# POLYNOMIAL AND PIECEWISE POLYNOMIAL FITTING IN TIGHT-BINDING MODEL OF CARBON MOLECULE

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# POLYNOMIAL AND PIECEWISE POLYNOMIAL FITTING IN TIGHT-BINDING MODEL OF CARBON MOLECULE

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# A**BSTRACT**

The tight-binding (TB) method is a semi-empirical method that is primarily used to calculate the energy band structure and single-particle Bloch states of material. Semi-empirical method is the method used in the electron system quantum mechanical involving the Schrödinger equation where the Hamiltonian is replaced with a parameterized model. The parameters of the model are fitted to reproduce the reference data which is obtained from the experimental data. The semi-empirical tight-binding method is one of the main approaches to compute the total energy of a system and it is computationally very fast. Therefore it tends to be used in the calculation of every large system, with more than a few thousand atoms in a unit cell. The main contribution of this research is to develop two new tight-binding energy models for carbon which associate with parameters fitting in the Hamiltonian system by using a minimization approach. This research aims to implement the polynomial and piecewise polynomial interpolation as new scaling function to the old TB model which denoted by Model 1 and Model 2, respectively. These new models are developed based on polynomial and piecewise polynomial approach. Mathematical techniques such as eigenvalues problem, minimization method, Newton iteration method and basic principles of the semi-empirical method are also applied in this research. The new methods obey the concept of semi-empirical approach which assumes that only one electron is free to move around the whole system. The elements of the overlapping Hamiltonian matrix in Model 1 and Model 2 are approximated by the polynomial function and piecewise polynomial function respectively. The models are then applied into 2-carbon, 3-carbon, and 4-carbon bond system with fixed geometry coordinates. Each parameter is calculated by using Newton iteration method which also involves differentiation of eigenvalues in the eigensystem. The energy of the bonding is then compared with the reference data from the well-established method of previous research. Both new models have been successfully reduced the computational time execution in the calculations by reducing the floating-point operations per second (FLOPS) in the algorithms. The results of Model 1 and Model 2 are compared whereby for 2-carbon simulation, the absolute error of these two models remains unchanged. For 3-carbon simulation, the absolute error has been reduced by 0.000006. Meanwhile, for 4-carbon simulation, the absolute error has been reduced by 0.116213. It is found that the efficiency of the new models has been significantly improved from Model 1 to Model 2 when the number of atom increases. The results suggest that Model 2 is more suitable for bigger molecule calculation due to its nature of piecewise polynomial advantages. Most of the results obtained gave positive feedback except some calculations which produced a trivial solution. Good agreement with data collection indicates that proposed models can be used as an alternative solution to the existing models and significant for the advancement of new knowledge.

# ABSTRAK

Kaedah pengikatan-ketat (TB) adalah kaedah separa empirikal yang digunakan terutamanya untuk mengira struktur jalur tenaga dan zarah-zarah tunggal jenis Bloch bahan. Kaedah separa empirikal adalah kaedah yang digunakan dalam sistem kuantum berelektron secara mekanikal yang melibatkan persamaan Schrödinger di mana Hamiltonian digantikan dengan suatu model berparameter. Parameter dalam model ini digunapakai untuk menghasilkan semula data rujukan yang diperoleh daripada data eksperimen. Kaedah pengikatan-ketat ini telah dilaporkan sebagai salah satu pendekatan utama untuk mengira jumlah tenaga sistem dan pengiraannya sangat cepat. Oleh itu ia biasa digunakan dalam pengiraan sistem yang besar, dengan lebih daripada ribuan atom dalam satu unit sel. Sumbangan utama penyelidikan ini ialah membina dua model pengikatan-ketat baharu untuk karbon yang berkaitan dengan pengiraan parameter dalam sistem Hamiltonian dengan menggunakan kaedah peminimuman. Tujuan dalam kajian ini ialah untuk menerapkan interpolasi polinomial dan polinomial cebis demi cebis sebagai fungsi penskalaan baru untuk model TB lama dan ditandakan masing-masing sebagai Model 1 and Model 2. Model-model baharu ini dibina berdasarkan pendekatan polinomial dan polinomial cebis demi cebis. Teknik matematik seperti masalah eigen, kaedah minimum, kaedah lelaran Newton dan prinsip asas kaedah separa empirikal juga digunakan dalam penyelidikan ini. Kaedah baharu ini mematuhi konsep pendekatan separa empirikal yang menganggap bahawa hanya satu elektron yang bebas bergerak di dalam keseluruhan sistem. Unsur-unsur matriks Hamiltonian yang bertindih di dalam Model 1 and Model 2 ini masing-masing dianggarkan oleh fungsi polinomial dan fungsi polinomial cebis demi cebis. Kedua-dua model baharu ini kemudiannya digunakan dalam sistem ikatan 2-karbon, 3-karbon, dan 4-karbon dengan kedudukan geometri yang tetap. Setiap parameter dikira dengan menggunakan kaedah lelaran Newton yang melibatkan juga pembezaan nilai eigen dalam sistem eigen. Tenaga dari ikatan kemudiannya dibandingkan dengan data rujukan daripada kaedah penyelidikan terdahulu yang telah mantap. Kedua-dua model baharu ini telah berjaya mengurangkan pelaksanaan masa pengiraan dengan mengurangkan operasi titik terapung per saat (FLOPS) dalam algoritma tersebut. Hasil daripada Model 1 dan Model 2 telah dibandingkan di mana untuk simulasi 2-karbon, ralat kesilapan mutlak kedua-dua model ini tidak berubah. Bagi simulasi 3-karbon, ralat kesilapan mutlak telah dikurangkan sebanyak 0.000006. Manakala, untuk simulasi 4-karbon, ralat kesilapan mutlak telah dikurangkan sebanyak 0.116213. Didapati bahawa kecekapan model baharu ini telah meningkat dengan ketara daripada Model 1 ke Model 2 apabila jumlah atom bertambah. Keputusan ini mencadangkan bahawa Model 2 lebih sesuai untuk pengiraan molekul yang lebih besar kerana kelebihan sifat polinomial cebis demi cebisnya. Kebanyakan keputusan yang diperoleh memberikan maklum balas positif kecuali beberapa pengiraan telah memberikan penyelesaian keputusan yang remeh. Kesepakatan yang baik dengan pengumpulan data menunjukkan bahawa model yang dicadangkan ini dapat digunakan sebagai penyelesaian alternatif kepada model yang sedia ada dan penting untuk kemajuan pengetahuan baharu.

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| | | |
|---|---|---|
| AO | - | Atomic Orbitals |
| CC | - | Coupled Cluster |
| CI | - | Configuration Interaction |
| CNDO | - | Complete Neglect of Differential Overlap |
| CNT | - | Carbon Nanotube |
| DFT | - | Density Functional Theory |
| FLOPS | - | Floating point operations per second |
| HF | - | Hartree-Fock |
| GTO | - | Gaussian Type Orbitals |
| INDO | - | Intermediate Neglect of Differential Overlap |
| LCAO | - | Linear Combination of Atomic Orbital |
| MD | - | Molecular Dynamics |
| MM | - | Molecular Mechanics |
| MO | - | Molecular Orbitals |
| MOPAC | - | Molecular Orbital PACkage |
| MPn | - | Møller-Plesset Perturbation |
| NDDO | - | Neglect of Diatomic Differential Overlap |
| QM | - | Quantum Mechanics |
| QMC | - | Quantum Monte Carlo |
| SCF | - | Self-Consistent Field |
| SK | - | Slater-Koster |
| STO | - | Slater Type Orbitals |
| TB | - | Tight-Binding |
| 1CA | - | One-center Approximation |
| 2CA | - | Two-center Approximation |
| 3CA | - | Three-center Approximation |

## LIST OF SYMBOLS

| | | |
|---|---|---|
| $\vec{a}$ | - | Vector of parameter to be fitted |
| $a_B$ | - | Bohr radius |
| $a_i$ | - | Coefficients of polynomial, $i = 1,\ldots,n$ |
| $\vec{a}^0$ | - | Initial values of $\vec{a}$ |
| $A_{p,q}$ | - | $p \times q$ matrix for minimization |
| $\vec{b}$ | - | Vector *b* for minimization |
| $c$ | - | Constant for LCAO wave functions |
| $e$ | - | Electron's charge |
| $\varepsilon$ | - | Energy of system |
| $\varepsilon_{\vec{k}}$ | - | Energy bands |
| $\varepsilon_v$ | - | Eigenenergy or eigenvalue at state $v = 1,2,3\ldots$ |
| $\varepsilon_K$ | - | Eigenvalues at state $K$ |
| $E_0$ | - | Ground state energy |
| $E_e$ | - | Born-Oppenheimer's energy of electrons |
| $E_K(\vec{a})$ | - | Eigenvalues from polynomial TB secular equation at state $K$ |
| $E_p$ | - | On-site energy for *s* orbital |
| $E_s$ | - | On-site energy for *p* orbital |
| $E_{tot}$ | - | Total energy of a system |
| $f_I$ | - | Force acting on ion $I$ |
| $g_K$ | - | Weight functions |
| $\hbar$ | - | Planck's constant |
| $\vec{h}$ | - | Changes of $\vec{a}$ |
| $h_{pq}$ | - | Hopping elements in Hamiltonian matrix |

| | | |
|---|---|---|
| $H$ | - | Hamiltonian operator or Hamiltonian matrix |
| $\hat{H}$ | - | Hamiltonian operator for either many particles or a single particle |
| $\hat{H}_e$ | - | Born-Oppenheimer's Hamiltonian operator of electrons |
| $\hat{H}_{TB}$ | - | TB Hamiltonian matrix |
| $i, j$ | - | Integers |
| $\vec{k}$ | - | *k*-points |
| $K$ | - | Index of both $\vec{k}$ and $\alpha$ |
| $l$ | - | Orbitals quantum number |
| $m$ | - | Magnetic quantum number |
| $m_e$ | - | Mass of the electron |
| $n$ | - | Principle quantum number |
| $N$ | - | No. of atoms |
| $r_a$ | - | Start-point of piecewise polynomial function |
| $r_b$ | - | Continuous-point of piecewise polynomial function |
| $r_c$ | - | End-point of piecewise polynomial function |
| $r_i$ | - | Location of electron at $i$ atom |
| $r_m$, $d_m$ | - | Cut-off distance |
| $p_n(r)$ | - | Polynomial functions |
| $R_I$ | - | Location of nuclei at $I$ atom |
| $R_{nl}(r)$ | - | Radial functions |
| $s, p, d, f$ | - | Angular-momentum states (atomic orbitals) |
| $s(r)$ | - | Scaling function |
| $S_{pq}$ | - | Overlapping elements in Hamiltonian matrix |
| $S_p(r)$ | - | Piecewise polynomial functions |
| $\hat{T}_e$ | - | Kinetic energy operator of electrons |

| | | |
|---|---|---|
| $\hat{T}_N$ | - | Kinetic energy operator of nuclei |
| $\hat{V}_{ee}$ | - | Electron-electron Coulomb interaction potential |
| $\hat{V}_{eN}$ | - | Electron-nucleus Coulomb interaction potential |
| $\hat{V}_{NN}$ | - | Nucleus-nucleus Coulomb interaction potential |
| $V_{pp\sigma}$ | - | TB parameter for *p*-*p* $\sigma$-bonds |
| $V_{pp\pi}$ | - | TB parameter for *p*-*p* $\pi$-bonds |
| $V_{sp\sigma}$ | - | TB parameter for *s*-*p* $\sigma$-bonds |
| $V_{ss\sigma}$ | - | TB parameter for *s*-*s* $\sigma$-bonds |
| $Y_{lm}(\theta,\phi)$ | - | Spherical harmonic functions |
| $\frac{\partial}{\partial a_n} E_K(\vec{a}^0)$ | - | Differentiation of eigenvalues with respect to $a_n$, $n = 1,2,3,\ldots.$ |
| $\alpha, \beta$ | - | Band indices for atomic orbitals |
| $\phi(r_{i,j})$ | - | Pairwise potential between atoms *i* and *j* |
| $\phi_\alpha(r,\theta,\phi)$ | - | Single-electron wave functions with atomic orbital $\alpha$ |
| $\psi_0$ | - | Ground states wave functions |
| $\psi_i(r)$ | - | Independent particle wave function of "orbital" where $i = 1,\ldots,N_{states}$ |
| $\psi_{\vec{k},\alpha}(\vec{r})$ | - | Bloch's sums wave function in periodic boundary condition |
| $\psi_v$ | - | Eigenvector of state $v = 1,2,3\ldots$ |
| $\langle\psi_i \mid \psi_i\rangle$ | - | Symbol of "bra-ket" |
| $\Psi$ | - | Many-body electronic wave functions |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of the Problem

Over the years, there are variety of interatomic potentials with different functional forms have been proposed for different purposes in molecular modelling. There are three types of main approaches that are frequently used in material science: *ab-initio*, semi-empirical and empirical approaches. Those approaches are successfully described the electronic properties in computational physics and chemistry which is highly demand in materials science. *Ab-initio* is first-principles approach which has high accuracy in energy evaluation. Density functional theory (DFT) is one of the well-known approaches that based on *ab-initio* method that kinetic potential, electrostatics or hartree potential, external potential and exchange-correlation potential are considered in the molecular interatomic calculations. Semi-empirical approaches are formulated normally based on *ab-initio* approach but some smaller integrals are neglected to speed up the calculations. So, semi-empirical approaches are designed for solving larger molecular system. Tight-binding (TB) model is one of the semi-empirical approaches that its parameters of Hamiltonian matrix are fitted by empirical results (experimental results or from first-principles approach). TB model has been used to describe the electronic band structure and electronic density of a system in quantum mechanical way. A parameterization scheme was proposed by Slater and Koster (1954) to illustrate frameworks that show how semi-empirical parameters fitting approach can be done by first-principles approximation. In 1992, Xu *et al* had introduced an analytical TB model with a scaling function in the Hamiltonian matrix of carbon element by using parameter fitting approach.

The above-mentioned approaches have intensively used in nano-based research activities, especially in science and engineering. The most popular carbon-based materials in recent research are carbon-nanotubes (CNTs) and graphene. Carbon-nanotube (CNTs) was discovered by Iijima in 1991. This material has mechanical properties like small size, low density, high stiffness and high strength. Published works related to carbon-nanotube research have been rapidly increased in rate of publication. It has influenced and improved the nano-science development over the years. For example, Bethune *et al*. (1993) described a single atomic layer wall carbon nanotube, Cornwell *et al.* (1997) and *Walter et al*. (1999) investigated the elastic strength properties of a single-walled carbon nanotube. Halicioglu (1998) had presented stress calculation on carbon nanotubes, Krishnan *et al.* (1998), Yao *et al* (1998) and Loujrie *et al.* (1998) introduced the calculation of Young's modulus of single-wall nanotube, Liew *et al.* (2004a, b; 2005a, b) interested in finding the elastic of the plastic properties, nano-mechanics, thermal stability, and buckling properties of multi-walled carbon nanotube, Mao *et al.* (1999) applied MD simulations on decorating of carbon nanotube, Yakobson *et al.* (1997) illustrated a high strain rate fracture in carbon nanotube, Wildoer *et al.* (1998) investigated the electronic structure of carbon nanotube structures, Van *et al.* (2000) introduced an *ab-initio* study on the elastic properties of single-walled carbon nanotube and graphene, Reich *et al*. (2002) had published a full description of TB approach on graphene study. Ban (2001) and Yang *et al*. (2008) had introduced the way to simulate and apply TB potential of hydrocarbon.

There are also some new research works related to carbon research within recent years such as Heeg *et al.* (2018) described about the properties of long linear carbon chains encapsulated inside the double-walled carbon nanotubes, Titus *et al.* (2015) has presented a detailed normal model analysis of suspended carbon nanotubes based on a non-orthogonal tight-binding formalism, Lu *et al.* (2015) has presented a three-center tight-binding potential model for carbon and silicon, Choi *et al.* (2010) investigated the effects of strain on electronic properties of graphene by using first-principles calculations, Andrade *et al.* (2015) investigated the linear carbon chain under high pressure conditions which encapsulated inside multi-walled nanotubes, Xu *et al.* (2014) investigated the two dimensional Dirac carbon allotropes from graphene by using the first-principles calculations, and Rezania (2015)

conducted an investigation on electronic properties of disordered zigzag carbon nanotubes by adding random on-site energy term to the tight binding model Hamiltonian in the system. All the above findings are interesting and implied that the importance of carbon in nano-technology research.

Hence, this research is conducted to model a new tight-binding (TB) approximation model regarding to carbon element as an extension research based on Yeak's PhD thesis (Yeak, 2007). Yeak has introduced a multiscale model in the implementation of coupling the three main approaches: molecular dynamic (MD), tight-binding (TB) method and density functional theory (DFT), which focused on carbon-nanotube (CNTs) study.

Molecular dynamics (MD) theory is most used particle method in scientific and engineering fields. Molecular dynamics can simulate a system of up to 100 million atoms with today's computational power. Unfortunately, molecular dynamics does not calculate the electron distribution. The forces acting on each atom are determined by a potential function which is determined from either empirical knowledge, or from *ab-initio* computations. Hence, any deformation of materials resulting in bond breaking is not accurately expressed by MD. In order to solve such problems, more robust and detail techniques such as tight-binding (TB) and density functional theory (DFT) are required to determine the electronic structure and electronic density of each atom.

It is generally acknowledged that DFT method is quite an accurate computational method to solve the potential energy of molecular structure. Unfortunately, it is too expensive to solve a large system. The limitation of this model is it can only solve for a system which from a few ten of atoms up to few hundred of atoms since it is the first-principles approach (*ab-initio*) of quantum mechanics. Nevertheless, this *ab-initio* approach provides a high level of accuracy in the energy simulation of system. TB method has the advantage of being quantum mechanical as well as being computationally efficient when compared with the DFT. But, the TB method is more expensive than the MD method due to the calculation of the complete eigensystem of all valence electrons in a cell. In fact, the matrix diagonalization as well as the calculation of atomic forces based on the Hellman-

Feynman theorem requires extensive computational effort (Yeak, 2007). But, with the help of better computer in recent years, the computational time can be reduced and be more efficient. However, the modelling of complex quantum mechanical systems is still an overwhelming challenge. We have sophisticated first-principles methods (DFT) for simulating reactions and electronic properties with high accuracy but these are limited to compute only small amount of molecules. Therefore significant progress is being made in the development of quantum mechanical approaches applicable to large systems. Hence, TB model is implemented in this work due to the range of the computational mechanical methodology (semi-empirical), accuracy and cost.

In this research, we are interested and focused on tight-binding model parameter fitting in carbon molecular simulation. Xu *et al*. (1992) had successfully introduced an analytical model with scaling function $s(r)$ in the Hamiltonian matrix elements to describe the TB potential of carbon. Xu's model is widely used by other researchers. But, the scaling function used in the model is too sophisticated. The amount of parameters used is large. It may slow down the computational time although with today's computer. In order to improve the model and apply it into the carbon-based system, a new tight-binding approximation is desirable. The basic idea behind the new model is to introduce and replace a new scaling function by piecewise polynomial function in the Hamiltonian matrix of the model. This challenge is to reproduce the same energy from the reference data seamlessly (accurately and efficiently) through the new parameters fitting frameworks.

## 1.2 Statement of the Problem

In 1954, Slater and Koster had contributed their idea in periodic potential problem based on a simplified linear combination of atomic orbital (LCAO) method. The investigation is widely accepted as a fundamental source or reference to the semi-empirical development in materials science to describe the potential behavior of a system. The tight-binding (TB) method is one of the semi-empirical methods that successfully utilized the performance of electronic potential of materials based on this Slater-Koster (SK) scheme. The main advantage of the TB method is its fast computational speed due to the use of minimal basis set and parameterized Hamiltonian and overlap matrices if compare to other semi-empirical methods. However, the transferability of the TB parameterization has been the key bottleneck in the applications of the TB method. Xu *et al.* (1992) had successfully introduced an analytical scaling function, $s(r)$ (Eq. (1.1)) for the SK Hamiltonian matrix elements to describe the TB potential of carbon. This model is commonly implemented and used to calculate properties of various carbon structures such as graphene, diamond, carbon-nanotube (CNTs) and so on.

$$s(r) = \left(\frac{r_0}{r}\right)^n \exp\left\{n\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right]\right\}, \tag{1.1}$$

$$\phi(r) = \phi_0\left(\frac{d_0}{r}\right)^m \exp\left\{m\left[-\left(\frac{r}{d_c}\right)^{m_c} + \left(\frac{d_0}{d_c}\right)^{m_c}\right]\right\}. \tag{1.2}$$

Those parameters $\phi_0$, $m$, $m_c$, $d_0$, $d_c$, $n$, $n_c$, $r_c$ and $r_0$ need to be fitted. $\phi(r)$ is pairwise potential function in short-ranged potential energy. Please refer to Chapter 2, Section 2.4.2 for further description of this model.

However, Xu's model seems too sophisticated in the way that there were too many parameters need to be fitted, although TB model always classify as semi-empirical approach that parameters fitting procedure is essentially important to the simulation. A large number of parameters in a system may describe the system more accurately or more closely to its nature but consequently it also make the

computational time heavier and expensive. In Xu's model, the number of floating point operations per second (FLOPS) in the calculation of the scaling function $s(r)$ is in quite high ($\geq 12$ FLOPS, it depends on the values $n$ and $n_c$ in the Eq. (1.1)). If the values of $n$ and $n_c$ increased, the FLOPS eventually will be increased relatively. The more FLOPS in the system or algorithms, the longer the computational time will take. Are there any possibilities that the disadvantages of this model can be improved? If yes, how this can be done? Some questions need to be answered.

To answer these questions on this matter, we decide to replace the model with new scaling functions $s(r)$ that can provide less parameter, simple, and easy to understand. After some discussions have been made, implementation of piecewise polynomial to the model seems more mathematically reasonable to describe the potential behavior due to its flexibility properties of the functions. Another reason is that a simple polynomial will reduce the FLOPS of the calculations and it is implied that the computational time can be reduced simultaneously. This idea can be done by modeling a new TB model with new Hamiltonian matrix with piecewise polynomial. To carry out the fitting procedures, some works may have to be done such as solve the eigenvalues problem, differential eigenvalues problem, minimization of the parameters by using Newton method, force and energy calculation and so on. Now, new question arises: Is this model better or worse? How about its efficiency? What is the difference between this model and the previous version? Well, we leave this question to final chapter in the discussion section.

## 1.3 Objective of the Research

The objectives are identified and can be summarized as:

i) To develop a new tight-binding (TB) Hamiltonian matrix with polynomial scaling functions.

ii) To implement the polynomial tight-binding (TB) model in two-carbon, three-carbon and four-carbon bond simulations. To compare the results with Xu' model generated by DFT.

iii) To develop a new tight-binding (TB) Hamiltonian matrix with piecewise polynomial scaling functions.

iv) To implement the piecewise polynomial tight-binding (TB) model in two-carbon, three-carbon and four-carbon bond simulations. To compare the results with Xu' model generated by DFT.

## 1.4 Significance of the Research

This work demonstrates an effective way to construct a new TB model by new concepts. It is significant for nano-sized materials study. New theory, new concepts, new technologies, new findings and new products can be developed. This model can be an alternative choice for nano-science study such as nano-material simulations and electronic structure study. Products fabricated from nanosize materials have gained much importance in recent years, especially carbon based nano-materials like graphene layer, nanotube, nano-fibre, nano-gear, and so on. Therefore, research associated with carbon has been dramatically important in this nano-teach development. This new model helps to improve the old model in calculating the energy in different perspectives. It also provides a faster (less FLOPS and less memory) model in the computational calculation in this field. This new

model also can be applied into different materials once we know the configuration of the substance.

## 1.5 Scope of the Research

In this work, the attention is focused on parameters fitting of carbon bond based on tight-binding (TB) approximation. The polynomial and piecewise polynomial functions are applied into the Hamiltonian matrix for generalization and parameterization purposes. The new models with associate independent variables or parameters based on approximation concept are proposed for energy calculations with computational algorithm. The factors such as degree of freedom of independent variables of the polynomials, accuracy of data collection and flexibility of fitting techniques will be reviewed and monitored. The minimization of the energy is based on the geometry properties of the atoms, generalization of Hamiltonian matrix, eigenvalues problem and differentiation of eigenvalues problem in the eigen-system. The algorithms of parameters fitting are emphasized with some rules of minimization method.

## 1.6 Organization of the Thesis

The layout of the thesis is concluded as follows:

In Chapter 1, the background of study is introduced. It highlights the reasons and objectives of this study to be conducted. The concepts, methodologies and scope are also briefly discussed. The new TB model is constructed to propose and introduce a new approach to reproduce the energy of carbon bond through the parameterized tight-binding fitting.

Chapter 2 covers the literature reviews and explores some previous research of published works and findings which related to the study. Three important

approaches in computational science material and electronic structure are also briefly introduced. Discussions on semi-empirical approach and some existing well-established semi-empirical methods are reviewed. A brief outline in TB approach is given and some papers related to carbon research are also reviewed. The source of data and important references are also briefly discussed.

Chapter 3 introduces the relevant mathematical formulation in molecular computation. The many-body Schrödinger equation in quantum mechanics is described which is simplified with the Born-Oppenheimer approximation. The method to reduce the many-body Schrödinger equation system to one-electron system semi-empirical TB method is reviewed. The mathematical formulation of TB model is also presented.

Chapter 4 provides the ideas of development and formulation to employ the new scaling function into the Hamiltonian matrix of TB model based on the basic principles of electronic structure, polynomial and piecewise polynomial concepts. The implementation of polynomial and piecewise polynomial into the new TB model to reproduce the predicted energies are presented. Parameters fitting procedures and algorithms are mathematically and theoretically derived.

In Chapter 5, the results and discussions are presented. The data are described in table and figure form for clarity purposes.

Lastly, the thesis is concluded with the summary of conclusions, contributions, limitation and recommendations for the future work in the last chapter.

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1. **Haa, W. K.,** & Yeak, S. H. (2017). Polynimial Fitting of Tight-Binding Method in Carbon. In *2017 AIP Conference Proceedings. Proceeding of the 4th International Conference on Mathematical Sciences (ICMS4)*( 1830, 020039-1-8). http://dx.doi.org/10.1063/1.4980902. **(Indexed by SCOPUS)**