



**Physical Properties of Novel  
Two-dimensional Materials and Their  
Modifications  
From first-principles studies**



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This dissertation is submitted for the degree of  
*Doctor of Philosophy*

Antwerp, Belgium

April 2017



*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.*



## **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.

Yierpan Aierken  
April 2017



## **Acknowledgements**

And I would like to acknowledge ...





## **Abstract**

This is where you write your abstract ...



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# Chapter 1

## Introduction

A new field of research in material science and condensed matter physics was formed after the synthesis of graphene in 2004 [1, 2]. This field is named Two-dimensional (2D) material due to the fact that graphene is a single atomic-layer crystal. The synthesis itself together with the phenomenal properties of graphene has led to a Nobel Prize in physics awarded to A. K. Geim and K. S. Novoselov [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 materials like graphite, fullerenes and carbon nanotubes which are strongly graphene related. In the last several years, researches focused on graphene and related topics increasing rapidly, see Fig. 1.1. While a part of these effects have been making to explore more on the graphene itself and its applications, some other parts were put on discovering new 2D materials. 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.

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 accessible. At the same time, given the accuracy of the calculations is the most crucial aspect of computational physics, especially when the results are related to the prediction the real properties of materials, 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

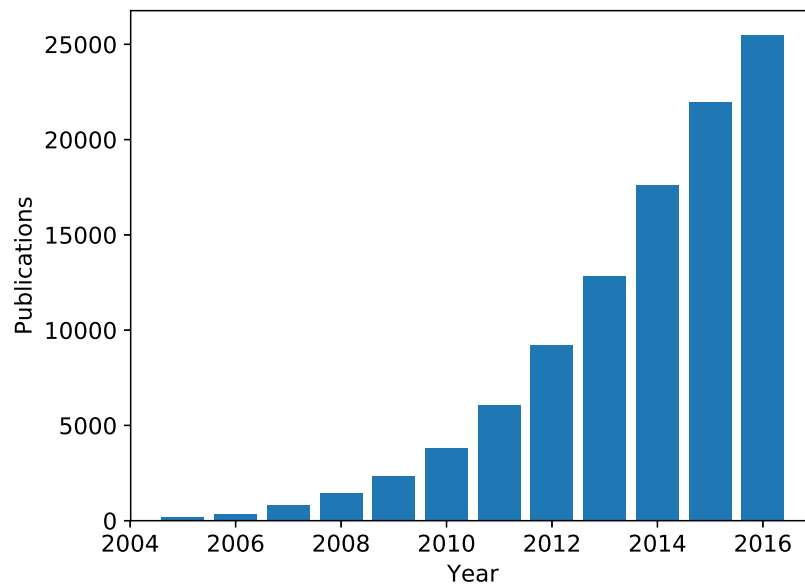


Fig. 1.1 Graphene related publications during the last decade. Data source: ISI Web of Science. <sup>1</sup>

scale benefits the experimental results to make it more convincing, or even sometimes to explain the unexpected results.

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 is a summary of several works which has accomplished during my PhD study and were initiated to this end. 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, 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 materails in [chapter 4](#), and followed by modification of physical properties of 2D materials in [chapter 5](#). Conclusions for the thesis will be given in the last chapter.

<sup>1</sup>This result is obtained by searching for "graphene" in the topic field of Web of Science.

## 1.1 Graphene

Graphene is composed of carbon (C) atoms arranged on a hexagonal lattice. Each C atoms bond to three neighbouring C atoms. Graphene is one single atomic layer of 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 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 are have been attempts[6, 7, 8, 9] to isolate graphene or ever grow it. However, they were mostly failed on 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 although these include certain types of characteristic defects that differ it from graphite, e.g. fullerene and nanotube, see Fig. 1.2. Flulerene is a C modelue has a quasispherical 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, hence 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. The method to produce a large quantity of fullerene, i.e. arc-discharge method[16], also results in another

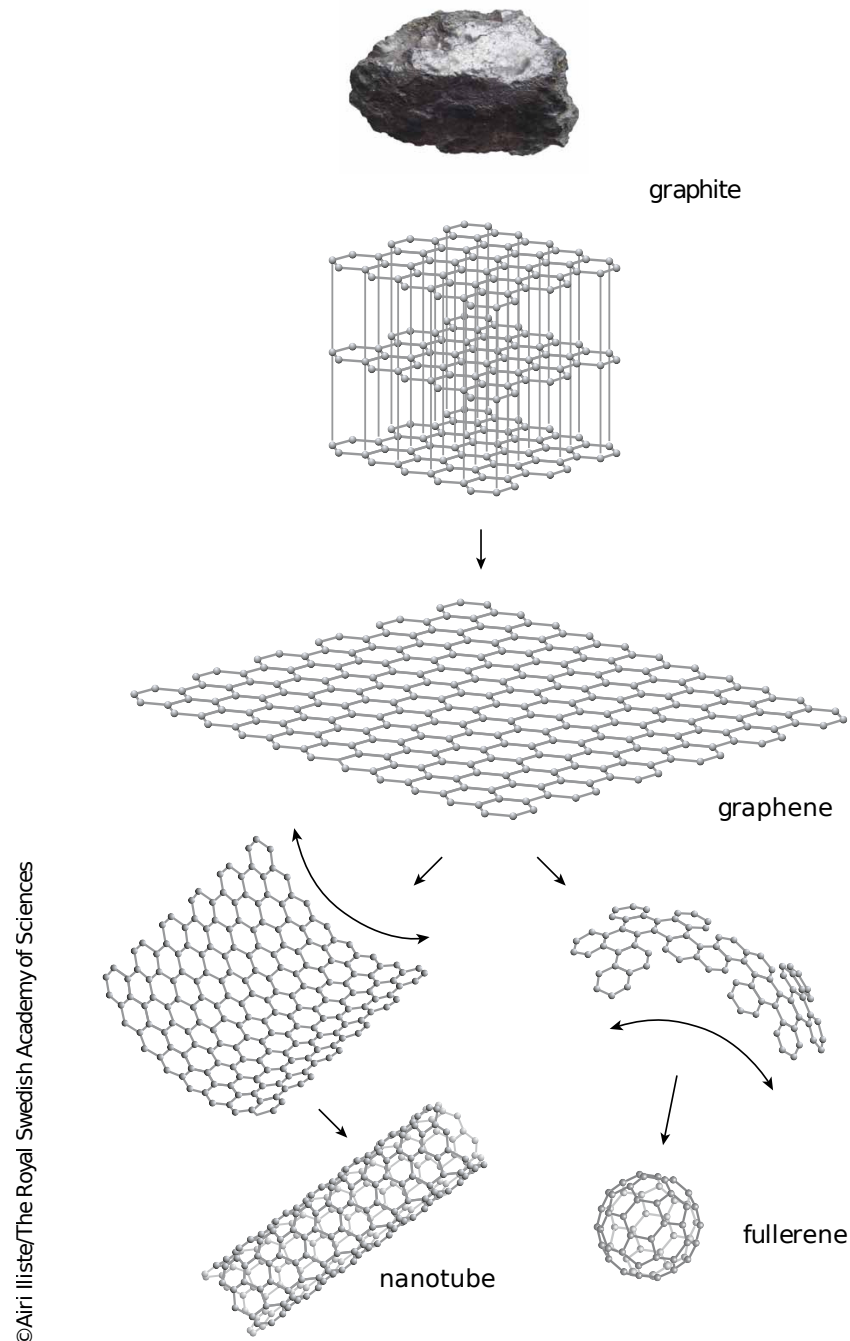


Fig. 1.2 Relation of graphite, graphene, fullerene and nanotube. Image source: the Nobel prize in physics 2010 [4].

important carbon allotrope: carbon nanotubes[17]. Despite sharing similar production method with fullerene, carbon nanotubes are actually more close to graphene in a sense it can be construct by rolling up finite graphene sheet into a hollow tube as its name suggested, and more importantly, these two both free of pentagonal C rings while fullerene must have a certain number. Carbon nanotubes are observed to have micrometer in lengths and nanometer in diameters and having either metallic or semiconducting nature depending on its edges. 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 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

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 lattice<sup>2</sup>, 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 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  $10^6\text{m/s}$ . Hence, the  $K$  and  $K'$  points are referred as Dirac

<sup>2</sup>honeycomb lattice is not a bravais lattice.

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 tunneling[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].

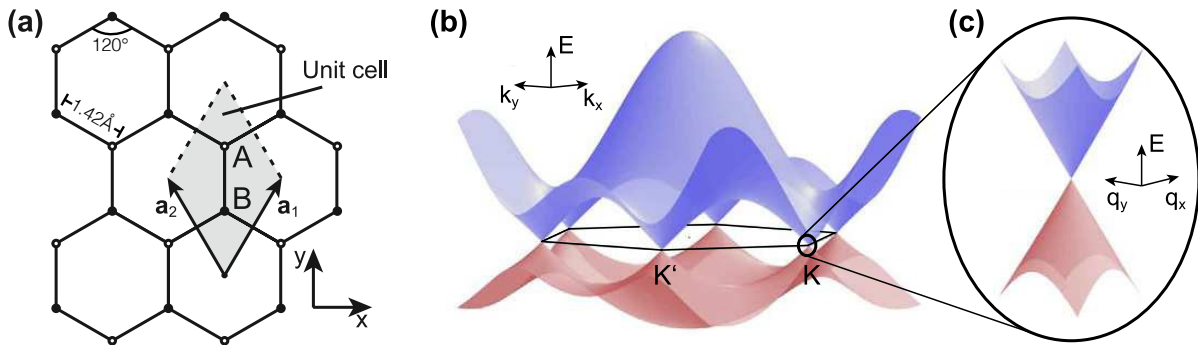


Fig. 1.3 (a) Graphene honeycomb lattice composed of A and B hexagonal Bravais sublattices. (b) Band structure of graphene where CBM and VBM touch each other only at the  $K$  and  $K'$  points. (c) Approximately linear dispersion at  $K$  and  $K'$  point. Image source: [22].

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  $130 \text{ Gpa}$ [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  $5000 \text{ W/mK}$  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, non-destructive 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

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, fluorographene and graphene oxide, respectively; On the other hand, inspired by graphite's layer structure, layered bulk materials are brought to the attention to isolate single layer just as it has done for graphene.

### 1.2.1 Functionized Graphene

#### Graphane

The fully hydrogenation of graphene gives a 2-D hydrocarbon called graphane. 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[36]. The C-C bond length in the chair structure is 1.52 Å larger 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[37].

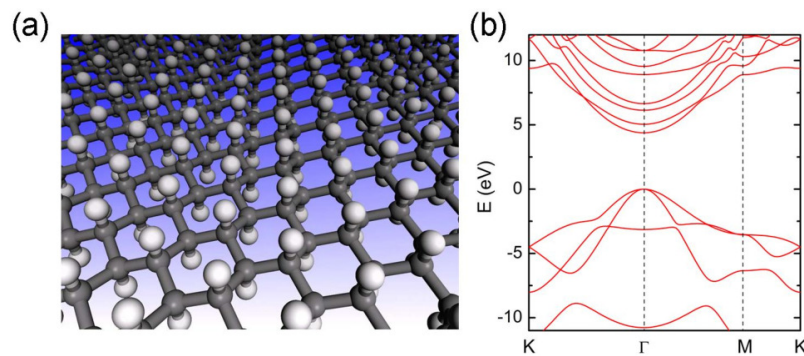


Fig. 1.4 (a) The chair structure of graphane. The white balls are H atoms and grey ones are C atoms. Image source: [38]. (b) Band structure of chair graphane. Image source: [39]

## 1 Fluorographene

### 1.2.2 Silicene and Germanene

### 1.2.3 2D from layered materials

## Boron Nitride

## Transition Metal Dichalcogenides

## 1.3 0D and 1D from 2D: buckyballs, nanotubes and nanoribbons

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#### **2.2.2 Software Packages**

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# 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

- 1 have a maximum distance between one and the other. Therefore, an optimal angle  
 2 between them is  $120^\circ$ , it will lead to the honeycomb structure of graphene. The  $p_z$   
 3 orbital left unchanged.

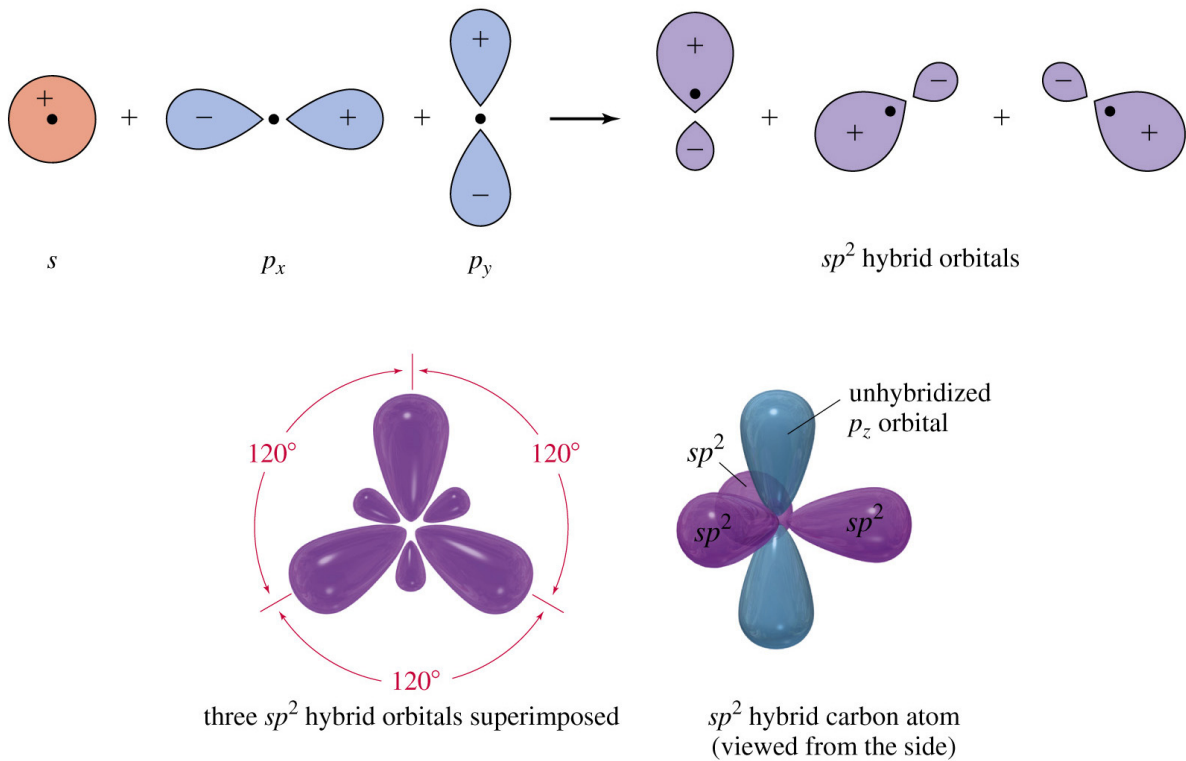


Fig. 3.1 The formation of  $sp^2$  hybridized orbitals with unhybridized  $p_z$  orbital. Image source: [40].

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

- 10 Every atom has same local environment, however, adjacent atoms are not equiv-  
 11 alent. They belong to different hexagonal sublattices  $A$  and  $B$  as indicated with blue  
 12 and yellow colors in Fig. 3.3.  $a_1$  and  $a_2$  are the basis vectors in real space connect-  
 13 ing equivalent sites.  $b_1$  and  $b_2$  are the basis vectors in reciprocal space connecting  
 14 equivalent k-points. The hexagon in the reciprocal space is the first Brillouin zone  
 15 where all inequivalent k-points are contained. These kpoints associate with different  
 16 parallel lines of atoms and thus also indicate different directions in the real space. The

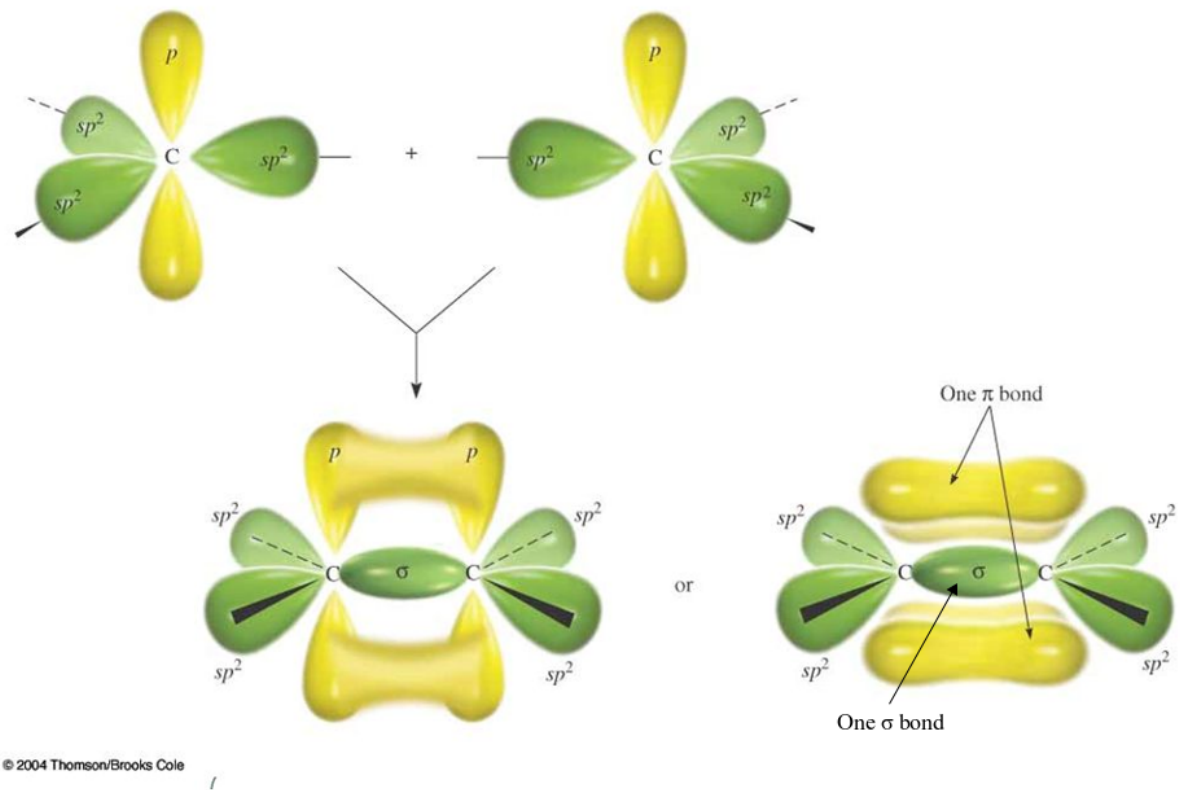


Fig. 3.2 The formation of  $sp^2$   $\sigma$  and  $p_z$   $\pi$  double bond. Image source: [41].

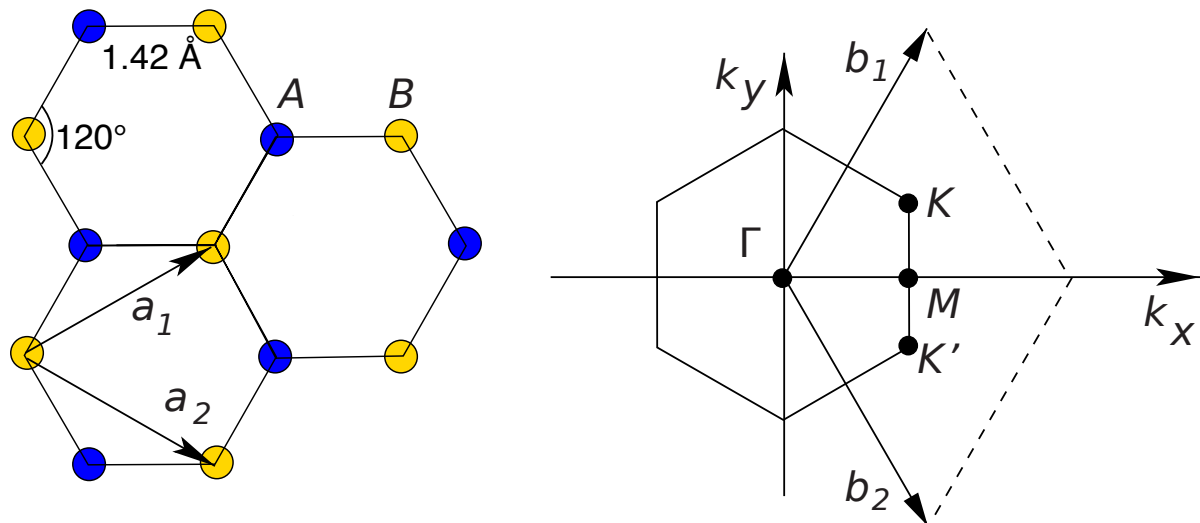


Fig. 3.3 Graphene lattice and its Brillouin zone. Image source: [14].

k wave vectors near the  $\Gamma$  point have longer wave length, while those at the boundary of the first Brillouin zone have wave length that is two times the unitcell dimension on that direction. For example, the most interesting k-point for graphene is the  $K$  and  $K'$  points. These directions correspond to the  $a_1$  and  $a_2$  directions in real space. It is only at these k-points in the Brioulloin zone, the antibinding and bonding  $\pi$  band touch each other.

As compared to  $\pi$  bond,  $\sigma$  bond originate from strong overlap of  $sp^2$  orbitals. The interaction is strong and the splitting of bonding and antibonding orbitals are large. Which makes the  $\sigma$  bonding orbitals deep in energy, or in other word, makes it strong and difficult to break. This feature contribute the most to the mechanical strength of graphene. On the other hand,  $p_z$  orbitals are less overlapped. This makes the  $pi$  bond energy close to Fermi level, i.e. the highest occupied state. Therefore, they contribute the most to the electronic properties of graphene.

## Clar's theory

### 3.2.3 Importance of interlayer interaction

### 3.2.4 Accurate description from DFT

## 3.3 Vibrational properties

### 3.3.1 Phonon dispersion of 2D materials

### 3.3.2 Dynamic stability from phonon dispersion

## 3.4 Mechanical properties

### 3.4.1 Elastic and engineering constants

### 3.4.2 Mechanical stability: Born stability criteria





# **Chapter 4**

## **Results of Physical Properties Calculations in Novel 2D materials**

### **4.1 Thermal properties**

#### **4.1.1 Thermal expansion and anharmonic oscillations**

#### **4.1.2 Quasi-harmonic approximation**

#### **4.1.3 Helmholtz free energy and specific heat**

### **4.2 Piezoelectric properties**

#### **4.2.1 Piezoelectric constants**

#### **4.2.2 Importance of internal relaxation**

### **4.3 Carrier transport properties**

#### **4.3.1 Carrier mobility**

#### **4.3.2 Deformation potential theory: non-polar materials**

#### **4.3.3 Deformation potential theory: polar materials**

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#### **4.4.1 Magnetic ordering**

#### **Stoner criterion of ferromagnetism**

### **4.5 Battery related properties**



# **Chapter 5**

## **Results of Physical Properties Modification in Novel 2D materials**

### **5.1 Number of layers and types of stackings**

#### **5.1.1 Electronic properties**

#### **5.1.2 Vibrational properties**

### **5.2 Mechanical strain**

#### **5.2.1 Carrier mobility**

#### **5.2.2 Magnetic properties**

### **5.3 Adatom adsorption**

#### **5.3.1 Electronic properties**

### **5.4 Heterostructures**

#### **5.4.1 Electronic properties**

#### **5.4.2 Li diffusion**

### **5.5 Defect induction**

#### **5.5.1 Structural properties**

#### **5.5.2 Electronic properties**

#### **5.5.3 Magnetic properties**

## **Chapter 6**

1

## **Conclusions**

2



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## **Appendix A**

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## **Appendix**

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