UNIVERSITI PUTRA MALAYSIA

THEORETICAL STUDY OF STRUCTURAL, ELECTRONIC, AND MAGNETIC PROPERTIES OF GRAPHENE WITH ADSORBED PALLADIUM AND VANADIUM BASED ON DENSITY FUNCTIONAL THEORY

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FS 2013 95

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By

YUSUF ZUNTU ABDULLAHI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

November 2013

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DEDICATION

This thesis is dedicated to my parents.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science.

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YUSUF ZUNTU ABDULAHI

November 2013

Chairman: Md Mahmudur Rahman, PhD

Faculty: Science

Graphene possesses interesting properties projected for various potential applications. The accurate understanding of how these properties are affected by the introducing foreign nanostructures into the sheet particularly transition metals (TM) has received the most attention. It is necessary to use theoretical method based on quantum mechanics to study the properties of graphene system with adsorbed metallic nanostructures. This thesis employs first principles calculations based on density functional theory implemented in the QUANTUM ESPRESSO simulation package to investigate the stable geometries and electronic and magnetic properties of graphene with adsorbed transition metals (palladium Pd and vanadium V).

The calculations are performed using ultrasoft pseudopotential and Perdew-Burke-Enzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functionals. For Brillouin zone (BZ) integrations, 8×8×1 set of *k*-points is sampled using Mankhorst-Pack scheme. In modeling a graphene sheet, 4×4×1 supercell containing 32 carbon atoms is constructed in a 3-dimensional periodic boundary conditions with 2.46 Å in plane lattice constant. Plain-wave basis with the kinetic energy cut-off of 500 eV is used to expand the wave functions. The structural optimizations of various configurations considered are performed to allow the structures to relax based on force and energy minimization. For the adsorption of Pd adatom and dimer, the results show significant covalent bonding with the graphene sheet. The density of states reveals that the system is semiconducting and metallic at low coverage adsorption of Pd adatom and dimer respectively. Moreover, it is found that Pd-Pd bond length is much weakened compared to an isolated Pd dimer with nearly symmetric height above the adsorption sites indicating that linear coverage can be achieved.

For adsorption of vanadium atoms, the findings show that the system is metallic and magnetic. The stable vanadium dimer configuration which has not been reported in the previous works has shown little enhancement of magnetic moment per unit cell

compared to isolated dimer whereas single V adatom adsorption has magnetic moment value per unit cell far more than that of an isolated V atomic value of $3\mu_B$. The orbital proportion in bonding between vanadium and carbon (C) is examined based on calculated projected density of states (PDOS). It is found that p_z of C is dominated by the spins states even at the vicinity of Fermi level and partial contribution from *d* orbital of V was also observed. This trend of orbital contributions appears to be uniform even for Pd atoms adsorption on graphene

Abstrak tesis ini dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi syarat keperluan untuk Ijazah Master Sains

KAJIAN TEORI BAGI SIFAT STRUKTUR, ELEKTRONIK DAN MAGNET GRAFIN DENGAN JERAPAN PALADIUM DANVANADIUM BERDASARKAN TEORI FUNGSIAN KETUMPATAN

Oleh

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Grafin mempunyai ciri-ciri menarik yang berpotensi diguna dalam pelbagai aplikasi. Kefahaman tepat tentang bagaimana ciri-ciri ini dipengaruhi oleh nanostruktur asing yang dimasukkan ke dalam lapisan grafin, khususnya logam peralihan, telah mendapat perhatian ramai. Adalah perlu untuk menggunakan kaedah teori berdasarkan mekanik kuantum bagi mengkaji ciri-ciri sistem grafin yang bernanostruktur logam terjerap. Tesis ini menggunakan pengiraan prinsip pertama berasaskan teori fungsian ketumpatan untuk diimplementasi dalam pakej simulasi QUANTUM ESPRESSO bagi mengkaji geometri stabil dan ciri elektronik dan magnet grafin dengan logam peralihan terjerap (paladium Pd dan vanadium V).

Pengiraan dilakukan mengguna pseudokeupayaan dan fungsian korelasi-pertukaran penghampiran cerun teritlak (GGA) Perdew-Burke-Enzerhof (PBE). Bagi kamiran zon Brillouin (BZ), set $8\times8\times1$ bagi titik-*k* disampel menggunakan skema Mankhorst-Pack. Dalam memodelkan lapisan grafit, supersel $4\times4\times1$ mengandungi 32 atom karbon dibangunkan dengan syarat sempadan berkala 3-dimensi dengan pemalar kekisi satah 2.46 Å. Asas gelombang satah dengan tenaga kinetik terpenggal 500 eV diguna untuk mengembangkan fungsi gelombang. Pengoptimuman berstruktur bagi pelbagai konfigurasi yang dipertimbangkan dilakukan untuk membenar struktur-struktur ini santai berdasarkan meminimumkan daya dan tenaga. Bagi jerapan adatom dan dimer Pd, keputusan menunjukkan ikatan kovalen yang signifikan dengan lapisan grafin. Ketumpatan keadaan menunjukkan bahawa sistem adalah bersifat semikonduktor dan logam masing-masing pada jerapan litupan rendah adatom dan dimer Pd. Tambahan itu, didapati juga panjang ikatan Pd-Pd sangat lemah berbanding dengan dimer Pd terasing dengan ketinggian hampir bersimetri di atas tapak jerapan, yang menunjukkan bahawa litupan linear dapat dicapai.

Bagi jerapan atom vanadium, dapatan menunjukkan sistem adalah bersifat logam dan bermagnet. Konfigurasi dimer vanadium yang stabil, tidak pernah dilaporkan dalam penyelidikan sebelum ini, menunjukkan hanya sedikit peninggian nilai momen magnet

per sel unit berbanding dengan dimer terpencil manakala jerapan adatom V tunggal mempunyai nilai momen magnet per sel unit jauh lebih tinggi daripada nilai atom V terpencil $3\mu_B$. Kadar orbital dalam ikatan anatara vanadium dan karbon (C) diteliti berdasarkan pengiraan ketumpatan keadaan terunjur (PDOS). Didapati bahawa p_z bagi C didominasi oleh keadaan spin walaupun di sekitar paras Fermi dan sumpangan separa dari orbital *d* juga diperolehi. Tren sumbangan orbital kelihatan lebih sekata walaupun untuk jerapan atom Pd ke atas grafin.

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ACKNOWLEDGEMENTS

I would like to extend my sincere gratitude to my supervisor, Dr. Md Mahmudur Rahman, for his helpful guidance, suggestions, swift feedback and support throughout my master's programme. His scholarly scrutiny, criticisms and vision kept me on the track when I got lost in the research work. Special thanks to my co-supervisors Prof. (madaya) Dr. H. Zainuddin for his role, swift replies and wonderful comments. I have also benefited a lot from various theoretical discussion groups, one of which is PWSCF forum. In this regards, many thanks go to the moderator Prof Paolo Giannozzi who is ever ready to address any problem related to open source package (ESPRESSO).

This research activity would have been more challenging without the immense moral support and encouragement of my parent, father, Alhaji Abdullahi Aliyu Zuntu and my mother, Hajiya Rabiatu Tukur, who have always been there for me in all circumstances. Appreciation goes also to my fellow research member, Shamsu Abubakar for his support and friendly approach. I will also like to specifically thank my friend Sultan Miyaki for his irreplaceable help in installation of Quantum ESPRESSO simulation package. The invaluable skills and the time you provided in this research activities are greatly appreciated. My warm regard goes to all colleagues at the university; friends and family back home for their unwavering supports and encouragement throughout the years. Special thanks to the entire Nigerian community in UPM for the high standard of cooperation and brotherhood extended to me.

I certify that a Thesis Examination Committee has met on 26 November 2013 to conduct the final examination of Yusuf Zuntu Abdullahi on his thesis entitled "Theoretical Study of Structural, Electronic, and Magnetic Properties of Graphene with Adsorbed Palladium and Vanadium Based on Density Functional Theory" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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TABLES OF CONTENTS

		Page
DEDICATION		ii
ABSTRACT		iii
ABSTRAK		v
ACKNOWLEDGEMENTS		vii
APPROVAL		viii
DECLARATION		x
LIST OF TABLES		xiii
LIST OF FIGURES		xiv
LIST OF ABBREVIATIONS		xix
CHAPTER		
1	**INTRODUCTION**	1
	1.1 Motivation and Background of the Study	1
	1.2 Problem Statement	4
	1.3 Objectives of the Study	5
	1.4 Scope of the Study	5
	1.5 Thesis Organization	6
2	**LITERATURE REVIEW**	7
	2.1 Introduction	7
	2.2 Background of Carbon Material	7
	2.3 The Graphene Structure	8
	2.4 The Electronic Properties of Pure Graphene	9
	2.5 Synthesis of Graphene	14
	2.6 Physical Properties and Application of Graphene	17
	2.7 Review on First Principle Calculations	18
3	**THEORETICAL BACKGROUND AND METHODOLOGY**	22
	3.1 Introduction	22
	3.2 Electronic Structure Calculations	22
	3.2.1 Independent-electron Approximation	23
	3.2.2 Hartree-Fock Approximation	24
	3.2.3 Density Functional Theory (DFT)	25
	3.2.3.1 Fundamentals of DFT	26
	3.2.3.2 The Kohn-Sham (KS) Equations	27
	3.2.4 The Exchange-Correlation Potential	29
	3.2.4.1 The Approximation to the Exchange-Correlation Potential 29	
	3.2.4.2 Self-consistent Field Procedure for Kohn-Sham Equation	30
	3.2.5 The Plane Wave Basis Sets	32
	3.2.6 K-point Sampling	33

3.2.7 Atomic Pseudopotential Approximation 34
3.3 Introduction to Quantum Espresso 36
3.4 Computational Methodology 37
3.4.1 Introduction 38
3.4.2 Computational Method and Model 38

4 RESULTS AND DISCUSSION 42
4.1 Introduction 42
4.2 Preliminary Convergences 42
4.3 Structural and Electronic Properties of Graphene Sheet 47
4.4 Structural Stabilities of Single/Dimer Transition Metal (V, Pd) 49
4.5 Adsorption of Palladium Adatom on Graphene 50
4.6 Adsorption of Palladium Dimer on Graphene 54
4.7 Adsorption of Vanadium Adatom on Graphene 98
4.8 Adsorption of Vanadium Dimer on Graphene 64

5 CONCLUSIONS AND RECOMMENDATIONS 71
5.1 Conclusions 71
5.2 Recommendations 73

REFERENCES 74
APPENDICES 83
BIODATA OF STUDENT 92
LIST OF PUBLICATIONS 93

LIST OF TABLES

Table		Page
2.1	Preparation methods and experimental techniques of adsorbed graphene on a various metal substrates.	15
4.1	The convergence of total energy of C, Pd and V as a function of K.E cut-off.	43
4.2	The convergence of total energy as a function of *k*-points.	45
4.3	The calculated adsorption energy for various adsorption sites as a function of Pd adatom separation on graphene sheet.	45
4.4	The calculated adsorption energy for various adsorption sites as a function of V adatom separation on graphene sheet.	47
4.5	Optimized structural properties of graphene with adsorbed palladium atom.	50
4.6	Optimized structural properties of graphene with adsorbed palladium dimer.	54
4.7	Optimized structural properties of graphene with adsorbed vanadium atom.	60
4.8	Löwdin charge analysis of graphene system with adsorbed vanadium atom.	61
4.9	Optimized structural properties of graphene with adsorbed vanadium dimer.	65
4.10	Löwdin charge analysis of graphene system with adsorbed vanadium dimer.	66

LIST OF FIGURES

Figure		Page
2.1	Graphitic allotropes derived from graphene: It can be wrapped into fullerenes, rolled into nanotubes, and staked into graphite.	8
2.2	The formation of sp^2 hybrid orbitals in graphene, the s, p_x and p_y orbitals hybridized to form the sp^2 orbital and p_z remain the same.	9
2.3	The graphene Lattice Structure. (a) Real space honeycomb lattice (b) Reciprocal lattice.	10
2.4	Graphene energy bands. The dispersion relation for graphene consists of six points touching at point where conduction and valence bands meet.	13
2.5	Density of states of pure graphene showing absence of states at the vicinity of Fermi level. Fermi energy set at zero.	13
2.6	(a) Chemical vapor deposition of graphene on a pattern Ni surface (b) and (c) Etching with different techniques and subsequent transfer to another substrate.	16
3.1	Self-consistent algorithms for solving Kohn-Sham equation.	31
3.2	The convergence of total energies of carbon as a function of cut-off energy.	33
3.3	The convergence of total energies as a function of k-points.	34
3.4	Schematic representation of pseudopotential (solid lines) and all electrons (dash lines) with their corresponding wave functions. The radius at which the pseudo-electron and all-electron values match is denoted as r_c .	35
3.5	Schematic diagram of computational procedure.	39
3.6	Single Pd adatom adsorption on carbon atom in the graphene Structure.	39
3.7	Possible adsorption sites for Pd atoms on a monolayer graphene and supercell models. Three different perpendicular adsorption sites for V and Pd dimer.	40

3.8	Side view of the adsorbed parallel configuration named R_T with two Pd atoms sitting directly above carbon atom in the graphene sheet.	40
3.9	Top view of the adsorbed parallel configuration named R_H with two V atoms located in the hexagonal site of graphene sheet.	41
3.10	Side view of the adsorbed perpendicular configuration on graphene sheet named P_H with two V atoms situated on the center of hexagon.	41
4.1	The convergence of total energies of carbon as a function of cut-off energy.	42
4.2	The convergence of total energy of palladium as a function of cut-off energy.	43
4.3	The convergence of total energies of vanadium as a function of cut-off energy.	44
4.4	The convergence of total energies as a function of k-points.	44
4.5	Adsorption energy for V adatom-graphene system as a function of distance between adatom and graphene sheet.	46
4.6	Adsorption energy for Pd adatom-graphene system as a function of distance between adatom and graphene sheet.	46
4.7	Top view charge density distribution of pure graphene with n(r) signifying ranges of electron density values in a.u	47
4.8	(a) Density of states of pure graphene showing the absence of states in the vicinity of Fermi level. (b) Projected density of states of pure graphene. Fermi energy set at zero. (c) Electronic band structure of pure graphene.	48
4.9	The optimized structure of graphene system with adsorbed Palladium atom.	51
4.10	Charge density plots: Scale n(r) signifying ranges of electron density values in a.u. top view charge distribution of the most stable adsorbed Pd-graphene configuration.	51
4.11	Charge density plots: Scale n(r) signifying ranges of electron density values in a.u. side view charge distribution of the most stable adsobed Pd atom-graphene configuration.	52
4.12	The spin-polarized total density of states for the energetically stable graphene system with si ngle adsorbed Pd.	52

4.13	The spin-polarized local density of states for carbon atom directly below Pd.	53
4.14	The spin-polarized local density of states for Pd adsorbed on graphene sheet.	53
4.15	The optimized structure of graphene system with adsorbed palladium dimer.	55
4.16	Charge density plots: Scale n(r) signifying ranges of electron density values in a.u. Top view charge distribution of the most stable graphene with adsorbed Pd dimer.	56
4.17	Charge density plots: Scale n(r) signifying ranges of electron density values in a.u. Side view of the perpendicular dimer adsorbed on carbon top site *i.e* P_T configuration with colors indicating charge accumulation and depletion.	57
4.18	The spin-polarized total density of states for the energetically stable graphene system with adsorbed Pd dimer.	57
4.19	The spin-polarized local density of states for carbon atom directly below one of the Pd in dimers adsorbed in the Graphene.	58
4.20	The spin-polarized local density of state for the most stable Graphene with adsorbed Pd dimer.	58
4.21	The optimized structure of graphene system with adsorbed vanadium atom.	60
4.22	Charge density plots: Scale n(r) signifying ranges of electron density values in a.u. Top view charge distribution of the most stable configurations of graphene with adsorbed. vanadium atom.	62
4.23	Charge density plots: Scale n(r) signifying ranges of electron density values in a.u. Side view charge distribution of the most stable graphene configurations with adsorbed single vanadium atom.	62
4.24	The spin-polarized total density of states for the energetically stable graphene system with adsorbed single vanadium atom.	63
4.25	The spin-polarized local density of states for carbon atom in the hexagonal site of graphene with adsorbed V.	63
4.26	The spin-polarized local density of states for the V *p* orbital.	64

4.27	The spin-polarized local density of states for the energetically stable single V *d* orbital.	64
4.28	The optimized structure of graphene system with adsorbed vanadium dimer.	65
4.29	Charge density plots: Scale n(r) signifying ranges of electron density values in a.u. Top view charge distribution of the most stable graphene with vanadium dimer configurations.	67
4.30	Side view of the perpendicular V dimer adsorbed on the hexagonal site *i.e.,* P_H of graphene sheet with colors indicating charge accumulation and depletion.	67
4.31	The spin-polarized total density of states for the energetically stable graphene system with adsorbed V dimer.	68
4.32	The spin-polarized local density of states for the V1 *p* orbital.	68
4.33	The spin-polarized local density of states for graphene with adsorbed V1 system.	68
4.34	The spin-polarized local density of states for C2 atom in the hexagonal site of graphene with adsorbed V dimer.	69
4.35	The spin-polarized local density of states for graphene system with adsorbed V2 for *p* orbital.	69
4.36	The spin-polarized local density of states for graphene system with adsorbed V2 for *d* orbital.	70
4.37	The spin-polarized local density of states for C1 atom in the hexagonal site of graphene with adsorbed V dimer.	70

LIST OF ABBREVIATIONS

BO	Born-Oppenheimer
C	Coulomb
DFT	Density-Functional Theory
GE	Gradient Expansion
GGA	Generalized Gradient Approximation
H	Hatree
HED	Homogeneous Electron Gas
HF	Hatree-Fock
HK	Hohenberg-Khon
KS	Khon-Sham
LDA	Local-Density Approximation
LSDA	Local Spin-Density Approximation
PBE	Perdew-Burke-Ernzerhof of GGA
PW91	Perdew-Wang 91 GGA
Ry	Rydberg
TF	Thomas-Fermi
SCCM	Standard Cubic Centimeters per Minute
XC	Exchange-Correlation

CHAPTER 1

INTRODUCTION

1.1 Motivation and Background of Study

Today, computational modeling at the atomistic level description serves as an alternative approach to experiments for understanding physical properties associated with nanoscale materials, for example carbon nanostructures and their derivatives. In various fields of research such as condensed matter physics, exploring these fundamental physical properties associated with a material has become an indispensable research interest for designing and predicting an excellent nanosystem to be used in many fields of applications such as modern nanotechnology. These rapid improvements in accurately predicting associated physical properties of nanosystems have stimulated advances which in return have given rise to the isolation of viable carbon materials. Nowadays, the leading nanoscale carbon material that has received intense attention in the wake of the silicon based industry is called graphene, a single layer of graphite in a hexagonal honey comb lattice made of carbon atoms (Novoselov *et al*., 2004).

The fascinating physics of graphene has been one of the central interests that fuelled this study (Zhang *et al*., 2005) since its isolation (Novoselov *et al*., 2004). Due to its peculiar two dimensional nature, it exhibits, unique properties such as magneto transport (Zhang *et al*., 2005), tunable band gap (Han *et al*., 2007), extremely high carrier mobility (Geim, 2009), electron confinement effects (Stander *et al*., 2009) and Klein tunneling nature (Phark *et al*., 2011). It has been demonstrated theoretically that these unusual physical properties of graphene are as a result of the strange linear band dispersion at the momentum or Fourier space known as Dirac points (Zhou, 2006). At these points, Dirac fermions (electrons) drift at high speeds that are independent of their energy and directions. Close to the Dirac points and at a room temperature, the mobility of charge carriers is approximately 15000 $cm^2V^{-1}s^{-1}$ which are more than the well-known established semi-conductors, for example silicon of nearly 1400 $cm^2V^{-1}s^{-1}$ (Novoselov *et al*., 2004). This massless behavior of electrons in graphene is responsible for the unique properties mentioned above.

While various groups have succeeded in getting isolated graphene sheets with different techniques (Berger *et al*., 2006; Sidorov *et al*., 2007), there have also been continuing efforts simultaneously to explore the effects of various adsorbed guest atoms (Krasheninnikov *et al*., 2009; Paulo *et al*., 2010) or molecules (Sanyal *et al*., 2009; Alzahrani, 2010) on graphene because potential applications and electronic transports properties experiments with graphene require contact with metal electrodes (Peres, 2010) and this may influence the target electronic properties of graphene. In this regard, graphene has been used experimentally as a substrate for growth of nanometer-sized crystal structures (Hupalo *et al*., 2011) which indicates the possibility of controlling the structure to produce viable future nanodevices.

Among the widely theoretically studied single atoms (Chan *et al*., 200□), dimers (Alzahrani, 2012) and molecules (Zhou *et al*., 2010) adsorption on graphene, research interest, particularly in transition metals (TM) adsorptions on graphene continues to grow fast and expand the ranges of applications from catalysis, spintronics to nanomagnetic devices. This is because additions of metallic nanostructures on graphene have the tendency to enhance the surface reactivity of graphene and hence the physical and chemical behaviors needed for desired applications will probably be more readily achieved as compared to pristine graphene. This further provides a promising feature for the development of graphene based nanodevices depending on the nature of interactions between graphene with the adsorbed nanostructures.

Theoretical works of TM atoms adsorption on graphene have provided a better understanding of the physical and chemical behavior associated to the changes in the electronic structure of graphene (Chan *et al*., 200□). Some of the TM, vanadium and palladium (V, Pd) adsorbents on carbon nanostructures and related structures that recently have received the attention of the scientists community are those that satisfy stoner criterion of magnetism, because their size and reduced dimensionality in coordination number are well known to influence their physical properties and hence may serve as good candidates for modern nanotechnology applications.

In their electron-beam evaporation and transmission electron microscopy (T□M) study, Zhang *et al.,* (2000) experimentally observed that linear coatings in the form of nanowire of palladium (Pd) on the outside wall of the suspended single-walled carbon nanotubes can be achieved. Their results also shed light on electrical coupling between nanotubes and metal contacts, an issue important to both fundamental electrical properties of nanotubes and their applications as high performance devices.

□n the other hand, Hu *et al.,* (2010) have theoretically investigated the geometry, electronic and magnetic properties of fifteen transition metals single atoms adsorbed on graphene. Their results indicated that the graphene properties can be effectively tuned by TM adsorption and further give an account based on strong covalent bonding such that palladium among others can be used as a functional material to coat uniformly graphene and carbon nanotubes. In another recent study, Thapa *et al.,* (2011) have been able to show appearance of magnetic moments for Palladium dimer adsorbed in perpendicular direction, although no magnetic moments have been confirmed for Pd single atom and parallel Pd dimer which is in perfect agreement with the previous works (Chan *et al*., 200□; Hu *et al*., 2010).

□such *et al*., 2005 have reported that appearance of magnetism in dimer perpendicular configurations is as a result of pattern hybridization of 4*d* orbital of Pd and 2*p* orbital of C. However, electronic properties of dimer in parallel configurations are importantly missing from the report. □nderstanding the effects of the parallel configuration on the properties of graphene is essential, since uniform coating of Pd has been predicted as an attractive property of Pd different from other metals which is useful in making contact between electrode and graphene for various applications (Hu *et al*., 2010).

Moreover, it has been also observed experimentally by ultraviolet photoelectron spectra that Pd among others deposited on graphite nucleated into a cluster, large enough to exhibit bulk properties even at low concentrations. In contrast, there are isolated adatom on amorphous carbon at low concentrations (□gelhoff and Tibbetts, 1979). In furtherance of the quest for possible formation of palladium planar surface on graphene, Sundaram *et al.,* (200□) coated graphene experimentally by electro deposition with palladium and the metal nucleated at edges and defects of the graphene sheets.

The peculiar properties exhibited by carbon nanostructures with adsorbed vanadium has triggered more interest to study the effects of V atoms on graphene due to its significance in discussing fundamental nanophysics of magnetic materials. The theoretical investigation of vanadium atom adsorption on graphene surface started long ago, before graphene was discovered, with the team of Duffy and Blackman (199□) whose investigations were on bonding site, adsorption energy and magnetic property of transition metal adatoms and dimers on graphite.

Their results have indicated that the adatoms in the lower part of the series preferred to position themselves above carbon (C) sites and their magnetic moments are higher than their free atom values. The atoms in the dimers were located either above the neighboring rings or above a line passing through the centers of C-C bonds at opposite sides of a ring. The magnetic moment of most of the dimers is similar to their free diatomic molecules because surface relaxation was not accounted for during the calculations.

Additionally, Hu *et al*., (2010) by means of spin-polarised first principle pseudopotential method have confirmed the chemisorption of vanadium on graphene, tunable electronic property and enhanced magnetic moments of the system. □iu *et al.,* (2011) have suggested new mechanism of charge transfer from metal atoms to graphene with values more than the previous works.

In spite of increasing number of metal-graphene studies, however, there is no prior theoretical study on graphene sheet with adsorbed small clusters of □*d* vanadium metal. In contrast, an investigation on carbon nanotube (CNT) and related nanostructures with adsorbed V have been performed (Durgun and Ciraci, 2006; □ie *et al*., 2011; Ma *et al*., 2012). It has been shown that vanadium on boron nitride (BN) sheet has 100□ spin polarization at the Fermi level which has potential in spin filtering material applications (□i *et al*., 2012), despite numerous disagreement with previous theoretical (□eddy *et al*., 1997; □amanathan *et al*., 2009) and experimental (Huttel *et al*., 200□; Benčok *et al*., 2006; Sheng *et al*., 2012) studies on various surfaces. This is expected, because different surfaces may have different charge exchange and thus the population of *s* and □*d* orbitals may be changed depending on the type of surface employed.

As predicted by the studies mentioned above, vanadium atom adsorption on various structures may have an attractive property different from other metals which is significance in making graphene related devices. Therefore, deeper understanding of

the effects on the properties of graphene by adsorbed vanadium atoms is essential particularly that graphene layer shares similar behavior in terms of interactions with metals the way BN and CNT do, especially CNT which has graphitic structure.

Thus, this research aims to contribute to the understanding of the geometrical stability and electronic and magnetic properties of the graphene system with low coverage adsorbed palladium and vanadium atoms and dimers based on structural changes, charge density distributions, magnetic moment per unit cell and electronic structure changes using first principles plane wave density functional theory calculations. The significance of understanding these changes will help both fundamental and applied physics to understand how properties of graphene are affected by deliberately introducing low coverage foreign atoms to the surface of pristine graphene.

In view of this the study will be performed in stages. Three known adsorption sites H (hollow site of the hexagon), B (bridge site) and T (atom top site) for both Pd and V adatoms on graphene configurations will be studied. Parallel and perpendicular configurations for both Pd and V dimer on these high symmetric adsorption sites (H, B and T) will be considered. In the first part, convergences and structural optimization for the equilibrium atomic positions on various configurations will first be examined as a necessary step to □ustify the chosen configurations as well as to have a bench mark of accuracy. Secondly, the stable structural properties of the various configurations will be determined. Finally, electronic and magnetic behaviors will be analyzed based on the most stable geometries of the graphene system with adsorbed TM atoms and dimers.

1.2 Problem Statement

Graphene, a single sheet of graphite has triggered a great research interest. Its unique physical properties such as ultrahigh electron mobility, low dimensionality and promising electronic properties make it an interesting as well as viable candidate in nanoscale industry. However, these fascinating properties can be modified, controlled and enhanced when combined with different guest materials depending on the technological end use. So far, adsorption of atoms, molecules or functional group on its sheet is one of the leading vectors toward realization of the quests. But despite numerous studies for understanding the effects of transition metals (TM) such as (palladium (Pd) and vanadium (V)) atomic adsorptions on graphene for both fundamental and applied research, there are many possibilities yet to be explored such as understanding the effects low coverage adsorptions of Pd and V adatoms and dimers on the graphene sheet. Therefore, this research proposes to give an account of the structural stabilities, electronic and magnetic properties of graphene system with adsorbed Pd and V atoms and dimers.

1.3 Aims and Objectives

The main aim of the thesis is to investigate and establish the geometric stabilities and electronic and magnetic properties of a graphene system with adsorbed transition metal (Pd, V) adatoms and dimers using first principle calculations. The objectives are:

i. To determine the structural stabilities of the graphene system with adsorbed Pd and V single atoms and dimers based on adsorption energy and bond length, charge density distributions and adsorption height.

ii. To analyze the electronic properties of the graphene system with adsorbed Pd and V single atoms and dimers based on total and projected density of states.

iii. To examine the magnetic properties of the graphene system with adsorbed Pd and V single atoms and dimers based on magnetic moment per unit cell.

1.4 Scope of Study

In this study, first principle calculations are performed to elucidate the structural stabilities of the graphene system with adsorbed palladium (Pd) and vanadium (V) single atoms and dimers in terms geometric stability parameter and the effects of these adsorbed atoms on the electronic, magnetic properties of graphene in terms of density of states, projected density of states and magnetic moment per unit cell respectively. Although, there are prior theoretical works on graphene with adsorbed Pd cluster, but none have studied the electronic structure changes of parallel Pd dimer adsorption on pure graphene. This is important because recent theoretical study (Hu *et al*., 2010) have predicted that uniform coating is an attractive property of Pd different from other metals which is the requirement needed in making contact between electrode and graphene.

For vanadium atom adsorption, none have reported the dimer model adsorption on graphene. This is also important as many interesting physical properties have been reported for the adsorption of vanadium adatom (Magi *et al*., 2004) dimer and metal chain (Durgun and Ciraci, 2006) on CNTs. Consequently, this research intends to reveal these effects of TM (V, Pd) on this system. All models and computational procedures will be tested for convergences to justify the accuracy of the calculations and experimental data will be compared where necessary. The preliminary results obtained serve as a basis for the subsequent calculations. Finally, results will be analyzed and discussed based on the available literatures.

1.5 Thesis Organization

Chapter 1 a brief overview of the research interest based on prior works and the existing challenges is presented. It highlights the research aims and ob ectives, scope and organization of thesis.

Chapter 2 presents a brief review of the carbon nanostructures and in particular electronic and structural properties of graphene are discussed. Moreover, the chapter summarizes previous theoretical works related to this research.

Chapter the basic concept and methods of the electronic structure calculations are summarized. The elements of density functional theory are reviewed. The Hohenberg-Kohn theory (Hohenberg and Kohn, 1964) and Kohn-Sham ansatz (Kohn and Sham, 1965) are described. The functional forms of the exchange and correlation in the local density approximation (Perdew and Zunger, 19 1) and the generalized gradient approximation (Perdew *et al*., 1996) are enumerated. Finally, the plane wave basis set in ANT M SP SS code (Giannozzi *et al*., 2009) and the computational method and models used in the research are discussed.

Chapter 4 presents the results and discussion on the ma or findings of the research for various models of the graphene with adsorbed transition metal adatoms and dimers.

Chapter 5 Summary of the results obtained is presented. It also highlights possible implications for future works.

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