Quantum Entrapment and Valence Charge Polarization in Ag, Cu, Pt, and Rh Nanoclusters

SHIDEH AHMADI

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY

2015
Quantum Entrapment and Valence Charge Polarization in Ag, Cu, Pt, and Rh Nanoclusters

Shideh Ahmadi

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University in fulfillment of the requirement for the degree of Doctor of Philosophy

July 2015
Acknowledgment

This thesis would not have been possible at all without the help and support of many people. First, I would like to express my deeply gratitude to my supervisor, Prof. Sun Chang Qing, for his continuous advice, support, encouragement, and patience throughout this research. His unique ideas, commitment, and determination towards research greatly inspired me. I have also learnt the disciplines in both education and socialist, which will benefit me not only in this work, but my life in general.

A special thanks goes to Dr. Xi Zhang from Shenzhen University and Dr. Yinyan Gong from China Jiliang University for solving problems that crop up along the way, and for their kind help, support, and patient instructions. I would like to thank Prof. Payam Kaghazchi from Free University Berlin for giving me a fruitful exchange experience. Working with Prof. Kaghazchi has been a wonderful learning experience. I would also like to thank Prof. Weiguang Zhu from Nanyang Technological University and Prof. Reza Khosrowabadi from Shahid Beheshti University for their support. I would also like to thank all my colleagues, in particular Dr. Ma Shouzhi, Dr. Nie Yanguang, Mr. Li Jiu, and Ms. Sara Panahian Jand for their support and countless help. Among of my friends, I would like to give special thanks for your listing, offering me advise, making me positive, and helping me countless to my friends, Ms. Sepideh Gholmakanian, Dr. Mehrnaz Afshang, Dr. Anantha, Mr. Ramtin Rabiee, Mr. Mahan Qwamizadeh, Dr. Mahnaz Arvaneh, and Dr. Hamed Ahmadi.
Additionally, I would like to express my gratitude to my dear husband Dr. Kasra Saeedfar for their endless continued support and encouragement during the challenges of graduate and life. I am truly thankful for having you in my life. I specially acknowledge my loving parents, my brother, and extended families, who have always loved me unconditionally and continued support and encouragement.

Finally, I would like to acknowledge Nanyang Technological University, especially NOVITAS, Nanoelectronics Centre of Excellence, School of Electronic and Electrical Engineering, and Singapore International Graduate Award (SINGA) on behalf of Agency for Science, Technology and Research (A*STAR) for giving me this opportunity to pursue my postgraduate studies.
This thesis is dedicated to my dear husband Kasra

and my beloved parents
Table of Contents

Acknowledgment .............................................................................................................. i

Table of Contents ............................................................................................................. iv

Summary ............................................................................................................................. ix

List of Figures .................................................................................................................... xi

List of Tables ...................................................................................................................... xvi

Nomenclatures ................................................................................................................... xviii

Chapter 1 Introduction ...................................................................................................... 1

1.1 Background .................................................................................................................. 1

1.2 Challenges .................................................................................................................... 3

1.3 Objectives ..................................................................................................................... 5

1.4 Achievements ............................................................................................................... 6

1.5 Organization of the Thesis .......................................................................................... 8

Chapter 2 Computational Approaches .............................................................................. 9

2.1 Theory: BOLS and NEP ............................................................................................ 9

2.1.1 Bond Relaxation in Length and Energy .............................................................. 10

2.1.2 Non-bonding Electron Polarization ................................................................. 20
2.2 BOLS-TB Theory .............................................................................................................. 23
  2.2.1 Hamiltonian and Energy Dispersion ................................................................. 23
  2.2.2 Hamiltonian Perturbation .................................................................................. 27
  2.2.3 BOLS: Coordination Resolution ...................................................................... 30

2.3 DFT Calculations ......................................................................................................... 33
  2.3.1 Problem of Many-body System ........................................................................ 33
  2.3.2 Thomas-Fermi Model ....................................................................................... 35
  2.3.3 Hohenberg-Kohn Theory .................................................................................. 36
  2.3.4 Kohn-Sham Theory .......................................................................................... 36
  2.3.5 Exchange-Correlation Functional .................................................................... 38
  2.3.6 Spin-DFT ........................................................................................................... 39

2.4 Summary ...................................................................................................................... 40

Chapter 3 Principles ........................................................................................................... 41

3.1 BOLS in Nanostructures .......................................................................................... 41

3.2 DFT in DMol³ .............................................................................................................. 42
  3.2.1 Introduction ....................................................................................................... 42
  3.2.1 Atomic Orbitals Basis Set ............................................................................... 43
3.2.2 Numerical Integration................................. 45

3.3 Application of BOLS in DFT ................................ 46
  3.3.1 DOS..................................................... 46
  3.3.2 Local and Partial DOS................................ 47
  3.3.3 Chemical and Physical Properties .................. 48

3.4 Summary ................................................................ 48

Chapter 4 Quantum Entrapment and Valence Polarization of Ag and Cu Nanoclusters
............................................................................................................. 50

4.1 Overview of Ag and Cu Nanoclusters ...................... 50

4.2 Computational Methods ........................................... 51
  4.2.1 COh and M-Dh structures.............................. 51
  4.2.2 DFT Calculations ........................................ 53

4.3 Discussions............................................................. 53
  4.3.1 Local Bond Length Contraction ..................... 53
  4.3.2 Charge Transfer and Magnetic Moment .......... 56
  4.3.3 CLS and Lattice Strain ................................. 57
  4.3.4 Shell-resolved Valence Charge Polarization ...... 62
4.4  Summary ........................................................................................................... 67

Chapter 5 Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters
................................................................................................................................. 68

5.1  Background of Pt and Rh Nanoclusters ......................................................... 68

5.2  Calculation Procedures.................................................................................... 69

5.2.1  COh and M-Dh structures.............................................................................. 69

5.2.2  DFT Calculation............................................................................................ 70

5.3  Discussions........................................................................................................ 71

5.3.1  Local Bond Length Contraction................................................................. 71

5.3.2  Charge Transfer............................................................................................ 74

5.3.3  Core Electron Entrapment and Lattice Strain.......................................... 74

5.3.4  Shell-resolved Valence Band Polarization................................................. 79

5.3.5  Magnetic Modulation.................................................................................. 83

5.4  Summary ......................................................................................................... 93

Chapter 6 Quantum Entrapment and Valence Polarization of Cationic, Neutral, and
Anionic Metallic Nanoclusters .................................................................................. 94

6.1  Overviews of Cationic, Neutral, and Anionic M\text{N} Nanoclusters............... 94
6.2 Computational Approaches ................................................................. 95

6.2.1 DFT Calculation............................................................................. 95

6.3 Discussions ....................................................................................... 96

6.3.1 Local Bond Length Contraction..................................................... 96

6.3.2 Charge of Core and Shell................................................................. 100

6.3.3 Quantum Entrapment and Valence Charge Polarization............... 104

6.3.4 Magnetization ............................................................................... 111

6.4 Summary .......................................................................................... 124

Chapter 7 Conclusions and Recommendations..................................... 125

7.1 Achievements ..................................................................................... 125

7.2 Limitations ......................................................................................... 126

7.3 Recommendations for Future Work................................................... 127

Author’s Publications ............................................................................. 129

References ............................................................................................. 131
Summary

Atomic under-coordination and non-bonding electrons are extensively used in nanomaterials and nanostructures. The bonds between the under-coordinated sites follow the rule of relaxation dynamics, although quantum confinement (QC) theory, Coulomb blockade, and size-dependent dynamic effects cannot describe the change in Hamiltonian and other magnitudes. The effect of under-coordinated atom on the electronic structures of nanomaterials was calculated in this study using the bond-order-length-strength (BOLS) correlation and non-bonding electron polarization (NEP) notations. The Hamiltonian perturbation of the atomic under-coordination entrapped the core electrons and polarized the valence charge.

Consistency between the BOLS-NEP notation and density functional theory (DFT) calculations on Ag, Cu, Pt, and Rh nanoclusters with cuboctahedral (COh) and Marks decahedral (M-Dh) structures confirmed that the shorter and stronger bonds between atomic under-coordination induced local densification, quantum entrapment, and valence charge polarization. The strong localization determined the intriguing catalytic, magnetic, and plasmonic attributes of these metallic nanoclusters.

The effect of excess charge states from (+2) to (-2) was determined using DFT calculations and BOLS correlation theories on the metallic nanoclusters with COh and M-Dh structures. Consistency between DFT calculations and experimental observations confirmed our BOLS predictions including the local bond length relaxation, charge...
densification, quantum entrapment, valence band polarization, and magnetization of the metallic nanoclusters with negative, neutral, and positive excess charge states. Magnetization behavior was observed in the even (positive/negative) excess charge states for all metallic nanoclusters and the odd (positive/negative) excess charge states in the Pt and Rh nanoclusters. By contrast, non-magnetization behavior was observed in the odd (positive/negative) excess charge states in the Ag and Cu nanoclusters. Furthermore, Rh and Pt were regarded as donors and acceptors in the catalytic reactions, respectively. This work elucidated the development of cationic, neutral, and anionic metallic nanoclusters for catalyst and magnetic applications.
List of Figures

Figure 2-1 Mechanism of the BOLS correlation and the ratio bond coefficient. The contraction coefficient $C_i$ is obtained from the notations of Goldschmidt (open circle) and Feibelman (open square). The bond energy at equilibrium atomic increases in the absolute energy $E_i = C_i^{-m} E_b$ because of spontaneous bond contraction. The nature of the bond is denoted as $m$. However, the atomic cohesive energy, $z_i E_i$, changes with both the m and $z_i$ values (Reprinted with permission from Ref. 3).................................11

Figure 2-2 Schematic of surface (a) a thin plate with thickness $t$, (b) a cylindrical rod, and (c) a sphere dot with radius $r$................................................13

Figure 2-3 Schematic of the BOLS-obtained nanosolid potential with multi-trap centers and CN induced local strain and quantum at terminating edges.\textsuperscript{45, 46} The charge density, energy, and mass are higher in the relaxed surface compared with their bulk interior.\textsuperscript{24} However, the atomic cohesive energy for the under-coordinated atoms decreases (Reprinted with permission from Ref. 3). ..................................................................................................................16

Figure 2-4 Entrapped bonding and core charges expressing the atomic under-coordination-induced local bond contraction ($d_i < d_b$), the related quantum
entrapment (T), and the nonbonding states polarization (P) based on BOLS correlation (Reprinted with permission from Ref. 30). ..........................

Figure 2-5 (a) Progress of the $v$th atomic energy level from $E_\nu(0)$ to the $v$th band $\Delta E_\nu$ ($z_b = 12$) with the shift of $\Delta E_\nu(z_b) = \alpha_\nu + z_b\beta_\nu$ and a width of $E_{\nu W} = 2z_b\beta_\nu\Phi_\nu(k, R)$ on bulk. Amounts of energy shift and band expansion is dependent on the cohesive energy per bond at equilibrium and the quantum number $\nu$ of the band. (b) The core band XPS spectrum, with the addition of entrapment (T) and polarization (P) components to the bulk (B) shifts (Reprinted with permission from Ref. 2).................................................................27

Figure 4-1 Schematic of metallic nanoclusters with (a-c) COh and (d-f) M-Dh structures. The number indicates the atom position in our calculation. ......................52

Figure 4-2 BOLS reproduction (solid and chained curves) and the measurement-extracted of XPS data (scattered data) CLS of (a) Ag-3d$^{5/2}$ and (b) Cu-2p$^{3/2}$ deposited on different substrates.................................................................60

Figure 4-3 Lattice stain of silver and copper nanoparticles shows consistency between theoretical prediction (solid line) and experimental data (scattered data).61

Figure 4-4 Shell-resolved LDOS for (a-b) COh$^{147}$ and (c-d) M-Dh$^{75}$ for silver and copper nanoclusters. The electronic binding energy shifts upward $E_f$ in the outermost layers, while those of the interior layers resemble the bulk. ...63
Figure 4-5 LDOS of the $s, p,$ and $d$ orbitals are shown by gray, blue, and black solid lines, respectively for (a-b) COh$_{147}$ and (c-d) M-Dh$_{75}$ of the silver and copper nanoclusters. The arrows indicate the state of spins, whether up or down. The $E_f$ is assumed to be zero. .............................................65

Figure 4-6 Size-resolved DOS of the (a, b) COh and the (c, d) M-Dh structures of the silver and copper nanoclusters, representing that the extent of polarization depends on the cluster size. This size-dependent polarization is agreement with the LDOS of the Au nanoclusters,$^{112}$ the end of Cu atomic chains,$^{15}$ and Ag.$^{85}$ .............................................................................................................66

Figure 5-1 shows the CLS predicted by the BOLS correlation and XPS measurements-extracted of the (a) Pt and (b) Rh nanoparticles.................................77

Figure 5-2 Consistency in the trend between theoretical predictions and various experimental observations of the mean lattice contraction of the Pt and Rh nanoparticles. ..........................................................78

Figure 5-3 Shell-resolved LDOS for the (a-b) COh-147 and the (c-d) M-Dh-75 structures of the Pt and Rh nanoclusters. The outermost shell electrons moved toward the upper edge near the $E_f$ whereas the interior shell electrons remained at the lower energy...........................................80
Figure 5-4 Size-resolved DOS of the (a, c, and e) COh and the (b, d, and f) M-Dh structures of the Pt\textsubscript{N} and Rh\textsubscript{N} nanoclusters (N = 13-147 atoms). E\textsubscript{f} is allocated at 0 eV..........................82

Figure 5-5 Spin-polarized DOS of (a-f) the Pt singlet state, (g-l) the Pt triplet state, and (m-r) the Rh quartet state. The inset shows the difference between spin-up (\(\alpha\)) and spin-down (\(\beta\)) states in DOS. The blue and red indicate the spin-up (\(\alpha\)) and spin-down (\(\beta\)) configurations. The E\textsubscript{f} is set at 0 eV..................87

Figure 5-6 Spin-polarized PDOS of (a-f) the 5d-Pt singlet state, (g-l) the 5d-Pt triplet state, and (m-r) the 4d-Rh quartet state. The inset shows the difference between the spin-up (\(\alpha\)) and spin-down (\(\beta\)) states in PDOS. The blue and red indicate the spin-up (\(\alpha\)) and spin-down (\(\beta\)) configurations. The E\textsubscript{f} is set at 0 eV.........................90

Figure 6-1 LDOS of d-band shown for (a-d) COh\textsubscript{13}, (e-h) COh\textsubscript{55}, (i-l) COh\textsubscript{147}, (m-p) M-Dh\textsubscript{13}, (q-t) M-Dh\textsubscript{49}, and (u-x) M-Dh\textsubscript{75} structures. The dash dot, dash, solid, short dash, and short dot indicate the excess charge states including (+2), (+1), (0), (-1), and (-2), respectively. The E\textsubscript{f} is considered to be 0 eV..109

Figure 6-2 Spin-polarized PDOS of 4d-Ag, 3d-Cu, 5d-Pt, and 4d-Rh for (a-d) COh\textsubscript{13}, (e-h) COh\textsubscript{55}, (i-l) COh\textsubscript{147}, (m-p) M-Dh\textsubscript{13}, (q-t) M-Dh\textsubscript{49}, and (u-z) M-Dh\textsubscript{75} structures. The excess charge states (+1) and (+2) were considered in the
singlet and double states for Ag and Cu nanoclusters, the doublet and triplet states for Pt nanoclusters, and the triplet and quartet states for Rh nanoclusters. The blue and red indicate the spin-up ($\alpha$) and spin-down ($\beta$) configurations. The $E_f$ is set at 0 eV.

Figure 6-3 Difference between spin-up and spin-down states in PDOS of 4$d$-Ag, 3$d$-Cu, 5$d$-Pt, and 4$d$-Rh for (a-d) COh$_{13}$, (e-h) COh$_{55}$, (i-l) COh$_{147}$, (m-p) M-Dh$_{13}$, (q-t) M-Dh$_{49}$, and (u-x) M-Dh$_{75}$ structures. The excess charge states (+1) and (+2) were considered in the singlet and double states for Ag and Cu nanoclusters, the doublet and triplet states for Pt nanoclusters, and the triplet and quartet states for Rh nanoclusters. The blue and red indicate the spin-up ($\alpha$) and spin-down ($\beta$) configurations. The $E_f$ is set at 0 eV.
List of Tables

Table 2-1 Related quantities with bond length ..........................................................19

Table 2-2 XPS and BOLS derived energy level of an isolated atom and its bulk shift. ........................................................................................................................................33

Table 4-1 Effective CN ($z_i$), Ag-Ag and Cu-Cu bond length ($d_i$), shell index ($i$), magnetic moment ($\mu$), and charge transfer ($e$) for silver and copper nanoclusters. 55

Table 4-2 $E_{\nu}(0)$ and $\Delta E_{\nu}(\infty)$ obtained from XPS $E_{\nu}(\infty)$ component and BOLS correlation for silver and copper nanoparticles. .................................................................58

Table 5-1 Effective CN ($z_i$), bond length ($d_i$), shell ($i$), magnetic moment ($\mu$), and charge transfer ($e$)................................................................................................................73

Table 5-2 BOLS derived $E_{\nu}(0)$ and $\Delta E_{\nu}(\infty)$ for Pt and Rh nanoparticles ............75

Table 5-3 Calculated gaps for the spin-up ($\alpha$) and spin-down ($\beta$) of Pt and Rh nanoclusters ........................................................................................................................................92

Table 6-1 Calculation of the M-M bond length $d_i(\text{Å})$ and charge of shell ($e$) at different position of $\text{M}_N$ metallic nanoclusters with COh and M-Dh structures and the excess charge states from (+2) to (-2). The shell index counts the atomic layer from the outermost inwards ........................................................................................98

Table 6-2 Calculation of the charge of core ($e$) of $\text{M}_N$ metallic nanoclusters with COh and M-Dh structures and excess charge states from (+2) to (-2). ........101
Table 6-3 Calculated gaps between spin-up and spin-down states of metallic nanoclusters with positive, neutral, and negative excess charge states. The magnetic behavior of $d$-band metallic nanoclusters was observed in the positive (negative) even excess charges for all metallic nanoclusters and the odd (positive/negative) excess charges for Pt and Rh nanoclusters, whereas no magnetic behavior was detected in the odd (positive/negative) excess charges for Ag and Cu nanoclusters.
Nomenclatures

- $\mu$: Magnetic moment
- $\gamma_i$: Surface-to-volume ratio
- $\tau$: Shape factor of surface-to-volume ratio
- $b$: Bulk

- BOLS: Bond-order-length-strength correlation
- $C_i$: Bond contraction coefficient
- CN: Coordination number
- CLS: Core-level shift
- CNTs: Carbon nanotubes
- COh: Cuboctahedral structure
- $d_i$: Bond length
- DN: Double numeric basis set
- DFT: Density functional theory
- DIIS: Direct inversion of the iterative subspace
- DOS: Density of states
- DND: Double numeric plus $d$-functions basis set
DNP  Double numeric plus polarization basis set

$E_b$  Cohesive energy per bond

$E_B$  Atomic cohesive energy

$E_F$  Fermi level

$E_v$  Core level energy

$E_v(0)$  $v$th energy level of an isolated atom

EXAFS  Extended X-ray-absorption fine structure spectroscopy

FCC  Face-centered cubic

G(E)  Density of energy states

HOMO  Highest occupied molecular orbital

HOPG  Highly ordered pyrolytic graphite

$K$  Dimensionless form of the radius of a sphere or thin film thickness

LDA  Local-density approximation

LDOS  Local density of states

LSDA  Local-spin-density approximation

LUMO  Lowest unoccupied molecular orbital

$m$  Bond nature indicator
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCNTs</td>
<td>Multiwall carbon nanotubes</td>
</tr>
<tr>
<td>MIN</td>
<td>Minimal basis set</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics method</td>
</tr>
<tr>
<td>M-Dh</td>
<td>Marks decahedral structure</td>
</tr>
<tr>
<td>NEP</td>
<td>Non-bonding electron polarization</td>
</tr>
<tr>
<td>PDOS</td>
<td>Partial density of states</td>
</tr>
<tr>
<td>PES</td>
<td>Photoelectron spectroscopy</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PRS</td>
<td>Photoelectron residual spectroscopy</td>
</tr>
<tr>
<td>PWC</td>
<td>Perdew-Wang function</td>
</tr>
<tr>
<td>Q(K)</td>
<td>Measurable quantity of a nanosolid</td>
</tr>
<tr>
<td>q(z)</td>
<td>Local detectable quantity at atomic sites with CN of z</td>
</tr>
<tr>
<td>QC</td>
<td>Quantum confinement theory</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent-field</td>
</tr>
<tr>
<td>SOC</td>
<td>Spin-orbit coupling</td>
</tr>
<tr>
<td>STM/S</td>
<td>Scanning tunneling microscopy/spectroscopy</td>
</tr>
<tr>
<td>TB</td>
<td>Tight-binding method</td>
</tr>
</tbody>
</table>
\( T_m \)  Melting temperature

UPS  Ultraviolet photoelectron spectra

\( V(r) \)  Periodic potential from ion-cores in crystal

\( V_{\text{atom}}(r) \)  Atomic potential

\( V_{\text{cry}}(r) \)  Crystal potential which equals to \( V(r) - V_{\text{atom}}(r) \)

XPDS  X-ray photoelectron differential spectroscopy

XPS  X-ray photoelectron spectroscopy

\( Y \)  Young’s modulus

\( z_i \)  Effective coordination number
Chapter 1 Introduction

1.1 Background

Nanomaterials exhibit unusual chemical and physical properties compared with their bulk counterparts. The ratio of atomic under-coordination at the surface, edges, and defects increases with the decrease in size. For instance, the ratio of surface atoms is around 20% and 50% in nanoscale systems with 8000 and 500 atoms, respectively.\(^1\) The effects of under-coordinated atoms induce these novel physical and chemical properties. Band-gap energy, core-level shift (CLS), melting temperature, surface stress, specific heat, and Young’s modulus, as well as the extensibility of a solid, are no longer constant, but become a variant of the solid size.\(^2\)\(^-\)\(^5\) The core binding energy level shifts to lower energies relative to those of the bulk energies as the size decreases or the atoms localize at under-coordination sites, including surfaces, edges, and nanoislands.\(^6\)

Nanomaterials demonstrate catalysis abilities and allow the transit of metallic nanoparticles from a conductor to an insulator for Ag and Pt, or a nonmagnetic-to-magnetic behavior for Pt and Rh nanoparticles, caused by pinning the conduction electrons.\(^7\)\(^-\)\(^11\) The red shift of valence band is detected with scanning tunneling microscopy/spectroscopy (STM/S), which includes Ag clusters and chains on the Ag(111) substrate,\(^12\)\(^-\)\(^13\) Cu adatom on the Cu(111) surface,\(^14\) Cu chains on the Cu(111) substrate,\(^15\) gold atomic chains,\(^16\) Rh nanoparticles,\(^17\) and Pt nanoclusters.\(^18\) The positive core level energy instantaneously shifts to higher binding energy level in nanomaterials
when measured using X-ray photoelectron spectroscopy (XPS) for Ag, Cu, Pt, and Rh nanoparticles,\textsuperscript{6, 19-23} resulting in perturbed Hamiltonian. The binding energy density perturbs the Hamiltonian of an extended solid that determines the entire band structure such as the band gap, core-level shift, and bandwidth. At the lower end of the size limit, the perturbation to the Hamiltonian of a nanosolid relates directly to the behavior of a single bond, being the cases of a surface and a monatomic chain.\textsuperscript{24} From a nanoscale perspective, the core level quantum entrapment is a function of particle size and oxidation. Quantum entrapment is global and polarization is subjective, depending on the electronic configuration in the valence band (Section 2.1.1.4). The low-energy component corresponds to the global quantum entrapment of the core electrons while the high energy component corresponds to potential screening by polarization of the otherwise conductive $s$-electrons of Rh or the lone $p$ electron of carbon.\textsuperscript{4}

Broken bond-induced valance charge entrapment and polarization splits the valence band, and the occupation of the upper branch dominates the catalytic ability of the under-coordinated systems. The non-bonding electron polarization at the site with even lower atomic CN than that of a flat surface is responsible for the emerging properties, such as increased catalytic ability of noble metals, dilute magnetism, and conductor–insulator transition. The catalytic properties are supported by nanoparticles and charge states, and can be adsorbed on the nanocluster surfaces, thereby inducing strains on the surface. Moreover, the catalyst behavior of Ag, Cu, Pt, and Rh nanoclusters has been investigated using excess charge states, including negative, neutral, and positive charges
on the surface in both theoretical and experimental observations.\textsuperscript{25-27} The excess charge states on the nanocluster surface play a significant role in the ability of catalysts in adjusting oxide support.

Bond-order-length-strength (BOLS) correlation\textsuperscript{28} has been used to refine the non-bonding electron polarization (NEP) theory,\textsuperscript{3, 29, 30} to solve associated problems,\textsuperscript{31, 32} including superfluidity in carbon nanotube channels,\textsuperscript{33} superlubricity in dry sliding,\textsuperscript{31, 34} and supersolidity of $^4$He with superelasticity and superfluidity.\textsuperscript{35} The effect of under-coordinated atoms and excess charge states on Ag, Cu, Pt, and Rh metallic nanoclusters are investigated in this study according to the BOLS-NEP theory. According to unique properties of these metallic nanoclusters such as magnetic and nonmagnetic order, and plasmon and catalyst applications, we are chosen Ag, Cu, Pt, and Rh metallic nanoclusters in this thesis. In addition, the results of Ag, Cu, Pt, and Rh metallic nanoclusters are presented separately, in Chapters 4 and 5, respectively, because Ag, Cu, Pt, and Rh belong to different elements such as Nobel and open metals.

1.2 Challenges

The concept of broken bonds and non-bonding in nanomaterials is complicated. According to theoretical and experimental observations, valence band polarization, CLS, lattice strain, charge transfer, magnetization, optical application, and electronic properties of metallic nanoclusters are dependent on size. However, basic advancement in principle remains behind the experimental and theoretical explorations, in which
questions are open to discussions in nanoscale systems. Moreover, the distribution of charge on the valence band, polarization of non-binding electrons, and interaction between bonding electrons are significant factors for material behaviors. The core level binding energy is regarded as a fingerprint of the interatomic interaction of the valence band electrons.

The quantum electronic properties of the macroscopic system can be analyzed using multi-scale modeling based on density functional theory (DFT) calculations, tight-binding (TB) approximation, and molecular dynamics (MD). Quantum modeling, such as DFT calculations utilized in atomic scale, explains the nanomaterial electronic properties for 100-atom using the Kohn-Sham equations. Force field modeling of similar MD is suitable for large-scale representation of 1000 atoms to model the mechanical, thermal, and chemical features through Newton’s motion equation. Moreover, the TB model is a quantum model, and encompasses 100-1000 atoms within systems that are faster than the DFT calculations and more accurate within the TB model.\textsuperscript{36, 37} The Hamiltonian can be simplified through the TB approximation rather than the DFT calculation, clearly representing the findings from the calculations. In a nanoscale system, atomic under-coordination perturbs to the Hamiltonian and changes the electronic structures. The BOLS correlation indicates that atomic coordination imperfection causes the remaining bonds of the under-coordinated atom to contract spontaneously associated with bond strength gain and the intra-atomic trapping potential well depression. Consequently, localized densification of charge, energy and mass
occurs to the surface skin, which modify the atomic coherency, electroaffinity, work function, and the Hamiltonian of the nanosolid. Therefore, any detectable quantity can be functionalized depending on the atomic coherency, electroaffinity, work function, Hamiltonian or their combinations. For instances, the perturbed Hamiltonian determines the entire band structure such as the band-gap expansion, core-level shift, Stokes shift, and dielectric suppression. The TB approximations are considered state-by-state without studying the physical origins, such as generation of the strong localized edge states of metallic nanoclusters and the band gap and vacancy of graphene nanoribbons; the band gap expansion lays because of the relatively short and strong bonds between under-coordinated atoms, making up the majority of the investigation in this model.

A model that correlates the classical macroscopic approach to the atomic quantum mechanics, allowing to circumvent the limitations induced by the effect of under-coordination, are also studies. By enlarging the BOLS mechanics, the BOLS-NEP and BOLS-TB methods in the form of quantum theories are suggested for applications in size-dependence and bond nature-dependence of electronic, lattice strain, catalytic, plasmonic, and magnetic properties of materials.

### 1.3 Objectives

This research aims to:
Chapter 1: Introduction

I. Connect 100 and 1000 atoms with a quantum calculation model at a faster rate than the DFT calculations, and at a rate that is more accurate than the MD model, while investigating the effect of under-coordination materials.

II. Combine the BOLS-TB quantum theory and incorporate the effect of under-coordination to tight-binding Hamiltonian for a positive core level binding energy in nanostructures.

III. Verify the BOLS-NEP notation to prove the valence electron polarization caused by the influence of under-coordination of Ag, Cu, Pt, and Rh nanoclusters.

IV. Discover the influence of positive, neutral, and negative charge states on the Ag, Cu, Pt, and Rh nanocluster surface.

V. Peruse the quantum entrapment and valence polarization of positive, neutral, and negative metallic nanoclusters using BOLS correlation and DFT calculations.

VI. Investigate the magnetic and non-magnetic orders of positive, neutral, and negative metallic nanoclusters with spin ground states through DFT calculations.

1.4 Achievements

This research achieved the following results:
Chapter 1: Introduction

I. Consistency between BOLS-NEP notation and DFT calculations confirmed the bond length contraction, charge transfer, positive CLS, lattice strain, magnetic momentum, and valence charge polarization of the Ag, Cu, Pt, and Rh nanoclusters.

II. Combining the BOLS-NEP theories confirmed that the shorter-and-stronger bonds between atomic under-coordination induced local densification and quantum entrapment of core electrons, which polarized the otherwise conducting electrons, and the binding energy shifts positively toward deeper energies.

III. The effect of atomic under-coordination verified the catalyst, magnetic, and plasmonic properties in these metallic nanoclusters for both cuboctahedral (COh) and Marks decahedral (M-Dh) structures through DFT calculations.

IV. Bond relaxation, core and shell charges, quantum entrapment, valence charge polarization, and magnetic momentum were investigated within the context of excess charge states, including positive, neutral, and negative of metallic nanoclusters by BOLS-NEP correlation and DFT calculations in both COh and M-Dh structures.

V. Magnetic and catalyst behaviors were verified in the cationic, neutral, and anionic metallic nanoclusters using DFT calculation and BOLS correlation, even though the ability of the catalyst plays a significant role in the acceptor or donor of these structures.
1.5 Organization of the Thesis

This thesis is organized into seven chapters. Chapter 1 discusses the current research on nanomaterials. Summaries of questions and problems in both classical and quantum mechanics approaches toward the understanding of size dependency and multiple properties of materials in the nanoscale system. The objectives and main contributions are discussed as well. Chapter 2 explains the theoretical models and the effect of atomic under-coordination by BOLS-NEP correlation theory, BOLS-TB approximation, and DFT calculations. Chapter 3 presents the BOLS model by combining the BOLS-NEP correlation and DFT calculations with the Dmol³ code to include the under-coordination effects. Chapters 4, 5, and 6 explain the effect of under-coordination and excess charge states by BOLS-NEP and BOLS-TB applications in positive, neutral, and negative Ag, Cu, Pt, and Rh nanoclusters to investigate the quantum entrapment, valence charge polarization, and magnetic and catalytic abilities. Chapter 7 provides the detailed achievements and limitations of the present approaches, as well as recommendations for metallic nanoclusters.
Chapter 2  Computational Approaches

2.1 Theory: BOLS and NEP

Finding the surface bond contraction in metal chemisorption studies, Sun C. Q. investigated the nanostructure dependency upon their size and its association to surfaces and defects. By developing the Goldschmidt and Pauling premise in the context of atomic coordination and radius to contain the energy and electronic response of the atomic bonds to atomic under-coordination, Sun C. Q. initiated the BOLS correlation notion, which renders the unification of adatoms, atomic chain, sheet and vacancies, defects, hollow tubes, grain boundaries, kink edges, surfaces, and varieties of nanostructures shapes in terms of bond order deficiency as the unique and common origin possible (Section 2.1.1.2).

Moreover, non-bonding electrons prompted the emergence of several interesting phenomena that polarize the interaction with bonding electrons. According to the advanced principles and the Anderson localization principle, Sun C. Q. (2007) suggested and confirmed the NEP hypothesis, showing the non-bonding electrons performance, including lone pairs of O, N, F, dipoles, C sp² unpaired electrons, and the otherwise s-conducting electrons of metals, such as Ag, Au, Pt, Ru, and Rh at boundaries, which indicate indicative unpredicted abnormalities (Section 2.1.2).
Chapter 2: Computational Approaches

2.1.1 Bond Relaxation in Length and Energy

2.1.1.1 Atomic coordination number

The defects, surfaces, and numerous shapes of nanostructures with fewer bonds were observed in atomic under-coordination as opposed to bulk components. For example, the atomic coordination number (CN) in face-centered cubic (FCC) structures is 12, which is the bulk standard.

According to Pauling\textsuperscript{34} and Goldschmidt’s notation,\textsuperscript{38} the ionic and metallic radius of an atom spontaneously contracts if the CN of an atom decreases. The high ratio of atoms is shown with an effective atomic CN (or $z_i$) value between 0 (for an isolated atom) and 12 (for an atom in the bulk with FCC structure) for nanoscale materials.\textsuperscript{3} The size of the nanomaterials is dependent on the atomic under-coordination and strong interaction between atoms.\textsuperscript{4}

2.1.1.2 BOLS notation

The physical properties of atomic under-coordination at sites differ from the bulk.\textsuperscript{2,39} Although the broken bonds do not affect the performance of materials at the boundaries, their effect on the remaining bonds is quite substantial.\textsuperscript{3} Broken bonds result in shrinkage of the remaining bonds of the atomic under-coordination alongside bond strength gain, inducing localized strain and potential well depression with charge, energy, and mass densification.
Figure 2-1 Mechanism of the BOLS correlation and the ratio bond coefficient. The contraction coefficient $C_i$ is obtained from the notations of Goldschmidt (open circle) and Feibelman (open square). The bond energy at equilibrium atomic increases in the absolute energy $E_i = C_i^{-m}E_b$ because of spontaneous bond contraction. The nature of the bond is denoted as $m$. However, the atomic cohesive energy, $z_iE_i$, changes with both the $m$ and $z_i$ values (Reprinted with permission from Ref. 3).

According to Figure 2-1, CN depends on the bond contraction coefficient ($C_i$), and in accordance with the Goldschmidt theory, the ionic radius contracted from 12%, 4%, and 3 % (solid curve) as the atomic CN decreased from 12 to 4, 6, and 8, respectively, compared to the standard value of the FCC structures. Feibelman$^{40}$ pointed out the contractions of Ti, Zr, and V dimer bonds. The shorter and stronger bonds between under-coordinated atoms enable perturbation of the Hamiltonian, atomic cohesive
energy, binding energy density, and corresponding properties as the ratio of the under-coordinated atoms is increased. The effect of broken bonds and principle of Goldschmidt-Pauling-Feibelman bond contraction adhere to the following BOLS correlation:  

\[
\begin{aligned}
C_i &= d_i / d_b = 2\left[1 + \exp\left(\frac{(12 - z_i)}{(8z_i)}\right)\right]^{-1} \quad \text{(BOLS Coefficient)} \\
E_i &= C_i^{-m} E_b \quad \text{(Single Bond Energy)} \\
E_{b,i} &= z_i E_i \quad \text{(Atomic Cohesive Energy)} \\
\varepsilon &= 1 + C_i \quad \text{(Strain)} \\
\end{aligned}
\]  

(2-1)

where \(C_i\) is the bond contraction coefficient; \(d_i\) and \(E_i\) are the bond length and energy between the under-coordinated atoms, respectively; and \(m\) indicates the bond nature index associated with the bond energy to bond length. For metals, such as Ag, Cu, Pt, and Rh, \(m\) is equal to 1, whereas for alloys and compounds, \(m\) is approximately 4. Subscripts \(i\) and \(b\) represent an atom in the \(i\)th atomic layer and the bulk, respectively. The \(i\) is numerated up to three from the outmost layer to the center of the solid. The \(C_i\) is anisotropic and varies with the effective CN rather than the apparent CN value. According to Schuppler et al.\textsuperscript{41} and Mason,\textsuperscript{42} \(z_1\) varies with the diameter of a spherical dot as \(z_1 = 4(1 - 0.75/K)\). \(z_2 = 6\) and \(z_3 = 8\) are assumed independent of the surface curvature. Further fine-tuning herewith shows that \(z_1 = 4(1 - 0.7836/K)\) and \(z_3 = 12\) improve the match between the predicted and the measured photoluminescence profile.
Chapter 2: Computational Approaches

(by ~ 1% only). Therefore, the CN atoms in the $i$th atomic layer of a substance are labelled $z_i$ taken by the curvature as follows:\textsuperscript{43}

$$z_1 = \begin{cases} 
4(1 - 0.75 / K) & \text{(Curved - surface; First Shell)} \\
4 & \text{(Flat - surface)}
\end{cases}$$

$z_2 = z_1 + 2$ \quad (Second Shell)

$z_3 = 12$ \quad (Third Shell : Bulk)

(2-2)

$K = R/d_b$ is the dimensionless form of size, which is the number of atoms aligned along the radius of a sphere, a cylinder rod, or cross thickness of a thin plate, with thickness $(t)$ and radius $(r)$ ($K = r/d_b$ or $K = t/d_b$) (see Figure 2-2).

Figure 2-2 Schematic of surface (a) a thin plate with thickness $t$, (b) a cylindrical rod, and (c) a sphere dot with radius $r$. 

13
2.1.1.3 Pauling’s theory

From an investigation of interatomic distances of the C–C bond in organic chemistry, Pauling obtained the following equation:\(^3\)

\[
r(1) - r(v/z_0) = 0.030 \log\left(\frac{v}{z_0}\right) \text{ (nm)}
\]

(2-3)

where \(r(1)\) is the dimer bond length, \(r(v/z)\) is the radius of an atom with \(v\)-fold bond \(z\) coordinate; \(v\) is the number of valence bonds, and \(z_0\) is the number of equivalent coordination.

As an illustration of the use of this relation, the radius of the hcp-structured Ti is obtained from the data of the bcc-structured Ti. The radius of the bcc-structured Ti is 0.1442 nm with eight bonds of each atom. The length of the next six shortest bonds is 0.1667 nm. These values are calculated from the known bcc lattice parameter of 0.333 nm. The valence, \(v\), of a Ti atom is four. The problem lies in determining the fraction of these four bonds that is associated with the eight nearest neighbors and the six next-nearest neighbors. From Eq. (2-3)

\[
r(1) - r(x/8) = 0.030 \log\left(\frac{x}{8}\right)
\]

(2-4)

and for the next-nearest neighbors,

\[
r(1) - r[(4-x)/6] = 0.030 \log\left(\frac{4-x}{6}\right)
\]

(2-5)
where \( x \) is the number of bonds associated with the eight near neighbors and \((4 - x)\) is the number associated with the other six neighbors. By subtracting (2-4) from (2-5) and using the value \((0.1667 - 0.1442)\) obtained from the lattice parameter, \( x = 3.75 \) and the dimer bond length \( r(1) = 0.13435 \text{ nm} \), which contracts by \(0.00985 \text{ nm} \). The bond number \( v/z \) is \(4/12\) in the hcp of \( CN = 12 \), and the corresponding bond length is \( r(4/12) = 0.13435 - 0.03 \log(4/12) = 0.1486 \text{ nm} \). From Eq. (2-3), the bond length of an atom with a reduced \( CN(z) \) can be denoted as follows:

\[
r(v/z) = r(v/z_o) + 0.030 \log(z/z_o)
\]

(2-6)

The values of electronegativity \((h)\), metallic (ionic) valencies, and metallic (ionic) radii of the elements were taken as a combination Goldschmidt and Paulings’ notations.\(^{34,38}\) Pauling’s theory introduced here contains numerous assumptions and it is somewhat empirical in nature. Compared to Eq. (2-3), Pauling’s notation is \( d_b \) and valence value dependent and relatively complicated, which gives

\[
C(z) = 1 + 0.060 \log(z/z_o)/d_b(v/z_o)
\]

(2-7)

This notation surprisingly provides good answers in certain cases.\(^{44}\) Both Eqs. (2-3) and (2-7) are valid; however relation (2-2) is universal and sufficient for purely CN effect, covers Feibelmens’s notation and element \((d_b)\) independent.
2.1.1.4 Quantum entrapment and densification

The potential well becomes deeper based on the general rule of energy minimization because the relaxation (expansion or contraction) is processed spontaneously. As a result, the relaxed bond energy will be greater, and bond expansion may occur. However, this process remains within the lower binding energy in the whole system, unless the relaxation is externally stimulated through heating, pressing, or stretching.

![BOLS correlation diagram](image)

Figure 2-3 Schematic of the BOLS-obtained nanosolid potential with multi-trap centers and CN induced local strain and quantum at terminating edges.\(^{45,46}\) The charge density, energy, and mass are higher in the relaxed surface compared with their bulk interior.\(^{24}\) However, the atomic cohesive energy for the under-coordinated atoms decreases (Reprinted with permission from Ref. 3).
The potential well of a nanosolid caused by the BOLS correlation is illustrated in Figure 2-3. The quantum confinement (QC) convention extends the monocenter trapping potential of an isolated atom as its size is rescaled. The BOLS correlation describes the distribution from individual atoms with multi center tapping potential and the effect of atomic CN on the surface of up to three atomic layers. The atomic CN induces the bond contraction, and the bond strength gain deepens the entrapment potential on the surface. Thus, the density of charge, energy, and mass in the relaxation surface are higher than those in the interior solid. Valence electron polarization and energy densification have been observed using STM/S at gold, silver, platinum, and rhodium atomic chains or clusters on different substrates.\textsuperscript{12-18} The highest localization of electron in the relaxed region has been observed, which may be due to the potential entrapment. Meanwhile, the core level binding energy and the bonding electrons shift when the potential deepens, causing quantum entrapment. This convention is utilized by monoatomic chains, atomic defects, terrace edges, and flat surfaces when the atomic CN decreases.

2.1.1.5 Scaling relations

For a nanosolid consisting of $N$ atoms with dimension $K$ (Section 2. 1. 1. 2), the dependence of a given quantity $Q(K)$ on the size can be related to $Q(\infty) = Nq_b$, with the effect of CN imperfection defined as follows:

$$Q(K) = Q(\infty) + \sum_{i \in \mathcal{S}} N_i (q_i - q_b) = Nq_b + \sum_{i \in \mathcal{S}} N_i (q_i - q_b)$$
where the $q_i$ and $q_b$ are the local density of $Q$ at the $i$th atomic layer from the surface and bulk, respectively. Table 2-1 shows that the $q_i(z_i, m, d, E_i)$, as macroscopic detectable quantities, is related to the bond parameters. Physical quantities of a bulk solid can normally be categorized as follows: (1) quantities that are related directly to bond length, including the mean lattice constant, mass density, binding energy density, and the mean free path in transport; (2) quantities that depend on atomic cohesive energy, including self-organization growth, thermal stability, Coulomb blockade, critical temperature for liquidation, evaporation and phase transition of a nanosolid and the activation energy for atomic dislocation, diffusion, and bond unfolding; (3) properties that vary with the binding energy density in the relaxed continuum region such as the Hamiltonian that determines the entire band structure and related properties such as bandgap, core-level energy, magnetization, and phonon frequency. The binding energy density is proportional to the single bond energy $E_i$ because the number of bonds per circumferential area between neighboring atomic layers in the relaxed region does not change; (4) properties related to the electroaffinity such as reactivity, iconicity, and toxicity; (5) properties contributed from the joint effect of the binding energy density and atomic cohesive energy such as mechanical strength, Young’s modulus, surface energy, surface stress, extensibility and compressibility of a nanosolid, and the magnetic performance of a ferromagnetic nanosolid; and (6) transport dynamics and scattering process such as thermal conductivity, electric conductivity, relate to the trapping
potential well of depth. The localized and depressed potential well will govern the transport processes.

<table>
<thead>
<tr>
<th>Table 2-1 Related quantities with bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Quantity</strong></td>
</tr>
<tr>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Elastic module ($Y_i$)</td>
</tr>
<tr>
<td>CLS ($\Delta E_v$)</td>
</tr>
<tr>
<td>Melting point ($T_m$)</td>
</tr>
<tr>
<td>Strain ($\varepsilon$)</td>
</tr>
<tr>
<td>Raman shift ($\Delta \omega$)</td>
</tr>
</tbody>
</table>

By equating the experimental scaling correlation with the theoretical illustration, the following equation can be obtained:

$$\frac{Q(K) - Q(\infty)}{Q(\infty)} = \begin{cases} bK^{-1} & \text{(Measurement)} \\ \Delta_q & \text{(BOLS theory)} \end{cases}$$

$$b = Q(\infty) \times \Delta_q \times K = Q(\infty) \times \sum_{i=3} \tau C_i \left(\frac{\Delta q_i}{q_b}\right) \equiv \text{constant}$$

$$\Delta_q = \sum_{i=3} \gamma_i \left(\frac{\Delta q_i}{q_b}\right)$$
Chapter 2: Computational Approaches

\[
\begin{align*}
\Delta_q &= \sum_{i=3}^{N_i} \frac{q_i - q_b}{Nq_b} = \sum_{i=3}^{N_i} \gamma_i \frac{\Delta q_i}{q_b} = \sum_{i=3}^{N_i} \gamma_i (C_i - 1) \quad \text{(Strain)} \\
\gamma_i &= \frac{N_i}{N} = \frac{\tau C_i}{K}
\end{align*}
\]

(2-9)

where \( Q(\infty) \) is the bulk value obtained by the intercept of measured \( Q(K) \) versus \( K^{-1} \) plot. Slope \( b \) is the core physical nanoscience; \( \gamma \) is surface-to-volume ratio; and \( N_i \) is the atom numbers of the \( i \)th atomic layer. \( \tau \) is the dimensionless geometrical factor, and equal to 1, 2, and 3 for a thin plate, a cylindrical rod, and a sphere dot, respectively. Therefore, the lattice strain and CLS consist of extrinsic and intrinsic variables of \((\tau, K, K^{-1}, m, z_i, d_i, E_i)\).

2.1.2 Non-bonding Electron Polarization

The bonds between under-coordinated atoms are shorter and stronger than its bulk counterpart, resulting in local strain densifications and quantum entrapment of binding energy and core electrons. In turn, the otherwise conductive charge is polarized by densely entrapped core and bonding electrons, such as half-filled \( s \)-orbital of Rh at the nanoscale.\(^{39}\) The polarized lone electrons neither follow the dispersion nor occupy the allowed states in the valence band and below, but they generate midgap impurity states close to Fermi level \((E_f)\).\(^{29}\)
Chapter 2: Computational Approaches

2.1.2.1 Features of non-bonding electrons

The ‘non-bonding’ electrons are referred as non-bonding lone pairs, antibonding dipoles, and non-bonding unpaired electrons, which include the π-bond in graphite, the dangling bond in silicon surface, the half-filled s-orbitals of metallic at the nanoscale system, and the H-like and C-H-like bonds. An ionic impurity induces dipoles. The van der Waals bond with a maximal energy of several tenths of an eV should be in this category because it represents dipole-dipole interaction instead of charge sharing. Such non-bonding electrons are only active when they are in positions adjacent to the broken bonds at the open edges of a material.

The non-bonding electrons adjust the impurity states between the conduction and the valence band, or generate tails for these bands that are dissimilar to the electrons of the core in the deeper bands or the bonding electrons in the valence band. The electrons become strongly localized and contribute to the Hamiltonian, exhibiting interesting properties. These types of electrons are polarized by dense core electron entrapment, or the electrons polarize the surroundings. The polarized states split and screen local crystal potentials, and calculate the band of energy such as the core level shift of XPS. These electrons cannot be explained quantum computational because of the localized and weak bounds. The presence of non-bonding states near the broken bonds dictates the behavior of the nanomaterials, biology, and organic molecules.
2.1.2.1 NEP theory

The bond order loss localizes the electrons based on the Anderson localization. It is scaling theory of localization. Polarization happens to the non-bonding electrons by the densely entrapped core and bonding electrons, which exemplifies Anderson’s localization due to bond order deficiency. The bond length contraction raises the local density of the electrons in the core bands and the electrons shared in the bonds. When the potential well becomes deep, it is called entrapment (T), and the core band shifts. The entrapment core and bonding electrons in turn polarize the non-bonding electrons and move near the $E_f$ energy. The electron polarization then splits and screens the potentials. This sequential occurrence of bond length contraction, entrapment, densification, and polarization (bonding–non-bonding electron repulsion and strong correlation) may elaborate the “strong-localization” of the Anderson for systems with bond order loss.

The non-bonding electrons dominate the terminating end of solid. According to BOLS-NEP, non-bonding lone electrons tend to become polarized by deep and dense trapped bonds and the core electrons of the under-coordinated atoms, as detailed in Figure 2-4. Therefore, the insulating and magnetic behaviors of Ag ($4d^{10} 5s^1$), Cu ($3d^{10}$), Pt ($5d^8 6s^1$), and Rh ($4d^8 5s^1$) nanoclusters are attributed to the localized polarization of $s$-electrons.
Figure 2-4 Entrapped bonding and core charges expressing the atomic undercoordination-induced local bond contraction \((d_i < d_b)\), the related quantum entrapment \((T)\), and the nonbonding states polarization \((P)\) based on BOLS correlation (Reprinted with permission from Ref. 30).

### 2.2 BOLS-TB Theory

#### 2.2.1 Hamiltonian and Energy Dispersion

The intra-atomic trapping potential confine electrons of a single atom that move around the central ion core inside the potential well. The Hamiltonian, eigen-wave functions, and eigen-energies are given by:
\[ \hat{H}_o = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{atom}}(r) \]

\[
\begin{align*}
\phi_n(r) &\propto \sin\left(\frac{2n\pi r}{d}\right) \\
E_v(n) &= \frac{2(n\pi \hbar)^2}{(m_e d^2)} \\
&= n = 1, 2, 3, \ldots
\end{align*}
\]

(2-10)

where the dimension of the potential well is \( d = 2r \), the electron mass is \( m_e \), and the different levels of energy are quantum number \( n \). The energy separation between the closest two levels depends on \( (n+1)^2 - n^2 = 2n + 1 \).

Given that a system includes two atoms, the interatomic binding energy determines the separation between sublevels, and the single energy level splits into two sublevels in the system. Meanwhile, the center of two levels shifts to lower level because of interatomic interaction. As the atom number increases to \( N \), the single energy level expands into a band with \( N \) sublevels. The number of sub-levels in a particular energy band is proportional to the number of atoms in the solid. Therefore, the classical band theories are valid for a nanometric solid that consist of at least two atoms. The density of states (DOS) of the core band for a nanosolid shows a band-like feature more than the separate line of single isolated atom, which can be detected using XPS. The energy level spacing of the sequential sublevels in the valence band is called the Kubo gap \( \delta_K = 4E_f/3N \), which is reduced as the number of valence electrons increases. The
fundamental changes in the nanoscale system, particularly those associated to the valence band, are caused by the discreteness of energy sublevel results.

According to the energy band theory, the Hamiltonian and wave function for an electron in the $v$th energy level inside solid are explained by:

$$\hat{H} = \hat{H}_0 + \hat{H}' = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{atom}}(r) + V_{\text{crys}}(r + R)$$

$$\phi_{v,j}(r) \equiv |v,i\rangle \exp(ikr) \approx |v,i\rangle$$

(2-11)

The Hamiltonian of an isolated atom, $\hat{H}_0$, contains the kinetic energy and the intra-atomic potential, $V_{\text{atom}}(r)$, whereas $\hat{H}'$ is the crystal potential, $V_{\text{crys}}(r) = V_{\text{crys}}(r + R)$. The crystal potential sums over the interatomic potentials of all neighbors. Both the intra- and the crystal potentials are periodic in real space, with $R$ being the lattice constant. The plain wave prefector $\exp(ikr)$ of the Bloch function is often deleted because of the strong localization of the core electrons. Thus, the wave function for the tightly bound core electron estimates the electron of an isolated atom. The eigen-wave function is described using the atomic position $i$ and $j$ as follows:

$$\langle v, j | v, i \rangle = \delta_{ij} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases}$$

Corresponding to the TB approximation, the energy dispersion of an electron inside bulk is expressed as follows:

$$E_v(z_b) = E_v(0) + (\alpha_v + z_b \beta_v) + 2z_b \beta_v \Phi_v(k, R)$$
Chapter 2: Computational Approaches

with,

\[
\begin{align*}
E_v(0) &= -\langle \nu, i | \hat{H}_0 | \nu, i \rangle \quad \text{(Atomic Core Level)} \\
\alpha_\nu &= -\langle \nu, i | \hat{H} | \nu, i \rangle \propto E_b \quad \text{(Exchange Integral)} \\
\beta_\nu &= -\langle \nu, i | \hat{H}^\prime | \nu, j \rangle \propto E_b \quad \text{(Overlap Integral)}
\end{align*}
\]

(2-12)

\(E_v(0)\) is the \(\nu\)th energy level of an isolated atom, which is determined by the interaction between the ion core and the particular electron. When the crystal potential is involved, or a liquid or bulk is formed, the core level \(E_v(0)\) becomes deeper by the amount of \(\Delta E_v(z_b)\) = \(E_v(z_b) - E_v(0)\) = \(\alpha_\nu + z_b \beta_\nu\) related to band broadening. The exchange integral \((\alpha_\nu)\) and overlap integral \((\beta_\nu)\) are functions of the cohesive energy per bond at equilibrium, \(E_b\). According to Figure 2-5a, if one shifts from the valence band downward, \(\Delta E_v(z_b)\) changes from 10\(^6\) eV to 10\(^{-1}\) eV and \(E_{\nu W}\) approaches a line of spin-resolved energy, such as 1s, 2p\(_{1/2}\), and 2p\(_{3/2}\) levels of copper. The core band shape follows the form, 2\(z_b\beta_\nu \Phi_\nu(k, R) \sim \sin^2(kR/2)\), for the FCC structure. Any perturbation to the interatomic potential at equilibrium, or any variation of the interatomic bond, will directly change the CLS changes with the effective atomic CN. Neither the band gap expansion nor the CLS would be possible without the crystal potential and neither a solid nor even a liquid would form without the interatomic binding.
Figure 2-5 (a) Progress of the $v$th atomic energy level from $E_v(0)$ to the $v$th band $\Delta E_v$ ($z_b = 12$) with the shift of $\Delta E_v(z_b) = \alpha_v + z_b \beta_v$ and a width of $E_{\nu W} = 2z_b \beta_v \Phi_{\nu}(k, R)$ on bulk. Amounts of energy shift and band expansion is dependent on the cohesive energy per bond at equilibrium and the quantum number $v$ of the band. (b) The core band XPS spectrum, with the addition of entrapment (T) and polarization (P) components to the bulk (B) shifts (Reprinted with permission from Ref. 2).

### 2.2.2 Hamiltonian Perturbation

Taking into consideration an assembly composed of $n$ particles with mean size $K$ and with each particle having $N_b$ atoms, the total binding energy, $V(r, n, N_b)$ is given by:

$$V(r, n, N_b) = \sum_{i \neq j} \sum_i v(r_{ij}) = \frac{n}{2} \left[ N_b \sum_{i=1} v(r_{ij}) + \sum_{k \neq l} V(K_{kl}) \right]$$

$$\approx \frac{n}{2} \left[ N_b^2 v(d) + nV(K) \right]$$
where $V(r, n, N_b)$ sums the $nN_b$ atoms and the $n$ particles. The high-order $r_{ij}$ is a certain fold of the nearest atomic spacing, $d$. In addition, the interaction between the nearest clusters $k$ and $l$, $V(K_k)$, should be considered. If $K_k$ is extremely large, the last term would be neglected that is, the case of an isolated particle. Usually, the intercluster interaction, $V(K)$, is much weaker than the interatomic interaction. In this study, the intercluster interaction is considerable, and Eq. (2-13) can be derived in terms of a core-shell structure as follows:

$$V_{cry}(r, n, N_b) = \frac{nN_b}{2} \left[ N_i v(d_i) + (N_b - N_i) v(d) + \frac{n}{N_b} V(K) \right]$$

$$= \frac{nN_b^2 v(d)}{2} \left[ \frac{N_i v(d_i)}{N^b v(d)} + (1 - \frac{N_i}{N^b}) + \frac{nV(K)}{N^b v(d)} \right]$$

$$= V_{cry}(d, n, N_b) \{1 + \gamma (\frac{v(d_i)}{v(d)} - 1) + \delta_k (K)\}$$

$$\frac{\Delta V_{cry}(N_b)}{V_{cry}(\infty)} = \sum_{i=1}^{3} \gamma_i \frac{\Delta v}{v} + \delta_k (K) = \sum_{i=1}^{3} \gamma_i (C_i^{nm} - 1) + \delta_k (K)$$

$$\delta_k = \frac{nV(R)}{N_b^2 v(d)}$$

(2-14)

The $i$ counts over the outermost up to three of the nanosolids. The crystal potential without the intercluster interaction is $V_{cry}(d, n, N_b)$. The pair of interatomic binding energy at equilibrium atomic separation, $v(d)$, is proportional to the binding energy (
Chapter 2: Computational Approaches

\[ E_i = C_i^{-m} E_b \], which results to perturbation in the crystal binding energy on assembly nanosolid. The perturbation covers the weighted sum of the contribution from individual surface layers \((C_i^{-m} - 1)\) of up to three outermost layers of nanosolid or intercluster interactions, \(\delta_i(K)\), which is negligible when the particle size is considerably large.

The total potential in Eq. (2-11) turns into \( V(\Delta_H) = V_{\text{atom}}(r) + V_{\text{cr}}(r)[1 + \Delta_H] \). In connection the corresponding Bloch wave functions, the atomic trapping potential, \( V_{\text{atom}}(r) \), describes the discrete core-level energies of an isolated atom, \( E_i(0) \). The crystal binding \( V_{\text{cr}}(r) \) defines the band gap and the CLS from the original position \( \Delta E_i(\infty) = E_i(\infty) - E_i(0) \). The dimensionless, \( \Delta_H \), is the contribution from the binding energy in the relaxed surface region, which is independent of interatomic potential particular form.

The Hamiltonian perturbation leads to changes in \( E_i(K) \), with following scaling relation:

\[
\frac{\Delta E_i(K) - \Delta E_i(\infty)}{\Delta E_{vy}(\infty)} = \Delta_H
\]

(2-15)

The Hamiltonian and the Bloch wave functions are key elements in the quantum theory for condensed matter. Nanosolid densification may slightly modify the wave functions as there no chemical reaction occurs.
2.2.3 BOLS: Coordination Resolution

The crystal potential modification deepens the core level by $\Delta E_c(z_b)$. The perturbation ($\Delta H$) will positively or negatively shift the bulk counterpart as entrapment ($T$, shift away from $E_b$) or polarization ($P$, shift toward $E_b$) occurs, respectively (see Figure 2-5). A mixed shift may occur if both entrapment and polarization occur simultaneously. Considering that the wave function varies insignificantly for the core electron localization, then Eq. (2-9) changes to the following formula by substituting $z_b$ to $x$ in the context of the effect of CN ($z$) atom variation or polarization:

$$\hat{H}' = V_{cxy}(r) (1 + \Delta H)$$

$$E_v(x) = E_v(0) + \alpha_{sv} (1 + x\beta_{sv} / \alpha_{sv}) + 2x\beta_{sv} \Phi_v(k, R)$$

where,

$$E_v(0) = -\langle v, i | \hat{H}_0 | v, i \rangle \quad \text{(Atomic Core Level)}$$

$$\alpha_{sv} = -\langle v, i | \hat{H}' | v, i \rangle \propto E_b(1 + \Delta H) \propto E_x \quad \text{(Exchange Integral)}$$

$$\beta_{sv} = -\langle v, i | \hat{H}' | v, j \rangle \propto E_b(1 + \Delta H) \propto E_x \quad \text{(Overlap Integral)}$$

$$\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ (2-16)$$

The exchange integral is the crystal potential effect on the specific core electron at site $r$. The overlap integral is the crystal potential effect on the coordinate neighboring electrons. Both the exchange integral and the overlap integral are proportional to the cohesive energy per bond at equilibrium. According to the energy band theory and the BOLS premise, the surface- and the size-induced energy shift of the energy level of an isolated atom explains the following fact:
Chapter 2: Computational Approaches

\[ V(\Delta_H) = V_{\text{atom}}(r) + V_{\text{cry}}(r)[1 + \Delta_H] \]

\[
\begin{align*}
E_v(\Delta_H) &= E_v(0) + [E_v(\infty) - E_v(0)](1 + \Delta_H) \\
\text{or} \\
E_v(\Delta_H) &= E_v(\infty) + [E_v(\infty) - E_v(0)]\Delta_H
\end{align*}
\]

(2-17)

where the intrinsic quantities, including \(E_v(0)\) and \(E_v(\infty)\) changes with chemical reaction and bond relaxation. The perturbation \((\Delta_H)\) is described as follows:

\[
\Delta_H = \begin{cases} 
\Delta_H(z) &= (E_z - E_b)/(E_b) = C^{-m} - 1 & \text{(Site of Surface and Defect)} \\
\Delta_H(K, \tau) &= \tau K^{-1} \sum_{i=3} E_i \Delta_H(z) & \text{(Shell Resolved in Shaped Nanosolid)}
\end{cases}
\]

(2-18)

where \(\Delta_H\) is the contribution from the interlayer bond contraction of up to three atomic layers for defects and surfaces and \(i\) counts from the outermost shell inwards up to three.

The CLS and its bulk shift, \(\Delta E_v(\infty) = E_v(\infty) - E_v(0)\) is derived using the BOLS correlation and XPS technique, as listed in Table 2-2. \(E_v(0)\) is the core level position of an isolated atom, \(\Delta E_v(K)\) is the atomic under-coordination induced CLS, \(E_v(K)\) is the XPS peak of the \(v\)th band, and \(E_v(\infty)\) is the bulk counterpart. Hence, \(E_v(0)\) and \(\Delta E_v(\infty)\) can be determined from the XPS spectra measurements. The size-induced binding energy shift of nanostructures is inversely proportional to its size \(K\) in the form of \(E_v(K) = A + BK^{-1}\), where constants \(A\) and \(B\) can be extracted from the measured \(E_v(K)\) versus size using the least-root-mean-square linearization method. By making the experimental scaling
correlation equal to the theoretical illustration, the following expression is obtained from Eq. (2-17):

\[ E_v(K) = \begin{cases} 
E_v(\infty) + [E_v(\infty) - E_v(0)]\tau\Delta_H K^{-1} & \text{(BOLS theory)} \\
A + BK^{-1} & \text{(Measurement)}
\end{cases} \]

(2-19)

By making the theoretical formulation equal to the experimental measurements, the following expression is obtained:

\[ \begin{align*}
A &= E_v(\infty) \\
B &= [E_v(\infty) - E_v(0)]\tau\Delta_H
\end{align*} \]

(2-20)

Therefore, the \( v \)th energy level of an isolated atom and its bulk shift can be expressed by

\[ \begin{align*}
E_v(0) &= A - \frac{B}{\tau\Delta_H} & \text{(Atomic energy level)} \\
\Delta E_v(\infty) &= \frac{B}{\tau\Delta_H} & \text{(Bulk shift)}
\end{align*} \]

(2-21)

Hence, BOLS-TB describes the reference and physical origins, the direction, and the correlation between the core level components for under-coordination systems.
Chapter 2: Computational Approaches

Table 2-2 XPS and BOLS derived energy level of an isolated atom and its bulk shift.

<table>
<thead>
<tr>
<th></th>
<th>eV</th>
<th>Au-4f$^{24}$</th>
<th>Ag-3d$^{49}$</th>
<th>Cu-2p$^{24}$</th>
<th>Cu-3d$^{24}$</th>
<th>Rh-3d$^{60}$</th>
<th>Pt-4f$^{39}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_\nu(0)$</td>
<td>81.15</td>
<td>363.03</td>
<td>931.00</td>
<td>5.11</td>
<td>302.16</td>
<td>67.21</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_\nu(\infty)$</td>
<td>2.87</td>
<td>4.63</td>
<td>1.70</td>
<td>2.12</td>
<td>4.37</td>
<td>3.28</td>
<td></td>
</tr>
</tbody>
</table>

2.3 DFT Calculations

DFT is a computational quantum mechanical simulation based on the electron density utilized in chemistry, physics, and materials science to study the electronic structures of many-body systems, particularly atoms, molecules, and condensed phases.

2.3.1 Problem of Many-body System

Prediction and understanding of material properties without experimental results is the fascinating aim of theoretical calculations. The many-body system consists of $N$ electrons and $M$ nuclei that provide all information pertaining to the system using the Schrödinger equation, with the following time-independent form:

$$\hat{H}\Psi(r,R) = E\Psi(r,R)$$

(2-22)

The many-body Hamiltonian is denoted as $\hat{H}$, which provides the total energy, $E$, by applying the many-body wave function $\Psi(r,R)$. The wave function relies on the electron coordination $r$ and nuclear position $R$. The Hamiltonian describes, in atomic units, the kinetic energy operators of electron ($T_e$) and nuclei ($T_n$), and the potential
operators, including electron-electron interaction \( (V_{e-e}) \), nuclei repulsive \( (V_{n-n}) \), and electron-nuclei interaction \( (V_{e-n}) \) in the following form:

\[
\hat{H} = \hat{T} + \hat{V} = \hat{T}_e + \hat{T}_n + \hat{V}_{e-e} + \hat{V}_{n-n} + \hat{V}_{e-n}
\]

\[
\hat{H} = \frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \frac{1}{2} \sum_{j=1}^{M} m_j \nabla_j^2 + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_i - r_j} + \sum_{i=1}^{M} \sum_{j=1}^{M} \frac{Z_i Z_j}{|R_i - R_j|} - \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{r_i - R_j}
\]

(2-23)

where the nuclei mass and charge are \( m_j \) and \( Z_j \), respectively.

Solving Eq. (2-22) is complicated because of the large number of variables in the many-body system with \( 3N + 3M \) degree-of-freedom. The first approximation was proposed by Born-Oppenheimer approximation. Assuming that the electron and nuclei have different masses, then the electrons move faster than the nuclei. If the nuclei are motionless, the kinetic energy is zero, and the nuclei-nuclei repulsion remains constant.\(^{52}\) The Hamiltonian and electronic Schrödinger with electronic wave function, \( \Psi_e(r) \), can be rewritten as follows:

\[
\hat{H}_e \Psi_e(r) = E_e \Psi_e(r)
\]

\[
\hat{H}_e = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-n} = \frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_i - r_j} - \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{r_i - R_j}
\]

(2-24)

The degree-of-freedom is reduced to \( 3N \), but remains unsolvable for this many-body Hamiltonian. Hartree and Fock\(^{53,54}\) achieved the first numerical model for this Hamiltonian equation based on the wave function to determine the total energy.
Moreover, some advanced approaches has been reported based on the wave function, including the Møller Plesset perturbation theory,\textsuperscript{55} coupled cluster methods,\textsuperscript{56} and multi self-consistent field methods.\textsuperscript{57} Furthermore, DFT calculations utilize the electron density instead of the wave function, rendering it a suitable quantum mechanical model capable of solving many-body problems.\textsuperscript{58-60}

\subsection*{2.3.2 Thomas-Fermi Model}

Electron density \((n)\) is defined by electron numbers \(N\) with spatial coordinates \((r_i)\) as follows:

\[
\begin{align*}
n(r) & = N\int dr_2\ldots dr_N \Psi^\ast(r_1, r_2, \ldots, r_N) \Psi(r_1, r_2, \ldots, r_N) \\
\int n(r) \, dr & = N
\end{align*}
\]

(2-25)

In this model, the total energy is a function of the electron density, the degree of freedom reduced to 3, and the fact that the molecules calculated with this model for many-body systems is unstable. The minimum energy of the ground states is obtained; however, the solution is not suitable for the many-body system because of the exchange and correlation energy being neglected. In 1930, Dirac\textsuperscript{61} added the exchange-correlation energy, but did not take it into account in their calculation.
2.3.3 Hohenberg-Kohn Theory

According to the two theorems proposed by Hohenberg and Kohn,\textsuperscript{62} DFT is the established and observed ground state energy ($E_0$) as a function of density ($n_0$) instead of the complex wave function

$$E_0 = E[n_0] = T_e[n_0] + E_{e-e}[n_0] + E_{e-n}[n_0] = E_{e-n}[n_0] + F_{HK}[n_0]$$

(2-26)

This equation is called the Hohenberg-Kohn functional $F_{HK}[n]$, where $E_{e-e}[n]$ is considered as a sum of the Hartree energy $E_{HH}[n]$, consisting of the self-interaction correction and exchange-correlation in the following form:

$$E_{HH}[n] = \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} drdr'$$

(2-27)

Taking into account all external potentials and the ground state density is the first Hohenberg-Kohn hypothesis. The second Hohenberg-Kohn hypothesis is that the minimum energy for the ground state density comes from an external potential. The $F_{HK}[n]$ is unknown, and is thus approximated, which makes it a problem.

2.3.4 Kohn-Sham Theory

DFT underwent an evolution from theory to tool, and Kohn and Sham were the ones responsible for this evolution.\textsuperscript{63} This approach uses the kinetic energy ($T_S$) of non-
interacting electrons instead of the unknown energy density functional $T_e[n]$ in the following manner:

$$ T_s = -\frac{1}{2} \sum_i \phi_i^*(r) \nabla_i^2 \phi_i(r) $$

(2-28)

The single particle Kohn-Sham orbitals ($\phi_i$) reproduce the full density of the many-body in a self-consistent Kohn-Sham operator $f_{KS}$ as follows:

$$ \begin{cases} f_{KS} \phi_i(r) = \varepsilon_i \phi_i(r) \\ f_{KS} = -\frac{1}{2} \nabla^2 + V_{ex}[n] + V_H[n] + V_{XC}[n] \end{cases} $$

(2-29)

where the external potential, the classic Hartree potential, and exchange-correlation potential is $V_{ex}[n]$, $V_H[n]$, and $V_{XC}[n]$, respectively. The eigenvalues ($\varepsilon_i$) are the Lagrange multipliers. The density constructed from the HK orbitals and their occupation numbers $f_i$ is same as the density of interacting systems represented as follows:

$$ n(r) = \sum_{i=1}^{N} \phi_i^*(r) \cdot \phi_i(r) \cdot f_i $$

(2-30)

The true kinetic energy is added to the electron-electron interaction in the exchange-correlation functional $E_{XC}[n]$. $E_{XC}[n]$ is related to the $V_{XC}[n]$ in Eq. (2-24), which is associated with density.
Chapter 2: Computational Approaches

\[ V_{xc}[n(r)] = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \]

(2-31)

Consequently, the Kohn-Sham equation is explained by the single-particle Schrödinger of non-interacting electrons and the effect of many-body included in \( E_{xc}[n] \).

\[ F_{HK} = T_s + E_H + E_{xc} \]

(2-32)

To solve the Kohn-Sham equation, the exchange-correlation function, which allows for the calculating of the state density and energy, must be obtained.

2.3.5 Exchange-Correlation Functional

\( E_{xc}[n] \) can be explained by homogenous electron gas in uniform electron distribution, which is dependent on the local density value, called the local-density approximation (LDA), assuming that \( E_{xc}[n] \) is at the position \( r \):

\[ E_{xc}^{LDA}[n] = \int n(r) \varepsilon_{xc}(n(r)) \, dr \]

(2-33)

where the exchange-correlation energy per particle of the homogenous electron gas is \( \varepsilon_{xc}[n(r)] \). The exchange part can be obtained analytically as follows:

\[ E_{x}^{LDA}[n] = \left(-\frac{3}{4}\right)\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int n(r)^{\frac{4}{3}} \, dr \]

(2-34)
Chapter 2: Computational Approaches

The correlation part is calculated by the Monte Carlo modeling and DFT calculations with LDA functions, such as Vosko-Wilk-Nusair and Perdew-Wang (PWC). The exchange-correlation function is only known in homogenous electron gas, which is a significant LDA approach. LDA functions agree with Hartree-Fock for many-body systems. The LDA function in exchange-correlation energy proved the validity of the results for metallic and semiconducting materials because of the slow changes in their densities. The PWC function has been utilized in this study to determine the bond length, charge transfer, valence band polarization, and magnetic behaviors.

2.3.6 Spin-DFT

Many systems that include even and odd electron numbers must behave as radicals because two electrons occupy a double-degenerate orbital. DFT calculations report reasonable results for closed-shell systems; however, similar calculations need to be developed for open-shell systems. Therefore, the new approximation is regarded as spin-density, including \( n^\uparrow \) and \( n^\downarrow \) in place of total density \( n \), which is called the spin-density-functional theory. According to the restricted and unrestricted Hartree-Fock calculations, the restricted and unrestricted Kohn-sham models can be defined based on similar or different spatial orbitals for both spin orientations, respectively, indicative of the non-spin-polarized and spin-polarized DFT. The spin-polarized LDA is called the local-spin-density approximation (LDSA), and the exchange-correlation functional is presented as follows:
DFT calculation is a method that can calculate multiple structures at reasonable accuracy and efficiency. Choosing the exchange-correlation function is vital to the success of the calculations.

2.4 Summary

In this study, we have addressed the notation of the BOLS-NEP theory, which verified the surface and nanosolid electronic properties. This theory focuses on the imperfection of the coordinated atoms and its results on the Hamiltonian at the surface shell. The BOLS-TB premise unified the core-level physical shift induced by surface relaxation and the formation of nanosolid into the same origin of the atomic CN imperfection, which allows the predicted size dependence of CLS to match the observations and enables the conventional XPS to provide comprehensive information about the behavior of electrons in the deeper shells of an isolated atom and the influence of crystal formation. Moreover, DFT calculations can be used for a nanocluster system with the exchange-correlation function to understand the nanocluster properties, such as bond length and charge densification. The understanding of the physical and chemical properties of nanoscale materials is made simpler with these theories.
Chapter 3  Principles

3.1  BOLS in Nanostructures

The gap between the traditional theory and quantum mechanics on behaviors of under-coordinated systems could be filled by BOLS correlation. The BOLS-NEP correlation theory with DFT and TB calculations are used in the metallic nanostructures. The properties of the nanomaterials differ from their bulk component, which needs to be taken into account in the calculations.

Nanostructure materials are classified based on structural dimensions, including zero-dimensional (nanoparticles, nanoclusters, quantum dots, and nanocrystals), one-dimensional (nanotubes, nanofibers, nanoribbons, and nanowires), two-dimensional (nanofilms and graphenes), and three-dimensional (polycrystals) nanomaterials. Electrons tend to localize at imperfect boundaries, such as edges, surfaces, and defects.

The numbers of electrons in the nanostructures are limited compared with those of the bulk materials. Therefore, the effect of electron interaction is average because of the electrons interaction around an electron does not resemble a “sea” of electrons. The electron-electron repulsion changes the electronic structures that cannot be ignored in a nanoscale system, mitigating a change from conductor to insulator.

Based on the unique properties of the nanostructures, the BOLS-NEP correlation theory with DFT calculations and DMol³ code are incorporated into the nanoscale systems in this study.
3.2 DFT in DMol³

3.2.1 Introduction

DFT can be used in many fields and large applications based on the theoretical principle, in which there are two main of implementation, either using plane waves or localized basis functions, as a basis set. For example, DMol³, in the form of DFT quantum mechanical code, can be used to accurately simulate the gas phase, a solvent, on the surfaces, and in solid systems through localized numerical orbitals. The DMol code is an abbreviation of “density functional calculations on molecules” that calculate on atoms, molecules, and clusters in non-periodic systems. In 2000, this code has been expanded for periodic systems, and its name has been changed to DMol³.

The localized basis set in all density functional codes is considered as the molecular orbitals \( \phi_i(\mathbf{r}) \), which are linear combinations of the basis function \( \chi_j(\mathbf{r}) \) for molecules, clusters, zeolites, and polymers:

\[
\begin{align*}
\phi_i(\mathbf{r}) &= \sum_{j=1}^{N} c_{ij} \chi_j(\mathbf{r}) \\
\chi_j(\mathbf{r}) &= \sum_{lm} R_{lj}(r) Y_{lm}(\vartheta, \varphi)
\end{align*}
\]

(3-1)

The expansion coefficients \( (c_{ij}) \) of these Kohn-Sham orbitals require optimization. DFT codes are based on Eq. (3-1) with different basic functions \( \chi(\mathbf{r}) \), including Gaussians, Slater, and numerical atomic orbitals in the following form:
Chapter 3: Principles

The basic functions $\chi(r)$ are taken numerically more than analytically, similar to the Gaussian type orbitals. The angular portion of each function is a function of spherical harmonic $Y_{lm}(\theta, \phi)$, while the radial portion $R_l(r)$ is realized by solving the atomic DFT equations numerically from the nucleus to an outer distance of 10 Bohrs ($\approx 5.3$ Å). The Gaussian type orbitals are practically used for Hartree-Fock, and the matrix elements for analytically evaluation, slater type orbitals numerical integration, and basis set are arbitrary. The DMol$^3$ shows a small basis set superposition error generation because of the quality of these orbitals. The basis set superposition effects$^{70}$ are minimized, and an excellent description can be obtained even for weak bonds.

### 3.2.1 Atomic Orbitals Basis Set

The use of localized atomic orbitals as basis function in DMol$^3$ has some advantages compared with the other basis sets. For instance, (1) some observed properties, such as a cusp at the nucleus, square integrality, and exponential decay, for large distance from the nucleus; (2) individual atoms consider their own atomic orbitals as basis function to minimize basis set error such as Gaussian functions$^{56}$ and (3) all kinds of components in periodic and non-periodic systems can be applied in this basis function.
Moreover, the basis set in DMol³ includes minimal (MIN), double numeric (DN), double numeric plus d-functions (DND), and double numeric plus polarization (DNP).\textsuperscript{70} The MIN basis set considers all occupied orbitals in the ground state of the free atoms, calculate the neutral atoms, and provide the results with less accuracy, whereas DN uses the ionic basis functions for the valence electrons in quantum chemistry. Meanwhile, the basis function can be developed by adding a high angular momentum, such as polarization function with high accuracy, which considers both DND and DNP as basis sets.

Unlike molecules orbitals, atomic orbitals are not orthonormal, which leads to DFT Eq. (2-26) being rewritten in the following form:

$$HC = \varepsilon SC$$

(3-3)

where \(C\) are the normalized linear coefficients, and the Hamiltonian and overlap matrix elements are calculated as follows:

$$H_{j\nu} = \left\langle \chi_j (\mathbf{r}_i) \left| -\frac{\nabla^2}{2} + V_{\text{el}} + V_{\text{hh}} + V_{\text{xc}}[n(\mathbf{r}_i)] \right| \chi_{\nu} (\mathbf{r}_i) \right\rangle$$

$$S_{j\nu} = \left\langle \chi_j (\mathbf{r}_i) \left| \psi_{\nu} (\mathbf{r}_i) \right\rangle$$

(3-4)

Therefore, the use of atomic orbitals as basic functions presents several advantages, such as (I) decreasing number of basis functions compared with other basis sets at
similar accuracy, (II) minimizing of basis set superposition errors, and (III) use of similar kind of basis functions for molecules and solids.

### 3.2.2 Numerical Integration

The atomic orbitals must be calculated by numerical treatments. The integrals in Eq. (3-5) are calculated by 3D numerical integration method, and the matrix elements are required to be approximated by finite sums as follows:

\[
\begin{align*}
H_{ij} &\approx \sum_i \chi_j(r_i)H_{ij}(r_i)\chi_i(r_i)w(r_i) \\
S_{ij} &\approx \sum_i \chi_j(r_i)\chi_i(r_i)w(r_i)
\end{align*}
\]

(3-5)

The sums considered on several numerical integration points are \( r_i \). The \( H_{\text{eff}}(r_i) \) and \( w(r_i) \) indicate the value of the integral of Eq. (3-5) at point \( r_i \) and a weight associated with each mesh point. The numerical integral is improved by increasing the number of mesh points and computational costs.

In this research, DNP as basis set was used to ensure the accuracy of the electronic properties and the core states that can be obtained by semi-core pseudopotential.\(^{74}\) The pseudopotential force accounts for the relativistic effect to explain the scale wave function within a nonrelativistic system. Furthermore, the PWC\(^{66}\) parameterization of the local exchange-correlation energy was applied to LSDA to describe the exchanges and the correlations (see Chapter 2 Section 2.3). Our calculation used the direct inversion of the iterative subspace method (DIIS) to accelerate the convergence of the
self-consistent field (SCF) procedures. In this study, we combined the DFT calculations using the DMol³ code and BOLS correlation theory to calculate the electronic properties such as bond length, charge transfer, quantum entrapment, valence electron polarization, and magnetic behavior in nanoclusters, consistent with other experimental observations (see Chapters 4, 5, and 6).

3.3 Application of BOLS in DFT

The BOLS correlation is a simulation theory that simulates the electronic structures of nanomaterials and predicts the nanomaterial behaviors in numerous applications.

3.3.1 DOS

A simple method of demonstrating the molecular orbitals is by plotting the DOS. For molecule systems, the molecular orbitals are functions of the molecular orbital eigenvalues. The DOS for n energy band, \( G(E) \), is achieved after calculating the energy bands, and given by:

\[
G(E) = \sum_n \delta(E - \varepsilon_n)
\]

where \( \varepsilon_n \) explains the distribution of the given band. The number of states falls between \( E \) and \( E + dE \).

For metallic systems, the simplest numerical technique to evaluate DOS involves histogram sampling based on Gaussian and Lorentzian broadening, which agrees with
Chapter 3: Principles

the experimental data, such as XPS and UPS. The energy levels of each band are as follows:

\[
G(E) = \begin{cases} 
\sum_{n=1}^{N} \exp \left(-\frac{E - \varepsilon_n}{\sigma}\right) & \text{(Gaussian)} \\
\sum_{n=1}^{N} \exp \left(-\frac{\alpha}{(\varepsilon_n - E)^2 + \sigma^2}\right) & \text{(Lorentzian)}
\end{cases}
\]

(3-7)

The sigma parameter displays the peak width and the changed value to represent the experimental data. The linear interpolation is an accurate method used in DMOl³, followed by histogram sampling of the resultant set of band energies.\(^7\)

3.3.2 Local and Partial DOS

The electronic properties in nanostructures are analyzed by local DOSs (LDOS) and partial DOSs (PDOS), which are the physical quantities that explain DOS, and can be achieved by computational modeling, such as DFT. According to the atomic orbitals, LDOS and PDOS can be defined as follows:

\[
\begin{align*}
G_j(E) &= \sum_{n} \langle \phi_n | i \rangle \langle i | \phi_n \rangle \delta(E - \varepsilon_n) \quad \text{(LDOS)} \\
G_j^\sigma(E) &= \sum_{n} \langle \phi_j^\sigma | \phi_n \rangle^2 \delta(E - \varepsilon_n) \quad \text{(PDOS)}
\end{align*}
\]

(3-8)

LDOS is interpreted by STM/S data, which is capable of imaging electron DOS with atomic resolution. For unrestricted Kohn-Sham models or spin-polarized system, DOS
Chapter 3: Principles

can be separated for electrons with spin-up (α) and spin-down (β). Their sum produces
the total DOS, and their difference are indicated as spin DOS. The contribution of atoms
in the electronic and the angular momentum states are shown by LDOS and PDOS,
respectively.

3.3.3 Chemical and Physical Properties

The chemical and physical properties of the nanomaterials can be predicted using the
BOLS-NEP correlation theory and DFT calculations in Chapter 2. The valence electron
polarization, quantum entrapment, magnetic, catalytic, and electronic structures of
metallic nanoclusters are consequential for their chemical and physical properties,
which will be elucidated in the following chapters.

3.4 Summary

Quantum calculations are crucial to chemists in their quest of elucidating chemical
bonds. Numerous analytical tools have developed within this context, such as Mulliken
population analysis, Mayer bond order analysis, and natural bond orbital analysis, which
aim to understand bonding analysis through electronic calculation findings. According
to these analytical tools, information on atomic charges, bond order, bonding types, and
other familiar valence explanations can be obtained.

BOLS-NEP correlation is advantageous in the design of nanomaterials and under-
coordinated systems. BOLS correlation theory emphasizes the bond length, energy,
elastic, electronic, optic, dielectric, and other properties of under-coordinated system
(Section 2.1). According to this theory, as the size of nanoparticles decrease, the shorter and stronger bonds between atomic under-coordination result in local densification and quantum entrapment of binding energy and core electrons, which in turn polarize the otherwise conductive charges and make the nanocrystals nonconductive and magnetic. Moreover, this theory can predict the physical and chemical properties of nanostructures, including the valence band of metals, induced by the enhancement of Hamiltonian integrals and the localized electron-electron repulsions.
Chapter 4  Quantum Entrapment and Valence Polarization of Ag and Cu Nanoclusters

4.1  Overview of Ag and Cu Nanoclusters

Ag and Cu nanoparticles have attracted a great deal of attention within the experimental and theoretical research community because of their interesting chemical and physical properties. However, these properties are absent in bulk counterparts$^{31}$ because the surface-to-volume ratio of the layers to the whole body of the nanoparticles increasing significantly when their sizes decrease. The interaction between the atomic under-coordination at the skin adjusts the electronic structure, and can differentiate between the performance of the nanoparticles and the bulk components. For instance, silver and copper nanoparticles demonstrate magnetic responses at diameters of 2-3 nm,$^{77}$ while their bulk components are diamagnetic. Ag nanoclusters are converted from conductors to insulators$^{31}$ because of the localized polarization of the non-bonding $s$-electrons. The decrease in size of both silver and copper nanoparticles increases the catalytic reaction in methanol synthesis,$^{78}$ H$_2$O oxidation, and CO reductions,$^{79, 80}$ as well as surface plasmon resonance.$^{81}$ These conversion mechanisms have become the hotspot of much attention and current research. Accompanied by the structure evolution from the FCC bulk structure to strained structures, such as icosahedral or decahedral,$^{82, 83}$ substantial bond contraction happens to the outermost few atomic shells, which can be explained as an elastic cover sheet of the “skin”.$^{3, 45}$
Aside from bond contraction, the charge and energy densification, as well as the enhancement of electronic binding energy of nanoparticles, differ from their respective bulk counterparts. For instance, the binding energies of the core levels of Ag-3d, Cu-1s, and Cu-2p shift to a higher binding energy when the particle size of Ag and Cu are reduced to nanometers, as shown by XPS. However, STM/S reveals a red shift of the valence LDOS in Cu monatomic chains on the Cu substrate and Ag nanoclusters and chains on the Ag(111) substrate, similar to that of the Au-Au atomic chains. Furthermore, the valence band polarization of Ag and Cu nanoclusters was detected by ultraviolet photoelectron spectra (UPS) measurements. A methodical investigation of the exotic changes induced by the effects of the under-coordination of Ag and Cu nanoparticles is rather attractive.

Despite possible mechanisms, such as s-d hybridization of Cu, s-p hybridization of Ag, and giant photon resonance, a predictable understanding of the size dependence of CLS, lattice contraction, and surface state creation of Ag and Cu nanoparticles remains quite challenging.

4.2 Computational Methods

4.2.1 COh and M-Dh structures

We used DFT calculations on Ag and Cu nanoclusters to confirm the BOLS predictions on the core level entrapment and the valence band polarization associated with under-
coordinated atoms. The metallic nanoparticle structures are distorted into icosahedral\textsuperscript{93} or decahedral\textsuperscript{94} with decrease in nanoparticle size.

Numerous theoretical and experimental efforts have been devoted to investigate the structures of Ag and Cu nanoclusters.\textsuperscript{93, 95-102} The M-Dh structures for Cu and Ag nanoclusters have been experimentally confirmed.\textsuperscript{99,97} Meanwhile, FCC-like COh structures are stable forms of Ag and Cu nanoparticles.\textsuperscript{96,98} Taking into account the fact that our primary purpose is to investigate the under-coordinated effect, selection of particular structures is immaterial to the conclusion. Therefore, we selected stable structures of silver and copper nanoclusters with COh (13, 55, and 147 atoms) and M-Dh structures (13, 49, and 75 atoms), as shown in Figure 4-1.

![Figure 4-1 Schematic of metallic nanoclusters with (a-c) COh and (d-f) M-Dh structures.](image)

The number indicates the atom position in our calculation.
4.2.2 DFT Calculations

DFT calculations were performed using the DMol³ code with a DNP basis set. During the DFT calculations, the potentials of the core electrons were assumed to be semi-core pseudopotential. The DFT exchange-correlation potential utilized the LSDA, with the PWC function for geometry and electronic structures. The spin states was calculated using Mulliken population analysis and the doublet state for Ag and Cu nanocluster with spin-unrestricted were considered in our calculation, which for spin-unrestricted wave-functions, different orbitals are used for different spins. The self-consistency threshold of the total energy was set at $10^{-6}$ Hartree. The tolerance energy, forces, and displacement in the geometry optimization were taken at $10^{-5}$ Hartree, 0.002 Hartree/Å, and 0.005 Å, respectively. The displacement specifies the maximum allowed step size during geometry optimization to minima or transition states. Moreover, PDOS and LDOS are used to analyze electronic structure. LDOS shows which atoms in the system contribute electronic states to various parts of the energy spectrum. PDOS further qualifies these results by resolving the contributions according to the angular momentum of the states.

4.3 Discussions

4.3.1 Local Bond Length Contraction

The current DFT calculations confirm the spontaneous bond contraction at the surface of Ag and Cu nanoclusters. The atomic CN affect the extent of bond contraction,
disregarding the sizes and structures used in the calculations. As listed in Table 4-1, the calculated Cu-Cu distance are 2.415, 2.341, 2.346, 2.517, 2.457, and 2.412 Å at the skin Cu atoms for COh13, COh55, COh147, M-Dh13, M-Dh49, and M-Dh75, respectively (see Eq. (2-1) and Eq. (2-2)), displaying significant decrease with respect to the bulk value of 2.556 Å. The calculated Ag-Ag distance is observed a similar trend. The calculated bond contraction coefficient falls within 0.7-0.9, which is in excellent agreement with Bahn et al. for Ag and Cu nanoclusters.

By combining the BOLS correlation with DFT calculations, the results are in good agreement with the previously reported results. For example, DFT and MD calculations revealed similar trends for dimer bonds of Ag and Cu metals by 15%, as well as Ag, Cu, Ni, Fe atomic chains by 12.5%, 13.2%, 13.6%, and 18.6%, respectively. Montano et al. pointed out that up to 13% bond contraction in small Cu nanoclusters are embedded in solid argon by X-ray-absorption fine structure spectroscopy (EXAFS), i.e., the Cu-Cu bond length contracts to 2.230 and 2.540 Å and 12.5% bond contraction of Ag dimers in small Ag nanoclusters. Apai et al. and Montano et al. also reported the size trend for Cu and Ni nanoclusters formed by vapor deposition, as well as Ag clusters formed in isolated in solid argon by EXAFS, i.e., the Ag-Ag bond shrinks to 2.470 (dimer), 2.49 (trimer), and 2.54 Å (quadrumer). The Ag and Cu dimer bond lengths contact spontaneously from their bulk value to 2.530 Å and 2.220 Å, respectively.
Table 4-1 Effective CN ($z_i$), Ag-Ag and Cu-Cu bond length ($d_i$), shell index ($i$), magnetic moment ($\mu$), and charge transfer ($e$) for silver and copper nanoclusters.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Position</th>
<th>$z_i$</th>
<th>$d_i$ (Å)</th>
<th>Shell</th>
<th>Magnetic moment ($\mu$)</th>
<th>Charge Transfer ($e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>atom</td>
<td>Ag</td>
<td>Cu</td>
<td>Ag</td>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>COh$_{13}$</td>
<td>1~2</td>
<td>2.00</td>
<td>2.778</td>
<td>2.415</td>
<td>1.0972</td>
<td>0.936</td>
</tr>
<tr>
<td>COh$_{55}$</td>
<td>1~2</td>
<td>2.80</td>
<td>2.703</td>
<td>2.341</td>
<td>0.883</td>
<td>0.852</td>
</tr>
<tr>
<td></td>
<td>2~3</td>
<td>4.80</td>
<td>2.824</td>
<td>2.470</td>
<td>0.108</td>
<td>0.144</td>
</tr>
<tr>
<td>COh$_{147}$</td>
<td>1~2</td>
<td>3.14</td>
<td>2.713</td>
<td>2.346</td>
<td>0.724</td>
<td>0.721</td>
</tr>
<tr>
<td></td>
<td>2~3</td>
<td>5.14</td>
<td>2.809</td>
<td>2.458</td>
<td>0.207</td>
<td>0.208</td>
</tr>
<tr>
<td></td>
<td>3~4</td>
<td>12.00</td>
<td>2.831</td>
<td>2.469</td>
<td>0.062</td>
<td>0.066</td>
</tr>
<tr>
<td>M-Dh$_{13}$</td>
<td>2~3</td>
<td>-</td>
<td>2.750</td>
<td>2.388</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1~3</td>
<td>2.43</td>
<td>2.902</td>
<td>2.517</td>
<td>0.974</td>
<td>0.947</td>
</tr>
<tr>
<td>M-Dh$_{49}$</td>
<td>2~4</td>
<td>-</td>
<td>2.773</td>
<td>2.420</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1~3</td>
<td>2.86</td>
<td>2.812</td>
<td>2.457</td>
<td>0.870</td>
<td>0.872</td>
</tr>
<tr>
<td>M-Dh$_{75}$</td>
<td>2~4</td>
<td>-</td>
<td>2.757</td>
<td>2.396</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1~3</td>
<td>3.10</td>
<td>2.778</td>
<td>2.412</td>
<td>0.860</td>
<td>0.835</td>
</tr>
<tr>
<td></td>
<td>4~5</td>
<td>-</td>
<td>2.818</td>
<td>2.456</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3~5</td>
<td>5.10</td>
<td>2.843</td>
<td>2.484</td>
<td>0.137</td>
<td>0.152</td>
</tr>
</tbody>
</table>

In current DFT calculations, the bond lengths of the outermost atomic layers, with smaller curvature-dependent CN, shrunk more than those within the core (see Table 4-1). For example, the Cu-Cu bond length of Cu$_{147}$ nanoclusters decreased from 2.458 Å to 2.346 Å for the interior and the outermost atomic layer when the effective CN decreased from 12.00 to 3.14. A similar trend was observed for M-Dh$_{75}$, i.e., the Cu-Cu bond shrunk from 2.484 Å to 2.412 Å when the effective CN decreased from 5.10 to 3.10. For nanoclusters with different sizes, the bond length varied in a similar tendency,
except for atoms with a comparable CN. The DFT underestimated the bond contraction, as predicted by BOLS notation approaching the measurements.\textsuperscript{3, 4}

### 4.3.2 Charge Transfer and Magnetic Moment

Based on the principal of least energy, any spontaneous process leads to energy reduction. Therefore, the spontaneous process of bond contraction is associated with the inter-atomic trapping potential well depression or the bond energy gain. Given the potential well entrapment, the valence charges prefer to flow from the interior layer to the outermost layer through polarization. Thus, the core level binding energy will go deeper, referred to as the “positive CLS”\textsuperscript{24} Consequently, the charge will be localized at the surface because of surface potential depression and core electron energy level deepening, which in turn polarize the loosely bound valence electrons.

The charge transfer of the Ag and Cu nanoclusters was estimated using the Mulliken population analysis,\textsuperscript{103} as listed in Table 4-1. The negative sign and positive sign represent the charge gain and charge loss, respectively. The outermost atomic layer gains excessive charges, whereas the interior layer experiences losses. For example, the COh\textsubscript{55} structure of Cu turns from -1.240 $e$ in the outermost atomic layer to 1.140 $e$ in the interior atomic layer. This phenomenon demonstrates that the electrons tend to flow from the inner to the outermost layer of the nanoclusters, in agreement with the previously reported results such as Au nanoclusters,\textsuperscript{112} Au(111) nanoclusters,\textsuperscript{113} Ag nanoclusters,\textsuperscript{114} and Cu-Ag clusters,\textsuperscript{115} which all obeyed the BOLS-NEP predictions. In
addition, the spin states of Ag and Cu nanoclusters was calculated, as listed in Table 4-1, and found that the spin states increased at the outermost shell compared with those at the interior shell. The localized spin states at the outermost shell of the nanoclusters are significantly reduced with increase in atomic CN, which is agreement with previously reported result by Jensen and Bennemann.116

4.3.3 CLS and Lattice Strain

The spectroscopy of Cu-1sK-edge,84 Cu-2p3/2,20 and Ag-3d5/219 showed consistency for the size-induced quantum entrapment. Table 4-2 lists the available observations using XPS and DFT calculations. Generally, the size-induced CLS of nanostructures is proportional to the nanosolid size, 1/K, in the form of, \( E_s(K) = A + BK^{-1} \), where \( A \) and \( B \) are constants and can be derived from the \( y \)-intercept and slope extracted by linearizing all the measured binding energy vs. nanosolid sizes with the least-root-mean-square optimization method. Figure 4-2 displays the BOLS reproduction (solid and chained curves) of the measured size dependence of the CLS (scattered data). The scattered data are XPS data from experimental results for Ag nanoparticles deposited on HOPG,19 CeO\(_2\),117 and Al\(_2\)O\(_3\)118 substrates, as well as, Cu nanoparticles deposited on HOPG/Ar\(^+\),21 CYCL/Ar\(^+\),21 Si,119 and Al\(_2\)O\(_3\)120 substrates. The intercepts may contain the effect of space charging or system error in the measurements, and thus can serve as a calibration to the measurements. The slopes are a major concern in the current decoding exercise.
because they depend on the surface treatment, particle size, and interaction between the particle and the substrate.\textsuperscript{90}

To elucidate the effect of size on the CLS of Ag and Cu nanoparticles, the dimensionality, $\tau$, and the bond nature indicator, $m$, were first calculated. The $E_{\nu}(0)$ and $\Delta E_{\nu}(\infty)$ of Cu-$2p_{3/2}$ can be achieved by calculating the Cu nanoparticles grown on highly ordered pyrolytic graphite (HOPG)/Ar$^+$ with $m = 1.0000$ using Eq. (2-17) and Eq. (2-18).\textsuperscript{21} The value of $m = 1.0000$, a value that holds for metallic solid,\textsuperscript{121} was chosen because Cu atoms barely react with carbon surfaces.\textsuperscript{122} The Cu-$2p_{3/2}$ binding energy shift for an isolated Cu atom and the bulk was 931.0 and 1.70 eV, respectively.\textsuperscript{90}

Table 4-2 $E_{\nu}(0)$ and $\Delta E_{\nu}(\infty)$ obtained from XPS $E_{\nu}(\infty)$ component and BOLS correlation for silver and copper nanoparticles.

<table>
<thead>
<tr>
<th></th>
<th>$A=E_{\nu}(\infty)$ (eV)</th>
<th>$B$ (eV)</th>
<th>$E_{\nu}(0)$ (eV)</th>
<th>$\Delta E_{\nu}(\infty)$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/HOPG</td>
<td>368.49</td>
<td>2.02</td>
<td>363.03</td>
<td>5.46</td>
</tr>
<tr>
<td>Ag/CeO$_2$</td>
<td>368.43</td>
<td>0.27</td>
<td>363.03</td>
<td>5.40</td>
</tr>
<tr>
<td>Ag/Al$_2$O$_3$</td>
<td>367.80</td>
<td>1.70</td>
<td>363.03</td>
<td>4.77</td>
</tr>
<tr>
<td>Cu/Si</td>
<td>932.50</td>
<td>3.99</td>
<td>931.00</td>
<td>1.50</td>
</tr>
<tr>
<td>Cu/Al$_2$O$_3$ (300K)</td>
<td>932.51</td>
<td>0.87</td>
<td>931.00</td>
<td>1.50</td>
</tr>
<tr>
<td>Cu/Al$_2$O$_3$ (80K)</td>
<td>932.67</td>
<td>0.39</td>
<td>931.00</td>
<td>1.67</td>
</tr>
<tr>
<td>Cu/HOPG/Ar$^+$</td>
<td>932.54</td>
<td>0.81</td>
<td>931.00</td>
<td>1.54</td>
</tr>
<tr>
<td>Cu/CYCL/Ar$^+$</td>
<td>932.53</td>
<td>1.32</td>
<td>931.00</td>
<td>1.53</td>
</tr>
</tbody>
</table>
Chapter 4: Quantum Entrapment and Valence Polarization of Ag and Cu Nanoclusters

According to Eq. (2-21), the $B$ and $E_v(\infty)$ values are achieved by linearizing the measured data of Ag and Cu binding energy with respect to $1/K$. Taking the obtained CLS value to the simulation iteration of the measured size-dependent $E_v(K)$ for Ag deposited on CeO$_2$ and HOPG substrates, $m = 1.0000$, similar to that of pure metals,$^4$ because of the lack of interaction between the Ag nanoclusters and the CeO$_2$ and HOPG substrates.$^{19,117}$ The bond nature of Ag was experimentally studied based on Ag on an Al$_2$O$_3$ substrate because of the interactions between the Ag nanoparticles and the substrate,$^{123}$ and we found that $m = 3.8200$. Similarly, the binding energy of an isolated Ag atom and its bulk shifts are 363.03 and 4.63 eV, respectively.$^{49}$

The Cu deposited on Dow Cyclotene 3022 (CYCL)/Ar$^+$ providing $m = 1.8175$ contributed to the interfacial reaction between Cu and the CYCL polymer substrate to $m = 1.0000$. However, $m$ may vary for different substrates; for instance, $m = 4.880^{119}$ for Cu on the Si surface, and $m = 1.9440^{120}$ at 300K, and $m = 1.2675^{124}$ at 80K for Cu on the Al$_2$O$_3$ substrate. Compared with their bulk counterparts, the experimentally observed positive CLS for Ag,$^{19}$ Au,$^{125}$ and Cu$^{21}$ nanoclusters indicated the intensification of the inter-atomic bonding between the under-coordinated atoms. Adjusting the $m$ values, our predications based on the BOLS correlation are in good agreement with the experimental observations.
Figure 4-2 BOLS reproduction (solid and chained curves) and the measurement-extracted of XPS data (scattered data) CLS of (a) Ag-3$d_{5/2}$ and (b) Cu-2$p_{3/2}$ deposited on different substrates.

The bonds between the neighboring atom experience lattice strain\textsuperscript{39} are caused by the influence of the initial state in XPS measurements. The mean lattice contracts instead of
expands in the bulk components. The lattice strains are plotted using Eq. (2-9) in Figure 4-3, based on the BOLS correlation (solid line) and the measured values of the mean lattice strain (scattered data). The experimental data were linearized with the least-root-mean-square optimization method to calculate the intercepts and slopes in the scaling law. Calculations were conducted for the experimental results of Ag(111) and Ag(220) surfaces\textsuperscript{126} and the Cu(111) and Cu(220) surfaces\textsuperscript{127}. The lattice strain is proportional to the nanoparticles size, which increases to larger percentage values with reduced $K$, indicating the effect of under-coordinated atoms on lattice strain.

Figure 4-3 Lattice stain of silver and copper nanoparticles shows consistency between theoretical prediction (solid line) and experimental data (scattered data).
4.3.4 Shell-resolved Valence Charge Polarization

According to the BOLS-NEP theory, the conductive $s$-electrons of Ag and Cu are expected to be polarized by the densely and tightly entrapped core charges. The magnitude of polarization increases as the electrons move from the inner to the edge with lower atomic CNs. This phenomenon has been observed for monatomic chains of gold, silver, and copper. Figure 4-4 shows the shell-resolved LDOS for the Ag and Cu nanoclusters with COh$_{147}$ and M-Dh$_{75}$ structures. The results exhibit that the valence electrons in the outermost shell shift towards $E_F$, while the entrapped electrons in the inner core remain at the lower edge. The maximum LDOS of the atoms at the outermost shell are polarized by the inner electrons. Therefore, the conducting electrons of the lower-coordinated atoms become localized and polarized at the nanometer scale.
Figure 4-4 Shell-resolved LDOS for (a-b) COh\textsubscript{147} and (c-d) M-Dh\textsubscript{75} for silver and copper nanoclusters. The electronic binding energy shifts upward E\textsubscript{f} in the outermost layers, while those of the interior layers resemble the bulk.

The LDOS for s, p, and d orbitals of Ag and Cu nanoclusters with COh\textsubscript{147} and M-Dh\textsubscript{75} structures (see Figure 4-5) revealed that this system is suitable for plasma resonance applications.\textsuperscript{88, 128, 129} The corresponding DOS in Figure 4-6 demonstrates that
the polarization is more important in the smaller nanoparticles. The DOS peak shifts from -2.06 eV for the Cu\textsubscript{147} nanocluster to -1.35 eV for the Cu\textsubscript{113} nanocluster in COh structures, as well as from -3.48 eV for the Ag\textsubscript{75} nanocluster to -3.18 eV for the Ag\textsubscript{13} nanocluster in M-Dh structures, indicate that the valence charge polarization is proportional to the inverse of the cluster size.

Moreover, the valence LDOS polarization was also confirmed, being consistent with experimental previous reports such as the STM observations of the Cu chains\textsuperscript{3}, Cu adatoms\textsuperscript{85} and Cu adatoms\textsuperscript{130} as well as Ag clusters and chains\textsuperscript{12}. STM/S observations of the Cu clusters\textsuperscript{15} exhibited the size-induced polarization with the LDOS at 3.2 eV (monomers), 2.6 eV (dimers), and 2.0 eV (trimers) through positive bias. The Ag clusters and chains on the Ag(111) substrate show a similar trend for the under-coordination-induced polarization\textsuperscript{12}. Ag adatoms on Ag(111) reveal that the unoccupied states of DOS are positioned at 3.0 (monomer), 2.7 (quasi-dimer), and 2.4 eV (dimer) through positive bias\textsuperscript{85}, indicating that the charge polarization depends on the CN of the system. The effect of strong polarization is more obvious in the monomer and quasi-dimer of the Ag adatoms than that in the dimer, because of one additional coordinated atom\textsuperscript{85}. Finally, the UPS spectra revealed that the Ag 4\textit{d} and the Cu 3\textit{d} bands expand and shift upwards because of polarization as the cluster size decreases\textsuperscript{86, 87, 131}. 

64
Figure 4-5 LDOS of the $s$, $p$, and $d$ orbitals are shown by gray, blue, and black solid lines, respectively for (a-b) COh$_{147}$ and (c-d) M-Dh$_{75}$ of the silver and copper nanoclusters. The arrows indicate the state of spins, whether up or down. The $E_f$ is assumed to be zero.
Figure 4-6 Size-resolved DOS of the (a, b) COh and the (c, d) M-Dh structures of the silver and copper nanoclusters, representing that the extent of polarization depends on the cluster size. This size-dependent polarization is agreement with the LDOS of the Au nanoclusters,\textsuperscript{112} the end of Cu atomic chains,\textsuperscript{15} and Ag.\textsuperscript{85}
4.4 Summary

Consistency in XPS measurements, STM/S observations, and DFT calculations confirmed our BOLS-NEP predictions on the atomic CN effect on local bond relaxation, and electron binding-energy shift of the Ag and Cu nanoclusters. Atomic undercoordination induced local bond contraction, local densification, and entrapment of core electrons, as well as valence charge polarization, resulting in unusual behavior of the Ag and Cu nanoclusters in terms of the size dependence of the known bulk properties and the emergence of properties that the parent bulk failed to show. The findings contribute to the understanding of the intrinsic properties, such as catalytic enhancement and surface plasmon response of the Ag and Cu nanoclusters.
Chapter 5 Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters

5.1 Background of Pt and Rh Nanoclusters

Pt and Rh metallic nanoparticles have attracted enormous interests because of their fascinating chemical and physical properties that cannot be observed in their bulk components. A significant difference between a nanosolid and its bulk counterpart is the high fraction of under-coordinated atoms in the surface consisting of a few atomic layers. The surface-to-volume ratio increases from 1% to 25% when the diameter of a spherical dot declines from 1 μm to 10 nm. The interaction between the under-coordinated atoms at the surface modifies the electronic structure and distinguishes the nanoparticles from their bulk counterparts in performance because of the bond contraction and bond energy elevation induced by atomic under-coordination. For instance, Rh nanoparticles show giant magnetic moments although the bulk Rh remains in the diamagnetism form. Similarly, Pt also transforms from non-magnetic to magnetic as the size is reduced from bulk to a few nanometres. The giant magnetic moments observed in these metallic nanoparticles make them potential candidates for nanospintronic applications and magnetic data storage. Furthermore, the catalytic ability of Au, Pt, Pd, and Rh nanoparticles is greatly enhanced and a phase transition from conductor to insulator occurs at the nanometre scale.
At the nanometre scale, the potential trap depth, charge density, energy density, and electronic configurations of the metallic nanoparticles differ from their bulk counterparts, accompanying the structural evolution from FCC to icosahedral\textsuperscript{135, 136} or decahedral,\textsuperscript{137, 138} as well as surface bond contraction. XPS measurements have revealed a positive CLS for Pt nanoclusters deposited onto pristine carbon nanotubes (CNTs)\textsuperscript{6, 22} and HOPG.\textsuperscript{23}

Moreover, the peaks of the valence LDOS of Ag nanoclusters,\textsuperscript{12} Rh nanoparticles,\textsuperscript{17} Au atomic chain,\textsuperscript{16} Au nanowires,\textsuperscript{139} Cu monatomic chain,\textsuperscript{15} and Pt nanoclusters\textsuperscript{18} all shifted to upper energies, as observed with STM/S. Although atoms that form nanoclusters, or those located at the edges or chain ends, demonstrate many fascinating properties, the related mechanisms remain unclear, which renders a thorough understanding of the under-coordination effects of Pt and Rh nanoclusters on their properties highly desirable.

### 5.2 Calculation Procedures

#### 5.2.1 COh and M-Dh structures

We conducted DFT calculations on Pt and Rh nanoclusters to verify the predications based on the BOLS correlation, such as quantum entrapment and the associated charge polarization. Numerous theoretical and experimental studies have been devoted to determine the structures of Pt and Rh nanoclusters.\textsuperscript{137, 140-143} Icosahedral\textsuperscript{135, 144} or
decahedral\textsuperscript{137,138} structures are stable structures of transitional metal nanoparticles, such as Pt and Rh nanoparticles. For example, M-Dh structures have been experimentally observed in Pt nanoparticles prepared by gas evaporation\textsuperscript{138} and Rh nanoparticles epitaxially deposited on NaCl(001).\textsuperscript{145} However, FCC-like COh structures are stable forms of Pt nanocrystals prepared by electrocatalytic hydrogenation\textsuperscript{141} and Rh nanocrystals grown on NaCl substrates.\textsuperscript{140} Previous DFT calculations also showed that the structures of multiple-twinned Pt\textsuperscript{146} and Rh\textsuperscript{147} clusters include COh. Hence, both COh structures (13, 55, and 147 atoms) and M-Dh structures (13, 49, and 57 atoms) have been adopted in our calculations (see Figure 4-1).

5.2.2 DFT Calculation

Details of the DFT calculations were mentioned in Chapter 4, Section 4.2.2. The singlet and triplet ground states for Pt nanoclusters and quartet ground state for Rh nanoclusters are considered to demonstrate the under-coordinated effects on the properties of nanoparticles. Thermal occupation was used instead of Fermi for open-shell system with unrestricted wave function to achieve SCF convergence. DMol\textsuperscript{3}, by default, finds the occupations that yield the lowest energy. This means that electrons occupy orbitals with the lowest orbital energies. The occupation numbers are integers. However, there may be a need to use a fractional occupancy, which effectively mixes some virtual orbitals into the occupied space. Therefore, in our calculation could achieve SCF convergence
by using smearing techniques, shifting up the virtual orbitals, or fixing (freezing) occupancy. In spin-unrestricted wave function, different orbitals are related to different spins, including spin-up ($\alpha$) and spin-down ($\beta$).

5.3 Discussions

5.3.1 Local Bond Length Contraction

The DFT calculation results are listed in Table 5-1 (see Eq. (2-1) and Eq. (2-2)). As expected, the spontaneous bond contraction at the surface of the Pt and Rh nanoclusters is observed, and the extent of bond contraction depends only on the atomic CN. For instance, the calculated Pt-Pt distance of the Pt nanoclusters in the outermost shell of COh is 2.663 and 2.685 Å for singlet and triplet states, respectively, which are significantly smaller than the bulk value of 2.770 Å. Similar trends are observed for other COh structures and multiple M-Dh structures. The results from the BOLS correlation and DFT calculations are in good agreement with the previous results. For instance, Sang et al. detailed through DFT calculations that Pt-Pt distance decreased to 2.400 and 2.580 Å for dimers and trimers, respectively. Up to 10%–15% and 13%, the bond contraction for the Pt dimer can also be determined through DFT and MD calculations, respectively.

The bond contraction of Pt clusters, Pt chains, and monoatomic chain was experimentally observed. For the Rh nanoclusters, the calculated bond length of the
outmost shell of COh\textsubscript{147} is about 2.685 Å, exhibiting a reduction compared with the bulk value of 2.690 Å.\textsuperscript{153} The observed trend of bond contraction at the surface is consistent with the previous report. For instance, bond contractions of up to 14\%,\textsuperscript{154} 4\%,\textsuperscript{153} and 4\%-8\%\textsuperscript{154} were observed by the local-spin-density-functional model and TB approximation for Rh dimer, Rh\textsubscript{13} clusters, and larger Rh clusters, respectively. Villaseñor-González et al.\textsuperscript{155} and Barreteau et al.\textsuperscript{156} also reported about 2 to 9\% bond contraction for Rh clusters and 3\%-5\% bond contraction for Rh clusters with 13, 55, 147, 309, and 561 atoms based on the TB approximation.

The bond lengths of the outermost shells, with smaller curvature-dependent CN, shrunk at a rate higher than the interior (see Table 5-1). For instance, for the singlet states of the Pt COh\textsubscript{147} nanoclusters, the calculated Pt-Pt distance decreases from 2.763 Å to 2.663 Å in the direction from the interior toward the outermost shells as the effective CN decreases from 12.00 to 3.14. For nanoclusters with different sizes, the bond length showed various similarities, except for atoms with comparable CN. The DFT calculations tend to underestimate the bond contraction compared with the expectation based on the BOLS correlation. However, the origin for this quantitative deviation remains unclear and requires systematic study.
Table 5-1 Effective CN \( (z_i) \), bond length \( (d_i) \), shell \( (i) \), magnetic moment \( (\mu) \), and charge transfer \( (e) \)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Position</th>
<th>( z_i )</th>
<th>( d_i ) (Å)</th>
<th>Shell ( i )</th>
<th>Magnetic moment ( \mu )</th>
<th>Charge Transfer ( e )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>Pt</td>
<td>Rh</td>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td>COh13</td>
<td>1~2</td>
<td>2.00</td>
<td>2.716</td>
<td>2.715</td>
<td>2.653</td>
<td>1</td>
</tr>
<tr>
<td>COh55</td>
<td>1~2</td>
<td>2.80</td>
<td>2.629</td>
<td>2.682</td>
<td>2.637</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2~3</td>
<td>4.80</td>
<td>2.679</td>
<td>2.737</td>
<td>2.694</td>
<td>2</td>
</tr>
<tr>
<td>COh147</td>
<td>1~2</td>
<td>3.14</td>
<td>2.673</td>
<td>2.663</td>
<td>2.685</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2~3</td>
<td>5.14</td>
<td>2.728</td>
<td>2.756</td>
<td>2.737</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3~4</td>
<td>12.00</td>
<td>2.763</td>
<td>2.763</td>
<td>2.753</td>
<td>3</td>
</tr>
<tr>
<td>M-Dh13</td>
<td>2~4</td>
<td>-</td>
<td>2.696</td>
<td>2.696</td>
<td>2.633</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1~3</td>
<td>2.43</td>
<td>2.793</td>
<td>2.792</td>
<td>2.715</td>
<td>1</td>
</tr>
<tr>
<td>M-Dh49</td>
<td>2~4</td>
<td>-</td>
<td>2.731</td>
<td>2.729</td>
<td>2.663</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1~3</td>
<td>2.86</td>
<td>2.797</td>
<td>2.805</td>
<td>2.712</td>
<td>1</td>
</tr>
<tr>
<td>M-Dh75</td>
<td>2~4</td>
<td>-</td>
<td>2.695</td>
<td>2.694</td>
<td>2.676</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1~3</td>
<td>3.10</td>
<td>2.741</td>
<td>2.734</td>
<td>2.695</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>4~5</td>
<td>-</td>
<td>2.763</td>
<td>2.744</td>
<td>2.721</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3~5</td>
<td>5.10</td>
<td>2.784</td>
<td>2.798</td>
<td>2.743</td>
<td>2</td>
</tr>
</tbody>
</table>
5.3.2 Charge Transfer

Details of the charge transfer was mentioned in Chapter 4, Section 4.3.2. The charge transfer of COh (13, 55, and 147 atoms) and M-Dh (13, 49, and 75 atoms) structures for the Pt and Rh nanoclusters was estimated using Mulliken population analysis;\textsuperscript{103} the results are listed in Table 5-1. The negative and positive signs in Table 5-1 represent the charge gain and loss, respectively. The outermost shells gain excessive charges, whereas the interior shells lose charges. For example, the calculated value of the charge transfer Pt COh\textsubscript{147} (triplet state) changes from -0.681 e in the outermost shell to 0.254 e in the interior shell, indicating that the electrons have higher density at the nanocluster surfaces. This is consistent with the previous work on Au(111) nanoclusters,\textsuperscript{113} Ag nanoclusters,\textsuperscript{114} Cu-Ag clusters,\textsuperscript{115} Au-Ag clusters,\textsuperscript{157} Au nanoclusters,\textsuperscript{112} and Ag and Cu nanoclusters.\textsuperscript{158}

5.3.3 Core Electron Entrapment and Lattice Strain

According to BOLS correlation, the core level binding energy of under-coordinated atoms shifts toward deeper energies. Previously, a positive binding energy shift of about 0.6, 0.5, and 0.65 eV has been reported by previous study for Pt nanoparticles on pristine CNTs,\textsuperscript{6,22} and HOPG,\textsuperscript{23} as well as the Rh(110) surface,\textsuperscript{159} respectively. Moreover, the deepening of the Pt 4f\textsubscript{7/2},\textsuperscript{160} and Rh 3d\textsubscript{5/2}\textsuperscript{161} core level binding energy was also confirmed by high energy resolution core level photoelectron spectroscopy and DFT calculations.
Table 5-2 lists the calculated $E_{\nu}(0)$ and $\Delta E_{\nu}(\infty)$ values for Pt-4f and Rh-3d based on Eq. (2-17) and Eq. (2-18), using the XPS measurements results reported in the references. Figure 5-1 plots the BOLS reproduction of the measured shape- and size-dependence of Pt-4f and Rh-3d CLS. The intercepts and slopes in the scaling law were obtained by linearizing the experimental data with the least-root-mean-square optimization method. The intercepts may contain the effect of space charging or the system error in the measurements, and can thus serve as a calibration to the measurements. The slopes are a major concern in the current decoding exercises because they depend on surface treatment, particles size, and interaction between the particles and the substrates for substantiate particles.  

<table>
<thead>
<tr>
<th></th>
<th>$A$</th>
<th>$B$</th>
<th>$E_{\nu}(0)$</th>
<th>$\Delta E_{\nu}(\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt- Pristine CNTs</td>
<td>71.26</td>
<td>0.66</td>
<td>67.21</td>
<td>4.05</td>
</tr>
<tr>
<td>Pt-HOPG$^{22}$</td>
<td>71.15</td>
<td>0.58</td>
<td>67.21</td>
<td>3.94</td>
</tr>
<tr>
<td>Pt-TiO$_2$(110)-300K$^{163}$</td>
<td>71.11</td>
<td>0.70</td>
<td>67.21</td>
<td>3.90</td>
</tr>
<tr>
<td>Pt-MCNTs-untreated$^6$</td>
<td>71.11</td>
<td>0.42</td>
<td>67.21</td>
<td>3.90</td>
</tr>
<tr>
<td>Pt-MCNTs-Ar$^{+6}$</td>
<td>71.19</td>
<td>0.88</td>
<td>67.21</td>
<td>3.98</td>
</tr>
<tr>
<td>Pt-MCNTs-O$_2$</td>
<td>71.26</td>
<td>0.63</td>
<td>67.21</td>
<td>4.05</td>
</tr>
<tr>
<td>Rh-TiO$_2$(110)-(1x1)-well ordered$^{164}$</td>
<td>306.70</td>
<td>0.09</td>
<td>302.16</td>
<td>4.54</td>
</tr>
<tr>
<td>Rh-TiO$_2$(110)-(1x1)-Slightly-Ar$^{+164}$</td>
<td>306.70</td>
<td>0.12</td>
<td>302.16</td>
<td>4.54</td>
</tr>
<tr>
<td>Rh-TiO$_2$(110)-(1x1)-Strongly- Ar$^{+164}$</td>
<td>306.40</td>
<td>0.11</td>
<td>302.16</td>
<td>4.24</td>
</tr>
<tr>
<td>Rh-TiO$_2$</td>
<td>307.50</td>
<td>0.13</td>
<td>302.16</td>
<td>5.34</td>
</tr>
<tr>
<td>Rh-TiO$_2$-300K$^{166}$</td>
<td>307.30</td>
<td>0.08</td>
<td>302.16</td>
<td>5.14</td>
</tr>
<tr>
<td>Rh-TiO$_2$-160K$^{166}$</td>
<td>307.40</td>
<td>0.05</td>
<td>302.16</td>
<td>5.24</td>
</tr>
</tbody>
</table>
We first calculated the dimensionality $\tau$ and the bond nature indicator $m$ to elucidate the size effect on the CLS of Pt and Rh nanoclusters. The $E_v(0)$ and $\Delta E_v(\infty)$ of the Pt-4$f_{7/2}$ can be obtained by applying Eq. (2-17) and Eq. (2-18) to the Pt nanoparticles deposited on pristine CNTs, the TiO$_2$(110) surface at room temperature, and the multiwall CNTs (MCNTs) without pretreatment at $m = 1.00$. The value of 1, a value that holds for metallic solid, was chosen because there is barely any reaction between the Pt nanoparticles and the substrates. The atomic trapping energy and the bulk shift for Pt are about 67.21 and 3.28 eV, respectively. According to Eq. (2-21), $B$ and $E_v(\infty)$ can be extracted by linearizing of the measured binding energies of Pt and Rh nanoclusters with respect to $1/K$. Taking the obtained CLS values to the simulation iteration of the measured size-dependent $E_v(K)$ for Pt on HOPG and MCNTs results in $m = 2.56$, which contributes to the interfacial reaction between Pt and the substrates to $m = 1.00$.

Similarly, for Rh nanoparticles deposited on the TiO$_2$(110)-(1x1) surface, the Ar$^+$-pretreated TiO$_2$(110) surface, and the TiO$_2$(110) surface at 300 and 160 K, the bond nature indicator $m = 1.00$ because of the weak interaction between the Rh nanoparticles and the substrates. The Rh 3$d_{5/2}$ binding energy of an isolated Rh atom and its bulk shift is equal to 302.163 and 4.37 eV, respectively. Compared with their bulk counterparts, the experimental results of Au, Cu, Pt, and Rh nanoclusters revealed a positive CLS, which is mainly attributed to the shorter and stronger bonds.
between the under-coordinated atoms. By adjusting the $m$ values, our predictions based on the BOLS correlation are in good agreement with the experimental observations.

Figure 5-1 shows the CLS predicted by the BOLS correlation and XPS measurements extracted of the (a) Pt and (b) Rh nanoparticles.
Furthermore, the plot of lattice strain values estimated based on the BOLS correlation and the measured size-dependent mean lattice contraction (scattered data) are shown in Figure 5-2. The intercepts and slopes in the scaling law were extracted by linearizing the experimental data with the least-root-mean-square optimization method. According to Eq. (2-9), the mean lattice strain of the Pt and Rh nanoparticles is inversely proportional to the size of the Pt and Rh nanoparticles. Our calculations include the experimental reported results on Pt deposition on the NiAl (110) substrate\textsuperscript{167} and Pt on the Cu(111) surface at 300K,\textsuperscript{168} the Pt(422) surface and the Pt(111) surface,\textsuperscript{169} and the Rh surface.\textsuperscript{170} The lattice contraction is a function of the nanoparticle size, and confirms that the bond-order loss and CN imperfection affect the lattice strain.

![Figure 5-2](image)

Figure 5-2 Consistency in the trend between theoretical predictions and various experimental observations of the mean lattice contraction of the Pt and Rh nanoparticles.
5.3.4 Shell-resolved Valence Band Polarization

According to the BOLS-NEP notation, the originally conductive $s$-electrons of Pt and Rh are expected to be polarized by the densely and tightly entrapped core charges. The magnitude of polarization increases as the electrons move from the inner toward the edge with lower atomic CNs. This phenomenon has been experimentally observed for the Ag, Au, and Cu chains, as well as for the Pt and Rh nanoparticles.

Figure 5-3 plots the shell-resolved LDOS for 147-atom and 75-atom Pt and Rh nanoclusters. The valence electrons in the outermost shell shifted toward $E_f$, whereas the entrapped electrons in the interior core remained at the lower edge. The maximum LDOS of the atoms at the outermost shell are polarized by the interior electrons. Therefore, the conducting electrons of the under-coordinated atoms became localized and polarized for Pt and Rh nanoclusters. Figure 5-4 shows the extracted DOS, indicating that polarization becomes more significant for smaller nanoparticles. The DOS peak shifted from -0.59 eV for the Rh$_{147}$ nanocluster to -0.07 eV for the Rh$_{13}$ nanocluster in the COh structures, and from -0.78 eV for the Pt$_{75}$ nanocluster to -0.34 eV for the Pt$_{13}$ nanocluster in the M-Dh structures, demonstrating that the valence charge polarization is inversely proportional to the nanocluster size.
Figure 5-3 Shell-resolved LDOS for the (a-b) COh-147 and the (c-d) M-Dh-75 structures of the Pt and Rh nanoclusters. The outermost shell electrons moved toward the upper edge near the $E_f$ whereas the interior shell electrons remained at the lower energy.

Moreover, the valence LDOS polarization of Pt and Rh nanoclusters was experimentally confirmed. For instance, Zheng et al.\textsuperscript{171} pointed out the under-
coordinated-induced valence polarization for Rh(111) and Rh adatoms through X-ray photoelectron differential spectroscopy (XPDS). For the Pt nanoparticles on pristine CNTs synthesized by oxygen-plasma treatment, the DOS shifted toward $E_f$ with the reduction of cluster size because of the spin-orbit coupling (SOC) effect.\textsuperscript{162, 172} Bianchettin et al.\textsuperscript{160} revealed that the LDOS shift of the Pt atoms on Pt(111) depends on the cluster size through high-energy resolution core level photoelectron spectroscopy and DFT calculations. Polarization is also observed by STM/S measurements for Ag clusters and chains on Ag(111),\textsuperscript{12} Ag adatoms on Ag(111),\textsuperscript{85} Au-Au atomic chains,\textsuperscript{16} Au nanowire,\textsuperscript{139} Cu chains on Cu(111),\textsuperscript{15} single Cu/Cu(111) adatoms,\textsuperscript{130} Pt nanoparticles on the TiO$_2$(110) surface,\textsuperscript{173} Pt clusters on HOPG,\textsuperscript{18} and Rh on TiO$_2$(110)-(1x2).\textsuperscript{17, 174}
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters

Figure 5-4 Size-resolved DOS of the (a, c, and e) COh and the (b, d, and f) M-Dh structures of the PtN and RhN nanoclusters (N = 13-147 atoms). E_f is allocated at 0 eV.
5.3.5 Magnetic Modulation

5.3.5.1 Magnetic moment

The difference between the occupied majority and minority spin band is called the magnetic moment, which is relative to the ferromagnetic exchange splitting between the bands.\textsuperscript{132} As listed in Table 5-1, the magnetic moment of the 147-atom COh structure of the Rh nanoparticles decreased from 2.067 \( \mu \) in the outermost shell with CN = 3.4, to 0.201 \( \mu \) in the interior core with CN = 12. A similar trend was observed for M-Dh structures of the Rh nanoclusters, and COh and M-Dh structures of the Pt nanoclusters. The magnetic moment value of the nanoclusters increased with decreasing CN,\textsuperscript{116} which is consistent with the previous results on Fe and Rh clusters.\textsuperscript{175 176, 177}

5.3.5.2 Magnetization

The magnetic behaviour is caused by the spin-up (\( \alpha \)-spin states) and spin-down (\( \beta \)-spin states) states of the metal \( d \)-band. The majority and minority spins of the \( d \)-band are occupied by the spin-up (\( \alpha \)) electrons and unoccupied by the spin-down (\( \beta \)) electrons located below and above \( E_f \), respectively. The positive and negative values represent the majority and minority spins, respectively. The \( E_f \) is allocated at 0 eV. The eigenvalue spectra were calculated by numerically integrating DOS for spin-up (\( \alpha \)) and spin-down (\( \beta \)) to understand the origin of the magnetic behaviours of Pt and Rh nanoclusters.
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters

Figure 5-5 and Figure 5-6 show the plot of the spin-resolved DOS and PDOS of the Pt and Rh nanoparticles consisting of 13-147 atoms for COh and M-Dh structures. Detailed results of the Pt and Rh nanoclusters made up of various sizes and structures are shown to illustrate the magnetization mechanism of the Pt and Rh nanoclusters with different structures. The DOS and PDOS distributions of spin-up ($\alpha$) and spin–down ($\beta$) states split near $E_f$ for the triplet state of the Pt nanoparticles and the quartet state of the Rh nanoparticles, whereas no split was detected for the singlet state of Pt. Hence, the exchange correlation of electrons forms the ordered spin arrangement of electrons that determines the magnetic moment of these materials.
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters

(c) COhPt_{147}

(d) M-DhPt_{13}

(e) M-DhPt_{49}

(f) M-DhPt_{75}

(g) COhPt_{13}

(h) COhPt_{55}
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters
Figure 5-5 Spin-polarized DOS of (a-f) the Pt singlet state, (g-l) the Pt triplet state, and (m-r) the Rh quartet state. The inset shows the difference between spin-up (α) and spin-down (β) states in DOS. The blue and red indicate the spin-up (α) and spin-down (β) configurations. The $E_f$ is set at 0 eV.
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters

(g) COhPt$_{13}$

(h) COhPt$_{55}$

(i) COhPt$_{147}$

(j) M-DhPt$_{13}$

(k) M-DhPt$_{49}$

(l) M-DhPt$_{75}$
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters

Figure 5-6 Spin-polarized PDOS of (a-f) the 5d-Pt singlet state, (g-l) the 5d-Pt triplet state, and (m-r) the 4d-Rh quartet state. The inset shows the difference between the spin-
up ($\alpha$) and spin-down ($\beta$) states in PDOS. The blue and red indicate the spin-up ($\alpha$) and spin-down ($\beta$) configurations. The $E_f$ is set at 0 eV.

The energy gap of the Pt and Rh nanoclusters between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the $\alpha$ and $\beta$ spin states was calculated by DFT calculations; and the results are listed in Table 5-3. The bonding and anti-bonding are referred to as the HOMO and the LUMO. The gap between the $\alpha$ and $\beta$ spin states of Pt (triplet state) and Rh (quartet state) was revealed for both COh and M-Dh structures, whereas no gap was observed for Pt (singlet state). These findings confirmed that the magnetic properties were enhanced when the size of the clusters decreased for Pt in the triple state and Rh in the quartet state because of the reduction of CN and the SOC effect.\textsuperscript{178} The magnetic ordering was consistent with the previous theoretical calculations on Pd, Rh, and Ru nanoclusters,\textsuperscript{179} Rh monolayers on Au,\textsuperscript{180} Rh\textsubscript{N} and Pd\textsubscript{N} cluster up to N = 13 atoms,\textsuperscript{181} transition metal monolayers on noble metal (001) substrates,\textsuperscript{182} Pt\textsubscript{N} (N = 2-55 atoms) clusters,\textsuperscript{133} Pt\textsubscript{13} clusters in a NaY zeolite,\textsuperscript{150} Tc, Ru, Rh, and Pd monolayers on Ag(001) surface,\textsuperscript{183} as well as Rh\textsubscript{N} clusters (N = 9, 13, 15, 17, and 19 atoms).\textsuperscript{105}
Chapter 5: Quantum Entrapment and Valence Polarization of Pt and Rh Nanoclusters

Table 5-3 Calculated gaps for the spin-up ($\alpha$) and spin-down ($\beta$) of Pt and Rh nanoclusters

<table>
<thead>
<tr>
<th></th>
<th>Gap spin-up alpha (eV)</th>
<th>Gap spin-down Beta (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt Singlet</td>
<td>Pt Triplet</td>
</tr>
<tr>
<td>COh$_{13}$</td>
<td>1.009</td>
<td>0.058</td>
</tr>
<tr>
<td>COh$_{55}$</td>
<td>0.305</td>
<td>0.252</td>
</tr>
<tr>
<td>COh$_{147}$</td>
<td>0.274</td>
<td>0.063</td>
</tr>
<tr>
<td>M-D$_{13}$</td>
<td>0.417</td>
<td>0.224</td>
</tr>
<tr>
<td>M-Dh$_{49}$</td>
<td>0.374</td>
<td>0.363</td>
</tr>
<tr>
<td>M-Dh$_{75}$</td>
<td>0.236</td>
<td>0.187</td>
</tr>
</tbody>
</table>

This phenomenon was also confirmed by experimental observations of Pt embedded in a polymer prepared by chemical reaction method,\textsuperscript{184} Pt clusters by ion exchange of a KL zeolite,\textsuperscript{185} Pt/Y$_3$Fe$_5$O$_{12}$ bilayers by X-ray magnetic circular dichroism,\textsuperscript{186} Pt nanoparticles induced by surface chemisorption,\textsuperscript{187} Rh$_N$ (N = 12-32 atoms) grown by laser vaporization,\textsuperscript{7} Rh monolayers deposited by the grown layer method on Fe,\textsuperscript{188} as well as Rh nanoparticles prepared by reducing cations in the solution.\textsuperscript{9} No magnetic behavior was reported for Pt clusters with 13-20 atoms in zeolite Y\textsuperscript{189} andPt clusters on graphene,\textsuperscript{190} consistent with our theoretical calculation for Pt in the singlet state. Consequently, the HOMO-LUMO gap and the magnetic behavior of
the Pt nanoclusters in the triplet state and Rh nanoclusters in the quartet state clusters correlated to the cluster size.

5.4 Summary

Consistency in trend between the DFT calculations and the experimental results, including the EXAFS, STM/S, XPDS, and XPS measurements, confirmed our predications based on the BOLS-NEP correlation that the atomic under-coordination affects the properties of Pt and Rh nanoclusters, including the bond relaxation, lattice strain, charge transfer, core electron entrapment, valence electron polarization, and magnetic moments. The atomic under-coordination induces local bond contraction, densification and entrapment of core electrons, valence charge polarization, as well as magnetization, giving rise to the unusual properties of Pt and Rh nanoclusters in terms of size dependence and emergence of new properties, which are lacking in their respective parent bulk materials. The results of this work will contribute to the understanding of the properties of Pt and Rh nanoclusters, such as catalytic enhancement and magnetization.
Chapter 6 Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

6.1 Overviews of Cationic, Neutral, and Anionic $M_N$ Nanoclusters

$M_N$ metallic nanoparticles ($M = \text{Ag, Cu, Pt, and Rh}; N = 13-147$ atoms) have attracted considerable interests because of their unique chemical and physical properties, such as enhanced catalytic activity, giant magnetic moments, and transition from conductor-to-insulator and non-magnetic-to-magnetic. Nanoparticles have high surface to volume ratio and large fraction of under-coordinated atoms, which modify their electronic structures and consequent material properties. In addition to reduced sizes, surface charge states also play a significant role on the nanoparticle properties. For instance, the catalytic performance of Ag nanoclusters, nitric oxide on Cu clusters, Pt clusters in gas phase, and nitric oxide on Rh clusters depends on their excess surface charges, and can thus be manipulated by controlling the oxide supports.

An upward shift of valence LDOS was revealed by scanning tunneling STM/S in neutral systems of metallic nanoparticles, such as Ag clusters on Ag (111) substrate, Cu chains on Cu(111), Pt clusters on highly oriented pyrolytic graphite, and Rh nanoparticles on TiO$_2$(110)-(1×2) surface. Moreover, an upward shift of $d$-band and $s$-$d$ hybridization for orbitals located close to $d$-band of UPS and PES measurements were observed in the cationic and anionic of the Ag, Cu, Pt, and Rh nanoclusters,
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

respectively. However, charge transfers between cluster and support, and the relationship between the excess charge states on the nanoparticle surface, and their properties, including catalytic performance and magnetization behaviors remain unclear. Although many experimental studies have been carried out on nanoparticles with cationic and anionic states, early theoretical work usually assume that nanoparticles are in a neutral state.

Therefore, studying the influence of excess charge states on bond length contraction, charge densification, quantum entrapment, polarization, and magnetization, as well as the electronic structure of metallic nanoparticles, is desirable.

6.2 Computational Approaches

6.2.1 DFT Calculation

To demonstrate the expectations on the framework of BOLS correlation, DFT calculations were used to investigate the bond length contraction, core and shell charge densification, entrapment and polarization, as well as the magnetization of the cationic, neutral, and anionic $M_N$ metallic nanoclusters. Our calculation results were then compared with previous experimental observations, such as EXAFS, STM/S, XPDS, PES, and UPS measurements. The metallic nanoparticles evolve into some distorted structures as the size decreases; the COh and M-Dh structures are stable forms for $M_N$ metallic nanoclusters. In this study, we considered COh structures...
with 13, 55, and 147 atoms and M-Dh structures with 13, 49, and 75 atoms (see Figure 4-1).

DFT calculations were carried out as mentioned in Chapter 4, Section 4.2.2. The amount of excess charge states in DMol$^3$ code was specified at the beginning of our calculations, including (+2), (+1), (0), (-1), and (-2) for $M_N$ metallic nanoclusters ($M = \text{Ag, Cu, Pt, and Rh; } N = 13-147 \text{ atoms}$). Spin states considered in our calculation include the doublet and singlet ground states for Ag and Cu nanoclusters, the triplet and doublets ground states for Pt nanoclusters, and the triplet and quartet ground states for Rh nanoclusters, respectively. In the spin-unrestricted wave function, different orbitals were attributed to different spins, including spin-up ($\alpha$) and spin-down ($\beta$).

6.3 Discussions

6.3.1 Local Bond Length Contraction

The DFT calculation results of $M_N$ metallic nanoclusters for positive, neutral, and negative excess charge states vary from (+2) to (-2), and listed in Table 6-1 (see Eq. (2-1) and Eq. (2-2)). Consistent with BOLS expectations, the bond length of the surface atomic layer was shortened compared with that in the bulk. For example, the calculated Ag-Ag, Cu-Cu, Pt-Pt, and Rh-Rh distance of the outermost shell is 2.711, 2.354, 2.680, and 2.645 Å for COh$_{55}$ with excess charge state of (+2), respectively, which are significantly smaller than their bulk values of Ag (2.890 Å),$^{104}$ Cu (2.556 Å),$^{104}$ Pt
(2.770 Å),\textsuperscript{149} and Rh (2.690 Å).\textsuperscript{153} For M-Dh\textsubscript{75} metallic nanoclusters with excess charge state of (+2), the calculated bond length of the outermost shell is 2.794, 2.419, 2.747, and 2.765 Å for Ag, Cu, Pt, and Rh, respectively, which are also smaller than their bulk counterparts. Similar trend was observed for all other COh and M-Dh structures with different sizes and excess charge states (see Table 6-1). The results were calculated by combining the BOLS correlation and DFT calculations, and confirmed to be consistent with previous theoretical calculations and experimental findings for cationic, neutral, and anionic metallic nanoparticles.\textsuperscript{8, 105-108, 156, 200-207}

For instance, Bonačić-Koutecký et al. reported that the bond length, estimated by coupled-cluster singles and doubles method, contracts in the cationic and neutral Ag clusters.\textsuperscript{202} Up to 8.30\%\textendash 13.20 \% and 11.20 \% of bond length contraction was observed in the anionic Ag and Cu clusters prepared by photodetachment, respectively.\textsuperscript{203} For neutral Ag, Cu, and Pt nanoparticles, EXAFS spectroscopy measurements revealed that the bond length was contracted by 2.83\textendash 2.87, 2.230\textendash 2.540, and 2.600 Å, respectively;\textsuperscript{8, 107, 108} and the XANES measurements revealed that the bond length was reduced to around 2.652 Å for Pt\textsubscript{13} clusters;\textsuperscript{150} around 2.300 Å for Pt clusters in monoatomic chains;\textsuperscript{149} and around 2.530 Å for Ag nanoparticles.\textsuperscript{110} Furthermore, the theoretical methods reported the contraction of bond length, for example, 2.590\textendash 2.830, 2.590\textendash 2.840, and 2.610\textendash 2.840 Å in cationic, neutral, and anionic silver clusters;\textsuperscript{206} 2.417\textendash 2.530,
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

2.269-2.522, and 2.388-2.520 Å in cationic, neutral, and anionic Cuₙ clusters with N = 3-13 atoms; 2.560-2.250, 2.570-2.300, and 2.580-2.360 Å in the cationic, neutral, and anionic Ptₙ (N = 2-14 atoms); and neutral Rhₙ (N = 13, 55, 147, 309, and 561 atoms) at around 3%-5%. Results showed that DFT calculations tend to underestimate bond length contraction with excess charge states compared with the expectation of the BOLS correlation and the aforementioned previous experimental observations.

Table 6-1 Calculation of the M-M bond length dᵢ(Å) and charge of shell (e) at different position of Mₙ metallic nanoclusters with COh and M-Dh structures and the excess charge states from (+2) to (-2). The shell index counts the atomic layer from the outermost inwards.

<table>
<thead>
<tr>
<th>Shell</th>
<th>Excess charge states</th>
<th>Bond length (Å)</th>
<th>Charge of Shell (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ag</td>
<td>Cu</td>
</tr>
<tr>
<td>COh₁₃</td>
<td>1~2</td>
<td>+2</td>
<td>2.798</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1</td>
<td>2.781</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>2.778</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1</td>
<td>2.788</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-2</td>
<td>2.785</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+2</td>
<td>2.711</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1</td>
<td>2.712</td>
</tr>
<tr>
<td>COh₅₅</td>
<td>1~2</td>
<td>0</td>
<td>2.703</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1</td>
<td>2.701</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+2</td>
<td>2.830</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1</td>
<td>2.825</td>
</tr>
</tbody>
</table>
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

|     | 0  | 2.824 | 2.470 | 2.737 | 2.694 | 0.960 | 1.140 | 0.564 | 1.556 |
|     | -1 | 2.822 | 2.467 | 2.742 | 2.693 | 1.032 | 1.188 | 0.594 | 1.605 |
|     | -2 | 2.820 | 2.465 | 2.737 | 2.693 | 1.080 | 1.212 | 0.624 | 1.645 |
|     | +2 | 2.719 | 2.349 | 2.668 | 2.685 | 1.359 | 1.602 | 1.230 | 1.918 |
|     | +1 | 2.711 | 2.347 | 2.667 | 2.682 | 0.372 | 0.620 | 0.265 | 0.742 |
| 1–2 | 0  | 2.713 | 2.346 | 2.663 | 2.685 | -0.554 | -0.300 | -0.681 | -0.007 |
|     | -1 | 2.717 | 2.342 | 2.660 | 2.684 | -1.601 | -1.370 | -1.736 | -1.341 |
|     | +2 | 2.810 | 2.468 | 2.739 | 2.738 | 0.725 | 0.478 | 0.877 | 0.322 |
|     | +1 | 2.808 | 2.464 | 2.731 | 2.731 | 0.712 | 0.495 | 0.087 | 0.419 |
| COH_{147} | 2–3 | 0  | 2.809 | 2.458 | 2.756 | 2.737 | 0.650 | 0.380 | 0.815 | 0.173 |
|     | -1 | 2.803 | 2.459 | 2.731 | 2.730 | 0.682 | 0.4396 | 0.858 | 0.416 |
|     | -2 | 2.809 | 2.457 | 2.729 | 2.731 | 0.670 | 0.4285 | 0.856 | 0.414 |
|     | +2 | 2.826 | 2.477 | 2.767 | 2.754 | 0.031 | 0.0362 | 0.029 | 0.001 |
|     | +1 | 2.825 | 2.476 | 2.766 | 2.753 | 0.033 | 0.036 | 0.027 | 0.007 |
| 3–4 | 0  | 2.831 | 2.469 | 2.763 | 2.753 | 0.036 | 0.037 | 0.254 | 0.066 |
|     | -1 | 2.826 | 2.475 | 2.767 | 2.751 | 0.036 | 0.037 | 0.045 | 0.005 |
|     | -2 | 2.826 | 2.474 | 2.765 | 2.753 | 0.038 | 0.038 | 0.030 | 0.004 |
|     | +2 | 2.766 | 2.404 | 2.701 | 2.635 | - | - | - | - |
|     | +1 | 2.757 | 2.393 | 2.697 | 2.625 | - | - | - | - |
| 2–4 | 0  | 2.750 | 2.388 | 2.696 | 2.633 | - | - | - | - |
|     | -1 | 2.749 | 2.389 | 2.704 | 2.626 | - | - | - | - |
|     | -2 | 2.757 | 2.397 | 2.706 | 2.631 | - | - | - | - |
|     | +2 | 2.898 | 2.532 | 2.809 | 2.731 | 2.052 | 1.871 | 1.965 | 1.852 |
|     | +1 | 2.898 | 2.526 | 2.799 | 2.721 | 0.856 | 0.835 | 0.940 | 0.812 |
| 1–3 | 0  | 2.902 | 2.517 | 2.792 | 2.715 | -0.184 | -0.128 | -0.087 | -0.224 |
|     | -1 | 2.899 | 2.509 | 2.790 | 2.714 | -1.224 | -1.230 | -1.109 | -1.258 |
|     | +2 | 2.770 | 2.415 | 2.736 | 2.658 | - | - | - | - |
|     | +1 | 2.775 | 2.416 | 2.713 | 2.656 | - | - | - | - |
| 2–4 | 0  | 2.773 | 2.420 | 2.729 | 2.663 | - | - | - | - |
|     | -1 | 2.775 | 2.419 | 2.729 | 2.678 | - | - | - | - |
|     | -2 | 2.783 | 2.422 | 2.717 | 2.650 | - | - | - | - |
|     | +2 | 2.807 | 2.453 | 2.800 | 2.719 | 1.505 | 1.236 | 1.750 | 0.839 |
|     | +1 | 2.809 | 2.454 | 2.797 | 2.716 | 0.495 | 0.239 | 0.346 | 0.278 |
| 1–3 | 0  | 2.812 | 2.457 | 2.805 | 2.712 | -0.482 | -0.128 | -0.686 | -1.226 |
|     | -1 | 2.813 | 2.461 | 2.796 | 2.711 | -1.390 | -1.774 | -1.791 | -2.253 |
| M-Dh_{13} | 2–4 | +2 | 2.755 | 2.404 | 2.690 | 2.684 | - | - | - | - |

99
### 6.3.2 Charge of Core and Shell

Details of the charge transfer was mentioned in Chapter 4, Section 4.3.2. The core and shell charge of M_N metallic nanoclusters were calculated by taking into account both COh and M-Dh structures with the positive, neutral, and negative excess charge states from (+2) to (-2) using Mulliken population analysis\(^{103}\) (see Table 6-1 and Table 6-2). The negative and positive signs indicate charge gain and charge loss, respectively.

Table 6-1 shows that the outermost shells of M_N metallic nanoclusters gain excessive charges with neutral and negative excess charge states and lose excessive charge with positive excess charge states, whereas the interior shells lose electrons regardless of the

<table>
<thead>
<tr>
<th></th>
<th>+2</th>
<th>+1</th>
<th>0</th>
<th>-1</th>
<th>-2</th>
<th>-3</th>
<th>-4</th>
<th>-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.759</td>
<td>2.397</td>
<td>2.703</td>
<td>2.681</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1~3</td>
<td>0</td>
<td>2.778</td>
<td>2.412</td>
<td>2.734</td>
<td>2.695</td>
<td>-1.105</td>
<td>-1.541</td>
<td>-1.241</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>2.775</td>
<td>2.409</td>
<td>2.743</td>
<td>2.752</td>
<td>-1.579</td>
<td>-1.892</td>
<td>-1.628</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>2.775</td>
<td>2.406</td>
<td>2.742</td>
<td>2.687</td>
<td>-2.596</td>
<td>-2.914</td>
<td>-3.242</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>2.813</td>
<td>2.458</td>
<td>2.766</td>
<td>2.714</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>2.812</td>
<td>2.460</td>
<td>2.766</td>
<td>2.700</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4~5</td>
<td>0</td>
<td>2.818</td>
<td>2.456</td>
<td>2.744</td>
<td>2.721</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>2.820</td>
<td>2.463</td>
<td>2.754</td>
<td>2.711</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>2.819</td>
<td>2.461</td>
<td>2.764</td>
<td>2.701</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>2.853</td>
<td>2.498</td>
<td>2.777</td>
<td>2.796</td>
<td>0.447</td>
<td>0.823</td>
<td>0.413</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>2.839</td>
<td>2.490</td>
<td>2.769</td>
<td>2.744</td>
<td>0.481</td>
<td>0.845</td>
<td>0.452</td>
</tr>
<tr>
<td>3~5</td>
<td>0</td>
<td>2.843</td>
<td>2.484</td>
<td>2.798</td>
<td>2.743</td>
<td>1.043</td>
<td>1.469</td>
<td>1.107</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>2.837</td>
<td>2.491</td>
<td>2.779</td>
<td>2.797</td>
<td>0.529</td>
<td>0.861</td>
<td>0.522</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>2.836</td>
<td>2.491</td>
<td>2.778</td>
<td>2.745</td>
<td>0.547</td>
<td>0.861</td>
<td>0.560</td>
</tr>
</tbody>
</table>
excess charge states. For instance, Ag, Cu, Pt, and Rh COh\textsubscript{147} nanoclusters at neutral excess charge state have calculated shell charge change of -0.554, -0.300, -0.681, and -0.007 e in the outermost shell, and 0.036, 0.037, 0.254, and 0.066 e in the interior shell. Moreover, for Ag, Cu, Pt, and Rh COh\textsubscript{55} nanoclusters at negative excess charge state (-1) the shell charge change is equal to -2.098, -2.274, -1.743, and -2.825 e in the outermost shell, and 1.032 e, 1.188 e, 0.594 e, and 1.605 e in the interior shell. Consequently, other COh and M-Dh nanoclusters with neutral and negative excess charge states follow the same trend for different sizes and structures. Therefore, the charge transfer was observed for the neutral and negative excess charge states of M\textsubscript{N} metallic nanoclusters, which is consistent with previous theoretical calculations and experimental observations.\textsuperscript{115, 158, 208-210}

Table 6-2 Calculation of the charge of core (e) of M\textsubscript{N} metallic nanoclusters with COh and M-Dh structures and excess charge states from (+2) to (-2).

<table>
<thead>
<tr>
<th>Excess charge states</th>
<th>Charge of Core (e)</th>
<th>COh\textsubscript{13}</th>
<th>COh\textsubscript{55}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ag</td>
<td>Cu</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>0.127</td>
<td>0.153</td>
</tr>
<tr>
<td>+1</td>
<td></td>
<td>0.171</td>
<td>0.191</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>0.214</td>
<td>0.228</td>
</tr>
<tr>
<td>-1</td>
<td></td>
<td>0.257</td>
<td>0.262</td>
</tr>
<tr>
<td>-2</td>
<td></td>
<td>0.288</td>
<td>0.286</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>0.068</td>
<td>0.089</td>
</tr>
<tr>
<td>+1</td>
<td></td>
<td>0.071</td>
<td>0.093</td>
</tr>
</tbody>
</table>
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

<table>
<thead>
<tr>
<th></th>
<th>COh_{147}</th>
<th>M-Dh_{49}</th>
<th>M-Dh_{75}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.070</td>
<td>0.062</td>
<td>0.062</td>
</tr>
<tr>
<td>-1</td>
<td>0.069</td>
<td>0.183</td>
<td>0.056</td>
</tr>
<tr>
<td>-2</td>
<td>0.064</td>
<td>0.222</td>
<td>0.062</td>
</tr>
<tr>
<td>+2</td>
<td>0.001</td>
<td>0.144</td>
<td>0.056</td>
</tr>
<tr>
<td>+1</td>
<td>0.001</td>
<td>0.183</td>
<td>0.056</td>
</tr>
</tbody>
</table>

On the contrary, the outermost and interior shell charge in positive excess charge states obtained positive signs for M_{N} metallic nanoclusters with different sizes and structures. For instance, the shell charge of Ag, Cu, Pt, and Rh COh_{55} nanoclusters in an excess charge state of (+1) change 0.046, 0.216, 0.316, and 1.565 e in the outermost shell, and 0.876, 0.720, 0.530, and 1.500 e in the interior shell which is regarded as a demonstration of a phenomenon called electrophilic behavior. The positive charge of nanoclusters attracts electrons, which can be utilized in chemisorption, such as H_{2}, CO_{2},
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

and NO2. These results are consistent with the core-shell structures for Au nanoclusters in catalyst application\textsuperscript{211} and Au-Ag nanoparticles in bacterial therapy.\textsuperscript{212}

Moreover, positive signs of core charges were determined for COh\textsubscript{13}, COh\textsubscript{55}, M-Dh\textsubscript{13}, and M-Dh\textsubscript{75} structures with the positive, neutral, and negative excess charge states (see Table 6-2). The magnitude of core charges increased for metallic nanocluster with COh\textsubscript{13} and M-Dh\textsubscript{13} structures as the excess charge states change from (+2) to (-2). For instance, the core charges of Ag are 0.127, 0.171, 0.214, 0.257, and 0.288 e for COh\textsubscript{13} structure, and 0.105, 0.144, 0.183, 0.222, and 0.260 e for M-Dh\textsubscript{13} structure, as the excess charge states vary from (+2) to (-2). The linear dependence of the variation of core charge on the excess charge states for metallic nanocluster with COh\textsubscript{13} and M-Dh\textsubscript{13} structures is consistent with the theoretical results of the Ag nanoclusters.\textsuperscript{209} Furthermore, the constant positive value of the core charge achieved for COh\textsubscript{55} and M-Dh\textsubscript{75} metallic nanoclusters with the positive, neutral, and negative excess charge states, showing that the excess charge states cannot directly affect the core charges because of the structures having two shells around of their core. However, the core charges of COh\textsubscript{147} structure with the excess charge states from (+2) to (-2) achieved constant positive values for Ag\textsubscript{147} and Cu\textsubscript{147} nanoclusters and constant negative values for Pt\textsubscript{147} and Rh\textsubscript{147}, which are in agreement with bimetallic nanoclusters, such as (AuAg)\textsubscript{147} nanoclusters co-catalysts for photocatalytic hydrogen reduction.\textsuperscript{213} These calculated
results are consistent with the aforementioned theoretical calculations and experimental observations with charge excess states of $M_N$ metallic nanoclusters, following the BOLS-NEP predictions.

### 6.3.3 Quantum Entrapment and Valence Charge Polarization

Figure 6-1 shows the plots of LDOS of $d$-bands for COh structures with 13, 55, 147 atoms and M-Dh structures with 13, 49, and 75 atoms, and the positive, neutral, and negative excess charge states from (+2) to (-2), respectively. The red dashed line in Figure 6-1 shows that the $d$-band of metallic nanoclusters move toward the Fermi level with the excess charge state (-1) on the outermost of Ag, Cu, and Rh nanoclusters with COh$_{13}$ structures and Ag and Cu nanoclusters with COh$_{55}$ structures, as well as the excess charge state (+2) on the outermost of Pt nanoclusters with COh$_{13}$ structures. The interior electrons can polarize the electrons at the valence band, thus the otherwise conducing electrons of the under-coordinated atoms become polarized for metallic nanoclusters. This result is consistent with BOLS-NEP expectation$^{2,31}$ and previous experimental observations on Ag clusters and chains on Ag (111), monatomic Cu chains on Cu (111), as well as single Pt atoms and clusters on highly oriented pyrolytic graphite and Rh NPs epitaxy on TiO$_2$(110)-(1×2) surface.$^{12,15,17,18}$
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

(a) Ag-COh$_{13}$

(b) Cu-COh$_{13}$

(c) Pt-COh$_{13}$

(d) Rh-COh$_{13}$

(e) Ag-COh$_{55}$

(f) Cu-COh$_{55}$
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

(g) Pt-CO$_{55}$

(h) Rh-CO$_{55}$

(i) Ag-CO$_{147}$

(j) Cu-CO$_{147}$

(k) Pt-CO$_{147}$

(l) Rh-CO$_{147}$

LDOS vs. Energy/eV
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

(m) Ag-M-Dh$_{13}$

(n) Cu-M-Dh$_{13}$

(o) Pt-M-Dh$_{13}$

(p) Rh-M-Dh$_{13}$

(q) Ag-M-Dh$_{49}$

(r) Cu-M-Dh$_{49}$
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

Figure 6-1 LDOS of $d$-band shown for (a-d) CO$_{13}$, (e-h) CO$_{55}$, (i-l) CO$_{147}$, (m-p) M-Dh$_{13}$, (q-t) M-Dh$_{49}$, and (u-x) M-Dh$_{75}$ structures. The dash dot, dash, solid, short dash, and short dot indicate the excess charge states including (+2), (+1), (0), (-1), and (-2), respectively. The $E_f$ is considered to be 0 eV.

Moreover, the interaction between the energy state of $d$-bands and $s$-bands for the excess charge state of (-1) are stronger than the other excess charge states, and induce strong $s$-$d$ hybridization, which is consistent with previously reported results.$^{88, 192-195, 205, 214}$ For instance, the PES measurement on anionic Cu clusters of up to 18 atoms observed multiplet splitting by the spin−spin interaction of the electrons in the nanocluster and $s$−$d$ hybridization for orbitals located close to the 3$d$-band.$^{214}$ Hybridization between $d$-band and $s$-band were also reported for the cationic, neutral, and anionic Cu clusters,$^{205}$ anionic Pt clusters,$^{192}$ cationic Rh clusters,$^{193}$ anionic Ag and Cu clusters,$^{194}$ neutral Cu clusters,$^{88}$ as well as neutral Ag clusters.$^{195}$

Furthermore, the entrapped states were observed in the Pt and Rh nanoclusters with CO$_{55}$ structures and all metallic nanoclusters with CO$_{147}$ and M-Dh$_{75}$ structures with excess charge states from (+2) to (-2) (see Figure 6-1). These findings are consistent with the XPDS observations by Zheng et al.$^{171}$ on Rh (111) and Rh adatoms, in which double valleys are related to the bulk and atoms, with CN of 3-4. The observed double
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

Valleys can be explained by considering the coupling of the polarization and quantum entrapment, which causes the loss of the initially trapped surface charge at under-coordinated atoms with CN values of 3-4. The extent of the polarization of the unpaired electrons can be enhanced by decreasing the atomic CN, which is mostly due to the bond length contraction and densification of the core and bonding charges. Consequently, the second valley demonstrates that the polarization becomes dominant for less-coordinated atoms, providing a stronger screening effect. The polarized charge screened the local crystal potential, resulting in the corresponding CLS. In addition, Sun et al.\textsuperscript{39} predicted the adatoms-induced quantum entrapment and charge polarization at Pt and Rh surface by photoelectron residual spectroscopy (PRS), which suggested that the electroaffinity increases by the quantum entrapment, whereas the polarization increased adversely and considered Pt and Rh adatom as an acceptor and a donor in the catalytic reactions, respectively. A catalyst reaction was reported by Nie et al.,\textsuperscript{215} which has enabled the finding of the similarity of the valence band of tungsten edges to that of Rh adatoms and Ag/Pd alloy and suggested that W under-coordinated atoms could be a suitable candidate for replacing the costly Rh adatoms and Ag/Pd alloy as a cheaper, richer, and efficient donor-type catalyst for CO and NO oxidation applications.\textsuperscript{10, 32, 39}

Finally, the valence LDOS polarization of metallic nanoclusters is consistent with the experimental findings, including the under-coordinated-induced valence
polarization for Rh(111) and Rh adatoms observed by XPDS, the DOS shift toward the Fermi level with the reduction of the size for Pt nanoparticles on pristine CNTs, the valence LDOS polarization observed by STM/S measurements on silver clusters, chains on the Ag(111) substrate, single copper on Cu(111) adatoms, Pt clusters on highly oriented pyrolytic graphite, and Rh on TiO$_2$(110)-(1x2). Moreover, an upward shift of $d$-band was observed by UPS measurements for the anionic copper cluster with 1–411 atoms and the anionic silver cluster with 1–60 atoms with the decrease in size of the nanoparticles. Furthermore, polarization of LDOS of the neutral copper monomers, dimers, and trimmers under positive bias and the unoccupied states of DOS of the neutral silver monomers, quasi-dimers, and dimer were also reported. The consistency between our calculations and experimental observations confirmed that quantum entrapment and valence charge polarization as BLOS predictions consider the effect of excess charge states.

6.3.4 Magnetization

The difference between the occupied majority and minority spin band is called the magnetic moment, which is related to the ferromagnetic exchange splitting between the bands. Magnetic behavior of a metal $d$-band in metallic nanoclusters originates from spin-up ($\alpha$-spin states) and spin-down ($\beta$-spin states) states. The occupied and unoccupied electrons by the spin-up and spin-down are called the majority and minority
spins of $d$-band below and above of the Fermi energy level, respectively. The majority and minority spins correspond to the positive and negative values, respectively, and the Fermi level is set at 0 eV. We simulated the eigenvalue spectra by numerically integrating the DOS for spin-up and spin-down to determine the origin of the magnetic behaviors of $M_N$ metallic nanoclusters with positive, neutral, and negative excess charges.

Figure 6-2 shows the PDOS of $M_N$ metallic nanoclusters with COh and M-Dh structures with excess charge states of (+1) and (+2). The detailed results of difference between spin-up and spin-down states in PDOS of 4$d$-Ag, 3$d$-Cu, 5$d$-Pt, and 4$d$-Rh for COh and M-Dh structures are given in Figure 6-3. The PDOS distributions of sin-up and spin–down states split near the Fermi level in even (positive/negative) excess charge states for Ag and Cu nanoclusters with doublet ground state, Pt nanoclusters with triplet ground state, and Rh nanoclusters with quartet ground state in both COh and M-Dh structures. However, odd (positive/negative) excess charge states show no split for the singlet ground state of Ag and Cu nanoclusters, whereas splits are detected near the Fermi level for the doublet ground state of Pt nanoclusters and the triplet ground state of Rh nanoclusters in both COh and M-Dh structures. These behaviors originate from the atomic electronic structure of Ag, Cu, Pt, and Rh, which consider $d$-band as Ag ($4d^{10} 5s^1$), Cu ($3d^{10} 4s^1$), Pt ($5d^8 6s^1$), and Rh ($4d^8 5s^1$). Therefore, the magnetic moment of
$M_N$ metallic nanoclusters is determined by the exchange correlation of electrons forming the ordered spin arrangement of electrons.
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

(e) PDOS (1/eV) for Ag-COH_{55} +1e and Ag-COH_{55} +2e.

(f) PDOS (1/eV) for Cu-COH_{55} +1e and Cu-COH_{55} +2e.

(g) PDOS (1/eV) for Pt-COH_{55} +1e and Pt-COH_{55} +2e.

(h) PDOS (1/eV) for Rh-COH_{55} +1e and Rh-COH_{55} +2e.

(i) PDOS (1/eV) for Ag-COH_{147} +1e and Ag-COH_{147} +2e.

(j) PDOS (1/eV) for Cu-COH_{147} +1e and Cu-COH_{147} +2e.
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

(k) PDOS (1/eV) vs. E(eV) for Pt-COH$_{147}$ +1e and Pt-COH$_{147}$ +2e.

(l) PDOS (1/eV) vs. E(eV) for Rh-COH$_{147}$ +1e and Rh-COH$_{147}$ +2e.

(m) PDOS (1/eV) vs. E(eV) for Ag-M-Dh$_{13}$ +1e and Ag-M-Dh$_{13}$ +2e.

(n) PDOS (1/eV) vs. E(eV) for Cu-M-Dh$_{13}$ +1e and Cu-M-Dh$_{13}$ +2e.

(o) PDOS (1/eV) vs. E(eV) for Pt-M-Dh$_{13}$ +1e and Pt-M-Dh$_{13}$ +2e.

(p) PDOS (1/eV) vs. E(eV) for Rh-M-Dh$_{13}$ +1e and Rh-M-Dh$_{13}$ +2e.
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

(q) PDOS (1/eV) vs. E(eV) for Ag-M-Dh_{49}^{+1e} and Ag-M-Dh_{49}^{+2e}

(r) PDOS (1/eV) vs. E(eV) for Cu-M-Dh_{49}^{+1e} and Cu-M-Dh_{49}^{+2e}

(s) PDOS (1/eV) vs. E(eV) for Pt-M-Dh_{49}^{+1e} and Pt-M-Dh_{49}^{+2e}

(t) PDOS (1/eV) vs. E(eV) for Rh-M-Dh_{49}^{+1e} and Rh-M-Dh_{49}^{+2e}

(u) PDOS (1/eV) vs. E(eV) for Ag-M-Dh_{75}^{+1e} and Ag-M-Dh_{75}^{+2e}

(v) PDOS (1/eV) vs. E(eV) for Cu-M-Dh_{75}^{+1e} and Cu-M-Dh_{75}^{+2e}
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

Figure 6-2 Spin-polarized PDOS of 4d-Ag, 3d-Cu, 5d-Pt, and 4d-Rh for (a-d) COh\textsubscript{13}, (e-h) COh\textsubscript{55}, (i-l) COh\textsubscript{147}, (m-p) M-Dh\textsubscript{13}, (q-t) M-Dh\textsubscript{49}, and (u-z) M-Dh\textsubscript{75} structures. The excess charge states (+1) and (+2) were considered in the singlet and double states for Ag and Cu nanoclusters, the doublet and triplet states for Pt nanoclusters, and the triplet and quartet states for Rh nanoclusters. The blue and red indicate the spin-up ($\alpha$) and spin-down ($\beta$) configurations. The $E_f$ is set at 0 eV.

The energy gap between the HOMO and the LUMO of $\alpha$ and $\beta$ spin states was calculated by DFT for $M_N$ metallic nanoclusters (see Table 6-3). The HOMO and LUMO states are related to the anti-bonding and bonding. Both COh and M-Dh structures show that the neutral and positive excess charge states of $M_N$ metallic nanoclusters exhibited the gap between $\alpha$ and $\beta$ spin states, whereas the odd excess charge states showed no gaps for Ag and Cu nanoclusters and a gap for Pt and Rh.
nanoclusters. The magnetic behavior is in good agreement with previous theoretical calculations and experimental results, including those of neutral Ag clusters,\textsuperscript{216} Cu on CeO$_2$,\textsuperscript{217} Pt clusters,\textsuperscript{185} and Rh nanoparticles,\textsuperscript{9} as well as cationic Rh nanoparticles and clusters of up to 12 atoms.\textsuperscript{218} 219 Therefore, the magnetic behaviors of M$_N$ metallic nanoclusters can be explained by considering the odd and even excess charge states.
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

\[ \text{PDOS (1/eV)} \]

\[ \text{E(eV)} \]

\[ \text{PDOS (1/eV)} \]

\[ \text{E(eV)} \]

\[ \text{PDOS (1/eV)} \]

\[ \text{E(eV)} \]

\[ \text{PDOS (1/eV)} \]

\[ \text{E(eV)} \]

\[ \text{PDOS (1/eV)} \]

\[ \text{E(eV)} \]

\[ \text{PDOS (1/eV)} \]

\[ \text{E(eV)} \]
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

\( q \)

\( r \)

\( s \)

\( t \)

\( u \)

\( v \)
Figure 6-3 Difference between spin-up and spin-down states in PDOS of 4d-Ag, 3d-Cu, 5d-Pt, and 4d-Rh for (a-d) COh\textsubscript{13}, (e-h) COh\textsubscript{55}, (i-l) COh\textsubscript{147}, (m-p) M-Dh\textsubscript{13}, (q-t) M-Dh\textsubscript{49}, and (u-x) M-Dh\textsubscript{75} structures. The excess charge states (+1) and (+2) were considered in the singlet and double states for Ag and Cu nanoclusters, the doublet and triplet states for Pt nanoclusters, and the triplet and quartet states for Rh nanoclusters. The blue and red indicate the spin-up (α) and spin-down (β) configurations. The E\textsubscript{f} is set at 0 eV.

Table 6-3 Calculated gaps between spin-up and spin-down states of metallic nanoclusters with positive, neutral, and negative excess charge states. The magnetic behavior of d-band metallic nanoclusters was observed in the positive (negative) even excess charges for all metallic nanoclusters and the odd (positive/negative) excess
Chapter 6: Quantum Entrapment and Valence Polarization of Cationic, Neutral, and Anionic Metallic Nanoclusters

charges for Pt and Rh nanoclusters, whereas no magnetic behavior was detected in the odd (positive/negative) excess charges for Ag and Cu nanoclusters.

<table>
<thead>
<tr>
<th>Excess charge states</th>
<th>Gap up-spin Alpha (eV)</th>
<th>Gap down-spin Beta (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
<td>Cu</td>
</tr>
<tr>
<td>COh₁₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+2</td>
<td>0.725</td>
<td>0.639</td>
</tr>
<tr>
<td>+1</td>
<td>0.702</td>
<td>0.610</td>
</tr>
<tr>
<td>0</td>
<td>0.695</td>
<td>0.611</td>
</tr>
<tr>
<td>-1</td>
<td>0.687</td>
<td>0.598</td>
</tr>
<tr>
<td>-2</td>
<td>0.689</td>
<td>0.598</td>
</tr>
<tr>
<td>+2</td>
<td>0.386</td>
<td>0.331</td>
</tr>
<tr>
<td>+1</td>
<td>0.383</td>
<td>0.326</td>
</tr>
<tr>
<td>COh₅₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.318</td>
<td>0.320</td>
</tr>
<tr>
<td>-1</td>
<td>0.380</td>
<td>0.310</td>
</tr>
<tr>
<td>-2</td>
<td>0.357</td>
<td>0.263</td>
</tr>
<tr>
<td>+2</td>
<td>0.251</td>
<td>0.194</td>
</tr>
<tr>
<td>+1</td>
<td>0.247</td>
<td>0.191</td>
</tr>
<tr>
<td>COh₁₄₇</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.255</td>
<td>0.174</td>
</tr>
<tr>
<td>-1</td>
<td>0.243</td>
<td>0.187</td>
</tr>
<tr>
<td>-2</td>
<td>0.243</td>
<td>0.185</td>
</tr>
<tr>
<td>+2</td>
<td>0.366</td>
<td>0.384</td>
</tr>
<tr>
<td>+1</td>
<td>0.123</td>
<td>0.342</td>
</tr>
<tr>
<td>M-Dh₁₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.301</td>
<td>0.317</td>
</tr>
<tr>
<td>-1</td>
<td>0.256</td>
<td>0.295</td>
</tr>
<tr>
<td>-2</td>
<td>0.572</td>
<td>0.487</td>
</tr>
<tr>
<td>+2</td>
<td>0.118</td>
<td>0.185</td>
</tr>
<tr>
<td>+1</td>
<td>0.114</td>
<td>0.185</td>
</tr>
<tr>
<td>M-Dh₄₉</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.134</td>
<td>0.171</td>
</tr>
<tr>
<td>-1</td>
<td>0.138</td>
<td>0.159</td>
</tr>
<tr>
<td>-2</td>
<td>0.102</td>
<td>0.118</td>
</tr>
<tr>
<td>+2</td>
<td>0.003</td>
<td>0.189</td>
</tr>
<tr>
<td>+1</td>
<td>0.015</td>
<td>0.193</td>
</tr>
<tr>
<td>M-Dh₇₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.128</td>
<td>0.232</td>
</tr>
<tr>
<td>-1</td>
<td>0.131</td>
<td>0.221</td>
</tr>
<tr>
<td>-2</td>
<td>0.122</td>
<td>0.239</td>
</tr>
</tbody>
</table>
6.4 Summary

Consistency between DFT calculations and experimental results, including EXAFS, STM/S, XPDS, PES, PRS, and UPS measurements, confirmed our BOLS-NEP predictions for the properties of cationic, neutral, and anionic $\text{M}_N$ metallic nanoclusters. The studies properties include bond length relaxation, charge densification, quantum entrapment, valence electron polarization, and magnetic moment. Magnetization can be explained by considering appropriate excess surface charges. The under-coordinated atoms induce the local bond contraction, charge densification, valence electron polarization, as well as magnetization and emergence of extraordinary properties of metallic nanoclusters depending on size and new properties. Our findings will help understand the intriguing properties of metallic nanoclusters of charge excess states, including catalytic and magnetization behaviors.
Chapter 7  Conclusions and Recommendations

7.1 Achievements

The BOLS-NEP theory, in the form of quantum calculations, has been modified in this research to explain size dependency of material properties and under-coordination. The effect of adatoms, defects, surface, and size of nanostructures on electronic and magnetic properties were incorporated as well. The surface effect plays a core role in demonstrating the size dependency of the nanostructures, whereas the interior core remains within the bulk behavior. Moreover, the polarization of non-bonding electrons results in the emergence of properties, such as transformation from conduction to insulation, catalytic enhancement, nanoplasmonics, and magnetisms at nanoscale systems. The results obtained using BOLS-NEP theory, and the combination between BOLS-TB and DFT calculations for cationic, neutral, and anionic metallic nanoclusters indicate that:

(1) The bond relaxation between atoms with fewer neighbors than the bulk components play an important role in relation to defects, surfaces, and various shapes of nanostructures.

(2) The difference between the nanostructures and its bulk counterparts was elucidated by the BOLS-NEP notation.

(3) The shorter bonds between atomic under-coordination increase the local density of the bonding electrons and binding energy, whereas the stronger
resulting bonds deepen the interatomic potential, resulting in quantum entrapment for under-coordinated systems.

(4) The atomic under-coordination of cationic, neutral, and anionic metallic nanoclusters induced local strain, quantum entrapments, charge densification, and valence charge polarization.

(5) The behavior of nanostructures was determined by the interaction between atomic under-coordination in the surface and the ratio of such atomic under-coordination with the BOLS correlation, which demonstrated the unusual performance of defects and surfaces, as well as the magnetic, electronic, and photonic properties.

(6) The polarization of non-bonding electrons resulted in difference in intrinsic properties of nanostructures and their bulk, such as surface plasmon response, and magnetization of cationic, neutral, and anionic metallic nanoclusters.

7.2 Limitations

Our BOLS correlation theory needs improvement in terms of analyzing the physical properties by involving other high-order effects. By considering atom-by-atom in a specific crystal structures, the theoretical curves at the lower end of the size limit should display oscillation features with “magic number” of atoms based on the surface-to-volume ratio. Therefore, utilizing the smooth function for the surface-to-volume ratio in the current approach is sufficient, because the nature, trend, origins, and limitations of
size-induced changes and the factors controlling the property changes should be given particular attention. Further studies may include mixed-elements and mixed-phases to obtain more precise predictions.

Although our BOLS-TB theory can calculate CLS certain limited properties remain, including the influence of trace impurities. If all the samples were prepared and measured under similar conditions, and the relative change of the quantities is utilized, then artifacts caused by impurities can be minimized, and the results can be considered purely size dependent.

Finally, our BOLS theory has not been developed to calculate the fluctuations of mechanical and thermal properties. Additional development of force field from the total energy will render the widespread usage of BOLS-TB.

7.3 Recommendations for Future Work

Current progress of BOLS-NEP theory and DFT calculations for metallic nanoclusters around the under-coordinated sites paves the way for the detailed study of nanomaterials.

For example, the dependency of size and the composition of bimetallic nanoclusters with core-shell structures are fascinating because of their unique chemical and physical properties, such as optical, magnetic, and catalytic properties. Geometrical optimization is crucial toward the investigation of catalysts, fuel cells, and optical materials for practical applications. Therefore, investigation of the anomalies of bimetallic nanoclusters by BOLS-NEP correlation theory is recommended.
Furthermore, the effect of size for small and large nanoclusters may be calculated with CO, O$_2$, and NO$_2$+CO adsorption$^{25,222,223}$ using BOLS-NEP correlation theory for catalytic applications of nanomaterials.
Author’s Publications

1. Shideh Ahmadi, Xi Zhang, Yinyan Gong, Chin Hua Chia and Chang Q. Sun, Skin-resolved local bond contraction, core electron entrapment, and valence charge polarization of Ag and Cu nanoclusters, Phys. Chem. Chem. Phys., 2014 (16), 8940-8948. (Chapter 4)

2. Shideh Ahmadi, Xi Zhang, Yinyan Gong, and Chang Q. Sun, Atomic Undercoordination Induced Catalytic and Magnetic Fascinations of Pt and Rh nanoclusters, Phys. Chem. Chem. Phys., 2014 (16), 20537-20547. (Chapter 5)


4. Shideh Ahmadi, Xi Zhang, Yinyan Gong, and Chang Q. Sun, Chemisorption of NO and O2 on M13 nanoclusters (M = Ag, Cu, Pt, and Rh). (Preparation for submission)

5. Shideh Ahmadi, Xi Zhang, Yinyan Gong, and Chang Q. Sun, Effect of atomic under-coordination on the properties of Ag and Cu nanoclusters, Proceedings of SPIE, 2014 (9165), 91650S-1-91650S-9. (Chapter 4)

6. Shideh Ahmadi, Xi Zhang, Yinyan Gong, and Chang Q. Sun, Local densification, quantum entrapment, and valence charge polarization at the surfaces of metallic nanoclusters, Hands-on workshop density-functional theory and beyond: First-
principles simulations of molecules and materials, Harnack House of the Max Planck Society, Berlin, Germany, July 13 - 23, 2015. (Chapter 4 and 5)
References


References


References


References


References


201. A. S. Chaves, G. G. Rondina, M. J. Piotrowski, P. Tereshchuk, and J. L. F. Da Silva, The role of charge states in the atomic structure of Cu$_n$ and Pt$_n$ ($n = 2$–14


207. G. Guzmán-Ramírez, F. Aguilera-Granja, and J. Robles, DFT study of the fragmentation channels and electronic properties of Cu$_n$$^\nu$ ($\nu = \pm 1,0,2$; $n = 3$-$13$) clusters. *Eur. Phys. J. D*, **57** (3), 335-342 (2010).


References


