DENSITY FUNCTIONAL THEORY SIMULATION OF MAGNETISM DUE TO ATOMIC VACANCIES IN GRAPHENE USING SIESTA

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I lovingly dedicate this thesis to my family, who supported me each step of the way.

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ABSTRACT

Spintronics generally refers to technology where devices utilise the spin of the electron in addition to its charge for information transmission, processing and storage. Graphene is a sheet of carbon atoms bound together with double bonds (called the sp^2 bonds) in a thin, one atom thick layer. It is a very special material because of the large spin relaxation length and ballistic transport characteristics that can provide a great platform for developing spin-polarized devices. The carbon atom itself does not own any magnetic moment, therefore, the researches on graphene-based spintronics mainly focus on the substantial magnetism in graphene due to the presence of defects. This study will investigate the magnetism originating from quasilocalised states induced by defects in graphene sheet using first principle approach. The density functional theory calculations were performed using SIESTA software in the spin-unrestricted manner, using the diagonalization-based method for solving Kohn-Sham equations. The calculation was done in parallel modes. The generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE) was used throughout this work. In addition, all the calculations for the models were carried out using the double-zeta plus one polarization (DZP) basis set. In this study, the magnetic moments generated due to atomic vacancies were calculated for supercells of different sizes namely 3×3, 4×4, 5×5, and 6×6 multiples of the graphene unitcell. The results show that the values of the magnetic moment in graphene supercells strongly depend on the size of the supercell, the number of the vacancies as well as on the sublattice where the vacancies are located. This is generally consistent with Lieb's theorem regarding the magnetism in materials with different sublattices. Furthermore the presence of exchange splitting in the density of states (DOS) for electrons with different spins can be considered as indication that this magnetism is of the itinerant type and this should enhance the potential of using graphene for spintronic devices.

ABSTRAK

Secara umumnya, spintronik merujuk kepada teknologi di mana sesebuah alat peranti menggunakan spin elektron sebagai tambahan kepada casnya bagi pemindahan, pemprosesan dan juga penyimpanan maklumat. Grafin adalah kepingan atom karbon yang terikat bersama dengan ikatan berganda (dikenali sebagai ikatan sp^2) dengan kenipisan satu atom. Ia adalah bahan yang sangat istimewa kerana keupayaan santaian spin yang panjang serta mempunyai ciri pemindahan balistik yang mampu menyediakan satu platform yang baik untuk membangunkan peranti-pengutuban spin. Atom karbon sendiri tidak mempunyai sebarang momen magnet, maka pengkajian mengenai spintronik berasaskan grafin diberikan perhatian terutama sekali kemagnetan disebabkan kehadiran kekosongan atom. Kajian ini dijalankan menggunakan pendekatan prinsip pertama pada kemagnetan yang berasal dari keadaan penyetempatkan-kuasi yang disebabkan oleh kecacatan pada kepingan grafin. Pengiraan teori berfungsi ketumpatan (DFT) telah dijalankan menggunakan perisian SIESTA mengikut cara yang tiada penghadan spin menggunakan kaedah berasaskan pepenjuruan untuk menyelesaikan persamaan Kohn-Sham. Pengiraan telah dilakukan dalam mod selari. Penghampiran kecerunan teritlak (GGA) dengan tukar ganti korelasi berfungsi Perdew, Burke dan Ernzerhof (PBE) telah digunakan sepanjang kajian ini. Di samping itu, semua pengiraan untuk model telah dijalankan menggunakan dua-zeta ditambah dengan pengutuban (DZP) set asas. Dalam kajian ini, momen magnet yang dijanakan berikutan kekosongan atom telah dikira untuk saiz supersel yang berbeza iaitu 3×3, 4×4, 5×5 dan 6×6 dalam gandaan unitsel grafin. Keputusan kajian menunjukkan bahawa nilai momen magnet pada supersel grafin sangat bergantung kepada saiz supersel, bilangan kekosongan serta kedudukan kekosongan pada subkekisi dan ini adalah selaras dengan teorem Lieb mengenai kemagnetan dalam bahan dengan subkekisi berbeza. Tambahan pula kehadiran tukar ganti pembelah dalam ketumpatan keadaan (DOS) bagi elektron dengan spin yang berbeza boleh dianggap sebagai petunjuk bahawa kemagnetan ini adalah jenis beredar dan ini mampu meningkatkan potensi menggunakan grafin sebagai peranti spintronik.

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LIST OF ABBREVIATIONS

BLACS	–	Basic Linear Algebra Communication Subprograms
BLAS	–	Basic Linear Algebra Subprograms
BO	–	Born Oppenheimer
CG	–	Conjugate Gradient
DFT	–	Density Functional Theory
DOS	–	Density of States
DZP	–	Double-Zeta-Polarized
FDF	–	Flexible Data Format
GGA	–	Generalize Gradient Approximation
GMR	–	Giant Magnetoresistance
HK	–	Hohenberg-Kohn
KS	–	Kohn-Sham
LAPACK	–	Linear Algebra PACKage
LDA	–	Local Density Approximation
LDOS	–	Local Density of States
LSDA	–	Local Spin Density Approximation
LYP	–	Lee, Yang, and Parr
MPI	–	Message Passing Interface
PBE	–	Perdew, Burke, and Ernzerhof
PDOS	–	Projected Density of States
ScaLAPACK	–	Scalable LAPACK
SCF	–	Self-Consistent Field
SIESTA	–	Spanish Initiative for Electronic Simulations with Thousands of Atoms
SZP	–	Single-Zeta-Polarized
TFD	–	Thomas Fermi Dirac

LIST OF SYMBOLS

$D(E)$	–	Density of states
E	–	Energy
E_F	–	Fermi energy
E_f	–	Formation energy
H	–	Hamiltonian operator
t	–	Hopping parameter
$E(k)$	–	Energy bands for tight-binding graphene
ρ	–	Density
M	–	Magnetic moment
ϵ_i	–	Eigenvalues
e	–	Electron
$\hbar$	–	Reduced Planck constant
Ψ	–	Wavefunction
T	–	Kinetic energy
V	–	Potential energy
m	–	Mass
$m(r)$	–	Magnetization density
F	–	Fock operator
w_i	–	weight factors
N	–	Number of states

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nanotechnology has become one of the interesting and most important fields in recent years. The direction of technological development will change as the nanotechnology shows great promise for providing many discoveries in various application. However as it was done in the past thirty years, the rapid increase cannot be compensated by simple downscaling of the semiconductor devices. In order to keep up with the demand, currently many researchers are working on systems which operate on the nanoscale and exploit quantum effects. One of the best option is to use the spin of the electron in addition to its charge for information transmission and storage, that is, going from the conventional electronics to spintronics.

1.1.1 Spintronics

Electronics and spintronics are two fields of technology which are very strongly coupled. This is due to the fact that both use the same elementary particles, that is electrons for their operations. But then each field uses a different fundamental property of particles. In electronics it is the charge while in spintronics it exploits the angular momentum, also better known as spin.

The term “spintronics” (a neologism meaning “spin transport electronics”) also known as magnetoelectronics. Spintronics burst on the scene when a much more powerful effect called giant magnetoresistance (GMR) discovered by Fert and Grünberg in 1988. It has already become reality in the field of data storage when the GMR effect is used in modern memory devices. They received the 2007 Nobel price.

The advantages of these new devices would be nonvolatility, increasing the data processing speed, decreasing the electric power consumption, long coherence or relaxation time, and reduced size of device structure compared to the conventional electronic devices.

1.1.2 Graphene as Spintronic Material

More than sixty years since the study of graphene was performed. However, graphene could not draw enough attention because it was presumed not exist in the free-state and was believed to be unstable. Then, in 2004, free-standing graphene was discovered by A.K. Geim in collaboration with the postdoctoral associate K. S. Nonoselov and his co-workers at the University of Manchester (Geim and Novoselov, 2007). Graphene is a sheet of carbon atoms bound together with double electron bonds (known as sp^2 bond) in a thin film only one atom thick. It is a very special material because in follow-up experiment confirmed that its charge carriers were indeed massless Dirac fermions.

Graphene contains no magnetic atoms, thus known as a metal-free material. However from the local states caused by the present of defect or molecular adsorption induced magnetism in graphenes(Kumazaki and Hirashima, 2007; Lehtinen *et al.*, 2004; Palacios *et al.*, 2008; Ugeda *et al.*, 2010; Yazyev and Helm, 2007; Zhang *et al.*, 2007). Arrangement of atoms of graphene in a honeycomb-style lattice pattern has captured the interest of the physics community because of its versatile application to microelectronics as it provides ballistic transport characteristics and large spin relaxation length. In the development of spintronic devices, it can be a great platform. Like d or f shell elements, carbon atoms do not own magnetic moment, thus the researches on graphene-based spintronics mainly pay attention to the magnetism in graphene.

1.1.3 Magnetism in Graphene

Electrons like all fundamental particles have a property called spin which can be oriented in one direction or the other called ‘spin-up’ or ‘spin-down’. The electron spins will create a large-scale net magnetic moment when they are aligned (all spin-up or all spin-down). Magnetism is an intrinsic physical property associated with the

spins of electrons in a material. Magnetism is already exploited in recording devices such as computer hard disks. The existence of unpaired electrons is the essential of a magnetic materials. More precisely the presence of a net spin that is spins associated with unpaired electrons. If the electron is seen as a classical charged particle literally spinning on the axis with angular momentum, L, its magnetic dipole moment,μ is given by :

$$\mu = \frac{-e}{2m_e} L \tag{1.1}$$

where m_e is the electron rest mass.

As a metal-free material, graphene can be visualized by honeycomb structure that contains two triangular interpenetrating sublattices. From previous studies, molecular adsorption or defects give rise to the magnetism that come from the local states. In the ideal graphene, defects can be introduced by both external doping and vacancies. The carbon atoms that removed from the sheet give quasilocalized states at Fermi level. Beside the vacancies, graphene can also show magnetism by doping defects. By introduced boron (B) and nitrogen (N) atoms, the π orbitals of the atoms around the border regions of graphite and BN are localized according to the result studied by (Okada and Oshiyama, 2001) on electronic structure of hexagonally bonded honeycomb.

Other than defects, atom or molecules adsorption also can lead to the occurrence of magnetic moments. Mainly the magnetic moment will localize around the adsorption of the atom or molecule(Yazyev and Helm, 2007).

1.1.4 Modelling and Simulation Approach Used in This Research

In the study of a solid state system, density functional theory (DFT) plays the role of providing the means to investigate the bulk properties of materials. The investigation of the electronic structure (principally the ground state) in physics and chemistry normally using quantum mechanical theory applied in DFT. DFT was developed by Hohenberg and Kohn in 1964 as well as Kohn and Sham in 1965 provided some hope of simple method for describing the effects of exchange and correlation

among the particles (Kohanoff, 2006). As such, DFT has become the main tools for calculation of electronic structure in condensed matter, and is increasingly important for quantitative studies of molecules and other finite system.

1.2 Statement of Problem

The introduction of defects to induce magnetic responce in graphene has been generating much interest. So far there have been many theoretical studies (Yazyev and Helm, 2007; Palacios *et al.*, 2008; Faccio and Mombru, 2012) predicting that point defects in graphene should carry magnetic moments. However, experimental evidence for such magnetism remains both scarce and controversial (Haase *et al.*, 2011; Matte *et al.*, 2009).

In this work, approximation methods implemented in density functional theory are used in order to simulate magnetism in graphene sheet. Approximation methods is one of the efficient methods to model the systems within density functional theory (DFT).

1.3 Objectives of Study

The objectives of the study are as follows:

i To determine from first-principle calculations the magnetic moment in graphene due to atomic vacancies.

ii To establish the dependence of the magnetic moment on other factors such as the number and location of the vacancies, the size of the supercell used in the calculations and the formation energy required to generate the vacancy

1.4 Scope of Study

This study will focus on graphene sheet as a test system of solid state. Graphene has been chosen partly because of its potentials in carbon-based nano-scale electronics.

To motivate the experimental study on graphene, first-principles calculation are used within the DFT using SIESTA code in parallel node. The magnetism of graphene due to local states in the presence of defect will be investigated using the first-principles calculations by removal the carbon atom from the graphene sheet. In general, the defect in graphene can be introduced by both atomic vacancies and external defects. This study only focused on magnetism due to the atomic vacancies.

1.5 Significance of Study

This research describe technique to investigate the emergence of magnetism in graphene due to the local defects. Besides, it can contribute to the knowledge that can enrich the understand in this area. Magnetic order in patterned or nanostructured graphene can also bring up new opportunities of research in spintronics.

REFERENCES

Artacho, E., Cela, J. M., Gale, J. D., Garcia, A., Junquera, J. Ordejon, P., Sanchez-Portal, D. and Soler, J. M. (2010). *User's Guide : SIESTA 3.0-rc2*.

Barzola-Quiquia, J., Esquinazi, P., Rothermel, M., Spemann, D., Butz, T. and Garc´, N. (2007). Experimental evidence for two-dimensional magnetic order in proton bombarded graphite. *Phys. Rev. B*. 76, 161403.

Castro, E. V., Peres, N. M. R., Stauber, T. and Silva, N. A. P. (2008). Low-Density Ferromagnetism in Biased Bilayer Graphene. *Phys. Rev. Lett.* 100, 186803.

Dai, X. Q., Zhao, J. H., Xie, M. H., Tang, Y. N., Li, Y. H. and Zhao, B. (2011). First-principle study of magnetism induced by vacancies in graphene. *The European Physical Journal B*. 80, 343–349. ISSN 1434-6028.

Faccio, R., Fernandez-Werner, L., Pardo, H., Goyenola, C., Ventura, O. N. and W Mombru, A. (2010). Electronic and Structural Distortions in Graphene Induced by Carbon Vacancies and Boron Doping. *Journal of Physical Chemistry C*. 114(44), 18961–18971.

Faccio, R. and Mombru, A. V. (2012). Magnetism in multivacancy graphene systems. *Journal of Physics: Condensed Matter*. 24(37), 375304.

Fürst, J. A., Pedersen, T. G., Brandbyge, M. and Jauho, A. (2009). Density functional study of graphene antidot lattices: Roles of geometrical relaxation and spin. *Phys. Rev. B*. 80, 115117.

Geim, A. K. and Novoselov, K. S. (2007). The rise of graphene.

Haase, P., Fuchs, S., Pruschke, T., Ochoa, H. and Guinea, F. (2011). Magnetic moments and Kondo effect near vacancies and resonant scatterers in graphene. *Phys. Rev. B*. 83, 241408.

Hubbard, J. (1963). Electron Correlations in Narrow Energy Bands. *Proceedings of the Royal Society of London Series A*. 276(1365), 238–257.

Kohanoff, J. (2006). *Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods*. Condensed matter physics, nanoscience and mesoscopic physics. Cambridge University Press. ISBN 9780521815918.

Kumazaki, H. and Hirashima, D. S. (2007). Nonmagnetic-Defect-Induced Magnetism in Graphene. *Journal of the Physical Society of Japan*. 76(6), 064713.

Lehtinen, P. O., Foster, A. S., Ma, Y., Krasheninnikov, A. V. and Nieminen, R. M. (2004). Irradiation-Induced Magnetism in Graphite: A Density Functional Study. *Phys. Rev. Lett.* 93, 187202.

Lieb, E. H. (1989). Two theorems on the Hubbard model. *Phys. Rev. Lett.* 62, 1201–1204.

Makarova, T. and Palacio, F. (2006). *Carbon Based Magnetism: An Overview of the Magnetism of Metal Free Carbon-based Compounds and Materials*. Carbon-based Magnetism: An Overview of the Magnetism of Metal Free Carbon-based Compounds and Materials. Elsevier Science.

Matte, H. S. S. R., Subrahmanyam, K. S. and Rao, C. N. R. (2009). Novel magnetic properties of graphene: Presence of both ferromagnetic and antiferromagnetic features and other aspects.

Nair, R. R., Sepioni, M., I-Ling, T., , O., Lehtinen, Keinonen, J., Krasheninnikov, A. K., Thomson, T., Geim, A. K. and Grigorieva, I. V. (2012). Spin-half paramagnetism in graphene induced by point defects. *Nature Physics*. 8, 199–202.

Nelayev, V. and Mironchik, A. (2010). Magnetism of Graphene with Vacancy Clusters. *Materials Physics and Mechanics*. 9(1).

Nolting, W. and Ramakanth, A. (2009). *Quantum Theory of Magnetism*. Berlin, Heidelberg: Springer-Verlag Berlin Heidelberg.

Okada, S. and Oshiyama, A. (2001). Magnetic Ordering in Hexagonally Bonded Sheets with First-Row Elements. *Phys. Rev. Lett.* 87, 146803.

Palacios, J. J., Fernández-Rossier, J. and Brey, L. (2008). Vacancy-induced magnetism in graphene and graphene ribbons. *Phys. Rev. B*. 77, 195428.

Perdew, J. P., Burke, K. and Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 77, 3865–3868.

Rode, A. V., Gamaly, E. G., Christy, A. G., Fitz Gerald, J. G., Hyde, S. T., Elliman, R. G., Luther-Davies, B., Veinger, A. I., Androulakis, J. and Giapintzakis, J. (2004). Unconventional magnetism in all-carbon nanofoam. *Phys. Rev. B*. 70, 054407.

Soler, J. M., Artacho, E., Gale, J. D., Garca, A., Junquera, J., Ordejn, P. and Snchez-Portal, D. (2002). The SIESTA method for ab initio order- N materials simulation. *Journal of Physics: Condensed Matter*. 14(11), 2745.

Thrower, P. A. and Mayer, R. M. (1978). Point defects and self-diffusion in graphite. *physica status solidi (a)*. 47(1), 11–37. ISSN 1521-396X.

Ugeda, M. M., Brihuega, I., Guinea, F. and Gómez-Rodr´, J. M. (2010). Missing Atom as a Source of Carbon Magnetism. *Phys. Rev. Lett.* 104, 096804.

Wallace, P. R. (1947). The Band Theory of Graphite. *Phys. Rev.* 71(9), 622–634.

Yang, X., Xia, H., Qin, X., Li, W., Dai, Y., Liu, X., Zhao, M., Xia, Y., Yan, S. and Wang, B. (2009). Correlation between the vacancy defects and ferromagnetism in graphite. *Carbon*. 47(5), 1399–1406.

Yazyev, O. V. and Helm, L. (2007). Defect-induced magnetism in graphene. *Phys. Rev. B*. 75, 125408.

Zhang, Y., Talapatra, S., Kar, S., Vajtai, R., Nayak, S. K. and Ajayan, P. M. (2007). First-Principles Study of Defect-Induced Magnetism in Carbon. *Phys. Rev. Lett.* 99, 107201.