



Physical Properties of Novel Two-dimensional Materials and Their Modifications

From first-principles studies



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*I would like to dedicate this thesis
to my loving parents Arkin and Perwin,
to my beloved wife Adila Dilshat,
to my cherished sons Efran and Wildan.*

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Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 65,000 words including appendices, bibliography, footnotes, tables and equations and has fewer than 150 figures.

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Acknowledgements

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Abstract

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Table of contents

List of figures	xv
List of tables	xvii
1 Introduction	1
1.1 Graphene	3
1.1.1 History	3
1.1.2 Physical properties	5
1.2 Post-graphene materials and their general properties	6
1.2.1 Functionalized graphene	7
1.2.2 Group IV 2D materials	9
1.2.3 2D from layered materials	10
1.3 1D from 2D: nanotubes and nanoribbons	13
1.4 Synthesis methods	14
2 Computational methods	19
2.1 Theory	19
2.1.1 Density Functional Theory	19
2.1.2 Exchange-correlation functional	22
2.2 Implementation	26
2.2.1 Basis set, Plane wave energy cut-off, K-points	26
2.2.2 Software Packages	26
3 General physical properties 2D materials	27
3.1 Structural properties	27
3.1.1 Layer structure	27
3.1.2 sp hybridization	27
3.1.3 Isotropic v.s. Anisotropic monolayer	27
3.1.4 Multiphase allotropes	27

3.2	Electronic properties	27
3.2.1	Polar bond	27
3.2.2	Importance of crystal symmetry	27
3.2.3	Importance of interlayer interaction	31
3.2.4	Accurate description from DFT	31
3.3	Vibrational properties	31
3.3.1	Phonon dispersion of 2D materials	31
3.3.2	Dynamic stability from phonon dispersion	31
3.4	Mechanical properties	31
3.4.1	Elastic and engineering constants	31
3.4.2	Mechanical stability: Born stability criteria	31
4	Results of Physical Properties Calculations in Novel 2D materials	33
4.1	Thermal properties	34
4.1.1	Thermal expansion and anharmonic oscillations	34
4.1.2	Quasi-harmonic approximation	34
4.1.3	Helmholtz free energy and specific heat	34
4.2	Piezoelectric properties	34
4.2.1	Piezoelectric constants	34
4.2.2	Importance of internal relaxation	34
4.3	Carrier transport properties	34
4.3.1	Carrier mobility	34
4.3.2	Deformation potential theory: non-polar materials	34
4.3.3	Deformation potential theory: polar materials	34
4.4	Magnetic properties	34
4.4.1	Magnetic ordering	34
4.5	Battery related properties	34
4.5.1	Principle of Lithium battery	34
4.5.2	Key quantities and their modelling	34
5	Results of Physical Properties Modification in Novel 2D materials	35
5.1	Number of layers and types of stackings	36
5.1.1	Electronic properties	36
5.1.2	Vibrational properties	36
5.2	Mechanical strain	36
5.2.1	Carrier mobility	36
5.2.2	Magnetic properties	36

Table of contents	xiii
5.3 Adatom adsorption	36
5.3.1 Electronic properties	36
5.4 Heterostructures	36
5.4.1 Electronic properties	36
5.4.2 Li diffusion	36
5.5 Defect induction	36
5.5.1 Structural properties	36
5.5.2 Electronic properties	36
5.5.3 Magnetic properties	36
6 Conclusions	37
References	39
Appendix A Appendix	47

Draft - v1.0

Friday 12th May, 2017 – 17:45

List of figures

1.1	Graphene publications	2
1.2	Relation of graphite, graphene, fullerene and nanotube. Image source: the Nobel prize in physics 2010 [4].	4
1.3	Graphene lattice and band structure.	6
1.4	Atomic and electronic structure of graphane	8
1.5	Graphite fluoride to fluorographene. Image source:[46]	8
1.6	Buckled hexagonal crystal structures of 2D group IV materials (X = Si, Ge, and Sn). Different colors represent different 2D planes. Their distance is the buckling parameter δ . Image adapted from:[51]	9
1.7	Layered hexagonal crystal structures of BN. Image adapted from:[65]	11
1.8	Layered structures of TMDs	11
1.9	Band structure variation of MoS ₂ from bulk to single layer. Image source: [78]	12
1.10	Chiral vector and different type of nanotubes. Image adapted from [79]	13
1.11	Graphene production setups. Image source [84]	15
1.12	Growth of graphene on SiC wafer. Image source [87]	16
1.13	A ultra-large-area graphene film. Image source [89]	17
2.1	Comparison of accuracy and capability of electronic structure calculation methods. Image source: [93].	20
2.2	Jacob's ladder for DFT approximations. Image source: [99].	23
2.3	MAE of the equilibrium lattice constants and band gaps of different functionals on SC40 solid test set. Data source: [102].	24
2.4	Schematic illustration of the relation between E_g and E_g^{KS} . Image adapted from: [104].	25
3.1	The formation of sp^2 hybridized orbitals with unhybridized p_z orbital. Image source: [106].	28
3.2	The formation of $sp^2 \sigma$ and $p_z \pi$ double bond. Image source: [107].	29

³3.3 Graphene lattice and its Brillouin zone. Image source: [14]. 30

List of tables

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Chapter 1

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Introduction

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A new field of research related to both material science and condensed matter physics has been formed since the synthesis of graphene in 2004 [1, 2]. Graphene is a sheet of carbon atoms in a crystal form having a single atom thickness. Given the thin plane-like structural nature of this type of materials the field is named two-dimensional (2D) material. The synthesis itself together with the phenomenal properties of graphene has leaded to a Nobel Price in physics rewarded to Andre Geim and Konstantin Novoselov in 2010 [3]. Since then, the field is expanding with the involvement of researcher not only from young community, but also from experts who have been working on graphene-related materials like graphite, fullerenes and carbon nanotubes. As a result, research focused on graphene and related topics increasing with unprecedeted speed, see Fig. 1.1. While a part of these effects have been making to explore more on the graphene itself and its applications, the other parts were put on discovering new 2D materials like graphene. It has been evidenced from graphene, same material having different dimensionality can have different properties. Therefore, many materials with hidden properties which will only manifest itself at other dimensions yet to be discovered.

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On the other hand, with the advent of powerful supercomputer facilities, calculations that seems impossible to finish in a reasonable time now has been made possible. The accuracy of such calculations is the most crucial aspect of computational physics, especially when the results are utilized to predict the real properties of materials. To make the time spend on costly supercomputer valuable, researchers and programmers have been making important progress to make sure theories and its implementation are correct and the results they yield are within acceptable precision. Equipped with these tools, theoretical predictions on the structure and the properties of material have served well on discovering unexplored features. Moreover, detailed characterizations at atomic scale benefits the experimental results as well, or even to explain the unexpected outcomes.

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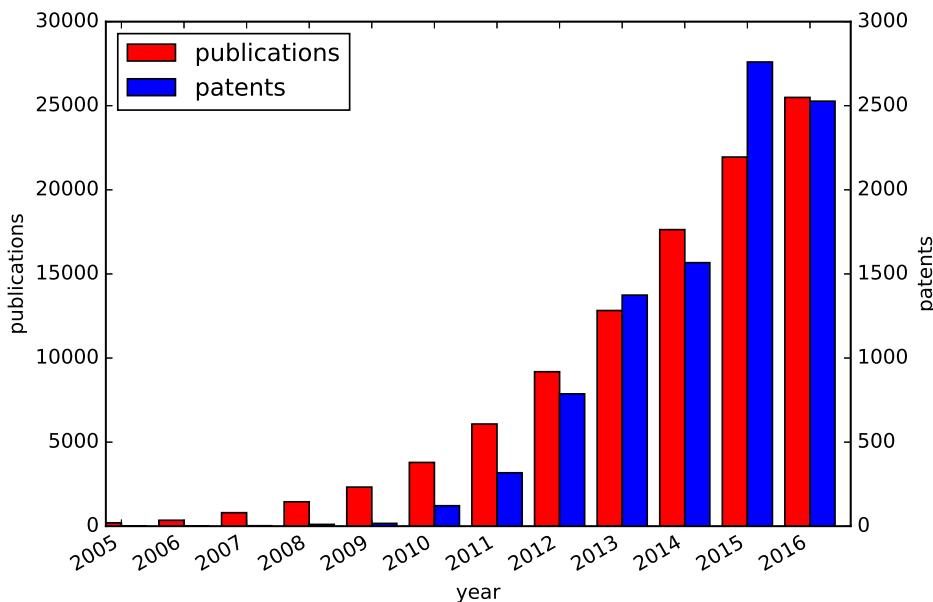


Fig. 1.1 Graphene related publications and patents during the last decade. Data source: ISI Web of Science and PATENTSCOPE.¹

Considering all mentioned, it is a sound approach to apply the state-of-the-art computational methods that accompanied with high-performance supercomputer facilities to investigate the physical properties of novel 2D materials. This thesis were initiated to this end and it is a summary of several works which has been accomplished during my PhD study. The thesis is organized as followed: For the rest of this chapter, I will first introduce graphene and some post-graphene materials that discovered right after graphene and, briefly, well-known methods used to synthesis 2D materials. The following [chapter 2](#) will present the computational methods, the theory behind and the implementations of them. In [chapter 3](#), I will discuss several general properties of 2D materials. The next two chapters will be the main results from my works. Starting from specific properties targeting at specific novel 2D materials in [chapter 4](#), and followed by modification of physical properties of 2D materials in [chapter 5](#). Overlapping of materials themselves and their properties is inevitable between chapters yet it will be minimized, such that each chapter will have a unique topic.

¹Publication and patent results are obtained by searching for "graphene" in the topic field of Web of Science and the title field of PATENTSCOPE, respectively.

1.1 Graphene

Graphene is composed of carbon (C) atoms arranged on a honeycomb lattice in a single atomic layer. Graphene is one of layers that construct graphite, see Fig. 1.2. These layers in graphite are stacked on top of another through weak physical bonding, whereas within each layer C atoms are hold together by strong chemical bonding. As a result, it is possible to just isolate single layer from graphite without damaging the layer itself.

1.1.1 History

The story of graphene can be trace back to the discover of graphite around 1564 in England[5]. Ever since, people have been using the graphite, the tip of a pencil, for writing and drawing. The black trace left behind by pencil they are actually stacks of graphite and graphene, by chance even a single layer graphene can present. Apart from being a part of a pencil, graphite certainly has been holding a more important position in technology and industry due to its rich chemistry, low friction, high electrical and thermal conductivity etc. . On the other hand, the synthesis of single layer graphene seems to be discouraged by both experimental and theoretical limitation. On the experiments, there have been attempts[6, 7, 8, 9] to isolate graphene from graphite or even grow it on a substrate. However, they were mostly failed on the control of the number of layers and identifying graphene itself. Addition to these experimental difficulties, on the theory, it was believed that strictly 2D material should not exist due to a divergence in the thermal fluctuation in 2D materials that will make them not stable [10, 11, 12]. Nevertheless, graphene was still considered as a theoretical model. for example, Wallace [13] was the first one to study the band structure of graphene [14] and found some of the interesting properties like semimetallic band structure.

Although not in the form of graphene, the single atomic layer of graphite has been already seen and studied in other forms, e.g. fullerenes and nanotubes, see Fig. 1.2. These material usually contain certain types of characteristic defects that differ it from graphite. Fullerene is a C molecule has a quasi-spherical hollow ball shape. It is composed of both six- and five-folded C rings, where the latter give positive curvature and made closed surface possible. The resulting shape resembles a football[15, 16]. The Nobel prize in chemistry of year 1996 was award to Harold W. Kroto, Robert F. Curl and Richard E. Smalley for their discovery of fullerene. Another important type of carbon allotrope: carbon nanotubes[17], was discovered using arc-discharge method[16] which was originally designed to produce a large quantity of fullerene. Despite sharing similar production method, carbon nanotubes are actually more close to graphene than fullerene due to the absence of pentagonal C rings in the former two. A carbon nanotube can be construct by rolling up graphene sheet into a hollow tube as its name

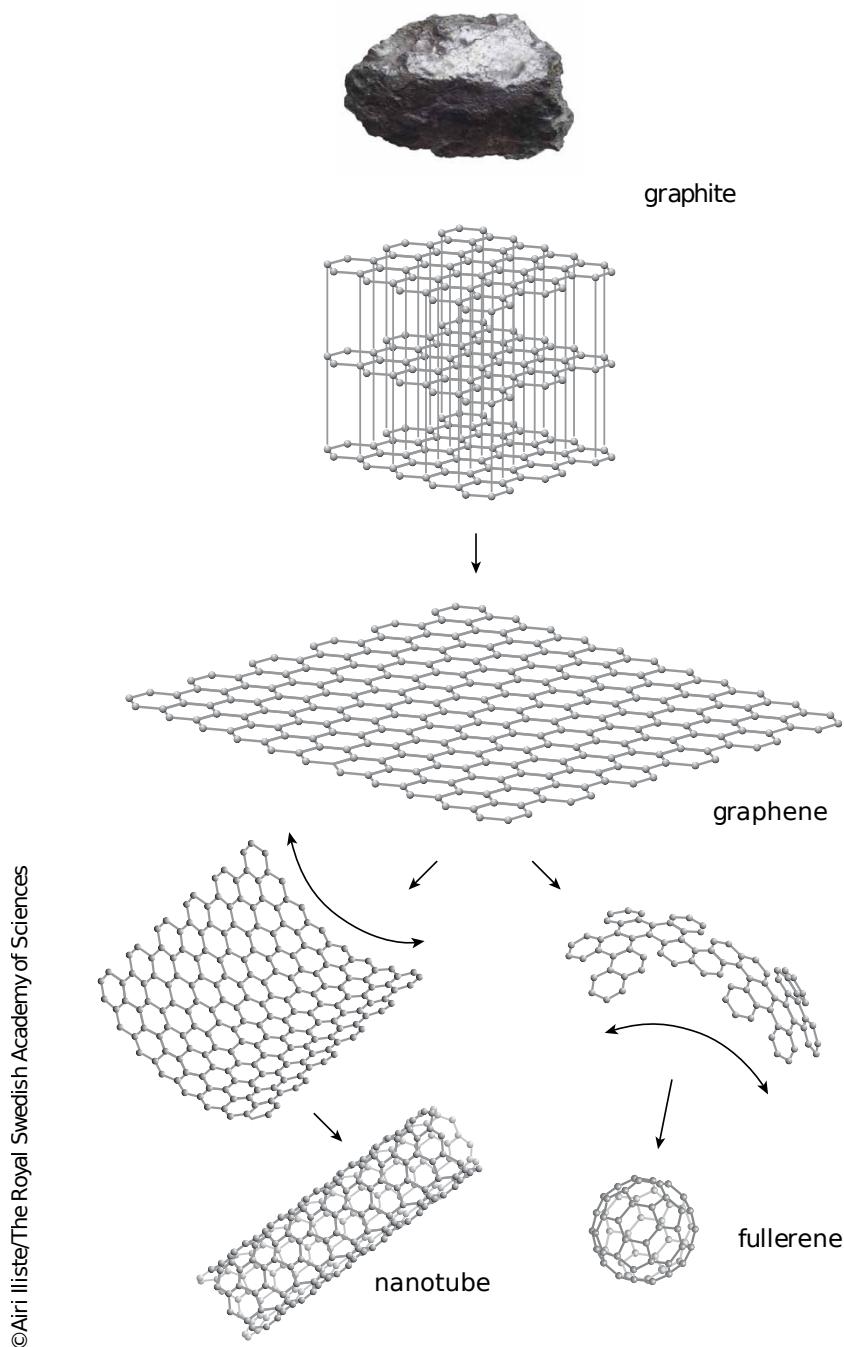


Fig. 1.2 Relation of graphite, graphene, fullerene and nanotube. Image source: the Nobel prize in physics 2010 [4].

1.1 Graphene

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suggested. Carbon nanotubes are observed to have micrometer in lengths and nanometre in diameters and having either metallic or semiconducting nature depending on its edges. They possess superior mechanical properties. Individual nanotube has a Young's modulus of 0.64 TPa and it is 56 times stronger than steel wire[18].

In 2004, the situation has changed completely for graphene with the successfully isolated single layer graphene from graphite by A. K. Geim and K. S. Novoselov at Manchester University using a simple micromechanical cleavage method. The key ingredient, except for the sophisticated experimental control, as compared to the previous failures[6, 7] in this case is that the Si wafer under the graphene made it easier to identify graphene[3]. The synthesis of graphene itself already is a ground-breaking achievement, however, what excited the researcher the most is the extraordinary properties of graphene. In the following section, I will summarized some of them to illustrate this point.

1.1.2 Physical properties

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As mentioned previously, graphene is the single atomic layer of graphite. It posses an interesting structure with high symmetry which many of its properties are attributed to. Each C atom has three neighbours to make chemical bonds. Because of this, C atoms are arranged in a honeycomb lattice², or a hexagonal Bravais lattice with two atoms per site, see (a) Fig. 1.3. Graphene has uniform bond lengths of 1.42Å and uniform bond angles of 120°. The band structure which characterizes the electronic properties of graphene has been calculated by P. R. Wallace in 1947 [13]. He discovered that graphene is a semimetal with conduction band minimum (CBM) and valence band maximum (VBM) only touch each other at the K and K' points in the first Brillouin zone as shown in (b) and (c) in Fig. 1.3. The energy-momentum dispersion is approximately linear in the vicinity of K and K' points. Due to this, the electron and hole in those states behave differently as they do in quadratic band. Several consequences of this can be concluded. First of all, considering the linear energy momentum relation, particles can be regard as Dirac particles and govern by relativistic Dirac equation[19], and they travel at constant speed of 10⁶m/s. Hence, the K and K' points are referred as Dirac points, its vicinities are called Dirac cone. Secondly, the carrier concentration can be tuned continuously from electron to hole with a perpendicular electric field[3]. Thirdly, the carrier in graphene can tunnel through finite height potential it normally incident to without reflection–Klein tunnelling[20]. Fourthly, under magnetic field, zero energy Landau level appears, and the large energy interval between zero to first level made it possible to observe quantum Hall effect at room temperature [21], etc..

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²honeycomb lattice is not a Bravais lattice.

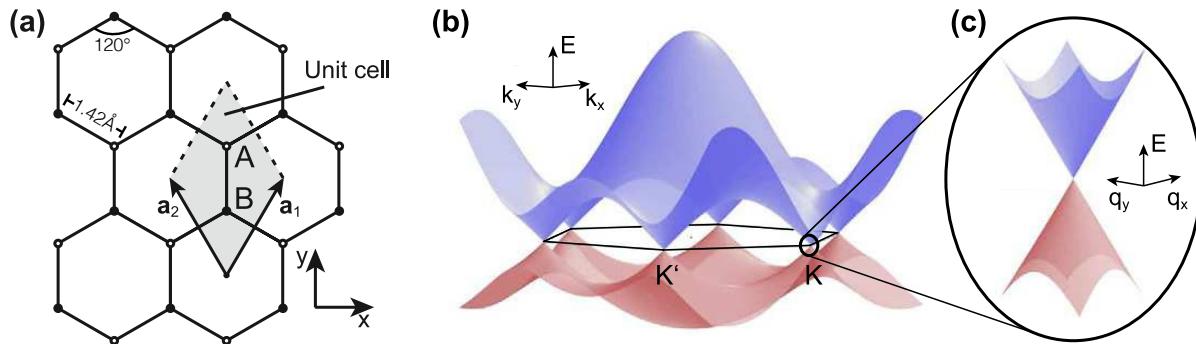


Fig. 1.3 (a) Graphene honeycomb lattice composed of A and B hexagonal Bravais sublattices. (b) Band structure of graphene where CBM and VBM touch each other only at the K and K' points. (c) Approximately linear dispersion at K and K' point. Image source: [22].

Graphene delivers more than just an interesting electronic property. For example, evidencing the extraordinary mechanical properties, graphene has a Young modulus $E = 1\text{ Tpa}$ and intrinsic strength of 130 Gpa [23]. This makes graphene the strongest material ever measured. More than 300 times stronger than steel and four times harder than diamond. Carrier high mobility is another exciting feature that has more applicative importance in electronic devices. Free standing graphene without substrate attached has been reported to have mobility of $230,000\text{ cm}^2/\text{Vs}$ at low temperature[24] and $120,000\text{ cm}^2/\text{Vs}$ at 240 Kelvin , the latter value is higher than any known semiconductor[25]. In addition, the thermal conductivity of graphene can reach up to 5000 W/mK at room temperature, which is 20 times higher than copper[26]. However, having a zero band gap means the application of graphene in digital logic gates is limited. The current controlled by the gate bias can not be turned off completely which would otherwise deliver distinct signal from when it is on. Efforts on band gap opening have been made, from substrate induction[27, 28], bilayer graphene[29, 30], chemical adsorption[31, 32], and chemical doping[33] to quantum confinements[34, 35]. While doping and adsorption usually come with a cost of reducing mobility by introducing scattering centres, chemically pure bilayer graphene and nanoribbon are thought to be promising approaches to open band gap as well as, to a great extent, preserve graphene's superior properties.

1.2 Post-graphene materials and their general properties

Excitements in the exploration of graphene properties drive the force to discover more types of 2D materials. Researchers have taken different approaches to this end. On one hand, aiming to open a band gap in graphene, chemical functionalizations on graphene have been carried out with adsorption of hydrogen, fluorine and oxygen, and they results in graphane, fluo-

1.2 Post-graphene materials and their general properties

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rographene and graphene oxide, respectively; On the other hand, inspired by graphite's layer structure, layered materials are brought to the attention to isolate single layer just as it has done for graphene. In this section, I will introduce some of these early post-graphene materials and their physical properties in general.

1.2.1 Functionalized graphene

Graphane

The fully hydrogenation of graphene gives a 2-D hydrocarbon called graphane. It can synthesized either by reduction of graphite then hydrogenation of left product (graphene, carbon nanotubes or graphite oxide) with liquid-based[36] or gas-based[37] environments, or grow by chemical vapour deposition[38].

graphane is not flat as graphene. In fact, the bonding character changed from sp^2 hybridization to sp^3 , which gives buckled structure, see Fig. 1.4. Neighbouring H atoms locate at the different sides of graphane plane. Among different phases of graphane, chair structure is the ground state. Others phases are metastable state like: boat, twist-boat and twist-boat-chair[39]. The C-C bond length in the chair structure is 1.52 Ålager than that in graphene. graphane is a semiconductor with 3.5 eV band gap in the chair form. Band gap are reported scale almost linearly with the hydrogen coverage[40]. The 2D Young's modulus of graphane is estimated 245 N/m[41], smaller than graphene' 340 N/m. The incomplete coverage of H atoms on graphene gives hydrogenated graphene. It has ferromagnetic magnetic state[42], tunable band gap[43] and reversible hydrogenation[31].

Fluorographene

More stronger binding between external atom and C atom can be realized using fluorine atom for adsorption . A full fluorinated graphene is called fluorographene, and it can be regards as a single layer of graphite fluoride. Actually, sonochemical exfoliation of fluorographene from graphite fluoride is one of the ways to synthesis it, see Fig. 1.5[46]. Fluorographene has a similar structure as graphane due to same sp^3 hybridization, and also different isomers where the again the chair type is the ground state configuration[47]. The unit cell of fluorographene us around 1% larger than that of graphene[48]. The formation energy of fluorographene is around 0.5 eV per fluorine atom lower than that of graphane per hydrogen atom[32]. The band gap of fluorographene is larger than 3 eV from optical measurement[48, 32], and band structure similar to that of graphane with a band gap at the Γ k-points. The 2D Young's modulus of Fluorographene is 100 N/m and the intrinsic strength is about 15 N/m. They both more than two times less than those for graphene due to weaker sp^3 bonds in fluorographene[48].

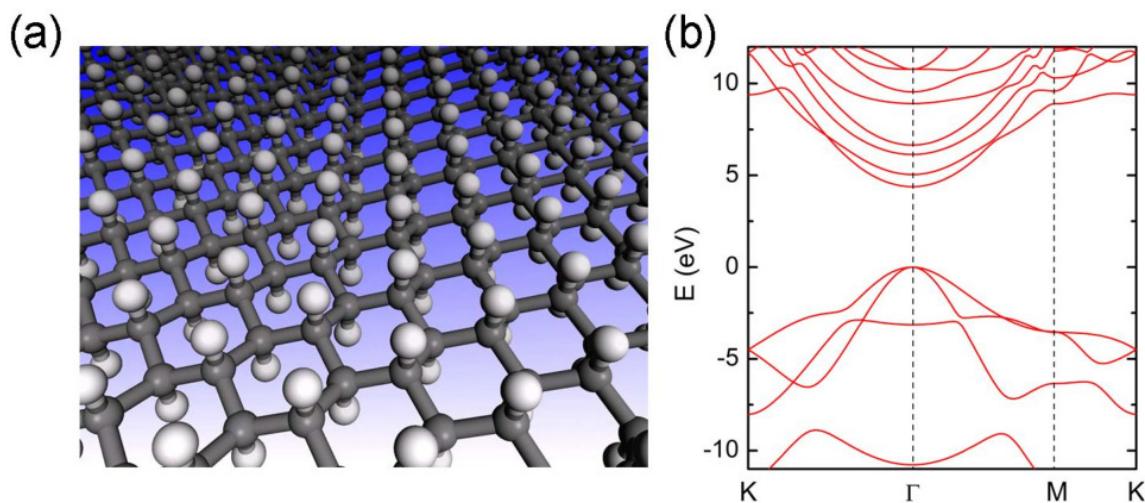


Fig. 1.4 (a)The chair structure of graphane. The white balls are H atoms and the grey ones are C atoms. Image source: [44]. (b) Band structure of chair graphane. Image source: [45]



Fig. 1.5 Graphite fluoride to fluorographene. Image source:[46]

1.2.2 Group IV 2D materials

In analogues to graphene, 2D material made of only single element from other members of group IV have been also proposed and synthesized. They are silicene, germanene, stanene made of silicon (Si), germanium (Ge) and tin (Sn) atoms, respectively. They generally suffer from less stability with respect to graphene. The free standing form of these material are hard to make, instead they usually need ordered substrates to support them. Therefore, the measurements done on these type of system can not exclusively speak for the target material, the influence of the substrate is not negligible[49]. This will in turns hinder the accurate characterization of the properties. Despite these experimental difficulties, theoretical studies have more freedom to investigate their physical properties. One of the most important differences of these materials as compared to graphene is their not-flat buckled structure, see Fig. 1.6. The buckling parameters δ is defined as the interlayer distance of layers at different 2D atomic planes. According to calculations, δ is 0.45Å for silicene, 0.69Å for germanene and 0.85 Å for stanene[50]. This change corresponds to more sp^3 character the orbitals have, and this degree increases with the atomic radius.

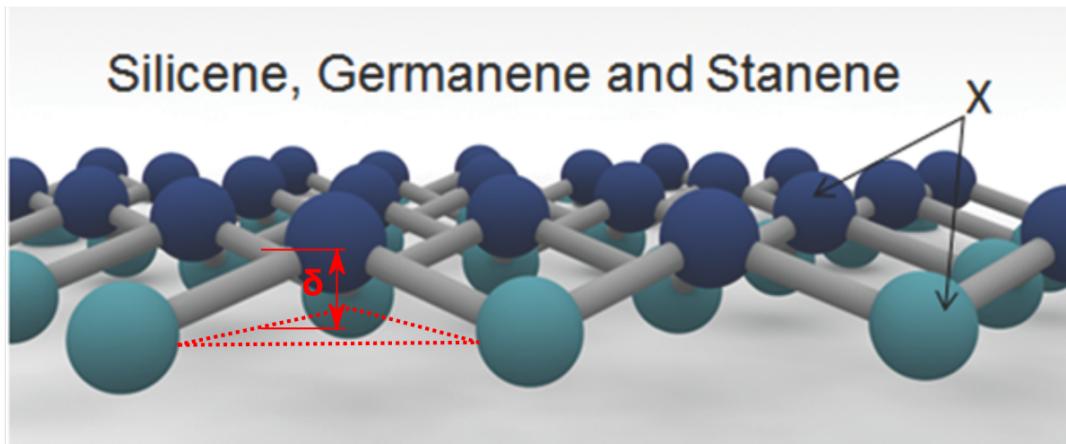


Fig. 1.6 Buckled hexagonal crystal structures of 2D group IV materials ($X = Si, Ge, and Sn$). Different colors represent different 2D planes. Their distance is the buckling parameter δ . Image adapted from:[51]

Although having a buckled structure, these materials also posses Dirac points with linear energy momentum dispersion around it[52]. However, as stated before, the substrate where the materials are supported will induce symmetry broken which leads to the lost of Dirac character for π electrons[49]. Moreover, spin-orbit coupling (SOC) in these materials are predicted to be larger than that in graphene due to larger atomic weights. With inclusion of SOC, this corresponds to 1.9 meV band gap in silicene and 101 meV of that in stanene[50]. The mechanical stiffness and strength are low as compared to graphene and has a reducing

1 trend with atomic number in this group. This is partially due to the less energetically costly
2 bond angle deformation in the buckled structure upon load rather than bond stretching[53].
3 For example, silicene has a 2D Young's modulus around 62 N/m, that is four times smaller
4 than graphene. Another important difference of these materials from graphene regards the
5 realization of monolayer. The lack of layered bulk materials for the former ones made the me-
6 chanical exfoliation inapplicable for them, which is believed to produce the highest quality
7 sample otherwise. Therefore, methods used in this case are either bottom-up decomposi-
8 tion techniques onto highly ordered substrates[54, 55], or top-down methods like chemical
9 exfoliation to isolate grown monolayer from substrate[56, 57].

10 **1.2.3 2D from layered materials**

11 The layered structure of graphite contribute the most to the isolation of graphene. If the
12 interlayer bonding were not weak vdW interaction rather a covalent type, even the concept
13 of layers can not stand let alone to break bonds only in one direction and keep others in the
14 other two directions. Therefore, a reasonable way to exploring the possibility to discover
15 other 2D materials is other layered materials, e.g. hexagonal boron nitrides (h-BN), transition
16 metal dichalcogenides (TMDs). In this section, I will discuss general physical properties of
17 these two material as examples for 2D materials from layered ones.

18 **Boron Nitride**

19 Among the multiple structural phases of BN, the layered hexagonal h-BN is the most stable
20 one, see Fig. 1.7 for the structure. A single layer extracted from it gives 2D h-BN. Because of
21 its structural similarity to graphene and its wide band gap it is often referred as the white
22 graphene[58]. 2D h-BN has a band gap of 6.1 eV according to calculations. A intuitive tight
23 binding analysis reveals the band gap, in the of 2D h-BN, is proportional to the difference of
24 p_z orbitals from B and N atoms. For silicene and graphene, this difference is zero thus so is
25 the band gap. Moreover, as a result of different electronegativity, i.e. 2.0 for B and 3.0 for N,
26 ionic character develops which further enlarge the band gap[59]. Several interesting features
27 of this material are reported: strong mechanical stiffness and strength close to graphene[60],
28 a good thermal conductivity of $100\text{--}270 \text{ W m}^{-1} \text{ K}^{-1}$ for few-layer h-BN[61] as an electrical
29 insulator, a high oxidation resistance up to 700 °C as contrast to 400°C for graphene[62], etc..
30 Benefit from its compatible bond length, i.e. 1. Å, with graphene, it is a perfect partner for
31 graphene to form heterostructure electronic device to serve as a dielectric substrate[63], the
32 result is better than using SiO_2 substrate[64] for instance.

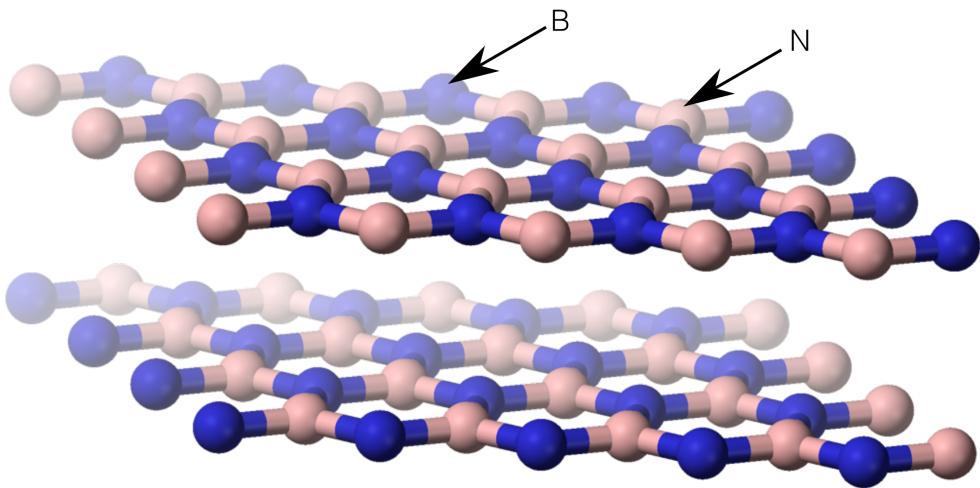


Fig. 1.7 Layered hexagonal crystal structures of BN. Image adapted from:[65]

Transition Metal Dichalcogenides

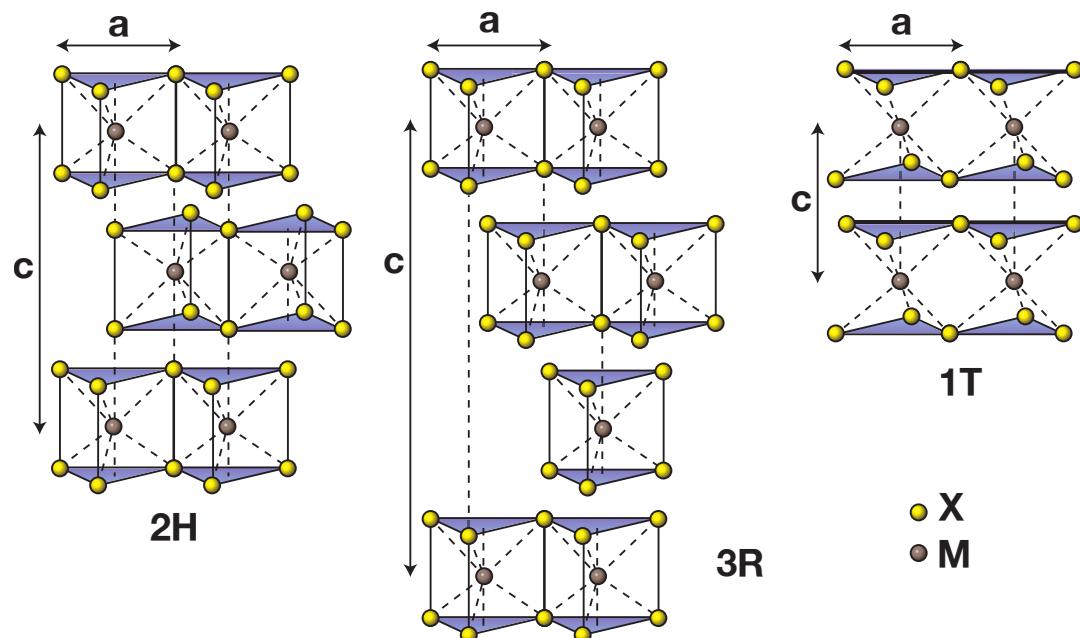


Fig. 1.8 Layered structures of TMDs. 2H: two layers per unit cell with hexagonal symmetry; 3R: three layers per unit cell with rhombohedral symmetry; 1T: one layer per unit cell with tetragonal symmetry. a is the in-plane lattice constant with a range from 3.1 to 3.7 Å. c is the vertical lattice constant. The interlayer distance has a typical length of 6.5 Å. Image source: [66]

1 Transition metal dichalcogenides (TMDs) have a generalized formula of MX_2 , where M
 2 stand for group 4-7 elements in the transition metal series in the periodic table, and X are
 3 the group VI elements. This is another type of layered materials, and single layer of some
 4 of them have been experimental realized. These materials typical existing in three different
 5 structural phases as shown in Fig. 1.8, which at monolayer level can be either H or T phase.
 6 One of the most important differences in these two phases is lack of inversion symmetry in
 7 H phase while T phase has it. Therefore, spin orbit coupling (SOC) is much important in H to
 8 induce spin-splitting than that in T phase, for instance 456 meV spin splitting in WSe_2 [67] has
 9 been reported. Note that, inversion symmetry is recovered in the layered bulk form hence
 10 suppresses SOC. Another important consequence of reduce dimensionality is the indirect-to-
 11 direct band gap transition from layered TMDs to its 2D counterpart, see for example in Fig. 1.9.
 12 2D-TMDs have a broad range of potential applications. Electrocatalysis[68, 69] benefit from
 13 adequate active sites, electronic devices[70, 71] benefit from typical band gap of 1-2 eV, Li or
 14 Na batteries[72, 73] benefit from high surface-to-volume ratio and short diffusion path, photo-
 15 catalysis benefit from high stability under extreme light intensity[74, 75], and biomedicine
 16 benefit from enhancement of the physiological stability and biocompatibility of polymers on
 17 2D-TMDs[76, 77].

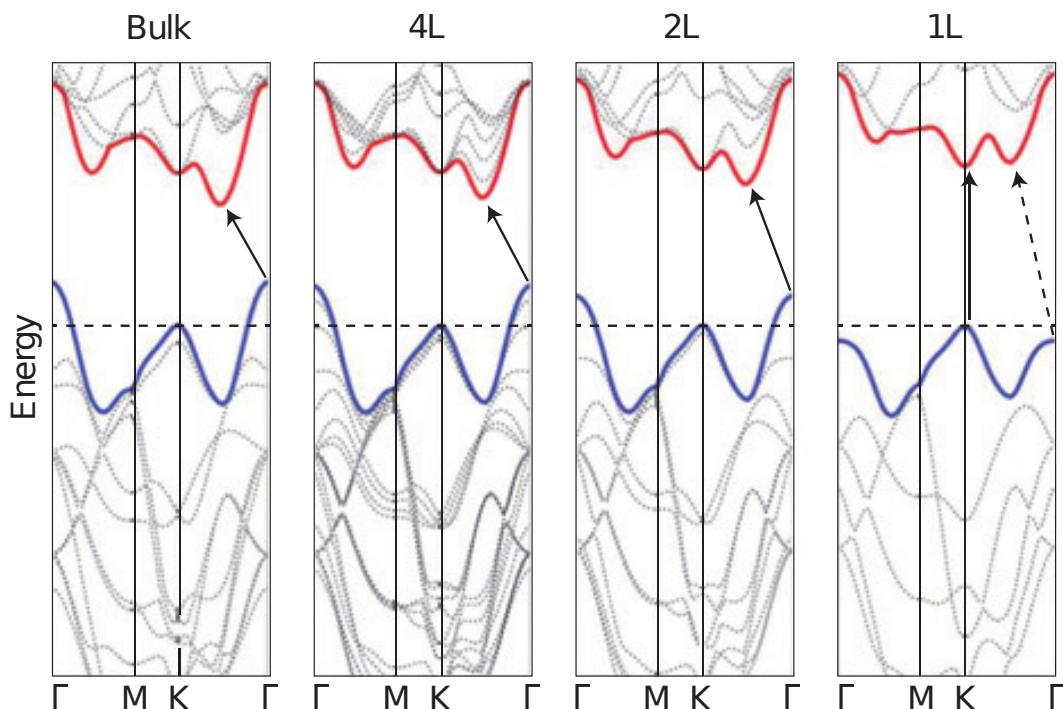


Fig. 1.9 Band structure variation of MoS_2 from bulk to single layer. Image source: [78]

1.3 1D from 2D: nanotubes and nanoribbons

The reduction of dimensionality of the materials did not stop at the 2D level. Further lowering it will result in 1D nanotubes or nanoribbons.

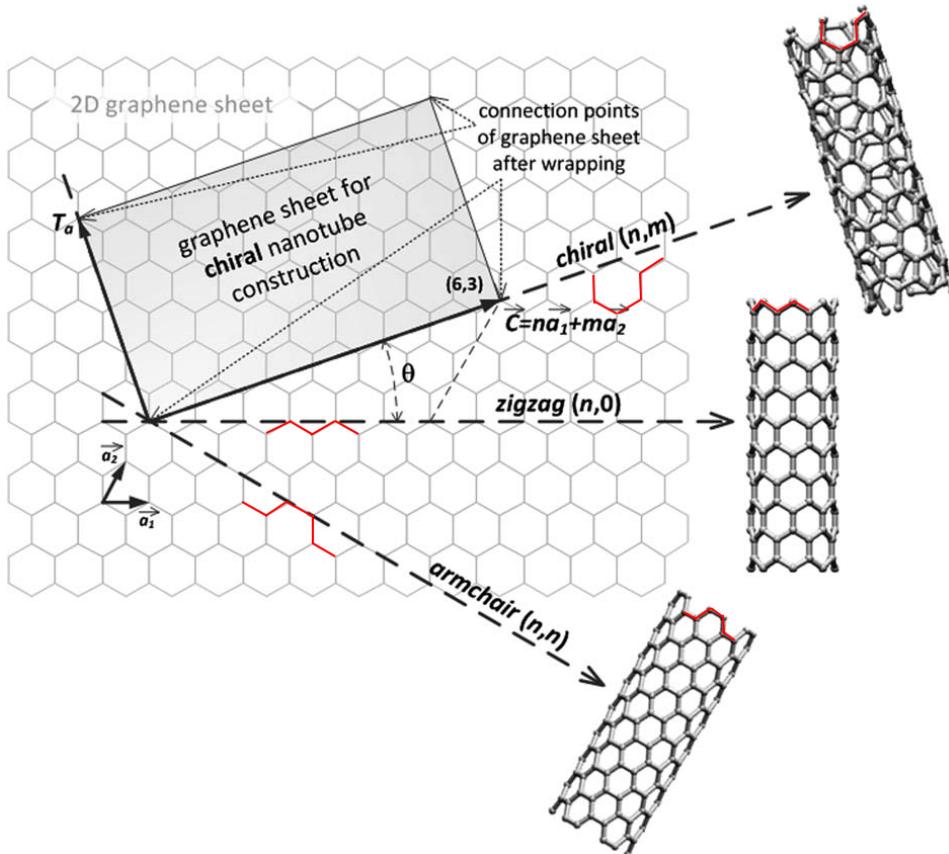


Fig. 1.10 Chiral vector and different type of nanotubes. Image adapted from [79]

A nanoribbon is a strip of 2D sheet with nano-scale width and micro-scale length and it is still flat. Whereas nanotubes are the rolling up of nanoribbons to have a tube structure. Each nanotube, also each nanoribbon but with different definition, is associated with a chiral vector that uniquely defines its structure parameters except the length which is considered to be infinite in theory. In the Fig. 1.10, a_1 and a_2 are the unit lattice vectors in graphene. Chiral vector, \vec{C} , is the superposition of these two unit vectors with indices pair (n,m) . Zigzag edge always has a $(n,0)$ form and (n,n) is always armchair edge. Everything else is called chiral type edge. This finite-length chiral vector also defines the radius of the tube. Nanoribbons, on the other hand, have these three types of edges as well. However, in this case, edges have infinite length.

With confinements from other directions, physical properties of these systems are expected to be different than their higher dimension counterparts. For example, graphene nanorib-

bonds have a finite band gap as contrast to zero band gap in graphene[80]. Moreover, control of this confinement will give tunable physical properties. For example, overall inverse band gap relation with the width of nanoribbon[81]. The zigzag edges in graphene nanoribbon form spin-polarized magnetic states give ferromagnetic ordering along the edge and anti-ferromagnetic ordering across edges[82]. For nanotubes, those have same edges belong to the same class of chirality and have same electronic structure. For instance, armchair carbon nanotubes are metallic, other types are semiconductor. But small radius tubes can be exceptional due to large curvature[83]. The strong mechanical strength and high thermal conductivity of graphene nanoribbon similar to those in graphene.

1.4 Synthesis methods

In this last section, I will briefly discuss some of the well-known synthesis methods for 2D materials. In Fig. 1.11, a overview of graphene production methods is displayed in Fig. 1.11.

13 Micromechanical cleavage

Micromechanical cleavage is also known as mechanical exfoliation, which was the method used to first successful isolation of graphene by Novoselov et al. [2] in 2004 using a adhesive tape. It involves separating layers in layered materials by mechanical, electrostatic, or electromagnetic forces. This method gives high quality product and suitable for laboratory-scale sample for fundamental studies. Large scale productions are impractical through this method. Room temperature mobility was measured up to $20,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [85] on graphene prepared with this method.

21 Liquid phase exfoliation

Liquid phase exfoliation is the extraction of layers in a proper solvent using ultrasounds. The cavitation-induced bubbles collapse around the graphite will generate compressive stress wave. As a primary result, this will cause a reflective tensile wave whose strength is proportional with the number of such bubbles. Intensive tensile stress is enough to break graphite into graphite flakes. Additionally, as a secondary effect, shear effect can be develop from unbalance lateral stress, and separate two adjacent layers. Liquid phase exfoliation is a promising method to synthesis cheap and scalable samples.

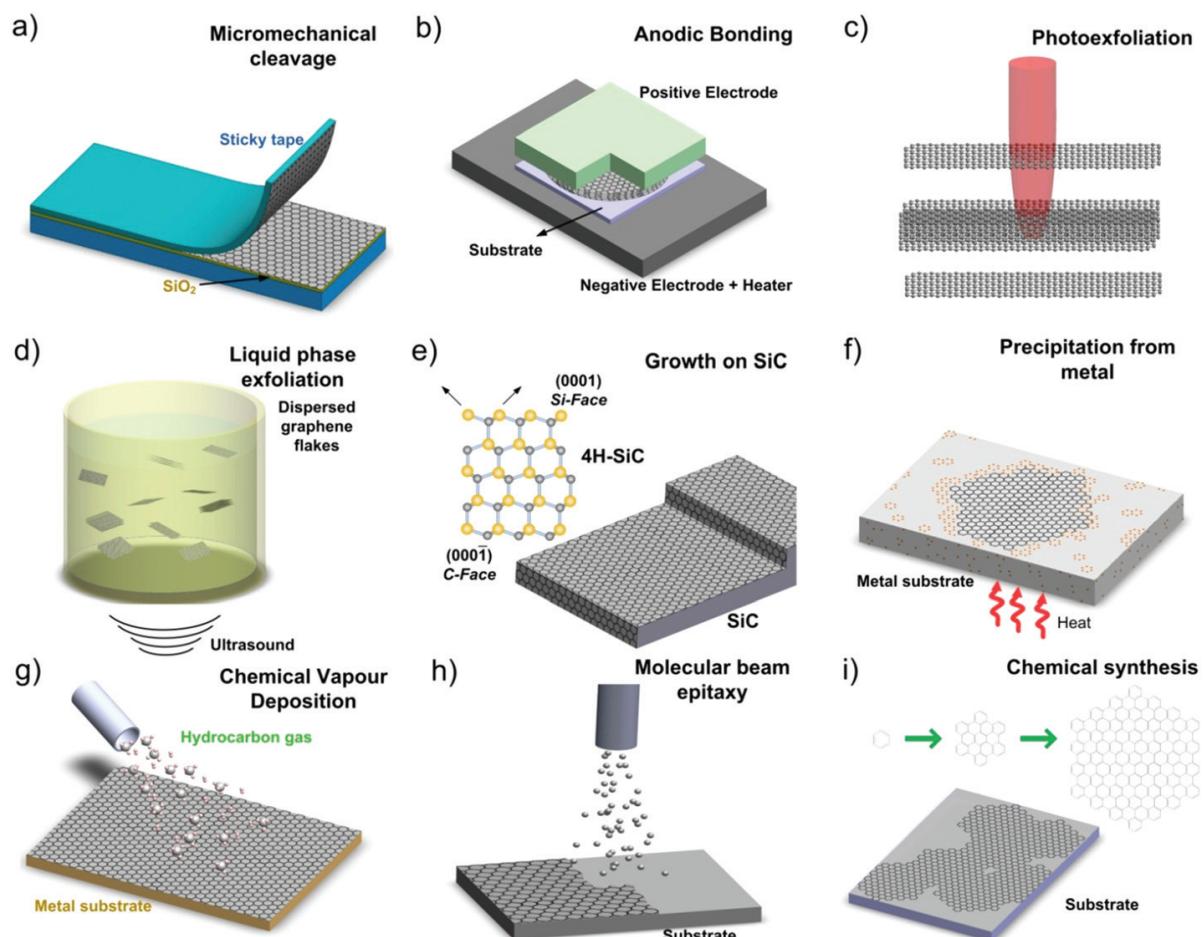


Fig. 1.11 Graphene production setups. Image source [84]

1 Growth on SiC

2 Growth of graphene on SiC involves SiC sample annealing at high temperature ($> 1400^{\circ}\text{C}$) in
3 vacuum or under atmospheric pressure. The sublimation of silicon atoms leave behind carbon
4 atoms on the surface which will rearrange to form graphitic layer[86], see Fig. 1.12. Apart from
5 high reproducibility and production of homogeneous large-area sample of this method, it has
6 an advantage that the graphene is available on semiconducting substrate for layer electronic
7 device integration.

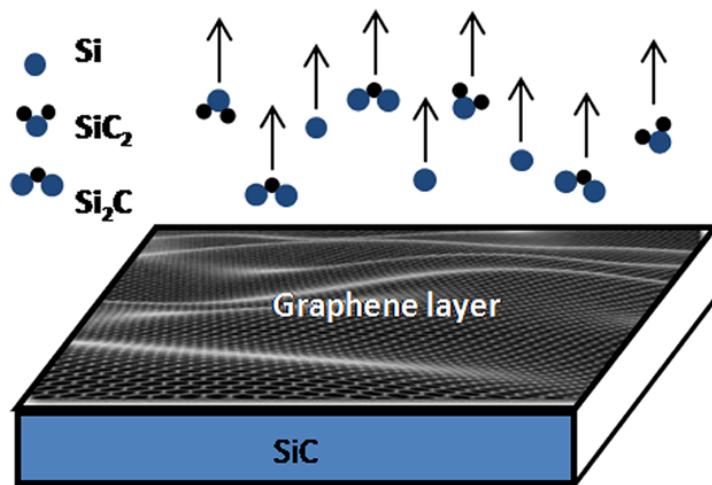


Fig. 1.12 Growth of graphene on SiC wafer. Image source [87]

8 Chemical vapor deposition

9 Chemical vapor deposition (CVD) is a popular method to grow amorphous or crystalline thin
10 film from solid, gaseous or liquid precursors. It is the direct deposition of vaporized desire
11 material onto a particular substrate. Various of CVD methods exist depending on their oper-
12 ating pressure, types of vaporization and whether it is plasma-assisted etc.. Graphene grown
13 on transition metals usually has a high quality. Carbon atoms from organic sources in the gas
14 phase are deposited on metal (Ni, Ru, Ir etc.) and convert to graphene at high temperature.
15 Then, for the characterization, graphene will be transferred to a appropriate substrate. Typical
16 mobility of such type of sample is around $1000\text{-}25000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [88]. A 30-inch graphene
17 film has been produced from roll-to-roll production through CVD methods by Bae et al. [89],
18 see Fig. 1.13. The product measured to be a better electrode than commercially available in-
19 dium tin oxides.

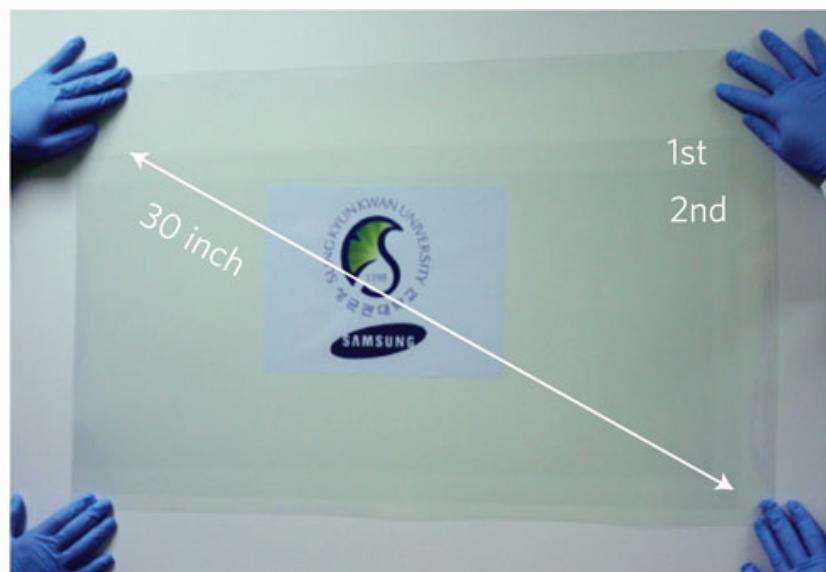


Fig. 1.13 A ultra-large-area graphene film. Image source [89]

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Chapter 2

Computational methods

As mentioned in the last chapter, theories behind the calculations are the most crucial component in the material properties determination process. Its correctness, accuracy and implementation directly influence the quality of its prediction. In this chapter, I will introduce relevant theoretical models, approximation and their implementation in commonly used software packages.

2.1 Theory

2.1.1 Density Functional Theory

Density functional theory (DFT) is one of the most widely used method to calculation material properties. Its applicable length and time scale are in nanometre and picoseconds. This is higher than quantum Monte Carlo simulation and lower than semi- or full-empirical methods in both scales. This order is also valid in the accuracy verse number-of-atoms-in-simulation plot in Fig. 2.1. It is reported that much of the inaccuracy attributes to the uncertainty of the experimental results that the methods are compared with[90]. For periodic bulk or nanostructure, DFT can be used to even quantitatively predict the properties of materials. DFT is based on two main basis: Hohenberg-Kohn theorems[91] and Kohn-Sham equations[92]. Here we briefly overview these without put too much effect for the derivation which have been extensively documented in other textbooks.

Materials are made from electrons and nuclei. Type of nuclei and interaction between these components give rise to various materials and their properties. The interactions are mainly electrostatic or Coulombic. While electrons must be described with quantum mechan-

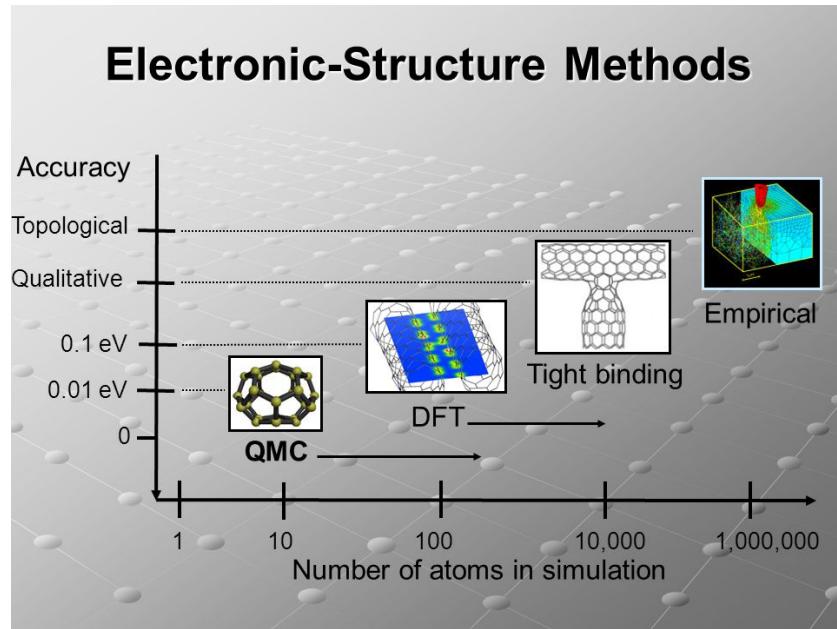


Fig. 2.1 Comparison of accuracy and capability of electronic structure calculation methods.
Image source: [93].

¹ ics, the nuclei can be treated as classical particles. The equation governs electrons behaviours
² is the Schrödinger equation, it can be written as following¹

$$\begin{aligned} \hat{H}\psi_k(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) &= \left[-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N v(\vec{r}_i) + \frac{1}{2} \sum_{i=1} \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \psi_k(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) \\ &= (\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}) \psi_k(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) \\ &= E_k \psi_k(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N). \end{aligned} \quad (2.1)$$

³
⁴ \hat{H} is the total Hamiltonian. \hat{T} is the kinetic energy. \hat{V}_{ext} is the interaction between elec-
⁵ trons and nuclei. Here we already started with the first approximation: Born–Oppenheimer
⁶ approximation[94]. Which neglect the dynamics of nuclei, instead electrons are moving in
⁷ a static potential generated by their interaction with all nuclei. \hat{V}_{ee} is interaction between
⁸ electrons. The first two sum over all N -electrons, and the last sums over all unique pairs of
⁹ N -electrons. \vec{r} is the electron position. σ is the z-component of spin on electron ($+\frac{1}{2}, -\frac{1}{2}$). ψ
¹⁰ is the N -electron wave function, and it should be antisymmetric under interchange of two
¹¹ electron orbital and spin coordinates (fermionic character for electrons) and it should also
¹² satisfy boundary condition of the system (quantum confinement for low-dimensional system).

¹equations in this chapter are written in cgs form, and the fundamental constants \hbar , e^2 and m are set to unity

E is the total energy. k is the complete set of N -electron quantum numbers. Following constrained search algorithm introduced by M. Levy[95], the ground-state energy E can be found by minimizing the expected value of total Hamiltonian with respect to wave function:

$$E = \min_{\psi} \langle \psi | \hat{H} | \psi \rangle. \quad (2.2)$$

Here we take two steps for the minimization. For the first step, we minimize with respect to all wave functions gives the same density $n(\vec{r})$:

$$E = \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle + \int dr^3 v(\vec{r}) n(\vec{r}). \quad (2.3)$$

Then with the resulting wave function ψ_n^{min} that yields minimum E and associate with density $n(\vec{r})$, we can construct universal functional:

$$\min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle = \langle \psi_n^{min} | \hat{T} + \hat{V}_{ee} | \psi_n^{min} \rangle = F[n(\vec{r})] \quad (2.4)$$

As seen in this equation, a functional, $F[n(\vec{r})]$, is a function of a function. For the second step, we minimized with respect to all densities $n(\vec{r})$:

$$E = \min_n \left\{ F[n(\vec{r})] + \int dr^3 v(\vec{r}) n(\vec{r}) \right\}, \quad (2.5)$$

where $v(\vec{r})$ is kept fix during minimization. The resulting density is the ground-state density that gives lowest ground state energy. This is known as density variational principle, also the main idea of the Hohenberg-Kohn theorems. For the completeness, they are present in the following:

Theorem 1 The external potential, $V_{ext}(\vec{r})$, of any system of interacting particles is uniquely determined (up to a constant) by the particle density, $n_0(\vec{r})$, of the ground state.

Theorem 2 The ground state energy of a system with an external potential $V_{ext}(\vec{r})$ is given by the minimum value of the energy functional $E_{HK}[n]$ and the density for which this minimum is reached corresponds with the ground state density $n_0(\vec{r})$.

Now, the main problem is to define the approximated expression of $F[n(\vec{r})]$. Kohn-Sham equation is a elegant way to do that. It aim to construct a non-interacting system, where density can be calculated exactly, and add local external potential $V_{KS}(\vec{r})$. The $F[n]$ decomposed into following and define $E_{EX}[n]$ as exchange-correlation (EX) energy:

$$F[n] = T_s[n] + E_H[n] + E_{EX}[n], \quad (2.6)$$

where $T_s[n]$ is the non-interacting kinetic energy functional, and $E_H[n]$ is the Hartree energy functional:

$$E_H[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (2.7)$$

Apart from the last term, $E_{EX}[n]$, everything else can be exactly calculated for non-interacting system for given density. By imposing a normalisation constraint on the electron density, $\int n(\vec{r})d\vec{r} = N$, we have

$$\frac{\delta F[n]}{\delta n(\vec{r})} = -v(\vec{r}). \quad (2.8)$$

Therefore, the effective local potential, $V_{KS}(\vec{r})$, will be

$$V_{KS}(\vec{r}) = v(\vec{r}) + \frac{\delta E_H[n]}{\delta n(\vec{r})} + \frac{\delta E_{EX}[n]}{\delta n(\vec{r})}, \quad (2.9)$$

and the Kohn-Sham equation reads

$$\left[-\frac{1}{2}\nabla_i^2 + V_{KS}(\vec{r}) + \frac{\delta E_H[n]}{\delta n(\vec{r})} + \frac{\delta E_{EX}[n]}{\delta n(\vec{r})} \right] \psi_k(\vec{r}\sigma) = \epsilon_k \psi_k(\vec{r}\sigma), \quad (2.10)$$

and ground-state density is

$$n(\vec{r}) = \sum_k^{\text{occ.}} \sum_{\sigma} |\psi_k(\vec{r}\sigma)|^2. \quad (2.11)$$

This can be solved self-consistently. An initial guess on the density $n(\vec{r})$ determines the effective potential $V_{KS}(\vec{r})$, from (2.10) a wave function $\psi_k(\vec{r}\sigma)$ can be calculate, which will give a new density through (2.11). This procedure is repeated until self-consistency is reached.

2.1.2 Exchange-correlation functional

The EX energy functional needs to be approximate. The choice of this directly influence the accuracy of the results. Since, although it is often the small fraction of the total energy, its contribution to chemical bonding and formation energy usually exclusive. The generalized gradient approximation (GGA) has become popular in solid state calculations. It is a further upgrade of its previous version, the local density approximation (LDA). The LDA has the following form:

$$E_{XC}^{LDA}[n] = \int n(\vec{r})\epsilon_{XC}[n(\vec{r})]d\vec{r}. \quad (2.12)$$

$\epsilon_{XC}[n(\vec{r})]$ is the EX energy for homogeneous electron gas having density of $n(\vec{r})$, and it is usually taken from Quantum Monte Carlo calculations. Whereas the GGA further includes the derivative of density, $\nabla n(\vec{r})$, as an argument for ϵ_{XC} , thus it reads

$$E_{XC}^{GGA}[n] = \int \epsilon_{XC}[n(\vec{r}), \nabla n(\vec{r})] d\vec{r}. \quad (2.13)$$

Contrast to LDA, there is no unique input for $\epsilon_{XC}(n(\vec{r}), \nabla n(\vec{r}))$. Different constructions for GGA usually named with the corresponding authors, e.g. PW91-GGA stands for Perdew and Wang's GGA construction in 1991[96, 97] and PBE-GGA stands for Perdew, Burke, and Ernzerhof [98]'s construction. They are the most popular GGA approximations for solid systems.

Jacob's ladder

Jacob's ladder is a ladder connecting earth and heaven that biblical Patriarch Jacob dreamed. Professor John P. Perdew, who is known for profound contribution to DFT and EX functionals, used it analogously to describe the hierarchy of density functional approximations in terms of their accuracies, see Fig. 2.2.

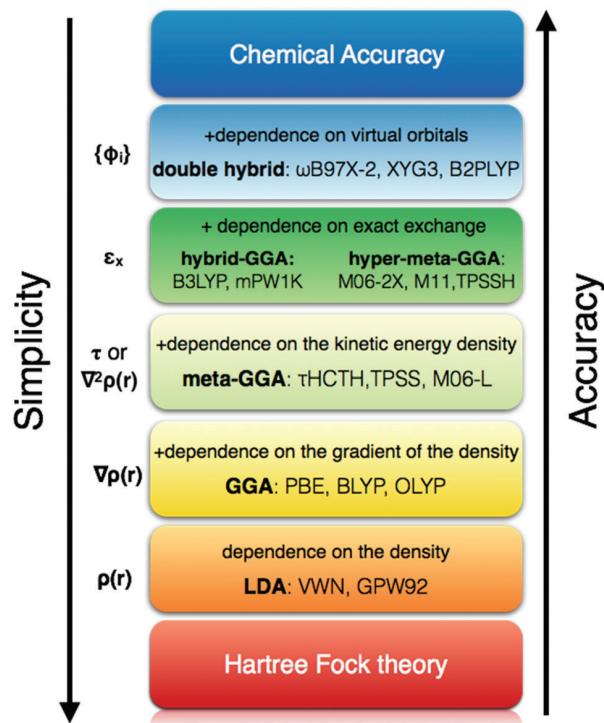


Fig. 2.2 Jacob's ladder for DFT approximations. Image source: [99].

Each rung is a level of approximation constructed with different formalisms. From LDA and GGA as mentioned to meta-GGA which includes the Kohn-Sham kinetic energy density. Next

14

15

- ¹ higher in the ladder is the hybrid functionals which incorporates a part of exact exchange from
² Hartree-Fock (HF) theory. For example, the PBE0 functional[100] has the following definition:

$$\text{3} \quad E_{XC}^{PBE0} = \frac{1}{4}E_X^{HF} + \frac{3}{4}E_X^{PBE} + E_C^{PBE}, \quad (2.14)$$

- ⁴ and the HSE06 (Heyd-Scuseria-Ernzerhof)[101] take into account the screen Coulomb po-
⁵ tential for the exact part:

$$\text{6} \quad E_{XC}^{HSE} = \alpha E_X^{HF,SR}(\omega) + (1 - \alpha)E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}, \quad (2.15)$$

- ⁷ where α is the mixing parameter and ω is the parameter to control the range which de-
⁸ fines the short-range, SR, and long-range, LR, parts. The values of $\alpha = 1/4$ and $\omega = 0.2$
⁹ corresponding to HSE06 functional which gives accurate band gaps and lattice constants, see
¹⁰ the Mean absolute error (MAE) of different functionals in Fig. 2.3.

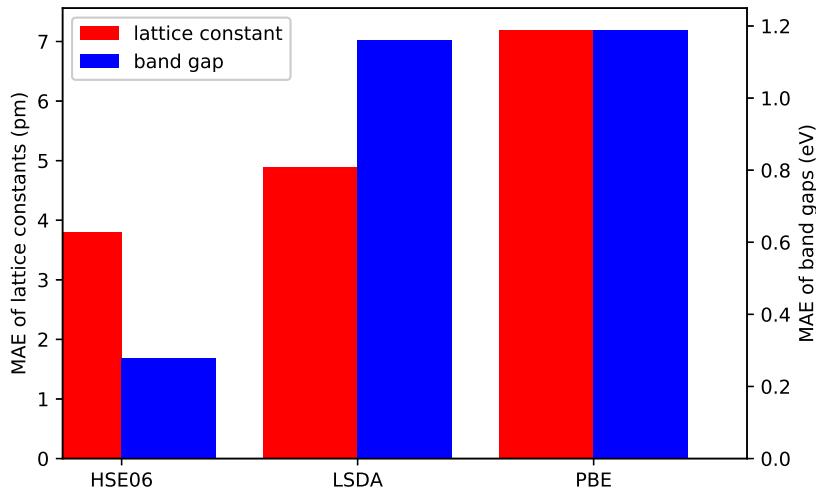


Fig. 2.3 MAE of the equilibrium lattice constants and band gaps of different functionals on SC40 solid test set. Data source: [102].

- ¹¹ The highest ranked functionals are the double hybrid which includes the unoccupied or-
¹² bitals as well, e.g. Random Phase Approximation[103].

¹³ Band gap problem

- ¹⁴ As shown in Fig. 2.3, band gap estimation in LDA and GGA is quite poor. This can be attributed
¹⁵ to the highly non-analytical and non-local behaviours of the EX energy functional. In other
¹⁶ words, it means the energy increase by adding an extra electron in the extended system is of

2.1 Theory

25

the order of 1 eV, even though, it is an infinitesimal density change. Let's look at the definite of band gap E_g :

$$E_g = I - A = \epsilon_{N+1}^{KS,HOMO} - \epsilon_N^{KS,HOMO}, \quad (2.16)$$

where I is the ionization energy, the energy change by removing one valence electron, A is the electron affinity, the energy change by add one electron to a neutral system, ϵ_N^{KS} Kohn-Sham orbital energy for N -electron system, and $HOMO$ stand for highest occupied molecular orbital. For a non-interacting Kohn-Sham system, E_g^{KS} can be calculated as following:

$$E_g^{KS} = \epsilon_N^{KS,LUMO} - \epsilon_N^{KS,HOMO}. \quad (2.17)$$

This leads to

$$E_g = E_g^{KS} + \Delta_{XC}, \quad (2.18)$$

where Δ_{XC} is the orbital shift caused by adding an extra electron: $\epsilon_{N+1}^{KS,HOMO} - \epsilon_N^{KS,LUMO}$.

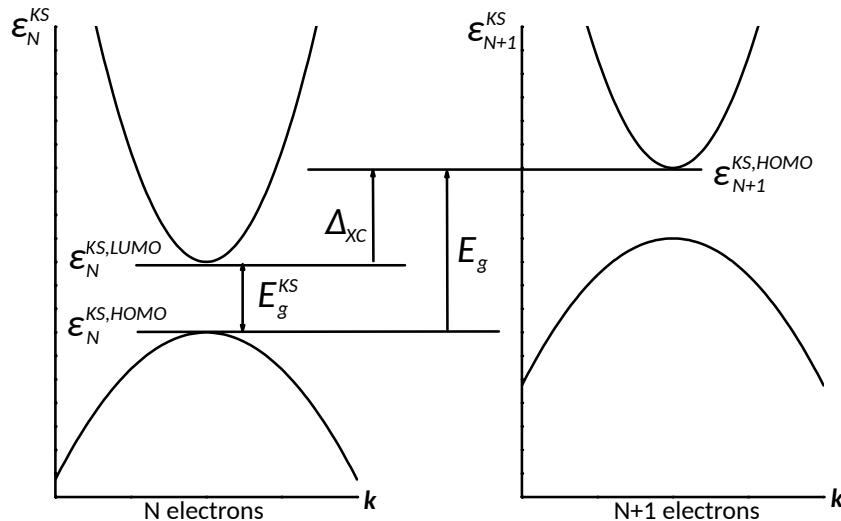


Fig. 2.4 Schematic illustration of the relation between E_g and E_g^{KS} . Image adapted from: [104].

The Δ_{XC} is exclusively depend on the non-analyticity of EX potential $\frac{\delta E_{EX}[n]}{\delta n(\vec{r})}$, since the Hartree potential explicitly depends on the density. If the EX energy functional were analytic, the infinitesimal density variation would not introduce large potential change, hence Δ_{XC} is small or equals to zero. Therefore, $E_g \approx E_g^{KS}$. The band gap accuracy when compared with experiment would be only limited inherently by different functionals. However, non-zero

- ¹ Δ_{XC} has been concluded on many materials and it is responsible for 80% of the LDA band gap
- ² error[105].

³ 2.2 Implementation

⁴ 2.2.1 Basis set, Plane wave energy cut-off, K-points

⁵ 2.2.2 Software Packages

Chapter 3

General physical properties 2D materials

3.1 Structural properties

3.1.1 Layer structure

3.1.2 sp hybridization

Coulson's theorem

3.1.3 Isotropic v.s. Anisotropic monolayer

3.1.4 Multiphase allotropes

3.2 Electronic properties

3.2.1 Polar bond

3.2.2 Importance of crystal symmetry

To understand this symmetry, we first need to discuss the hybridization of bonds. C atom has six electron, where two of them strongly localized near the nuclei core, they are called core electrons, such that their interaction with other electrons from other C atoms are suppressed. This only left us with four valence electrons to interact with others and then form bonds. As shown in Fig. 3.1, the s orbital will hybrid with p_x and p_y orbitals and form three equivalent sp^2 hybridized orbitals. They repel each other to have a maximum distance between one and the other. Therefore, an optimal angle between them is 120°, it will lead to the honeycomb structure of graphene. The p_z orbital left unchanged.

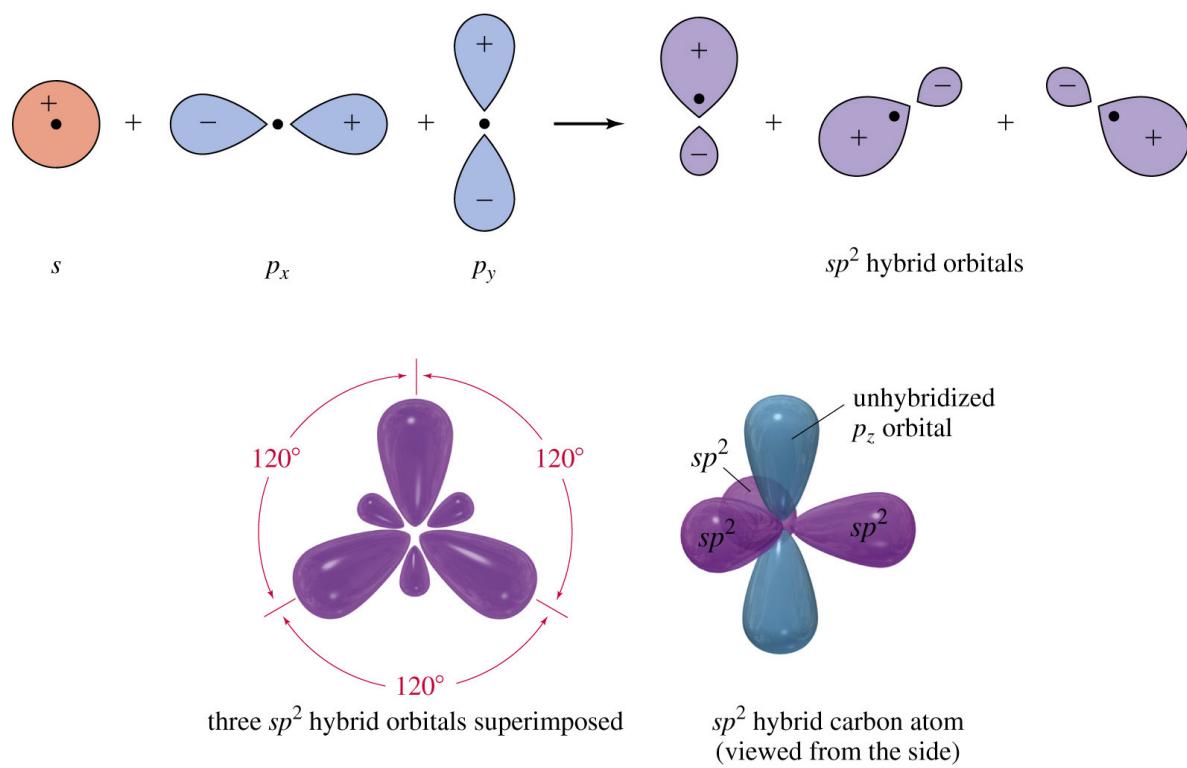
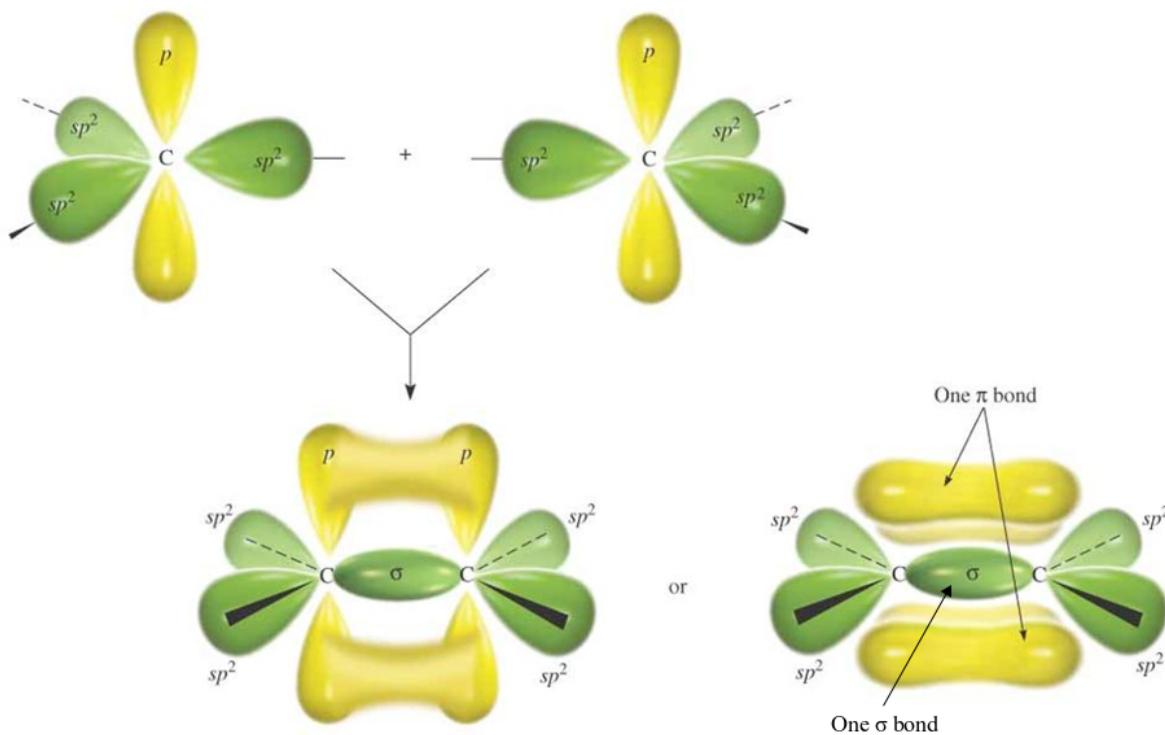


Fig. 3.1 The formation of sp^2 hybridized orbitals with unhybridized *p_z* orbital. Image source: [106].

Now C atoms are ready for bonding. The results of bonding is shown in Fig. 3.2. One sp^2 hybridized orbital with another one from adjacent atom form strong σ bond, while p_z orbitals form π bonds. It may look like an alternative single and double bonds between atoms, actually the bond order in graphene is $4/3$ and it is uniform. We will talk about how a delocalized π bond is more stable than alternative single and double bonds in the later chapter where Clar's theory is discussed.



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Fig. 3.2 The formation of $sp^2 \sigma$ and $p_z \pi$ double bond. Image source: [107].

Every atom has same local environment, however, adjacent atoms are not equivalent. They belong to different hexagonal sublattices *A* and *B* as indicated with blue and yellow colors in Fig. 3.3. a_1 and a_2 are the basis vectors in real space connecting equivalent sites. b_1 and b_2 are the basis vectors in reciprocal space connecting equivalent k-points. The hexagon in the reciprocal space is the first Brillouin zone where all inequivalent k-points are contained. These kpoints associate with different parallel lines of atoms and thus also indicate different directions in the real space. The k wave vectors near the Γ point have longer wave length, while those at the boundary of the first Brillouin zone have wave length that is two times the

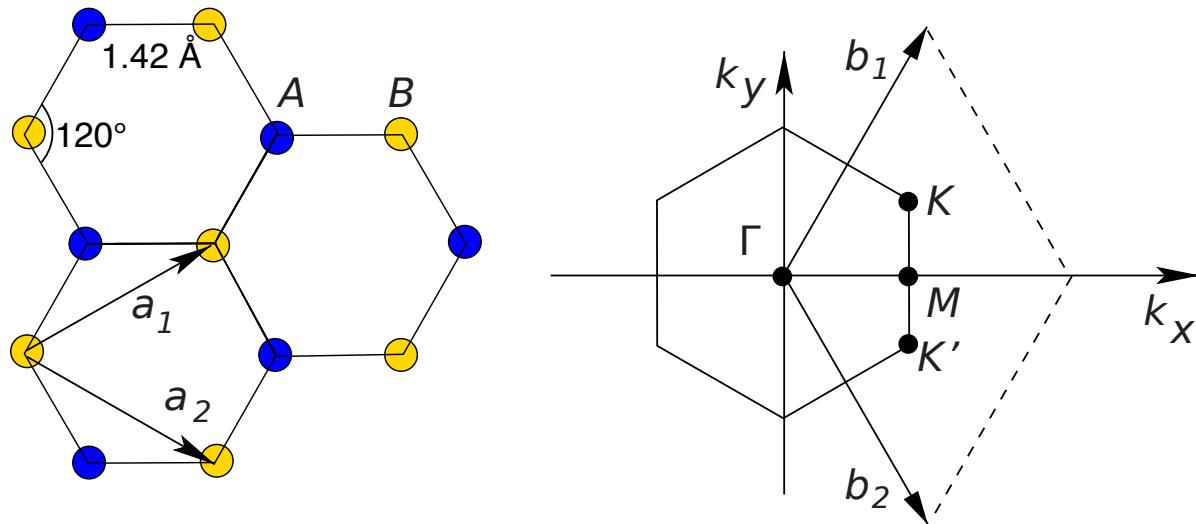


Fig. 3.3 Graphene lattice and its Brillouin zone. Image source: [14].

1 unitcell dimension on that direction. For example, the most interesting k-point for graphene
 2 is the K and K' points. These directions correspond to the a_1 and a_2 directions in real space.
 3 It is only at these k-points in the Brioulloin zone, the antibinding and bonding π band touch
 4 each other.

5 As compared to π bond, σ bond originate from strong overlap of sp^2 orbitals. The inter-
 6 action is strong and the splitting of bonding and antibonding orbitals are large. Which makes
 7 the σ bonding orbitals deep in energy, or in other word, makes it strong and difficult to break.
 8 This feature contribute the most to the mechanical strength of graphene. On the other hand,
 9 p_z orbitals are less overlapped. This makes the π bond energy close to Fermi level, i.e. the
 10 highest occupied state. Therefore, they contribute the most to the electronic properties of
 11 graphene.

Clar's theory 1

3.2.3 Importance of interlayer interaction 2

3.2.4 Accurate description from DFT 3

3.3 Vibrational properties 4

3.3.1 Phonon dispersion of 2D materials 5

3.3.2 Dynamic stability from phonon dispersion 6

3.4 Mechanical properties 7

3.4.1 Elastic and engineering constants 8

3.4.2 Mechanical stability: Born stability criteria 9

Draft - v1.0

Friday 12th May, 2017 – 17:45

Draft - v1.0

Friday 12th May, 2017 – 17:45

¹ Chapter 4

² Results of Physical Properties Calculations ³ in Novel 2D materials

⁴ 4.1 Thermal properties

⁵ 4.1.1 Thermal expansion and anharmonic oscillations

⁶ 4.1.2 Quasi-harmonic approximation

⁷ 4.1.3 Helmholtz free energy and specific heat

⁸ 4.2 Piezoelectric properties

⁹ 4.2.1 Piezoelectric constants

¹⁰ 4.2.2 Importance of internal relaxation

¹¹ 4.3 Carrier transport properties

¹² 4.3.1 Carrier mobility

¹³ 4.3.2 Deformation potential theory: non-polar materials

¹⁴ 4.3.3 Deformation potential theory: polar materials

¹⁵ 4.4 Magnetic properties

¹⁶ 4.4.1 Magnetic ordering

¹⁷ Stoner criterion of ferromagnetism

¹⁸ 4.5 Battery related properties

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Friday 12th May, 2017 – 17:45

¹ Chapter 5

² Results of Physical Properties Modification ³ in Novel 2D materials

⁴ 5.1 Number of layers and types of stackings

⁵ 5.1.1 Electronic properties

⁶ 5.1.2 Vibrational properties

⁷ 5.2 Mechanical strain

⁸ 5.2.1 Carrier mobility

⁹ 5.2.2 Magnetic properties

¹⁰ 5.3 Adatom adsorption

¹¹ 5.3.1 Electronic properties

¹² 5.4 Heterostructures

¹³ 5.4.1 Electronic properties

¹⁴ 5.4.2 Li diffusion

¹⁵ 5.5 Defect induction

¹⁶ 5.5.1 Structural properties

¹⁷ 5.5.2 Electronic properties

¹⁸ 5.5.3 Magnetic properties

Chapter 6

1

Conclusions

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Friday 12th May, 2017 – 17:45

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Appendix A

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Appendix

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