STRUCTURAL AND MAGNETIC PROPERTIES OF RHODIUM CLUSTERS

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STRUCTURAL AND MAGNETIC PROPERTIES OF RHODIUM CLUSTERS

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LIST OF ABBREVIATIONS

Ag	silver
Au	gold
BFGS	Broyden–Fletcher–Goldfarb–Shanno
BH	basin hopping
BHGA	basin hopping plus genetic algorithm
BO	Born-Oppenheimer approximation
bcc	body-centered cubic
Co	cobalt
Cu	copper
DFT	density functional theory
DFTB	density functional based tight binding
ECP	effective core potential
Fe	iron
fcc	face-centered cubic
GA	genetic algorithm
GGA	generalized gradient approximation
GTO	Gaussian-type-orbitals
HF	Hartree-Fock
HOMO	highest occupied molecular orbital

KS	Kohn-Sham
LCAO	linear combinations of atomic orbitals
LCGTO	linear combination of Gaussian-type orbital
LDA	local-density approximation
LUMO	lowest unoccupied molecular orbital
MCP	model core potential
Ni	nickel
PES	potential energy surface
Pd	palladium
PT	parallel tempering
Pt	platinum
PTMBHGA	parallel tempering multicanonical basin hopping plus genetic algorithm
QECP	quasi-relativistic effective core potential
RMCP	relativistic model core potential
RMS	root mean square
SCF	self-consistent field
SK	Slater-Koster
Rh	rhodium
TF	Thomas-Fermi

LIST OF SYMBOLS

α	up spin
β	down spin
ρ	electron density
μ	total spin magnetic moment
$\tilde{\nu}$	vibrational frequency
η	basis function
χ	spin orbital
φ	spatial orbital
ε	energy of spin orbital
ε_0	vacuum dielectric constant
Ψ	wavefunction
Ψ_{elec}	electronic wavefunction
ν	random number in GA
ϕ	sorting parameter in GA
δ	space between stationary energy levels
N	cluster size (number of atoms)
n	number of electrons
N_{c}	number of individuals (atomic configurations)
N_q	number of charges

e	charge of an eletron
Z	charge of a nucleus
m	mass of a nucleus
m_e	mass of an electron
m_r	reduced mass
$\mathbf{R}$ or $\mathbf{r}$	position vector
$\mathbf{s}$	position vector of a charge
r_{ij}	pair distance between atoms i and j
r_0	nearest-neighbour distance
$\bar{d}$	average radial bond distance
$\mathbf{P}$	momentum of a nucleus
$\mathbf{p}$	momentum of an electron
M	spin multiplicity
M	total spin angular momentum
$\hat{H}$	Hamiltonian operator
$\hat{H}_\mathrm{elec}$	electronic Hamiltonian operator
f	normalized fitness in GA
C	any configuration
C_TF	constant for TF model
g	gradient matrix
$\mathbf{H}$	Hessian (force constant matrix)

k	force constant of a vibration mode
E	energy
E_F	Fermi energy
E_b	binding energy
E_tot	total energy
E_elec	total electronic energy
E_kin	total kinetic energy
E_xc	exchange-correlation energy
E_TF	energy of an atom in TF model
T_TF	kinetic energy in TF model
ΔE	relative energy with respect to lowest energy level
$\Delta^2 E$	second-order difference of energies
D_e	dissociation energy
J	Coulomb repulsion
V	potential energy of opriginal PES in BH
$\tilde{V}$	potential energy of transformed PES in BH
V_rep	repulsive potential in Gupta potential
V_att	attractive potential in Gupta potential
V_Ne	attractive potential ecerted by nuclei on electrons
V_xc	exchange-correlation potential
V_ext	external potential

V_{eff}	external potential in KS approach

SIFAT-SIFAT STRUKTUR DAN MAGNETIK KLUSTER RHODIUM

ABSTRAK

Kluster nano merupakan satu sistem yang amat menarik sejak dekad akhir-akhir ini kerana, jika dibandingkan dengan keadaan pukal, ia memperlihatkan kelakaun yang luar biasa di mana sifat-sifat tabiinya bergantung kepada saiz. Sejauh yang unsur-unsur peralihan *4d* dipertimbangkan, kluster rhodium (Rh) merukapan salah satu sistem yang paling banyak diperbahaskan. Rh dalam bentuk pukal adalah bahan paramagnet, tetapi apabila ia dikurangkan kepada dimensi berskalar atomik, sifat-sifat struktur dan magnetiknya akan berubah-ubah mengikuti saiz kluster. Projek ini bertujuan untuk mengaji dan menyiasat secara sistematik sifat-sifat yang pelik tersebut bagi kluster Rh_N yang berada pada keadaan tenaga yang paling rendah, di mana N adalah bilangan atom di antara 2 hingga 23. Untuk melanjutkan pemahaman dalam kluster-kluster yang besar, Rh_{26}, Rh_{30} dan Rh_{38} juga termasuk dalam kajian tersebut. Konfigurasi kluster-kluster pada keadaan tenaga yang paling rendah diperolehi dengan menjalankan pengoptimuman berperingkat dua. Mula-mula sekali, satu konfigurasi rawak dioptimumkan secara global dengan menggunakan satu algoritma carian yang tidak berat sebelah, BHGA (keupayaan empirikal Gupta sebagai kalkulator tenaga), diikuti dengan pengoptimuman secara lokal melalui pengiraan berprinsip pertama DFT dengan formalisma spin-polarisasi LCAO. Kesan-kesan kontaminasi spin tidak diambil kira dalam pengiraan. Dengan menjalankan analisis energik, kluster-kluster Rh dengan bilangan atom genap didapati lebih stabil, berbanding dengan kluster-kluster yang mempunyai bilangan atom ganjil. Sifat-sifat struktur kluster-kluster telah dikaji daripada aspek geometri, seperti purata jarak bon jejarian, purata jarak jiran terdekat dan simetri molekul. Sifat-sifat magnetik yang bergantung kepada saiz kluster telah dibentangkan dan berkaitan dengan simetri kluster-kluster tersebut. Struktur elektronik kluster-kluster Rh juga dikaji supaya dapat memahami dengan lebih lanjut mengenai bagaimana elektron ditaburkan dalam struktur-struktur kluster malalui analisis populasi. Secara umum, hasil kajian ini bersetuju dengan kerja-kerja lain yang dilaporkan sebelum ini. Hasil-hasil baru yang diperoleh dalam tesis ini termasuk (i) konfigurasi yang telah dioptimum bagi kluster-kluster besar yang jarang dilaporkan seperti Rh_{26}, Rh_{30} dan Rh_{38}, (ii) kluster-kluster Rh menjadi lemah dalam magnetik apabila bilangan atom melebihi 19, serta (iii) order makgetik yang luar jangkaan dalam beberapa kluster didedahkan, di mana spin-spin negatif dijumpai dalam atom-atom terpilih dalam kluster-kluster tersebut. Khususnya, tesis ini meramalkan anomali momen magnet yang besar untuk Rh_{38}, pada nilai 30 μ_B, yang tidak pernah dilaporkan dalam literatur. Tesis ini melaporkan satu kajian yang sistematik untuk pemodelan komputasi bagi kluster Rh di peringkat atomik dengan menggunakan strategi komputasi dua peringkat dan pelbagai perkakas teori, yang boleh pada dasarnya digunakan untuk sistem kluster yang lain untuk memperolehi pemahaman yang berharga pada tahap DFT.

STRUCTURAL AND MAGNETIC PROPERTIES OF RHODIUM CLUSTERS

ABSTRACT

Nanocluster has been a system of interest for the past decades due to its peculiar size-dependent properties as compared to its bulk counterparts. As far as 4*d* transition elements are concerned, rhodium (Rh) cluster is one of the most-debated systems. Bulk Rh is a paramagnetic material, but when it is reduced to atomic dimension, its structural and magnetic properties vary with the cluster size. This project is aimed to perform systematic study to investigate the unusual properties at the lowest energy state of Rh_N clusters, where N is the number of atoms ranged from 2 to 23. To study large Rh clusters, Rh_{26}, Rh_{30} and Rh_{38} are also included in the study. The lowest-energy configurations of the clusters were obtained by performing two-stage optimization. A random configuration was first globally optimized using an unbiased search algorithm, BHGA (empirical Gupta potential as energy calculator), followed by local optimization via first-principles DFT calculations with spin-polarized LCAO formalism. The effect of spin contamination was not considered in the calculations. By performing energetic analysis, Rh clusters with even number of atoms are found to be relatively stable, compared to those with odd number of atoms. Structural properties of the clusters were studied from their geometrical aspects, such as average radial bond distance, average nearest neighbour distance and molecular symmetry. Size-dependent magnetic properties of the clusters were presented and related to their symmetries. Electronic structures of Rh clusters were studied to further understand how are the electrons distribute over the structures via population analysis. In general, the results from current study agree with previous works. The new results obtained in this thesis include (i) optimized configurations of larger clusters that are rarely reported previously such as Rh_{26}, Rh_{30} and Rh_{38}, (ii) Rh clusters become weakly magnetic when the number of atoms exceeds 19, and (iii) unexpected magnetic ordering in some clusters are revealed, in which negative spins are found in selected atoms in these clusters. In particular this thesis predicted an anomalously large total magnetic moment for Rh_{38} at a value of 30 μ_B, which has not been reported in the literature. This thesis reports a systematic study to computational modelling of Rh clusters at atomistic level using a two-stage computational strategy and multitude of theoretical tools, which can be in principle applied to other cluster systems to gain valuable DFT-level insight.

CHAPTER1

INTRODUCTION

Why can't we manufacture these small computers somewhat like we manufacture the big ones? What are the limitations as to how small a thing has to be before you can no longer mold it? - Feynman (1960) -

1.1 Overview

It has been decades after the early concept of miniaturization is introduced, yet its development does not arrive at the saturation stage. In fact, engineers and researchers are still trying to manufacture ever smaller electronic, optical and mechanical devices. The greatest motivation of developing nanotechnology is due to its wide range of promising technological applications, from industrial (as in catalytic process) to medical (as in cancer diagnosis) applications.

Nowadays, thanks to modern technological advances, experimentalists are able to fabricate, manipulate and even visualize particles at the atomic scale, specifically nanoparticles with diameters much less than 100 nm. On the other hand, with powerful high-performance computing resources, theorists are able to suggest new insights, investigate thoroughly properties and applications of nanoparticles, as well as design a new material by carrying out *in silico* experiments. As a result of the synergy between interdisciplinary experimental and theoretical point of views, material science in low dimension is still the field of interest and worthwhile for further study.

As far as theoretical investigation is concerned, theorists have been studying a variety of materials, including organic and inorganic materials, particularly the transition elements. In previous studies, it has been shown that nanoclusters, especially for those comprised of 3*d* and 4*d* transition elements, exhibit peculiar properties as compared to their bulk counterparts (Billas, Chatelain, & de Heer, 1994; Cox, Louderback, Apsel, & Bloomfield, 1994). Despite the existence of many theoretical works to predict ground-state structures of clusters, they are difficult to be confirmed experimentally due to scarcity of experimental evidence. Among all, rhodium (Rh), which has great applications in catalysis, is one of the most discussed 4*d* transition elements for more than two decades (Hang, Hung, Thiem, & Nguyen, 2015; Reddy, Khanna, & Dunlap, 1993).

1.2 Problem Statements

Although there have been a number of theoretical works reported on the unusual size-dependent properties of Rh clusters, there are still unsettled inconsistencies in existing published studies concerning their lowest-energy structures and ground-state properties. This is mainly due to the lack of experimental evidence on measured geometrical structures of the clusters.

Density functional theory (DFT) calculations of clusters are commonly categorised into two types of formalisms, namely, plane-wave basis and linear combinations of atomic orbitals (LCAO) approaches. It is generally agreed that the former is more suitable for periodic systems meanwhile the latter is for finite systems. In the literature, both formalisms have been used to calculate clusters at DFT level. Most of the previous studies of Rh clusters based on LCAO formalism concentrated only on small clusters ($\lesssim$ Rh_{13}). In addition, electronic structures and magnetic ordering of Rh clusters for sizes larger than 13 using LCAO approach are also seldom reported in details.

1.3 Objectives of Study

This thesis is aspired to provide a detailed density functional theory (DFT) computational study on the Rh clusters with a selected range of sizes measured in terms of the number of atom comprising the clusters. The first objective of this study is to determine the lowest-energy configurations of Rh clusters, up to 23 atoms. In addition, clusters with 26, 30 and 38 atoms are selectively chosen for the study. Rh_{26} and Rh_{38} are selected due to their high symmetry orders, while Rh_{30} acts as a connection point in exploring large clusters within this range of cluster size ($26 \leq N \leq 38$). This work located the global minimum of each cluster by performing a two-stage optimization: (i) unbiased search for the lowest-energy structure of a cluster in the Gupta empirical potential energy surface, and followed by (ii) optimization of the structures obtained from (i) using first-principles DFT calculation.

The next objective is to derive the structural and magnetic properties of the DFT-optimized Rh clusters, targeting large cluster sizes ($N \geq 20$) that have rarely been reported in the literature.

Last but not least, the present work endeavours to derive the very physically-pertinent information of the electronic structures of the clusters, including their molecular orbitals, distributions of charges and spins over the clusters, and hence, their magnetic orderings.

1.4 Organization of Thesis

Up to this point, a brief introduction about the motivation and objectives of this thesis has been given in Sections 1.2 and 1.3.

The following chapter (Chapter 2) is separated into two major parts to review available literature: (i) a general introduction of atomic clusters and magnetism of nanoparticles, and (ii) previous works related to Rh clusters. In this chapter, it highlights the gap in the theoretical understanding of Rh clusters, which becomes the motivation of this project.

Chapter 3 discusses the theoretical frameworks that form the basis of the methods employed in this project. It starts from the fundamental understanding in computational modelling techniques, followed by the conventional optimization approaches to locate the global minimum in a potential energy surface. The basic ideas and theoretical basis of DFT are also covered in this chapter.

The methodology (computational details), including the computational protocol employed, parameters and approximations used in this project, is given in Chapter 4. Vibrational frequency analysis, which was performed to check whether a given configuration is a true global minimum, is also discussed in this chapter. Moreover, the geometrical structures and associated magnetic moments of the DFT-optimized Rh clusters obtained are reported. The results are then discussed and compared with that reported in the literature.

The unusual size-dependence magnetic properties of Rh clusters are discussed in

Chapter 5. Following this, the optimized configurations are investigated from energetic (binding energy and relative stabilities) and geometrical aspects (average radial bond distance, average nearest-neighbour distance and molecular symmetry) in order to study the structural properties of the Rh clusters.

The electronic structures of the optimized Rh clusters are explored in Chapter 6. In this chapter, molecular orbitals of the clusters are investigated in order to understand the arrangement of electrons in spin-polarized environment. This is followed by the discussion on the electronic stability of the clusters. Subsequently, the distributions of charges and spins of the electrons over the clusters, which in turn suggest their magnetic orderings, are discussed in this chapter.

Lastly, the thesis is concluded in Chapter 7. The chapter also gives suggestions on how to improve the present computational modelling technique and other possible directions as extensions to the work done in this thesis. This thesis presents two appendices: Appendix A illustrates the optimized Rh clusters at empirical level, while Appendix B displays displays the zero-point energies and infrared spectra of Rh clusters optimized from DFT.

CHAPTER2

LITERATURE REVIEW

This chapter gives an overview of nanoparticles. Next, optimization methods generally used in theoretical frameworks are tabled, followed by topics related to magnetism of nanoparticles. The last section reviews previous works, both theoretical and experimental ones, that are related to rhodium (Rh) clusters.

2.1 Overview of Nanoparticles

Nanoscience has encountered vast development for the past decades following the vision of Feynman (1960). This field is not only limited to the understanding of basic sciences, but it also addresses issues about new technological applications (Baletto & Ferrando, 2005). The materials that are involved in these studies and applications are called nanomaterials. One of the nanomaterials of great interest are nanoparticles, and they are ultra-fine particles in the size of nanometer order (Nogi, Naito, & Yokoyama, 2012). Comparison with other small particles whose sizes are below 1 mm is shown in Figure 2.1 (Roduner, 2006). In general, nanoparticles can exist in various forms like spherical, rod-like, film or more complex geometries.

Nanoparticles play an important role of being a bridge connecting atoms or molecules and bulk materials. This is because these particles behave very much differently as compared to their bulk counterparts. In fact the properties of nanoparticles, such as structural, thermal and magnetic properties, change drastically with size. Such unusual

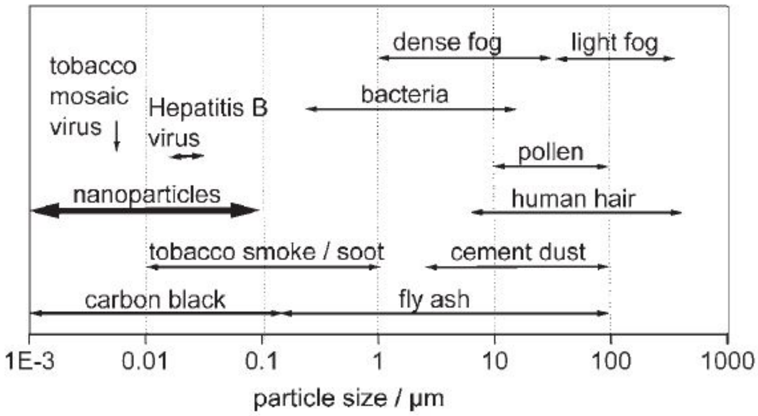

Figure 2.1: Comparison of the size of nanoparticles with other small particles. The dimension of nanoparticles is in the regime below 0.1 μm.(Roduner, 2006)

size dependence has prompted much interest among researchers to provide theoretical explanations and gather more in-depth experimental data to this phenomena, as well as finding a way to control their properties by controlling their formation process (Baletto & Ferrando, 2005).

On the other hand, what really interest engineers are the applications of nanoparticles. Nanoparticles, especially nanoclusters, have a wide range of applications, including skincare cosmetics, cancer treatment, light emitting diodes, microelectronics packaging and etc. Nanoclusters not only can be used in homogeneous catalytic reactions, they also useful in designing nanocatalysts with specific reactivity. In addition, a variety of nanoparticles such as carbon nanotubes, metal and semiconductor nanoclusters, have been synthesized and proposed as potential building blocks for optical and electronic devices (Castleman Jr & Khanna, 2009; Fedlheim & Foss, 2001; Nogi et al., 2012; Tsutsui, 2012).

Nanocluster (in short, cluster) is referred to a particle that aggregates between a few and many millions of identical or various types of atoms or molecules, with size about 1 – 10 nm (Fedlheim & Foss, 2001; Ferrando, Jellinek, & Johnston, 2008). It can be in

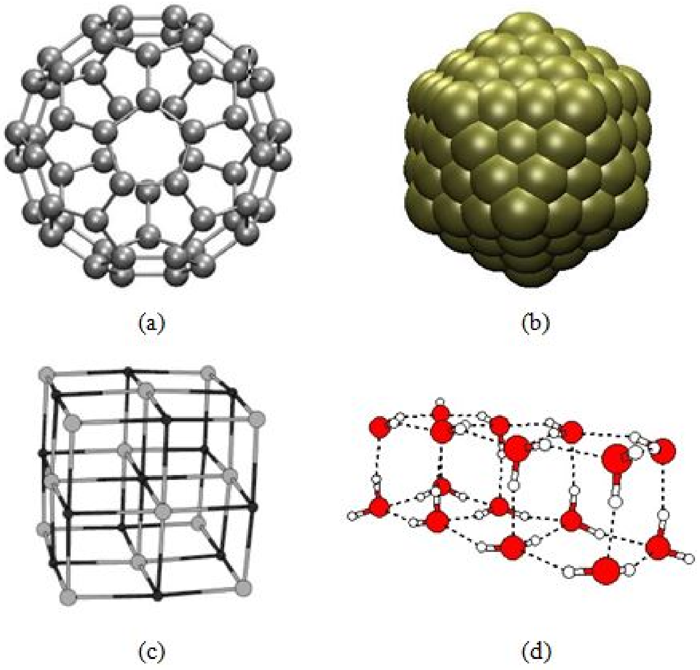

Figure 2.2: Examples of cluster types: (a) fullerenes [C_{60} (Yen & Lai, 2015)], (b) metal clusters [Ag_{147} (Huang et al., 2011)], (c) ionic clusters [$(NaCl)_{13}Cl^{-}$(Doye & Wales, 1999)], and (d) molecular clusters [$(H_2O)_{16}$ (D. J. Wales & Hodges, 1998)].

different shapes, for example a sphere and a plane that are very symmetric or irregular shape as in amorphous (Roduner, 2006). There are assorted types of clusters that have been studied experimentally or through computer simulation, such as fullerenes, metal, ionic and molecular clusters as illustrated in Figure 2.2 (Johnston, 2002). In contrast to a simple molecule, a cluster does not have a fixed size or composition. For instance, an oxygen and two hydrogen atoms are placed at a well-defined angle to each other in a water molecule, whilst a water cluster may contain a number of water molecules, binding together to form in overall a specific shape as displayed in Figure 2.2(d) (Baletto & Ferrando, 2005). The most important feature that draws attentions from scientists and engineers is their size-dependent properties, at which their geometric shape and energy stability as well as electronic properties are drastically changed with size (Ferrando et al., 2008). Hence, studying the clusters of chosen composition and size allows ones to investigate their unique physical and chemical behaviour, as well as exploring the fundamental mechanisms governing their chemical reactivity (Castleman Jr & Khanna, 2009).

The extensive studies in this field involve various types of material, which have covered most of the elements in the periodic table, from alkali metals to late-transition metals as well as non-metals and rare gases. Among all, metal clusters are the most investigated because of their wide range of applications and the advantage of being comparatively easier to be synthesized and modified chemically (Fedlheim & Foss, 2001). Attentions are especially drawn to the transition metals that have been proved to have great industrial applications. Going down the transition block, clusters of ferromagnetic 3*d* elements like iron (Fe), cobalt (Co) and nickel (Ni) were shown to have enhancement in magnetic moments and this is found to be caused by the increase in localization of electrons and their narrow band widths (Billas et al., 1994). On the other hand in period 5 and 6, 4*d* and 5*d* elements are non-magnetic in bulk form. However, 4*d* metal like rhodium (Rh) and palladium (Pd), and 5*d* metal like platinum (Pt) were shown to become magnetic when their dimensions were reduced to atomic scale (Cox et al., 1994; Di Paola, D'Agosta, & Baletto, 2016; Kumar & Kawazoe, 2003). The clusters composed of coinage metal from group 11, especially the copper (Cu), silver (Ag) and gold (Au), are of great interests to researchers. In particular, Au cluster draws the most attention as it was reported for transformation from a planar structure to a three-dimensional structure (Xiao & Wang, 2004) when it arrives at certain number of atoms.

Apart from pure metal clusters, there are also vast studies in nanoalloys, comprised of more than one type of atoms. Ferrando et al. (2008) reviewed different kind of works related to bimetallic cluster, from experimental techniques for generating and characterizing the nanoalloys to theoretical studies of their geometrical and dynamical properties. Works also have been extended to ternary clusters, and they are more complex compared to pure metal and bimetallic clusters in terms of interatomic interactions, and hence searching of their ground-state configurations is a nightmare. One of the most-studied clusters is Cu-Ag-Au. It was fabricated by physical vapour deposition (Chatterjee, Howe, Johnson, & Murayama, 2004). Its segregation was later studied by computational modelling at the empirical level by using different methods (Cheng, Liu, Wang, & Huan, 2007; Liu, Espinosa-Medina, Sosa, & la Torre, 2009; Wu, Wu, Chen, & Qiao, 2011).

Nanoparticles have great potentials for advanced applications. Theoretical study is as important as fabrication and synthesis of the nanoparticles, as it allows one to peek more fundamentally into the size-dependence properties of the clusters. It allows ones to understand the transformation of these properties as the system grows, which in turn can be references for the experimentalists and engineers for further applications in real life.

2.2 Magnetism of Nanoparticles

Magnetism, due to its wide application in practice, is one of the most interesting and important properties for a given material. Magnetic property is widely applied in medical fields, including the magnetic resonance imaging (MRI), cancer treatment and targeted drug delivery. The concept of magnetism is also used in environmental treatment, in which the contaminants are seperated from a solution through the use

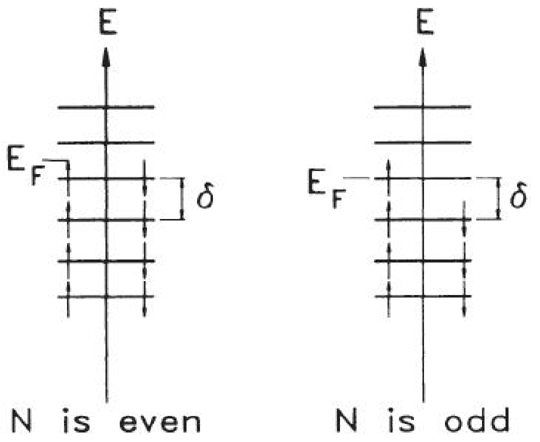

Figure 2.3: Schematic representation of the spin occupation of a set of equally spaced levels in a cluster (de Jongh, 2013).

of an external magnetic field (Binns, 2014). Nowadays, the development of new technological processes permits the production of smaller magnetic particles, as they are used in increasing information density in data storage (Roduner, 2006). These are the practical motivations that make magnetism of nanoparticles a continual hot research topic.

Consider a cluster which is in equilibrium, and its stationary energy levels as obtained from Hamiltonian are equally spaced with δ, as shown in Figure 2.3. According to Hund's rules, the n electrons will occupy the energy levels until they arrive at the last and highest level, at which is known as Fermi energy (E_F). It is shown that for an even number of n, there are two electrons with opposite spins occupied at E_F, cancelling each other and resulted in a non-magnetic cluster. On the other hand, when n is odd, there is an unpaired spin at E_F which makes the cluster magnetic (de Jongh, 2013).

There are two main factors that contribute to the magnetic behaviour of magnetic clusters, namely intra-atomic and interatomic charge transfer (Di Paola et al., 2016). The intra-atomic charge transfer is induced by the intraband splitting between up and down spins around E_F. Tsukerblat (2008) have discussed the group-theoretical approaches based on the spin and point symmetries which might results in molecular magnetism in metal clusters. On the contrary, the interatomic contribution indicates the charge transfer between adjacent atoms. In other words, it depends on the immediate environment of the atoms which relates directly to the geometrical structure of the cluster itself (Roduner, 2006).

The local geometrical environment has been shown to be one of the factors that dominates the magnetism of metal clusters. For instance, local dimensionality and structural symmetry might enhance or reduce magnetic effect of a cluster. In this respect, Dunlap (1990) linked the structural symmetry to the magnetism of 13-atom Fe clusters, suggesting high-symmetrical icosahedral structure with greatest magnetic moments is the ground-state configuration. It was suggested that the highly symmetric clusters are more likely to have degenerate energy levels. The degeneracy allows different spins to occupy the orbitals according to Hund's rule which promotes more unpaired spins and hence, each atom is expected to carry a larger magnetic moment (Roduner, 2006). In recent study, Yen and Lai (2016) also found uncommonly net magnetic moments in highly symmetric coinage metal clusters, Ag_{38} and Cu_{38}, also in bimetallic cluster $Ag_{24}Cu_{14}$. Besides the effect of symmetry, the splitting of electronic bands which consequently affects the spin occupation, can also be caused by strong distortion of next-nearest neighbour (commonly known as second-nearest neighbour) with respect to that of a bulk system (Mohn, 2006). This was shown recently by Di Paola et al. (2016) that the magnetism in Pt clusters, especially for those with more than 100 atoms, are enhanced. The authors suggested the strong dependence of total magnetization of the clusters on the local atomic arrangements, in particular the nearest and second-nearest neighbour distances.

Despite previous works that reported the geometrical factors which affect magnetism of clusters, as discussed in the above, these works concentrated only on specific materials. Hence, what had been discussed in their context may not be applicable to other chemical species. In fact, the understanding of magnetic properties by DFT calculation becomes increasingly difficult when itinerant electrons are involved, such as in the case of transition metals. This is due to the possibility of forming complex structures when the system contains a significant number of *d* and *f* electrons (van Dijk, 2011).

Magnetism of metal clusters is an interesting topic that is worth to investigate further, both experimentally and theoretically. Apparently, geometrical effect on the magnetism is more commonly studied as compared to intra-atomic contribution. However, how geometry influences magnetism in a cluster is not exactly known, especially for the transition metal clusters. The state of matter hence warrants the necessity to carry out more study on how geometrical environment influences the magnetism of a metal cluster.

2.3 Works Related to Rhodium Clusters

Being a noble transition metal element, rhodium (Rh) which has partially filled 4*d* orbital, is paramagnetic in bulk system. In low dimension, Rh nanoparticles have been proved to behave very differently than bulk form. Promising applications of these nanoparticles, especially in homogeneous catalysis (Tsutsui, 2012), draw attentions of researchers to study their unique characteristics.

Nevertheless, there are not much experimental works done on Rh clusters. Using high-temperature Knudsen effusion mass spectrometry, Gingerich and Cocke (1972) and Cocke and Gingerich (1974) provided the first experimental study on Rh dimer (Rh_2). Later, H. Wang et al. (1997) and Langenberg and Morse (1998) also reported their study on Rh_2 by using mass selected ion deposition and resonant two-photo ionization techniques respectively. Using the Stern-Gerlach experiment, it had been found that Rh clusters had large magnetic moments, which became approximately zero when the clusters have more than 60 atoms (Cox et al., 1994; Cox, Louderback, & Bloomfield, 1993). Consistent with this study, Ma, Moro, Bowlan, Kirilyuk, and de Heer (2014) who suggested the multiferroic behaviour of Rh clusters, presented the similar and temperature-independence magnetic behaviour as the cluster grows in number. These experimental works only reported measurements of the magnetism of specific free-standing Rh clusters. Quantitative aspects of the geometrical structures of the measured clusters were not addressed. The only work that mentioned about cluster geometry was done by Sessi et al. (2010), which measured the magnetic moment of Rh clusters on inert xenon buffer layers and suggested biplanar geometries for the clusters with an average size of 20 atoms. A thorough literature search suggests that there is no [except Sessi et al. (2010)] experimental measurement made on the geometries of stable free-standing Rh clusters.

On the other hand, inspired by Reddy et al. (1993) who found remarkably magnetic moment per atom in a stable icosahedral Rh_{13}, Rh clusters are studied theoretically intensively over these years, especially after experimental confirmations reported by Cox et al. (1993). The main concern of theorists is to determine the ground-state configurations, including geometries and physical properties, of the clusters.

To determine the ground-state configuration of a cluster, the choice of initial configuration for first-principle calculation is crucial. In earlier works, due to limitation in computational abilities, theorists put the attention mainly on simple structures such as body-centered cubic (bcc), face-centered cubic (fcc), icosahedral and octahedral structures. Later, intelligent search algorithm such as basin hopping (BH) and genetic algorithm (GA), as well as optimization technique using molecular dynamics like simulated annealing, were used to generate the initial atomic configurations. However, without experimental evidence, it is still a controversial topic even though dozens of works have been reported and the root of this debate is the modelling approach.

In the early days, Rh clusters were studied using discrete-variational local-density-functional method by Jinlong, Toigo, and Kelin (1994) and Li, Yu, Ohno, and Kawazoe (1995), in which both of them agreed with a ferromagnetic icosahedral Rh_{13}. In other work, Rh clusters were calculated using tight-binding model within Hartree-Fock (HF) approximation in order to study their electronic structures. By using this approximation, Guirado-López, Spanjaard, and Desjonqueres (1998) was able to study large clusters and found the antiferromagnetic behaviour Rh_{55} and Rh_{79}. While H. Sun, Ren, Luo, and Wang (2001) and Aguilera-Granja, Rodríguez-López, Michaelian, Berlanga-Ramírez, and Vega (2002) reported icosahedral growth of Rh clusters, Aguilera-Granja, Montejano-Carrizalez, and Guirado-López (2006) studied the non-compact growth of the clusters by combining the HF and DFT approaches.

Likewise, DFT which includes electronic correlation that is not included in HF approximation, is claimed to be more reliable and has been widely applied in recent years. As a whole, most of the DFT software packages available today use either plane-wave basis or LCAO approach to solve the Kohn-Sham (KS) equations. Both approaches could in practice be applied to calculate clusters, but there are concerns about which approach describes a cluster system better. By using plane wave method, Kumar and Kawazoe (2003) was the first to explore a large Rh cluster, up to 147 atoms. Even though this approach has been proved to be able to handle large clusters, the following works that used the similar method do not increase the cluster size, where the largest size was up to 64 atoms only (Bae, Kumar, Osanai, & Kawazoe, 2005). On the contrary, studies on Rh clusters by employing LCAO approach, do not exceed 13 atoms even in the recent study done by Hang et al. (2015). This is because increasing of the cluster size increases the number of atomic orbitals, which in turn increases the complexity of computation. Although in principle it is possible to do similar modelling for a large cluster using LCAO method, the interest to do so somewhat fades away due to the expensive computational cost (i.e. long computational duration and demanding hardware resources).

DFT calculations can be carried out by expanding the electron density functional in either plane-wave or LCAO basis sets. As a well-known norm, the absolute values of the resultant output from these calculations could be strongly dependent on the type of basis set employed, as well as the initial configurations used. For example, consider the specific case of Rh_{13} cluster.

Chou, Hsing, Wei, Cheng, and Chang (2013) and Hang et al. (2015) considered a number of different 13-atom configurations as initial structures of Rh_{13}, and performed calculations based on plane-wave basis and LCAO approach respectively. Although both of these studies reported a similar geometry (capped double cube) as lowest-energy

Rh_{13}, the magnetic moments reported are numerically different. This example illustrates a common dilemma often encountered by routine DFT practitioners. Hence, as a rule of thumb in the practice of DFT calculations, the quality of theoretical results is opened to be better judged by comparing against experimental data rather than existing theoretical studies.

As a whole, theoretical studies of Rh clusters over the years mainly hover on some specifically interesting small clusters, such as Rh_{13} and Rh_{19}. Apparently, the choice of approach in modelling a cluster is an important factor that might affect directly the ground-state configurations obtained. This can be seen from the various ground-state configurations reported on Rh_{13}, which include icosahedral, cubic and bilayer structures. Besides, the lack of studies on large clusters leaves a gap in connecting the unique behaviour of atomic clusters with those in bulk. These controversies open up a venue for investigation into Rh clusters, especially those with more than 20 atoms by employing LCAO approach. We believe that the present study would provide additional insight into Rh clusters and fill up the missing gaps in this topic which has been initiated more than two decades.

CHAPTER3

THEORETICAL BACKGROUND

This chapter covers the theoretical background of the modelling techniques adopted in this work. These include a discussion on semi-empirical potential, followed by the optimisation methods employed to achieve one of the main goals of obtaining the global minimum of metallic cluster. *Ab initio* calculation using density functional theory (DFT), being a major part of this study, is described in detail.

3.1 Computational Modelling Techniques

One of the main objectives in this study is to obtain the structural configurations of rhodium (Rh) clusters, which are metallic, with the lowest total potential energy, known as global minimum structure, without considering electronic contribution. Today, experimentalists might be able to determine structures of nanoparticles with advance technology. Experimental determination of ground-state structures of nanoparticles with advanced technology, however accurate it may be, would be best complemented by theoretical predictions.

From theoretical point of view, the interactions between atoms in a system can be described by different forcefield. Different forcefield yields different potential energy surface(PES). PES of a cluster, as a function of coordinates, can be represented in diagram form (D. Wales, 2003). For a cluster with number of atoms N, it leads to a $(3N+1)$-dimensional PES, where $3N$ represents the degrees of freedom while the

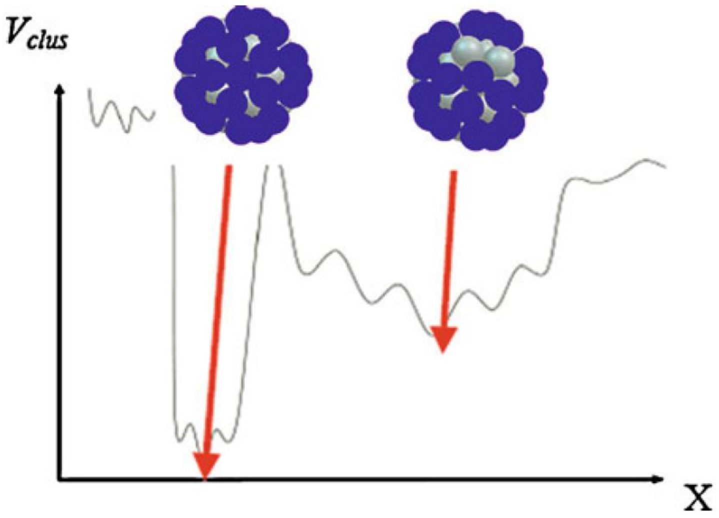

Figure 3.1: Schematic representation of a PES of two bimetallic cluster homotops (Borbón, 2011). Both clusters have the same number of atoms A (grey) and B (blue) but with different chemical ordering.

extra dimension is the potential energy of the system. Figure 3.1 shows the PES of two bimetallic cluster homotops as a function of $3N$-dimensional vector of Cartesian coordinates. Both clusters are fixed in size and composition, comprising of two types of chemical species A (grey) and B (blue), but different chemical ordering changes the energy states of the system. As shown in the diagram, configuration with lowest potential energy (left) represents the global minimum structure whilst another configuration (right) is one of the local minima of the system.

Over the years, various approaches have been utilised to describe the atom-atom interactions in a system and they can be characterised into two major groups: first-principles and empirical potential. First-principles calculations are known to be computationally intensive method. Hartree-Fock approximation (HF) and density functional theory (DFT) are the most popular first-principles methods. On the other hand, using empirical potential to describe the interatomic interactions is much cheaper than first-principles calculations in terms of computational cost. A simple empirical two-body potential, such as Lennard-Jones potential which describes interactions among the atoms through attractive and repulsive terms with interaction parameters that are fitted to experimental data. Unfortunately, this potential can only be used to describe simple systems which have no electron involved in the bonding or of atoms that are bounded by van der Waals forces, as in rare gases. Many-body potential, like Gupta and Sutton-Chen potentials, take into account the effect of metallic bonding by including additional physical contributions such as cohesive energy. It is in principle possible to locate the global minimum of a metallic cluster by using first-principles calculations, but the cost would be daunting. As a good compromise, the global minimum search could be performed by using many-body potential that couples to a global-optimisation tool which is able to explore large areas in the PES. This alternative definitely requires a much lower computation cost while still providing a reasonably well-described atom-atom interactions.

3.2 Many-Body Gupta Potential

Introduced by Gupta (1981), this potential was initially proposed to study relaxation near surfaces and impurities in bulk transition metals. In recent decades, being an alternative for the first-principles model, Gupta potential has been extensively applied to describe metallic systems.

Gupta potential is derived from the second moment approximation in the tight-binding model, which takes into account the essential band character of the metallic bond. In tight-binding scheme, valence electrons wave functions are written as a linear combination of atomic orbitals centred on each site. This model is particularly suitable for transition metals, in which their valence states are occupied with delocalised d-electrons while their core electrons are, relatively, remaining localised.

For a system with N atoms and denoting the pair distance between atoms i and j as r_{ij}, Gupta potential for a mono-metallic cluster is written as the sum of a repulsive potential (V_{rep}) and an attractive potential (V_{att}), over all the atoms:

$$V = \sum_{i=1}^{N} [V_{\text{rep}}(i) + V_{\text{att}}(i)]. \tag{3.1}$$

The repulsive term, also known as the Born-Mayer potential, is given by

$$V_{\text{rep}}(i) = A \sum_{j=1}^{N} \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right] \tag{3.2}$$

while the attractive term is defined as

$$V_{\text{att}}(i) = -\sqrt{\xi^2 \sum_{j=1}^{N} \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right]}. \tag{3.3}$$

Based on the work by Cleri and Rosato (1993), the parameters A, ξ, p and q in Equation (3.2) and Equation (3.3) were fitted to experimental values of cohesive energy, lattice parameters and elastic constants for respective bulk system at temperature of 0 K, whilst the r_0 is taken as the nearest-neighbour distance of the metallic cluster in this study.

3.3 Optimisation Techniques

Given a simple potential well, its global minimum can be located easily using a direct search algorithm, without knowing the gradient or higher derivatives as in conventional optimisation methods. However, when the system is getting larger in size (number of atoms) or more complex (comprising of different chemical species), the PES becomes increasingly complex due to the presence of many local minima. The task of global minimum search in large system becomes very demanding, necessitating the use of more powerful search algorithm.

In general, global optimisation algorithms are categorized into two types, namely, deterministic and stochastic optimisations. Deterministic methods, such as branch-and-bound algorithm, provide a theoretical guarantee for locating the global minimum; whilst stochastic methods like simulated annealing, generate and use random variables. This makes stochastic methods capable of locating a global optimum faster than deterministic ones (Liberti & Kucherenko, 2005), and have been widely applied in scientific and engineering studies.

The optimisation approach employed in this work is the combination of BH and GA as implemented in a novel search algorithm introduced by Hsu and Lai (2006). Short introductions to BH and GA are respectively given in the following sections.

3.3.1 Basin Hopping

Introduced by D. J. Wales and Doye (1997), basin hopping (BH) is an optimisation approach integrating deterministic and stochastic methods, and has been widely employed in numerous theoretical works to locate global minimum of a system. The fundamental idea of this method is to transform a given PES with energy V into a multidimensional staircase topology without changing the global minimum nor the

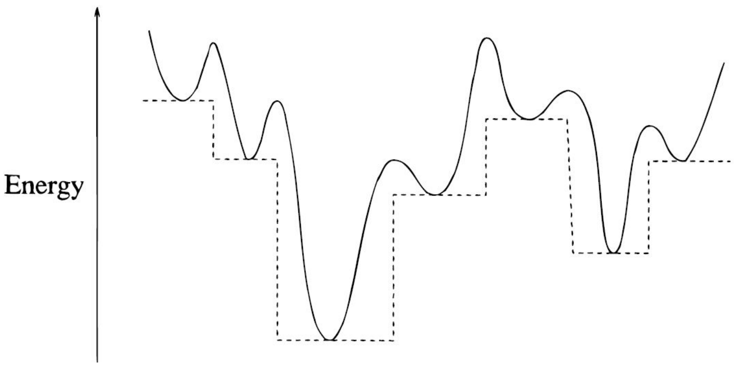

Figure 3.2: A schematic diagram showing the transformation of PES using BH approach for a one-dimensional example (D. J. Wales & Doye, 1997).

relative energies of any local minimum. The transformed PES is given by,

$$\tilde{V}(\mathbf{X}) = \min\{V(\mathbf{X})\} \tag{3.4}$$

where $\mathbf{X}$ is a set of N-atoms position coordinates $\{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\}$, while the local energy minimisation is represented by min. The transformation of PES via BH algorithm for a one-dimensional example is illustrated schematically in Figure 3.2.

3.3.2 Genetic Algorithm

In a complex potential energy surface (PES), the searching for global optimum depends on the initial point of the search algorithm. There is a high chance that the single starting point will roll into a local minima with high energy barrier. Hence, it is always beneficial if the algorithm starts from a series of starting points. This strategy has been adopted by a stochastic method known as genetic algorithm (GA), which has been widely employed in searching global optimum of complex space (Coley, 1999).

GA is initialised with a population of guesses, which are spread randomly in a search space. These initial guesses (individuals) are called "parents". A selection process is performed by determining the fitness of each of these individuals and as a result, discarding individuals with poor performance while keeping the others for the next generation. Then, genetic operators are applied to those "parents" who are retained from selection process. These operators may transform an individual into another form or create a "child" from two individuals by exchanging information of each other. The population is remained at certain number throughout the optimization. The selection and "child-generating" processes are repeated and direct the population to converge at the global minimum until specific convergence criterion has been met.

3.3.3 Coupling of Basin Hopping and Genetic Algorithm

Basin hopping (BH) and genetic algorithm (GA) are two conventional optimization algorithms used in obtaining the ground-state structures of metallic clusters. Lai, Hsu, Wu, Liu, and Iwamatsu (2002) compared the performances of these two methods and the results were found to agree excellently with each other. Later, Hsu and Lai (2006) improved the optimizers by coupling both methods to obtain lowest-energy configurations of bimetallic nanoalloy, where the potential energy surface (PES) of a nanoalloy is more complex than mono-metallic clusters. In present work, the initial configurations of Rh clusters for first-principles calculations were obtained by using the program code developed by these authors, named parallel tempering multicanonical basin hopping plus genetic algorithm (PTMBHGA).

In fact, PTMBHGA is a complete program that is equipped with several computational techniques. Besides the canonical Monte Carlo BH and GA used by Lai et al. (2002), it contains also multicanonical BH and parallel tempering methods as described