Quantum entrapment and valence charge polarization in Ag, Cu, Pt, and Rh nanoclusters

Ahmadi, Shideh

2016

Ahmadi, S. (2016). Quantum entrapment and valence charge polarization in Ag, Cu, Pt, and Rh nanoclusters. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/69223>

<https://doi.org/10.32657/10356/69223>

**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 DMol ³	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_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. ^{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).	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).	23
Figure 2-5 (a) Progress of the ν th atomic energy level from $E_\nu(0)$ to the ν th band ΔE_ν ($z_b = 12$) 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 ν 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 _N and Rh _N nanoclusters (N = 13-147 atoms). E _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 (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.	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 (α) and spin-down (β) states in PDOS. The blue and red indicate the spin-up (α) and spin-down (β) configurations. The E _f is set at 0 eV.	90
Figure 6-1 LDOS of d-band shown 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 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. .	109
Figure 6-2 Spin-polarized PDOS of 4d-Ag, 3d-Cu, 5d-Pt, and 4d-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-z) 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 (α) and spin-down (β) configurations. The E_f is set at 0 eV..... 117

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) COh₁₃, (e-h) COh₅₅, (i-l) COh₁₄₇, (m-p) M-Dh₁₃, (q-t) M-Dh₄₉, and (u-x) M-Dh₇₅ 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_f is set at 0 eV..... 122

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 (μ), and charge transfer (e) for silver and copper nanoclusters. .	55
Table 4-2 $E_v(0)$ and $\Delta E_v(\infty)$ obtained from XPS $E_v(\infty)$ 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 (μ), and charge transfer (e).....	73
Table 5-2 BOLS derived $E_v(0)$ and $\Delta E_v(\infty)$ for Pt and Rh nanoparticles	75
Table 5-3 Calculated gaps for the spin-up (α) and spin-down (β) of Pt and Rh nanoclusters	92
Table 6-1 Calculation of the M-M bond length d_i (Å) and charge of shell (e) at different position of 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 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 <i>d</i> -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.....	122
-----------	---	-----

Nomenclatures

μ	Magnetic moment
γ_i	Surface-to-volume ratio
τ	Shape factor of surface-to-volume ratio
b	Bulk
BOLS	Bond-order-length-strength correlation
C_z	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

MCNTs	Multiwall carbon nanotubes
MIN	Minimal basis set
MD	Molecular dynamics method
M-Dh	Marks decahedral structure
NEP	Non-bonding electron polarization
PDOS	Partial density of states
PES	Photoelectron spectroscopy
PL	Photoluminescence
PRS	photoelectron residual spectroscopy
PWC	Perdew-Wang function
$Q(K)$	Measurable quantity of a nanosolid
$q(z)$	Local detectable quantity at atomic sites with CN of z
QC	Quantum confinement theory
SCF	Self-consistent-field
SOC	Spin-orbit coupling
STM/S	Scanning tunneling microscopy/spectroscopy
TB	Tight-binding method

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,^{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.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.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.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) correlation²⁸ has been used to refine the non-bonding electron polarization (NEP) theory,^{3, 29, 30} to solve associated problems,^{31, 32} including superfluidity in carbon nanotube channels,³³ superlubricity in dry sliding,^{31, 34} and supersolidity of ⁴He with superelasticity and superfluidity.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.^{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:

- 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:

- 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,⁵ Sun C. Q. investigated the nanostructure dependency upon their size and its association to surfaces and defects.³ By developing the Goldschmidt and Pauling premise^{34, 38} 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.³⁻⁵ 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,³³ Sun C. Q. (2007)⁴ suggested and confirmed the NEP hypothesis,³¹ 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).

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 Pauling³⁴ and Goldschmidt's notation,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.³ The size of the nanomaterials is dependent on the atomic under-coordination and strong interaction between atoms.⁴

2.1.1.2 BOLS notation

The physical properties of atomic under-coordination at sites differ from the bulk.^{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.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, $z_i E_i$, 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. Feibelman⁴⁰ 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:²⁻⁵

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

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.⁴¹ and Mason,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

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

$$\begin{aligned} z_1 &= \begin{cases} 4(1 - 0.75/K) & \text{(Curved - surface; First Shell)} \\ 4 & \text{(Flat - surface)} \end{cases} \\ z_2 &= z_1 + 2 & \text{(Second Shell)} \\ z_3 &= 12 & \text{(Thirs Shell : Bulk)} \end{aligned}$$

(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 .

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:³⁴

$$r(1) - r(v/z_0) = 0.030 \log(v/z_0) \quad (nm) \quad (2-3)$$

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)

$$r(1) - r(x/8) = 0.030 \log(x/8) \quad (2-4)$$

and for the next-nearest neighbors,

$$r(1) - r[(4-x)/6] = 0.030 \log[(4-x)/6] \quad (2-5)$$

Chapter 2: Computational Approaches

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 $r(1) = 0.13435$ nm, which contracts by 0.00985 nm. The bond number v/z is $4/12$ in the hcp of CN = 12, and the corresponding bond length is $r(4/12) = 0.13435 - 0.03 \log(4/12) = 0.1486$ nm. From Eq. (2-3), the bond length of an atom with a reduced CN(z) can be denoted as follows:

$$r(v/z) = r(v/z_0) + 0.030 \log(z/z_0) \quad (2-6)$$

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

$$C(z) = 1 + 0.060 \log(z/z_0) / d_b(v/z_0) \quad (2-7)$$

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 Feibelman'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.

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 trapping 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.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:

$$Q(K) = Q(\infty) + \sum_{i \leq 3} N_i (q_i - q_b) = Nq_b + \sum_{i \leq 3} N_i (q_i - q_b)$$

(2-8)

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 $q_i(z_i, m, d_i, E_i)$, 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

Chapter 2: Computational Approaches

potential well of depth. The localized and depressed potential well will govern the transport processes.

Table 2-1 Related quantities with bond length

Quantity	q_i	$\Delta q_i / q_b$
Elastic module (Y_i)	$\propto d_i^{-\tau} E_i$	$C_i^{-(m+\tau)} - 1$
CLS (ΔE_v)	$\propto z_i E_i$	$C_i^{-m} - 1$
Melting point (T_m)	$\propto z_i E_i$	$z_{ib} C_i^{-m} - 1$
Strain (ϵ)	-	$C_i - 1$
Raman shift ($\Delta\omega$)	$\propto \frac{z_i}{d_i} \left(\frac{E_i}{\mu} \right)^{1/2}$	$z_{ib} C_i^{-(m/2)+1} - 1$

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

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

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

$$\Delta_q = \sum_{i \leq 3} \gamma_i \left(\frac{\Delta q_i}{q_b} \right)$$

$$\begin{cases} \Delta_q = \sum_{i \leq 3} \frac{N_i (q_i - q_b)}{N q_b} = \sum_{i \leq 3} \gamma_i \frac{\Delta q_i}{q_b} = \sum_{i \leq 3} \gamma_i (C_i - 1) & \text{(Strain)} \\ \gamma_i = \frac{N_i}{N} = \frac{\tau C_i}{K} \end{cases} \quad (2-9)$$

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; γ_i is surface-to-volume ratio; and N_i is the atom numbers of the i th atomic layer. τ 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

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.⁴⁷ 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.³⁸

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 ($3d^{10} 4s^1$), Pt ($5d^9 6s^1$), 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 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).

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:

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

$$\begin{cases} \phi_v(r) \propto \sin^2\left(\frac{2n\pi r}{d}\right) \\ E_v(n) = \frac{2(n\pi\hbar)^2}{(m_e d^2)} \end{cases} \quad n = 1, 2, 3, \dots$$

(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,⁴⁸ the Hamiltonian and wave function for an electron in the ν th energy level inside solid are explained by:

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}' = -\frac{\hbar^2 \nabla^2}{2m} + V_{atom}(r) + V_{cry}(r + R) \\ \phi_{\nu,i}(r) &\equiv |\nu, i\rangle \exp(ikr) \approx |\nu, i\rangle\end{aligned}\tag{2-11}$$

The Hamiltonian of an isolated atom, $\hat{H}_0$, contains the kinetic energy and the intra-atomic potential, $V_{atom}(r)$, whereas $\hat{H}'$ is the crystal potential, $V_{crys}(r) = V_{crys}(r + R)$. 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.⁴⁸ 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:

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

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

$$E_\nu(z_b) = E_\nu(0) + (\alpha_\nu + z_b \beta_\nu) + 2z_b \beta_\nu \Phi_\nu(k, R)$$

with,

$$\begin{cases} E_v(0) = -\langle \nu, i | \hat{H}_0 | \nu, i \rangle & \text{(Atomic Core Level)} \\ \alpha_v = -\langle \nu, i | H' | \nu, i \rangle \propto E_b & \text{(Exchange Integral)} \\ \beta_v = -\langle \nu, i | H' | \nu, j \rangle \propto E_b & \text{(Overlap Integral)} \end{cases} \quad (2-12)$$

$E_v(0)$ is the ν 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 $\Delta E_v(z_b) = E_v(z_b) - E_v(0) = \alpha_v + z_b \beta_v$ related to band broadening. The exchange integral (α_v) and overlap integral (β_v) 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 10^0 eV to 10^{-1} eV and E_{vW} 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, $2z_b \beta_v \Phi_v(k, R) \sim \sin^2(kR/2)$, 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 ν th atomic energy level from $E_v(0)$ to the ν th band ΔE_v ($z_b = 12$) with the shift of $\Delta E_v(z_b) = \alpha_v + z_b\beta_v$ and a width of $E_{vW} = 2z_b\beta_v\Phi_v(k, R)$ on bulk. Amounts of energy shift and band expansion is dependent on the cohesive energy per bond at equilibrium and the quantum number ν 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:

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

$$\cong \frac{n}{2} [N_b^2 v(d) + nV(K)]$$

(2-13)

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:

$$\begin{aligned} V_{cry}(r, n, N_b) &= \frac{nN_b}{2} \left[N_i v(d_i) + (N_b - N_i) v(d) + \frac{n}{N_b} V(K) \right] \\ &= \frac{nN_b^2 v(d)}{2} \left[\frac{N_i v(d_i)}{N_b v(d)} + \left(1 - \frac{N_i}{N_b}\right) + \frac{nV(K)}{N_b^2 v(d)} \right] \\ &= V_{cry}(d, n, N_b) \left\{ 1 + \gamma_i \left(\frac{v(d_i)}{v(d)} - 1 \right) + \delta'_k(K) \right\} \end{aligned}$$

$$\frac{\Delta V_{cry}(N_b)}{V_{cry}(\infty)} = \sum_{i \leq 3} \gamma_i \frac{\Delta v}{v} + \delta'_k(K) = \sum_{i \leq 3} \gamma_i (C_i^{-m} - 1) + \delta'_k(K)$$

$$\delta'_{kl} = \frac{nV(R)}{N_b^2 v(d)}$$

(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, $v(d_i)$, 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, $\delta_k(K)$, which is negligible when the particle size is considerably large.

The total potential in Eq. (2-11) turns into $V(\Delta_H) = V_{atom}(r) + V_{cry}(r)[1 + \Delta_H]$. In connection the corresponding Bloch wave functions, the atomic trapping potential, $V_{atom}(r)$, describes the discrete core-level energies of an isolated atom, $E_v(0)$. The crystal binding $V_{cry}(r)$ defines the band gap and the CLS from the original position $\Delta E_v(\infty) = E_v(\infty) - E_v(0)$. The dimensionless, Δ_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 $E_v(K)$, with following scaling relation:

$$\frac{\Delta E_v(K) - \Delta E_v(\infty)}{\Delta E_{vy}(\infty)} = \Delta_H \quad (2-15)$$

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 $\Delta E_v(z_b)$. The perturbation (Δ_H) will positively or negatively shift the bulk counterpart as entrapment (T, shift away from E_f) or polarization (P, shift toward E_f) 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_i) atom variation or polarization:

$$\hat{H}' = V_{cry}(r)(1 + \Delta_H)$$

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

where,

$$\begin{cases} E_v(0) = -\langle \nu, i | \hat{H}_0 | \nu, i \rangle & \text{(Atomic Core Level)} \\ \alpha_{xv} = -\langle \nu, i | H' | \nu, i \rangle \propto E_b (1 + \Delta_H) \propto E_x & \text{(Exchange Integral)} \\ \beta_{xv} = -\langle \nu, i | H' | \nu, j \rangle \propto E_b (1 + \Delta_H) \propto E_x & \text{(Overlap Integral)} \end{cases} \quad (2-16)$$

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:

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

$$\begin{cases} E_v(\Delta_H) = E_v(0) + [E_v(\infty) - E_v(0)](1 + \Delta_H) \\ or \\ E_v(\Delta_H) = E_v(\infty) + [E_v(\infty) - E_v(0)]\Delta_H \end{cases}$$

(2-17)

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

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

(2-18)

where Δ_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

Chapter 2: Computational Approaches

correlation equal to the theoretical illustration, the following expression is obtained from Eq. (2-17):

$$E_v(K) = \begin{cases} E_v(\infty) + [E_v(\infty) - E_v(0)]\tau\Delta'_H K^{-1} & \text{(BOLS theory)} \\ A + BK^{-1} & \text{(Measurement)} \end{cases} \quad (2-19)$$

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

$$\begin{cases} A = E_v(\infty) \\ B = [E_v(\infty) - E_v(0)]\tau\Delta'_H \end{cases} \quad (2-20)$$

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

$$\begin{cases} E_v(0) = A - \frac{B}{\tau\Delta'_H} & \text{(Atomic energy level)} \\ \Delta E_v(\infty) = \frac{B}{\tau\Delta'_H} & \text{(Bulk shift)} \end{cases} \quad (2-21)$$

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

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

eV	Au-4f ²⁴	Ag-3d ⁴⁹	Cu-2p ²⁴	Cu-3d ²⁴	Rh-3d ⁵⁰	Pt-4f ³⁹
$E_v(0)$	81.15	363.03	931.00	5.11	302.16	67.21
$\Delta E_v(\infty)$	2.87	4.63	1.70	2.12	4.37	3.28

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:

$$\hat{H}\Psi(r, R) = E\Psi(r, R) \quad (2-22)$$

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 .⁵¹ 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:

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} = \hat{T}_e + \hat{T}_n + \hat{V}_{e-e} + \hat{V}_{n-n} + \hat{V}_{e-n} \\ \hat{H} &= -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{j=1}^M \frac{1}{m_j} \nabla_j^2 + \sum_{i=1}^N \sum_{j,i}^N \frac{1}{|r_i - r_j|} + \sum_{i=1}^M \sum_{j,i}^M \frac{Z_i Z_j}{|R_i - R_j|} - \sum_{i=1}^N \sum_{j=1}^M \frac{Z_j}{|r_i - R_j|}\end{aligned}\tag{2-23}$$

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, $\Psi_e(\mathbf{r})$, can be rewritten as follows:

$$\begin{aligned}\hat{H}_e \Psi_e(\mathbf{r}) &= E_e \Psi_e(\mathbf{r}) \\ \hat{H}_e &= \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-n} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j,i}^N \frac{1}{|r_i - r_j|} - \sum_{i=1}^N \sum_{j=1}^M \frac{Z_j}{|r_i - R_j|}\end{aligned}\tag{2-24}$$

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,⁵⁵ coupled cluster methods,⁵⁶ and multi self-consistent field methods.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.⁵⁸⁻⁶⁰

2.3.2 Thomas-Fermi Model

Electron density (n) is defined by electron numbers N with spatial coordinates ($\mathbf{r}_i$) as follows:

$$\begin{cases} n(\mathbf{r}) = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ \int n(\mathbf{r}) d\mathbf{r} = N \end{cases} \quad (2-25)$$

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, Dirac⁶¹ 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,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

$$E_0 = E[n_0] = T_e[n_0] + E_{e-e}[n_0] + E_{e-n}[n_0] = E_{e-n}[n_0] + F_{HK}[n_0] \quad (2-26)$$

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 $E_H[n]$, consisting of the self-interaction correction and exchange-correlation in the following form:

$$E_H[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (2-27)$$

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.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:

$$T_S = -\frac{1}{2} \sum_i \phi_i^*(\mathbf{r}) \nabla_i^2 \phi_i(\mathbf{r}) \quad (2-28)$$

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

$$\begin{cases} f_{KS} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \\ f_{KS} = -\frac{1}{2} \nabla^2 + V_{ext}[n] + V_H[n] + V_{XC}[n] \end{cases} \quad (2-29)$$

where the external potential, the classic Hartree potential, and exchange-correlation potential is $V_{ext}[n]$, $V_H[n]$, and $V_{XC}[n]$, respectively. The eigenvalues (ε_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:

$$n(\mathbf{r}) = \sum_{i=1}^N \phi_i^*(\mathbf{r}) \cdot \phi_i(\mathbf{r}) \cdot f_i \quad (2-30)$$

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.

$$V_{xc}[n(\mathbf{r})] = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (2-31)$$

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

$$F_{HK} = T_s + E_H + E_{xc} \quad (2-32)$$

To solve the Kohn-Sham equation, the exchange-correlation function, which allows for the calculating of the sate 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 $\mathbf{r}$:

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) d\mathbf{r} \quad (2-33)$$

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

$$E_X^{LDA}[n] = \left(-\frac{3}{4}\right) \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int n(\mathbf{r})^{\frac{4}{3}} d\mathbf{r} \quad (2-34)$$

The correlation part is calculated by the Monte Carlo modeling⁶⁴ and DFT calculations with LDA functions, such as Vosko-Wilk-Nusair⁶⁵ and Perdew-Wang (PWC).⁶⁶ 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.⁶⁷ 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.⁶⁸ 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.⁶⁹ The spin-polarized LDA is called the local-spin-density approximation (LSDA), and the exchange-correlation functional is presented as follows:

$$E_{XC}^{LSDA}[n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{XC}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r})) d\mathbf{r} \quad (2-35)$$

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.^{70, 71} The DMol code⁷⁰ 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 DMol³.⁷¹

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:

$$\begin{cases} \phi_i(\mathbf{r}) = \sum_{j=1}^N c_{ij} \chi_j(\mathbf{r}) \\ \chi_j(\mathbf{r}) = \sum_{lm} R_l(r) Y_{lm}(\vartheta, \varphi) \end{cases} \quad (3-1)$$

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,⁷² Slater,⁷³ and numerical atomic orbitals⁷¹ in the following form:

$$\left\{ \begin{array}{ll} R_j(r) = N_j e^{-a_j r^2} & \text{(Gaussians)} \\ R_j(r) = N_j r^{n^*-1} e^{-\zeta_j r} & \text{(Slater)} \\ \frac{1}{2r} \frac{d^2}{dr^2} [r R_{nl}(r)] + \left[-\frac{l(l+1)}{2r^2} + E_{nl} - V_{eff}(r) \right] R_{nl}(r) = 0 & \text{(Dmol)} \end{array} \right.$$

(3-2)

The basic functions $\chi(\mathbf{r})$ are taken numerically more than analytically, similar to the Gaussian type orbitals. The angular portion of each function is a function of spherical harmonic $Y_{lm}(\vartheta, \varphi)$, while the radial portion $R_l(\mathbf{r})$ is realized by solving the atomic DFT equations numerically from the nucleus to an outer distance of 10 Bohrs ($\approx 5.3 \text{ \AA}$). 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 DMol³ shows a small basis set superposition error generation because of the quality of these orbitals. The basis set superposition effects⁷⁰ 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 DMol³ 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).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:

$$HC = \mathcal{E}SC \quad (3-3)$$

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

$$\begin{cases} H_{j\nu} = \langle \chi_j(\mathbf{r}_1) | -\frac{\nabla^2}{2} + V_{ext} + V_H + V_{xc}[n(\mathbf{r}_1)] | \chi_\nu(\mathbf{r}_1) \rangle \\ S_{j\nu} = \langle \chi_j(\mathbf{r}_1) | \chi_\nu(\mathbf{r}_1) \rangle \end{cases} \quad (3-4)$$

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:

$$\begin{cases} H_{jv} \cong \sum_i \chi_j(\mathbf{r}_i) H_{eff}(\mathbf{r}_i) \chi_v(\mathbf{r}_i) w(\mathbf{r}_i) \\ S_{jv} \cong \sum_i \chi_j(\mathbf{r}_i) \chi_v(\mathbf{r}_i) w(\mathbf{r}_i) \end{cases} \quad (3-5)$$

The sums considered on several numerical integration points are $\mathbf{r}_i$. The $H_{eff}(\mathbf{r}_i)$ and $w(\mathbf{r}_i)$ indicate the value of the integral of Eq. (3-5) at point $\mathbf{r}_i$ 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 PWC⁶⁶ 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.⁷⁵ 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:

$$G(E) = \sum_n \delta(E - \varepsilon_n) \quad (3-6)$$

where ε_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

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

$$G(E) = \begin{cases} \sum_{n=1}^N \exp\left(-\frac{E - \epsilon_n}{\sigma}\right) & \text{(Gaussian)} \\ \sum_{n=1}^N \exp\left(-\frac{\alpha}{(\epsilon_n - E)^2 + \sigma^2}\right) & \text{(Lorentzian)} \end{cases} \quad (3-7)$$

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.⁷⁶

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:

$$\begin{cases} G_i(E) = \sum_n \langle \phi_n | i \rangle \langle i | \phi_n \rangle \delta(E - \epsilon_n) & \text{(LDOS)} \\ G_i^\sigma(E) = \sum_n \left| \langle \phi_i^\sigma | \phi_n \rangle \right|^2 \delta(E - \epsilon_n) & \text{(PDOS)} \end{cases} \quad (3-8)$$

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

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 counterparts³¹ 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 insulators³¹ 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 H₂O 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.⁴ For instance, the binding energies of the core levels of Ag- $3d$,¹⁹ Cu- $1s$,⁸⁴ and Cu- $2p$ ²¹ 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 substrate¹⁵ and Ag nanoclusters and chains on the Ag(111) substrate,^{12, 85} similar to that of the Au-Au atomic chains.¹⁶ Furthermore, the valence band polarization of Ag and Cu nanoclusters was detected by ultraviolet photoelectron spectra (UPS) measurements.^{86, 87} 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,⁸⁸ $s-p$ hybridization of Ag,¹² and giant photon resonance,⁸⁹ a predictable understanding of the size dependence of CLS,⁹⁰ lattice contraction,⁹¹ and surface state creation of Ag and Cu nanoparticles remains quite challenging.⁹²

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 icosahedral⁹³ or decahedra⁹⁴ with decrease in nanoparticle size.

Numerous theoretical and experimental efforts have been devoted to investigate the structures of Ag and Cu nanoclusters.^{93, 95-102} The M-Dh structures for Cu and Ag nanoclusters have been experimentally confirmed.^{99,97} Meanwhile, FCC-like COh structures are stable forms of Ag and Cu nanoparticles.^{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.

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.⁷⁰ During the DFT calculations, the potentials of the core electrons were assumed to be semi-core pseudopotential.⁷⁴ The DFT exchange-correlation potential utilized the LSDA, with the PWC function for geometry and electronic structures.⁶⁶ The spin states were calculated using Mulliken population analysis¹⁰³ 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.¹⁰⁴ 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.¹⁰⁵ 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%,¹⁰⁵ as well as Ag, Cu, Ni, Fe atomic chains by 12.5%, 13.2%, 13.6%, and 18.6%, respectively.¹⁰⁶ Montano et al.^{107, 108} 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.⁸⁴ and Montano et al.¹⁰⁹ 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 (quadramer). The Ag and Cu dimer bond lengths contract spontaneously from their bulk value to 2.530 Å¹¹⁰ and 2.220 Å,¹¹¹ respectively.

Chapter 4: Quantum Entrapment and Valence Polarization of Ag and Cu Nanoclusters

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

Structure	Position atom	z_i	d_i (Å)		Shell i	Magnetic moment (μ)		Charge Transfer (e)	
			Ag	Cu		Ag	Cu	Ag	Cu
COh ₁₃	1~2	2.00	2.778	2.415	1	0.972	0.936	-0.216	-0.228
COh ₅₅	1~2	2.80	2.703	2.341	1	0.883	0.852	-1.034	-1.240
	2~3	4.80	2.824	2.470	2	0.108	0.144	0.960	1.140
COh ₁₄₇	1~2	3.14	2.713	2.346	1	0.724	0.721	-0.554	-0.300
	2~3	5.14	2.809	2.458	2	0.207	0.208	0.650	0.380
	3~4	12.00	2.831	2.469	3	0.062	0.066	0.036	0.037
M-Dh ₁₃	2~3	-	2.750	2.388	-	-	-	-	-
	1~3	2.43	2.902	2.517	1	0.974	0.947	-0.184	-0.128
M-Dh ₄₉	2~4	-	2.773	2.420	-	-	-	-	-
	1~3	2.86	2.812	2.457	1	0.870	0.872	-0.482	-0.768
M-Dh ₇₅	2~4	-	2.757	2.396	-	-	-	-	-
	1~3	3.10	2.778	2.412	1	0.860	0.835	-1.105	-1.541
	4~5	-	2.818	2.456	-	-	-	-	-
	3~5	5.10	2.843	2.484	2	0.137	0.152	1.043	1.469

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 Cu₁₄₇ 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-Dh₇₅, *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.^{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”.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,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 COh₅₅ 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,¹¹² Au(111) nanoclusters,¹¹³ Ag nanoclusters,¹¹⁴ and Cu-Ag clusters,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-1*sk*-edge,⁸⁴ Cu-2*p*_{3/2},²⁰ and Ag-3*d*_{5/2}¹⁹ 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, $E_v(K) = A + BK^{-1}$, 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 CeO₂,¹¹⁷ and Al₂O₃¹¹⁸ substrates, as well as, Cu nanoparticles deposited on HOPG/Ar⁺,²¹ CYCL/Ar⁺,²¹ Si,¹¹⁹ and Al₂O₃¹²⁰ 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.⁹⁰

To elucidate the effect of size on the CLS of Ag and Cu nanoparticles, the dimensionality, τ , and the bond nature indicator, m , were first calculated. The $E_v(0)$ and $\Delta E_v(\infty)$ of Cu-2 $p_{3/2}$ 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).²¹ The value of $m = 1.0000$, a value that holds for metallic solid,¹²¹ was chosen because Cu atoms barely react with carbon surfaces.¹²² The Cu-2 $p_{3/2}$ binding energy shift for an isolated Cu atom and the bulk was 931.0 and 1.70 eV, respectively.⁹⁰

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

	$A=E_v(\infty)$ (eV)	B (eV)	$E_v(0)$ (eV)	$\Delta E_v(\infty)$ (eV)
Ag/HOPG	368.49	2.02	363.03	5.46
Ag/CeO ₂	368.43	0.27	363.03	5.40
Ag/Al ₂ O ₃	367.80	1.70	363.03	4.77
Cu/Si	932.50	3.99	931.00	1.50
Cu/Al ₂ O ₃ (300K)	932.51	0.87	931.00	1.50
Cu/Al ₂ O ₃ (80K)	932.67	0.39	931.00	1.67
Cu/HOPG/Ar ⁺	932.54	0.81	931.00	1.54
Cu/CYCL/Ar ⁺	932.53	1.32	931.00	1.53

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 CeO₂ 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 CeO₂ and HOPG substrates.^{19, 117} The bond nature of Ag was experimentally studied based on Ag on an Al₂O₃ substrate because of the interactions between the Ag nanoparticles and the substrate,¹²³ and we found that $m = 3.8200$.¹¹⁸ 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 $m = 1.8175$ ²¹ 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 Al₂O₃ substrate. Compared with their bulk counterparts, the experimentally observed positive CLS for Ag,¹⁹ Au,¹²⁵ and Cu²¹ 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-3d_{5/2} and (b) Cu-2p_{3/2} deposited on different substrates.

The bonds between the neighboring atom experience lattice strain³⁹ 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) surfaces¹²⁶ and the Cu(111) and Cu(220) surfaces.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,¹⁶ silver,¹² and copper.¹⁵ Figure 4-4 shows the shell-resolved LDOS for the Ag and Cu nanoclusters with COh₁₄₇ and M-Dh₇₅ 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) COh₁₄₇ and (c-d) M-Dh₇₅ 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.

The LDOS for s , p , and d orbitals of Ag and Cu nanoclusters with COh₁₄₇ and M-Dh₇₅ structures (see Figure 4-5) revealed that this system is suitable for plasma resonance applications.^{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 Cu₁₄₇ nanocluster to -1.35 eV for the Cu₁₃ nanocluster in COh structures, as well as from -3.48 eV for the Ag₇₅ nanocluster to -3.18 eV for the Ag₁₃ 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,³ Cu adatoms,⁸⁵ and Cu adatoms,¹³⁰ as well as Ag clusters and chains.¹² STM/S observations of the Cu clusters¹⁵ 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.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,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.⁸⁵ Finally, the UPS spectra revealed that the Ag 4*d* and the Cu 3*d* bands expand and shift upwards because of polarization as the cluster size decreases.^{86, 87, 131}

Figure 4-5 LDOS of the s , p , and d orbitals are shown by gray, blue, and black solid lines, respectively for (a-b) CO₁₄₇ and (c-d) M-Dh₇₅ 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,¹¹² the end of Cu atomic chains,¹⁵ and Ag.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 under-coordination 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.² 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.² For instance, Rh nanoparticles show giant magnetic moments^{7, 9} 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.^{7, 8} The giant magnetic moments observed in these metallic nanoparticles make them potential candidates for nanospintronic applications¹³² and magnetic data storage.¹³³ Furthermore, the catalytic ability of Au, Pt, Pd, and Rh nanoparticles is greatly enhanced;¹³⁴ and a phase transition from conductor to insulator occurs at the nanometre scale.^{10, 11}

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^{135, 136} or decahedral,^{137, 138} as well as surface bond contraction. XPS measurements have revealed a positive CLS for Pt nanoclusters deposited onto pristine carbon nanotubes (CNTs)^{6, 22} and HOPG.²³

Moreover, the peaks of the valence LDOS of Ag nanoclusters,¹² Rh nanoparticles,¹⁷ Au atomic chain,¹⁶ Au nanowires,¹³⁹ Cu monatomic chain,¹⁵ and Pt nanoclusters¹⁸ 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.^{137, 140-143} Icosahedral^{135, 144} or

decahedral^{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 evaporation¹³⁸ and Rh nanoparticles epitaxially deposited on NaCl(001).¹⁴⁵ However, FCC-like COh structures are stable forms of Pt nanocrystals prepared by electrocatalytic hydrogenation¹⁴¹ and Rh nanocrystals grown on NaCl substrates.¹⁴⁰ Previous DFT calculations also showed that the structures of multiple-twinned Pt¹⁴⁶ and Rh¹⁴⁷ 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. DMol³, 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,¹⁴⁸ shifting up the virtual orbitals, or fixing (freezing) occupancy. In spin-unrestricted wave function, different orbitals are related to different spins, including spin-up (α) and spin-down (β).

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 COh₁₄₇ 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.¹⁴⁹ 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.^{8, 105, 149-152} For instance, Sang et al.¹⁵¹ 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%¹⁰⁵ and 13%,¹⁵² the bond contraction for the Pt dimer can also be determined through DFT and MD calculations, respectively.

The bond contraction of Pt clusters,⁸ Pt chains,¹⁵⁰ and monoatomic chain¹⁴⁹ was experimentally observed. For the Rh nanoclusters, the calculated bond length of the

outmost shell of COH₁₄₇ is about 2.685 Å, exhibiting a reduction compared with the bulk value of 2.690 Å.¹⁵³ The observed trend of bond contraction at the surface is consistent with the previous report. For instance, bond contractions of up to 14%,¹⁵⁴ 4%,¹⁵³ and 4%-8%¹⁵⁴ were observed by the local-spin-density-functional model and TB approximation for Rh dimer, Rh₁₃ clusters, and larger Rh clusters, respectively. Villaseñor-González et al.¹⁵⁵ and Barreteau et al.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 COH₁₄₇ 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 (μ), and charge transfer (e)

Structure	Position atom	z_i	d_i (Å)			Shell i	Magnetic moment (μ)		Charge Transfer (e)		
			Pt Singlet	Pt Triplet	Rh		Pt Triplet	Rh	Pt Singlet	Pt Triplet	Rh
COh ₁₃	1~2	2.00	2.716	2.715	2.653	1	1.896	2.856	-0.120	-0.120	-0.240
COh ₅₅	1~2	2.80	2.629	2.682	2.637	1	1.638	2.472	-1.404	-0.716	-1.768
	2~3	4.80	2.679	2.737	2.694	2	0.336	0.492	1.150	0.564	1.556
COh ₁₄₇	1~2	3.14	2.673	2.663	2.685	1	1.387	2.067	-0.682	-0.681	-0.007
	2~3	5.14	2.728	2.756	2.737	2	0.477	0.714	0.800	0.815	0.173
	3~4	12.00	2.763	2.763	2.753	3	0.126	0.201	0.026	0.254	0.066
M-Dh ₁₃	2~4	-	2.696	2.696	2.633	-	-	-	-	-	-
	1~3	2.43	2.793	2.792	2.715	1	1.894	2.852	-0.088	-0.087	-0.224
M-Dh ₄₉	2~4	-	2.731	2.729	2.663	-	-	-	-	-	-
	1~3	2.86	2.797	2.805	2.712	1	1.754	2.670	-0.686	-0.685	-1.226
M-Dh ₇₅	2~4	-	2.695	2.694	2.676	-	-	-	-	-	-
	1~3	3.10	2.741	2.734	2.695	1	1.598	2.440	-1.215	-1.241	-2.553
	4~5	-	2.763	2.744	2.721	-	-	-	-	-	-
	3~5	5.10	2.784	2.798	2.743	2	0.384	0.534	1.084	1.107	2.376

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;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 COh₁₄₇ (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,¹¹³ Ag nanoclusters,¹¹⁴ Cu-Ag clusters,¹¹⁵ Au-Ag clusters,¹⁵⁷ Au nanoclusters,¹¹² and Ag and Cu nanoclusters.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,^{6, 22} and HOPG,²³ as well as the Rh(110) surface,¹⁵⁹ respectively. Moreover, the deepening of the Pt 4*f*_{7/2}¹⁶⁰ and Rh 3*d*_{5/2}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 $E_v(0)$ and $\Delta E_v(\infty)$ values for Pt-4*f* and Rh-3*d* 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-4*f* and Rh-3*d* 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.⁹⁰

Table 5-2 BOLS derived $E_v(0)$ and $\Delta E_v(\infty)$ for Pt and Rh nanoparticles

	<i>A</i> (eV)	<i>B</i> (eV)	$E_v(0)$ (eV)	$\Delta E_v(\infty)$ (eV)
Pt- Pristine CNTs ¹⁶²	71.26	0.66	67.21	4.05
Pt-HOPG ²²	71.15	0.58	67.21	3.94
Pt-TiO ₂ (110)-300K ¹⁶³	71.11	0.70	67.21	3.90
Pt-MCNTs-untreated ⁶	71.11	0.42	67.21	3.90
Pt-MCNTs-Ar ⁺ ⁶	71.19	0.88	67.21	3.98
Pt-MCNTs-O ₂ ⁶	71.26	0.63	67.21	4.05
Rh-TiO ₂ (110)-(1x1)-well ordered ¹⁶⁴	306.70	0.09	302.16	4.54
Rh-TiO ₂ (110)-(1x1)-Slightly-Ar ⁺ ¹⁶⁴	306.70	0.12	302.16	4.54
Rh-TiO ₂ (110)-(1x1)-Strongly- Ar ⁺ ¹⁶⁴	306.40	0.11	302.16	4.24
Rh-TiO ₂ ¹⁶⁵	307.50	0.13	302.16	5.34
Rh-TiO ₂ -300K ¹⁶⁶	307.30	0.08	302.16	5.14
Rh-TiO ₂ -160K ¹⁶⁶	307.40	0.05	302.16	5.24

We first calculated the dimensionality τ 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- $4f_{7/2}$ can be obtained by applying Eq. (2-17) and Eq. (2-18) to the Pt nanoparticles deposited on pristine CNTs,¹⁶² the TiO₂(110) surface at room temperature,¹⁶³ and the multiwall CNTs (MCNTs) without pretreatment⁶ 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.¹²¹ The atomic trapping energy and the bulk shift for Pt are about 67.21 and 3.28 eV, respectively.³⁹ 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 $m = 1.00$.^{6, 22}

Similarly, for Rh nanoparticles deposited on the TiO₂(110)-(1x1) surface,¹⁶⁴ the Ar⁺-pretreated TiO₂(110) surface,¹⁶⁵ and the TiO₂(110) surface at 300 and 160 K,¹⁶⁶ the bond nature indicator $m = 1.00$ because of the weak interaction between the Rh nanoparticles and the substrates. The Rh $3d_{5/2}$ binding energy of an isolated Rh atom and its bulk shift is equal to 302.163 and 4.37 eV, respectively.⁵⁰ Compared with their bulk counterparts, the experimental results of Au,¹²⁵ Cu,²¹ Pt,¹⁶⁰ and Rh⁵⁰ 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) substrate¹⁶⁷ and Pt on the Cu(111) surface at 300K,¹⁶⁸ the Pt(422) surface and the Pt(111) surface,¹⁶⁹ and the Rh surface.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 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,¹² Au,¹⁶ and Cu chains,¹⁵ as well as for the Pt¹⁷ and Rh nanoparticles.¹⁸

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 Rh₁₄₇ nanocluster to -0.07 eV for the Rh₁₃ nanocluster in the COh structures, and from -0.78 eV for the Pt₇₅ nanocluster to -0.34 eV for the Pt₁₃ 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.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.^{162, 172} Bianchetti et al.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),¹² Ag adatoms on Ag(111),⁸⁵ Au-Au atomic chains,¹⁶ Au nanowire,¹³⁹ Cu chains on Cu(111),¹⁵ single Cu/Cu(111) adatoms,¹³⁰ Pt nanoparticles on the TiO₂(110) surface,¹⁷³ Pt clusters on HOPG,¹⁸ and Rh on TiO₂(110)-(1x2).^{17, 174}

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_N and Rh_N 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.¹³² As listed in Table 5-1, the magnetic moment of the 147-atom COh structure of the Rh nanoparticles decreased from 2.067μ in the outermost shell with CN = 3.4, to 0.201μ 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,¹¹⁶ which is consistent with the previous results on Fe and Rh clusters.^{175 176, 177}

5.3.5.2 Magnetization

The magnetic behaviour is caused by the spin-up (α -spin states) and spin-down (β -spin states) states of the metal d -band. The majority and minority spins of the d -band are occupied by the spin-up (α) electrons and unoccupied by the spin-down (β) 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 (α) and spin-down (β) to understand the origin of the magnetic behaviours 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 (α) and spin-down (β) 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.

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.

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 (α) and spin-down (β) states in PDOS. The blue and red indicate the spin-up (α) and spin-down (β) 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 α and β 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 α and β 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.¹⁷⁸ The magnetic ordering was consistent with the previous theoretical calculations on Pd, Rh, and Ru nanoclusters,¹⁷⁹ Rh monolayers on Au,¹⁸⁰ Rh_N and Pd_N cluster up to N = 13 atoms,¹⁸¹ transition metal monolayers on noble metal (001) substrates,¹⁸² Pt_N (N = 2-55 atoms) clusters,¹³³ Pt₁₃ clusters in a NaY zeolite,¹⁵⁰ Tc, Ru, Rh, and Pd monolayers on Ag(001) surface,¹⁸³ as well as Rh_N clusters (N = 9, 13, 15, 17, and 19 atoms).¹⁰⁵

Table 5-3 Calculated gaps for the spin-up (α) and spin-down (β) of Pt and Rh nanoclusters

	Gap spin-up alpha (eV)			Gap spin-down Beta (eV)		
	Pt	Pt	Rh	Pt	Pt	Rh
	Singlet	Triplet		Singlet	Triplet	
COh ₁₃	1.009	0.058	0.976	1.009	1.005	0.982
COh ₅₅	0.305	0.252	0.092	0.305	0.253	0.055
COh ₁₄₇	0.274	0.063	0.013	0.274	0.091	0.034
M-D ₁₃	0.417	0.224	0.334	0.417	0.416	0.105
M-Dh ₄₉	0.374	0.363	0.068	0.374	0.361	0.022
M-Dh ₇₅	0.236	0.187	0.028	0.236	0.054	0.052

This phenomenon was also confirmed by experimental observations of Pt embedded in a polymer prepared by chemical reaction method,¹⁸⁴ Pt clusters by ion exchange of a KL zeolite,¹⁸⁵ Pt/Y₃Fe₅O₁₂ bilayers by X-ray magnetic circular dichroism,¹⁸⁶ Pt nanoparticles induced by surface chemisorption,¹⁸⁷ Rh_N (N = 12-32 atoms) grown by laser vaporization,⁷ Rh monolayers deposited by the grown layer method on Fe,¹⁸⁸ as well as Rh nanoparticles prepared by reducing cations in the solution.⁹ No magnetic behavior was reported for Pt clusters with 13-20 atoms in zeolite Y¹⁸⁹ and Pt clusters on graphene,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 ($M = \text{Ag, Cu, Pt, and Rh}$; $N = 13\text{-}147$ 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.^{2, 9, 11, 25-27, 31, 77, 191} 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,²⁵ nitric oxide on Cu clusters,²⁶ Pt clusters in gas phase,¹⁹¹ and nitric oxide on Rh clusters²⁷ 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,⁸⁵ Cu chains on Cu(111),¹⁵ Pt clusters on highly oriented pyrolytic graphite,¹⁸ and Rh nanoparticles on $\text{TiO}_2(110)\text{-(1}\times\text{2)}$ surface.¹⁷ 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.^{87, 192-195} 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,^{196, 197} early theoretical work usually assume that nanoparticles are in a neutral state.^{198, 199}

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;^{93, 94} the COh and M-Dh structures are stable forms for M_N metallic nanoclusters.^{95, 97, 144, 200, 201} In this study, we considered COh structures

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

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 DMol³ code was specified at the beginning of our calculations, including (+2), (+1), (0), (-1), and (-2) for M_N metallic nanoclusters (M = Ag, Cu, Pt, and Rh; N = 13-147 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 (α) and spin-down (β).

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 COh₅₅ 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

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

(2.770 Å),¹⁴⁹ and Rh (2.690 Å).¹⁵³ For M-Dh₇₅ 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.^{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.²⁰² Up to 8.30%-13.20 % and 11.20 % of bond length contraction was observed in the anionic Ag and Cu clusters prepared by photodetachment, respectively.²⁰³ For neutral Ag, Cu, and Pt nanoparticles, EXAFS spectroscopy measurements revealed that the bond length was contracted by 2.83-2.87, 2.230-2.540, and 2.600 Å, respectively;^{8, 107, 108} and the XANES measurements revealed that the bond length was reduced to around 2.652 Å for Pt₁₃ clusters,¹⁵⁰ around 2.300 Å for Pt clusters in monoatomic chains,¹⁴⁹ and around 2.530 Å for Ag nanoparticles.¹¹⁰ Furthermore, the theoretical methods reported the contraction of bond length, for example, 2.590-2.830, 2.590-2.840, and 2.610-2.840 Å in cationic, neutral, and anionic silver clusters;²⁰⁶ 2.417-2.530,

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 Cu_N clusters with N = 3-13 atoms;²⁰⁷ 2.560-2.250, 2.570-2.300, and 2.580-2.360 Å in the cationic, neutral, and anionic Pt_N (N = 2-14 atoms);²⁰¹ and neutral Rh_N (N = 13, 55, 147, 309, and 561 atoms) at around 3%-5 %.¹⁵⁶ 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 d_i (Å) and charge of shell (e) at different position of 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

	Shell	Excess charge states	Bond length (Å)				Charge of Shell (e)			
			Ag	Cu	Pt	Rh	Ag	Cu	Pt	Rh
COh ₁₃	1~2	+2	2.798	2.431	2.723	2.665	1.872	1.848	1.932	1.836
		+1	2.781	2.420	2.726	2.655	0.828	0.804	0.900	0.792
		0	2.778	2.415	2.715	2.653	-0.216	-0.228	-0.120	-0.240
		-1	2.788	2.415	2.718	2.648	-1.260	-1.260	-1.152	-1.284
		-2	2.785	2.419	2.723	2.658	-2.292	-2.280	-2.165	-2.316
COh ₅₅	1~2	+2	2.711	2.354	2.680	2.645	1.146	0.844	1.361	0.353
		+1	2.712	2.346	2.681	2.641	0.046	0.216	0.316	1.565
		0	2.703	2.341	2.682	2.637	-1.034	-1.240	-0.716	-1.768
		-1	2.701	2.338	2.672	2.636	-2.098	-2.274	-1.743	-2.825
		-2	2.705	2.340	2.677	2.636	-3.150	-3.306	-2.773	-3.852
	2~3	+2	2.830	2.477	2.745	2.698	0.792	1.020	0.493	1.440
		+1	2.825	2.473	2.741	2.696	0.876	0.720	0.530	1.500

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

COh ₁₄₇	1~2	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
	2~3	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	2.712	2.341	2.667	2.683	-2.570	-2.157	-2.736	-2.252
		+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
	3~4	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
	M-Dh ₁₃	2~4	0	2.831	2.469	2.763	2.753	0.036	0.037	0.254
-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	-	-	-	-
1~3		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
2~4		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	2.889	2.502	2.791	2.717	-2.261	-2.259	-2.129	-2.188
		+2	2.770	2.415	2.736	2.658	-	-	-	-
		+1	2.775	2.416	2.713	2.656	-	-	-	-
M-Dh ₄₉		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	
M-Dh ₇₅	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	
	-2	2.825	2.465	2.799	2.710	-2.474	-1.892	-2.732	-3.005	
	2~4	+2	2.755	2.404	2.690	2.684	-	-	-	-

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

	+1	2.759	2.397	2.703	2.681	-	-	-	-
	0	2.757	2.396	2.694	2.676	-	-	-	-
	-1	2.762	2.402	2.716	2.689	-	-	-	-
	-2	2.762	2.401	2.689	2.675	-	-	-	-
	+2	2.794	2.419	2.747	2.765	1.487	1.114	1.485	1.447
	+1	2.780	2.413	2.738	2.698	0.460	0.100	0.444	0.024
1~3	0	2.778	2.412	2.734	2.695	-1.105	-1.541	-1.241	-2.553
	-1	2.775	2.409	2.743	2.752	-1.579	-1.892	-1.628	-2.048
	-2	2.775	2.406	2.742	2.687	-2.596	-2.914	-3.242	-3.699
	+2	2.813	2.458	2.766	2.714	-	-	-	-
	+1	2.812	2.460	2.766	2.700	-	-	-	-
4~5	0	2.818	2.456	2.744	2.721	-	-	-	-
	-1	2.820	2.463	2.754	2.711	-	-	-	-
	-2	2.819	2.461	2.764	2.701	-	-	-	-
	+2	2.853	2.498	2.777	2.796	0.447	0.823	0.413	0.791
	+1	2.839	2.490	2.769	2.744	0.481	0.845	0.452	0.841
3~5	0	2.843	2.484	2.798	2.743	1.043	1.469	1.107	2.376
	-1	2.837	2.491	2.779	2.797	0.529	0.861	0.522	0.100
	-2	2.836	2.491	2.778	2.745	0.547	0.861	0.560	1.440

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 analysis¹⁰³ (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

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

excess charge states. For instance, Ag, Cu, Pt, and Rh COh₁₄₇ 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 COh₅₅ 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_N metallic nanoclusters, which is consistent with previous theoretical calculations and experimental observations.^{115, 158, 208-210}

Table 6-2 Calculation of the charge of core (*e*) of M_N metallic nanoclusters with COh and M-Dh structures and excess charge states from (+2) to (-2).

Excess charge states		Charge of Core (<i>e</i>)			
		Ag	Cu	Pt	Rh
COh ₁₃	+2	0.127	0.153	0.067	0.161
	+1	0.171	0.191	0.096	0.205
	0	0.214	0.228	0.122	0.244
	-1	0.257	0.262	0.146	0.281
	-2	0.288	0.286	0.166	0.312
COh ₅₅	+2	0.068	0.089	0.148	0.205
	+1	0.071	0.093	0.150	0.208

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

COh ₁₄₇	0	0.070	0.095	0.151	0.209
	-1	0.069	0.095	0.152	0.210
	-2	0.064	0.092	0.152	0.211
	+2	0.001	0.003	-0.003	-0.001
	+1	0.001	0.003	-0.003	-0.001
	0	0.001	0.002	-0.003	-0.001
	-1	0.001	0.002	-0.003	-0.001
	-2	0.001	0.004	-0.003	-0.001
	+2	0.105	0.130	0.034	0.146
	+1	0.144	0.165	0.062	0.187
M-Dh ₁₃	0	0.183	0.199	0.086	0.224
	-1	0.222	0.231	0.108	0.258
	-2	0.260	0.260	0.127	0.287
	+2	-	-	-	-
	+1	-	-	-	-
	0	-	-	-	-
M-Dh ₄₉	-1	-	-	-	-
	-2	-	-	-	-
	+2	0.056	0.059	0.102	0.134
	+1	0.056	0.059	0.105	0.137
M-Dh ₇₅	0	0.062	0.075	0.132	0.176
	-1	0.054	0.056	0.107	0.138
	-2	0.052	0.054	0.108	0.168

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 COh₅₅ 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 H₂, CO₂,

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 application²¹¹ and Au-Ag nanoparticles in bacterial therapy.²¹²

Moreover, positive signs of core charges were determined for COh₁₃, COh₅₅, M-Dh₁₃, and M-Dh₇₅ structures with the positive, neutral, and negative excess charge states (see Table 6-2). The magnitude of core charges increased for metallic nanocluster with COh₁₃ and M-Dh₁₃ 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 COh₁₃ structure, and 0.105, 0.144, 0.183, 0.222, and 0.260 *e* for M-Dh₁₃ 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 COh₁₃ and M-Dh₁₃ structures is consistent with the theoretical results of the Ag nanoclusters.²⁰⁹ Furthermore, the constant positive value of the core charge achieved for COh₅₅ and M-Dh₇₅ 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 COh₁₄₇ structure with the excess charge states from (+2) to (-2) achieved constant positive values for Ag₁₄₇ and Cu₁₄₇ nanoclusters and constant negative values for Pt₁₄₇ and Rh₁₄₇, which are in agreement with bimetallic nanoclusters, such as (AuAg)₁₄₇ nanoclusters co-catalysts for photocatalytic hydrogen reduction.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 COh₁₃ structures and Ag and Cu nanoclusters with COh₅₅ structures, as well as the excess charge state (+2) on the outermost of Pt nanoclusters with COh₁₃ structures. The interior electrons can polarize the electrons at the valence band, thus the otherwise conducting 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 TiO₂(110)-(1×2) surface.^{12, 15, 17, 18}

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) COh₁₃, (e-h) COh₅₅, (i-l) COh₁₄₇, (m-p) M-Dh₁₃, (q-t) M-Dh₄₉, and (u-x) M-Dh₇₅ 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 COh₅₅ structures and all metallic nanoclusters with COh₁₄₇ and M-Dh₇₅ 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.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.,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.^{10, 32, 39}

Finally, the valence LDOS polarization of metallic nanoclusters is consistent with the experimental findings, including the under-coordinated-induced valence

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

polarization for Rh(111) and Rh adatoms observed by XPDS,¹⁷¹ the DOS shift toward the Fermi level with the reduction of the size for Pt nanoparticles on pristine CNTs,¹⁶² the valence LDOS polarization observed by STM/S measurements on silver clusters, chains on the Ag(111) substrate,¹³ single copper on Cu(111) adatoms,¹³⁰ Pt clusters on highly oriented pyrolytic graphite,¹⁸ and Rh on TiO₂(110)-(1x2).¹⁷ 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.⁸⁷ Furthermore, polarization of LDOS of the neutral copper monomers, dimers, and trimers under positive bias¹⁵ and the unoccupied states of DOS of the neutral silver monomers, quasi-dimers, and dimer⁸⁵ 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.¹³² Magnetic behavior of a metal *d*-band in metallic nanoclusters originates from spin-up (α -spin states) and spin-down (β -spin states) states. The occupied and unoccupied electrons by the spin-up and spin-down are called the majority and minority

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

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 4d-Ag, 3d-Cu, 5d-Pt, and 4d-Rh for COh and M-Dh structures are given in Figure 6-3. The PDOS distributions of spin-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 ($5d^9 6s^1$), and Rh ($4d^8 5s^1$). Therefore, the magnetic moment of

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

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

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) COh₁₃, (e-h) COh₅₅, (i-l) COh₁₄₇, (m-p) M-Dh₁₃, (q-t) M-Dh₄₉, and (u-z) M-Dh₇₅ 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_f is set at 0 eV.

The energy gap between the HOMO and the LUMO of α and β 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 α and β spin states, whereas the odd excess charge states showed no gaps for Ag and Cu nanoclusters and a gap for Pt and Rh

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

nanoclusters. The magnetic behavior is in good agreement with previous theoretical calculations and experimental results, including those of neutral Ag clusters,²¹⁶ Cu on CeO₂,²¹⁷ Pt clusters,¹⁸⁵ and Rh nanoparticles,⁹ as well as cationic Rh nanoparticles and clusters of up to 12 atoms.^{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

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

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) COH₁₃, (e-h) COH₅₅, (i-l) COH₁₄₇, (m-p) M-Dh₁₃, (q-t) M-Dh₄₉, and (u-x) M-Dh₇₅ 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_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.

	Excess charge states	Gap up-spin Alpha (eV)				Gap down-spin Beta (eV)			
		Ag	Cu	Pt	Rh	Ag	Cu	Pt	Rh
COh ₁₃	+2	0.725	0.639	1.018	0.833	2.156	1.069	1.010	0.851
	+1	0.702	0.610	1.048	0.954	0.702	0.610	1.044	0.958
	0	0.695	0.611	0.058	0.976	0.688	0.597	1.005	0.982
	-1	0.687	0.598	0.190	0.992	0.687	0.598	0.892	0.995
	-2	0.689	0.598	0.233	0.993	0.706	0.615	0.302	0.968
COh ₅₅	+2	0.386	0.331	0.181	0.099	0.510	0.393	0.182	0.067
	+1	0.383	0.326	0.218	0.099	0.383	0.326	0.219	0.062
	0	0.318	0.320	0.252	0.092	0.319	0.321	0.253	0.055
	-1	0.380	0.310	0.285	0.090	0.380	0.310	0.284	0.030
	-2	0.357	0.263	0.307	0.071	0.248	0.305	0.308	0.041
COh ₁₄₇	+2	0.251	0.194	0.009	0.019	0.252	0.196	0.062	0.027
	+1	0.247	0.191	0.011	0.016	0.247	0.191	0.080	0.015
	0	0.255	0.174	0.063	0.013	0.256	0.176	0.091	0.034
	-1	0.243	0.187	0.066	0.010	0.243	0.187	0.003	0.015
	-2	0.243	0.185	0.057	0.011	0.246	0.188	0.108	0.013
M-Dh ₁₃	+2	0.366	0.384	0.705	0.319	0.112	1.356	0.693	0.079
	+1	0.123	0.342	0.554	0.330	0.123	0.342	0.549	0.006
	0	0.301	0.317	0.224	0.334	0.137	0.309	0.416	0.105
	-1	0.256	0.295	0.225	0.335	0.256	0.295	0.227	0.336
	-2	0.572	0.487	0.914	0.332	0.242	0.295	0.227	0.012
M-Dh ₄₉	+2	0.118	0.185	0.453	0.067	0.452	0.318	0.451	0.013
	+1	0.114	0.185	0.413	0.068	0.114	0.185	0.412	0.057
	0	0.134	0.171	0.363	0.068	0.128	0.175	0.361	0.022
	-1	0.138	0.159	0.335	0.061	0.138	0.159	0.334	0.053
	-2	0.102	0.118	0.278	0.036	0.146	0.150	0.293	0.032
M-Dh ₇₅	+2	0.003	0.189	0.291	0.054	0.213	0.187	0.034	0.063
	+1	0.015	0.193	0.255	0.014	0.015	0.193	0.054	0.037
	0	0.128	0.232	0.187	0.028	0.041	0.231	0.054	0.052
	-1	0.131	0.221	0.190	0.027	0.131	0.221	0.090	0.021
	-2	0.122	0.239	0.157	0.022	0.128	0.238	0.103	0.030

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 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,¹²⁸ magnetic,²²⁰ and catalytic properties.²²¹ 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, O₂, and NO₂+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 Under-coordination Induced Catalytic and Magnetic Fascinations of Pt and Rh nanoclusters, *Phys. Chem. Chem. Phys.*, 2014 (16), 20537-20547. (Chapter 5)
3. Shideh Ahmadi, Xi Zhang, Yinyan Gong, Weiguang Zhu, and Chang Q. Sun, Catalytic and Magnetic Behaviors of Excessively-Charged Ag, Cu, Pt, and Rh Atomic Clusters, *J. Phys. Chem. C*, 2016 (120), 17527–17536. (Chapter 6).
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

1. Catherine Bréchnignac, Philippe Houdy, and M. Lahmani, *Nanomaterials and nanochemistry*. 2006: Berlin, Heidelberg: Springer-Verlag Berlin Heidelberg.
2. C. Q. Sun, *Relaxation of the Chemical Bond*. Vol. 108. 2014: Springer Series in Chemical Physics.
3. C. Q. Sun, Thermo-mechanical behavior of low-dimensional systems: the local bond average approach. *Prog. Mater. Sci.*, **54** (2), 179-307 (2009).
4. C. Q. Sun, Size dependence of nanostructures: impact of bond order deficiency. *Prog. Solid State Chem.*, **35** (1), 1-159 (2007).
5. C. Q. Sun, Oxidation electronics: bond–band–barrier correlation and its applications. *Prog. Mater. Sci.*, **48** (6), 521-685 (2003).
6. D.-Q. Yang and E. Sacher, Strongly enhanced interaction between evaporated Pt nanoparticles and functionalized multiwalled carbon nanotubes via plasma surface modifications: effects of physical and chemical defects. *J. Phys. Chem. C*, **112** (11), 4075-4082 (2008).
7. A. J. Cox, J. G. Louderback, and L. A. Bloomfield, Experimental observation of magnetism in rhodium clusters. *Phys. Rev. Lett.*, **71** (6), 923-926 (1993).
8. X. Liu, M. Bauer, H. Bertagnolli, E. Roduner, J. van Slageren, and F. Phillipp, Structure and magnetization of small monodisperse platinum clusters. *Phys. Rev. Lett.*, **97** (25), 253401-253404 (2006).

References

9. Y. T. Jeon and G. H. Lee, Magnetism of the fcc Rh and Pd nanoparticles. *J. Appl. Phys.*, **103** (9), 094313-094315 (2008).
10. E. Roduner, Size matters: why nanomaterials are different. *Chem. Soc. Rev.*, **35** (7), 583-592 (2006).
11. F. Porrati, R. Sachser, and M. Huth, Magnetoresistance of granular Pt–C nanostructures close to the metal–insulator transition. *J. Phys.: Condens. Matter*, **26** (8), 085302-085308 (2014).
12. A. Sperl, J. Kröger, N. Néel, H. Jensen, R. Berndt, A. Franke, and E. Pehlke, Unoccupied states of individual silver clusters and chains on Ag(111). *Phys. Rev. B*, **77** (8), 085422-085428 (2008).
13. A. Sperl, J. Kröger, and R. Berndt, Conductance of Ag atoms and clusters on Ag(111): spectroscopic and time-resolved data. *Phys. Status Solidi B*, **247** (5), 1077-1086 (2010).
14. F. E. Olsson, M. Persson, A. G. Borisov, J. P. Gauyacq, J. Lagoute, and S. Fölsch, Localization of the Cu(111) surface state by single Cu adatoms. *Phys. Rev. Lett.*, **93** (20), 206803-206806 (2004).
15. S. Fölsch, P. Hyldgaard, R. Koch, and K. H. Ploog, Quantum confinement in monatomic Cu chains on Cu(111). *Phys. Rev. Lett.*, **92** (5), 056803-056806 (2004).
16. J. N. Crain and D. T. Pierce, End states in one-dimensional atom chains. *Science*, **307** (5710), 703-706 (2005).

References

17. A. Berkó and F. Solymosi, Method for independent control of particle size and distance in rhodium epitaxy on $\text{TiO}_2(110)-(1 \times 2)$ surface: an STM study. *Surf. Sci.*, **400** (1–3), 281-289 (1998).
18. U. Müller, K. Sattler, J. Xhie, N. Venkateswaran, and G. Raina, Scanning tunneling microscopy of single platinum atoms and small platinum clusters on highly oriented pyrolytic graphite. *J. Vac. Sci. Technol. B*, **9** (2), 829-832 (1991).
19. I. Lopez-Salido, D. C. Lim, and Y. D. Kim, Ag nanoparticles on highly ordered pyrolytic graphite (HOPG) surfaces studied using STM and XPS. *Surf. Sci.*, **588** (1–3), 6-18 (2005).
20. D.-W. Shin, C. Dong, M. Mattesini, A. Augustsson, S. Mao, C. L. Chang, C. Persson, R. Ahuja, J. Nordgren, S. X. Wang, and J. H. Guo, Size dependence of the electronic structure of copper nanoclusters in SiC matrix. *Chem. Phys. Lett.*, **422** (4–6), 543-546 (2006).
21. D. Q. Yang and E. Sacher, Initial- and final-state effects on metal cluster/substrate interactions, as determined by XPS: copper clusters on Dow Cyclotene and highly oriented pyrolytic graphite. *Appl. Surf. Sci.*, **195** (1–4), 187-195 (2002).
22. P. Marcus and C. Hinnen, XPS study of the early stages of deposition of Ni, Cu and Pt on HOPG. *Surf. Sci.*, **392** (1–3), 134-142 (1997).

23. D.-Q. Yang and E. Sacher, Platinum nanoparticle interaction with chemically modified highly oriented pyrolytic graphite surfaces. *Chem. Mater.*, **18** (7), 1811-1816 (2006).
24. C. Q. Sun, Surface and nanosolid core-level shift: impact of atomic coordination-number imperfection. *Phys. Rev. B*, **69** (4), 045105-045112 (2004).
25. D. Tang, Z. Chen, J. Hu, G. Sun, S. Lu, and C. Hu, CO oxidation catalyzed by silver nanoclusters: mechanism and effects of charge. *PCCP*, **14** (37), 12829-12837 (2012).
26. S. Hirabayashi and M. Ichihashi, Reactions of size-selected copper cluster cations and anions with nitric oxide: enhancement of adsorption in coadsorption with oxygen. *J. Phys. Chem. A*, **118** (10), 1761-1768 (2014).
27. S. L. Romo-Ávila and R. A. Guirado-López, Adsorption of nitric oxide on small $\text{Rh}_n^\pm$ clusters: role of the local atomic environment on the dissociation of the N–O bond. *J. Phys. Chem. A*, **116** (3), 1059-1068 (2012).
28. Y. Wang, X. Zhang, Y. Nie, and C. Q. Sun, Under-coordinated atoms induced local strain, quantum trap depression and valence charge polarization at W stepped surfaces. *Physica B: Condens. Matter*, **407** (1), 49-53 (2012).
29. C. Q. Sun, S.-Y. Fu, and Y. G. Nie, Dominance of broken bonds and unpaired nonbonding π -electrons in the band gap expansion and edge states generation in graphene nanoribbons. *J. Phys. Chem. C*, **112** (48), 18927-18934 (2008).

References

30. C. Q. Sun, Y. Sun, Y. Ni, X. Zhang, J. Pan, X.-H. Wang, J. Zhou, L.-T. Li, W. Zheng, S. Yu, L. K. Pan, and Z. Sun, Coulomb repulsion at the nanometer-sized contact: a force driving superhydrophobicity, superfluidity, superlubricity, and supersolidity. *J. Phys. Chem. C*, **113** (46), 20009-20019 (2009).
31. C. Q. Sun, Dominance of broken bonds and nonbonding electrons at the nanoscale. *Nanoscale*, **2** (10), 1930-1961 (2010).
32. C. Q. Sun, Y. Wang, Y. G. Nie, B. R. Mehta, M. Khanuja, S. M. Shivaprasad, Y. Sun, J. S. Pan, L. K. Pan, and Z. Sun, Interface quantum trap depression and charge polarization in the CuPd and AgPd bimetallic alloy catalysts. *PCCP*, **12** (13), 3131-3135 (2010).
33. E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Scaling theory of localization: absence of quantum diffusion in two dimensions. *Phys. Rev. Lett.*, **42** (10), 673-676 (1979).
34. L. Pauling, Atomic radii and interatomic distances in metals. *J. Am. Chem. Soc.*, **69** (3), 542-553 (1947).
35. Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang, and T.-S. Kuo, Remarkably Short Metal–Metal Bonds: A Lantern-Type Quintuply Bonded Dichromium(I) Complex. *Angew. Chem. Int. Ed.*, **47** (38), 7250-7253 (2008).
36. C. M. Goringe, D. R. Bowler, and E. Hernández, Tight-binding modelling of materials. *Rep. Prog. Phys.*, **60** (12), 1447-1512 (1997).

References

37. W. A. Harrison, Overlap interactions and bonding in ionic solids. *Phys. Rev. B*, **34** (4), 2787-2793 (1986).
38. V. M. Goldschmidt, Krystallbau und chemische zusammensetzung. *Berichte der deutschen chemischen Gesellschaft (A and B Series)*, **60** (5), 1263-1296 (1927).
39. C. Q. Sun, Y. Wang, Y. Nie, Y. Sun, J. Pan, L. Pan, and Z. Sun, Adatoms-induced local bond contraction, quantum trap depression, and charge polarization at Pt and Rh surfaces. *J. Phys. Chem. C*, **113** (52), 21889-21894 (2009).
40. P. J. Feibelman, Relaxation of hcp (0001) surfaces: a chemical view. *Phys. Rev. B*, **53** (20), 13740-13746 (1996).
41. S. Schuppler, S. L. Friedman, M. A. Marcus, D. L. Adler, Y. H. Xie, F. M. Ross, Y. J. Chabal, T. D. Harris, L. E. Brus, W. L. Brown, E. E. Chaban, P. F. Szajowski, S. B. Christman, and P. H. Citrin, Size, shape, and composition of luminescent species in oxidized Si nanocrystals and H-passivated porous Si. *Phys. Rev. B*, **52** (7), 4910-4925 (1995).
42. M. G. Mason, Electronic structure of supported small metal clusters. *Phys. Rev. B*, **27** (2), 748-762 (1983).
43. C. Q. Sun, L. K. Pan, Y. Q. Fu, B. K. Tay, and S. Li, Size Dependence of the 2p-Level Shift of Nanosolid Silicon. *J. Phys. Chem. B*, **107** (22), 5113-5115 (2003).
44. M. J. Sinnott, *The Solid State for Engineers*. 1963, Wiley, New York.

References

45. W. J. Huang, R. Sun, J. Tao, L. D. Menard, R. G. Nuzzo, and J. M. Zuo, Coordination-dependent surface atomic contraction in nanocrystals revealed by coherent diffraction. *Nat. Mater.*, **7** (4), 308-313 (2008).
46. Y. Wang, Y. Nie, L. Wang, and C. Q. Sun, Atomic-Layer- and Crystal-Orientation-Resolved $3d_{5/2}$ Binding Energy Shift of Ru(0001) and Ru(10 $\bar{1}$ 0) Surfaces. *J. Phys. Chem. C*, **114** (2), 1226-1230 (2009).
47. F. G. Shi, Size dependent thermal vibrations and melting in nanocrystals. *J. Mater. Res.*, **9** (5), 1307-1314 (1994).
48. M. A. Omar, *Elementary solid state physics: principles and applications*. 1993, Reading, Mass.: Addison-Wesley, New York.
49. W. Qin, Y. Wang, Y. Huang, Z. Zhou, C. Yang, and C. Q. Sun, Bond order resolved $3d_{5/2}$ and valence band chemical shifts of Ag surfaces and nanoclusters. *J. Phys. Chem. A*, **116** (30), 7892-7897 (2012).
50. Y. Wang, Y. G. Nie, J. S. Pan, L. K. Pan, Z. Sun, L. L. Wang, and C. Q. Sun, Orientation-resolved $3d_{5/2}$ binding energy shift of Rh and Pd surfaces: anisotropy of the skin-depth lattice strain and quantum trapping. *PCCP*, **12** (9), 2177-2182 (2010).
51. A. Groß, *Theoretical surface science: a microscopic perspective*. 2009: Berlin, Heidelberg : Springer-Verlag Berlin Heidelberg.
52. M. Born and R. Oppenheimer, Zur Quantentheorie der Molekeln. *Ann. Phys.*, **389** (20), 457-484 (1927).

References

53. V. Fock, Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Z. Phys.*, **61** (1-2), 126-148 (1930).
54. D. R. Hartree, A theory of Hartree's atomic fields. *Proc. Camb. Phil. Soc.*, **24** (2), 328-342 (1928).
55. C. Møller and M. S. Plesset, Note on an approximation treatment for many-electron systems. *Phys. Rev.*, **46** (7), 618-622 (1934).
56. A. Szabo and N. S. Ostlund, *Modern quantum chemistry: introduction to advanced electronic structure theory*. 1996, New York: McGraw-Hill: Dover.
57. B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, A complete active space SCF method (CASSCF) using a density matrix formulated super-CI approach. *Chem. Phys.*, **48** (2), 157-173 (1980).
58. R. G. Parr and Y. Weitao, *Density-functional theory of atoms and molecules*. 1989: New York: Oxford University Press; Oxford.
59. E. K. U. Gross and R. M. Dreizler, *Density functional theory*. 1990: Springer, Berlin.
60. W. Koch and M. C. Holthausen, *A chemist's guide to density functional theory*. 2001: Weinheim; New York: Wiley-VCH
61. P. A. M. Dirac, Note on exchange phenomena in the Thomas atom. *Math. Proc. Cambridge*, **26** (03), 376-385 (1930).
62. P. Hohenberg and W. Kohn, Inhomogeneous electron gas. *Phys. Rev.*, **136** (3B), B864-B871 (1964).

References

- 63. W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, **140** (4A), A1133-A1138 (1965).
- 64. D. M. Ceperley and B. J. Alder, Ground state of the electron gas by a stochastic method. *Phys. Rev. Lett.*, **45** (7), 566-569 (1980).
- 65. S. H. Vosko, L. Wilk, and M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.*, **58** (8), 1200-1211 (1980).
- 66. J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, **45** (23), 13244-13249 (1992).
- 67. L. V. Slipchenko and A. I. Krylov, Singlet-triplet gaps in diradicals by the spin-flip approach: a benchmark study. *J. Chem. Phys.*, **117** (10), 4694-4708 (2002).
- 68. O. Gunnarsson and B. I. Lundqvist, Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism. *Phys. Rev. B*, **13** (10), 4274-4298 (1976).
- 69. A. A. Ovchinnikov, C. F. Bender, and J. K. Labanowski, *A simple method of removing spin contamination from unrestricted Kohn-Sham density functional calculations*, in *Theoretical and Computational Chemistry*, J.M. Seminario, Editor. 1996, Elsevier. p. 359-388.
- 70. B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.*, **92** (1), 508-517 (1990).

References

- 71. B. Delley, From molecules to solids with the DMol³ approach. *J. Chem. Phys.*, **113** (18), 7756-7764 (2000).
- 72. J. Andzelm, E. Wimmer, and R. S. Dennis, *Spin density functional approach to the chemistry of transition metal clusters*, in *The Challenge of d and f Electrons*. 1989, American Chemical Society. p. 228-245.
- 73. L. Versluis and T. Ziegler, The determination of molecular structures by density functional theory. The evaluation of analytical energy gradients by numerical integration. *J. Chem. Phys.*, **88** (1), 322-328 (1988).
- 74. B. Delley, Hardness conserving semilocal pseudopotentials. *Phys. Rev. B*, **66** (15), 155125-155133 (2002).
- 75. P. Pulay, Convergence acceleration of iterative sequences. The case of SCF iteration. *Chem. Phys. Lett.*, **73** (2), 393-398 (1980).
- 76. G. J. Ackland, Embrittlement and the bistable crystal structure of zirconium hydride. *Phys. Rev. Lett.*, **80** (10), 2233-2236 (1998).
- 77. J. S. Garitaonandia, M. Insausti, E. Goikolea, M. Suzuki, J. D. Cashion, N. Kawamura, H. Ohsawa, I. Gil de Muro, K. Suzuki, F. Plazaola, and T. Rojo, Chemically induced permanent magnetism in Au, Ag, and Cu nanoparticles: localization of the magnetism by element selective techniques. *Nano Lett.*, **8** (2), 661-667 (2008).

78. J. D. Grunwaldt, A. M. Molenbroek, N. Y. Topsøe, H. Topsøe, and B. S. Clausen, In situ investigations of structural changes in Cu/ZnO catalysts. *J. Catal.*, **194** (2), 452-460 (2000).
79. D. C. Lim, I. Lopez-Salido, and Y. D. Kim, Size selectivity for CO-oxidation of Ag nanoparticles on highly ordered pyrolytic graphite (HOPG). *Surf. Sci.*, **598** (1-3), 96-103 (2005).
80. P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, and H. Topsøe, Atom-resolved imaging of dynamic shape changes in supported copper nanocrystals. *Science*, **295** (5562), 2053-2055 (2002).
81. J. Sancho-Parramon, Surface plasmon resonance broadening of metallic particles in the quasi-static approximation: a numerical study of size confinement and interparticle interaction effects. *Nanotechnology*, **20** (23), 235706-235712 (2009).
82. J. Urban, H. Sack-Kongehl, K. Weiss, I. Lisiecki, and M. P. Pileni, Structures of clusters. *Cryst. Res. Technol.*, **35** (6-7), 731-743 (2000).
83. C. Mottet, J. Goniakowski, F. Baletto, R. Ferrando, and G. Treglia, Modeling free and supported metallic nanoclusters: structure and dynamics. *Phase Transitions*, **77** (1-2), 101-113 (2004).
84. G. Apai, J. F. Hamilton, J. Stohr, and A. Thompson, Extended X-ray-absorption fine structure of small Cu and Ni clusters: binding-energy and bond-length changes with cluster size. *Phys. Rev. Lett.*, **43** (2), 165-169 (1979).

85. A. Sperl, J. Kröger, R. Berndt, A. Franke, and E. Pehlke, Evolution of unoccupied resonance during the synthesis of a silver dimer on Ag(111). *New J. Phys.*, **11** (6), 063020-063027 (2009).
86. O. Cheshnovsky, K. J. Taylor, J. Conceicao, and R. E. Smalley, Ultraviolet photoelectron spectra of mass-selected copper clusters: evolution of the 3*d* band. *Phys. Rev. Lett.*, **64** (15), 1785-1788 (1990).
87. K. J. Taylor, C. L. Pettiette-Hall, O. Cheshnovsky, and R. E. Smalley, Ultraviolet photoelectron spectra of coinage metal clusters. *J. Chem. Phys.*, **96** (4), 3319-3329 (1992).
88. C. Massobrio, A. Pasquarello, and R. Car, Structural and electronic properties of small copper clusters: a first principles study. *Chem. Phys. Lett.*, **238** (4–6), 215-221 (1995).
89. J. Tiggesbäumker, L. Köller, H. O. Lutz, and K. H. Meiwes-Broer, Giant resonances in silver-cluster photofragmentation. *Chem. Phys. Lett.*, **190** (1–2), 42-47 (1992).
90. C. Q. Sun, L. K. Pan, H. L. Bai, Z. Q. Li, P. Wu, and E. Y. Jiang, Effects of surface passivation and interfacial reaction on the size-dependent 2*p*-level shift of supported copper nanosolids. *Acta Mater.*, **51** (15), 4631-4636 (2003).
91. J. Schiøtz, Atomic-scale modeling of plastic deformation of nanocrystalline copper. *Scripta Mater.*, **51** (8), 837-841 (2004).

References

92. V. G. Grigoryan, D. Alamanova, and M. Springborg, Structure and energetics of Cu_N clusters with ($2 \leq N \leq 150$): An embedded-atom-method study. *Phys. Rev. B*, **73** (11), 115415-115427 (2006).
93. F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, and C. Mottet, Crossover among structural motifs in transition and noble-metal clusters. *J. Chem. Phys.*, **116** (9), 3856-3863 (2002).
94. Marks L. D, Modified Wulff constructions for twinned particles. *J. Cryst. Growth*, **61** (3), 556-566 (1983).
95. M. Chen, J. E. Dyer, K. Li, and D. A. Dixon, Prediction of structures and atomization energies of small silver clusters, $(\text{Ag})_n$, $n < 100$. *J. Phys. Chem. A*, **117** (34), 8298-8313 (2013).
96. S. Giorgio and J. Urban, Structure of 1 nm silver clusters. *J. Phys. F: Met. Phys.*, **18** (8), L147-L152 (1988).
97. C. R. Li, N. P. Lu, Q. Xu, J. Mei, W. J. Dong, J. L. Fu, and Z. X. Cao, Decahedral and icosahedral twin crystals of silver: formation and morphology evolution. *J. Cryst. Growth*, **319** (1), 88-95 (2011).
98. J. Oviedo and R. E. Palmer, Amorphous structures of Cu, Ag, and Au nanoclusters from first principles calculations. *J. Chem. Phys.*, **117** (21), 9548-9551 (2002).

References

99. C. Salzemann, I. Lisiecki, J. Urban, and M. P. Pileni, Anisotropic copper nanocrystals synthesized in a supersaturated medium: nanocrystal growth. *Langmuir*, **20** (26), 11772-11777 (2004).
100. K. Michaelian, N. Rendón, and I. L. Garzón, Structure and energetics of Ni, Ag, and Au nanoclusters. *Phys. Rev. B*, **60** (3), 2000-2010 (1999).
101. M. N. Blom, D. Schooss, J. Stairs, and M. M. Kappes, Experimental structure determination of silver cluster ions (Ag_n^+ , $19 < n < 79$). *J. Chem. Phys.*, **124** (24), 244308-244310 (2006).
102. A. M. Angulo and C. Noguez, Atomic structure of small and intermediate-size silver nanoclusters. *J. Phys. Chem. A*, **112** (26), 5834-5838 (2008).
103. M. D. Segall, Population analysis in plane wave electronic structure calculations. *Mol. Phys.*, **89** (2), 571-577 (1996).
104. Ş. Erkoç and R. Shaltaf, Monte Carlo computer simulation of copper clusters. *Phys. Rev. A*, **60** (4), 3053-3057 (1999).
105. S. R. Bahn and K. W. Jacobsen, Chain formation of metal atoms. *Phys. Rev. Lett.*, **87** (26), 266101-266104 (2001).
106. A. Kara and T. S. Rahman, Vibrational properties of metallic nanocrystals. *Phys. Rev. Lett.*, **81** (7), 1453-1456 (1998).
107. P. A. Montano, G. K. Shenoy, E. E. Alp, W. Schulze, and J. Urban, Structure of copper microclusters isolated in solid argon. *Phys. Rev. Lett.*, **56** (19), 2076-2079 (1986).

- 108. P. A. Montano, W. Schulze, B. Tesche, G. K. Shenoy, and T. I. Morrison, Extended x-ray-absorption fine-structure study of Ag particles isolated in solid argon. *Phys. Rev. B*, **30** (2), 672-677 (1984).
- 109. P. A. Montano, J. Zhao, M. Ramanathan, G. K. Shenoy, W. Schulze, and J. Urban, Structure of silver microclusters. *Chem. Phys. Lett.*, **164** (2–3), 126-130 (1989).
- 110. B. Simard, P. A. Hackett, A. M. James, and P. R. R. Langridge-Smith, The bond length of silver dimer. *Chem. Phys. Lett.*, **186** (4–5), 415-422 (1991).
- 111. M. D. Morse, Clusters of transition-metal atoms. *Chem. Rev.*, **86** (6), 1049-1109 (1986).
- 112. X. Zhang, J.-l. Kuo, M. Gu, X. Fan, P. Bai, Q.-G. Song, and C. Q. Sun, Local structure relaxation, quantum trap depression, and valence charge polarization induced by the shorter-and-stronger bonds between under-coordinated atoms in gold nanostructures. *Nanoscale*, **2** (3), 412-417 (2010).
- 113. A. Moghaddasi, M. Zahedi, and P. Watson, Theoretical study of site dependency on charge transfer at Au(111) nanoclusters. *J. Phys. Chem. C*, **116** (8), 5014-5018 (2012).
- 114. D. Liu, J. S. Lian, and Q. Jiang, Surface energy and electronic structures of Ag quasicrystal clusters. *J. Phys. Chem. C*, **113** (4), 1168-1170 (2009).
- 115. C. J. Heard and R. L. Johnston, A density functional global optimisation study of neutral 8-atom Cu-Ag and Cu-Au clusters. *Eur. Phys. J. D*, **67** (2), 1-6 (2013).

References

116. P. J. Jensen and K. H. Bennemann, Theory for the atomic shell structure of the cluster magnetic moment and magnetoresistance of a cluster ensemble. *Z. Phys. D*, **35** (4), 273-278 (1995).
117. D. Kong, G. Wang, Y. Pan, S. Hu, J. Hou, H. Pan, C. T. Campbell, and J. Zhu, Growth, structure, and stability of Ag on CeO₂(111): synchrotron radiation photoemission studies. *J. Phys. Chem. C*, **115** (14), 6715-6725 (2011).
118. K. Luo, X. Lai, C. W. Yi, K. A. Davis, K. K. Gath, and D. W. Goodman, The growth of silver on an ordered alumina surface. *J. Phys. Chem. B*, **109** (9), 4064-4068 (2005).
119. N. Ferretti, *X-ray photoelectron spectroscopy of size selected copper clusters on silicon*, in *Fakultät II - Mathematik und Naturwissenschaften*. 2008, Technische Universität Berlin. p. 1-101.
120. Y. Wu, E. Garfunkel, and T. E. Madey, Initial stages of Cu growth on ordered Al₂O₃ ultrathin films *J. Vac. Sci. Technol. A*, **14** (3), 1662-1667 (1996).
121. C. Q. Sun, B. K. Tay, X. T. Zeng, S. Li, T. P. Chen, Z. Ji, H. L. Bai, and E. Y. Jiang, Bond-order–bond-length–bond-strength (bond-OLS) correlation mechanism for the shape-and-size dependence of a nanosolid. *J. Phys.: Condens. Matter*, **14** (34), 7781-7795 (2002).
122. W. F. Egelhoff, Jr. and G. G. Tibbetts, Growth of copper, nickel, and palladium films on graphite and amorphous carbon. *Phys. Rev. B*, **19** (10), 5028-5035 (1979).

References

123. N. C. Hernández, J. Graciani, A. Márquez, and J. F. Sanz, Cu, Ag and Au atoms deposited on the α -Al₂O₃ surface: a comparative density functional study. *Surf. Sci.*, **575** (1–2), 189-196 (2005).
124. D. Schmeißer, O. Böhme, A. Yfantis, T. Heller, D. R. Batchelor, I. Lundstrom, and A. L. Spetz, Dipole moment of nanoparticles at interfaces. *Phys. Rev. Lett.*, **83** (2), 380-383 (1999).
125. T. Ohgi and D. Fujita, Consistent size dependency of core-level binding energy shifts and single-electron tunneling effects in supported gold nanoclusters. *Phys. Rev. B*, **66** (11), 115410-115415 (2002).
126. H. J. Wasserman and J. S. Vermaak, On the determination of a lattice contraction in very small silver particles. *Surf. Sci.*, **22** (1), 164-172 (1970).
127. H. J. Wasserman and J. S. Vermaak, On the determination of the surface stress of copper and platinum. *Surf. Sci.*, **32** (1), 168-174 (1972).
128. Wenqiang Ma and F. Chen, Optical and electronic properties of Cu doped Ag clusters. *J. Alloys Compd.*, **541**, 79-83 (2012).
129. M. Tomak, O. Ü. Aktürk, and O. Gülseren, Vibrational modes in small Ag_n, Au_n clusters: a first principle calculation. *Int. J. Mod. Phys. B*, **23** (31), 5819-5834 (2009).
130. J. Lagoute, X. Liu, and S. Fölsch, Link between adatom resonances and the Cu(111) shockley surface state. *Phys. Rev. Lett.*, **95** (13), 136801-1368014 (2005).

References

131. G. K. Wertheim, S. B. DiCenzo, and D. N. E. Buchanan, Noble- and transition-metal clusters: the d bands of silver and palladium. *Phys. Rev. B*, **33** (8), 5384-5390 (1986).
132. D. Sellmyer and S. Ralph, *Advanced magnetic nanostructures*. 2006, New York: Springer.
133. L. Xiao and L. Wang, Structures of platinum clusters: planar or spherical? *J. Phys. Chem. A*, **108** (41), 8605-8614 (2004).
134. Y. Liu and W. E. Mustain, Structural and electrochemical studies of Pt clusters supported on high-surface-area tungsten carbide for oxygen reduction. *ACS Catalysis*, **1** (3), 212-220 (2011).
135. T. Imaoka, H. Kitazawa, W.-J. Chun, S. Omura, K. Albrecht, and K. Yamamoto, Magic number Pt₁₃ and misshapen Pt₁₂ clusters: Which one is the better catalyst? *J. Am. Chem. Soc.*, **135** (35), 13089-13095 (2013).
136. S. H. Lee, S. S. Han, J. K. Kang, J. H. Ryu, and H. M. Lee, Phase stability of Pt nanoclusters and the effect of a (001) graphite surface through molecular dynamics simulation. *Surf. Sci.*, **602** (7), 1433-1439 (2008).
137. G. Rupprechter, K. Hayek, and H. Hofmeister, Microstructural study of epitaxially grown rhodium model catalyst particles. *Vacuum*, **46** (8-10), 1035-1040 (1995).

138. A. Renou and M. Gillet, Growth of Au, Pt and Pd particles in a flowing argon system: observations of decahedral and icosahedral structures. *Surf. Sci.*, **106** (1–3), 27-34 (1981).
139. K. Schouteden, E. Lijnen, D. A. Muzychenko, A. Ceulemans, F. C. Liviu, P. Lievens, and C. V. Haesendonck, A study of the electronic properties of Au nanowires and Au nanoislands on Au(111) surfaces. *Nanotechnology*, **20** (39), 395401-395408 (2009).
140. G. Rupprechter, K. Hayek, and H. Hofmeister, Characterization of oxide supported rhodium nanocrystals: habit, surface structure and catalytic activity. *Nanostruct. Mater.*, **9** (1–8), 311-314 (1997).
141. C. Kim and H. Lee, Shape effect of Pt nanocrystals on electrocatalytic hydrogenation. *Catal. Commun.*, **11** (1), 7-10 (2009).
142. T. Fukushima, K. Matshzawa, H. Yamada, A. Tasaka, and M. Inaba. *Preparation of cuboctahedral Pt nanoparticles and their electrochemical properties*. in *ECS Meeting Abstracts*. 2008.
143. S. Dobrin, CO oxidation on Pt nanoclusters, size and coverage effects: a density functional theory study. *PCCP*, **14** (35), 12122-12129 (2012).
144. A. V. Myshlyavtsev and P. V. Stishenko, Relative stability of icosahedral and cuboctahedral metallic nanoparticles. *Adsor*, **19** (2-4), 795-801 (2013).

145. G. Rupprechter, K. Hayek, and H. Hofmeister, Electron microscopy of thin-film model catalysts: activation of alumina-supported rhodium nanoparticles. *J. Catal.*, **173** (2), 409-422 (1998).
146. N. Watari and S. Ohnishi, Atomic and electronic structures of Pd₁₃ and Pt₁₃ clusters. *Phys. Rev. B*, **58** (3), 1665-1677 (1998).
147. B. Piveteau, M.-C. Desjonquères, A. M. Oles, and D. Spanjaard, Magnetic properties of 4d transition-metal clusters. *Phys. Rev. B*, **53** (14), 9251-9266 (1996).
148. B. Delley, *Modern Density Functional Theory: A Tool for Chemistry; Seminario*. Theoretical and Computational Chemistry ed. J.M. Seminario, Politzer, P., Eds. Vol. 2. 1995, Elsevier Science: Amsterdam
149. R. H. M. Smit, C. Untiedt, A. I. Yanson, and J. M. van Ruitenbeek, Common origin for surface reconstruction and the formation of chains of metal atoms. *Phys. Rev. Lett.*, **87** (26), 266102-266105 (2001).
150. J. Bartolomé, F. Bartolomé, L. M. García, E. Roduner, Y. Akdogan, F. Wilhelm, and A. Rogalev, Magnetization of Pt₁₃ clusters supported in a NaY zeolite: A XANES and XMCD study. *Phys. Rev. B*, **80** (1), 014404-014413 (2009).
151. H. Y. Sang, A. D. David, B. A. James, O. Pablo, and G. Keith, Density functional studies of small platinum clusters. *J. Phys.: Condens. Matter*, **9** (5), L39-L45 (1997).

- 152. K. Balasubramanian, Electronic states of Pt₂. *J. Chem. Phys.*, **87** (11), 6573-6578 (1987).
- 153. L. Zhi-Qiang, Y. Jing-Zhi, K. Ohno, and Y. Kawazoe, Calculations on the magnetic properties of rhodium clusters. *J. Phys.: Condens. Matter*, **7** (1), 47-53 (1995).
- 154. Y. Jinlong, F. Toigo, and W. Keln, Structural, electronic, and magnetic properties of small rhodium clusters. *Phys. Rev. B*, **50** (11), 7915-7924 (1994).
- 155. P. Villaseñor-González, J. Dorantes-Dávila, H. Dreyssé, and G. M. Pastor, Size and structural dependence of the magnetic properties of rhodium clusters. *Phys. Rev. B*, **55** (22), 15084-15091 (1997).
- 156. C. Barreteau, M. C. Desjonquères, and D. Spanjaard, Theoretical study of the icosahedral to cuboctahedral structural transition in Rh and Pd clusters. *Eur. Phys. J. D*, **11** (3), 395-402 (2000).
- 157. R. L. J. Fuyi Chen, Charge transfer driven surface segregation of gold atoms in 13-atom Au–Ag nanoalloys and its relevance to their structural, optical and electronic properties. *Acta Mater.*, **56** (10), 2374-2380 (2008).
- 158. S. Ahmadi, X. Zhang, Y. Gong, C. H. Chia, and C. Q. Sun, Skin-resolved local bond contraction, core electron entrapment, and valence charge polarization of Ag and Cu nanoclusters. *PCCP*, **16** (19), 8940-8948 (2014).
- 159. M. Zacchigna, C. Astaldi, K. C. Prince, M. Sastry, C. Comicioli, R. Rosei, C. Quaresima, C. Ottaviani, C. Crotti, A. Antonini, M. Matteucci, and P. Perfetti,

- Photoemission from atomic and molecular adsorbates on Rh(100). *Surf. Sci.*, **347** (1–2), 53–62 (1996).
160. L. Bianchettin, A. Baraldi, S. de Gironcoli, E. Vesselli, S. Lizzit, L. Petaccia, G. Comelli, and R. Rosei, Core level shifts of undercoordinated Pt atoms. *J. Chem. Phys.*, **128** (11), 114706–114711 (2008).
161. A. Baraldi, L. Bianchettin, E. Vesselli, S. d. Gironcoli, S. Lizzit, L. Petaccia, G. Zampieri, G. Comelli, and R. Rosei, Highly under-coordinated atoms at Rh surfaces: interplay of strain and coordination effects on core level shift. *New J. Phys.*, **9** (5), 143–154 (2007).
162. C. Bittencourt, M. Hecq, A. Felten, J. J. Pireaux, J. Ghijsen, M. P. Felicissimo, P. Rudolf, W. Drube, X. Ke, and G. Van Tendeloo, Platinum–carbon nanotube interaction. *Chem. Phys. Lett.*, **462** (4–6), 260–264 (2008).
163. H.-P. Steinrück, F. Pesty, L. Zhang, and T. E. Madey, Ultrathin films of Pt on TiO₂(110): growth and chemisorption-induced surfactant effects. *Phys. Rev. B*, **51** (4), 2427–2439 (1995).
164. A. Berkó, I. Ulrych, and K. C. Prince, Encapsulation of Rh nanoparticles supported on TiO₂(110)-(1 × 1) surface: XPS and STM studies. *J. Phys. Chem. B*, **102** (18), 3379–3386 (1998).
165. H. R. Sadeghi and V. E. Henrich, Rh on TiO₂: model catalyst studies of the strong metal-support interaction. *Appl. Surf. Sci.*, **19** (1–4), 330–340 (1984).

166. L. Óvári and J. Kiss, Growth of Rh nanoclusters on TiO₂: XPS and LEIS studies. *Appl. Surf. Sci.*, **252** (24), 8624-8629 (2006).
167. M. Klimenkov, S. Nepijko, H. Kuhlenbeck, M. Bäumer, R. Schlögl, and H. J. Freund, The structure of Pt-aggregates on a supported thin aluminum oxide film in comparison with unsupported alumina: a transmission electron microscopy study. *Surf. Sci.*, **391** (1–3), 27-36 (1997).
168. Y. G. Shen, D. J. O'Connor, and R. J. MacDonald, Stacking and structure of platinum on Cu(1 1 1) up to five monolayers. *Nucl. Instr. Meth. Phys. Res. Sec. B*, **135** (1–4), 361-365 (1998).
169. C. Solliard and M. Flueli, Surface stress and size effect on the lattice parameter in small particles of gold and platinum. *Surf. Sci.*, **156, Part 1**, 487-494 (1985).
170. J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, and N. K. Szymczak, When is a nanoparticle a cluster? an operando EXAFS Study of amine borane dehydrocoupling by Rh₄₋₆ clusters. *J. Am. Chem. Soc.*, **129** (39), 11936-11949 (2007).
171. W. Zheng, J. Zhou, and C. Q. Sun, Purified rhodium edge states: undercoordination-induced quantum entrapment and polarization. *PCCP*, **12** (39), 12494-12498 (2010).
172. K. A. Mills, R. F. Davis, S. D. Kevan, G. Thornton, and D. A. Shirley, Angle-resolved photoemission determination of *M*-line valence bands in Pt and Au using synchrotron radiation. *Phys. Rev. B*, **22** (2), 581-592 (1980).

- 173. J. Szöko and A. Berkó, Tunnelling spectroscopy of Pt nanoparticles supported on TiO₂ surface. *Vacuum*, **71** (1–2), 193-199 (2003).
- 174. A. Berkó, G. Ménesi, and F. Solymosi, STM study of rhodium deposition on the TiO₂(110)-(1 × 2) surface. *Surf. Sci.*, **372** (1–3), 202-210 (1997).
- 175. F. Aguilera-Granja, J. M. Montejano-Carrizales, and J. L. Morán-López, Magnetic moments of iron clusters: a simple theoretical model. *Phys. Lett. A*, **242** (4–5), 255-260 (1998).
- 176. H. Sun, Y. Ren, Y.-H. Luo, and G. Wang, Geometry, electronic structure, and magnetism of Rh_n (n = 9, 13, 15, 17, 19) clusters. *Physica B: Condens. Matter*, **293** (3–4), 260-267 (2001).
- 177. E. O. Berlanga-Ramírez, F. Aguilera-Granja, A. Díaz-Ortiz, J. L. Rodríguez-López, and A. Vega, Effects of the structural deformations on the magnetism of Rh₆ and Rh₁₃ clusters. *Phys. Lett. A*, **318** (4–5), 473-479 (2003).
- 178. S. N. Khanna, F. Cyrot-Lackmann, Y. Boudeville, and J. Rousseau-Voilet, Electronic structure of cubooctahedral clusters of platinum. *Surf. Sci.*, **106** (1–3), 287-292 (1981).
- 179. B. V. Reddy, S. N. Khanna, and B. I. Dunlap, Giant magnetic moments in 4d clusters. *Phys. Rev. Lett.*, **70** (21), 3323-3326 (1993).
- 180. M. J. Zhu, D. M. Bylander, and L. Kleinman, Rhodium monolayer on gold: A 4d ferromagnet. *Phys. Rev. B*, **43** (5), 4007-4010 (1991).

References

181. T. Futschek, M. Marsman, and J. Hafner, Structural and magnetic isomers of small Pd and Rh clusters: an ab initio density functional study. *J. Phys.: Condens. Matter*, **17** (38), 5927-5963 (2005).
182. S. Blügel, Two-dimensional ferromagnetism of 3d, 4d, and 5d transition metal monolayers on noble metal (001) substrates. *Phys. Rev. Lett.*, **68** (6), 851-854 (1992).
183. O. Eriksson, R. C. Albers, and A. M. Boring, Prediction of ferromagnetism and metamagnetism in 4d transition-metal overlayers on the (001) surface of Ag (4d = Tc, Ru, Rh, and Pd). *Phys. Rev. Lett.*, **66** (10), 1350-1353 (1991).
184. Y. Yamamoto, T. Miura, Y. Nakae, T. Teranishi, M. Miyake, and H. Hori, Magnetic properties of the noble metal nanoparticles protected by polymer. *Physica B: Condens. Matter*, **329–333, Part 2**, 1183-1184 (2003).
185. C. Jensen, J. van Slageren, P. Jakes, R.-A. Eichel, and E. Roduner, Support effects on hydrogen desorption, isotope exchange, chemical reactivity, and magnetism of platinum nanoclusters in KL Zeolite. *J. Phys. Chem. C*, **117** (44), 22732-22745 (2013).
186. S. Geprägs, S. Meyer, S. Altmannshofer, M. Opel, F. Wilhelm, A. Rogalev, R. Gross, and S. T. B. Goennenwein, Investigation of induced Pt magnetic polarization in Pt/Y₃Fe₅O₁₂ bilayers. *Appl. Phys. Lett.*, **101** (26), 262407-262410 (2012).

References

187. Y. Sakamoto, Y. Oba, H. Maki, M. Suda, Y. Einaga, T. Sato, M. Mizumaki, N. Kawamura, and M. Suzuki, Ferromagnetism of Pt nanoparticles induced by surface chemisorption. *Phys. Rev. B*, **83** (10), 104420-104432 (2011).
188. T. Kachel, W. Gudat, C. Carbone, E. Vescovo, S. Blügel, U. Alkemper, and W. Eberhardt, Ferromagnetic order in ultrathin Rh layers on Fe(100). *Phys. Rev. B*, **46** (19), 12888-12891 (1992).
189. J. de Graaf, A. J. van Dillen, K. P. de Jong, and D. C. Koningsberger, Preparation of highly dispersed Pt particles in Zeolite Y with a narrow particle size distribution: characterization by hydrogen chemisorption, TEM, EXAFS spectroscopy, and particle modeling. *J. Catal.*, **203** (2), 307-321 (2001).
190. H. D. Ozaydin, H. Sahin, R. T. Senger, and F. M. Peeters, Formation and diffusion characteristics of Pt clusters on graphene, 1H-MoS₂ and 1T-TaS₂. *Ann. Phys.*, **526** (9-10), 423–429 (2014).
191. C. Kerpel, D. J. Harding, D. M. Rayner, and A. Fielicke, Small platinum cluster hydrides in the gas phase. *J. Phys. Chem. A*, **117** (34), 8230-8237 (2013).
192. K. M. Ervin, J. Ho, and W. C. Lineberger, Electronic and vibrational structure of transition metal trimers: photoelectron spectra of Ni₃⁻, Pd₃⁻, and Pt₃⁻. *J. Chem. Phys.*, **89** (8), 4514-4521 (1988).
193. D. J. Harding, T. R. Walsh, S. M. Hamilton, W. S. Hopkins, S. R. Mackenzie, P. Gruene, M. Haertelt, G. Meijer, and A. Fielicke, Communications: The structure of Rh₈⁺ in the gas phase. *J. Chem. Phys.*, **132** (1), 011101-011104 (2010).

194. H. Häkkinen, M. Moseler, and U. Landman, Bonding in Cu, Ag, and Au clusters: relativistic effects, trends, and surprises. *Phys. Rev. Lett.*, **89** (3), 033401-033404 (2002).
195. Y. Lei, G.-F. Zhao, and Z. Zeng, The electronic structure of silver clusters. *JNN*, **10** (8), 5483-5489 (2010).
196. A. Shayeghi, R. L. Johnston, and R. Schafer, Evaluation of photodissociation spectroscopy as a structure elucidation tool for isolated clusters: a case study of Ag_4^+ and Au_4^+ . *PCCP*, **15** (45), 19715-19723 (2013).
197. P. Weis, Structure determination of gaseous metal and semi-metal cluster ions by ion mobility spectrometry. *Int. J. Mass spectrom.*, **245** (1–3), 1-13 (2005).
198. M. J. Piotrowski, P. Piquini, and J. L. F. Da Silva, Density functional theory investigation of $3d$, $4d$, and $5d$ 13-atom metal clusters. *Phys. Rev. B*, **81** (15), 155446-155459 (2010).
199. J. L. F. Da Silva, M. J. Piotrowski, and F. Aguilera-Granja, Hybrid density functional study of small Rh_n ($n = 2-15$) clusters. *Phys. Rev. B*, **86** (12), 125430-125435 (2012).
200. K. Jug, B. Zimmermann, P. Calaminici, and A. M. Koster, Structure and stability of small copper clusters. *J. Chem. Phys.*, **116** (11), 4497-4507 (2002).
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 ($n = 2-14$

- atoms) clusters: a DFT investigation. *J. Phys. Chem. A*, **118** (45), 10813-10821 (2014).
202. V. Bonačić-Koutecký, J. Pittner, M. Boiron, and P. Fantucci, An accurate relativistic effective core potential for excited states of Ag atom: an application for studying the absorption spectra of Ag_n and Ag_n^+ clusters. *J. Chem. Phys.*, **110** (8), 3876-3886 (1999).
203. J. Ho, K. M. Ervin, and W. C. Lineberger, Photoelectron spectroscopy of metal cluster anions: Cu_n^- , Ag_n^- , and Au_n^- . *J. Chem. Phys.*, **93** (10), 6987-7002 (1990).
204. V. E. Matulis, O. A. Ivashkevich, and V. S. Gurin, DFT study of electronic structure and geometry of neutral and anionic silver clusters. *Journal of Molecular Structure: THEOCHEM*, **664–665** (0), 291-308 (2003).
205. K. A. Jackson, First-principles study of the structural and electronic properties of Cu clusters. *Phys. Rev. B*, **47** (15), 9715-9722 (1993).
206. E. M. Fernández, J. M. Soler, I. L. Garzón, and L. C. Balbás, Trends in the structure and bonding of noble metal clusters. *Phys. Rev. B*, **70** (16), 165403-165416 (2004).
207. G. Guzmán-Ramírez, F. Aguilera-Granja, and J. Robles, DFT study of the fragmentation channels and electronic properties of Cu_n^v ($v = \pm 1, 0, 2$; $n = 3-13$) clusters. *Eur. Phys. J. D*, **57** (3), 335-342 (2010).

References

208. S. Ahmadi, X. Zhang, Y. Gong, and C. Q. Sun, Atomic under-coordination fascinated catalytic and magnetic behavior of Pt and Rh nanoclusters. *PCCP*, **16** (38), 20537-20547 (2014).
209. D. H. Kim, K. Shin, and H. M. Lee, CO oxidation on positively and negatively charged Ag₁₃ nanoparticles. *J. Phys. Chem. C*, **115** (50), 24771-24777 (2011).
210. C. Berg, M. Beyer, U. Achatz, S. Joos, G. Niedner-Schatteburg, and V. E. Bondybey, Effect of charge upon metal cluster chemistry: Reactions of Nb_n and Rh_n anions and cations with benzene. *J. Chem. Phys.*, **108** (13), 5398-5403 (1998).
211. Y. Zhu, R. Jin, and Y. Sun, Atomically monodisperse gold nanoclusters catalysts with precise core-shell structure. *Catalysts*, **1** (1), 3-17 (2011).
212. M. Banerjee, S. Sharma, A. Chattopadhyay, and S. S. Ghosh, Enhanced antibacterial activity of bimetallic gold-silver core-shell nanoparticles at low silver concentration. *Nanoscale*, **3** (12), 5120-5125 (2011).
213. A. L. Gould, C. J. Heard, A. J. Logsdail, and C. R. A. Catlow, Segregation effects on the properties of (AuAg)₁₄₇. *PCCP*, **16** (39), 21049-21061 (2014).
214. C. Y. Cha, G. Ganteför, and W. Eberhardt, Photoelectron spectroscopy of Cu_n⁻ clusters: Comparison with jellium model predictions. *J. Chem. Phys.*, **99** (9), 6308-6312 (1993).

References

215. Y. Nie, X. Zhang, S. Ma, Y. Wang, J. Pan, and C. Q. Sun, XPS revelation of tungsten edges as a potential donor-type catalyst. *PCCP*, **13** (27), 12640-12645 (2011).
216. M. Pereiro and D. Baldomir, Structure of small silver clusters and static response to an external electric field. *Phys. Rev. A*, **75** (3), 033202-033211 (2007).
217. S. Suri, *Synthesis, Structural and Magnetic Properties of Copper Doped Cerium Oxide Nanoparticles*, in *Electronic Engineering*. 2010, West Virginia University: Ann Arbor. p. 1-63.
218. G. H. Lee, Y. T. Jeon, S. H. Huh, B. Kim, J. Park, and S. J. Oh, Paramagnetism in (Rh)_n (n~1100) nanoparticles. *J. Korean Phys. Soc.*, **46** (2), 556-558 (2005).
219. D. J. Harding, P. Gruene, M. Haertelt, G. Meijer, A. Fielicke, S. M. Hamilton, W. S. Hopkins, S. R. Mackenzie, S. P. Neville, and T. R. Walsh, Probing the structures of gas-phase rhodium cluster cations by far-infrared spectroscopy. *J. Chem. Phys.*, **133** (21), 214304-214312 (2010).
220. F. Aguilera-Granja, R. C. Longo, L. J. Gallego, and A. Vega, Structural and magnetic properties of X₁₂Y (X, Y = Fe, Co, Ni, Ru, Rh, Pd, and Pt) nanoalloys. *J. Chem. Phys.*, **132** (18), 184507-6 (2010).
221. J. Kaiser, L. Leppert, H. Welz, F. Polzer, S. Wunder, N. Wanderka, M. Albrecht, T. Lunkenbein, J. Breu, S. Kummel, Y. Lu, and M. Ballauff, Catalytic activity of nanoalloys from gold and palladium. *PCCP*, **14** (18), 6487-6495 (2012).

References

222. D. Tang and J. Zhang, Theoretical investigation on CO oxidation catalyzed by a copper nanocluster. *RSC Advances*, **3** (35), 15225-15236 (2013).
223. M.-S. Liao, J. D. Watts, and M.-J. Huang, Theoretical comparative study of oxygen adsorption on neutral and anionic Ag_n and Au_n clusters ($n = 2-25$). *J. Phys. Chem. C*, **118** (38), 21911-21927 (2014).