ELECTRONIC STRUCTURES OF SILICON QUANTUM DOTS AS NANOCLUSTERS FOR SINGLE-ELECTRON TRANSISTORS

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Specially dedicated to my beloved parents, sisters, brother, brother-in-laws and my little nephews. Thanks for setting me on the path towards intellectual pursuits and giving me absolute support along the way

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ABSTRACT

Nanostructures such as quantum dot and nanocluster have occupied the centre of scientific interest because of their unique electronic nature. In this research, the electronic structures of silicon quantum dot were studied. The quantum dot was homologized with nanocluster since there is no strict distinction between these two nanostructures. The simulations in this research were carried out by using VASP (Vienna Ab-Initio Software Package) which utilizes the method of density functional theory and plane wave basis set. In order to speed up the computational time, parallelization was implemented on VASP. First, silicon clusters with surface passivated by hydrogen, Si_nH_m were simulated and the density of states (DOS) as well as bandstructure for each cluster was yielded. From the DOS graphs, discrete spectrum was observed instead of bulk-like continuous DOS which is the evolvement from bulk to nano-size. Bandstructure graphs also showed the discrete energy level in consistence with the discrete energy spectrum from DOS. It was found that the bandgap for hydrogenated silicon clusters increases with the decrease in size. Bare silicon clusters, Si_n were also simulated from 1 to 15 number of silicon atom (n). Optimization was performed to obtain the ground state structure. The bandgaps for the ground state silicon clusters do not show a decreasing trend with the increment of cluster size as that of hydrogenated silicon cluster. The electronic structures of optimized clusters are affected by the surface orientation of the clusters. A comparison of the bandgap values for Si_nH_m and Si_n was made. Finally, the current-voltage (I-V) characteristic and conductance-voltage spectrum (G-V) of single-electron transistor (SET) were studied with a simple toy model. These transport properties have shown the relativity of the electronic structure and the electron transport, where the conductance gap increases with the energy difference between Fermi level of the gold lead and the nearest molecular energy level of silicon cluster.

ABSTRAK

Nanostruktur seperti bintik kuantum dan nano kluster telah menjadi matlamat kajian dalam bidang sains disebabkan sifat elektronik semulajadinya. Dalam kajian ini, struktur elektronik bintik kuantum silikon telah dikaji. Bintik kuantum telah dianggap sama dengan nano kluster, oleh kerana tiada perbezaan yang ketara antara kedua-dua nanostruktur ini. Simulasi kajian telah dijalankan dengan menggunakan perisian VASP (*Vienna Ab-Initio Software Package*) yang menggunakan teori fungsian ketumpatan dan set basis gelombang satah. Untuk menyingkatkan masa pengiraan, keselarian telah dilaksanakankan ke atas VASP. Simulasi ke atas kluster silikon yang permukaannya dipasifkan dengan hidrogen, Si_nH_m telah dilakukan dan ketumpatan keadaan dengan struktur jalur telah diperolehi. Daripada graf ketumpatan keadaan, spektrum diskrit telah didapati. Perubahan ketumpatan keadaan daripada selanjar bagi struktur pukal ke diskrit spektrum bagi nanostruktur merupakan evolusi nano. Jalur struktur juga menunjukkan aras tenaga diskret yang selaras dengan spektrum diskrit daripada ketumpatan keadaan. Jurang jalur untuk silikon terhidrogenasi telah didapati semakin mengurang semasa saiz kluster meningkat. Simulasi ke atas kluster silikon tulen (tak terhidrogenasi), Si_n yang mempunyai bilangan atom (n) dari 1 ke 15 juga dilakukan. Pengoptimuman dilakukan untuk mendapatkan struktur keadaan dasar. Jurang jalur bagi struktur keadaan dasar kluster-kluster itu tidak mempunyai aliran yang menurun dengan peningkatan saiz kluster seperti yang berlaku pada kluster silikon terhidrogenasi. Struktur elektronik kluster-kluster optimum dipengaruhi oleh orientasi permukaan kluster. Perbandingan nilai jurang jalur bagi Si_nH_m dan Si_n dilakukan. Akhirnya, ciri arus-voltan (I-V) dan konduktans-voltan (G-V) bagi transistor elekron tunggal dikaji dengan menggunakan satu model yang mudah. Sifat-sifat pengangkutan elektron itu menunjukkan perkaitan antara struktur elektronik dengan pengangkutan elektron, di mana jurang konduktans semakin bertambah apabila perbezaan tenaga antara aras Fermi elektrod emas dengan aras tenaga molekular yang paling dekat bertambah.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SET	-	Single-electron transistor
RTD	-	Resonant tunneling diodes
QCA	-	Quantum cellular automata
ATLAS	-	Automatically Tuned Linear Algebra Software
BLAS	-	Basic Linear Algebra Subprograms
BO	-	Born Oppenheimer
BP	-	Becke-Perdew
BSSE	-	Basis set superposition error
CC	-	Coupled cluster theory
CG	-	Conjugate gradient
CI	-	Configuration Interaction
CMOS	-	Complementary metal oxide semiconductor
CMS	-	Computational materials science
CNT	-	Carbon nanotubes
DFT	-	Density functional theory
DIIS	-	Direct inversion in the iterative subspace
DOS	-	Density of states
ETB	-	Empirical tight binding
EPM	-	Empirical pseudopotential method
EMA	-	Effective mass approximation
2DEG	-	Two-dimensional electron gas
FFT	-	Fast-fourier transform
GEA	-	Gradient expansion approximation

GGA	-	Generalized gradient approximation
GTO	-	Gaussian-type orbital
GVB	-	Generalized valence bond
HF	-	Hartree Fock theorem
HK	-	Hohenberg-Kohn
HOMO	-	Highest Occupied Molecular Orbital
HPC	-	High-performance cluster
IFC	-	Intel Fortran Compiler
Intel® MKL	-	Intel Math Kernel Library
KS	-	Kohn-Sham theorem
LCAO	-	Linear combination of atomic orbitals
LDA	-	Local density approximation
LAPACK	-	Linear Algebra PACKage
LM	-	Langreth-Mehl
LSDA	-	Local spin density approximation
LUMO	-	Lowest Unoccupied Molecular Orbital
LYP	-	Lee-Yang-Parr
MCSCF	-	Multi-Configurations Self Consistent Field
MD	-	Molecular dynamics
MGGA	-	Meta-Generalized Gradient Approximation
MOSFET	-	Metal-oxide-semiconductor field-effect transistor
MPI	-	Message Passing Interface
NC-PP	-	Norm-conserving pseudopotential
NFS	-	Network file system
PAW	-	Projected Augmented Wave
PBE	-	Perdew-Burke-Ernzernhof
PES	-	Potential energy surfaces
PP	-	Pseudopotential
PW	-	Plane Wave
PW91	-	Perdew-Wang 1991

RMM	-	Residual minimization scheme
rPBE	-	Revised-Perdew-Burke-Ernzernhof
RPA	-	Random phase approximation
SA	-	Simulated annealing
SCF	-	Self-consistent functional
SSH	-	Secure Shell
STO	-	Slater-type orbitals
US-PP	-	Ultrasoft Vanderbilt pseudopotential
VASP	-	Vienna Ab-Initio Software Package
VWN	-	Vosko-Wilk-Nusair
QMC	-	Quantum Monte Carlo
WF	-	Wavefunction

LIST OF SYMBOLS

C	-	Capacitance
E	-	Energy
E_F	-	Fermi Energy
E_g	-	Energy gap / bandgap
E_n	-	Energy of nth confined state
E_C	-	Charging energy
E_{XC}	-	Exchange-correlation energy
$f(E)$	-	Fermi energy
F	-	Force
$g(E)$	-	Density of states
g	-	Spin-scaling factor
G	-	Capacitance
G	-	Reciprocal lattice vector
$h, \hbar$	-	Planck's constant
H	-	Hamiltonian
I_{SD}	-	Source-drain current
j_l	-	Spherical Bessel function
$J[n]$	-	Coulomb interaction
k	-	Wavenumber
k_B	-	Boltzmann's constant
L	-	Edge length
$\hat{L}$	-	Angular momentum operator
m	-	Mass

n	-	Quantum number of state (integer)
N	-	Total number of states
N	-	Number of electron
$n(\vec{r})$	-	Electron density
p	-	Momentum
$\hat{p}_r$	-	Linear momentum operator
$\tilde{p}_{lm\varepsilon}$	-	Projector function
Q	-	Charge
r, $\vec{r}$	-	Position vector
r_i	-	Electron spatial coordinates
r_s	-	Wigner-Seitz radius
$R_{nl}(r)$	-	Radial wavefunction
R	-	Radius
R	-	Resistance
R_A	-	Nuclei spatial coordinates
s, t	-	Dimensionless density gradient
t	-	time
T	-	Kinetic energy
T	-	Temperature
$T(E)$	-	Transmission
u_k	-	Bloch function
V	-	Volume
V	-	Potential Energy
V_{DS}	-	Drain-source voltage
V_T	-	Threshold voltage
V_G	-	Gate voltage
$Y_l^m(\theta,\varphi)$	-	Spherical harmonic
Z_A	-	Nuclei charge
λ	-	Wavelength
λ	-	Coupling constant

Ψ	-	Wavefunction
υ	-	Velocity
ω	-	Angular frequency
ν	-	Frequency
$\phi(r)$	-	Envelope function
Θ	-	Unit step function
ε	-	Energy
ε_i	-	Single-particle energy level
Γ	-	Tunneling rates
μ	-	Chemical potential
∇	-	Laplacian operator
ξ	-	Spin-polarization
$\tau(\vec{r})$	-	Kinetic energy density
Ω	-	Volume of unit cell
η	-	Voltage division factor
ρ	-	Density matrix
Si	-	Silicon
Si_n	-	Silicon cluster with n silicon atom
Si_nH_m	-	Hydrogenated silicon cluster with n silicon atom and m hydrogen atom
S_N	-	Speedup
E_N	-	Efficiency

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Nanotechnology and Nanoscience

Nanotechnology and nanoscience had emerged as a very popular and important issue in every field including science (physics, chemistry and biology) and engineering over the decade. This is the trend of technology as many things get smaller and smaller by time and when it exceeds the ability of microtechnology, it comes to nanotechnology. This is the phenomenon of miniaturization which consequently leads to the brand new era of technology with novel concepts and devices.

The word “nano” refers to the size of 10^{-9} meter. One can imagine how small a nanometer is when a human hair with diameter approximately 100 µm is sliced 10^5 times, a bacterial cell is divided 100 times, and ten hydrogen atoms are lined up. Nanoscience is concerned with study of objects which is anywhere from hundreds to tens of nanometer in size, whilst nanotechnology is related to the practical application of materials and devices in the same size range. Nanotechnology is sometimes called molecular manufacturing which is a branch engineering that deals with the design and manufacture of extremely small electronic circuits and mechanical device built at molecular level of matter.

Indeed, the emergence of nanotechnology already happened in the late 19th century when colloidal science started but it is not referred to nanotechnology at the time. In year 1959, Richard Feynman in his talk "There's Plenty of Room at the Bottom" had firstly mentioned some of the nanotechnology concepts [1]. He described a process by which the ability to manipulate individual atoms and molecules might be developed. In 1947, the term "nanotechnology" was defined by Professor Norio Taniguchi from Tokyo Science University.

When things shrink into nanoscale, quantum effects come into play and classical theory unable to explain what happens in this extremely small size. Hence, the attributes of nanoscale particles are in between the atom and bulk materials. These attributes will vary by size which leads to the ability of material behavior engineering. This revolution have made nanotechnology and nanoscience a very exotic field which still need a lot more efforts in research to open up and reveal its under covered ability.

1.2 Application of Nanotechnology

The advancements in science and technology have allowed the miniaturization of amazingly complex devices. A lot of the nano-devices are being researched widely and intensively, hence its market potential is bright. A portion of it is as yet conceptual, though realization is not an impossible matter. It is worth to point out that nanotechnology has remarkably brought together technologies from physics, biology and chemistry.

1.2.1 Nanoelectronics, Nanocomputing and Nanophotonics

According to Moore's law, the number of transistors on a microprocessor would double periodically approximately every 18 months. Without taking account of the cost, this prediction had indicated that the transistors will be smaller in order to obey the law. To increase the density of transistors on one chip, the size of transistors must be small enough. Nanotechnology can achieve this target and open up the new phase of Moore's law with nanoelectronics and nanocomputing.

Nanocomputing is the use of the structures on the scale of within 100 nanometers to accomplish any of the tasks that modern computers can do. This kind of computing will adopt a new concept of operation, which is quantum principle. Thus, nanocomputing can also be termed as quantum computing. In making computers faster, power consumption and heat dissipation are the problems that need to be concerned. Amazingly, nanotechnology may overcome these problems. There was an analysis with unbelievable outcome: A CPU-scale system containing a million transistors would fit within a 400 nm cube, run at 1 GHz, and consume 60 nanoWatts [2]. A desktop nanocomputer consuming 100 watts of power would process 10^{18} instructions per second. Indubitably, the memory would increase in consistent with the power and speed. The factor that contributes to these distinct abilities is quantum bits or qubits. Classical computers rely on bits, which 1 represent ON state and 0 represent OFF state. Quantum computing consumes the law of quantum mechanics that allow an atom to be arranged in a coherent superposition of states 0 and 1. This means an atom can be in both states at the same time. While N bits can store a single number out of 2^N possibilities, a qubit can store all 2^N number available.

In order to create quantum computers, nanoelectronics are needed. There are plenty of nanoelectronic devices have been proposed, among which are: single-electron transistor (SET), resonant tunneling diodes (RTD), spin transistor, quantum cellular automata (QCA), carbon nanotubes (CNT), ultra-scaled FETs, superlattice

arrays, and molecular electronic devices. The nanostructures that build these nanoelectronics can be categorized into three: quantum well, quantum wires and quantum dots. The operations of these devices are governed by quantum principles. CNT is one of the popular research targets owing to its special attributes, for instance, it is stronger than steel and it can be used in a lot of applications in field of biology, chemistry as well as physics.

Fabricating nanoelectronics could open new way of making nanophotonic devices. Nanophotonic is the manipulation and emission of light includes near field and far field light using nano-scale materials. It could revolutionize the fields of telecommunication, computing as well as sensing. Its applications includes storing data, as switch operating in computers, and converting electrical energy into light of variable wavelength for the purpose of light sources.

1.3 Introduction to Modeling and Simulation

Modeling is the technique of representing a real-word syste or phenomenon with a set of mathematical equations or physical model. A computer simulation then attempts to use the models on a computer so that it can be studied to see how the system works. Prediction may be made about the behavior and performance of the system by changing its variables. In this research, nanostructures are the system targets of the modeling and simulation.

Simulation is a useful and important part of modeling nanostructures to gain insight into the attributes of a structure or a whole system with several structures connected. It is a method to predict the behavior transformation for a variable changing before performing a practical experiment. The simulation can then be proven by the results of experiment. This is also a beneficial approach to test the

most optimal and the best performance of a device which is built by those nanostructures before the real fabrication.

Besides, simulation can give detailed theoretical explanation to the phenomenon that could not be explained by experiment solely. Among the examples are the reconstruction of the nanostructures and the occupation of the electrons. With the 3D graphical viewer and animation, we can view the atomic structure models and the process of the structure transformation. With computer simulation done prior to experiment, the mastering of the nanostructures principles is improved and 'trial and error' could be reduced during experiment.

However, there isn't a comprehensive simulator which can take into account every factor that would contribute to the system changes. Many of those only adopt the approximation which is the most optimal and closest to the real system for the representation. For nanostructures, first principle calculation is an appropriate simulation approach for studying the electronic structures and properties. The advantage of this calculation is that, it can be done without any experimental data. However, it could be a massive calculation that consumes a very long time to accomplish.

Computational science becomes an essential tool in modeling and simulation. It is the application of computational and numerical technique to solve large and complex problem, for example, complex mathematics that involved a large number of calculations. Therefore, modeling and simulation are commonly accomplished by the aid computational science and therefore they are always referred to computer modeling and computer simulation. Computational science could be defined as an interdisciplinary approach that uses concepts and skills from the science, computer science and mathematic disciplines to solve complex problems which allow the study of various phenomena. It can be illustrated by Figure 1.1. To improve the performance and speed of large computation, one of the approaches is parallel computing. Parallel computing can reduce the computing time of computational

costly calculations such as first principle calculations mentioned above, where it distributes the calculation to two or more processors or computers.

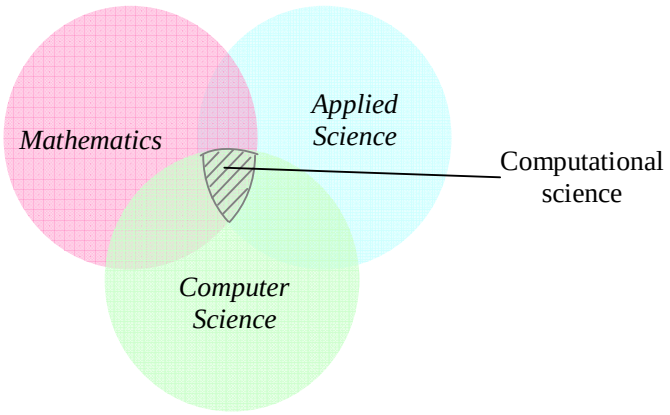

Figure 1.1. Computational science is defined as the intersection of the three disciplines, i.e. computer science, mathematics and applied science.

1.4 Research Objectives

The main interest of this research is to study the electronic structures of silicon quantum dots in the form of clusters. The objectives of this research can be summarized as the following:

a) to study the electronic structures of quantum dots with variable size and structures.

b) to study the relation between the bandgap and the size as well as the effect of structure of the quantum dot, and

c) to study the relation between the electronic structure of the quantum dot and the I-V characteristic of single-electron transistor.

1.5 Scopes of Study

The study scopes of this research are as the following:

a) Quantum dot is simulated as isolated small range nanocluster.

b) Silicon is adopted as the material of the quantum dot.

c) Bandstructure and energy spectrum are studied for the electronic structures of quantum dot.

d) Density functional theory is used to calculate and simulate the electronic structures of quantum dot.

e) To build a parallel computing system to speed up the calculation.

1.6 Thesis Overview

Quantum dot is a crucial part in single-electron transistor (SET) that govern the performance of the device. In the next chapter, SET is introduced and its operation principle is discussed. From this chapter, the characteristics of quantum dot in SET could be understood, where the objective of modeling and simulating quantum dot is manifested.

In chapter 3, theory of nanostructures and quantum dot is discussed. The attribute of the evolvement from bulk to nanoscale structure is showed. In this extremely small size, the theory that governs its properties is quantum theory. There are a lot of approaches to simulate the electronic structures of quantum dot. Density

functional theory is a sufficient method in doing this. Its theory is discussed in the next chapter, Chapter 4.

Chapter 5 is discussing the methodology of the simulation. Vienna Ab-initio Software Package which is utilized in this study is introduced. The steps and process of simulation is explained. Following this, Chapter 6 would be results and discussion. Figures and graphs showing the electronic structures of quantum dot are showed, and the results are discussed and interpreted.

Finally Chapter 7 which is the conclusion. Theories and results discussed in the previous chapters are summarized and concluded here. Furthermore, suggestion is given on how to make the simulation work better and more complete.

REFERENCES

[1] R. P. Feynman. There's Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics. In: William A. Goddard. III, Donald W. Brenner, Sergey Edward Lyshevski, Gerald J. Iafrate. *Handbook of Nanoscience Engineering and Technology*. U.S.: CRC Press. 1-9; 2003.

[2] K. Eric Drexler. *Nanosystems:Molecular Machinery, Manufacturing and Computation*. New York: John Wiley & Sons, 1992.

[3] Richard L. Liboff. *Introductory Quantum Mechanics.* Fourth Edition. Addison Wesley: San Francisco, 2003.

[4] Robert W. Kelsall, Ian W. Hamley and mark Geoghegan. *Nanoscale Science and Technology*. Chichester: John Wiley & Sons. 2005.

[5] Charles P. Poole Jr., Frank J. Owens. *Introduction to Nanotechnology*. New Jersey: John Wiley & Sons. 2003.

[6] Thomas Heinzel. *Mesoscopic Electronics in Solid State Nanostructure*. Weinheim: Wiley-VCH. 2003.

[7] Alexander L. Efros, David J. Lockwood, Leonid Tsybeskov. *Semiconductor Nanocrystals: From Basic Principles to Applications*. New York: Kluwer Academic/Plenum Publisher. 2003.

[8] Julio A. Alonso. *Structrues and Properties of Atomic Nanoclusters*. London: Imperial College Press. 2005.

[9] Akhlesh Lakhtakia. *Nanometer Structures: Theory, Modeling and Simulation*. New York: ASME Press. 2004.

[10] Serdar Öğüt. First Principles Modeling of Nanostructures. *Turkish Journal of Physics*. 2003. vol. **27.** Issue 5. p.443-458.

[11] C. Delerue and M. Lannoo. *Nanostructures: Theory and Modelling*. Berlin: Springer. 2004.

[12] Enrico Lipparini. *Modern Many-Particle Physics: Atomic Gases, Quantum Dots and Quantum Fluids*. Singapore: World Scientific, 2003.

[13] Takeyce K. Whittingham. *Scaling Relations in Density Functional Theory and Applications of Electronic Structure Methods*. PhD Dissertation. The State University of New Jersey; 2004.

[14] Attila Szabo and Neil S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Revised Edition. US: McGraw-Hill. 2003.

[15] L. H. Thomas. The calculation of atomic fields. *Proc. Cambrigde Philos. Soc*. 1927. 23: 542.

[16] E. Fermi. Application of statistical gas methods to electronic systems. *Atti. Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend*. 1927. 6: 602.

[17] J. Harris. Adiabatic-connection approach to Kohn-Sham theory. *Phys. Rev. A*. 1984. 29(4):1648.

[18] R. O. Jones and O. Gunnarsson. The density functional formalism, its applications and prospects. *Rev. Mod. Phys.* 1989. 61(3): 689 – 746.

[19] O. Gunnarsson and B. I. Lundqvist. Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism. *Phys. Rev. B*. 1976. 13(10): 4274.

[20] W. Kohn, A. D. Becke and R. G. Parr. Density Functional Theory Of Electronic Structure. *J. Phys. Chem*. 1996. 100(31): 12974-12980.

[21] D. M. Ceperley and B. J. Alder. Ground State of the Electron Gas by a Stochastic Method. *Phys. Rev. Lett.* 1980. 45(7): 566.

[22] P. A. M. Dirac. Quantum Mechanics of Many-Electron Systems. *Proc. Royal Soc.(London) A*. 1929. 123(792)**:** 714-733.

[23] J. P. Perdew and Y. Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*. 1992. 45(23): 13244.

[24] S. J. Vosko, L. Wilk and M. Nusair. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys.* 1980. 58: 1200.

[25] J. P. Perdew and A. Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*. 1982. 23(10):5048-5079.

[26] J. Kohanoff and N.I. Gidopoulos, Density Functional Theory: Basics, New Trends and Applications. In: Stephen Wilson. *Handbook of Molecular Physics and Quantum Chemistry*. Chichester: John Wiley & Sons. Volume **2**, Part 5, Chapter 26, 532–568; 2003.

[27] D. C. Langreth and M. J. Mehl. Easily Implementable Nonlocal Exchange-Correlation Energy Functional. *Phys. Rev. Lett.* 1981. 47(6): 446-450.

[28] Langreth, D.C. and Mehl, M.J. Beyond the local-density approximation in calculations of ground-state electronic properties. *Phys. Rev. B.* 1983, 28(4): 1809.

[29] Perdew, J.P. and Wang, Y. Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation. *Phys. Rev. B.* 1986. 33(12): 8800-8802.

[30] J. P. Perdew. Density-functional approximation for the correlation energy of the inhomogeneous electron gas,*Phys. Rev. B*. 1986. 33(12): 8822-8824.

[31] J. P. Perdew and Y. Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, 1992. 45(23): 13244-13249.

[32] A. D. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A.* 1988. 38(6): 3098-3100.

[33] Chengteh Lee, Weitao Yang, and Robert G. Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* 1988. 37(2): 785-789.

[34] J. P. Perdew, K. Burke and M. Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996. 77(18): 3865-3868.

[35] J. P. Perdew, K. Burke and M. Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*1997. 78**:** 1396 (E).

[36] A. D. Becke. Density Functional Calculations of Molecular-Bond Energies, *J. Chem. Phys.*1986. 84(8): 4524-4529.

[37] Yingkai Zhang and Weitao Yang. Comment on “Generalized Gradient Approximation Made Simple”. *Phys. Rev. Lett.* 1998. 80(4): 890 – 890.

[38] M. Levy and J. P. Perdew. Hellmann-Feynman, virial, and scaling requisites for the exact universal density functionals. Shape of the correlation potential and diamagnetic susceptibility for atoms, *Phys. Rev. A.* 1985. 32(4):2010-2021.

[39] E. H. Lieb and S. Oxford. An Improved Lower Bound on the Indirect Coulomb Energy. *Int. J. Quantum Chem*. 1981. 19:427.

[40] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B.* 1992. 46(11): 6671-6687.

[41] Y. Wang and J. P. Perdew. Spin scaling of the electron-gas correlation energy in the high-density limit. *Phys. Rev. B*. 1991. 43(11): 8911-8916.

[42] J. P. Perdew and Y. Wang. Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling. *Phys. Rev. B.* 1991. 44(24)**:** 13298-13307.

[43] J. P. Perdew, Unified Theory of Exchange and Correlation Beyond the Local Density Approximation. In: P. Ziesche and H. Eschrig. *Electronic Structure of Solids '91*, Berlin: Akademie Verlag, 11-20; 1991.

[44] J. P. Perdew, Stefan Kurth, Ales Zupan, and Peter Blaha, Accurate Density Functional with Correct Formal Properties: A Step Beyond the Generalized Gradient Approximation, Phys. Rev. Lett. 1999. 82(12):2544-2547.

[45] Jianmin Tao, John P. Perdew, Viktor N. Staroverov and Gustavo E. Scuseria, Climbing the Density Functional Ladder: Nonempirical Meta–Generalized Gradient Approximation Designed for Molecules and Solids, *Phys. Rev. Lett.* 2003. 91(14): 146401.

[46] T. Van Voorhis and G. E. Scuseria, A novel form for the exchange-correlation energy functional. *J. Chem. Phys*. 1998. 109(2): 400-410.

[47] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993. 98(7): 5648-5652.

[48] A. D. Becke, A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.* 1993. 98(2): 1372-1377.

[49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. H.-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. L. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople. *GAUSSIAN92*©. Pittsburgh: Gaussian Inc. 1993.

[50] P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas. *Phys. Rev.* 1964. 136(3B): B864 - B871.

[51] Georg Kresse and Jürgen Furthmüller. *VASP the GUIDE*. Institut für Materialphysik, Universität Wien. 2005. (retrieved from: http://cms.mpi.univie.ac.at/VASP/)

[52] W. J. Hehre, R. F. Stewart, and J. A. Pople. Self-Consistent Molecular Orbital Methods. I. Use of Gaussian Expansions of Slater Type Atomic Orbitals, *J. Chem. Phys*. 1969. 51(6): 2657-2664.

[53] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, *Gaussian 70*, Quantum Chemistry Program Exchange, Program No. 237, 1970.

[54] J. C. Slater. Atomic Shielding Constants. *Phys. Rev*. 1930. 36(1): 57 – 64.

[55] M. T. Yin and Marvin L. Cohen. Theory of ab initio pseudopotential calculations. *Phys. Rev. B.* 1982. 25(12): 7403 – 7412.

[56] G. Kresse and J. Joubert. From ultrasoft pseudopotentials to the projector augmented wave method. *Phys. Rev. B*. 1999. 59(3): 1758-1775.

[57] P. E. Blöch. Projector augmented-wave method. *Phys. Rev. B.* 1994. 50(24): 17953.

[58] G. Kresse and J. Hafner. Ab initio molecular dynamics for liquid metals. *Phy. Rev. B.* 1993. 47(1): 558-561; 1994. ibid. 49: 14251.

[59] G. Kresse and J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mat. Sci.* 1996. 6(1): 15-50.

[60] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B.* 1996. 54(16): 11169-11186.

[61] M. P. Teter, M. C. Payne, and D. C. Allan. Solution of Schrödinger's equation for large systems. *Phys. Rev. B*. 1989. 40(18): 12255-12263.

[62] A.R. Tackett, N.A.W. Holzwarth and G.E. Matthews. A Projector AugmentedWave (PAW) code for electronic structure calculations, Part II: pwpaw for periodic solids in a plane wave basis. *Computer Physics Communications*. 2001. 135(3): 348–376.

[63] H. J. Monkhorst and J. D. Pack. Special points for Brillouin-zone integrations. *Phys. Rev. B*. 1976. 13(12): 5188-5192.

[64] R. P. Feynman. Forces in Molecules. *Phys. Rev*. 1939. 56(4): 340 – 343.

[65] R. O. Jones. Cluster Geometries From Density Functional Calculations – Prospects and Limitations. Eur. Phys. J. D. 1999. 9: 81-84.

[66] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth. A.H. Teller and E. Teller. Equation of State Calculations by Fast Computing Machines. *J. Chem. Phys.* 1953. 21(6): 1087-1092.

[67] Andréia Luísa da Rosa. *Density-Functional Theory Calculations on Anti-Surfactants at Gallium Nitride Surfaces*. Master Dissertation. Universität Berlin; 2003.

[68] S. F. Li and X. G. Gong. First-Principles Studies On The Reactions of O_2 with Silicon Clusters. *J. Chem Phys.* 2005. 122(17): 174311.

[69] Jürgen Müller, Bei Liu, Alenxandra A. Shvartsburg, Serdar Ögut, James R. Chelikowsky, K. W. Michael Siu, Kai Ming Ho, and Gerd Gantefor. Spectroscopic Evidence for the Tricapped Trigonal Prism Structure Of Semiconductor Clusters. *Phys. Rev. Lett.* 2000. 85(8): 1666-1669.

[70] L. A. Bloomfield, R. R. Freeman, and W. L. Brown. Photofragmentation of Mass-Resolved $Si_{2\text{-}12}^{+}$ Clusters. *Phys. Rev. Lett.* 1985. 54(20), 2246-2249.

[71] J. R. Heath, Y. Liu, S. C. O'Brien, Q. L. Zhang, R. G. Curl, F. K Tittel, and R. E. Smalley, Semiconductor Cluster Beams: One and two color ionization studies of Six and Gex, *J. Chem. Phys*. 1985. 83: 5520.

[72] Krishnan Raghavachari and Celeste McMichael Rohlfing, Electronic Structures of The Negative Ion Si_2^- - Si_{10}^- : Electron Affinities of Small Silicon Clusters, *J. Chem. Phys.* 1991. 94(5): 3670-3678.

[73] Siqing Wei, R. N. Barnett, and Uzi Landman. Energetics and structures of neutral and charged Si_n ($n \leq 10$) and sodium-doped Si_nNa clusters. *Phys. Rev. B.* 1997. 55(12): 7935-7944.

[74] Krishnan Raghachari. Theoretical Study of Small Silicon Clusters: Equilibrium Geometries and Electron Structures of Si_n (n = 2-7,10). *J. Chem. Phys*. 1986. 84(10): 5672-5686.

[75] J. A. Stroscio, R. M. Feenstra and A. P. Fein. Electronic Structure of the Si(111)2 × 1 Surface by Scanning-Tunneling Microscopy. *Phys. Rev. Lett*. 1986. 57(20): 2579-2582.

[76] R. H. Hamers. Atomic-Resolution Surface Spectroscopy with the Scanning Tunneling Microscope. *Annu. Rev. Phys. Chem*. 1989. 40: 531.

[77] F. J. Himpsel, T. Fauster. Probing Valence States with Photoemission and Inverse Photoemission. *J. Vac. Sci. Technol*. 1984. A2: 815.

[78] Klaus Sattler. The Energy Gap of Clusters Nanoparticles, And Quantum Dots. In: H. S. Nalwa. *Handbook of Thin Films Materials*, Academic Press. vol 5. p.61-97, 2002.

[79] Ferdows Zahid, Magnus Paulsson and Supriyo Datta. *Electrical Conduction through Molecules*, In: H. Morkoc, *Advances Semiconductors and Organic Nano-Techniques.* U.S.:Academic Press, 2003.

[80] L. Kouwenhoven. Coupled Quantum Dots as Artificial Molecules. *Science*. 1995. 268: 1440-1441.

[81] Konstantin K. Likharev. Single-Electron Devices and Their Application. *Proceedings of the IEEE*. 1999. 87(4): 606-632.

[82] V. Ranjan, ManishKapoor and VijayASingh. The Bandgap in Silicon Nanocrystallites. *J.Phys.:Condens.Matter*. 2002. 14(26): 6647–6655.

[83] D. V. Averin and K. K. Likharev. Single Electronics: a Correlated Transfer of Single Electrons and Copper Pairs in Systems of Small Tunnel Junctions. In: B. L. Altshuler, P. A. Lee and R. A. Webb. *Mesoscopic Phenomena in Solids*. Amsterdam: Elsevier. 173-271; 1991.

[84] Wolfgang Johann Parak, Liberato Manna, Friedrich Christian Simmel, Daniele Gerion, and Paul Alivisatos. Quantum Dots. In: Günter Schmid, *Nanoparticles: From Theory to Application*. Weinheim: Wiley-VCH. 4-44; 2004.

[85] S. Li, R. J. Van Zee, W. Weltner Jr., Krishnan Raghavachari. Si_3-Si_7 Experimetal and Theoritical Infrared Spectra. *Chem. Phys. Lett*. 1995. 243(3): 275-280.

[86] Kurt A. Johnson and N. W. Ashcraft. Corrections to Density-Functional Theory Band Gaps. *Phys. Rev. B*. 1998. 58(23): 15548-15556.

[87] Krishnan Raghavachari and Celeste McMichael Rohlfing. Bonding and stabilities of small silicon clusters: A theoretical study of Si_7–Si_{10}. *J. Chem. Phys*. 1988. 89**(**4): 2219-2234.

[89] Krishnan Raghavachari and Veronika Logovinsky. Structure and bonding in small silicon clusters. *Phys. Rev. Lett*. 1985. 55(26): 2853 – 2856.

[90] C.Delerue ,G.Allan and M.Lannoo, Optical bandgap of Si nanoclusters, *Journal of Luminescence.* 1999. 80(1): 65-73.

[91] S. Katircioglu and S. Erkoc. Structural and Electronic Properties of bare and hydrogenated silicon clusters. *Physica E*. 2001. 9: 314-320.

[92] B. Marsen, M. Lonfat, P. Scheier and K. Sattler. The energy gap of pristine silicon clusters. *Journal of Spectroscopy and Related Phenomena.* 2000. 109: 157-168.

[93] X. L. Zhu, X. C. Zeng, and Y. A. Lei. Structures and stability of medium silicon cluster. II. Ab initio molecular orbital calculation of Si_{12}-Si_{20}. *J. Chem. Phys*. 2004. 120(19): 8985-8995.

[94] Bei Liu, Zhong-Yi Liu, Bicai Pan, Cai-Zhuang Wang and Kai-Ming Ho. Ionization of medium-sized clusters and the geometries of the cations. *J. Chem. Phys*. 1998. 109(21): 9401-9409.

[95] Kai-Ming Ho, Alexandre A. Shvartsburg, Bicai Pan, Zhong-Yi Lu, Cai-Zhuang Wang, Jacob G. Wacker, James L. Fye, and Martin F. Jarrold. Structures of medium-sized silicon clusters. *Nature*. 1998. 392(6676): 582-585.

[96] Krishnan Raghavachari. Theoritical study of small silicon clusters: Cyclic ground state structure of Si_3. *J. Chem. Phys*. 1985. 83(7): 3520-3525.

[97] Bernd Hartke. Global geometry optimization of small silicon clusters at the level of density functional theory. *Theoritical Chemistry Accounts*. 1998. 99:241-247.

[98] Eleonora Luppi, Elena Degoli, G. Cantele, Stefano Ossicini, Rita Magri, D. Ninno, O. Bisi, O. Pulci, G. Onida, M. Gatti, A. Incze and R. Del Sole. The electronic and optical properties of silicon nanoclusters: absorption and emission. *Optical Materials*. 2005. 27: 1008-1013.

[99] K. P. Huber and G. Herzberg. *Molecular Spectra and Molecular Structure I. Spectra of diatomic molecules.* New York: Van Nostrand Reinhold, 1950. 658 p.

[100] C. Chatillon, M. Allibert and A. Pattoret, High temperature Knudsen cell mass spectrometry. Atomization energies determination of Si_2, Si_3, Al_2, AlSi and $AlSi_2$. *C. R. Acad. Sci. Ser. C.* 1975. v 280, 1505.

[101] J. C. Grossman and L. Mitas. Quantum Monte Carlo Determination of Electronic and Structural Properties of Si_n Clusters ($n \leq 20$). *Phys. Rev. Lett*. 1995. 74(8), 1323; J. C. Grossman, I. Stich and J. Tobik, Silicon Clusters of Intermediate Size: Energetics, Dynamics, and Thermal Effects, *Phys. Rev. Lett.* 2000. 84(7). 1479.

[102] JuCai Yang ,WenGuo Xu and WenSheng Xiao. The small silicon clusters Si_n (n =2–10) and their anions: structures, themochemistry, and electron affinities. Journal of Molecular Structure:THEOCHEM . 2005. 719. 89–102

[103] Norahanim Mohd Jais, Ujian Prestasi Pembangunan Makmal Pemprosesan Selari Dengan Antaramuka Laluan Pesanan (MPI) Kaedah Pengenduran Berturut-turut Merah Hitam (SOR RED BLACK), Degree Dissertation, Universiti Teknologi Malaysia, 2002.

[104] Motoyuki Oishi, 5nm CMOS Transistor, 1MHz Organic Circuits Draw Attention, *Nikkei Electronics Asia*, March 2004.

[105] J. Donahue, *The Structure of Elements*, Wiley, New York, 1974.

[106] Igor Vasiliev, Serdar Öğüt and James R. Chelikowsky. Ab Initio Absorption and Optical Gaps in Nanocystalline Silicon. *Phys. Rev. Lett*. 2000. 86(9). 1813.

[107] E. C. Honea et.al. Structures and coalescence behavior of size-selected silicon nanoclusters studied by surface-plasmon-polariton enhanced Raman spectroscopy. *J. Chem. Phys.* 1999. 110(24). 12161-12172.

[108] Giovanni Meloni, Michael J. Ferguson, Sean M. Sheehan, Daniel M. Neumark. Probing structural transitions of nanosize silicon clusters via anion photoelectron spectroscopy at 7.9 eV. *Chem. Phys. Lett.* 2004. 399. 389-391.

[109] Thomas Bachels, Rolf Schäfer. Binding energies of neutral silicon clusters. *Chem. Phys. Lett.* 2004. 324. 365-372.