Theoretical studies on electronic structure and x-ray spectroscopies of 2D materials

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To my family.
Abstract

Extraordinary chemical and physical properties have been discovered from the studies of two-dimensional (2D) materials, ever since the successful exfoliation of graphene, the first 2D material. Theoretical investigations of electronic structure and spectroscopies of these materials play a fundamental role in deep understanding the various properties. In particular, the band structure and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy can provide critical information near the Fermi level. In this thesis, we performed first-principles density functional theory calculations to study the electronic structure and NEXAFS spectra of four materials, including three 2D materials and one bulk material. The three 2D materials are atomically thin bismuth telluride, nitrogen and boron nitride doped graphenes. The bulk material is lithium intercalated graphite, an analogue of lithium doped graphene.

Atomically thin bismuth telluride is first studied. This is a material obtained following the same exfoliation procedure as for graphene. Band structure calculations show that the quintuple layers of Bi$_2$Te$_3$ is semiconducting with localized shallow bands, while bilayer and trilayer are metallic. Charge density difference analysis proves the stronger bonding between Bi and surface Te than that between Bi and Te in the middle layer.

Doping is one of the most efficient way to tune the electronic structure of graphene. Electronic structures of nitrogen doped graphene, based on a hexagonal vacancy and three major dopant configurations namely quaternary, pyridinic and pyrrolic nitrogens have been studied in combination with N 1s NEXAFS spectroscopy. The obtained spectra show that the $\pi^*$ peak observed in experiments originated from the pyridinic type doping, while the peak at 401 eV is from the quaternary doping. Pyrrolic doping configuration exhibits broad $\pi^*$ feature with no intensive peak. The relationship between NEXAFS spectra and ground state density of states are discussed for each dopant configuration.

Boron nitride doped graphenes with different dopant domain sizes have been studied by electronic structure and N 1s NEXAFS spectra calculations. Five quantum dot and one phase-separated zigzag-edged type doping configurations were considered. Nitrogens in the dopant domain center result in blue-shift of the $\pi^*$ peak in the spectrum in comparison with those at or near the domain boundary, which are consistent with the finding in band structure calculation, namely the
interfacial nitrogens dominate the lowest conduction bands of the system. Upon increasing the domain size, the bad gap of the system opens up and the ratio of domain center to interfacial nitrogens increases, leading to further blue-shift of the $\pi^*$ peak in the total NEXAFS spectrum.

C 1s NEXAFS spectra of graphite and lithium intercalated graphite have been studied using first principle simulations, supported by the ground state electronic structure investigations. The charge transfer from lithium to carbon leads to significant reduction of the $\pi^*$ peak and obvious red-shift of the $\sigma^*$ peak. Further calculations for the structure effect on NEXAFS spectra show that the small in-plane lattice change leads to large red-shift (ca. 0.5 eV) of the $\sigma^*$ peak, whereas the contribution from the interlayer spacing change is negligible.

Our studies provide important electronic property information of the studied materials, and are helpful for understanding their properties and developing potential applications.
Preface

The work presented in this thesis was carried out at the Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology (KTH), Stockholm, Sweden

List of papers included in the thesis


**Paper IV**  **X. Li**, D. Prendergast, J. H. Guo, and Y. Luo, Electronic Structure of Lithium Intercalated Graphite from First-Principles Simulations, In manuscript.
List of papers not included in the thesis


Comments on my contribution to the papers included

I have taken the major responsibility in all papers included.
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Chapter 1

Introduction

1.1 2D materials

The discovery of graphene by K. S. Novoselov and A. K. Geim in 2004 has opened a new era of the two dimensional (2D) functional materials. Graphene is a crystalline allotrope of carbon in the form of one atom thick sheet. The structure of graphene can be considered as a single layer of the bulk graphite, and the first graphene indeed was produced by using adhesive tape to lifting the flakes from bulk graphite. Nowadays, the most employed method to prepare graphene is by the chemical vapor deposition method (CVD) with methane as the carbon source. It has been proved that graphene exhibits various extraordinary properties, such as strong mechanical strength, excellent thermal and electrical conductivity, and optical transparent, which lead to vast potential applications. It can be applied in many fields such as medical drug delivery, electronic devices, optical modulator, energy generation and storage, and environment cleaning, just name a few. Many of these applications have been not only realized in laboratories, but also in industry. Figure 1.1 illustrates part of the applications that have been achieved so far.

Inspired by the isolation of graphene, many efforts were dedicated to the study of derived materials of this first 2D material. Such efforts can be generally classified into two categories, one is to find other non-carbon materials that can be exfoliated or synthesized down to 2D, and the other is to modify carbon based materials such as graphene to obtain desired chemical and physical properties. So far the family of 2D materials has been greatly extended. For non-carbon 2D materials, researchers have proposed borophene, germanene, silicene, phosphorene, etc.
Figure 1.1: Illustration of the applications realized by graphene. Insert figures adapted from the Wikipedia with the Creative Commons Licenses or in public domain.

and compounds such as the hexagonal boron nitride\textsuperscript{15} and monolayer molybdenum disulfide.\textsuperscript{16} These materials exhibit unique properties. For instance, the monolayer hexagonal boron nitride is shown to be an excellent proton conductor which yields unexpectedly high proton transport rates.\textsuperscript{15} The monolayer molybdenum disulfide has been demonstrated to be a good conductive channel candidate in the field-effect transistor device.\textsuperscript{16} There are also many more studies focusing on modifying the pristine graphene to open its zero band gap and to achieve desired electronic properties. Such modification can be realized by different approaches, for example, the pristine graphene can be tailored geometrically into nanoribbons,\textsuperscript{17} substituted doped with foreign atoms,\textsuperscript{18} and chemically absorbed by atoms or small molecules.\textsuperscript{19} These modifications have greatly enhanced graphene’s applicational potential in various fields. Geometrically, graphene can be cut, by using a sharp diamond knife, into blocks with exfoliation procedure afterwards to obtain graphene nanoribbons (GNR) which show highly edge structure-dependent electronic properties. The substitution of carbon with foreign atoms, \emph{i.e.,} substitutional doping, forms another class of graphene modification. Since graphene has zero band gap, doping provides a path to open the band gap and leads to controllable electronic structures. It has shown that nitrogen doped graphene exhibits impressive performance in hydrogen storage,\textsuperscript{20} lithium battery,\textsuperscript{21} biosensing,\textsuperscript{22} oxygen reduction reactions,\textsuperscript{23} and ultracapacitor\textsuperscript{24}. The capacitance of nitrogen doped graphene has
shown four times larger than that of pristine graphene. Graphene absorbed with atoms or molecules can also improve the chemical and physical properties. It is shown that graphene absorbed with calcium can be a good candidate of hydrogen storage material at room temperature.

1.2 Experimental techniques

In principle, the mystery of various properties of a 2D material depend on its atomic and electronic structure. Hence, to achieve desired properties, the fundamental approach is to realize the control of the atomic and electronic structures, which naturally is the goal for both experimentalists and theoreticians. The past century has witnessed the development of both experimental techniques and fundamental theories. There already have been adequate tools to characterize the atomic and topological structures. The atomic and topological structure of 2D materials can be characterized by means of approaches, for example, the scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) can give information about the microstructure, and the scanning tunneling microscopy (STM) can provide the information of local density of states. The electronic structure information, however, is not easy to be obtained directly by the above approaches. The electronic structure of a certain materials describes its electronic state that resulted from the electrostatic field created by the stationary nuclei of that material. The chemical and physical properties of the material are then determined by its electronic structure. Hence, it is fundamentally important to investigate the electronic structure of materials for understanding their various properties and developing applications. It is not a trivial task to measure the electronic structure directly, but its reflection, the electronic state, can be characterized by various of x-ray related techniques.

X-ray radiation is core level spectroscopic techniques, with high energy comparable with the core-electron binding energies. Depending on the incident photon energy, a core electron is pumped out of its orbital and leads to various consequences including x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES), etc. In 1895, W. C. Röntgen, who later received the first Nobel Prize in Physics, found out an new ray emanating from Crookes tubes, and firstly brought out the concept of x-ray. This discovery is a revolutionary change in our understanding of the nature. Soon after
Figure 1.2: Illustration of the synchrotron accelerator set up.

Röntgen’s discovery, x-ray was employed by doctors for examining patients. It was not until more than one decade later when William Henry Bragg and his son William Lawrence Bragg began to use x-ray in characterizing the atomic structures\textsuperscript{26}. Their method then developed as an standard tool to insightfully characterizing the crystal structure, so-called x-ray crystallography, which is the first scientific reason of using x-ray. However, the application of x-ray did not take off until the employing of synchrotron radiation. Initially, the synchrotron accelerator facilities were build up for studying particle physics, and not long since it was found that the undesired energy loss in particle physics was an useful light source for x-ray related experiments.

In the late 1960s’, synchrotron radiation based x-ray became an independent tool for investigating matter, and has contributed significantly to our understanding of materials. The general set up of a synchrotron radiation facility is illustrated in figure 1.2. The so powerful potential of x-ray in practical applications is lying in its wavelength (covering a range of $0.1 \sim 100 \text{ Å}$) which falls in the length scale of atoms and the time scale of nuclei movements. The interaction between the x-ray photon and matter results in electronic transitions and absorption/emission of specific wavelength photons which carry the information of corresponding electronic state.
1.2. EXPERIMENTAL TECHNIQUES

The obtained x-ray through beamline is filtered to abstract photons with certain wavelength, and then concentrated to get beam with high intensity. The final obtained x-ray beam can then be used to perform measurements, as illustrated in Figure 1.3. With the advantages of the high intense, brightness, and controllable wavelength, many applications have been developed, such as the above mentioned XRD, XAS, XES and XPS. Some derivations of these tools are also innovated, for example, the resonant inelastic x-ray scattering (RIXS) and x-ray magnetic circular dichroism (XMCD), etc. All these techniques are based on the interaction of incident x-ray photon with matter, more specifically, electrons in matter. Different types of interaction provide different electronic information, which can be adopted as desired during measurement. In a XPS measurement, the core electron is excited to the vacuum and collected to get the core level binding energy, while in a XAS process, a core electrons is excited to the unoccupied orbitals above the Fermi level which can provide the unoccupied states information. The core-hole created from the excitation process will be filled by a valence electron and emit photon with

![Figure 1.3: Schematic view of the procedure from synchrotron ring to experimental detector for x-ray beam.](image)

![Figure 1.4: Different x-ray experimental techniques.](image)
CHAPTER 1. INTRODUCTION

Among the many techniques of applying synchrotron x-ray radiation, XAS, which is often referred as near-edge x-ray absorption spectroscopy (NEXAFS), plays an important role due to its capability of detecting the unoccupied states right above the Fermi level. Since being introduced in 1980s,\textsuperscript{27} it has become an efficient way in probing the electronic and chemical structures of molecules, bulk materials and solutions due to its element and environment sensitivities. The energy of soft x-ray can be matched to the atomic orbitals of different elements, thus the core energy of a certain element can be characterized by introducing the x-ray photon with corresponding energy. Depending on the orbital of the excited core electron, the excitation is commonly named as K-, L-, and M-edges, corresponding to the principal quantum numbers of $n = 1$, $2$, and $3$ respectively. For example, the excitation of $1s$ electron of carbon is called carbon K-edge, while the excitation of $2s/2p$ electrons of silicon is called silicon L-edge. L- and M-edges can be further split into sub-level edges (figure 1.5). K-edge is the most employed measurement for the first two rows of elements. There are two modes to collect the XAS excitation signals, total electron yield (TEY) and total fluorescence yield (TFY). The TEY mode is more surface sensitive, while the TFY mode is more bulk.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_5.png}
\caption{Illustration of different absorption edges and sub-level edges for XAS. Adapted from the Wikipedia with the Creative Commons Licenses.}
\end{figure}
sensitive. Thus the XAS technique can be applied to study both the surface and the bulk of a material, providing complementary electronic structure information. The transition of the excited electron in XAS follows the dipole selection role, which means the transition only occurs when the angular momentum differs by 1 or -1, and the absorption cross-sections show a polarization dependent angular anisotropy. Due to the unique advantages of XAS, it has become a powerful tool for electronic structure studies on innovative materials.

1.3 Theoretical simulations

Along with the development of experimental techniques, theoretical approaches for studying electronic structure have also been greatly developed. Especially, after the birth of quantum theory, it began to be possible to accurately investigate the chemical and physical properties of matter, which is an enormous advancement. Theories based on quantum mechanics have been extensively developed, forming the foundation of not only the scientific world, but also our daily practical applications. From laser to electron microscope, from nuclear magnetic resonance imaging to diode in semiconductors, quantum theory plays as the fundamental role in every modern scientific and technological development. Meanwhile, our understanding on the electronic nature of matter is also dramatically accelerated,

Figure 1.6: Scheme of relations between experiment, theory and simulation.
CHAPTER 1. INTRODUCTION

wherein electronic structure simulation as an practical way to implement theories has became more and more critical. In the past decades, powerful supercomputers have provide us the ability of fast computing, so that simulation has become an important cornerstone in modern scientific research. It can not only help to understand the results from experiments, but also verify the accuracy of theories. Therefore we can obtain the abilities of both material interpretation and design (Fig. 1.6) from simulations. Experiments and theories can in turn improve the methodology and efficiency of simulations.

![Figure 1.7: The increasing publications related to "density of functional theory", and the percentage of DFT publications over the total publications in all fields. Data from the Web of Science.](image)

The density functional theory (DFT), has been proven to be an extreme powerful tool to theoretically interpret the electronic structure of materials. Its principle philosophy is to consider the properties of a studied system as functional of the corresponding electron density, which is promising in achieving the goal of maximizing both efficiency and accuracy. After significant development for the past decades, DFT now has became the most widely used theory for electronic structure study. Fig.1.7 shows the number of publications that contain density functional theory in the topic since 1990, and the ratio of DFT publications over the total publications in all fields. The significant increasing trend reveals the importance of DFT to the scientific community. In particular, DFT method has been extremely efficient in condensed phase physics since 1970s. The success of
DFT in solid state physics is directly related to the great compatibility of the local density approximation to the model of homogeneous electron gas in condensed phase. The electron density can be satisfactorily described with the LDA functional when dispersion or correlation effects are not strong which is common in solid state materials. More sophisticated approximations based on LDA, such as generalized gradient approximations (GGA) or hybrid functionals, have been proposed during the past decades and shown significant improvement in predicting the electronic structure of molecules. It is also shown that hybrid functionals also have better description on the band gap of condensed phase semiconductors. The state-of-art theoretical level of DFT and programs that implementing DFT already can give good description on the novel two dimensional materials. One of the enormous popular program is the VASP\textsuperscript{32,33} package.

Apart from the progress in functionals, there are also enormous efforts dedicated on various x-ray spectroscopic simulations. Due to the x-ray spectroscopy is usually related to the core excited state, while the normal DFT treats only the ground state or valence excited states, the simulation of x-ray spectra requires more complex considerations. In this regard, the efforts of searching more accurate and efficient solution for the core excited state fall into different directions, including DFT based $\Delta$SCF\textsuperscript{34} and time-dependent density functional theory (TDDFT), many-body perturbation theory based Green’s function method, semi-empirical methods based the crystal field multiplet (CFM) and the charge transfer multiplet (CTM) models, as well as some other post-HF methods, etc. The Green’s function method and the post-HF methods have high requirements on computational cost, which limits their application in large systems. The CFM and CTM models are usually employed to treat the transition metals which sometime hard for DFT to describe accurately, yet these models are generally system and parameter dependent, and the insightful electronic structure information is absent as well. The DFT based methods, however, provide compromised solution on the accuracy and efficiency to the problem. Especially, the equivalent core-hole method, which also referred as the Z+1 method, has shown great success in simulating the core excitation process with low computational cost and high accuracy. Figure 1.8 shows the simulated N K-edge NEXAFS spectra for nitrogen doped carbon nanocages, which was done based on the Z+1 approximation. We can see that the theoretical spectra well reproduced the experimental features and provide insightful information on the origin of different features, indicating the validity of method.
1.4 Contents of the thesis

With the increasing attention on the two dimensional materials, enormous efforts have been dedicated to the searching of novel chemical and physical properties from these materials. This thesis, in this regard, is devoted to the electronic structure study on the two dimensional materials by first-principles simulations. Both of the two categories of 2D materials have been considered: atomically thin Bi$_2$Te$_3$ that following the idea of exfoliation of graphene, and allotropes of carbon, including graphene and graphite, doped with foreign atoms.

This thesis is organized as follows. The basis concept and theory of ground state and NEXAFS spectroscopy calculations are firstly introduced in the following chapters 2 and 3, respectively. Applications using DFT simulations on the under-studied two dimensional materials are presented in chapter 4. The conclusion of included papers and future outlook of the current studies are introduced in the last chapter 5.
Soon after the quantum mechanics being introduced, it had been applied to chemistry such as H\textsubscript{2} and He since the 1920s to study the chemical bonds, which can be considered as the beginning of quantum chemistry. The electronic structure of a material is determined by the solution of Schrödinger equation, however, the equation for any real material with multiple electrons is still too complicated to be solved exactly. Thus the development of quantum chemistry at the initial stage was slow. To address this issue, many efforts were dedicated to the study of simplifying the equation to achieve approximate solution with high accuracy and reliability, and acceptable cost. So far there are different methods available to calculate electronic structures such as the wave function based methods\textsuperscript{36} including Hartree-Fock (HF) self-consistent field (SCF) theory, configuration-interaction theory, many-body perturbation theory, coupled-cluster theory and so on, however, the most widely used method nowadays is the electron density based DFT, which provides promising efficiency and accuracy for large systems. Significant accomplishments have been achieved in electronic structure study of condensed phase materials by using DFT, in particular the novel 2D materials. Same as other methods, DFT employs the Born-Oppenheimer (BO) approximation\textsuperscript{37} introduced by Born and Oppenheimer in 1927, which allows the wave function of a Schrödinger equation divided into electronic and nuclear components. In this chapter, we first introduce the fundamental BO approximation, followed by the basic concept of DFT. Then, we present the general concepts in condensed phase DFT calculations, including Brillouin Zone, reciprocal lattice, band structure theory, pseudopotential and plane-wave basis set.
2.1 BO approximation

For the first three row of elements, of which the speed of electrons is much less than the speed of light, the relativistic effect can be neglected. The Hamiltonian of the system thus can be written in terms of nuclei and electron contributions separately, in the form of:

$$\hat{H}_{\text{tot}} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{Ne}. \quad (2.1)$$

Here, N and e donate nuclei and electron respectively, and $\hat{T}_N$, $\hat{T}_e$, $\hat{V}_{NN}$, $\hat{V}_{ee}$, and $\hat{V}_{Ne}$ represent operators for the nuclear and electron kinetic energies, nuclear-nuclear, electron-electron, and nuclei-electron interaction potentials, respectively. They can be expressed in the following forms:

$$\hat{T}_N = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2;$$
$$\hat{T}_e = -\sum_A \frac{\hbar^2}{2M_A} \nabla_A^2;$$
$$\hat{V}_{NN} = \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi \epsilon_0 R_{AB}};$$
$$\hat{V}_{ee} = \sum_{i>j} \frac{e^2}{4\pi \epsilon_0 r_{ij}};$$
$$\hat{V}_{Ne} = -\sum_{A,i} \frac{Z_A e^2}{4\pi \epsilon_0 r_{Ai}}; \quad (2.2)$$

where $Z_A$ and $Z_B$ stand for the atomic number of atom A and B, $m$ and $M_A$ stand for the mass of electron and nuclei A, and $r_{ij}$, $r_{Ai}$ and $R_{AB}$ stand for the distances between electron-electron, electron-nuclei, and nuclei-nuclei, respectively.

Considering the fact that the mass of electron is much less than any nuclei and the significant higher speed of electrons, the total wave function can be separated into nuclei and electrons in the form of,

$$\Psi_{\text{tot}}(r, R) = \phi_e(r, R) \chi_N(R). \quad (2.3)$$

Such separation is called Born-Oppenheimer approximation.

The corresponding total Hamiltonian can be divided as the following form,

$$\hat{H}_{\text{tot}} = \hat{H}_N + \hat{H}_e,$$
$$\hat{H}_e = \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{Ne}. \quad (2.4)$$
2.2. THE BASICS OF DFT

The wave function of electrons can be obtained by,

\[ H_e \phi_e(r, R) = E_e(R)\phi_e(r, R), \quad (2.5) \]

and the total wave function thus can be obtained by,

\[ (T_N + E_e(R))\Psi_e(r, R) = E_{tot}\Psi_e(r, R). \quad (2.6) \]

The electronic wave function from Eq. 2.5 gives the potential energy surface that nuclei move on.

2.2 The basics of DFT

The concept of using electron density to solve the electronic structure of many-body systems, which named as Thomas-Fermi (TF) model, was first brought up by Llewellyn Thomas and Enrico Fermi, soon after the introduction of the Schrödinger equation in 1920s. It formed the root for the modern density functional theory. The era of DFT began in 1964, when Hohenberg and Kohn published their landmark paper in Physics Review.\textsuperscript{38} This paper brought out two theorems, so-called Hohenberg-Kohn theorems (H-K theorems), which served as fundamental theorems in modern DFT. The practical realization of Hohenberg-Kohn theorems soon appeared in 1965 when Kohn and Sham introduced their solution to the universal functional in H-K theorems.\textsuperscript{39} The Kohn-Sham formulation (K-S formulation) reduces the complicity of energy calculation. All parts in the total energy can be calculated accurately, except one small part which is determined by an approximate functional.

2.2.1 The Hohenberg-Kohn theorems

To calculate the electronic structure of a system, the normal approach is to solve the Schrödinger equation for the eigenstates of system, wherein in principle all the properties of the system are determined by the external potential. In Hohenberg-Kohn’s paper, they presented the major principles that used by all modern density functional theories. Here we introduce the two Hohenberg-Kohn theorems and discuss their consequences.
The first Hohenberg-Kohn theorem demonstrates that the external potential \( v_{\text{ext}}(r) \) and the corresponding total energy are unique functionals of the electron density \( \rho(r) \). The Hamiltonian is fixed upon the given \( \rho(r) \), so the ground state of given system is a unique functional of \( \rho(r) \). The energy functional \( E[\rho(r)] \) can be written in terms of the external potential \( v_{\text{ext}}(r) \) in the form of,

\[
E[\rho(r)] = \int \rho(r) v_{\text{ext}}(r) \, dr + F[\rho(r)],
\]

where \( F[n(r)] \) is an universal functional of the electron density \( \rho(r) \). The ground state energy is then determined by minimizing the expectation of the system’s Hamiltonian,

\[
E[\rho(r)] = \langle \Psi|\hat{H}|\Psi \rangle.
\]

The Hamiltonian can be written as,

\[
\hat{H} = \hat{F} + \hat{V}_{\text{ext}},
\]

where \( \hat{F} \) is the electronic Hamiltonian constructed from a kinetic energy operator term \( \hat{T} \) and an interaction operator term \( \hat{V}_{\text{ee}} \). For any \( N \)-electron systems, the electron operator \( \hat{F} \) is always the same. Thus \( \hat{H} \) is defined by the total number of electrons \( N \), and the external potential \( v_{\text{ext}}(r) \).

The second Hohenberg-Kohn theorem demonstrates that the ground state energy can be obtained by variational principle: the density which gives the minimum total energy is the exact ground state density.

### 2.2.2 Kohn-Sham formulation

The two Hohenberg-Kohn theorems are very useful, however, they do not provide directly how to compute the ground state density of a system in practice. About one year after the landmark DFT paper by Hohenberg and Kohn, Kohn and Sham developed an easy way of performing DFT calculations. This method is so-called Kohn-Sham (KS) formulation. The main idea of the KS formulation is replacing the interacting system with the real potential by a non-interacting system built fictitiously, in consequence the electrons move within an effective single particle potential \( v_{\text{KS}}(r) \). The KS formulation provides a practical easy way to calculate the exact ground state energy.
2.2. THE BASICS OF DFT

As a result of the Hohenberg-Kohn theorems, the ground state wavefunction \( \Psi_{KS} \) of a system can be described exactly by a determinant of single particle orbitals \( \psi_i(r_i) \).

\[
\Psi_{KS} = \frac{1}{\sqrt{N!}} \det[\psi_1(r_1)\psi_2(r_2)\ldots\psi_N(r_N)],
\]

(2.10)

The universal functional \( F[\rho(r)] \) consists of three terms,

\[
F[\rho(r)] = T_s[\rho(r)] + E_H[\rho(r)] + E_{XC}[\rho(r)],
\]

(2.11)

where \( T_s[\rho(r)] \) is the kinetic energy of a reference system density with electron density \( \rho(r) \), and \( E_H[\rho(r)] \) is the classical Coulomb interaction of electrons.

\[
T_s[\rho(r)] = \frac{1}{2} \sum_{i=1}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle,
\]

(2.12)

\[
E_H[\rho(r)] = \frac{1}{2} \int \int \rho(r)\rho(r') \left| \frac{r-r'}{|r-r'|} \right| dr dr'.
\]

(2.13)

The third term is exchange-correlation term which is unknown and need to be approximated. An implicit definition of \( E_{XC}[\rho(r)] \) can be described as,

\[
E_{XC}[\rho(r)] = T[\rho(r)] - T_s[\rho(r)] + E_{ee}[\rho(r)] - E_H[\rho(r)],
\]

(2.14)

where \( T[\rho(r)] \) and \( E_{ee}[\rho(r)] \) are the exact energies of kinetic and electron-electron interaction, respectively. The intention of KS formulation is to make the \( E_{XC} \) of the non-interacting system as small as possible compare to the total energy, which is indeed true. However, this small contribution is still comparable to the order of binding energies of many systems, which makes it very important to find an accurate description of the exchange-correlation. Thus developing satisfiable exchange-correlation functionals is essential for studying various electronic structure properties.

2.2.3 Exchange and correlation

So far many efforts have been dedicated to the development of exchange-correlation functionals, and there are already some mature approximations. Here
we introduce briefly some of them that used in this thesis including the local density approximation (LDA) and the generalized gradient approximation (GGA).

Local density approximation

In Hohenberg and Kohn’s original DFT paper, they already proposed the so-called local density approximation, which is the oldest, simplest and probably the most important functional. The central idea of LDA is a hypothetical uniform electron gas, in which electrons move in a positive background charge distribution and the total charge is electrically neutral. The reason that LDA has such a good popularity is that it is the only system for which we can calculate the exchange and correlation energy functionals accurately, and it has been successfully applied on the solid phase problems such as simple metals. However, it is not hard to find out that this homogeneous electron gas approach is not a good approximation in many realistic situations such as atoms or molecules due to their rapidly varying electronic densities. Base on the uniform electron gas assumption, the $E_{\text{XC}}$ can be wrote in the following simple form

$$E_{\text{XC}}^{\text{LDA}}[\rho(r)] = \int \rho(r) \varepsilon_{\text{XC}}[\rho(r)] \, dr,$$

(2.15)

here $\varepsilon_{\text{XC}}$ corresponds to the exchange-correlation energy of a uniform electron gas with density $\rho(r)$, which can be further decomposed into exchange and correlation contributions,

$$\varepsilon_{\text{XC}}[\rho(r)] = \varepsilon_X[\rho(r)] + \varepsilon_C[\rho(r)],$$

(2.16)

$\varepsilon_X$ represents the exchange energy of an electron and can be obtained from

$$\varepsilon_X[\rho(r)] = -\frac{3}{4} \sqrt{\frac{3\rho(r)}{\pi}}.$$

(2.17)

There is no explicit expression for the correlation part $\varepsilon_C$, however it can be obtained from interpolation schemes.

Generalized gradient approximation

Generalised gradient approximation (GGA), which mainly contributed by Perdew and co-workers,\textsuperscript{40,41} is nowadays the most widely used exchange-correlation
2.3 2D PERIODIC CONDENSED PHASE

functional in condensed matter physics. It can be written in the form of an analytic function

$$E_{\text{GGA}}^{\text{XC}}[\rho(r)] = \int \rho(r) \varepsilon_{\text{XC}}[\rho(r)] F_{\text{XC}}[\rho(r), \nabla \rho(r)] dr. \quad (2.18)$$

Here $F_{\text{XC}}[n(r), \nabla n(r)]$ is called the enhancement factor, which can modify the energy from LDA directly and can be written in terms of the dimensionless reduced density gradient $s(r)$,

$$s(r) = \frac{|
abla \rho(r)|}{2k_F(r)\rho(r)}. \quad (2.19)$$

$$k_F(r) = [3\pi^2 \rho(r)]^{1/3}. \quad (2.20)$$

Recently, Perdew, Burke and Ernzerhof developed an improved functional so-called PBE,\textsuperscript{42} whose exchange enhancement factor has a simple form

$$F_{\text{X}}^{\text{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}. \quad (2.21)$$

LDA and GGA functionals have been successfully applied in condensed phase electronic structure calculations.

2.3 2D periodic condensed phase

Due to the success of uniform electron gas model, DFT method has natural advantage in solving the electronic structure of periodic solid phase problems. Different from molecules, periodic boundary condition exists in solid crystal. The crystal is described in terms of the primitive lattice vectors $a_1$, $a_2$, and $a_3$ in real space (Bravais lattice), as well as the position of atoms within a primitive unit cell. All the possible combinations of $a_1$, $a_2$, and $a_3$ then build up the all lattice vectors $R$ as in Eq. 2.22.

$$R_n = n_1 \cdot a_1 + n_2 \cdot a_2 + n_3 \cdot a_3, \quad (2.22)$$

with $n_1$, $n_2$ and $n_3$ being integrals.

For 2D materials, the third vector $a_3$ can be considered as infinite, and only the in-plane vectors ($a_1$ and $a_2$) are needed to build up the lattice. Take the honeycomb
lattice with lattice constant $a$ shown in figure 2.1 as an example, the lattice vector $a_1: a(\frac{3}{2}, \frac{\sqrt{3}}{2})$ and $a_2: a(\frac{3}{2}, -\frac{\sqrt{3}}{2})$ build up a rhombus shape primitive lattice unit cell consisting both the non-equivalent atoms, and the periodic repeating of this cell forms the whole crystal lattice.

![Honeycomb lattice and its primitive vectors in real space.](image)

**Figure 2.1:** Honeycomb lattice and its primitive vectors in real space.

The electrons in the crystal travel across the whole lattice, and due to the periodicity they follow the following Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi = E\psi,$$  \hspace{1cm} (2.23)

$$V(r) = V(r + R_n),$$  \hspace{1cm} (2.24)

where $R_n$ is any lattice vector. The eigenfunction $\psi$ of equation 2.23 is called Bloch function, which satisfies the following condition,

$$\psi(r) = e^{ik\cdot r}u(r).$$  \hspace{1cm} (2.25)

Here $u(r)$ represents a periodic function that sharing the same periodicity as the crystal, $k$ is the crystal wave vector.
2.3. 2D PERIODIC CONDENSED PHASE

2.3.1 Reciprocal lattice and Brillouin zone

A direct result of the Bloch function is that we can solve the electronic structure of crystal by dealing with only one periodic unit, leading to the introduction of reciprocal lattice and the first Brillouin zone. Due to the periodicity of crystals, the Bloch function also satisfies $\psi(k) = \psi(k + G)$, with $G$ is the reciprocal lattice vector in k-space (also called momentum space). The electronic band structure of the crystal in consequence can be obtained through the relationship between $k$ and energy.

**Reciprocal lattice**

Reciprocal lattice, which is the inverse space of the real lattice, is the foundation to describe the behavior of electrons in a crystal. The derivation of reciprocal lattice is by the Fourier transform of real lattice, which can be written in the form of Eq. 2.26

\[
\begin{align*}
    b_1 &= 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}, \\
    b_2 &= 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_3 \times a_1)}, \\
    b_3 &= 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)},
\end{align*}
\] (2.26)

Any lattice vector in momentum space can be written as,

\[
G_m = m_1 \cdot b_1 + m_2 \cdot b_2 + m_3 \cdot b_3,
\] (2.27)

with $m_1, m_2$ and $m_3$ being integrals.

**Brillouin zone**

In practice, it is not convenient to use arbitrary lattice unit to calculate the electronic structure, but use the unique cell call Brillouin zone. The Brillouin zone is built by Wigner-Seitz cell method for a crystal in the reciprocal lattice. The electronic structure of crystal can be described by solving the electronic structure of the first Brillouin zone due to the periodicity. For the 2D honeycomb lattice shown in figure 2.1, the corresponding reciprocal lattice is also in honeycomb configuration as shown in figure 2.2a. The first Brillouin zone is built upon the primitive vectors
Figure 2.2: (a) Honeycomb lattice in k-space and the corresponding construction of first Brillouin zone. (b) Zoomed view of the first Brillouin zone in (a) with high symmetry lines and points indicated.

$b_1$ and $b_2$. Base on the first Brillouin zone, high symmetry points and lines, which is important for solving the electronic structure, can be determined. For honeycomb lattice, there are three high symmetry points $\Gamma$ at $\frac{2\pi}{a}(0,0)$, $M$ at $\frac{2\pi}{a}(\frac{1}{3}, 0)$ and $K$ at $\frac{2\pi}{a}(\frac{1}{3}, \frac{\sqrt{3}}{3})$, with the lines connecting them as high symmetry lines.

2.3.2 Band structure and density of states

2D materials provide an excellent demonstration of the close relationship between quantum mechanics and invention of novel materials. The electrons in crystal follows the equation,

$$H_n(k)\Psi_n = E_n(k)\Psi_n. \quad (2.28)$$

The eigenenergies obtained from above give the dispersion relationship between $k$ and eigenenergies, which is commonly called band structure. The formation of bands in solid is similar to the formation of energy level in molecule orbitals. When the atoms in a solid joint together, they form discrete energy levels which is so dense that they can be considered as continuum.\textsuperscript{43} Band structure is very useful in explain different physical and chemical properties of the material, such as optical absorption and electrical resistivity, \textit{etc}, and is the foundation of understanding and developing devices based on the material.
Combining simulated band structures base on modern DFT theory and experimental measurements, we already can obtain insightful understanding on electronic structure of materials. Such understandings not only allow us to look inside of the electronic structure, but also provides us the ability to manipulate it to achieve the desired physical and chemical properties. Take graphene as an example, figure 2.3 shows the calculated band structure compared with the experimental measurement of graphene on copper. We can see that the calculated band structure generally agrees well with the experiment, indicating the validity of theory and the reliability of the method in interpreting the electronic structure of graphene.

Band structure provides the information of the dispersion relation between $k$ and energy for each band, however, we can not observe directly how the energy states distributed in the energy scale, which can be given by density of states (DOS). DOS describes the number of states per interval of energy. If the DOS at a specific energy is high, it means that there are many available states for occupation, while a zero DOS indicates zero occupancy. Experimentally, XES and XAS are powerful tools to characterize the occupied and unoccupied states, respectively. However, the spectral measurement process involves core-hole and screening effects, which is not considered in ground state DOS calculations.
2.3.3 Basis set and pseudopotential

When solving electronic structures with DFT, a basis set is always needed to construct wave functions. Localized Gaussian type basis set is commonly adopted for molecules, while for crystals where periodic boundary conditions exists, plane-wave basis set becomes a natural choice. The number of plane-wave functions describing all electrons in an atom is usually extremely large especially for the many core electrons with higher oscillation, and it is hard to be implemented in practice. Since the core electrons have less effect on the chemical bonding between atoms, the complex interactions between them can be replaced by an effective core potential, so-called pseudopotential. In this way, only the valence electrons need to be calculated with plane-wave basis functions, resulting in significant higher computational efficiency. The pseudopotential used nowadays was first introduced in late 1950s, and extensively applied in band structure calculations since then. Both plane-wave basis set and pseudopotential have been implemented in many programs that dealing with the electronic structure calculations under periodic boundary condition, such as VASP which is the major tool used in this thesis.
Near Edge X-ray Absorption Fine Structure spectra

Reliable and precise knowledge of the electronic structure of materials are of fundamental importance in understanding their properties, where synchrotron radiation based techniques have played an outstanding role. The synchrotron facilities were first built in the 1940s for particle physics studies. It was not devoted to materials characterization after about two decades. Nowadays, the synchrotron facilities have been developed to the third generation, and contributed significantly to the study of materials at macroscopic scale. Among all the synchrotron related techniques, NEXAFS spectroscopy is of great importance due to its excellent capability in identifying the unoccupied electronic structure, especially for the low Z elements, such as C, N, O. The absorption edges of these elements fall in the soft X-ray region (ca. 0.1 ~ 5 keV). NEXAFS is powerful not only with the advantage of element-specificity, but also environment-sensitivity, so that different type of bondings can be characterized efficiently. There are two modes of collecting signals for material characterization, including the total electron yield (TEY) detection mode which is sensitive to the surface, and the total fluorescence yield (TFY) which is sensitive to the bulk. The measured samples can be in all of the gas, liquids and solid phases. The target samples can be for biology, life science, functional materials, etc. For 2D materials like graphene, the two modes are near equivalent. Furthermore, due to the dipole selection rule and the linear polarized x-ray source in NEXAFS measurements, the angle dependent spectra can be obtained by varying the incident beam angle to the surface. In this chapter, we first introduce the basic concepts for calculating the NEXAFS spectra. Then, we present the three approximations used in this thesis with corresponding examples. The post procedures for the calculated raw spectra are explained at last.
3.1 Basics of NEXAFS spectra

NEXAFS serves as a reliable tool to investigate the chemical and electronic structure of materials. The physical picture of the measurement process is depicted in Fig. 3.1. When the X-ray photon $h\omega$ is absorbed, the core electron is excited to an unoccupied orbital, with a core-hole left. This excited state subsequently decays into a lower energy state, either by de-excitation of the exited electron with emission of a fluorescent photon, or by excitation of an Auger electron non-radiatively. These two decay ways can be detected as the TFY and TEY, respectively. The interaction between the x-ray and the core electron can be described by the Fermi’s Golden rule as introduced below.

![Electron excitation scheme](image)

**Figure 3.1:** Electron excitation scheme, with solid and dash lines represent the energy levels and the Fermi level, respectively. The excited core electron is shown in blue.

Fermi’s golden rule

The interaction between light and matter can be considered as a harmonic time-dependent perturbation governed by

$$\hat{V}(t) = \frac{e}{mc} A(t) \cdot \hat{p},$$

where $\hat{p} = \sum \hat{p}_i$ represents the sum of the momentum operators for the electrons, and $A(t)$ is the vector potential in the following form,

$$A = \epsilon A_0 \cos(k \cdot r - \omega t) = \frac{\epsilon A_0}{2} (e^{i(k \cdot r - \omega t)} + e^{-i(k \cdot r - \omega t)}),$$

where $\epsilon = \frac{e}{m}$ and $A_0 = \frac{eA_0}{2c}$.
where $\epsilon$, $k$ and $\omega$ represent the polarization unit vector, the plane wave electromagnetic wave vector, and the incident frequency, respectively. Using Eq. 3.2, we can rewrite Eq. 3.1 in the following form,

$$\hat{V}(t) = \hat{v}e^{-i\omega t} + \hat{v}^\dagger e^{i\omega t},$$  (3.3)

where $\hat{v}$ is a time-independent term in the form of

$$\hat{v} = \epsilon \frac{eA_0}{2mc} e^{ikr} \hat{p}.$$  (3.4)

Here $\hat{v}^\dagger$ is the Hamiltonian complex conjugate of $\hat{v}$. Therefore, for an absorption process that an initial state $i$ is excited to a final state $f$ by absorbing a photon with energy $\hbar \omega$, the transition probability can be expressed by the Fermi’s golden rule:

$$P_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle \Phi_f | \hat{v} | \Phi_i \rangle|^2 \delta(E_i - E_f + \hbar \omega)$$

$$= \frac{\pi e^2}{2\hbar m^2 c^2} A_0^2 |\langle \Phi_f | e^{ikr} \epsilon \cdot \hat{p} | \Phi_i \rangle|^2 \delta(E_i - E_f + \hbar \omega),$$  (3.5)

where $E_i$ and $E_f$ are the electron energies of initial and final states, respectively. The $\delta$ function indicates that nonzero transition happens only when $E_f = E_i + \hbar \omega$ is satisfied.

The dipole approximation

The $e^{ikr}$ term can be expanded into Taylor series as

$$e^{ikr} = \sum_{n=0}^{\infty} \frac{(-i)^n (k \cdot r)^n}{n!}.$$  (3.6)

For soft x-ray, we have the conditions of $k \cdot r \ll 1$, and $e^{ikr} \approx 1$, which is often called the dipole approximation. Eq. 3.5 can then be rewritten as

$$P_{i \rightarrow f} = \frac{\pi e^2}{2\hbar m^2 c^2} A_0^2 |\langle \Phi_f | \epsilon \cdot \hat{p} | \Phi_i \rangle|^2 \delta(E_i - E_f + \hbar \omega).$$  (3.7)

By using the relation of

$$\langle \Phi_f | \hat{p} | \Phi_i \rangle = im\omega_{fi} \langle \Phi_f | r | \Phi_i \rangle,$$  (3.8)
Eq. 3.7 can further be rewritten in the position operator representation,

$$P_{i \rightarrow f} = \frac{\pi e^2 \omega^2}{2 \hbar c^2} A^2_{\|} \langle \Phi_f | \epsilon \cdot r | \Phi_i \rangle^2 \delta (E_i - E_f + \hbar \omega),$$  \hspace{1cm} (3.9)

where \( r = \sum r_i \) is the sum of coordination operators for the electrons.

Absorption cross section and oscillator strength

The cross section and oscillator strength are two basic concepts of absorption. The cross section describes the transition probability per unit photon flux, such as for a transition from the initial state \( i \) to the final state \( f \). The cross section can be written as

$$\sigma_{\text{abs}} = \frac{P_{i \rightarrow f}}{F_{\text{ph}}},$$  \hspace{1cm} (3.10)

where

$$F_{\text{ph}} = \frac{A^2_{\|}\omega}{8\pi\hbar c},$$  \hspace{1cm} (3.11)

stands for the photon flux, that is, the number of incident photons per unit time per unit area. Using Eq. 3.9 we have

$$\sigma_{\text{abs}} = \frac{4\pi^2 e^2}{m^2 \omega c} |\langle \Phi_f | \epsilon \cdot \hat{p} | \Phi_i \rangle|^2 \delta (E_i - E_f + \hbar \omega),$$  \hspace{1cm} (3.12)

$$\int d\omega \sigma_{\text{abs}} = \frac{2\pi^2 e^2}{mc} \cdot \frac{2}{m\hbar \omega f_i} |\langle \Phi_f | \epsilon \cdot \hat{p} | \Phi_i \rangle|^2,$$  \hspace{1cm} (3.13)

with

$$f_{fi} = \frac{2}{m\hbar \omega} |\langle \Phi_f | \epsilon \cdot \hat{p} | \Phi_i \rangle|^2,$$  \hspace{1cm} (3.14)

defined as the oscillator strength, and can also be written in terms of the position operator

$$f_{fi} = \frac{2m\omega}{\hbar} |\langle \Phi_f | \epsilon \cdot r | \Phi_i \rangle|^2.$$  \hspace{1cm} (3.15)

The total oscillator strengths satisfy a basic sum rule, the Thomas-Reiche-Kuhn sum rule, which states that the sum of all oscillator strengths for all possible transitions of an electron should be unity. As a consequence, the total oscillator
strengths for the excitation in an atom or molecule should be equal to the number of electrons $N$.

$$\sum_f f_{fi} = N.$$ (3.16)

### 3.2 Approximations

In NEXAFS calculations, it is impossible to compute all possible final states to generate transitions for a large or even moderate system. A practical solution is to find a reference final state which can generate all transitions. Many efforts have been dedicated to the study of such reference final states. There are already a number of effective methods available, such as the full core-hole (FCH), half core-hole (HCH), Slater’s transition-state (TS), excited core-hole (XCH), and equivalent core-hole (ECH), etc. In this section, we only discuss three of them which have been used in our works, namely FCH, XCH, and ECH. All these approximations are representatively illustrated in Fig. 3.2. More details on DFT-based and other methods can be found in recent reviews in refs 59, 60.

#### 3.2.1 Full core-hole approximation

In the full core-hole approximation, the core electron is ionized which creates a hole in the core level, as illustrated in Fig. 3.2a. Practically this method has already been implemented in the StoBe\textsuperscript{34,52} package, which is based on the Gaussian basis sets. Normally, this approximation needs special attention on the
choice of basis sets for the excited atom, while the triple-\(\zeta\) quality individual gauge for localized orbital (IGLO-III) basis set is commonly recommended. The FCH method has shown its success in many studies. For large systems like polymers, a simple solution is to choose a small fraction of the entire system which contains the excitation center. This is especially efficient for systems with significant localized orbitals. However, this is not enough for systems with largely delocalized orbitals, such as the two dimensional graphene. Here we illustrate an example of the FCH method as applied in the poly (9,9-diocetylfluorene-co-benzothiadiazole) (abbreviated as F8BT) NEXAFS spectra simulations.

The F8BT (Fig. 3.3) is commonly used as a semiconductor material\(^{61}\) in organic light-emitting diodes due to its advantages in flexibility, low cost, and tunable

![Figure 3.3: The chemical structure of F8BT polymer.](image)

![Figure 3.4: (a) Different fraction sizes of F8BT models for N K-edge NEXAFS simulations, with corresponding spectra shown in (b). Color scheme: grey, C; pink, H; blue, N; yellow, S.](image)
3.2 APPROXIMATIONS

band gap. We simulated the N K-edge NEXAFS spectra by adopting different fraction sizes (Fig. 3.4a) as model structures, with results shown in Fig. 3.4b. The spectra are convoluted using Gaussian broadening with 0.1 eV half width at half maximum (HWHM). As the model size increases, the low energy peaks are near constant, and the peak at ~401 eV splits into two and approaches convergence for the biggest model. Thus, the FCH method gives acceptable results. However, for many 2D materials, such as graphene, the FCH calculation is quite expensive as very large models should be included. The reason is that the largely conjugated planer π orbitals can not be accurately described by small clusters. In this case, alternative more efficient core-hole method is needed.

3.2.2 Excited core-hole approximation

Prendergast and Galli implemented another approximation with the periodic boundary conditions in 2006, which considers not only the core-hole but also the excited electron. The picture can be described from Fig. 3.2b that the final state of the system is simulated in the presence of a core-hole resulting from the x-ray excitation and a photoelectron at the lowest unoccupied state. Due to their implementation based on plane-wave basis set in periodic boundary conditions using the Quantum Espresso program, a special modified pseudopotential is needed for the representation of core-electron potential of the excited atom with one electron form the 1s orbital removed. It has been proved that this approximation works well for many systems including solid states, solutions, and gas phase molecules. For gas phase molecules, large supercell method is needed to avoid interactions between the excited atom and its images in neighboring supercells. Due to the advantage of plane wave basis in periodic conditions, their implementation is naturally suitable for condensed phase NEXAFS spectra calculations and capable for very large systems.

The XCH method is similar to the FCH method, except that the inclusion of the photoelectron is considered. The study on water has shown that the FCH method tends to overestimate the absorption intensity at and near the absorption edge, leading to underestimation of the main peak intensity due to the Thomas-Reiche-Kuhn sum rule, while the XCH approximation in this case gives better description of the excitation. Here we illustrate an example of Mg K-edge NEXAFS calculation for magnesium boron hydride in tetrahydrofuran solution. Mg(BH$_4$)$_2$
is commonly used as an effective hydrogen storage material,\textsuperscript{64} and recently realized as the electrolyte for novel magnesium batteries.\textsuperscript{65}

First-principles molecular dynamics for the solution of Mg(BH$_4$)$_2$ in THF was first carried out, and then periodic snapshots were abstracted for NEXAFS calculations after the system reached equilibrium. Figure 3.5a shows one equilibrium snapshot, with corresponding Mg K-edge NEXAFS spectrum shown in b (spectra convoluted using Gaussian broadening with 0.1 eV HWHM). Although there are 255 non hydrogen atoms in total for the model structure, the efficient parallel computing algorithm makes such type of calculations doable. However, despite of the significant success of the XCH approximation, very large computational resource is usually needed which rises the barrier of applying it widely. Cheaper approximation with high accuracy is thus needed.

### 3.2.3 Equivalent core-hole approximation

A good balance between accuracy and computational time can be realized in the equivalent core-hole (also called Z+1) approximation.\textsuperscript{56-58} The central idea of the approximation is that the effect of an excited state of element Z with a core-hole and an excited electron is equivalent to the effect of element Z+1 with +1 charged, \textit{i.e.}, using a increased nucleus to model the electronic potential of the core-hole excited state. For example, replacing N as O$^+$ can be used to model
the NEXAFS spectra for N atoms. The implementation of this approximation on NEXAFS calculations was firstly introduced by Agren and coworkers\textsuperscript{58} for carbon based molecules, and it has been successfully applied on many other systems.\textsuperscript{66–69} Similar to the FCH method, the basis set for the excited atom need to be particularly specified and IGLO-III is usually chosen for the study in this thesis. Since the ECH method considers only ground state electronic structures, it is more efficient and easy to handle in practical computations. The approximation has been implemented in our in-house code, which is employed in this thesis, based on the the molecular orbital coefficients and multipole integrals outputs from the Gaussian program. Here we take C K-edge NEXAFS spectrum calculation for graphene as an example to illustrate this approximation. Graphene as the first single atomic layer thin 2D material has attracted enormous attentions since its discovery. To calculate its NEXAFS, we adopted a molecular-like large size truncated model with hydrogen saturation as shown in Fig. 3.6a with result shown in panel b (spectra convoluted using Gaussian broadening with 0.4 eV HWHM). Large model (568 non-hydrogen atoms) helps to reduce the edge effect to the final spectrum, and the resulting spectrum well reproduced the $\pi^*$ and $\sigma^*$ peaks measured in experiment. ECH method significantly reduced the computational requirement, yet keep good description to the final state, leading it to be a reliable tool to calculate NEXAFS spectra.

![Graphene model and spectrum](image)

**Figure 3.6:** (a) Model structure used for graphene C K-edge calculation, with result shown in panel (b).
CHAPTER 3. NEAR EDGE X-RAY ABSORPTION FINE STRUCTURE SPECTRA

3.3 Spectral alignment and broadening

Depending on the approximations employed, the raw spectra obtained usually cannot be directly compared with experiment. Post process for the calculated raw spectra is needed including energy alignment and spectral broadening. The energy alignment is to shift the calculated raw spectra by a constant value $\Delta E$ so that features from calculation can be compared correspondingly with those observed in experiment, while the spectral broadening helps to consider the broadening effect introduced by the core-hole life time, vibronic, and many other thermal or optical effects.

Energy alignment

For the FCH approximation implemented in the StoBe program, the $\Delta$SCF method is used for the energy alignment. For a $1s \rightarrow$ LUMO (K-edge) transition, the shift value $\delta$ can be calculated by the energy difference between the transition energy from FCH approximation and the energy from $\Delta$SCF

$$\delta = \epsilon_{FCH} - E_{\Delta SCF},$$

$$E_{\Delta SCF} = E_{1s \rightarrow LUMO} - E_{GS}, \quad (3.17)$$

where $\epsilon_{FCH}$ represents the first transition energy from the FCH approximation, $E_{1s \rightarrow LUMO}$ and $E_{GS}$ represent the total energies for $1s \rightarrow$ LUMO excited state and the ground state, respectively. This scheme is implemented in the StoBe program. The relativistic effect is neglected during the spectral calculation process, which is usually accounted by adding a constant small shift. For the common C, N and O atoms, this value is usually taken as 0.2, 0.3 and 0.4 eV respectively.

For approximations that the absolute transition energies are hard to get, another energy alignment method is applied by shifting the first peak of simulated spectra to the experiment. This method is quite straightforward and was adopted for the XCH and ECH calculations in this thesis.

Linear broadening

No matter what approximation is employed, the obtained raw spectra are in terms of the oscillation strengths at different energies, i.e., the stick bar spectra, which need to be convoluted to compare with experiments. The theoretical reason
is mentioned above. In practice, the most commonly used broadening method is
by using the Gaussian distribution. The Lorentzian distribution also appear in
literatures but less often. The mathematical formulas are given by

\[
\begin{align*}
\text{f}_G(\varepsilon; \varepsilon_0, \gamma) &= \frac{1}{\gamma} \sqrt{\frac{\ln 2}{\pi}} \exp\left[-\frac{(\varepsilon - \varepsilon_0)^2 \ln 2}{\gamma^2}\right], \\
\text{f}_L(\varepsilon; \varepsilon_0, \gamma) &= \frac{1}{\pi} \frac{\gamma}{(\varepsilon - \varepsilon_0)^2 + \gamma^2},
\end{align*}
\] (3.18)

where \(f_G\) and \(f_L\) represent the Gaussian and Lorentzian distributions respectively,
\(\gamma\) stands for the HWHM, and the bar spectra are convoluted centering at each
transition energy \(\varepsilon_0\). The choice of broadening method does not change the spectral
features, and for convenience the Gaussian type broadening is employed in this
thesis.

3.4 Angular dependence

Eq. 3.15 can be rewritten as,

\[
\text{f}_{ji} = \frac{2m\omega}{3\hbar} \left( |\langle \Phi_f | \varepsilon \cdot \Phi_i \rangle |^2 + |\langle \Phi_f | \varepsilon \cdot y | \Phi_i \rangle |^2 + |\langle \Phi_f | \varepsilon \cdot z | \Phi_i \rangle |^2 \right). \tag{3.19}
\]

This formula works for systems with random orientated molecules, such as gas
phase molecules, liquids, and amorphous materials. 2D materials have ordered

![Figure 3.7](image_url)

**Figure 3.7:** (a) Schematic illustration of h-BN and incident linear polarized x-ray. 
\(\theta\) and \(\varphi\) describe the angle of incident photons and the azimuthal angle, respectively.
(b) Simulated polarization dependent N K-edge NEXAFS spectra of h-BN. Dashed lines, \(1s \rightarrow \sigma^*(1s \rightarrow \pi^*)\) corresponds to \(\theta=0^\circ (90^\circ)\); Solid line, orientally averaged spectra.
structures. The incident angle of linear polarized x-ray $\theta$ (the angle between the x-ray beam and surface normal, see Fig. 3.7a) holds an important parameter which adjusts the relative intensities of $\pi^*$ and $\sigma^*$ peaks in the NEXAFS spectrum. Another angle, so-called grazing angle, is also often used, which is defined as the complementary angle of the incident angle, i.e., $90^\circ - \theta$. The azimuthal angle $\varphi$ is usually not resolved in NEXAFS measurements. Here we illustrate an example to show the clear difference between in- and out-of-plane contributions to spectra. Figure 3.7b shows the calculated N K-edge NEXAFS spectra of monolayer $h$-BN, with 1s to $\pi^*$ and $\sigma^*$ contributions plotted separately. 1s to $\pi^*$ transitions correspond to $\theta=90^\circ$, while 1s to $\sigma^*$ transitions correspond to $\theta=0^\circ$. By tuning the incident angle, spectra with varying $\pi^*$ and $\sigma^*$ peak intensities can be obtained.
Applications on 2D Materials

Our studies in this thesis mainly focus on the electronic structure and NEXAFS spectroscopy of 2D materials by using the first-principles DFT method. Four types of material are considered, including atomically thin bismuth telluride, nitrogen doped graphene, boron nitrided doped graphene, and lithium intercalated graphite. The first one is a novel non-carbon 2D material that can be exfoliated similar as for graphene. Nitrogen and boron nitride doped graphenes are graphene based materials with non-metal dopant. Lithium intercalated graphites (LIGs) is a metal doped carbon material. Although being bulk material, the electronic properties of LIGs are analogue to that of lithium doped graphene that used in lithium-graphene batteries.

4.1 Atomically thin bismuth telluride layer

Bismuth telluride (Bi$_2$Te$_3$) is a narrow gap semiconductor material\textsuperscript{70} that often used in efficient thermoelectric applications such as power generation in industry. The thermoelectric performance is defined by the thermoelectric figure of merit (ZT), which can be significantly enhanced by reducing the material thickness down to $\sim$1 nm.\textsuperscript{71-74} Bi$_2$Te$_3$ has also been proven to be a topological insulator (TI) material after the discovery of its time reversal symmetry property and topological surface states.\textsuperscript{75,76} TI materials have wide potential in applications, such as electronic devices with low energy consumption, spintronic devices, infrared detectors, etc.\textsuperscript{77,78} Thus Bi$_2$Te$_3$ has drawn enormous attentions to investigate its various properties.\textsuperscript{79-84}
Following the simple but efficient idea of exfoliation of graphene, atomic layered Bi$_2$Te$_3$ was realized in experiments. The thickness of the obtained layer was found to be $\sim$1 nm by scanning electron microscopy (SEM), atomic force microscopy (AFM), and optical inspection. Furthermore, thinner layers was also observed with thickness down to 2-3 atomic layers, indicating the possibility of further exfoliation. High electrical conductivity, low thermal conductivity, and enhanced thermoelectric properties have been observed for the obtained layers. Despite many characterizations on this two dimensional Bi$_2$Te$_3$ from experiments, its electronic structure was still unclear. The electronic structure is essential for understanding the chemical and physical properties of materials, and developing related applications. Therefore, we performed first-principles calculations to understand the electronic structure of such atomic layered Bi$_2$Te$_3$.

The unit cell of bulk Bi$_2$Te$_3$ belongs the rhombohedral crystal structure, consisting three building blocks of five-fold (quintuple) atomic layers (Te$^1$-Bi-Te$^2$-Bi-Te$^1$). The three building blocks, as shown in Fig. 4.1a, are bonding together with van der Waals interactions. The weak interaction leads to the probability of exfoliation from the bulk material to the atomically thin layered structure, similar to the exfoliation of graphene. The 2D Bi$_2$Te$_3$ layer, with thickness of about 1 nm, is a quintuple structure with two types of non-equivalent Te atoms, Te$^1$ and Te$^2$ as shown in Fig. 4.1b.

![Figure 4.1: Crystal structure of Bi$_2$Te$_3$ (a), with one building block shown in (b).](image)

The calculated interlayer spacings between Te$^1$ and Bi, and Te$^2$ and Bi, are 1.72 and 2.06 Å, respectively. The larger interlayer spacing between Te$^2$ and Bi layers implies their weaker interaction than that between Te$^1$ and Bi. Such
4.1. ATOMICALLY THIN BISMUTH TELLURIDE LAYER

Figure 4.2: Calculated band structure and density of states (DOS) of (a) quintuple, (b) bilayer and (c) trilayer. Projected density of states (PDOS) of \( p \) orbitals on inequivalent atoms are shown as dashed lines differing in colors. Adapted with permission from ref. 85. Copyright 2011 American Institute of Physics.

difference supports the existence of further exfoliation of the quintuple structure into two or three-fold structures (bilayer and trilayer) which have been observed in the experiment.\textsuperscript{79}

Figure 4.2 shows the calculated band structures and density of states (DOSs) for quintuple layer, bilayer and trilayer structures of \( \text{Bi}_2\text{Te}_3 \). It can be seen that the quintuple structure retains as semiconductor with a indirect band gap of \( \sim 0.9 \text{ eV} \). The top of valence bands locates between \( \Gamma \) and K, while the bottom of conduction bands locates at the \( \Gamma \) point. In contrast, the bilayer and trilayer structures are metallic. In experiments, atomically thin layer \( \text{Bi}_2\text{Te}_3 \) was characterized as high electrical conductivity. This, from theoretical point of view, can be explained by the mixture of all of quintuple, bilayer and trilayer structures. From the projected density of states result of quintuple layer, we can see that the valence bands mainly contributed by the Te (both Te\textsuperscript{1} and Te\textsuperscript{2}) 5\textit{p} orbitals, while the conduction bands mainly come from the Te\textsuperscript{1} 5\textit{p} and Bi 6\textit{p} orbitals. The s orbitals of each element have no contribution to the near-Fermi bands.

From the quintuple layer band structure, we can see that there are three shallow bands below and above the Fermi level, respectively, which show less dispersion than other bands. These bands are localized in real space and directly related with the bonding between Te and Bi atoms. We hence calculated the local density of states (LDOS) for these three bands above and below the Fermi level, respectively, with results shown in Fig. 4.3. We can see that the electronic density locates at the Te atoms for the valence bands (Fig. 4.3a), and locates at the Te\textsuperscript{1} and Bi atoms for the conduction bands (Fig. 4.3b), which is consistent with the PDOS
calculation. Furthermore, the bader charge analysis gives -0.4e, -0.6e and +0.7e for Te$_1$, Te$_2$ and Bi atoms, respectively, indicating a greater charge transfer from Bi to Te$_2$ than to Te$_1$.

The bond strength difference between Bi-Te$_1$ and Bi-Te$_2$ can be visualized by calculating the charge density difference (CDD). Here we calculated the CDD

Figure 4.3: LDOS of (a) the highest three valence bands and (b) the lowest three conduction bands for the quintuple layer. contour value set to 0.02. Adapted with permission from ref. 85. Copyright 2011 American Institute of Physics.

Figure 4.4: Charge density difference (CDD) for quintuple layer shown in the (110) cross section, with contour value set to 0.02. Dash circles indicate the atomic position. Adapted with permission from ref. 85. Copyright 2011 American Institute of Physics.
using the following relation,

\[ \delta_{p} = \rho_{sc} - \rho_{atom}, \]  

(4.1)

where \( \rho_{sc} \) represents the charge density after self-consistent convergence, and \( \rho_{atom} \) represents the superposition of neutral atomic charge densities before self-consistent.

Fig. 4.4 shows the calculated CDD in the (110) cross section. The accumulation of charge density around the Te\(^2\) atom is less obvious than around the Te\(^1\) atom, while the charge depletion for the two Bi layers are identical. This means that the bond between Bi and Te\(^2\) is weaker than that between Bi and Te\(^1\). We may assign the former as weak covalent bond and the later strong covalent bond. This also indicates the probability of further exfoliation of quintuple layer into bilayer and trilayer.

4.2 N-doped graphene

Ever since the discovery of graphene in 2004, this 2D carbon material that opened a new era for materials study has drawn enormous attentions by researchers and has shown various physical and chemical properties. Due to the 2D structure, every carbon atom in the lattice is available for chemical reactions, especially those atoms at the edges can show particular reactivity.\(^{86,87}\) Tailoring the electronic structure of pristine graphene has continuously been the goal of researchers to develop novel materials with higher performance in electronic or chemical reactions.\(^{88-91}\) In this regard, doping is an efficient way to achieve the goal. Doping foreign atoms into allotropes of carbon has been an important approach to realize desired chemical and physical properties.\(^{92-99}\) Following the same idea, graphene doped with nitrogen was first successfully synthesized by Wei et al. in 2009,\(^{18}\) and soon by many others.\(^{100-110}\)

Extraordinary properties of N doped graphene have been explored, leading to many potential applications. It has shown impressive capabilities in lithium battery,\(^{21}\) hydrogen storage,\(^{20}\) and biosensing.\(^{22}\) It can be also used as efficient metal-free catalyst in oxygen reduction reaction giving high performance,\(^{111}\) and as high-performance ultracapacitor showing four times capacitance than pristine graphene.\(^{24}\) Many theoretical efforts have also been dedicated to the study of this material, leading to wide understandings on its fundamental electronic properties such as band structure,\(^{112-114}\) and spin charge density,\(^{115}\) as well as applications
such as properties in oxygen reduction reaction\textsuperscript{116}, lithium air battery\textsuperscript{117}, etc. During the synthesis process of N doped graphene, different doping configurations exist depending on experimental conditions. Various characterizations have identified that there are mainly three doping configurations exist, including quaternary, pyridinic and pyrrolic N.\textsuperscript{18,90,101} For quaternary type doping, a nitrogen atom substitutes a carbon atom in the lattice forming graphite-like (quaternary) structure, while pyridinic and pyrrolic doping exist at a vacancy site that they form six or five member ring, respectively. Despite the extensive studies on this material, some understandings on the fundamental electronic structure especially the unoccupied states above the Fermi level are still missing. NEXAFS spectroscopy, in this regard, provides an powerful tool.

We performed electronic structure and spectroscopic studies on N doped graphene, considering the three most common doping configurations. In our calculations, large vacancy that appears in experiment\textsuperscript{119} was chosen as the basis to build pyridinic and pyrrolic configurations. Our electronic structure calculations are based on large supercells (11 × 11, Fig. 4.5) with a hexagonal vacancy (6V). The calculated spin-polarized band structures for the models in Fig. 4.5 are shown in Fig. 4.6. We can see that, for pristine graphene and graphene with 6V vacancy (Fig. 4.6a), the original Dirac point stays at K point after Brillouin zone folding. The bands near the Fermi level is degenerated for pristine graphene, while splitting

![Diagram of graphene models](image-url)
occurs when a vacancy is introduced. The original Dirac point for 6V shifts up by $\sim 0.4$ eV indicating the hole doping character of the vacancy. Dangling bonds exist in the 6V structure and these dangling bonds contribute six spin up and six spin down flat bands, which indicates that the current model size is large enough to neglect the vacancy-vacancy interaction. The carbon atoms of those dangling bands are highly active in chemical reactions. Fig. 4.6b shows the band structure of quaternary N doped graphene, there is no band splitting and the Fermi level shift up by $\sim 0.5$ eV. There is a band gap opening on the original Dirac point of

![Band Structures](image)

**Figure 4.6:** Calculated band structures for (a) ideal graphene and graphene with hexavacancy, (b) quaternary, (c) pyridinic, and (d) pyrrolic dopings. Adapted with permission from ref. 118. Copyright 2015 American Chemical Society.
\( \sim 0.04 \) eV. The rise of the Fermi level is simply due to the one extra electron of nitrogen than carbon. When nitrogen is doped in the 6V center, the one extra electron reduces one dangling bond, leaving a lone pair electrons at the nitrogen atom. Fig. 4.6c shows great similarity with Fig. 4.6a, indicating that the doping effect on the electronic structure is much weaker than that from vacancy. Upon changing the six- to five-membering, the Dirac point shifts up of \( \sim 0.1 \) eV, and shifts away from the high symmetric K point to the \( K \rightarrow \Gamma \) direction.

Our NEXAFS simulations were based on the ECH approximation. Test calculations for quaternary N doping was first investigated with results shown in Fig. 4.7, comparing with experimental measurement (Fig. 4.7a). The calculated N 1s \( \rightarrow \pi^* \) (Fig. 4.7b) and 1s \( \rightarrow \sigma^* \) (Fig. 4.7c) transitions are given separately. Here we considered three sizes of model, 1.1 \( \times \) 1.5 nm (size A), 2.0 \( \times \) 2.2 (size B) and 2.7 \( \times \) 2.9 nm (size C), to compare the influence of concentration to the spectra. Size C was chosen for calculating other doping concentrations. From Fig. 4.7b, we can see that the intensity of the main \( \pi^* \) peak at 401 eV decreases as increasing the model size. This is due to the fact that the \( \pi^* \) states are more delocalized, which gives smaller transition dipole moment from the N 1s orbitals for the large size model. The oscillation in higher energies is weaker in large size model, which is

![Figure 4.7: (a) Experimental spectrum of N doped graphene. Calculated N 1s \( \rightarrow \pi^* \) (b) and 1s \( \rightarrow \sigma^* \) (c) NEXAFS spectra of quaternary N doping under sizes A, B, and C (see insert in panel c). Adapted with permission from ref. 118. Copyright 2015 American Chemical Society.](image-url)
4.2. N-DOPED GRAPHENE

Figure 4.8: Calculated N 1s NEXAFS spectra for all doping configurations with size C, with 1s → π* and 1s → σ* plotted separately. Adapted with permission from ref. 118. Copyright 2015 American Chemical Society.

similar to that of graphene. The N 1s → σ* transitions are shown in Fig. 4.7c. The spectral shape is much less affected by the model size, only a slight increase of intensity and energy position is observed for size C. This is because the σ* orbitals of the excited atom is very localize compared with the π* orbitals. Comparing the calculated results to the experiment, we can see that the peak 2 and 3 in the experiment can be assigned to the π* and σ* peaks of quaternary N in Fig. 4.7b and c, respectively.

We performed further calculations for all doping configurations with spin polarized and the obtained spectra are shown in Fig. 4.8, with 1s → π* and σ* transitions plotted separately. Upon vacancy, the pyrrolic N doping gives very broad π* feature ranging from 395 to 405 eV. The π* peak of pyridinic N, however, is clear and shifts to lower energy by ~2.6 eV at 398.6 eV, which can be
assigned to the experimental peak 1 at 398.6 eV in Fig. 4.7c. For the \( \sigma^* \) feature, both pyridinic and pyrrolic N have red-shifted \( \sigma^* \) peaks compared to quaternary N, with one additional weak peak for each at lower energies. This peak splitting is probably due to the lowering of local symmetry around the excitation center. In the experiment (Fig. 4.7c), there is a clear feature at 407.1 eV, which can be attributed to be originated from the quaternary N. However, the variation of \( \sigma^* \) peaks from all three configurations can cover a broad range from 402 eV to 407 eV. The significant difference between different doping configurations can be used to identify the doping degree of certain configuration.

4.3 BN co-doped graphene

As can be seen from the study of N doped graphene, doping is an efficient approach to manipulate the electronic structure of this unique 2D material. Due to the zero band gap behavior of pristine graphene, many attempts have been dedicated to the study of opening the zero band gap for semiconducting applications, wherein hexagonal boron nitride (h-BN) has drawn particular attentions as dopant candidate.\(^{120-129}\) h-BN has the same lattice symmetry and close lattice constants as graphene, thus can be suitably doped in to the graphene lattice. It was first successfully synthesized in experiment in 2010\(^{130}\) and soon followed by other studies.\(^{89,123,131-135}\) It has been proven that the doping level is an important parameter in controlling the band gap of the outcome.\(^{131,136}\) To understand the mechanism of how the doping level influences the properties of such semiconducting materials is of great importance for the design of new generation electronics. Therefore, we performed electronic structure and NEXAFS spectroscopic studies on this material to investigate the effect of dopant domain size on the electronic properties. Based on the fact that the BN dopant tend to form domains growing in size with increasing doping level, we consider a series of model structures with increasing the cluster type dopant domain size as shown in Fig. 4.9. For the largest domain size (v), an alternative configuration (vi) is considered based on the same dopant concentration. This consideration is because the cluster type dopant domain is possible to merge together when the dopant concentration is high enough, as well as the energetic calculations show small difference (8 meV/atom) between the two configurations.

The calculated band structures for the six doping configurations are shown in
4.3. BN CO-DOPED GRAPHENE

Figure 4.9: Supercells employed for different doping configurations of BN doped graphenes i-vi. The periodic cells from i to vi correspond to dopant concentrations of 0.7, 2.1, 8.3, 18.8, 33.3 and 33.3%, respectively. Color scheme for atoms: gray, C; orange, B; blue, N. Dash line in configuration vi indicates the corresponding unit cell. Adapted from ref. 137.

Fig. 4.10a. The contributions from interfacial atoms (Fig. 4.10b) are plotted in circles with circle size representing the corresponding weight. The contributions approach equal at the valence band maximum and conduction band minimum. We can see that for configurations i-v, the band structures near the Fermi level are quite similar in profile while distinct in band gap. The projected band structures show that it is the interfacial atoms, rather than those in the dopant domain, determine the electronic structure near the Fermi level. Furthermore, the valence and conduction bands mainly come from the interfacial boron and nitrogen atoms, respectively, which highlights the importance of interfacial structures.\textsuperscript{138} The band gap opening for all configurations is plotted in Fig. 4.10c, which shows a non-linear increasing upon increasing dopant size for configuration i-v. The band gap ranges from 0.02 to 0.52 eV for concentration from 0.7% to 33.3%. The phase separated configuration vi, however, gives a merely opening of $\approx$0.03 eV which is close to the room temperature thermal energy. The comparison between different configurations i-vi illustrates the importance of doping concentration and configuration to the final band gap. This indeed provides an idea of controlling the performance of such semiconducting material by tailoring the geometry of dopant.

NEXAFS spectra studies were performed using the ECH method. We first
Figure 4.10: (a) Band structures for configuration i-vi, with circles represent the contribution from interfacial dopant atoms as indicated in (b). The size of circle represents the corresponding weight. (c) The band gap opening for all configurations (i-vi). Adapted from ref. 137.
calculated the N 1s spectrum for pristine monolayer h-BN and compare that with the experimental measurement. It worth to mention that the polarization setting in our experiment was fixed at the angle of 45° between the electric field vector and the surface normal, which is close to our setting of the theoretical spectra of spacial oriental average. The calculated spectrum of h-BN (Fig. 4.11a top) well reproduced the main $\pi^*$ and $\sigma^*$ features, validating the theoretical method and models employed. The measured pre-shoulder at ca. 400 eV (peak 0) is not found from the calculation, which is attributed to the edge effect and/or defects. The calculated spectrum gives very close energy position to the experiment for peak 2, while the peak 3 in experiment is split into 3a and 3b in calculation. As the NEXAFS spectroscopy is a sensitive tool of the local bonding, we compared the atom specific contributions for nitorgens at different non-equivalent sites (Fig. 4.11b) for the largest dopant domain configuration. N1-N4 locate in the interfacial boundary, and N1-N2 bond with 2 borons and 1 carbon, while N3-N4 bond to 3

**Figure 4.11:** (a) Measured (black) and calculated (grey) N 1s NEXAFS spectra of h-BN, and calculated atom specific spectra for boron nitride doped graphene for doping configuration v, with the ten considered non-equivalent atom sites label as N1-N10 as shown in (b). Weight of each non-equivalent atomic site is indicated on the right. Adapted from ref. 137.
borons with carbon as the second nearest neighbors. N5-N10 are nitrogens located inside the dopant domain. These three groups are also reflected in the calculated N 1s spectra. N1-N2 give the lowest absorption edge at ca. 399.1 eV, which blue shifts to 400.1 eV for N3-N4, and further to 401.0 eV for N5-N10. The lowest absorption energy of N1-N2 is consistent with the band structure results that the interfacial nitrogens contribute the lowest conduction bands. The blue shift can also be found in the $\sigma^*$ peak from ca. 405.1 eV for N1 to 408.2 eV for N10. The blue shift is understandable as nitrogen has stronger bonding with boron than carbon, and stronger bonding results in larger splitting between the bonding and antibonding orbitals. The higher anti-bonding unoccupied orbital thus leads to higher absorption edge. An energy difference between $h$-BN and N10 can be found for the $\sigma^*$ peak 4. Generally, N10 should experience a $h$-BN like chemical environment given the very center position in the dopant domain. The peak energy difference, however, indicates that the B-N bond length plays an critical role, as $h$-BN has slight longer B-N bond length (1.444 Å) than that in boron nitride doped graphene (1.425 Å).

To obtain the total spectra for each configuration, we performed N 1s NEX-AFS calculations for each non-equivalent nitrogens in each dopant configuration i-vi, and made sum according to their weight. The obtained spectra compared with experiment are shown in Fig. 4.12. From the experiment results shown in Fig. 4.12, we can see that with the increase of concentration from 6% to 26%, the $\pi^*$ peak blue shifts from 398.9 to 400.2 eV. The $\sigma^*$ peak also shows a slight blue shift. Similar peak evolution can be observed from calculations as well. As increasing dopant domain size from i to v, the $\pi^*$ peak blue shifts about 1.6 eV from 399.3 to 400.9 eV. The $\sigma^*$ peaks, which are more sensitive to the N-C and N-B $\sigma$ bond, show complicate features. For configuration i and ii, there is only one non-equivalent nitrogen, and the obtained $\sigma^*$ peak is very intensive, which is not observed clearly from the experiment. This is mainly due to the low experimental resolution at low dopant concentration. As the domain size increases, we can see a clear main $\sigma^*$ peak 4 at higher energy. In consequence, the evolution of the $\pi^*$ peak 1 and $\sigma^*$ peak 4 can be considered as the following: the boron nitride presents as small dimers or clusters (configuration i and ii) at low dopant concentration with lower peak energies, where interfacial nitrogens have more contribution; at high concentration, boron nitride forms large domains where N5-N10 type nitrogens dominate the total spectra, leading to blue shift of both $\pi^*$ and $\sigma^*$ peaks.
4.4 Lithium intercalated graphite

The increasing global warming issue and potential energy crisis due to the consumption of fossil energy that in inevitable depletion highlight the demand of innovating novel energy generation and storage approaches. In this regard, lithium ion batteries have played an important role in energy storage ever since its invention. It now has become a part of our life due to its enormous applications in cell phones, electronic watches, medical equipments, satellites, and even vehicles like the Tesla. Despite such intensive applications, lithium ion batteries now face a bottleneck due to the difficulties of increasing its capacity, charge density, and charging efficiency. These difficulties prevent its more widely application in areas where large storage capacity and short charging time are needed. Thus enormous

Figure 4.12: (a) Experimental N 1s NEXAFS spectra of different doping concentrations. (b) Calculated total spectra for the configurations i-vi, with increasing dopant domain sizes. Dashed lines are to guide the eyes. Intensity of config. i has been multiplied by 1/2 for better visualization. Reproduced from ref. 137.
attempts have been dedicated to develop novel batteries, covering a wide range of topics.\textsuperscript{142–147} The investigation on the graphite intercalation compounds (GICs), a prototype of anode electrode, has drawn particular attentions,\textsuperscript{148–152} as thoroughly understanding on its electronic properties provides the fundamental information. Furthermore, the understanding on GICs benefits the electronic property study of lithium doped graphene that used in lithium graphene batteries.\textsuperscript{153,154}

The working process of charge-discharge (lithiation and dilithiation) process has been characterized by many experiments.\textsuperscript{155–157} It is shown that there are many complex compounds exist in the anode graphite, such as LiC\textsubscript{6}, LiC\textsubscript{12}, LiC\textsubscript{18}, and LiC\textsubscript{24}, etc.\textsuperscript{148,158–161} At the stage of fully lithiation, the lithium and graphite form a stable structure with least anisotropic and highest in-plane density of lithium, i.e., LiC\textsubscript{6}. In consequence, LiC\textsubscript{6} became the critical target for both theoreticians and experimentalists, and many achievements have been obtained including its superconductivity property\textsuperscript{162,163}, thermo stability\textsuperscript{164,165}, charge transfer\textsuperscript{166,167}, and interlayer states\textsuperscript{163}, etc. However, despite the vast applications and investigations, there are still some mysteries remaining in understanding the fundamental electronic structure of LiC\textsubscript{6}. For example, it has shown that the $\pi^*$ peak gets reduced and the $\sigma^*$ peak presents a red-shift upon lithiation.\textsuperscript{157,168} Theoretical explanation for such phenomenon is still absent. Thus our scope on the current study is to understand the electronic structure modification of graphite upon lithiation and address the origin of the spectral change.

The most common graphite lattice is well-known as ABAB stacking layered structure with $\sim$1.42 Å for C-C bond length and $\sim$3.36 Å for interlayer spacing, respectively. Upon lithiation, the graphite lattice experiences an intercalation process, resulting in a significant structural change that the stacking sequence changed

| Table 4.1: The lattice parameters of graphite and LiC\textsubscript{6} after relaxation comparing with experiment value. C1 and C2 correspond to two different carbon bond lengths as stated in the text. The experimental values are from references 163 and 164. |
|-----------------|--------|----------|--------|--------|
| graphite        | LiC\textsubscript{6} |
|                 | Theory | Experiment | Theory | Experiment |
| C-C bond length (Å) | 1.413 | 1.423 | 1.441\textsuperscript{C1} | 1.435 |
| Interlayer spacing (Å) | 3.314 | 3.356 | 3.654 | 3.680 |
4.4. LITHIUM INTERCALATED GRAPHITE

to AAAA and the interlayer spacing significantly increased. To understand such structural change, lattice optimizations were performed for both graphite and LiC$_6$, with results shown in table 4.1. It shows that the interlayer spacing is significantly enlarged by $\sim$10%, while the C-C bond length does not present obvious change. However, due to the intercalation of lithium, there are two inequivalent types of carbon ring, leading to two C-C bond lengths as indicated in the table. The experimental values are from corresponding experiments.$^{169,170}$

Ground state electronic structure is fundamental to understand the modification by intercalation. Band structure and projected density of states of carbon calculations were first performed for pristine graphite and LiC$_6$ with results shown in Fig. 4.13a and b. Upon intercalation, the Fermi level increases for $\sim$1.3 eV, indicating the charge transfer from lithium to carbon $p$ orbital, and a small band

![Figure 4.13: Calculated band structure and projected density of states of carbon for graphite (a) and LiC$_6$ (b). Charge density difference for 1e/C$_6$ charged AAAA stacking graphite, i.e. C$_6$ (c) and LiC$_6$ (d).](image-url)
CHAPTER 4. APPLICATIONS ON 2D MATERIALS

A gap (~0.3 eV) opens at the original Dirac point similar to lithium absorbed on graphene.\textsuperscript{171} The charge transfer effect is studied by charge density difference calculations for 1e/C\textsubscript{6} charged AAAA stacking graphite (Fig. 4.13c) and LiC\textsubscript{6} (Fig. 4.13d). For the former the extra electrons uniformly distributed along the lattice plane filling the unoccupied \textit{p}\textsubscript{z} orbital, while for LiC\textsubscript{6} the electrons are accumulated between lithium and carbon atoms indicating a chemical bonding between them.

C K-edge NEXAFS spectra for graphite and LiC\textsubscript{6} were calculated using the XCH approximation. From the results shown in Fig. 4.14, we can see that upon intercalation, the \(\pi^*\) peak intensity reduces significantly, and the \(\sigma^*\) peak red shifts about 1 eV. The spectral change is mainly due to the charge transfer effect. The transferred electron fills in the \textit{p}\textsubscript{z} orbital of carbon, leaving it partly occupied. Apart from the charge transfer, crystal structure change spontaneously happens during intercalation, which may also contributes to the spectrum. To investigate this structural effect, we performed a series of calculations by changing the lattice parameters (C-C bond length and interlayer spacing) from AAAA stacking graphite to LiC\textsubscript{6}. The two parameters were examined separately. The peak energy positions for both \(\pi^*\) and \(\sigma^*\) are extracted shown in Fig. 4.15. As can be seen from Fig. 4.15a, the energy positions for both \(\pi^*\) and \(\sigma^*\) show little change upon intercalation, indicating that the interlayer spacing merely has influence to

![Figure 4.14](image_url)

**Figure 4.14:** Calculated N 1s NEXAFS spectra for graphite and LiC\textsubscript{6}. Insets show the crystal structure of LiC\textsubscript{6}.
the spectra even experienced a change of \(\sim 10\%\). The in-plane change shown in Fig. 4.15b, however, is different. The \(\sigma^*\) peak clearly shows a red shift of \(\sim 0.5\) eV for lattice expanding from graphite to LiC\(_6\), together with mere change to the \(\pi^*\) peak. The difference for interlayer spacing and in-plane lattice can be understood from the fact that, the interaction between graphite layers is weak van der Waals interaction, while the in-plane lattice is strong \(\sigma\) bond which is more sensitive to the change.

Thus the significant spectral change from graphite to LiC\(_6\) is due to two factors, charge transfer and structure change, and the former plays the dominative role.
Conclusion and Outlook

We have studied the electronic structure and NEXAFS spectroscopies of various materials using first-principles calculations. Four types of materials are considered: atomically thin bismuth telluride, nitrogen doped graphene, boron nitrided doped graphene, and lithium intercalated graphite, representing the typical carbon and non-carbon based materials, with metallic and non-metallic dopings.

**Paper I.** It is found that quintuple layer sheets of Bi$_2$Te$_3$ are semiconductor materials, which is the same as bulk. The bonding between Te$^1$ and Bi layers is stronger than that between Te$^2$ and Bi, which suggests the possibility to further exfoliate quintuple layer into bilayer and trilayer. Bilayer and trilayer show metallic band structures, and a mixture of different types of sheet may be responsible to the high electric conductivity observed in the experiment.

**Paper II.** We have studied the electronic structure of nitrogen doped graphene based on ideal and 6V-defected graphene. N K-edge NEXAFS spectra, combined with ground state band structure and density of states, provide the complementary understanding of the electronic structure of nitrogen doped graphene, as well as the interplay between dopant nitrogen and vacancy defects. The vacancy defect and dopant N act as p and n type dopings respectively. Simulated spectra show that the experimental peak at 398.6 eV can be assigned to the pyridinic N configuration at vacancy center. The pyrrolic N contributes broad $\pi^*$ feature covering an energy range of 395 – 405 eV. The splitting of $\sigma^*$ peaks for different dopant configurations can be used to evaluate the degree of defects.

**Paper III.** The electronic structure of BN doped graphene in both the ground and core excited states have been studied and the influence of different dopant do-
main size has been analyzed. It is found that the interfacial nitrogens and borons mainly contribute to the lowest conduction bands and highest valence bands, respectively. This leads to the conclusion that the interfacial nitrogens produce $\pi^*$ peak in lower energy than those from the domain center in the K-edge NEXAFS spectra. As increasing the dopant domain size, spectral evolutions can be found in both theoretical simulation and experimental measurement. Blue shift of $\pi^*$ peak in simulation is found similar to the experiment, which is useful to identify the relative dopant domain size. The observed spectral evolution in experiment can be explained by the size effect of dopant domains.

**Paper IV.** Lithium intercalated graphite has been studied by C K-edge NEXAFS spectra combined with ground state electronic structure analysis. The $\pi^*$ peak intensity of graphite is significantly reduced upon lithium intercalation, and a red-shift of the $\sigma^*$ peak is observed. Such spectral change is mainly due to the charge transfer from lithium to the unoccupied graphite $p$ orbital. It is also found that the $\sigma^*$ peak is sensitive to the C-C bond length, but insensitive to the interlayer spacing. The spectral change of C K-edge from graphite to LiC$_6$ can be used to evaluate the intercalation degree.

The unique electronic structure of 2D materials provides us tremendous opportunities to develop novel materials with excellent chemical and physical properties. Further investigation based on our current study is of important. For example, our paper II considered only single atom dopant for each doping configuration, and neglect the possible interaction between different doping configurations that may have impact to the electronic structure as well as the spectra. Thus our future plan is to investigate such interactions and examine the corresponding effects. Besides, our study in paper IV were based on static models and the thermal effects on the mobility of Li ions was completely neglected. The molecular dynamics simulations that can provide insightful understanding on how the lithium atoms diffuse between the graphite layers will be on our next plan. This is important for understanding the lithiation and dilithiation processes.

So far, most of my works focus on unoccupied states. In the future, occupied state electronic structure and corresponding x-ray emission spectroscopy will also be studied to obtain more comprehensive understanding of the states both above and blew the Fermi level.
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