A NEW HYDROCARBON EMPIRICAL POTENTIAL FOR MOLECULAR DYNAMICS SIMULATION

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A NEW HYDROCARBON EMPIRICAL POTENTIAL FOR MOLECULAR
DYNAMICS SIMULATION

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Special dedicated to

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ABSTRACT

Molecular dynamics utilize energy model to solve the Newton's equation of motion for a system of interacting particles. Ab-initio, semi-empirical and empirical approaches have been reported as main approaches to compute total energy of a system for describing its molecular structures and properties. In these approximation methods, the calculations achieved the level of accuracy in descending manner and in ascending order for computational time. Ab-initio approach also known as first principles method solved the complex energy evaluations in Schrödinger equation to account for electronic structures with limitation on the size of the system. Molecular mechanics (MM) is a conventional empirical approach that defined energy calculations in terms of functions with fitted parameters. The simple algorithm in MM allowed it to simulate larger system. Consequently, new potential function is always required either to produce higher accuracy result or to reduce the computational time. It is believed that there should be a compromise between the accuracy and the computational time depending on the simulation. The main contribution of this study is to propose a new hydrocarbon potential energy model which consist of bond stretching and angle bending function, where both functions are important components of short range potential for the force fields based on MM principle. The existing bond stretching and angle bending functions are found correlated to the piecewise polynomial concept. New models were then proposed based on piecewise polynomial concept and basic principles. Firstly, by neglecting the motion of electrons for fast computation purpose. Secondly, only the necessity independent variables are involved. Thirdly, structural properties such as symmetry and degeneracy are considered. In this regard, the interatomic distance was determined as the independent variable in bond stretching model since single independent variable is assumed sufficient in reproducing the chemical reaction for one motion involvement. Angle was selected as independent variable when the interactions were treated as a plane with triangle shape. However, there is more than one motion involvement in angle bending model, thus, the deviation for angle is also considered as independent variable. The selection rules were developed and independent variables were coupled with the interatomic distance to account for structural properties. Hence, the angle bending model is developed based on the triangle and selection rules. The parameters were estimated by using least square method. The proposed model was then compared with data collected from two well-established methods and applied to the carbon nanotube application for validation. Most of the results obtained achieved a good agreement except for carbon nanotube application where the discussions were given. Good agreement with data collection indicates that proposed models can be alternative solution to the existing force fields. The results are significant for advancement of new knowledge.

ABSTRAK

Dinamik molekul menggunakan model tenaga untuk menyelesaikan persamaan pergerakan Newton untuk sistem zarah yang berinteraksi. Ab-initio, semi-empirikal dan empirikal telah dilaporkan sebagai pendekatan utama untuk mengira jumlah sistem tenaga demi menggambarkan struktur dan sifat molekulnya. Dalam kaedah penghampiran ini, pengiraan mencapai tahap ketepatan mengikut tertib menurun dan masa pengiraan dalam urutan menaik. Pendekatan ab-initio juga dikenali sebagai kaedah prinsip pertama menyelesaikan penilaian tenaga yang rumit dalam persamaan Schrödinger yang mengambilkira struktur elektronik yang terhad pada saiz sistem. Mekanik molekul (MM) adalah pendekatan empirikal konvensional yang mendefinasi pengiraan tenaga sebagai fungsi parameter suaian. Algoritma yang mudah dalam MM membenarkan simulasi sistem yang lebih besar. Akibatnya, rekaan potensi baharu diperlukan sama ada untuk menghasilkan ketepatan yang lebih tinggi atau untuk mengurangkan masa pengiraan. Adalah dipercayai bahawa mesti ada tolak ansur antara ketepatan dan masa pengiraan yang bergantung pada simulasi. Sumbangan utama kajian ini adalah untuk mencadangkan model tenaga hidrokarbon baharu yang terdiri daripada fungsi regangan ikatan dan sudut lenturan, di mana kedua-dua fungsi adalah komponen penting bagi potensi berjarak pendek untuk medan daya berdasarkan prinsip MM. Fungsi ikatan regangan dan sudut lenturan didapati berkorelasi dengan konsep polinomial cebis demi cebis. Model baharu ini dicadangkan berdasarkan konsep polinomial cebis demi cebis dan prinsip-prinsip asas. Pertama, mengabaikan pergerakan elektron untuk tujuan kelajuan pengiraan. Kedua, melibatkan hanya pembolehubah bebas yang berkaitan. Ketiga, sifat-sifat struktur seperti simetri dan degenerasi dipertimbangkan. Dalam hal ini, jarak antara dua atom ditentukan sebagai pembolehubah bebas dalam model ikatan regangan kerana pembolehubah bebas tunggal diandaikan mampu untuk menghasilkan reaksi kimia bagi satu penglibatan gerakan. Sudut dipilih sebagai pembolehubah bebas apabila interaksi antaranya dianggap sebagai satah berbentuk segitiga. Walau bagaimanapun, terdapat lebih daripada satu penglibatan gerakan dalam model lenturan sudut, oleh itu, sudut sisihan juga dipertimbangkan sebagai pembolehubah bebas. Peraturan pemilihan telah dibangunkan dan pembolehubah bebas digandingkan pula dengan jarak antara dua atom untuk menangani sifat-sifat struktur. Oleh itu, model lenturan sudut dibangunkan berdasarkan peraturan segi tiga dan pemilihan. Parameter tersebut dianggarkan dengan menggunakan kaedah kuasa dua terkecil. Model yang dicadangkan dibandingkan dengan data yang dikumpul dari dua kaedah yang mantap dan digunakan untuk aplikasi tiub nano karbon untuk pengesahan. Kebanyakan hasil diperoleh dicapai dengan baik kecuali untuk aplikasi tiub nano karbon di mana perbincangan telah diberikan. Persetujuan yang baik dengan data yang dikumpul menunjukkan bahawa model yang dicadangkan boleh menjadi penyelesaian alternatif kepada medan daya yang wujud. Hasil kajian ini adalah penting untuk kemajuan pengetahuan baharu.

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LIST OF SYMBOLS

a	-	Second derivative of position with respect to time or acceleration
b	-	Third derivative of position with respect to time or the rate of change of acceleration
C	-	Cubic spline interpolant
$C(x)$	-	Cubic polynomial
d	-	Number of degree
E	-	Energy
e	-	Charge of the electrons
F	-	Universal functional
$F(x)$	-	Force function for a particle that located at coordinate x
f	-	Function
$G(\cos(\theta_{ijk}))$	-	Fifth-order polynomial
$\mathbf{g}$	-	Generalized derivative of variable vector
$H(x_{ik})$	-	Switching function
$H(x_{jl})$	-	Switching function
I	-	Integer
i	-	Integer
J	-	Integer
j	-	Integer
K	-	Integer
k	-	Integer
M	-	Total nuclei in a system
m	-	Integer

N	-	Total electrons in a system
n	-	Integer
p	-	Number of piecewise
Q	-	Repulsion parameter
$Q(N_i^t)$	-	Switching function for revised angular function
R	-	Distance between two particles or position, where particles are nuclei
$\mathbf{R}$	-	Position vector
r	-	Distance between two particles or position, where particles could be atoms or electrons.
$\mathbf{r}$	-	Position vector
S	-	Piecewise polynomial with least square approach
T	-	Kinetic energy of the electron
t	-	Time
$U(x)$	-	Potential energy function for a particle that located at coordinate x
v	-	First derivative of position with respect to time or velocity
W	-	Work done
$\mathbf{w}$	-	Variable vector
Z	-	Charge of the nuclei
a^C	-	Corrector for acceleration
a^P	-	Predictor for acceleration
b^C	-	Corrector for the rate of change of acceleration
b^P	-	Predictor for the rate of change of acceleration
E^{bend}	-	Energy calculation for angle bending interactions
E^{LJ}	-	Lennard-Jones 6-12 interaction function (non-bonded repulsion interactions)
$E^{non-bonded}$	-	Energy calculated for non-bonded interactions between atoms or groups
$E^{stretch}$	-	Energy calculation for bond stretching interactions

$E^{torsion}$	-	Energy calculation for torsional motion around single bonds interactions
E^{REBO}	-	REBO potential
k^{LJ}	-	Lennard-Jones coefficient
m^{LJ}	-	The sixth-power term in Lennard-Jones 6-12 interaction function
n^{LJ}	-	The twelfth-power term in Lennard-Jones 6-12 interaction function
r^{C}	-	Corrector for position
r^{P}	-	Predictor for position
v^{C}	-	Corrector for velocity
v^{P}	-	Predictor for velocity
V^{R}	-	Repulsion pair interaction
V^{A}	-	Attraction pair interaction
a_n	-	n-th fitting parameter
B_E	-	Bond Stretching Model (BSM) for approximating energy calculation
B_F	-	Bond Stretching Model (BSM) for approximating force calculation
B_n	-	Attraction parameters
b_{ij}	-	Bond order between atoms i and j
C_E	-	Penalty function for energy model
C_F	-	Penalty function for force model
$C_i(x_i)$	-	Cubic i-th piecewise polynomial
c_i	-	i-th coefficient
c_s	-	Coefficients for strain energy
c_{-1}	-	Coefficients for strain energy from previous step
c_{-2}	-	Coefficients for strain energy from two previous steps
D_c	-	Directive coefficient
D_e	-	Dissociation energy

E_b	-	Chemical binding energy in the Abell-Tersoff formalism
E_{DFT}	-	Total energy functional of the density
E_{EE}	-	Electron-electron repulsive energy
E_{elec}	-	Electronic energy
E_I	-	Energy for I-th data set
E_{II}	-	Classical interaction of nuclei with one another
$E_{M=0}$	-	First version of Angle Bending Model (ABM)
$E_{M=1}$	-	Equilateral model, part of second version of Angle Bending Model (ABM)
$E_{M=2}$	-	Isosceles model, part of second version of Angle Bending Model (ABM)
$E_{M=3}$	-	Scalene model, part of second version of Angle Bending Model (ABM)
E_{NE}	-	Nuclear-electron attraction energy
E_{NN}	-	Nuclear repulsion energy
E_s	-	Strain energy
E_{total}	-	Total energy
E_{XC}	-	Exchange-correlation energy
E_0	-	Ground state energy
E_{-1}	-	Previous stage strain energy
E_{-2}	-	Previous two stage strain energy
E_υ	-	A υ-representable energy functional
e_{ik}	-	Residuals for each piecewise polynomial of i-th observation based on k-th piecewise
e_{jik}	-	Unit vectors in the perpendicular direction to the planes jik
e_{ijl}	-	Unit vectors in the perpendicular direction to the plane ijl
F_I	-	Force for I-th data set

F_i	-	Force acting on i-th dynamics particle
$F_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right)$	-	Tricubic spline
f_i	-	Thomas-Fermi function
G_I	-	Molecular geometry for I-th data set
g_j	-	Derivative of j-th variable
k_f	-	Force constants
k_i	-	i-th function for Runge-Kutta integration
k_j	-	j-th coefficients for special case of polynomial function
m_e	-	Mass of electron
m_n	-	Mass of nucleus
m_i	-	Mass of i-th dynamics particle
$P_{ij}\left(N_i^C, N_i^H\right)$	-	Bicubic spline
P_m	-	m-th piecewise polynomial
P_m'	-	Differentiation form of piecewise polynomial
r_c	-	Cut-off points
r_e	-	Interatomic distance at equilibrium state
r_i	-	Position of i-th dynamics particle
r_{ij}	-	Interatomic distances between atoms i and j
r_{jk}	-	Interatomic distances between atoms j and k
r_{ki}	-	Interatomic distances between atoms k and i
r_{ij}'	-	Differentiation forms for interatomic distance with respect to the position of each atom
r_{LN}	-	Largest interatomic distance who is neighbour with θ_L
r_N	-	Interatomic distance that is neighbour to θ_L
T_a	-	Total atoms in a system
T_b	-	Number of building blocks that bundled as a group

$T_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right)$	-	Tricubic spline
T_p	-	Total interacting particles in a system
V_{EE}	-	Electron-electron repulsive energy
V_{eff}	-	Effective potential
V_{NE}	-	Nuclear-electron attraction energy
V_{XC}	-	Exchange-correlation potential
v_i	-	Velocity of i-th particle
w_j	-	j-th variable
x_i	-	Coordinate of i-th particle located on at x-axis
x_{ijk}	-	j-th independent variable for i-th observation based on k-th piecewise of the polynomial
x_j	-	Coordinate of j-th particle located on at x-axis
x_k	-	Coordinate of k-th particle located on at x-axis
x_n	-	n-th nodes
y_i	-	Coordinate of i-th particle located on at y-axis
y_{ik}	-	The dependent variable of i-th observation based on k-th piecewise
y_j	-	Coordinate of j-th particle located on at y-axis
y_k	-	Coordinate of k-th particle located on at y-axis
z_i	-	Coordinate of i-th particle located on at z-axis
z_j	-	Coordinate of j-th particle located on at z-axis
z_k	-	Coordinate of k-th particle located on at z-axis
b_{ij}^{DH}	-	bond order function account for the dihedral angle of carbon-carbon double bonds
b_{ij}^{RC}	-	influence towards the bond energy between bonding atoms i and j due to the possible presence of radical character and π bond conjugations
$b_{ij}^{\sigma-\pi}$	-	Bond orders depend on the local coordination and bond angles between bonding atoms i and j

$b_{ji}^{\ \sigma-\pi}$	-	Bond orders depend on the local coordination and bond angles between bonding atoms j and i
$D_{ij}^{\ min}$	-	Cut-off points of switching function
$D_{ij}^{\ max}$	-	Cut-off points of switching function
E_X^{Becke}	-	Energy contribution from Becke exchange functional
E_{XC}^{B3LYP}	-	Energy contribution from B3LYP
E_X^{HF}	-	Energy contribution from Hartree-Fock exchange functional
E_X^{LSDA}	-	Energy contribution from Local Spin Density Approximation exchange functional
E_C^{LYP}	-	Energy contribution from Lee-Yang-Parr correlation functional
E_C^{VWN}	-	Energy contribution from Vosko-Wilk-Nusair correlation functional
$f_{ij}^{\ c}$	-	Switching function for pairwise interactions
$f_{ik}^{\ c}$	-	Switching function
$f_{il}^{\ c}$	-	Switching function
$f_{jl}^{\ c}$	-	Switching function
$g_C(\cos(\theta_{ijk}))$	-	Revised angular function
N_i^C	-	The numbers of nearest-neighbour carbon atoms for atom i
N_i^H	-	The numbers of nearest-neighbour hydrogen atoms for atom i
N_i^t	-	Total number of neighbours of bonded atoms i
N_{ij}^{conj}	-	A local measure of conjugation in the bonding atom i and j
$\hat{F}$	-	Summation of kinetic energy operator and electron-electron interaction potentials operator
$\hat{H}$	-	Hamiltonian operator
$\hat{T}$	-	Kinetic energy operator for the electrons

$\hat{H}_{elec}$	-	Electronic Hamiltonian operator
$\hat{V}_{EE}$	-	Electron-electron interaction potentials operator
$\hat{V}_{ext}$	-	External potential operator acting on the electrons due to nuclei
$\hat{V}_{NE}$	-	Electron-nuclei interaction potentials operator
$\vec{r}$	-	Vector that connecting the atoms
α	-	Repulsion parameter
β_n	-	Attraction parameters
Δa	-	Small change in acceleration
Δr	-	Change in position
Δr_N	-	Change in interatomic distance that is neighbour to θ_L
ΔT	-	Correction to the kinetic energy
Δt	-	Small change in time
$\Delta \theta_N$	-	Change in angle who is neighbour with θ_L
$\Delta U(x)$	-	Small change in potential energy function for a particle that located at coordinate x
ΔV_{EE}	-	Correction to the electron-electron repulsion energy
Δx	-	Small change in coordinate x
δE	-	Change in the energy
$\delta \rho$	-	small change in the true density
$d\boldsymbol{\tau}$	-	Volume element appropriate to the coordinate system
χ	-	System dependent parameter
ε	-	System dependent parameter
γ	-	Weighting parameter
μ	-	Lagrange multipliers
ψ	-	Wavefunction
ρ	-	Density
$\hbar$	-	Reduced Planck's constant, Planck's constant over 2π
θ_{ijk}	-	Angle of the bonds between atoms i and j and atoms j and k

θ_{jki}	-	Angle of the bonds between atoms j and k and atoms k and i
θ_{kij}	-	Angle of the bonds between atoms k and i and atoms i and j
θ_L	-	Largest angle in system with triangle structure
Θ_{ijkl}	-	Rotation angle around double bond
ε_{ik}	-	Positive residuals for each piecewise polynomial of i-th observation based on k-th piecewise
ε_0	-	Vacuum permittivity
ψ_0	-	Ground state wavefunction
ψ_{elec}	-	Electronic wavefunction
ρ_0	-	Density functional of the ground state energy
υ_{ext}	-	External potential

LIST OF ABBREVIATIONS

ABM	-	Angle Bending Model
AMBER	-	Assisted Model Building with Energy Refinement
BSM	-	Bond Stretching Model
B3LYP	-	Becke 3-parameters Exchange and Lee-Yang-Parr Correlation Hybrid Functional
CCH	-	One hydrogen and two carbon atoms interaction
CFF	-	Consistent Force Field
CH	-	Carbon-hydrogen bonding
CHARMM	-	Chemistry at HARvard Macromolecular Mechanics (Academic Version)
CHARMm	-	Chemistry at HARvard Macromolecular Mechanics (Commercial Version)
CHH	-	One carbon and two hydrogen atoms interaction
COSMIC	-	COmputation and Structure Manipulation In Chemistry
CVFF	-	Consistent – Valence Force field
DFT	-	Density Functional Theory
EFF	-	Empirical Force Field
ESFF	-	Extensible Systematic Force Field
HC	-	Hydrogen-carbon bonding
HHC	-	One carbon and two hydrogen atoms interaction
HCH	-	One carbon and two hydrogen atoms interaction
HF	-	Hartree-Fock
MD	-	Molecular Dynamics
MM	-	Molecular Mechanics
MMFF	-	Merck Molecular Force Field
MP	-	Møller-Plesset

MP4(SDQ)	-	Møller-Plesset Fourth Order Perturbation Theory with Single, Double and Quadruple Substitutions
OPLS	-	Optimized Potentials for Liquid Simulation
QM	-	Quantum Mechanics
REBO	-	Reactive Empirical Bond Order
UFF	-	Universal Force Field
Br_2	-	Bromine molecule
C_2	-	Carbon-carbon bonding
Cl_2	-	Chlorine molecule
F_2	-	Fluorine molecule
H_2	-	Hydrogen molecule
I_2	-	Iodine molecule
N_2	-	Nitrogen molecule
O_2	-	Oxygen molecule

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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter comprises of several sections. The first section introduces the main approaches for finding the potential energy and the basic principles of molecular mechanics approach for creating the functional forms that relevant to the research problem. In the subsequent sections, the problem statement, objectives, significance, and scope of this research are stated, respectively. Finally, the content is provided in the last section, organization of the thesis, for clarity purpose.

1.2 Background of the Problem

In molecular modelling, a wide variety of interatomic potentials in different functional form have been proposed for different intention over the years. These computational methods for finding the potential energy curve of molecular structures can be categorized into three main approaches, which are *ab-initio*, semi-empirical and empirical approaches. The word *ab-initio* is a Latin term means from the beginning or from first principles, thus, *ab-initio* approach also known as first principles theory. It takes Schrödinger equation as a starting point and solved the Schrödinger equation without the inclusion of empirical parameters in the equation (Yeak, 2006). Among the computational methods, the *ab-initio* approach able to

provide the highest level of accuracy in the energy evaluation. The variational principle and perturbation theory are two most notable methods used in the *ab-initio* approach to perform direct electronic structure calculations. However, the limitation of the *ab-initio* approach is size of the system. It just capable to solve the system comprising up to hundreds of atoms even facilitated it with the powerful computers. Even though semi-empirical approach is assigned for solving the larger molecular system, it is also high computing demands for most systems (Yeak et al, 2005; Yip, 2005). Hence, empirical approach is applied to model the system behavior which avoided quantum mechanics (QM) totally in the calculation (Young, 2001). The strengths and weaknesses for each approach have created critical breakthroughs into research area. Especially for *ab-initio* and empirical approaches, high accuracy and fast computational speed were concluded as two main characteristics for ones to select the proper interatomic potential for handling different problems. The former is critical for studying the electronic properties in computational chemistry and the latter is extremely demanding in materials science.

The simplification of energy system of molecular mechanics (MM) methods allows its utility in molecular dynamics (MD) simulation, where MD simulation required a large number of energy calculations. MD simulation is a computer simulation method for studying the atomics motions in a system. In principle, it is known that real materials shall behave according to the laws of quantum mechanics (QM), so that the electronic motions are included in the calculation. The simulation work in the classical mechanics ignore the electronic effects, ones might suspect that it is unable to validate with any real application. Born Oppenheimer approximation has diminished the skepticism by filling the gap between them. Hamiltonian in Schrödinger equation considered the motions of system contributes from two particles, that is nuclei and electrons. Born and Oppenheimer noticed that the mass of nuclei is much heavier than the mass of electrons, force is mass times acceleration, this indicates electron move at least 1000 times faster than nuclei. Therefore, in their approximation, they considered to separate the electronic part and nuclei part that this separation is approximately correct. Born Oppenheimer approximation treated nuclei are fixed with respect to electron interactions in the system, the electronic part can be solved at an accumulate set of fixed positions of the nuclei. Then, the nuclei

part can be solved by treated the electron in terms of an effective Hamiltonian with electronic energy. Solution for nuclei separation is indirectly equivalent to the MD, in which requires coordinates of atoms for calculating the energy system. This is an important remark that supports the diversity progress for the development of MD simulation using potential function of any force field approaches. Also, many force field methods have consistently increased in the progress of diversity, complexity, and sophistication over time.

One of the famous applications is the artificial products made by Carbon based nano-materials. NASA is still working on to turn science fiction concept into reality, which is to build an elevator to the Moon from Earth's surface (Artyukhov *et al*., 2013) by using Carbon based nano-materials. Hence, the time execution for energy calculation is extremely large. Empirical approach is able to handle system comprising up to a few millions of atoms (Yeak et al, 2005; Yip, 2005). The MM methods still widely extend and recommended today for use, especially for work before or after fabricated the nano-products, and for studying in planetary science. The similarity for both phenomena is treating an extraordinary large system, and thus, a simpler form of energy calculation for solving larger system is always required.

As mentioned before, any conventional molecular mechanics (MM) method in the empirical approach is an approximation solution that returns less accurate results, but yet, it is still a preferable option for solving the large system. The energy calculation in conventional MM methods can be subdivided into several functional forms with fitted parameters. Parameters of the potential were fitted accordingly to the experimental data in the calculation, so that the potential with parameters obtained able to approximate the experimental data. The basic principle of MM methods considered the energy calculation as the summation of bonded and non-bonded terms (Lewars, 2011). In fact, bonded and non-bonded terms also named as short range and long range potential in the different application fields. Both consist of several combinations of functional forms. The short range potential may comprises of 4 functional forms such as bond stretching, angle bending, dihedrals motion (improper or torsion dihedrals), and cross over terms of bond stretching,

angle bending and dihedrals motion. The long range potential may consist of the van der Waals, electrostatic and polarization interaction. Variety MM methods were categorized into three classes, where the first two classes only include the bonded terms in the calculation. The first class is called Class I or first-generation; no cross terms are involved this class and the rest of functional terms are able to be expressed in the form of quadratic Taylor series expansion or harmonic potential or polynomial with degree two. The second class is named as Class II or second-generation, it contains higher order in the Taylor series expansion or polynomial and the presence of cross terms in the potential function. Similarly, the third class is termed as Class III or third-generation which account for electronegativity, polarizability and hyperconjugation. Conventionally, classical force fields classified MM methods into either Class I or Class II (Schlick, 2010).

There are four significant factors that affect the performance in this procedure for construction of new potential. The complexity functional form of the energy expression is the first factor. The number of independent variables and the calculation for finding assigned independent variables in the functional forms are main concerns which affect the implementation for the complexity of the energy calculation. As a result, only essential independent variables are involved in the calculation. Second factor refers to the data selected to parameterize the constants. As mentioned earlier, an ideal situation for MM is to produce high accurate result whilst the time execution and complexity of potential function remain unchanged. The accuracy of the approximation solution is substantially depends on the accuracy of data collection. However, as discussed earlier, the *ab-initio* approach produced higher accuracy result for data collection due to it involved more independent variables in the calculation. Hence, there should have a compromise between the independent variables with the level of accuracy for the data selection. Thirdly, the fitting technique for parameters estimation, or more succinctly, the technique used to optimize constants from that data collection. Finally, ability of new potential to be applied in such a way that it show consistent with its strengths and weaknesses (Young, 2001).

In real situation and the limited resources, the experimental results are initially considered in averaging or ensemble amount as it is hard to probe the molecules especially for any unstable state. Therefore, molecular mechanics (MM) methods worked out by giving best description to the molecules that distorted from idealized geometry where molecules are initially distorted from stable state in order to study its behaviour near the equilibrium distance. Considered a ball attached to a fixed spring, Newton's third law states that whenever there is a force acted towards the ball, there exists an inner force in opposite direction which rebounces the ball back to the stable state (Leach, 2001). By treating particles like a ball attached to the spring, the ideal geometry or equilibrium distance separates the energy curve into two parts. The first part of energy curve illustrates the repulsion part, when a force is applied to the system in order to squeeze the particles uniformly, the particles tends to repulse each other in order to get back to the stable behaviour. The second part demonstrates the attraction part, when a force is enforced in the system to pull the particles away, the particles tends to attract each other in order to form the stable state. The repulsive and attractive forces are not uniform when same amount in increment of distance was applied (Hinchliffe, 2003). This implies that there must at least two different equations to distinguish these behaviors. Thus, piecewise polynomial (Davis, 1984) is found most suitable to capture this scenario.

Taking the affecting factors as considerations, in this thesis, piecewise polynomial is proposed to approximate the functional forms of bond stretching and angle bending, where only important independent variables are employed. The second-generation of reactive empirical bond order (REBO) potential energy (Brenner *et al.*, 2002) is used as the main source of data collection for the parameters estimation, since it showed some flexibilities to be recognized as empirical potentials for the first-generation (Brenner, 1990), and semi-empirical for the improvement version of second-generation (Brenner *et al.*, 2002) for studying hydrocarbon compounds. The level of accuracy for second-generation of REBO potential (Brenner *et al.*, 2002) is in the middle range, where it allows forming and breaking for covalent bonding with associated changes in atomic hybridization within a classical potential. It is a powerful method in modelling complex chemistry for large system by providing a better definition for bond lengths, energies, and force

constants of molecules, as well as interstitial defect energies, elastic properties, and surface energies for different arrangement of carbon system. In numerical methods, there are plenty of choices for parameters estimation. The least square approach is well known as the best fitting technique, since it only gives unique solution by searching the global minima in the whole optimization process for parameters. If local minima should be allowed for filling the interstitial causes by independent variables in the optimization process, other methods such as truncated Newton method is a good option. The new model with fitted parameter sets is used to reproduce the set of experimental data. In this work, general piecewise polynomial is employed as fundamental principle for building new models. Theoretical derivations for comparing general piecewise polynomial with the existing potential functions are presented. Some derivations were utilized as a theoretical evident for describing the generalization of the new model. The new function for bond stretching interaction is found able to contribute itself as an alternative method in computational chemistry softwares. The flexibilities and weaknesses for general piecewise polynomial are discussed.

1.3 Statement of the Problem

The development of force fields or potential function is always required either to obtain result at high accuracy or to reduce the computational cost for large system. The present work intends to produce the force fields based on molecular mechanics (MM) principle. Conventional force fields in MM ignored the electron motions and expressed the energy calculation as the combination from several contributions of functions with fitted parameters, where only necessary independent variables are considered. Mimic the concept from crystal structure in solid state physics, electrons were replaced by atoms in a building block (imagine a box). The building block could be an atom or groups of atoms in specific location (Kittel, 1996). Thus, when identical building blocks were added continuously, the system forms the crystal structure in a 3-dimensional periodic array of atoms. In present study, single atom was treated in a building block. The system is said with an assortment of T_a

building blocks indicates that there is a total of T_a atoms in a system. If T_b building blocks are bundled together as a group where T_a is divisible by T_b, then, the energy calculation also expressed as summation of $\dfrac{T_a}{T_b}$ functions of bundled group. The problem statements can be written as below:

1. What is the necessary independent variable best describe for the case if $\dfrac{T_a}{T_b} = 1$, $T_a = T_b$ and two building blocks $T_b = 2$ are bundled together as a group? The energy as well as their forces of individual atom for each contribution can be approximated by using the proposed model that based on piecewise polynomials concept? How good is this empirical potential function for approximating the chemical reaction and structural property?

2. What are the essential independent variables best describe for the case if $\dfrac{T_a}{T_b} = 1$, $T_a = T_b$ and three building blocks $T_b = 3$ are bundled together as a group? The energy as well as their forces of individual atom for each contribution can be approximated by using the new model that based on piecewise polynomials concept? How good is this new empirical potential function for approximating the chemical reaction and structural properties?

3. If $T_b = 3$ building blocks are bundled together as a group, is it possible to approximate larger system?

1.4 Objectives of the Research

The classical short range potential in conventional molecular mechanics (MM) methods considered bond stretching, angle bending and dihedrals motion as three important contributions of energy evaluation in ascending order. The present work intends to study and develop models for covering first and second main models with its structural properties, respectively. Symmetry and degeneracy are two basic

structural properties to the bond stretching and angle bending interactions, especially the latter is significant to connect both interactions for validation purpose. A mathematical function is symmetric if there is an operation that alters its coordinates in some manner but leaves the graph of the function unchanged. The degeneracy of an energy level is defined as the number of distinct quantum states that share that energy (Cooksy, 2014). These fundamental definitions are widely applicable in quantum chemistry; nevertheless, the definitions for both properties have been slightly modified to suit the case studies in this work. Both properties are found can be achieved by choosing the appropriate independent variables and creating the proper selection rules for piecewise polynomial (Davis, 1984). The objectives of this research are summarized as:

1. To develop and implement Bond Stretching Model (BSM) for approximating energy and forces. In this regard independent variables to be employed must be determined and symmetry of structure considered.
2. To develop and implement Angle Bending Model (ABM) for approximating energy and forces. In this regard independent variables to be employed must be determined and symmetry of structure considered.
3. To propose degeneracy embedded in the independent variables for bond stretching and bond angle interaction.
4. To implement second-generation of reactive empirical bond order (REBO) potential in the tension of carbon nanotube simulation for calibration purpose.

1.5   Significance of the Research

This work is significant for nanosized materials study. Products that fabricated by nanosized particles will exhibit different kind of properties from the products fabricated by larger particles, even both using same materials. These properties are called size-dependent properties. In the vast literature, empirical potentials for different intentions have been proposed and applied to explore the system properties especially for nanosized materials properties. New theories, new

concepts, new questions, new findings, new technologies and new products have been developed. These products are created to improve quality of life. In order to study the energy and motion for large system such as nanosized materials, new models for calculating the empirical potential and forces based on bond stretching and angle bending interaction are required, basically it needs to be:

1. Fast in calculation due to less memory.
2. Able to capture symmetry for the structure.
3. Embedded with degeneracy.
4. Ability to be generalized to general problem.

Flexibilities for the proposed potential based on piecewise polynomial (Davis, 1984) concept show that the models are potentially to be generalized to tackle for general problem. And also, there is still numerous ways to improve the model, for instance, the multiscale concept at critical region.

1.6 Scope of the Research

In this work, the attention are focused on interatomic interactions of 3-dimensional multi molecular based on the geometric structures of system. The factors such as degree of freedom for independent variables, accuracy for data collection and flexibility for fitting techniques which affect the performance and time execution in computation algorithm are reviewed and monitored. The new models with its associated independent variables based on approximation concept are proposed for energy and force calculations since it is considered simple computation algorithm. The new models are then used to approximate the bond stretching and bond angle interaction as well as study the structural properties. Structural properties such as symmetry for the geometric structures and degeneracy between bond stretching and bond angle interaction are emphasized with selection rules. The bond stretching model is applied with electronic structure calculation for generalization purpose. The tension for carbon nanotube is simulated by molecular dynamics (MD)

via short range potential namely second-generation of reactive empirical bond order (REBO) potential.

1.7   Organization of the thesis

The pros and cons for three main approaches of energy evaluations as well as the significant linkage between classical and quantum mechanics were briefly discussed in this chapter. Chapter 2 introduces the relevant mathematical formulation in molecular computation. Chapter 3 consists of three sections. First section elucidates three main approaches for finding the energy calculation in different point of view; it starts with general problem and end up with the significant of this study. Second section reviews the remarkable evolution from molecular mechanics (MM) methods to molecular dynamics (MD) simulation where the recent development and applications of force fields are given. Third section discusses the main source of data collection, second-generation of reactive empirical bond order (REBO) potential energy. The development of REBO potential energy from the first-generation up to second-generation are described. Chapter 4 provides the ideas and basic principles employed for model development and formulations. The capability of general piecewise polynomial concept to reproduce predicted energies are theoretically derived and justified for bond stretching model (BSM) and angle bending model (ABM). Particular details such as how to determine and identify the essential independent variables involved in the function, and how to derive the differentiation forms that related to the forces calculation based on interatomic potential energy are also described in this chapter. Chapter 5 represents the results and discussions for BSM and ABM. The affecting factors of general piecewise polynomial are manipulated by using BSM. Lastly, conclusions, contributions, limitation and recommendations for this thesis are presented in last chapter.

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