Pseudo-permittivity in simulation of nonlocal effects in optical properties of metallic nanoparticles

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NANYANG
TECHNOLOGICAL
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**PSEUDO-PERMITTIVITY IN SIMULATION OF NONLOCAL
EFFECTS IN OPTICAL PROPERTIES OF METALLIC
NANOPARTICLES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

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EFFECTS IN OPTICAL PROPERTIES OF METALLIC
NANOPARTICLES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
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Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

18-Jun-2018

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Date

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Abstract

Metallic nanoparticles exhibit localized surface plasmonic resonance (LSPR) with peak energy dependent on particle size. Under the frame of classical electrodynamics, this size effect would diminish for nanoparticles whose dimension is much shorter than the wavelength of incident light, and quasistatic approximation can be applied. By the prediction of *ab initio*, however, remarkable LSPR peak shift with size variation can be observed for metallic nanoparticles with radius less than 10 nm, indicating the failure of classical approach at nanometer and sub-nanometric scale.

In this work, we systematically studied three quantum effects (s-band electron spilling out, d-band electron screening and surface atom relaxation) that may cause failure of classical electromagnetic models in contrast simulations. We also proposed a machine learning enhanced semi-classical semi-quantum approach, valence electron density dependent pseudo-permittivity model.

This new model describes ground state valence electron densities by incorporating s-band electron spilling out effect and d-band screening effect into shell region and core region of metallic nanoparticles and successfully predicted different trends in size dependent peak shifts in LSPR for dissimilar metallic nanoparticles. The core-shell description of nanoparticles can also be used to explain quantum tunneling effect, and has good prediction of charge transfer plasmons in dimer systems. For very large plasmonic systems, our model can be accelerated by machine learning algorithms without losing accuracy. The optical spectra got from this model show excellent agreements with *ab initio* calculations, and the extrapolation of LSPR energies to nanometer scale also agrees classical electrodynamics.

The employ of core-shell model and machine learning approach are expected to eliminate the long-existing contradiction of accuracy and efficiency in quantum plasmonics, providing a new ideology in simulation of wave-matter interactions for nanometer and sub-nanometric scaled metallic nanostructures.

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Abbreviations

AETRS	Approximated Enforced Time-Reversal Symmetry
AgNP	Silver Nanoparticle
BDP	Bonding Dipolar Plasmon
BQP	Bonding Quadrupolar Plasmon
CTP	Charge Transfer Plasmon
CEM	Classical Electrodynamic Model
DFT	Density Functional Theory
EELS	Electron Energy Loss Spectroscopy
ELM	Extreme Learning Machine
FDTD	Finite-Difference Time-Domain
GGA	Generalized Gradient Approximation
GNOR	General Nonlocal Optical Response
HCTP	Higher-order Charge Transfer Plasmon
HDM	Hydrodynamic Models
HM	High-order Mode
LDA	Local Density Approximation
LRA	Local Response Approximation
LSPR	Localized Surface Plasmon Resonance
MEEP	MIT Electromagnetic Equation Propagation
MNP	Metallic Nanoparticles
NaNP	Sodium Nanoparticle
PAW	Projector Augmented Wave
PBE	Perdew–Burke–Ernzerhof
QCM	Quantum Corrected Model
SE-CEM	Spilling-out Effected Classical Electrodynamic Model
SSE-CEM	Screening and Spilling-out Effected Classical Electrodynamic Model
TDDFT	Time-Dependent Density Functional Theory
VASP	Vienna Ab Initio Simulation Package

Chapter 1

Introduction

This chapter gives a brief introduction to the whole thesis. Starting with the concept of localized surface plasmon resonance, some problems and existing issues of the area are stated. With the rapid progress in manufacturing of nano-technology and fabrication of nano-plasmonic devices, current theoretical approaches like classical electrodynamics and quantum mechanics are becoming insufficient and inefficient to predict optical properties of the nanometer scaled plasmonic structures. To address these issues, a semi-quantum semi-classical approach has been proposed, together with three possible hypotheses. The objective of this project is to discover a general approach to calculate optical response in quantum plasmonic systems, for both alkaline metals and transition metals, and solve the long contradiction between accuracy and efficiency of numerical simulation in quantum optics. The basic introduction of each chapter in this thesis are listed. At the end, our main findings are stated.

1.1 Hypothesis/Problem Statement

1.1.1 Problem statement

Localized surface plasmon resonance (LSPR) is a process of collective oscillations of valence electrons¹⁻⁴ especially free electrons localized at the surface of lattice of metallic nanoparticles (MNPs)⁵, when external periodical oscillate electromagnetic fields is applied. One interesting phenomenon of LSPR is that its peak energy depends on the size of MNPs^{6,7}. Previously, by prediction of classical electrodynamic model (CEM), obvious size dependent shift in LSPR peak energy could be observed if the radius of the MNPs is larger than 20 nm^{3,8}. For MNPs whose radius is less than 20 nm, when the dimension of MNP is much less than the incident wavelength, however, CEM would evolve into quasistatic approximation. By the theory of quasistatic approximation, when the size of nanoparticle is much smaller than wavelength of surrounding electromagnetic wave, the phase of electromagnetic wave inside the MNP can be approximated taken the same value, and the LSPR energy would be independent of particle size in this case⁹⁻¹¹. This conclusion obtained from CEM, however, is in contradiction with experimental phenomena. Recently, experimental studies have pointed out that both alkaline metallic nanoparticles and noble metallic nanoparticles with diameter less than 20 nm exhibit remarkable size dependent LSPR peak shift^{9,12,13}. For example, silver nanoparticles (AgNPs) would experience blueshift in LSPR peak energy if their diameter is decreased from 20 nm to around 5 nm, as was discovered by Electron Energy Loss Spectroscopy (EELS)¹⁴. On the other hand, sodium nanoparticles (NaNPs) show different size effect compared with AgNP^{3,15}. By the measurements of photoabsorption methods, NaNPs would have redshift with particles' size decrease¹⁶. This kind of size dependent peak shifting phenomenon is promising in playing significant roles to realize programmably tunable nano-plasmonic devices¹⁶⁻¹⁸. These plasmonic devices are at nanometer or sub-nanometric scale, and there is a need for proper theoretical tools that can be used to calculate. Despite the widely usage of CEM, the contradiction of CEM and experimental phenomenon has indicated that CEM would fail for the nano-plasmonic structures whose nonlocal effects contribute a significant part, especially for nanoparticles whose dimension is less than 5 nm^{3,7,15}. To achieve accurate

description on optical properties of these nano-plasmonic structure, we need a powerful tool that can use quantum mechanics to take fully consideration of nonlocal effects. One excellent example is named as time-dependent density functional theory (TDDFT)^{3,7,18-20}. Recently, some theoretical studies on TDDFT simulations have reported optical response of MNPs of nanometer and sub-nanometric scale. By TDDFT, with a decrease of particle size, the LSPR energies of NaNPs and AgNPs show redshift and blueshift, respectively, same as the discoveries from experiments⁸. The limitation of TDDFT, however, lies in its high consumption of computational resources^{13,21}. Due to this reason, the practical application of TDDFT is limited to quite small MNPs, which contain no more than several thousands of valence electrons. For typical nano-plasmonic systems, there're usually hundreds of thousands or even millions of valence electrons, making TDDFT a powerless tool under these conditions. Since both CEM and TDDFT cannot fulfill the requirement to predict nano-plasmonic devices within nanometer and sub-nanometric scale, innovative approaches are highly desirable.

It is generally accepted that the break down of CEM for nanometer and sub-nanometric scaled structures originates from its approximation for local response. Local response approximation is an intuitive treatment of wave-particle interactions in local regions of all the points inside the structures spatially. To stress this issue, a new branch of simulation methods named as semi-quantum semi-classical approach has come into birth²²⁻²⁵. This kind of approaches manage to take account of nonlocal effect to certain degree by doing certain modifications upon the Maxwell's equations. Some popular examples are hydrodynamic models (HDM)²⁴, general nonlocal optical response model (GNOR)²⁴, and quantum tunneling corrected model (QCM)²⁵. As a pioneer in semi-classical model, HDM manages to take nonlocal effect into account to a certain degree, and this novelty was achieved by considering pressure-driven flow of free electrons. Being an updated version of HDM, GNOR has also introduced entropy driven flow of free elections into the frame of CEM, besides the pressure driven ones. Compared with HDM, GNOR has made a big progress²⁶, since GNOR manages to account for a full description of convections of free electrons inside MNPs, but both HDM and GNOR are limited to nonlocal effect of conduction electrons only, and neglected other bonded valence electrons. They cannot tell

the difference between alkaline metals and transition metals, and their quantitative agreements with TDDFT in calculating far field spectra of noble metallic nanoparticles have been regarded as fortuitous issues in following literatures²⁷. Another family of semi-classical models mainly focus on the electron tunneling issues in multi-particles structures, since in quantum mechanics, it has been predicted that electrons are able to tunnel through sub-nanometric vacuum gaps between two metallic surfaces^{28,29}. The QCM method, being an excellent pioneer in tunneling enabled semi-classical model, has exhibited rather successful predictions in plasmonic properties of dimer structures. For more complicated multi-particle plasmonic structures, such as trimers or tetramers, however, QCM may become less fruitful. Nonlocal effect is a natural result of wave-particle duality of electrons, while the tunneling effect is only one phenomenon of this theory. In more complex plasmonic structures, more nonlocal effects other than tunneling also need to be considered.

According to above-mentioned research background, the problems existed in current researches are summarized and listed. Firstly, a semi-quantum semi-classical method is needed to predict optical response of nanometer or sub-nanometric scale MNPs, since both CEM and TDDFT are not satisfactory choices. The new model should achieve both accuracy and efficiency in numerical calculations. Secondly, this semi-quantum semi-classical model should focus on the wave-particle duality of electrons to keep its generality, not account for a single phenomenon due to nonlocal effect.

1.1.2 Hypotheses

From the study of different plasmonic structures and different approaches in plasmonics simulations, three hypotheses have been proposed to explain the failure of CEM.

Firstly, CEM does not consider the spilling out effect of free electrons^{1,30}. In CEM, electrons are treated as classical rigid particles, and the motion of electrons are localized inside the surface boundary of MNPs. In quantum mechanics, however, due to the wave property of electrons, they can spill out of the surface boundary of MNPs, especially under external fields. For nanometer or sub-nanometric sized MNPs, the amount of spilled out

electrons may take up a considerable amount. Therefore, neglect of spilling out effect of valence electrons may be one of the factors that causing failure of CEM.

Secondly, CEM does not accurately describe the d-band electrons' screening effect³¹. Unlike conduction electrons, the d-band valence electrons are localized near their nuclei. External oscillated electromagnetic field will also cause bounded oscillations of d-band valences, and the motion of these d-band electrons would screen the field generated by conduction electrons. Some CEM model such as Drude model failed to consider d-band electrons screening effect, while some others like Drude-Lorentz model make d-band electrons homogeneously distributed inside the whole particle. Both these treatments fail to account for screening effect correctly and may be another cause of failure of CEM.

Finally, CEM does not take relaxation of surface atoms^{2,30}. When larger particles are divided into smaller ones, atoms at surface would undergo a relaxation process to achieve a new optimal structure. In CEM, on the contrary, particles are described as rigid bodies with perfect surfaces. In this way, the electron density in CEM would be different from that of quantum mechanical models, and we think this may be the third issue that lead to the failure of CEM.

1.2 Objectives and Scope

The overall of this study is to discover an innovative approach to calculate optical responses of MNPs of both alkaline metal and noble metal in nanometer and sub-nanometric scale. This approach is aimed to eliminate the existing contradiction of efficiency and accuracy in simulation of quantum plasmonics.

Based on current issues and our hypotheses discussed above, the detailed objectives should be:

- (1) To conduct a series of control simulations to test whether s-band electrons' spilling out effect, d-band electrons' screening effect and surface relaxation of atoms should

- be the key factors that lead to the failure of CEM in quantum plasmonics.
- (2) To design a general approach that could potentially account for all possible nonlocal effect in quantum plasmonics. This innovative approach should remain the form of Maxwell equations, since we need a semi-quantum semi-classical approach. Thus, the design of this approach should pay more attention on wave-particle duality of electrons but not individual nonlocal phenomena.
 - (3) To introduce possible technologies into this semi-quantum semi-classical approach to accelerate the simulation process. The accuracy of the accelerated calculations should be at the same level of the original ones, otherwise the acceleration would be abandoned since almost all numerical simulation methods could improve efficiency at the cost of accuracy.

In summary, the main difficulty this project is to find a great balance between efficiency and accuracy in calculation of nanophotonic structures. On the success of this work, large amount of time and human resource and computational resource can be saved on conducting simulations on optical properties of MNPs.

1.3 Dissertation Overview

This thesis contains seven chapters.

Chapter 1 Introduction

This chapter includes problem statement, hypotheses, research objectives and scopes, dissertation overview and findings and significances.

Chapter 2 Literature Review

This chapter presents a comprehensive literature review, including classical analytical dielectric function models, Lorenz-Mie theory, quasi-static approximation, size effect, nonlocal effect, and quantum tunneling effect. Based on the works discussed in literature review, the research gaps and PhD in context of literature have also been list at the end of

this chapter

Chapter 3 Experimental Methodology

This chapter contains theoretical approaches and simulation tools used in this study, including MIT Electromagnetic Equation Propagation, Vienna Ab Initio Simulation Package and Octopus real-space, real-time TDDFT implementation.

Chapter 4 Size-dependent Energy Shift in Localized Surface Plasmon Resonance of Alkaline Metallic Nanoparticles

This chapter studies the LSPR peak energy shift of alkaline metallic nanoparticles and finds that spilling out effect of s-band valence electrons would be the major cause of LSPR peak shift. A approach named as spilling-out effected classical electrodynamic model (SE-CEM) has been proposed to describe optical response in alkaline metallic nanoparticles, and a machine learning method has been introduced to accelerate the calculations.

Chapter 5 Size-dependent Energy Shift in Localized Surface Plasmon Resonance of Noble Metallic Nanoparticles

This chapter studies the LSPR peak energy shift of noble metallic nanoparticles and finds that spilling out effect of s-band valence electrons together with screening effect of d-band valence electrons determine the optical properties of noble metallic nanoparticles. Based on SE-CEM, an updated version called screening and spilling-out effected classical electrodynamic model (SSE-CEM) has been proposed to address issues emerged in noble metals. The validity of SSE-CEM has been proved by extrapolation of LSPR peak energies to nanoscale particles.

Chapter 6 Optical responses of dimer structures studied by semi-quantum semi-classical model

This chapter investigates the plasmon modes in dimer structures. The quantum tunnelling effect has been studied and incorporated into SE-CEM/SSE-CEM naturally. The dimer structures present five characteristic plasmon modes, and all of them are shown. The enhancement of local electric field of dimers is also studied in detail for each mode.

Chapter 7 Discussion and future work

This chapter summaries the whole thesis and gives some suggestions about the future works.

1.4 Findings and Outcomes

This research leads to three significant outcomes:

(1) The results of control simulations indicate that both spilling out effect of s-band valence electrons and screening effect of d-band valence electrons are critical factors in determination of LSPR phenomena of nanometre or sub-nanometric scaled metallic nanoparticles. The surface relaxation of nuclei, on the contrary, plays an insignificant role in affecting LSPR peak energies. Our findings show that in wave-matter interactions, the behaviour of valence electrons is much more important than that of nuclei and core electrons. In set up new models for semi-quantum semi-classical approaches, the correct description of both s-band and d-band valence electrons should be the major consideration.

(2) In the process of setting up semi-quantum semi-classical models, we propose that the ideology of pseudo-permittivity is an innovative description of nonlocal effect. By introducing pseudo-permittivity, we manage to incorporate nonlocal properties of valence electrons from both s-band and d-band into classical electrodynamics effectively, while remaining the basic forms of Maxwell's equations. Since the calculation of pseudo-permittivity is based on electron density of the MNPs, quantum mechanical regimes can be naturally included, such as spilling out effect or tunnelling effect.

(3) Finally, the current approach of SE-CEM/SSE-CEM can be accelerated by machine learning tools without any cost of accuracy. Due to the valence electron density dependent properties of pseudo-permittivity, we could use machine learning method to predict density of valence electrons to get the value of pseudo-permittivity of MNPs. Our calculation results showed that machine learning predicted electron density agrees with ground state DFT calculations remarkably, making machine learning enhanced SE-CEM/SSE-CEM

powerful tools in theoretical studies of quantum plasmonics.

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Chapter 2

Literature Review

This chapter gives a comprehensive literature review. The concept of dielectric functions and two classical models to analytically illustrate dielectric functions are firstly introduced, with. The size effect of LSPR in both classical electrodynamics and quantum mechanics is also presented. Then, two critical issues leading to failure of classical electrodynamics, the nonlocal effect and quantum tunneling effects, are reviewed, together with some semi-classical models that could solve these issues. Currently, the research gap in quantum plasmonics is that quantum mechanical tools are inefficient in prediction optical properties of typical plasmonic systems containing millions of valence electrons and the available semi-quantum approaches can only be applied to a few particular structures. To address the issue, a new concept of pseudo-permittivity was established in this study. Finally, the PhD in context of literature is also stated.

2.1 Classical analytical dielectric function models

For a certain range of wavelengths, the interaction between metals and electromagnetic waves can be described as a plasma model. Upon the incident electromagnetic wave, free electrons are drifted by the local oscillating electronic fields and leaving ion cores as positive charged materials¹. In plasma model, an increase or decrease of free electron density may alter the optical properties of metals significantly², while the motion of nuclei would not make an obvious different³⁻⁸. Thus, behavior of lattice potential and nuclei properties play insignificant roles and the volume density of free electrons become the dominated factor. The scope of applications of plasma model is quite large in spectrum^{3,9-11}. For noble metals, almost the whole spectrum of visible light is appropriate for plasma model, and this range can be extended to ultraviolet region for metals without d-band electrons

2.1.1 Drude Model

A simple equation can be written down to show the motion of free electrons under external electronic field:

$$m\ddot{\mathbf{x}} + m\gamma\dot{\mathbf{x}} = -e\mathbf{E} \quad (2-1)$$

In Equation 2-1, $\mathbf{E}$ represents the applied external field, and it is a sinusoidal function of time t , for the incident electromagnetic wave with a certain angular frequency ω . Thus, the internal field can be represented as:

$$\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t} \quad (2-2)$$

By substitution Equation 2-2 into Equation 2-1, the partial differential equation can be solved:

$$\mathbf{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)} \mathbf{E}(t) \quad (2-3)$$

Where

$$\mathbf{x}(t) = \mathbf{x}_0 e^{-i\omega t} \quad (2-4)$$

In this situation, the polarization $\mathbf{P}$ and dielectric displacement $\mathbf{D}$ of the material can be explicitly expressed as:

$$\mathbf{P}(t) = -\frac{ne^2}{m(\omega^2 + i\gamma\omega)} \mathbf{E}(t) \quad (2-5)$$

$$\mathbf{D}(t) = \left(\epsilon_0 - \frac{e^2}{m(\omega^2 + i\gamma\omega)} \right) \mathbf{E}(t) \quad (2-6)$$

If a new physical quantity, the plasma frequency, ω_p , is defined as:

$$\omega_p = \frac{n e^2}{\epsilon_0 m} \quad (2-7)$$

then the dielectric displacement $\mathbf{D}$ can be rewritten as

$$\mathbf{D}(t) = \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \right) \epsilon_0 \mathbf{E}(t) \quad (2-8)$$

The form of Equation 2-8 states a linear relationship between $\mathbf{D}$ and $\mathbf{E}$, which is the definition of dielectric constant, or permittivity. As reflected in Equation 2-8, the dielectric constant is function of frequency, therefore, it is also referred as dielectric function or more accurately, frequency dependent permittivity, as is shown below:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_p\omega} \quad (2-9)$$

This representation of frequency dependent permittivity of free electron gas is also referred as Drude model⁶.

Since Drude model only predicts motion of free electrons under external oscillating electric field, it may lose its accuracy at high frequencies when photon energies are able to cause electron interband transitions¹²⁻¹⁵. Thus, for simple metals without d-band electrons, such as sodium and potassium, Drude model can works well for most frequencies below 10eV, and a well-agreement can be found in Figure 2.1^{16,17}.

As is reflected in Equation 2-9, frequency dependent permittivity of metals are complex functions, with their real and imaginary part labelled as ϵ_1 and ϵ_2 , respectively:

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma_p^2} \quad (2-10)$$

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \gamma_p}{\omega (\omega^2 + \gamma_p^2)} \quad (2-11)$$

Figure 2.1 Dielectric function $\varepsilon(\omega)$ of the sodium calculated by Drude model (solid line) fitted to the literature data obtained by experiment ¹⁸ (dots).

For noble metals with d-band electrons, however, a highly polarized background can be created when subjected to external electric field^{12,14,15}, this polarization is referred as $\mathbf{P}_\infty$:

$$\mathbf{E}_\infty = \varepsilon_0(\varepsilon_\infty - 1)\mathbf{E}_\infty \quad (2-12)$$

The physical quantities $\mathbf{E}_\infty$ and ε_∞ in Equation 2-12 represent the applied electric field with infinite high oscillating frequency and the relative dielectric constant under this infinite high frequency. Therefore, by adding the term $\mathbf{E}_\infty$ to Equation 2-5 a modified expression of frequency dependent permittivity of noble metals can be achieved:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma_p\omega} \quad (2-13)$$

For noble metals, such as gold, silver and copper, their ε_∞ are usually less than 10 and

greater than 1.0^{18} .

This modification only considers d-band electron polarizations, cannot provide satisfactory prediction at high frequency regions, as shown in Figure 2.2.

Figure 2.2 Real and imaginary part of dielectric function $\epsilon(\omega)$ of the gold calculated by Drude model (black line) fitted to the literature data obtained by experiment¹⁸ (red line).

From Figure 2.2, it can be seen that Drude model can only be adopted for low frequencies, and the model would fail completely for photons with energy larger than 2eV, because

such energetic photons would stimulate electron interband transitions actively, causing a decrease in polarization and an increase in damping¹⁹⁻²¹.

2.1.2 Lorentzian Model

To improve the behavior of Drude model, a new term can be added to Equation (2-1)^{6,22,23}:

$$m\ddot{x} + m\gamma\dot{x} + m\omega_i^2x = -eE \quad (2-14)$$

In Equation (2-14), the new term $m\omega_i^2x$ describes restoring force with a resonance frequency of ω_0 , which can be used to represent a screen effect of d-band electrons. Equation (2-14) can also be solved explicitly, with solutions having the form of :

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{A_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega} \quad (2-15)$$

The second term in Equation (2-13) is a Lorentzian peak, it is a result the restoring force whose resonant frequency is ω_i . In real materials, the restoring forces have many resonance frequencies, and a series functions with the form of Equation 2-12 should be solved and a series of Lorentz peaks may be added together to achieve an accurate description:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_{i=1}^n \frac{A_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega} \quad (2-16)$$

By comparing Figure 2.2 and Figure 2.3, it can be seen that adding Lorentzian peaks can show better description of both real and imaginary parts of frequency dependent permittivity of noble metals compared with Drude model, and this improved model is also referred as Lorentzian model.

Figure 2.3 Dielectric function $\epsilon(\omega)$ of the gold calculated by Lorentzian model (black line) fitted to the literature data obtained by experiment¹⁸ (red dots).

2.2 Quasi-Static Approximation

Lorentz models can give accurate descriptions of optical properties of bulk parts of metal materials. The big advantage of Lorentz model is using only a few parameters to give out a quite accurate analytical expression of dielectric functions, $\epsilon(\omega)$, making it readily and

efficiently to be incorporated into all kinds of numerical and analytical solvers for Maxwell equations, such as Lorentz-Mie theory^{19,24-28}.

In ancient Roman times, people can observe fantastic behavior of plasmon produced by noble nanoparticles. The mechanism behind this phenomenon, plasmonics, has been fully understood after the establishment of Lorenz-Mie theory in 1908²⁴. In this classical paper, Mie described a method to calculate scattering of electromagnetic fields by small particles with perfect spherical geometry based on Maxwell's equations. Based on his own calculations, Mie managed to explain the color change of gold nanoparticles with various diameters. Thus, the scatterings of electromagnetic waves by nanospheres are usually referred as Mie theory. However, Clebsch and Lorenz were considered to establish similar scattering models earlier than Mie, thus the name of Lorenz-Mie theory is also very popular. Lorenz-Mie theory is a mathematically rigorous solution of Maxwell equations under the condition that electromagnetic plane wave scattered by a perfect sphere with homogeneous frequency dependent permittivity, $\epsilon(\omega)$ ²⁹⁻³¹. If the size of nanoparticles is very small so that the wavelength of electromagnetic wave is several times larger than the diameter of the sphere, the phase difference of wave inside the nano-sphere is then negligible. In this case, the rigorous dynamic approach of Mie theory can be simplified to the quasi-static approximation^{31,32}.

Considering a homogeneous, isotropic metallic sphere positioned in a homogeneous, isotropic medium, as is shown in Figure 2.4. The electrostatic potential Φ can be calculated of the system shown in Figure 2.4. Suppose the permittivity of the metallic nanosphere is ϵ_m and that of surrounding vacuum is ϵ_v , the potential inside and outside the nanosphere can be expressed as:

$$\Phi_{in} = -\frac{3\epsilon_v}{\epsilon_m+2\epsilon_v}E_0r \cos \theta \quad (2-17)$$

$$\Phi_{out} = -E_0r \cos \theta + \frac{\epsilon_m-\epsilon_v}{\epsilon_m+2\epsilon_v}E_0a^3 \frac{\cos \theta}{r^2} \quad (2-18)$$

The potential shown in Equation (2-17) and (2-18) is the overall effect of applied external electric field E_0 and the electric field generated by induced charges inside the metallic sphere, as is shown in Figure 2.5.

Figure 2.4 Illustration of a homogeneous, isotropic metallic nanosphere surrounded by vacuum, with external electric field applied in the surrounding environment.

The potential shown in Equation (2-17) and (2-18) is the overall effect of applied external electric field E_0 and the electric field generated by induced charges inside the metallic sphere, as is shown in Figure 2.5. The induced charges forming a dipole moment p inside the nano-sphere, the polarizability α of the dipole is

$$\alpha = 4\pi r_0^3 \frac{\epsilon_m - \epsilon_v}{\epsilon_m + 2\epsilon_v} \quad (2-19)$$

The quantity r_0 in Equation 2-19 is the radius of the nanosphere. By interpreting Equation (2-19), it can be found that the polarizability α is a function of permittivity of the metal, ϵ_m .

Since frequency dependent permittivity of metals are complex functions of photon energy, which has been discussed in Drude and Lorentz models, the polarizability, α , is also a complex function, and achieve its maximum when $|\epsilon_m + 2\epsilon_v|$ achieve its minimum. From Figure 2.2 and Figure 2.3, it is apparent that the real part of Drude and Lorentz models are

always negative values, while the imaginary part is always positive and have smaller derivatives compared with that of real part.

Figure 2.5 Distribution of positive(blue) and negative (red) charges inside a metallic nanosphere with external electric field E_0 applied.

Thus, by Frohlich condition, the dipole polarizability can achieve maximum when

$$\text{Re}[\varepsilon(\omega)] + 2\varepsilon_m = 0 \quad (2-20)$$

Upon this condition, a resonance between external electric field and oscillation of free electrons can be observed, this resonance mode is referred as dipole surface plasmon.

If the a metallic nanosphere is placed in vacuum and its dielectric property can be described by Drude model in Equation 2-9, its resonant frequency, ω_o , can be approximated as:

$$\omega_o = \omega_p / \sqrt{3} \quad (2-21)$$

This conclusion draw from quasi-static approximation is consider by to reasonably accurate if the diameter of nanosphere is well below 100nm under the illumination of visible light, and become inaccurate for larger nanoparticles due to the failure of quasi-static approximation³³.

Thus, for these metallic nanosphere, their LSPR resonance frequency will remain constant, as is shown in Figure 2.6.

Figure 2.6 Absorption Spectra of NaNP with radius of 8nm, 12 nm, 16 nm and 20 nm, respectively. A constant peak position around 3.4 eV can be observed.

If the radius of NaNP is further decreased below 5nm, the peak position of absorption spectra cannot remain constant anymore³⁴, since the permittivity of such small particles can be inflected by quantum effects significantly.

2.3 Quantum Size Effect from Experiment

According to Mie theory and quasi-static approximation, the LSPR resonance frequency of nano-spheres with diameters between 10nm and 100nm can be well determined as constants³².

The behavior of smaller particles, of nanometric or sub-nanometric scale, will become much more complex, since the classical electrodynamic description of free electrons in such small particles is not appropriate anymore, and the quantum behavior of these electrons must be taken into consideration^{2,13,25,34-51}.

As reported by literatures, measuring the LSPR properties of metals experimentally can be very difficult issues, since the absorption cross-sections scales third power of the particles dimension, and the signals can be significantly damped for such small particles²⁴. Moreover, the detailed geometry information of particles can also hardly be clearly detected due to the limit of optical diffraction^{2,19,52}.

Despite of the hardship mentioned above, some valuable experimental results have been published by researchers.

2.3.1 Electron Energy Loss Spectroscopy of Silver Nanoparticles

The plasmon properties of individual silver particles(AgNP) has been investigated via Electron Energy Loss Spectroscopy (EELS)^{36,53-58}, as is shown in Figure2.7. From the experimental results, a blue shift of 0.5 eV of LSPR resonance frequency can be observed as diameter of the AgNP decrease from 20 nm to 1.7 nm.

The authors came up with an analytical quantum theory of particle permittivity to explain the blue shift, by express the permittivity as the summation of all the possible electron transitions from occupied states to unoccupied states:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \omega_p^2 \sum_i \sum_f \frac{B_{if}}{\omega_i^2 - \omega^2 - i\gamma_i \omega} \quad (2-22)$$

By the analytical theory of particle permittivity, the permittivity under this model should be highly dependent on particles size, as is shown in Figure 2.7 and the LSPR resonance peak should have an obvious blue shift, which agrees well with the experimental EELS spectrum.

Based on the analytical theory of particle permittivity, the permittivity under this model should be highly dependent on particles size, as is shown in Figure 2.8, and the LSPR resonance peak should have an obvious blue shift, which agrees well with the experimental EELS spectrum.

Figure 2.7 EELS spectrum of AgNP of various diameters³⁶. a) Normalized EELS data from particles with size diameter ranging from 11 nm to 1.7 nm in diameter b) Surface plasmon resonance energy (with inset the resonance energy of bulk materials).

Figure 2.8 An analytical form of quantum theory of permittivity of silver particles³⁶. a) The real and imaginary parts of the permittivity of silver nanoparticles with diameters ranging from 2 to 8 nm, calculated by Equation 2-22. b) Absorption spectra of corresponding particles calculated by Mie theory.

2.3.2 Photoabsorption spectra of Sodium Nanoparticles

Although the EELS spectrum of AgNP suggests that decreasing of nanoparticle size would result in a redshift of LSPR, the detection of absorption cross sections of sodium clusters showed that sodium nanoparticles (NaNP) would show a reverse trend^{59,60}, as is shown in Figure 2.9.

Figure 2.9 Photoabsorption cross sections for a) Na_{20} and b) Na_{92} , a significant 0.4 eV red shift of Na_{20} (2.5 eV) can be observed compared with Na_{92} (2.9 eV).

From Figure 2.9, a red shift of around 0.5 of LSPR resonance frequency can be observed, as the size of NaNP decrease, which is quite different from that of AgNP.

2.4 Nonlocal Effect in Nanoparticles

The partial differential equations such as Equation 2-1 and Equation 2-14 used to derive Drude model and Lorentz reveals an ideology of linear response, which assumes that a response caused by external fields is always very short in time evolution and local in spatial coordinates, and the latter is also referred as local response⁴⁶. Although local response is

always intuitively correcting in macroscopic view, it would become incorrect in the regime of quantum mechanics^{61,62}. For metallic materials, free electrons may create responses over a finite region that alter the optical properties of nanoparticles⁶³⁻⁶⁸.

Based on Maxwell equations, the response subjected to external electric field can decoupled and expressed as

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}) = (\omega/c)^2 \int d\mathbf{r}' \varepsilon(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}') \quad (2-23)$$

The term $\varepsilon(\mathbf{r}, \mathbf{r}')$ in Equation 2-23 is the nonlocal response function, where $\mathbf{r}'$ indicate the finite around the position vector $\mathbf{r}$.

Despite the opposite trend of peak shifting of NaNP and AgNP, the origin of these size effects can be attributed to nonlocal effect. From Maxwell's equations, the electric displacement at a certain point is determined by surrounding materials and external electric field⁶⁹.

$$\mathbf{D}(\mathbf{r}, \omega) = \varepsilon_0 \int d\mathbf{r}' \varepsilon(\mathbf{r}, \mathbf{r}', \omega) \mathbf{E}(\mathbf{r}', \omega) \quad (2-24)$$

In Equation (2-23), ε_0 is the vacuum permittivity, and the electric permittivity is a spatial integration of the electric field $\mathbf{E}$, and the term $\varepsilon(\mathbf{r}, \mathbf{r}', \omega)$ is the nonlocal relative permittivity of the surrounding material. For bulk materials or large particles, local response approximation(LRA) can be reasonably adopted and Equation 2-23 can be rewritten as

$$\mathbf{D}(\mathbf{r}, \omega) = \varepsilon_0 \varepsilon(\omega) \mathbf{E}(\mathbf{r}, \omega) \quad (2-25)$$

Upon Equation 2-25, both Drude model and Lorentz model can be achieved directly. Since current observations of size effect cannot be explained by LRA, nonlocal effects have been taken into account to explain LSPR of small nanoparticles.

2.4.1 Hydrodynamic Model (HDM)

Hydrodynamic model is a famous pioneer work studying nonlocal effect^{40,44,62,70-74}. In this model, the origin of nonlocal response is contributed to convective flow of free electrons, and the expression of nonlocal function can be reduced:

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}) = (\omega/c)^2 [\varepsilon_D + (\beta/\omega)^2 \nabla^2] \mathbf{E}(\mathbf{r}') \quad (2-26)$$

In Equation 2-26, the nonlocal response function is divided into two parts. The term ε_D , the local response term, is same as $\varepsilon(\omega)$ in Equation 2-13 and is also referred as Drude dielectric function. The other term, $(\beta/\omega)^2 \nabla^2$, is the nonlocal term in Laplacian type, where β is the character velocity associated with the pressure waves in the electron gas⁴⁴. This nonlocal term has been reported to cause blue shifts in LSPR^{41,42}, as is illustrated by Extinction cross section in Figure 2.10.

Figure 2.10 Extinction spectra in cross-section of cylindrical nanorods: (a) 2nm, (b) 25nm calculated for local response(Blue), and nonlocal response(Red).

2.4.2 General Nonlocal Optical Response (GNOR)

Apart from convective flow, it has also been reported that diffusion of free electron may also contribute to nonlocal response. Based on this assumption, a more generalized model referred as GNOR has been proposed^{40,75}. In GNOR, the Equation 2-26 should be further modified as

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}) = (\omega/c)^2 [\varepsilon_D + \xi^2 \nabla^2] \mathbf{E}(\mathbf{r}') \quad (2-27)$$

The new parameter ξ in Equation 2-27 is the nonlocal parameter, which contains the nonlocal response contributed by both convection and diffusion:

$$\dots \quad (2-28)$$

Figure 2.11 Extinction cross-sections for nanosphere monomers⁴⁰. a) LRA vs NLHD b) LRA vs GNOR. With the size of nanoparticles decrease, blue shifts in LSPR peak energy are predicted by GNOR.

In Equation 2-28, β is the character velocity same as in Equation 2-27, and the parameter D is the diffusion constant for free electrons, which could cause line broadening of LSPR peaks, as is shown in Figure 2.2. When comparing LRA and HDM, more significant blue shifts can be observed for HDM results^{76,77}. For GNOR, when both convection and diffusion are considered, both blue shifting and line broadening of peaks can be achieved.

2.4.3 Recent Progress in Hydrodynamic Models

Based on GNOR, some recent works on hydrodynamic models have been put forward since 2014. In 2014, Researchers found that surface plasmon of noble metals are dependent on the electron density profile at metal surfaces⁷⁸, and they further extend this feature to gap plasmons. In 2016, a methodology has been developed to calculate optical response of two-dimensional plasmonic crystals under the model of hydrodynamic nonlocal approximations⁷⁹. In 2017, generalized hydrodynamic models was used to study plasmons of holey gold films, and extraordinary optical transmissions were reported⁷⁵. The applications of hydrodynamic models have been spread to various nanostructures, but for each case, sophisticated modelling works must be done for the implementation of hydrodynamic model.

2.5 Quantum Tunneling Effect in Nanoparticles

Another kind of quantum treatment of plasmonics lies in gaps between two particles in a dimer system. In classical model, the conductivity in gaps between two particles is zero⁴⁰. The zero-conduction means that there is no charge transfer between particles when external electric field is applied. In quantum mechanics, however, electrons are described as wave functions that the probability of an electron to tunnel through a vacuum gap should be a positive value^{37,80-83}.

To address this quantum tunneling issue, a quantum corrected model (QCM) has been denoted⁸⁰. By QCM, electron tunneling between subnanometric gaps are non-negligible effect, and is can be represented by a reasonable conductivity, as is shown in Figure 2.12. The conductivity of the gap region can be derived by assuming a Drude model to

characterize the optical response of the gap region, with frequency dependent permittivity expressed as

$$\varepsilon(l, \omega) = 1 - \frac{\omega_p^2}{\omega^2 + i \omega \gamma_p(l)} \quad (2-29)$$

In Equation 2-29, $\gamma_p(l)$ is the tunneling damping, a function of gap distance, l . Since the tunneling probability decrease with increase of gap distance, we can expect an increasing damping with gap distance^{80,84}.

The QCM treatment of subnanometric gaps making it possible to calculated optical response of dimer systems in classical FDTD codes with proper quantum treatments^{80,85}. For small dimer systems, the typical plasmon modes such as bonding dipolar plasmon (BDP), bonding quadrupolar plasmon (BQP), charge transfer plasmon (CTP) and higher-order charge transfer plasmon (HCTP) can all be accurately predicted by QCM, with extinction spectra shown in Figure 2.12⁸⁴.

Figure 2.12 Schematics that illustrate the treatment of optical properties at gap regions of dimer structures. a) Classical electrodynamics, b) Quantum mechanical approaches, c) Quantum corrected model (QCM).

2.6 Machine Learning in Semi-Quantum Model

Besides semi-classical models, the rapidly emerging data driven approaches have also been used to study nanophotonic structures. These approaches are based on machine learning algorithms and deep neural networks. In 2008, researchers put forward Neural Network Inverse Modeling to design Microwave Filters⁸⁶, pointing out a new approach that people could utilise to study photonics. In 2017, there were publications dealing with inverse design of nanophotonic structures with help of deep neural networks⁸⁷ and bidirectional neural network models^{88,89}. But these inverse models are all very computationally expensive, and more efficient models based on machine learning methods are more desirable.

2.7 Research Gaps Based on Literature Review

Although quite a few simulation results of Hydrodynamic models show good quantitative agreements with that of TDDFT and some experiments, some researchers regard the success of Hydrodynamics models as a fortuitous issue⁹⁰. Moreover, GNOR can only predict the blue shift of AgNPs caused by decreasing of size, but not the red shift of NaNPs⁴⁰. The quantum tunneling effect emphasized by QCM and other models is practical solution to add quantum treatment for structures with sub-nanometric gaps like dimer systems^{37,80}, but it also cannot explain the LSPR energy shift of different kinds of MNPs. For a general semi-quantum semi-classical approach, nonlocal effects other than tunneling of electrons should also be considered. Thus, for theoretical studies of nanometer and subnanometric scale plasmonic structures, classical models would lose accuracy, quantum mechanical tools would be insufficient in efficiency and semi-quantum semi-classical approaches now available cannot fully account for nonlocal effects occurred in wave-matter interactions in LSPR process. An innovation in theoretical tools that could give consideration to both generality and efficiency is highly desirable.

2.8 PhD in Context of Literature

To solve the research gaps shown in part 2.7, the following listed works have been conducted accordingly during my PhD study:

- (1) Set up control simulations to find out possible effects that cause the failure of classical electron dynamics in quantum plasmonics.

Firstly, absorption spectra of NaNPs have been studied, using different simulation tools. The effect of s-band electrons' spilling out can be shown by comparison of the results of CEM and quantum jellium model, and the effect of surface atoms' relaxation can be reflected by comparing spectra calculated by quantum jellium model and quantum atomistic model.

Secondly, absorption spectra of AgNPs have been studied, using different simulation tools. The effect of d-band electrons' screening out can be shown by comparison of the absorption spectra predicted by CEM, quantum jellium model and quantum atomistic model.

- (2) Find proper relationships between pseudo-permittivity and density of valence electrons.

The introduction of pseudo-permittivity of MNPs into Maxwell's equations needs information of ground state information of valence electron densities. However, the bulky information of electron density cannot be used as parameters of optical properties by MNPs directly, and a mathematic treatment needs to be done before we could calculate the value of pseudo-permittivity. We've designed a core-shell model to store the information of s-band and d-band valence electrons in shell and core regions of a MNP, respectively. The following calculations of far field spectra of MNPs have proved the success of this treatment.

- (3) Exploring optical properties of MNP dimers

To test the generality of our semi-quantum semi-classical approach, the near field and for field spectra of a series of sodium nanowires has been calculated. We demonstrated that there're five characteristic plasmon modes in dimer structures with various gap separations and find the enhanced of localized electric field in that gap of dimers is as high as the prediction of classical electrodynamics. The extreme compress in the value of gap separation is not a necessary term on achieve extreme field enhancement, but gap separation dependent LSPR modes of dimers could provide tuneable properties in nano-devices.

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Chapter 3

Simulation Methodology

This chapter gives comprehensive introductions to all simulation tools and theoretical approaches that have been used in this study. Four different simulation packages, MIT Electromagnetic Equation Propagation (Meep), Vienna Ab Initio Simulation Package (VASP), and Octopus real-space, real-time TDDFT implementation (Octopus) are presented, with the essential physical background that has been implanted into these packages also discussed.

3.1 MIT Electromagnetic Equation Propagation (Meep)

The MIT Electromagnetic Equation Propagation (Meep) is an open source simulation software that implements the finite-difference time-domain (FDTD) methods for solving Maxwell's equations¹⁻⁵. FDTD is a widely-used time-domain electromagnetic simulation method⁶⁻¹⁰. It manages to grab Maxwell's equation over finite time periods within finite special regions. This method can calculate electromagnetic quantities in classical electrodynamic framework efferently. In electrodynamic numerical experiment, transmission and reflection spectra, resonant modes and frequency and field patterns are frequently studied quantities by FDTD.

In this project, Meep is used to calculate the absorption spectra of MNPs in classical framework.

3.1.1 Maxwell's Equations

The Maxwell's equations are the foundations of classical electrodynamics, classical optics, and electric circuits¹¹⁻¹³. The solutions of the Maxwell's equations can describe the between incident light and any materials. In linear, isotropic and nonmagnetic medium, Maxwell's electric flux dependent equations are given by

$$\nabla \cdot \mathbf{E} = \rho / \varepsilon_0 \quad (3-1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (3-2)$$

$$\nabla \times \mathbf{E} = -\partial \mathbf{B} / \partial t \quad (3-3)$$

$$\nabla \times \mathbf{B} = \mu_0 (\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}) \quad (3-4)$$

Maxwell's equations deal with two electromagnetic field quantities, where $\mathbf{E}$ is the electric field, and $\mathbf{B}$ is the magnetic induction. The nature of these field quantities relates to charge density ρ and current density $\mathbf{J}$. There are two constants involved in these equations, the vacuum electric permittivity, ε_0 , and the vacuum magnetic permeability, μ_0 .

For the convenience of application, another two quantities have been introduced, the dielectric displacement $\mathbf{D}$ and the magnetic field $\mathbf{H}$, which are defined as

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (3-5)$$

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \quad (3-6)$$

The new quantity $\mathbf{D}$ and $\mathbf{H}$ are connected with the two original field quantities $\mathbf{E}$ and $\mathbf{B}$ by polarization $\mathbf{P}$ and magnetization $\mathbf{M}$. By substitute Equation 3-5 and 3-6 into Maxwell's equations, a modified set of Maxwell equations can be achieved.

$$\nabla \cdot \mathbf{D} = \rho_{\text{ext}} \quad (3-7)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (3-8)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (3-9)$$

$$\nabla \times \mathbf{H} = \mathbf{J}_{\text{ext}} + \frac{\partial \mathbf{D}}{\partial t} \quad (3-10)$$

For most metallic plasmonic materials, their electromagnetic properties are considered linear media with no obvious magnetic permeability. If the material is assumed to be isotropic, then there're linear relationship between $\mathbf{D}$ and $\mathbf{E}$, $\mathbf{B}$ and $\mathbf{H}$, respectively.

$$\mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} \quad (3-11)$$

$$\mathbf{H} = \frac{1}{\mu_0 \mu} \mathbf{B} \quad (3-12)$$

Since only nonmagnetic properties are considered, the electric field $\mathbf{E}$ can be decoupled from by applying curl operator to both sides of Equation 3-9. For the left side

$$\nabla \times (\nabla \times \mathbf{E}) = \nabla \times \nabla \times \mathbf{E} \quad (3-13)$$

For the right side, curl operator is also applied with equation 3-10 substituted into:

$$\nabla \times \left(-\frac{\partial \mathbf{B}}{\partial t} \right) = -\frac{\partial}{\partial t} (\nabla \times \mu_0 \mathbf{H}) = -\frac{\partial}{\partial t} \left(\mu_0 \mathbf{J} + \mu_0 \frac{\partial \mathbf{D}}{\partial t} \right) = \left(\frac{\omega}{c} \right)^2 \varepsilon \mathbf{E}(\mathbf{r}) + i\omega \mu_0 \mathbf{J}(\mathbf{r}) \quad (3-14)$$

By equalize Equation 3-13 and 3-14, and neglect current density $\mathbf{J}(\mathbf{r})$, a partial differential equation about electric field, $\mathbf{E}$, can be finally obtained:

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}) = \left(\frac{\omega}{c} \right)^2 \varepsilon \mathbf{E}(\mathbf{r}) \quad (3-15)$$

In Equation 3-14 and 3-15, ω is the angular frequency of the incident electromagnetic wave and c is the speed of light in vacuum.

3.1.2 Introduction of Finite-Difference Time-Domain Method

The time and spatial evaluation of electric field can be evaluated by solving Maxwell's equations. Theoretical solutions of Maxwell's equations can only be obtained for limited kinds of systems, such as Mie theory^{10,14}, which is only capable to deal with spherical geometries in three-dimensional space and circles in two-dimensional space (planar projection of infinite long cylinders in three-dimensional space). If more complex geometries are to be investigated, numerical approaches should be employed instead of analytical ones. Among variety of numerical analysis tools for computational electrodynamics, Finite-Difference Time-Domain Method (FDTD) is accepted as one of the most general and robust algorithms^{6,15}.

Proposed by Kane Yee in 1966 as a simply programmed algorithm, FDTD can be realized by replacing all derivatives in Maxwell's equations by ratio of corresponding finite-difference terms¹⁵⁻¹⁷. Space and time are then segmented into small rectangular grids with finite dimensions by FDTD, resulting in three major advantages. Firstly, the universality and generality of Maxwell's equations has been inherited by FDTD, making FDTD applicable to all kinds of electrodynamic problems. Secondly, structures in FDTD simulation regions are described as accumulation of cuboids in space, a methodology that can greatly increase efficiency in modelling process. Finally, the conciseness of FDTD algorithm guarantees a robust program, with all source of errors well known and well handled. The disadvantage of FDTD comes from its computational efficiency. The generality of FDTD make it less efficient than some other electrodynamic simulation tools, such as discrete dipole approximation (DDA)¹⁸ or coupled dipole approximation (CDA)¹⁹. This shortcoming, however, is becoming negligible with the fast development of supercomputing technology.

3.1.3 Technological details of FDTD

The special cuboids in FDTD simulation regions are referred Yee cells, in memory of Kane Yee, with a simple illustration in Figure 3.1.

Figure3.1 A simulation region containing a nano-sphere with Yee cells represented by dashed lines, with unit cuboids inside Yee cells.

These cubic Yee cells are represented as three dimensional vectors in FDTD, corresponding to their Cartesian coordinates in space, with each element a multiple of finite spatial difference in one direction

$$(i, j, k) = (i\Delta x, j\Delta y, k\Delta z) \quad (3-16)$$

Propagation time in FDTD is also represented as multiples of the finite time difference,

$$T = n\Delta t \quad (3-17)$$

Thus, for any other physical quantities, they can be generally described as functions of the finite spatial and time difference, in the form of

$$F(i\Delta x, j\Delta y, k\Delta z, n\Delta t) = F_{i,j,k}^n \quad (3-18)$$

The first partial difference of any physical quantities can then be derived from Equation 3-18,

$$\frac{\partial F_{i,j,k}^n}{\partial x} = \frac{F_{i+1/2,j,k}^n - F_{i-1/2,j,k}^n}{\Delta x} + O(\Delta x^2) \quad (3-19)$$

$$\frac{\partial F_{i,j,k}^n}{\partial y} = \frac{F_{i+1/2,j,k}^n - F_{i-1/2,j,k}^n}{\Delta y} + O(\Delta x^2) \quad (3-20)$$

$$\frac{\partial F_{i,j,k}^n}{\partial z} = \frac{F_{i+1/2,j,k}^n - F_{i-1/2,j,k}^n}{\Delta z} + O(\Delta x^2) \quad (3-21)$$

$$\frac{\partial F_{i,j,k}^n}{\partial t} = \frac{F_{i,j,k}^{n+1/2} - F_{i,j,k}^{n-1/2}}{\Delta t} + O(\Delta t^2) \quad (3-22)$$

These four differential equations are in the form of Taylor series expansion with second order accuracy in space or time incremental of finite difference. The accuracy of FDTD can be controlled by manipulating size of Yee cells.

3.1.4 Computational Details in Meep

Developed from 1960s in last century, FDTD now can be realized by a variety of commercial softwares and free softwares. The open source FDTD simulation software package developed at MIT, Meep, has been used in this project. Since source code of Meep has been released by MIT, it is convenient to locate source of errors and to make proper modifications without arousing copyright issues^{1,3}.

Firstly, it comes with boundary conditions. For numerical experiments in computers, only a finite simulation region can be built. Therefore, simulations would terminate at certain boundaries, and these boundaries must be designed properly to simulate physical realities. Three kinds of boundary conditions are available: Bloch-periodic boundary condition²⁰, metallic wall boundary condition and perfectly matched layer boundary condition.

In normal periodic boundary conditions along x direction, if the periodic length is L, then the field quantities should satisfy

$$\mathbf{F}(x + L) = \mathbf{F}(x) \quad (3-23)$$

The Bloch-periodic boundary condition, on the other hands, the periodicity of field quantities is expressed as

$$\mathbf{F}(x + L) = e^{iK*L} \mathbf{F}(x) \quad (3-24)$$

The K value in Equation 3-24 is the Bloch wave-vector. The adoption of Bloch periodicity could convert the periodic real space into a finite k -space via Fourier transformations, an excellent tool to solve problems involving plasmonic arrays.

For non-periodical systems, the boundary of the simulation region can be set as a metallic wall, or perfect matched wall. This kind of boundary behaves like perfect metal sheet with zero skin depth that can perfect reflect all the incident waves, which can be achieved by simply force the field to be zero at all boundaries.

If open boundary conditions are preferred rather than closed ones, the boundaries should be able to absorb all incident waves instead of reflection. This kind of boundary is known as perfectly matched layer, or PML for abbreviation. PML can be achieved by adding absorbing material layers outside the boundary of simulation region. The special absorbing material is actually a fictitious material created by computers, with a high imaginary value in permittivity to absorb incident waves. The thickness of PML layer can be increased to realize better absorption effectiveness.

The unity system is another special feature of Meep. The International System of Units (SI) is the most common adopted unit system in electrodynamics. The Maxwell's equations, however, have three worrisome tedious constants, vacuum permittivity, ϵ_0 , vacuum permeability, μ_0 and speed of light in vacuum, c , with their approximate values shown below.

$$\epsilon_0 = 8.854187817... \times 10^{-12} \text{F} \cdot \text{m} - 1 \quad (3-25)$$

$$\mu_0 = 1.2566370614... \times 10^{-6} \text{H} / \text{m} \quad (3-26)$$

$$c = 299792458... \text{m/s} \quad (3-27)$$

FDTD algorithm solving Maxwell's equation iteratively, while approximations are made in each step, errors will grow up quickly in the overall process. If more accurate values are employed, the load of floating-point calculation would also increase. Meep, however, introduces a dimensionless system of units, in which all these three constants are of unity value, 1. The unit of distance in Meep is also a dimensionless value, a , a unit that can be

whatever lengthscale favored by users. Since the speed of light, c , is also of unity value, the unit of time, t , in Meep should also be the value a :

$$t = a/c = a \quad (3-28)$$

Since both time and space are divided into finite grids in FDTD, Meep uses the Courant factor³, S , to relates time step Δt and spatial discretization Δx :

$$S = \frac{c * \Delta t}{\Delta x} = \frac{\Delta t}{\Delta x} \quad (3-29)$$

In this project, the characteristic length scale, a , has been set to be 1000 nm. The simulation region is a cubic space whose edge-length equals to 20nm. Since the open boundary conditions were simulated, 10-nm-thick PML layers have been attached to all faces of the simulation region. The resolution in simulation was 5000 pixels per a , or 2.0 Å in each direction. The Courant factor, S , is set to be 0.5 for numerical stability.

The incident electromagnetic wave is a Gaussian-pulse source, and the spectra with of the source range from 1eV to 7eV.

The material dispersion in optical media of Meep is also treated by frequency dependent permittivity, $\varepsilon(\omega)$. For the convenience of computation, the Drude-Lorentz model was adopted, in the form of

$$\varepsilon(\omega) = \sum_{i=0}^N \frac{f_i * \omega_p^2}{\omega_i^2 - \omega^2 - i\gamma_i \omega} \quad (3-30)$$

There're totally $N+1$ terms in Equation 3-30, and starting from $i = 0$. Thus, the 0th term in Equation 3-30 is a Drude term, while all the other N terms are Lorentzian terms. For alkaline metals, like Na and K, there is only one s-band electron is treated valence electron in each atom, therefore only one Drude term should be enough to describe optical dispersions of alkaline metals. For noble metals, like Ag and Au, However, 11 valence electrons are to be considered in each atom, with one s-band valence electron and ten d-band valence electrons. The behavior of d-band valence electrons is much more complex

than s-band free electrons, and several Lorentzian terms must be added. Parameters of Silver in Drude-Lorentz model used in this project are listed in Table 3.1.

Table 3.1 Fitting Parameters of Silver in Drude-Lorentz model used in this study

N	$\omega_i(eV)$	$\gamma_i(eV)$	f_i
0 (Drude term)	0.000	0.048	0.990
1	0.816	3.886	0.065
2	4.481	0.452	0.124
3	8.185	0.065	0.011
4	9.083	0.916	0.840
5	20.29	2.419	5.646

3.2 Vienna Ab Initio Simulation Package (VASP)

The Vienna Ab Initio Simulation Package (VASP)²¹⁻²³ [ENREF 11 21](#) is a commercialized program for *ab initio* calculations at atomic scale. VASP manages to solve many-body Schrödinger equations numerically. There're several approached that can be realized by VASP, like density functional theory (DFT)²¹, Hartree-Fock (HF) approximation^{24,25}, Green's functions methods^{26,27} [ENREF 11 26](#), many-body perturbation theory²⁸, and Hybrid functionals^{29,30}. The central physical quantities in VASP are electron density and local potential and both are expressed in plane wave basis sets, making VASP a powerful tool dealing with periodical crystalline structures.

In this project, VASP is used to calculate electronic structures and optimized atomic structures of MNPs.

3.2.1 Time Independent Schrödinger Equation

The Schrödinger equation is generally accepted as the fundamental equation of quantum physics. It is a partial differential equation that quantifies how wave functions evolve in universe with time included:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t) \quad (3-31)$$

For static systems, or ground state properties, the Schrödinger equation can be separated into temporal part and spatial part by separation of variables to extract the time independent Schrödinger equation:

$$E\Psi(\mathbf{r}) = \hat{H}\Psi(\mathbf{r}) \quad (3-32)$$

The symbol $\hat{H}$ in Equation 3-31 and 3-32 is the Hamiltonian operator, E is the ground-state energy, and $\Psi(\mathbf{r}, t)$ is the eigenstate wave function. If more than one electrons and several nuclei are involved, the interaction among these particles would be more complicated, and the time independent Schrödinger equation can be rewritten into a longer form:

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<1}^N U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E\psi \quad (3-33)$$

There're two constants in Equation 3-33, m is the electron mass and $\hbar$ is the Planck constant. The Hamiltonian operator has been replaced by three terms in bracket at the left side of Equation 3-33. The first term, $-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2$, represents kinetic energy of electrons. The second term, $\sum_{i=1}^N V(\mathbf{r}_i)$, is the potential energy of interaction between electrons and nuclei. The last term, $\sum_{i=1}^N \sum_{j<1}^N U(\mathbf{r}_i, \mathbf{r}_j)$, is the potential energy of interactions between different electrons. In time independent Schrödinger, the wave function $\Psi(\mathbf{r}, t)$ can be rewritten into a position dependent function $\psi(\mathbf{r})$. If multi-electron system is under evaluation, such as in Equation 3-33, the wave function, ψ is the function of spatial coordinates of all the electrons involved. Therefore, the wave function ψ should be expressed as

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2 \dots \dots, \mathbf{r}_N) \quad (3-34)$$

These quantum treatment of electrons, however, would increase the dimension of the wave function, ψ , dramatically, since each atom may contain several electrons and each electron has three dimensions in Cartesian coordinates. A small molecule with less than 10 atoms may need more than 1000 dimensions to describe its wave function. This is why it has been very impractical to solve Schrödinger equation for large systems, and a functional with less

dimensions has been highly desirable to describe physical systems in quantum mechanical regimes.

3.2.2 Density Functional Theory

The wave function, ψ , describes quantum states of any systems by telling the probability that whether electrons would appear at certain coordinate, $\mathbf{r}$. This quantity, mathematically, can be related to density of electrons at certain coordinate, $n(\mathbf{r})$, by

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \quad (3-35)$$

where $\psi_i^*(\mathbf{r})$ in Equation 3-35 is the complex conjugate of $\psi_i(\mathbf{r})$. More rigorous mapping relationships between electron density, $n(\mathbf{r})$, and wave function, $\psi(\mathbf{r}_1, \mathbf{r}_2 \dots \dots, \mathbf{r}_N)$, have establish by Khon and Sham in 1960s by Kohn-Sham theorems, as shown below.

Kohn-Sham theorem 1: The external potential is a unique functional of the electron density.

Kohn-Sham theorem 2: The functional that delivers the ground state energy of the system, gives the lowest energy if and only if the input density is the true ground state density.

These two theorems are fundamental theorems of density functional theory. The first Kohn-Sham theorem says the ground states density functional uniquely determines ground state wave function of the system, so does all the other information contained by ground state wave function, such as ground-state energy. The second Kohn-Sham theorem tells that if the functional is already known, then electron density, $n(\mathbf{r})$, can be achieved when the ground state energy is minimized.

Unfortunately, the exact form of energy functional is still unknown, can it can be represented as:

$$E[\psi] = E_{exact}[\psi] + E_{XC}[\psi] \quad (3-36)$$

Equation 3-36, the energy functional can be divided into two parts, $E_{exact}[\psi]$ is the summary of terms with analytical expressions, and $E_{XC}[\psi]$ is the summary of terms that cannot be found in $E_{exact}[\psi]$. Since the exact form of $E_{XC}[\psi]$ is still not known, some approximation must be taken to find out approximated solutions of Kohn-Sham equations.

That is to define a trial electron density, $n(\mathbf{r})$, initially. With the initial guessing of $n(\mathbf{r})$, the wave function, $\psi_i(\mathbf{r})$, can be calculated via Kohn-Sham equations. Then a new set of electron density can be derived from the solution of Kohn-Sham equations, which is denoted as $n_{KS}(\mathbf{r})$. Thus, we can compare the value of the initial trial value of $n(\mathbf{r})$ and the Kohn-Sham equations derived value, $n_{KS}(\mathbf{r})$. If these two set of electron densities are the same, then $n(\mathbf{r})$ should be the correct solution. Otherwise, the value of $n(\mathbf{r})$ should be properly modified to calculate the $n_{KS}(\mathbf{r})$ one more time. These steps should be repeated until the difference between $n(\mathbf{r})$ and $n_{KS}(\mathbf{r})$ can be decreased to be smaller than a predetermined value, and this value is often referred as cutoff value. After certain loops of iterations, if the difference can be decreased to less than the cutoff, then the calculation achieves a convergence, otherwise the calculation diverges. Since the form of Kohn-Sham equations are fixed, whether a calculation can achieve convergence or not depends on how to make an initial guess and how to modify the guess if the criteria of convergence is not met.

One fundamental method is the local density approximation (LDA)³¹. In this method, the initial trial is that the electron density is constant for all points, which can be represented as:

$$n(\mathbf{r}) \equiv \text{Constant} \quad (3-37)$$

Although this assumption cannot reflect the physical reality for most cases, it does provide a practical approach that people can solve the Kohn-Sham equations somehow. Based on this assumption, the term of $E_{XC}[\psi]$ can be calculated out approximately. Since this approximation only evolves the local density of each point, people call this functional local density approximation.

Another functional that can be used to solve Kohn-Sham equations effectively is the generalized gradient approximation (GGA)²¹⁻²³. In general, the trial of $n(\mathbf{r})$ from GGA contains more information than that of LDA, since gradient of the functionals would always contain some nonlocal information. Thus, in practical simulations, GGA is much more widely used than LDA. With two sub-families, Perdew–Wang (PW91) functional

and Perdew–Burke–Ernzerhof (PBE) functional being most famous ones^{32,33}. In this study, the PBE functional is adapted as the default functional in DFT calculations.

3.2.3 Projector Augmented Wave (PAW) Method

The working process of DFT is solving Kohn-Sham equations iteratively. To do this work on computers, proper mathematical tools are needed to represent the Kohn-Sham wave functions in binary files. Generally, there are two approaches. One way is to use a three-dimensional matrix to store the value of wave functions in real space in Cartesian coordinate. Another way is to use a series of special functions to represent wave functions, and the most common used special functions are plane wave functions. Since wave functions equals to linear combinations of plane wave functions, these plane wave functions are also referred as plane-wave basis set:

$$\psi = \sum \alpha_i \phi_i \quad (3-38)$$

Thus, Equation 3-33 can be rewritten as

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(\mathbf{r}_i) + U(\mathbf{r}_i, \mathbf{r}_j)\right] \phi_i = \epsilon_i \phi_i \quad (3-39)$$

In Equation 3-38, ψ is the Kohn-Sham wave function, ϕ_i are plane wave functions, and ϵ_i is the eigenvalues of each state.

The computational requirement of a basis set is its efficiency. A basis set with a higher efficiency value manages to use fewer numbers of plane wave functions to describe the targeting wave function without losing accuracy. In this way, plane wave basis set performs well for systems with smooth potential evaluations. For regions close to nuclei, where spatial differentials of potentials have very high values, many more plane waves are needed to describe the local wave functions accurately, which in turn lowers the efficiency. The local wave functions near nuclei come from nuclei and core electrons, and these particles hardly contribute to the chemical properties. Therefore, the concept of ‘pseudopotentials’ can be used to stress this issue.

Pseudopotentials treat every nuclear and its surrounding core electrons as a frozen unity. Therefore, local potentials near nuclei can be described by smooth potentials that produce same effect on valence electrons, and Kohn-Sham equations are set up for valence electron only. A very popular method adopting this ideology to solve Kohn-Sham equations is projector augmented wave (PAW) method proposed by Bloch²⁰.

In PAW method, wavefunctions are categorized as inner partial wave expansion functions and outer envelope functions, representing the spherical regions around nuclei and interstitial regions between atoms, respectively. Wavefunctions of these two kinds of regions are represented differently and are smoothly matched at surface boundaries. The spherical regions surrounding nuclei are called augmentation spheres. The basic requirement of PAW methods is that the pseudo-wave functions should be numerically same as the real wave functions outside augmentation spheres, and the pseudo-wave functions inside augmentation spheres should be same for nuclei belong to same elements.

3.2.4 Computational Details in VASP

VASP is a commercial *ab initio* simulation package coded mainly with Fortran. In this work, VASP 5.4.1 was compiled using Inter Fortran compiler on Linux distribution of Red Hat Linux Server (RHEL) release 6.3, the operation of VASP also needs Intel MKL libraries and Intel MPI libraries installed.

Several import parameters used in the input file of VASP are also presented here.

Pseudopotential

The PAW method was used to describe the electron-ion interaction and the exchange correlation between electrons was described by the GGA in the PBE form. The cut-off energy for plane waves is 500 eV for all the simulations, which should be enough for sodium and silver clusters.

Supercell and K-points

Since atomic clusters are all non-periodic structures, while VASP could only do simulations in periodic boundary conditions, a supercell with dimension of ($25 \text{ \AA} \times 25 \text{ \AA} \times 25 \text{ \AA}$) was set up to box each cluster. In this way, the separation of a cluster in each supercell would always be more than $15 \text{ \AA}$ away from its nearest neighbors, making interactions between clusters negligible. The setting of k -mesh was $(1 \times 1 \times 1)$ in Monkhorst-Pack scheme, since the k -space for a large supercell is very small, and a mesh of $(1 \times 1 \times 1)$ could provide the required accuracy.

Optimization

The algorithm for electronic minimization was set to be ALGO = FAST. In this option, the Davison algorithm³⁴ should be used in the initial phase of each ionic step, and after 10 electronic steps, the algorithm would be switched to RMM-DIIS³⁴. This option can achieve a balance between accuracy and efficiency in structure optimization of metallic structure.

Convergence

The error in free energy was set the criteria in determination of convergence, the simulation would achieve convergence when error in free energy is smaller than 10^{-4} eV between two successive ionic steps.

3.3 Octopus real-space, real-time TDDFT implementation (Octopus)

Octopus is an open-sourced free software for real-space *ab initio* virtual experimentation on atomic scales in 3D finite systems. The code Octopus is written based on time-dependent density-functional theory (TDDFT)³⁵ established on Kohn-Sham theorems^{36,37}, in which electrons are quantum-mechanically defined and nuclei are classically described as points, and pseudopotential is adopted to describe electron-nucleus interactions. Physical quantities in Octopus are expressed in mesh grids in real space and evolutions of simulations are done in real time³⁸. Therefore, Octopus is good at dealing with finite systems such as atomic clusters and dimer systems.

In this project, Octopus is used to calculate ground state electron densities of MNPs and their absorption spectrum at *ab initio* level.

3.3.1 Finite-difference Grid Methods

Besides basis set representations of wavefunctions, the information of wavefunction can also be stored in 3D point arrays that representing real simulation space, which can be shown in matrix form:

$$\psi = [\psi_{x1,y1,z1}, \psi_{x1,y1,z2}, \psi_{x1,y2,z2}, \dots, \psi_{xn,yn,zn}] \quad (3-40)$$

$\psi_{x1,y1,z1}$ is the value of wavefunction ψ in space with Cartesian coordinate (x_1, y_1, z_1) . To ensure normalization, the wavefunction should satisfy the normalization constraint:

$$\psi^* \psi = 2 \quad (3-41)$$

on conditions that spin polarization of electrons is considered. With the initial guess of wavefunction written in matrix, the initial electron density can also be expressed as

$$\rho = [\rho_{x1,y1,z1}, \rho_{x1,y1,z2}, \rho_{x1,y2,z2}, \dots, \rho_{xn,yn,zn}] \quad (3-42)$$

Based on initial ground state density, the Hamiltonian Operator $\hat{H}$ can be determined. By applying $\hat{H}$ on the initial wavefunction ψ_0 , a new wavefunction ψ_1 :

$$\hat{H}\psi_1 = E\psi_1 \quad (3-43)$$

The wavefunction ψ_1 give rise to new set of Hamiltonian and energy, which can be used to calculated $\psi_2, \psi_3, \dots, \psi_n$ until the entire system can achieve convergence.

The advantage of finite-difference grid methods is that it is a general straightforward description of wavefunctions that can be used by both periodic and non-periodic systems, and the periodicity may be in 1D 2D or 3D. The computation quality can be systematically improved by decreasing the grid sizes or increasing the simulation region whenever needed. When written as computer codes, the simulation system described by finite-difference grid

method can be easily divided into different domains and each domain can be separately calculated by different computers. This treatment could improve the efficiency of parallel computing, making finite-difference grid methods very suitable for large non-periodical systems containing isolated particles.

3.3.2 Time Dependent Density Functional Theory

By Kohn-Sham theorems, the calculation of density functionals apply to ground states only, thus description of excited states under DFT may have limited accuracy in many situations. For optical properties, which are the behaviors of valence electrons upon external excitations, time dependent density functional theory (TDDFT) should be introduced, which was first pointed out by Runge-Gross theorem^{39,40}.

From the statement of Runge-Gross theorem, it can be deduced that there is a one-to-one mapping relationship from the time evolution of external potential $V_{ext}(\mathbf{r}, t)$ to the time-dependent electron density $n(\mathbf{r}, t)$ for any arbitrary systems. Similar to Kohn-Sham theorems, there is no analytical expression of time-dependent electron density functionals provided by Runge-Gross theorem. Thus, numerical approaches must be applied to find $n(\mathbf{r}, t)$. The time-dependent Schrödinger equation should be used instead,

$$\hat{H}(t)\psi(t) = E(t)\psi(t) \quad (3-44)$$

Since the time-dependent wavefunction $\psi(t)$ can be uniquely determined by initial wavefunction $\psi(t_0)$ together with the applied external potential $V_{ext}(\mathbf{r}, t)$, a propagator can be found to calculate $\psi(t)$ from $\psi(t_0)$

$$\psi(t) = U(t, t_0) \psi(t_0) \quad (3-45)$$

Substituting Equation 3-45 into Equation 3-44, the time-dependent Schrödinger equation can be rephrased as

$$\hat{H}(t)U(t, t_0) \psi(t_0) = E(t)U(t, t_0) \psi(t_0) \quad (3-46)$$

The time propagator $U(t, t_0)$ in Equation 3-45 and Equation 3-46 is in terms of time-ordered exponential expressions:

$$U(t, t_0) = U_0 e^{-i \int H(\delta) d\delta} \quad (3-47)$$

The equations discussed above is just a general outline of how theory of TDDFT can be expressed mathematically and how Hamiltonian of time-dependent systems can be achieved numerically. Octopus is a realization of TDDFT with finite-difference grid method, which can be used to calculate absorption cross-sections of isolated particles.

3.3.3 Computational Details in Octopus

Being an open-sourced software distributed under GNU GPL, Octopus is a real-time real-space *ab initio* simulation package coded mainly with Fortran, and partially with C. In this work, Octopus-5.0.1 was compiled using GNU Compiler Collections (gcc) on Linux distribution of Red Hat Enterprise Linux Server (RHEL) release 6.3. the operation of Octopus codes need the following libraries: libxc-2.2.0, fftw-3.3.4, gsl-1.1.6, openmpi-1.6.4, lapack-3.4.2, which are all compiled with gcc compilers.

Several import parameters used in the input file of Octopus are also presented here.

Box

In Octopus, the box represents the real space region inside which simulations occur. The box should be large enough to contain all the atoms to be calculated, and ensured proper boundary conditions. The box shape was chosen to sphere, since spherical box shape should be proper for isolated metallic nanoparticles whose geometries are spherical-like. For non-periodical systems, electron density should approach zero at boundary of the box, otherwise there will be a significant increase in total energy of the system under simulation. To ensure this, the radius of box was set to be 8Å larger than the radius of the particle.

Gird

For finite-difference grid simulations, the determination of grid spacing is of immense importance. In principle, the quality of calculation can be improved by increasing the density of grids, at the cost of consuming more computational resource. In our calculations,

the grid spacing of ground state calculations was set to be 0.2 Å, and the grid spacing of time-dependent calculations was set to be 0.5 Å, both of which can guarantee an excellent convergence without waste of computational time.

Pseudopotential

In our calculations, LDA exchange-correlation potential has been adopted, which is generally faster than GGA. For NaNPs, norm-conserving Troullier-Martins pseudopotential has been adopted in SIESTA format⁴⁰. The maximum angular momentum considered is $l = 0$, such that only the one s-band electron is considered as the valence electron each sodium atom. For AgNPs, norm-conserving Troullier-Martins pseudopotential in SIESTA format has also been used. The d-electrons are included in the calculations, such that each silver atom contains 11 valence electrons, with one s-band electron and 10 d-band electrons.

Convergence

The relative error in density was set the criteria in determination of convergence, the simulation would achieve convergence when error in relative electron density is smaller than 10^{-6} Å^{-3} between two successive electronic steps.

External Field

A delta pulse with a strength of 0.01 V/Å was set to act as the external electromagnetic perturbation, and the time propagation for this incident wave is calculated. The propagation of the delta pulse is treated using approximated enforced time-reversal symmetry (AETRS). The time step of this propagation is set to be 0.000827 fs, and the total propagation length is 20000 time steps.

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Chapter 4

Size-dependent LSPR of Sodium Nanoparticles

When size of a sodium nanoparticles is reduced to less than 10nm, with its size further decreasing, remarkable red shift in LSPR peak energy can be observed. This phenomenon cannot be predicted by classical electrodynamics and we refer it as quantum plasmonics. By conducting a series of control simulations, we've found that it is the spilling out of s-band valence electrons that lead to the red shift of LSPR for nanoparticles made of alkaline metals. Therefore, a new method, spilling-out effected classical electrodynamic model(SE-CEM), has been developed to study optical response of alkaline metallic materials in quantum plasmonics. Furthermore, to increase the efficiency of the new model, machine learning algorithm has been introduced for acceleration. The calculated results of our new model agree well with the TDDFT benchmarks, exhibiting a promising approach in theoretical studies of quantum plasmonics.

4.1 Introduction

When exposed to incident light, free electrons in metals are subjected to periodic oscillating external fields, resulting in periodic oscillations of these free electrons. If the frequency of the incident lights becomes close to nature frequencies of the free electrons, resonance occurs. For metallic nanoparticles (MNPs) immersed in transparent media, electron oscillations exist at the surface boundaries between the two materials, and is referred as localized surface plasmon resonance (LSPR)¹⁻³. The frequency at which LSPR occurs is referred as LSPR frequency (in unit of Hz), LSPR wavelength (in unit of nm) or LSPR energy (in unit of eV). There're two remarkable effects brought by LSPR. The first one is extreme enhancement of local electric field near the surface boundary⁴⁻⁸, and the second one is local maximum in spectra of extinction spectra⁹⁻¹³.

For particles made up from same kinds of metal, predicted by classical electrodynamics(CEM), their LSPR energy differs as the size and morphology changes, as is shown in Figure 4.1, showing the extinction spectra of sodium nanoparticles (NaNPs) with radius ranging from 1nm to 10nm. For NaNPs with radius larger than 10nm, their LSPR energy in dipole plasmon mode decrease with increase of size, from 3.3eV to 1.8 eV as the radius increases from 10nm to 100nm, together with the emergence of quadrupole model with higher LSPR energy. For NaNPs smaller than 10nm in radius, the calculated LSPR energy keeps being a constant around 3.4 eV, which also agrees well with conclusion of quasi static approximation¹⁴⁻¹⁷. Recent studies on optical response of small MNPs found that remarkable shift in LSPR peak energies can be observed¹⁷⁻²¹, especially for MNPs whose radius are below 1nm. These findings declared the failure of CEM in optical properties of MNPs within nanometer or sub-nanometric scale²²⁻²⁵.

To study LSPR phenomenon for subnanometric MNPs, we've calculated absorption spectra for a series of subnanometric MNPs by approach of CEM and TDDFT, as is shown in Figure 4.2. Though CEM approach shows constant LSPR energy for these small NaNPs, spectra calculated by TDDFT tell a very different story, which showing red shift of LSPR energy as the size of NaNPs decreases.

Figure 4.1 Extinction spectra of NaNPs with various radius value. a) NaNPs with radius ranging from 10nm to 100 nm b) NaNPs with radius ranging from 1 nm to 10 nm.

Figure 4.2 Absorption spectra of sub-nanometric NaNPs contains 92, 138, 198 and 268 atoms, respectively, calculated by a) TDDFT b) CEM.

The failure of CEM for sub-nanometric NaNPs proved that quantum mechanical effect must be to be considered when the optical response of plasmonic systems with subnanometric geometries are to be investigated. Although full quantum approaches such as TDDFT²⁶⁻³⁰ are very powerful theoretical tools in dealing with optical response accurately, however, these kinds of ab initio simulation packages are extremely resource consuming, and would become unacceptable inefficient for those plasmonic systems containing thousands of valence electrons or even larger systems^{27,31-33}. To better understand mechanisms of plasmonic systems with sub-nanometric structural features, semi-quantum semi-classical optical response simulation approaches with a general scope of applications are highly desirable^{24,34-36}.

In this work, by studying descriptions of free valence electrons of NaNPs by TDDFT and CEM, we concluded that it is the spilling out effect of free electrons that leads to the failure of CEM. Based on this achievement, a spilling out correction has been added into Maxwell's Equations to create a semi-quantum semi-classical model called spilling-out effected classical electrodynamic model (SE-CEM). From the conclusion of SE-CEM, the LSPR peak shifting of small NaNPs can be well explained. To improve the efficiency of SE-CEM, machine learning methods have been introduced, and we've found that the

machine learning enhanced SE-CEM manage to finish simulation works at cost of much less CPU hours compared with original SE-CEM, while no loss of accuracy has been reported.

4.2 Spilling-out Effectuated Classical Electrodynamic Model (SE-CEM)

The buildup of SE-CEM can be illustrated in Figure 4.3. Currently, to describe a metallic nanocluster shown in Figure 4.3a, which is composed by positively charged nuclei and negatively charged free electrons, there're two popular models. The first one is the classical quantum model shown in Figure 4.3c, and the second one is the quantum jellium model shown in 4.3b. In classical description, nanoparticles are regarded as rigid objects, and there is a definite boundary to separate the particles with their environments. Inside the particle boundary, the particle is fulfilled by homogeneous metallic material, while outside the particle boundary, the media is the vacuum environment. The optical properties of metallic materials can be described as a frequency dependent by Drude model shown in Equation 4-1:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_p\omega} \quad (4-1)$$

In Equation 4-1, there two important parameters, the plasmon frequency, ω_p , and the damping frequency, γ_p . These two parameters are all dependent on free electron densities of the material under study:

$$\omega_p = \frac{N_e e^2}{\varepsilon_0 m} \quad (4-2)$$

$$\gamma_p = \alpha_p \sqrt{N_e}^{-5} \quad (4-30)$$

Since the materials inside the boundary have homogenous optical properties, a single equation should be enough to describe one kind of metal.

In quantum jellium model, however, the free electron are no more classical particles, but have wave-like properties as stated in quantum mechanics. The nuclei lattice is described as a background with positive charges uniformly distributed inside a definite jellium boundary. The electrons, however, due to their wave-like properties, are not limited inside jellium boundary. Therefore, electrons under a jellium model could spill out of the jellium boundary, and the electron density outside the jellium boundary attenuates to zero gradually. For alkaline metals whose valence electron are make up by s-band electrons only, the performance of jellium model show excellent agreement with experimental results and based on the success of jellium model for alkaline metals, we proposed the semi-quantum semi-classical model SE-CEM.

Figure 4.3 Schematic illustration of descriptions of electron density in different models a) Quantum atomistic model, b) Quantum jellium model, c) CEM, d) SE-CEM.

The description of electron density distributions in SE-CEM model act as a combination of classical description and jellium description. A MNP has been divided into two parts, a core region and a shell region outside the core region. In core region, the value of electron density has been take the averaged value, regardless the periodic fluctuations. Thus, a constant value N_{core} was used to represent core electron density. In shell region, where electron spilling out effect occurs, the local electron density is denoted as $N_{shell}(\mathbf{r})$. The value of $N_{shell}(\mathbf{r})$ gradually vanishes with the increase of $\mathbf{r}$, as shown in Figure 4.3d. In summary, the electron density profile, $N_e(\mathbf{r})$, was separately represented as N_{shell} and N_{core} for core region and shell region, respectively. By Hohenberg-Kohn theorems and Runge-Gross theorems, all observable physical quantities can be derived from $N_e(\mathbf{r})$, thus the optical properties can also be calculated from $N_e(\mathbf{r})$.

This core-shell structure in description of permittivity of MNPs comes from the concept of pseudopotentials, which also use distinct functions to represent potentials of atoms for different regions. As a result, we call the permittivity in SE-CEM of a MNP as pseudo-permittivity. To calculation of pseudo-permittivity in shell region for different MNPs, the averaged value of $N_e(\mathbf{r})$ in their shell region are to be known:

$$N_e(n) = \frac{1}{V} \int_{R_{core}}^{R_{shell}} N_{shell}(n, r) dV \quad (4-4)$$

In Equation 4-4, n represent the number of atoms contained by a MNP, and V is the volume of shell region of the MNP.

After pseudo-permittivity achieved, the far-field properties of NaNPs can be simulated via FDTD method. An area source was chosen to provide the incident plane wave. The simulation region is a cubic space in vacuum environment, and the edge-length of the cubic space is 200nm, with a 10-nm-thick perfect matched layer added at each face. The light source gave out a Gaussian-pulse at initial stage of each simulation, and the width of the Gaussian source was set to be 1eV to 5eV in frequency. To ensure convergence of the simulations, the resolution was set to be 1/10 of the radius of the NaNP under study, with a reasonable value of Courant factor being 0.5. In this work, FDTD simulations are

calculated by MEEP. All the important parameters used by MEEP are listed in Chapter 3 of this thesis.

4.3 Results and discussions

4.3.1 Absorption spectra of NaNP under SE-CEM

To validate SE-CEM model, absorption spectra of NaNPs were calculated. The NaNPs under study have been carefully chosen, all of which contain magic number of sodium atoms. The magic number for NaNPs, is a series of even numbers (92, 138, 198, 338, 440, 562, 694...), and NaNPs with magic numbers are also called closed shell particles, since electron cloud of these particles are well distributed in spherical symmetry, which are exactly same as electron cloud in jellium particles. We've chosen TDDFT as a benchmark to test the validity of SE-CEM for NaNPs whose atom numbers ranging from 92 to 440. NaNPs smaller than 92 atoms were not in consideration of SE-CEM, as core-shell description of pseudo-permittivity should not be used for very small nanoparticles with less than 80 atoms, since in these extremely tiny structures, we cannot find a proper boundary splitting core and shell regions. Figure 4.4 (a) and (b) present the blue shift of LSPR energy for NaNPs calculated by TDDFT and SE-CEM, respectively. These two approaches agree well with each other, and both predict a blue shift of 0.15 in unit of electron-Volt.

Figure 4.4 Absorption spectra of sub-nanometric NaNPs with closed shell structures from 92 atoms to 440 atoms calculated by a) TDDFT b) CEM.

The TDDFT benchmarks of absorption spectra are calculated by Octopus, with computational details listed in Chapter 3.

4.3.2 Machine learning enhanced SE-CEM model

The central ideology in SE-CEM is the concept of pseudo-permittivity in adopted in core-shell description of MNPs. To calculate pseudo-permittivity of a MNP, ground-state DFT calculations must be conducted to achieve its spatial distribution of valence electron density, based on the electron density distributions, the following optical properties can be derived by SE-CEM model. Although this approach would be much faster than TDDFT, the ground-state DFT calculations are not favorable as well. To calculate the absorption spectrum of an NaNP with 2000 sodium atoms, more than 4500 CPU hours are needed. To get rid of these tedious DFT calculations, we've decided to turn to the fashionable machine learning methods for a new solution. A very efficient neural network based algorithm called Extreme Learning Machine (ELM)³⁷ has been chosen to learn and predict density of valence electrons in shell region of MNPs. The raw learning data needed for ELM was generated by previous ground-state DFT calculations.

For closed shell NaNPs, spherical symmetry on density of s-band valence electrons can be satisfied. Therefore, ELM has been used to study the electron density profiles along radical direction, $N_e(\mathbf{r})$, of NaNPs with various size. It has been found that a brief function containing a Cosine function and a Fermi-Dirac distribution formula can be used to approximate $N_e(\mathbf{r})$:

$$N_{shell}(r) = (N_{core} + A \cos[\omega(r - R_{core})]) * \frac{1}{1 + E^{B(r - R_{jellium})}} \quad (4-5)$$

$$\left. \frac{dN_{shell}(r)}{dr} \right|_{r=R_{core}} = 0 \quad (4-6)$$

$$\frac{N_{shell}(R_{shell})}{N_{core}} = 0.1 \quad (4-7)$$

Figure 4.5 Fitting parameters calculated from Machine learning algorithms. a, b) Evolution of parameter A and B in Equation 4-5. c) Spilling out of s-band free electrons in radical direction of NaNP, predicted by DFT (dots) and ELM (lines). d) LSPR energy calculated by VEDDPP vs. jellium model, red circles are based on DFT and green squares based on ELM.

The parameter $R_{jellium}$ and R_{core} in Equation 4-5 represent the radius of jellium sphere and the radius of core region of each NaNP, respectively, and the R_{shel} in Equation 4-6 & 4-7 represent the radius of shell region of the NaNPs. The definition of R_{core} is the surface boundary where $N_e(\mathbf{r})$ achieve local maximum as stated in Equation 4-6. The

determination of R_{shell} , on the other hand, is the location where $N_e(\mathbf{r})$ is attenuated to less than 10% of N_{core} as stated in Equation 4-7. Another parameter in Equation 4-5 is the wave number, ω , which is related to the periodicity of fluctuations of $N_e(\mathbf{r})$ in core region calculated by ground-state DFT. The other two parameters, A and B, are two fitting parameters generated by ELM automatically, whose physical meanings are not clear to us yet.

The evolutions of parameters A and B with increase of NaNPs' size have been shown in Figure 4.5a and 4.5b. With size of NaNPs increase continuously, the fluctuation in values of both A and B decrease and these two parameters tend to approach some fixed values asymptotically. For NaNPs who are large enough (i.e. contain more than 2000 sodium atoms), the value of parameters A and B can approximately be adopted as 0.0037 and 2.005, respectively. The electron density profiles along radical direction of NaNPs predicted by ELM show agreement with TDDFT calculations, which has been clearly plotted in Figure 4.5c. The error tolerance of ELM prediction is less than 10^{-5} electrons per cubic angstrom, which reach the same level of most ground-state DFT calculations for large metallic nanoparticles. Based on the electron density predicted by ELM, the pseudo-permittivity needed for SE-CEM can also be provided. We refer this approach of SE-CEM as ELM-enhanced SE-CEM (ELM-SE-CEM), different from the previous DFT-enhanced SE-CEM (DFT-SE-CEM). The LSPR peak energies obtained by ELM-SE-CEM, as shown in Figure 4.5d, are quite similar with those obtained from DFT-SE-CEM, with differences less than 0.01 eV for all calculations. Although both ELM-SE-CEM and DFT-SE-CEM underestimate the LSPR peak energy slightly compared the TDDFT benchmark, the absolute deviations are also well below 0.03 eV. The accuracy of SE-CEM should be sufficient for current applications on plasmonic technologies.

4.4 Conclusions

Plasmonic structures in subnanometric scales show unique performances quite different from trinational plasmonic systems. To study the optical response of these plasmonics

structure, quantum tools must be used instead of classical electrodynamics, thus plasmonics of these structures are also referred as quantum plasmonics. Current *ab initio* tools that can be used to study quantum plasmonics such as TDDFT are very insufficient, so we've proposed a SE-CEM to calculate optical response in quantum plasmonics for alkaline metals. SE-CEM stress the spilling out effect of s-band valence electrons in NaNPs, and introduce the concept of pseudo-permittivity in a core-shell model. This model manages to characterize the spatial distribution of density of s-band valence electrons in NaNPs quantitatively. Under SE-CEM, we predict a blue shift in LSPR energy as the size of NaNPs increases, and our results agree well with TDDFT benchmarks. Since our SE-CEM needs ground-state DFT calculations to provide information of electron density, its efficiency is still not so satisfactory. One feasible solution is the machine learning method. We've proved that the accuracy of ELM-SE-CEM should be at the same level of DFT-SE-CEM, while the former approach consumes much less computational resource. Starting from SE-CEM, a semi-quantum semi-classical are expected to be setup to act as a more efficient tool in simulation of quantum plasmonics.

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Chapter 5

Size-dependent LSPR of Silver Nano-Particles

When size of a silver nanoparticle is reduced to less than 10nm, remarkable blue shift in LSPR peak energy can be observed, which is very different from the case of sodium ones discussed in the previous chapter. This kind of blue shift cannot be explained by classical electrodynamics, and we found that it is the effect of spilling out of s-band valence electrons and screening effect of d-band electrons together determined the nonlocal effect in LSPR of silver nanoparticles. A more general model, screening and spilling-out effected classical electrodynamic model (SSE-CEM) has been set up to study the optical response of metallic nanoparticles with d-band valence electrons in transition metals. The calculated results SSE-CEM agree well with the TDDFT benchmarks, and the extrapolation of radius of nanoparticles into nanometer scale also showed an excellent agreement between SSE-CEM and CEM

5.1 Introduction

Due to the fast development in nano-fabrication technologies, quantum plasmonics has becoming a hot topic in recent researches¹⁻⁶. In our previous studies, we've found that spilling out effect of s-band valence electrons plays key roles in optical response processes in quantum plasmonics and proposed a semi-quantum semi-classical model named as SC-CEM to investigate MNPs made from alkaline metals. The scope of SC-CEM, however, can be limited to alkaline metallic materials only, while in real quantum plasmonic applications the MNP are usually made from noble metals. For noble metallic atoms, such as Cu, Ag and Au, besides s-band valence electrons, they also contain d-band valence electrons, and these d-band valence electrons could lead to screening effects inside plasmonic, making their optical properties quite different from alkaline metallic nanoparticles⁷⁻¹¹.

Figure 5.1 Absorption spectra of calculated by TDDFT jellium model (red) and TDDFT cluster model (cyan). a) NaNP of 198 atoms, b) NaNP of 268 atoms, c) AgNP of 21 atoms, d) AgNP of 59 atoms.

The existence of d-band valence electrons would cause failure of Drude model and jellium model, both of which do not take d-band electrons into account¹². To calculate absorption spectra with TDDFT, quantum atomic model should be used instead of quantum jellium model^{13,14}. The difference of atomic model and jellium model has been shown in Figure 5.1. For closed shell nanoparticles^{15,16}, our TDDFT calculations showed that NaNPs under atomic model and jellium model have almost same absorption spectra, in Figure 5.1a and 5.1b. For silver nanoparticles (AgNPs), however, LSPR peaks calculated by jellium model have remarkable blue shift compared with that of atomic model, and the peak intensities in jellium model were also much higher.

This discrepancy between jellium and atomic model for optical response of AgNPs originates from the effect of d-band electron screening^{11,17}. On applying of external electric field, free electrons in s-band would move along the direction of electric field and accumulate at the surface region of AgNPs to form polarizations^{18,19}. The valence electrons in d-band, however, would polarize in the opposite directions in the inner region of the AgNPs to screen the polarity induced by s-band electrons^{14,20-22}. This screening effect could lead to remarkable decrease in LSPR energy. It has been reported that in TDDFT calculations, overestimating on d-band screening effect would also cause undersetting of LSPR frequency and intensity¹⁴. To setup a semi-quantum semi-classical model for noble metals, screening effect from d-band electrons must be considered.

In this work, based on the description of d-band electrons of quantum mechanical models and classical models, we've found that the distributions of d-band electrons are limited to the inner part of nanoparticles, or the core region in SE-CEM model. therefore, we improved our SE-CEM model by adding Lorentzian terms to pseudo-permittivity of core regions and rename the new model as screening and spilling-out effected classical electrodynamic model (SSE-CEM). This upgraded new SSE-CEM model, manages to describe optical responses of noble metallic nanoparticles accurately with no trade off in efficiency.

5.2 Spilling-out Effect Classical Electrodynamics Model (SSE-CEM)

Even though the Drude model is a classical approach without considering d-band electrons, it can be upgraded to Drude-Lorentz model by adding Lorentzian terms to solve this issue. This classical approach, however, can only be applied to bulk materials. For nanoparticles in subnanometric size, it would also cause severe error, as is shown in Figure 5.2. By adding Lorentzian term to permittivity of AgNPs, we can eliminate the false overestimations of LSPR energy predict by jellium model, but unexpected underestimations were observed, compared with TDDFT benchmark in Figure 5.2(a). Moreover, as the size of AgNPs decrease, blue shift in LSPR energy can be observed under TDDFT, but not reflected under Drude-Lorentz model²³⁻²⁶.

Figure 5.2 Absorption spectra of sub-nanometric AgNPs contains 21, 35, 41 and 93 atoms, respectively, calculated by a) TDDFT b) CEM.

The false of Drude-Lorentz model of AgNPs lies in overestimating of d-band electron screening effect, which would in turn lead to underestimation of LSPR energy²⁷⁻²⁹. In our SSE-CEM model, d-band screening effect is only considered in core regions of AgNPs, where d-band electrons are localized, as illustrated in Figure 5.3.

In classical Drude-Lorentz model, the whole particle is treated as a solid metallic material inside the surface boundary of the particle³⁰. This description of AgNPs has two

disadvantages. Firstly, s-band valence electrons are localized inside the surface boundary, without incorporation of spilling-out effect. Secondly, d-band electrons are uniformly distributed inside the surface boundary, which does not reflect the true case^{31,32}. The jellium model, on the other hand, has totally ignored the existence of d-band electrons, but fully described spilling-out effect of s-band electrons^{33,34}. The core-shell description adopted by SSE-CEM has addressed the shortcomings of Drude-Lorentz model and jellium model. In SSE-CEM, the change of pseudo-permittivity caused by d-band electrons' screening is accounted in core region of each AgNP and the s-band electrons' spilling-out occurring in shell region.

Figure 5.3 Schematic illustration of descriptions of d-band valence electrons in different models a) CEM, d-band valence electrons are uniformly distributed, as is for bulk solid materials, b) Jellium model, only conduction s-band electrons are considered, without taking d-band electrons into account, c) SSE-CEM, d-band valence electrons are localized in core regions of MNPs, with shell regions containing those spilled-out s-band electrons only.

The construction of pseudo-permittivity in shell region is same as what has been done in SE-CEM, as described in Chapter 4.2. In core region, extra Lorentzian terms must be added after the Drude term in Equation 4-1. Therefore, the pseudo-permittivity in core region of noble nanoparticles can be expressed as:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_p\omega} + \sum_{i=1}^N \frac{A_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega} \quad (5-1)$$

In our calculation, five Lorentzian terms were used ($N = 5$). The parameters of all these five terms were achieved by fitting the Experimental data of Johnson and Christy using

Differential evolution method. All parameters configuring pseudo-permittivity of AgNPs are listed in Table 3.1.

After pseudo-permittivity achieved, the far-field properties of NaNPs can be simulated via FDTD method. An area source was chosen to provide the incident plane wave. The simulation region is a cubic space in vacuum environment, and the edge-length of the cubic space is 200nm, with a 10-nm-thick perfect matched layer added at each face. The light source gave out a Gaussian-pulse at initial stage of each simulation, and the width of the Gaussian source was set to be 1eV to 5eV in frequency. To ensure convergence of the simulations, the resolution was set to be 1/10 of the radius of the AgNP under study, with a reasonable value of Courant factor being 0.5. In this work, FDTD simulations are calculated by MEEP. All the important parameters used by MEEP are listed in Chapter 3 of this thesis.

Figure 5.4 Absorption spectra of sub-nanometric AgNPs with closed shell structures containing atoms ranging from 139 to 441 atoms, respectively, calculated by a) TDDFT jellium model, b) SSE-CEM.

5.3 Results and discussions

5.3.1 Absorption spectra of NaNP under SSE-CEM

To test the validity of SSE-CEM model, we calculated absorption spectra of AgNPs containing magic numbers of silver atoms. Different from NaNPs, the magic number of AgNPs is a series of odd numbers, which can be taken as 93, 139, 199, 339, 441.... These magic number can also guarantee closed shell structures in electron clouds of AgNPs.

Figure 5.5 Size-dependent LSPR energy of MNPs. a) Extrapolation of LSPR energy vs. inverse radius ($1/R$) of NaNPs, calculated by ELM based SE-CEM (red circles), DFT based SE-CEM model (cyan rhombus), jellium model (purple triangles) and classical CEM (black squares), b) As panel (a), now for the AgNPs.

Absorption spectra under quantum jellium model have also be calculated to act as comparisons. From Figure 5.4, we can see jellium model has predicted blue shifts of LSPR peak energy with size of AgNPs increasing, whereas SSE-CEM model has showed an opposite trend, red shifts in LSPR peak energy. From the calculation of quantum atomistic model and experimental results published in literatures, it is obvious that LSPR peak energy should have red shift with size increasing; on the contrary, NaNPs show blue shift under same conditions. Thus, we know how jellium model succeeds in NaNPs but fails for AgNPs, the key point is ignorance of d-band electron screening.

For nanoparticles made of noble metals with several d-band electrons, screening effect from these d-band electrons must be taken into account for setup of models. As is known, introducing d-band electrons into a plasmonic system would cause remarkable red-shifts in LSPR peak energy, so either overestimating or underestimating of effects from d-band electron may cause wrong evaluation of LSPR energies. The screening effect of d-band electrons can well explain LSPR energy shifts of AgNPs. As size of AgNPs decreases, volume ratio of the core region where d-band electrons are localized also decreases, resulting in less significant screening effect. Therefore, we could observe blue shift in LSPR peak energy for smaller AgNPs.

5.3.2 Size-dependent LSPR energy of MNPs

Different from the SE-CEM model, an appliance for alkaline metal only, the SSE-CEM can be applied on noble metal as well. The NaNPs and AgNPs investigated by SE-CEM and SSE-CEM, respectively, both have shown remarkable energy shifts in LSPR modes. By applying mathematical analysis on our simulation results, a linear relationship between LSPR energy and the inverse value of radius ($1/R$) of the MNPs has been found^{14,35}. By doing extrapolating for LSPR peak energy vs $1/R$, LSPR peak energy of MNPs at quasistatic limit can be reached. The best fitting for both NaNPs and AgNPs are shown in Figure 5.5. To check to which extent these extrapolations agree with CEM predictions, we also conducted FDTD simulations for AgNPs and NaNPs within the scale requirement of quasistatic limit (less than 10nm in radius). The fitting parameters have been listed in Table 5.1, from which we see both DFT-SSE-CEM and ELM-SSE-CEM's extrapolation

predictions of LSPR peak energy are very close to CEM's predictions. The success of this series of extrapolations show that SSE-CEM are compatible with both TDDFT and CEM. the scope of application of this semi-quantum semi-classical model ranges from down to 100-atom clusters and up to 10-nm radius particles.

Table 5. 1 Extrapolation limit for LSPR peak energy for Na and Ag

Element	DFT-SSE-CEM	ELM-SSE-CEM	CEM-FDTD
Sodium	3.36	3.38	3.40
Silver	3.38	3.36	3.37

5.4 Conclusions

Plasmonics are caused by collective oscillations of valence electrons. For noble metals, besides s-band valence electrons, those d-band valence electrons also account for MNPs behavior in wave-particle interactions. To setup a semi-quantum semi-classical model dealing with typical quantum plasmonics, we upgraded the SE-CEM to SSE-CEM, and the latter model manage to incorporate effects of d-band electrons into pseudo-permittivity of MNP in a reasonable way. The birth of SSE-CEM explained why NaNPs show redshift in LSPR peak energy when size decreases while AgNPs show blueshift. The calculation results obtained from SSE-CEM also agree with TDDFT bench marks for closed shell AgNPs. Both NaNPs and AgNPs' LSPR peak energies present a linear dependence on inverse of their radius ($1/R$). By extrapolating this linear relationship to mesoscopic scale, the results also agree with CEM simulations. In this work, we've shown that SSE-CEM is compatible with both CEM and TDDFT, and its scope of applications containing most of typical quantum plasmonic systems currently under study. As a semi-quantum semi-classical model, SSE-CEM always gives considerations to productivity in simulations, making this tool applicable to more complex bio-plasmonics in future.

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Chapter 6

Optical Responses of Dimer Structures By SSE-CEM

When subjected to external oscillating field, dimer structures would exhibit plasmon modes in various forms compared with individual particles. In classical electrodynamics, these plasmon modes are explained by interactions of dipoles or quadrupoles in each particle. For quantum plasmonics, however, electron transfers between nanoparticles also affect behaviors of LSPR in dimer structures. In this chapter, we use SSE-CEM set up in previous chapters to study the optical responses of dimer structures. Five characteristic plasmon modes have been illustrated, and the local electric field enhancement in gap regions of dimers has also been discussed. In this study, it has been found that multipoles form in dimers could be very different with the increasing of photon energy, and the field enhancement at sub-nanometric gap is actually not as high as predicted by classical electrodynamics

6.1 Introduction

One of the most interesting topics in quantum plasmonics should be the various plasmon modes of plasmonic dimers¹⁻⁴. As the gap distance separating the two MNPs varies, diverse kinds of plasmon may arise, determined by frequency of external electric field and transfers of charge carriers within the dimer system⁵⁻⁸. If the gap distance is reduced to less than 5 Å, charge carriers may tunnel through the gap and significantly alter the plasmon properties. This phenomenon is also referred as electron tunneling effect, which is common in quantum mechanics but not included in classical electrodynamics⁹. Previously, related works regarding these dimer systems have investigated by *ab initio* calculations and proposed as plasmon ruler for the characteristic plasmon modes under different gap distance. Almost all these researches focused on far field spectra of the dimers and recognized different LSPR modes by peaks in extinction spectra¹⁰⁻¹⁴. The near field spectra, such electric field near the gap region of those dimers, however, also have very interesting properties, while remain unrevealed^{7,15-19}.

In this work, a detailed study of plasmonic dimer systems was conducted under the semi-quantum semi-classical SSE-CEM model. The far field extinction spectra and near field local electric field spectra have been calculated.

6.2 Dimer Structures in SSE-CEM

The buildup of SSE-CEM for dimers are shown in Figure 6.1. When two separated MNPs are moving towards each other until finally merge into one nanoparticle, three characteristic regimes can be achieved during this process, name as separation regime, tunneling regime and contact regime, respectively.

In separation regimes, there is no charge transfer between the two MNPs due to the large separation created by the gap. The interactions between the two MNPs can only be realized by dipole interactions induced by the applied external field. In tunneling regime, the gap distance is reduced to sub-nanometric level and electron now can be transported by the

external field from one MNP to the other one via tunneling effect, even though these two MNPs have no physical contact at all. In contact mode, the two MNPs physically touch each other and the description of electron transfers between the two MNPs can now be done under CEM. The modelling of these three regimes, however, can be easily realized by the core-shell pseudo-permittivity system in SSE-CEM. When two MNPs are far away from each other such that their shell regions do not overlap, then this situation is defined as separation regime. If the two MNPs are placed very close to each other, and there're overlaps of their shell regions but not core regions, the situation is referred as tunneling regime^{6,20-22}. If the core regions of the two MNPs also in contact with each other, the requirement of contact regime then has been reached.

In simulation part, two nanowires made of sodium (NaNW) act as the two geometries of the dimer system. the radius of each nanowire is 5 Å as stated in Figure 6.1. Under different condition of gap distance, the spatial distribution of s-band electron densities have been calculated firstly, then the pseudo-permittivity of the dimer systems can be determined. With pseudo-permittivity known, both near-field and far-field spectra of the dimer systems can be easily calculated by FDTD method.

6.3 Results and Discussion

6.3.1 Far field spectra of plasmonic dimers

The evolution of plasmon modes starts from separation mode, when the gap distance equals to 20 Å. Under this distance, no tunneling current can be detected, and the resonance are induced by interactions of dipoles or quadrupoles formed inside each NaNW. Therefore, the extinction spectrum mainly present two modes: bonding dipole plasmon (BDP) and bonding quadrupole plasmon (BQP), and LSPR energy of BQP is about 0.5 eV higher than that of BDP for the same dimer configuration. There is also another mode may appear, which is refer as high-order mode(HM). This mode is generated by interactions of higher-order multipoles inside each NaNW. For gap separations larger than 15 Å, BQP and HM

would merge into one mode. By continuously decrease the gap distance, the LSPR energy of both BDP and BQP decrease accordingly, which can be clearly seen in Figure 6.2. Another indication of decrease in gap distance is the better resolution of BQP and HM. The LSPR energy of HM stays at constant around 3.9 eV. when the LSPR energy of BQP can be decrease below 3.6 eV, these two plasmon modes can then be well resolved. If the gap distance is further reduced to less than 5 Å, shell regions of the two NaNWs start to overlap and the tunneling regime takes over the issue.

In this case, the overlap of shell regions can be regarded as overlap the electron clouds of the two nanowires. Electrons inside the gap region now cannot be localized inside a certain nanowire but may be transferred from one to the other easily under external electric field. Therefore, tunneling current can be detected across the gap, and this kind of current can decrease the strength of dipoles and quadrupoles formed in each NaNW, which in turn lead to decrease of LSPR energy for both BDP and BQP. The intensity of tunneling current will increase dramatically as the gap distance keeps decreasing in tunneling regime. As a result, both BDP and BQP vanish and new modes named charge transfer plasmon (CTP) and higher order charge transfer plasmon (HCTP) emerge. Different from BDP and BQP, LSPR energies of CTP and HCTP show blue shifts as the gap distance continuously decreases. This trend has been kept in contact regime also. In contact regime, gap distance is expressed in negative values, and the intensity transfer current becomes larger than the tunneling current under tunneling regime, with increase of LSPR energy of both CTP and HCTP to even higher levels. The HCTP mode, however, would merge into HM again if the gap distance becomes very negative or smaller than -20 Å.

From Figure 6.2, it could be shown that plasmon modes in dimer structures show greater diversity than that of monomers, and the LSPR peak energies would be decreased if the gap separation between the geometries is extremely expressed, for both BDP/CTP series in low energy resonance and BQP/HCTP series in high energy resonance, providing potential applications in tunable functional plasmonic nano-devices.

Figure 6.1 Schematic illustration of descriptions of s-band valence electrons under different regime of a dimer structure. a) Separation regime, b) Tunneling regime, c) Contact regime.

Though there is no specific description of tunneling, this effect has been included by the core-shell description of pseudo-permittivity. when the spilled-out electrons of one particle could reach the shell region of the other particle, then there is a chance that electron could tunneling through the gap between the two particles. Since spilling out effect and quantum tunneling effect are both reflect the wave properties of electrons, they can be described by the same set of pseudo-permittivity.

Figure 6.2 Extinction cross-section and Schematic illustration for nanowire dimers calculated by SE-CEM, the radius of each nanowire is 5 Å, and the gap separation ranging from -16 Å to 20 Å.

6.3.2 Near field spectra of plasmonic dimers

Besides far field spectra, near field spectra also present interesting properties that help to reveal the physical scenarios hidden in dimer systems. As shown in Figure 6.3, electric field patterns at LSPR frequencies have been calculated for dimer systems whose gap distance ranges from $-8 \text{ \AA}$ to $8 \text{ \AA}$.

For the CTP/BDP mode series (upper panel in Figure 6.3), the LSPR energies are relatively lower than that of HCTP/BQP mode series (lower panel in Figure 6.3), and two hot spots can be formed within the gap region. When the gap distance equals to $8 \text{ \AA}$, a typical electric field pattern of BDP mode can be observed. The two hot spots are near the two electric poles inside the gap region, while the extreme enhancement of localized electric field is found at the center of the gap. When gap distance is reduced to $4 \text{ \AA}$, electron tunneling effect become such significant that field enhancement in the center of gap has been weakened by the tunneling current, which separates the hot spots into left and right parts.

In contact regime, the field pattern for CTP mode also has characteristic features, with two hot spots located at the two cavities neck of the connected dimer. For the HCTP/BQP mode series, four hot spots can be found in each structure due to higher LSPR energies. Though all these four are still located inside the gap/cavity regions, their separation distance are obviously larger than that of CTP/BDP series.

To study the local field enhancement at the gap of dimers, a rectangular monitor with size of $80 \text{ \AA} \times 40 \text{ \AA}$ on gap region of the dimers to record field patterns of hot spots quantitatively was placed. Thus, the local field enhancement can be quantitatively expressed as the averaged electric field enhancement factor inside the monitor box, E_{Fac} , which is defined as:

$$E_{Fac} = \int |\mathbf{E}/\mathbf{E}_0|^2 ds / \int ds \quad (6-1)$$

Figure 6.3 Enhancement of local electric field of CTP/BDP mode series (upper panel) and HCTP/BQP mode series (lower panel) of nanowire dimer structures, the radius of each nanowire is $5 \text{ \AA}$, and the gap separation ranging from $-8 \text{ \AA}$ to $8 \text{ \AA}$.

In Equation 6-1, the physical quantity is the local electric field intensity inside monitor box, and the quantity E_0 is the electric field intensity at the source position. The value of E_{Fac} has been calculated for BDP/CTP mode and BQP/HCTP mode with the gap distance increasing from -16 to $20 \text{ \AA}$, as illustrated in Figure 6.4. For the BDP/CTP mode, a series with relatively lower LSPR energies, only two hot spots can be formed. As the gap distance decreases from $20 \text{ \AA}$, E_{Fac} value decreases moderately until the gap distance reaches $6 \text{ \AA}$. When the gap distance is continuously decreased from $6 \text{ \AA}$, the value of E_{Fac} experiences a sudden decrease from 100 to 40 and achieves a minimum when tunneling regime is converted to contact regime. After that, E_{Fac} value begins to increase as the gap distance

continuous to decrease to more negative values to $-8 \text{ \AA}$, and remains almost unchanged all the way to $-16 \text{ \AA}$. This dramatic decrease appears around $6 \text{ \AA}$ -separation gap distance is believed to be caused by emergence of electron tunneling effect. Electrons tunneling through the gap may decrease the dipole moment inside each nanowire, which would in turn cause reduction in enhancement of electric field. When tunneling regime is gradually converted to contact regime, conducting current rises while tunneling current vanishes, and the E_{Fac} value also increases due to hot spots are strengthened at neck region of the dimer structure. Based on E_{Fac} curve for BDP/CTP mode, it clearly indicates that extreme compression of gap distance is not a smart choice if extreme electric field enhancement is to be achieved, since strong tunneling current would weaken the strength of localized electric field. Moreover, for metallic structures, high electric field are favored to be localized in the regions where the value of permittivity is at modest level, such as vacuum surrounding or shell regions in SSE-CEM model. A very narrow gap certainly compresses the living space of hot spots.

In BQP/HCTP mode, where higher photon energy is required, a different physical picture can be presented. As shown in the lower panel in Figure 6.3, there should be four hot spots under each case, forming quadrupolar resonances. In these quadrupolar modes, separations of any two poles could hardly decreased to be less than $4 \text{ \AA}$, which in turn would limit the strength of tunneling currents. Therefore, the field enhancement would not undergo a decrease as we diminish the gap separations between the two nanowires, and the E_{Fac} value achieves a maximum around $0 \text{ \AA}$ in gap distance. If the value of gap distance is too positive or too negative, inter-polar distance between different poles increases and their interaction strength decreases, and the value of E_{Fac} also decreases.

From the all the pictures included in Figure 6.3 and Figure 6.4, we could not find any characteristic signals that can distinguish contact regime, tunneling regime or separation regimes from the other two regimes, due to continuous evolution of electron density distributions as the gap distance varies. Smooth transitions between different regimes can reflect the physical realities and are also well predicted by TDDFT calculations, while both

near field and for field spectra calculated by CEM show abrupt changes during regime transitions. These smooth transitions further proved the validity of SSE-CEM model.

Figure 6.4 Factor of enhancement of local electric field in inside the monitor, E_{Fac} , of CTP/BDP mode series (yellow curve) and HCTP/BQP mode series (blue curve) of nanowire dimer structures, the radius of each nanowire is 5 Å, and the gap separation ranging from -16 Å to 20 Å.

6.4 Conclusions

Dimer structures exhibit various unique properties in plasmonic phenomena, which are promising in practical applications of nano-plasmonic devices. The multiformity of dimers in plasmonics originates from variation of the gap distance. As the gap distance changes from 20 Å to -16 Å, three different regimes, separation regime, tunneling regime and contract regime are experienced the system successively. Under the frame of SSE-CEM, transitions between these regimes are quite smooth, indicating the quantum-mechanical

feature of SSE-CEM. Our calculations have also shown that three series of plasmon modes could be observed for dimer systems, BDP/CTP series, BQP/HTCP series and HM series, from low LSPR energy to high, respectively. By compressing the gap separation, we could get maximum field enhancement in BQP/HCTP series, but not BDP/CTP series. On the contrary, the E_{Fac} value reaches its minimum around the 0 Å gap in BDP/CTP modes. For plasmonic systems containing multiple MNPs, the dominant factor in each plasmon mode may change, but our central ideology is to follow the change of valence electron densities only, which leads to the success of SSE-CEM model. Followed by the same ideology, the scope of application for SSE-CEM in dimers could also be extended to oligomers and even more complexed plasmonic systems.

For noble metals, although there're d-band electrons inside core regions of MNPs, the existence of these d-band electrons would not have much influence on gap regions of dimer sys structures, thus the method on study NaNW dimers and AgNW dimers should be similar. The details of optical properties of AgNW are to be listed in future works.

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Chapter 7

Discussion and Future Work

This chapter draws together the threads of this thesis. The two hypotheses presented in Chapter 1, about the effect of s-band electrons' spilling out and d-band electrons' screening in quantum plasmonics, have been verified in control simulations. The main achievement in this study, setting up the ideology of pseudo-permittivity, was based on these two hypotheses, together with applications of semi-quantum approach, SE-CEM/SSE-CEM, for MNPs made of alkaline metals and transition metals. The introduction of pseudo-permittivity and machine learning has built up a general semi-quantum semi-classical model that can predict optical responses for complex nanometer scaled plasmonic structures, and the validity of SE-CEM/SSE-CEM has also been verified by TDDFT and extrapolation. In addition, the opportunities for future work about extending the scope of pseudo-permittivity to semiconductors and 3D multi-particle systems are also discussed in this chapter.

7.1 Discussions

This project is aimed to setup a new semi-quantum semi-classical model to accurately describe optical response of plasmonic systems with sub-nanometric features, since both CEM and TDDFT have been proved ineffective in related fields¹⁻³. We investigated models in classical approaches and quantum mechanical approaches, and finally find three critical issues that may lead to failure of CEM: spilling out effect of s-band valence electrons, screening effect of d-band valence electrons, and surface relaxations of nuclei. By designing control simulations, it has been concluded that for sub-nanometric NaNPs, the dominant factor in size dependent LSPR peak shift is the spilling out effect of s-band valence electrons, while this effect together with screening effect from d-band valence electrons determine size dependent LSPR peak energies for sub-nanometric AgNPs. The surface relaxation of nuclei, however, play very insignificant roles in optical response of closed shell MNPs. With these conclusions drawn, we've developed SE-CEM and SSE-CEM successively, to describe optical response of nanometer scale and sub-nanometric nanoparticles for alkaline metals and noble metals, respectively. In SE-CEM model, the spilling out effect of s-band valence electrons are stressed using a core-shell structured model. We've introduced the concept of pseudo-permittivity to describe the optical properties of the shell regions where spilling out effect occurs.

By calculating absorption spectra of NaNPs under SE-CEM, a red-shift of LSPR energies could be observed with decreasing of particle size. To simulate optical response of noble metals, the SE-CEM has been upgraded to SSE-CEM, and the new SSE-CEM model has incorporated d-band valence electrons' screening effect into the pseudo-permittivity of core-regions of MNPs. By this modification in SSE-CEM, we've found that it is the screening effect in core regions that makes LSPR peak energy of AgNPs blue shift with decrease of particle size. All the predictions made by SE-CEM and SSE-CEM agree well with that of TDDFT, and the concept of pseudo-permittivity within the core-shell model plays the key role in success of our models. Moreover, for MNPs of nanometer and sub-nanometric scale, there is a linear relationship between the LSPR peak energy and the inverse value of particles' radius ($1/R$). Therefore, the validity of SE-CEM and SSE-CEM

can be further improved by extrapolating LSPR peak energies to nanometer scale. The extrapolated LSPR energies, as shown in Figure 5.5, are also accurate benchmarked by CEM simulations. Thus, we concluded that SE-CEM/SSE-CEM can be regarded as a general simulation approach to predict optical properties of nanoparticles within nanometer and sub-nanometric scale made of either alkaline metals or noble metals.

Another improvement of our SE-CEM/SSE-CEM model is that the performance of this semi-quantum semi-classical model can also be enhanced by machine learning methods. In this project, we've chosen ELM algorithm as an example to accelerate our SE-CEM/SSE-CEM. In prediction of spatial distribution electron density, it has been illustrated that the tolerance of error is same for ground DFT calculation and ELM machine learning prediction, at the level of less than 10^{-5} electrons per cubic angstrom. Since pseudo-permittivity in SE-CEM/SSE-CEM depends on electron density functional only, the accuracy of ELM enhanced approach is also same as that of original approach. The efficiency of ELM enhanced one, however, is much better than the original ground state DFT supported one. According to our test, to calculate absorption spectra of a NaNP containing 2048 sodium atoms, DFT-SE-CEM spent more than 500 CPU hours while it takes less than 5 CPU hours for ELN-SE-CEM to complete the same task. As the fast development of nanotechnology, more complex plasmonic systems are to be studied in future, and a more efficient simulation tool is by no means favored in theoretical calculations.

7.1.1 SE-CEM for alkaline MNPs

The establishment of SE-CEM was based on the outstanding spilling out effect of valence s-band electrons in LSPR. This effect has long been ignored by classical models, since the relative number of spilled-out electrons is extremely remote for bulk materials. As the size of materials decreases, however, the ratio of spilled-out valence electrons increases dramatically, and becomes a significant factor for MNPs whose diameter is less than 10 nm. Based on our calculations, for a 1-nm-diameter NaNP at ground state, about 5% of its s-band valence electrons are in spilled-out state, and this value would increase to 10% for

a 5-Å-diameter NaNP. With more valence electrons spilling out of the atomic lattice region, free electron density N_e of small nanoparticles would become lower than the value of bulk materials. From Equation 4-2, it can be easily derived that the value of plasmon frequency of metallic materials is largely dependent on the value of N_e . Therefore, as the value of N_e continuously decrease as the size of NaNP decrease, the value of plasmon frequency decreases simultaneously. Based on our calculations, this is the main cause of red shift of LSPR peak for nanometer and sub-nanometric scale NaNPs.

Based on Drude model, a classical model that work well for bulk alkaline metals, we found that permittivity of materials depends on the density of electrons. This deduction could be rigorously proved by Hohenberg-Kohn theorems and Runge-Gross theorems. The conclusion can be rephrased in a more comprehensive way: permittivity of metallic materials is a unique functional of electron density, and if the effect of core electron can be neglected, then permittivity is a unique functional of valence electron density. For nanoparticles made of alkaline metallic atoms, such as NaNPs, there're only s-band valence electrons, thus permittivity of these materials depends on density of s-band valence electrons.

Spatial distribution of s-band electrons of NaNPs can be achieved from ground state DFT calculations. After analysis of distribution of s-band electrons of a series NaNPs with closed shell structure, we found that s-band valence electron density inside the atomistic lattice of NaNPs show periodic fluctuations, and decays gradually outside the lattice. This kind of spatial distribution can be well described by a core-shell model. Core region of a NaNP represents the space inside the atomistic lattices, and shell region is the space outside. In this way, the pseudo-permittivity of core and shell region can be described by different functionals of s-band electron density. We named this model as spilling-out effected classical electrodynamic model (SE-CEM), and the prediction in LSPR peak of SE-CEM showed remarkable agreements with that of TDDFT. The conclusion of SE-CEM indicates that spilling out effect of s-band valence electrons is the main source of non-local effect of nanometer and sub-nanometric scaled alkaline metallic nanoparticles.

7.1.2 SSE-CEM for alkaline MNPs

The light-matter interactions inside noble metallic materials would be much more complex than that of alkaline metallic materials, due to more complicated structure of electron orbitals. If the SE-CEM was used to calculate far field spectra of noble metallic materials, the predicted LSPR peak energy should be much larger than the value obtained from experiments or TDDFT calculations, as mentioned in Chapter 5. We've calculated the absorption spectra of AgNPs with closed shell structures using SE-CEM, and found that the peak value is more than 0.5 eV compared with TDDFT's calculation. The possible cause of discrepancy between SE-CEM and TDDFT is believed to be the d-band electrons' screening effect, a prominent issue in plasmonics for noble metals but failed to be considered by either Drude model nor SE-CEM. In AgNPs, there're 10 d-band valence electrons in each silver atoms, and they're 4d electrons. The energy of these 4d electrons is lower than that of 5s electrons but higher than all the other electrons. As a result, these d-band electrons cannot be treated as frozen electrons nor totally free electrons. They're partially free but also localized near atomic nuclei. When external electric field is applied, those free s-band valence electrons would be drifted to localize at surface of the particle, and d-band valence electron would be polarized at the opposite directions of s-band electrons near nuclei. In this way, d-band valence electrons manage to form a counteracting screening field in the core region, and this screening effect would significantly decrease the LSPR peak energy.

Previously, Drude model has been modified by adding Lorentzian terms to describe the influence of d-band valence electrons. This approach assumes that d-band electrons are uniformly distributed inside MNPs and would overestimate the screening effect contributed by d-band electrons, since d-band electrons are localized within the core regions. To stress this issue, we've proposed SSE-CEM (screening and spilling-out effected classical electrodynamic model), an improvement of SE-CEM by adding d-band valence electron's screening effect into the pseudo-permittivity of core regions of MNPs, with parameters used in Lorentzian terms obtained from publication of Johnson and Christy. Again, the LSPR peak energy of AgNPs with closed shell structures predicted by SSE-

CEM agree excellently with TDDFT calculations. The success of SSE-CEM in optical response for noble metallic nanoparticles has confirmed our assumption that both s-band valence electrons' spilling out effect and d-band valence electrons' screening effect are important in describing plasmonics. If either one is underestimated or overestimated, a major error may occur in prediction of LSPR peak energy.

7.1.3 Machine learning enhanced SE-CEM/SSE-CEM

To calculate the pseudo-permittivity used in SE-CEM/SSE-CEM model, ground state DFT calculations are needed to provide information of electron density of certain structures. Although efficiency of ground state DFT is much better than that of TDDFT, it still consumes considerable amount of computational resource for each simulation work. To get free of DFT calculations in our semi-quantum semi-classical model, we turned to machine learning for innovative solutions. Current machine learning approaches are widely available in function prediction, while electron density is a unique function of optimized atomic structure, therefore machine learning could be applied to predict electron density of MNPs. Generally, to predict the electron density of an NaNP containing 500 atoms with convergence's requirement at the level of 10^{-5} electrons per cubic angstrom, a typical ground state DFT calculation would take more than 5000 CPU hours while a machine learning approach cost less than 1 CPU hour. We regard the potential of machine learning as a key to solve the long-lived contradiction between efficiency and accuracy for computational physics.

Among various machine learning tools, we've chosen the Extreme Learning Machine (ELM) to enhance our SE-CEM/SSE-CEM. One advantage of ELM is that it is a matrix-based algorithm, which is compatible with most *ab initio* simulation packages who use matrix to describe wave functions. Since machine learning needs raw data of electron density as learning materials, the compatibility between these two tools bring a lot of convenient in the development of machine learning enhanced approach.

7.1.4 Plasmonic dimer structures

The development of SE-CEM/SSE-CEM was aimed to predict optical response of complex quantum plasmonic structures, and the most popular one is dimer structures. Compared with single MNPs, dimers present various plasmon modes, making it possible to design tunable plasmonic nano-devices. The key feature in study dimers is quantum tunneling effect, which electrons can be transported between the two MNPs via the gap. Since tunneling effect is forbidden in CEM, it become a main source of error for CEM in describe optical responses of multi-particle systems. This issue, however, can be figured out by SE-CEM/SSE-CEM easily through the overlapping of shell regions. If two MNPs are very closed to each other, then there should be an overlap of their shell regions, which could enable transition of electrons through these two MNPs even though contact regime is not reached.

Another advantage of SE-CEM/SSE-CEM in multi-particle plasmonics is that the transition between different regime can be smoothly realized. This phenomenon reflects the physical reality. With the gap separation decreased gradually to zero, based on our prediction, the local field enhancement cannot be significantly increased. If the separation of poles is less than 5 Å, the field enhancement would even decrease due to tunneling effect.

7.2 Future work

Inspired by the achievements obtained in this work, more future works are to be conducted to setup a more generalized semi-quantum semi-classical model.

7.2.1 More complex multi-particle structures

Multi-particle plasmonic structures made by noble metals are promising to exhibit various interesting plasmonic modes^{4,5}, however, due to the limitation of theoretical tools, current studies focus on dimers only. One advantage of SE-CEM/SSE-CEM is that it naturally

includes a lot of quantum nonlocal effects by the core-shell pseudo-permittivity. Therefore, SE-CEM/SSE-CEM is readily to be applied to more complex structures without further modifications.

One of the interesting plasmonic structures is the equilateral trimer, as is shown in Figure 7.1. The equilateral trimer structure contains three MNPs, and the geometry center of each MNP would form an equilateral triangle. With the inter-particle separation decreases, tunneling of electron would occur between all the three MNPs, and up to six poles may be formed at resonance mode, forming bonding hexapole plasmon modes. Unlike dimer structures, if gap distance of equilateral trimers is extremely depressed, there is still some vacuum region in the center of the structures, making it easier for greater enhancement of local electric field.

Figure 7.1 Schematic illustration for MNP equilateral trimer structures with various interparticle distance.

Figure 7.2 Schematic illustration for MNP regular tetramer structure in 3D space.

Besides the equilateral trimers, another family of multi-particle structures should be the regular tetramers, as is shown in Figure 7.2. Compared with dimers and equilateral trimers, the regular tetramers can be regarded as 3D plasmonic systems, since the geometry center of the four MNPs in one regular tetramer structure could form a regular tetrahedron in space. What kinds of plasmon mode would these kind of 3D plasmonic system exhibit has not been systematically studied yet, and our SE-CEM/SSE-CEM is promising to complete these tasks.

7.2.2 Semi-quantum approach for Semiconductors

In this project, SE-CEM/SSE-CEM approach focuses on pure alkaline or transition metallic nanoparticles only. For these two elements, their valence electrons contain s-band electrons and d-band electrons only, while p-band electrons are as inner electrons that contribute little in plasmonic resonances.

Although these two kinds of metallic materials are very popular in related studies of plasmonics, other plasmonic materials also exhibit attractive properties. For those materials whose optical properties are not dominated by behaviour of s-band and d-band valence electrons, SE-CEM/SSE-CEM cannot be used. The optical properties of these materials, however, as discussed in Chapter 4, are also functionals of valence electron densities, and optical response of these valence electrons can also be described as pseudo-permittivity in the same manner as SE-CEM/SSE-SEM. By next step, we're planning to study the behaviour of p-band electrons⁶⁻⁸, a very important valence electrons in optical properties of semi-conducting materials⁹⁻¹¹.

Moreover, current SE-CEM and SSE-CEM can only be used to predict optical response of electrons inside 3D materials within a core-shell structured model. As a new uprising field, semiconductors with 2D structures also show competitive performance and novel perspective in applications of plasmonics. Due to the unique structural configuration of 2D materials, a lamellar model is to be setup to store the pseudo-permittivity. The challenge of this work lies in coupling of s-band electrons and p-band electrons at the surface of 2D materials. These valence electrons are also referred as sp-coupling electrons, whose properties is very different from either s-band or p-band electrons in bulk materials¹²⁻¹⁵.

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