Multiscale molecular modeling and simulation of carbon nanotubes

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2007

Yeak, S. H. (2007). Multiscale molecular modeling and simulation of carbon nanotubes.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/36048>

<https://doi.org/10.32657/10356/36048>

a529 608

Multiscale Molecular Modeling and Simulation of Carbon Nanotubes

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A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2007

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May all beings be happy.

May they be joyous and live in safety.

*All living beings, whether weak or strong, in high or middle or low realms of existence,
small or great, visible or invisible, near or far, born or to be born, may all beings be
happy.*

*Let no one deceive another, nor despise any being in any state; Let none by anger or
hatred wish harm to another.*

*Even as a mother at the risk of her life watches over and protects her only child, so with
a boundless mind should one cherish all living things, suffusing love over the entire
world, above, below and all around without limit; so let one cultivate an infinite good
will toward the whole world.*

*Standing or walking, sitting or lying down, during all one's waking hours let one
cherish the thought that this way of living is the best in the world.*

⋮
⋮
⋮

Metta Sutta

ACKNOWLEDGEMENTS

The author would like to take this opportunity to acknowledge the numerous people without whom this project would not have been possible. First and foremost, the author wants to express his deepest gratitude to his project supervisors, Associate Professor Ng Teng Yong and Professor Liew Kim Meow, who have provided him the opportunity to venture into this new and challenging area. Their ideas, guidance as well as support on this project have been remarkable.

In addition, the author would like to acknowledge the financial support, as well as permission of study leave, from the Universiti Teknologi Malaysia.

The author would also like to thank all research staff as well as colleagues for their assistance and support.

Finally, I thank my family and wife Lew Ai Lee for their unwavering love and support, without whom the completion of this project would not have been possible.

SUMMARY

Due to their excellent mechanical properties, carbon nanotubes (CNTs) have undergone intense scrutiny by the research community at large since their discovery in 1991. In this thesis, we propose and implement an overlapping scheme to concurrently couple empirical molecular dynamics (MD) with both semi-empirical tight-binding (TB) and *ab initio* density-functional theory (DFT). The multiscale of these three approaches is then used to numerically study the mechanical properties and dynamic characteristics of CNTs. Since MD is based on empirical potential functions, it is relatively “cheap” in terms of computational intensity, and is therefore the technique of choice throughout most of the domains in the CNT during simulation. However, when there is large deformation and/or bond breaking, more robust and refined techniques are required, namely TB or DFT. Basically, the TB technique is a simplification of the *ab initio* method, where a minimal basis set is used in the Hamiltonian system. The hopping integrals are calculated empirically and cut off at a prescribed interatomic distance. The DFT, which was first proposed by Nobel laureate Walter Kohn in 1965, is a fully *ab initio* method based on first-principles, which take into account the electron structure. It is computationally very intensive technique compared with MD and TB, and although it has taken more than thirty years to make these calculations feasible, the DFT method has phenomenally progressed to be the most widely used in computational quantum physics/chemistry today. Generally, the DFT method is solved by iteratively diagonalizing the Hamiltonian. The entire global basis (plane-wave basis set) requires a computational effort which scales to the cube of the system-size, and a memory requirement which scales to the square.

In order to reduce the computation time (to enable the calculations to become feasible) without incurring accuracy penalties, a multiscale approach is developed whereby we define overlap handshaking regions between MD and TB techniques, and also between MD and DFT. The basic idea behind the multiscale model is that for non-bond breaking regions, the MD method is sufficient (and also efficient) and therefore

employed, whereas for areas where there is severe bond extension/compression or bond-breaking, TB or DFT techniques will be deployed.

In order to further reduce the calculation time as well as increase the number of atoms which form the problem domain, we parallelize the DFT method by parallelizing the Kohn-Sham equation based on the k -points. Also, for the MD model, we parallelize the entire program according to the atomic sub-domains. This parallelization of the MD and DFT results in significant computational speed-up, but it was also revealed that as the number of processors increase, communication costs and load imbalance also become critical considerations.

In addition to the development of the TB/MD and DFT/MD multiscale techniques, this thesis also offers several refinements to the techniques employed. In the present MD model, a smooth cutoff Lennard-Jones (LJ) potential with switch function is introduced. The main objective of this switch function is to transform the non-smooth objective function to a smooth one during minimization of the total energy. Our simulation results show that smoothness of the LJ potential is important in certain cases, especially when buckling occurs in CNTs when subjected to axial compression. Finally, our present simulation results revealed that the truncated-Newton via Lanczos minimization performs significantly better than the conjugate gradient method both in terms of the smoothness of the results, as well as reduced computational time.

LIST OF KEYWORDS

Multiscale Technique; Concurrent Coupling; Carbon Nanotubes (CNT); Molecular Dynamics (MD); Tight-Binding (TB); Density Functional Theory (DFT); Parallel Programming.

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NOMENCLATURE

$ a\rangle$	element in Hilbert space H
$\mathbf{a}_i$	primitive translation vectors
$\mathbf{b}_i$	primitive vectors of reciprocal lattice
E_{tot}	energy of a system of ion cores and valence
E_i	energy of many-body state
E_H	classical Hartree energy
$E_{xc}[\mathbf{n}]$	exchange-correlation energy in Kohn-Sham theory
ε_i	independent-particle eigenvalue, $i=1, \dots, N_{states}$
$\varepsilon_{xc}(\mathbf{r})$	exchange-correlation energy per electron
$\varepsilon_{i,\mathbf{k}}$	eigenvalues that define bands as a function of $\mathbf{k}$
E_{ij}^{REBO}	energy using REBO potential between atoms i and j
E_{ij}^{vdw}	van der Waals energy between atoms i and j
$f_i=f(\varepsilon_i)$	occupation of state i where f is the Fermi function
$F[f]$	general notational of F as functional of the function f
$\mathbf{G}$ or $\mathbf{G}(\mathbf{m})=\mathbf{G}(m_1, m_2, m_3)$ $=m_1\mathbf{b}_1+m_2\mathbf{b}_2+m_3\mathbf{b}_3$	reciprocal lattice vectors
$\hat{H}$	Hamiltonian for either many particles or a single particle
$\hat{H}_{tot}$	Hamiltonian of a system of ion cores and valence
	electrons in tight-binding
$\hat{H}_{TB}$	reduced one-electron Hamiltonian in tight-binding
$\mathbf{k}$	wavevector in first Brillouin zone (BZ)
$\psi_i(\mathbf{r})$	independent-particle wavefunction or “orbital” where $i=1, \dots, N_{states}$
$\psi_{n,\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r})$	Bloch function in crystal, with $u_{n,\mathbf{k}}(\mathbf{r})$ periodic where n is good quantum number
$\langle\psi_1 \psi_2\rangle=\int_{-\infty}^{\infty}\psi_1^*\psi_2dV$	inner product in Hilbert space, symbol of ‘bra-ket’ (bracket)

l	orbital quantum number
m_l	magnetic quantum number
n	principal quantum number
$n(\mathbf{r})$	density of electrons
N_e	total electrons to be calculated
N_{pw}	total number of plane waves
(n,m)	pair of integers that define the type of CNT
Ω_{cell}	volume of primitive cell
$\mathbf{q}$	general wavevector ($\mathbf{q}=\mathbf{k}+\mathbf{G}$)
$S(r)$	switch function that couples with LJ potential
s, p, d, f	angular-momentum states, exactly same with l
$\mathbf{T}$ or $\mathbf{T}(\mathbf{n})=\mathbf{T}(n_1,n_2,n_3)$ $=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$	lattice translations
U_{rep}	effective repulsive potential
$V_{ext}(\mathbf{r})$	static external potential
$V_{KS}(\mathbf{r})$	Kohn-Sham potential
$V_{xc}(\mathbf{r})$	exchange-correlation potential in Kohn-Sham theory
V_A	interatomic attraction from the valence electrons in REBO
V_R	interatomic repulsion from the valence electrons in REBO

PUBLICATIONS

The following papers are related to the present research:

1. Yeak S. H., "Multiscale Models of Carbon Nanotubes under Axial Tension", 3rd International Conference on Materials for Advanced Technologies "ICMAT", Suntec SICEC, Singapore, 3-8 July, 2005.
2. Yeak S. H., Ng T. Y. and Liew K.M., "Multiscale modeling of carbon nanotubes under axial tension and compression", Physical Review B, 72, 165401, 2005.
3. Ng T. Y., Yeak S. H., Ren Y. X. and Liew K. M., Book chapter on "Multiscale Modeling of Carbon Nanostructures", in contribution to Fundamentals & Applications of Multiscale Materials Modeling, Edited by Z. X. Guo (Queen Mary, University of London), Woodhead Publishing, Cambridge, UK.
4. Ng T. Y., Yeak S. H. and Liew K. M., "Coupling of ab initio density functional theory and molecular dynamics for the multiscale modeling of carbon nanotubes", - Submitted.

CHAPTER ONE

INTRODUCTION

In this chapter, a brief history of carbon nanotubes (CNTs) is presented. Some published works on the simulation of CNTs are then briefly discussed. Next, the background of problem is reviewed, with the need for multiscale methodology discussed. Thirdly, the objectives of this research are defined. Lastly, for clarity, the layout of this thesis is briefly outlined.

CHAPTER 1 - INTRODUCTION

1.1 NUMERICAL SIMULATION OF CARBON NANOTUBES

The discovery of multi-walled carbon nanotubes in 1991 by Iijima (1991) has stimulated very broad and intense research activities in science and engineering of carbon nanotubes (CNTs). This intense research is due to excellent mechanical properties namely small size, low density, high stiffness and high strength. This broad research includes the numerical simulation of mechanical properties of CNTs. Yakobson *et al.* (1996) studied CNT behavior under axial compression using the Tersoff-Brenner potential. Their simulations showed that at large deformations, an abrupt release of energy is accompanied by a reversible switch into a different morphological pattern. Liew *et al.* (2004, 2005) examined the buckling behavior of single-walled and multi-walled CNTs under axial compression. Their thermal stability analysis showed that single-walled CNTs are thermally more stable than multi-walled CNTs. In addition, they found that critical buckling loads of CNT bundles are much higher than individual single-walled CNT.

The above-mentioned works are based upon empirical molecular dynamics. However, as pointed out by Abraham *et al.* (1998, 2000, 1999), a more refined description is necessary especially in the bond-breaking area. In other words, potentials due to electron-electron, electron-ion as well as ion-ion interactions should be considered. In this respect, tight-binding (TB) and density-functional theory (DFT) (an *ab initio* method¹) are used since they are respectively semi-empirical and fully quantum mechanical, where the latter takes into account the kinetic potential, electrostatic or Hartree potential, external potential and exchange-correlation potential. In the present study, a multiscale model is developed by introducing near and far regions in order to achieve a seamless coupling between MD and DFT, and between MD and TB.

¹ The Latin term *ab initio* means “from the beginning” and is used in several contexts: in sciences (especially physics and chemistry) meaning from first principles. A calculation is considered to be “*ab initio*” (or “from first principles”) if it relies on the most basic and established laws of nature without additional assumptions or special models. Experimental inputs to *ab initio* calculations are limited to the values of fundamental physical constants such as the Planck’s constant.

CHAPTER 1 - INTRODUCTION

In *ab initio* methods, prediction of the electronic and geometric structures of molecular systems require calculation of the quantum mechanical total energy of the system and subsequent minimization of that energy with respect to the electronic and nuclear coordinates. Due to the large difference in mass between the electrons and nuclei and the fact that the forces on the particles are the same, the electrons respond essentially instantaneously to the motion of the nuclei. Thus the nuclei can be treated adiabatically, leading to a separation of electronic and nuclear coordinates in the many-body wavefunction – the so-called Born-Oppenheimer approximation. This “adiabatic principle” reduces the many-body problems to that of the dynamics of the electrons in a “frozen” configuration of the nuclei. Further simplifications are required in order to allow total energy calculations to be performed accurately and efficiently. These include density-functional theory to model the electron-electron interactions, pseudopotential theory to describe valence states by smooth wavefunctions ignoring core electrons, supercells² to model systems with periodic geometries, and iterative minimization techniques to relax the electronic structures.

1.2 BACKGROUND OF THE PROBLEM

Molecular dynamics (MD) theory is arguably the most widely used particle method in scientific and engineering fields. Molecular dynamics can simulate a system of up to 10 million atoms with today’s computational power. In molecular dynamics, one does not calculate the electron distribution, and the forces acting on each atom are determined by a potential function which is determined from either empirical knowledge, or from *ab initio* computations.

However, as pointed out earlier, deformation of nanostructures resulting in bond breaking is not accurately expressed by MD. In order to solve such problems, more robust and detail techniques such as TB or DFT are required to determine the electronic structure and electronic density of each atom. The TB method has the

² The size of a supercell is bigger than that of a unit cell. In many cases it is convenient to simulate an aperiodic (or ‘almost-periodic’) system with a periodically repeated fictitious supercell.

CHAPTER 1 - INTRODUCTION

advantage of being quantum mechanical as well as being computationally efficient when compared with the DFT. The TB method is more expensive than the MD method due to the calculation of the complete eigensystem of all valence electrons in a supercell. In addition, matrix diagonalization as well as the calculation of atomic forces based on the Hellman-Feynman theorem requires extensive computational effort.

At present, *ab initio* methods are restricted to the simulations of only several hundreds of atoms, and furthermore within the nano-second time scale. To simulate a system of larger than that is beyond the limit of current computing hardware. In order to study a nanostructure system like carbon nanotubes (CNTs) with large numbers of atoms for longer time duration, a multiscale model is desirable. The basic idea behind the multiscale model is that for the non-bond breaking regions, the MD method is sufficient whereas the bond-breaking areas will be solved by the *ab initio* methods such as DFT or semi-empirical methods such as TB. The challenge is to seamlessly (accurately and efficiently) couple the different methodologies.

1.3 RESEARCH OBJECTIVES

The objectives of this research are summarized as:

- (i) Implementation of *ab initio* DFT method which incorporates plane-wave basis set and the pseudopotential method. This includes source code development for subsequent multiscale modeling.
- (ii) Implementation of seamless coupling of empirical short-range potential and semi-empirical quantum mechanics, the handshaking between MD and TB.
- (iii) Implementation of seamless coupling of empirical short-range potential and fully quantum mechanics method, the handshaking between MD and DFT.
- (iv) Calculation of mechanical properties of carbon nanotubes (CNTs) using molecular dynamics (MD) and the multiscale models developed.

CHAPTER 1 - INTRODUCTION

- (v) Parallelization of DFT method by parallelizing k -points as well as MD method by domain decomposition.

1.4 LAYOUT OF THE THESIS

The layout of the thesis is as follows:

In chapter 1, published works on the mechanical properties of CNTs are briefly reviewed. The multiscale methodology is proposed and introduced as an approach to obtain quantum mechanical description at significantly reduced computational cost. The general concepts in quantum mechanics as well as DFT are also briefly introduced.

In chapter 2, some background information and characteristics of CNTs is presented. A brief outline of the molecular dynamics approach is also given. Some details are also provided for the associated numerical integration of motion techniques, the choice of short-range empirical bond-order potential, the Verlet neighbor list as well as the long-range Lennard-Jones (LJ) potential.

In chapter 3, the many-body Schrödinger equation is described which is simplified with the Born-Oppenheimer approximation. The second part is devoted to the semi-empirical TB method with emphasis given to the calculation of the empirical hopping integrals.

Chapter 4 is devoted to outlining the salient aspects of the DFT formulation. These include the Hohenberg-Kohn theorems and the resulting Kohn-Sham equations. We discuss in detail the Bloch's theorem which will leads to Fourier transform of the wavefunction. We briefly explain the plane-wave basis which involves the implementation of fast Fourier transform. The exchange-correlation potentials by the generalized gradient approximation is also discussed. Then the Pseudopotential method which enables the calculation of only the valence electrons of the supercell is

CHAPTER 1 - INTRODUCTION

presented. Finally, the reciprocal space integration and special points techniques leading to Brillouin zone calculations will be briefly explained.

In chapter 5 we describe the TB/MD and DFT/MD multiscale schemes and their implementations. The multiscale modeling, nearest distance and density of point (DOP) are discussed. One of the important numerical tasks involves minimization which will be investigated using different schemes. In this chapter we present and compare the computation time of these different minimization schemes. Parallelization of the computations is also discussed, including MD parallelization and k -points parallelization of the DFT.

In chapter 6 we present the simulation results of the pure MD and multiscale TB/MD and DFT/MD models in the analysis of CNTs. The presently developed MD and multiscale schemes are thoroughly validated. In addition, they are mutually compared and the individual characteristics of each method is assessed.

The final chapter concludes this thesis with a summary of achievements of the present work. The recommendation for future work is also proposed.

CHAPTER TWO

CARBON NANOTUBES AND MOLECULAR DYNAMICS MODELING

The discovery of multi-walled carbon nanotubes (MWCNTs) by Iijima (1991) sparked intensive and extensive research in science and engineering of carbon nanotubes (CNTs). This is mainly due to the impressive physical and mechanical properties of CNTs namely small size, low density, high stiffness, high strength and excellent electronic properties. As a result, CNTs have been used in a wide range of applications such as material reinforcement, field emission panel display, chemical sensing, drug delivery, nanoelectronics and hydrogen storage systems.

The present research in CNT studies will focus on the mechanical properties. In this chapter, the mechanical properties will be studied using molecular dynamics (MD) approach. In MD, the short-range interaction force between atoms is modeled using the second-generation reactive empirical bond-order (REBO) potential. Furthermore, the Lennard-Jones (LJ) 12-6 potential is adopted for long-range interaction, which are the van der Waals forces. The LJ potential is integrated via a switch function in order to achieve a smooth objective function. The integration of the equations of motion is also briefly reviewed. The Verlet neighbour list, which is introduced so as to speed up the computational time, is briefly discussed.

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2.1 MOLECULAR STRUCTURE OF CARBON NANOTUBES

The REBO potential takes into account of the molecular structure of CNTs including the bonding mechanisms, namely the π -bond and σ -bond. The REBO potential also takes into account the bond angles between atoms. These different bond angles will determine different types of CNTs as defined by a pair of integers (n,m) .

2.1.1 Bonding Mechanisms

Basically, the bonding mechanism in a CNT is very close to graphite since a CNT can be considered as a rolled-up graphene sheet. Each carbon in a CNT has six electrons which occupy the $1s^2$, $2s^2$, and $2p^2$ atomic orbitals. When carbon atoms combine to form graphite, sp^2 hybridization occurs. In this process, one s -orbital and two p -orbitals combine to form three hybrid sp^2 -orbitals at 120° to each other within a plane as shown in Figure 2.1.1.

Figure 2.1.1. Hexagonal bonding structure for graphene sheet; out-of-plane π -bonds represented as delocalized, whereas σ -bonds connect the carbon nuclei in-plane.

This in-plane bond is referred to as a σ -bond. It is a strong covalent bond that binds the atoms in the plane resulting in the high stiffness and high strength of a CNT. The remaining π -orbital is perpendicular to the plane of the σ -bonds. It introduces the

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interlayer interaction and is called the π -bond. These much weaker, out-of-plane, delocalized π -bonds interact with the π -bonds on the neighboring layer.

2.1.2 Physical Structure of Carbon Nanotubes

Generally, a CNT can be considered as a rolled-up graphene sheet. Subsequently, each unique structure of a CNT can be determined by specifying the direction of rolling and the circumference of the cross-section. Depicted in Figure 2.1.2 is a graphene sheet with defined roll-up vector $\mathbf{C}$ (or wrapping angle).

Figure 2.1.2. Definition of roll-up vector, $\mathbf{C}$ as linear combinations of base vectors $\mathbf{a}_1$ and $\mathbf{a}_2$.

After rolling to form a CNT, the two end nodes coincide. As shown in the figure, vector $\mathbf{C}$ can be decomposed as a linear combination of base vectors $\mathbf{a}_1$ and $\mathbf{a}_2$

$$\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (2.1)$$

with n and m being integers. Different types of CNT are defined by this pair of integers (n,m) as shown in Figure 2.1.3 and the ends are closed with caps of certain types of fullerenes (Qian *et al.*, 2002).

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Figure 2.1.3. Zigzag, arm chair, and chiral CNT.

Basically, CNTs are divided into three major categories based on the chiral angle θ (see Figure 2.1.2)

- $\theta=0^\circ$, “Zigzag”, $m=0$
- $0<\theta<30^\circ$, “Chiral”
- $\theta=30^\circ$, “ArmChair”, $n=m$

Using some geometrical properties, the diameter d and the chiral angle θ of the CNTs can be derived as

$$d = 0.783\sqrt{n^2 + nm + m^2} \quad (2.2)$$

$$\theta = \sin^{-1}\left(\frac{\sqrt{3}m}{2(n^2 + nm + m^2)}\right) \quad (2.3)$$

Based on the Euler’s theorem of polyhedra, Fujita *et al.* (1992) and Dresselhaus *et al.* (1993, 1996) concluded that any cap must contain six pentagons that are isolated from each other.

Wildöer *et al.* (1998) revealed that for an armchair CNT with $n=m$, the CNT behaves as a metallic material. For chiral and zigzag CNT, there exist two possibilities. When $n-m = 3l$ (where l is an integer), the CNT behaves as a metallic material. However, in

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the case where $n-m \neq 3l$, the CNT behaves as a moderate band-gap semiconductor with an energy gap of the order of ~ 0.5 eV.

2.2 ELASTIC BEHAVIOUR OF CARBON NANOTUBES

The elastic behavior of CNTs can be simulated successfully, including the elastic buckling and local deformation behavior. Based on the simple Newton's second law with the integration of the equations of motion, the derivation of force and energy from the REBO and LJ potentials enables the calculation of new atomic positions. The relaxation of total energy (REBO and LJ energies) will produce the structural response of the CNT.

2.2.1 Elastic Properties of Carbon Nanotubes

In order to model this atomic-scale CNT, we have to make an assumption that the CNT has similar mechanical characteristics as that of an elastic beam. Lourie and Wagner (1998) carried out axial loading experiments and successfully measured the compressive deformation of a nanotube embedded in an epoxy matrix. They obtained a Young's modulus of 2.8-3.6 TPa for single-wall carbon nanotubes (SWCNTs). Yu *et al.* (2000) presented results for SWCNTs undergoing tensile loading. Their experiments reveal that the Young's modulus values vary in the range of 320 to 1470 GPa. Figure 2.2.1 shows some results of the stress-strain relationships.

The Young's modulus of CNT can be determined experimentally by depositing the CNT on a well-polished alumina ultrafiltration membrane proposed by Salvétat *et al.* (1999), see Figure 2.2.2. A CNT will occasionally span across pores present in the membrane, approximately forming a suspended nanoscale fixed-fixed beam configuration. In the measurement process, the tip of an atomic force microscope (AFM) applies a load to the mid-portion of a suspended CNT, and the maximum deflection at the center of the beam is directly recorded from the topographic image. The slope of the resulting plot of force versus deflection will provide the Young's

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modulus of the CNT, which was found within experimental error to be 0.81 ± 0.41 TPa.

Figure 2.2.1. Stress versus strain curves obtained from the tensile-loading experiments on individual SWCNT ropes. Thickness of SWCNTs is assumed 0.34nm. The strain is the engineering strain. D is the diameter of the rope and ϵ the breaking strain. Yu *et al.* (2000).

Figure 2.2.2. An AFM image of a CNT suspended over a pore of alumina ultrafiltration membrane, Salvetat *et al.* (1999).

By observing the CNT free-standing room temperature vibrations through a transmission electron microscope (TEM), Krishnan *et al.* (1998) reported an average SWCNT Young's modulus of 1.25 TPa. However, the diameter and length of the samples of the CNT used in this technique are restricted to a limited range, i.e., those

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that do not possess too small or too large thermally excited vibrations. This is necessary for a reliable TEM detection.

From numerical means, Hernández *et al.* (1998) employed a nonorthogonal TB method and obtained a Young's modulus value in the region of 1.22 TPa. They also showed that the Young's modulus of CNTs have a slight dependence on their chiralities and diameters. Srivastava *et al.* (1999) investigated the mechanical properties of CNT using a generalized TB formulation and reported a Young's modulus value of 1.3 TPa. More accurate *ab initio* calculations on SWCNTs by Hernández (1998) have yielded corresponding values of 1.06-1.14 TPa. Belytschko *et al.* (2002) calculated the mechanical properties of CNT using a modified Morse function and obtained a value of 0.94 TPa for the Young's modulus.

Robertson *et al.* (1992) studied the energetic and elastic properties of SWCNTs with radii less than 0.9 nm using both Brenner potential (Brenner, 1990) and first-principle techniques. They found a consistent linear proportionality to $1/R^2$ for the strain energy, where R is the radius of CNT. This implies that small deformation beam theory is still valid even for the lower radius limit of CNTs.

2.2.2 Elastic Buckling and Local Deformation of CNT

Generally, buckling in CNT can occur in both the axial and transverse modes. It can also occur globally or locally. Yakobson *et al.* (1996) successfully modeled buckling of CNT under axial compression using the Brenner potential in MD simulation. Their results showed that the first buckling mode starts at a nominal compressive strain of 0.05. When the CNT is under torsion, flattening of the tube or collapse of the cross-section can occur. Qian *et al.* (2002) obtained these buckling modes using MD simulation as shown in the Figure 2.2.3.

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Figure 2.2.3. (i) Buckling of SWCNT under bending load,
(ii) Buckling of SWCNT under torsional load.
Qian *et al.* (2002).

2.2.3 Strength Under Bond Breaking and/or Plastic Yielding

Pristine CNTs have very high strength which strongly depends on the synthesis process. There are several major categories of synthesis methods, namely carbon evaporation by arc current discharge, laser ablation or chemical vapor deposition. By laterally stretching suspended SWCNT bundles fixed at both ends using an AFM (atomic force microscopy) operated in lateral force mode, Walters *et al.* (1999) were able to determine the maximum elongation of the bundle, and thus the breaking strain. The tensile strength of an SWCNT was estimated to be 45 ± 7 GPa. Yakobson *et al.* (1996) performed a set of MD simulations on the tensile loading of nanotubes. Following the application of very high strain rate, the CNT did not break completely in half, but the two separated parts were instead connected by a chain of atoms.

One of the major observations by quantum molecular dynamics simulations of plastic yielding in CNT is the effect of pentagon/heptagon (5/7) defects as shown in Figure 2.2.4. The bond rotation effect leading to the 5-7-7-5 defect initially formed, is referred to as the Stone-Wales bond-rotation (Dresselhaus, 1996). As shown by Yakobson (1997), for certain types of SWCNTs, sufficiently high temperature loading can lead to plastic yielding.

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Figure 2.2.4. The “5-7-7-5” dislocation evolves into two possibilities: crack or as a couple of dislocations gliding away along the spiral slip plane (plastic yield). Qian *et al.* (2002).

Nardelli *et al.* (1998) used MD and quantum molecular dynamics (QMD) to study the mechanism of strain release under tensile loading. Their results show that in the case of tension, the 5-7-7-5 defect tends to form when the strain is greater than 5% in order to achieve relaxation of the structure. Srivastava *et al.* (1999) showed that a local reconstruction leading to the formation of sp^3 bonds can occur under compressive loading, and also obtained a compressive strength of approximately 153 GPa.

2.3 NUMERICAL SIMULATION OF CARBON NANOTUBES

Generally, the major limitation of atomic/molecular simulation is the huge computational time involved, especially those related to *ab initio* methods. In other words, the application of *ab initio* methods is limited by the size of the atoms in the system. Presently, our research focuses on three methods namely MD, TB and DFT methods. Among the three methods, the MD method is the most simple and most inexpensive technique.

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Basically, the MD method is based on Newton's second law with the integration of equation of motion to obtain the velocities and displacements. In our MD model, the short-range potential is based on the REBO potential while the long-range potential is the van der Waals Lennard-Jones 12-6 (LJ) potential. The LJ potential with switch function is also implemented.

2.3.1 Molecular Dynamics

Presently, we perform a microcanonical ensemble¹ molecular dynamics (MD) model. The essence of molecular dynamics (MD) is to solve the governing equations of particle dynamics based on Newton's second law

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i = -\nabla V \quad (2.4)$$

where m_i and $\mathbf{r}_i$ are the mass and spatial coordinates of the i^{th} atom while V is the empirical potential for the system.

The main principle of MD simulation is as follows: given the system state $S(t_0)$, which relates to the position $\mathbf{r}$ and velocity $\mathbf{v}$ of every particle in the system at time t_0 , the subsequent states $S(t_0+\Delta t)$, $S(t_0+2\Delta t)$, ..., are calculated based on Equation (2.4). In order to calculate accurate results we will use small timesteps Δt . When we want to advance to $S(t_0+(n+1)\Delta t)$ from $S(t_0+n\Delta t)$, then for every particle i , $\mathbf{F}_i(t_0+n\Delta t)$ is calculated. $\mathbf{F}_i(t_0+n\Delta t)$ is the sum of the forces on particle i as exerted by the other particles in the system at time $t_0+n\Delta t$. For every particle i the force $\mathbf{F}_i(t_0+n\Delta t)$ is then integrated to get the new velocity $\mathbf{v}_i(t_0+n\Delta t)$. Using this velocity, the new position $\mathbf{r}_i(t_0+(n+1)\Delta t)$ can be calculated for every particle i .

¹ The microcanonical ensemble is the simplest of the ensembles of statistical mechanics, where each system of the ensemble is assumed to have the same total energy. It is a degenerate canonical ensemble. On the other hand, a canonical ensemble in statistical mechanics is an ensemble of dynamically similar systems, where each can share its energy with a large heat reservoir, or heat bath. In other words, a canonical ensemble is assumed to have constant temperature. The grand canonical ensemble is a generalization of this, whereby the systems may share particles as well as energy.

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2.3.2 Integration of Equations of Motion

Here we describe the leapfrog algorithm, which is widely used, simple and numerically stable. Here, particle positions are calculated at time $t_0 + n\Delta t$ and velocities at midpoints, i.e. at $t_0 + (n+1/2)\Delta t$. Using the notation $t_n = t_0 + n\Delta t$, the formulas for leapfrog integration can be written as

$$\mathbf{v}_i(t_n + \Delta t / 2) = \mathbf{v}_i(t_n - \Delta t / 2) + m_i^{-1} \mathbf{F}_i(t_n) \Delta t \quad (2.5)$$

$$\mathbf{r}_i(t_n + \Delta t) = \mathbf{r}_i(t_n) + \mathbf{v}_i(t_n + \Delta t / 2) \Delta t \quad (2.6)$$

Note that in Equations (2.5) and (2.6), the ratio of the first and second terms on the right-hand side is only of order Δt . In the leapfrog method, the updates of the velocity and position are shifted by $\Delta t/2$. First, one calculates the force from the coordinate data at time t . Then, using this force, we can estimate the velocity at time $t + \Delta t/2$. Subsequently, using this velocity, we can derive the position at $t + \Delta t$. Basically, the leapfrog method is more tractable than the Verlet method when applied in periodic boundary conditions. This is because, even if the new position is outside the cell boundary, the velocity is not affected.

Since the leapfrog method cannot handle the velocities in an appropriate manner, a modified method is introduced, namely the velocity Verlet method. The modification is given as

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{1}{2m_i} \mathbf{F}_i(t) \Delta t^2 \quad (2.7)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2m_i} [\mathbf{F}_i(t + \Delta t) + \mathbf{F}_i(t)] \Delta t^2 \quad (2.8)$$

Generally, the above algorithm requires the storage of coordinates, velocities and forces at every time step, but it minimizes round-off errors. It involves two stages since the forces must be evaluated after the updating of the coordinates but before the updating of the velocities.

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Another integration method used in MD is the Gear's predictor-corrector algorithm. Since the trajectory of the atomic motions is a continuous function of time, the position, velocity and acceleration at time $t+\Delta t$ can be expanded as Taylor series

$$\begin{aligned} \mathbf{r}_i^P(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{(\Delta t)^2}{2} \mathbf{a}_i + \frac{(\Delta t)^3}{6} \mathbf{b}_i(t) + \dots \\ \mathbf{v}_i^P(t + \Delta t) &= \mathbf{v}_i(t) + \Delta t \mathbf{a}_i(t) + \frac{(\Delta t)^2}{2} \mathbf{b}_i(t) + \dots \\ \mathbf{a}_i^P(t + \Delta t) &= \mathbf{a}_i(t) + \Delta t \mathbf{b}_i(t) + \dots \\ \mathbf{b}_i^P(t + \Delta t) &= \mathbf{b}_i(t) + \dots \end{aligned} \quad (2.9)$$

Using the new predicted position $\mathbf{r}_i^P(t + \Delta t)$, one can obtain the force $\mathbf{F}(t+\Delta t)$ at time $t+\Delta t$, as well as $\mathbf{a}_i^C(t + \Delta t)$, which is then used as a corrector. Using this corrector, we can estimate the error in the predicted acceleration, $\mathbf{a}_i^P(t + \Delta t)$

$$\Delta \mathbf{a}_i(t + \Delta t) = \mathbf{a}_i^C(t + \Delta t) - \mathbf{a}_i^P(t + \Delta t) \quad (2.10)$$

Assuming the difference between the predicted and corrected quantities is small, one can say that they are all proportional to each other and, therefore, to $\Delta \mathbf{a}$. Adding this difference to the predicted values, one obtains the following corrected quantities

$$\begin{aligned} \mathbf{r}_i^C(t + \Delta t) &= \mathbf{r}_i^P(t + \Delta t) + c_0 \Delta \mathbf{a}_i(t + \Delta t) \\ \mathbf{v}_i^C(t + \Delta t) &= \mathbf{v}_i^P(t + \Delta t) + c_1 \Delta \mathbf{a}_i(t + \Delta t) \\ \mathbf{a}_i^C(t + \Delta t) &= \mathbf{a}_i^P(t + \Delta t) + c_2 \Delta \mathbf{a}_i(t + \Delta t) \\ \mathbf{b}_i^C(t + \Delta t) &= \mathbf{b}_i^P(t + \Delta t) + c_3 \Delta \mathbf{a}_i(t + \Delta t) \end{aligned} \quad (2.11)$$

Gear (1971) has determined the coefficients c_0 to c_5 in order to achieve the best accuracy and stability. These values are given in Table 2.4.1. The predictor-corrector method is one of the more superior methods for solving nonlinear ordinary differential equations. Beside the above three algorithms, there exist a very accurate and stable algorithm called the Runge-Kutta (RK) method. As pointed out by Haile (1992), the popular RK method possesses good stability characteristics. However, they are less used since for large numbers of molecules and long simulation period, the RK algorithms are too inefficient. In our problem, the evaluation of intermolecular forces

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is the most time-consuming calculation. Since a fourth-order RK algorithm would require four force evaluations per atom per time step, such an algorithm becomes very slow and not suitable for large molecular systems.

Table 2.4.1. Values of coefficients for the Gear's predictor-corrector algorithm.

Order	c_0	c_1	c_2	c_3	c_4	c_5
3	0	1	1			
4	1/6	5/6	1	1/3		
5	19/120	3/4	1	1/2	1/12	
6	3/20	251/360	1	11/18	1/6	1/60

2.3.3 Bond-Order and Long Range Potentials

The basic formulation of MD requires that the spatial gradient of the empirical potential function V be evaluated. Different empirical potentials for a CNT system have been developed to satisfy this requirement. In this thesis, we employ the second-generation reactive empirical bond order (REBO) potential energy expression first introduced by Brenner *et al.* (2002).

The characteristics of carbon must be accurately expressed, especially its strong bonds in both sp^2 and sp^3 configurations. The REBO potential has been specially derived to match closely with carbon's characteristics, which allows for bond breaking and forming with appropriate changes in atomic hybridization. The REBO potential contains improved analytic functions and a more comprehensive database. These therefore provide a better description of bond energies, bond lengths, force constants, elastic properties, interstitial defect energies, and surface energies. Srivasta *et al.* (1999a), Liew *et al.* (2004, 2004a, 2005, 2005a) and Ni *et al.* (2002) have successfully applied the REBO potential in CNTs.

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In this research, the short-range interaction force between atoms is modeled using the Brenner REBO potential. In addition, the van der Waals potential is applied (Lennard-Jones, 1924) as²

$$E = \sum_i \sum_{j>i} (E_{ij}^{REBO} + E_{ij}^{vdw}) \quad (2.12)$$

$$E_{ij}^{REBO} = [V_R(r_{ij}) + b_{ij}V_A(r_{ij})] \quad (2.13)$$

where V_R and V_A are pair-additive interactions that represent all interatomic repulsions and attractions respectively from valence electrons, and b_{ij} is the reactive empirical bond order between atoms where i and j are the indices of the atoms. E is the total energy including short-range REBO potentials and long-range van der Waals potentials.

The repulsive and attractive pair terms are given as

$$V_R(r) = f^c(r)(1 + Q/r)Ae^{-\alpha r} \quad (2.14)$$

$$V_A(r) = f^c(r) \sum_{n=1,3} B_n e^{-\beta_n r} \quad (2.15)$$

where r denotes the scalar distance between atoms, Q the effective charge in the screened Coulomb potential, and the function $f^c(r)$ limits the range of the interactions which assumes a value of one for nearest neighbors and zero for all other interatomic distances. The function $f^c(r)$ is defined as

$$f_{ij}^c(r) = \begin{cases} 1 & r < D_{ij}^{\min} \\ \left[1 + \cos(\pi(r - D_{ij}^{\min})/(D_{ij}^{\max} - D_{ij}^{\min}))\right]/2 & D_{ij}^{\min} < r < D_{ij}^{\max} \\ 0 & r > D_{ij}^{\max} \end{cases} \quad (2.16)$$

where $D_{ij}^{\max} - D_{ij}^{\min}$ is the distance over which the function goes from one to zero. All the above parameters are provided by Brenner (2002) for C-C and is given in Table 2.4.2.

² In this chapter, the subscript index “ ij ” is optional and will be shown when it is required for clarity.

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Table 2.4.2. Values of parameter for C-C pair in Brenner REBO.

$B_1=12355.79197798 \text{ eV}$	$B_2=17.56740646509 \text{ eV}$	$B_3=30.71493208065 \text{ eV}$
$\beta_1=4.7204523127 \text{ \AA}^{-1}$	$\beta_2=1.4332132499 \text{ \AA}^{-1}$	$\beta_3=1.3826912506 \text{ \AA}^{-1}$
$Q=0.3134602960833 \text{ \AA}$	$A=10953.544162170 \text{ eV}$	$\alpha=4.7465390606595 \text{ \AA}^{-1}$
$D_{\min}=1.7$	$D_{\max}=2.0$	

The empirical bond order function between atoms i and j in Equation (2.12) is given as

$$\bar{b}_{ij} = \frac{b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}}{2} + b_{ij}^{\pi} \quad (2.17)$$

where the values for the functions $b_{ij}^{\sigma-\pi}$ and $b_{ji}^{\sigma-\pi}$ are dependent on the local coordinate and bond angles, for atoms i and j . The function b_{ji}^{π} can also be written as

$$b_{ij}^{\pi} = \pi_{ij}^{RC} + b_{ij}^{DH} \quad (2.18)$$

The value of the first term π_{ij}^{RC} is dependent on whether a bond between atoms i and j has radical character, and if it is part of the conjugated system. The value of b_{ij}^{DH} depends on the torsional angle of the C-C bonds. It is worthwhile to note that for bonds that are not part of the conjugated system, as well as planar double bonds, both terms are equal to zero. For solid-state carbon, the function $b_{ij}^{\sigma-\pi}$ for CNT in Equation (2.17) is given as

$$b_{ij}^{\sigma-\pi} = \left\{ 1 + \sum_{k(\neq i, j)} f_{ik}^c(r_{ik}) G_C [\cos(\theta_{ijk})] \right\}^{-1/2} \quad (2.19)$$

The angular function $G_C[\cos(\theta)]$ modulates the contribution that each nearest neighbour makes to the empirical bond order according to the cosine of the bond angles, between atoms i and k as well as between atoms i and j . However, according to Brenner (2002), the values for $G_C[\cos(\theta)]$ determined for θ equal to 90° and 60° are too large for under-coordinated carbon atoms. In order to allow for both over-coordinated and under-coordinated atoms, a second spline function $\gamma_c[\cos(\theta)]$ was required for

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angles less than 109.47° which was coupled into the original angular function $G_c[\cos(\theta)]$. Therefore the revised angular function between 109.47° and 0° for carbon atom i is given as

$$g_c = G_c[\cos(\theta_{ijk})] + Q(N_i^t) \{ \gamma_c[\cos(\theta_{ijk})] - G_c[\cos(\theta_{ijk})] \} \quad (2.20)$$

where the function Q is given as

$$Q(N_i^t) = \begin{cases} 1 & N_i^t \leq 3.2 \\ \{1 + \cos[2\pi(N_i^t - 3.2)]\} / 2 & 3.2 < N_i^t \leq 3.7 \\ 0 & N_i^t > 3.7 \end{cases} \quad (2.21)$$

and since CNT consists of pure carbon³,

$$N_i^t = N_i^C \quad (2.22)$$

$$N_i^C = \sum_{k(\neq i,j)}^{carbon} f_{ik}^c(r_{ik}) \quad (2.23)$$

The term π_{ij}^{RC} in Equation (2.18) represents the effects of radical energies and π -bond conjugation on the bond energies. This is essential as it accurately describes radical structures and it accounts for non-local conjugation effects such as those that govern the different properties of the C-C bonds in graphite. This function is represented as a tricubic spline F_{ij}

$$\pi_{ij}^{RC} = F_{ij}(N_i^t, N_j^t, N_{ij}^{conj}) \quad (2.24)$$

which involves the neighboring atoms i and j , and N_{ij}^{conj} that determines if a bond is part of a conjugated system as

$$N_{ij}^{conj} = 1 + \left[\sum_{k(\neq i,j)}^{carbon} f_{ik}^c(r_{ik}) F(X_{ik}) \right]^2 + \left[\sum_{l(\neq i,j)}^{carbon} f_{jl}^c(r_{jl}) F(X_{jl}) \right]^2 \quad (2.25)$$

where

³ Since REBO potential was initially designed to model hydrocarbon molecules, thus in our simulation model, we only use carbon atoms which was labeled as “carbon”.

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$$F(X_{ik}) = \begin{cases} 1 & X_{ik} \leq 2 \\ [1 + \cos(2\pi(X_{ik} - 2))]/2 & 2 < X_{ik} \leq 3 \\ 0 & X_{ik} > 3 \end{cases} \quad (2.26)$$

with

$$X_{ik} = N_k^t - f_{ik}^c(r_{ik}) \quad (2.27)$$

The term b_{ij}^{DH} in Equation (2.18) which describes the torsion angle for C-C bonds is given as

$$b_{ij}^{DH} = T_{ij}(N_i^t, N_j^t, N_{ij}^{conj}) \left[\sum_{k(\neq i, j)} \sum_{l(\neq i, j)} (1 - \cos^2 \Theta_{ijkl}) f_{ik}^c(r_{ik}) f_{jl}^c(r_{jl}) \right] \quad (2.28)$$

where

$$\Theta_{ijkl} = \hat{\mathbf{e}}_{jik} \cdot \hat{\mathbf{e}}_{ijl} \quad (2.29)$$

The function $T_{ij}(N_i^t, N_j^t, N_{ij}^{conj})$ is tricubic spline, where $\hat{\mathbf{e}}_{jik}$ and $\hat{\mathbf{e}}_{ijl}$ are unit vectors in the direction of the cross products $\mathbf{R}_{ji} \times \mathbf{R}_{ik}$ and $\mathbf{R}_{ij} \times \mathbf{R}_{jl}$ respectively, and $\mathbf{R}$'s are vectors connecting the associated atoms.

One feature that is not considered by the REBO potential is the interlayer potential. It is a non-bonding, van der Waals interactions between atoms. Presently, the long-range Lennard-Jones12-6 (LJ) potential is employed

$$E_{ij}^{vdw} = 4\varepsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2.30)$$

where ε denotes the well depth parameter and is 4.55meV, and σ_{ij} is the collision diameter between two atoms.

As pointed out by Mao *et al.* (1999), it is advisable to incorporate the van der Waals potential only when the short-range potential becomes zero. This is to prevent an

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artificial reaction barrier⁴ from forming due to the steep repulsive wall of the Lennard-Jones 12-6 potential in the short range. If E^{vdw} were activated in the short range as well, the sum effect of $(E^{REBO} + E^{vdw})$ will be erroneously high due to the additional accounting, thus forming the artificial force barrier that restricts unbonded atoms from undergoing chemical reaction.

Mathematically, the above barrier will produce nonsmooth potential energy profiles and interatomic forces, leading to a nonsmooth optimization problem during energy relaxation. Since the nonsmooth optimization algorithm is very time consuming, it is proposed here to modify the above van der Waals potential such that it behaves smoothly around the cutoff distance, $D_{\max}$. The current work employs the conjugate-gradient method and truncated-Newton via Lanczos minimization. Both methods are subjected to smooth objective minimization using the gradient of the objective function. Details of these methods will be discussed in Chapter 5.

The original Equation (2.30) will be modified by adding a switch function $S(r)$ as shown below,

$$E^{vdw,s} = E^{vdw} \cdot S(r) \quad (2.31)$$

which must satisfy the following conditions:

$$\begin{aligned} E^{vdw,s}(D_{\max}) &= 0 \\ E^{vdw,s}(D_{\max} + d) &= E^{vdw}(D_{\max} + d) \\ \left. \frac{\partial}{\partial r} E^{vdw,s} \right|_{D_{\max}} &= 0 \\ \left. \frac{\partial}{\partial r} E^{vdw,s} \right|_{D_{\max} + d} &= \left. \frac{\partial}{\partial r} E^{vdw} \right|_{D_{\max} + d} \end{aligned} \quad (2.32)$$

⁴ Short range potential becomes zero mean that the attractive and repulsive pair terms versus interatomic distance, becomes zero. It occurs when the interatomic distance is more than 2 Å. As a result, before this interatomic distance, there exists a difference or gap between the LJ and short range potentials. This is referred as the artificial barrier.

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where $D_{\max}$ is the distance at which the REBO potential becomes zero, and d is the neighbor distance that causes the switch function to vary from zero to one⁵.

The switch function is given by

$$S(r) = a_0 + a_1 r + a_2 r^2 + a_3 r^3 \quad (2.33)$$

The conditions stated in Equations (2.32) results in the following linear system of equations

$$\begin{bmatrix} 1 & D_{\max} & D_{\max}^2 & D_{\max}^3 \\ 1 & D_{\max} + d & (D_{\max} + d)^2 & (D_{\max} + d)^3 \\ 0 & 1 & 2D_{\max} & 3D_{\max}^2 \\ 0 & 1 & 2(D_{\max} + d) & 3(D_{\max} + d)^2 \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \quad (2.34)$$

Thus the unknown coefficients in the switch function can be calculated by solving the above linear system simultaneously.

Finally, we derive a smooth cutoff van der Waals potential as

$$E^{vdw,s} = \begin{cases} 0, & r < D_{\max} \\ E_{ij}^{vdw} \cdot S(r), & D_{\max} \leq r \leq D_{\max} + d \\ E_{ij}^{vdw}, & r > D_{\max} + d \end{cases} \quad (2.35)$$

2.3.4 Verlet Neighbour List

The most time consuming part of MD simulation is the calculation of energy and force of each atom interacting with others. Generally, for a system with N atoms, there are $N(N-1)/2$ pair interactions in order to calculate energy and force of each atom. In order to reduce the total pair of interactions, it is advantageous to introduce the cutoff of

⁵ In Mao *et al.*'s work, they employed the long-range Lennard-Jones potential, E^{vdw} , only after the short-ranged REBO potential, goes to zero and beyond. This occurs when the interatomic distance is $2\text{\AA}$ or higher. As E^{REBO} is specially designed for accurately modeling short-range effects and does not appropriately handle long-range effects, the long-range E^{vdw} is thus introduced to specifically enhance the long-range effects. Therefore it is only activated at interatomic distances above $D_{\max}$ ($2\text{\AA}$).

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energy and force of each atom. Hence, for the long-range potential, the original LJ potential is modified as

$$E_{ij}^{vdw} = \begin{cases} 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] & , r_{ij} \leq r_{cut} \\ 0 & , r_{ij} > r_{cut} \end{cases} \quad (2.36)$$

where r_{cut} is typically 2.5σ . This truncated version of the LJ potential is used throughout this research. Please note that the above cutoff is attributed to the long distance whereas the cutoff using switch function in Equation (2.31) belongs to short distance at the intersection between the LJ and REBO potentials.

Since the force equals to zero for any $r_{ij} > r_{cut}$, the total interaction pairs can be dramatically reduced by using a book-keeping scheme introduced by Verlet (1967). In the Verlet neighbour list (or simply neighbour list) method, a second cutoff radius $r_{verlet} > r_{cut}$ is introduced. For each atom i , a neighbour list of neighbouring atoms that lie within a distance r_{verlet} is maintained. As a result, this neighbour list identifies those atoms that contribute to the force on atom i and thus reduce the total interactions pair. In the real time simulation, if the maximum displacement of the atoms is less than $r_{diff} = r_{verlet} - r_{cut}$, then the neighbour list remains unchanged. However, as soon as one of the atoms is displaced more than r_{diff} , the neighbour list has to be updated. Presently, we use $r_{verlet} = 2.6\sigma$. As our present objectives focuses on multiscale models as well as TB and DFT methods, we did not perform a detailed study on the relationship between r_{verlet} and computation time.

In order to further describe the MD method, a flow chart of MD simulation is given in Figure 2.3.1.

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Figure 2.3.1. Flow chart of MD simulation.

2.4 CONCLUSIONS

In this chapter, the molecular structure of CNT is presented. It is shown that different types of CNT will display different band energy leading to metallic or semiconductor characteristics. It is pointed out that the elastic properties as well as buckling characteristics can be simulated using the MD method with REBO potential.

In the integration of the equations of motion, even though the Runge-Kutta (RK) method possesses very accurate and stable algorithm, we eventually adopted the Gear's predictor-corrector algorithm. This is due to the inefficiency of the RK method making it unsuitable for large molecular systems. In order to further speed-up the computation time, the Verlet neighbour list is introduced to reduce the total interaction pairs.

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Finally, the LJ potential with switch function is presented. Theoretically, it will produce more accurate results since the objective function become differentiable and smooth. This is very suitable for our present smooth optimization algorithms, namely the conjugate-gradient method and the truncated-Newton via Lanczos minimization.

CHAPTER THREE

TIGHT-BINDING METHOD

In this chapter, the many-body Schrödinger equation is reviewed. This equation is simplified using the Born-Oppenheimer approximation which leads to the separation of electron and nuclei functions.

In the tight-binding (TB) method, we only use localized orbitals with minimal basis set approximation. The matrix elements constitute the most important part in the TB model. The matrix elements consist of hopping integrals which are cut off to zero for a certain interatomic distance due to the localized orbitals. The calculation of the matrix elements is further simplified by adopting a two-center approximation in the evaluation of the hopping integrals. It is important to point out that these matrix elements will not be evaluated but will be approximated as analytical functions of the atoms' coordinates.

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3.1 MANY-BODY SCHRÖDINGER EQUATION

The general Hamiltonian for a system of electrons and nuclei is given by

$$\begin{aligned} \hat{H}\Psi(\{\mathbf{r}_i\}) = & \left[-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right. \\ & \left. - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \right] \Psi(\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{r}_i\}) \end{aligned} \quad (3.1)$$

where the electrons are denoted by lower case subscripts and nuclei, with charge eZ_I and mass M_I , are denoted by upper case subscripts. Ψ is the many-body electronic wavefunction. $\hbar$ is Planck's constant divided by 2π , while m_e is the mass of the electron, and e is the electron charge (please refer to Appendix C for more details). $\mathbf{r}_i$ is the location of electron at i and $\mathbf{R}_I$ is the location of nuclei at I .

The challenge for modern electronic structure theories is to overcome the independent electron approximation and to find a solution to the many-body Schrödinger equation for a fully interacting system of electrons bound by positively charged nuclei. Within the Born-Oppenheimer approximation¹, there is a strong disparity of timescales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude, see Leach (2001).

Ignoring the nuclear kinetic energy, the fundamental Hamiltonian for the theory of electronic structure can be written as

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} + \hat{V}_{NN} \quad (3.2)$$

Here, we adopt (Hartree) atomic units unless otherwise stated. Please refer to Appendix C for details on atomic units and Appendix G for the “bra-ket” notation as well as a brief introduction to Hilbert space.

¹ Due to the masses of the nuclei being much greater than the masses of electrons, the electrons can adjust almost instantaneously to any changes in the positions of the nuclei. Thus, under the Born-Oppenheimer approximation the total wavefunction can be separated as $\psi_{\text{tot}}(\text{nuclei, electrons}) = \psi(\text{electron}) \psi(\text{nuclei})$.

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The kinetic energy operator for the electrons is given as

$$\hat{T} = \sum_i -\frac{1}{2} \nabla_i^2 \quad (3.3)$$

and $\hat{V}_{ext}$ is the external potential acting on the electrons due to the nuclei

$$\hat{V}_{ext} = \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (3.4)$$

the electron-electron interaction, $\hat{V}_{ee}$ is

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (3.5)$$

while $\hat{V}_{NN}$ is the nuclear-nuclear interaction,

$$\hat{V}_{NN} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (3.6)$$

The final term $\hat{V}_{NN}$ is the electrostatic nucleus-nucleus interaction, which is essential in the total energy calculation, but is only a classical additive term in the theory of electronic structure.

The total energy is the expectation value of the Hamiltonian,

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + \hat{V}_{NN} \quad (3.7)$$

where the expectation value of the external potential has been explicitly written as a simple integral over the density function. The eigenstates of the many-body Hamiltonian are stationary points (saddle or minimum) of the energy in Equation (3.7). These may be found by applying the Ritz variational method in inner product space as

$$\delta(E) = \delta \left(\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right) = 0 \quad (3.8)$$

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As shown in Appendix D, we finally obtain

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (3.9)$$

which is exactly the Schrödinger equation.

The ground state wavefunction Ψ_0 is the state with lowest energy, which can be determined, in principle, by minimizing the total energy with respect to all the parameters in $\Psi(\{\mathbf{r}_i\})$, with the constraint that Ψ must obey the particle symmetry and any conservation laws.

3.2 TIGHT-BINDING MODEL

Generally, the tight-binding (TB) method of modeling materials is a very efficient computational technique. The TB approach works by replacing the many-body Hamiltonian operator with a parameterized Hamiltonian matrix and solving the Schrödinger equation in an atomic-like localized basis set. Within the TB approach, the many-body system is simplified into a system of ion cores and valence electrons. The Hamiltonian² of a system of ion cores and valence electrons in the adiabatic approximation can be written as

$$\hat{H}_{tot} = \hat{T}_i + \hat{T}_e + U_{ee} + U_{ei} + U_{ii} \quad (3.10)$$

where $\hat{T}_i, \hat{T}_e$, U_{ee} , U_{ei} and U_{ii} are respectively the kinetic energy operators of the ions and electrons, and the potential energies due to electron-electron, electron-ion, and ion-ion interactions. Within the adiabatic one-electron assumption, the many-body electron Hamiltonian can be reduced to that of one electron moving in the average field due to the other valence electrons and ions. Core electrons are treated as frozen and they will be attached to the nuclei and thus forming ions. The reduced one-electron Hamiltonian $\hat{H}_{TB}$ and its n^{th} eigenfunction $|\Psi_n\rangle$ can therefore be written as

² The Hamiltonian is represented by operators. In quantum mechanics, an operator maybe assigned as any observable quantity. Please refer to Appendix G for details.

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$$\hat{H}_{TB}|\Psi_n\rangle = \varepsilon_n|\Psi_n\rangle \quad (3.11)$$

where ε_n is the energy of the n^{th} single-particle state.

The reduced one-electron Hamiltonian $\hat{H}_{TB}$ can be written as

$$\hat{H}_{TB} = \hat{T}_e + U_{ee} + U_{ei} \quad (3.12)$$

The wavefunctions $|\Psi_n\rangle$ can be approximated by linear combination

$$|\Psi_n\rangle = \sum_{l\alpha} c_{l\alpha}^n |\phi_{l\alpha}\rangle \quad (3.13)$$

where l is the quantum number index and α labels the ions. The computational load will increase significantly if the basis set, $|\phi_{l\alpha}\rangle$ is not orthogonal. However, it is possible to obtain a new orthogonal basis set $\{\varphi_{l\alpha}\}$ through the Löwdin transform

$$|\Psi_n\rangle = \sum_{l\alpha} b_{l\alpha}^n |\varphi_{l\alpha}\rangle \quad (3.14)$$

and orthogonal constraint,

$$\langle \varphi_{l'\beta} | \varphi_{l\alpha} \rangle = \delta_{l'l} \delta_{\alpha\beta} \quad (3.15)$$

Finally, we obtain the eigensystem

$$H' b^n = \varepsilon_n b^n \quad (3.16)$$

where $b^n = \{b_{l\alpha}^n\}$ and H' is the matrix elements of $\langle \varphi_{l'\beta} | \hat{H}_{TB} | \varphi_{l\alpha} \rangle$. Please note that the basis set $|\phi_{l\alpha}\rangle$ or $\{\phi_{l\alpha}\}$ are localized orbitals. This is different from the plane wave basis set in DFT which are global orbitals. Normally a local orbital basis set can be written as

$$|\varphi_{l\alpha}\rangle = \chi_l(\mathbf{r} - \mathbf{R}_\alpha) \quad (3.17)$$

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where $\mathbf{R}_\alpha$ is the position of the atom or ion. In order to simplify the notation, we let m denote both the quantum number l and site α , so that $m=1, \dots, N_{\text{basis}}$ labels all the states in the basis (N_{basis} is the total number of basis). Thus, we can write

$$|\varphi_{l\alpha}\rangle = \chi_m(\mathbf{r} - \mathbf{R}_m) \quad (3.18)$$

In order to take into consideration the symmetries of the basis orbitals, the appropriate choice for basis functions is a set of atomic-like functions centered on the atom sites. Each basis function can be written as the product of radial functions and spherical harmonics functions

$$|\varphi_{l\alpha}\rangle = \chi_l(\mathbf{r} - \mathbf{R}_\alpha) = \chi_{nlm}(\mathbf{r} - \mathbf{R}_\alpha) = \chi_{nl,\alpha}(r)Y_{lm}(\Omega_{\mathbf{r}}) \quad (3.19)$$

where n, l, m indicate quantum numbers. Real basis functions can also be defined using the real angular functions $S_{lm}^+ = \frac{1}{\sqrt{2}}(Y_{lm} + Y_{lm}^*)$ and $S_{lm}^- = \frac{1}{\sqrt{2}i}(Y_{lm} - Y_{lm}^*)$. These spherical harmonics functions can account for the s, p, d orbitals as well as their orientation along the bond axis (please refer to Figure 3.1). The implementation of spherical harmonics function will produce the two-center and three-center approximations in the evaluation of the $\langle \varphi_{l'\beta} | \hat{H}_{TB} | \varphi_{l\alpha} \rangle$ integrals. In the present TB approach, as all the integration are performed entirely in real space, and so periodicity is not necessary. Thus, the Bloch theorem is not applied here.

For the eigensystem in TB, the matrix elements $\langle \varphi_{l'\beta} | \hat{H}_{TB} | \varphi_{l\alpha} \rangle$ constitute the most important part of the TB model. We do not require the explicit forms of these basis set functions because we will approximate them as analytical functions of the atomic coordinates. The off-diagonal matrix elements $\langle \varphi_{l'\beta} | \hat{H}_{TB} | \varphi_{l\alpha} \rangle$, when $l'\beta \neq l\alpha$, are termed the hopping integrals, while the diagonal on-site elements $\langle \varphi_{l\alpha} | \hat{H}_{TB} | \varphi_{l\alpha} \rangle$ are termed the atomic orbital energies. The fitting procedure is carried out based on the following approximation:

- a) Only atomic orbitals whose energy is close to that of the energy bands of interest are considered, and this is the minimal basis set approximation. For

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instance, only the $2s$ (one orbital) and $2p$ (three orbitals: p_x , p_y , and p_z) orbitals are considered in the case of diamond or graphite and $3s$ and $3p$ orbitals for silicon, in order to describe the occupied (valence) bands. For these two materials there are only 16 possible hopping integrals. However, only hopping integrals between orbitals with similar angular momentum about the bond axis become non-vanishing. Thus, there remains only four nonzero hopping integrals namely $ss\sigma$, $sp\sigma$, $pp\sigma$, and $pp\pi$. σ ($m=0$) refers to orbitals with zero angular momentum about the bond axis while π ($m=\pm 1$) refers to orbitals with angular momentum ± 1 as shown in Figure 3.1.

Figure 3.1. The four fundamental hopping integrals between s and p orbitals. Positive and negative lobes are denoted by solid and dashed lines, respectively. Note that the sign of the p orbitals must be fixed by convention; the positive p_x lobe is along the positive x -axis, etc.

- b) the hopping integrals are cut off to zero for any interatomic distance, $|\mathbf{R}_\alpha - \mathbf{R}_\beta|$, larger than a given range due to the localized orbital. In order to reduce the number of parameters to be fitted, a cutoff distance which is inclusive of the nearest neighbors is appropriate. However, the orthogonalized (Löwdin) functions should extend further than those non-orthogonal from which they are derived, because the orthogonalization procedure involves orbitals of nearby atoms only. Thus, interactions extending beyond first nearest neighbors have to be considered when an orthogonal basis is used.
- c) Two-center approximation is used in the evaluation of the $\langle \phi_{l\beta} | \hat{H}_{TB} | \phi_{l\alpha} \rangle$ integrals. Slater and Koster (1954) proposed to neglect the three-center integrals and only account for the two-center integrals. The three-center integrals involve two orbitals located at two different atoms, as well as a

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potential component of the Hamiltonian due to a third atom. Thus, in the Slater and Koster's approach, only spherical potentials located on atom α or β are considered.

Generally, the reduced one-electron Hamiltonian $\hat{H}_{TB}$ consists of kinetic and potential terms and can be written as

$$\hat{H}_{TB} = -\frac{1}{2}\nabla^2 + \sum_{\mathbf{T}, \kappa, j} V^{\kappa} \left[\left| \mathbf{r} - (\boldsymbol{\tau}_{\kappa, j} + \mathbf{T}) \right| \right] \quad (3.20)$$

where the first term is the usual kinetic energy and the second term is the potential decomposed into a sum of spherical terms centered on each site κ, j in the unit cell. In a crystal, the atoms in a unit cell are at positions $\boldsymbol{\tau}_{\kappa, j}$, where $\boldsymbol{\tau}_{\kappa, j}$ is the position of $j=1, \dots, n^{\kappa}$ atoms of type κ . $\mathbf{T}$ in Equation (3.20) is a translation vector. However, these potential terms may depend upon the positions of other atoms. They can be divided into the following:

- One-center, where both orbitals and the potential are centered on the same site. These terms have the same symmetry as an atom in free space.
- Two-center, where the orbitals are centered on different sites and the potential is on one of the two. These terms have the same symmetry as other two-center terms. For Slater-Koster two-center approximation, the Hamiltonian matrix elements can be approximated with the two-center form and fitted to theoretical calculations (or empirical data).
- Three-center, where the orbitals and the potential are all centered on different sites. Presently, this three-center approximation is not applied.

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Figure 3.2. Calculation of the hopping integrals between two atoms. (a) 3-D representation. (b) Projection onto x - y plane. (c) Overlap between $2s$ orbitals centered on different atoms. (d) Overlap between s and p_x orbitals.

The matrix elements can be written as

$$\langle \varphi_{l\beta} | \hat{H}_{TB} | \varphi_{l\alpha} \rangle = \int d\mathbf{r} \chi_l(\mathbf{r} - \mathbf{R}_\beta) \hat{H}_{TB} \chi_l(\mathbf{r} - \mathbf{R}_\alpha) = h_{pq} \quad (3.21)$$

where p, q is the indices indicating the quantum number.

Now consider two atoms separated by a distance r as shown in Figure 3.2. For the sake of illustration, let them be carbon atoms with the $2s$ and $2p$ basis states on the first atom $|\varphi_{s,1}\rangle, |\varphi_{x,1}\rangle, |\varphi_{y,1}\rangle, |\varphi_{z,1}\rangle$ and on the second atom $|\varphi_{s,2}\rangle, |\varphi_{x,2}\rangle, |\varphi_{y,2}\rangle$ and $|\varphi_{z,2}\rangle$. Let the on-site matrix elements be (on-site means that orbitals localized on one and the same atom):

$$h_{qq} = E_s = \langle \varphi_{0\alpha} | \hat{H}_{TB} | \varphi_{0\alpha} \rangle \quad (3.22)$$

where q is the s orbital,

$$h_{qq} = E_p = \langle \varphi_{1\alpha} | \hat{H}_{TB} | \varphi_{1\alpha} \rangle \quad (3.23)$$

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where q is any of the p orbitals. E_s and E_p are empirical parameters that fit results of experiments or first-principle simulations.

Next we consider the off-diagonal matrix elements for s orbitals centered on different atoms which can be calculated as

$$h_{p_s q_s} = s(r)E_{s,s} = s(r)V_{ss} = \langle \varphi_{0\alpha} | \hat{H}_{TB} | \varphi_{0\beta} \rangle \quad (3.24)$$

where $s(r)$ is an analytic function which depends only on the atom separation as shown in Figure 3.2(c). V_{ss} is a parameter chosen to fit the reference system. This integrals are called hopping integrals due to the second-quantization formalism where the corresponding elements of the Hamilton matrix describe “hopping” of electrons between orbitals localized on different atoms.

For s and p_x orbitals centered on different atoms we get

$$h_{q_s q_{p_x}} = s(r)E_{s,x} = s(r)V_{sp\sigma}l' = \langle \varphi_{0\alpha} | \hat{H}_{TB} | \varphi_{1\beta} \rangle \quad (3.25)$$

where $l' = \cos(\theta_x) = x/r$ is the direction cosine of the vector between the atoms. l' reflects the anisotropy of p orbitals and the fact that the sign of the orbitals is different in different “leaves” of the orbitals (please refer to Figures 3.1 and 3.2). Thus, if $\theta_x = 90^\circ$ the overlap integral between the s and p_x orbitals is zero (please note that $2p$ spherical harmonics function change its sign at the origin). $V_{sp\sigma}$ is an empirical parameter that depends on the atom type.

As discussed above, all states except the s state have positive and negative lobes or “leaves”. Their sign must be fixed by convention where typically the positive lobe is assumed along the positive axis. Interchange of indices will lead to

$$V_{l'm} = (-1)^{l+l'} V_{l'm} \quad (3.26)$$

where l and l' are the orbital quantum numbers and m is the magnetic quantum number. Please note that σ -bond occurs for $m=0$ and π -bond occurs for $m=\pm 1$. For example,

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after the interchange of indices, the integral of s and p_x orbitals centered on different atoms is given as

$$V_{sp\sigma} = -V_{ps\sigma} \quad (3.27)$$

For s and p_x orbitals centered on-site we get

$$h_{q_s q_{p_x}} = 0 = \langle \varphi_{0\alpha} | \hat{H}_{TB} | \varphi_{1\alpha} \rangle \quad (3.28)$$

which is due to the cancellation of the positive and negative lobes.

For two p_x orbitals centered on different atoms we have

$$h_{p_x p_x} = s(r)E_{x,x} = s(r)[l'^2 V_{pp\sigma} + (1-l'^2)V_{pp\pi}] = \langle \varphi_{1\alpha} | \hat{H}_{TB} | \varphi_{1\beta} \rangle \quad (3.29)$$

As usual, $V_{pp\sigma}$ and $V_{pp\pi}$ are empirical parameters.

Similarly, all the overlap integrals for s and p orbitals can be expressed in terms of four non-zero parameters (as shown in Figure 3.1) and direction cosines $l'=x/r$, $m'=y/r$, $n'=z/r$. For instance,

$$h_{p_x p_y} = s(r)E_{x,y} = s(r)[l'm'V_{pp\sigma} - l'm'V_{pp\pi}] = \langle \varphi_{1\alpha} | \hat{H}_{TB} | \varphi_{1\beta} \rangle \quad (3.30)$$

$$h_{p_x p_z} = s(r)E_{x,z} = s(r)[l'n'V_{pp\sigma} - l'n'V_{pp\pi}] = \langle \varphi_{1\alpha} | \hat{H}_{TB} | \varphi_{1\beta} \rangle \quad (3.31)$$

$$h_{p_z p_z} = s(r)E_{z,z} = s(r)[n'^2 V_{pp\sigma} + (1-n'^2)V_{pp\pi}] = \langle \varphi_{1\alpha} | \hat{H}_{TB} | \varphi_{1\beta} \rangle \quad (3.32)$$

A complete list of hopping integrals can be found in Slater and Koster (1954).

Finally, the Schrödinger equation for the single-particle states becomes

$$\sum_{l'\beta} (\langle \varphi_{l'\beta} | \hat{H}_{TB} | \varphi_{l\alpha} \rangle - \varepsilon_n \delta_{ll'} \delta_{\alpha\beta}) c_{l'\beta}^n = 0 \quad (3.33)$$

Upon knowing the single-particle energies through solving Equation (3.33), the total potential energy of ion cores and valence electrons can be written as

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$$E_{tot} = \sum_n \varepsilon_n f(\varepsilon_n, T) + U_{ii} - U_{ee} = E_{bs} + U_{rep} \quad (3.34)$$

where $f(\varepsilon_n, T)$ is the Fermi-Dirac distribution functions (Please refer to Appendix C for details). The sum over all the single-particle energies is commonly named the band structure energy, E_{bs} . The U_{ee} term corrects the double counting of the electron-electron interactions in the first term. The last two terms constitute the effective repulsive potential, $U_{rep} = U_{ii} - U_{ee}$. This repulsive potential can be expressed as a sum of two-body potentials as

$$U_{rep} = U_{ii} - U_{ee} = \sum_i f \left(\sum_j \phi(r_{ij}) \right) \quad (3.35)$$

where r_{ij} is the distance between atoms located at i and j . This pairwise potential $\phi(r_{ij})$ between atoms at i and j , can be solved using the transferable TB potential introduced by Xu *et al.* (1992). Xu's model has successfully been used to calculate properties of various carbon structures. f is a functional expressed as a 4th-order polynomial with argument $\sum_j \phi(r_{ij})$. This pairwise potential is expressed as

$$\phi(r) = \phi_0 (d_0 / r)^m \exp \left\{ m \left[- (r / d_c)^{m_c} + (d_0 / d_c)^{m_c} \right] \right\} \quad (3.36)$$

The scaling function $s(r)$ for the Slater-Koster Hamilton matrix elements has the form

$$s(r) = (r_0 / r)^n \exp \left\{ n \left[- (r / r_c)^{n_c} + (r_0 / r_c)^{n_c} \right] \right\} \quad (3.37)$$

All the parameters in Equations (3.36) and (3.37), as well as the Slater-Koster parameters were determined by fitting first-principles results of energy versus nearest-neighbor interatomic separation for different carbon polytypes, namely diamond, graphite, linear chain, simple cubic and face-centered cubic structures. These parameters are listed in Table 3.1 and 3.2.

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Table 3.1 Parameters for the functions $s(r)$ and $\phi(r)$.

n	n_c	r_c (Å)	r_0 (Å)	r_1 (Å)
2.0	6.5	2.18	1.536329	2.45

ϕ_0 (eV)	m	m_c	d_c (Å)	d_0 (Å)	d_1 (Å)
8.18555	3.30304	8.6655	2.1052	1.64	2.57

Table 3.2 Coefficients of the polynomial functions $t_s(r-r_1)$, $t_\phi(r-d_1)$ and $f(x)$.

	$t_s(r-r_1)$	$t_\phi(r-d_1)$	$f(x)$
c_0	$6.7392620074314 \times 10^{-3}$	$2.2504290109 \times 10^{-8}$	-2.5909765118191
c_1	$-8.1885359517898 \times 10^{-2}$	$-1.4408640561 \times 10^{-6}$	0.5721151498619
c_2	0.1932365259144	$2.1043303374 \times 10^{-5}$	$-1.7896349903996 \times 10^{-3}$
c_3	0.3542874332380	$6.6024390226 \times 10^{-5}$	$2.3539221516757 \times 10^{-5}$
c_4			$-1.24251169551587 \times 10^{-7}$

In order to ease the computational intensity, scaling functions $s(r)$ and $\phi(r)$ were required to cutoff to zero smoothly at some designated cutoff distance. This was achieved by replacing the tails of $s(r)$ with a third-order polynomial $t_s(r-r_1)$ whose coefficients are determined by requiring the intersection between $s(r)$ and $t_s(r)$ at r_1 (match point, $r_1 \leq r_m$) to be smooth up to the first derivative, and $t_s(r)$ with its first derivative to be zero at r_m . The same procedure is used to determine $t_\phi(r-d_1)$ which replaces the tail of $\phi(r)$. The cutoff distances were chosen to be $r_m = d_m = 2.6$ Å (standard cutoff radius for carbon). The TB parameters are given in Table 3.3

Table 3.3 The TB parameters.

E_s	E_p	$V_{ss\sigma}$	$V_{sp\sigma}$	$V_{pp\sigma}$	$V_{pp\pi}$
-2.99 eV	3.71 eV	-5.0 eV	4.7 eV	5.5 eV	-1.55 eV

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The coefficients for the tail functions $t_s(r-r_1)$, $t_\phi(r-d_1)$ and polynomial function $f(x)$ are expressed as

$$t_s(r-r_1) = \sum_{n=0}^3 c_n (r-r_1)^n \quad (3.38)$$

$$t_\phi(r-d_1) = \sum_{n=0}^3 c_n (r-d_1)^n \quad (3.39)$$

and

$$f(x) = \sum_{n=0}^4 c_n x^n, \quad \text{with } x = \sum_j \phi(r_{ij}) \quad (3.40)$$

The coefficients for Equations (3.38) to (3.40) are given in Table 3.1 and 3.2.

When a suitable repulsive potential is added in the total energy expression of Equation (3.34), the TB method can be used for tight-binding molecular dynamics (TBMD) simulation. In our present TBMD scheme, the forces $\bar{f}_\alpha (\alpha = 1, 2, \dots, N_{at})$ that are required in the simulation can be calculated from the Hamiltonian function H_{TBMD} as

$$H_{TBMD} = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} + \sum_n \varepsilon_n f(\varepsilon_n, T) + U_{rep} \quad (3.41)$$

where p_{α} and m_{α} is the momentum and mass of the ion. The first term is the kinetic energy of the ions. The relaxation of energy is performed on H_{TBMD} .

The forces are thus given as

$$\bar{f}_{\alpha} = - \sum_n \langle \Psi_n | \frac{\partial \hat{H}_{TB}}{\partial \bar{r}_{\alpha}} | \Psi_n \rangle f(\varepsilon_n, T) - \frac{\partial U_{rep}}{\partial \bar{r}_{\alpha}} \quad (3.42)$$

It is found that the second term in Equation (3.42) is short ranged and can be solved analytically. The first term however is solved using the Hellmann-Feynman theorem

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$$\sum_n \langle \Psi_n | \frac{\partial \hat{H}_{TB}}{\partial \vec{r}_\alpha} | \Psi_n \rangle f(\epsilon_n, T) = -2 \sum_n f(\epsilon_n, T) \sum_{l\gamma} \sum_{l'\beta} c_{l'\beta}^n \frac{\partial \hat{H}_{l'\beta, l\gamma}(r_{\beta\gamma})}{\partial \vec{r}_\alpha} c_{l\gamma}^n \quad (3.43)$$

where

$$\hat{H}_{l'\beta, l\gamma}(r_{\beta\gamma}) = g(r_{\beta\gamma}) \langle \phi_{l'\beta} | \hat{H}_{TB} | \phi_{l\gamma} \rangle \Big|_{r_{\beta\gamma}=r_0} \quad (3.44)$$

and $g(r_{\beta\gamma})$ is a scaling function. It is important to note that the Hellmann-Feynman forces require the full set of eigen-system solutions and is therefore very compute intensive.

The TB simulation is summarized in the flow chart in Figure 3.3.

Figure 3.3. Flow chart of TB simulation.

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3.3 CONCLUSIONS

In this chapter, the Born-Oppenheimer approximation is presented which leads to the separation of electron and nuclei functions. The mean field potential in Schrödinger equation is further simplified into potential decomposition in the tight-binding (TB) method.

In the tight-binding method, the Schrödinger equation is further simplified by using the localized orbitals and the minimal basis set approximation. The empirical hopping integrals are cut off to zero for a certain interatomic distance due to localized orbitals. Generally, the hopping integrals are derived from real space integration of spherical harmonics functions. Two-center approximation is used in the evaluation of the hopping integrals significantly reducing the computational time. Finally, the forces of ions are calculated using the Hellmann-Feynman theorem.

CHAPTER FOUR

DENSITY-FUNCTIONAL THEORY

A different approach to the quantum many-body problem is provided by the density-functional theory (DFT) which was first proposed by Kohn and Sham (1965), and this enabled the determination of the ground-state properties of a system without having to deal with the many-body wavefunction. The DFT has long been the mainstay of electronic structure calculations in solid state physics, and has recently become popular in quantum chemistry. It also provides a useful balance between accuracy and computational cost, allowing much larger systems to be treated compared to using traditional *ab initio* methods. The DFT is not just another way of solving the Schrödinger equation. It is a completely different way of approaching an interacting problem, which is mapping it exactly to a much simpler non-interacting problem.

In this chapter, the basic Hohenberg-Kohn theorem is presented. It is the prerequisite theorem for the DFT that proves the uniqueness of the external potential through the ground state electronic density. The Bloch theorem is discussed which leads to implementation of FFT. The Kohn-Sham equation is briefly discussed with exchange-correlation potential using LDA or GGA. The implementation of plane waves as basis with Bloch's theorem further simplifies the complexity of the DFT. Using the frozen-core approximation, the DFT is yet further simplified by introducing pseudopotentials which replace the all-electron external potential. Next, the characteristics of reciprocal lattice and Brillouin zone will enhance the calculation by introducing reciprocal space integration and special points techniques. Finally, the solution of the Kohn-Sham equation for self-consistency is discussed.

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4.1 THE HOHENBERG-KOHN THEOREMS

According to the Born-Oppenheimer approximation, the Coulomb potential arising from the nuclei can be treated as a static external potential

$$V_{ext}(\mathbf{r}) = -\sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \quad (4.1)$$

The Hamiltonian for kinetic energy and electron-electron interaction potentials are given

$$\hat{F} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (4.2)$$

such that $\hat{H} = \hat{F} + \hat{V}_{ext}$, where

$$\hat{V}_{ext} = \sum_i V_{ext}(\mathbf{r}_i) \quad (4.3)$$

$\hat{F}$ takes the same form for all N -electron systems, so that the Hamiltonian, and hence the ground-state $|\Psi_0\rangle$, are entirely determined by N and $V_{ext}(\mathbf{r})$. The ground-state $|\Psi_0\rangle$ for this Hamiltonian results in a ground-state electronic density $n_0(\mathbf{r})$

$$n_0(\mathbf{r}) = \langle \Psi_0 | \hat{n} | \Psi_0 \rangle = \int \prod_{i=2}^N d\mathbf{r}_i |\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 \quad (4.4)$$

Both the ground-state $|\Psi_0\rangle$ and density $n_0(\mathbf{r})$ are functionals of the number of electrons N as well as the external potential $V_{ext}(\mathbf{r})$. Basically, the Hohenberg-Kohn theorem consists of two remarkable statements:

- The external potential $V_{ext}(\mathbf{r})$ is uniquely determined by the corresponding ground-state electronic density, to within an additive constant. Given

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$F[n] = \langle \Psi | \hat{F} | \Psi \rangle$ which is unique, then a functional for an arbitrary external potential $V(\mathbf{r})$, unrelated to $V_{ext}(\mathbf{r})$, and determined by $n(\mathbf{r})$, can be defined as

$$E_v[n] = F[n] + \int d\mathbf{r} V(\mathbf{r}) n(\mathbf{r}) \quad (4.5)$$

- For all v -representable¹ densities $n(\mathbf{r})$, $E_v[n] \geq E_0$ where E_0 is the ground-state energy for N electrons under the influence of the external potential $V(\mathbf{r})$.

In conclusion, the Hohenberg-Kohn theorem tells us that the electron density in principle contains all the information of the ground state wavefunction and that finding the ground state energy can be cast into a variational problem of minimizing the energy functional with respect to the density. The main advantage is that instead of having to deal with a function of $3N$ variables (the N -electron wavefunction) we can instead determine the ground state properties using just a function of three variables (the density). Thus, the complexity of the quantum mechanical problem is significantly reduced and, in principle, scales linearly with system size.

4.2 THE KOHN-SHAM EQUATION

Unfortunately, the exact form of the universal functional $F[n]$ introduced by Hohenberg-Kohn theorem is not known. This is due to the complexity of the interactions between the electrons in a many-electron system which makes it difficult to treat them as independent particles. Exchange and correlation effects must be taken into account and this is the aim of the Kohn-Sham method. In this method, the total energy functional $E[n]$ is given as

$$E[n] = T_s[n] + E_H[n] + E_{e-nuc}[n] + E_{xc}[n] + E_{nuc-nuc} \quad (4.6)$$

¹ A density $n(\mathbf{r})$ is v -representable if it is associated with an antisymmetric ground state wavefunction of some Hamiltonian H_e distinguished by a particular external potential $V(\mathbf{r})$.

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where T_s is the kinetic energy of the non-interacting electrons, E_H the Hartree energy, E_{e-nuc} the electron-nuclei energy, E_{xc} the exchange-correlation energy, and $E_{nuc-nuc}$ the nuclei-nuclei interaction energy. The classical Hartree energy is given as

$$E_H[n] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (4.7)$$

and the kinetic energy of non-interacting electron is

$$T_s[n] = -\frac{1}{2} \sum_i f_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \quad (4.8)$$

where f_i is the Fermi function². i is all occupation states.

The energy of the electron-nuclei and nuclei-nuclei interactions are respectively

$$E_{e-nuc}[n] = \int d\mathbf{r} V_{e-nuc}(\mathbf{r})n(\mathbf{r}), \quad \text{and} \quad E_{nuc-nuc} = \frac{1}{2} \sum_{(I,J), I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (4.9)$$

where Z_I and Z_J are the charges of the corresponding nuclei. V_{e-nuc} is also known as external potential $V_{ext}(\mathbf{r})$ which is the potential acting on the electrons due to the nuclei. For a free atom, external potential $V_{ext}(\mathbf{r})$ known as nuclear potential, $-Z/r$.

The minimization of the Kohn-Sham functional is obtained by varying the energy functional of Equation (4.6) for a fixed number of electrons with respect to the orbitals subject to the orthonormality constraints. Since T_s is explicitly expressed as a functional of the orbitals but all other terms are considered to be functionals of the density, we can vary the wavefunctions and use the chain rule to derive the variational equation

$$\frac{\delta E[n]}{\delta \psi_i^*(\mathbf{r})} = \frac{\delta T_s}{\delta \psi_i^*(\mathbf{r})} + \left[\frac{\delta E_{ext}}{\delta n} + \frac{\delta E_{Hartree}}{\delta n} + \frac{\delta E_{xc}}{\delta n} \right] \frac{\delta n(\mathbf{r})}{\delta \psi_i^*(\mathbf{r})} = 0 \quad (4.10)$$

We found that

$$\frac{\delta T_s}{\delta \psi_i^*(\mathbf{r})} = -\frac{1}{2} \nabla^2 \psi_i(\mathbf{r}); \quad \frac{\delta n(\mathbf{r})}{\delta \psi_i^*(\mathbf{r})} = \psi_i(\mathbf{r}) \quad (4.11)$$

² $f_i = f(\epsilon_i)$ is the occupation of state i where f is the Fermi function. Please refer to Appendix C for details.

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Using the Lagrange multiplier method, finally we get the Kohn-Sham equations that describes a system of non-interacting particles moving in an effective potential $V_{KS}(\mathbf{r})$, subject to one-electron Schrödinger equations

$$H_{KS}(\mathbf{r})\psi_i(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (4.12)$$

where $|\psi_i\rangle$ are the orthonormal single-particle states and ε_i the energies associated with states $i=1, \dots, N_{\text{states}}$ (total number of states). Please refer to Appendix D for details of variational method in Kohn-Sham equation. The electron-electron interaction is embedded in the effective potential. We note here that the effective potential is non-linear and a self-consistent approach is required. The density is therefore given by

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 \quad (4.13)$$

where f_i is the Fermi function for state i .

The Kohn-Sham potential $V_{KS}(\mathbf{r})$ is given by

$$V_{KS}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r}) \quad (4.14)$$

where the first term related to electrostatic or Hartree potential from electron-electron repulsion. The exchange-correlation potential $V_{xc}(\mathbf{r})$ is

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad (4.15)$$

Thus, through the Kohn-Sham scheme, the fully interacting problem can be mapped uniquely via the Hohenberg-Kohn theorem onto a fictitious system of non-interacting fermions³ with the same density.

³ Fermions are particles of odd half-integral spin which have wavefunctions that are antisymmetric to an exchange of any pair of them. Such particles, which include protons and neutrons as well as electrons obey the exclusion principle when they are in the same system.

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4.3 LOCAL DENSITY APPROXIMATION (LDA)

The problem of determining the functional form of the universal Hohenberg-Kohn density functional has now been transferred to just one unknown term, which is $V_{xc}(\mathbf{r})$. It is possible to make simple approximations for the exchange-correlation energy which can actually work very well, and the simplest of these is the local density approximation (LDA).

In the LDA, the contribution to the exchange-correlation energy from each infinitesimal volume in space, $d\mathbf{r}$, is equivalent to the value it would have if that entire space was filled with a homogeneous electron gas with the same density as is found in $d\mathbf{r}$ i.e.

$$E_{xc}[n] = \int d\mathbf{r} \varepsilon_{xc}(n(\mathbf{r}))n(\mathbf{r}) \quad (4.16)$$

where $\varepsilon_{xc}(n(\mathbf{r}))$ is the exchange-correlation energy per electron in a homogeneous electron gas environment with density $n(\mathbf{r})$. The exchange-correlation potential $V_{xc}(\mathbf{r})$ can be written in the form

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \varepsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r}) \frac{d\varepsilon_{xc}(n)}{dn} \bigg|_{n=n(\mathbf{r})} \quad (4.17)$$

A parameterisation procedure can then be employed to calculate the exchange-correlation energy for the homogeneous electron gas, Perdew and Zunger (1981).

4.4 GENERALIZED GRADIENT APPROXIMATION (GGA)

The LDA is motivated by the notion that the interaction between the electrons and the nuclei creates only weak inhomogeneities in the electron density. The LDA has been successfully employed in numerous important applications in solid state physics, including studies on semiconductors and metals. In many important chemistry

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applications, however, the electron density possesses sufficient inhomogeneities such that the LDA breaks down. One example is in hydrogen-bonded systems. In such cases, the LDA can be improved by adding an additional dependence on the lowest order gradients of the density which is known as the generalized gradient approximation (GGA). GGA denotes a variety of ways proposed for functions that modify the behavior at large gradients in such a way as to preserve the desired properties (see Perdew *et al.* 1992).

It is convenient to define a GGA as

$$E_{xc}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r} \quad (4.18)$$

where ε_{xc} at $\mathbf{r}$ depends on the density and its gradient plus higher terms at $\mathbf{r}$.

The corresponding exchange-correlation potential $V_{xc}(\mathbf{r})$ can then be written as

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \frac{\partial F_{xc}}{\partial n(\mathbf{r})} - \sum_{i=1}^3 \frac{\partial}{\partial \mathbf{r}_i} \left[\frac{\partial F_{xc}}{\partial (\partial_i n(\mathbf{r}))} \right] \quad (4.19)$$

where $F_{xc} = \varepsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) n(\mathbf{r})$ and $\partial_i n(\mathbf{r})$ is the i -component of the density gradient. Please refer to Appendix D for the Gâteaux-derivative of Euler-Lagrange equation in Banach space. The functionals have to be evaluated on a real space grid because they are only in the local real space, and not the Fourier space. Presently, we use the GGA functionals by Perdew *et al.* (1992).

4.5 PERIODIC SYSTEMS

An ordered state of matter in which the positions of the nuclei are repeated periodically in space results in a crystal. The elemental-types and nuclear-positions of the nuclei in one repeat unit (primitive unit cell), and the rules that describe the repetition (translations) completely specify a crystal. In the study of bulk crystals, the volume becomes infinite but periodic. Thus, it becomes necessary to reduce the problem to a finite periodic system. This approach is so advantages that it has even been employed to study aperiodic systems through the introduction of some false periodicity. The

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system is contained within a supercell which is then replicated periodically throughout the space. However, the supercell must be large enough in order to ensure there is no interaction between supercells.

4.5.1 Bloch Theorem

In a perfect crystal, the nuclei are arranged in a periodic array which can be described by a set of Bravais lattice vectors $\{\mathbf{R}\}$. Being infinite, the system is invariant under translation by any linear combination of these lattice vectors; in particular the potential is also periodic such that

$$V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r}) \quad (4.20)$$

for all Bravais lattice vectors $\mathbf{R}$.

The Schrödinger equation which describes the motion of a single particle in such a potential can therefore be written as

$$\hat{H}|\psi\rangle = \left[-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right]|\psi\rangle = \varepsilon|\psi\rangle \quad (4.21)$$

and the translation operators $\hat{T}_{\mathbf{R}}$ for each lattice vector $\mathbf{R}$ are defined as

$$\hat{T}_{\mathbf{R}}f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}) \quad (4.22)$$

Since the potential and hence the Hamiltonian⁴ are periodic, namely $\hat{H}(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})$, these operators will commute with the translation operators

$$\hat{T}_{\mathbf{R}}\hat{H}(\mathbf{r})\psi(\mathbf{r}) = \hat{H}(\mathbf{r} + \mathbf{R})\psi(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})\psi(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})\hat{T}_{\mathbf{R}}\psi(\mathbf{r}) \quad (4.23)$$

From Equation (4.23) it is obvious that both operators commute⁵, which is written as

$$[\hat{H}, \hat{T}_{\mathbf{R}}] = 0. \text{ In addition, the translation operators commute with each other}$$

⁴ Due to periodic system.

⁵ Two operators commute if, and only if

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0.$$

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$$\hat{T}_{\mathbf{R}}\hat{T}_{\mathbf{R}'} = \hat{T}_{\mathbf{R}'}\hat{T}_{\mathbf{R}} = \hat{T}_{\mathbf{R}+\mathbf{R}'} \quad (4.24)$$

According to the properties of commute operators, there exists a quantum number corresponding to each lattice vector $\mathbf{R}$, and it is feasible to select the eigenstates of the Hamiltonian to be simultaneous eigenstates of all the translation operators as shown here

$$\hat{H}|\psi\rangle = \varepsilon|\psi\rangle \quad (4.25)$$

$$\hat{T}_{\mathbf{R}}|\psi\rangle = c(\mathbf{R})|\psi\rangle \quad (4.26)$$

Using the commutation relations $\hat{T}_{\mathbf{R}}\hat{T}_{\mathbf{R}'} = \hat{T}_{\mathbf{R}+\mathbf{R}'}$ of the translation vectors, the eigenvalues must satisfy

$$c(\mathbf{R} + \mathbf{R}') = c(\mathbf{R})c(\mathbf{R}') \quad (4.27)$$

Now let $\mathbf{a}_i$ be three primitive vectors for the Bravais lattice. We can then write $c(\mathbf{a}_i)$ in the form

$$c(\mathbf{a}_i) = e^{2\pi i x_i} \quad (4.28)$$

As all the lattice vectors can be written in the form $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where n_i are integers, then it follows from Equation (4.27) that

$$c(\mathbf{R}) = c(\mathbf{a}_1)^{n_1} c(\mathbf{a}_2)^{n_2} c(\mathbf{a}_3)^{n_3} \quad (4.29)$$

which can be rewritten as

$$c(\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \quad (4.30)$$

$$\mathbf{k} = x_1\mathbf{g}_1 + x_2\mathbf{g}_2 + x_3\mathbf{g}_3 \quad (4.31)$$

We call this expression a commutator and can be written as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

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where $\{\mathbf{g}_i\}$ are the reciprocal lattice vectors⁶ which are required to satisfy $\mathbf{g}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$, and $\{x_i\}$ are in general vectors of complex numbers.

According to Equation (4.30), we obtain

$$\hat{T}_{\mathbf{R}}\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R}) = c(\mathbf{R})\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}}\psi(\mathbf{r}) \quad (4.32)$$

which is the Bloch theorem. Now consider the function $u(\mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{r}}\psi(\mathbf{r})$. We can write

$$u(\mathbf{r} + \mathbf{R}) = e^{-i\mathbf{k} \cdot [\mathbf{r} + \mathbf{R}]} \psi(\mathbf{r} + \mathbf{R}) = u(\mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{r}} \psi(\mathbf{r}) \quad (4.33)$$

which indicates that function $u(\mathbf{r})$ also possesses the lattice periodicity, and the wavefunction $\psi(\mathbf{r})$ can therefore be expressed as

$$\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}) \quad (4.34)$$

where $u(\mathbf{r})$ obeys the relationship $u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r})$.

As shown in Equation (4.34), the general wavefunction should be complex unless the vector $\mathbf{k}$ is set to zero. For clarity, we label the eigenstates of the Hamiltonian as $|\psi_{n\mathbf{k}}\rangle$ where n is the quantum number label of the different eigenstates of the Hamiltonian related to the corresponding quantum vector $\mathbf{k}$, and associated with the translational symmetry.

In terms of Fourier series⁷ expansion, we note that any periodic function can be expressed as

$$u(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \quad (4.35)$$

⁶ Reciprocal lattice vectors are derived from primitive translation vectors and are defined as

$$\mathbf{g}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{g}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}, \quad \mathbf{g}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}.$$

⁷ 3-D Fourier transforms are defined as

$$\tilde{n}(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}} \int_{\text{cell}} d\mathbf{r} e^{-i\mathbf{G} \cdot \mathbf{r}} n(\mathbf{r}); \quad n(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}.$$

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where $\mathbf{G}$ is the reciprocal lattice vector $\mathbf{G} = m_1\mathbf{g}_1 + m_2\mathbf{g}_2 + m_3\mathbf{g}_3$ and m_i are integers. We can now express the state $|\psi_{n\mathbf{k}}\rangle$ as a linear combination of plane-waves as shown below

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (4.36)$$

As a result, the solution for a wavefunction over infinite space now becomes the problem of solving for wavefunctions only within a single supercell. The transformation between real space and reciprocal space is important in the solution of the plane-waves, especially in the *ab initio* DFT.

4.6 PLANE WAVES AND GRIDS

Plane waves and grids provide general methodologies for the solution of differential equations including the Schrödinger equations. Plane waves are especially appropriate for periodic crystals which are amenable to simpler algorithms for practical calculations. Unlike the Gaussian basis set, the plane wave basis set produces a complete basis set. Plane waves can be expanded in terms of a set of Fourier components. Thus, the fast Fourier transform (FFT) can be introduced in the transformation between real space and reciprocal space. Besides the plane wave basis, the Slater Type Orbitals (STO) are also quite often used where its shape is close to the true orbitals of the hydrogen atom. However, the weakness of STO is that the calculation of inner product (or evaluation of integral) is expensive. The third generally used basis is the Gaussian Type Orbitals (GTO) where the evaluation of inner product is “cheaper”. However, its shape is different from the true orbital shape and it is not a complete space as well.

The eigenfunction of the Kohn-Sham equation is represented by a plane wave basis set as

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$$\psi_i(\mathbf{r}) = \sum_{\mathbf{q}} c_{i,\mathbf{q}} \frac{1}{\sqrt{\Omega}} e^{i\mathbf{q}\cdot\mathbf{r}} = \sum_{\mathbf{q}} c_{i,\mathbf{q}} |\mathbf{q}\rangle \quad (4.37)$$

where $c_{i,\mathbf{q}}$ are the expansion coefficients of the wavefunction in the basis of orthonormal plane waves $|\mathbf{q}\rangle$. $\mathbf{q}$ is the reciprocal space and $i=1,\dots,N_{\text{states}}$ (number of states, for pseudopotential it is number of valence electrons). These orthonormal plane waves $|\mathbf{q}\rangle$ must satisfy orthonormal condition

$$\langle \mathbf{q}' | \mathbf{q} \rangle = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{-i\mathbf{q}'\cdot\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} = \delta_{\mathbf{q},\mathbf{q}'} \quad (4.38)$$

Please refer to Appendix A for the proof of orthonormal condition.

Inserting Equation (4.37) into (4.12), and multiplying by $\langle \mathbf{q}' |$ followed by integrating in the supercell real space leads to the Schrödinger equation in Fourier space

$$\sum_{\mathbf{q}} \langle \mathbf{q}' | H_{KS} | \mathbf{q} \rangle c_{i,\mathbf{q}} = \varepsilon_i \sum_{\mathbf{q}} \langle \mathbf{q}' | \mathbf{q} \rangle c_{i,\mathbf{q}} = \varepsilon_i c_{i,\mathbf{q}'} \quad (4.39)$$

The matrix elements of the kinetic energy operator become

$$\langle \mathbf{q}' | -\frac{1}{2} \nabla^2 | \mathbf{q} \rangle = \frac{1}{2} |\mathbf{q}|^2 \delta_{\mathbf{q},\mathbf{q}'} \quad (4.40)$$

For a crystal or supercell, the potential $V_{KS}(\mathbf{r})$ is periodic and can be expressed as a sum of Fourier components

$$V_{KS}(\mathbf{r}) = \sum_m V_{KS}(\mathbf{G}_m) \exp(i\mathbf{G}_m \cdot \mathbf{r}) \quad (4.41)$$

where $\mathbf{G}_m$ are the reciprocal lattice vectors, and

$$V_{KS}(\mathbf{G}_m) = \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} V_{KS}(\mathbf{r}) \exp(-i\mathbf{G}_m \cdot \mathbf{r}) d\mathbf{r} \quad (4.42)$$

where Equations (4.41) and (4.42) are the inverse FFT and forward FFT respectively, and Ω_{cell} is the volume of the primitive cell. Thus the matrix elements of the potential become

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$$\begin{aligned}\langle \mathbf{q}' | V_{KS} | \mathbf{q} \rangle &= \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{-i\mathbf{q}' \cdot \mathbf{r}} \cdot e^{i\mathbf{q} \cdot \mathbf{r}} \sum_m V_{KS}(\mathbf{G}_m) e^{i\mathbf{G}_m \cdot \mathbf{r}} = \frac{1}{\Omega} \sum_m V_{KS}(\mathbf{G}_m) \int_{\Omega} d\mathbf{r} e^{-i\mathbf{q}' \cdot \mathbf{r}} e^{i\mathbf{q} \cdot \mathbf{r}} e^{i\mathbf{G}_m \cdot \mathbf{r}} \\ &= \sum_m V_{KS}(\mathbf{G}_m) \delta_{\mathbf{q}' - \mathbf{q}, \mathbf{G}_m}\end{aligned}\quad (4.43)$$

and it is non-zero only if $\mathbf{q}$ and $\mathbf{q}'$ differ by some reciprocal lattice vector $\mathbf{G}_m$. If we define

$$\mathbf{q} = \mathbf{k} + \mathbf{G}_m, \quad \mathbf{q}' = \mathbf{k} + \mathbf{G}_{m'} \quad (4.44)$$

then the Schrödinger equation for any given $\mathbf{k}$ can be written as the matrix equation

$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}) \quad (4.45)$$

where,

$$H_{m,m'}(\mathbf{k}) = \langle \mathbf{k} + \mathbf{G}_m | H_{KS} | \mathbf{k} + \mathbf{G}_{m'} \rangle = \frac{1}{2} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{KS}(\mathbf{G}_m - \mathbf{G}_{m'}) \quad (4.46)$$

The eigenvalues and eigenfunctions are labeled by $i=1,2,\dots, N_e$ (total number of electrons) for the discrete set of solutions of the matrix equation for a given $\mathbf{k}$. Equations (4.45) and (4.46) are the basic Schrödinger equations for a periodic crystal⁸.

According to the Bloch theorem in Equation (4.36), the eigenfunction solution of the Schrödinger equation (4.45), for a given $\mathbf{k}$ is given by Equation (4.37), with the sum over $\mathbf{q}$ restricted to $\mathbf{q} = \mathbf{k} + \mathbf{G}_m$

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_m c_{i,m}(\mathbf{k}) \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k} + \mathbf{G}_m) \cdot \mathbf{r}} = e^{i\mathbf{k} \cdot \mathbf{r}} \frac{1}{\sqrt{N_{cell}}} u_{i,\mathbf{k}}(\mathbf{r}) \quad (4.47)$$

where $\Omega = N_{cell} \Omega_{cell}$ and

$$u_{i,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{cell}}} \sum_m c_{i,m}(\mathbf{k}) e^{i\mathbf{G}_m \cdot \mathbf{r}} \quad (4.48)$$

which possesses the periodicity of the crystal. For the plane wave using Bloch theorem, $m=1,\dots, N_{pw}$ (total number of plane waves) and $i=1,\dots, N_e$ (total number of

⁸ Equations (4.45) and (4.46) are derived by interchanging the symbols.

$$\langle \mathbf{q} | V_{KS} | \mathbf{q}' \rangle = \sum_{m'} V_{KS}(\mathbf{G}_{m'}) \delta_{\mathbf{q} - \mathbf{q}', \mathbf{G}_{m'}} = \sum_{m'} V_{KS}(\mathbf{G}_{m'}) \delta_{\mathbf{G}_m - \mathbf{G}_{m'}, \mathbf{G}_{m'}} = \sum_{m'} V_{KS}(\mathbf{G}_m - \mathbf{G}_{m'})$$

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electrons to be calculated, for the pseudopotential it becomes the total number of valence electrons).

According to the Bloch theorem, any eigenvector is a product of $\exp(i\mathbf{k}\cdot\mathbf{r})$ and a periodic function. Since $\psi_{i,\mathbf{k}}(\mathbf{r})$ is orthonormal over the volume Ω , then $u_{i,\mathbf{k}}(\mathbf{r})$ should be orthonormal in a primitive cell

$$\frac{1}{\Omega_{cell}} \int_{cell} d\mathbf{r} u_{i,\mathbf{k}}^*(\mathbf{r}) u_{i',\mathbf{k}}(\mathbf{r}) = \sum_m c_{i,m}^*(\mathbf{k}) c_{i',m}(\mathbf{k}) = \delta_{i,i'}, \quad (4.49)$$

where the $c_{i,m}(\mathbf{k})$ are orthonormal vectors in the discrete index m of the reciprocal lattice vectors.

Calculation of electron density

One of the most important operations in the DFT is the calculation of the density of electrons, n . The electron density can be written as

$$n(\mathbf{r}) = \frac{1}{N_k} \sum_{\mathbf{k},i} f(\varepsilon_{i,\mathbf{k}}) n_{i,\mathbf{k}}(\mathbf{r}) \quad (4.50)$$

where,

$$n_{i,\mathbf{k}}(\mathbf{r}) = |\psi_{i,\mathbf{k}}(\mathbf{r})|^2 \quad (4.51)$$

Equation (4.50) is averaged over $\mathbf{k}$ points, with i denoting the bands at each $\mathbf{k}$ point and $f(\varepsilon_{i,\mathbf{k}})$ denoting the Fermi function. The total number of $\mathbf{k}$ points is denoted by N_k . For a plane wave basis, Equation (4.47), leads to

$$n_{i,\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{m,m'} c_{i,m}^*(\mathbf{k}) c_{i,m'}(\mathbf{k}) \exp(i(\mathbf{G}_{m'} - \mathbf{G}_m) \cdot \mathbf{r}) \quad (4.52)$$

and

$$n_{i,\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega} \sum_m c_{i,m}^*(\mathbf{k}) c_{i,m}(\mathbf{k}) \quad (4.53)$$

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where m'' refers to the $\mathbf{G}$ vector for which $\mathbf{G}_{m''} = \mathbf{G}_m + \mathbf{G}$. Equation (4.53) is derived from Fourier transform formulation. The symmetry operations of the supercell can be used to find the density in terms of only the $\mathbf{k}$ points (or simply k -points) in the irreducible Brillouin zone (IBZ) (to be discussed in Section 4.8).

4.7 PSEUDOPOTENTIALS

In the pseudopotential approach, only the valence electrons, which are chemically active, are considered explicitly. The inert core electrons are eliminated within the frozen-core approximation, being considered together with the nuclei as rigid non-polarizable ion cores. Angular momentum dependent pseudopotentials are then used to account for all electrostatic and quantum mechanical interactions of the valence electrons with the cores, such as the nuclear Coulomb attraction screened by the core electrons, and the Pauli repulsion and exchange and correlation between core and valence electrons. These replicate the true potential and valence orbitals exterior to a chosen core region but remain significantly weaker and smoother in the interior. Pseudopotentials effectively replace the electronic degrees of freedom in the Hamiltonian through an effective potential. This leads to the reduction of the number of electrons in the system thus enabling faster calculations and the treatment of larger molecular systems. The use of pseudopotentials thus considerably reduces the size of the basis set. Furthermore, valence states are generally smoother than core states and therefore require fewer basis functions for an accurate description.

Now, we construct the pseudopotentials from atomic wavefunctions. Let the wavefunctions $|\psi_c\rangle$ = core states and $|\psi_v\rangle$ = valence states, we get

$$\hat{H}|\psi_c\rangle = E_c|\psi_c\rangle \quad (4.54)$$

$$\hat{H}|\psi_v\rangle = E_v|\psi_v\rangle \quad (4.55)$$

Due to orthogonality condition,

$$\langle \psi_v | \psi_c \rangle = 0 \quad (4.56)$$

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and this leads to oscillations in wavefunctions $|\psi_v\rangle$. Mathematically, the oscillations in wavefunctions will increase the total number of wavefunctions in the numerical calculation making it very expensive. As a result, we try to obtain smooth pseudo valence wavefunctions $|\psi_v^{ps}\rangle$ from atomic valence wavefunctions, projecting away the oscillation components from $|\psi_v\rangle$.

Firstly, we define the pseudo wavefunction for the valence electrons as

$$|\psi_v^{ps}\rangle = |\psi_v\rangle + \sum_c |\psi_c\rangle \langle \psi_c | \psi_v^{ps} \rangle = |\psi_v\rangle + \sum_c |\psi_c\rangle \alpha_{cv} \quad (4.57)$$

Now we apply the pseudo wavefunction on the atomic Hamiltonian and obtain

$$\begin{aligned} \hat{H} |\psi_v^{ps}\rangle &= E_v |\psi_v\rangle + \sum_c E_c |\psi_c\rangle \alpha_{cv} \\ &= E_v |\psi_v^{ps}\rangle - E_v \sum_c |\psi_c\rangle \alpha_{cv} + \sum_c E_c |\psi_c\rangle \alpha_{cv} \\ &= E_v |\psi_v^{ps}\rangle + \sum_c (E_c - E_v) |\psi_c\rangle \alpha_{cv} \end{aligned} \quad (4.58)$$

Finally

$$\left\{ \hat{H} + \sum_c (E_v - E_c) |\psi_c\rangle \langle \psi_c| \right\} |\psi_v^{ps}\rangle = E_v |\psi_v^{ps}\rangle \quad (4.59)$$

The pseudo wavefunction fulfills the Schrödinger-like equation with a Hamiltonian that is dependent on energy and contains an additional repulsive nonlocal part. The new Hamiltonian can be written as

$$\hat{H}_{ps} = \hat{H} + \sum_c (E_v - E_c) |\psi_c\rangle \langle \psi_c| \quad (4.60)$$

Using the above Hamiltonian, we get

$$\hat{H}_{ps} |\psi_v^{ps}\rangle = E_v |\psi_v^{ps}\rangle \quad (4.61)$$

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in the pseudoatom condition. By comparing Equations (4.55) and (4.61), we note that both produce the same energies. The external potential acting on the pseudo valence electrons becomes

$$\hat{V}_{ps} = \hat{V}_{ext}^{core} + \sum_c (E_v - E_c) |\psi_c\rangle \langle \psi_c| \quad (4.62)$$

and the core potential is given

$$\hat{V}_{ext}^{core}(r) = \frac{-Z_v e^2}{r} \quad (4.63)$$

where $\hat{V}_{ps}$ is weaker than $\hat{V}_{ext}^{core}$. Z_v is the number of valence electrons in neutral atom. If we use atomic units, then $\hat{V}_{ext}^{core}(r) = -Z_v/r$. All the components $\hat{V}_{ps}$ at large r reduce to $-Z_v/r$, and become independent of angular momentum l . As a result, we can examine the pseudopotential in two regions:

- Within the core region ($0 \leq r \leq r_c$)

The core potential and atomic valence wavefunctions are substituted by pseudopotential $\hat{V}_{ps}$ and knot free pseudowavefunction ψ_v^{ps} .

- Outside the core region ($r > r_c$)

$$\psi_v^{ps} = \psi_v, \quad \hat{V}_{ps} = -\frac{Z_v}{r} \quad (4.64)$$

However, it is important to note that for both regions, the construction procedure keeps the energies of atomic and pseudoatomic states unchanged. The pseudopotential method is further refined by introducing the norm-conserving concept. In the final step, the pseudopotential is further simplified by the separation of the long-ranged local and short-ranged nonlocal components. Even though the nonlocal potential is more complex than a simple local potential, the fact that it is weaker and smoother has significant advantages, both conceptually and computationally since it can be expanded in just a small number of Fourier components.

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Norm-conserving Pseudopotentials

Pseudopotentials generated by calculations on atoms are termed “*ab initio*” because they are not fitted with empirical parameters. It simplifies the application of the pseudopotentials and it makes them more accurate and transferable. Norm-conserving pseudopotentials are normalized and are solutions of a model potential chosen to reproduce the valence properties of an all-electron calculation.

The first step involves the construction of the pseudopotentials in an all-electron calculation of the free atom in a reference state, usually its neutral ground state. The total energy of N electrons in an external potential $V_{\text{ext}}(\mathbf{r})$ (for an atom, it is the nuclear $-Z/r$ potential where Z is the charge on the nucleus) can be represented as a functional of the electron density n ,

$$E^{\text{tot}}[n] = T_s[n] + E_{\text{xc}}[n] + E_H[n] + \int -\frac{Z}{r} n(\mathbf{r}) d\mathbf{r} \quad (4.65)$$

where $T_s[n]$ is the non-interacting kinetic energy, $E_{\text{xc}}[n]$ the exchange and correlation energy, and $E_H[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$ the electrostatic or Hartree energy from the electron-electron repulsion. The ground state corresponds to the minimum of $E^{\text{tot}}[n]$, and is found from the self-consistent solution of the Kohn-Sham equations

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{KS}}(n; \mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (4.66)$$

$$V_{\text{KS}}(n; \mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) \quad (4.67)$$

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \quad \int n(\mathbf{r}) d\mathbf{r} = N \quad (4.68)$$

$$f_i = 1 \text{ if } \varepsilon_i \leq \varepsilon_N, \quad 0 \leq f_i \leq 1 \text{ if } \varepsilon_i = \varepsilon_N, \quad \text{and } f_i = 0 \text{ if } \varepsilon_i > \varepsilon_N \quad (4.69)$$

where f_i is the Fermi function for state i . For a free atom environment, the electron density behaves in a spherically symmetric manner. Since the potential acting on the electron is spherically symmetric, we can write

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$$V_{ext}(\mathbf{r}) = V_{ext}(r) = -Z/r \quad (4.70)$$

where Z is the charge on the nucleus.

Here, we introduce a new wavefunction

$$\psi_i(\mathbf{r}) = [u_{nl}(\varepsilon_i; r)/r] Y_{lm}(\Omega_r) \quad (4.71)$$

where $Y_{lm}(\Omega_r)$ are spherical harmonics functions (please refers to Appendix B for details). Using the Laplacian in spherical coordinates (please refers to Appendix B), and substituting Equation (4.71) into Equation (4.66), we obtain

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{KS}(r) - \varepsilon_i \right] u_{nl}(\varepsilon_i; r) = 0 \quad (4.72)$$

Due to the spherical symmetry, the effective all-electron potential is thus simplified as

$$V_{KS}(n; \mathbf{r}) = V_{KS}(r) = V_{XC}[n; r] + V_H[n; r] - \frac{Z}{r} \quad (4.73)$$

where the exchange-correlation potential is

$$V_{XC}[n; r] = \frac{\delta E_{XC}(n)}{\delta n(r)} \quad (4.74)$$

and the Hartree potential becomes

$$V_H[n; \mathbf{r}] = V_H[n; r] = \frac{\delta E_H(n)}{\delta n(r)} = 4\pi \frac{1}{r} \int_0^r n(r') r'^2 dr' + 4\pi \int_r^\infty n(r') r' dr' \quad (4.75)$$

Relativistic effects are treated by using a scalar-relativistic kinetic energy operator as introduced by Koelling and Harmon (1977). The radial wavefunction u_{nl} then become the self-consistent eigenfunctions of the scalar-relativistic Schrödinger equation

$$\left[\frac{1}{M(r)} \left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{4M(r)c^2} \frac{dV_{KS}(r)}{dr} r \frac{d}{dr} \frac{1}{r} + \frac{l(l+1)}{2r^2} \right) + V_{KS}(r) - \varepsilon_i \right] u_{nl}(\varepsilon_i; r) = 0 \quad (4.76)$$

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where the relativistic electron mass is given as $M(r) = 1 + (\varepsilon_i - V_{KS}(r))/2c^2$, and the finestructure constant is $1/c = 1/137.036$. The scalar-relativistic Schrödinger equation is transformed into the nonrelativistic Schrödinger equation by setting the finestructure constant, $1/c$, to zero.

Having obtained the all-electron potential and valence states, we employ the approach by Hamann (1989) or Troullier and Martins (1991) for constructing the intermediate screened pseudopotential. It is an effective potential for the pseudo valence states

$$\psi_{lm}^{ps}(\mathbf{r}) = [u_l^{ps}(\varepsilon_l^{ps}; r)/r] Y_{lm}(\Omega_r) \quad (4.77)$$

where the radial part for the angular momentum l represents the lowest eigenfunction of the nonrelativistic Schrödinger equation

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l^{ps,scr}(r) - \varepsilon_l^{ps} \right] u_l^{ps}(\varepsilon_l^{ps}; r) = 0 \quad (4.78)$$

Initially, a radial pseudo wavefunction $u_l^{ps}(r)$ is derived from the all-electron valence level with angular momentum l such that

- The pseudo wavefunction and the all-electron wavefunction have the same eigenvalue

$$\varepsilon_l^{ps} = \varepsilon_{nl} \quad (4.79)$$

and their logarithmic derivatives and potentials are similar beyond a chosen core cutoff radius r_l^c ,

$$\frac{d}{dr} \ln u_l^{ps}(\varepsilon_l^{ps}; r) \rightarrow \frac{d}{dr} \ln u_{nl}(\varepsilon_{nl}; r) \quad \text{for } r > r_l^c \quad (4.80)$$

- The radial pseudo wavefunction has the same amplitude as the all-electron wavefunction beyond the core cutoff radius,

$$u_l^{ps}(\varepsilon_l^{ps}; r) \rightarrow u_{nl}(\varepsilon_{nl}; r) \quad \text{for } r > r_l^c \quad (4.81)$$

and is normalized as

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$$\int_0^\infty |u_l^{ps}(\varepsilon_l^{ps}; r)|^2 dr = \int_0^\infty |u_{nl}(\varepsilon_{nl}; r)|^2 dr = 1 \quad (4.82)$$

This implies the following norm-conservation constraint condition

$$\int_0^{r'} |u_l^{ps}(\varepsilon_l^{ps}; r)|^2 dr = \int_0^{r'} |u_{nl}(\varepsilon_{nl}; r)|^2 dr \quad \text{for } r' \geq r_l^c \quad (4.83)$$

- The pseudo wavefunction does not consist of any radial nodes. A continuous pseudopotential which is regular at the origin should be twice differentiable and complies with

$$\lim_{r \rightarrow 0} u_l^{ps}(r) \propto r^{l+1} \quad (4.84)$$

The wavefunction outside the radius r_l^c is the same as the true function (all-electron function) and at r_l^c it is matched to a parameterized analytic function. Since the energy ε is fixed (often it is the eigenvalue from the all-electron calculation, but this is not essential) it is straightforward to rearrange the Schrödinger equation for a nodeless function for each l separately as

$$V_l^{ps,scr}(r) = \varepsilon_l^{ps} - \frac{l(l+1)}{2r^2} + \frac{1}{2u_l^{ps}(r)} \frac{d^2}{dr^2} u_l^{ps}(r) \quad (4.85)$$

The assumption for the radial function $u_l^{ps}(r)$ at energy ε_l^{ps} requires three coefficients to fulfill the above constraints. The spatial radial functions are knot free and twice differentiable. The Hamann scheme is of this minimal type, while the Troullier-Martins scheme requires additional constraints, whereby the pseudopotential's curvature vanish at the origin. In addition, the first four derivatives of the pseudo and all-electron wavefunction coincide at the core cutoff radius. Both schemes differ somewhat technically with regard to the radii where the pseudo wavefunctions and pseudopotentials match their all-electron results. In the Troullier-Martins scheme, the pseudo wavefunction in the core region ($r < r_l^c$) can be written as

$$u_l^{ps}(r) = r^{l+1} \exp[p_l(r^2)] \quad (4.86)$$

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where p_l is a polynomial of 6th-order.

In general, increasing r_l^c results in softer pseudopotentials, which converge faster in a plane wave basis. However, it will become less transferable as the pseudo wavefunctions become less accurate at radii associated with bonding. When setting the value of r_l^c , it cannot be lower than the radius of the outermost radial node in the respective all-electron orbital.

The final ionic pseudopotentials are obtained by subtracting the electrostatic and the exchange-correlation screening contributions (due to the valence electrons⁹), from the screened pseudopotentials

$$V_l^{ps}(r) = V_l^{ps,scr}(r) - V_H[n_v^{ps};r] - V_{xc}[n_v^{ps};r] \quad \text{with} \quad n_v^{ps}(r) = \frac{1}{4\pi} \sum_{l=0} f_l \left| \frac{u_l^{ps}(\varepsilon_l^{ps};r)}{r} \right|^2 \quad (4.87)$$

and for atomic density we have

$$n(\mathbf{r}) = n_c + n_v \quad (4.88)$$

where n_c is the core electron density and n_v the valence electron density.

Although E_{xc} is a nonlinear functional of the total electron density n , the above linearization of its core-valence contribution is a common and usually sufficient approximation for calculations within both LDA and GGA.

With the ionic pseudopotential (substituting external potential $V_{ext}(\mathbf{r})$), the iterative solution of Kohn-Sham equation will produce the eigenvalues of valence electrons only thus reducing the computational time. The weakness of norm conservation is nonlocality, i.e., the ionic pseudopotential is dependent on the angular momentum l .

⁹ As shown in Appendix B, $\sum_{m=-l}^l [Y_{lm}(\theta, \phi)]^2 = \frac{2l+1}{4\pi}$. Thus, due to orthogonal condition we obtain

$$\sum_{l=0} \sum_{m=0} \left| \frac{u_l^{ps}}{r} Y_{lm} \right|^2 = \sum_{l=0} \left| \frac{u_l^{ps}}{r} \right|^2 |Y_{lm}|^2 = \sum_{l=0} \left| \frac{u_l^{ps}}{r} \right|^2 \frac{1}{4\pi} = \frac{1}{4\pi} \sum_{l=0} \left| \frac{u_l^{ps}}{r} \right|^2.$$

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In general to generate the *ab initio* pseudopotential, the Kohn-Sham equations for the isolated atom are firstly solved with an all-electron technique in order to obtain the all-electron potential and valence wavefunctions. Then within a selected scheme (Hamann or Troullier-Martins scheme) an intermediary screened pseudopotential is created by inverting the Schrödinger equation for the radial pseudo wavefunctions. These wavefunctions are subject to the above-mentioned cutoff requirements plus norm-conservation. Finally the intermediary potential is unscreened by subtracting the exchange-correlation and the Hartree contribution of the valence shell. In order to further reduce computational effort, the semilocal part of the constructed pseudopotential is brought to a fully nonlocal (both in the angular momentum l and in the $\mathbf{r}$ coordinate) separable form suggested by Kleinman and Bylander (1982). In transforming a semilocal to the corresponding Kleinman-Bylander (KB) pseudopotential, it is necessary to ensure that the KB-form does not lead to unphysical “ghost” states at energies close to or below those of the physical valence states as these would adversely affect its transferability. Such false states can occur if unfavorable choices are made for the underlying semilocal and local pseudopotentials. Ghost states can be averted through the use of more than one reference state or an appropriate choice of the local component and cutoff radii in the semilocal pseudopotentials. The appearance of ghost states can be analyzed by investigating the following properties:

- Discrepancies between the logarithmic derivatives of the energy of the KB-pseudopotential and those of the respective semilocal pseudopotential or all-electron potential.
- Ghost states below the valence states have been identified through a rigorous criteria by Gonze *et al.* (1991).

The transferability of carbon which is of interest in this thesis has been tested and the ghost states have been eliminated. The logarithmic derivative graphs have been generated in Figures 4.1-4.3 for verification.

A ghost state is indicated by a marked deviation of the logarithmic derivatives of the KB-pseudopotential from those of the respective semilocal pseudopotential or all-

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electron potential. Figures 4.1-4.3 show a good transferability (no ghost state) and without significant deviation.

A requirement when the checking the transferability is to carry out the Gonze’s ghost state criteria test and plot the logarithmic derivatives of the s , p and d orbitals. Figures 4.1-4.3 indicate that the pseudopotential and all-electron logarithmic derivatives are in close agreement in the vicinity of the atomic valence eigenvalues. Furthermore, as expected, there are some discrepancies for excited configurations. The ghost states below the valence states are identified by a rigorous criterion by Gonze *et al.* (1991) as shown in Table 4.1. Currently the d -component is set as the local potential.

Table 4.1. Gonze’s criteria analysis of pseudopotential.

Analysis of KB potentials: s orbital		Analysis of KB potentials: p orbital	
KB energy	54.6667 eV	KB energy	-41.1747 eV
local potential groundstate	-32.6757 eV	local potential groundstate	-2.6210 eV
reference energy	-13.6395 eV	reference energy	-5.4159 eV
1 st excited state	-0.9976 eV	1 st excited state	0.0 eV
Criteria for Nonexistence of ghost state: KB energy > 0; Local potential groundstate < reference energy < 1 st excited state Conclusion : No ghost state		Criteria for Nonexistence of ghost state: KB energy < 0; Reference energy < local potential groundstate Conclusion : No ghost state	

The final form of the pseudopotential can be generalized in terms of local and nonlocal parts using an operator for every l as

$$V_l^{ps}(\mathbf{r}) = V^{loc}(\mathbf{r}) + \delta V_l^{sl}(\mathbf{r}) = V^{loc}(\mathbf{r}) + \sum_{l=0}^{l_{\max}} V_l^{ps, nl}(\mathbf{r}) \hat{P}_l \quad (4.89)$$

$$\hat{P}_l |\psi(\mathbf{r})\rangle = \sum_{m=-l}^l \langle Y_{lm}(\Omega_{\mathbf{r}}) | \psi(\mathbf{r}) \rangle Y_{lm}(\Omega_{\mathbf{r}}) \quad (4.90)$$

They are nonlocal because it is usually impossible to mimic the effect of orthogonalization to core states on different angular momentum l with a single function.

The above pseudopotentials are set up and derived in terms of an angular momentum dependent, semilocal operator $\delta V^{sl}(\mathbf{r})$. The local pseudopotential is $V^{loc}(\mathbf{r})$ and is then

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taken as one of the semilocal pseudopotential components, $V^{loc}(\mathbf{r}) = V_{l=l_{loc}}^{ps}(\mathbf{r})$, and $\delta V_l^{sl}(\mathbf{r}) = V_l^{ps}(\mathbf{r}) - V_{l_{loc}}^{ps}(\mathbf{r})$ vanishes beyond r_l^c (the cutoff radius in angular momentum l), and we get $V^{loc}(\mathbf{r}) \cong -Z_v e^2/r$ for large r (beyond r_l^c). Typically one truncates the expansion at $l_{max} = 2$ (the maximum angular momentum), whereby the core effects on the valence states with the same symmetries as the core states are accounted for. The number of projections is reduced most if we pick the $l_{loc} = l_{max}$ component as local potential (l_{loc} is the local angular momentum)

$$V^{loc}(\mathbf{r}) = V_{l_{loc}}^{ps}(\mathbf{r}) = V_{l_{max}}^{ps}(\mathbf{r}) \quad (4.91)$$

Here, we use $l_{loc} = l_{max} = 2$, which is the common practice for sp -type materials like carbon and silicon.

Figure 4.1. Transferability tests of the carbon for the s orbital.

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Figure 4.2. Transferability tests of the carbon for the p orbital.

Figure 4.3. Transferability tests of the carbon for the d orbital.

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4.8 RECIPROCAL SPACE INTEGRATION AND SPECIAL POINTS TECHNIQUES

Before we proceed to reciprocal space integration, we will briefly discuss the supercell approximation. By a simple calculation, we find that plane waves are eigenfunctions of the kinetic energy operator

$$\frac{1}{2} \nabla^2 e^{i\mathbf{G}\cdot\mathbf{r}} = -\frac{1}{2} |\mathbf{G}|^2 e^{i\mathbf{G}\cdot\mathbf{r}} \quad (4.92)$$

Based on the eigenfunction in Equation (4.47)

$$\frac{1}{2} \nabla^2 e^{i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}} = -\frac{1}{2} |\mathbf{k} + \mathbf{G}_m|^2 e^{i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}} \quad (4.93)$$

Theoretically, the Bloch states can be expanded in plane waves with the sum runs over an infinite number of Bravais $\mathbf{G}$ -vectors of the reciprocal lattice. In practice, however as shown in Equation (4.93), one uses a truncated plane-wave expansion to include N_{PW} (total number of plane waves) terms with kinetic energies only up to certain cutoff E_{cut} ,

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{cut} \quad (4.94)$$

where $\mathbf{k}$ is the reciprocal space. The truncation of the plane-wave basis due to the Kohn-Sham potential V_{KS} shows faster rate of convergence with increasing modulus of $\mathbf{G}$. The plane-wave energy cutoff is dependent on the transferability of the pseudopotentials when ghost states have been eliminated. This cutoff energy is calculated to be approximately 30.0 Rydberg.

Finally, the plane wave basis in Equation (4.47) can be written as

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}_m, \frac{1}{2}|\mathbf{k}+\mathbf{G}_m|^2 \leq E_{cut}} c_{i,m}(\mathbf{k}) \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}} \quad (4.95)$$

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where the wavevector $\mathbf{k}$ is a vector in the Brillouin zone¹⁰.

The Reciprocal Lattice and Brillouin Zone

Consider any periodic function $f(\mathbf{r})$ defined for a crystal, such as the density of the electrons, which is similar in each unit cell

$$f(\mathbf{r}+\mathbf{T}(n_1, n_2, n_3)) = f(\mathbf{r}) \quad (4.96)$$

where $\mathbf{T}$ is any translation operator. It is well-known that such a periodic function can be represented by Fourier transforms in terms of Fourier components at wavevectors $\mathbf{q}$ defined in reciprocal space. Let us then consider that the large volume of crystal Ω_{crystal} (entire crystal) is composed of $N_{\text{cell}}=N_1 \times N_2 \times N_3$ cells. Then each component must satisfy the Born-Von Karmen periodic boundary conditions in each of the dimensions

$$\exp(i\mathbf{q} \cdot N_1 \mathbf{a}_1) = \exp(i\mathbf{q} \cdot N_2 \mathbf{a}_2) = \exp(i\mathbf{q} \cdot N_3 \mathbf{a}_3) = 1 \quad (4.97)$$

so that $\mathbf{q}$ is restricted to the set of vectors satisfying $\mathbf{q} \cdot \mathbf{a}_i = 2\pi m / N_i$ ($m=\text{integer}$) for each of the primitive vectors $\mathbf{a}_i$.

The Fourier transform into $\mathbf{q}$ space is therefore

$$f(\mathbf{q}) = \frac{1}{\Omega_{\text{crystal}}} \int_{\Omega_{\text{crystal}}} d\mathbf{r} f(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) \quad (4.98)$$

which, for periodic functions, can be written as

$$\begin{aligned} f(\mathbf{q}) &= \frac{1}{\Omega_{\text{crystal}}} \sum_{n_1, n_2, n_3} \int_{\Omega_{\text{cell}}} d\mathbf{r} f(\mathbf{r}) e^{i\mathbf{q} \cdot (\mathbf{r} + \mathbf{T}(n_1, n_2, n_3))} \\ &= \frac{1}{N_{\text{cell}}} \sum_{n_1, n_2, n_3} e^{i\mathbf{q} \cdot \mathbf{T}(n_1, n_2, n_3)} \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} d\mathbf{r} f(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} \end{aligned} \quad (4.99)$$

The sum over all lattice points in the middle line vanishes for all $\mathbf{q}$ except those which fulfill the relationship, $\mathbf{q} \cdot \mathbf{T}(n_1, n_2, n_3) = 2\pi m$ ($m=\text{integer}$) for all translation $\mathbf{T}$. $\mathbf{T}(n_1, n_2, n_3)$ is defined as sum of integer multiples of the primitive translations $\mathbf{a}_i$, and it indicates

¹⁰ Brillouin zone (BZ) or first Brillouin zone is the volume of the primitive cell in the reciprocal lattice. If $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are reciprocal lattice vectors, then $\Omega_{\text{BZ}} = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|$.

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that $\mathbf{q} \cdot \mathbf{a}_i = 2\pi m$. Please refer to Appendix E for the further elaboration of Equation (4.99).

The set of Fourier components of $\mathbf{q}$ that satisfy the above condition is called the “reciprocal lattice”. Here we define the vectors $\mathbf{b}_i$, $i=1,\dots,d$ (d is the dimension) that are reciprocal to the primitive translations $\mathbf{a}_i$ as

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad (4.100)$$

and we can therefore obtain $f(\mathbf{q})$, the only non-zero Fourier components of $f(\mathbf{r})$ when $\mathbf{q}=\mathbf{G}$, where the $\mathbf{G}$ vectors are a lattice of points in reciprocal space defined by

$$\mathbf{G}(m_1, m_2, \dots) = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + \dots m_d\mathbf{b}_d \quad (4.101)$$

and m_i are integers. For each $\mathbf{G}$, the Fourier transform of the periodic function can be written as

$$f(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} d\mathbf{r} f(\mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (4.102)$$

The unit cell is closely related to Brillouin zone. The first Brillouin zone (denoted as simply the “Brillouin zone” or BZ) is the Wigner-Seitz cell of the reciprocal lattice, which is defined by the planes that are the perpendicular bisectors of the vectors from the origin to the reciprocal lattice points. The well-known Bragg condition is satisfied for elastic scattering on these planes. For incident particles with wavevectors inside the BZ there can be no Bragg scattering.

Reciprocal space integration and special points techniques

In the Kohn-Sham calculation scheme, there is a need to determine the valence electron density, and the band-structure energy whereby

$$n(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k}, i} f(\varepsilon_{i,\mathbf{k}}) |\psi_{i,\mathbf{k}}(\mathbf{r})|^2 = \frac{1}{N} \sum_v^{N_v} \sum_{\mathbf{k} \in \text{BZ}}^N f(\varepsilon_{i,\mathbf{k}}) |\psi_{i,\mathbf{k}}(\mathbf{r})|^2 \quad (4.103)$$

and

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$$E_{band} = \frac{1}{N} \sum_v \sum_{\mathbf{k} \in BZ}^N \mathcal{E}_{v,\mathbf{k}} \quad (4.104)$$

where we have to sum over an infinite number of wavevectors $\mathbf{k}$ for each state i . v and N_v denote the index of the valence electron and total number of valence electrons respectively. The wavevector $\mathbf{k}$ (or $\mathbf{q}$) is expressed as

$$\mathbf{k} = \frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3 = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 \quad (4.105)$$

where n_i are integers, ranging from 0 to N_i-1 . There is exactly the same number of values of $\mathbf{k}$ as the number of cells, $N_1 \times N_2 \times N_3$ (N or N_k). In a large crystal of volume $\Omega_{crystal}$ composed of N cells, then there is exactly one wavevector $\mathbf{k}$ for each cell. Thus in a sum over states to find an intrinsic property of a crystal expressed as “per unit cell” we can simply has a sum over values of $\mathbf{k}$ divided by the number of cells N . For a general function $f_i(\mathbf{k})$, where i denotes any of the discrete set of states at each $\mathbf{k}$, the average value per cell becomes

$$\bar{f}_i = \frac{1}{N} \sum_{\mathbf{k}} f_i(\mathbf{k}) = \frac{1}{N_1 N_2 N_3} \sum_{\mathbf{k}} f_i(\mathbf{k}) \quad (4.106)$$

According to Equation (4.105), we obtain

$$\begin{aligned} \Delta \mathbf{k} &= \left(\Delta \frac{n_1}{N_1} \right) \mathbf{b}_1 + \left(\Delta \frac{n_2}{N_2} \right) \mathbf{b}_2 + \left(\Delta \frac{n_3}{N_3} \right) \mathbf{b}_3 = \frac{1}{N_1} \mathbf{b}_1 + \frac{1}{N_2} \mathbf{b}_2 + \frac{1}{N_3} \mathbf{b}_3 \\ &= \Delta \mathbf{k}_1 + \Delta \mathbf{k}_2 + \Delta \mathbf{k}_3 \end{aligned} \quad (4.107)$$

Following the approach in Appendix A, we obtain

$$\begin{aligned} dk^3 &= d\mathbf{k} = |(\Delta \mathbf{k}_1) \cdot (\Delta \mathbf{k}_2) \times (\Delta \mathbf{k}_3)| = |\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3| \frac{1}{N_1 N_2 N_3} \\ &= \Omega_{BZ} \frac{1}{N_1 N_2 N_3} \end{aligned} \quad (4.108)$$

Following the PBC averaging technique shown in Appendix F, we can derive

$$\bar{f}_i = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} f_i(\mathbf{k}) \frac{1}{N_1 N_2 N_3} = \sum_{\mathbf{k}_1=0}^{\frac{N_1-1}{N_1} \mathbf{b}_1} \sum_{\mathbf{k}_2=0}^{\frac{N_2-1}{N_2} \mathbf{b}_2} \sum_{\mathbf{k}_3=0}^{\frac{N_3-1}{N_3} \mathbf{b}_3} f_i(\mathbf{k}) \frac{1}{\Omega_{BZ}} \Delta k^3 \quad (4.109)$$

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In the thermodynamic limit ($N \rightarrow \infty$) the discrete sums are replaced by integrals over the BZ,

$$\begin{aligned}\bar{f}_i &= \int_{\mathbf{k}_1=0}^{b_1} \int_{\mathbf{k}_2=0}^{b_2} \int_{\mathbf{k}_3=0}^{b_3} f_i(\mathbf{k}) \frac{1}{\Omega_{BZ}} d\mathbf{k}^3 = \frac{1}{\Omega_{BZ}} \int_{BZ} f_i(\mathbf{k}) d\mathbf{k} \\ &= \frac{\Omega_{cell}}{(2\pi)^3} \int_{BZ} f_i(\mathbf{k}) d\mathbf{k}\end{aligned}\quad (4.110)$$

Equation (4.110) effectively performs an average over the BZ of the $\mathbf{k}$ -dependent functions.

The wavevector $\mathbf{k}$ in the Equation (4.47) is restricted to the BZ. In the infinite periodic system, which is a natural choice for solids and liquids, the plane wave basis sets obey the Bloch theorem that finally leads to averaging over the BZ.

It is possible to approximate the integral over the BZ by using a selected set of $\mathbf{k}$ -points, using both the space group of the crystal and sampling of the BZ. Due to the group symmetry, the sum over $\mathbf{k}$ can be restricted to the irreducible part of the BZ (IBZ), and we then sample this zone with a special point technique.

If $f(\mathbf{k})$ does not have the same symmetry of the crystal, it can be symmetrized as

$$f(\mathbf{k}) = \frac{1}{N_s} \sum_{m=1}^{N_s} f(S^m \mathbf{k}) \quad (4.111)$$

where S^m are the N_s rotation operations that map the crystal onto itself. If $\mathbf{R}$ and $\mathbf{R}'$ are related by symmetry operations, the Fourier components satisfy $f(\mathbf{R})=f(\mathbf{R}')$ because $f(\mathbf{k})$ is invariant with respect to the operations of the point group. Therefore we can divide the direct lattice vectors into shells of symmetry-related vectors: $C_n = \{\mathbf{R}_m = S^m \mathbf{R} | m=1, \dots, N_s\}$, where the index n is used to order the shells according to increasing modulus of their $\mathbf{R}$ vectors. For all the elements of a given shell, C_n , $f(\mathbf{R})$ has the same value f_n . It is therefore possible to rewrite the Fourier expansion of $f(\mathbf{k})$ as

$$f(\mathbf{k}) = \sum_{n=0}^{\infty} f_n \sum_{|\mathbf{R}| \in C_n} e^{i\mathbf{k} \cdot \mathbf{R}} = f_0 + \sum_{n=1}^{\infty} f_n A_n(\mathbf{k}) \quad (4.112)$$

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Suppose that we have a set of N_k special points and relative weights such that

$$\sum_{i=1}^{N_k} w_i A_n(\mathbf{k}_i^*) = 0, \quad n = 1, \dots, N_p \quad \text{and} \quad \sum_{i=1}^{N_k} w_i = 1 \quad (4.113)$$

then we can approximate the integral over the BZ with a weighted sum over the special points as

$$\bar{f} \approx \sum_{i=1}^{N_k} f(\mathbf{k}_i^*) w_i \quad (4.114)$$

The error, ε , associated with the above approximation can be derived by substituting the above expression into the Fourier expansion of Equation (4.112)

$$\begin{aligned} \sum_{i=1}^{N_k} f(\mathbf{k}_i^*) w_i &= \sum_{i=1}^{N_k} f_0 w_i + \sum_{n=1}^{\infty} f_n \sum_{i=1}^{N_k} w_i A_n(\mathbf{k}_i^*) = f_0 + \sum_{n=N_k+1}^{\infty} f_n \sum_{i=1}^{N_k} w_i A_n(\mathbf{k}_i^*) \\ &= f_0 + \varepsilon \end{aligned} \quad (4.115)$$

The magnitude of ε depends on the values of the Fourier transform f_n for $n > N_p$. For sufficiently smooth functions, the values of f_n tend rapidly to zero as n becomes large. The precision of the calculation can be increased simply by increasing the number of sampling points and, therefore, of shells N_p . Different procedures have been developed to determine the sets of special points $\mathbf{k}_i^*$ (called k -points) that satisfy the conditions of Equation (4.113), and the scheme by Monkhorst-Pack (1976) is employed with a $2 \times 2 \times 2$ k -points mesh in the present study.

4.9 SELF-CONSISTENT KOHN-SHAM EQUATIONS

The Kohn-Sham equations are summarized in the flow chart in Figure 4.4. They are a set of Schrödinger-like independent-particle equations which must be solved subject to the condition that the effective potential $V_{KS}(\mathbf{r})$ and electron density $n(\mathbf{r})$ are consistent. Generally, except at the exact solution, the input and output potentials as well as

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densities are not consistent. In order to move towards the ground state solution we define a new potential $n^{\text{out}} \rightarrow V^{\text{new}}$, which can then start a new cycle with V^{new} as the new input potential. Basically, the procedure shown in Figure 4.4 can be defined as an iterative progression

$$V^i \rightarrow n^i \rightarrow V^{i+1} \rightarrow n^{i+1} \rightarrow \dots \quad (4.116)$$

where i labels the iteration step in the solution process.

In achieving self-consistency, an important aspect is the choice of procedure for updating the potential V_{KS} or the density $n(\mathbf{r})$ in each loop of the Kohn-Sham equations as shown in Figure 4.4. Mathematically we can vary either V or n , but it is simpler to describe in terms of n (since n is unique whereas V is subject to shift by a constant).

One of the simplest approaches is linear mixing

$$n_{in}^{i+1} = \alpha n_{out}^i + (1 - \alpha)n_{in}^i = n_{in}^i + \alpha(n_{out}^i - n_{in}^i) \quad (4.117)$$

where α is determined from the linear analysis of the behavior near the minimum energy conditions. This is the optimal choice and is essentially moving in an approximate “steepest descent” direction for minimizing the energy.

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Figure 4.4. Flow chart for self-consistent solution of Kohn-Sham equations.

Besides solving the consistency of electron density, we also need to move any atom based on the derived forces in the Hamiltonian. Feynman (1939) derived the force theorem and explicitly pointed out that the force on a nucleus is given strictly in terms of the electron density, and is independent of the electron kinetic energy, exchange, and correlation. This theorem is generally known as “Hellmann-Feynman theorem” or “force theorem”.

The force conjugate to any parameter describing a system, such as the position of a nucleus $\mathbf{R}_I$, can be written generally as

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$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} \quad (4.118)$$

Since the only terms that depend explicitly upon the positions of the nuclei are the nucleus-nucleus interaction $E_{nuc-nuc}$ and the external potential

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\int d\mathbf{r} n(\mathbf{r}) \frac{\partial V_{ext}(\mathbf{r})}{\partial \mathbf{R}_I} - \frac{\partial E_{nuc-nuc}}{\partial \mathbf{R}_I} \quad (4.119)$$

4.10 CONCLUSIONS

In this chapter, the Hohenberg-Kohn theorems and Kohn-Sham equation are presented. A summary of how the DFT successfully simplifies the many-electron system into one electron Schrödinger equations is shown. The Bloch theorem will simplify the Schrödinger equation and introducing the Fourier series which leads to fast Fourier transform (FFT). The plane wave basis which is adopted is expanded in a complete set of Fourier components. Thus, the fast Fourier transform (FFT) can be introduced in the transformation between real space and reciprocal space. All of these will speed up the calculation.

The introduction of norm-conserving pseudopotential further simplifies the complexity of the system by reducing the total numbers of states by considering only the valence electrons. The main problem of the norm-conserving pseudopotential is the possibility of ghost states which must be eliminated. The transferability of carbon atoms is also tested.

The combination of Bloch theorem and reciprocal space integration technique leads to the k -points calculation in BZ. This will further simplify the calculation and is also ideal for code parallelization.

CHAPTER FIVE

MULTISCALE COMPUTATIONAL IMPLEMENTATION

In this chapter, the multiscale modeling, minimization methods, as well as parallelization approach, are discussed. The multiscale model developed involves the concurrent and seamless coupling between MD and TB, as well as between MD and DFT. In the present work, both the conjugate-gradient minimization and truncated-Newton with Lanczos minimization are implemented. The stability and speed of both methods are reviewed. Parallelization of MD and DFT is also carried out. The speed-up of parallelization as well as time consumption breakdown in each multiscale model are discussed. The numerical results of long-range LJ potential with a switch function are also discussed.

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5.1 MULTISCALE MODEL

Sherwood (Grotendorst, 2000) demonstrated a successful multiscale approach in the form of a hybrid quantum mechanics/molecular mechanics (QM/MM) model. They introduce outer, boundary, and inner regions in order to achieve seamless coupling. Their subtractive schemes have the advantage of relative simplicity of implementation, with no requirement for validating the QM/MM interactions, but requires the use of link atoms.

Rafii-Taber *et al.* (1998) introduced a multiscale model for simulating brittle-crack propagation. Their model seamlessly couples the crack dynamics at the macroscales and nanoscales via an intermediate mesoscale continuum using a combination of finite elements (FE) and MD. Abraham *et al.* (1998, 2000) studied the rapid brittle fracture of a silicon slab, flawed by a central microcrack and subject to uniaxial tension. They labeled the atomic length scale as the mesoscopic regime, but pointed out that treating bond breaking with an empirical MD potential may be questionable, and a quantum-mechanical treatment would be highly desirable. A multiscale method which successfully couples FE or meshfree methodology with MD was introduced by Dong *et al.* (2002). A multiple-scale decomposition of the atomic displacements in terms of FE nodal displacements and MD displacements is first carried out. The total scale is then calculated based on the usual FE interpolation, MD displacements, and the projection of the MD displacements onto the FE basis. Dong *et al.* (2004) also introduced a virtual atom cluster (VAC) in the coarse-scale treatment, where the number of quadrature points used in the VAC is far less than the actual number of atoms. An “isoparametric-like” meshfree approximation was also formulated and this approximation was found to be valid for interpolating a general class of low-dimensional nanostructured materials such as 2D graphite.

In the presently developed overlap multiscale approach, interpolation scaling is not required. Both the MD and TB methods utilize the information available at the atomic locations. However, unlike the TB method, the MD method does not consider the contributions of valence electrons.

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Figure 5.1. Terminology for regions used in the present multiscale model.

As shown in Figure 5.1, the TB domain comprises the near and far regions. The overlap far region constitutes a relatively small subdomain and is used to achieve a seamless coupling between the TB (near region) and MD potentials.

The MD method is applied to both the pure MD and TB far regions. The resultant forces and motions of the atoms in these two regions are therefore determined by the MD method. The TB method is applied to both the TB near and far regions but only the motions of the atoms in the near region are determined by the TB method. The model is therefore not affected by the periodic boundary conditions (PBC) of the TB analysis as the motions of the atoms in the TB far region are based on MD calculations. For the TB analysis of the TB near and far regions, the forces acting on the atoms at the boundary of the TB far region are derived from the MD analysis. The average width of the far region is 2.6 Å since it is the standard cutoff radius of carbon. With the introduction of this far region, the concept of a link “silogen atom” is not required in the present model. Silogen is a terminology used by Abraham *et al.* (1998, 2000) to describe TB terminating silicon atoms which bond like silicon but are monovalent like hydrogen.

For multiscale model between MD and TB, the entire energy can be written as

$$E_{MD/TB}^{entire} = E_{MD}^{pure} + E_{MD}^{far} + E_{TB}^{near} \quad (5.1)$$

where the superscripts *pure*, *far*, *near* respectively indicate pure MD region, far TB region and near TB region. The subscripts indicate the computational method used.

The force on each atom can be written as

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$$F_I = \begin{cases} F_{MD}^I, & I \in (pure \cup far) \\ F_{TB}^I, & I \in near \end{cases} \quad (5.2)$$

where the atom is located at nucleus $\mathbf{R}_I$.

The above multiscale TB/MD approach will be used for multiscale DFT/MD where all the TB term replaced by DFT. All the other conditions will remain the same. As a result, the entire energy and force of each atom in multiscale model between MD and DFT can be written as

$$E_{MD/DFT}^{entire} = E_{MD}^{pure} + E_{MD}^{far} + E_{DFT}^{near} \quad (5.3)$$

and

$$F_I = \begin{cases} F_{MD}^I, & I \in (pure \cup far) \\ F_{DFT}^I, & I \in near \end{cases} \quad (5.4)$$

5.2 NEAREST DISTANCE AND DENSITY OF POINT

The nearest mutual distance between two carbon atoms will determine whether their bond is single, double, or if it is broken. Thus, it is useful to calculate the nearest distance among carbon atoms. The nearest distance is indicated as $ndist(i,j)$. The $ndist(i,j)$ table is derived based on the double partial sorting of the entire CNT subject to the constraint of the order $i < j$, where i and j are the indexes of the atoms. The constraint is required to avoid the double counting of each pair of atoms.

Figure 5.2. Nearest distances a and b .

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Initially in its undeformed state, each atom in the CNT will have three nearest mutual distances, and two for those atoms at the boundary. However, during the simulation, as the CNT deforms, each atom will have at least one nearest mutual distance. From the standard graphene hexagon structure shown in Figure 5.2, we have

$$b = 2a \cdot \sin(60^\circ) \approx 1.732a \quad (5.5)$$

All the distances larger or equal to the designated nearest distance cutoff value of $1.732a$ will be excluded.

The density of point (DOP) is defined and calculated so as to detect the buckling, kink shape occurrences as well as bond breaking. All the distances larger than or equal to a designated cutoff distance should be excluded. For instance, if we set the cutoff radius as $2.6 \text{ \AA}$, each carbon atom will initially have a DOP value of 9, indicating that it has nine neighboring carbons within the cutoff radius. However, when the SWCNTs start to buckle sideways, it is expected that at the regions of relative larger deformations, some carbon atoms will have DOP values higher than 9. This region will be automatically detected and designated as the near region.

In order to better describe the multiscale technique, a flow chart of multiscale simulation is given in Figure 5.3. Please note that the flow chart is similar for both the multiscale MD/TB and MD/DFT formulations, where the TB and DFT are interchangeable in the present context.

In a canonical ensemble, the absolute temperature of a system is proportional to the average of the kinetic energy

$$\langle E_k \rangle = \frac{3}{2} N k_B T \quad (5.6)$$

where k_B is the Boltzmann's constant, N the number of particles in system, and T the temperature in Kelvin.

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If we wish to control the temperature, Woodcock (1971) proposed a simple way in altering the temperature of the system by scaling the particles' velocity. If the temperature at time t is $T(t)$ and the velocities are multiplied by a factor λ , then the associated temperature change can be calculated as follows

$$\Delta T = \frac{1}{2} \sum_{i=1}^N \frac{2}{3} \frac{m_i (\lambda v_i)^2}{N k_B} - \frac{1}{2} \sum_{i=1}^N \frac{2}{3} \frac{m_i v_i^2}{N k_B} = (\lambda^2 - 1) T(t) \quad (5.7)$$

and

$$\lambda = \sqrt{T_{new} / T(t)} \quad (5.8)$$

where m_i and v_i are mass and velocity of particle i with total number of particle N .

Thus the simplest way to control the temperature is to multiply the velocities at each time step by the factor λ where $T(t)$ is the current temperature as calculated from the kinetic energy and T_{new} is the desired temperature.

Figure 5.3. Flow chart of MD/TB or MD/DFT multiscale simulation.

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In the present work, we are not considering a constant temperature system. There is no attempt to control the temperature and it is thus left to fluctuate. In other words, in the present finite temperature system (where the temperature is induced by the velocities of carbon nuclei), the zero-temperature Fermi-Dirac distribution assumption is used in the TB and DFT calculations solely to determine the electronic structure and thus the interatomic forces. As this is a dynamic problem, the resulting velocities changes will of course result in temperature fluctuations. In this work, these fluctuations are not of interest. However, they can be calculated from the kinetic energies of the nuclei.

5.3 MINIMIZATION

In our present research, we examine both the conjugate-gradient method and the truncated-Newton via Lanczos minimization. The conjugate gradient algorithm does not use prespecified conjugate directions, but computes the search directions as the algorithm progresses. At each stage, the direction is calculated as a linear combination of the previous direction and the current gradient, in such a way that all the directions are mutually $\mathbf{Q}$ -conjugate¹. For a quadratic function of n variables, we can locate the function minimizer by performing n searches along mutually conjugate directions.

Let us consider a quadratic function

$$f(\mathbf{x}) = \frac{1}{2} \mathbf{x}^T \mathbf{Q} \mathbf{x} - \mathbf{x}^T \mathbf{b}, \quad \mathbf{x} \in R^n \quad (5.9)$$

where $\mathbf{Q} = \mathbf{Q}^T > 0$. $\mathbf{Q}$ is a positive definite symmetric matrix² and $\mathbf{b} \in R^n$. The initial direction at an initial point $\mathbf{x}^{(0)}$ is in the direction of steepest descent as

$$\mathbf{d}^{(0)} = -\mathbf{g}^{(0)} \quad (5.10)$$

where the gradient at point $\mathbf{x}^{(i)}$ is given as

¹ Let $\mathbf{Q}$ be a real symmetric $n \times n$ matrix. The directions $\mathbf{d}^{(0)}, \mathbf{d}^{(1)}, \mathbf{d}^{(2)}, \dots, \mathbf{d}^{(m)}$ are $\mathbf{Q}$ -conjugate if, for all $i \neq j$, we have $\mathbf{d}^{(i)T} \mathbf{Q} \mathbf{d}^{(j)} = 0$.

² So that the objective function, $f(\mathbf{x})$ has a single global minimum.

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$$\mathbf{g}^{(i)} = \nabla f(\mathbf{x}^{(i)}) = \mathbf{Q}\mathbf{x}^{(i)} - \mathbf{b} \quad (5.11)$$

Subsequently

$$\mathbf{x}^{(1)} = \mathbf{x}^{(0)} + \alpha_0 \mathbf{d}^{(0)} \quad (5.12)$$

where

$$\alpha_0 = \min_{\alpha \geq 0} f(\mathbf{x}^{(0)} + \alpha \mathbf{d}^{(0)}) = -\frac{\mathbf{g}^{(0)T} \mathbf{d}^{(0)}}{\mathbf{d}^{(0)T} \mathbf{Q} \mathbf{d}^{(0)}} \quad (5.13)$$

In the next stage, we search in a direction $\mathbf{d}^{(1)}$ that is $\mathbf{Q}$ -conjugate to $\mathbf{d}^{(0)}$. We choose $\mathbf{d}^{(1)}$ as a linear combination of $\mathbf{g}^{(1)}$ and $\mathbf{d}^{(0)}$ which can be written as

$$\mathbf{d}^{(k+1)} = -\mathbf{g}^{(k+1)} + \beta_k \mathbf{d}^{(k)}, \quad k=0,1,2,\dots \quad (5.14)$$

where the coefficients β_k , ($k=1, 2, \dots$) are chosen in such a way that $\mathbf{d}^{(k+1)}$ is $\mathbf{Q}$ -conjugate to $\mathbf{d}^{(0)}$, $\mathbf{d}^{(1)}$, ..., $\mathbf{d}^{(k)}$. We can set β_k as

$$\beta_k = \frac{\mathbf{g}^{(k+1)T} \mathbf{Q} \mathbf{d}^{(k)}}{\mathbf{d}^{(k)T} \mathbf{Q} \mathbf{d}^{(k)}} \quad (5.15)$$

The whole processes will be repeated until the point $\mathbf{x}$ or quadratic function $f(\mathbf{x})$ converge.

Truncated-Newton methods are a family of optimization methods suitable for solving large nonlinear problems. In each iteration, the current estimate of the solution is updated by approximately solving the Newton equations using an iterative algorithm. The truncated-Newton method will be effective if only a small number of inner iterations is sufficient to produce a converged step. The implementation of preconditioning will accelerate the convergence of the inner iterations.

The present truncated-Newton method will minimize a twice continuously-differentiable function, $f(\mathbf{x})$. The first-order optimality condition leads to

$$\nabla f(\mathbf{x}) = 0 \quad (5.16)$$

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$$\nabla^2 f(\mathbf{x}_k) \mathbf{p}_k = -\nabla f(\mathbf{x}_k) \quad (5.17)$$

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \mathbf{p}_k \quad (5.18)$$

where Equation (5.16) is a system of nonlinear equations. Newton's method computes a step $\mathbf{p}_k$ in Equation (5.17).

In a truncated-Newton method, an iterative method is applied to Equation (5.17). The main emphasis in a truncated-Newton method is the choice of an inner iterative algorithm for solving Equation (5.17). We note here that the Hessian matrix $\nabla^2 f(\mathbf{x}_k)$ in Equation (5.17) is always symmetric.

The truncated-Newton method is embedded with the following techniques:

- conjugate-gradient method is used to solve a large system, such as Equation (5.17), by solving a large linear system $\mathbf{A}\mathbf{p}=\mathbf{b}$ where $\nabla^2 f(\mathbf{x}_k)=\mathbf{A}$. Iteration is truncated before the exact solution is attained.
- line-search method (1-D minimization) is used to find α_k :
for $k=0,1,\dots$
 - stop if stopping rule satisfied
 - compute a search direction $\mathbf{p}_k$
 - determine an improved estimate, $\mathbf{x}_{k+1}=\mathbf{x}_k+\alpha_k\mathbf{p}_k$.
- trust-region method is used where we specify some initial guess of the solution $\mathbf{x}_0$, and specify Δ_0 , the bound on the size of the trust-region. The global convergence to a local solution can be achieved in either a line search or trust-region method.
for $k=0,1,\dots$
 - stop if stopping rule satisfied
 - choose $\mathbf{p}_k$ so as to minimize $\psi_k(\mathbf{p})\approx f(\mathbf{x}_k+\mathbf{p})$,
 - subject to $\|\mathbf{p}\| \leq \Delta_k$,
 - compute $\mathbf{x}_{k+1}$ and Δ_{k+1} using $\mathbf{p}_k$.

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- Lanczos shift is used when Hessian matrix, $\nabla^2 f(\mathbf{x})$, is indefinite. The Lanczos method can be applied to any symmetric matrix $\mathbf{A}$. It determines a sequence of orthogonal matrices $\mathbf{V}_i$ and tridiagonal matrices $\mathbf{T}_i$ such that

$$\mathbf{V}_i^T \mathbf{A} \mathbf{V}_i = \mathbf{T}_i \quad (5.19)$$

If $\mathbf{A} = \nabla^2 f(\mathbf{x}_k)$, then $\mathbf{p}_i$ in Equation (5.17) can be derived as

$$\mathbf{p}_i = -\mathbf{V}_i \mathbf{T}_i(\mathbf{x}_k)^{-1} \mathbf{V}_i^T \nabla f(\mathbf{x}_k) \quad (5.20)$$

5.4 PARALLELIZATION OF COMPUTATION

In our parallelization approach, we adopt the single program multiple data (SPMD) programming model. MPI 1.2 (Message Passing Interface) is employed for the parallelization, while each processor executes the same executable in serial. Normally, each processor works on different set of data on a defined sub-domain, which for this case are the k -points domain for DFT, and the group of atoms for MD. Finally, data is shared among processors by message passing within the defined ‘communicator’ which is the core component of MPI programming.

Generally, the main challenges in parallel computing are communication cost, memory performance and load balancing. Communication cost becomes critical as CPU speeds continue to increase. Load imbalance occurs when all processor wait for the “slowest” one. It happens especially in files handling which is performed in serial mode. Since DFT is very compute intensive, it is important to parallelize their computation in order to simulate bigger systems and/or over longer time periods. As shown in Appendix F, using Bloch function the Kohn-Sham equation can be transformed to

$$\left[\frac{1}{2} (-i\nabla + \mathbf{k})^2 + v_{eff}(\mathbf{r}) \right] u_{i,\mathbf{k}} = \varepsilon_{i,\mathbf{k}} u_{i,\mathbf{k}} \quad (5.21)$$

where $u_{i,\mathbf{k}}$ is a Bloch function, and $\varepsilon_{i,\mathbf{k}}$ is an eigenvalue for wavevector $\mathbf{k}$ and state i . $v_{eff}(\mathbf{r})$ is an effective potential which corresponds to $V_{KS}(\mathbf{r})$ in section 4.2. Please note

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that i in $i\nabla$ is $\sqrt{-1}$. These separate diagonalisations of the wavevector $\mathbf{k}$ are ideal for iterative methods. Theoretically, we can parallelize the FFT calculations as well, but in the present case, most of the FFT calculations are carried out within each independent k -points loop. Thus, in our present research, we parallelize over k -points in the entire DFT calculation, where one of the most intensely calculated components is the evaluation of electron density.

In this work, we perform speed-up comparison when using 2 and 4 processors. The parallel speed-up ratio is defined as

$$\text{speed - up} = \frac{\{\text{elapsed time of serial execution}\}}{\{\text{elapsed time of parallel execution}\}} \tag{5.22}$$

Table 5.1 shows the speed-up in the DFT calculation of 91 atoms for a SWCNT (7,0). It is evident that as the number of processors increase, communication cost and load imbalance become more pronounced, resulting in the reduction of the speed-up.

Table 5.1. Parallel speed-up in DFT simulation.

No. of run	2 processors	4 processors
1	1.99	3.07
2	1.98	3.00
3	1.91	2.98
4	1.93	3.32
5	1.95	3.52
Average	1.95	3.18

Here, we also perform parallel speed-up for the MD simulations, and this is achieved by parallelization of the short-range REBO and long-range LJ potentials, as well as the neighbor list. Basically, we divide the total number of atoms in the atomic structure by the number of processors available, and each processor will then perform the MD calculations on each sub-group of atoms. Figure 5.4 shows the speed-up of the simulations for a SWCNT (7,0).

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Figure 5.4. Parallel speed-up in MD simulation.

As shown in Figure 5.4, too small a simulation size results in reduction of parallel efficiency as the complexity of the calculations are reduces significantly. For sub-grouping of 2800 atoms and above, we achieve average speed-up values of 1.7 and 3.0, for 2 and 4 processors, respectively.

Finally, we perform time consumption studies for the individual MD and DFT components in the multiscale simulation of a SWCNT (7,0) with a total 476 atoms. The results of the breakdown are shown in Table 5.2, and it is obvious, and expected as well, that the DFT calculation is the most expensive part in the entire simulation. Thus, it becomes the crucial component for parallelization in the multiscale model.

Table 5.2. Time consumption breakdown in DFT/MD multiscale model.

	MD region	DFT region
Average time consumption per simulation run (sec.)	1665	1006904
Percentage of time consumption.	0.17 %	99.83%

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5.5 SIMULATION RESULTS OF LJ POTENTIAL WITH SWITCH FUNCTION

Here, we investigate the effects of implementing the switch function into the LJ potential as discussed in chapter 2. Obviously, the existence of this switch function will not affect the results for a SWCNT under axial tension, where all the atoms are moving away from each other. However, we would expect some differences for the case of axial compression as distance between atoms are near to the cutoff of switch function. From Figures 5.5-5.8, we observe that this is indeed the case.

Figure 5.5. Strain energy using original Lennard-Jones for SWCNT (8,0) in axial compression.

Figure 5.6. Strain energy using Lennard-Jones with switch function for SWCNT (8,0) in axial compression.

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Figure 5.7. Nearest distance of SWCNT (8,0) in axial compression using original Lennard-Jones potential.

Figure 5.8. Nearest distance of SWCNT (8,0) in axial compression using Lennard-Jones with switch function.

According to Figures 5.5-5.8, we find that both sets of results have the same collapse strain of 0.1. However, we also find that after the initial collapse, results via the smooth cutoff LJ show lower strain energy as well as less fluctuation. It is also the same case for maximum nearest distance $\text{ndist}(i,j)$ where results using the smooth cutoff LJ show less fluctuation in maximum distance. Obviously, this switch function plays important role immediately after the initial collapse. All subsequent simulations in chapter 6 will employ the smooth cutoff LJ potential.

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5.6 SIMULATION RESULTS USING DIFFERENT MINIMIZATION SCHEMES

Here, we examine the two minimization schemes described earlier, namely, the conjugate-gradient method and the truncated-Newton via the Lanczos algorithm (Nash, 1984). Both schemes are applicable only to smooth solution fields. Theoretically, the truncated-Newton scheme shows superior convergence properties if the starting coordinates are in the vicinity of the solution.

From the simulation results for SWCNT(8,0), we observe that both schemes produce similar profiles for the strain energy and stress-strain curves. However, in terms of computational time, we find that the truncated-Newton method is significantly more efficient.

Table 5.3. Comparison of computational time of two minimization schemes.

Strain	Time consumption (s-clock time)	
	Conjugate gradient	Truncated-Newton
0-0.118	398	463
0.118-0.236	5952	852
0.236-0.32	25716	682

As can be observed from Table 5.3, the truncated-Newton scheme is relatively more efficient over the entire simulation range. The conjugate-gradient method, on the other hand, is very computationally intensive especially in the bond breaking regime. It is also interesting to note that prior to reaching the yield strain, the conjugate-gradient method is somewhat faster. Finally, we present the smoothness of stress-strain curves when using both the minimization schemes.

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Figure 5.9. Smoothness of stress-strain curve when using truncated-Newton minimization.

Figure 5.10. Smoothness of stress-strain curve when using conjugate-gradient minimization.

From Figures 5.9-5.10, we note that the conjugate-gradient method produces results which are somewhat oscillatory. Results from the truncated-Newton scheme are significantly smoother. Thus, all subsequent simulations in Chapter 6 will employ the truncated-Newton method.

5.7 CONCLUSIONS

The first section of this chapter describes the development of the multiscale model. Basically, the present multiscale model introduces three regions, namely pure MD, (TB or DFT) near and (TB or DFT) far regions. The region for TB or DFT activation is detected and calculated based on the density of point (DOP). The nearest distance

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$\text{ndist}(i,j)$ can be used to characterize the mechanical behaviour of CNTs during simulation and will be used in Chapter 6.

Simulation results in this chapter reveal that the truncated-Newton with Lanczos minimization is superior to the conjugate-gradient minimization in terms of numerical stability and speed. The parallelization of MD and DFT shows that as the number of processors increase, communication cost and load imbalance become more critical and thus reduce the rate of speed-up. In addition, the time consumption breakdown in the multiscale simulations reveals the importance of parallelization in DFT. The numerical results for the long-range LJ potential with switch function also show that the switch function does not affect the cases of CNTs under axial tension. However, when under axial compression, simulation results show that after the initial collapse, the switch function will produce lower strain energy as well as less fluctuation. It is also shows less fluctuation in the maximum nearest distance $\text{ndist}(i,j)$.

CHAPTER SIX

MULTISCALE MODELING OF CNT – RESULTS AND DISCUSSION

In this chapter, the applicability and viability of the presently developed multiscale TB/MD and DFT/MD models for SWCNT is illustrated and validated. In axial compression simulation, a constant axial compression plus linear velocity increasing along diameter is applied to induce sideways buckling and avoid the symmetrical modes. Most of the validations and comparisons are based on the characteristics of nearest distance, strain energy per atom and stress-strain relations of SWCNT under axial loading. Comparison of the simulation results are also made between the pure MD model, multiscale TB/MD and DFT/MD models.

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6.1 VALIDATION OF PRESENT RESULTS

For the simple validation test, we conducted a patch test with a linear arrangement of three carbon atoms (C1, C2 and C3), see Figure 6.1 for the initial configuration.

Figure 6.1. Initial conditions of a linear arrangement of three carbon atoms.

Table 6.1 presents the simulation results of this patch test for the converged energy as well as the final positions of atoms using the MD, TB and DFT approaches.

Table 6.1. Simulation results for linear arrangement of three carbon atoms by different approaches.

Method	Initial distance between C (Å)	Final distance between C (Å)	Total energy per atom (eV)
MD	1.90	1.31	-4.30
TB	1.90	1.31	-5.88
DFT	1.90	1.27	-5.63

The bond length of a typical C=C double bond is around 1.34Å (bond length may vary slightly in different molecular structures). Thus the above simple simulation displays the correct and expected double bond linear arrangement of three carbon atoms.

Figure 6.2. Lewis structure of linear arrangement of three carbon atoms.

Next we examine the formal charge of the molecular structure (Zumdahl, 2006). The formal charge is defined as

Formal charge = (Number of valence electrons on free atom) –
(Number of valence electrons assigned to the atom in the molecule) (6.1)

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For a carbon atom, the number of assigned valence electrons is calculated as

$$(\text{Valence electrons})_{\text{assigned}} = (\text{Number of lone pair electrons}) + \frac{1}{2} (\text{Number of shared electrons}) \quad (6.2)$$

Therefore:

$$\text{Valence electrons assigned to C1} = 2 + \frac{1}{2}(4) = 4$$

$$\text{Formal charge on C1} = 4 - 4 = 0$$

$$\text{Valence electrons assigned to C2} = 0 + \frac{1}{2}(8) = 4$$

$$\text{Formal charge on C2} = 4 - 4 = 0$$

$$\text{Valence electrons assigned to C3} = 2 + \frac{1}{2}(4) = 4$$

$$\text{Formal charge on C3} = 4 - 4 = 0$$

The two fundamental assumptions on the formal charges are used in order to validate Lewis structures:

- Atoms in molecules will attempt to achieve formal charges as close to zero as possible.
- Any negative formal charges are expected to reside on the most electronegative atoms.

Figure 6.2 shows the preferred Lewis structure since all the carbons produce zero formal charge. In addition, we shall use a simple method for determining the molecular structure. This model is termed the Valence Shell Electron-Pair Repulsion (VSEPR) model. The main postulate of this model is that the structure around a given atom is determined principally by minimizing electron-pair repulsions. Please note that a double bond should be counted as one effective pair when using the VSEPR model. According to Lewis structure in Figure 6.2, the centre of carbon shows two effective bonding pairs. To minimize repulsions, these are best arranged in a linear structure with a 180° bond angle. The same argument applies to C1 and C3.

In the validation of our DFT code, we have generated the following Figures 6.3 to 6.5. We observe that the electronic density obtained is consistent with the preferred Lewis structure and VSEPR model. Figure 6.3 shows the total electron density calculated by

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DFT which best describes the linear structure as predicted above. Figure 6.4 shows the lowest energy state of electron which represents the σ bond arising from the hybridized sp orbitals. Figure 6.5 shows the higher energy state of electron which represents the $2p$ orbital, and it indicates the π bond between the carbon atoms.

Figure 6.3. 2-D Electron density of total electron at $Z=0$ using DFT.

Figure 6.4. 2-D Electron density for state=1 at $Z=0$ using DFT.

Figure 6.5. 2-D Electron density for state=5 at $Z=0$ using DFT.

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In our following validation test case, we apply a velocity of 20 m/s (see Liew *et al.*, 2004) at both ends of the CNT in order to obtain the stress-strain relationship. The atoms located at the ends of the CNT are moved according to this velocity at very small time steps of 1 femto-second (fs). In this MD simulation, the locations of the atoms are calculated according to Gear's fifth-order predictor-corrector algorithm. The whole tube was relaxed by truncated-Newton with Lanczos algorithm in order to minimize the energy of CNTs but without affecting the atoms at the two ends.

To validate the presently developed multiscale model, we carry out several comparisons with published data of existing methodologies. Of interest in these comparisons are the Young's modulus and strain energy.

In the microcanonical ensemble MD simulations of CNTs, strain is derived as

$$\varepsilon = |(L-L_0)| / L_0 \quad (6.3)$$

where L_0 and L are the undeformed and deformed lengths of the CNT. The stress is calculated as

$$\sigma = F/S \quad (6.4)$$

where F is axial force and the cross-sectional area is given by $S=\pi dh$, with d being the CNT diameter and h the thickness, which is usually taken to be 0.34 nm.

To date, there is no agreement on the true value of the CNT thickness. Yakobson *et al.* (1996) obtained a value of 0.66 Å through an equivalent continuum shell model. Vodenitcharova and Zhang (2003) arrived at a value of 0.617 Å through inference from an equivalent continuum ring theory. An equivalent Euler-Bernoulli beam theory was used by Sear and Batra (2004) and they obtained different thickness values of 1.34 Å and 0.98 Å, when different potentials were used in the initial atomistic simulation. In yet another work, Halicioglu (1998) used a thickness of 6.8 Å for predicting the CNT Young's modulus. In the present thesis, we employ the most commonly used thickness value of 3.4 Å, which is the separation distance between adjacent walls in a multiwall carbon nanotube. Some of these works include Robertson

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et al. (1992), Cornwell and Wille (1997), Lu (1997), Hernandez *et al.* (1998), Yao and Lordi (1998), Ozaki *et al.* (2000), Van Lier *et al.* (2000) and Belytschko *et al.* (2002).

For the validation, we compare the strain energy of SWCNT (8,0) undergoing axial compression. Here, 352 atoms were considered with length-to-diameter ratio, $L/D=7.2$. This comparison is made against results obtained via the quantum GTBMD method, as well as MD results computed with Tersoff-Brenner potential reported by Srivastava *et al.* (1999) in Figure 6.6.

Figure 6.6. Comparison of strain energy curve of SWCNT (8,0) under axial compression.

The results show that collapse occurs at the respective strains of 0.12 and 0.8-0.9 for GTBMD and MD (using Tersoff-Brenner potential), whereas the present MD (using second-generation REBO potential) yields a collapse strain of 0.1 (the collapse strain here refers to the buckling strain). The present results are thus in reasonable agreement and are actually more refined than those obtained using the Tersoff-Brenner potential. The validation of the present MD algorithm is also made for SWCNT under axial tension. We also examine the stress-strain relations of SWCNT (12,12) with $L/D=9.1$. The comparison is made with the MD (using modified Morse potential) results of Belytschko *et al.* (2002), as shown in Figure 6.7. The present results yield a slightly higher collapse strain at a lower stress value. For the tensile case, the collapse strain refers to the strain at which bond-breaking first occurs.

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Figure 6.7. Comparison of stress-strain curve of a SWCNT (12,12) under axial tension.

The third comparison carried out is for the Young’s modulus and is made against the *ab initio* results of Kudin *et al.* (2001). These results are tabulated in Table 6.2, and it can be observed that the four sets of results are comparable with an average discrepancy of about 4.9%, 4.5% and 2.9% respectively.

Table 6.2. Comparison of Young’s modulus when using MD, TB and DFT.

CNT geometry	$\frac{\partial^2 E}{\partial \varepsilon^2}$ (eV)			
	Present (MD)	Present (TB)	Present (DFT)	<i>ab initio</i> (Kudin, 2001)
(4,4)	53.1	53.6	54.0	56.4
(7,0)	54.6	54.9	54.7	56.3
(7,7)	52.7	53.1	54.9	56.5
(12,0)	53.0	52.7	54.4	55.2

The Young’s modulus Y is calculated as $Y = \frac{\rho_b}{m} \frac{\partial^2 E}{\partial \varepsilon^2}$, where ρ_b is the bulk density, ε the strain, m the mass of a carbon atom, and E the strain energy per atom, Kudin (2001).

The validation is also carried out for pseudopotential as explained in section 4.6. As shown in Figures 4.1 to 4.3 (in Chapter 4), the ghost state is eliminated and the transferability of carbon is validated. To visualize the electron density distribution, we plot the electron density for a SWCNT (4,4) evaluated on the x - y plane at $z=10.4 \text{ \AA}$ in Figures 6.8 and 6.9.

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Figure 6.8. 2-D plot of electronic density at $z=10.4$ Å for SWCNT (4,4).

Figure 6.9. Contour plot of electronic density at $z=10.4$ Å for SWCNT (4,4).

For the choice of time step, a convergence study was first carried out for the strain energy per atom with respect to the time step. This was done for a SWCNT (4,4) under axial compression. Table 6.3 shows the strain energy per atom at strain $\varepsilon=0.05$. From this study, it is obvious that a time step of 1.0 fs provides sufficiently converged results, and it was thus used in all subsequent simulations. Please note that the use of the large time step of 2.5 fs results in erroneous large displacements that cause the incorrect instantaneous collapse of the CNT.

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Table 6.3. Convergence characteristics of the time step used at $\varepsilon=0.05$.

Time Step (fs)	Strain energy per atom (eV/atom)
2.5	6.4
2.0	0.083
1.5	0.081
1.0	0.080
0.5	0.080

6.2 SIMULATION RESULTS OF THE TB/MD MULTISCALE MODEL

In order to compare the pure MD and multiscale TB/MD schemes, we simulate the case of a SWCNT (7,7) with length-to-diameter ratio $L/D=7.1$, under axial tension. In this problem, the total number of atoms is 784, with 616 atoms located in the MD region when multiscaling first occurs. First we perform the pure MD simulation and examine the elastic and plastic behaviors of the SWCNT.

Figure 6.10. Strain energy per atom using MD for SWCNT (7,7) under axial tension.

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Figure 6.11. Stress-strain curve of SWCNT (7,7) under axial tension using MD.

Figure 6.12. Nearest distance of SWCNT (7,7) under axial tension using MD.

Upon observation of above Figures 6.10-6.12, it is found that after the ultimate load point S , the $\text{ndist}(i,j)$ tends to converge to two values, namely a minimum value of 1.3 Å and a maximum value of 1.75 Å. The collapse of the SWCNT occurs at the point where a sudden drop in strain energy is observed and at strain $\varepsilon=0.235$. It is interesting to note that the variations of the maximum and minimum $\text{ndist}(i,j)$ distances are linear for strain values lower than the ultimate load strain occurring at the point S in the stress-strain curve.

The straight line from the origin to the point P represents the linear elastic region. The points P and S are calculated using the least squares fitting of stress-strain data points (see Press *et al.*, 1992). The fitting curves are based on $\sigma=A_p\varepsilon$ and $\sigma=A_s\varepsilon^2+B_s\varepsilon$, respectively, where A_p , A_s , and B_s are the fitting coefficients. In general, the linear least squares is defined as

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$$\sigma(\varepsilon) = \sum_{k=1}^M a_k X_k(\varepsilon) \quad (6.5)$$

where $X_1(\varepsilon), \dots, X_M(\varepsilon)$ are arbitrary basis functions of ε , and $\sigma(\varepsilon)$ is a polynomial of degree $M-1$.

The linear least squares method attempts to minimize a merit function which is related to measurement error

$$\chi^2 = \sum_{i=1}^N \left[\frac{\sigma_i - \sum_{k=1}^M a_k X_k(\varepsilon_i)}{\sigma_i^s} \right]^2 \quad (6.6)$$

where σ_i^s is the measurement error (standard deviation) of the i^{th} data point $(\varepsilon_i, \sigma_i)$. Here we set standard deviation, $\sigma_i^s = 1$ (Press *et al.*, 1992) and $\chi^2=10$ as the acceptable error margin.

Using the same SWCNT under similar axial tension, we perform the corresponding multiscale model simulation. This multiscale model involves handshaking between MD and TB where 56 atoms are located in the far region and 112 atoms in the near region. Thus, the TB method is used to solve for 168 atoms and this requires the solution of an eigensystem of dimension 672 (168×4). For the multiscale modeling of the axial tension case, the TB near and far regions are implemented, after detecting from initial MD simulations the maximum $\text{ndist}(i,j)$ distance exceeding 1.71 Å. From the current comparison of Figures 6.10, 6.11, 6.13, and 6.14 it is observed that for both pure MD and multiscale simulations, the SWCNT collapses at strain $\varepsilon=0.235$.

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Figure 6.13. Strain energy per atom using multiscale method for SWCNT (7,7) under axial tension.

Figure 6.14. Stress-strain curve of SWCNT (7,7) under axial tension using multiscale method.

Figure 6.15. Nearest distance of SWCNT (7,7) under axial tension using multiscale method.

From Figure 6.15, it is observed that after the ultimate load point S , the minimum and maximum $ndist(i,j)$ distances converge to 1.31 and 1.78 Å, respectively. The above results also show that for the multiscale method, the SWCNT collapses at higher strain energy per atom (0.935 eV/atom) compared with the pure MD case (0.918 eV/atom).

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As shown in Figures 6.12 and 6.15, the oscillations of maximum distance curves occur due to the occurrence of a “dangling” carbon atom as depicted in Figure 6.16, which results in high amplitude vibrations leading to the oscillations observed in Figures 6.12 and 6.15.

Figure 6.16. Oscillations of a “dangling” carbon atom.

Figure 6.17 depicts the collapse mode of this case study when implementing the multiscale model. As can be observed, the near and handshaking regions are applied only to the critical regions so as to significantly reduce the computational time.

Figure 6.17. Multiscale model showing the pure MD, handshaking TB far, and TB near regions in SWCNT: (a) before collapse and (b) after collapse.

We now move on to compare the numerical results of a SWCNT under axial compression using MD and multiscale TB/MD. In this case study, a SWCNT (7,7) with the length-to-diameter ratio $L/D=7.4$ is used. The total number of carbon atoms is 812, with 644 atoms located in the MD region when multiscaling first occurs. For the first 800 fs of this simulation, we apply a constant velocity of 20 ms^{-1} to the left boundary while the other boundary is applied with a constant velocity of 20 ms^{-1} plus a linear velocity increase along the diameter with gradient 1. All the velocities act in the

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compressive sense. After 800 fs, all velocities are set to the constant value of 20 ms^{-1} . In the corresponding multiscale simulation, again we initially perform a full MD analysis. The full MD model will shift to a multiscale model after detecting a DOP higher than nine. The above setting acts as the necessary trigger to induce the sideways buckling and avoid the symmetrical modes.

Figure 6.18. Strain energy per atom using MD for SWCNT (7,7) under axial compression.

Figure 6.19. Stress-strain curve of SWCNT (7,7) under axial compression using MD.

Figure 6.20. Nearest distance of SWCNT (7,7) under axial compression using MD.

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Basically, in the present work, the near and handshaking far TB regions are implemented after detecting a DOP exceeding 9. In this case study, this shift occurs at strain $\varepsilon=0.0518$. Figures 6.18-6.20 show the MD results for the variation of the strain energy per atom with compressive strain, the stress-strain curve, and the maximum/minimum $\text{ndist}(i,j)$ distances, respectively. The corresponding multiscale results are presented in Figures 6.21-6.23. We observe that the maximum $\text{ndist}(i,j)$ distance behaves in a more stable manner for the multiscale model.

Figure 6.21. Strain energy per atom using multiscale method for SWCNT (7,7) under axial compression.

Figure 6.22. Stress-strain curve of SWCNT (7,7) under axial compression using multiscale method.

Figure 6.23. Nearest distance of SWCNT (7,7) under axial compression using multiscale method.

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The strain-energy/atom-strain and stress-strain curves (Figures 6.18, 6.19, 6.21 and 6.22) represent the global characteristics of energy or stress of the CNT as the strain varies. For the strain energy curves as in Figures 6.18 and 6.21, the first drop in the curve around 0.05 strain indicates the initial occurrence of sideways buckling. For the stress-strain curves as in Figure 6.19 and 6.22, the first sharp drop in the curves around 0.05 strain also indicates the occurrence of sideways buckling.

Theoretically, since the quantum mechanical TB and DFT take into account of the effects of valence electrons, they will therefore provide more accurate description of critical area where breaking and formation of bonds occur. Thus the multiscale model will provide a better estimation of the deformation profile since quantum mechanical theories are used to model the reaction bond order.

Figure 6.24 below depicts the sideways buckling modes when respectively implementing the MD and multiscale models. Comparing these two figures, we observe that both deformations are very similar at strain values below $\varepsilon=0.072$. However, at strain values higher than $\varepsilon=0.072$, the results from the multiscale model shows more severe deformations.

MD results for sideways buckling at strain values of:
(a) $\varepsilon=0.0569$; (b) $\varepsilon=0.0683$; (c) $\varepsilon=0.078$.

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Multiscale results for sideways buckling at strain values of:
(a) $\varepsilon=0.0569$; (b) $\varepsilon=0.0683$; (c) $\varepsilon=0.078$.

Figure 6.24. Comparison of MD and TB/MD results for sideways buckling of a SWCNT (7,7).

6.3 SIMULATION RESULTS OF THE DFT/MD MULTISCALE MODEL

In order to compare the two presently developed MD and multiscale DFT/MD schemes, we first simulate the case of a SWCNT (7,0) with length-to-diameter ratio $L/D=12.9$, and under axial compression. For the first 800 fs of this simulation, we apply a constant velocity of 20 m/s to the left boundary while the right boundary undergoes the application of a constant velocity of 20 m/s plus a linear velocity increase along the diameter with gradient 1. All the velocities act in the compressive sense. After 800 fs, all velocities are set to the constant magnitude of 20 m/s. In the corresponding multiscale simulation, we initially execute a full MD analysis. The full MD model will switch to the multiscale model upon the detection of a DOP higher than 9. The present velocity setting acts as the necessary trigger to induce the sideways buckling, and avoid the symmetrical modes. In this problem, the total number of atoms is 476, with 91 atoms located in DFT region when multiscaling first occurs. First we perform the pure MD simulation and examine the elastic and plastic behaviors of SWCNTs.

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Figure 6.25. Nearest distance of SWCNT (7,0) under axial compression using MD.

Figure 6.26. Strain energy per atom for SWCNT (7,0) under axial compression using MD.

Figure 6.27. Stress-strain curve of SWCNT (7,0) under axial compression using MD.

As observed in Figures 6.25 and 6.28, both the MD and multiscale models show similar convergence behavior, and the maximum and minimum $ndist(i,j)$ values are respectively 1.75 and 1.35. For strain energy per atom, as shown in Figures 6.26 and 6.29, both models produce very similar physical behavior. Both models also produce almost same constitutive stress-strain curves, as observed in Figures 6.27 and 6.30. It

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is therefore not surprising that the global responses of the SWCNT based on each of the two computational techniques show very similar global symmetrical bending characteristics, see Figures 6.31 and 6.32.

Figure 6.28. Nearest distance of SWCNT (7,0) under axial compression when using multiscale method.

Figure 6.29. Strain energy per atom for SWCNT (7,0) under axial compression when using multiscale method.

Figure 6.30. Stress-strain curve of SWCNT (7,0) under axial compression using multiscale method.

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Figure 6.31. MD results for sideways buckling of a SWCNT (7,0) at strain values of (a) $\varepsilon=0.0594$; (b) $\varepsilon=0.0662$; and (c) $\varepsilon=0.0679$.

Figure 6.32. Multiscale results for sideways buckling of a SWCNT (7,0) at strain values of (a) $\varepsilon=0.0594$; (b) $\varepsilon=0.0662$; and (c) $\varepsilon=0.0679$.

Next we perform corresponding calculations for a broader SWCNT (7,7) with the length-to-diameter ratio $L/D=7.4$ under axial compression, using both the presently described MD and multiscale DFT/MD methods. In this case, the total number of carbon atoms is 812, with 644 atoms located in MD region when multiscale first occurs. Here, the application of velocities at the both boundaries is similar to that in the preceding case for the narrower SWCNT. In the corresponding multiscale simulation, again we initially perform a full MD analysis with the switch to the multiscale model occurring when a DOP higher than 9 is detected. As shown in Figures 6.33 and 6.36, we observe that the multiscale model generally generates higher maximum $\text{ndist}(i,j)$ values, while the MD model show more stable convergence behavior with distinctly

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less fluctuations in the region of $0.075 < \varepsilon < 0.1$. Figures 6.34, 6.35, 6.37 and 6.38 indicate that the multiscale model produces somewhat higher values for the strain energy curve and stress-strain curve compared to the MD model.

Figure 6.33. Nearest distance of SWCNT (7,7) under axial compression using MD.

Figure 6.34. Strain energy per atom for SWCNT (7,7) under axial compression using MD.

Figure 6.35. Stress-strain curve of SWCNT (7,7) under axial compression using MD.

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Figure 6.36. Nearest distance of SWCNT (7,7) under axial compression when using multiscale method.

Figure 6.37. Strain energy per atom for SWCNT (7,7) under axial compression when using multiscale method.

Figure 6.38. Stress-strain curve of SWCNT (7,7) under axial compression using multiscale method.

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MD results for sideways buckling at strain values of:
(a) $\varepsilon=0.0569$; (b) $\varepsilon=0.0683$; and (c) $\varepsilon=0.0780$.

Multiscale results for sideways buckling of at strain values of:
(a) $\varepsilon=0.0569$; (b) $\varepsilon=0.0683$; and (c) $\varepsilon=0.0780$.

Figure 6.39. Comparison of MD and DFT/MD results for sideways buckling of a SWCNT (7,7).

Figure 6.39 depicts the global sideways buckling modes for the SWCNT (7,7) based on the MD and multiscale models. Comparing these two figures, we note that the deformation characteristics are very similar at strain values below $\varepsilon=0.072$. However, at strain values higher than $\varepsilon=0.072$, the results from the multiscale model shows more severe deformations. This clearly indicates the multiscale DFT/MD model being relatively less stiff compared to the MD model. In addition, if we compare the severity of the deformations with the corresponding multiscale TB/MD results of section 6.2,

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we find that the multiscale DFT/MD results fall between those of the pure MD model and multiscale TB/MD model.

6.4 CONCLUSIONS

In this chapter, the applicability and viability of the presently developed TB/MD and DFT/MD multiscale models in CNTs is illustrated and validated. Generally, both multiscale schemes generate different results at higher strain values compared to the pure MD method. It was also observed that the nearest distance converges to two values for all cases studies, when using both MD and multiscale models.

Both pure MD and multiscale models show a high level of correspondence for relatively low strain values. However, for higher strain values, both TB/MD and DFT/MD multiscale schemes display more severe deformations and exhibit relatively lower stiffnesses, with the TB/MD scheme having the lowest stiffness.

CHAPTER SEVEN

CONCLUSIONS AND FUTURE WORK

This chapter summarizes the major achievements and contributions of the present research project. It consists of three parts, namely MD refinements, multiscale methodology and numerical techniques. This chapter also outlines possible future work resulting from the present works.

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7.1 CONCLUSIONS

The contributions of this thesis consists of three main parts. The first is the investigation and refinement of MD method by introducing switch function for long-range potential. The second is the implementation of multiscale model between MD/TB and MD/DFT. The third is the numerical techniques for efficient computation, which include the parallelization of MD and DFT. The main achievements and contributions are summarized as follows.

7.1.1 Refinement of the MD Method for CNT Calculations

In this study, we have performed a microcanonical ensemble MD as well as developed a novel multiscale model for the study of elastic and plastic deformations of SWCNT under axial compression and tension. In these case studies, a switch function has been introduced to ensure the smoothness of the LJ potential. Our simulation results show that smoothness of the van der Waals potential (LJ potential) is not essential for tensile cases but is important when buckling occurs in axial compression. Subsequently, under axial compression, simulation results showed that after the initial collapse, the switch function will produce lower strain energy as well as less fluctuation. It also resulted in less fluctuation in maximum distance $\text{ndist}(i,j)$. It was also observed that the nearest distance $\text{ndist}(i,j)$ converges to two values for all cases studied, when using both MD and multiscale models.

7.1.2 Implementation of TB/MD and DFT/MD Multiscale Models

In the present work, we adopt a concurrent and seamless overlap multiscale technique to couple empirical MD with semi-empirical TB. This overlap approach was also adopted to couple MD and DFT. This technique requires three sub-region types, namely the pure MD region, the DFT (or TB) near region and the DFT (or TB) far region.

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We also introduce the nearest distance in order to study the mechanical behaviour of the CNT. The nearest distance is derived based on the double partial sorting of the entire CNT subject to the constraint of the order $i < j$, where i and j are the indexes of the atoms. Beside nearest distance, we also introduce the density of point (*DOP*) so as to detect buckling, kink shape occurrences as well as bond breaking. All the distances larger than or equal to a designated cutoff distance should be excluded. Initially, each carbon atom will have a *DOP* value of 9 indicating that it has nine neighboring carbons within the cutoff radius. However, when the SWCNTs start to buckle sideways, it is expected that at the regions of relative larger deformations, some carbon atoms will have *DOP* values higher than 9. This region will be automatically detected and designated as the near region. As a result, the pure MD model will be triggered to upgrade to a multiscale model, either TB/MD or DFT/MD.

The applicability and viability of the presently developed multiscale TB/MD and DFT/MD models are then presented and validated. Generally, both TB/MD and DFT/MD show different results at higher strain values comparing to the pure MD method. Both the TB/MD and DFT/MD multiscale models show more severe deformations while exhibiting relatively lower stiffnesses in the SWCNT, when compared to the corresponding pure MD simulation. For relatively low strain values, both MD and multiscale results display high level of correspondence.

7.1.3 Numerical Techniques for Computational Efficiency and Speed-up

Our present simulation results reveal that the truncated-Newton via Lanczos minimization performs significantly better than the conjugate gradient method both in terms of the smoothness of the results, as well as computational time.

In our parallelization approach, we adopt the single program multiple data (SPMD) programming model by using MPI 1.2. For DFT, we parallelize according to k -points domain. However, for MD model, we parallelize the whole program according to sub-domain of atoms. The parallelization of MD and DFT show that as the number of

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processors increase, communication costs and load imbalance become more critical issues which may reduce the scalability. In our DFT/MD multiscale model, the DFT calculation was noted to be the most expensive part in the whole simulation. Thus, it became the hot-spot for parallelization in the multiscale model.

7.2 FUTURE WORK

In the present research, a MD model and two multiscale models (TB/MD and DFT/MD) were developed and/or implemented to simulate the mechanical behaviour of SWCNT. However, the multiscale models, being novel approaches, there remains much to be investigated and many challenges to overcome. In the face of these challenges, the future work includes the following:

- First and foremost, the parallelization of the *ab initio* DFT needs to be further enhanced. Presently, MPI 1.2 with collective communication is employed. This only allows one parallelization at any one time. In future, different topology can be introduced in order to allow two or more parallelizations at the same loops. Parallelization of the files handling processes in order to improve the load imbalance is also an important future aspect.
- In future, we intend to study the thermal effects on CNT using MD, TB or DFT methods.
- The DFT method is extremely time consuming. Haynes (1997, 1998) introduced the localized spherical wave basis set which claim to achieve linear-scaling in the DFT and thus attaining further speed-up in computation time. Future works can investigate this exciting claim.

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APPENDIX A

ORTHONORMAL PLANE WAVE

Here, we prove the orthonormal condition of plane waves in Chapter 4. As shown in Figure A.1, the periodic crystal is defined by three primitive translational vectors.

Figure A.1. Crystal defined by three primitive translations vectors.

With given primitive translational vectors of crystal, $\mathbf{a}_i$, the reciprocal vectors, $\mathbf{b}_i$, are defined by

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad (\text{A.1})$$

where δ_{ij} is the Kronecker delta function.

The objective is to prove the following relationship

$$\frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i\mathbf{r} \cdot (\mathbf{k}_1 - \mathbf{k}_2)} = \delta_{\mathbf{k}_1, \mathbf{k}_2} \quad (\text{A.2})$$

where,

$$\int_{\Omega} d\mathbf{r} = \int_{\Omega} dV = \Omega \quad (\text{A.3})$$

$$\mathbf{k}_1 = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \quad (\text{A.4})$$

$$\mathbf{k}_2 = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \quad (\text{A.5})$$

and m_i, n_i ($i=1,2,3$) are integers.

APPENDIX A – ORTHONORMAL PLANE WAVE

In order to validate the result of Equation (A.2), we have to prove the following condition which is simplified from Equation (A.2) as

$$\frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i\mathbf{r} \cdot m\mathbf{b}_j} = 0, \text{ for } j=1,2,3 \text{ and } m \text{ is a non-zero integer} \quad (\text{A.6})$$

In order to integrate the volume integral in Equation (A.6), we have to transform the normal xyz axes to the primitive vector space axis.

From,

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3 \quad (\text{A.7})$$

we have

$$d\mathbf{r} = \frac{\partial \mathbf{r}}{\partial u} du + \frac{\partial \mathbf{r}}{\partial v} dv + \frac{\partial \mathbf{r}}{\partial w} dw = \mathbf{a}_1 du + \mathbf{a}_2 dv + \mathbf{a}_3 dw \quad (\text{A.8})$$

The small volume of the parallelepiped is given by

$$dV = |(\mathbf{a}_1 du) \cdot (\mathbf{a}_2 dv) \times (\mathbf{a}_3 dw)| = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| dudv dw \quad (\text{A.9})$$

Noting that the determinant in Equation (A.9) is similar to the Jacobian of the transformation, if the determinant is identically zero, then there is no parallelepiped. In other words, the three primitive vectors are not linearly independent and thus fails to span the whole real space.

Finally, we derive the volume integral from Equation (A.9) as

$$\int d\mathbf{r} = \int dV = \int |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| dudv dw = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| \int dudv dw \quad (\text{A.10})$$

Since the size of crystal is constant, the three primitive vectors are thus constant. Hence, the determinant is always constant.

Using Equations (A.6), (A.7) and (A.10), we find that for $j=1$

$$\frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i\mathbf{r} \cdot m\mathbf{b}_j} = \frac{1}{\Omega} \int_{\Omega} dV e^{i(m\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3) \cdot m\mathbf{b}_1} = \frac{1}{\Omega} |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| \iiint dudv dw e^{imv2\pi} \quad (\text{A.11})$$

APPENDIX A – ORTHONORMAL PLANE WAVE

Equation (A.11) can be solved using trigonometric functions,

$$\int_{u=0}^{u=1} e^{i2\pi mu} du = \int_{u=0}^{u=1} \cos(2\pi mu) + i \sin(2\pi mu) du = 0 \quad (\text{A.12})$$

The result is also valid for $j=2$ and 3. Thus, Equation (A.6) is proved to be valid for $j=1, 2$ and 3, and Equation (A.2) is thus validated as well.

APPENDIX B

SPHERICAL HARMONICS FUNCTION

The spherical harmonics function is generally used as the basis set in the TB or DFT methodologies, especially in the pseudopotential approach. Thus, in this appendix, we briefly outline some important formulae related to spherical harmonics function.

The spherical harmonics is defined as

$$Y_n^m(\theta, \phi) = Y_{nm}(\theta, \phi) = (-1)^m \sqrt{\frac{(2n+1)(n-m)!}{4\pi(n+m)!}} P_n^m(\cos\theta) e^{im\phi} \quad (\text{B.1})$$

where θ is measured from the z -axis and ϕ from the x -axis. $P_n^m(x)$ is the associated Legendre function, see Andrews (1998) for details of special functions.

Some important properties of the associated Legendre function are

$$P_n^{-m}(x) = (-1)^m \frac{(n-m)!}{(n+m)!} P_n^m(x) \quad (\text{B.2})$$

$$Y_n^m(\Omega_{-\mathbf{k}}) = (-1)^n Y_n^m(\Omega_{\mathbf{k}}) \quad (\text{B.3})$$

$$\left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y_{lm}(\theta, \phi) = -l(l+1) Y_{lm}(\theta, \phi) \quad (\text{B.4})$$

The left operator in Equation (B.4) derived from the Laplacian in spherical coordinates can be written as

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (\text{B.5})$$

One of the important summation formulae for the spherical harmonics function is

$$\sum_{m=-l}^l [Y_{lm}(\theta, \phi)]^2 = \frac{2l+1}{4\pi} \quad (\text{B.6})$$

APPENDIX B – SPHERICAL HARMONICS FUNCTION

Table B.1. Real spherical harmonics for $l=0,1,2$ and 3.

$l=0, m=0$	$\bar{Y}_{0,0} = \sqrt{\frac{1}{4\pi}}$
$l=1, m=-1$	$\bar{Y}_{1,-1} = \sqrt{\frac{3}{4\pi}} \frac{y}{r}$
$l=1, m=0$	$\bar{Y}_{1,0} = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$
$l=1, m=1$	$\bar{Y}_{1,1} = \sqrt{\frac{3}{4\pi}} \frac{x}{r}$
$l=2, m=-2$	$\bar{Y}_{2,-2} = \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2}$
$l=2, m=-1$	$\bar{Y}_{2,-1} = \sqrt{\frac{15}{4\pi}} \frac{yz}{r^2}$
$l=2, m=0$	$\bar{Y}_{2,0} = \sqrt{\frac{5}{16\pi}} \left(2 \frac{z^2}{r^2} - \frac{x^2}{r^2} - \frac{y^2}{r^2} \right)$
$l=2, m=1$	$\bar{Y}_{2,1} = \sqrt{\frac{15}{4\pi}} \frac{xz}{r^2}$
$l=2, m=2$	$\bar{Y}_{2,2} = \sqrt{\frac{15}{16\pi}} \frac{(x^2 - y^2)}{r^2}$
$l=3, m=-3$	$\bar{Y}_{3,-3} = \sqrt{\frac{35}{32\pi}} \frac{(3x^2y - y^3)}{r^3}$
$l=3, m=-2$	$\bar{Y}_{3,-2} = \sqrt{\frac{105}{4\pi}} \frac{(xyz)}{r^3}$
$l=3, m=-1$	$\bar{Y}_{3,-1} = \sqrt{\frac{21}{32\pi}} \left(4 \frac{yz^2}{r^3} - \frac{x^2y}{r^3} - \frac{y^3}{r^3} \right)$
$l=3, m=0$	$\bar{Y}_{3,0} = \sqrt{\frac{7}{16\pi}} \left(2 \frac{z^3}{r^3} - 3 \frac{x^2z}{r^3} - 3 \frac{y^2z}{r^3} \right)$
$l=3, m=1$	$\bar{Y}_{3,1} = \sqrt{\frac{21}{32\pi}} \left(4 \frac{xz^2}{r^3} - \frac{x^3}{r^3} - \frac{xy^2}{r^3} \right)$
$l=3, m=2$	$\bar{Y}_{3,2} = \sqrt{\frac{105}{16\pi}} \left(\frac{x^2z}{r^3} - \frac{y^2z}{r^3} \right)$
$l=3, m=3$	$\bar{Y}_{3,3} = \sqrt{\frac{35}{32\pi}} \left(\frac{x^3}{r^3} - 3 \frac{xy^2}{r^3} \right)$

APPENDIX B – SPHERICAL HARMONICS FUNCTION

Please note that if $r \rightarrow 0$, then $\bar{Y}_{l,m} = k$, where $k = \sqrt{\frac{1}{4\pi}}$ for $(l,m)=(0,0)$, otherwise $k = \text{finite number}$.

Table B.2. Some associated Legendre functions and polynomials.

$n=1, m=1$	$P_1^1(x) = (1-x^2)^{1/2}$
$n=2, m=1$	$P_2^1(x) = 3x(1-x^2)^{1/2}$
$n=2, m=2$	$P_2^2(x) = 3(1-x^2)$
$n=3, m=1$	$P_3^1(x) = \frac{3}{2}(5x^2-1)(1-x^2)^{1/2}$
$n=3, m=2$	$P_3^2(x) = 15x(1-x^2)$
$n=3, m=3$	$P_3^3(x) = 15(1-x^2)^{3/2}$
$n=0$	$P_0(x) = 1$
$n=1$	$P_1(x) = x$
$n=2$	$P_2(x) = \frac{1}{2}(3x^2-1)$
$n=3$	$P_3(x) = \frac{1}{2}(5x^3-3x)$
$n=4$	$P_4(x) = \frac{1}{8}(35x^4-30x^2+3)$

Please refer to Dahl (2001) or Greiner (2000) for the details on the derivation of spherical harmonics functions.

APPENDIX C

ATOMIC UNIT, QUANTUM NUMBER AND FERMI-DIRAC DISTRIBUTION

Atomic Unit

The Schrödinger equation for the electron in a hydrogen atom (with infinitely heavy nuclear mass) is given as

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = E\psi \quad (\text{C.1})$$

where,

- m_e is the mass of the electron, $m_e = 9.10938 \times 10^{-31}$ kg
- e is the elementary electric charge, $e = 1.60218 \times 10^{-19}$ C
- $\hbar$ is Planck's constant (the quantum of action) divided by 2π
- $\hbar = 1.05457 \times 10^{-34}$ Js or $\hbar = (p\lambda)/2\pi$, where p is the momentum of the particle and λ the wavelength of the particle
- ϵ_0 is the permittivity of vacuum, where $4\pi\epsilon_0 = 1.11265 \times 10^{-10}$ Fm⁻¹

The Bohr radius, is defined as

$$a_0 = \frac{\hbar^2}{m_e} \frac{4\pi\epsilon_0}{e^2} = 0.52918 \times 10^{-10} \text{ m} \quad (\text{C.2})$$

In order to simplify all the calculations, we usually normalize these base units such that the values of the four dimensionally independent quantities m_e , e , $\hbar$, and $4\pi\epsilon_0$ are equal to 1. From Equation (C.2), we note that the value of a_0 also becomes 1. The resulting system of units is termed (Hartree) atomic units.

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For the sake of simplicity, we write¹:

- $m_e=1$ au of mass,
- $e=1$ au of charge,
- $\hbar=1$ au of action,
- $4\pi\epsilon_0=1$ au of permittivity,
- $a_0=1$ au of length=1 bohr,
- $E_0=-1/2$ au of energy=-1/2 hartree,

where E_0 defines the ground state solution of Equation (C.1)

$$E_0 = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m_e}{2\hbar^2} \quad (\text{C.3})$$

Please note that atomic unit is used through out the whole thesis unless it is stated otherwise.

Some important values that are frequently used include

- 1 bohr=0.52918 Å=0.52918×10⁻¹⁰ m,
- Energy in unit of 1 hartree =27.2116 eV,
- Energy in unit of 1 Rydberg = 2.1798741 × 10⁻¹⁸ J ≅ 13.6 eV.

Quantum Number

The hydrogen wavefunction of Equation (C.1) can be solved analytically using separation of variables

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (\text{C.4})$$

where θ is the angle between the point and the +z axis, and ϕ is that between the point and the +x axis. Please refer to Greiner (2000) for more details. The final analytical solution reveals the three quantum numbers n, l, m_l which is described in Table C.1.

¹ au means atomic unit

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Table C.1. Quantum numbers of an atomic electron.

Name	Symbol	Possible values	Quantity determined
Principal quantum number	n	1, 2, 3, ...	Electron energy
Orbital quantum number	l	0, 1, 2, ..., $n-1$	Orbital angular-momentum magnitude
Magnetic quantum number	m_l	0, ± 1 , ± 2 , ..., $\pm l$	Orbital angular-momentum direction
Spin magnetic quantum number	m_s	$-\frac{1}{2}$, $+\frac{1}{2}$	Electron spin direction

It is customary to specify electron angular-momentum states by a letter according to the following scheme

l	0	1	2	3	4	5	6
Angular-momentum states	s	p	d	f	g	h	i

The famous Pauli exclusion principle states that no two electrons in an atom can exist in the same quantum state. In other words, each electron must have a different set of quantum numbers n , l , m_l , m_s .

Electrons that have the same principal quantum number n usually (though not always) average approximately the same distance from the nucleus. These electrons therefore interact with roughly the same electric field and have similar energies. Thus, it is conventional to speak of such electrons as occupying the same atomic shell. Shells are denoted by capital letters according to the following scheme:

n	1	2	3	4	5
Atomic shells	K	L	M	N	O

APPENDIX C – ATOMIC UNIT, QUANTUM NUMBER AND FERMI-DIRAC DISTRIBUTION

With the above notation we can write the electron configuration of any atom. For instance, we get

$$\text{hydrogen} = 1s^1; \quad \text{carbon} = 1s^2 2s^2 2p^2.$$

Finally, the Figures C.1 and C.2 show the electronic density of the hydrogen atom at several energy eigenstates.

Figure C.1. Photographic representation of the electron probability density distribution for several energy eigenstates of hydrogen (part 1).

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Figure C.2. Electronic density of hydrogen (part 2).

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Fermi-Dirac Distribution

The theory of electrons in condensed matter is a many-body problem in which one must use statistical concepts to describe the intrinsic properties of materials in the large system “thermodynamic limit”. Development toward quantitative theories requires approximations, namely the independent-electron approximation. Within this approximation each electron moves independently of others, except that the electrons obey the exclusion principle and each moves in some average effective potential which may be determined by the other electrons.

The ground state is the state of the N -electron system at absolute zero temperature. Thus, according to elementary statistical mechanics, as the temperature increases, the electron distribution is given by the Fermi-Dirac distribution function or simply the Fermi function.

The kinetic energy of the electron gas increases as the temperature is increased: some energy levels are occupied which were vacant at absolute zero, and some levels are now vacant which were occupied at absolute zero. The Fermi-Dirac distribution gives the probability that an orbital at energy ε_i will be occupied in an ideal electron gas in thermal equilibrium

$$f_i = f(\varepsilon_i) = f(\varepsilon_i, T) = \frac{1}{\exp[(\varepsilon_i - \mu) / k_B T] + 1} \quad (\text{C.5})$$

where generally, f_i is the probability of finding an electron in state i . Normally the Fermi function is denoted as f_i or $f(\varepsilon_i)$. The quantity μ is a function of the temperature; μ is to be chosen for the particular problem in such a way that the total number of particles in the system turns out correctly – that is, equal to the total number of electrons N . At absolute zero, $\mu = \varepsilon_F$ (Fermi energy ε_F is defined as the energy of the topmost filled level in the ground state of the N electron system), because in the limit $T \rightarrow 0$ the function $f(\varepsilon_i)$ changes discontinuously from the value 1 (filled) to the value 0 (empty) at $\varepsilon_i = \varepsilon_F = \mu$. At all temperatures $f(\varepsilon_i)$ is equal to $\frac{1}{2}$ when $\varepsilon = \mu$, then the denominator of Equation (C.5) has the value 2.

APPENDIX C – ATOMIC UNIT, QUANTUM NUMBER AND FERMI-DIRAC DISTRIBUTION

The quantity μ is the chemical potential, and we see that at absolute zero the chemical potential is equal to the Fermi energy, defined as the energy of the topmost filled orbital at absolute zero.

The high energy tail of the distribution is that part for which $\varepsilon - \mu \gg k_B T$; here the exponential term is dominant in the denominator of $f(\varepsilon_i)$ in Equation (C.5), so that $f(\varepsilon_i) \cong \exp[(\mu - \varepsilon_i)/k_B T]$. This limit is called the Boltzmann or Maxwell distribution.

The temperature of the artificial Fermi smearing of the electrons in eV is represented by $k_B T$. In the computation, it is convenient to use an artificial temperature of $k_B T = 0.01 - 0.10$ eV since a broadening of the occupation improves the stability and convergence rate of the calculation.

Figure C.3 Fermi-Dirac distribution function at various temperatures, for $T_F \equiv \varepsilon_F/k_B = 50,000$ K.

According to Figure C.3, it is obvious that at absolute zero, $T=0$, all the energy states up to the Fermi energy ε_F are occupied. At a low temperature, some electrons will leave states just below ε_F and move into states just above ε_F . However, at a higher temperature, electrons from any state below ε_F may move into states above ε_F .

APPENDIX D

FUNCTIONAL CALCULUS AND VARIATIONAL PRINCIPLE

In this appendix, we briefly discuss the functional space and functional derivative which is frequently used in quantum mechanics. We will show two important examples, the first is related to the well-known Euler-Lagrange equations and the second is the Hartree potential in the DFT. The variational principle is also discussed, leading to the famous Kohn-Sham equations.

Banach Spaces

Generally, the Banach space is a complete normed space (complete in the metric defined by the norm) which is the solution space in DFT. The completeness of the space is required to ensure the convergence behaviour in the iteration procedure.

First of all a Banach space, B , is a vector space which means that if $x, y \in B$ and $\lambda \in R$ or C then

$$\begin{aligned} x, y \in B &\Rightarrow x + y \in B \\ x \in B \text{ and } \lambda \in R \text{ or } C &\Rightarrow \lambda x \in B \end{aligned} \tag{D.1}$$

Secondly a Banach space is a normed space which means that we have on B a function to the positive real numbers including zero with the following properties

$$\begin{aligned} \|\lambda x\| &= |\lambda| \|x\| \\ \|x + y\| &\leq \|x\| + \|y\| \\ \|x\| &= 0 \Leftrightarrow x = 0 \end{aligned} \tag{D.2}$$

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These properties are similar to that of the length of an ordinary vector in three-dimensional space. The introduction of a norm now allows us to define the distance between two points by the following formula

$$d(x, y) = \|x - y\| \quad (\text{D.3})$$

Thus, we obtain the following result

$$d(x, y) = 0 \Leftrightarrow x = y \quad (\text{D.4})$$

Thirdly a Banach space is a complete space. A complete space is a space in which every Cauchy sequence converges to an element of the space. For instance, the real number, R is complete but the rational number, Q is not. We can choose a sequence of rational numbers such as $\langle 1, 1.4, 1.41, 1.412, \dots \rangle$ which converges to real number $\sqrt{2}$, which is not a rational number, and therefore does not belong to Q .

Basically, there are two types of Banach spaces which are relevant to quantum mechanics and DFT in particular. The first Banach space of importance is the space of functions for which the Lebesgue integral

$$\int |f(x)|^p dx \quad (\text{D.5})$$

exists where x is usually a n -dimensional real vector and p is a positive real number. This space is usually denoted as $L^p(R^n)$. Another space is the space of real functions for which the Lebesgue integral

$$\int |f(x)|^2 + |\nabla f(x)|^2 dx \quad (\text{D.6})$$

exists and this is called the Sobolev space $H^1(R^n)$ (the n in H^n denotes the order of the derivative).

Operators and Functionals

Every map $F: B_1 \rightarrow B_2$ in which B_1 and B_2 are Banach spaces is called an operator. For the special case $B_2 = R$ this operator is called a functional. Generally, the space B_1 and

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B_2 are in different spaces with different norms. We consider for instance the operator, $F: C[a,b] \rightarrow C[a,b]$ given by

$$F[f] = f^2 \quad (D.7)$$

or the functional,

$F: C[a,b] \rightarrow R$ given by

$$F[f] = \int_a^b f^2(x) dx \quad (D.8)$$

Linear operators are special operators. These operators have the property that if $f, g \in B_1$ and $\lambda \in R$, then

$$F[\lambda f] = \lambda F[f] \quad (D.9)$$

$$F[f+g] = F[f] + F[g] \quad (D.10)$$

The space of linear operators from B_1 to B_2 is also a vector space. On this space we can also introduce a norm

$$\|F\| = \sup_{f \in B_1} \left\{ \frac{\|F[f]\|_2}{\|f\|_1} \right\} \quad (D.11)$$

where $\| \cdot \|_1$ and $\| \cdot \|_2$ are the norms on the spaces B_1 and B_2 . If the above operator norm exists for an operator F then this operator is considered bounded.

Functional Differentiation

Analogous to conventional vector calculus, on the vector space R^n , we can define two types of derivatives. The first is the Fréchet-derivative, which is analogous to the total derivative in vector calculus, and the second is the Gateaux-derivative which is analogous to the directional derivative in vector calculus.

An operator $F: D_F \rightarrow B_2$ with $D_F \subseteq B_1$ in which B_1 and B_2 are Banach spaces with norms $\| \cdot \|_1$ and $\| \cdot \|_2$, is differentiable in $f \in D_F$ if there exists a linear operator

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$$\frac{\delta F}{\delta f}(f) \in [B_1, B_2] \quad (D.12)$$

such that for $f+h \in D_F$, we obtain

$$\lim_{\|h\|_1 \rightarrow 0} \frac{\|F[f+h] - F[f] - \frac{\delta F}{\delta f}(f)[h]\|_2}{\|h\|_1} = 0 \quad (D.13)$$

If $\frac{\delta F}{\delta f}(f)$ exists for all $f \in D_F$, then this linear functional is called the Fréchet-derivative of F . Here we provide some examples. Consider the operator defined in Equation (D.7), its Fréchet-derivative is a linear operator $\frac{\delta F}{\delta f}(f): B_1 \rightarrow B_2$ defined by

$$\frac{\delta F}{\delta f}(f)[h] = 2fh \in C[a, b] \quad (D.14)$$

This result can be verified according to the definition

$$\begin{aligned} \lim_{\|h\| \rightarrow 0} \frac{\|(f+h)^2 - f^2 - \frac{\delta F}{\delta f}(f)[h]\|}{\|h\|} &= \lim_{\|h\| \rightarrow 0} \frac{\|h^2\|}{\|h\|} = \\ \lim_{\|h\| \rightarrow 0} \frac{1}{\|h\|} \max_{x \in [a, b]} |h^2(x)| &\leq \lim_{\|h\| \rightarrow 0} \frac{1}{\|h\|} \left(\max_{x \in [a, b]} |h(x)| \right)^2 = \lim_{\|h\| \rightarrow 0} \|h\| = 0 \end{aligned}$$

We have defined the derivative of an operator as a linear operator. This is in accordance with the result that the derivative of a function is a linear approximation to that function.

The Gâteaux-derivative of an operator $F: B_1 \rightarrow B_2$ in the direction $h \in B_1$ is a linear operator $\frac{\delta F}{\delta f} \in [B_1, B_2]$ defined by

$$\frac{\delta F}{\delta f}(f)[h] = \lim_{t \rightarrow 0} \frac{F[f+th] - F[f]}{t} \quad (D.15)$$

The limit should be calculated in the norm $\|\cdot\|_2$ of B_2 . As a result, we should check the following condition

$$\lim_{t \rightarrow 0} \left\| \frac{F[f+th] - F[f]}{t} - \frac{\delta F}{\delta f}(f)[h] \right\|_2 = 0 \quad (D.16)$$

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The existence of the Gâteaux-derivative is guaranteed if F is also Fréchet-differentiable and in that case they are of equivalence. However, the existence of the Gâteaux-derivative does not guarantee the existence of the Fréchet-derivative. In other words, F might be differentiable in some directions but not in all directions, or those derivatives might not be equal.

Here we provide some examples of Gâteaux-derivative. Let us consider $F: C[a,b] \rightarrow R$ defined by

$$F[f] = \int_a^b f^{4/3}(x) dx \quad (D.17)$$

Then the Gâteaux-derivative $\frac{\delta F}{\delta f}(f): C[a,b] \rightarrow R$ is given by

$$\begin{aligned} \frac{\delta F}{\delta f}(f)[h] &= \lim_{t \rightarrow 0} \frac{1}{t} \left(\int_a^b (f + th)^{4/3} dx - \int_a^b f^{4/3} dx \right) = \\ &= \lim_{t \rightarrow 0} \frac{1}{t} \left(\int_a^b f^{4/3} \left(1 + \frac{4}{3} t \frac{h}{f} + O(t^2) \right) dx - \int_a^b f^{4/3} dx \right) = \\ &= \lim_{t \rightarrow 0} \int_a^b \frac{4}{3} f^{1/3} h dx + O(t) = \int_a^b \frac{4}{3} f^{1/3} h dx \end{aligned}$$

which can be rewritten as

$$\frac{\delta F}{\delta f}(f)[h] = \int_a^b h \frac{d}{df} (f^{4/3}(x)) dx = \int_a^b h \frac{4}{3} f^{1/3} dx$$

Another important example is the derivation of the Euler-Lagrange equations. Let us consider the Banach space of continuously differentiable functions on some subspace V of 3-D space, denoted by $C^1(V)$. We can then define the functional $F: C^1(V) \rightarrow R$ by

$$F[f] = \int L(f, \nabla f) d\mathbf{r} \quad (D.18)$$

where L is a local function of f and ∇f . The functions f and ∇f are supposed to disappear on the edge of V . Then the Gâteaux-derivative of F is given by¹

¹ Let $\frac{\partial L}{\partial \nabla f} = A$, if A is a vector and h a scalar, then $\nabla \cdot (hA) = (\nabla h) \cdot A + h(\nabla \cdot A)$.

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$$\begin{aligned}
 \frac{\delta F}{\delta f}(f)[h] &= \lim_{t \rightarrow 0} \frac{1}{t} \left(\int L(f + th, \nabla f + t \nabla h) - L(f, \nabla f) d\mathbf{r} \right) \\
 &= \lim_{t \rightarrow 0} \frac{1}{t} \left(\int t \frac{\partial L}{\partial f} h + t \frac{\partial L}{\partial \nabla f} \cdot \nabla h + O(t^2) d\mathbf{r} \right) \\
 &= \int \frac{\partial L}{\partial f} h + \frac{\partial L}{\partial \nabla f} \cdot \nabla h d\mathbf{r} = \int \left(\frac{\partial L}{\partial f} - \nabla \cdot \frac{\partial L}{\partial \nabla f} \right) h d\mathbf{r}
 \end{aligned}$$

If we are looking for extreme values of F , then $\frac{\delta F}{\delta f}(f)[h]$ must be zero for all variations of h . Thus, we obtain

$$\frac{\partial L}{\partial f} - \nabla \cdot \frac{\partial L}{\partial \nabla f} = 0 \quad (\text{D.19})$$

which yields the well-known Euler-Lagrange equations.

The last example of the Gâteaux-derivative is the functional derivative of the Hartree energy in DFT. The Hartree energy of a charge distribution interacting with itself via Coulomb's law is given by

$$U[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (\text{D.20})$$

In the DFT, we set or assign the directional h as $\delta(\mathbf{r} - \mathbf{r}_0)$, t as ε and $\delta n = \varepsilon \delta(\mathbf{r} - \mathbf{r}_0)$. After interchanging the symbols, we arrive at

$$\begin{aligned}
 \frac{\delta U}{\delta n}(n)[h] &= \frac{\delta U}{\delta n}(n)[\delta] = \frac{\delta U}{\delta n}(n) \\
 &= \lim_{\varepsilon \rightarrow 0} \frac{U[n + \varepsilon h] - U[n]}{\varepsilon} = \lim_{\varepsilon \rightarrow 0} \frac{U[n + \delta n] - U[n]}{\varepsilon}
 \end{aligned} \quad (\text{D.21})$$

From Equation (D.20)

After applying divergence theorem and volume integral, we get

$$\begin{aligned}
 \iiint (\nabla h) \cdot A dV &= \iiint \nabla \cdot (hA) dV - \iiint h(\nabla \cdot A) dV = \iint (hA) \cdot \mathbf{n} dS - \iiint h(\nabla \cdot A) dV \\
 &= - \iiint h(\nabla \cdot A) dV,
 \end{aligned}$$

where the divergence theorem or Green's theorem is given as

$$\int \nabla \cdot A d\mathbf{r} = \iiint \nabla \cdot A dV = \iint A \cdot \mathbf{n} dS.$$

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$$U[n + \delta n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\{n(\mathbf{r}) + \delta n(\mathbf{r})\} \{n(\mathbf{r}') + \delta n(\mathbf{r}')\}}{|\mathbf{r} - \mathbf{r}'|} \quad (\text{D.22})$$

where $\delta n(\mathbf{r}') = \varepsilon \delta(\mathbf{r}' - \mathbf{r}_0)$. Expanding the Equation (D.22)

$$U[n + \delta n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}') + \delta n(\mathbf{r})n(\mathbf{r}') + n(\mathbf{r})\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \delta n(\mathbf{r})\delta n(\mathbf{r}') \quad (\text{D.23})$$

The last term of right hand side of Equation (D.23) is ignored. Thus,

$$\begin{aligned} U[n + \delta n] - U[n] &= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\delta n(\mathbf{r})n(\mathbf{r}') + n(\mathbf{r})\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\varepsilon \delta(\mathbf{r} - \mathbf{r}_0)n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\varepsilon \delta(\mathbf{r}' - \mathbf{r}_0)n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{1}{2} \int d\mathbf{r}' \varepsilon \frac{n(\mathbf{r}')}{|\mathbf{r}_0 - \mathbf{r}'|} + \frac{1}{2} \int d\mathbf{r} \varepsilon \frac{n(\mathbf{r})}{|\mathbf{r}_0 - \mathbf{r}|} = \int d\mathbf{r} \varepsilon \frac{n(\mathbf{r})}{|\mathbf{r}_0 - \mathbf{r}|} \end{aligned}$$

Finally, we obtain the Hartree potential as

$$\frac{\delta U(n)}{\delta n(\mathbf{r})} = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}_0 - \mathbf{r}'|} \quad (\text{D.24})$$

Basic of Variational Calculus

Analogous with the total differential operator d of ordinary functions, the variational operator δ acts like the total differential operator with respect to the independent variables of the system. For example, if

$$F = F(x, u, u') \quad (\text{D.25})$$

where x is an independent variable while u and u' are dependent variables. The first variation of F is defined by

$$\delta F = \varepsilon \left[\frac{d}{d\varepsilon} F(x, u + \varepsilon h, u' + \varepsilon h') \right]_{\varepsilon=0} = \varepsilon \left(\frac{\partial F}{\partial u} h + \frac{\partial F}{\partial u'} h' \right) = \frac{\partial F}{\partial u} \delta u + \frac{\partial F}{\partial u'} \delta u' \quad (\text{D.26})$$

where

$$\delta u = (u + \varepsilon h) - u = \varepsilon h, \quad \delta u' = (u' + \varepsilon h') - u' = \varepsilon h' \quad (\text{D.27})$$

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Please note that in Equation (D.26), x is fixed during the variation of u to $u+\delta u$. h and h' are arbitrary. However, for integrals, these two functions are still arbitrary but they must pass through the two fixed end points.

For the case of just one independent variable and one dependent variable, say

$$F = F(x, u) \quad (\text{D.28})$$

we obtain

$$\delta F = \frac{\partial F}{\partial u} \delta u \quad (\text{D.29})$$

The following are some relations of variational calculus which are analogous to those of differential calculus. Letting $F_1=F_1(u)$, $F_2=F_2(u)$, and $G=G(u,v)$, where u and v are dependent variables. We have

$$\delta(F_1 \pm F_2) = \delta F_1 \pm \delta F_2 \quad (\text{D.30})$$

$$\delta(F_1 F_2) = (\delta F_1) F_2 + F_1 \delta F_2 \quad (\text{D.31})$$

$$\delta\left(\frac{F_1}{F_2}\right) = \frac{(\delta F_1) F_2 - F_1 \delta F_2}{F_2^2} \quad (\text{D.32})$$

$$\delta(F_1)^n = n(F_1)^{n-1} \delta F_1 \quad (\text{D.33})$$

$$\delta G = \frac{\partial G}{\partial u} \delta u + \frac{\partial G}{\partial v} \delta v \quad (\text{D.34})$$

$$\frac{d}{dx}(\delta u) = \delta\left(\frac{du}{dx}\right) \quad (\text{D.35})$$

$$\delta\left(\int u dx\right) = \int \delta u dx \quad (\text{D.36})$$

General Ritz Variational Method in Inner Product Space

Here, the objective is to determine the energy of the ground state and using variational method we obtain

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$$\delta(E) = \delta\left(\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}\right) = 0 \quad (\text{D.37})$$

Using Equation (D.32)

$$\delta\left(\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}\right) = \frac{(\delta\langle\psi|\hat{H}|\psi\rangle)\langle\psi|\psi\rangle - \langle\psi|\hat{H}|\psi\rangle(\delta\langle\psi|\psi\rangle)}{\langle\psi|\psi\rangle^2} = 0 \quad (\text{D.38})$$

$$(\delta\langle\psi|\hat{H}|\psi\rangle)\langle\psi|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle(\delta\langle\psi|\psi\rangle) \quad (\text{D.39})$$

As ψ is a complex function, we can look at ψ and its complex conjugate ψ^* as two independent functions. The minimization of the Kohn-Sham functional is obtained by varying the energy functional for a fixed number of electrons with respect to the orbitals subject to the orthonormality constraints. Thus

$$\begin{aligned} \delta \int d\mathbf{r} \psi^* (\hat{H}\psi) &= \frac{\delta\langle\psi|\hat{H}|\psi\rangle}{\delta\psi^*}[h] = \lim_{\varepsilon \rightarrow 0} \frac{\int d\mathbf{r} (\psi^* + \varepsilon h)(\hat{H}\psi) - \int d\mathbf{r} \psi^* (\hat{H}\psi)}{\varepsilon} \\ &= \lim_{\varepsilon \rightarrow 0} \frac{\int d\mathbf{r} \varepsilon h(\hat{H}\psi)}{\varepsilon} = \int d\mathbf{r} h(\hat{H}\psi) \end{aligned} \quad (\text{D.40})$$

As usual, we fix the directional h as $\delta(\mathbf{r}-\mathbf{r}_0)$, and obtain

$$\delta \int d\mathbf{r} \psi^* (\hat{H}\psi) = \int d\mathbf{r} h(\hat{H}\psi) = \int d\mathbf{r} \delta(\mathbf{r}-\mathbf{r}_0)(\hat{H}\psi(\mathbf{r})) = \hat{H}\psi(\mathbf{r}_0) \quad (\text{D.41})$$

Using the same technique,

$$\delta \int d\mathbf{r} \psi^* \psi = \frac{\delta}{\delta\psi^*} \int d\mathbf{r} \psi^* \psi = \psi(\mathbf{r}_0) \quad (\text{D.42})$$

Substituting Equations (D.41) and (D.42) into Equation (D.39),

$$\langle\psi|\psi\rangle\hat{H}\psi(\mathbf{r}_0) = \langle\psi|\hat{H}|\psi\rangle\psi(\mathbf{r}_0) \quad (\text{D.43})$$

and simplifying,

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$$\hat{H}\psi(\mathbf{r}_0) = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \psi(\mathbf{r}_0) = E\psi(\mathbf{r}_0) \quad (\text{D.44})$$

which is exactly the Schrödinger equation.

Variational Principle for the Kohn-Sham Equation

The total ground state energy of the interacting system of electrons with classical nuclei fixed at positions $\{\mathbf{R}_I\}$ can be obtained from

$$\min_{\Psi_0} \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \min_{\{\phi_i\}} E^{KS}[\{\phi_i\}] \quad (\text{D.45})$$

where the new non-interacting system is separable and, therefore, described by a set of single-particle orbitals ϕ_i , $i=1, \dots, N_e$ (total number of electrons). This set of auxiliary functions (Kohn-sham orbitals) $\{\phi_i(\mathbf{r})\}$ must satisfy the orthonormality relation

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (\text{D.46})$$

This is a dramatic simplification since the minimization with respect to all possible many-body wavefunctions $\{\Psi_0\}$ is replaced by a minimization with respect to a set of orthonormal one-particle functions.

The Kohn-Sham energy can be written as

$$E^{KS}[\{\phi_i\}] = -\frac{1}{2} \sum_j \int d\mathbf{r} \phi_j^*(\mathbf{r}) \nabla^2 \phi_j(\mathbf{r}) + \int d\mathbf{r} V_{KS}(\mathbf{r}) n(\mathbf{r}) + E_{nuc-nuc} \quad (\text{D.47})$$

Using the Lagrange multiplier method, the minimization of the Kohn-Sham functional is obtained by varying the energy functional for a fixed number of electrons with respect to the orbitals subject to the orthonormality constraints. Thus, the variational problem can now be formulated as

$$\begin{aligned} \frac{\delta}{\delta \phi_i^*(\mathbf{r})} \left[-\frac{1}{2} \sum_j \int d\mathbf{r} \phi_j^*(\mathbf{r}) \nabla^2 \phi_j(\mathbf{r}) + \int d\mathbf{r} V_{KS}(\mathbf{r}) n(\mathbf{r}) \right. \\ \left. - \sum_{j,k} \lambda_{jk} \left(\int d\mathbf{r} \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r}) - \delta_{ij} \right) \right] = 0 \end{aligned} \quad (\text{D.48})$$

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Now, consider the first term, using Equation (D.41) we obtain

$$\frac{\delta}{\delta\phi_i^*} \sum_j \int d\mathbf{r} \phi_j^*(\mathbf{r}) \nabla^2 \phi_j(\mathbf{r}) = \frac{\delta}{\delta\phi_i^*} \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) = \nabla^2 \phi_i(\mathbf{r}_0) \quad (\text{D.49})$$

For the second term, using the chain rule with Equation (D.42), we obtain

$$\frac{\delta}{\delta\phi_i^*} \int d\mathbf{r} V_{KS}(\mathbf{r}) n(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})} \int d\mathbf{r} V_{KS}(\mathbf{r}) n(\mathbf{r}) \frac{\delta n(\mathbf{r})}{\delta\phi_i^*} = V_{KS}(\mathbf{r}_0) \phi_i(\mathbf{r}_0) \quad (\text{D.50})$$

For the last term, with the use of orthonormality and Equation (D.42), we obtain

$$\frac{\delta}{\delta\phi_i^*} \sum_{j,k} \lambda_{j,k} \int d\mathbf{r} \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r}) = \frac{\delta}{\delta\phi_i^*} \sum_{i,i} \lambda_{i,i} \int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) = \lambda_{ii} \phi_i(\mathbf{r}_0) \quad (\text{D.51})$$

Finally, with the exchange of notation, we obtain the famous Kohn-Sham equation

$$\left\{ -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \lambda_i \phi_i(\mathbf{r}) \quad (\text{D.52})$$

where the Lagrange multiplier can be interpreted as the energy eigenvalues.

APPENDIX E

RECIPROCAL LATTICE AND FOURIER TRANSFORM

In this appendix, we briefly discuss reciprocal lattice and Fourier transform since all the wavefunctions can be expanded in Fourier series in PBC. We also discuss the relationship between the whole crystal and the supercell which will lead to the Brillouin zone (BZ) used in Chapter 4.

For a function $f(x)$ which is p -periodic on R , the Fourier transform is defined as

$$F[k] = \frac{1}{p} \int_0^p f(x) e^{-2\pi i k x / p} dx \quad (\text{E.1})$$

$$f(x) = \sum_{k=-\infty}^{\infty} F[k] e^{2\pi i k x / p} \quad (\text{E.2})$$

and the Plancherel identity is

$$\int_0^p |f(x)|^2 dx = p \sum_{k=-\infty}^{\infty} |F[k]|^2 \quad (\text{E.3})$$

However, we can modify the notation in order to deal with the reciprocal lattice problem. Letting $-k=k^*$, we obtain

$$F[-k^*] = \frac{1}{p} \int_0^p f(x) e^{2\pi i k^* x / p} dx \quad (\text{E.4})$$

and

$$f(x) = \sum_{k^*=-\infty}^{\infty} F[-k^*] e^{-2\pi i k^* x / p} \quad (\text{E.5})$$

If we further let $F[-k^*]=F^*[k^*]$

$$F^*[k^*] = \frac{1}{p} \int_0^p f(x) e^{2\pi i k^* x / p} dx \quad (\text{E.6})$$

and

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$$f(x) = \sum_{k^*=-\infty}^{\infty} F^*[k^*] e^{-2\pi i k^* x / p} \quad (\text{E.7})$$

Finally, letting $F^*[k^*]=F[k]$ and $k^*=k$, we obtain

$$F[k] = \frac{1}{p} \int_0^p f(x) e^{2\pi i k x / p} dx \quad (\text{E.8})$$

and

$$f(x) = \sum_{k=-\infty}^{\infty} F[k] e^{-2\pi i k x / p} \quad (\text{E.9})$$

We also get a slightly modified Plancherel identity

$$\int_0^p |f(x)|^2 dx = p \sum_{k=-\infty}^{\infty} |F[k]|^2 \quad (\text{E.10})$$

Here we solve a reciprocal lattice problem by considering a crystal consists of 4 cells.

This is a 1-D problem (for illustration only) where $N=4$ with primitive vector $a=2\pi$.

A function $f(r)$ is defined for the crystal as

$$f(r) = \begin{cases} \sin(r), & 0 < r < \pi \\ 0, & \pi < r < 2\pi \end{cases} \quad (\text{E.11})$$

The Fourier transform is defined as

$$F[k] = \frac{1}{8\pi} \int_0^{8\pi} f(r) e^{2\pi i k r / 8\pi} dr = \frac{1}{8\pi} \int_0^{8\pi} f(r) e^{i k r / 4} dr \quad (\text{E.12})$$

Note that the wavevector, $\mathbf{q}=k/N=k/4$. The Fourier transform is performed over the whole crystal. However, since the function $f(r)$ is periodic over the whole crystal as well as the cell,

$$f(r) = f(r+\mathbf{T}(n_1)) = f(r+2\pi) \quad (\text{E.13})$$

We breakdown the Fourier transform defined in Equation (E.13) into four regions as

APPENDIX E – RECIPROCAL LATTICE AND FOURIER TRANSFORM

$$F[k] = \frac{1}{8\pi} \left[\int_0^{2\pi} f(r) e^{ikr/4} dr + \int_{2\pi}^{4\pi} f(r) e^{ikr/4} dr + \dots + \int_{6\pi}^{8\pi} f(r) e^{ikr/4} dr \right] \quad (E.14)$$

Subsequently, by substituting $r=r^*+2\pi, \dots, r=r^*+6\pi$ into Equation (E.14) accordingly, we obtain

$$F[k] = \frac{1}{8\pi} \left[\int_0^{2\pi} f(r) e^{ikr/4} dr + \int_0^{2\pi} f(r^*) e^{ik(r^*+2\pi)/4} dr + \dots + \int_0^{2\pi} f(r^*) e^{ik(r^*+6\pi)/4} dr \right] \quad (E.15)$$

Let us examine second term on right hand side of Equation (E.15) and setting $r=r^*$,

$$\int_0^{2\pi} f(r) e^{ik(r+2\pi)/4} dr = \int_0^{2\pi} f(r) e^{ikr/4} \cdot e^{ik2\pi/4} dr = e^{ik2\pi/4} \int_0^{2\pi} f(r) e^{ikr/4} dr \quad (E.16)$$

Following the relationship established in Equation (E.16), Equation (E.15) can be simplified as

$$F[k] = \frac{1}{8\pi} \left[\int_0^{2\pi} f(r) e^{ikr/4} dr + e^{ik2\pi/4} \int_0^{2\pi} f(r) e^{ikr/4} dr + e^{ik4\pi/4} \int_0^{2\pi} f(r) e^{ikr/4} dr + e^{ik6\pi/4} \int_0^{2\pi} f(r) e^{ikr/4} dr \right] \quad (E.17)$$

By letting

$$\alpha = \int_0^{2\pi} f(r) e^{ikr/4} dr \quad (E.18)$$

Equation (E.17) can then be simplified as

$$\begin{aligned} F[k] &= \frac{1}{8\pi} \left[\alpha + e^{ik2\pi/4} \alpha + e^{ik4\pi/4} \alpha + e^{ik6\pi/4} \alpha \right] \\ &= \frac{1}{8\pi} \left[1 + e^{ik2\pi/4} + e^{ik4\pi/4} + e^{ik6\pi/4} \right] \alpha \end{aligned} \quad (E.19)$$

Using the below simple trigonometry formulae

$$\sin(\alpha) + \sin(\beta) = 2 \sin((\alpha+\beta)/2) \cos((\alpha-\beta)/2) \quad (E.20)$$

$$\cos(\alpha) + \cos(\beta) = 2 \cos((\alpha+\beta)/2) \cos((\alpha-\beta)/2) \quad (E.21)$$

we can break down the right hand side of Equation (E.19).

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Let $g(k) = 1 + e^{ik2\pi/4} + e^{ik4\pi/4} + e^{ik6\pi/4}$, we can expand the function $g(k)$ as

$$\begin{aligned} g(k) &= (\cos 0 + i \sin 0) + (\cos k2\pi/4 + i \sin k2\pi/4) + \\ &(\cos k4\pi/4 + i \sin k4\pi/4) + (\cos k6\pi/4 + i \sin k6\pi/4) = A(k) + iB(k) \end{aligned} \quad (E.22)$$

Using the formula in Equation (E.21), we obtain

$$\begin{aligned} A(k) &= (\cos 0 + \cos k6\pi/4) + (\cos k2\pi/4 + \cos k4\pi/4) \\ &= 2 \cos(k3\pi/4) \cos(k3\pi/4) + 2 \cos(k3\pi/4) \cos(k\pi/4) \\ &= 2 \cos(k3\pi/4) 2 \cos(k2\pi/4) \cos(k\pi/4) \end{aligned} \quad (E.23)$$

Since

$$\cos(\pi/2 + n\pi) = \cos\left(\frac{2n+1}{2}\pi\right) = 0, \quad n = \text{integer} \quad (E.24)$$

we arrive at the solution set of $\cos(k3\pi/4)=0$ based on Equation (E.24).

We find that

$$\cos(k3\pi/4) = \cos\left(\frac{2n+1}{2}\pi\right) \rightarrow k = \frac{4n+2}{3} \quad (E.25)$$

Due to k being an integer, the solution set is $\{\dots, 2, 6, 10, \dots\}$. Using the same technique, we found that the solution set for $\cos(k2\pi/4)=0$ is $\{\dots, 1, 3, 5, 7, \dots\}$. Lastly, the solution set for $\cos(k\pi/4)=0$ is $\{\dots, 2, 6, 10, \dots\}$. In conclusion, $A(k)$ is always zero for the union of the above three solution set namely $\{\dots, 1, 2, 3, 5, 6, 7, 9, 10, \dots\}$ or $\{k: k/4=\text{integer}\}$.

Following the same approach, using the formula of Equation (E.20), we obtain correspondingly for $B(k)$

$$\begin{aligned} B(k) &= (\sin 0 + \sin k6\pi/4) + (\sin k2\pi/4 + \sin k4\pi/4) \\ &= 2 \sin(k3\pi/4) \cos(k3\pi/4) + 2 \sin(k3\pi/4) \cos(k\pi/4) \\ &= 2 \sin(k3\pi/4) 2 \cos(k2\pi/4) \cos(k\pi/4) \end{aligned} \quad (E.26)$$

Using the above technique, we also find that $B(k)$ is always zero for any integer k .

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Finally, following the interception of solution sets for $A(k)$ and $B(k)$, we conclude that $F[k]$ is always zero except when $k=0,4,\dots$ (or $k/N=\text{integer}$). Since $N=4$, $\mathbf{q}=k/N$ and $\mathbf{a}_i=2\pi$, we can therefore establish the following relationship, $\mathbf{q}\cdot\mathbf{a}_i=2\pi\times\text{integer}$.

Thus, we can write

$$F[k] = \frac{1}{2\pi} \int_0^{2\pi} f(r) e^{ikr/4} dr, \quad k = 0, 4, \dots (\text{or } k/4 = \text{integer}) \quad (\text{E.27})$$

Finally, the Equation (4.99) in Chapter 4 is validated for the 1-D case where $\Omega_{\text{crystal}}=8\pi$ and $\Omega_{\text{cell}}=2\pi$.

Next we discuss the Fourier transform in 3-D space. In the 3-D space, we obtain the Fourier transform as

$$\tilde{f}(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}} \int_{\text{cell}} d\mathbf{r} e^{-i\mathbf{G}\cdot\mathbf{r}} f(\mathbf{r}); \quad f(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{f}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \quad (\text{E.28})$$

where $\mathbf{G}$ is the reciprocal lattice vector. The function $f(\mathbf{r})$ has the periodicity of a Bravais lattice, $f(\mathbf{r}+\mathbf{R})=f(\mathbf{r})$ for all $\mathbf{R}$ in the Bravais lattice.

In a large crystal of volume Ω_{crystal} composed of N cells, we can write

$$\tilde{f}(\mathbf{k}) = \frac{1}{\Omega_{\text{crystal}}} \int_{\text{crystal}} d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}); \quad f(\mathbf{r}) = \sum_{\mathbf{k}} \tilde{f}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (\text{E.29})$$

where the wavevector $\mathbf{k}$ is explained in Section 4.8. Please note that the relationship between Equations (E.28) and (E.29) follow exactly the result of Equation (4.99). The function $f(\mathbf{r})$ satisfies the Born-von Karman boundary condition

$$f(\mathbf{r}+N_i\mathbf{a}_i) = f(\mathbf{r}), \quad i=1, 2, 3 \quad (\text{E.30})$$

where $\mathbf{a}_i$ are the primitive vectors and N_i the number of cell divisions in the i -axis.

For discrete Fourier transform in 3-D space, we obtain

$$f_{i_1, i_2, i_3} = \sum_{j_1=0}^{N_1-1} \sum_{j_2=0}^{N_2-1} \sum_{j_3=0}^{N_3-1} g_{j_1, j_2, j_3} e^{i2\pi j_1 / N_1} e^{i2\pi j_2 / N_2} e^{i2\pi j_3 / N_3} = \sum_{j_1, j_2, j_3} g_{j_1, j_2, j_3} e^{i\mathbf{g}_j \cdot \mathbf{r}_i} \quad (\text{E.31})$$

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where we modify the notation for simplicity and consistency. The new notations are

$$\mathbf{g}_j = j_1 \mathbf{g}_1 + j_2 \mathbf{g}_2 + j_3 \mathbf{g}_3 \quad (\text{E.32})$$

where $\mathbf{g}_i$ are the reciprocal lattice vectors and

$$\mathbf{r}_i = \frac{i_1}{N_1} \mathbf{a}_1 + \frac{i_2}{N_2} \mathbf{a}_2 + \frac{i_3}{N_3} \mathbf{a}_3 \quad (\text{E.33})$$

The respective inverse Fourier transform is defined as

$$\begin{aligned} g_{j_1, j_2, j_3} &= \frac{1}{N_1 N_2 N_3} \sum_{i_1=0}^{N_1-1} \sum_{i_2=0}^{N_2-1} \sum_{i_3=0}^{N_3-1} f_{i_1, i_2, i_3} e^{-i2\pi i_1 j_1 / N_1} e^{-i2\pi i_2 j_2 / N_2} e^{-i2\pi i_3 j_3 / N_3} \\ &= \frac{1}{N_1 N_2 N_3} \sum_{i_1, i_2, i_3} f_{i_1, i_2, i_3} e^{-i\mathbf{g}_j \cdot \mathbf{r}_i} \end{aligned} \quad (\text{E.34})$$

From Equation (E.33) we obtain

$$\Delta \mathbf{r}_i = \frac{\Delta i_1}{N_1} \mathbf{a}_1 + \frac{\Delta i_2}{N_2} \mathbf{a}_2 + \frac{\Delta i_3}{N_3} \mathbf{a}_3 = \frac{1}{N_1} \mathbf{a}_1 + \frac{1}{N_2} \mathbf{a}_2 + \frac{1}{N_3} \mathbf{a}_3 \quad (\text{E.35})$$

Following the discussion in Appendix A, the small volume of the parallelepiped is given by

$$dV = d\mathbf{r} = \left| \frac{\mathbf{a}_1}{N_1} \cdot \frac{\mathbf{a}_2}{N_2} \times \frac{\mathbf{a}_3}{N_3} \right| = \frac{1}{N_1 N_2 N_3} \Omega_{\text{cell}} \quad (\text{E.36})$$

From Equation (E.34) we obtain

$$g_{j_1, j_2, j_3} = \frac{1}{\Omega_{\text{cell}}} \sum_{i_1, i_2, i_3} \frac{\Omega_{\text{cell}}}{N_1 N_2 N_3} f_{i_1, i_2, i_3} e^{-i\mathbf{g}_j \cdot \mathbf{r}_i} = \frac{1}{\Omega_{\text{cell}}} \sum_{i_1, i_2, i_3} dV f_{i_1, i_2, i_3} e^{-i\mathbf{g}_j \cdot \mathbf{r}_i} \quad (\text{E.37})$$

In the thermodynamic limit ($N_1, N_2, N_3 \rightarrow \infty$), the discrete sums are replaced by integrals over the unit cell

$$g_{j_1, j_2, j_3} = \frac{1}{\Omega_{\text{cell}}} \int_{\text{cell}} d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{g} \cdot \mathbf{r}} \quad (\text{E.38})$$

The above Equation (E.38) is exactly similar to Equation (E.28). Practically, (N_1, N_2, N_3) must be sufficiently large to include all available Fourier components. In other words, the more Fourier components, the larger the grid in the reciprocal space and the finer the grid in the real space.

APPENDIX F

PERIODIC BOUNDARY CONDITIONS

Here we will employ a simple example to illustrate the k -points calculation. We will also discuss the Bloch theorem in a PBC (periodic boundary conditions) system and its application in the Kohn-Sham equations which lead to the k -points diagonalisations.

The use of periodic boundary conditions in electronic structures leads to a number of special features. Here we illustrate it using a simple 1-D system. Suppose we have a 1-D system of $2N$ spinless electrons in a periodic box of length a , and no potential energy exists ($V=0$). Our objective is to determine its energy $E(a,2N)$. Since we assume no potential exists and if plane wave basis set is used, we can write

$$\hat{T}\phi_i = \varepsilon_i \phi_i \rightarrow -\frac{1}{2}\nabla^2 \phi_i = \varepsilon_i \phi_i \quad (\text{F.1})$$

Letting

$$\phi_i = e^{i(2\pi m/a)x} \quad (\text{F.2})$$

will lead to

$$\phi_i(x+a) = e^{i(2\pi m/a)(x+a)} = e^{i(2\pi mx/a) + i2\pi m} = e^{i(2\pi mx/a)} \quad (\text{F.3})$$

which satisfies the periodic condition. Substituting Equation (F.2) into (F.1), we obtain

$$-\frac{1}{2}\nabla^2 \phi_i = \varepsilon_i \phi_i \rightarrow -\frac{1}{2}(i2\pi m/a)^2 e^{i(2\pi m/a)x} = \varepsilon_i \cdot e^{i(2\pi m/a)x} \quad (\text{F.4})$$

Therefore we determine energy to be

$$\varepsilon_i = \frac{1}{2}(2\pi m/a)^2, \quad m = 0, \pm 1, \pm 2, \dots \quad (\text{F.5})$$

Filling the level from $m=-N+1$ to $m=N$ gives us $2N$ electrons, and so we might simply assume that the total kinetic energy is

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$$E(a, 2N) = \frac{1}{2} \sum_{m=-N+1}^N \left(\frac{2\pi m}{a} \right)^2 \quad (\text{F.6})$$

However, the above result must be verified. By evaluating the sums, we get

$$E(a, 2N) = \left(\frac{2\pi}{a} \right)^2 \frac{2N^3 + N}{6} \quad (\text{F.7})$$

Unfortunately, we find that this energy expression has a serious fault as it does not obey the periodic condition, i.e.

$$E(Ma, 2NM) \neq ME(a, 2N) \quad (\text{F.8})$$

where M is any integer larger than 1 for duplication. In other words, if we double the supercell length $a \rightarrow 2a$ and number of electrons $2N \rightarrow 4N$, it does not lead the desired result of $E \rightarrow 2E$.

A more reasonable definition of the kinetic energy would take the energy of an assembly of large number M of unit cells, and divide it by M . In this way, extensivity would be built in automatically

$$E'(a, 2N) = \lim_{M \rightarrow \infty} \frac{E(Ma, 2NM)}{M} \quad (\text{F.9})$$

leading to

$$E'(a, 2N) = \left(\frac{\pi}{a} \right)^2 \frac{(2N)^3}{6} \quad (\text{F.10})$$

which is extensive. Comparing Equations (F.10) and (F.7), we note that the latter result eliminates the troublesome $O(N)$ term.

Physically, the above exercise indicates that we are introducing long wavelength plane waves into our system by taking larger supercells. Please note that these modes are absent in a supercell that has only one unit cell.

APPENDIX F – PERIODIC BOUNDARY CONDITIONS

Here we try to illustrate a form of ‘ k -points’ averaging. An alternative way to obtain this result would be as follows. Suppose we take a supercell of dimension Ma consisting of $2MN$ electrons. The states then have wavevectors

$$\frac{2\pi n}{Ma}, \quad n = -MN+1, \dots, MN \quad (\text{F.11})$$

These wavenumbers can be decomposed into integer and fractional parts

$$\frac{2\pi n}{Ma} = \frac{2\pi}{a} \frac{(n+m)}{M} - \frac{2\pi m}{aM} \quad (\text{F.12})$$

Now, letting

$$q = \frac{n+m}{M} \quad (\text{F.13})$$

where m is chosen so that q is an integer (or $n+m$ is a multiple of M)

$$q = -N+1, \dots, 0, \dots, N \quad (\text{F.14})$$

We examine the minimum value of q

$$q_{\min} = \frac{n_{\min} + m}{M} = \frac{-MN+1+m}{M} = -N + \frac{1+m}{M} \quad (\text{F.15})$$

Since $q_{\min} = -N+1$

$$q_{\min} = -N+1 = -N + \frac{1+m}{M} \rightarrow 1 = \frac{1+m}{M} \quad (\text{F.16})$$

As a result, it is obvious that $q_{\min}$ corresponds to $m=M-1$.

For the maximum value of q

$$q_{\max} = \frac{n_{\max} + m}{M} = \frac{MN+m}{M} = N + \frac{m}{M} \quad (\text{F.17})$$

Since $q_{\max}=N$, we note that $q_{\max}$ corresponds to $m=0$.

The above decomposition enables us to split the single sum over n , from $-MN+1$ to MN , into a double sum as

APPENDIX F – PERIODIC BOUNDARY CONDITIONS

$$\begin{aligned} \frac{E(Ma, 2NM)}{M} &= \frac{1}{2M} \sum_{n=-NM+1}^{NM} \left(\frac{2\pi n}{aM} \right)^2 = \frac{1}{2M} \sum_{n=-NM+1}^{MN} \left(\frac{2\pi}{a} q - \frac{2\pi m}{aM} \right)^2 \\ &= \frac{1}{2M} \sum_{m=0}^{M-1} \sum_{q=-N+1}^N \left(-\frac{2\pi m}{aM} + \frac{2\pi}{a} q \right)^2 \end{aligned} \quad (\text{F.18})$$

Taking the limit of $M \rightarrow \infty$ and applying the concept of a definite integral, let us define

$$k = -\frac{2\pi m}{aM} \quad (\text{F.19})$$

and therefore

$$m=0 \rightarrow k=0; \quad \text{and} \quad m=M-1 \rightarrow k = -\frac{2\pi}{a} \frac{(M-1)}{M} \quad (\text{F.20})$$

The small increment of k becomes

$$\Delta k = -\frac{2\pi}{aM} \Delta m = -\frac{2\pi}{aM} \quad (\text{F.21})$$

since m is an integer, $\Delta m=1$.

Rearranging, we can write

$$\frac{1}{M} = -\frac{a}{2\pi} \Delta k \quad (\text{F.22})$$

and noting that Equation (F.22) obeys the condition

$$\text{if } M \rightarrow \infty, \text{ then } \Delta k \rightarrow 0 \quad (\text{F.23})$$

Thus, the summation can be transformed as

$$\frac{1}{M} \sum_m^{M-1} \rightarrow \sum_m^{M-1} \frac{1}{M} = \sum_{k=0}^{\frac{2\pi(M-1)}{a}} \frac{1}{M} = \sum_{k=0}^{\frac{2\pi(M-1)}{a}} -\frac{a}{2\pi} \Delta k = -\frac{a}{2\pi} \sum_{k=0}^{\frac{2\pi(M-1)}{a}} \Delta k \quad (\text{F.24})$$

Now let $M \rightarrow \infty$, so that $\Delta k \rightarrow 0$, then we obtain

APPENDIX F – PERIODIC BOUNDARY CONDITIONS

$$\frac{1}{M} \sum_m^{M-1} \rightarrow -\frac{a}{2\pi} \sum_{k=0}^{\frac{2\pi}{a}} \Delta k \Bigg|_{\Delta k \rightarrow 0} = -\frac{a}{2\pi} \int_{k=0}^{\frac{2\pi}{a}} dk \equiv \frac{a}{2\pi} \int_{k=0}^{\frac{2\pi}{a}} dk \quad (\text{F.25})$$

Finally, we arrive at

$$\lim_{M \rightarrow \infty} \frac{E(Ma, 2NM)}{M} = E(a, 2N) = \frac{1}{2} \frac{a}{2\pi} \int_{k=0}^{\frac{2\pi}{a}} \sum_{q=-N+1}^N \left(k + \frac{2\pi}{a} q \right)^2 dk \quad (\text{F.26})$$

The above expression is an example of a k -points averaged energy. Equation (F.26) shows that we can treat our system of $2NM$ electrons as consisting of M systems of $2N$ electrons, where each system is characterized by particular k -points. Their energy levels are given by $(k+2\pi q/a)^2/2$. Please note that the above k -points is not exactly the special points $\mathbf{k}_i^*$ (also sometimes called k -points) where the former is simply the integration path in reciprocal space whereas the latter is the special points used in the reciprocal space integration.

Bloch Theorem

In the calculation of a PBC system, the external potential and the effective potential are periodic functions. Their periodicity are defined by the supercell translational vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ such that

$$v(\mathbf{r}+\mathbf{T}) = v(\mathbf{r}) \quad (\text{F.27})$$

$$\mathbf{T} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (\text{F.28})$$

where v is the potential and n_i are any integers. The translational invariance associated with this periodicity immediately leads to a set of quantum numbers that label our one-electron orbitals as

$$\phi_i \rightarrow \phi_{i,\mathbf{k}} \quad (\text{F.29})$$

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The Kohm-Sham orbitals ϕ are in general complex values, whereas the density $n(\mathbf{r})$ constructed from $|\phi_{i,\mathbf{k}}|^2$ is a real value. As a result, if we translate the vector $\mathbf{T}$, the wavefunction $\phi_{i,\mathbf{k}}$ will acquire a phase

$$\phi_{i,\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}} \phi_{i,\mathbf{k}}(\mathbf{r}) \quad (\text{F.30})$$

without changing the electron density. Another way to express the wavefunction is

$$\phi_{i,\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i,\mathbf{k}}(\mathbf{r}) \quad (\text{F.31})$$

where $u_{i,\mathbf{k}}$ is a periodic function which obeys the following condition

$$u_{i,\mathbf{k}}(\mathbf{r}+\mathbf{T}) = u_{i,\mathbf{k}}(\mathbf{r}) \quad (\text{F.32})$$

The periodic function $u_{i,\mathbf{k}}$ is a Bloch function. The actual orbital is constructed out of a Bloch function by multiplying it with the phase factor $e^{i\mathbf{k}\cdot\mathbf{r}}$.

We can derive the equivalent equations which the Bloch functions obey by substituting Equation (F.31) into the following Kohm-Sham equation

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_{i,\mathbf{k}} = \varepsilon_{i,\mathbf{k}} \phi_{i,\mathbf{k}} \quad (\text{F.33})$$

where $v_{\text{eff}}(\mathbf{r})$ is same with $V_{KS}(\mathbf{r})$ in Section 4.2.

The result is a set of equations very similar to the Kohm-Sham equations as

$$\left[\frac{1}{2} (-i\nabla + \mathbf{k})^2 + v_{\text{eff}}(\mathbf{r}) \right] u_{i,\mathbf{k}} = \varepsilon_{i,\mathbf{k}} u_{i,\mathbf{k}} \quad (\text{F.34})$$

Note that this is an eigenvalue problem for each $\mathbf{k}$, resulting in a set of energy levels $\varepsilon_{i,\mathbf{k}}$ and Bloch functions $u_{i,\mathbf{k}}$. Thus when we are doing a calculation over wavevector $\mathbf{k}$, we are actually performing separate diagonalisations.

The above Bloch functions also obey a periodicity in reciprocal space which is defined over the reciprocal space lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ as

$$\mathbf{b}_1 = \frac{2\pi}{\Omega} (\mathbf{a}_2 \times \mathbf{a}_3) \quad (\text{F.35})$$

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$$\mathbf{b}_2 = \frac{2\pi}{\Omega}(\mathbf{a}_3 \times \mathbf{a}_1) \quad (\text{F.36})$$

$$\mathbf{b}_3 = \frac{2\pi}{\Omega}(\mathbf{a}_1 \times \mathbf{a}_2) \quad (\text{F.37})$$

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (\text{F.38})$$

$$\mathbf{K} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \quad (\text{F.39})$$

The Bloch functions as well as energy levels $\varepsilon_{i,\mathbf{k}}$ are periodic in the reciprocal lattice vectors $\mathbf{K}$

$$u_{i,\mathbf{k}+\mathbf{K}}(\mathbf{r}) = u_{i,\mathbf{k}}(\mathbf{r}) \quad (\text{F.40})$$

$$\varepsilon_{i,\mathbf{k}+\mathbf{K}} = \varepsilon_{i,\mathbf{k}} \quad (\text{F.41})$$

This periodicity over $\mathbf{K}$ implies that we need not compute the Bloch functions $u_{i,\mathbf{k}}$ over all $\mathbf{k}$, but can restrict our attention over one periodic element of it. Generally, we will restrict our calculation to the first Brillouin Zone (FBZ or BZ). The BZ is normally defined as the Wigner-Seitz cell of the periodic lattice, a k -vector $\mathbf{k}$ lies within the BZ if it is closer to the origin $\mathbf{k}=0$ (called Γ region) than any other reciprocal lattice vector $\mathbf{K}$.

We would need to calculate any $\mathbf{k}$ vector inside the BZ as it is a continuously varying “quantum number”. For a 1-D chain of atoms with lattice spacing a , the BZ is spanned by $-\pi/a < k < \pi/a$, see Ashcroft (1976).

APPENDIX G

MATHEMATICAL FOUNDATION OF QUANTUM MECHANICS

The inner product operation in Hilbert space is used in both TB and DFT. In this appendix, we summarize the basic mathematical principles of quantum mechanics with some examples. We present some basic properties of the Hilbert space, and also point out the necessity of the self-adjoint or Hermitian operator used in the DFT, see also Greiner (2000).

A Hilbert space is a complete inner product space. In a Hilbert space H , its abstract number of elements, which are called vectors, $|a\rangle$, $|b\rangle$ etc., has the following properties:

(1) The space H is a linear vector space above the body of the complex numbers μ and ν . It has three properties:

$$(a) \quad |a\rangle + |b\rangle = |b\rangle + |a\rangle \quad (\text{commutative law}) \quad (G.1)$$

$$(|a\rangle + |b\rangle) + |c\rangle = |a\rangle + (|b\rangle + |c\rangle) \quad (\text{associative law}) \quad (G.2)$$

(b) a zero vector $|0\rangle$ exists, with the property

$$|a\rangle + |0\rangle = |a\rangle \quad (G.3)$$

(c) to each vector $|a\rangle$ of H , an antivector $|-a\rangle$ exists, with property

$$|a\rangle + |-a\rangle = |0\rangle \quad (G.4)$$

In addition,

$$\mu(|a\rangle + |b\rangle) = \mu|a\rangle + \mu|b\rangle$$

$$(\mu + \nu)|a\rangle = \mu|a\rangle + \nu|a\rangle$$

$$\mu\nu|a\rangle = \mu(\nu|a\rangle)$$

$$1|a\rangle = |a\rangle \quad (G.5)$$

(2) An inner product operation defined in the space H is denoted by

APPENDIX G – MATHEMATICAL FOUNDATION OF QUANTUM MECHANICS

$$(|a\rangle, |b\rangle) \text{ or } \langle a|b\rangle \quad (\text{G.6})$$

yielding a complex number¹. The inner product has to fulfill the relations

$$\begin{aligned} (|a\rangle, \lambda|b\rangle) &= \lambda(|a\rangle, |b\rangle) \\ (|a\rangle, |b\rangle + |c\rangle) &= (|a\rangle, |b\rangle) + (|a\rangle, |c\rangle) \\ (|a\rangle, |b\rangle) &= (|b\rangle, |a\rangle)^* \text{ or } \langle a|b\rangle = \langle b|a\rangle^* \end{aligned} \quad (\text{G.7})$$

It is easily shown that

$$(\lambda|a\rangle, |b\rangle) = \lambda^* (|a\rangle, |b\rangle) = \lambda^* \langle a|b\rangle \quad (\text{G.8})$$

The norm of the vectors is defined by

$$\|a\| = \sqrt{\langle a|a\rangle} \quad (\text{G.9})$$

In the normed space, Schwartz's inequality holds true

$$\|a\| \cdot \|b\| \geq |\langle a|b\rangle| \quad (\text{G.10})$$

(3) For every vector $|a\rangle$ of H , a series of vectors $|a_n\rangle$ exists, with the property that for every $\varepsilon > 0$, there is at least one vector $|a_n\rangle$ of the series with

$$\|a\rangle - |a_n\rangle\| < \varepsilon \quad (\text{G.11})$$

A series with this property is called compact, or $|a_n\rangle$ of the space H is separable.

(4) The Hilbert space is complete. This means that every vector $|a\rangle$ of H can be arbitrarily and exactly approximated by a series $|a_n\rangle$

$$\lim_{n \rightarrow \infty} \|a\rangle - |a_n\rangle\| = 0 \quad (\text{G.12})$$

The series $|a_n\rangle$ thus has a unique limiting value $|a\rangle$.

¹ In quantum mechanics, we adopt $\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{\infty} \psi_1^* \psi_2 dV$. This is interpreted to be a product of two elements, $\langle \psi_1 |$ and $|\psi_2\rangle$. The element $\langle \psi_1 |$ is termed 'bra' and $|\psi_2\rangle$ termed 'ket', together forming the 'bra-ket' notation. Both are vectors (state vectors) in a linear vector space.

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Here we discuss some properties which are frequently used in quantum mechanics.

Orthogonality of vectors

Two vectors $|f\rangle$ and $|g\rangle$ are orthogonal if

$$\langle f|g\rangle = 0 \quad (\text{G.13})$$

Orthonormal system

The set $\{|f_i\rangle\}$ of vectors is an orthonormal system if

$$\langle f_i|f_j\rangle = \delta_{ij} \quad (\text{G.14})$$

where i and j are integer.

Complete orthonormal system

The orthonormal system $\{|f_n\rangle\}$ is complete in H if an arbitrary vector $|f\rangle$ of H can be expressed by

$$|f\rangle = \sum_n \alpha_n |f_n\rangle \quad (\text{G.15})$$

In general, α_n are complex numbers. Due to the orthonormality of the system,

$$\langle f_m|f\rangle = \left\langle f_m \left| \sum_n \alpha_n f_n \right. \right\rangle = \sum_n \alpha_n \langle f_m|f_n\rangle = \sum_n \alpha_n \delta_{mn} = \alpha_m \quad (\text{G.16})$$

Substituting Equation (G.16) into Equation (G.15),

$$|f\rangle = \sum_n |f_n\rangle \langle f_n|f\rangle \quad (\text{G.17})$$

The complex numbers α_n are called the f_n representation of $|f\rangle$. If the sum encloses an infinite number of terms, then we speak of a Hilbert space of infinite dimensions.

Operators in Hilbert Space

A linear operator $\hat{A}$ induces a mapping of H upon itself or upon a subspace of H .

$$\hat{A}(\alpha|f\rangle + \beta|g\rangle) = \alpha\hat{A}|f\rangle + \beta\hat{A}|g\rangle \quad (\text{G.18})$$

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The operator $\hat{A}$ is bounded, if

$$\|\hat{A}|f\rangle\| \leq C\|f\rangle\| \quad (\text{G.19})$$

for all $|f\rangle$ of H , with C being the same constant for all the $|f\rangle$. Bounded linear operators are continuous. This means that

$$\hat{A}|f_n\rangle \rightarrow \hat{A}|f\rangle \text{ if } |f_n\rangle \rightarrow |f\rangle, \text{ for } n \rightarrow \infty \quad (\text{G.20})$$

The following definitions are often used:

(1)	unity operator	$\hat{1}$	:	$\hat{1} f\rangle = f\rangle$	
(2)	zero operator	$\hat{0}$	:	$\hat{0} f\rangle = 0\rangle$	
(3)	sum operator	$\hat{A} + \hat{B}$	:	$(\hat{A} + \hat{B}) f\rangle = \hat{A} f\rangle + \hat{B} f\rangle$	
(4)	product operator	$\hat{A}\hat{B}$	:	$(\hat{A}\hat{B}) f\rangle = \hat{A}(\hat{B} f\rangle)$	(G.21)

In general

$$\hat{A}\hat{B} \neq \hat{B}\hat{A} \quad (\text{G.22})$$

The adjoint of a restricted operator

If an operator $\hat{A}^+$ exists for the operator $\hat{A}$ for all $|f\rangle$ and $|g\rangle$ of H in such a way that

$$(|g\rangle, \hat{A}|f\rangle) = (\hat{A}^+|g\rangle, |f\rangle) \quad (\text{G.23})$$

which can be rewritten as

$$\langle g|\hat{A}|f\rangle = \langle \hat{A}^+g|f\rangle \quad (\text{G.24})$$

then $\hat{A}^+$ is the adjoint operator of $\hat{A}$. This relation can be expressed by²

$$\langle g|\hat{A}|f\rangle = \langle \hat{A}^+g|f\rangle = \langle f|\hat{A}^+|g\rangle^* \quad (\text{G.25})$$

The adjoint of an operator possesses the following properties:

² $|\psi\rangle^* = \langle \psi|$. $\langle \psi|\hat{L}|\xi\rangle = \int \psi^* \hat{L}\xi dV$. $\langle \hat{L}\psi|\xi\rangle = \int (\hat{L}\psi)^* \xi dV$.

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$$\begin{aligned}
 (1) \quad & (\alpha \hat{A})^+ = \alpha^* \hat{A}^+ \\
 (2) \quad & (\hat{A} + \hat{B})^+ = \hat{A}^+ + \hat{B}^+ \\
 (3) \quad & (\hat{A}\hat{B})^+ = \hat{B}^+ \hat{A}^+ \\
 (4) \quad & (\hat{A}^+)^+ = \hat{A}
 \end{aligned} \tag{G.26}$$

A Hermitian operator (or self-adjoint operator) is an operator that fulfills the relation

$$\hat{A} = \hat{A}^+ \tag{G.27}$$

The expectation values of Hermitian operator are real

$$\langle f | \hat{A} | f \rangle = \langle f | \hat{A}^+ | f \rangle^* = \langle f | \hat{A} | f \rangle^* = \text{real} \tag{G.28}$$

Eigenvalues and Eigenvectors

For the eigen problem

$$\hat{A} |a\rangle = \lambda |a\rangle \tag{G.29}$$

where λ , is a complex eigenvalue. For a Hermitian operator $\hat{A}$, the following hold true:

- (a) The eigenvalues of Hermitian operators are real.

Multiplying $\langle a |$ to Equation (G.29)

$$\langle a | \hat{A} | a \rangle = \lambda \langle a | a \rangle \tag{G.29a}$$

Now, applying the complex conjugate to Equation (G.29a)

$$\langle a | \hat{A} | a \rangle^* = \lambda^* \langle a | a \rangle^* \rightarrow \langle a | \hat{A} | a \rangle = \lambda^* \langle a | a \rangle \tag{G.29b}$$

According to Equations (G.29a) and (G.29b)

$$\lambda = \lambda^*, \rightarrow \lambda = \text{real}$$

As a result, the entire potential operators in quantum mechanics as well as DFT must be self-adjoint or Hermitian.

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(b) If $|a'\rangle$ and $|a''\rangle$ are two eigenvectors of a Hermitian operator $\hat{A}$ with two different eigenvalues, $\lambda' \neq \lambda''$, then

$$\langle a' | a'' \rangle = 0$$

In the DFT, the eigenvalue represents energy. Thus, for different energy levels their wavefunctions are mutually orthogonal.

(c) The normalized eigenvectors of a bounded Hermitian operator $\hat{A}$ create a countable, complete orthonormal system. In this case the eigenvalues are discrete. Therefore, for a complete orthonormal system $|a\rangle$ of Hermitian $\hat{A}$, we obtain for an arbitrary vector $|\psi\rangle$

$$|\psi\rangle = \sum_a |a\rangle \langle a | \psi \rangle \quad (\text{G.30})$$

The inner product of two vectors $|\xi\rangle$ and $|\psi\rangle$ can thus be expressed in the A representation using Equation (G.30)

$$\langle \xi | \psi \rangle = \sum_a \langle \xi | a \rangle \langle a | \psi \rangle \quad (\text{G.31})$$

Here, if we introduce the unity (or completeness) operator $\hat{1}$,

$$\hat{1} = \sum_a |a\rangle \langle a| \quad (\text{G.32})$$

then we obtain

$$|\psi\rangle = \hat{1} |\psi\rangle = \sum_a |a\rangle \langle a | \psi \rangle \quad (\text{G.33})$$

and,

$$\langle \xi | \psi \rangle = \langle \xi | \hat{1} | \psi \rangle = \sum_a \langle \xi | a \rangle \langle a | \psi \rangle \quad (\text{G.34})$$

Now applying a self-adjoint operator $\hat{B}$ to $|\psi\rangle$ yields

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$$\langle a' | \hat{B} | \psi \rangle = \sum_{a''} \langle a' | \hat{B} | a'' \rangle \langle a'' | \psi \rangle \quad (\text{G.35})$$

Thus the operator $\hat{B}$ can be written in the A representation as the matrix

$$\hat{B} \rightarrow \langle a' | \hat{B} | a'' \rangle = \begin{pmatrix} \langle a_1 | \hat{B} | a_1 \rangle & \langle a_1 | \hat{B} | a_2 \rangle & \cdots & \vdots \\ \langle a_2 | \hat{B} | a_1 \rangle & \langle a_2 | \hat{B} | a_2 \rangle & & \vdots \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \end{pmatrix} \quad (\text{G.36})$$

and the vector ψ in A representation as

$$|\psi\rangle \rightarrow \langle a'' | \psi \rangle = \begin{pmatrix} \langle a_1 | \psi \rangle \\ \langle a_2 | \psi \rangle \\ \vdots \\ \langle a_n | \psi \rangle \\ \vdots \end{pmatrix} \quad (\text{G.37})$$

Therefore the operator $\hat{B}$ in A representation is a quadratic matrix; and the vector $|\psi\rangle$ is a column matrix.

The operator $\hat{A}$ itself is given in the A representation as

$$\langle a' | \hat{A} | a'' \rangle = \lambda' \delta_{a' a''} \quad (\text{G.38})$$

For any arbitrary operator $\hat{B}$, we can write

$$\hat{B} = \hat{1} \hat{B} \hat{1} = \sum_{a', a''} |a'\rangle \langle a' | \hat{B} | a'' \rangle \langle a'' | \quad (\text{G.39})$$

The choice of the representation depends on the choice of the coordinate system in the Hilbert space.

Now, if we introduce the second eigen equation as

$$\hat{B} |b\rangle = \beta |b\rangle \quad (\text{G.40})$$

then we can introduce the transformation of the A representation into B representation.

In analogy to Equation (G.38)

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$$\langle b' | \hat{B} | b'' \rangle = \beta' \delta_{b' b''} \quad (\text{G.41})$$

In Hilbert space (complete inner product space), we can write

$$\hat{1} = \sum_{a'} |a'\rangle \langle a'| = \sum_{b'} |b'\rangle \langle b'| \quad (\text{G.42})$$

The following relations are valid:

$$\langle b' | \psi \rangle = \langle b' | \hat{1} | \psi \rangle = \sum_{a'} \langle b' | a' \rangle \langle a' | \psi \rangle \quad (\text{G.43})$$

$$\langle a' | \psi \rangle = \langle a' | \hat{1} | \psi \rangle = \sum_{b'} \langle a' | b' \rangle \langle b' | \psi \rangle \quad (\text{G.44})$$

$$\langle b' | \hat{C} | b'' \rangle = \langle b' | \hat{1} \hat{C} | b'' \rangle = \sum_{a', a''} \langle b' | a' \rangle \langle a' | \hat{C} | a'' \rangle \langle a'' | b'' \rangle \quad (\text{G.45})$$

We also obtain

$$\langle a' | \hat{B} \hat{C} | a'' \rangle = \langle a' | \hat{B} \hat{1} \hat{C} | a'' \rangle = \sum_{a'''} \langle a' | \hat{B} | a''' \rangle \langle a''' | \hat{C} | a'' \rangle \quad (\text{G.46})$$

This means that for the matrix element of the product of two operators $\hat{B}\hat{C}$, the normal rules for matrix multiplication are valid. Please note that the so-called transformation matrix $\langle a|b \rangle$ plays an important role in the above equations.

Operator Functions

Operator functions $f(\hat{A})$ may be defined as a power series if the function $f(x)$ can be expanded in this way. Thus if

$$f(x) = \sum_{n=0}^{\infty} C_n x^n \quad (\text{G.47})$$

then the corresponding operator function $f(\hat{A})$ can be defined as

$$f(\hat{A}) = \sum_{n=0}^{\infty} C_n \hat{A}^n \quad (\text{G.48})$$

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where $x^0=1$ and $\hat{A}^0 = \hat{1}$. Another way of defining operator functions is obtained via their eigenvalues.

If

$$\hat{A} |a'\rangle = \lambda' |a'\rangle \quad (\text{G.49})$$

then

$$f(\hat{A}) |a'\rangle = f(\lambda') |a'\rangle \quad (\text{G.50})$$

For example,

$$\begin{aligned} \langle b' | f(\hat{A}) | b'' \rangle &= \langle b' | \hat{1} f(\hat{A}) \hat{1} | b'' \rangle = \sum_{a', a''} \langle b' | a' \rangle \langle a' | f(\hat{A}) | a'' \rangle \langle a'' | b'' \rangle \\ &= \sum_{a', a''} \langle b' | a' \rangle f(\lambda'') \delta_{a', a''} \langle a'' | b'' \rangle = \sum_{a'} \langle b' | a' \rangle f(\lambda') \langle a' | b'' \rangle \end{aligned} \quad (\text{G.51})$$

For the second example, we try to solve $e^{i(\beta/2)\hat{\sigma}_x}$ where

$$\hat{\sigma}_x = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(a) For the first solution, we use the power series of the exponential function and obtain

$$e^{i(\beta/2)\hat{\sigma}_x} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{i\beta}{2} \right)^n \hat{\sigma}_x^n \quad (\text{G.52})$$

and we have $\hat{\sigma}_x^2 = \hat{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and therefore $\hat{\sigma}_x^3 = \hat{\sigma}_x$. Thus, the series of Equation (G.52) can be split into even and odd powers as

$$\begin{aligned} e^{i(\beta/2)\hat{\sigma}_x} &= \hat{1} \sum_{n=\text{even}} \frac{1}{n!} \left(\frac{i\beta}{2} \right)^n + \hat{\sigma}_x \sum_{n=\text{odd}} \frac{1}{n!} \left(\frac{i\beta}{2} \right)^n \\ &= \hat{1} \cos(\beta/2) + i \hat{\sigma}_x \sin(\beta/2) = \begin{pmatrix} \cos(\beta/2) & i \sin(\beta/2) \\ i \sin(\beta/2) & \cos(\beta/2) \end{pmatrix} \end{aligned} \quad (\text{G.53})$$

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(b) However, this problem can also be solved using eigen problem with matrix transformation. Let us introduce two vectors as

$$\begin{aligned} |z, +1\rangle &= |z, j = 1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ |z, -1\rangle &= |z, j = 2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ \langle z, i = 1| &= \left(|z, i = 1\rangle^* \right)^T = (1 \quad 0) \\ \langle z, i = 2| &= \left(|z, i = 2\rangle^* \right)^T = (0 \quad 1) \end{aligned} \quad (G.54)$$

Please note that the above vectors are the eigenstates of the matrix $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ (however this matrix is not being used here). By introducing the above vectors, we can easily get

$$\langle z, i | \hat{\sigma}_x | z, j \rangle = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \hat{\sigma}_x \quad (G.55)$$

In order to use the method of eigenvalues, we need to solve the eigensystem of $\hat{\sigma}_x$ as

$$\hat{\sigma}_x |x, \lambda\rangle = \lambda |x, \lambda\rangle \quad (G.56)$$

where $|x, \lambda\rangle$ are orthonormal space. We easily establish that

$$|x, \lambda = 1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |x, \lambda = -1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (G.57)$$

Thus, we get

$$\begin{aligned} \langle z, i | e^{i(\beta/2)\hat{\sigma}_x} | z, j \rangle &= \sum_{\lambda=+1,-1} \langle z, i | \hat{1} e^{i(\beta/2)\hat{\sigma}_x} \hat{1} | z, j \rangle = \\ &= \sum_{\lambda=-1,1} \langle z, i | x, \lambda \rangle \langle x, \lambda | e^{i(\beta/2)\hat{\sigma}_x} | x, \lambda \rangle \langle x, \lambda | z, j \rangle \\ &= \sum_{\lambda=-1,1} \langle z, i | x, \lambda \rangle e^{i(\beta/2)\lambda} \langle x, \lambda | z, j \rangle \end{aligned} \quad (G.58)$$

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For example, we obtain the first element (1,1) of the matrix as

$$\begin{aligned}
 \langle z,1|e^{i(\beta/2)\hat{\sigma}_x}|z,1\rangle &= \sum_{\lambda=-1,1} \langle z,1|x,\lambda\rangle e^{i(\beta/2)\lambda} \langle x,\lambda|z,1\rangle \\
 &= \langle z,1|x,\lambda=1\rangle e^{i(\beta/2)1} \langle x,\lambda=1|z,1\rangle + \langle z,1|x,\lambda=-1\rangle e^{i(\beta/2)(-1)} \langle x,\lambda=-1|z,1\rangle \\
 &= \frac{1}{\sqrt{2}}(1 \ 0) \begin{pmatrix} 1 \\ 1 \end{pmatrix} e^{i(\beta/2)} \frac{1}{\sqrt{2}}(1 \ 1) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}}(1 \ 0) \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-i(\beta/2)} \frac{1}{\sqrt{2}}(1 \ -1) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\
 &= \frac{1}{2} e^{i(\beta/2)} + \frac{1}{2} e^{-i(\beta/2)} = \cos\left(\frac{\beta}{2}\right)
 \end{aligned} \tag{G.59}$$

In a similar manner we derive the other three matrix elements and finally obtain

$$\langle z,i|e^{i(\beta/2)\hat{\sigma}_x}|z,j\rangle = \begin{pmatrix} \cos\frac{\beta}{2} & i\sin\frac{\beta}{2} \\ i\sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix} \tag{G.60}$$

Quantum Mechanical Operators

In the nonrelativistic case we have for the kinetic energy $T=p^2/2m$, where p is momentum and m is mass. In analogy, we obtain the kinetic energy operator $\hat{T}$ as

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{(-i\hbar\nabla)^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \tag{G.61}$$

where the momentum $\mathbf{p}$ is related to the momentum operator $\hat{\mathbf{p}}$ by

$$\hat{\mathbf{p}} = -i\hbar\nabla \tag{G.62}$$

and its components are

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar\frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z} \tag{G.63}$$

It is easy to verify the relation

$$\hbar\mathbf{k}\psi(\mathbf{r}) = -i\hbar\nabla\psi(\mathbf{r}) = \hat{\mathbf{p}}\psi(\mathbf{r}) \tag{G.64}$$

by using the wave function

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$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \quad (\text{G.65})$$

where $\mathbf{k}$ is reciprocal space as discussed in Chapters 3 and 4.

The classical angular momentum of a particle is defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, where $\mathbf{r}$ is the position vector and $\mathbf{p}$ the momentum. In analogy, we obtain the quantum mechanical angular momentum operator as

$$\hat{L} = \mathbf{r} \times (-i\hbar\nabla) = -i\hbar \mathbf{r} \times \nabla \quad (\text{G.66})$$

In classical mechanics, the total energy of time-independent physical systems is described by the Hamiltonian function,

$$H = T + V(\mathbf{r}) \quad (\text{G.67})$$

where T denotes the kinetic energy and $V(\mathbf{r})$ the potential energy. In quantum mechanics, the Hamiltonian operator (or simply called Hamiltonian) is,

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\mathbf{r}) \quad (\text{G.68})$$

Please note that all the above equation can be further simplified by adopting atomic units (see Appendix C).

In quantum mechanics, an operator is assigned to any observable quantity. For example, letting $A(\mathbf{r}, \mathbf{p})$ be a function of $\mathbf{r}$ and $\mathbf{p}$ (position vector and momentum), we can construct the corresponding operator by replacing the quantities $\mathbf{r}$ and $\mathbf{p}$ by the assigned operators $\hat{r} = \mathbf{r}$ and $\hat{p} = -i\hbar\nabla$. Thus

$$A(\mathbf{r}, \mathbf{p}) \rightarrow \hat{A}(\hat{r}, \hat{p}) \quad (\text{G.69})$$

Here the position operator $\hat{r}$ is identical with the position vector $\mathbf{r}$. However, this is not generally valid. It is only true in the Cartesian coordinate representation.