to generate femtosecond white light probe pulses that are refocused to a spatial overlap with the pump pulse at the sample.
Figure 5.2: TEM images of gold-silver-gold core-shell-shell nanoparticles with (a) 12-12-12 nm, (b) 12-18-10 nm, (c) 12-24-10 nm, (d) 12-12-5 nm, (e) 12-18-10 nm, and (f) 12-24-10 nm core-shell-shell sizes, respectively.

The colloidal sample is contained in a 3 mm fused quartz cell under constant stirring. Several time-resolved spectral scans are taken for statistical analysis.

5.6 Results And Discussion

The extinction spectra of the gold-silver-gold nanoparticles as a function of the silver and gold shell sizes are first investigated. The different average sizes and distributions of the gold- silver-gold core-shell-shell nanoparticles studied are listed in Appendix A. Figure 5.2a-f shows selected HRTEM images of the gold-silver-gold core-shell-shell nanoparticles with a 12.1±0.9 nm gold core and various silver and gold shell thicknesses. After the addition of the silver shell, the surface plasmon resonance peak blue shifts from 513 nm for the gold core to approximately 420 nm for the gold-silver core- shell nanoparticles. The plasmon extinction peak broadens and increases in intensity as the thickness of the silver shell is increased, as
Figure 5.3: Normalized extinction spectra of different samples of the colloidal gold-silver-gold core-shell-shell nanoparticles obtained by varying the thickness of the gold and silver shells. The size of the gold core is $12.1 \pm 0.9$ nm, and the thickness of the silver shell is (a) $11.7 \pm 1.1$ nm, (b) $18.2 \pm 1.6$ nm, and (c) $23.8 \pm 2.1$ nm, respectively. (d) The position of the plasmon extinction peak wavelength varies linearly with the ratio of the gold shell thickness to the overall particle size.

shown in Appendix A. Figure 5.3 shows the extinction spectra of the colloidal gold-silver-gold core-shell-shell nanoparticles with a $12.1 \pm 0.9$ nm gold core and various silver and gold shell thicknesses. After the formation of the outer gold shell, the plasmon peak red shifts, leading to enhanced extinction in the near-infrared region. Figure 5.3a shows the normalized extinction spectra of gold-silver-gold core-shell-shell nanoparticles with a $12.1 \pm 0.9$ nm gold core, a $11.7 \pm 1.1$ nm silver shell, and an outer gold shell of thickness $5.3 \pm 0.6$, $15.0 \pm 0.9$, $20.4 \pm 1.6$, and $29.8 \pm 2.4$ nm, respectively. For the thinnest gold shell of 5 nm, the plasmon peak is centered near 565 nm and extends to the near-infrared. As the thickness of the outer gold shell is increased, the plasmon peak broadens and red shifts to the near-infrared. At an outer gold shell thickness of $29.8 \pm 2.4$ nm, the plasmon peak is centered near 850 nm.

The effect of varying the thickness of the silver shell is also studied. Figure 5.3b shows the extinction spectra of gold-silver-gold core-shell-shell nanoparticles with a $12.1 \pm 0.9$ nm gold
core, a 18.2 ± 1.6 nm silver shell, and an outer gold shell thickness of 5.1 ± 0.5, 7.5 ± 0.8, and 10.3 ± 1.1 nm, respectively. Similarly to Figure 5.3 a, the gold-shell-shell nanoparticles with the thinnest gold shell of 5 nm has a plasmon peak centered near 565 nm that extends to the nearinfrared. Increasing the thickness of the outer gold shell to 10 nm red shifts the plasmon peak wavelength to approximately 585 nm. Figure 5.3c shows the extinction spectra of the gold-silver-gold core-shell-shell nanoparticles with a 12.1 ± 0.9 nm gold core, a 23.8 ± 2.1 nm silver shell, and an outer gold shell thickness of 5.4 ± 0.7, 7.5 ± 0.9, and 10.4 ± 1.1 nm, respectively. For the thinnest gold shell of 5 nm, the plasmon peak is centered at 610 nm and extends to the near-infrared. As the thickness of the gold shell is increased, the plasmon peak first blue shifts, then an additional peak centered in the NIR rises and increases in intensity. The plasmon-enhanced extinction spectra can be controlled from the UV to the NIR wavelengths by varying the silver and gold shell sizes, making these nanoparticles ideal for many biologically relevant applications such as photothermal therapy and bioimaging. Importantly, as shown in Figure 5.3d, the plasmon extinction peak wavelength depends linearly on the ratio of thickness of the outer gold shell to the overall size of the nanoparticle. The equation of the best fit line is given by a slope of 8.1 × 10^{-4} ± 1 × 10^{-5} nm^{-1} and a y-intercept of −0.35 ± 0.01. This relationship provides a mechanism to control the plasmonic optical properties of the colloidal gold-silver-gold core-shell-shell nanoparticles depending on the desired application. Future studies will compare these experimental results to computation modeling using a Finite-Difference Time-Domain (FDTD) approach to investigate the underlying plasmonic interactions that give rise to these controlled optical properties.

Figure 5.4 displays the results of the photothermal study of different nanoparticle samples. The temperature of the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticle sample with a 12 nm core, a 12 nm silver shell, and a 30 nm outer gold shell as a function of time after irradiation with 800 nm laser light is shown. The results are compared to corresponding measurements on colloidal gold nanorods with a 10 nm width and a 35 nm length
Figure 5.4: Temperature change over time upon irradiation with 1.7 W of 800 nm laser light of (black dots) water, (red dots) 54 nm colloidal gold nanoparticles, (green dots) colloidal gold nanorods, and (blue dots) 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles. The laser beam is unblocked at time 0 s.
in water, 54 nm colloidal gold nanospheres in water, and an ultrapure water control sample. The extinction spectra of these samples are shown in Appendix A. The water and spherical colloidal gold nanoparticle samples do not exhibit any detectable temperature change, to within experimental uncertainty, after laser irradiation. Here, the negligible absorption coefficient of the gold nanospheres at 800 nm corresponds to negligible heating under the laser irradiation. The colloidal core-shell-shell nanoparticles show a temperature change of $5.2 \pm 0.2^\circ C$ at a rate of $1.5^\circ C/min$ due to the conversion of the absorbed NIR light to heat by the plasmonic nanoparticles. The gold nanorods show a temperature change of $3.7 \pm 0.2^\circ C$ at a rate of $0.75^\circ C/min$. It is important to note that previous photothermal studies of gold nanorods of these same dimensions were compared to silica-gold core-shell nanoparticles as well as gold nanoparticles coated with reduced graphene oxide. Our results indicate that gold-silver-gold core-shell-shell nanoparticles have the largest plasmonic photothermal effects in the NIR for potential advances in photothermal cancer therapy.

Femtosecond transient absorption is used to investigate the excited-state dynamics of gold-silver-gold core-shell-shell nanoparticles for comparison to gold nanospheres and gold nanorods. The excited-state dynamics and spectral features of the transient absorption measurements of gold nanoparticles have been extensively studied. Figure 5.5a displays the transient absorption spectra of 54 nm colloidal gold nanospheres at different time delays using 400 nm, 5 J pump pulses. A positive band centered at 480 nm arises from an electronic interband transition. A negative band centered at 535 nm is attributed to the depletion of the plasmon electrons. Another positive band after 578 nm is due to the absorption of thermally excited plasmon electrons, which are attributed to nonequilibrium electron distributions near the Fermi level according to a two-temperature model. Representative transient absorption time profiles measured at 480 and 535 nm are shown in Figure 5.5b. The time-dependent transient absorption profiles are analyzed over the wavelength range of 410 to 550 nm using a global analysis technique shown in Appendix A. Three lifetimes are required to adequately
Figure 5.5: (a) Transient absorption spectra of 54 nm colloidal gold nanospheres at different time delays after excitation with a 400 nm pump pulse. (b) Transient absorption time profiles of 54 nm colloidal gold nanospheres at 480 and 535 nm probe wavelengths with corresponding fits.
describe the relaxation dynamics of the gold nanosphere sample. The time profile at 480 nm is characterized by a single exponential function with a lifetime of $8.0 \pm 0.6$ ps. The time profile corresponding to the plasmon depletion band centered at 535 nm is characterized by two exponential functions with lifetimes of $2.6 \pm 0.3$ and $94.0 \pm 7.3$ ps attributed to electron-phonon scattering and phonon-phonon scattering, respectively. The excited-state dynamics of gold nanorods show similar excited-state relaxation dynamics.

Figure 5.6a and b displays the transient absorption spectra of the colloidal gold nanorods at different pump-probe time delays using 400 and 800 nm, 5 J pump pulses, respectively. Two negative bands near 530 and 750 nm are attributed to the depletion of the transverse and longitudinal plasmon modes, respectively. A positive transient absorption band centered near 625 nm is caused by thermally excited plasmonic electrons.\(^{33,34}\) Representative transient absorption time profiles at 750 nm using 400 and 800 nm pump pulse excitation wavelengths are shown in Figure 5.6c. The longitudinal and transverse bands have similar excited-state relaxation lifetimes, in concurrence with the same electron-phonon and phonon-phonon relaxation pathways of the two orthogonal oscillations.\(^{33}\) The time-dependent transient absorption profiles are analyzed over the wavelength range of 490-770 nm using a global analysis technique shown in Appendix A. Three lifetimes are required to adequately describe the relaxation dynamics of the gold nanorod sample. The electron-phonon and phonon-phonon scattering lifetimes obtained from global analysis using 400 nm pump pulses are $2.8 \pm 0.3$ and $102 \pm 7$ ps, respectively. The electron-phonon and phonon-phonon scattering lifetimes obtained from global analysis using 800 nm excitation pulses are $3.2 \pm 0.4$ and $104 \pm 12$ ps, respectively. An important observation is that the plasmon depletion dynamics corresponding to the electron-phonon and phonon-phonon scattering lifetimes for the gold nanorod sample are shown to be the same when exciting with either 400 or 800 nm, to within experimental uncertainty.

Pump-probe transient absorption spectroscopy is used to investigate the enhanced pho-
Figure 5.6: Transient absorption spectra of colloidal gold nanorods at different time delays using (a) 400 nm and (b) 800 nm excitation pulses. (c) Transient absorption time profiles of colloidal gold nanorods at a probe wavelength of 750 nm using 400 and 800 nm pump pulse excitation wavelengths with corresponding fits.
Figure 5.7: Transient absorption spectra of 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles at different time delays using (a) 400 nm and (b) 800 nm pump pulse excitation wavelengths. (c) Transient absorption time profiles of these nanoparticles measured at 750 nm using 400 and 800 nm pump pulse excitation wavelengths with corresponding fits.
tothermal effect of the colloidal gold-silver-gold core-shell-shell nanoparticles. Figure 5.7 shows the transient absorption spectra of 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles with a 12 nm core, a 12 nm silver shell, and a 30 nm outer gold shell at different time delays using (a) 400 nm and (b) 800 nm, 5 J pump pulses. A positive band centered at 470 nm is observed using 400 nm excitation pulses and is attributed to the electronic interband transition. A broad plasmon depletion band is observed for wavelengths greater than 500 nm, extending to the NIR, using 400 and 800 nm pump pulse excitation wavelengths. The transient absorption time profiles measured at 750 nm using 400 and 800 nm excitation pulses are shown in Figure 5.7c. The time-dependent transient absorption profiles are analyzed over the wavelength range of 450-770 nm using a global analysis technique shown in Appendix A. Three lifetimes are required to adequately describe the relaxation dynamics of the core-shell-shell nanoparticle sample. The electronic interband transition observed after 400 nm pump pulses is characterized by a lifetime of $5.0 \pm 0.3$ ps. The plasmon depletion band is described by the two lifetimes of $3.0 \pm 0.2$ and $23.5 \pm 0.6$ ps using 400 nm excitation pulses and $2.8 \pm 0.2$ and $23.9 \pm 0.5$ ps using 800 nm excitation pulses. These two lifetimes are attributed to electron-phonon scattering and phonon-phonon scattering, respectively. Again, we observe that the electron-phonon and phonon-phonon scattering lifetimes are the same using either 400 or 800 nm excitation pulses, to within experimental uncertainty. However, the decay lifetimes of the plasmon band are dependent on the fluences of the excitation pulses. The power-dependent study of the three samples under study is shown in Appendix A. The lifetime associated with the electron-phonon scattering is identical within the standard deviation for the gold nanoparticles, gold nanorods, and gold-silver-gold core-shell-shell nanoparticles under study. Electron-phonon scattering and phonon-phonon scattering in the umklapp processes are known to limit the thermal conductivity of materials. Importantly, the lifetime of the phonon-phonon scattering is remarkably faster in the case of the core-shell-shell nanoparticles, which is a contributing factor that leads to more
efficient energy relaxation for the photothermal effect. More work is needed to fully characterize the crystal structure of the gold-silver-gold core-shell-shell nanoparticles, especially at the gold-silver interfaces, since some degree of lattice imperfection may exist and may contribute to enhanced photothermal effects.

Figure 5.8: Normalized extinction spectra of 12 nm colloidal gold nanoparticles (black line), 30 nm colloidal gold-silver core-shell nanoparticles (red line), 35 nm colloidal gold-silver-gold core-shell-shell nanoparticles (blue line), 47 nm colloidal gold-silver-gold-silver core-shell-shell-shell nanoparticles (green line), and 53 nm colloidal gold-silver-gold-silver-gold core-shell-shell-shell-shell nanoparticles (purple line).

This reported synthesis technique also allows for the continuation of alternating gold/silver shells for advanced plasmonic engineering. Figure 5.8 shows the normalized extinction spectra of 12 nm colloidal gold nanoparticles, 30 nm colloidal gold-silver core-shell nanoparticles, 35 nm colloidal gold-silver-gold core-shell-shell nanoparticles, 47 nm colloidal gold-silver-gold-silver core-shell-shell-shell nanoparticles, and 53 nm colloidal gold-silver-gold-silver-gold core-shell-shell-shell-shell nanoparticles, respectively. Each successive sample uses the previous sample as its corresponding core, for direct comparison. Here, the plasmon extinction peak wavelength closely correlates with the composition of the outer shell of the nanopar-
article. For example, when the outer shell composition is gold, the plasmon extinction peak wavelength ranges from about 550 to 600 nm. Similarly, when the outer shell is silver, the plasmon extinction peak wavelength ranges from about 400 to 450 nm. In addition, every sequential shell of alternating gold or silver composition broadens the plasmon extinction peak while red shifting it further to the NIR wavelengths. It is also important to point out that the extinction peak wavelength of the extended gold-silver-gold-silver-gold nanoparticles with multiple alternating gold and silver shells does not follow the linear trend reported in Figure 5.3d. Therefore, these extended core-shell architectures with controllable core and shell dimensions of alternating gold and silver compositions provide additional spectral tunability for advanced plasmonic nanoparticle engineering.

5.7 Conclusion

In summary, the development of a new synthesis technique for colloidal gold-silver-gold core-shell-shell nanoparticles is reported. These nanoparticles exhibit plasmon enhancement and controllable NIR absorption that are very advantageous for biologically relevant applications such as photothermal cancer therapy and biosensing. The plasmon extinction peak wavelength of the gold-silver-gold core-shell-shell nanoparticles depends linearly on the ratio of the thickness of the outer gold shell to the overall size of the nanoparticle. A photothermal study shows a significant temperature increase of colloidal 12-12-30 nm gold-silver-gold core-shell-shell nanoparticle sample upon irradiation with NIR laser light, demonstrating a larger photothermal effect compared to gold nanorods and gold nanospheres. Transient absorption measurements show that the phonon-phonon scattering lifetime for colloidal gold-silver-gold core-shell-shell nanoparticles is much faster than the corresponding lifetimes for gold nanospheres and nanorods, which contributes to the higher photothermal efficiencies of the core-shell-shell nanoparticles. In addition, the continuation of alternating gold/silver shells around a gold core is reported, providing the possibility of advanced and controllable plasmonic nanoparticle engineering.
5.8 Modeling

Elucidating the origins of the optical properties of these core-shell-shell nanostructures requires developing predictive simulations for the dynamics and spectral response of the plasmonic modes. The large size of the NPs precludes a quantum description and allows for classical modeling via Maxwell’s Equations. Classically, plasmons can be described as a coherent oscillation of free-electron density. Consider a metal sphere wherein an electric field is applied. Electrons will begin to move to one side of the metal, until the restoring force (uncovered positive ions of the metal) pulls the electrons back to the other side. When the frequency of light is in resonance with the plasmon frequency, electrons oscillate until the energy is lost due to some resistance or damping. Traditionally, for spherical nanospheres, the optical properties can be calculated via Mie theory. This technique does not refer to any physical theory, but is rather a solution to Maxwell’s equations for the scattering of an electromagnetic wave by a dielectric sphere or infinite cylinder. However, this solution is only valid in the case where the size of the scatterer is much smaller than the wavelength of light \((d < \lambda)\) and limited in terms of the shape and size of the scatterer and offers little flexibility.\(^{36}\)

5.9 References


Appendix A: Gold-Silver-Gold Core-Shell-Shell NP Characterization

A.1 Additional TEM Images and Spectroscopy of CSS NPs

The different average sizes and distributions of the synthesized gold-silver-gold core-shell-shell nanoparticles are shown in Table A.1. All gold cores presented here have sizes of 12.1 ± 0.9 nm. Figure A.1 displays representative HR-TEM images of the 12 nm gold core, and the 36 nm, 48 nm, and 60 nm gold-silver core-shell nanoparticles, as well as their corresponding extinction spectra. The spectrum of the 12 nm gold core is fit using Mie Theory at a concentration of 2.9 × 10^{11} nanoparticles/mL. Additional HR-TEM images of the gold-silversgold core-shell-shell nanoparticles are shown in Figure A.2.

TEM images of the multi-layer gold-silver-gold-silver core-shell-shell-shell nanoparticles and gold-silver-gold-silver-gold core-shell-shell-shell-shell nanoparticles are shown in Figure A.3. Figure A.4 shows the energy dispersive X-ray spectroscopy (EDS) results obtained from 12-12-30 nm gold-silver-gold core-shell-shell nanoparticles deposited on a carbon film. The characteristic peaks of gold and silver are observed in the spectrum, which shows that the silver shell is still present after the formation of the gold outer shell.

The emission spectra of the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles, the gold nanorods, and the 54 nm gold nanospheres after 400 nm excitation are shown in Figure A.5. Gold nanospheres exhibit the highest fluorescence, while gold-silver-gold core-shell-shell nanoparticles show the lowest fluorescence. These results demonstrate another contributing factor for the high efficiency of the photothermal effect in core-shell-shell nanoparticles since a lower percentage of energy is lost to fluorescent emission.
Table A.1: Average core and shell sizes of the synthesized gold-silver-gold core-shell-shell nanoparticles.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Size of gold core</th>
<th>Thickness of silver shell</th>
<th>Thickness of gold shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSS1</td>
<td>5.3 ± 0.6 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CSS2</td>
<td>11.7 ± 1.1 nm</td>
<td>15.0 ± 0.9 nm</td>
<td></td>
</tr>
<tr>
<td>CSS3</td>
<td></td>
<td>20.4 ± 1.6 nm</td>
<td></td>
</tr>
<tr>
<td>CSS4</td>
<td></td>
<td>29.8 ± 2.4 nm</td>
<td></td>
</tr>
<tr>
<td>CSS5</td>
<td>12.1 ± 0.9 nm</td>
<td>5.1 ± 0.5 nm</td>
<td></td>
</tr>
<tr>
<td>CSS6</td>
<td>18.2 ± 1.6 nm</td>
<td>7.5 ± 0.8 nm</td>
<td></td>
</tr>
<tr>
<td>CSS7</td>
<td></td>
<td>10.3 ± 1.1 nm</td>
<td></td>
</tr>
<tr>
<td>CSS8</td>
<td></td>
<td>5.4 ± 0.7 nm</td>
<td></td>
</tr>
<tr>
<td>CSS9</td>
<td>23.8 ± 2.1 nm</td>
<td>7.4 ± 0.9 nm</td>
<td></td>
</tr>
<tr>
<td>CSS10</td>
<td></td>
<td>10.4 ± 1.3 nm</td>
<td></td>
</tr>
</tbody>
</table>

A.2 Photothermal Study

Figure A.6 shows a schematic diagram of the experimental setup used for the photothermal study. Figure A.7 displays the extinction spectra of the colloidal gold nanospheres at a concentration of $3.1 \times 10^{10}$ nanoparticles/mL, the colloidal gold nanorods at a concentration of $3.0 \times 10^{11}$ nanoparticles/mL, and the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles at a concentration of $3.6 \times 10^{10}$ nanoparticles/mL (sample CSS4) used in the photothermal study. The extinction of the spherical gold nanoparticles is overlapped with the best fit using Mie theory (dotted black line) at a concentration of $2.8 \times 10^{10}$ nanoparticles/mL.

A.3 Power-Dependent Transient Absorption Study

Figure A.8 shows the transient absorption time profiles of (a) the colloidal gold nanospheres, (b) the colloidal gold nanorods, and (c) the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles using 400 nm pump pulses. The magnitude of the transient absorption signal increases with the increase of the excitation power. The transient absorption time

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Figure A.1: TEM images of (a) 12 nm gold nanoparticles, (b) 36 nm gold-silver core-shell nanoparticles, (c) 48 nm gold-silver core-shell nanoparticles, and (d) 60 nm gold-silver core-shell nanoparticles. Extinction spectra of (e) 12 nm gold nanoparticles and (f) 24 nm, 30 nm, and 36 nm gold-silver core-shell nanoparticles are shown. The extinction spectrum of the 12 nm colloidal gold nanoparticles is fit using Mie theory at a concentration is $2.9 \times 10^{11}$ nanoparticles/mL.

Profiles in Figure A.9 are all normalized for comparison. The time profiles are measured at 550 nm for the gold nanosphere sample and at 750 nm for gold nanorod and core-shell-shell samples. As the excitation pulse energy is increased, the electron-phonon and phonon-phonon scattering lifetimes become slower due to an increase of the heat capacity of the electron gas.$^{1,2}$

The excited-state decay lifetimes shown in Table A.2 are obtained by fitting the time-dependent transient depletion spectra using a bi-exponential function for the three samples at different excitation energies. Figure A.9 shows the decay spectra obtained using the global analysis technique$^3$ where all time profiles over the extended wavelength range of the probe
pulse measurements are fit to sums of exponential functions for (a) the gold nanospheres, (b) the gold nanorods, and (c) the 12-12-30 nm gold-silver-gold core-shell-shell nanoparticles using 400 nm, 5 µJ pump pulses. The lifetimes determined by global analysis for the gold nanospheres are 8.0 ± 0.6 ps, 2.6 ± 0.3 ps, and 94.0 ± 7.3 ps. The time traces obtained from the transient absorption measurements of the gold nanorods are fit using global analysis with two lifetimes of 2.8 ± 0.3 ps and 102 ± 7 ps. The time traces obtained from the transient absorption measurements of the core-shell-shell nanoparticles are fit using global analysis with three lifetimes of 5.0 ± 0.3 ps, 3.0 ± 0.2 ps, and 23.5 ± 0.6 ps. The thermally excited plasmon electrons corresponding to the positive transient absorption band in the gold nanorods are described by the same electron-phonon and phonon-phonon scattering lifetimes.
as the negative plasmon depletion bands, so two lifetimes are sufficient for describing the gold nanorod dynamics. However, the electronic interband transition lifetimes for both the gold nanospheres and the gold-silver-gold core-shell-shell nanoparticles near 470 nm are described by different lifetimes, so three lifetimes are needed when exciting with 400 nm pump pulses. Figure A.10 shows the decay spectra obtained using the global analysis technique for (a) the gold nanorods and (b) the 12-12-30 nm gold-silver-gold core-shell-shell nanoparticles using 800 nm, 5 µJ pulse. The time profiles of the gold nanorod sample can be fit using two
Table A.2: The excited-state decay lifetimes are obtained by fitting the time-dependent transient absorption spectra using a bi-exponential function for the three samples at different excitation energies.

<table>
<thead>
<tr>
<th>Excitation Energy</th>
<th>Gold Nanospheres</th>
<th>Gold Nanorods</th>
<th>Core-Shell-Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 µJ/pulse</td>
<td>2.6 ± 0.3 ps</td>
<td>2.9 ± 0.2 ps</td>
<td>3.0 ± 0.2 ps</td>
</tr>
<tr>
<td></td>
<td>94 ± 7 ps</td>
<td>100 ± 9 ps</td>
<td>23.5 ± 0.5 ps</td>
</tr>
<tr>
<td>7 µJ/pulse</td>
<td>3.2 ± 0.2 ps</td>
<td>3.2 ± 0.2 ps</td>
<td>3.8 ± 0.2 ps</td>
</tr>
<tr>
<td></td>
<td>114 ± 8 ps</td>
<td>116 ± 7 ps</td>
<td>25.0 ± 0.3 ps</td>
</tr>
<tr>
<td>9 µJ/pulse</td>
<td>3.7 ± 0.1 ps</td>
<td>3.5 ± 0.1 ps</td>
<td>4.7 ± 0.3 ps</td>
</tr>
<tr>
<td></td>
<td>121 ± 11 ps</td>
<td>119 ± 9 ps</td>
<td>26.8 ± 0.4 ps</td>
</tr>
</tbody>
</table>

lifetimes of 3.2 ± 0.4 ps and 104 ± 12 ps. The time profiles of the core-shell-shell sample can be fit using two lifetimes of 2.8 ± 0.2 ps and 23.9 ± 0.5 ps. The 800 nm pulse excitation is not energetic enough to excite electronic interband transitions, so the dynamics of both the gold nanorods and the gold-silver-gold core-shell-shell nanoparticles are sufficiently described by only two characteristic lifetimes.

Table A.3 shows the electron-phonon and phonon-phonon scattering lifetimes obtained from the transient absorption time profiles of the gold nanorods and the 12-12-30 nm gold-
Figure A.6: Schematic diagram of the experimental setup used for the photothermal study.

<table>
<thead>
<tr>
<th>Excitation Energy</th>
<th>$\tau_{ps}$(ps)</th>
<th>$\tau_{pp}$(ps)</th>
<th>$\Delta T_{max}$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold Nanospheres</td>
<td>N/A</td>
<td>N/A</td>
<td>0.3 ± 0.3</td>
</tr>
<tr>
<td>Gold Nanorods</td>
<td>3.2 ± 0.4</td>
<td>104 ± 12</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td>Core-Shell-Shell</td>
<td>2.8 ± 0.2</td>
<td>23.9 ± 0.5</td>
<td>5.2 ± 0.2</td>
</tr>
</tbody>
</table>

Table A.3: Electron-phonon and the phonon-phonon scattering lifetimes obtained from the transient absorption time profiles of the gold nanorods and the 12-12-30 nm gold-silver-gold core-shell-shell nanoparticles using 800 nm excitation pulses, along with corresponding temperature changes from the photothermal analysis results.

silver-gold core-shell-shell nanoparticles using 800 nm excitation pulses. The maximum change in temperature obtained from the photothermal measurements using 800 nm laser irradiation is also listed for the three plasmonic nanoparticle samples tested. Corresponding transient absorption with 800 nm excitation pulses is not obtained and no change in temperature is observed, to within experimental uncertainty, for the colloidal gold nanospheres because the absorption coefficient of this sample at 800 nm is negligible. For comparison, the electron-phonon and phonon-phonon scattering lifetimes of the gold nanospheres using 400 nm excitation pulses are 2.6 ± 0.3 ps and 94.0 ± 7.3 ps, respectively. Figures 5 and 6
Figure A.7: Extinction spectra of (red line) the colloidal gold nanospheres, (green line) the colloidal gold nanorods, and (blue line) the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles. The extinction of the spherical gold nanoparticles is overlapped with the best fit using Mie theory (dotted black line).

show that electron-phonon and phonon-phonon scattering lifetimes are the same, to within experimental uncertainty, when using either 400 nm or 800 nm excitation pulses. The gold-silver-gold core-shell-shell nanoparticles show the largest temperature increase as well as the fastest phonon-phonon scattering lifetimes.
Figure A.8: Time-dependent transient absorption spectra of (a) the colloidal gold nanospheres, (b) the colloidal gold nanorods, and (c) the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles using 400 nm pump pulses at different excitation energies. The transient absorption time profiles are measured at 550 nm for the gold nanospheres and at 750 nm for the gold nanorods and gold-silver-gold core-shell-shell nanoparticles. The time profiles are all normalized for comparison.
Figure A.9: Decay spectra obtained using a sum of exponential fits for the time-dependent transient absorption spectra of (a) the colloidal gold nanospheres, (b) the colloidal gold nanorods, and (c) the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles using 400 nm, 5 µJ pump pulses.
Figure A.10: Decay spectra obtained using a sum of exponential fits for the time-dependent transient absorption spectra of (a) the colloidal gold nanorods and (b) the 12-12-30 nm colloidal gold-silver-gold core-shell-shell nanoparticles using 800 nm, 5 µJ pump pulses.
A.4 References


Appendix B: 1D FDTD Code

This appendix contains a one-dimensional FDTD algorithm written in Fortran90, employing a plane wave injection via a TF/SF boundary (Section 2.3.3) as well as first and second order ABC’s (Section 2.3.4). This code was based on the derivations used in Taflove, Allen, and Susan C. Hagness. Computational electrodynamics: the finite-difference time-domain method. Artech house, 2005.¹

```fortran
module common_data
    implicit none

    double complex, parameter :: zi = (0d0, 1d0) ! complex i
    integer, parameter :: nx = 6000
    integer, parameter :: i0 = nx/3, i1 = nx - nx/3
    integer, parameter :: inc_start = nx/4

    double precision :: dt, dtxi
    double precision, parameter :: dx = 1d0
    double precision, parameter :: tmax = 80d0
    integer :: allocstat

    ! constants
    double precision, parameter :: pi = 3.14159265d0
    double precision, parameter :: epsr = 1.335d0**2
    double precision, parameter :: eps0 = 0.07957747154594767d0 * epsr, mu0 = 0.0006691762496807159d0
    double precision :: c = 1d0 / sqrt(eps0 * mu0)
    double precision :: c1, c2

    ! variables

    integer :: it
    double precision :: t

    double precision :: f_w
    double precision, parameter :: wmin = 0d0, wmax = 6d0 / 27.2114d0
    integer, parameter :: nw = 100
    double precision :: wvals(nw)
```

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double precision, parameter :: dw = (wmax - wmin) / dble(nw)

double precision, dimension (:), allocatable :: E_z, H_y
double precision, dimension(:), allocatable :: Ez_inc_1D, Hy_inc_1D ! 1D incident
double precision :: pulse
double complex :: Ew(nw), Ew1(nw), Hw(nw), Hw1(nw)
double complex :: fw
double precision :: fw_target
double precision :: ez_old_left, ez_old_right, hy_old_left, hy_old_right
double precision :: abc_c1, abc_c2
double precision, dimension (:) :: abc_coef (0:2)

!1D abc main grid
double precision, dimension (: :: ez_left11(1:3), ez_left22(1:3),
   ez_right11(nx-1:nx+1), ez_right22(nx-1:nx+1)

! !1D ABC incident
!
double precision, dimension (:) :: abc_coef_1 (0:2)
double precision, dimension (:) :: ez_old_left11 (1:3), ez_old_left22 (1:3)
double precision, dimension (:) :: ez_old_right11 (nx-1:nx+1), ez_old_right22 (nx-1:nx+1)

real(4) :: t1, t2, t3

end module common_data

!####################################
!
!Program Main
!
program main
  use common_data
  implicit none

  integer :: i

  call alloc_arrays
  call init/constants
  call init_1D_abc
  call init_fields
  write(6,*) "dt = ", dt, "au"
it = 0
t = 0d0
t3 = secnds(0.0)
do while (t < tmax)
    call source
    call inc_1D_hy
    call update_Hy
    call hfield_tfsf
    call inc_1D_Ez
    call update_Ez
    call efield_tfsf
    call inc_1d_abc ! 2nd order ABC applied on the 1D auxiliary incident field--no reflections
    call first_order_abc ! 2nd order ABC on the main 1D update equations
    write(1000,*) E_z(:) ! prints slices of electric field in time
    write(4000,*) t, E_z(nx / 4) ! print value of electric field outside of the TF/SF region
    it = it + 1
    t = t + dt
end do

end program main

subroutine alloc_arrays
    use common_data
    implicit none

allocate(E_z(1:nx+1), stat=allocstat)
if (allocstat /= 0) then
    write (6,*) "Failed to allocate E_z, not enough memory?"
    stop
endif
allocate(H_y(1:nx+1), stat= allocstat)
if ( allocstat /= 0) then
  write (6,*) "Failed to allocate H_y, not enough memory?"
  stop
endif

! 1D incident field arrays
allocate(Ez_inc_1D(1:nx+1), stat= allocstat)
if ( allocstat /= 0) then
  write (6,*) "Failed to allocate Ez_inc_1D, not enough memory?"
  stop
endif
allocate(Hy_inc_1D(1:nx), stat= allocstat)
if ( allocstat /= 0) then
  write (6,*) "Failed to allocate Hy_inc_1D, not enough memory?"
  stop
endif
end subroutine alloc_arrays

subroutine init_1D_abc
  use common data
  implicit none

  ez_old_left11 = 0d0
  ez_old_left22 = 0d0
  ez_old_right11 = 0d0
  ez_old_right22 = 0d0
  ez_left11 = 0d0
  ez_left22 = 0d0
  ez_right11 = 0d0
  ez_right22 = 0d0
end subroutine init_1D_abc

subroutine source
  use common_data
  implicit none
  double precision :: frequency
  integer, parameter :: n_cycles = 25
  double precision :: Sc ! Courant Stability Constant
  double precision, parameter :: Md = 1.5d0 ! Delay Multiple
  double precision :: N_points, delay, arg1, arg2 ! # points per wavelength

  !
  ! RICKER WAVELET
! \texttt{frequency = 0.12d0 / pi !dummy molecule freq}

\begin{verbatim}
Sc = c * dt / dx
N_points = 10d0

delay = Md * 1d0 / frequency

arg1 = 1d0 - 2d0 * ((pi * frequency * (t - delay))**2)
arg2 = -(pi * frequency * (t - delay))**2

!DISCRETIZED VERSION
N_points = Sc / frequency / dt

delay = Md * N_points * dt / Sc

arg1 = 1d0 - 2d0 * pi**2 * (Sc * it / N_points - Md)**2
arg2 = - pi**2 * (Sc * it / N_points - Md)**2

pulse = arg1 * exp(arg2)
end subroutine source
\end{verbatim}

!#####################################################

!Incident 1D: x directed z-polarized electric field
!#####################################################

subroutine inc_1d_ez
use common_data
implicit none
integer :: i
double precision :: dtdxeps
double precision :: junk

double precision, parameter :: frequency = 0.12d0!3.09960d0/ 27.2114d0 / 2d0 / pi! silver
double precision, parameter :: center_pulse = 20.d0, width = 3d0

classic pulse = exp(-0.5d0 * ( ( t - center_pulse ) / width )**2 )

junk = 1.5d0 * 1d0 / frequency + 2d0 * pi / frequency !ensures the full pulse
has entered the TF region

dtdxeps = dt / eps0 / dx ! = dt / (eps0 * dx)

\begin{verbatim}
do i = 2, nx
   Ez_inc_1D(i) = Ez_inc_1D(i) + &
      dtdxeps * (Hy_inc_1D(i) - Hy_inc_1D(i-1))
enddo
\end{verbatim}
if (t < junk) then
    Ez_inc_1D (inc_start) = pulse
endif

end subroutine inc_1d_ez

subroutine inc_1d_hy
    use common_data
    implicit none
    integer :: i

    do i = 1, nx
        Hy_inc_1D(i) = Hy_inc_1D(i) + &
        dt / mu0 / dx * (Ez_inc_1D(i+1) - Ez_inc_1D(i))
    endo
end subroutine inc_1d_hy

subroutine efield_tfsf
    use common_data
    implicit none
    E_z(i0) = E_z(i0) - c1 * Hy_inc_1D(i0-1) !left start of the TFSF
    E_z(i1) = E_z(i1) + c1 * Hy_inc_1D(i1) !right end of the TFSF
end subroutine efield_tfsf

subroutine hfield_tfsf
    use common_data
    implicit none

    H_y(i0-1) = H_y(i0-1) - c2 * Ez_inc_1D(i0) !left start of the TFSF
    H_y(i1) = H_y(i1) + c2 * Ez_inc_1D(i1) !right end of the TFSF
end subroutine hfield_tfsf

subroutine init_constants
    use common_data
    implicit none
    double precision :: imp0, temp

    dtxi = c / dx
    dt = 1d0 / sqrt (dtxi ** 2)
    c1 = dt / (eps0) / dx
    c2 = dt / mu0 / dx
    imp0 = sqrt (mu0 / eps0)
!abc coefficients
      temp = sqrt((1/c) * c) ! equals 1 for free space
      abc_c1 = (temp - 1d0) / (temp + 1d0)
      abc_c2 = (temp - 1d0) / (temp + 1d0)

end subroutine init_constants

subroutine init_fields
  use common_data
  implicit none

  E_z = 0d0
  H_y = 0d0
  Ew = 0d0
  Hw = 0d0

  Ew = 0d0
  Ew1 = 0d0

  Hw = 0d0
  Hw1 = 0d0

  Ez_inc_1D = 0d0
  Hy_inc_1D = 0d0

end subroutine init_fields

subroutine update_Ez
  use common_data
  implicit none
  integer :: i

  do i = 2, nx
    E_z(i) = E_z(i) + c1 * (H_y(i) - H_y(i-1))
  enddo

end subroutine update_Ez

subroutine update_Hy
  use common_data
  implicit none
  integer :: i

  do i = 1, nx
    H_y(i) = H_y(i) + c2 * (E_z(i+1) - E_z(i))
  enddo

end subroutine update_Hy
enddo

end subroutine update_Hy

!Incident 1D ABC: 2nd Order Absorbing Boundary
!##########################################################

subroutine first_order_abc
  use common_data
  implicit none
  double precision :: temp1, temp2
  double precision :: eta0
  integer :: i
  double precision :: S_c

  eta0 = sqrt(mu0 / (eps0))
  S_c = c * dt / dx !courant number

  ! 2nd Order ABC
  temp1 = (eta0 / epsr) / eta0
  temp2 = 1d0 / temp1 + 2d0 + temp1

  abc_coef_1(0) = -(1d0 / temp1 - 2d0 + temp1) / temp2
  abc_coef_1(1) = -2d0 * (temp1 - 1d0 / temp1) / temp2
  abc_coef_1(2) = 4d0 * (temp1 + 1d0 / temp1) / temp2

  /* Second order ABC for left side of grid */
  Ez(0) = abc_coef_1(0) * (Ez(3) + ez_left22(1)) + &
       abc_coef_1(1) * (ez_left11(1) + ez_left11(3) - Ez(2) - ez_left22(2)) + &
       abc_coef_1(2) * ez_left11(2) - ez_left22(3)

  do i = 1, 3
    ez_left22(i) = ez_left11(i)
    ez_left11(i) = Ez(i)
  enddo

  !first order ABC
  !Ez(1) = ez_left11(2) + (temp1 - 1d0)/(temp1 + 1d0) * (Ez(2) - Ez(1))
  !ez_left11(2) = Ez(2)

  /* Second order ABC for right side of grid */
  Ez(nx+1) = abc_coef_1(0) * (Ez(nx-1) + ez_right22(nx+1)) + &
       abc_coef_1(1) * (ez_right11(nx+1) + ez_right11(nx-1) - Ez(nx) -
       ez_right22(nx)) + &
       abc_coef_1(2) * ez_right11(nx) - ez_right22(nx-1)
do i = nx-1, nx+1
  ez_right22(i) = ez_right11(i)
  ez_right11(i) = E_z(i)
enddo

!first order ABC
!E_z(nx+1) = ez_right11(nx) + (temp1 - 1d0)/(temp1 + 1d0) * (E_z(nx) - E_z(nx+1))
!ez_right11(nx) = E_z(nx)

end subroutine first_order_abc

! Incident 1D ABC: 2nd Order Absorbing Boundary
!---------------------------------------------------------
subroutine inc_1d_abc
  use common_data
  implicit none
  double precision :: temp1, temp2
  double precision :: c_r, eta0
  integer :: i

  c_r = sqrt(1d0 / (eps0 * mu0))
  eta0 = sqrt(mu0 / (epsr * eps0))

  ! 2nd Order ABC
  temp1 = (eta0 / epsr) / eta0!((dt * c_r) / dx)
  temp2 = 1d0 / temp1 + 2d0 + temp1
  abc_coef(0) = -(1d0 / temp1 - 2d0 + temp1) / temp2
  abc_coef(1) = -2d0 * (temp1 - 1d0 / temp1) / temp2
  abc_coef(2) = 4d0 * (temp1 + 1d0 / temp1) / temp2

  !ABC Left Side
  Ez_inc_1D(1) = abc_coef(0) * (Ez_inc_1D (3) + ez_old_left22(1)) + &
                 abc_coef(1) * (ez_old_left11(1) + ez_old_left11(3) - &
                Ez_inc_1D(2) - ez_old_left22(2)) + &
                 abc_coef(2) * ez_old_left11(2) - ez_old_left22(3)

  !update stored fields
  do i = 1, 3
ez_old_left22(i) = ez_old_left11(i)
ez_old_left11(i) = Ez_inc_1D(i)
end do

!ABC Right Side
Ez_inc_1D(nx+1) = abc_coef(0) * (Ez_inc_1D (nx - 1) + ez_old_right22(nx+1)) + &
abc_coef(1) * (ez_old_right11(nx+1) + ez_old_right11(nx-1) - &
Ez_inc_1D(nx) - ez_old_right22(nx)) + &
abc_coef (2) * ez_old_right11(nx) - ez_old_right22(nx-1)

do i = nx-1, nx+1
  ez_old_right22(i) = ez_old_right11(i)
ez_old_right11(i) = Ez_inc_1D(i)
end do
end subroutine inc_1d_abc

B.1 References

Appendix C: Publication Agreements and Permissions

Title: Enhanced Photothermal Effects and Excited-State Dynamics of Plasmonic Size-Controlled Gold–Silver–Gold Core–Shell–Shell Nanoparticles

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Vita

Holden T. Smith studied chemistry at the University of Louisiana at Monroe, where he received his B.S. in chemistry with a concentration in biochemistry in 2013. He is currently a Ph.D. candidate in both the Haber and Lopata research groups at Louisiana State University in Baton Rouge, LA. His research interests focus on the synthesis, ultrafast characterization and modeling of molecules adsorbed to the surface of plasmonic nanoparticles to study the processes of molecular adsorption and plasmon-molecule interaction for the design and advancement of devices in the fields photovoltaics, photothermal cancer therapy, bioimaging and molecular sensing.