Theoretical studies of the electromagnetic response of metal nanoparticles

Xuan, Fengyuan

2017

Xuan, F. (2017). Theoretical studies of the electromagnetic response of metal nanoparticles.
Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69938>

<https://doi.org/10.32657/10356/69938>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**THEORETICAL STUDIES OF THE
ELECTROMAGNETIC RESPONSE OF
METAL NANOPARTICLES**

XUAN FENGYUAN

INTERDISCIPLINARY GRADUATE SCHOOL

ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)

2017

**THEORETICAL STUDIES OF THE
ELECTROMAGNETIC RESPONSE OF METAL
NANOPARTICLES**

XUAN FENGYUAN

Interdisciplinary Graduate School

Energy Research Institute @NTU (ERI@N)

A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of

Doctor of Philosophy

2017

Acknowledgements

I would like to thank my supervisors, Claude Guet and Su Haibin, for their inspiring and patient guidance of my PhD work. Discussions with my friends, Zhang Chaodong, Wang Jianfeng, Sun Zhiyuan and Wu Can are also very helpful and I appreciate their help very much. I also wish to express my thanks to my mentor, Zhang Baile. This PhD project is supported by Energy Research Institute at Nanyang Technological University (ERI@N). Calculations are performed on cluster of High Performance Computing Centre in Nanyang Technological University (HPCC/NTU).

Table of Contents

Acknowledgments	i
Table of Contents	iii
Abstract	vii
Table Captions	ix
Figure Captions	xi
Abbreviations	xv
Chapter 1 Introduction	1
1.1 Problem Statement	2
1.2 Objectives and Scope	4
1.3 Dissertation Overview	5
1.4 Findings and Outcomes	6
Chapter 2 Literature Review	9
2.1 Classical Approach	10
2.2 Electronic Shell Structure	13
2.3 Jellium Model	14
2.3.1 HF-RPAE Approach	15
2.3.2 KS-TDLDA Approach	18
2.4 Lithium Cluster	25
2.5 Silver Cluster	25
2.6 Rare-gas Matrix Effect	30
2.7 Questions to Answer	31
Chapter 3 Theoretical Methods	33
3.1 Hatree-Fock Equations	34
3.2 Radial Hatree-Fock Term	35
3.3 B-spline Method	38

3.4	Random Phase Approximation with Exact Exchange	40
3.5	Energy-weighted Sum Rule	46
3.5.1	Sum Rule for Hartree-Fock Approximation	47
3.5.2	Sum Rule for Random Phase Approximation	48
Chapter 4	Pseudopotential Method	51
4.1	Model	52
4.2	Numerical Details	53
4.2.1	Modified Radial Hatree-Fock Equations	55
4.2.2	Modified f-sum Rule	56
4.3	Numerical Results for Li Clusters	61
4.4	Conclusion	66
Chapter 5	Core Polarization Corrections	67
5.1	Polarizable Jellium Model	69
5.1.1	Core Polarizability	70
5.2	Numerical Results	71
5.3	Effective Dielectric Screening	81
5.4	Conclusion	83
5.5	Appendix A: Jellium Averaging Approach	84
5.5.1	Cutoff Function	85
5.5.2	Two-body Correction	85
5.6	Appendix B: Jellium Polarization Interaction	87
Chapter 6	Matrix Effect	89
6.1	Model	90
6.1.1	Screened Coulomb Interaction	91
6.1.2	Dielectric One-body Term	91
6.1.3	Conduction Band Minima	92
6.2	Numerical Results	94
6.3	Conclusion	97
6.4	Appendix A: Derivation of the Dielectric Potential	98
6.4.1	When $r_i > R_J$	99
6.4.2	When $r_i < R_J$	100
6.5	Appendix B: Another Approach to Matrix Polarization Effect . .	101
6.5.1	Classical theory	107

Chapter 7	Discussion and Future Work	113
7.1	Discussion	114
7.2	Future Work	118
References		121

Abstract

This PhD project develops a set of theoretical models to explain and predict the electromagnetic response, mainly optical, of metal nanoparticles with sizes ranging from sub-nanometer to hundreds of nanometers and bulk. The focus is on the transition from purely quantum effects to classical description. For sake of clarity the project aims at identifying and modeling the hierarchy of effects that control the optical response of metal clusters. Therefore simple metals such as sodium and lithium will be considered in spite of their lack of interest for practical applications. They serve to define the zeroth approximation in which important effects can be revealed. The next step will be to consider noble metal nanoparticles and focus on the particular role of d-electrons and how it can be modeled while keeping the optical response driven by fully delocalized valence electrons. In order to estimate this effect we introduce a modified HF-RPAE (RPA with exact exchange). The jellium background of Ag cores is treated as a polarizable sphere, which screens the dipole component of the electron-electron interaction. Our model gives the blue shift as cluster size decreases for cationic Ag clusters which is in good agreement with experimental data. As a lot of experimental photo absorption measurements are done for silver clusters embedded in rare-gas matrix, we propose a dielectric screening model for the delocalized valence electrons. The dipole surface resonance peak of large clusters is shifted to lower energy significantly as the dielectric constant increases from $\epsilon_{He} = 1.05$ to $\epsilon_{Ar} = 1.6$. An alternative quantum mechanical description of the matrix polarization effect is also presented and shows good agreement with classical dielectric screening model.

Table Captions

Table 2.1	Hartree-Fock eigenvalues of Na39- 40 and 41+.	18
Table 2.2	Static dipole polarizabilities (a_0^3) for sodium clusters Na_N	18
Table 4.1	f-sum comparison with previous work (1) on Li clusters. Good agreement can be found.	65
Table 5.1	Change of the eigenvalues of Ag20 by the core-polarization correction.	72
Table 5.2	Change of the eigenvalues of Ag21+ by the core-polarization correction.	73
Table 5.3	Change of the eigenvalues of Ag58 by the core-polarization correction.	73
Table 5.4	Static dipole polarizabilities (a_0^3) for silver clusters Ag_N	73
Table 6.1	Parameters for rare-gas matrices. (2, 3, 4)	97
Table 6.2	Calculated HF ionization potential (IP) of Ag8 embedded in argon matrix.	97
Table 6.3	Calculated HF ionization potential (IP) of Ag198 embedded in argon matrix.	98

Figure Captions

Figure 1.1	Reproduced from Ref. (5).	2
Figure 2.1	Optical absorption spectrum using Equation 2.1 with experiment Na dielectric function.	11
Figure 2.2	Optical absorption spectrum using Equation 2.1 with experiment Li dielectric function.	11
Figure 2.3	Optical absorption spectrum using Equation 2.1 with experiment Ag dielectric function.	12
Figure 2.4	Optical absorption spectrum using Equation 2.1 with experiment Au dielectric function.	12
Figure 2.5	Oscillator strength of sodium clusters ($N=8, 20, 58, 92, 138, 198$). Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength. Also the experimental photo absorption spectra results from Ref. (6) for Na_8 and Na_{20} are provided, as shown by the black errorbars. . .	19
Figure 2.6	Oscillator strength of sodium clusters ($N=39-, 40, 41+$). Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.05\omega_k$) of the oscillator strength. Also the experimental photo absorption spectra results from Ref. (7) for Na_{41}^+ are provided, as shown by the black errorbars.	20
Figure 4.1	Non-local pseudo-potential corrected Jellium Model results for free lithium clusters: $Li_8; Li_{20}; Li_{40}; Li_{58}; Li_{92}$. Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength.	62

Figure 4.2	Non-local pseudo-potential corrected Jellium Model results for free lithium clusters: Li9+; Li21+; Li41+; Li59+; Li93+. Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength.	63
Figure 4.3	Experimental data (black circles) for Li9+ and Li21+ compared with previous RPAE calculation results (dash-dotted line), which used the same method as discussed in this chapter. This figure is replotted from reference (8).	64
Figure 4.4	Non-local pseudo-potential corrected (red) and pure (blue) Jellium Model results for free Li139+ compared with experimental data (black). Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.060\omega_k$) of the oscillator strength. Black dots with error bars are experimental data from reference (9).	65
Figure 5.1	Photo absorption cross section ($\text{\AA}^2$) of free silver cationic clusters as function of dipole transition energy (eV). Red dots with errorbars are experiment results (10). The blue vertical lines give the discrete oscillator strength distribution calculated by RPAE with the core polarization modified jellium model. The continuous blue line is a Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength distribution. Note that the Lorentzian shape convolution of Ag_{59}^+ is rescaled by a factor of 50/58 to compare with experimental data for Ag_{50}^+	75
Figure 5.2	Photo absorption cross section ($\text{\AA}^2$) of free silver anionic clusters as a function of dipole transition energy (eV). Red dots with errorbars are experiment results (11). The blue vertical lines give the discrete oscillator strength distribution calculated by RPAE with the core polarization modified jellium model. The continuous blue line is a Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength distribution.	76

- Figure 5.3 Photo absorption cross section ($\text{\AA}^2$) of free silver cationic clusters as a function of dipole transition energy (eV). Blue vertical drop lines are oscillator strengths calculated by RPAE within a pure jellium model. Red vertical drop lines are oscillator strengths calculated by RPAE within a core polarization modified jellium model. The continuous lines are Lorentzian shape convolutions ($\gamma=0.065\omega_k$) of the corresponding oscillator strength distributions. 78
- Figure 5.4 Photo absorption cross section ($\text{\AA}^2$) of free silver anionic clusters as a function of dipole transition energy (eV). Ag_9^+ ; Ag_{19}^+ ; Ag_{57}^+ ; Ag_{137}^+ ; Ag_{197}^+ . Blue vertical drop lines are oscillator strengths calculated by RPAE within a pure jellium model. Red vertical drop lines are oscillator strengths calculated by RPAE within a core polarization modified jellium model. The continuous lines are Lorentzian shape convolutions ($\gamma=0.065\omega_k$) of the corresponding oscillator strength distributions. 79
- Figure 5.5 Photo absorption cross section of free silver neutral clusters as a function of dipole transition energy (eV). Blue vertical drop lines are oscillator strengths calculated by RPAE within a pure jellium model. Red vertical drop lines are oscillator strengths calculated by RPAE within a core polarization modified jellium model. The continuous lines are Lorentzian shape convolutions ($\gamma=0.065\omega_k$) of the corresponding oscillator strength distributions 80
- Figure 5.6 Theoretical evolution of the surface plasmon peak (eV) as a function of the inverse radius $\text{\AA}^{-1}$ of silver clusters: cationic clusters (green), anionic clusters (red), neutral clusters (blue). RPAE calculations with the core polarization modified jellium model. 81
- Figure 6.1 Vertical drop lines are oscillator strength distribution calculated by RPAE for: free Na8, Na8Ar without V_{se} , Na8Ar without V_0 , Na8Ar. Continuous line is Lorentzian shape convolution ($\Gamma = 0.01\omega_k$ and $d = r_{mWS}$) 96

Figure 6.2	Blue vertical drop lines are oscillator strength distribution calculated by RPAE for: free Ag8, Ag8 in He, Ag8 in Ne, Ag8 in Ar. Red solid lines indicate the experiment peak position from references(12, 13, 14). Continuous blue line is Lorentzian shape convolution ($\Gamma = 0.01\omega_k$ and $d = r_{mWS}$)	108
Figure 6.3	Vertical drop lines are oscillator strength distribution calculated by RPAE for: Ag198 in Ar with parameter $d=0.0, 0.5, 0.8$ and 1.0 . Continuous line is Lorentzian shape convolution ($\Gamma = 0.065\omega_k$)	109
Figure 6.4	Vertical drop lines are oscillator strength distribution calculated by RPAE for: free Ag138, Ag138 in He, Ag138 in Ne, Ag138 in Ar. Continuous line is Lorentzian shape convolution ($\Gamma = 0.065\omega_k$)	110
Figure 6.5	Vertical drop lines are oscillator strength distribution calculated by RPAE for: free Ag198, Ag198 in He, Ag198 in Ne, Ag198 in Ar. Continuous line is Lorentzian shape convolution ($\Gamma = 0.065\omega_k$)	111
Figure 6.6	(a) Local field factor f_L for uniform rare-gas matrix; (b) Local field factor f_L^m and f_L^c for embedded cluster.	111

Abbreviations

CI	Configuration Interatction
CP	Core Polarization
DFT	Density Functional Theory
HF	Hartree-Fock approximation
IP	Ionization Potential
JM	Jellium Model
KS	Kohn-Sham
LDA	Local Density Approximation
LSPR	Localized Surface Plasmon Resonance
RPA	Random Phase Approximation
RPAE	Random Phase Approximation with exact Exchange
SP	Surface Plasmon
TDDFT	Time Dependent Density Functional Theory
TDHF	Time Dependent Hartree-Fock approximation
WS	Wigner Seitz
XC	Exchange-Correlation

Chapter 1

Introduction

In this chapter, the motivation and objectives of this PhD project are introduced. They are to be found in the rapid development of nano-devices providing a strong electromagnetic field enhancement for energy harvesting in photovoltaics, molecule detection, etc. A short overview of this thesis is given. Major outcomes are summarized, that is, core-polarization-modified RPAE for jellium silver clusters and dielectric screening effect on the electron-electron electron-ion interaction for metal clusters embedded in rare-gas matrices.

Figure 1.1: Reproduced from Ref. (5).

1.1 Problem Statement

During the last three decades, metal nanoparticles (15, 16, 17) have attracted extensive attention due to their promising applications (18, 19, 20). Among them, the possibility of using metal nanoparticles to enhance electric field is a very hot topic because of its use in increasing light trapping in photovoltaic devices, and therefore improved absorption efficiency, which is the motivation of this PhD project. Along with experimental research there is a strong need of better theoretical understanding of the optical properties of such metal nanoparticles and how they vary with size, structure, shape, assembly.

As the main cost of photovoltaic devices comes from semiconductor materials such as Si, GaAs which convert light to electricity, plenty of research work has been devoted to designing thin film solar cells. However, thin layers of semiconductor materials in photovoltaic devices usually mean short effective path of light which further leads to low light absorption efficiency. Two strategies of using metal nanoparticles to increase effective optical path in thin film solar cell have been proposed. In Fig 2a of reference(5) (for clarity, it is reproduced in Figure 1.1), the top layer of metal nanoparticles prefers to scatter sunlight into the semiconductor materials below and reflect the light transmitting in the devices back. In Fig 2b of reference (5), the middle layer of metal nanoparticles prefers to localize the light in the semiconductor materials by surface plasmon excitation and enhance the electric field around them. To realize these designs, one needs to ask several questions: which metal shall be chosen; which size of nanoparticle shall be made; or more generally, under what condition does a metal nanoparticle behave in controlled way. Noble metals, like Ag and Au, have absorption reso-

nance frequency in the optical range which means that they are good candidates for sunlight harvesting and ideal for photovoltaic devices. On the other hand, noble metals are expensive which makes people search for substitute like copper. To answer the second question, one needs to understand the physical phenomena that rule the size dependence of the optical response of different metal nanoparticles and of the excitation relaxation process. This is what this PhD project is about, theoretical study of optical response of noble metal nanoparticles.

Classical, semi-classical and quantum mechanical modelings of the optical response of a wide range of metal nanoparticles have been done (15, 21, 22). Typically when the radius of nanoparticle is much larger than 10 nm, a classical description based on Maxwell equations can give the right results. As the size of nanoparticles reach the scale of nanometers, quantum mechanical methods become necessary. For example, the Mie theory for about 1 nm radius sodium nanoparticles gives 3.4 eV for the resonance frequency, which is significantly larger than the experimental result, 2.8 eV. Discrepancies of classical surface plasmonic frequencies and experimental values are observed for all nanometric particles (lithium, silver and gold,), however the shifts can be either red or blue and do not show a systematic trend that would barely scale with radius.

The quantum study of sodium clusters has shown that the red-shift of resonance frequencies compared to Mie theory is due to both the spill-out electrons and the coupling between collective motion and intrinsic motion of valence electrons, which are all quantum effects (23). The random phase approximation with exact exchange energy for Na Jellium Model directly generates the oscillator strength distribution with a peak around 2.8 eV. Indeed, the simple Jellium Model works extremely well for sodium clusters as it easily explains the magic number of atoms in sodium clusters (24). The Schrodinger equation for the valence electrons of sodium in Jellium Model predicts shell structure just like in an atom. Closed electronic shell clusters are more stable than partially filled shell clusters. For these small clusters it is not the atomic arrangement but rather the electronic shell filling that governs the overall stability.

Unfortunately, sodium is the only metal that can be described by simple Jellium Model. The very same theoretical calculation for lithium clusters still could

not give the right absorption spectrum. To extend Jellium Model to the case of lithium, researchers have proposed to use a non-local pseudo-potential to describe the interaction between delocalized valence electrons and localized core electrons, and obtained quite good results (1, 25, 26). However, only simple elements such as Lithium and Sodium have received successful quantum mechanical treatment. For noble metal nanoparticles, such as Au and Ag, a theoretical description that is reliable over a large range of sizes is still an open question due to the difficulty of dealing with the $5s$ - $4d$ and $6s$ - $5d$ electron interaction and relativistic effects of inner shell electrons.

1.2 Objectives and Scope

Previous studies have shown that the simple Jellium Model works extremely well for Sodium nanoparticle (15). One only needs to treat one electron per atom for Na clusters which reduces the computation time to a large extent. This is because the valence electron of Na is highly separated from the other core electrons which are closely attached to the nucleus. Although Lithium seems an even simpler element, Jellium Model is not accurate enough to describe it. Nevertheless the Jellium Model for Li can still be corrected with a non-local potential (1) in order to treat one electron per atom. Although one could get accurate results for noble metal clusters by quantum chemistry method or simply taking care of 11 electrons ($4d$ and $5s$) per atom, it gives no physical understanding of the motion of electrons and remains limited to very small clusters. Up to now, no satisfying result of modified Jellium Model based HF-RPAE approach for silver cluster has been reported.

The main objective of this PhD project is to develop a core-polarization corrected RPAE formalism for the delocalized valence electrons of silver clusters. One need to investigate how the localized $4d$ electrons of the silver core screen the delocalized $5s$ electrons in silver clusters and distinguish the present model from TDLDA approach. Reason for the size-dependency of the dipole surface plasmon peak will be identified according to the core-polarization corrected RPAE formalism. Experimentally, silver clusters that are embedded in rare-gas matrices are more suitable for photo absorption measurements. However only a few

theoretical studies of the media effect exist (27, 28, 29) and no quantum mechanical calculation has been reported for embedded large metal clusters. To have a complete understanding of the optical response for both free and embedded metal clusters from a jellium model based HF-RPAE point of view, the second objective is to study the dielectric effect of the rare-gas matrices and show how the surface plasmon spectrum is shifted by this effect. The present model for the inert environment could also help understanding the optical response of metal clusters embedded in thin film solar cell. Hopefully this thesis could serve as a quite complete review of and fill the gaps in metal cluster physics.

1.3 Dissertation Overview

Chapter 1: A general introduction of the motivation for this PhD project is given. Objectives of this project are stated and major findings are summarized. Overview of this thesis is presented.

Chapter 2: A detailed literature review on the development of theoretical metal cluster physics is provided. Jellium model based density functional theory (DFT) time-dependent density functional theory (TDDFT) are reviewed and compared to Random Phase Approximation with exact Exchange (RPAE). Several important experimental work are also discussed to support the theoretical model.

Chapter 3: The three theoretical methods, that is, Hartree-Fock approximation, B-spline method and Random Phase Approximation with exact Exchange (RPAE) are presented in detail and simplified to several radial problems. These are the fundamental theoretical basis for the codes that are used in the present thesis.

Chapter 4: A repetition of theoretical work in the reference of (1) is presented. This chapter shows numerical calculations of the oscillator strength for lithium clusters with non-local ionic pseudo-potential and the comparison with the original work. A good agreement on both the distribution pattern and summation of the oscillator strength is found, which serves as a benchmark.

Chapter 5: A core-polarization-corrected Random Phase Approximation matrix equation is presented for the surface plasmon in silver clusters. A Jellium-like

model for the valence electrons in silver clusters is developed. The background of Ag cores is considered as a spherical polarizable Jellium which leads to a core-polarization two-body interaction and a self-energy potential for the valence electrons. The core-polarization corrections are implemented into Hartree-Fock equations and matrix Random Phase Approximation equation. Oscillator strength of anionic, neutral and cationic Ag clusters have been calculated and are compared with pure Jellium calculations. The effects of the one-body and two-body corrections on the oscillator strength distribution are identified. A clear blue shift is found for cationic Ag clusters as clusters size decreases which is in good agreement with experimental results.

Chapter 6: The effect on the optical response of metal clusters from the surrounding rare-gas media is discussed. A dielectric potential is presented for the extra free electrons in the media. This dielectric potential, which is written into a multipole expansion form, has been frequently used in quantum mechanics calculations inside quantum dots. It further reduces to a two-body interaction, which screens the bare Coulomb interaction, and a self-energy potential. The singularity of one-body self-energy potential on the interface between the metal clusters and the rare-gas media is corrected by a position dependent dielectric function of the rare-gas matrix.

Chapter 7: A general discussion of this PhD work in the last four years time is given. Connection between the dielectric matrix effect and silver core polarization corrections is made. Possible future work is presented.

1.4 Findings and Outcomes

There are mainly two outcomes in this PhD project: study of core-polarization-modified Random Phase Approximation for silver clusters and that of dielectric screening effect on the electron-electron and electron-ion interaction for metal clusters embedded in rare-gas matrices.

Finding 1: One takes into account the d -electron screening effect in silver clusters by adding a core-polarization correction term to the Hamiltonian for the valence electrons. The core-polarization correction further leads to a one-body

self-energy attractive potential and a two-body screening term on the dipole component of bare Coulomb interaction $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$. These effects lead to a modified Hartree-Fock equation, where only the exchange potential is screened. Meanwhile one is left with a core-polarization corrected matrix Random Phase Approximation equation, where the Hartree term of the matrix element is strongly screened. The one-body and two-body corrections are competing effects and they give a blue and red shift, respectively, to the plasmon peak position. Core-polarization-modified Random Phase Approximation calculation is done for neutral and cationic ($N=8 - 198$) Ag clusters. A significant size-dependence red shift of the collective dipole oscillation peak is found due to core-polarization correction, which means that the two-body dipole screening dominates the core-polarization correction. The size-dependence of the correction comes from two aspects: (i) the effect from the one-body polarization correction is getting stronger as cluster size decreases; the effect from the two-body polarization correction remains the same. Since the one-body polarization correction shifts the plasma peak to high energy, the total core-polarization correction contributes to the blue shift. (ii) As cluster size increases, there are more embedded Ag ions, which have larger polarizability than free ion. As discussed above, the total core-polarization correction gives a red shift, which will become less significant as cluster size decreases and thus a blue shift. The larger the polarizability, the stronger screening the valence electrons will feel.

Finding 2: Since there is a lack of theoretical study on large embedded metal clusters and for a complete understanding of metal cluster physics, the rare-gas environment is modeled as a macroscopic infinite dielectric media. The electron-electron (e-e) and electron-ion (e-i) Coulomb interaction are both screened. The conduction band minima of the the rare-gas matrix modifies the vacuum zero energy and can be included as an energy barrier for the delocalized electrons of the metal cluster. The dielectric screening and the energy barrier are implemented into the HF-RPAE. The screening on the e-e interaction and e-i interaction lead to opposite direction shift of the collective dipole oscillation peak. Calculations on Na and Ag clusters embedded in He Ne Ar matrix were done. A significant red shift of the oscillator strength peak is found for large clusters due to dielectric matrix effect. The screening on the Coulomb interaction between electrons makes

the electrons more bounded and shifts the plasmon peak to higher energy, which is the major correction for small embedded clusters, while that on the jellium background unbound the electrons and shifts the plasmon peak to lower energy and it dominates rare-gas dielectric effect for large embedded clusters. The energy barrier effect is only a minor effect compared to the dielectric screening. The largest magnitude of the shift reaches 1eV for Ar matrix with a dielectric constant of $\epsilon_{Ar} = 1.6$, while the He droplet with a dielectric constant closed to 1 ($\epsilon_{He} = 1.05$) almost gives no change. The present model should work for large metal clusters embedded in rare-gas matrix and could serve as a theoretical tool for a systematic study of the optical response of various metal clusters embedded in an inert environment.

Chapter 2

Literature Review

In this chapter, first a general review on metal cluster physics will be given. Then the development of Jellium Model will be shown, which is the main method the present thesis uses. Two approaches, HF-RPAE and KS-TDLDA, are compared. Finally, a more detailed literature review on silver clusters, from both experimental and theoretical sides, is presented and how this work differs from the previous ones is discussed.

2.1 Classical Approach

As mentioned in Chapter 1, the objective of this PhD project is to study the optical response of metal nanoparticles from a quantum mechanical point of view. To start with, one needs to know the most important classical electrodynamics conclusions on the metal sphere-light interaction, which can be seen as a benchmark for the quantum mechanical calculations. For a detailed review of the classical approach to cluster physics one could use reference (30). In long wave length limit, classically, the metal sphere-light interaction can be considered as a response problem of a dielectric sphere to a oscillating uniform electric field. By solving the Maxwell equations one could find the scattering field. If there is an imaginary part of the dielectric function, the absorption cross section can be written as,

$$\sigma(\omega) = \frac{4\pi\omega R^3}{c} \text{Im} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \quad (2.1)$$

Here the optical absorption spectrum of Na, Li, Ag and Au are provided using the experimental dielectric function data in Figure 2.1-2.4. The photo absorption spectrum calculated by quantum mechanical method should converge to these classical results for large cluster limit. If one inserts a Drude model for the dielectric function of metal cluster,

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \quad (2.2)$$

one gets the classical Mie formula for the surface plasmon peak position:

$$\omega_{\text{Mie}}^2 = \frac{\omega_p^2}{3}, \quad (2.3)$$

where,

$$\omega_p = \sqrt{\frac{\rho_e e^2}{\epsilon_0 m_e}}. \quad (2.4)$$

Figure 2.1: Optical absorption spectrum using Equation 2.1 with experiment Na dielectric function.

Figure 2.2: Optical absorption spectrum using Equation 2.1 with experiment Li dielectric function.

Figure 2.3: Optical absorption spectrum using Equation 2.1 with experiment Ag dielectric function.

Figure 2.4: Optical absorption spectrum using Equation 2.1 with experiment Au dielectric function.

2.2 Electronic Shell Structure

In 1984, the mass-spectra experiment, conducted by Knight (24), showed that Sodium atoms tend to aggregate with magic numbers ($N=8, 20, 40, 58, 92, \dots$ Fig 1a of reference (24)). The authors argued that this phenomenon is governed by the electronic shell structure of sodium clusters rather than the atom packing pattern once had been used to explained the 'magic numbers' of rare-gas clusters. A one-electron potential well picture is used for the $3s$ valence electrons of the sodium atoms to fill in. The effective one-particle potential, which takes into account of the electron-ion and electron-electron interactions, is approximated by Woods-saxon potential under a spherical symmetry. Eigenvalues of the effective one particle Schrodinger equation was solved and summed to get the total electronic energy $E(N)$. The energy difference is defined by $\delta(N) = E(N) - E(N - 1)$ and $\delta(N + 1) - \delta(N)$ was plotted against N (please see Fig 1b of reference (24)).

$$\delta(N + 1) - \delta(N) = E(N + 1) + E(N - 1) - 2E(N) \quad (2.5)$$

The peak at N means that $2E(N)$ is much smaller than $E(N + 1) + E(N - 1)$ which suggests that clusters constructed by N atoms is much stable than its neighbours. And they occur when the electronic shell with a certain azimuthal quantum number L is fully filled, which corresponds to the magic number of sodium atom aggregation. Thus electronic shell structure in alkali clusters was discovered and ever since then much attention has been paid to metal cluster physics, both experimentally and theoretically. First ionization potential and optical absorption spectrum for alkali clusters have been measured (6, 31, 32, 33, 34, 35, 36, 37). The most important feature of Na clusters from Knight's mass-spectra experiment and the one-electron potential well picture, is that all of the sodium $3s$ valence electrons move freely inside the cluster. And the binding of the ground state of these $3s$ electrons is roughly captured by a Woods-saxon potential well which means that the arranging of the sodium ions is not important. The sodium cluster with N atoms is like a super-atom, with a distributed ionic charge of N . This leads to the fundamental Jellium Model (JM) approximation in the present quantum calculations(see next section). At this stage, one can only conclude that the ground state properties of sodium cluster is governed by the nearly free $3s$ electrons.

Soon after, optical absorption experiments on sodium clusters were reported and compared with quantum calculation based on JM, which has been used to calculate the ionization energy of metal clusters(38). Although the ionic structure is completely neglected in Jellium Model, it reproduces the position of plasma resonance peak and its red shift as cluster size decreases surprisingly well. It was thus settled that the optical properties of small Sodium clusters, to a first approximation, can be understood by a quantum description of the nearly free valence electrons in a uniformly distributed ion background (Jellium Model(39, 40, 41)). Therefore JM could also serve as a starting point of further study of the electronic structure in more complex metal clusters like lithium, silver and gold clusters. (The giant peak in the photo absorption spectra of metal clusters were named as surface plasmon. Later volume plasmon at high energy range have also been measured (42, 43, 44, 45). This thesis is only focused on surface plasmon.)

2.3 Jellium Model

Firstly the theoretical Jellium Model will be presented in this section, and then discuss about RPAE and TDLDA. Finally some important numerical results are compared with experiment data. (Note that from now on, the many body effect, that is, Coulomb direct interaction and exchange-correlation effect, is considered by a self-consistent calculation, which differs from the very early Knight's Woods-saxon one-particle picture.) In a pure JM, cluster of N metal atoms with one valence electron can be regarded as a system of N electrons (one valence electron per atom) confined by a uniformly charged ionic background. The ground state and excited state properties of the cluster can be obtained by solving the Schrodinger equation of these N electrons. The Hamiltonian is given by,

$$H = \sum_i \left(-\frac{\hbar^2}{2m_e} \nabla^2 \right) + \sum_i V_{JM}(\mathbf{r}_i) + \sum_{i < j} k_e \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.6)$$

One would adopt atomic units from now on without special statement,

$$H = \sum_i \left(-\frac{1}{2} \nabla^2 \right) + \sum_i V_{JM}(\mathbf{r}_i) + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = T + V_{bkg} + V_{ee} \quad (2.7)$$

The jellium background potential $V_{JM}(r)$ is easily found for a uniformly charged sphere,

$$V_{JM}(r) = \begin{cases} -\frac{N}{2R_J}(3 - (\frac{r}{R_J})^2) & \text{if } r < R_J \\ -\frac{N}{r} & \text{if } r > R_J. \end{cases}$$

As the confining Jellium potential deviates from a harmonic oscillator potential only outside, one can use the Kohn theorem for a zeroth order estimate. The Kohn theorem states that for a system with interacting particles in a confining external harmonic oscillator potential, a single state contains the whole dipole strength (46, 47, 48, 49, 50). The frequency of this collective mode is equal to that of the confining potential, independently of the interaction among the particles and of the number of particles. The electron-ion potential inside the jellium sphere is a harmonic oscillator with a frequency given by:

$$\omega_{ho}^2 = \frac{k_e e^2}{m_e r_s^3}, \quad (2.8)$$

where r_s is the Wigner-Seitz radius.

2.3.1 HF-RPAE Approach

Now one is left with a quantum many body problem, N electrons confined by a spherically symmetrized potential $V_{JM}(r)$. There are two approaches to solve this problem numerically. The first one is approximating the ground state by a single determinant and using Hartree-Fock approximation (HF) to obtain the one-electron orbital. Since the jellium potential has spherical symmetry, the one-particle wave function is,

$$\phi_i(\mathbf{r}) = \frac{R_{nl}(r)}{r} Y_{lm}(\Omega) \quad (2.9)$$

The one-particle HF equations (51, 52) is,

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + v_{HF} + v_{JM} + \frac{l(l+1)}{2r^2}\right) R_{nl}(r) = \epsilon_{nl} R_{nl}(r) \quad (2.10)$$

where v_{HF} contains HF direct and exchange potential. Note that the HF exchange potential automatically corrects the self-interaction in the direct part and overall

it gives the correct $-1/r$ asymptotic behaviour at long distance. The HF ground state energy is,

$$\langle E \rangle = \sum_i (\epsilon_i - \frac{1}{2} \langle i | v_{HF} | i \rangle) \quad (2.11)$$

By confining the N electron system in a large sphere wall one can find a complete set of occupied and unoccupied HF orbitals, with which the matrix Random Phase Approximation with exact Exchange (RPAE) equation below gives the many-body excited states.

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X^k \\ Y^k \end{pmatrix} = \omega_k \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X^k \\ Y^k \end{pmatrix} \quad (2.12)$$

where,

$$A_{mi,nj} = (\epsilon_m - \epsilon_i) \delta_{mn} \delta_{ij} + \langle mj | \frac{1}{r_{12}} | in \rangle \quad (2.13)$$

$$B_{mi,nj} = \langle mn | \frac{1}{r_{12}} | ij \rangle \quad (2.14)$$

In the RPAE matrix equation, the many-body excited states are approximated by linear combination of single excitation Slater determinant (one-particle one-hole state). The eigenvalues ω_k correspond to the excitation energy of the N electron system and the eigenvectors, X_{ma}^k, Y_{ma}^k , represent the excited states, satisfying the normalization equation. Note that the ground state of the N electron is also corrected by double excitation Slater determinants through matrix elements B . The dipole transition amplitude from many-body ground state $|0\rangle$ to excited state $|k\rangle$ and its oscillator strength f_k can be calculated by

$$\langle k | Z | 0 \rangle = \sum_{i,m} [X_{mi}^k \langle m | z | i \rangle + Y_{mi}^k \langle i | z | m \rangle] \quad (2.15)$$

$$f_k = \frac{4}{3} \omega_k |\langle k | Z | 0 \rangle|^2 \quad (2.16)$$

The total energy of the metal cluster in a Jellium Model will be

$$E_{tot} = E_{ion-ion} + E_{e-e} + E_{e-ion} \quad (2.17)$$

The HF ground state calculation gives the electron-electron energy E_{e-e} and the electron-ion E_{e-ion} energy. The ionic self-energy $E_{ion-ion}$ is,

$$E_{ion-ion} = \frac{1}{2} \int \rho_{ion}(r) V_{JM}(r) dr = \frac{3N^2}{5R_J} \quad (2.18)$$

The present calculation are all based on the HF-RPAE approach and the details of the theoretical methods will be given in the next Chapter. Red shift of experiment surface plasmon peak with respect to classical Mie frequency ($\sqrt{\frac{4\pi\rho_e e^2}{3m_e}}$) can be understood by the well-accepted spill-out effect of the delocalized valence electrons to the vacuum and a many body effect which couples the center of mass and intrinsic electron motions(23).

$$\langle \omega^2 \rangle = \frac{4\pi\rho_0}{3} \left(1 - \frac{1}{N} \int_R^\infty \rho_e(\mathbf{r}) d\mathbf{r}\right) \quad (2.19)$$

$$\sqrt{\langle \omega^2 \rangle} = \omega_{Mie} \sqrt{\left(1 - \frac{\delta N}{N}\right)} \quad (2.20)$$

The oscillator strength fragmented distribution pattern was explained by Landau damping (53). To compare with experiment absorption spectrum results and the previous theoretical calculations, a Lorentzian shape convolution is made for the discrete oscillator strength peaks, which has been used to model the peak broadening (54, 55).

$$\sigma(E) = \frac{2\pi^2}{c} \sum_k f_k \delta(E - E_k + E_0) \quad (2.21)$$

$$f_k = \frac{f_k}{\pi} \frac{\Gamma}{\Gamma^2 + (E - \omega_k)^2} \quad (2.22)$$

where one sets $\Gamma = 0.065\omega_k$ for most of the calculated results without special notification. Figure 2.5 and 2.6 shows some RPAE results for sodium clusters. One can see that as cluster size increase, the collective resonance peak shifts to higher energy. For a fixed number of electrons, the cationic cluster has a narrow spectrum at higher energy, while anionic cluster has a broader spectrum at lower energy. Table 2.1 compares the HF eigenvalues for Na39- 40 and 41+ and shows

Table 2.1: Hartree-Fock eigenvalues of Na39- 40 and 41+.

nl	1s	2p	3d	2s	4f	3p
Na39- (eV)	-6.47	-5.53	-4.16	-3.45	-2.29	-1.51
Na40 (eV)	-8.25	-7.33	-5.96	-5.24	-4.10	-3.29
Na41+ (eV)	-10.07	-9.16	-7.80	-7.06	-5.93	-5.09

Table 2.2: Static dipole polarizabilities (a_0^3) for sodium clusters Na_N .

N	8	20	34	40	58	92	138
This work	755	1808	2807	3529	4619	7178	10667
Ref.(54)	755	1808	2806	3529	4619	7178	10667
Exp.(31)	879±17	2138±43	3520±17	4090±77			

that the electrons in Na41+ is much more bounded. Table 2.2 shows that the static polarizabilities calculated in this work agree well with previous theoretical work (54). Compared with experimental results, the static polarizabilities are systematically lowered which is due to the limitation of Jellium Model.

2.3.2 KS-TDLDA Approach

As a contrast, the second approach to the N-electron many body problem is based on Density Functional Theory (DFT). According to the famous Hohenberg-Kohn theorem (56, 57) the ground state energy of an interacting N-electron system in the external potential V_{ext} is a functional of ground state density. In the case of Jellium background $V_{ext} = V_{JM}$. From here one could adopt the constrained search approach by Levy (58). The ground state energy E can be written as,

$$E = \min_{\Psi} \langle \Psi | H | \Psi \rangle = \min_{\rho} \min_{\Psi \in \rho} \langle \Psi | H | \Psi \rangle \quad (2.23)$$

The minimising search over the Ψ within a density ρ is,

$$\begin{aligned} \min_{\Psi \in \rho} \langle \Psi | H | \Psi \rangle &= \min_{\Psi \in \rho} \langle \Psi | T + V_{ee} | \Psi \rangle + \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \\ &= F[\rho] + \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (2.24)$$

Figure 2.5: Oscillator strength of sodium clusters ($N=8, 20, 58, 92, 138, 198$). Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength. Also the experimental photo absorption spectra results from Ref. (6) for Na_8 and Na_{20} are provided, as shown by the black errorbars.

Figure 2.6: Oscillator strength of sodium clusters ($N=39^-$, 40 , 41^+). Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.05\omega_k$) of the oscillator strength. Also the experimental photo absorption spectra results from Ref. (7) for Na_{41}^+ are provided, as shown by the black errorbars.

where the Hamiltonian is,

$$H = \sum_i \left(-\frac{1}{2}\nabla^2\right) + \sum_i V_{JM}(\mathbf{r}_i) + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = T + V_{bkg} + V_{ee} \quad (2.25)$$

Therefore one sees that the ground state density E is a functional of ρ ($F[\rho]$ is a universal functional for N interacting electrons). Given that the number of electrons is fixed to N .

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad (2.26)$$

Variational principle with a lagrange multipliers μ gives the ground state energy by the Lagrangian equation

$$\frac{\delta F[\rho]}{\delta \rho} + V_{ext}(\mathbf{r}) = \mu \quad (2.27)$$

Now consider a non-interacting ($V_{ee} = 0$) Kohn-Sham N -electron system in a different external potential $V_s = 0$. The Lagrangian equation of this system is,

$$\frac{\delta T_s[\rho]}{\delta \rho} + V_s(\mathbf{r}) = \mu \quad (2.28)$$

One defines exchange correlation functional $E_{xc}[\rho]$ as,

$$F[\rho] = T_s[\rho] + U[\rho] + E_{xc}[\rho] \quad (2.29)$$

where,

$$U[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.30)$$

If there exists a such a non-interacting N -electron system that its ground state energy is same with the target interacting N -electron system, one will have.

$$V_s(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\delta U[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (2.31)$$

Then the ground state energy of the N electron can be obtained by solving non-interacting Kohn-Sham system, which leads to the single particle Kohn-Sham

equation,

$$\left(-\frac{1}{2}\nabla^2 + \sum_i V_{JM}(\mathbf{r}) + V_{Hxc}[\rho, \mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \quad (2.32)$$

And the ground state energy is,

$$\begin{aligned} E = F[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} &= T_s[\rho] + U[\rho] + E_{xc}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \\ &\quad \sum_{i \in occupied} \epsilon_i - U[\rho] + E_{xc}[\rho] - \int V_{xc}[\rho](\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \end{aligned} \quad (2.33)$$

The exchange-correlation functional $E_{xc} = E_x + E_c$ can be separated into exchange part and correlation part. Usually the exchange functional is approximated by the exact expression of uniform electron gas, while there many choice for the correlation functional. For example (59),

$$\begin{aligned} V_{xc}[\rho, \mathbf{r}] &= \frac{\delta[\rho(\mathbf{r})(\epsilon_{xc}\rho(\mathbf{r}))]}{\delta\rho(\mathbf{r})} \\ &= -\left(\frac{9}{4\pi^2}\right)^{1/3} \frac{1}{r_s(\mathbf{r})} - 0.0333 \ln\left(1 + \frac{11.4}{r_s}\right) \end{aligned} \quad (2.34)$$

where,

$$\epsilon_{xc} = -\frac{3}{4}\left(\frac{9}{4\pi^2}\right)^{1/3} \frac{1}{r_s(\mathbf{r})} - 0.0333G\left(r_s\left(\frac{\mathbf{r}}{11.4}\right)\right) \quad (2.35)$$

$$G(x) = (1 + x^3)\ln\left(1 + \frac{1}{x}\right) - x^2 + \frac{x}{2} - \frac{1}{3} \quad (2.36)$$

From Eq. 2.35 one knows that the asymptotic behaviour of the exchange functional at large r is $\rho(r)^{1/3}$. Since the long range behaviour of the radial wave function is e^{-r} , the exchange potential decays exponentially. Although the $1/r$ behaviour can be restored by self-interaction correction (SIC), the HF approach still gives a better ionization potential for sodium clusters(38).

The optical response of N interacting electron system to the external perturbation $H_1(t) = \sum_i \delta V(\mathbf{r}_i, t)$ is given by the linear response theory. (For a detailed

review please see reference (60)) The total Hamiltonian is separated into a time-independent part and a time-dependent perturbation $H(t) = H_0 + H_1(t)$. One defines the density operator in the space coordinate as,

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (2.37)$$

and the time-dependent density operator in the interaction picture

$$\hat{\rho}(\mathbf{r}, t) = e^{iH_0 t} \hat{\rho}(\mathbf{r}) e^{-iH_0 t} \quad (2.38)$$

Under the perturbation $H_1(t)$, the linear response of the electron density is

$$\delta\rho(\mathbf{r}, t) = \int dt \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', t) \delta V(\mathbf{r}', t) \quad (2.39)$$

the density-density response function $\chi(\mathbf{r}, \mathbf{r}', t)$ is

$$\chi(\mathbf{r}, \mathbf{r}', t) = -i\theta(t - t') < \Phi_0 | [\hat{\rho}(\mathbf{r}, t - t'), \hat{\rho}(\mathbf{r}')] | \Phi_0 > \quad (2.40)$$

In the frequency domain, one found the Lehmann representation

$$\delta\rho(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega) \delta V(\mathbf{r}', \omega) \quad (2.41)$$

where

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_i \left(\frac{< \Phi_0 | \hat{\rho}(\mathbf{r}) | \Phi_n > < \Phi_n | \hat{\rho}(\mathbf{r}') | \Phi_0 >}{\omega - \Omega_n + i\eta} - \frac{< \Phi_0 | \hat{\rho}(\mathbf{r}') | \Phi_n > < \Phi_n | \hat{\rho}(\mathbf{r}) | \Phi_0 >}{\omega + \Omega_n + i\eta} \right) \quad (2.42)$$

where Φ_n is the eigen wave function of the interacting N-electron system with the Hamiltonian of H_0 , and Ω_n is the exact excitation energy.

In the same spirit of DFT, Time Dependent Density Functional Theory (TDDFT) gives the time-dependent density $\rho(\mathbf{r}, t)$. According to Van Leeuwen Theorem (which is an analog of KS theorem) the time dependent density $\rho(\mathbf{r}, t)$ of an interacting N-electron system can be found by solving a time dependent non-

interacting N-electron Kohn-Sham system,

$$\left(-\frac{1}{2}\nabla^2 + \sum_i V_s[\rho](\mathbf{r}, t)\right)\phi_i(\mathbf{r}, t) = i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t) \quad (2.43)$$

where,

$$V_s[\rho](\mathbf{r}, t) = V_{ext}(\mathbf{r}, t) + \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}[\rho](\mathbf{r}, t) \quad (2.44)$$

and the time-dependent density for the interacting system is,

$$\rho(\mathbf{r}, t) = \sum_i |\phi_i(\mathbf{r}, t)|^2 \quad (2.45)$$

The linear response function of this KS system is,

$$\delta\rho(\mathbf{r}, t) = \int dt \int d\mathbf{r}' \chi_s(\mathbf{r}, \mathbf{r}', t) \delta V_s(\mathbf{r}', t) \quad (2.46)$$

where,

$$\delta V_s(\mathbf{r}', t) = \delta V_{ext}(\mathbf{r}', t) + \int d\mathbf{r} \frac{\delta\rho(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} + \delta V_{xc}[\rho](\mathbf{r}, t) \quad (2.47)$$

$$\delta V_{xc}[\rho](\mathbf{r}, t) = \int f_{xc}(\mathbf{r}, t, \mathbf{r}', t') \delta\rho(\mathbf{r}', t') d\mathbf{r}' dt' \quad (2.48)$$

equalizing Eqn 2.38 and Eqn 2.46 gives the relation of the density-density response function between the KS system and the interacting system in the frequency domain,

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \chi_s^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad (2.49)$$

where the non-interacting density-density response function $\chi_s(\mathbf{r}, \mathbf{r}', \omega)$ is

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{j,k} (f_k - f_j) \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - \omega_{jk} + i\eta} \quad (2.50)$$

and the exchange correlation kernel in frequency domain is

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \int d(t - t') e^{i\omega(t-t')} \frac{\delta V_{xc}[\rho](\mathbf{r}, t)}{\delta\rho(\mathbf{r}', t')} \quad (2.51)$$

The Random Phase Approximation with exact exchange approach and Time De-

pendent Density Functional Theory approach have been carefully investigated and shown to give similar optical properties for Na clusters (38, 54, 61).

2.4 Lithium Cluster

Compared with classical Mie theory and quantum chemistry calculation, Jellium Model not only keep the quantum nature of electronic structure, but also is computational efficient and can be extended to large systems (cluster of hundreds of atoms). The weakness of Jellium Model is that it treats the valence-core interaction as a pure Coulomb potential, which in many cases is too broad an approximation. In order to extend Jellium Model to metal clusters other than Sodium and Potassium, real valence-core interaction must be taken into account. For example, simple Jellium Model predicts a plasma resonance peak position much higher than experimental measurement for lithium clusters. Also the oscillator strength of the valence electrons of Lithium atoms, clusters and bulk are constantly reduced by 30 percent. Given that the $2s$ electron of Lithium feels a strong L -dependent ionic pseudo-potential, all of these discrepancies can be solved by including a nonlocal norm-conserving pseudo-potential to the Jellium Model (1).

$$V_{ps} = \sum_{L=0}^{\infty} v_L(r) \sum_m |Lm\rangle \langle Lm| \quad (2.52)$$

Effective mass of the delocalized $2s$ valence electrons can be defined from the nonlocality of the pseudo-potential, and it is shown that the difference of the pseudo-potential for the s - and p - waves determines its effective mass. The effective mass obtained by this method agrees well with that from band structure calculation for Lithium. Detailed repetition of this work is given in Chapter 4.

2.5 Silver Cluster

Besides lithium, silver cluster has also been investigated frequently. A specific analysis of experimental techniques is not the goal of this PhD project. For a review, one could refer to (16). The important experimental results will be stressed below. Treating the silver cluster as a classical dielectric sphere the absorption

cross section in the long wavelength can be written as:

$$\sigma(\omega) = \frac{4\pi\omega R^3}{c} \text{Im} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \quad (2.53)$$

Using experimental data for dielectric function one gets the classical limit of the surface plasmon resonance in Figure 2.3. Inserting Drude mode for the dielectric function, one obtains classical Mie frequency at 5.18eV :

$$\omega_{\text{Mie}}^2 = \frac{e^2}{mr_{\text{WS}}^3}, \quad (2.54)$$

where r_{WS} is the Wigner-Seitz radius. From figure 2.3 one knows that the classical limit of the surface plasmon resonance peak of free Ag clusters is at about 3.5eV . Obviously there is huge difference between the Mie frequency and experiment classical limit. Typically a pure JM calculation will give 5.18eV for large clusters. How to modify the JM for silver clusters is one of the objectives.

In 1970, Kreibig and Zacharias conducted electron surface plasma losses and optical extinction bands measurement for embedded and colloid Ag nanoparticles with diameter from about $100\text{\AA}$ to $800\text{\AA}$ (62). They then used the hydrodynamical equations by Fujimoto and Komaki (63) to study the interaction between electron and metal sphere. Electron passing through the metal sphere will lose energy to a sequence of surface plasma oscillation mode, with oscillation frequency,

$$\omega_l = \frac{\omega_p}{\sqrt{1 + \frac{l+1}{l}\epsilon_a}}, l = 1, 2, 3, \dots \quad (2.55)$$

where, ω_p is the bulk plasma frequency and ϵ_a is the dielectric constant of the medium around the metal sphere. The blue shift of electron energy loss maxima as particle size increases observed in Kreibig's experiment is explained by the increasing probability of exciting larger l mode as particle size increases. Meanwhile, Kreibig and Zacharias found the optical extinction band maxima are shifted to lower energy as particle size increases and they explained it by Mie theory. For larger particles, radiation damping and scattering occurs so that the optical extinction maxima shifts to lower energy. However since the low resolution of their experiment, different surface plasma oscillation modes cannot

be distinguished, which makes the explanation not very convincing. Later, blue shift of the dipolar plasma resonance as size decreases was observed for silver clusters on alumina surface(64), explained by the d-electron contribution to the silver cluster dielectric function, which is further used in a non-local response with a smoothly varying surface approximation(65). This experiment was followed by the absorption spectra measurement of Ag clusters ($20\text{\AA} < D < 100\text{\AA}$) embedded in Argon matrix (66), which is explained in the same manner. Soon after, photoabsorption spectra of very small Ag clusters (Ag_n $n=2-21$) embedded in Argon matrix (14) were obtained. It showed no clear shift trend of plasma peak in this range. And the authors proposed a core-shell model for the dielectric function of silver cluster, which reproduced quite well the size dependence of both Charle and their experimental results. In the interior region ($0 < r < R-d$), bulk dielectric function is used for ϵ_1 . Drude dielectric function ϵ_2 is used in the surface region. The absorption cross section is,

$$\sigma(\omega) = \frac{9V\omega\epsilon_m^{1/2}}{c} \text{Im} \frac{(\epsilon_2 - \epsilon_m)(\epsilon_1 + 2\epsilon_2) + f(\epsilon_1 - \epsilon_2)(\epsilon_m + 2\epsilon_2)}{(\epsilon_2 + 2\epsilon_m)(\epsilon_1 + 2\epsilon_2) - f(\epsilon_1 - \epsilon_2)(2\epsilon_m - 2\epsilon_2)} \quad (2.56)$$

where,

$$f = \left(\frac{R-d}{R+t}\right)^3 \quad (2.57)$$

At this point, all of Ag clusters are neutral and embedded in some matrix or colloid solution and are neutral. In 1993, Tiggesbaumker first conducted a Photodepletion spectroscopy experiment for small free positively charged Ag clusters, which showed that the absorption spectrum of Ag cationic clusters has a blue shift from 3.8eV to 4.4eV as the number of atoms in cluster decreases from 70 to 5 (10). They argued that the strong s-d interaction in Ag clusters shifts the plasmon peak to lower energy and as cluster size decreases, there are more spill-out electrons, which leads to a weaker s-d interaction, and therefore a higher frequency of plasmon resonance peak. The s-d interaction is presented by an extra term in the dielectric function of Ag cluster,

$$\epsilon(R, \omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Sigma(R, \omega)} + \Delta(\omega) \quad (2.58)$$

$\Delta(\omega)$ shifts the bulk plasmon frequency of silver from $\omega_p = 9.2\text{eV}$ to $\omega_p^* =$

$\omega_p/\sqrt{1+Re\Delta} = 3.76eV$, which is the observed value. Later, Tiggesbaumer conducted the same measurement for negatively charged silver clusters and explained the results in the manner (11). In a more sophisticated two-region model (67, 68), which is basically the same as reference(14), silver clusters are separated into a core-region ($0 < r < R - a$), where a bulk-like local dielectric function ϵ_b is used, and a surface-region ($R - a < r < R + \delta$), where only the free-electron dielectric function ϵ_0 is used. The absorption cross section is written as,

$$\sigma(\omega) = \frac{4\pi\omega(R+\delta)^3}{c} Im \frac{(\epsilon_0 - 1)(\epsilon_b + 2\epsilon_0) + f(1 + 2\epsilon_0)(\epsilon_b - \epsilon_0)}{(2 + \epsilon_0)(\epsilon_b + 2\epsilon_0) - 2f(1 - \epsilon_0)(\epsilon_b - \epsilon_0)} \quad (2.59)$$

where,

$$\epsilon_0(\omega) = 1 - \frac{\tilde{\omega}_p^2}{\omega^2 + i\Gamma\omega} \quad (2.60)$$

$$\tilde{\omega}_p = \omega_p \left(\frac{R}{R + \delta} \right)^2 \quad (2.61)$$

$$f = \left(\frac{R - a}{R + \delta} \right)^3 \quad (2.62)$$

δ takes into account the spill-out effect. By a good choice of the parameters a and δ , this model explains the experiment results quite well.

Quantum mechanically, a generalized time dependent density functional theory (TDDFT) has also been proposed to take into account of the polarization effect of silver core(69). As the induced valence electron density polarizes the silver cores, which are mainly the $4d$ electrons, the effective potential felt by the valence electrons in the normal linear response formalism will include a dipole core-polarization potential $\phi^{dip}(r)$. The radial part of the total effective potential is,

$$\phi^{tot}(r) = \phi^{ext}(r) + \int dr' r'^2 K(r, r') \delta\rho_v(r') + \phi^{dip}(r) \quad (2.63)$$

where, $K(r, r')$ is the radial residual interaction of TDDFT. In order to understand the fundamental expression of the polarization correction and for the sake

of simplicity, one rewrites the total effective potential as,

$$\phi^{tot}(\mathbf{r}) = \phi^{ext}(\mathbf{r}) + \int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') \delta\rho_v(\mathbf{r}') + \phi^{dip}(\mathbf{r}) \quad (2.64)$$

where,

$$\phi^{dip}(\mathbf{r}) = -N\alpha \int d\mathbf{r}' \frac{\mathbf{r}}{r^3} \frac{\mathbf{r}'}{r'^3} \delta\rho_v(\mathbf{r}') \quad (2.65)$$

which leads to a modified residual interaction,

$$K'(\mathbf{r}, \mathbf{r}') = K(\mathbf{r}, \mathbf{r}') - N\alpha \frac{\mathbf{r}}{r^3} \frac{\mathbf{r}'}{r'^3} \quad (2.66)$$

where the polarizable silver cluster background is approximated by one dipole located at the origin. (Note that the ground state of the valence electrons and exchange-correlation functional are not changed by the core polarization. What is corrected is the Hartree term of the residual interaction. As a contrast, the present model, which fundamentally modified the bare Coulomb interactions between valences electrons, ends up with a correction not only to the Hartree term, but also the exact exchange term in both Hartree-Fock equations and the matrix elements of RPAE.) Also, for Ag core sitting on the surface of the cluster, free ion polarizability is used, which is smaller than the embedded polarizability (70, 71) of Ag core inside the cluster. Their calculation showed that the core polarization screens the interaction between valence electrons and shifts the surface plasmon peak to lower energy. And the blue shift of the plasmon peak as cluster size decreases is assigned to an increasing percentage of surface Ag cores, with free ion polarizability. Later 11-electron TDLDA calculations results were reported for small silver clusters (72, 73). Reduction on the Mie frequency and oscillator strength were found as

$$\omega'_M = \sqrt{1 - \frac{\alpha_d}{r_s^3}} \omega_M \quad (2.67)$$

and

$$f = N(1 - \frac{\alpha_d}{r_s^3})^2 \quad (2.68)$$

In 2000s, optical absorption spectra for Ag clusters embedded in Helium nanodroplet (12, 74, 75) were measured. Coupled cluster CCSD calculations (76) with 11-electron relativistic effective core potentials were performed for free Ag₈, and compared to experimental results for Ag₈ embedded in Helium droplet. Clear discrepancy can be seen. However good agreement was found between experimental optical spectra of small Ag clusters embedded in Neon matrix and TDDFT calculations without taking into account the matrix effects (13). Although matrix effects on the shift of optical absorption spectra of Sodium clusters were claimed to depend on the details of matrix configuration by Gervais(28, 29), conductor-like screening model was implemented in TDDFT and shown that argon matrix shifts the optical spectra of silver clusters to lower energy by about 0.17eV (77), which is in the same direction of experimental estimated value 0.24eV (14). Meanwhile, from a pure theoretical point of view, atomic packing symmetry effects on the absorption spectrum of silver clusters were studied by TDDFT calculation with 11-electron pseudo-potential and different exchange correlation functionals were tested for use in TDDFT calculations (78, 79, 80, 81). In reference (79), different XC functionals and basis sets lead to significant difference on the optical absorption spectrum of silver cluster and the classical limit of 3.5eV is not found. Thus a 11-electron TDDFT calculation may not be a good approach. More recently, Donnie conducted an energy-loss spectroscopy experiment for ligand-free neutral Ag clusters deposit on a substrate and also found a blue shift as cluster radius decreases from 20nm to 2nm (82). A free electron gas model confined by infinite potential wall is used to calculate the dielectric function of silver clusters, which is further applied into the Mie scattering theory. The theoretical calculations showed good agreement with their experimental results. A similar experiment was conducted by Raza for free Ag clusters with size ranging from 3.5nm to 26nm and consistent result was found (83)

2.6 Rare-gas Matrix Effect

As has been reviewed above, in contrast to alkali metal clusters, many photo absorption experiments are conducted for silver clusters embedded in rare-gas

matrix (12, 13, 14, 75, 80, 84, 85, 86), which allows temperature to be controlled and a high cluster density for photo absorption measurement. Meanwhile, there is a lack of theoretical understanding of the matrix effect. The first quantum description of the cluster-matrix interaction is considered by Gross (27), where each metal atom core and argon atom was considered as a polarizable dipole. The polarization effect of Argon atoms was taken into account in the Hamiltonian for the valence electrons of the metal cluster embedded in argon matrix. However, the calculation is limited to sodium dimer due to high computation cost of Configuration Interaction (CI) method they used. In 2004, Gervis implemented the Gross's cluster-matrix polarization interaction into the density functional theory and calculation Na(2 4 8) embedded in up to 1396 argon atoms. A significant change on the absorption spectrum is found for Na4 due to the argon matrix, while a very slight shift for Na8.

2.7 Questions to Answer

Although there are many TDDFT calculations for Ag clusters, where $5d$ and $6s$ electrons are treated equally, the 11 electrons per Ag atom calculation gives no physical understanding of the d electron screening on the valence s electrons. Moreover different exchange correlation functionals and basis sets lead to huge discrepancy on the photo absorption spectrum. As a first part of this PhD work, one needs to know how the polarizable cores of silver cluster (mainly d electrons) affect the ground state and the collective dipole excitations of the delocalized s electrons. By using HF-RPAE approach, one can see how the polarizable localized d electrons screen the exchange potential in the HF equation and the residue interaction in the RPAE matrix equation. One step further, one would study the size-dependency of the dipole surface plasmon and find the origin of the blue shift of the plasmon peak in cationic silver clusters.

Compared to the abundant photo absorption measurements for silver clusters embedded in rare-gas matrices, there exists very few quantum mechanical study for the optical response of embedded metal clusters. The second question is to show, quantum mechanically, the screening by the rare-gas matrix effect on electron-electron and electron-ion interaction in the metal cluster. One would identify

how much shift different rare-gas matrices would affect the absorption spectrum of embedded metal clusters and examine the size dependency of the matrix effect. The study of the dielectric media should be helpful for understanding the optical properties of metal clusters embedded in thin film solar cells.

Chapter 3

Theoretical Methods

In this chapter, the three basic theoretical methods, HF approximation, B-spline method and RPAE are introduced. These include the fundamental equations implemented in the three codes, which serve as the computational tools in the following chapters of the present thesis. Since the present codes are developed under spherical symmetry, how these theoretical methods can be reduced to radial problems will be shown. Finally a short discussion on the f-sum rule is presented.

As has been introduced in Chapter 2, there are two competing approaches, KS-TDLDA and HF-RPAE, to solve the response problem an N interacting electron system. Since one is investigating electronic structure in metal clusters with tens to hundreds of atoms, the binding potential has $1/r$ asymptotic behaviour at long range and exchange effect will be important and cannot be well captured by a density approximation. Therefore one adopts HF-RPAE approach, which treats the exchange exactly. The present numerical codes contains three steps: 1, finding the HF ground state; 2, using B-spline method to find the complete set of HF wave functions; 3, solving the matrix RPAE problem.

3.1 Hatree-Fock Equations

Consider an interacting N electron system in external potential V_{ext} .

$$H = \sum_i \left(-\frac{1}{2}\nabla^2\right) + \sum_i V_{ext}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = T + V_{bkg} + V_{ee} \quad (3.1)$$

If one approximates the ground state as a Slater determinant of a set of single particle wave function $\phi_i(\mathbf{r}_i)$.

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \det|\phi_1(\mathbf{r}_1) \dots \phi_n(\mathbf{r}_n)| \quad (3.2)$$

The ground state energy can be found by,

$$\begin{aligned} E = \langle \Psi | H | \Psi \rangle = & \sum_i \int \phi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}_i)\right) \phi_i(\mathbf{r}) d\mathbf{r} \\ & + \sum_{i,j} \frac{1}{2} \int \frac{|\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & - \sum_{i,j} \langle s_i | s_j \rangle \frac{1}{2} \int \frac{\phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}) \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (3.3)$$

taking the variation with respect to $\phi_i(\mathbf{r})$ one finds a set of coupled Hartree-Fock equations

$$\begin{aligned} & \left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \sum_j \int \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \phi_i(\mathbf{r}) \\ & - \sum_j \langle s_i | s_j \rangle \int \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}') \phi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \epsilon_i \phi_i(\mathbf{r}) \end{aligned} \quad (3.4)$$

3.2 Radial Hartree-Fock Term

Since the present calculation are based on Jellium model with spherical symmetry, the Hartree-Fock single particle wave functions can be written as.

$$\phi_i(\mathbf{r}) = \frac{R_{nl}(r)}{r} Y_{lm}(\Omega) \quad (3.5)$$

Replacing the external potential V_{ext} with Jellium background potential V_{JM} in Equation 3.4:

$$\left(-\frac{1}{2}\nabla^2 + V_{JM}(\mathbf{r}_i) + U_{HF} \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (3.6)$$

where the HF potential is defined by

$$U_{HF} \phi_i(\mathbf{r}) = V_H \phi_i(\mathbf{r}) - V_{ex} \phi_i(\mathbf{r}) \quad (3.7)$$

Now one can see how a radial HF equation is derived. Insert Equation 3.5 into the exchange potential.

$$\begin{aligned} V_{ex} \phi_i(r) &= \sum_j^{core} \int \frac{\phi_j^*(r') \phi_i(r')}{|r - r'|} d^3 r' \phi_j(r) = \\ & \sum_{n'l'm'} \int \frac{R_{n'l'}^*(r')}{r'} \frac{R_{nl}(r')}{r'} Y_{l'm'}^*(\Omega') Y_{lm}(\Omega') \frac{1}{|\vec{r} - \vec{r}'|} r'^2 dr' d\Omega' \frac{R_{n'l'}(r)}{r} Y_{l'm'}(\Omega) \end{aligned} \quad (3.8)$$

Note that exchange happens only between same spin electrons. So there is a factor of 1/2 that cancel the factor 2 in the summation over core orbitals. Given

that the Coulomb interaction can be expanded as,

$$\frac{1}{|\vec{r} - \vec{r}'|} = \sum_{LM} \frac{r_{<}^L}{r_{>}^{L+1}} \frac{4\pi}{2L+1} Y_{LM}^*(\Omega') Y_{LM}(\Omega) \quad (3.9)$$

One finds that,

$$\begin{aligned} V_{ex}\phi_i(r) &= \sum_{n'l'm'} \sum_{LM} \int (angularpart) \int (radialpart) \\ &= \sum_{n'l'} \sum_L \left(\sum_{m'M} \int (angularpart) \right) \int (radialpart) \end{aligned} \quad (3.10)$$

where the radial part is easily found as

$$\int (radialpart) = \int R_{n'l'}^*(r') R_{nl}(r') \frac{r_{<}^L}{r_{>}^{L+1}} \frac{4\pi}{2L+1} \frac{R_{n'l'}(r)}{r} dr' \quad (3.11)$$

Use the 3-j symbol to simplify the angular part,

$$\begin{aligned} Y_{l'm'}(\Omega')^* Y_{LM}^*(\Omega') &= \sum_{L'M'} Y_{L'M'}^*(\Omega') \sqrt{\frac{(2L'+1)(2l'+1)(2L+1)}{4\pi}} \\ &\quad (-1)^{M'} \begin{pmatrix} l'LL' \\ m'M - M' \end{pmatrix} \begin{pmatrix} l'LL' \\ 000 \end{pmatrix} \end{aligned} \quad (3.12)$$

Then angular part is transformed into:

$$\begin{aligned} \sum_{m'M} \int (angularpart) &= \sum_{m'M} \sqrt{\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}} \\ &\quad (-1)^m \begin{pmatrix} l'LL \\ m'M - m \end{pmatrix} \begin{pmatrix} l'LL \\ 000 \end{pmatrix} Y_{LM}(\Omega) Y_{l'm'}(\Omega) \end{aligned} \quad (3.13)$$

Apply the same expression as equation 3.12:

$$\begin{aligned} Y_{l'm'}(\Omega) Y_{LM}(\Omega) &= \sum_{L'M'} Y_{L'M'}(\Omega) \sqrt{\frac{(2L'+1)(2l'+1)(2L+1)}{4\pi}} \\ &\quad (-1)^{M'} \begin{pmatrix} l'LL' \\ m'M - M' \end{pmatrix} \begin{pmatrix} l'LL' \\ 000 \end{pmatrix} \end{aligned} \quad (3.14)$$

And using orthogonality of 3-j symbol:

$$\sum_{m'M} \begin{pmatrix} l' L l \\ m' M - m \end{pmatrix} \begin{pmatrix} l' L L' \\ m' M - M' \end{pmatrix} = \frac{1}{(2l+1)} \delta_{lL'} \delta_{mM'} \quad (3.15)$$

one finds the expression for the angular part of the exchange potential.

$$\begin{aligned} \sum_{m'M} \int (angularpart) &= \sum_{L'M'} Y_{L'M'}(\Omega) \frac{\delta_{lL'} \delta_{mM'} (2l'+1)(2L+1)}{4\pi(2l+1)} \\ &\quad \sqrt{(2L'+1)(2l+1)} \begin{pmatrix} l' L L' \\ 000 \end{pmatrix} \begin{pmatrix} l' L l \\ 000 \end{pmatrix} (-1)^m (-1)^{M'} \\ &= Y_{lm}(\Omega) \frac{(2l'+1)(2L+1)}{4\pi} \begin{pmatrix} l' L l \\ 000 \end{pmatrix}^2 \end{aligned} \quad (3.16)$$

Therefore,

$$\begin{aligned} V_{ex} \phi_i(r) &= \sum_{n'l'} \sum_L \left(\sum_{m'M} \int (angularpart) \right) \int (radialpart) \\ &= \sum_{n'l'L} \int (radialpart) Y_{lm}(\Omega) \frac{(2l'+1)(2L+1)}{4\pi} \begin{pmatrix} l' L l \\ 000 \end{pmatrix}^2 \\ &= \frac{Y_{lm}(\Omega)}{r} \sum_{n'l'L} \int R_{n'l'}^*(r') R_{nl}(r') \frac{r_{\leq}^L}{r_{>}^{L+1}} dr' R_{n'l'}(r) (2l'+1) \begin{pmatrix} l' L l \\ 000 \end{pmatrix}^2 \end{aligned} \quad (3.17)$$

The radial Hartree-Fock equation for Jellium Model is:

$$\begin{aligned} &\left(-\frac{1}{2} \frac{d^2}{dr^2} + V_{Local} + \frac{l(l+1)}{2r^2} \right) R_{nl}(r) \\ &+ \sum_{n'l'L} \int R_{n'l'}^*(r') R_{nl}(r') \frac{r_{\leq}^L}{r_{>}^{L+1}} dr' R_{n'l'}(r) (2l'+1) \begin{pmatrix} l' L l \\ 000 \end{pmatrix}^2 = \epsilon_{nl} R_{nl}(r) \end{aligned} \quad (3.18)$$

In a more compact form.

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + V_{JM} + V_{HF} + \frac{l(l+1)}{2r^2} \right) R_{nl}(r) = \epsilon_{nl} R_{nl}(r) \quad (3.19)$$

At this point let us make a digression. Two equalities for 3-j symbols were proposed by us and mathematical proof has not been found:

1, for any integer n , the equality below holds:

$$\sum_{L_1=0}^n \sum_{L_2=0}^n (L_1, L_2, 2n - L_1 - L_2)^2 = 1 \quad (3.20)$$

2, for any integer n , the equality below holds:

$$\begin{aligned} \sum_{L_1=0}^n \sum_{L_2=0}^n & \left[(L_1, L_2, 2n - L_1 - L_2 - 2)^2 \frac{2n - 1 - L_1 - L_2}{2(2n - 1 - L_1 - L_2) + 1} \right. \\ & \left. + (L_1, L_2, 2n - L_1 - L_2)^2 \frac{2n - L_1 - L_2}{2(2n - 1 - L_1 - L_2) + 1} \right] = 1 \end{aligned} \quad (3.21)$$

Now back to the HF equation, the first step code (HFcode) solves the radial HF equation self consistently. The total energy of the metal cluster in a Jellium Model can be written as:

$$E_{tot} = E_{ion-ion} + E_{e-e} + E_{e-ion} \quad (3.22)$$

The HF ground state calculation gives the electron-electron energy E_{e-e} and the electron-ion E_{e-ion} energy. The ionic self-energy $E_{ion-ion}$ is derived analytically by classical electrodynamics.

$$E_{ion-ion} = \frac{1}{2} \int \rho_{ion}(r) V_{JM}(r) dr = \frac{3N^2}{5R_J} \quad (3.23)$$

3.3 B-spline Method

In order to get a complete set of HF wave functions, which includes both occupied and unoccupied orbitals, one could confine the jellium in a cavity of radius R_{max} . Boundary condition requires the wave function and its first order of derivative to be zero at R_{max} . Then one expands the radial wave function in a set of B-spline functions (87).

$$R_{nl}(r) = \sum_i^n c_i B_{i,k}(r) \quad (3.24)$$

where the n ($i=1, 2, \dots, n$) B-spline functions $B_{i,k}(r)$ of order k are a set of piece-wise polynomials of degree $k - 1$, which can be defined on a knot sequence

$t_j, j = 1, \dots, n + k$ recursively

$$B_{i,1}(x) = \begin{cases} 1 & \text{if } t_i \leq x < t_{i+1} \\ 0 & \text{if otherwise} \end{cases}$$

$$B_{i,k}(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i=1}} B_{i+1,k-1}(x) \quad (3.25)$$

The knot sequence t_j is defined on the r axis by,

$$t_1 = \dots = t_k = 0, t_n = \dots = t_{n+k} = R_{max} \quad (3.26)$$

and

$$t_i = (i - k) \frac{R_{max}}{n - k + 1} \text{ for } i = k + 1, n \quad (3.27)$$

From the definition of B-splines one knows that $B_{i,k}(r)$ is zero except in the range of $[t_i, t_{i+k}]$. In most of the calculations in this thesis, one chooses $n = 50$ and $k = 9$, which gives accurate enough results. According to action principle, solving the radial HF eigenvalue problem, is the exactly the same as taking the variation of action S , which is defined by.

$$S = \int \frac{1}{2} \left(\frac{d}{dr} R_{nl}(r) \right)^2 dr + \int \left(V_{JM} + \frac{l(l+1)}{2r^2} + V_{HF} \right) (R_{nl}(r))^2 dr - \epsilon \int (R_{nl}(r))^2 dr = 0 \quad (3.28)$$

where ϵ is the Lagrange multiplier to fulfill the normalization requirement. Inserting the expansion of $R_{nl}(r)$ into s ,

$$\begin{aligned} S &= \int \frac{1}{2} \sum_{ij} \frac{d}{dr} B_{i,k}(r) \frac{d}{dr} B_{j,k}(r) c_i c_j dr \\ &+ \int \sum_{ij} \left(V_{JM} + \frac{l(l+1)}{2r^2} + V_{HF} \right) B_{i,k}(r) B_{j,k}(r) c_i c_j dr \\ &- \epsilon \int \sum_{ij} B_{i,k}(r) B_{j,k}(r) c_i c_j dr = 0 \end{aligned} \quad (3.29)$$

taking the functional derivative with respect to $R_{nl}(r)$ means taking the derivative with respect to c_i . One is left with a matrix equation for c_i ,

$$AC^{nl} = \epsilon_{nl}BC^{nl} \quad (3.30)$$

where the matrix elements of A and B is defined by,

$$a_{ji} = \int \frac{1}{2} \frac{d}{dr} B_{j,k}(r) \frac{d}{dr} B_{i,k}(r) dr + \int B_{j,k}(r) (V_{JM} + \frac{l(l+1)}{2r^2} + V_{HF}) B_{i,k}(r) dr \quad (3.31)$$

and

$$b_{ji} = \int B_{j,k}(r) B_{i,k}(r) dr \quad (3.32)$$

The second step code (SPLcode) generates A and B matrix and solves the matrix eigenvalue problem. The eigenvalues calculated by the B-spline method is found in excellent agreement with that of HF calculation.

3.4 Random Phase Approximation with Exact Exchange

The excitation energies and oscillator strength of an N interacting electron system can be found by Random Phase Approximation with exact Exchange. For a detail review please see reference (88). Here one way is provided to derive the RPAE, which is basically time-dependent Hartree-Fock equation. The time dependent many-body wave function is approximated by a Slater determinant of N time dependent single particle wave function.

$$|\Psi(t)\rangle = |\phi_1(t)\phi_2(t)\dots\phi_i(t)\dots\phi_N(t)\rangle \quad (3.33)$$

Each time dependent single particle wave function is approximated by,

$$|\phi_i(t)\rangle = c_i(t)|\phi_i(0)\rangle + \sum_{m>F} c_{mi}(t)|\phi_m(0)\rangle, \quad (3.34)$$

where the coefficient fulfills normalization requirement,

$$|c_i(t)|^2 + \sum_{m>F} |c_{mi}(t)|^2 = 1. \quad (3.35)$$

$|\phi_i(0) >$ and $|\phi_m(0) >$ are occupied and unoccupied Hartree-Fock orbitals, which for convenience will be noted as $|i >$ and $|m >$. Later on, i and j denote occupied state while m and n denote unoccupied state.

$$\int < \Psi(t) | H - i\hbar \frac{\partial}{\partial t} | \Psi(t) > dt \quad (3.36)$$

The Random Phase Approximation can be obtained by applying variational principle to equation (3.34) with respect to c_{mi} .

Simplification of $< \Psi(t) | H | \Psi(t) >$:

$$\begin{aligned} < \Psi(t) | H | \Psi(t) > &= \sum_i < \phi_i(t) | h_{HF}(t) | \phi_i(t) > \\ &- \frac{1}{2} \sum_{ij} (< \phi_i(t) \phi_j(t) | \frac{1}{r_{12}} | \phi_i(t) \phi_j(t) > - < \phi_j(t) \phi_i(t) | \frac{1}{r_{12}} | \phi_i(t) \phi_j(t) >) \\ &= \sum_i < \phi_i(t) | h_{HF}(t) | \phi_i(t) > - \frac{1}{2} \sum_{ij} < \phi_i(t) \phi_j(t) | \frac{1}{r_{12}} | \phi_i(t) \phi_j(t) > \end{aligned} \quad (3.37)$$

The first part of equation 3.35:

$$\begin{aligned} < \phi_i(t) | h_{HF}(t) | \phi_i(t) > &= |c_i|^2 < i | h_{HF} | i > - \sum_{nj} |c_i|^2 |c_{nj}|^2 < ij | \frac{1}{r_{12}} | ij > \\ &+ \sum_{mn} c_{mi}^* c_{ni} < m | h_{HF} | n > + < \phi_i(t) | \Delta | \phi_i(t) > \\ &= (1 - \sum_m |c_{mi}|^2) \varepsilon_i + \sum_m |c_{mi}|^2 \varepsilon_m \\ &- \sum_{nj} |c_i|^2 |c_{nj}|^2 < ij | \frac{1}{r_{12}} | ij > + < \phi_i(t) | \Delta | \phi_i(t) > \end{aligned} \quad (3.38)$$

where ε_i and ε_m are Hartree-Fock energies for occupied and unoccupied orbital,

while Δ is defined by,

$$\Delta = h_{HF}(t) - h_{HF}. \quad (3.39)$$

It is easy to find

$$\begin{aligned} \langle \phi_i(t) | \Delta | \phi_i(t) \rangle &= |c_i|^2 \langle i | \Delta | i \rangle + \sum_{mn} c_{mi}^* c_{ni} \langle m | \Delta | n \rangle \\ &+ \sum_m c_i^* c_{mi} \langle i | \Delta | m \rangle + \sum_m c_{mi}^* c_i \langle m | \Delta | i \rangle \end{aligned} \quad (3.40)$$

Since c_{mi} is small, one only considers the second order terms. (Noted Δ contains only first and second order terms.)

$$\begin{aligned} \langle \phi_i(t) | \Delta | \phi_i(t) \rangle &= \sum_{mnj} c_{mj}^* c_{nj} |c_i|^2 \langle im | \frac{1}{r_{12}} | in \rangle \\ &+ \sum_{mnj} c_{mi} c_{nj}^* \langle in | \frac{1}{r_{12}} | mj \rangle + \sum_{mnj} c_{mi} c_{nj} \langle ij | \frac{1}{r_{12}} | mn \rangle \\ &+ \sum_{mnj} c_{mi}^* c_{nj} \langle mj | \frac{1}{r_{12}} | in \rangle + \sum_{mnj} c_{mi}^* c_{nj}^* \langle mn | \frac{1}{r_{12}} | ij \rangle \end{aligned} \quad (3.41)$$

The second part of equation 3.35:

$$\begin{aligned} \langle \phi_i(t) \phi_j(t) | \frac{1}{r_{12}} | \phi_i(t) \phi_j(t) \rangle &= |c_i|^2 |c_j|^2 \langle ij | \frac{1}{r_{12}} | ij \rangle \\ &+ \sum_{mn} |c_i|^2 c_{mj}^* c_{nj} \langle im | \frac{1}{r_{12}} | in \rangle + \sum_{mn} |c_j|^2 c_{mi}^* c_{ni} \langle mj | \frac{1}{r_{12}} | nj \rangle \\ &+ \sum_{mn} c_{mi}^* c_{nj}^* c_i c_j \langle mn | \frac{1}{r_{12}} | ij \rangle + \sum_{mn} c_i^* c_j^* c_{mi} c_{nj} \langle ij | \frac{1}{r_{12}} | mn \rangle \\ &+ \sum_{mn} c_{mi}^* c_j^* c_i c_{nj} \langle mj | \frac{1}{r_{12}} | in \rangle + \sum_{mn} c_i^* c_{mj}^* c_{ni} c_j \langle im | \frac{1}{r_{12}} | nj \rangle \end{aligned} \quad (3.42)$$

Variation of $\int \langle \Psi(t) | H | \Psi(t) \rangle dt$: Using Euler-Lagrange equation, the variation of $\int \langle \Psi(t) | H | \Psi(t) \rangle dt$ with respect to c_{mi} is equivalent to differentiation

of equation (5) with respect to c_{mi}^*

$$\begin{aligned}
 \frac{\delta \int \langle \Psi(t) | H | \Psi(t) \rangle dt}{\delta c_{mi}} &= \frac{d \langle \Psi(t) | H | \Psi(t) \rangle}{dc_{mi}^*} \\
 &= \frac{d \sum_i \langle \phi_i(t) | h_{HF}(t) | \phi_i(t) \rangle}{dc_{mi}^*} - \frac{d}{2dc_{mi}^*} \sum_{ij} \langle \phi_i(t) \phi_j(t) | \frac{1}{r_{12}} | \phi_i(t) \phi_j(t) \rangle \\
 &= c_{mi}(\varepsilon_m - \varepsilon_i) + \sum_{nj} c_{nj} \langle mj | \frac{1}{r_{12}} | in \rangle + \sum_{nj} c_{nj}^* \langle mn | \frac{1}{r_{12}} | ij \rangle
 \end{aligned} \tag{3.43}$$

If c_{mi} is transformed into frequency domain,

$$c_{mi}(t) = X_{mi}e^{-i\omega t} + Y_{mi}^*e^{i\omega t}, \tag{3.44}$$

one finds that:

$$\begin{aligned}
 \frac{\delta \int \langle \Psi(t) | H | \Psi(t) \rangle dt}{\delta c_{mi}} &= \frac{d \langle \Psi(t) | H | \Psi(t) \rangle}{dc_{mi}^*} \\
 &= (X_{mi}e^{-i\omega t} + Y_{mi}^*e^{i\omega t})(\varepsilon_m - \varepsilon_i) + \sum_{nj} (X_{nj}e^{-i\omega t} + Y_{nj}^*e^{i\omega t}) \langle mj | \frac{1}{r_{12}} | in \rangle \\
 &\quad + \sum_{nj} (X_{nj}^*e^{i\omega t} + Y_{nj}e^{-i\omega t}) \langle mn | \frac{1}{r_{12}} | ij \rangle
 \end{aligned} \tag{3.45}$$

Simplification of $\langle \Psi(t) | i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle$:

$$\begin{aligned}
 \langle \Psi(t) | \frac{\partial}{\partial t} | \Psi(t) \rangle &= \sum_i \langle \phi_i(t) | \frac{\partial}{\partial t} | \phi_i(t) \rangle = \sum_i c_i^* \frac{\partial}{\partial t} c_i + \\
 \sum_{mi} c_i^* \langle i | \frac{\partial}{\partial t} c_{mi} | m \rangle &+ \sum_{mi} c_{mi}^* \langle m | \frac{\partial}{\partial t} c_i | i \rangle + \sum_{mni} c_{mi}^* \langle m | \frac{\partial}{\partial t} c_{ni} | n \rangle \\
 &= \sum_i c_i^* \frac{\partial}{\partial t} c_i + \sum_{mi} c_{mi}^* \frac{\partial}{\partial t} c_{mi}
 \end{aligned} \tag{3.46}$$

From the normalization requirement below,

$$|c_i(t)|^2 = 1 - \sum_m |c_{mi}(t)|^2, \quad (3.47)$$

and the fact that $|c_i(t)|^2$ is a positive real number, one can always choose $c_i(t)$ to be real.

$$c_i(t) = \sqrt{1 - \sum_m |c_{mi}(t)|^2} \quad (3.48)$$

Therefore,

$$\begin{aligned} \langle \Psi(t) | \frac{\partial}{\partial t} | \Psi(t) \rangle &= \sum_i \frac{\partial}{\partial t} |c_i(t)|^2 + \sum_{mi} c_{mi}^* \frac{\partial}{\partial t} c_{mi} \\ &= - \sum_{mi} \frac{\partial}{\partial t} |c_{mi}(t)|^2 + \sum_{mi} c_{mi}^* \frac{\partial}{\partial t} c_{mi}. \end{aligned} \quad (3.49)$$

Variation of $\int \langle \Psi(t) | i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle dt$:

$$\begin{aligned} \frac{\delta \int \langle \Psi(t) | i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle dt}{\delta c_{mi}} &= \frac{i\hbar \delta \int (-\sum_{mi} \frac{\partial}{\partial t} |c_{mi}(t)|^2 + \sum_{mi} c_{mi}^* \frac{\partial}{\partial t} c_{mi}) dt}{\delta c_{mi}} \\ &= i\hbar \frac{\partial c_{mi}}{\partial t} = \hbar\omega (X_{mi} e^{-i\omega t} - Y_{mi}^* e^{i\omega t}) \end{aligned} \quad (3.50)$$

where,

$$c_{mi}(t) = X_{mi} e^{-i\omega t} + Y_{mi}^* e^{i\omega t} \quad (3.51)$$

Matrix RPA Equation: The matrix RPA equation is obtained by setting the variation of $\int \langle \Psi(t) | H - i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle dt$ to zero.

$$\frac{\delta \int \langle \Psi(t) | H - i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle dt}{\delta c_{mi}} = 0 \quad (3.52)$$

therefore one finds that:

$$\begin{aligned}
 (X_{mi}e^{-i\omega t} + Y_{mi}^*e^{i\omega t})(\varepsilon_m - \varepsilon_i) + \sum_{nj} (X_{nj}e^{-i\omega t} + Y_{nj}^*e^{i\omega t}) < mj | \frac{\widetilde{1}}{r_{12}} | in > \\
 + \sum_{nj} (X_{nj}^*e^{i\omega t} + Y_{nj}e^{-i\omega t}) < mn | \frac{\widetilde{1}}{r_{12}} | ij > = \hbar\omega (X_{mi}e^{-i\omega t} - Y_{mi}^*e^{i\omega t})
 \end{aligned} \tag{3.53}$$

Equating the coefficient of $e^{-i\omega t}$ leads to:

$$(\varepsilon_m - \varepsilon_i)X_{mi} + \sum_{nj} < mj | \frac{\widetilde{1}}{r_{12}} | in > X_{nj} + \sum_{nj} < mn | \frac{\widetilde{1}}{r_{12}} | ij > Y_{nj} = \hbar\omega X_{mi} \tag{3.54}$$

Equating the complex conjugate of the coefficient of $e^{i\omega t}$ leads to:

$$(\varepsilon_m - \varepsilon_i)Y_{mi} + \sum_{nj} < in | \frac{\widetilde{1}}{r_{12}} | mj > Y_{nj} + \sum_{nj} < ij | \frac{\widetilde{1}}{r_{12}} | mn > X_{nj} = -\hbar\omega Y_{mi} \tag{3.55}$$

The above two sets of equations can be written as one matrix equation:

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \hbar\omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \tag{3.56}$$

where,

$$A_{mi,nj} = (\varepsilon_m - \varepsilon_i)\delta_{mn}\delta_{ij} + < mj | \frac{\widetilde{1}}{r_{12}} | in > \tag{3.57}$$

and,

$$B_{mi,nj} = < mn | \frac{\widetilde{1}}{r_{12}} | ij > . \tag{3.58}$$

The eigenvalues ω_k corresponds to the excitation energy of the N electron system and the eigenvectors, X_{ma}^k, Y_{ma}^k , represent the excited states satisfying the normalization equation. Note that the ground state of the N electron is also corrected by double excitation slater determinants through matrix elements B . The dipole transition amplitude from many-body ground state $|0 >$ to excited state

$|k\rangle$ and its oscillator strength f_k can be calculated by

$$\langle k|Z|0\rangle = \sum_{i,m} [X_{mi}^k \langle m|z|i\rangle + Y_{mi}^k \langle i|z|m\rangle] \quad (3.59)$$

$$f_k = 2\omega |\langle k|Z|0\rangle|^2 \quad (3.60)$$

The last step code (RPAEcode) generates A and B matrix elements and solves the matrix RPAE eigenvalue problem.

3.5 Energy-weighted Sum Rule

For a general many body system, the energy-weighted sum rule for a operator Z is defined by,

$$2 \sum_k (E_k - E_0) |\langle k|Z|0\rangle|^2 = \langle 0|[[Z, H], Z]|0\rangle, \quad (3.61)$$

where E_k and $|k\rangle$ are many-body excited energy and excited state. Proof:

$$(E_k - E_0) \langle k|Z|0\rangle = \langle k|HZ|0\rangle - \langle k|ZH|0\rangle = \langle k|[H, Z]|0\rangle \quad (3.62)$$

and,

$$(E_k - E_0) \langle 0|Z|k\rangle = \langle k|HZ|0\rangle - \langle k|ZH|0\rangle = \langle 0|[Z, H]|k\rangle. \quad (3.63)$$

Thus,

$$\begin{aligned} & 2 \sum_k (E_k - E_0) |\langle k|Z|0\rangle|^2 \\ &= \sum_k (\langle 0|Z|k\rangle \langle k|[H, Z]|0\rangle + \langle 0|[Z, H]|k\rangle \langle k|Z|0\rangle) \quad (3.64) \\ &= \langle 0|Z[H, Z]|0\rangle + \langle 0|[Z, H]Z|0\rangle = \langle 0|[[Z, H], Z]|0\rangle. \end{aligned}$$

If the operator Z is defined as,

$$Z = \sum_i z_i \quad (3.65)$$

then,

$$[Z, H] = - \sum_{ij} \frac{1}{2} [z_i, p_{zj}^2] = - \sum_{ij} p_{zj} [z_i, p_{zj}] = -i \sum_i p_{zi} = -iP_z \quad (3.66)$$

$$2 \sum_k (E_k - E_0) | \langle k | Z | 0 \rangle |^2 = \langle 0 | [[Z, H], Z] | 0 \rangle = N \quad (3.67)$$

Therefore, for the dipole excitation $Z = \sum_i z_i$ the sum of the oscillator strength should be equal to the number of valence electrons.

3.5.1 Sum Rule for Hartree-Fock Approximation

If one replaces E_k and $|k\rangle$ with Hartree-Fock excited energy and excited state, then

$$\begin{aligned} & 2 \sum_k (E_k - E_0) | \langle k | Z | 0 \rangle |^2 = \langle 0 | [[Z, H_{HF}], Z] | 0 \rangle \\ &= N + \sum_i \langle 0 | [[z_i, U_{HF}], z_i] | 0 \rangle = N + \sum_i \langle i | [[z_i, U_{HF}], z_i] | i \rangle \\ &= N - \sum_i \langle i | z_i^2 U_{HF} + U_{HF} z_i^2 - 2z_i U_{HF} z_i | i \rangle \quad (3.68) \\ &= N + \frac{1}{2} \sum_{ij} \int \phi_i(1)^* \phi_j(2)^* \left(z_{1i}^2 \frac{1}{r_{12}} + \frac{1}{r_{12}} z_{2i}^2 - 2z_{1i} \frac{1}{r_{12}} z_{2i} \right) \phi_i(2) \phi_j(1) \\ &= N + \frac{1}{2} \sum_{ij} \int \phi_i(1)^* \phi_j(2)^* \frac{(z_{1i} - z_{2i})^2}{r_{12}} \phi_i(2) \phi_j(1) \end{aligned}$$

The factor 1/2 comes from HF exchange potential. (note that the sum has to include spin) This shows that Hartree-Fock approximation does not fulfill energy-weighted sum rule.

3.5.2 Sum Rule for Random Phase Approximation

If one replaces $E_k - E_0$ and $|k\rangle$ with RPA excitation energy and excited state, then

$$\begin{aligned}
 (E_k - E_0) \langle k|Z|0 \rangle &= \omega_k \sum_{mi} (\langle m|z|i \rangle X_{mi}^{k*} + \langle i|z|m \rangle Y_{mi}^{k*}) \\
 &= \sum_{mi} (\langle m|[h_{HF}, z]|i \rangle X_{mi}^{k*} + \langle i|[h_{HF}, z]|m \rangle Y_{mi}^{k*}) \\
 &+ \sum_{mni} \langle in|\frac{1}{r_{12}}|mj \rangle \langle m|z|i \rangle X_{nj}^{k*} - \sum_{mni} \langle mn|\frac{1}{r_{12}}|ij \rangle \langle i|z|m \rangle X_{nj}^{k*} \\
 &+ \sum_{mni} \langle ij|\frac{1}{r_{12}}|mn \rangle \langle m|z|i \rangle Y_{nj}^{k*} - \sum_{mni} \langle mj|\frac{1}{r_{12}}|in \rangle \langle i|z|m \rangle Y_{nj}^{k*}
 \end{aligned} \tag{3.69}$$

All the direct Hartree terms cancel with each other.

$$\begin{aligned}
 (E_k - E_0) \langle k|Z|0 \rangle &= \sum_{mi} (\langle m|[h_{HF}, z]|i \rangle X_{mi}^{k*} + \langle i|[h_{HF}, z]|m \rangle Y_{mi}^{k*}) \\
 &- \sum_{mni} \langle in|\frac{1}{r_{12}}|jm \rangle \langle m|z|i \rangle X_{nj}^{k*} + \sum_{mni} \langle mn|\frac{1}{r_{12}}|ji \rangle \langle i|z|m \rangle X_{nj}^{k*} \\
 &- \sum_{mni} \langle ij|\frac{1}{r_{12}}|nm \rangle \langle m|z|i \rangle Y_{nj}^{k*} + \sum_{mni} \langle mj|\frac{1}{r_{12}}|ni \rangle \langle i|z|m \rangle Y_{nj}^{k*}
 \end{aligned} \tag{3.70}$$

where one needs to evaluate the exchange part in $\langle m|[h_{HF}, z]|i \rangle$,

$$\begin{aligned}
 \sum_{mi} \langle m|V_x z|i \rangle &= \sum_{mij} \int \phi_m^*(1) \phi_j^*(2) \left(-\frac{1}{r_{12}} z_2\right) \phi_i(2) \phi_j(1) \\
 &= \sum_{mij} \int \phi_m^*(1) \left(-\frac{1}{r_{12}}\right) \phi_i(2) \phi_j(1) \phi_j^*(3) z_3 \delta(2-3) \\
 &= \sum_{mni} \langle mn| -\frac{1}{r_{12}} |ji \rangle \langle i|z|m \rangle
 \end{aligned} \tag{3.71}$$

α sums over all state. Note that:

$$\langle i|z|j \rangle = 0 \tag{3.72}$$

one finds,

$$\begin{aligned}
 (E_k - E_0) \langle k|Z|0 \rangle &= \sum_{mi} (\langle m|[\frac{p^2}{2}, z]|i \rangle X_{mi}^{k*} + \langle i|[\frac{p^2}{2}, z]|m \rangle Y_{mi}^{k*}) \\
 &= - \sum_{mi} (\langle m|[z, p_z]p_z|i \rangle X_{mi}^{k*} + \langle i|[z, p_z]p_z|m \rangle Y_{mi}^{k*}) = -i \langle k|P_z|0 \rangle
 \end{aligned} \tag{3.73}$$

where,

$$P_z = \sum_i p_{iz}. \tag{3.74}$$

Thus,

$$\begin{aligned}
 &2 \sum_k (E_k - E_0) |\langle k|Z|0 \rangle|^2 \\
 &= -i \sum_k (\langle 0|Z|k \rangle \langle k|P_z|0 \rangle - \langle 0|P_z|k \rangle \langle k|Z|0 \rangle) \tag{3.75} \\
 &= -i (\langle 0|ZP_z|0 \rangle - \langle 0|P_zZ|0 \rangle) = -i \langle 0|[Z, P_z]|0 \rangle = N.
 \end{aligned}$$

Therefore Random Phase Approximation with exact exchange fulfills energy-weighted sum rule.

Chapter 4

Pseudopotential Method

As a starting point, the first part of this PhD project is to repeat a previous work on the non-local pseudo-potential method for lithium clusters. By reproducing all numerical results in reference (1), the Hartree-Fock, B-spline and matrix Random Phase Approximation codes are benchmarked, which are needed in later work on the core polarization effects of silver clusters. This chapter shows numerical calculations of the oscillator strength for lithium clusters with non-local ionic pseudo-potential and the comparison with the original work. A good agreement on both the distribution pattern and the oscillator strength summation is found.

4.1 Model

Compared to classical Mie theory and quantum chemistry methods, Jellium Model not only keeps the quantum mechanical properties of electronic structure, but also is computational efficient and can be extent to larger systems (cluster of hundreds atoms). The weakness of Jellium Model is that it treats the valence-core interaction as a pure Coulomb potential, which in many cases is too broad a approximation. In order to extend Jellium Model to metal clusters other than Sodium and Potassium, real valence-core interaction has to be taken into account. As has been shown in previous work, simple Jellium Model predicts a plasma resonance peak position much higher than experimental measurement for lithium clusters. Using the effective mass (at the bottom of conduction band) from band structure calculation 1.33 a.u. in $\sqrt{\frac{4\pi\rho_e e^2}{3m_e^*}}$, the effective Mie frequency agrees better with experimental results. Another experimental fact about lithium is that the oscillator strength of the valence electrons of lithium atoms, clusters and bulk are constantly reduced by 30 percent (8). Given that the 2s electron of Lithium feels a strong angular-momentum-dependent ionic pseudo-potential, all of these discrepancy between Mie frequency theory and experiments can be solved by including a nonlocal norm-conserving pseudo-potential to the Jellium Model (1).

In a spherical Jellium Model, cluster of N Li atoms is considered as a system of N electrons and a sphere of uniformly distributed N positive charges. Each Li ion generates a angular-momentum-dependent pseudo-potential.

$$V_{ps} = \sum_{L=0}^{\infty} v_L(r) \mathcal{P}_L \quad (4.1)$$

where $\mathcal{P}_L$ is the angular momentum projection operator,

$$\mathcal{P}_L = \sum_{m=-L}^L |Lm\rangle\langle Lm| \quad (4.2)$$

In configuration space,

$$\mathcal{P}_L(\mathbf{r}, \mathbf{r}') = \frac{1}{r^2} \delta(r - r') \sum_{m=-L}^L Y_{Lm}(\hat{\mathbf{r}}) Y_{Lm}^*(\hat{\mathbf{r}}') \quad (4.3)$$

Since lithium atom only has s core orbitals, all $v_L(r)$ except $L=0$ component is given by a ionic potential calculated by Hartree-Fock or Kohn-Sham method.

$$v_L(r) = v_{ion}(r), L > 0 \quad (4.4)$$

Therefore the total lithium ionic pseudo-potential can be written as,

$$V_{ps} = v_{ion}(r) + \delta v(r) \mathcal{P}_0 \quad (4.5)$$

Using atomic units, the Hamiltonian for this N-electron system is given by,

$$H = \sum_i \left(-\frac{1}{2} \nabla^2 \right) + \sum_i V_{JM}(\mathbf{r}_i) + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = T + V_{bkg} + V_{ee} \quad (4.6)$$

where the usual Jellium background potential is replaced by a summation of the angular-momentum-dependent lithium ionic pseudo-potential (Eqn. 4.7)

$$V_{JM}(r) = \begin{cases} -\frac{N}{2R_J} \left(3 - \left(\frac{r}{R_J} \right)^2 \right) & \text{if } r < R_J \\ -\frac{N}{r} & \text{if } r > R_J. \end{cases}$$

N is the number of atoms in the cluster and $R_J = N^{1/3} r_s$ is the cluster radius. r_s is the Wigner-Seitz radius of Li atom.

$$V_{bkg}(\mathbf{r}, \mathbf{r}') = \sum_{I=1}^N V_{ps}(\mathbf{r} - \mathbf{R}_I, \mathbf{r}' - \mathbf{R}_I) \quad (4.7)$$

4.2 Numerical Details

In order to implement the pseudo-potential into the Jellium codes, it is averaged by spherical Jellium ionic distribution,

$$\begin{aligned} \langle V_{bkg}(\mathbf{r}, \mathbf{r}') \rangle &= \delta(\mathbf{r} - \mathbf{r}') \int d\mathbf{x} \rho_{ion}(x) v(|\mathbf{r} - \mathbf{x}|) \\ &+ \int d\mathbf{x} \rho_{ion}(x) \delta v(|\mathbf{r} - \mathbf{x}|) \mathcal{P}_0(\mathbf{r} - \mathbf{x}, \mathbf{r}' - \mathbf{x}) \\ &= \langle v_{ion}(r) \rangle \delta(\mathbf{r} - \mathbf{r}') + \mathbf{K}_{av}(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (4.8)$$

where,

$$\mathbf{K}_{av}(\mathbf{r}, \mathbf{r}') = \rho_{ion}(q) K(s) \quad (4.9)$$

$$s = |\mathbf{r} - \mathbf{r}'| \quad (4.10)$$

$$q = \frac{|\mathbf{r} + \mathbf{r}'|}{2} \quad (4.11)$$

Apparently the angular-momentum-dependent pseudo-potential is separated into local and non-local parts. The local part of the pseudo-potential $\langle v_{ion}(r) \rangle$ is very similar to the usual Jellium background potential. Next multipole expansion is done for the non-local part, so that $\mathbf{K}_{av}(\mathbf{r}, \mathbf{r}')$ can be added into the radial Hartree-Fock equations:

$$\rho_{ion}(q) K(s) = \frac{1}{rr'} \sum_l k_l(r, r') P_l(\cos \theta_{r,r'}) \quad (4.12)$$

where $k_l(r, r')$ is calculated numerically by:

$$\begin{aligned} k_l(r, r') &= rr' \frac{2l+1}{2} \int_{-1}^1 P_l(t) [\rho_{ion}(q) K(s)] dt \\ &= \frac{2l+1}{4} \int_{|r-r'|}^{r+r'} P_l(t) \rho_{ion}(q) \left[\int_{\frac{s}{2}}^{\frac{s}{2}} \delta v(x) dx \right] ds \end{aligned} \quad (4.13)$$

where,

$$s^2 = r^2 + r'^2 - 2rr't \quad (4.14)$$

$$4q^2 = r^2 + r'^2 + 2rr't \quad (4.15)$$

using Legendre polynomials,

$$P_l(t) = \sum_{k=0,l} c_k t^k = \sum_k y_k s^{2k} \quad (4.16)$$

$k_l(r, r')$ is further simplified into a form that can be evaluated numerically,

$$\begin{aligned}
 k_l(r, r') &= \frac{2l+1}{4} \rho_{ion} \int_{b_2}^{b_1} \sum_k (y_k s^{2k}) \left[\int_{\frac{s}{2}}^s \delta v(x) dx \right] ds \\
 &= \frac{2l+1}{4} \rho_{ion} \sum_k \frac{y_k}{2k+1} \left(\left[s^{2k+1} \int_{\frac{s}{2}}^s \delta v(x) dx \right] \Big|_{b_2}^{b_1} + \frac{1}{2} \int_{b_2}^{b_1} s^{2k+1} \delta v\left(\frac{s}{2}\right) ds \right).
 \end{aligned} \tag{4.17}$$

4.2.1 Modified Radial Hartree-Fock Equations

In this section, the derivation of the non-local pseudo-potential modified radial Hartree-Fock equations is presented. The normal Hartree-Fock equations is,

$$\left(-\frac{1}{2} \nabla^2 + V_{bkg} + U_{HF} \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \tag{4.18}$$

where under a spherical symmetry approximation,

$$\phi_i(\mathbf{r}) = \frac{R_{nl}(r)}{r} Y_{lm}(\Omega) \tag{4.19}$$

one get the normal radial Hartree-Fock equations.

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + V_{bkg} + U_{HF} + \frac{l(l+1)}{2r^2} \right) R_{nl}(r) = \epsilon_{nl} R_{nl}(r) \tag{4.20}$$

Apply the non-local background potential of Eqn. (4.12) to Eqn. (4.21).

$$\begin{aligned}
 &\left(-\frac{1}{2} \nabla^2 + U_{HF} \right) \phi_i(\mathbf{r}) + \int (\langle \mathbf{v}_{ion}(\mathbf{r}) \rangle \delta(\mathbf{r} - \mathbf{r}') + \\
 &\quad K_{av}(\mathbf{r}, \mathbf{r}')) \phi_i(\mathbf{r}') d\mathbf{r}' = \epsilon_i \phi_i(\mathbf{r})
 \end{aligned} \tag{4.21}$$

Now one needs to evaluate the angular part of the non-local pseudo-potential.

$$\begin{aligned}
 \int K_{av} \phi_i &= \sum_{l'=0}^{\infty} \int \frac{1}{r r'} k_{l'}(r, r') P_{l'}(\cos \theta_{r, r'}) \left(\frac{R_{nl}(r')}{r'} Y_{lm}(\Omega') \right) d\Omega' r'^2 dr' \\
 &= \sum_{l'=0}^{\infty} \int P_{l'}(\cos \theta_{r, r'}) \frac{k_{l'}(r, r') R_{nl}(r')}{r} Y_{lm}(\Omega') d\Omega' dr'
 \end{aligned} \tag{4.22}$$

Given that:

$$P_{l'}(\cos \theta_{r,r'}) = \sum_{m'=-l'}^{l'} \frac{4\pi}{2l'+1} Y_{l'm'}(\Omega) Y_{l'm'}^*(\Omega') \quad (4.23)$$

one has.

$$\begin{aligned} \int K_{av} \phi_i &= \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \int \frac{4\pi}{2l'+1} Y_{l'm'}(\Omega) Y_{l'm'}^*(\Omega') \frac{k_{l'}(r, r') R_{nl}(r')}{r} Y_{lm}(\Omega') d\Omega' dr' \\ &= \int \frac{4\pi}{2l+1} Y_{lm}(\Omega) \frac{k_l(r, r') R_{nl}(r')}{r} dr' = \frac{Y_{lm}(\Omega)}{r} \frac{4\pi}{2l+1} \int k_l(r, r') R_{nl}(r') dr' \end{aligned} \quad (4.24)$$

Therefore the radial Hartree-Fock equations with non-local background potential is:

$$\begin{aligned} & \left(-\frac{1}{2} \frac{d^2}{dr^2} + V_{Local} + \frac{l(l+1)}{2r^2} \right) R_{nl}(r) \\ & + \frac{4\pi}{2l+1} \int k_l(r, r') R_{nl}(r') dr' + U_{HF} R_{nl}(r) = \epsilon_{nl} R_{nl}(r) \end{aligned} \quad (4.25)$$

4.2.2 Modified f-sum Rule

The optical response of lithium cluster is calculated by matrix Random Phase Approximation with exact exchange:

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \hbar\omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (4.26)$$

where,

$$A_{mi,nj} = (\varepsilon_m - \varepsilon_i) \delta_{mn} \delta_{ij} + \langle mj | \frac{1}{r_{12}} | in \rangle \quad (4.27)$$

and

$$B_{mi,nj} = \langle mn | \frac{1}{r_{12}} | ij \rangle \quad (4.28)$$

For a local background potential, the Thomas-Reiche-Kuhn f sum rule gives the number of valence electrons (see chapter 3). With a non-local pseudo-potential, the f-sum rule is modified. The HF equation with the non-local background po-

tential is,

$$(T + V_{ext} + U_{HF} + V_{ps})|\alpha\rangle = h_{HF}|\alpha\rangle = \varepsilon_\alpha|\alpha\rangle \quad (4.29)$$

To evaluate the f-sum rule, one needs to calculate:

$$\begin{aligned} (E_k - E_0) \langle k|Z|0\rangle &= -i \langle k|P_z|0\rangle \\ &+ \sum_{mi} (\langle m|[V_{ps}, z]|i\rangle X_{mi}^{k*} + \langle i|[V_{ps}, z]|m\rangle Y_{mi}^{k*}) \\ &= -i \langle k|P_z|0\rangle + \langle k|\sum_i [V_{ps}, z]|0\rangle \end{aligned} \quad (4.30)$$

Thus

$$\begin{aligned} 2 \sum_k (E_k - E_0) |\langle k|Z|0\rangle|^2 &= N + \\ \sum_k (\langle 0|Z|k\rangle \langle k|\sum_i [V_{ps}, z]|0\rangle - \langle 0|\sum_i [V_{ps}, z]|k\rangle \langle k|Z|0\rangle) \\ &= N - \sum_i \int \phi_i^*(\mathbf{r}) (z^2 V_{ps}(\mathbf{r}, \mathbf{r}') + V_{ps}(\mathbf{r}, \mathbf{r}') z'^2 - 2z V_{ps}(\mathbf{r}, \mathbf{r}') z') \phi_i(\mathbf{r}') d^3r d^3r' \\ &= N - \sum_i \int \phi_i^*(\mathbf{r}) V_{ps}(\mathbf{r}, \mathbf{r}') (z - z')^2 \phi_i(\mathbf{r}') d^3r d^3r' \end{aligned} \quad (4.31)$$

Therefore one can see that the energy-weighted f-sum rule is violated by the non-local potential.

Simplification for Jellium Model

Replace the single particle wave function by,

$$\phi_i = \frac{R_{nl}(r)}{r} Y_{lm}(\Omega) \quad (4.32)$$

and given that the non-local potential can be expanded as,

$$\rho_{ion}(q)K(s) = \frac{1}{rr'} \sum_L k_L(r, r') P_L(\cos \theta_{r,r'}) \quad (4.33)$$

one has,

$$\sum_k f_k = N - \sum_{nlm} \int dr dr' d\Omega d\Omega' R_{nl}(r) R_{nl}(r') Y_{lm}^*(\Omega) Y_{lm}(\Omega') (r \cos \theta - r' \cos \theta')^2 \left(\sum_{LM} k_L(r, r') \frac{4\pi}{2L+1} Y_{LM}(\Omega) Y_{LM}^*(\Omega') \right). \quad (4.34)$$

Since,

$$P_L(\cos \theta_{r,r'}) = \sum_{M=-L}^L \frac{4\pi}{2L+1} Y_{LM}(\Omega) Y_{LM}^*(\Omega') \quad (4.35)$$

Consider r^2 term

$$\begin{aligned} \sum_{nlL} \frac{4\pi}{2L+1} \int (radial)_{nlL} \sum_{Mm} \int Y_{lm}^*(\Omega) Y_{lm}(\Omega') \cos^2 \theta Y_{LM}(\Omega) Y_{LM}^*(\Omega') d\Omega d\Omega' \\ = \sum_{nl} \frac{4\pi}{2l+1} \int (radial)_{nl} \sum_m \int Y_{lm}^*(\Omega) \left(\frac{4\pi}{3} Y_{10}^*(\Omega) Y_{10}(\Omega) \right) Y_{lm}(\Omega) d\Omega \end{aligned} \quad (4.36)$$

The radial part is,

$$(radial)_{nlL} = R_{nl}(r) R_{nl}(r') k_L(r, r') r^2 \quad (4.37)$$

and,

$$(radial)_{nl} = R_{nl}(r) R_{nl}(r') k_l(r, r') r^2. \quad (4.38)$$

Given that

$$\begin{aligned} Y_{lm}(\Omega) Y_{LM}(\Omega) = \sum_{L'M'} Y_{L'M'}^*(\Omega) \\ \sqrt{\frac{(2L'+1)(2l+1)(2L+1)}{4\pi}} \begin{pmatrix} l & L & L' \\ m & M & M' \end{pmatrix} \begin{pmatrix} l & L & L' \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (4.39)$$

and,

$$Y_{lm}(\Omega) Y_{10}(\Omega) = \sum_{LM} \sqrt{\frac{3(2l+1)(2L+1)}{4\pi}} Y_{LM}^*(\Omega) \begin{pmatrix} l & 1 & L \\ m & 0 & M \end{pmatrix} \begin{pmatrix} l & 1 & L \\ 0 & 0 & 0 \end{pmatrix}. \quad (4.40)$$

one finds that,

$$\begin{aligned}
 \int Y_{lm}^*(\Omega) \left(\frac{4\pi}{3} Y_{10}^*(\Omega) Y_{10}(\Omega) \right) Y_{lm}(\Omega) d\Omega &= \sum_{LM} \sum_{L'M'} \sqrt{(2l+1)(2L+1)} \\
 \sqrt{(2l'+1)(2L'+1)} \int Y_{LM}^*(\Omega) Y_{L'M'}(\Omega) \begin{pmatrix} l1L \\ m0M \end{pmatrix} \begin{pmatrix} l1L \\ 000 \end{pmatrix} \begin{pmatrix} l'1L' \\ m0M \end{pmatrix} \begin{pmatrix} l'1L' \\ 000 \end{pmatrix} d\Omega \\
 &= \sum_{LM} (2l+1)(2L+1) \begin{pmatrix} l1L \\ m0M \end{pmatrix}^2 \begin{pmatrix} l1L \\ 000 \end{pmatrix}^2
 \end{aligned} \tag{4.41}$$

Therefore the r^2 term is

$$\begin{aligned}
 \sum_{nl} \frac{4\pi}{2l+1} \int (radial)_{nl} \sum_m \int Y_{lm}^*(\Omega) \left(\frac{4\pi}{3} Y_{10}^*(\Omega) Y_{10}(\Omega) \right) Y_{lm}(\Omega) d\Omega \\
 = 4\pi \sum_{nl} \int (radial)_{nl} \sum_L (2L+1) \left(\sum_{Mm} \begin{pmatrix} l1L \\ m0M \end{pmatrix}^2 \right) \begin{pmatrix} l1L \\ 000 \end{pmatrix}^2 \\
 = \frac{4\pi}{3} \sum_{nl} \int (radialpart)_{nl}
 \end{aligned} \tag{4.42}$$

Next consider rr' term

$$\begin{aligned}
 \sum_{nlL} \frac{4\pi}{2L+1} \int (radial)_{nlL} \\
 \sum_{Mm} \int Y_{lm}^*(\Omega) Y_{lm}(\Omega') 2 \cos \theta \cos \theta' Y_{LM}(\Omega) Y_{LM}^*(\Omega') d\Omega d\Omega' \\
 = \sum_{nlL} \frac{4\pi}{2L+1} 2 \frac{4\pi}{3} \int (radial)_{nlL} \\
 \sum_{Mm} \int Y_{lm}^*(\Omega) Y_{10}(\Omega) Y_{LM}(\Omega) Y_{lm}(\Omega') Y_{10}^*(\Omega') Y_{LM}^*(\Omega') d\Omega d\Omega'
 \end{aligned} \tag{4.43}$$

The radial part is,

$$(radialpart)_{nlL} = R_{nl}(r) R_{nl}(r') k_L(r, r') rr'. \tag{4.44}$$

Given that,

$$Y_{lm}(\Omega)Y_{LM}(\Omega) = \sum_{L'M'} Y_{L'M'}(\Omega) \sqrt{\frac{(2L'+1)(2l+1)(2L+1)}{4\pi}} (-1)^{M'} \begin{pmatrix} lL L' \\ m' M - M' \end{pmatrix} \begin{pmatrix} lL L' \\ 000 \end{pmatrix} \quad (4.45)$$

and,

$$Y_{10}(\Omega)Y_{LM}(\Omega) = \sum_{L'M'} Y_{L'M'}(\Omega) \sqrt{\frac{(2L'+1)3(2L+1)}{4\pi}} (-1)^{M'} \begin{pmatrix} 1L L' \\ 0M - M' \end{pmatrix} \begin{pmatrix} 1L L' \\ 000 \end{pmatrix} \quad (4.46)$$

one has,

$$\int Y_{lm}^*(\Omega)Y_{10}(\Omega)Y_{LM}(\Omega)d\Omega = \sqrt{\frac{(2l+1)3(2L+1)}{4\pi}} (-1)^m \begin{pmatrix} 1L l \\ 0M - m \end{pmatrix} \begin{pmatrix} 1L l \\ 000 \end{pmatrix} \quad (4.47)$$

and

$$\int Y_{lm}(\Omega')Y_{10}^*(\Omega')Y_{LM}^*(\Omega')d\Omega' = \sqrt{\frac{(2l+1)3(2L+1)}{4\pi}} (-1)^m \begin{pmatrix} 1L l \\ 0M - m \end{pmatrix} \begin{pmatrix} 1L l \\ 000 \end{pmatrix} \quad (4.48)$$

Therefore the rr' term is

$$\begin{aligned} & \sum_{nlL} \frac{4\pi}{2L+1} \int (radial)_{nlL} \sum_{Mm} \int Y_{lm}^*(\Omega)Y_{lm}(\Omega')2 \cos \theta \cos \theta' \\ &= \sum_{nlL} 8\pi \int (radial)_{nlL} \sum_{Mm} (2l+1) \begin{pmatrix} 1L l \\ 0M - m \end{pmatrix}^2 \begin{pmatrix} 1L l \\ 000 \end{pmatrix}^2 \\ &= \frac{8\pi}{3} \sum_{nl} \sum_L (2l+1) \begin{pmatrix} 1L l \\ 000 \end{pmatrix}^2 \int (radial)_{nlL} \end{aligned} \quad (4.49)$$

So the radial equation for the modified f-sum rule is,

$$\begin{aligned} \sum_k f_k &= N - \frac{4\pi}{3} \sum_{nl} \int R_{nl}(r) R_{nl}(r') k_l(r, r') (r^2 + r'^2) dr dr' \\ &+ \frac{8\pi}{3} \sum_{nl} \sum_L (2l+1) \left(\frac{1Ll}{000} \right)^2 \int R_{nl}(r) R_{nl}(r') k_L(r, r') r r' dr dr' \end{aligned} \quad (4.50)$$

4.3 Numerical Results for Li Clusters

Use norm-conserving pseudo-potential for v_0 (89)

$$v_0 = -\frac{1}{r} \sum_{i=1}^2 c_i \exp(\beta_i r) + \sum_{i=1}^3 (A_i + r^2 A_{i+3}) \exp(-\alpha_i r^2) \quad (4.51)$$

However the norm-conserving pseudo-potential converges to $-1/r$ not fast enough, so that $k_l(r, r')$ at large r and r' is not small enough, which makes the HF code fail.

$$\begin{aligned} k_l(r, r') &= r r' \frac{2l+1}{2} \int_{-1}^1 P_l(t) [\rho_{ion}(q) K(s)] dt \\ &= r r' \frac{2l+1}{4} \int_{-1}^1 P_l(t) \rho_{ion}(q) \left[\frac{1}{s} \int_{\frac{s}{2}}^1 \delta v(x) dx \right] dt \end{aligned} \quad (4.52)$$

So a damping factor is multiplied to the nonlocal potential

$$dk_l(r, r') = k_l(r, r') / (e^{a*(\sqrt{r^2+r'^2}/b-1)} + 1) \quad (4.53)$$

To compare with experiment absorption spectrum results and the previous theoretical calculations, one makes a Lorentzian shape convolution for the oscillator strength.

$$\sigma(E) = \frac{2\pi^2}{c} \sum_k f_k \delta(E - E_k + E_0) \quad (4.54)$$

Figure 4.1: Non-local pseudo-potential corrected Jellium Model results for free lithium clusters: Li_8 ; Li_{20} ; Li_{40} ; Li_{58} ; Li_{92} . Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength.

Figure 4.2: Non-local pseudo-potential corrected Jellium Model results for free lithium clusters: Li_9^+ ; Li_{21}^+ ; Li_{41}^+ ; Li_{59}^+ ; Li_{93}^+ . Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength.

Figure 4.3: Experimental data (black circles) for $\text{Li}9+$ and $\text{Li}21+$ compared with previous RPAE calculation results (dash-dotted line), which used the same method as discussed in this chapter. This figure is replotted from reference (8).

Table 4.1: f-sum comparison with previous work (1) on Li clusters. Good agreement can be found.

Cluster	current results	previous results
8	0.792	0.792
9+	0.770	0.771
20	0.782	0.781
21+	0.772	0.771
40	0.777	0.776
41+	0.771	0.772
58	0.770	0.769
59+	0.766	0.765
92	0.766	0.766
93+	0.764	0.762
138	0.763	0.763
139+	0.761	0.761

Figure 4.4: Non-local pseudo-potential corrected (red) and pure (blue) Jellium Model results for free Li139+ compared with experimental data (black). Vertical drop lines are oscillator strength calculated by RPAE. Continuous line is Lorentzian shape convolution ($\gamma=0.060\omega_k$) of the oscillator strength. Black dots with error bars are experimental data from reference (9).

$$f_k = \frac{f_k}{\pi} \frac{\Gamma}{\Gamma^2 + (E - \omega_k)^2} \quad (4.55)$$

Good agreement with experiment absorption spectrum is found for Li139+ (Figure 4.3). A clear red shift of the plasmon peak can be seen due to the non-local pseudo-potential. Table 4.1 shows that the present calculation results agree very well with the original work. Figure 4.1 and 4.2 show the oscillator strength distribution for neutral and cationic lithium clusters. The size dependency does not change by the non-local pseudo-potential. As cluster size increase, the plasmon peak moves to higher energy.

4.4 Conclusion

To conclude this chapter, a repetition of a previous work on pseudo-potential method for lithium clusters is presented. Detailed numerical procedure is given. Good agreement with the original work and experimental results is found. Oscillator strength distribution is significantly shifted to lower energy by the non-local pseudo-potential compared to pure Jellium Model prediction. The only *s* core shell of Li leads to a large difference of *s*- and *p*- wave pseudo-potential, which has been shown determining the effective mass (1, 90).

Chapter 5

Core Polarization Corrections

This chapter presents the major work of this PhD project, that is, core-polarization-corrected Random Phase Approximation for the surface plasmon in neutral and charged silver clusters. A Jellium-like model for the valence electrons in silver clusters is developed. The background of Ag cores is considered as a spherical polarizable Jellium which leads to a core-polarization two-body interaction and a self-energy potential for the valence electrons. The core-polarization corrections are implemented into Hartree-Fock equations and matrix Random Phase Approximation equation. Oscillator strength of anionic, neutral and cationic Ag clusters have been calculated and are compared with pure Jellium calculations. The effects of the one-body and two-body corrections on the oscillator strength distribution are identified. A clear blue shift is found for cationic Ag clusters as clusters size decreases which is in good agreement with experimental results. (This part of work has been published (91).)

In a pure Jellium Model, cluster of N metal atoms can be regarded as a system of N electrons (one valence electron per atom) confined by a uniformly charged background. Using atomic units, the Hamiltonian for this N -electron system is given by,

$$H = \sum_i \left(-\frac{1}{2} \nabla^2 \right) + \sum_i V_{JM}(\mathbf{r}_i) + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = T + V_{bkg} + V_{ee} \quad (5.1)$$

where,

$$V_{JM}(r) = \begin{cases} -\frac{N}{2R_J} \left(3 - \left(\frac{r}{R_J} \right)^2 \right) & \text{if } r < R_J \\ -\frac{N}{r} & \text{if } r > R_J. \end{cases}$$

N is the number of atoms in the cluster and $R_J = N^{1/3} r_s$ is the cluster radius. r_s is the Wigner-Seitz radius of the metal atom. One could take jellium background potential V_{JM} as a first approximation for the valence-core interaction, which requires that the valence electron is well separated from the core. Since there is a large overlap between 5s and 4d electron wave functions in Ag atom, simple Jellium Model for silver clusters will not be as accurate as for Sodium clusters. Noticing the fact that silver core (Ag+) has a rather large polarizability than Sodium core (Na+), the valence-core interaction of silver is treated as core-polarization effect. The picture is that delocalized 5s electrons polarize the jellium background (mainly constructed by the 4d electrons from each silver core) to form a dipole. The induced dipole will further generate a dipole potential which is then felt by the delocalized valence electrons. The total polarizability of the jellium background is $N\alpha$, where α is the polarizability of Ag+, which can be found by an atomic calculation. Therefore to include the core-polarization effect from the 4d electrons of Ag atom, one adds a correction term V_{cp} to the total Hamiltonian (cp stands for core-polarization),

$$H_{cp} = T + V_{ee} + V_{ext} + V_{cp} = H + V_{cp} \quad (5.2)$$

Of course the most accurate expression for V_{cp} would be a sum of atomic dipole energy over all the silver cores.

$$V_{cp} = \sum_a v_{cp}(a) = \sum_a \left(-\frac{1}{2} \alpha_a |\mathbf{E}_a|^2 \right) \quad (5.3)$$

where α_a is the polarizability of core a and $\mathbf{E}_a$ is the electric field at core a , generated by all the delocalized valence electrons $\mathbf{E}_a^e$ and other silver cores $\mathbf{E}_a^{ion}$.

$$\mathbf{E}_a = \mathbf{E}_a^{ion} + \mathbf{E}_a^e \quad (5.4)$$

Near core electric field can be approximated by a cutoff function $C(|\mathbf{r}_i - \mathbf{r}_a|, r_0)$, which has a adjustable parameter r_0 .

$$\mathbf{E}_a^e = \sum_i C(|\mathbf{r}_i - \mathbf{r}_a|, r_0) \frac{\mathbf{r}_i - \mathbf{r}_a}{|\mathbf{r}_i - \mathbf{r}_a|^3} \quad (5.5)$$

In the Appendix A of this chapter, it is shown that, other than a simple dipole correction, Eqn (5.3) leads to higher multipole terms. Since our numerical calculation ensures that the dipole term dominates V_{cp} , one could look for a simple straight forward dipole core-polarization correction. Moreover, we are not trying to compete with a quantum chemistry 3-dimension calculation. What we start from is the simple Jellium Model and we want to know how the atomic core polarization would affect the giant collective dipole response of the delocalized valence electrons by screening the exact exchange potential. The overall contribution from each silver core to the V_{cp} can be considered as a polarizable jellium, which is big dipole oscillating with the valence electrons.

5.1 Polarizable Jellium Model

Given all the considerations above a simple parameter free model for V_{cp} is proposed.

$$V_{cp} = \sum_{i,j} \left(-\frac{1}{2} N \alpha \mathbf{f}_i \mathbf{f}_j \right) \quad (5.6)$$

where,

$$\mathbf{f}_i = \begin{cases} \frac{\mathbf{r}_i}{R_J^3} & \text{if } r_i < R_J \\ \frac{\mathbf{r}_i}{r_i^3} & \text{if } r_i > R_J \end{cases}$$

In fact, different cutoff function with adjustable parameters for the electric field inside the cluster have been tried. It can be shown that they all lead to very similar results as in the atomic case(92, 93, 94, 95). Therefore one concludes that a linear

approximation for the electric field $\mathbf{f}$ inside the cluster would be enough as long as it has a correct long range behaviour. It needs to be stressed that the present model is parameter-free so that it is easy to analyse the magnitude of the core-polarization correction. (A mathematical justification is presented in Appendix B of this chapter.)

Equation 5.6 can be further divided into a one-body and a two-body term.

$$V_{cp} = \sum_i \left(-\frac{1}{2} N \alpha \mathbf{f}_i \mathbf{f}_i \right) + \sum_{i < j} \left(-N \alpha \mathbf{f}_i \mathbf{f}_j \right) = V_{cp1} + V_{cp2} \quad (5.7)$$

As has been argued by Serra (69), the polarizability of Ag^+ on the surface of the cluster is different from that embedded in the cluster. To account for this difference, a shell model is applied for large clusters ($N=58, 138, 198$),

$$H_{cp} = T + V_{ee} + V_{ext} + V_{shellcp} = H + V_{shellcp} \quad (5.8)$$

$$\begin{aligned} V_{shellcp} = \sum_{i,j} \left(-\frac{1}{2} N_{total} \alpha_{freeion} \mathbf{f}_i \mathbf{f}_j \right) - \sum_{i,j} \left(-\frac{1}{2} N_{core} \alpha_{freeion} \mathbf{f}_i \mathbf{f}_j \right) \\ + \sum_{i,j} \left(-\frac{1}{2} N_{core} \alpha_{embedded} \mathbf{f}_i \mathbf{f}_j \right) \end{aligned} \quad (5.9)$$

The silver cores in the inner part of the cluster and on the surface shell have embedded polarizability and free-ion polarizability, respectively. The surface shell contribution is modeled by subtracting the core-polarization correction of the total cluster with a free-ion polarizability from that of the inner sphere, also with a free-ion polarizability.

5.1.1 Core Polarizability

The free-ion polarizability of Ag^+ is $8.281 a.u.$, which is obtained by an atomic calculation. The 46 core electrons are confined by the bare nuclear potential $-Z/r$. The ground state is calculated by HF approximation. Unoccupied HF states are generated by B-spline method. Finally the polarizability is calculated by RPAE. As for the embedded polarizability, the situation is that the target silver

core is surrounded by all metallic delocalized valence electrons(70, 71), most of which are neutralized by other silver cores and left with a uniformly distributed Wigner-Seitz sphere of one unit negative charge with a density $\rho = 3/4\pi r_s^3$. Thus the potential felt by the 46 core electrons is $V = -Z/r + V_{ws}(r)$ where,

$$V_{ws}(r) = \begin{cases} \frac{1}{2r_s}(3 - (\frac{r}{r_s})^2) & \text{if } r < r_s \\ \frac{1}{r} & \text{if } r > r_s. \end{cases}$$

The HF-RPAE calculation gives the embedded polarizability $11.272a.u.$. For small clusters AgN ($N \leq 21$), all the silver cores are considered as staying on the surface and the α in Equation 5.6 is set to free-ion polarizability $8.281a.u.$. For $Ag58$ and $Ag59+$ the number of embedded silver cores is obtained by using the atomic structure in Fig 2 of reference(96) for the core part, $N_{core} = 13$. In the same way, for $Ag138$ and $Ag139+$ the number of embedded silver cores is 55. For $Ag198$ and $Ag199+$, an approximation is made that the surface shell has the same thickness as that of $Ag138$. Thus N_{core} fulfills

$$r_s * 198^{1/3} - r_s * N_{core}^{1/3} = r_s * 138^{1/3} - r_s * 55^{1/3} \quad (5.10)$$

which gives $N_{core} = 89$.

5.2 Numerical Results

Starting from the modified total Hamiltonian (Eq. 5.2 and 5.6) for the delocalized valence electrons (the Wigner-Seitz radius of Ag is $r_s = 3.02a_0$), ground state calculation is carried out by Hartree-Fock approximation, which leads to a set of coupled one-particle Schrodinger equations,

$$(-\frac{1}{2}\nabla^2 + V_{bkg} + U_{HFdx} + V_{cp1} + V_{cp2x})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \quad (5.11)$$

where U_{HFdx} is usual Hartree-Fock direct and exchange term. V_{cp1} is the one-body correction and serves as a correction to the jellium background potential V_{bkg} . V_{cp2x} originates from the two-body core-polarization correction V_{cp2} , which

Table 5.1: Change of the eigenvalues of Ag20 by the core-polarization correction.

Ag20(nl)	1s	2p	3d	2s	Ecluster
Pure JM (eV)	-10.81	-8.46	-5.27	-4.44	-18.91
CP JM (eV)	-10.64	-8.22	-5.36	-4.52	-21.20

is proportional to $\cos(\theta_{\mathbf{r}_i \mathbf{r}_j})$

$$V_{cp2} = \sum_{i < j} (-N\alpha \mathbf{f}_i \mathbf{f}_j) \propto \cos(\theta_{\mathbf{r}_i \mathbf{r}_j}) \quad (5.12)$$

therefore V_{cp2} only screens the bare Coulomb interaction in the exchange term

$$V_{cp2x} = \sum_j^{core} \int \phi_j^*(\mathbf{r}') (-N\alpha \mathbf{f} \mathbf{f}') \phi_i(\mathbf{r}') d\mathbf{r}' \phi_j(\mathbf{r}) \quad (5.13)$$

For further use in the matrix RPA calculation, the occupied and unoccupied orbitals are expanded by a finite number of B-splines. The optical response is described by Random Phase Approximation with exact exchange (RPAE) modified by the two-body core-polarization interaction.

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \hbar\omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (5.14)$$

where,

$$A_{mi,nj} = (\varepsilon_m - \varepsilon_i) \delta_{mn} \delta_{ij} + \langle mj | \frac{1}{r_{12}} | in \rangle - N\alpha \langle mj | \widetilde{\mathbf{f}_1 \mathbf{f}_2} | in \rangle \quad (5.15)$$

$$B_{mi,nj} = \langle mn | \frac{1}{r_{12}} | ij \rangle - N\alpha \langle mn | \widetilde{\mathbf{f}_1 \mathbf{f}_2} | ij \rangle \quad (5.16)$$

The third term in A and second term in B come from the core-polarization two-body term. Dipole transitions ($F = \sum f = \sum_i z_i$) amplitude is given by,

$$\langle k | F | 0 \rangle = \sum_{i,m} [X_{mi}^k \langle m | f | i \rangle + Y_{mi}^k \langle i | f | m \rangle] \quad (5.17)$$

Numerical calculations were performed for closed shell free anionic, neutral and

Table 5.2: Change of the eigenvalues of Ag21+ by the core-polarization correction.

Ag21(nl)	1s	2p	3d	2s	Ecluster
Pure JM (eV)	-13.76	-11.44	-8.24	-7.35	-15.98
CP JM (eV)	-13.60	-11.21	-8.34	-7.44	-18.21

Table 5.3: Change of the eigenvalues of Ag58 by the core-polarization correction.

Ag58(nl)	1s	2p	3d	2s	4f	3p	5g	Ecluster
Pure JM (eV)	-11.99	-10.58	-8.89	-8.30	-6.85	-5.45	-4.18	-52.39
CP JM (eV)	-11.79	-10.35	-8.62	-8.12	-6.59	-5.49	-4.22	-56.92

cationic silver clusters (Ag7-, Ag19-, Ag57-, Ag137-, Ag197-; Ag8, Ag20, Ag58, Ag138, Ag198; Ag9+, Ag21+, Ag59+, Ag139+, Ag199+). For clusters with atom number larger than 58, a shell model is applied to distinguish embedded and free ion polarizability of silver core inside and on the surface of the clusters. The static polarizabilities of neutral silver clusters are significantly increased as shown by Table 5.4. A clear red shift of surface plasma peak compared to pure Jellium prediction can be seen for all cluster size due to the core-polarization correction (figure 5.3, 5.4 and 5.5). As shown before that the core polarization correction splits into a one-body and a two-body term.

$$V_{cp} = \sum_i \left(-\frac{1}{2} N \alpha \mathbf{f}_i \mathbf{f}_i \right) + \sum_{i < j} \left(-N \alpha \mathbf{f}_i \mathbf{f}_j \right) = V_{cp1} + V_{cp2} \quad (5.18)$$

The one-body correction serves as a self-energy term and is an attractive potential, which makes the valence electrons more bounded and shifts the plasma resonance peak to higher energy. The two body term can be seen as a screening effect for the bare Coulomb interaction $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$. If one does a multipole expansion for Coulomb interaction, one could see that the core polarization two-body interaction screens

Table 5.4: Static dipole polarizabilities (a_0^3) for silver clusters Ag_N .

N	8	20	58	92	138	198
CP	430	1059	2819	4475	6768	9823
JM	361	856	2109	3262	4854	6976

only L=1 component of Coulomb interaction.

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_L \frac{r_{<}^L}{r_{>}^{L+1}} P_L(\cos\theta_{\mathbf{r},\mathbf{r}'}) \quad (5.19)$$

$$v_{cp2} = -N\alpha\mathbf{f}\mathbf{f}' \propto \cos(\theta_{\mathbf{r}\mathbf{r}'}) = P_1(\cos\theta_{\mathbf{r}\mathbf{r}'}) \quad (5.20)$$

This two-body polarization correction shifts the plasma resonance peak to lower energy and contributes more than the one-body term. Therefore the overall polarization corrections, that is, the one-body and two-body terms, give a red shift. And Table 5.1 to 5.3 show that the HF eigenvalues are affected by core polarization corrections. The inner shell orbital is slightly less bounded and the outer shell orbital is slightly more bounded. And overall the cluster total energy is lowered.

To compare with experimental absorption spectrum results, one makes a Lorentzian shape convolution for the oscillator strength of Ag9+ Ag21+ and Ag59+.

$$\sigma(E) = \frac{2\pi^2}{c} \sum_k f_k \delta(E - E_k + E_0) \quad (5.21)$$

$$f_k = \frac{f_k}{\pi} \frac{\Gamma}{\Gamma^2 + (E - \omega_k)^2} \quad (5.22)$$

Good agreement with experiment absorption spectrum is found for Ag9+ Ag21+ (figure 5.1 upper and middle panel). For Ag59+ we rescaled it to compare with experiment result of Ag50+ (figure 5.1 lower panel).

For negatively charged clusters (Ag7 and Ag19-) an agreement of peak position is found (figure 5.2 and 5.4). However, the present results have rather large broadening than the experiments. The discrepancy is probably due to the approximation one makes for the core-polarization correction inside the cluster, which in principle should have small corrections to L=0 L=2 ... components of the Coulomb interaction. These small corrections in total serves as a slight dielectric screening which should make the oscillator strength distribution narrow. Another possible reason is the limitation of Jellium Model, which does not take into ac-

Figure 5.1: Photo absorption cross section ($\text{\AA}^2$) of free silver cationic clusters as function of dipole transition energy (eV). Red dots with errorbars are experiment results (10). The blue vertical lines give the discrete oscillator strength distribution calculated by RPAE with the core polarization modified jellium model. The continuous blue line is a Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength distribution. Note that the Lorentzian shape convolution of Ag_{59}^+ is rescaled by a factor of 50/58 to compare with experimental data for Ag_{50}^+

Figure 5.2: Photo absorption cross section ($\text{\AA}^2$) of free silver anionic clusters as a function of dipole transition energy (eV). Red dots with errorbars are experiment results (11). The blue vertical lines give the discrete oscillator strength distribution calculated by RPAE with the core polarization modified jellium model. The continuous blue line is a Lorentzian shape convolution ($\gamma=0.065\omega_k$) of the oscillator strength distribution.

count of the relaxation of ionic core distribution to adjust to the extra negative charge. Consequently the larger fragmentation of the collective dipole excitation which is expected from the larger spill-out as compared with a neutral or cationic cluster is possibly overestimated. As cluster size decreases, the present calculation shows a blue shift of the plasma resonance peak for cationic Ag clusters and is in very good agreement with Tiggesbaumer's and Charle's experiments (figure 5.6). This trend comes from three aspects: (i) From the maximum value of the ratio of the Jellium background potential to the one-body polarization correction, one finds that the effect from the one-body polarization correction is getting stronger as cluster size decreases; from the maximum value of the ratio of the Coulomb interaction to the two-body polarization correction, one finds that the effect from the two-body polarization correction keep the same. Since the one-body polarization correction shifts the plasma peak to high energy, the total core-polarization correction contributes to the blue shift.

$$\max \frac{v_{bkg}}{v_{cp1}} = \frac{2Nr_s^3}{\alpha} \sim N \quad (5.23)$$

$$\max \frac{\frac{r_{\leq}}{r_{>}^2} P_1(\cos\theta_{r,r'})}{v_{cp2}} = \frac{r_s^3}{\alpha} = const \quad (5.24)$$

(ii) As cluster size increases, there are more embedded Ag ions, which has a larger polarizability than free ion. As discussed above, the total core-polarization correction gives a red shift, which will become less significant as cluster size decreases. (iii) The cationic clusters are all positively one unit charged, which means the 5s valence electrons are more bound in cationic clusters than in neutral clusters. A deeper Jellium background potential leads to a blue shift of the plasma peak. This charge effect will be more important in small clusters than in large clusters when they are all one unit charged. For large neutral Ag clusters (Ag199 138 58), a slight blue shift is found as cluster size decreases. However for small neutral Ag clusters (Ag58 20 8), a slight red shift is found (see figure 5.5 and 5.6). Therefore, the blue shift of Mie plasma frequency in small cationic Ag clusters is assigned to the third reasoning discussed above, while the blue shift of Mie plasma frequency in large Ag clusters (neutral or cationic) originates from the first two reasonings. The third reasoning is also responsible for the red shift with

Figure 5.3: Photo absorption cross section ($\text{\AA}^2$) of free silver cationic clusters as a function of dipole transition energy (eV). Blue vertical drop lines are oscillator strengths calculated by RPAE within a pure jellium model. Red vertical drop lines are oscillator strengths calculated by RPAE within a core polarization modified jellium model. The continuous lines are Lorentzian shape convolutions ($\gamma=0.065\omega_k$) of the corresponding oscillator strength distributions.

Figure 5.4: Photo absorption cross section ($\text{\AA}^2$) of free silver anionic clusters as a function of dipole transition energy (eV). Ag_9^+ ; Ag_{19}^+ ; Ag_{57}^+ ; Ag_{137}^+ ; Ag_{197}^+ . Blue vertical drop lines are oscillator strengths calculated by RPAE within a pure jellium model. Red vertical drop lines are oscillator strengths calculated by RPAE within a core polarization modified jellium model. The continuous lines are Lorentzian shape convolutions ($\gamma=0.065\omega_k$) of the corresponding oscillator strength distributions.

Figure 5.5: Photo absorption cross section of free silver neutral clusters as a function of dipole transition energy (eV). Blue vertical drop lines are oscillator strengths calculated by RPAE within a pure jellium model. Red vertical drop lines are oscillator strengths calculated by RPAE within a core polarization modified jellium model. The continuous lines are Lorentzian shape convolutions ($\gamma=0.065\omega_k$) of the corresponding oscillator strength distributions

decreasing cluster size in anionic clusters (see figure 5.4 and 5.6).

Figure 5.6: Theoretical evolution of the surface plasmon peak (eV) as a function of the inverse radius $\text{\AA}^{-1}$ of silver clusters: cationic clusters (green), anionic clusters (red), neutral clusters (blue). RPAE calculations with the core polarization modified jellium model.

5.3 Effective Dielectric Screening

The above analysis of the core-polarization correction is based on its maximum value. Since two-body core-polarization correction contains only a dipole term, it can be seen as a screening of the dipole component of the bare Coulomb interaction $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$. In this section the magnitude of the screening is shown in detail and an effective dielectric constant can be found by the Clausius-Mossotti relation. Rewrite the two-body core-polarization correction

$$v_{cp2} = -N\alpha\mathbf{f}\mathbf{f}' = -N\alpha f(r)f(r')\cos(\theta_{\mathbf{r}\mathbf{r}'}) \quad (5.25)$$

where

$$f(r) = \begin{cases} \frac{r}{R_J^3} & \text{if } r < R_J \\ \frac{1}{r^2} & \text{if } r > R_J \end{cases}$$

Therefore the dipole term $\frac{r_{<}}{r_{>}^2}$ is screened to,

$$\Delta_{dipole} = \frac{r_{<}}{r_{>}^2} - N\alpha f(r)f(r') \quad (5.26)$$

Inserting $N = \frac{R_J^3}{r_s^3}$

$$\Delta_{dipole} = \begin{cases} \frac{r_{<}}{r_{>}^2} \left(1 - \frac{\alpha}{r_s^3} \frac{R_J^3}{r_{<}^3}\right) & \text{if } R_J < r_{<} \\ \frac{r_{<}}{r_{>}^2} \left(1 - \frac{\alpha}{r_s^3}\right) & \text{if } r_{<} < R_J < r_{>} \\ \frac{r_{<}}{r_{>}^2} \left(1 - \frac{\alpha}{r_s^3} \frac{r_{>}^3}{R_J^3}\right) & \text{if } r_{>} < R_J \end{cases}$$

In a more compact form

$$\Delta_{dipole} \leq \frac{r_{<}}{r_{>}^2} \left(1 - \frac{\alpha}{r_s^3}\right) \quad (5.27)$$

if one defines an effective dielectric constant ϵ_{eff} for the silver core background by ClausiusMossotti relation

$$\frac{\epsilon_{eff} - 1}{\epsilon_{eff} + 2} = \frac{\alpha}{r_s^3} \quad (5.28)$$

one is left with

$$\Delta_{dipole} \leq \frac{r_{<}}{r_{>}^2} \frac{3}{\epsilon_{eff} + 2} \quad (5.29)$$

If one uses the general Drude model in Equation 2.1 and replaces ϵ_{∞} with ϵ_{eff} ,

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \quad (5.30)$$

one obtains the modified Mie frequency ω_{Mie}^* ,

$$\omega_{Mie}^* = \frac{\omega_p}{\sqrt{\epsilon_{eff} + 2}} = \frac{\omega_p}{\sqrt{3}} \sqrt{1 - \frac{\alpha}{r_s^3}}. \quad (5.31)$$

Using the embedded core polarizability $\alpha_{emb} = 11.27$ of Ag+ in the above equation, one has $\epsilon_{eff} = 3.08$ and $\omega_{Mie}^* = 3.95eV$ (as shown in Fig 5.6), which is still larger than the classical limit $3.5eV$. To reach $3.5eV$ one needs an effective dielectric constant of 4.57. One possibility for the reason of this discrepancy is

due to the underestimation of the value of embedded silver core polarizability. In the work of Yabana (73), the authors took $\alpha = 15.25$.

Another way to look at the classical prediction is that the effective electron charge is screened from one to $e^* = \sqrt{1 - \frac{\alpha}{r_s^3}}$, so that the plasma frequency in Drude Model becomes $\omega_p^* = \sqrt{1 - \frac{\alpha}{r_s^3}} \omega_p$. Therefore the Mie frequency will be $\omega_{Mie}^* = \sqrt{1 - \frac{\alpha}{r_s^3}} \omega_{Mie}$, which is the same with Eqn. 5.31.

5.4 Conclusion

Unlike Lithium and Sodium, the core part of silver atom (Ag+) has a non-negligible polarizability. In silver clusters the Jellium background, which is constructed by Ag+, can be polarized by the valence electrons. One treats the core-polarization effect of silver cores as a two-body interaction and a self-energy potential. As a major correction, the two-body interaction screens the L=1 component of Coulomb interaction in a multipole expansion, which makes it impossible to include this effect in the Kohn-Sham formalism. The one-body self-energy potential binds the valence electrons more. Overall the core-polarization corrections keep the HF states and eigenvalues almost unchanged. However, the two-body dipole correction to the Coulomb interaction leads to a strong screening in the direct matrix elements $\langle m_j | V' | in \rangle$ of RAPE. This screening finally gives rise to a red shift of the dipole surface plasmon peak.

Core-polarization-modified Random Phase Approximation calculation is done for (N=8 - 198) Ag clusters. Compared with a pure Jellium calculation, the oscillator strength shifts to lower energy due to the core-polarization correction. Good agreement with experimental optical absorption results is found for Ag9+ 21+ 59+ clusters. A blue shift of oscillator strength of cationic Ag clusters is identified. The magnitude of the two-body correction does not vary with cluster size, while the one-body correction decreases as clusters size increases. With an increasing percentage of embedded Ag cores, the cp-caused red shift gets stronger as clusters size increases.

5.5 Appendix A: Jellium Averaging Approach

In Eqn. (5.3) E is the electric field on the site of silver core i , generated by the other silver cores and all the valence electrons.

$$\mathbf{E} = \sum_i \frac{\mathbf{R} - \mathbf{R}_i}{|\mathbf{R} - \mathbf{R}_i|^3} - \sum_i \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \quad (5.32)$$

Under spherical distribution approximation, the core polarization term can be written,

$$\begin{aligned} V_{cp}(t) &= \int \left(-\frac{1}{2}\alpha\rho_{ion}(\mathbf{R})|\mathbf{E}(\mathbf{R})|^2\right)d\mathbf{R} = -\frac{1}{2}\alpha \int |\mathbf{E}(\mathbf{R})|^2\rho_{ion}(\mathbf{R})d\mathbf{R} \\ &= -\frac{1}{2}\alpha \int \left(\sum_i \frac{\mathbf{R} - \mathbf{R}_i}{|\mathbf{R} - \mathbf{R}_i|^3}\right)^2\rho_{ion}(\mathbf{R})d\mathbf{R} - \frac{1}{2}\alpha \int \left(\sum_i \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3}\right)^2\rho_{ion}(\mathbf{R})d\mathbf{R} \\ &\quad + \frac{1}{2}\alpha \int \left(2\sum_i \frac{\mathbf{R} - \mathbf{R}_i}{|\mathbf{R} - \mathbf{R}_i|^3} \sum_i \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3}\right)\rho_{ion}(\mathbf{R})d\mathbf{R} \\ &= V_{cp0}(t) + V_{cp1}(t) + V_{cp2}(t) \end{aligned} \quad (5.33)$$

Therefore the total core polarization correction reduces to three terms: zero-body, one-body and two-body terms. The first term is a zero-body constant which can be neglected.

$$V_{cp0}(t) = -\frac{1}{2}\alpha \int \left(\sum_i \frac{\mathbf{R} - \mathbf{R}_i}{|\mathbf{R} - \mathbf{R}_i|^3}\right)^2\rho_{ion}(\mathbf{R})d\mathbf{R} \quad (5.34)$$

$$\begin{aligned} V_{cp1}(t) &= \sum_i \left[\frac{1}{2}\alpha \int \left(2\sum_I \frac{\mathbf{R} - \mathbf{R}_I}{|\mathbf{R} - \mathbf{R}_I|^3} \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3}\right)\rho_{ion}(\mathbf{R})d\mathbf{R} \right. \\ &\quad \left. - \frac{1}{2}\alpha \int \left(\frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3}\right)^2\rho_{ion}(\mathbf{R})d\mathbf{R}\right] \end{aligned} \quad (5.35)$$

$$V_{cp2}(t) = \sum_{i < j} \left(-\alpha \int \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3} \rho_{ion}(\mathbf{R})d\mathbf{R}\right) = \sum_{i < j} g(i, j) \quad (5.36)$$

$$g(i, j) = -\alpha \int \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3} \rho_{ion}(\mathbf{R}) d\mathbf{R} \quad (5.37)$$

5.5.1 Cutoff Function

Since each silver core has a finite size, one may take an approximation for the electric field inside each silver core (94).

$$\frac{1}{r^3} \rightarrow f_D(r) \frac{1}{r^3} = \frac{r^3}{r^3 + d^3} \frac{1}{r^3} = \frac{1}{r^3 + d^3} \quad (5.38)$$

To evaluate Eqn. (5.10) and (5.11) with a cutoff function of Eqn. (5.13) numerically, one expands the two major factors by Legendre polynomials so that the angular part can be calculated analytically.

$$\begin{aligned} \frac{1}{|\mathbf{r} - \mathbf{r}'|^3 + d^3} &= \sum_L A_L(r, r') P_L(\cos\theta_{r,r'}) \\ &= \sum_{LM} A_L(r, r') \frac{4\pi}{2L+1} Y_{LM}^*(\Omega') Y_{LM}(\Omega) \end{aligned} \quad (5.39)$$

$$\begin{aligned} \frac{\mathbf{r}\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3 + d^3} &= \sum_L B_L(r, r') P_L(\cos\theta_{r,r'}) \\ &= \sum_{LM} B_L(r, r') \frac{4\pi}{2L+1} Y_{LM}^*(\Omega') Y_{LM}(\Omega) \end{aligned} \quad (5.40)$$

where $L=0,1,2, \dots$, $M=-L, \dots, L$.

5.5.2 Two-body Correction

Given that the Coulomb interaction can be expanded as,

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{LM} \frac{r_{<}^L}{r_{>}^{L+1}} \frac{4\pi}{2L+1} Y_{LM}^*(\Omega') Y_{LM}(\Omega) \quad (5.41)$$

in order to take into account the two-body polarization correction to the Coulomb interaction, one needs to expand it in the form of

$$g(i, j) = \sum_{LM} C_L(r, r') \frac{4\pi}{2L+1} Y_{LM}^*(\Omega_i) Y_{LM}(\Omega_j) \quad (5.42)$$

Now one needs to evaluate the expansion coefficient $C_L(r, r')$ numerically.

$$g(i, j) = -\alpha \int \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3 + d^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3 + d^3} \rho_{ion}(\mathbf{R}) d\mathbf{R} \quad (5.43)$$

First $g(i, j)$ can be separated into four terms. The angular part of each term is calculated analytically.

$$\begin{aligned} term1 &= -\alpha \int \frac{\mathbf{R}}{|\mathbf{R} - \mathbf{r}_i|^3 + d^3} \frac{\mathbf{R}}{|\mathbf{R} - \mathbf{r}_j|^3 + d^3} \rho_{ion}(\mathbf{R}) d\mathbf{R} \\ &= \sum_{LM} \left[-\alpha \int R^4 \rho_{ion}(R) A_L(R, r_i) A_L(R, r_j) \frac{4\pi}{2L+1} dR \right] \frac{4\pi}{2L+1} Y_{LM}^*(\Omega_j) Y_{LM}(\Omega_i) \end{aligned} \quad (5.44)$$

$$\begin{aligned} term2 &= \alpha \int \frac{\mathbf{R} \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3 + d^3} \frac{1}{|\mathbf{R} - \mathbf{r}_j|^3 + d^3} \rho_{ion}(\mathbf{R}) d\mathbf{R} \\ &= \sum_{LM} \left[\alpha \int R^2 \rho_{ion}(R) B_L(R, r_i) A_L(R, r_j) \frac{4\pi}{2L+1} dR \right] \frac{4\pi}{2L+1} Y_{LM}^*(\Omega_j) Y_{LM}(\Omega_i) \end{aligned} \quad (5.45)$$

$$term3 = term2 \quad (5.46)$$

$$\begin{aligned} term4 &= -\alpha \int \frac{\mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3 + d^3} \frac{\mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3 + d^3} \rho_{ion}(\mathbf{R}) d\mathbf{R} \\ &= \sum_l \sum_L \left[-\alpha \int R^2 r_i r_j \rho_{ion}(R) A_L(R, r_i) A_L(R, r_j) \frac{4\pi}{2L+1} dR \right. \\ &\quad \left. (2l+1)(L1l)^2 \right] P_l(ij) \end{aligned} \quad (5.47)$$

where the following facts have been used.

$$\cos\theta_{r,r'} = \frac{4\pi}{3} \sum_m Y_{1m}(\Omega) Y_{1m}^*(\Omega') \quad (5.48)$$

$$P_L(x) P_{L'}(x) = \sum_l (2l+1) (LL'l)^2 P_l(x) \quad (5.49)$$

Numerical evaluation shows that the dipole component $L = 1$ is significantly larger than other terms.

5.6 Appendix B: Jellium Polarization Interaction

Let N silver cations and N electrons form a bound system. The electric field $\mathbf{E}(\mathbf{R}_a)$ on the site of a silver cation a located at position $\mathbf{R}_a$, generated by the other silver cations at positions $\mathbf{R}_j$ and the valence electrons at positions $\mathbf{r}_i$ is,

$$\mathbf{E}(\mathbf{R}_a) = \sum_j \frac{\mathbf{R}_a - \mathbf{R}_j}{|\mathbf{R}_a - \mathbf{R}_j|^3} - \sum_i \frac{\mathbf{R}_a - \mathbf{r}_i}{|\mathbf{R}_a - \mathbf{r}_i|^3}. \quad (5.50)$$

Let α be the atomic dipole polarizability of a single silver cation. The induced polarization leads to a polarization energy:

$$V_p = -\frac{1}{2} \alpha \sum_a |\mathbf{E}(\mathbf{R}_a)|^2. \quad (5.51)$$

Within the spherical jellium approximation, we average the core polarization energy over the cation distribution of constant number density n_i , $n_{ion}(\mathbf{R}) = n_i \theta(R_J - R) = \frac{3}{4\pi r_J^3} \theta(R_J - R)$, where $\theta(x)$ is the step function equal to 1 for $x > 0$ and to 0 for $x < 0$ and R_J is the jellium radius. This gives:

$$V_p = -\frac{1}{2} \alpha n_i \int_0^{R_J} d\mathbf{R} |\mathbf{E}(\mathbf{R})|^2. \quad (5.52)$$

Only the part depending on the electron position enters the jellium Hamiltonian (Eq. 5.2). Therefore the core-polarization potential in this Hamiltonian has two terms, namely a one-electron term V_{cp} and a two-electron term u_{cp} . Expanding

Eq. 5.52, the one-body term reads as:

$$V_{cp}(\mathbf{r}_i) = \frac{1}{2}\alpha n_i \int_0^{R_J} d\mathbf{R} \left[\sum_I 2 \frac{\mathbf{R} - \mathbf{R}_I}{|\mathbf{R} - \mathbf{R}_I|^3} \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} - \left(\frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \right)^2 \right], \quad (5.53)$$

and the two-body term as:

$$u_{cp}(\mathbf{r}_i, \mathbf{r}_j) = -\alpha n_i \int_0^{R_J} d\mathbf{R} \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3}. \quad (5.54)$$

Dealing with dipole transitions only, we need to pick up the dipole component of the two-body interaction. Other multipoles may contribute to the exchange RPAE matrix elements but they are much smaller and can be neglected with regard to the set of approximations underlying the jellium approximation. Expanding the functions $\frac{1}{|\mathbf{R}-\mathbf{r}|}$ in Legendre polynomials, it is clearly seen that the dipole term reduces to:

$$u_{cp}^{L=1}(\mathbf{r}_i, \mathbf{r}_j) = -\alpha n_i \int_0^{R_J} d\mathbf{R} \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_{>i}^3 r_{>j}^3} = -\alpha N \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_{>i}^3 r_{>j}^3}, \quad (5.55)$$

where $r_{>i}$ denotes the largest of r_i and R_J as explicit in Eq. 5.6.

As to the one-body potential of Eq. 5.53, which enters the jellium Hamiltonian we need to retain the monopole leading contribution only; it clearly is:

$$V_{cp}^{L=0}(\mathbf{r}_i) = -\frac{1}{2}\alpha n_i \int_0^{R_J} d\mathbf{R} \frac{r_i^2}{r_{>i}^6} = -\frac{1}{2}\alpha N \frac{r_i^2}{r_{>i}^6}. \quad (5.56)$$

Chapter 6

Matrix Effect

In this chapter, the effect on the optical response of metal clusters from the surrounding rare-gas medium will be discussed. A dielectric potential is presented for the interaction between two electrons in an embedded dielectric sphere. This dielectric potential, which is written into a multipole expansion form, has been frequently used in quantum mechanics calculations inside quantum dots. It further reduces into a two-body interaction, which screens the bare Coulomb interaction, and a self-energy potential. The singularity of one-body self-energy potential on the interface between the metal clusters and the rare-gas media is corrected by a position dependent dielectric function of the rare-gas matrix. In Appendix B of this chapter an alternative approach to the matrix polarization effect is also presented.

As has been reviewed in Chapter 2, photo absorption spectrum measurements are often conducted for silver clusters that are embedded in rare-gas matrix. However there are only a few theoretical studies of the medium effect (27, 28, 29) and no quantum mechanical calculation was done for embedded large silver clusters. To have a complete understanding of the optical response for both free and embedded metal clusters from a HF-RPAE point of view, a dielectric model for the rare-gas matrix effect is proposed.

The rare-gas matrix is treated as a uniform dielectric media, which screens the Coulomb interaction between the valence electrons of the metal atoms. Since the Jellium Model is used for the metal cluster, the rare-gas matrix will also screen the Jellium background potential, which represents the valence electron-ion interaction. The dielectric screening will lead to a modified Coulomb two-body interaction and a one-body correction in the Hamiltonian for the valence electrons. The energy barrier arising from the conduction band minima (97) is also included in the present calculation. The new Hamiltonian is solved by the HF-RPAE approach. Numerical calculations have been done for Na, Ag clusters embedded in He, Ne and Ar matrix. Red shift of the oscillator strength peak is found due to matrix effect. The magnitude of the shift increases as the dielectric constant of the rare-gas matrix increase from He ($\epsilon_{He}=1.05$) to Ar($\epsilon_{Ar}=1.6$) and the energy barrier serves as a minor effect compared to the dielectric screening.

6.1 Model

Consider a Jellium metal cluster sphere with radius R embedded in rare-gas (He Ne Ar) matrix. For a simple alkali metal, such as Na K, a pure Jellium Model shall be enough. For silver clusters, the core-polarization correction in chapter 5 will be adopted to model the Hamiltonian of the 5s valence electrons. In the same spirit of Jellium Model, the rare-gas matrix is treated as an infinite uniform dielectric media. The optical response of the metal-matrix system is determined by the delocalized valence electrons from the metal clusters. The Coulomb interaction between the delocalized electrons and the Jellium background potential should be screened by the dielectric media. A Hamiltonian for the delocalized valence electrons of the metal cluster with a screened Coulomb interaction and

ionic potential will be presented.

The dielectric constants of the Jellium sphere and the media are $\epsilon_1 = 1.0$ and ϵ_2 , respectively. The dielectric effect for the valence electrons of the metal clusters contains a two-body and a one-body self-energy correction. From a macroscopic image charge formula one knows that the Coulomb interaction between the valence electrons is screened.

6.1.1 Screened Coulomb Interaction

The two-body bare Coulomb interaction changes from

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{LM} \frac{r_{<}^L}{r_{>}^{L+1}} \frac{4\pi}{2L+1} Y_{LM}^*(\Omega') Y_{LM}(\Omega) \quad (6.1)$$

to

$$V(\mathbf{r}_1, \mathbf{r}_2) = \sum_{LM} \Phi_L(r_1, r_2, R) \frac{4\pi}{2L+1} Y_{LM}^*(\Omega') Y_{LM}(\Omega) \quad (6.2)$$

where,

$$\Phi((r_1, r_2) < R) = \frac{r_{<}^L}{\epsilon_1 r_{>}^{L+1}} + \frac{(\epsilon_1 - \epsilon_2)(L+1)(r_1 r_2)^L}{\epsilon_1 (L\epsilon_1 + L\epsilon_2 + \epsilon_2) R^{2L+1}} \quad (6.3)$$

$$\Phi((r_1, r_2) > R) = \frac{r_{<}^L}{\epsilon_2 r_{>}^{L+1}} + \frac{(\epsilon_2 - \epsilon_1) L R^{2L+1}}{\epsilon_2 (L\epsilon_1 + L\epsilon_2 + \epsilon_2) (r_1 r_2)^{L+1}} \quad (6.4)$$

$$\Phi((r_1 < R < r_2)) = \frac{(2L+1)r_{<}^L}{(L\epsilon_1 + L\epsilon_2 + \epsilon_2)r_{>}^{L+1}} \quad (6.5)$$

For a detailed derivation of the screened form, please see the appendix in the end of this chapter.

6.1.2 Dielectric One-body Term

If one sets $r_1 = r_2$, a self-energy potential v_{se} for the delocalized electrons can be found

$$v_{se}(r < R) = \sum_n \frac{1}{\epsilon_1} \frac{(n+1)(\epsilon_1 - \epsilon_2)}{\epsilon_1 n + \epsilon_2(n+1)} \frac{1}{R} \left(\frac{r}{R}\right)^{2n} \quad (6.6)$$

$$v_{se}(r > R) = -\frac{1}{R\epsilon_2} \left(\frac{R}{r}\right)^2 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \sum_{n=0}^{\infty} \frac{n}{n+b} a^n \quad (6.7)$$

where,

$$a = \left(\frac{R}{r_i}\right)^2 \quad (6.8)$$

$$b = \frac{\epsilon_2}{\epsilon_1 + \epsilon_2} \quad (6.9)$$

Since there is a breakdown region for the dielectric function of rare-gas matrix(98),

$$\frac{1}{\epsilon(r)} = \frac{1}{\epsilon_0} + \left(1 - \frac{1}{\epsilon_0}\right) e^{-r/a} \quad (6.10)$$

the singularity of the one-body term should be removed. For the same reason, one needs to know that the screened Coulomb interaction applies only to large clusters where the interface effect between the cluster and rare-gas matrix will not be a problem.

$$v_{se}(r) = (1 - e^{-(r-R/r_{mWS})^2}) v_{se}(r) \quad (6.11)$$

where r_{mWS} is the WS radius of rare-gas element.

6.1.3 Conduction Band Minima

Since the valence electrons of the metal cluster is treated as free electrons, which can spill out and the rare-gas is an infinite media, the vacuum zero point shall be corrected by an energy barrier V_0 coming from the conduction band minimum of the rare-gas matrix. The conduction band minima serves as an energy barrier. (97, 99, 100, 101, 102, 103)

$$V_0(r) = -\frac{V_0}{1 + e^{c*(r-R_J)}} \quad (6.12)$$

Therefore the effects from the rare-gas matrix contains two parts: 1, uniform dielectric effect (DE); 2, energy barrier (EB) V_0 coming from the conduction band minima. The dielectric constants of the Jellium ionic background and the

media are $\epsilon_1 = 1.0$ and ϵ_2 , respectively. Using atomic units, the Hamiltonian for this N-electron system is given by,

$$H = T + V_{JM} + \tilde{V}_{ee} + V_{e1b} + V_{ind} + V_0 \quad (6.13)$$

where T and V_{JM} take the form of a pure Jellium Model (see eqn). Use Equation 6.2 for the screened Coulomb interaction

$$\tilde{V}_{ee} = \sum_{i < j} V(\mathbf{r}_i, \mathbf{r}_j) \quad (6.14)$$

The one-body term from the effect of rare-gas to a Jellium metal sphere has two parts: 1, electron self-energy term (simply use $\epsilon_1 = 1.0$ in the dielectric one-body term discussed above);

$$V_{e1b} = \sum_i v_{e1b}(r_i) \quad (6.15)$$

2, the Jellium ionic background also polarize the rare-gas matrix. For the same reason of removing the singularity in the one-body self-energy term, the screening charges are sitting on a sphere with radius $R_{ind} = R + d$, which should be larger than the Jellium sphere. The parameter d here is to take into account of the breakdown region for the dielectric function of rare-gas matrix.

$$V_{ind} = \sum_i v_{ind}(r_i) \quad (6.16)$$

where,

$$v_{ind}(r) = \begin{cases} -\frac{1-\epsilon_2}{\epsilon_2} \frac{N}{R+d} & \text{if } r < R + d \\ -\frac{1-\epsilon_2}{\epsilon_2} \frac{N}{r} & \text{if } r > R + d \end{cases}$$

To determine the exact value of d , one could adjust it to fit the experimental ionization potential(37). For small clusters, the effect of parameter d should be non-negligible, while for large clusters, the macroscopic screening formula should be good enough so that one may take $d = 0$.

6.2 Numerical Results

Numerical calculations are conducted for Na8, Ag8, Ag138 and Ag198 embedded in Helium, Neon and Argon matrix. (The core-polarization correction is adopted for the treatment of silver core background polarization effect.) To compare with experimental absorption spectrum results, one makes a Lorentzian shape convolution for the oscillator strength.

$$\sigma(E) = \frac{2\pi^2}{c} \sum_k f_k \delta(E - E_k + E_0) \quad (6.17)$$

$$f_k = \frac{f_k}{\pi} \frac{\Gamma}{\Gamma^2 + (E - \omega_k)^2} \quad (6.18)$$

The rare-gas matrix effect is quite different for small and large clusters. First, for small Na clusters, Figure 6.1 shows that the one-body corrections from V_0 and the electron self-energy term V_{se} are small corrections, the magnitude of which is about 0.1eV. The major correction comes from the two body interaction. This is because argon matrix has rather large dielectric constant and small energy barrier $-0.35eV$. Figure 6.2 shows that the two peaks of Ag8 oscillator strength are getting closer as the dielectric constant of the matrix is getting larger. (One found that if one takes the WS radius of the matrix for the parameter d , the ionization potential of Ag8Ar agrees with experimental results for gas phase silver clusters (104).) To compare with experiment, one may refer to reference (12) for Ag8He (one major peak at 3.99eV), reference (13) for Ag8Ne (three peaks at 3.12eV 3.65eV and 4.00eV) and reference (14) for Ag8Ar (two peaks at 3.60eV and 3.90eV). Excellent agreement can be seen in Figure 6.2. For Ag8 embedded in He droplet, the dielectric effect can be neglected since $\epsilon_{He} = 1.05$, which is very closed to one. The major correction from He droplet is the energy barrier 1.05eV from its conduction band minima(97). For Neon matrix, the energy barrier 0.67eV and the dielectric screening effect both contribute.

Now consider large clusters, that is, Ag138 and Ag198 embedded in Helium, Neon and Argon matrices. The rare-gas dielectric screening on the jellium back-

ground potential contributes a lot. From figure 6.3, one can see how the oscillator strength distribution of Ag198 embedded in Ar vary with the parameter d . As d decreases from one to zero, the oscillator strength become more and more fragmented and red shifted. The difference of parameter d for small and large clusters is related to the spill-out effect. Small clusters have a large percentage of spill-out electrons which could feel the induced charges on a larger sphere. Since the breakdown region of the dielectric function and the spill-out electrons for large clusters can be neglected, one takes $d = 0.0$. It is found that the surface plasmon resonance peak shifts to lower energy significantly by almost $1eV$ due to the dielectric effect of the rare-gas matrix environment (Figure 6.4 and 6.5). The larger dielectric constant the matrix has, the larger shift of the plasmon peak will present. If one chooses the parameter d (Table 6.2 and 6.3) to fit the ionization potential(37), then $d = 4.0$ for Ag8 and $d = 1.0$ for Ag198. In this case, the dipole collective resonance peak of Ag198 shifts to lower energy by about $0.4eV$ and the peak position agrees well with the experimental results in reference (66).

Classically, for a metal cluster embedded in argon matrix medium with $\epsilon_{Ar} = 1.6$, the absorption cross section is,

$$\sigma(\omega) = \frac{4\pi\omega R^3}{c} \text{Im} \frac{\epsilon(\omega) - \epsilon_{Ar}}{\epsilon(\omega) + 2\epsilon_{Ar}} \quad (6.19)$$

Therefore, if one uses general Drude model (Eqn. 5.30) for $\epsilon(\omega)$, the surface resonance peak position can be found by $\epsilon(\omega) + 2\epsilon_{Ar} = 0$, which gives,

$$\omega = \frac{\omega_p}{\sqrt{\epsilon_\infty + 2}} \sqrt{\frac{\epsilon_\infty + 2}{\epsilon_\infty + 2\epsilon_{Ar}}} \quad (6.20)$$

For silver clusters embedded in argon, one could replace $\frac{\omega_p}{\sqrt{\epsilon_\infty + 2}}$ by $3.5eV$ and obtain $\omega = 3.2eV$, which is exactly the large cluster limit of Ag clusters embedded in Ar in reference(66). Thus argon matrix should shift the surface plasmon peak of large silver cluster to lower energy by about $0.3eV$, which agrees with the present calculation if one fits parameter d by setting HF ionization potential to experimental data. Therefore it is concluded that this model for rare-gas matrices can be applied to both small and large embedded metal clusters.

Figure 6.1: Vertical drop lines are oscillator strength distribution calculated by RPAE for: free Na8, Na8Ar without V_{se} , Na8Ar without V_0 , Na8Ar. Continuous line is Lorentzian shape convolution ($\Gamma = 0.01\omega_k$ and $d = r_{mWS}$)

Table 6.1: Parameters for rare-gas matrices. (2, 3, 4)

Rare-gas	ϵ	V_0 (eV)	r_{mWS}
He	1.05	1.05	3.68
Ne	1.24	0.67	3.30
Ar	1.6	-0.35	4.00

Table 6.2: Calculated HF ionization potential (IP) of Ag8 embedded in argon matrix.

Parameter d (a.u.)	0.0	2.0	4.0
IP(eV)	3.50	5.38	7.66

6.3 Conclusion

In this PhD work, previous calculations on simple metal clusters and the pseudo-potential method for lithium clusters are repeated. After that the core-polarization effect on the optical response of silver clusters is considered and it is included in the HF-RPAE formalism. For a thorough understanding of metal cluster physics we present in this chapter a screened Coulomb interaction for the rare-gas matrix, which has been frequently used to hold metal clusters in photo absorption experiment. The matrix effect on the surface plasmon peak position was evaluated experimentally. However, existing theoretical work only modeled for very small embedded clusters. The present model for large metal clusters embedded in rare-gas matrix could serve as a theoretical tool for a systematic study of the optical response of various metal clusters embedded in an inert environment.

Calculations on Na and Ag clusters embedded in He Ne Ar matrix were done. For small clusters, the surface plasmon has slightly blue shift and a narrower distribution because of the dielectric two-body screening effect. For large clusters, a significant red shift of the oscillator strength peak is found due to and the matrix dielectric screening effect, especially the induced charges. The screening on the Coulomb interaction between electrons makes the electrons more bounded and shifts the plasmon peak to higher energy, while the that on the jellium background unbound the electrons and shifts the plasmon peak to lower energy. The energy barrier effect is only a minor effect compared to the dielectric effect in large clusters. The largest magnitude of the shift reaches 1eV for Ar matrix with a dielectric constant of $\epsilon_{Ar}=1.6$ and parameter $d = 0.0$, while the He droplet with

Table 6.3: Calculated HF ionization potential (IP) of Ag198 embedded in argon matrix.

Parameter $d(\text{a.u.})$	0.0	0.5	0.8	1.0
IP(eV)	1.88	2.89	4.07	5.00

a dielectric constant closed to one $\epsilon_{He}=1.05$ almost leads to no change. If one adjusts d to fit HF IP to experiment, the classical shift $0.3eV$ of surface plasmon by argon matrix can be found in the calculation of Ag198 embedded in Ar.

6.4 Appendix A: Derivation of the Dielectric Potential

This appendix presents the derivation of the dielectric screened two-body interaction. In a uniform dielectric media (ϵ'), the potential $V_i(r_j)$ generated by a free charge q located at $(r_i, 0, 0)$ (spherical coordinate) is

$$\begin{aligned}
 V_{i,q}(r_j) &= \frac{q}{\epsilon' |\mathbf{r}_i - \mathbf{r}_j|} \\
 &= \frac{q}{\epsilon'} \sum_{LM} \frac{r_{<}^L}{r_{>}^{L+1}} \frac{4\pi}{2L+1} Y_{LM}^*(\Omega_j) Y_{LM}(\Omega_i) = \frac{q}{\epsilon'} \sum_n \frac{r_{<}^n}{r_{>}^{n+1}} P_n(\cos\theta_{ij})
 \end{aligned} \tag{6.21}$$

which can be written in another way,

$$V_{i,q}(r_j) = \begin{cases} \sum_n \frac{q}{\epsilon' r_i} \left(\frac{r_j}{r_i}\right)^n P_n(\cos\theta_{ij}) & \text{if } r_j < r_i \\ \sum_n \frac{q}{\epsilon' r_i} \left(\frac{r_i}{r_j}\right)^{n+1} P_n(\cos\theta_{ij}) & \text{if } r_j > r_i. \end{cases}$$

Now consider a dielectric sphere cluster with radius R_J embedded in a uniform dielectric media. The dielectric constants of the cluster and the media are ϵ and ϵ' , respectively. The potential $V_{i,tot}(r_j)$ generated by a free charge q located at $(r_i, 0, 0)$ is

$$V_{i,tot}(r_j) = V_{i,q}(r_j) + V_{i,ind}(r_j) \tag{6.22}$$

$V_{i,ind}(r_j)$ is generated by the induced charge on the interface, which can be expanded in a similar way

$$V_{i,ind}(r_j) = \begin{cases} \sum_n A_n \left(\frac{r_j}{R_J}\right)^n P_n(\cos\theta_{ij}) & \text{if } r_j < R_J \\ \sum_n B_n \left(\frac{R_J}{r_j}\right)^{n+1} P_n(\cos\theta_{ij}) & \text{if } r_j > R_J. \end{cases}$$

To calculate A_n , use the fact that the electric displacement is continuous across the boundary and $V_{i,tot}(r_j)$ is continuous on the boundary:

$$\epsilon \frac{\partial V(R_J^-)}{\partial r} = \epsilon' \frac{\partial V(R_J^+)}{\partial r} \quad (6.23)$$

and

$$V_{i,tot}(R_J^-) = V_{i,tot}(R_J^+). \quad (6.24)$$

6.4.1 When $r_i > R_J$

$$V_{i,q}(r_j) = \begin{cases} \sum_n \frac{q}{\epsilon' r_i} \left(\frac{r_j}{r_i}\right)^n P_n(\cos\theta_{ij}) & \text{if } r_j < r_i \\ \sum_n \frac{q}{\epsilon' r_i} \left(\frac{r_i}{r_j}\right)^{n+1} P_n(\cos\theta_{ij}) & \text{if } r_j > r_i. \end{cases}$$

$$V_{i,outside,ind}(r_j) = \begin{cases} \sum_n A_n \left(\frac{r_j}{R_J}\right)^n P_n(\cos\theta_{ij}) & \text{if } r_j < R_J \\ \sum_n B_n \left(\frac{R_J}{r_j}\right)^{n+1} P_n(\cos\theta_{ij}) & \text{if } r_j > R_J. \end{cases}$$

Boundary conditions:

$$\begin{aligned} & \epsilon \sum_n \left[\frac{nq}{\epsilon' r_i R_J} \left(\frac{R_J}{r_i}\right)^n + \frac{nA_n}{R_J} \right] P_n(\cos\theta_{ij}) \\ &= \epsilon' \sum_n \left[\frac{nq}{\epsilon' r_i R_J} \left(\frac{R_J}{r_i}\right)^n - \frac{(n+1)B_n}{R_J} \right] P_n(\cos\theta_{ij}) \end{aligned} \quad (6.25)$$

and

$$\sum_n \left[\frac{q}{\epsilon' r_i} \left(\frac{R_J}{r_i}\right)^n + A_n \right] P_n(\cos\theta_{ij}) = \sum_n \left[\frac{q}{\epsilon' r_i} \left(\frac{R_J}{r_i}\right)^n + B_n \right] P_n(\cos\theta_{ij}) \quad (6.26)$$

Thus one obtains the coefficient:

$$A_n = B_n = -\frac{q}{\epsilon'} \frac{n(\epsilon - \epsilon')}{n(\epsilon + \epsilon') + \epsilon'} \frac{R_J^n}{r_i^{n+1}} \quad (6.27)$$

Self-energy one-body term due to the induced charge can be found by setting $\mathbf{r}_j = \mathbf{r}_i$

$$\begin{aligned} V_{ioutside,ind}(r_i) &= \sum_n B_n \left(\frac{R_J}{r_i}\right)^{n+1} P_n(1) \\ &= -\frac{q}{R_J \epsilon'} \left(\frac{R_J}{r_i}\right)^2 \frac{\epsilon - \epsilon'}{\epsilon + \epsilon'} \sum_{n=0}^{\infty} \frac{n}{n+b} a^n \end{aligned} \quad (6.28)$$

where,

$$a = \left(\frac{R_J}{r_i}\right)^2 \quad (6.29)$$

and

$$b = \frac{\epsilon'}{\epsilon + \epsilon'} \quad (6.30)$$

For behaviour near the boundary:

$$\sum_{n=0}^{\infty} \frac{n}{n+b} a^n = \sum_{n=0}^{\infty} \left(1 - \frac{b}{n+b}\right) a^n = \sum_{n=0}^{\infty} a^n - \frac{b}{a^b} \sum_{n=0}^{\infty} \frac{1}{n+b} a^{n+b} \quad (6.31)$$

which will be infinite when $r_i = R_J$. Therefore one needs to remove the singularity by the position dependent dielectric function.

$$\frac{1}{2(1-a)} < \sum_{n=0}^{\infty} \frac{n}{n+b} a^n < \frac{1}{1-a} \quad (6.32)$$

6.4.2 When $r_i < R_J$

$$V_{i,q}(r_j) = \begin{cases} \sum_n \frac{q}{\epsilon r_i} \left(\frac{r_j}{r_i}\right)^n P_n(\cos\theta_{ij}) & \text{if } r_j < r_i \\ \sum_n \frac{q}{\epsilon r_i} \left(\frac{r_i}{r_j}\right)^{n+1} P_n(\cos\theta_{ij}) & \text{if } r_j > r_i. \end{cases}$$

$$V_{iinside,ind}(r_j) = \begin{cases} \sum_n A_n \left(\frac{r_j}{R_J}\right)^n P_n(\cos\theta_{ij}) & \text{if } r_j < R_J \\ \sum_n B_n \left(\frac{R_J}{r_j}\right)^{n+1} P_n(\cos\theta_{ij}) & \text{if } r_j > R_J. \end{cases}$$

Boundary conditions:

$$\begin{aligned} & \epsilon \sum_n \left[-\frac{(n+1)q}{\epsilon r_i R_J} \left(\frac{r_i}{R_J} \right)^{n+1} + \frac{nA_n}{R_J} \right] P_n(\cos\theta_{ij}) \\ &= \epsilon' \sum_n \left[-\frac{(n+1)q}{\epsilon r_i R_J} \left(\frac{r_i}{R_J} \right)^{n+1} - \frac{(n+1)B_n}{R_J} \right] P_n(\cos\theta_{ij}) \end{aligned} \quad (6.33)$$

and

$$\begin{aligned} & \sum_n \left[\frac{q}{\epsilon r_i} \left(\frac{r_i}{R_J} \right)^{n+1} + \frac{nA_n}{R_J} \right] P_n(\cos\theta_{ij}) \\ &= \sum_n \left[\frac{q}{\epsilon r_i} \left(\frac{r_i}{R_J} \right)^{n+1} - \frac{(n+1)B_n}{R_J} \right] P_n(\cos\theta_{ij}) \end{aligned} \quad (6.34)$$

One obtains the coefficient:

$$A_n = B_n = \frac{q(n+1)(\epsilon - \epsilon')}{\epsilon \epsilon n + \epsilon'(n+1)} \frac{r_i^n}{R_J^{n+1}} \quad (6.35)$$

Self-energy one-body term due to the induced charge can be found by setting $\mathbf{r}_j = \mathbf{r}_i$

$$\begin{aligned} V_{inside,ind}(r_i) &= \sum_n A_n \left(\frac{r_i}{R_J} \right)^n P_n(1) \\ &= \sum_n \frac{q(n+1)(\epsilon - \epsilon')}{\epsilon \epsilon n + \epsilon'(n+1)} \frac{1}{R_J} \left(\frac{r_i}{R_J} \right)^{2n} \end{aligned} \quad (6.36)$$

6.5 Appendix B: Another Approach to Matrix Polarization Effect

The approach in this chapter uses classical electrodynamics for the matrix dielectric correction to Coulomb interaction. To illustrate the matrix polarization effect quantum mechanically, we propose another model. In the alternative model, the cluster of N silver atoms is considered as a super-atom with N valence electrons,

and polarizability of $\alpha_c = N\alpha_I$. The two-body term thus reads:

$$u_{cp}(\mathbf{r}_i, \mathbf{r}_j) = -\gamma^I \alpha_I n_I \int_0^{R_J} d\mathbf{R} \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3} - \gamma^m \alpha_m n_m \int_{R_J}^{\infty} d\mathbf{R} \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3} \quad (6.37)$$

where, the two terms in the above expression are the ionic core contribution and rare-gas contribution respectively. Dealing with dipole transitions only, we need to pick up the dipole component of the two-body interaction. Other multipoles may contribute to the exchange RPAE matrix elements but they are much smaller and can be neglected with regard to the set of approximations underlying the jellium approximation. Expanding the functions $\frac{1}{|\mathbf{R}-\mathbf{r}|}$ in Legendre polynomials, it is clearly seen that the dipole two-body term reduces to:

$$u_{cp}^{L=1}(\mathbf{r}_i, \mathbf{r}_j) \approx -\alpha_I^* \gamma^I R_J^3 f(\mathbf{r}_i) f(\mathbf{r}_j) - 2\alpha_m^* \gamma^m R_J^3 f(\mathbf{r}_i) f(\mathbf{r}_j). \quad (6.38)$$

where the interaction form factor is:

$$f(\mathbf{r}) = \begin{cases} \frac{\mathbf{r}}{R_J^3} & \text{if } r < R_J \\ \frac{\mathbf{r}}{r^3} & \text{if } r > R_J, \end{cases} \quad (6.39)$$

and a corresponding one-body term by setting $\mathbf{r} = \mathbf{r}_i = \mathbf{r}_j$:

$$V_{cp}(\mathbf{r}) = \frac{1}{2} u_{cp}^{L=1}(\mathbf{r}, \mathbf{r}). \quad (6.40)$$

Note that there is a factor of 2 for the matrix contribution since the integral is from R_J to ∞ . The electric field on the super-atom like cluster when the valence electron is inside the cluster is approximated as in our previous work (91).

To evaluate $\gamma(\mathbf{R})$, one may first consider the local field factor γ for a uniform rare-gas media as has been discussed in reference (105). As shown in Fig6.6(a) the local field at site $\mathbf{R}$ due to a point charge e^- is the sum of its direct field and

all the contribution from other dipoles,

$$\begin{aligned} \frac{\gamma(R)\mathbf{R}}{R^3} &= \frac{\mathbf{R}}{R^3} - \int dt \frac{3(\mathbf{p}(t)\hat{\mathbf{s}})\hat{\mathbf{s}} - \mathbf{p}(t)}{s^3} \\ &= \frac{\mathbf{R}}{R^3} - \lim_{\sigma \rightarrow 0} \pi n \alpha \int_0^\infty \frac{\gamma(t)\mathbf{R}dt}{R^3 t^2} \int_{|R-t|}^{R+t} \frac{\theta(t,s)g(s)ds}{s^2} \end{aligned} \quad (6.41)$$

where n and α are the density and polarizability of argon atom. The function $\theta(t,s)$ takes into account of the indirect dipole field:

$$\theta(t,s) = \frac{3}{2s^2}(R^2 + t^2 - s^2)(s^2 + R^2 - t^2) + (R^2 + t^2 - s^2) \quad (6.42)$$

and the pair correlation function $g(s)$ is defined by,

$$g(s) = \begin{cases} 0 & \text{if } s < \sigma \\ 1 & \text{if } s > \sigma \end{cases} \quad (6.43)$$

Thus γ fulfills a self-consistent equation:

$$\begin{aligned} \gamma &= 1 - \lim_{\sigma \rightarrow 0} \pi n \alpha \int_0^\infty \frac{\gamma(t)dt}{t^2} \int_{|R-t|}^{R+t} \frac{\theta(t,s)g(s)ds}{s^2} \\ &= 1 - \lim_{\sigma \rightarrow 0} \pi n \alpha \int_{R-\sigma}^{R+\sigma} \frac{\gamma(t)dt}{t^2} \int_\sigma^{R+t} \frac{\theta(t,s)ds}{s^2} \\ &= 1 - \lim_{\sigma \rightarrow 0} \pi n \alpha \int_{R-\sigma}^{R+\sigma} \frac{\gamma(t)dt}{2t^2} \left[s - \frac{2R^2 + 2t^2}{s} + \frac{(R^2 - t^2)^2}{s^3} \right] \Big|_\sigma^{R+t} \\ &= 1 - \frac{8\pi n \alpha}{3} \gamma = 1 - 2\alpha^* \gamma \end{aligned} \quad (6.44)$$

where $\alpha^* = \frac{4\pi n \alpha}{3}$ is a local property. What can be extracted from Eq. 6.44 is that all the dipole screening effect to the local field at $\mathbf{R}$ comes from its immediate neighborhood, that is, the atoms between $R - \sigma$ to $R + \sigma$. The problem we are dealing with is a metallic super-atom surrounded by rare-gas atoms. The valence electrons are mainly located near the interface. Rare-gas atoms that are far away from the cluster see no electric field, that is $\mathbf{E}(\mathbf{R}_m \rightarrow \infty) = 0$ since the cluster is a neutral system. Thus when $R > R_J$, $\gamma(\mathbf{R})$ can be replaced with $\gamma(\mathbf{R}_J)$. And we assumes that the local field corrections on the silver ions comes only from the matrix. The magnitude can be determined by a point-like model

for the embedded cluster using Lekner's approach. which means when $R < R_J$, $\gamma(\mathbf{R}) = \gamma^I$. Therefore, for simplicity, it is reasonable that one defines an averaged local field $\gamma^m = \gamma(\mathbf{R}_J)$ for the rare-gas atoms near the surface and γ^I for silver cations as shown in fig1(b). Following Lekner (105) the self consistent equation for γ^m fulfils:

$$\gamma^m = 1 - \alpha_I^* \gamma^I - \alpha_m^* \gamma^m, \quad (6.45)$$

since the contribution to the local field γ^m on the interface comes from its immediate neighborhood α_c and α_m . The integration in Eq. 6.44 is separated into from $R - \sigma$ to R and from R to $R + \sigma$ which leads to Eq. 6.46. In a point-like model for the embedded cluster γ^I satisfies:

$$\gamma^I = 1 - 2\alpha_m^* \gamma^m. \quad (6.46)$$

Therefore from Eq. 6.46 and 6.47 one gets:

$$\gamma^m = \frac{1 - \alpha_I^*}{1 - 2\alpha_I^* \alpha_m^* + \alpha_m^*} \quad (6.47)$$

$$\gamma^I = \frac{1 - \alpha_m^*}{1 - 2\alpha_I^* \alpha_m^* + \alpha_m^*} \quad (6.48)$$

where α_I^* and α_m^* are polarizability of metal and rare-gas atom respectively. Only the part depending on the electron position enters the jellium Hamiltonian. Finally, we present the Hamiltonian for delocalized valence electrons of the metal cluster with a polarization two-body interaction $u_{cp}(\mathbf{r}_i, \mathbf{r}_j)$ and a one-body self-energy term $V_{cp}(\mathbf{r}_i)$:

$$H = \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_i V_{JM}(\mathbf{r}_i) + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i < j} u_{cp}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i V_{cp}(\mathbf{r}_i) \quad (6.49)$$

where $V_{JM}(r)$ is the simple Jellium background potential,

$$V_{JM}(r) = \begin{cases} -\frac{N}{2R_J}(3 - (\frac{r}{R_J})^2) & \text{if } r < R_J \\ -\frac{N}{r} & \text{if } r > R_J. \end{cases} \quad (6.50)$$

One can see that there are two contributions to the polarization two-body interaction and the one-body self-energy potential from the ionic cores and the rare-gas media:

$$\begin{aligned} u_{cp}(\mathbf{r}_i, \mathbf{r}_j) &= -\alpha_I^* \gamma^I R_J^3 f(\mathbf{r}_i) f(\mathbf{r}_j) - 2\alpha_m^* \gamma^m R_J^3 f(\mathbf{r}_i) f(\mathbf{r}_j) \\ &= u_{cp}^c(\mathbf{r}_i, \mathbf{r}_j) + u_{cp}^m(\mathbf{r}_i, \mathbf{r}_j), \end{aligned} \quad (6.51)$$

and

$$V_{cp}(\mathbf{r}_i) = V_{cp}^c(\mathbf{r}_i) + V_{cp}^m(\mathbf{r}_i). \quad (6.52)$$

In the above model, the polarization two-body correction screens the dipole component of the Coulomb interaction, which can be rewritten as:

$$\sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i < j} u_{cp}(\mathbf{r}_i, \mathbf{r}_j) = \sum_{i < j} V_{screened}(\mathbf{r}_i, \mathbf{r}_j). \quad (6.53)$$

One could extract an effective screening factor β from the dipole term of a multipole expansion,

$$V_{screened}^{L=1} = \beta V_{Coulomb}^{L=1}, \quad (6.54)$$

where,

$$\beta = \begin{cases} 1 - \gamma^I \alpha_I^* \frac{R_J^3}{r_{<}^3} - 2\gamma^m \alpha_m^* \frac{R_J^3}{r_{<}^3} & \text{if } R_J < r_{<} \\ 1 - \gamma^I \alpha_I^* - 2\gamma^m \alpha_m^* & \text{if } r_{<} < R_J < r_{>} \\ 1 - \gamma^I \alpha_I^* \frac{r_{>}^3}{R_J^3} - 2\gamma^m \alpha_m^* \frac{r_{>}^3}{R_J^3} & \text{if } r_{>} < R_J \end{cases} \quad (6.55)$$

The screening factor β on the electron-electron interaction can be seen as a screening on the electron charge $e^* = \beta e$. If one defines a dielectric constant for the metal cluster background and the rare-gas media ϵ_i and ϵ_m by Clausius-

Mossotti relation.

$$\frac{\epsilon_I - 1}{\epsilon_I + 2} = \alpha_I^* \quad (6.56)$$

$$\frac{\epsilon_m - 1}{\epsilon_m + 2} = \alpha_m^* \quad (6.57)$$

the local field factor reads,

$$\gamma^m = \frac{\epsilon_m + 2}{\epsilon_I + 2\epsilon_m} \quad (6.58)$$

$$\gamma^I = \frac{\epsilon_I + 2}{\epsilon_I + 2\epsilon_m}. \quad (6.59)$$

Given that the spill-out electrons are located near surface $r_< \approx r_> \approx R_J$, one obtains the factor β for the screening on Coulomb interaction

$$\beta \approx \frac{3}{\epsilon_I + 2\epsilon_m} \quad (6.60)$$

As a conclusion our model predicts the Mie frequency for metal clusters embedded in rare-gas matrix as,

$$\omega_M^* = \sqrt{\beta} \omega_M = \omega_M \sqrt{\frac{3}{\epsilon_I + 2\epsilon_m}}. \quad (6.61)$$

The absorption cross section can thus be found by

$$\sigma(\omega) = 2\pi^2 \frac{e^2 \hbar \epsilon_m^{\frac{3}{2}}}{m_e c} \frac{1}{4\pi\epsilon_0} \sum_k f_k \delta(E - E_k + E_0) \quad (6.62)$$

in atomic unit

$$\sigma(\omega) = \frac{2\pi^2 \epsilon_m^{\frac{3}{2}}}{c} \sum_k f_k \delta(E - E_k + E_0) \quad (6.63)$$

where the oscillator strength is defined by

$$f_k = \left(\frac{3}{\epsilon_I + 2\epsilon_m} \right)^2 \frac{2m_e \omega | \langle k | Z | 0 \rangle |^2}{\hbar} \quad (6.64)$$

Sum rule is modified:

$$\sum_k f_k = \left(\frac{3}{\epsilon_I + 2\epsilon_m}\right)^2 N \quad (6.65)$$

and can be calculated from RPAE. Eq. fulfils normalization relation

$$\int \sigma(\omega) dE = 2\pi^2 \frac{\hbar e^2}{4\pi\epsilon_0 m_e c} N \epsilon_m^{\frac{3}{2}} \left(\frac{3}{\epsilon_I + 2\epsilon_m}\right)^2. \quad (6.66)$$

6.5.1 Classical theory

Classically, for a metal cluster embedded in rare-gas matrix with dielectric constant of ϵ_m , the absorption cross section is,

$$\sigma(\omega) = \frac{4\pi\omega R^3 \sqrt{\epsilon_m}}{c} \text{Im} \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m} \quad (6.67)$$

Using Drude model for $\epsilon(\omega)$, the surface resonance peak position can be found by $\epsilon(\omega) + 2\epsilon_m = 0$, which gives,

$$\omega_M^* = \omega_M \sqrt{\frac{3}{1 + 2\epsilon_m}}. \quad (6.68)$$

If one takes into account of the dielectric constant of the ionic cores of the metal cluster ϵ_I , the surface plasmon frequency reads (81):

$$\omega_M^* = \omega_M \sqrt{\frac{3}{\epsilon_I + 2\epsilon_m}}. \quad (6.69)$$

The prediction of the plasmon peak position by the present model Eq.30 agrees with classical limit. The normalization relation for Eq. is

$$\int \sigma(\omega) dE = 2\pi^2 \frac{\hbar e^2}{4\pi\epsilon_0 m_e c} \frac{N}{\sqrt{\epsilon_m}} \left(\frac{3\epsilon_m}{\epsilon_I + 2\epsilon_m}\right)^2. \quad (6.70)$$

From Appendix we know that our polarization screening correction is in fact the $L = 1$ component of the classical dielectric screening correction.

Figure 6.2: Blue vertical drop lines are oscillator strength distribution calculated by RPAE for: free Ag₈, Ag₈ in He, Ag₈ in Ne, Ag₈ in Ar. Red solid lines indicate the experiment peak position from references(12, 13, 14). Continuous blue line is Lorentzian shape convolution ($\Gamma = 0.01\omega_k$ and $d = r_{mWS}$)

Figure 6.3: Vertical drop lines are oscillator strength distribution calculated by RPAE for: Ag₁₉₈ in Ar with parameter $d=0.0, 0.5, 0.8$ and 1.0 . Continuous line is Lorentzian shape convolution ($\Gamma = 0.065\omega_k$)

Figure 6.4: Vertical drop lines are oscillator strength distribution calculated by RPAE for: free Ag138, Ag138 in He, Ag138 in Ne, Ag138 in Ar. Continuous line is Lorentzian shape convolution ($\Gamma = 0.065\omega_k$)

Figure 6.5: Vertical drop lines are oscillator strength distribution calculated by RPAE for: free Ag198, Ag198 in He, Ag198 in Ne, Ag198 in Ar. Continuous line is Lorentzian shape convolution ($\Gamma = 0.065\omega_k$)

Figure 6.6: (a) Local field factor f_L for uniform rare-gas matrix; (b) Local field factor f_L^m and f_L^c for embedded cluster.

Chapter 7

Discussion and Future Work

This chapter reviews what has been achieved in this PhD program and makes a conclusion. Link between the two major outcomes, core-polarization correction and the dielectric screening formalism, is made. Extensions of the present theoretical model will also be discussed and potential opportunities in the future will be presented.

7.1 Discussion

Metal cluster made of tens to hundreds of atoms is the bridge between atom and bulk material. The size-dependence of their electronic properties has attracted much attention both experimentally and theoretically. Distinguished optical properties of different kinds of metal clusters have been found in this size range (nanoscale). Electronic shell structure and surface plasmon in metal clusters are the most important discoveries. The objective of this PhD project is to systematically investigate the electromagnetic responses of metal nanoparticles. We hope to have a complete understanding of one-valence-electron metal clusters, containing from tens to hundreds of atoms. For large clusters classical electrodynamics (Mie theory) is typically enough for a quite accurate prediction of the surface plasmon resonance. As cluster size goes below nanometer (a few hundreds of atoms) quantum mechanical effects emerge and pure classical approach is not enough. For very small clusters made of tens of atoms, quantum chemistry method can be a good theoretical tool. But computation cost will be unaffordable when there are hundreds of atoms. Another competitive theoretical approach is TDDFT calculation. The variety choices of XC functionals and the long range $1/r$ behavior of the self consistent potential make TDDFT not accurate in predicting the dipole surface plasmon. Therefore we recall a very early model, Jellium Model, which could be a good candidate to describe the quantum nature of the electronic structure of metal clusters in the desired size range.

One starts from the pure jellium model, which has been widely accepted to be a good model for Na and K clusters. This can be regarded as a zeroth order of approximation to the electronic structure in metal clusters. The delocalized s-electrons are treated quantum mechanically in a uniformly distributed ionic potential. In the framework of JM, there are two competing approaches, TDLDA and RPAE, to calculate the excitation energies. Noticing that the JM background potential has a $1/r$ large range behaviour, we choose RPAE, which, although neglecting correlation, treats electron exchange effect exactly and has been shown producing similar results as TDLDA (54). Jellium Model based RPAE can bring quantum effects and its prediction should converge to the classical limit. Simple size dependency of Sodium cluster optical property is well understood by this

simple model. The red shift of surface plasmon resonance peak with respect to the classical Mie theory is explained by spill-out and many body effect (23). The replacement of real valence-core interaction with a simple $1/r$ Coulomb potential makes the quantum mechanical calculation efficient. But it also limits itself to Na and K where the s -valence electron is well separated from the core. To extend Jellium Model to lithium clusters, one needs to include an angular momentum dependent pseudo-potential, which further leads to a non-local background potential for the delocalized valence electrons. It has been shown that the effective mass of $2s$ electron depends on the difference of s - and p - wave pseudo-potential (1). The absence of the p core shell in lithium leads to quite different s - and p -wave pseudo-potential. In contrast, sodium cluster has an effective mass closed to unity. In fact the pseudo-potential method has also been used in quantum chemistry frozen core. However in Jellium Model the ions is smeared out uniformly so that we are left with a radial problem, which is much easier to solve. Repetition of the work for lithium helps benchmark our numerics and is the step going beyond Jellium Model.

When one goes further to silver clusters, the simplicity of JM can still be used in understanding the d -electron screening effect of silver cores. As the first part of the original work of this PhD program, we developed a core-polarization corrected JM. Of course there will be some non-locality like the case in lithium cluster. Since the effective mass of bulk silver is closed to one, we neglect this effect and focus on the core polarization effect. We treat jellium background of Ag cores as a polarizable sphere. The core-polarization correction to the total Hamiltonian separates into a one-body self-energy term and a two-body dipole screening term. We implemented the core-polarization corrections into Hartree-Fock calculation and the matrix Random Phase Approximation. Numerical calculations are done for anionic, neutral and cationic silver clusters with closed shell number of atoms ($N=7-,19-; 8,20,58,138,198;9+,21+,59+,139+,199+$). As a major correction, the two-body interaction screens the dipole component of Coulomb interaction in a multipole expansion, which makes it impossible to include this effect in the Kohn-Sham formalism from the very beginning. The one-body self-energy potential bounds the valence electrons more. Overall the core-polarization corrections keep the HF states and eigenvalues almost unchanged. However, the

two-body dipole correction to the Coulomb interaction leads to a strong screening in the direct matrix elements $\langle m,j|V'|in \rangle$ of RPAE. This screening finally gives a red shift of the dipole surface plasmon peak. Excellent agreement with experimental photo absorption measurements is found for cationic Ag₉₊ 21+ 59+ clusters. A blue shift (as size decreases) trend of oscillator strength in cationic Ag clusters is identified and agrees well with experiments. We explain this unusual size dependent absorption spectrum of Ag clusters by: the magnitude of the two-body correction does not vary with cluster size, while the one-body correction decreases as clusters size increases. With an increasing percentage of embedded Ag cores, the CP-caused red shift gets stronger as clusters size increases.

As many photo absorption experiments are conducted for embedded silver clusters, we would like to have a complete theoretical description of the optical response for both free and embedded metal clusters. As far as we know the existing theoretical treatment for the inert environment is only designed for very small metal clusters. Therefore the second part of this original work is to include the rare-gas matrix into the jellium model based HF-RPAE approach so that we have a model for large embedded clusters. We proposed a dielectric model for the rare-gas matrix. It is regarded as an infinite uniform dielectric media. The Coulomb interaction between the valence electrons of the metal atoms is screened. Since we are in the framework of JM, the rare-gas matrix will also screen the Jellium background potential, which represents the valence electron-ion interaction. To take into account of the r -dependency of rare-gas dielectric function, we include a parameter d , which defines the distance between the induced charges and cluster surface. The dielectric screening will lead to a modified Coulomb two-body interaction and a one-body correction in the Hamiltonian for the valence electrons. The energy barrier arising from the conduction band minima (97) is also included in the present calculation. The new Hamiltonian is solved by HF-RPAE approach. Numerical calculations have been done for Na, Ag clusters embedded in He, Ne and Ar matrix. Significant red shift of the oscillator strength peak due to matrix effect was found in Ag₁₃₈ and Ag₁₉₈. For small embedded clusters, the one-body corrections are minor effect compared to the dielectric screening on the two-body Coulomb interaction. For larger embedded clusters, the screening charges on the ionic background is the main contribution. To determine parame-

ter d , one could fit the HF IP to the experimental value. The present calculation results for Ag8 embedded in He Ne and Ar matrices agree well with experiments. Moreover, the classical prediction of $0.3eV$ redshift by argon matrix can be found in the calculation of Ag198 embedded in Argon. It is concluded that the present model works in a wide range of cluster size. Here, we would like to recall the light trapping methods in reference (5), which is the motivation of this PhD project. The metal nanoparticles are always embedded in a dielectric media, which highlights the importance of studying rare-gas matrix effect.

As has been discussed in Chapter 5, the core-polarization two-body correction screens the dipole component of the Coulomb interaction and we found an effective dielectric constant ϵ_{eff} .

$$\frac{\epsilon_{eff} - 1}{\epsilon_{eff} + 2} = \frac{\alpha}{r_s^3} \quad (7.1)$$

One may notice that the silver core background can be generalized into a dielectric media and the dielectric screening formalism can be used. If one replaces ϵ_1 with the effective dielectric constant ϵ_{eff} in the expansion form of the screened Coulomb interaction of Chapter 6, that is, Equation 6.2 and replaces ϵ_2 with one for a free Ag cluster, one can easily obtain:

$$\Phi_{L=1}(r_1, r_2, R) = \begin{cases} \frac{r_{<}}{r_{>}^2} \left(1 - \frac{\epsilon_{eff}-1}{\epsilon_{eff}+2} \frac{R_J^3}{r_{<}^3}\right) & \text{if } R_J < r_{<} \\ \frac{r_{<}}{r_{>}^2} \left(1 - \frac{\epsilon_{eff}-1}{\epsilon_{eff}+2}\right) & \text{if } r_{<} < R_J < r_{>} \\ \frac{r_{<}}{\epsilon_{eff} r_{>}^2} \left(1 + 2 \frac{\epsilon_{eff}-1}{\epsilon_{eff}+2} \frac{r_{>}^3}{R_J^3}\right) & \text{if } r_{>} < R_J \end{cases}$$

where $\Phi_{L=1}(r_1, r_2, R)$ is the dipole term in the screened Coulomb interaction below

$$V(\mathbf{r}_1, \mathbf{r}_2) = \sum_{LM} \Phi_L(r_1, r_2, R) \frac{4\pi}{2L+1} Y_{LM}^*(\Omega') Y_{LM}(\Omega) \quad (7.2)$$

Since the spill-out electrons are near the cluster surface, $r_{>} \approx R_J$, one gets:

$$\Phi_{L=1}(r_1, r_2, R) \approx \frac{r_{<}}{r_{>}^2} \left(1 - \frac{\epsilon_{eff}-1}{\epsilon_{eff}+2} \frac{r_{>}^3}{R_J^3}\right) \quad (7.3)$$

when $r_{>} < R_J$. Comparing the above expression with Equation 5.26, one finds

that the core-polarization screening correction (Equation 5.6) is in fact the dipole ($L = 1$) component of the dielectric screening correction.

In conclusion, during the four years PhD time, a previous non-local pseudopotential work for Li clusters has been repeated. Calculation for both free and embedded Ag clusters are made by modifying jellium model using HF-RPAE approach. One should be aware of the advantages and disadvantages of this model compared to commercial quantum chemistry package. Hopefully the present dielectric model for rare-gas matrices could serve as a theoretical tool for a systematic study of the optical response of various metal clusters embedded in an inert environment. It needs to be stressed that there are extensions from the present theoretical study of metal clusters. In the next section discussion on possible future work on gold clusters and semiconductor nanoparticles will be given.

7.2 Future Work

As mentioned in Chapter 1, noble metals are more suitable for photovoltaic devices. After successfully treating Na, Li and Ag clusters in the framework of simple and modified Jellium Model, one needs to go further into more complicated noble metals. Experimental measurement has been done for gold clusters (106, 107, 108). The ground state electron configuration of Au atoms is [Xe] $4f^{14} 5d^{10} 6s^1$. At a first glance, one may notice that if [Xe] can be seen as a polarizable core, we could use the same core-polarization correction as Ag for the extra d -orbital electrons in Au. However, by using the core-polarizability from a non-relativistic atomic calculation for Au⁺ in the present CP formalism for silver clusters, the oscillator strength peak is still blue shifted compared to the experimental photo absorption spectrum. Although a relativistic calculation would give a larger core-polarizability, it is not enough to reach the classical Mie limit of $2.7eV$. In the last two decades, there are many TDDFT calculations(13, 96, 109, 110, 111) for Au clusters by treating all the 11 electrons ($5d^{10} 6s^1$) equally with a pseudo-potential for the frozen core. Range separated density functional was applied to large gold clusters(112). However contradictory results are reported, which makes the theoretical description of the optical response in gold clusters an open question. We would like to keep the one-valence electron picture so that the

how the core electron affect the s electron can be seen clearly. Studies on lithium clusters, although it is much simpler metal than gold, indeed give some insight picture of the physical process of quantum excitation in noble metal nanoparticles. For example, the non-local potential proposed for Li clusters indicates that the ionic structure in metal nanoparticles always leads to increase of effective mass of valence electrons and a non-local pseudo-potential can be used to describe the interaction between core and valence electrons. A combination of the angular momentum dependent pseudo-potential method and the core polarization formalism could be an attractive way. One unclear part of the core-polarization formalism is the analytical form of the cutoff function. If one uses a jellium averaging process for the core-polarization correction, it is still difficult to determine the cutoff function of an atomic core. The cutoff function becomes l -dependent:

$$V_{ps} = \sum_{L=0}^{\infty} \left(-\frac{1}{2} N \alpha \mathbf{f} \right) \mathcal{P}_L \quad (7.4)$$

where $\mathcal{P}_L$ is the angular momentum projection operator,

$$\mathcal{P}_L = \sum_{m=-L}^L |Lm\rangle \langle Lm| \quad (7.5)$$

$$\mathbf{f} = \sum_i \frac{\mathbf{r}_i}{r_i^3} C_L(r_i) \quad (7.6)$$

The relativistic effect may be further included by a spin-dependent pseudopotential (113). How to present a pseudo-potential which contains core-polarization effect, non-local effect and spin-orbital coupling effect and implement it into the JM could be a very challenging work. Another possible future work is about the localized surface plasmon resonance (LSPR) in semiconductor materials. In the past ten years, there is a huge interest in the size-dependency of LSPR and controlling its free carrier density (114, 115, 116, 117, 118). We wish that our Jellium Model based RPAE approach, beside metal clusters, can be extended to even semiconductor nanoparticles where free carrier density is large enough to hold the LSPR. Indeed, Jellium Model has already been used for a TDDFT calculation of the absorption spectra in doped quantum dots(119). One can look at the effective mass and dielectric screening effect on the optical properties of colloidal semi-

conductor nanocrystals. Does a position dependent effective mass (98, 120) play an important role? Is the free charge carrier density achieved by the photodoping technique high enough that many-body effect become non-negligible? Is the plasma-like collective excitation or exciton-like excitation dominating the optical response in such systems (121)?

References

- [1] S. A. BLUNDELL AND C. GUET. *Z. Phys. D*, **33**:153, 1995. ix, 4, 5, 25, 51, 52, 65, 66, 115
- [2] D. R. JOHNSTON, G. J. OUDEMANS, AND R. H. COLE. *J. Chem. Phys.*, **33**(5):1310, 1960. ix, 97
- [3] RALPH L. AMEY AND ROBERT H. COLE. *J. Chem. Phys.*, **40**(1):146, 1964. ix, 97
- [4] M. ROSENBLIT AND J. JORTNER. *J. Phys. Chem. A*, **101**:751, 1997. ix, 97
- [5] H. A. ATWATER AND A. POLMAN. *Nat. Mater.*, **9**:205, 2010. xi, 2, 117
- [6] KATHY SELBY, VITALY KRESIN, JUN MASUI, MICHAEL VOLLMER, WALT A. DE HEER, ADI SCHEIDEMANN, AND W. D. KNIGHT. *Phys. Rev. B*, **43**(6):4565, 1991. xi, 13, 19
- [7] TH. REINERS, W. ORLIK, CH. ELLERT, M. SCHMIDT, AND H. HABERLAND. *Chem. Phys. Lett.*, **215**:357, 1993. xi, 20
- [8] C. ELLERT, M. SCHMIDT, C SCHMITT, H HABERLAND, AND C. GUET. *Phys. Rev. B*, **59**:R7841–R7844, 1999. xii, 52, 64
- [9] C. BRECHIGNAC, PH. CAHUZAC, J. LEYGNIER, AND A. SARFATI. *Phys. Rev. Lett.*, **70**(13):2036, 1993. xii, 65
- [10] JOSEF TIGGESBUMKER, LARS KLLER, KARL-HEINZ MEIWES-BROER, AND ANSGAR LIEBSCH. *Phys. Rev. A*, **48**(3):R1749, 1993. xii, 27, 75
- [11] JOSEF TIGGESBUMKER, LARS KLLER, AND KARL-HEINZ MEIWES-BROER. *Chem. Phys. Lett.*, **260**:428, 1996. xii, 28, 76
- [12] THOMAS DIEDERICH, JOSEF TIGGESBAUMKER, AND KARL-HEINZ MEIWES-BROER. *J. Chem. Phys.*, **116**(8):3263, 2002. xiv, 30, 31, 94, 108

-
- [13] S. LECOULTRE, A. RYDLO, C. FELIX, J. BUTTET, S. GILB, AND W. HARBICH. *J. Chem. Phys.*, **134**(7):074302, 2011. xiv, 30, 31, 94, 108, 118
- [14] S. FEDRIGO, W. HARBICH, AND J. BUTTET. *Phys. Rev. B*, **47**(16):10706, 1993. xiv, 27, 28, 30, 31, 94, 108
- [15] M. BRACK. *Rev. Mod. Phys.*, **65**(3):677, 1993. 2, 3, 4
- [16] W. A. DE HEER. *Rev. Mod. Phys.*, **65**(3):611, 1993. 2, 25
- [17] F. BALETTO AND R. FERRANDO. *Rev. Mod. Phys.*, **77**:371, 2005. 2
- [18] H. XU, E. J. BJERNELD, M. KALL, AND L. BORJESSON. *Phys. Rev. Lett.*, **83**:4357, 1999. 2
- [19] J. N. ANKER, W. P. HALL, O. LYANDRES, N. C. SHAH, J. ZHAO, AND R. P. VAN DUYN. *Nat. Mater.*, **7**:442, 2008. 2
- [20] K. R. CATCHPOLE AND A. POLMAN. *Opt. Express*, **16**:21793, 2008. 2
- [21] F. BALETTO AND R. FERRANDO. *Rev. Mod. Phys.*, **77**, 2005. 3
- [22] J. M. PITARKE, V. M. SILKIN, E. V. CHULKOV, AND P. M. ECHENIQUE. *Rep. Prog. Phys.*, **70**(1):1, 2007. 3
- [23] L. G. GERCHIKOV, C. GUET, AND A. N. IPATOV. *Phys. Rev. A*, **66**:053202, 2002. 3, 17, 115
- [24] W. D. KNIGHT, KEITH CLEMENGER, WALT A. DE HEER, WINSTON A. SAUNDERS, M. Y. CHOU, AND MARVIN L. COHEN. *Phys. Rev. Lett.*, **52**(24):2141, 1984. 3, 13
- [25] S. A. BLUNDELL AND C. GUET. *Z. Phys. D*, **28**:81, 1993. 4
- [26] K. YABANA AND G. F. BERTSCH. *Z. Phys. D*, **32**:329, 1995. 4
- [27] M. GRO AND F. SPIEGELMANN. *J. Chem. Phys.*, **108**(10):4148, 1998. 5, 31, 90

-
- [28] B. GERVAIS, E. GIGLIO, E. JACQUET, A. IPATOV, P. G. REINHARD, AND E. SURAUD. *J. Chem. Phys.*, **121**(17):8466, 2004. 5, 30, 90
- [29] B. GERVAIS, E. GIGLIO, E. JACQUET, A. IPATOV, P. G. REINHARD, F. FEHRER, AND E. SURAUD. *Phys. Rev. A*, **71**(1):015201, 2005. 5, 30, 90
- [30] U. KREIBIG AND VOLLMER M. *Optical properties of metal clusters*. Berlin: Springer. 10
- [31] W. D. KNIGHT, KEITH CLEMENGER, WALT A. DE HEER, AND WINSTON A. SAUNDERS. *Phys. Rev. B*, **31**(4):2539, 1985. 13, 18
- [32] M. M. KAPPES, M. SCHAR, U. ROTH LISBERGER, C. YERETZIAN, AND E. SCHUMACHER. *Chem. Phys. Lett.*, **143**(3):251, 1988. 13
- [33] C. BRECHIGNAC, P. CAHUZAC, F. CARLIER, AND J. LEYGNIER. *Phys. Rev. Lett.*, **63**(13):1368, 1989. 13
- [34] KATHY SELBY, MICHAEL VOLLMER, JUN MASUI, VITALY KRESIN, WALT A. DE HEER, AND W. D. KNIGHT. *Phys. Rev. B*, **40**(8):5417, 1989. 13
- [35] M. L. HOMER, J. L. PERSSON, E. C. HONEA, AND R. L. WHETTEN. *Z. Phys. D*, **22**:441, 1991. 13
- [36] PH. DUGOURD, D RAYANE, P. LABASTIE, B. VEZIN, J. CHEVALEYRE, AND M. BROYER. *Chem. Phys. Lett.*, **197**(4,5):433, 1992. 13
- [37] C. JACKSCHATH, I. RABIN, AND W. SCHULZE. *Phys. Chem.*, **96**:1200, 1992. 13, 93, 95
- [38] SUSUMU SAITO, GEORGE F. BERTSCH, AND DAVID TOMNEK. *Phys. Rev. B*, **43**(8):6804–6807, 1991. 14, 22, 25
- [39] D. E. BECK. *Phys. Rev. B*, **30**(12):6935, 1984. 14
- [40] W. EKARDT. *Phys. Rev. B*, **29**(4):1558, 1984. 14
- [41] W. EKARDT. *Phys. Rev. Lett.*, **52**(21):1925, 1984. 14

-
- [42] C. XIA, C. YIN, AND V. V. KRESIN. *Phys. Rev. Lett.*, **102**:156802, 2009. 14
- [43] K. HOFlich, U. GOSELE, AND S. CHRISTIANSEN. *Phys. Rev. Lett.*, **103**:087404, 2009. 14
- [44] L. HENRARD, C. VANDENBEM, PH. LAMBIN, AND A. A. LUCAS. *Phys. Rev. Lett.*, **104**:149701, 2010. 14
- [45] K. HOFlich, U. GOSELE, AND S. CHRISTIANSEN. *Phys. Rev. Lett.*, **104**:149702, 2010. 14
- [46] W. KOHN. *Phys. Rev.*, **123**:1242, 1961. 15
- [47] N. F. BREY, L. AND JOHNSON AND B. I. HALPERIN. *Phys. Rev. B*, **40**:10647, 1989. 15
- [48] J. BREY, L. AND DEMPSEY, N. F. JOHNSON, AND B. I. HALPERIN. *Phys. Rev. B*, **42**:1240, 1990. 15
- [49] S. K. YIP. *Phys. Rev. B*, **43**:1707, 1991. 15
- [50] J. F. DOBSON. *Phys. Rev. Lett.*, **73**:2244, 1994. 15
- [51] D. R. HARTREE AND W. HARTREE. *Proc. R. Soc. A*, **150**(869):9, 1935. 15
- [52] J. C. SLATER. *Phys. Rev.*, **81**(3):385, 1951. 15
- [53] C. YANNOULEAS, R. A. BROGLIA, M. BRACK, AND P. F. BORTIGNON. *Phys. Rev. Lett.*, **63**(3):255, 1989. 17
- [54] M. MADJET, C. GUET, AND W. R. JOHNSON. *Phys. Rev. A*, **51**(2):1327, 1995. 17, 18, 25, 114
- [55] G. F. BERTSCH AND D. TOMANEK. *Phys. Rev. B*, **40**:2749, 1989. 17
- [56] P. HOHENBERG AND W. KOHN. *Phys. Rev.*, **136**(3B):864, 1964. 18
- [57] W. KOHN AND L. J. SHAM. *Phys. Rev.*, **140**(4A):1133, 1965. 18
- [58] M. LEVYL. *Natl. Acad. Sci. USA*, **76**:6062, 1979. 18

-
- [59] O. GUNNARSSON AND B. I. LUNDQVIST. *Phys. Rev. B*, **13**(10):4274, 1976. 22
- [60] C. A. ULLRICH. *Time-dependent density-functional theory - concepts and applications*. Oxford University Press. 23
- [61] C. GUET AND W. R. JOHNSON. *Phys. Rev. B*, **45**:11283, 1992. 25
- [62] U. KREIBIG AND P. ZACHARIAS. *Z. Physik*, **231**:128, 1970. 26
- [63] F. FUJIMOTO AND K. KOMAKI. *J. Phys. Soc. Japan*, **25**:1679, 1968. 26
- [64] Y. BORENSZTEIN, P. DE ANDRS, R. MONREAL, T. LOPEZ-RIOS, AND F. FLORES. *Phys. Rev. B*, **33**(4):2828, 1986. 27
- [65] P. APELL AND A. LJUNGBERT. *Solid State Commun.*, **44**(9):1367, 1982. 27
- [66] K. P. CHARLEL, W. SCHULZE, AND B. WINTER. *Z. Phys. D*, **12**:471, 1989. 27, 95
- [67] V. V. KRESIN. *Phys. Rev. B*, **51**:1844, 1995. 28
- [68] V. KASPEROVICH AND V. V. KRESIN. *Philos. Mag. B*, **78**(4):385, 1998. 28
- [69] L. SERRA AND A. RUBIO. *Phys. Rev. Lett.*, **78**:1428, 1997. 28, 70
- [70] K. STURM, E. ZAREMBA, AND K. NUROH. *Phys. Rev. B*, **42**(11):6973, 1990. 29, 71
- [71] E. ZAREMBA AND K. STURM. *Phys. Rev. Lett.*, **55**(7):750, 1985. 29, 71
- [72] K. YABANA AND G. F. BERTSCH. *Phys. Rev. B*, **54**:4484, 1996. 29
- [73] K. YABANA AND G. F. BERTSCH. *Phys. Rev. A*, **60**:3809, 1999. 29, 83
- [74] J. TIGGESBAUMKER AND F. STIENKEMEIER. *Phys. Chem. Chem. Phys.*, **9**(34):4748, 2007. 30

-
- [75] E. LOGINOV, L. F. GOMEZ, N. CHIANG, A. HALDER, N. GUGGEMOS, V. V. KRESIN, AND A. F. VILESOV. *Phys. Rev. Lett.*, **106**(23):233401, 2011. 30, 31
- [76] VLASTA BONACIC-KOUTECKY, VINCENT VEYRET, AND ROLAND MITRIC. *J. Chem. Phys.*, **115**(22):10450, 2001. 30
- [77] L JENSEN, L. L. ZHAL, AND G. C. SCHATZ. *J. Phys. Chem. C*, **111**:4756, 2007. 30
- [78] KOPINJOL BAISHYA, JUAN C. IDROBO, SERDAR T, MINGLI YANG, KOBLAR JACKSON, AND JULIUS JELLINEK. *Phys. Rev. B*, **78**(7):075439, 2008. 30
- [79] GEORGE C. SCHATZ CHRISTINE M. AIKENS, SHUZHOU LI. *J. Phys. Chem. C*, **112**:11272, 2008. 30
- [80] M. HARB, F. RABILLOUD, D. SIMON, A. RYDLO, S. LECOULTRE, F. CONUS, V. RODRIGUES, AND C. FELIX. *J. Chem. Phys.*, **129**(19):194108, 2008. 30, 31
- [81] J. LERME, B. PALPANT, B. PREVEL, M. PELLARIN, M. TREILLEUX, J. L. VIALLE, A. PEREZ, AND M. BROYER. *Phys. Rev. Lett.*, **80**:5105, 1998. 30, 107
- [82] J. A. SCHOLL, A. L. KOH, AND J. A. DIONNE. *Nature*, **483**(7390):421, 2012. 30
- [83] S. RAZA, N. STENGER, S. KADKHODAZADEH, S. V. FISCHER, N. KOSTESHA, A. P. JAUHO, A. BURROWS, M. WUBS, AND N. A. MORTENSEN. *Nanophotonics*, **2**:131, 2013. 30
- [84] W. HARBICH, S. FEDRIGO, AND J. BUTTET. *Chem. Phys. Lett.*, **195**:613, 1992. 31
- [85] S. LECOULTRE, A. RYDLO, C. FELIX, J. BUTTET, S. GILB, AND W. HARBICH. *J. Chem. Phys.*, **134**:074303, 2011. 31
- [86] C YU. *Optical properties of small metal clusters*. PhD Thesis. 31

- [87] W. R. JOHNSON, S. A. BLUNDELL, AND J. SAPIRSTEIN. *Phys. Rev. A*, **37**(2):307, 1988. 38
- [88] D. J. ROWE. *Rev. Mod. Phys.*, **40**(1):153, 1968. 40
- [89] G. B. BACHELET, D. R. HAMANN, AND M. SCHLUTER. *Phys. Rev. B*, **26**(8):4199, 1982. 61
- [90] N. F. MOTT AND H. S. W. MASSEY. *The theory of atomic collisions*. Oxford University Press. 66
- [91] F. XUAN AND C. GUET. *Phys. Rev. A*, **94**:043415, 2016. 67, 102
- [92] JOSEPH CALLAWAY. *Phys. Rev.*, **106**(5):868, 1957. 69
- [93] C. D. H. CHISHOLM AND U. OPIK. *Proc. Phys. Soc.*, **83**:541, 1964. 69
- [94] W. R. JOHNSON AND C. GUET. *Phys. Rev. A*, **49**(2):1041, 1994. 69, 85
- [95] W. MULLER, J. FLESCH, AND W. MEYER. *J. Chem. Phys.*, **80**(7):3297, 1984. 69
- [96] J. C. IDROBO AND S. T. PANTELIDES. *Phys. Rev. B*, **82**:085420, 2010. 71, 118
- [97] MILTON W. COLE. *Rev. Mod. Phys.*, **46**(3):451–464, 1974. 90, 92, 94, 116
- [98] J HERMANSON. *Phys. Rev.*, **150**:660, 1966. 92, 120
- [99] W. T. SOMMER. *Phys. Rev. Lett.*, **12**(11):271, 1964. 92
- [100] MICHAEL A. WOOLF AND G. W. RAYFIELD. *Phys. Rev. Lett.*, **15**(6):235, 1965. 92
- [101] BRET HALPERN, JOHN LEKNER, STUART A. RICE, AND ROBERT GOMER. *Phys. Rev.*, **156**(2):351, 1967. 92
- [102] B. RAZ AND J. JORTNER. *Chem. Phys. Lett.*, **4**:155, 1969. 92

-
- [103] N. SCHWENTNER, F. J. HIMPSEL, V. SAILE, M. SKIBOWSKI, W. STEINMANN, AND E. E. KOCH. *Phys. Rev. Lett.*, **34**(9):528, 1975. 92
- [104] C. JACKSCHATH, I. RABIN, AND W. SCHULZE. *Z. Phys. D*, **22**:517, 1992. 94
- [105] J. LEKNER. *Phys. Rev.*, **158**:130, 1967. 102, 104
- [106] C. A. FOSS, G. L. HORNYAK, J. A. STOCKERT, AND C. R. MARTIN. *J. Phys. Chem.*, **98**:2963, 1994. 118
- [107] G. L. HORNYAK, C. J. PATRISSI, AND C. R. MARTIN. *J. Phys. Chem. B*, **101**:1548, 1997. 118
- [108] B. PALPANT, B. PREVEL, J. LERME, E. COTTANCIN, M. PELLARIN, M. TREILLEUX, A. PEREZ, J. L. VIALLE, AND M. BROYER. *Phys. Rev. B*, **57**:1963, 1998. 118
- [109] H. HAKKINEN, M. MOSELER, AND U. LANDMAN. *Phys. Rev. Lett.*, **89**(3):033401, 2002. 118
- [110] K. IIDA, M. NODA, K. ISHIMURA, AND K. NOBUSADA. *J. Phys. Chem. A*, **118**(47):11317, 2014. 118
- [111] R. W. BURGESS AND V. J. KEAST. *J. Phys. Chem. C*, **118**:3194, 2014. 118
- [112] J. V. KOPPEN, M. HAPKA, AND M. M. SZCZESNIAK. *J. Chem. Phys.*, **137**:114302, 2012. 118
- [113] L. KLEINMAN. *Phys. Rev. B*, **21**(6):2630, 1980. 119
- [114] D. DORFS, T. HARTLING, K. MISZTA, N. C. BIGALL, M. R. KIM, A. GENOVESE, A. FALQUI, M. POVIA, AND L. MANNA. *J. Am. Chem. Soc.*, **133**(29):11175, 2011. 119
- [115] J. M. LUTHER, P. K. JAIN, T. EWERS, AND A. P. ALIVISATOS. *Nat. Mater.*, **10**:361, 2011. 119

- [116] M. J. POLKING, P. K. JAIN, Y. BEKENSTEIN, U. BANIN, O. MILLO, R. RAMESH, AND A. P. ALIVISATOS. *Phys. Rev. Lett.*, **111**(3):037401, 2013. 119
- [117] J. A. FAUCHEAUX, A. L. STANTON, AND P. K. JAIN. *J. Phys. Chem. Lett.*, **5**(6):976, 2014. 119
- [118] G. M. CARROLL, A. M. SCHIMPF, E. Y. TSUI, AND D. R. GAMELIN. *J. Am. Chem. Soc.*, **137**(34):11163, 2015. 119
- [119] H. ZHANG, V. KULKARNI, E. PRODAN, P. NORDLANDER, AND A. O. GOVOROV. *J. Phys. Chem. C*, **118**:16035, 2014. 119
- [120] O. V. ROOS. *Phys. Rev. B*, **27**:7547, 1983. 120
- [121] S. CHATTERJEE, C. ELL, S. MOSOR, G. KHITROVA, H. M. GIBBS, W. HOYER, M. KIRA, S. W. KOCH, J. P. PRINEAS, AND H. STOLZ. *Phys. Rev. Lett.*, **92**:067402, 2004. 120