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**NANYANG
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**FIRST-PRINCIPLES CALCULATIONS OF THE
NOVEL PROPERTIES OF TWO-DIMENSIONAL
MATERIALS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
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Abstract

Two-dimensional (2D) materials such as graphene have inspired a worldwide upsurge of research interests since 2004 when graphene were firstly obtained by Andre Geim using mechanical exfoliation from highly oriented pyrolytic graphite. In spite of the excellent carrier mobility of graphene, the lack of a band gap impedes its applications in areas like nanoelectronics and solar cell. Although various methods have been developed to realize the band gap opening, the resulting structures are accompanied by adverse side effects, such as dramatically increased effective mass, distorted lattice, and/or damaged layer integrity, resulting in the loss of majority of its superior properties. Parallel to the intensive world-wide effort to engineer the band structure of graphene, scientists start to study other 2D materials beyond graphene. For example, molybdenum oxide and molybdenum sulfide, which possesses the layered structure as graphene, can be viewed as the potential candidates. Inspired by graphene, such 2D materials beyond graphene now have drawn more attention for its electrical and optical properties. My studies can be divided into five parts in this thesis.

In the first part of the thesis, we systematically explore the mechanism of the stacking order transformation from ABC to ABA in trilayer graphene by evaporating triazine molecules onto its surface. Based on the experimental observation, we first construct the most plausible stacking sequence, i.e. one wrinkle separated the ABA and ABC flakes. Then, we perform the density function theory (DFT) calculations to compare the energy difference between two stacking orders including the van der Waals interaction. Our results show that this energy difference after triazine decoration become larger and serves as the driving force to promote such transformation. Further molecular dynamics (MD)

simulations demonstrate that absorbed triazine molecules effectively drive the wrinkle moving towards the ABC domains.

In the second part, we study the novel properties of AB-stacking closed-edge bilayer graphene (CEBG) employing the first-principles calculations, such as the band gap opening and spatial charge separation. The former originates from the pseudospin interaction, while the latter arises from geometrical asymmetry. The quasiparticle band structures are also calculated using the GW approximation. We also demonstrate theoretically that CEBG can be used as bricks for developing the future graphene-functionalized electronic devices, such as solar cells.

In the third part, we thoroughly investigate the electronic and optical properties of molybdenum trioxide, α -MoO₃. Although α -MoO₃ has been widely applied in chemical batteries and catalysis, the full understanding about its electronic and particularly optical properties is still lacking so far. We calculate the optical absorption spectra by solving the Bethe-Salpeter equations (BSE), which match the experimental data well. Our results claim the discrepancy of the band gaps obtained from experiments and calculations. Our results also show a distinct anisotropy of the excitons along the different polarized direction.

In the fourth part, we calculate the band structures of MoS₂ including the spin-orbit coupling (SOC) effects and explore the mechanism behind the enhancement of intensities of overtone peaks excited by 325 nm laser. We then attribute such enhancement to the triply resonant Raman mechanism and the energy of phonons corresponds to the energy splitting due to the SOC. By studying the strain effects on the SOC, we find that the value of the splitting induced by SOC exhibits monotone features with the applied strain, while the band gap shows non-monotonic strain dependence.

In the last part, we explore the possible new phases of molybdenum oxide (including MoO₂ and MoO₃) and carbon allotropes employing the particle swarm optimization (PSO) algorithm. For MoO₂, we find one semiconducting phase with the similar structure of MoS₂. For MoO₃, we report one novel hexagonal phase with an open tunnel framework: h' -MoO₃. For carbon allotropes, we propose one novel superhard carbon allotrope

U-carbon, which is found to be matched better with the XRD data for cold-compressed graphite than all previous proposed carbon allotropes.

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Chapter 1

Introduction

1.1 Graphene

Although graphite has been widely used for thousands of years, its mono layer, i.e. graphene, is now a rising star and draws a myriad of interests for scientists worldwide because of its unusual electronic properties [1, 2, 3]. Its 2D honeycomb lattice with bond provides the building block to form 0D fullerence, 1D nanotube, and even 3D graphite, as shown in Fig.1.1. Tracing back to more than half a century ago, a pioneer study on graphene by Wallace [4] in 1947 first reported the linear dispersion band structure near K point. Subsequent theoretical studies also remarked on graphene's unusual charge carriers that mimic massless Dirac fermions and predicted relativistic-like effects in this two-dimensional condensed matter system, such as the unusual landau levels under magnetic field [5, 6]. On the other hand, due to various technical difficulties, the early experiments on graphene were mainly observational, and did not reveal substantially its unique electronic properties. The breakthrough finally emerged in 2004, when Geim obtained this film by mechanically exfoliating the highly oriented pyrolytic graphite [7], which formally sparked the graphene gold rush. The experiments had not only confirmed various predictions on graphene's usual electronic properties, but also discovered many unexpected novel characteristics of the material. Prof. Geim and Dr. Novoselov were awarded the 2010 Nobel Prize in physics because of the pioneer contributions in related

fields. The award was also the best confirmation on the impact of graphene on science and technology.

Figure 1.1: Single layer graphene provides the building block to form 0D fullerenes, 1D nanotubes and 3D graphite [1].

Graphene presents remarkable electronic properties, resulting from its unique energy band structure. As present in Fig.1.2, graphene possesses one unit cell including two atoms that accounts for two conical points per Brillouin zone, called Dirac points (K' and K). The valence and conduction bands contact with the Fermi energy passing through the points. The energy dispersion near such points can be approximated to introduce a linear relationship with momentum and is given by the Eq.1.1, where v_f is the Fermi velocity.

$$H = \hbar v_f \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_f \boldsymbol{\sigma} \cdot \mathbf{k} \quad (1.1)$$

The associated energy spectrum is

$$E(\vec{k}) = \pm t \sqrt{1 + 4 \cos^2(\sqrt{3}ak_y/2) + 4 \cos(\sqrt{3}ak_y/2) \cos(\sqrt{3}ak_x/2)} \quad (1.2)$$

Figure 1.2: (a) Crystal structures of graphene and the corresponding Brillouin zone (b) Blue and red dots denote its two inequivalent sub-lattices. The lattice vectors are given. (c) Tight-binding (TB) band structures of graphene. The linear dispersion near K point is present. The figures are adapted from Ref.[8].

While graphene presents various remarkable properties, its bilayer counterpart is equally interesting. By placing an extra graphene layer on top of graphene, the inter-layer interaction will modify the material's properties significantly. The bilayer graphene possesses the hyperbolic energy bands, compared with the linear bands in monolayer graphene. The carriers in bilayer graphene are governed by a peculiar Hamiltonian with combined features of the Dirac and Schrödinger equations [1, 2]. That means that the carriers in bilayer have the chirality of Dirac fermions, also carry masses as the Schrödinger particles. Such massive chiral fermions have no analogy in other systems. Bilayer graphene exhibits unique quantum Hall effects (QHE) [9, 10], which is different from that in monolayer graphene and conventional semiconductors. In addition, though bilayer graphene is a gapless semiconductor, a perpendicular applied electric field can modify its band structure and open a band gap. Its gap value can be turned from zero up to 250 meV by an applied electrical gate [11, 12].

Based on TB approach, the carriers of bilayer graphene in the K points can be described by using a low-energy effective Hamiltonian within four basis (A1, B2, A2, and B1). U is the potential difference between the two layers. To illustrate the effects of U , let's consider a simplified Hamiltonian with only γ_1 and U at the K point

$$H_{bi} = \begin{pmatrix} U/2 & 0 & 0 & v\pi^* \\ 0 & -U/2 & v\pi & 0 \\ 0 & v\pi^* & -U/2 & \gamma_1 \\ v\pi & 0 & \gamma_1 & U/2 \end{pmatrix} \quad (1.3)$$

where $\pi = p_x + ip_y$, $\pi^* = p_x - ip_y$. The eigenenergies are

$$E_{c1,v1} = \pm U/2 \quad (1.4)$$

$$E_{c2,v2} = \pm \sqrt{\gamma_1^2 + U^2/4} \approx \pm \gamma_1 \quad (1.5)$$

where c_1 , c_2 , ν_1 and ν_2 denote the first and second conduction bands and valence bands [green lines in Fig.1.3]. We found that the interlayer potential difference U induces the

inversion asymmetry of two layers and lifts up the degeneracy at K points. As the degeneracy of bands is destroyed, there is a band gap opening in bilayer graphene [13, 14, 15, 16, 17, 18]. Experimentally, such band gap can be realized through a perpendicular electric field using double-gate devices [19, 8, 20, 21], in which the back and top gates are applied with opposite voltages.

Figure 1.3: (a) atomic structure of bilayer graphene. The yellow and blue circles are the two sub-lattices of graphene. γ_0 represents the TB hopping parameter between two nearest-neighbor atoms. γ_1 , γ_2 and γ_3 are three TB hopping parameters between atoms in different graphene plane. (b) Band gap opening in bilayer graphene due to interlayer potential difference induced by the shift of Fermi level. The red (green) line represents the band structure at zero (finite) doping level.

Figure 1.4: (a) the movement of a top graphene layer versus the bottom layer. (b, c) two different stacking sequence of ABA (b) and ABC (c). The yellow and blue dots are two inequivalent sublattices. The figures are adapted from Ref.[13].

Trilayer graphene is another type of configurations attracting researchers' interest recently due to its more stacking formats (Fig.1.4). The different symmetry of the crystal structure results in distinct electronic structures of ABA and ABC trilayer systems. The

Figure 1.5: Low energy band structures of trilayer graphene. $\sqrt{2}\gamma_1$ and γ_1 are the energy spacing among low- and high-lying bands at K points in ABA and ABC trilayer, respectively.

corresponding electronic structures for trilayer graphene are distinct, as present in Fig.1.5. ABA trilayer has four low-energy bands that follow either linear or quadratic dispersion [22, 23], while ABC trilayer has only two low-energy bands that follow the cubic dispersion [23, 24]. Under a uniform electric field, no band gap occurs in ABA trilayer while there is a small band gap in ABC trilayer [25].

1.2 2D materials beyond graphene

The transition metal oxides generally are of great technical interest and highly important in commercial catalysts. In the case of molybdenum oxides, they have attracted considerable attention owing to its wide band gap nature and exhibit various promising applications, such as catalysis [26, 27, 28], Li-ion batteries [29, 30, 31, 32, 33], gas sensors [34, 35, 36, 37, 38, 39], recording materials [40, 41], solar cells [42, 43, 44], photochromic and electrochromic devices [45, 46, 47]. Therefore, the understanding of the electronic and optical properties in molybdenum oxides are important for both fundamental studies and applications.

Molybdenum can form two stable binary oxides, namely, molybdenum trioxide MoO_3 and molybdenum dioxide MoO_2 . MoO_3 has been known to exist three crystalline polymorphs: thermodynamically stable orthorhombic $\alpha\text{-MoO}_3$, metastable monoclinic $\beta\text{-MoO}_3$, and triclinic $\gamma\text{-MoO}_3$.

MoO_3 and hexagonal $h\text{-MoO}_3$. As shown in Fig.1.6, all found polymorphs are basically built up of MoO_6 octahedra merely in different ways. For $\alpha\text{-MoO}_3$, its space group is $Pbnm$ with lattice constants: $a = 3.962 \text{ \AA}$, $b = 13.855 \text{ \AA}$, and $c = 3.699 \text{ \AA}$. Two layers of distorted MoO_6 octahedrons oriented along the $[010]$ axis through a weak van der Waals interaction. Each layer can be viewed as edge sharing zig-zag chains of MoO_6 along the $[001]$ axis, while the chains are mutually linked by corner O sites along the $[100]$ directions. The $\beta\text{-MoO}_3$ can be viewed as distorted variants of the 3D ReO_3 structure [48], where the MoO_6 octahedrons are corner-connected to form a distorted cube, as shown in Fig.1.6(a). It crystallizes with lattice constants $a = 7.122 \text{ \AA}$, $b = 5.366 \text{ \AA}$, and $c = 5.556 \text{ \AA}$ and $\beta = 92.01^\circ$ with the space group $P2_1/c$. Among other polymorphs, $h\text{-MoO}_3$ ($P6_3/m$) exhibits a distinct 1D open tunnel structure [49, 50], where the MoO_6 octahedra interlinked through the *cis*-position, giving an open framework structure with 1D tunnels, as shown in Fig.1.6(c).

Figure 1.6: Schematic representation of (a) orthorhombic $\alpha\text{-MoO}_3$ (b) monoclinic $\beta\text{-MoO}_3$ and hexagonal $h\text{-MoO}_3$ from the top view and side view. The figures are adapted from Ref.[49, 51, 52].

Unlike other rutile-structure transition metal dioxides, MoO_2 crystallizes in a distorted

rutile monoclinic phase, as shown in Fig.1.7. Similar structures can also be found in WO_2 , TcO_2 , and the low-temperature forms of VO_2 . MoO_2 crystallizes with lattice constants $a = 5.611 \text{ \AA}$, $b = 4.856 \text{ \AA}$, and $c = 5.629 \text{ \AA}$ and $\beta = 120.95^\circ$ with the space group $P2_1/c$. In MoO_2 , distorted MoO_6 octahedra result in two inequivalent types of oxygen atoms, where Mo-O bonds vary in length between 1.97 and 2.07 $\text{\AA}$. The corresponding Mo-Mo distances are 2.51 $\text{\AA}$ within pairs or 3.02 $\text{\AA}$ between the pairs.

Figure 1.7: Schematic representation of monoclinic MoO_2 from the side view (a) and top view (b). The figures are adapted from Ref.[49].

The electronic structure is crucial for the catalytic activity as the transition energies in absorption spectra are mainly determined by the valence and the conduction bands. Despite a great deal of investigations on the band structures of such oxides, their properties are by far less well known than its sulfide counterpart MoS_2 [53, 54, 55, 56] and a corresponding deep understanding is still lacking.

Recently, molybdenum disulfide (MoS_2) which is a member of 2D layered metal chalcogenide materials [57, 58], such as MoSe_2 , WS_2 and WSe_2 , have attracted considerable attention due to their unique properties [59, 60, 61, 62, 63, 64, 65, 66]. Bulk MoS_2 is abundant in nature and was used as solid lubricant because of the low friction and me-

chanic robustness [67, 68]. MoS₂ has also proven to be useful in photocatalysts [69, 70], solar cells [71, 72, 73], Li ion batteries [74, 75] and catalysts for hydrogen evolution [76, 77] for decades. Similar with the fabrication of graphene [7], MoS₂ can be grown or mechanically exfoliated down to a single layer. Comparing to its bulk phase, few layer MoS₂ present very distinctive physical properties, particularly in lattice dynamics, energy band structure and optical properties. Unlike graphene, monolayer MoS₂ with the direct bandgap makes it a promising candidate in the optoelectronic applications, such as transistors with an extra-high on/off ratio at room temperature [60]. More importantly, coupled spin and valley in 1L-MoS₂ due to strong spin-orbital coupling (SOC) and inversion symmetry breaking introduce new controllable degree of freedom beyond charge and spin, leading to valleytronics [78, 79].

MoS₂ show a graphene-like layered structure consisting of S-Mo-S sandwiched layers bonded together by van der Waals forces in Fig.1.8(a). In each layer, Mo atoms have triangular prismatic coordination between two planes of hexagonally arranged sulfur atoms connected through covalent S-Mo-S bonds. Each layer is about 0.65 nm thick and the in-plane lattice constants of MoS₂ are 3.2 Å [58]. Depending on the different stacking sequence, the S-Mo-S sandwiched layer stacking along *c* axis will form two different polytypes, i.e., 2H with hexagonal symmetry and 3R with rhombohedral symmetry. Actually, the central Mo atoms can form octahedral prismatic coordination configuration, which gives the third polytype of 1T with tetragonal symmetry. The schematics of the three structure polytypes are depicted in Fig.1.8(b). The symmetry difference between monolayer of 2H-MoS₂/3R-MoS₂ (with point group D_{3h}) and 1T-MoS₂ (with point group D_{3d}) can be differentiated by Raman analysis [80].

MoS₂ is indirect-gap semiconductors in bulk, but transformed into direct-gap semiconductors when thinned down to monolayers. (see Fig.1.9(a)) [81]. For Bulk MoS₂, VBM states are located at the Γ point, while CBM states are located halfway along the $\Gamma-K$ direction. In monolayer case, the direct band gap is located at K point of about 1.9 eV. Such transition can be probed by a variety of spectroscopic tools [81, 82, 83, 84, 85]. As an indirect-gap semiconductor, PL in bulk MoS₂ is a weak phonon-assisted process

Figure 1.8: Schematic representation of (a) MoS₂ and (b) three typical structure polytypes: 2H, 3R and 1T. a and c represent lattice constants. The figures are adapted from Ref.[57, 60].

and have negligible quantum yield. Appreciable PL is observed in few-layer MoS₂ and surprisingly bright PL is detected in 1L-MoS₂, which is indicative of being a direct-gap semiconductor. The indirect transition (I) is revealed in 2L-, FL- and bulk TMDs, which is found to change significantly with layer number in WS₂ and WSe₂ flakes [86]. Indirect-to-direct transition is attributed to the absence of the weak interlayer coupling in 1L. Two peaks (A and B) are observed in absorption spectra of 1L- and 2L-MoS₂, corresponding to transitions between split valence bands (VBs) and conduction band (CBs). The energy splitting between A and B in bulk MoS₂ arises from combined effect of interlayer coupling and SOC, but solely comes from SOC in 1L-MoS₂ due to the absence of interlayer coupling [81].

Figure 1.9: (a) Calculated electronic structure for the bulk phase and single-layer of MoS₂. The arrows indicate the band gap (direct or indirect). (b) Photoluminescence spectra of MoS₂ with increasing number of layers, showing evolution of A and B excitons as well as the I peak of indirect transition. The figures are adapted from Ref.[87, 81].

1.3 Cold-compressed graphite

Researchers have been struggling to shed light on the intriguing transition process in cold-compressed graphite for decades [88]. Experimental observations including the increase of electrical resistivity [89] and optical transmittance [90], sharp drop in optical reflectivity [91, 92], in-plane displacements [93], changes in near K -edge spectroscopy [94] and x-ray diffraction (XRD) pattern [94, 95, 96] as well as the indentation of diamond anvils [94] indicate that such transparent and superhard phase is distinct from hexagonal and cubic diamond.

Due to the difficulty in identifying the transition process in cold-compressed graphite by experiment, theoretical efforts have been made to uncover the nature of this mysterious superhard phase. The monoclinic polymorph M-carbon obtained by using the ab initio evolutionary algorithm was firstly proposed to be a possible candidate for cold-compressed graphite in 2009 [97]. Later, bct- C_4 was designated as the coexistence phase with M-carbon and seemed to be one plausible solution [98]. By calculating the enthalpy barriers for the various phase transitions, W-carbon was revealed to possess a lower barrier than both bct- C_4 and M-carbon [99]. Soon after, three groups reported independently one novel allotrope with the same structure using different methods, which was named as oC16-II in Ref. [100], Cco- C_8 in Ref. [101] and Z-carbon in Ref. [102]. Z. Zhao et al. argued that there was a matching problem with the XRD peaks of cold-compressed graphite for Cco- C_8 , whereas the other two groups considered this new phase as a product of graphite cold compression. In addition to these structures mentioned above, numerous other carbon phases (e.g., R-, H-, S-, X-, Y-carbon, etc.) have also been proposed by various methods and fit the XRD data to some extent [103, 104, 105]. Scientists attempted to identify the observed superhard phase in cold-compressed graphite among above predicted allotropes, but none of them can match the experimental XRD data satisfactorily. Frankly, the simulated XRD for all above potential candidates can merely fit the experimental data to some extent [97, 99, 100, 101, 102, 103, 106]. In other words, up to now, identified structure for the cold-compressed graphite have not been revealed.

Figure 1.10: Schematic representation of various carbon allotropes predicted via different methods. The figures are adapted from Ref.[97, 98, 99, 102, 103, 104, 105].

Chapter 2

Theoretical background

2.1 Tight-binding approach

Tight-binding approach, a basic semi-empirical method for the calculations of electronic band structures, affords a satisfying description in covalent systems based on basis sets of localized wave functions. The name of “tight-binding” suggests that the electrons in this approximation should be tightly bound to each atomic site and possess finite interactions with the surrounding atoms. As such, wave functions of electrons should have the similar form with atomic orbitals for free atoms. The energies of electrons should be compared with the ionization energies for the electrons of free atoms due to the finite interactions with the states on surrounding atoms. As a result, tight-binding methods should be particularly useful for the calculation of solids for which the electronic states remain rather close to the unperturbed atomic orbitals, such as insulators with weak hybridization among neighbors, or d - and f - states in transition metal materials, which are compact and hence remain somewhat “atomic-like” [107].

Tight-binding method is close tied to Linear Combination of Atomic Orbitals (LCAO) methods [108]. This method was first developed by Bloch [109] considering only the s -symmetry function in 1928. Then, Jones, Mott, and Skinner [110] considered a basis of different atomic orbitals in 1934. Compared with the first-principles calculations, the tight-binding approach is at least 10 to 100 times faster with a loss in transferability. On

the other hand, tight-binding approach is generally 10 to 100 times slower than empirical methods, but the bonds retain the quantum feature. Therefore, tight-binding methods based on one-electron models, with relative computational efficiency, are useful for the calculation of large or highly complex systems in which first-principles calculations would be impractical [111, 112, 113, 114, 115, 116, 117].

2.1.1 The Tight-binding Hamiltonian

In tight-binding approach, the electronic states for a crystal structure are given by the Schrödinger equation in atomic unit,

$$\hat{H}\Psi_{\vec{k}}(\vec{r}) = \left[-\frac{1}{2}\nabla^2 + V(\vec{r}) \right] \Psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\Psi_{\vec{k}}(\vec{r}) \quad (2.1)$$

where the two items in the Hamiltonian stand for the kinetic energy and the effective periodic potentials; $\Psi_{\vec{k}}(\vec{r})$ and $E_{\vec{k}}$ denote the single-electron wave functions and eigenvalue for the state $\vec{k}$, respectively.

Given a periodically replicated cell with a lattice vector $\vec{R}$, atom l is located at the position $\vec{t}_l$. The atomic-like orbitals $\phi_{\mu,s}$ are centered on each atom, in which s is the spin state for the μ th orbital. In principle, orbitals for different atoms are not orthogonal to others. Following Bloch's theorem, the expansion for the wave functions could be a linear combination of the atomic orbitals $\phi_{\mu,s}$ using Löwdin's method [118]:

$$\Psi_{\vec{k}l\mu s}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi_{\mu,s}(\vec{r} - \vec{t}_l - \vec{R}) \quad (2.2)$$

where N indicates the number of unit cells of the system. We can easily verify that this function Eq.2.2 satisfies Bloch condition:

$$\begin{aligned} \Psi_{\vec{k},j}(\vec{r} + \vec{R}) &= \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} e^{i\vec{k}(\vec{R}-\vec{R})} \phi_j(\vec{r} - (\vec{R} - \vec{R})) \\ &= e^{i\vec{k}\vec{R}} \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi_j(\vec{r} - \vec{R}) = e^{i\vec{k}\vec{R}} \Psi_{\vec{k},j}(\vec{r}) \end{aligned} \quad (2.3)$$

where $\vec{R} = \vec{R} - \vec{R}$ and $j = l\mu s$ are used to simplify the notation. In a solid, the crystal wave functions $\Psi_{\vec{k}}(\vec{r})$ can be expressed as a linear combination of Bloch functions:

$$\Psi_{\vec{k}}(\vec{r}) = \sum_{j=1} A_{\vec{k},j} \psi_{\vec{k},j}(\vec{r}) \quad (2.4)$$

The eigenvalues for the system described by the Hamiltonian is given by

$$E_{\vec{k}} = \frac{\langle \Psi_{\vec{k}} | H | \Psi_{\vec{k}} \rangle}{\langle \Psi_{\vec{k}} | \Psi_{\vec{k}} \rangle} = \frac{\int \Psi_{\vec{k}}^*(\vec{r}) H \Psi_{\vec{k}}(\vec{r}) d\vec{r}}{\int \Psi_{\vec{k}}^*(\vec{r}) \Psi_{\vec{k}}(\vec{r}) d\vec{r}} \quad (2.5)$$

Now, substituting $\Psi_{\vec{k}}(\vec{r})$ as defined in Eq.2.4 leads to

$$E_{\vec{k}} = \frac{\sum_{i,j} A_{\vec{k},i}^* A_{\vec{k},j} \langle \psi_{\vec{k},i}(\vec{r}) | H | \psi_{\vec{k},j}(\vec{r}) \rangle}{\sum_{i,j} A_{\vec{k},i}^* A_{\vec{k},j} \langle \psi_{\vec{k},i}(\vec{r}) | \psi_{\vec{k},j}(\vec{r}) \rangle} = \frac{\sum_{i,j} A_{\vec{k},i}^* A_{\vec{k},j} H_{i,j}(\vec{k})}{\sum_{i,j} A_{\vec{k},i}^* A_{\vec{k},j} S_{i,j}(\vec{k})} \quad (2.6)$$

where $H_{i,j}(\vec{k})$ and $S_{i,j}(\vec{k})$ are transfer and overlap matrices, respectively, and defined by

$$H_{i,j}(\vec{k}) = \langle \psi_{\vec{k},i}(\vec{r}) | H | \psi_{\vec{k},j}(\vec{r}) \rangle \quad (2.7)$$

$$S_{i,j}(\vec{k}) = \langle \psi_{\vec{k},i}(\vec{r}) | \psi_{\vec{k},j}(\vec{r}) \rangle \quad (2.8)$$

Above Eq.2.6 can be solved by minimizing the eigenvalues $E_{\vec{k}}$, when the coefficients $A_{\vec{k},j}$ are optimized such that

$$\frac{\partial E_{\vec{k}}}{\partial A_{\vec{k},i}^*} = \frac{\sum_j H_{i,j}(\vec{k}) A_{\vec{k},j}}{\sum_{i,j} S_{i,j}(\vec{k}) A_{\vec{k},i}^* A_{\vec{k},j}} - \frac{\sum_{i,j} H_{i,j}(\vec{k}) A_{\vec{k},i}^* A_{\vec{k},j}}{(\sum_{i,j} S_{i,j}(\vec{k}) A_{\vec{k},i}^* A_{\vec{k},j})^2} \sum_j S_{i,j}(\vec{k}) A_{\vec{k},j} = 0 \quad (2.9)$$

Multiply both sides in Eq.2.9 by $\sum_{i,j} S_{i,j}(\vec{k}) A_{\vec{k},i}^* A_{\vec{k},j}$, we get:

$$\sum_j H_{i,j}(\vec{k}) A_{\vec{k},j} - \frac{\sum_{i,j} H_{i,j}(\vec{k}) A_{\vec{k},i}^* A_{\vec{k},j}}{\sum_{i,j} S_{i,j}(\vec{k}) A_{\vec{k},i}^* A_{\vec{k},j}} \sum_j S_{i,j}(\vec{k}) A_{\vec{k},j} = 0 \quad (2.10)$$

Given the expression of $E_{\vec{k}}$ in Eq.2.6, and non-trivial solutions require

$$\sum_j [H_{i,j}(\vec{k}) - \varepsilon_{\vec{k}} S_{i,j}(\vec{k})] c_{\vec{k},j} = 0 \quad (2.11)$$

This equation is known as the secular equation, in which eigenvalues $E_{\vec{k}}$ give the band structures.

2.1.2 Classification of Slater-Koster integrals

Consider $V(r)$ as the single-particle potential in the Hamiltonian $\hat{H}$,

$$V(\vec{r}) = \sum_{\vec{R},l} v_l(\vec{r} - \vec{t}_l - \vec{R}) \quad (2.12)$$

Where the atomic potential v_l is located in the l th atom. Substituting $V(r)$ into Eq.2.11, the integrals of potentials will depend upon the coordinates of sites and involve in three different components: the potential at $\vec{t}_l$ and the two atomic-like wave functions $\Psi_{\vec{k},j}(\vec{r})$ and $\Psi_{\vec{k},i}(\vec{r})$. They can be classified into the following categories:

1. One-center, in which all three locations are on the same site.
2. Two-center, in which the potential locates in one of coordinates of the wave functions and orbitals are located in individual sites.
3. Three-center, in which the potential and locates in different sites, as well as the wave functions.
4. The fourth class exists when the wave functions both centered in the same sites but the potential is located in a different site.

2.1.3 Slater-Koster (SK) approximation

The crucial factor in SK approximation is to deal with the integrals using a simplified parameter which determined by only the atomic space and the involved symmetry of

the orbitals. Suggested by Slater and Koster, the potentials $v_l(\vec{r})$ should be spherically symmetric. The Hamiltonian matrix elements are proposed to be approximated within the two-centre form by neglecting the three-centre integrals [108].

This approximation offers a simple but reasonable picture of electronic states. Within this two-centre approximation, the integrals are determined by only the displacement between the two sites,

$$h_{\alpha\beta}^{ij} = \int \phi_{i\alpha}^*(\vec{r} - \vec{\chi}) H_{\alpha\beta} \phi_{j\beta}(\vec{r}) d^3r \quad (2.13)$$

$H_{\alpha\beta}$ is the two-center Hamiltonian. Obviously, the integrals depend only on the direction of $\vec{\chi}$, the distance between sites ($\chi = |\vec{\chi}|$), and the angular momentum. Slater and Koster provided 14 SK parameters, if the atomic orbitals ϕ_i are contained to s , p , and d orbitals. To simplify the discussion, here we adopted the notation $H_{ab\gamma}(\vec{\chi})$, with the angular momenta a and b instead of s , p , d and $\gamma = \sigma, \pi, \delta$ denoting the angular momentum relative to $\vec{\chi}$. When the two atoms are identical, ten independent parameters are reserved since four pairs will be disappeared due to the symmetry. For example, in transition metals, we then have 10 parameters: $ss\sigma$, $sp\sigma$, $sd\sigma$, $pp\sigma$, $pp\pi$, $pd\sigma$, $pd\pi$, $dd\sigma$, $dd\pi$ and $dd\delta$. In a binary alloy AB, there are, in addition to the ten parameters cited before, $ps\sigma$, $ds\sigma$, $dp\sigma$ and $dp\pi$.

2.2 Density Functional Theory (DFT)

Considering a periodic system including N electrons and M nuclei with the positions of electrons $\vec{r}_i$ and nuclei $\vec{R}_A$, the Hamiltonian operator can be expressed as follows in atomic units,

$$H = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{p=1}^M \frac{1}{2M_p} \nabla_p^2 - \sum_{i=1}^N \sum_{p=1}^M \frac{Z_p}{r_{ip}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{p=1}^M \sum_{q>p}^M \frac{Z_p Z_q}{R_{qp}} \quad (2.14)$$

where M_p stands for the mass ratio between nuclei and electrons; Z_p is the charge of nucleus p ; R_{qp} and r_{ij} are the distance between two nuclei and between two electrons, respectively. In the right part of Eq.2.14, these terms represent the kinetic energy operator

of the electrons and nuclei, the Coulomb interaction between nuclei and electrons, as well as Coulomb repulsions between electrons and between nuclei.

2.2.1 Born-Oppenheimer Approximation

Since the mass ratio between nuclei and electrons is extremely high, one can consider that the electrons equilibrate in the field of “frozen” nuclei, which named as Born-Oppenheimer approximation. For such approximation, the kinetic energy for nuclei (the second item in Eq.2.14 can be neglected and the Coulomb interactions among nuclei (the last item in Eq.2.14 degenerate to a constant. The rest of items in Eq.2.14 are formally written as,

$$H = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{p=1}^M \frac{Z_p}{r_{ip}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (2.15)$$

which stands for N electrons running within the potential encased by the “frozen” nuclei and interacting each other.

Despite the above approximation, the electron-electron interactions remain complex. In practice, the motion of electrons is correlated with involving spin states. In solving electronic Schrödinger equations, there are two main approaches. One is to find the solution expressed in the many-electron wave functions $\Psi = \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ ($\vec{r}_i$ represents the electron coordinates including spins), such as the Hartree-Fock theory. An alternative method to solve Eq.2.15 is using the electron density in a system, which termed as Density-Functional Theory (DFT).

2.2.2 Hartree-Fock (HF) method

Within Hartree approximation, the Hamiltonian for N particles is simply the gross of the Hamiltonians of single-particle and the wavefunction Ψ is the product of wavefunctions of each particle,

$$H = \sum_i^N h(i) \quad (2.16)$$

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \psi(\vec{r}_1) \psi(\vec{r}_1) \cdots \psi(\vec{r}_N) \quad (2.17)$$

where $h(i)$ is the Hamiltonian describing the kinetic energy and external potential for the i th electron.

Therefore, the Schrödinger equation for one particle can be rewritten as:

$$\left(-\frac{1}{2}\nabla^2 + V(\vec{r}_i)\right)\psi(\vec{r}_i) = \varepsilon\psi(\vec{r}_i) \quad (2.18)$$

Since electrons are fermions, the wavefunctions should be anti-symmetric concerning the exchange for every pair of particles, in other words, the Hartree product takes no account of the indistinguishability of electrons. To add the exchange energy to the Hartree equation, one may construct the wavefunctions by one single Slater determinant using a linear combination of the wavefunctions, instead of the product of them. In N -electron systems the generalization of the Slater determinant is

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \cdots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \psi_2(\vec{r}_2) & \cdots & \psi_2(\vec{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\vec{r}_1) & \psi_N(\vec{r}_2) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix} \quad (2.19)$$

where $\frac{1}{\sqrt{N!}}$ is a normalization factor. Such Slater determinant in Eq.2.19 describes N electrons possessing N spin states $(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ without showing which electron locates in which orbital. One can easily check that Slater determinants meet the requirement of the anti-symmetry principle (or Pauli Exclusion Principle). It also implies that Slater determinants incorporate exchange energies in a system.

Based on the variational principle, the ground state energies are obtained through minimising the total energy with respect to the spin orbitals, which have to remain orthogonal. Using the variational method, the single-particle Hartree-Fock equations for a given orbital, λ , can be defined as

$$\left\{-\frac{1}{2}\nabla^2 + V_{e-ion}(\vec{r}) + V_H(\vec{r}) + V_\lambda^{ex}(\vec{r}) - E_\lambda\right\}\psi_\lambda(\vec{r}) = \sum_{\mu \neq \lambda} E_{\lambda\mu} \psi_\mu(\vec{r}) \quad (2.20)$$

$$V_H(\vec{r})\psi_\lambda(\vec{r}) = \int \frac{n(\vec{r}_1)\psi_\lambda(\vec{r})}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 \quad (2.21)$$

$$V_\lambda^{ex}(\vec{r})\psi_\lambda(\vec{r}) = \int \psi_\mu^*(\vec{r}_1)\psi_\lambda(\vec{r}_1) \frac{1}{|\vec{r} - \vec{r}_1|} \psi_\mu(\vec{r}) d\vec{r}_1 \quad (2.22)$$

In Eq.(2.20), the former two items describe the kinetic and potential energies. The third item means the Coulomb energy: the Coulomb interaction between one electron and the average potential of other electrons. Thus, the Hartree-Fock theory is considered as a mean field theory. The fourth term is the exchange energy due to the antisymmetric features of the wavefunctions. The solution for the Hartree-Fock equation depends on the chosen spin orbitals. Initial spin orbitals are given, they are refined through the variational method iteratively. Therefore, the Hartree-Fock approximation is also known as a self-consistent-field. The exact solution to the Hartree-Fock equation is obtained only if we know the exact spin orbital.

2.2.3 Hohenberg-Kohn theorem

Due to the complexity of computing Eq.2.20 within the HF approach, introduced in 1964 [119] and then developed later in 1965 [120], DFT reduced the solution of the many-electron problem to a self-consistent solution for a group of single-electron equations.

In DFT, the electron density for a system is given by,

$$\rho(\vec{r}) = N \int d\vec{r}_2 d\vec{r}_3 \cdots \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) \psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) \quad (2.23)$$

Such equation was presented based on two Hohenberg-Kohn theorems. According to the first theorem, the external potential $V(\vec{r})$ can be viewed as the unique functional of the electron density $\rho(\vec{r})$, except a trivial constant. It indicates that the electron density $\rho(\vec{r})$ for the ground state and the Hamiltonian in a system are corresponding one by one.

As mentioned above, the energy for the ground state can be expressed in terms of the

electron density $\rho(\vec{r})$

$$\begin{aligned} E[\rho] &= T[\rho] + E_{ne}[\rho] + E_{ee}[\rho] \\ &= \int \rho(\vec{r})v(\vec{r})d\vec{r} + F_{HK}[\rho] \end{aligned} \quad (2.24)$$

where $T[\rho]$ is the functional of kinetic energies; $E_{ne}[\rho]$ and $E_{ee}[\rho]$ are the functional of nuclei-electron interaction energies and electron-electron interaction energies, respectively; $F_{HK}[\rho]$, independent of any external potential, is a universal functional of $\rho(\vec{r})$ that is applicable for any arbitrary systems.

The second Hohenberg-Kohn theorem claims the minimum $E[\rho]$ yielding the correct density $n(\vec{r})$, under the charge conservation condition,

$$N[\rho] = \int \rho(\vec{r})d\vec{r} = N \quad (2.25)$$

This theorem can be mathematically expressed via the variational principle. For a trial density $\rho_1(\vec{r}) > 0$, such that $\int \rho_1(\vec{r})d\vec{r} = N$, one will have

$$E_0 \leq E[\rho_1] \quad (2.26)$$

where $E[\rho_1]$ represents the energy functional and E_0 indicates the ground-state energy. It indicates that the ground-state electron density equals to the density which minimizes the energy functional $E[\rho]$.

Once the universal functional $F_{HK}[\rho]$ is given and sufficiently simple, the ground state energies for the many-body system in an external potential can be easily obtained. However, the main complexity of many-electron problems in practice is always accompanied by the explicit forms for the universal functional $F_{HK}[\rho]$.

2.2.4 Kohn-Sham equations

One still has to face the full intricacies for the many-electron puzzle, as the Hohenberg-Kohn methods offer no accessible hints to the explicit forms of the universal functional $F_{HK}[\rho]$. The extensive practical implementation of the DFT was proposed through Kohn-

Sham approach. In the scheme of Kohn-Sham method, the complicated many-body problem is then simplified to a simpler problem of non-interaction fictitious particles moving in a proper, fictitious and density-dependent potential $V_{eff}(r)$. This allows a Hamiltonian of the form

$$H_{KS} = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_i^N V_{eff}(\vec{r}) = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 + V_{eff}(\vec{r}) \right) = \sum_i^N h_{si} \quad (2.27)$$

Since the Hamiltonian can be expressed as a summation of the Hamiltonians of single electrons (similar to the Hartree method), the many-electron Schrödinger equation can be simplified to a one-electron Schrödinger equation, called Kohn-Sham equation,

$$h_s \psi_i = \left[-\frac{1}{2} \nabla^2 + V_{eff}(r) \right] \psi_i = \varepsilon_i \psi_i \quad (2.28)$$

where h_s denotes the one-electron Hamiltonian; ε_i and ψ_i represent the orbital energy and wavefunction for an electron occupying the state i . The exact ground-state wavefunctions for an N -electron system are described by the determinant of the occupied spin orbitals:

$$\psi_s = \frac{1}{\sqrt{N!}} \det |\psi_1 \psi_2 \cdots \psi_N| \quad (2.29)$$

The ground-state electron density $\rho(\vec{r})$ can be given by the N occupied orbitals ψ_i

$$\rho(\vec{r}) = \sum_{i=1}^N \left| \psi_i(\vec{r}) \right|^2 \quad (2.30)$$

The kinetic energy functional $T_s[\rho]$ for the reference system is

$$\begin{aligned} T_s[\rho] &= \langle \psi_s | \sum_{i=1}^N -\frac{1}{2} \nabla_i^2 | \psi_s \rangle \\ &= \sum_{i=1}^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle \end{aligned} \quad (2.31)$$

where the kinetic energy $T_s[\rho]$ means the non-interacting particles in the ground state with density $\rho(\vec{r})$, rather than the real kinetic energy of the interacting electron systems

$T[\rho]$. Thus, the universal functional $H_{HK}[\rho]$ is rewritten as

$$\begin{aligned} F_{HK}[\rho] &= T[\rho] + E_{ee}[\rho] \\ &= T_s[\rho] + J[\rho] + (T[\rho] - T_s[\rho] + E_{ee}[\rho] - J[\rho]) \\ &= T_s[\rho] + J[\rho] + E_{xc}[\rho] \end{aligned} \quad (2.32)$$

where $J[n]$ represents the classical electron Coulomb interaction,

$$J[\rho] = \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \quad (2.33)$$

where $E_{xc}[\rho]$ denotes the so called exchange-correlation energy,

$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \quad (2.34)$$

where the exchange-correlation energy $E_{xc}[\rho]$ includes two parts. The first part arises from the correction of the kinetic energy for the fictitious system without interactions (the former two terms in Eq.2.34). The other part comes from non-classical effects for the electron-electron interactions (the latter two terms in Eq.2.34). Kohn-Sham effective potential $V_{eff}(r)$ in Eq.2.28 is defined as

$$\begin{aligned} V_{eff}(\vec{r}) &= V(\vec{r}) + \frac{\partial J[\rho]}{\partial \rho(\vec{r})} + \frac{\partial E_{xc}[\rho]}{\partial \rho(\vec{r})} \\ &= V(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}(\vec{r}) \end{aligned} \quad (2.35)$$

In the above equation, $V(r)$ describes the external Coulomb potential for nuclei. The second term in the right-hand side,

$$\frac{\partial J[\rho]}{\partial \rho(\vec{r})} = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (2.36)$$

is the potential resulted from the electron-electron Coulomb repulsion. The last term,

$$V_{xc}(\vec{r}) = \frac{\partial E_{xc}[\rho]}{\partial \rho(\vec{r})} \quad (2.37)$$

is named as the exchange-correlation potential.

From Eq.2.37 the effective potential $V_{eff}(r)$ is found as the functional of the electron density $\rho(r)$. In other words, the Hamiltonian term in Eq.2.28 itself depends on the electron density $\rho(r)$. Thus, the Kohn-Sham equation could be solved through employing self-consistent methods. The computation scheme of Kohn-Sham approach is shown in the flowchart in Fig.1.2. One constructs first a guessing density $\rho_0(r)$. Then the effective potential $V_{eff}(r)$ is calculated through Eq.2.35 based on the initial density $\rho(r)$. Subsequently, use this effective potential to construct the Kohn-Sham equation in Eq.2.28. By solving Eq.2.28 one obtains a new electron density $\rho(r)$ via the Eq.2.30. This new electron density $\rho(r)$ is then compared with $\rho_0(r)$ and then the above procedures iterate. Once the convergence is achieved, one can compute the energy of the system through above equations.

2.2.5 Local Density Approximation (LDA)

The Kohn-Sham procedure induces a one-body-like Hamiltonian, which has the natural interpretation as describing "electrons" in the effective mean field. The exact format of the exchange correlation energy, however, is unclear. Even if it is known, it is probably so complicated that it is not manageable in practical calculations. Practical calculations require further approximations.

One of the most common approximations should be the Local Density Approximation (LDA). By given the exchange-correlation energy density $\varepsilon_{xc}([n]; \vec{r})$, then

$$E_{xc}[n] = \int dr n(\vec{r}) \varepsilon_{xc}([n]; \vec{r}) \quad (2.38)$$

We assume that the system locally appears as the homogeneous electron gas. We can split $\varepsilon_{xc}([n]; \vec{r})$ as composed of $\varepsilon_{xc}^{hom o}(n) = \varepsilon_x^{hom o}(n) + \varepsilon_c^{hom o}(n)$ with $\varepsilon_x^{hom o}(n)$ bare

Figure 2.1: The calculation flowchart in Kohn-Sham DFT.

exchange and $\epsilon_c^{\text{hom } o}(n)$ correlation energy density. While $\epsilon_x^{\text{hom } o}(n)$ is an analytic function of n , *e.g.* $\epsilon_x^{\text{hom } o}(n) = -\frac{3}{4}[\frac{3n}{\pi}]^{1/3}$, the correlation part can be obtained approximately using Many-Body perturbation theory [121] or via quantum Monte Carlo methods [122]. The first method gives an analytic function of n while the results from numerical Monte Carlo have been metrized by, *e.g.*, Perdew and Zunger [123].

2.3 Many-body Perturbation Theory

Given the poor performance of DFT for the calculation of excited properties, such as photoemission, electron loss spectrum, and optical absorption, *etc*, many-body perturbation theory (MBPT) has showed as an invaluable tool over recent decades which based upon a group of Green's function equations, by starting from a single-particle propagator. One term named as “self-energy” Σ is critical for describing the electron-hole interaction. An elegant approximation for Σ was constructed by Hedin, which is known as the GW

approximation (GWA), by introducing the concept of “quasiparticles” (QP) consisting of screen charge and bare electron. Based on the single-particle Green’s function (G), the self-energy of quasiparticles will be expanded linearly as the Coulomb screening (W), $\Sigma \approx GW$, which implies the name of this approximation. To go beyond simple DFT, the GW approximation offers a satisfactory picture of band structure in semiconductors and insulators.

When considering the optical absorption of semiconductors, the above GW is not enough. In this case, the excited particles interact with each other and form the exciton or e - h pair. In this situation, we need to construct the two-particle Green’s functions and the corresponding equations are named as the Bethe-Salpeter equation (BSE) [124, 125, 126]. The derivation of BSE can be thought as the second order expansion of the self-energy Σ .

In general, the whole first-principles MBPT (GW+BSE) can be divided into three steps: (i) the ground-state energy using DFT calculation; (ii) the quasiparticle excitations within the GW approximation; (iii) optical absorption spectra by solving the e - h interaction in the BSE. Following such scheme, the absorption spectra of various materials has been obtained and the calculation results match excellent with the experimental data [127, 128, 129, 130].

2.3.1 Hedin Equations

Still starting from the Schrödinger equation, we can easily split the many-body Hamiltonian into two parts: a single-particle term H° and a perturbation term Σ . i.e. $H = H^\circ + \Sigma$. Here $H^\circ = -\frac{1}{2}\nabla^2 + V_{ext} + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}$ denotes the non-interacting Hamiltonian including the kinetic energy, external potentials, and the Hartree energy. Σ is named as self-energy operator which consists of interactions among the electrons. By principle, the imaginary part of Σ is described as the finite lifetime for quasi-particles.

Introduced by Hedin [131], we can derive a series of coupled equations for Σ termed

as the screened Coulomb operator W , vertex function Γ , and polarization propagator P :

$$G(1, 2) = G^\circ(1, 2) + G^\circ(1, 3)\Sigma(3, 4)G(4, 2) \quad (2.39)$$

$$\Sigma(1, 2) = i\hbar \int d(3, 4)G(1, 4)W(1, 3)\Gamma(4, 2; 3) \quad (2.40)$$

$$W(1, 2) = v(1, 2) + \int d(3, 4)W(1, 3)P(3, 4)v(4, 2) \quad (2.41)$$

$$P(1, 2) = -i\hbar \int d(3, 4)G(2, 3)G(4, 2+)\Gamma(3, 4; 1) \quad (2.42)$$

$$\Gamma(1, 2; 3) = \delta(1, 2)\delta(1, 3) + \frac{\delta\Sigma(1, 2)}{\delta V(3)} \quad (2.43)$$

where $(1, 2)$ is the shorthand notation for a combined space and time coordinate, and v is the bare Coulomb interaction. Above five equations can be corporately defined as the Hedin equations, and in principle, G can be obtained self-consistently through iterating these coupled equations. Obviously, such iterations are hardly onerous for solving of G , and we need further approximation to these equations in practice.

2.3.2 GW approximation

The first approximation for the vertex function Γ is to consider only the zero order:

$$\Gamma(1, 2; 3) = \delta(1, 2)\delta(1, 3) \quad (2.44)$$

Within this approximation, the polarization P is given by

$$P(1, 2) = -i\hbar G(2, 1)G(1, 2+) \quad (2.45)$$

And the self-energy Σ adopted the form of $\Sigma(1, 2) = i\hbar G(1, 2)W(1^+, 2)$. This approximation is thus the well-known GW approximation. In practice, given a trial Green's Function G° , the Hedin equations are only calculated once to obtain the screening W° using the polarization $P^\circ(1, 2) = -i\hbar G^\circ(2, 1)G^\circ(1, 2+)$. This is the $G^\circ W^\circ$ approximation. Another approximation is re-evaluating the screening self-consistently, which named as

$G^\circ W$ approximation.

2.3.3 Bethe-Salpeter Equation (BSE)

As we mentioned early, when dealing with the e - h pair interaction, the picture of one-electron Green's function becomes not insufficient. The next order expansion for the self-energy beyond the GWA is needed and such movement for two-particle Green's function is described by Bethe-Salpeter equations (BSE).

The two-particle Green's function has the form as

$$G(1, 2; 1', 2') = -\langle N, 0 | T(\varphi(1)\varphi(2)\varphi^\dagger(2')\varphi^\dagger(1')) | N, 0 \rangle \quad (2.46)$$

Then the correlation function can be expressed as

$$L(1, 2; 1', 2') = [G(1, 2; 1', 2') - G(1, 1')G(2, 2')] |_{\omega=0} \quad (2.47)$$

This e - h correlation function fullfills a Dyson-like equation [125], i.e. BSE.

$$L(1, 2; 1', 2') = G(1, 2')G(2, 1') + \int G(1, 3)G(4, 1')K(3, 5; 4, 6)L(6, 2; 5, 2')d(3)d(4)d(5)d(6) \quad (2.48)$$

where $G(1, 2')G(2, 1')$ can be defined as the disconnected term $L_0(1, 2; 1', 2')$; $K(3, 4; 5, 6)$ denotes the e - h interaction kernel.

In practice, to make the solving of BSE accessible, we can adopt the expression for the self-energy using the single-particle wave functions as the 0 -order approximation. Then we rewrite L_0 in terms of wavefunctions of conduction band $\varphi_c(\vec{r})$ and valence band $\varphi_v(\vec{r})$:

$$L_0(1, 2; 1', 2'; \omega) = i \sum_{c,v} \left\{ \frac{\varphi_c(\vec{r}_1)\varphi_v^*(\vec{r}_1')\varphi_v(\vec{r}_2)\varphi_c^*(\vec{r}_2')}{(E_v - E_c) - \omega} - \frac{\varphi_v(\vec{r}_1)\varphi_c^*(\vec{r}_1')\varphi_c(\vec{r}_2)\varphi_v^*(\vec{r}_2')}{(E_v - E_c) + \omega} \right\} \quad (2.49)$$

and likewise, the correlation function L can be rewrite using the corresponding excitonic

wavefunctions:

$$L(1, 2; 1', 2'; \omega) = i \sum_{e-h} \left\{ \frac{\chi_{e-h}(\vec{r}_1, \vec{r}'_1) \chi_{e-h}^*(\vec{r}_2, \vec{r}'_2)}{\Omega_{e-h} - \omega} - \frac{\chi_{e-h}(\vec{r}_2, \vec{r}'_2) \chi_{e-h}^*(\vec{r}_1, \vec{r}'_1)}{\Omega_{e-h} + \omega} \right\} \quad (2.50)$$

where $\chi_S(\vec{r}, \vec{r}') = -\langle N, 0 | \varphi^\dagger(\vec{r}') \varphi(\vec{r}) | N, S \rangle$

As the valence (conduction) bands are occupied (empty) in semiconductors, the $e-h$ wave function $\chi_S(\vec{r}, \vec{r}')$ then be modified further as

$$\chi_S(\vec{r}, \vec{r}') = \sum_c^{\text{empty}} \sum_v^{\text{occ}} \{ A_{vc}^S \varphi_c(\vec{r}) \varphi_v^*(\vec{r}') + B_{vc}^S \varphi_v(\vec{r}) \varphi_v^*(\vec{r}') \} \quad (2.51)$$

Substituting above Eq.2.51 in Eq.2.48, the BSE is adopted as a generalized matrix form:

$$(E_c - E_v) A_{cv}^S + \sum_{c'v'} \{ K_{cv,c'v'}^{AA}(\Omega_S) A_{c'v'}^S + K_{cv,c'v'}^{AB}(\Omega_S) B_{c'v'}^S \} = \Omega_S A_{cv}^S \quad (2.52)$$

$$(E_c - E_v) B_{cv}^S + \sum_{c'v'} \{ K_{cv,c'v'}^{BB}(\Omega_S) B_{c'v'}^S + K_{cv,c'v'}^{BA}(\Omega_S) A_{c'v'}^S \} = -\Omega_S B_{cv}^S \quad (2.53)$$

In actual calculations, the off-diagonal blocks of K^{AB} or K^{BA} can be ignored. Thus, we obtain the simplified BSE form:

$$(E_c - E_v) A_{cv}^S + \sum_{c'v'} K_{cv,c'v'}^{AA}(\Omega_S) A_{c'v'}^S = \Omega_S A_{cv}^S \quad (2.54)$$

The diagonal blocks K^{AA} are given by

$$\langle cv | K^{AA, \vec{r}} | c'v' \rangle = \int d\vec{r} d\vec{r}' \varphi_c^*(\vec{r}) \varphi_v(\vec{r}) v(\vec{r}, \vec{r}') \varphi_{c'}(\vec{r}) \varphi_{v'}^*(\vec{r}') \quad (2.55)$$

The direct interaction term $K^{AA,d}$ are simplified by

$$\begin{aligned} \langle cv | K^{AA,d}(\Omega_S) | c'v' \rangle &= \int d\vec{r} d\vec{r}' \varphi_c^*(\vec{r}) \varphi_v(\vec{r}) v(\vec{r}, \vec{r}') \varphi_{c'}(\vec{r}) \varphi_{v'}^*(\vec{r}') \frac{i}{2\pi} \int d\omega e^{-i\omega 0^+} W(\vec{r}, \vec{r}', \omega) \\ &\times \left\{ \frac{1}{\Omega_S + i0^+ - (E_{c'}^{QP} - E_{v'}^{QP}) - \omega} + \frac{1}{\Omega_S + i0^+ - (E_c^{QP} - E_v^{QP}) + \omega} \right\} \end{aligned} \quad (2.56)$$

Using single-plasmon pole-model, a simplification for the screening can be given

$$W(\vec{r}, \vec{r}', \omega) = \sum_l W_l(r, r') \frac{\omega_l}{2} \left(\frac{1}{\omega + i0^+ - \omega_l} - \frac{1}{\omega - i0^+ + \omega_l} \right) \quad (2.57)$$

where ω_l stands for the Plasmon frequency.

Then Eq.2.56 becomes:

$$\begin{aligned} \langle cv | K^{AA,d}(\Omega_S) | c'v' \rangle = & - \sum_l \int d\vec{r} d\vec{r}' \varphi_c^*(\vec{r}) \varphi_v(\vec{r}) \varphi_{c'}(\vec{r}) \varphi_{v'}^*(\vec{r}') W_l(\vec{r}, \vec{r}') \\ & \times \frac{\omega_l}{2} \left\{ \frac{1}{\omega_l - [\Omega_S - (E_{c'}^{QP} - E_{v'}^{QP})]} + \frac{1}{\omega_l - [\Omega_S - (E_c^{QP} - E_v^{QP})]} \right\} \end{aligned} \quad (2.58)$$

Since $\omega_l \gg \Omega_S - (E_c^{QP} - E_v^{QP})$ for most semiconductors, above equation for the interaction kernel can be changed to

$$\langle cv | K^{AA,d} | c'v' \rangle = - \int d\vec{r} d\vec{r}' \varphi_c^*(\vec{r}) \varphi_v(\vec{r}) \varphi_{c'}(\vec{r}) \varphi_{v'}^*(\vec{r}') W_l(\vec{r}, \vec{r}', \omega = 0) \quad (2.59)$$

Until now, all items in BSE calculations have been specified. Clearly, the BSE for the inclusion of e - h interactions is a simple extension of the GWA beyond the single-particle picture. The flowchart of a whole MBPT calculation is shown in Fig.2.2. The calculation starts from DFT, solving the Kohn-Sham equations which include the electron exchange and correlations by using approximated functionals such as LDA. The solutions of Kohn-Sham equations are then applied to build up the one-particle Green's function and static dielectric matrix at the 0th order. Using the GPP model, the frequency-dependent dielectric matrix is constructed and the dynamic screening is obtained. After the RPA, the self-energy is obtained by the GWA as product of the one-particle Green's function and screened Coulomb interactions. Then the QP equations are solved with the self-energy replacing the LDA approximated functionals. As the self-energy lies on the QP energies, it can first use Kohn-Sham energies as the 0th-order input, and then solve the QP energies by the self-consistent scheme. For the optical excitations of e - h pairs, the QP energies and wavefunctions are used to calculate the interaction kernel with the dynamic screening. In realistic calculations, QP wavefunctions are approximated by the Kohn-

Sham wavefunctions since they are very close to each other for most materials. With the interaction kernel and the Tamm-Dancoff approximation [129], the BSE is solved and the excitation energies and the e - h amplitudes are obtained. Finally, based on the BSE solutions, the optical absorption spectrum can be evaluated including the coupling coefficients of e - h amplitudes.

Figure 2.2: The flowchart of MBPT in calculating the QP band structure and optical absorption spectra.

Chapter 3

Stacking transformation in trilayer graphene

3.1 Introduction

Single layer graphene, as well as its bilayer counterpart, have attracted intense attention due to its unique electronic structures [132, 133, 134] and huge application potential in high frequency electronics [135], flexible display screens [136, 137] and sensors [138, 139]. In sharp contrast, trilayer graphene and other thicker few layer graphene just began to attract increasing attention [140, 141, 142, 43, 143, 144, 145] since the stacking configuration of graphene offers one more degree of freedom for managing the electronic properties [146, 147, 148, 149]. The Bernal (i.e. ABA) and rhombohedral (i.e. ABC) stacking orders are known as the most two stable crystallographic configurations. While ABA-stacking trilayer graphene remains semi-metallic, ABC-stacking trilayer is predicted to be semiconducting with a tuneable band gap by an applied electric field [150, 143, 144, 145]. The graphene trilayers are considered to present various behaviour at low energies near the Fermi level because of competing symmetries and different interlayer interactions [144]. Although people believe that ABA-stacking order is the most favourable phase, ABC-stacking graphite were found to be steady and still maintain their stacking orders in practice, even at a high temperature [151, 152], *e.g.* 1000-1200 °C. These experimental

findings reveal an insurmountable energy barrier between ABC- and ABA-stacking order through the thermal transformation. Such huge energy barriers from ABC- to ABA-stacking graphene is reduced by our experimental collaborators via triazine decoration [153]. Previously, they have reported that 1,3,5-triazine molecule, which is abbreviated as triazine in the following discussion, can be formed one homogeneous film on the bilayer graphene and open the band gap due to the induced inversion asymmetry [154]. Inspired by that, they thermally deposited triazine molecules onto the trilayer graphene sample under 150 °C for 7 hours in a vacuum chamber. As presented in Fig.3.1(a), the Raman 2D FWHM mapping for the selected area of a pristine trilayer graphene are given, as well as AFM topology images in Fig.3.1(b). Fig.3.1(c) and (d) are shown as the corresponding results for the same area after triazine decoration. It is observed that the ABA domains still maintain as the ABA-stacking order after triazine decoration. However, the area identified originally as the ABC has converted to ABA, which is labelled as “X”. It could be directly explained by the fact of the lower energy of ABA domains compared with that of ABC domains. Interestingly, as shown in the triangle area in Fig.3.1, the new formed ABA domains always operates starting from the original ABA domains. Fig.3.1(e) and (f) present the Raman mapping and AFM image for the triazine decorated sample after annealing at 500 °C for 5 hours, where the ABA and ABC domain remain their original stacking order with that of before triazine removal. It is therefore concluded that the converted ABA-domain is very stable, even after thermal annealing at 500 °C.

3.2 Method and model

To shed the lights on the mechanism behind the observed ABC- to ABA-stacking transformation, our simulations are carried out using various calculation methods, such as the density functional theory (DFT) calculations [119, 120], van der Waals density functional (vdW-DF) approximation [155], density functional tight binding-molecular dynamics (DFTB-MD) approach [156, 157], as well as the adiabatic-connection fluctuation-dissipation theory based on the random-phase approximation (ACFDT-RPA) [158, 159,

Figure 3.1: The stacking order transformation from ABC to ABA in trilayer graphene. Left panel: Raman mappings of 2D band FWHM for pristine sample, after the triazine deposition and then after thermal annealing at 500 °C for 5 hours, respectively. Right panel: the corresponding AFM images, respectively. The black dotted lines indicate the boundaries separated the ABA and ABC domains in trilayer graphene.

160]. We will first discuss the possible configurations including both ABA and ABC domains which is important to our further simulation and discussions. Fig.3.2(a) presents schematically three possible constructions for an ABA/ABC structure. In such structures, the carbon atoms in ABA (or ABC) domains need to move along the armchair direction by $2.84 + 2.65 \times n$ Å ($n = 0, 1, 2, 3, \dots$) as present in Fig.3.2(b), where the 2.84 Å means two carbon bonds. Model I shows that the additional third layer on top of the continuous Bernal stacking bilayer is discontinuous and divided by a little gap. The model II represents that a grain boundary (GB) is used to connect the ABA and ABC domains, which mainly are constitutive of pentagon and octagon carbon rings to compromise the junction between two domains. The model III shows that the two domains are constructed from a continuous third layer of grapheme through a wrinkle. In such model, a wrinkle is used to reconcile the $2.84 + 2.65 \times n$ Å movement between the two different domains. Raman cannot identify these models due to the limit of spatial resolution and AFM as well. However, simulations can help to differentiate understand the observed transformation.

Figure 3.2: Identification of the layer stacking of trilayer graphene which contains both ABA- and ABC-domains.

We have compared the formation energies for possible configurations which include

ABA and ABC domains in Fig.3.2(c). The first-principles calculations were carried out by using the plane wave basis Vienna *ab initio* simulation package (VASP) code [161]. The projector augmented wave (PAW) method was adopted to describe electron-ion interactions and the exchange correlation potential was given by the generalized-gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) form [123]. A plane-wave basis set with a cut-off of 400 eV was set. The calculated models contain a trilayer graphene with a wrinkle of 224 atoms and one vacuum region of 10 Å and two hydrogen atoms terminated at the edges of top layer. The formation energy is given as: $E_f = E_{system} - mE_C - nE_H$, where E_C indicates the total energy for bulk graphite; E_H is the total energy for hydrogen molecule. Compared with other models, the Model II that is separated by various point defects, i.e. 5-5-8-5-5 grain boundary, is energetically unfavourable. Note that we use $n = 0$ in the calculation of E_f since the other cases (i.e. $n > 0$) would introduce more defects and become even less stable. In many bulk materials, point defects, *e.g.* vacancies and interstitials, are attracted by the strained grain boundaries and then concentrated therein, which in turn might block the GB migration. As for the case of graphene, T. Yu *et al.* found that the tensile strain could induce G and 2D modes softening near GB regions in the trilayer graphene [161, 162, 163, 164]. Nevertheless, in the case of graphene the GB migration is challenging since such process involves a series of damaging and recombining of the carbon bonds in the pentagon or octagon carbon rings. Even vacancies in the GB region can diffuse and coalesce under a high temperature, *e.g.* 2000K, which is much higher than the temperature we have adopted [40]. Thus the Model II is very unlikely and can be excluded. For the Model III with a wrinkle, a wrinkle in third top layer graphene was constructed first. We then minimized the model energy using DFT calculations and found the wrinkle with a separation when $n = 3$ is the most favourable. For purposes of comparison, the Model I with a separated gap is also constructed using $n = 3$. Clearly, the Model III possesses a slight lower formation energy than the Model I.

After identification of the trilayer model, we now consider the configuration of the model when absorbing the triazine molecules. As listed in Table 3.1, we compared the

total energies for one triazine adopted in the different orientation (parallel or perpendicular with the graphene sample) for both ABA- and ABC-stacking domains. We explored the most stable adsorption positions for comparison. As expected, triazine molecules prefer to parallel to a trilayer graphene sample, regardless of the stacking order.

Table 3.1: Comparison of the total energy (eV) for one triazine molecule deposited onto the ABA- and ABC-stacking graphene.

	ABA	ABC
Perpendicular	-1014.785	-1014.785
Parallel	-1015.463	-1015.459

3.3 MD simulation results

Next, we have performed the MD simulation to reveal the structural evolution of trilayer graphene after triazine decoration at 500 K, as shown in Fig.3.3(a). For the simulation study, trilayer graphene flakes with a wrinkle grain boundary were calculated by the DFTB-MD method [156, 157]. The simulation system is coupled to an Andersen thermostat in order to maintain an invariant temperature of 500 K. A small time step of 0.1 *fs* is adopted to ensure the integration stability for the higher frequency C-H stretch vibrations. The model containing 1076 atoms was initially constructed according to the reliability. The triazine molecules are adopted with the most stable configurations for ABC- and ABA-domains, where carbon atoms in triazine molecules overlap with graphene lattice. The van der Waals interaction between the atoms is took into account via a Lennard-Jones potential.

After the triazine molecules deposition, the triazine molecules above the wrinkle region in the ABA/ABC trilayer model start to tilt and provide a chief driving force to move the wrinkle towards ABC domains, leading to the instability of the ABC domains. For the ABA domains, the atomic stacking shows little remarkable modification, as present in Fig.3.3(b). Unlike the stable ABA domains, the atomic arrangements of carbon atoms in the ABC domains show a significant shift. This can be understood that the small movement of the wrinkle induce the carbon atoms in the third layer in ABC domains

Figure 3.3: MD simulations for the structural evolution of trilayer graphene after triazine decoration at 500 K. (a) Atomic configurations of the model at 0 *ps*, (solid trace) and 30 *ps* (shaded trace). Atomic colours are shown as: H, white; C, cyan; N, blue. (b) Top view of configurations of trilayer graphene during the MD simulation at the wrinkle region. For clarity, the triazine molecules are not shown.

deviating from their original sites, which serves as the final conversion from ABC to ABA domains. As for the Model I, to interpret the growth-like behaviour of ABA domains as observed in Fig.3.1, one would expect to move the carbon atoms in the top layer graphene at the edge of ABC domains by widening the gap, which is not consistent with our experimental observations. Therefore, the Model I is excluded. As for our observed smooth and incremental transformations, the model that separated the ABA- and ABC-stacking domains by a wrinkle is the most reasonable configuration.

3.4 Discussion

To further reveal the role of triazine molecules, we have performed DFT calculations to investigate whether the conversion from ABC to ABA domains is favourable from an energetic standpoint. Our LDA results show that the energy difference between pristine ABA and ABC domains is 4 meV and the value is doubled to 8 meV after triazine deposition, as listed in Table 3.2. However, when we introduce the vdW correction using van der Waals density functional (vdW-DF) method, the energy difference between ABA- and ABC-domains is 35 meV (68 meV) before (after) triazine deposition. We accounted for the non-local correlation energies by employing the vdW density functional method. As a benchmark, we have also calculated the energy difference between ABA- and ABC-stacking trilayer graphene (6 carbon atoms per unitcell) by using the adiabatic-connection fluctuation-dissipation theory within the random-phase approximation (ACFDT-RPA). The in-plane lattice constant and the interplane distance along the stacking direction are both adopted the experimental values (2.46 Å and 3.34 Å), while the trilayer graphene slabs were separated by a vacuum layer of 10 Å. Hence, only one variable is involved in the energy difference, i.e. stacking sequence. Following Dobson’s recipe [165], for the Hartree-Fock part we adopted a high plane wave cut-off of 800 eV and 600 eV for the correlation part. For the HF part, $16 \times 16 \times 2$ k -grid was used. In the Fig.3.4, the energy difference between ABA- and ABC-stacking trilayer graphene unitcell is shown as a function of k -point mesh. Like the graphene RPA results [166], our calculated RPA

energy starts to converge also at $8 \times 8 \times 1$ k -point grid where the energy difference is 0.6 meV in favour of the ABA-stacking. Such a stacking preference is consistent with our LDA results using the large supercell model (4 meV in favor of the ABA-stacking).

Table 3.2: The energy difference (eV) between ABA and ABC domains with or without the triazine molecule decoration computed within the VdW-DF approach compared with LDA calculations.

	LDA	VdW-DF
$\Delta E_{(ABA-ABC)}$ without triazine	-0.004	-0.035
$\Delta E_{(ABA-ABC)}$ with triazine	-0.008	-0.068

Figure 3.4: k -point convergence of the energy difference between ABA- and ABC-stacking trilayer graphene.

On the other hand, we note that the triazine molecules prefer to adopt the C-top configuration: the nitrogen atoms of the molecules lie upon the hollow of carbon rings of the third graphene layer. For ABA domains, the triazine molecules thus construct an additional fourth layer within Bernal-like stacking order, i.e., ABAB. For ABC domains, the additional molecule layer with the underneath rhombohedral trilayer graphene will be arranged into ABCA or ABCB configurations. Such intuitive picture maybe serves as a plausible explanation for the increased energy difference.

3.5 Summary

The goal of our study is not only at understanding, but also at controlling. The results indicate that the electronic properties of graphene can be controlled by simply changing the layer stacking order and the stacking order offers an additional parameter for tuning the electronic properties for graphene. Such unveiled striking insights will guide the future possible graphene electronics fabrication using ABA and ABC-stacking trilayer graphene blocks.

As mentioned before, the way how the layers are stacked affects drastically the electrical prosperities of the system. By engineering the stacking of trilayer grapheme (ABA or ABC), we can experimentally realize graphene-based field-effect transistors (FET) [167, 168]. In such designed transistors as shown in Fig.3.5, ABA-stacking domain exhibits a semi-metallic behaviour, while the ABC-stacking domain shows semiconducting. In addition, ABA- and ABC-stacking trilayer graphene are expected to show the peculiar nature of the Quantum Hall Effect (QHE) phases and related quantum phase transitions, which is critical for the grapheme-based spintronics [169, 170]. Another possible application is considered as one attractive platform for detecting molecules attached to the trilayer system, which can be used in gas-sensor devices [171, 172].

One of the most promising applications of this new technique is graphene-based nanodevices and even integrated circuits [173, 174, 175]. Choosing an ABC-stacking trilayer graphene sheet, the researchers can design and realize the device architectures by selectively decorating the modules at the different portions to form artificial ABA or ABC patterns. Going further still, such process of patterning can be used to build Carbon-based integrated circuits. Compared with conventional devices, such proposed graphene-based nanodevices can be joined to the circuits by metallic ABA trilayer graphene, which serve as extensions of metal electrodes. The defect-free interfaces between these building blocks will retain the excellent electronic performance of graphene.

Figure 3.5: (a) Schematic illustration for the structural transformation of trilayer graphene decorated with triazine molecules. (b) Schematics of graphene-based FET, made from ABA (as source or drain electrodes) and ABC (as tunable semiconductors) building blocks.

Chapter 4

Closed-edge bilayer graphene (CEBG)

4.1 Introduction

The excitement about graphene lies in that it brings relativistic quantum phenomena into conventional condensed-matter physics, such as room-temperature quantum Hall effects [176], and Klein tunneling [177, 178]. From the viewpoint of application, the superior transport properties exhibited by graphene that the room-temperature mobility of $\sim 15,000 \text{ cm}^2/\text{Vs}$ and ballistic transport of the submicrometer scale, make it as ideal candidates for the next generation electronics. Such merits come from the characteristic behaviors of its low-energy excitations. Due to the massless Dirac fermions, charge carriers in graphene will transport faster and travel longer than in other semiconductors. Therefore, graphene is expected to present better performance than conventional semiconductors in building low-power faster-switching transistors [179, 180] or high-speed optoelectronic devices [181]. In spite of the excellent carrier mobility of graphene, lacking a band gap limited its applications in nanoelectronics. Hence, the band gap opening of graphene is the critical key step towards the wider graphene-based electronic device applications.

Up to now, various attempts have been proposed to realize the band gap opening

in graphene, such as hydrogenation [182], electrically gated bilayer graphene [183, 184], nanoribbons [185, 186], defects [187], substrate interactions [188], and molecules adsorption [189, 190]. However, these methods also bring unpleasant side effects to graphene after band gap opening, such as dramatically increased effective mass, distorted lattice, and damaged layer integrity. With such side effects, the resulted graphene will lose its superior transport performance. Another question in making electronic or optoelectronic devices of graphene is how to realize p - n junctions. As graphene is normally p -doped by adsorbates, it is rather hard to be n -doped at the same time [191]. Although this problem seems being solved by controlling the chemical bonding of graphene nanoribbon edges, it would be much more desirable to separate the electrons and holes in a more direct and efficient way for device applications. In this chapter, we further demonstrate theoretically that both obstacles which hinder the electronic application of graphene can be overcome by properly folding graphene layers.

4.2 CEBG Model

Recently, Liu *et al.* reported a novel graphene structure that the edge-open AB stacking bilayer graphene transforms to edge-closed AA stacking structure after annealing at extremely high temperature [190]. Actually, for AB-stacking bilayer graphene (CEBG), armchair edges cannot realize the closed edges with sp^2 hybridized carbon bonds due to the geometry incompatibility in Fig.4.1(c) and (d), while zigzag edges are allowed to close their edges as shown in Fig.4.1(a) and (b). To validate our prediction, we performed a DFT calculation for understanding the formation of AB-stacking CEBG. As shown in Fig.4.2, the system energy for AB-stacking bilayer graphene evolves from its initial open edges to the final optimized structures with closed edges through a series of intermediate states. In such evolution process, no energy barrier from the initial open edge states to closed edge states is observed, instead, the system energy decrease by more than 2 eV when the carbon atoms on the top and bottom layer firstly bonded. Then, the system energy further drop slightly in Fig.4.2(g) by structure optimization as shown in

Fig.4.2(b) to (f). Therefore, we can conclude that the AB-stacking CEBG is dynamically and energetically favorable. Moreover, Cruz-Silva, E. *et al.* also found that AB-stacking bilayer graphene can be transformed to CEBG along the zigzag direction rapidly using the quantum molecular dynamics simulation [192].

Figure 4.1: Atomic structures of AB-stacking bilayer graphene edges. (a,b) Compatible edges along the zigzag direction; (c,d) Incompatible edges along the armchair direction.

Figure 4.2: Simulation of evolution of CEBG from its initial open-edged structures. (a,b) Structure evolution from open edges to closed edges; (c-f) Energy relaxation of CEBG by optimizing the curvature. (g) Calculated energy versus the configurations as shown in (a-f).

4.3 Electronic structure of CEBG

The bonding (π) and anti-bonding (π^*) orbitals touch each other at opposite Brillouin zone corners of K and K' , and also gives an extra degree of freedom (i.e. pseudospin) to its low-energy (LE) quasi-particles as shown schematically in Fig.4.3(a). Being an elementary property, real spins in graphene are inert against the overall morphological

changes. However, as a direct product of graphene's lattice symmetry, pseudospins have to comply with the chiral alignment of the graphene sheet and therefore behave differently. For example, after closing its edges, its top and bottom layers may not have the same pseudospin chirality, such as the AB stacking case as shown in Fig.4.3(b). As the effect of pseudospin interaction is explored in the ascendant by now [193, 194, 195, 196], the studies on the consequent electronic structures of graphene would be fundamentally meaningful to the pseudospin physics.

Figure 4.3: (a) Schematic LE electronic band structure in graphene. (b) AB-stacking graphene folded along zigzag edge. The red (green) ball with a rightward (leftward) pointer represents pseudospin up (down). (c) Calculated band structures of AB-stacking (top) and AA-stacking CEBG (bottom).

In this work, a periodic AB stacking CEBG, as shown in Fig.4.3(b), is selected to investigate the interlayer pseudospin interaction. In this model, the interlayer distance for the three central carbon hexagons of CEBG is fixed to 3.4 Å which is the typical layer distance of graphite. Our first-principles calculations have been performed within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof form [197] using the Vienna *ab initio* simulation package (VASP) [198, 199, 200]. A plane-wave basis with the energy cut-off of 400 eV was used. The K -points were meshed using a $24 \times 1 \times 1$ Monkhorst-Pack grid. We adopted a vacuum layer of 10 Å to eliminate the

“image” models and the energy converged to be less than 1 meV. Fig.4.3(c) shows the band structures for CEBG, which presents the expected band gap of 0.113 eV at $k \approx 0.33$. The band gap for the AB stacking CEBG is crucial, as bilayer graphene is always metallic regardless of its stacking.

Although a finite band gap can be opened for bilayer graphene nanoribbons with zigzag edges, that happens only when the edge states become spin-polarized [200]. As the finite curvature of the graphene sheets may also induce energy gaps like in carbon nanotubes [201], the role of curved edges in the band gap opening of AB stacking CEBG has been examined as well. For comparison, we evaluated such edge effect by studying the band structure of the same CEBG model structure, but with AA stacking. As both top and bottom layers in AA stacking CEBG sustain the same chirality, the interlayer pseudospin scattering in AA stacking CEBG will vanish. Fig.4.3(c) presents the band structure of AA stacking CEBG, where conduction bands and valence bands intersect at the Dirac point and present no band gap opening. While the curvature does not introduce the band gap opening for the AA stacking CEBG, the contribution from curved edges can be eliminated. Therefore, the energy spectrum is gapless for the AA stacking CEBG but has a finite gap for the AB stacking case.

In order to verify the pseudospin repulsion induced band gap opening, we compared bilayer zigzag graphene nanoribbons with AA and AB stacking, as well as folded zigzag graphene nanoribbons as shown in Fig.4.4. For bilayer zigzag graphene nanoribbons, as the single layer counterpart, it is always metallic regardless of its stacking as shown in Fig.4.4(a) and (b). For folded zigzag graphene nanoribbons, there is no band gap in the AA stacking case but it has a finite pseudo-gap in AB stacking case in Fig.4.4(c) and (d). Note that all calculations are performed non-spinpolarized to eliminate the spin polarization induced band gap opening effect. These results further confirm the new mechanism we proposed that band gap opening is indeed by pseudospin interaction.

We then adopt the van der Waals density functional (vdW-DF) [202] which includes long-range dispersion interactions to investigate the nature of the interlayer bonding in our CEBG models. The optimized geometries using vdW-DF are relatively similar to DFT

Figure 4.4: Calculated band structures of bilayer and folded zigzag nanoribbons for AA stacking (a,c) and AB stacking (b,d).

Figure 4.5: DFT eigenvalues (hollow line) and GW quasiparticle energies (solid line) of AA stacking and AB stacking CEBG close to the Dirac point.

calculations except some expansions in interlayer distance for the both cases (AA stacking: 3.759 Å; AB stacking: 3.632 Å). More importantly, as well as the DFT calculations, the vdW-DF calculations give a small gap (0.1eV) for AB stacking and gapless for AA stacking. Next we inspect the robustness of our results using a more rigorous approach such as GW approximation [203]. The G_0W_0 calculations were carried out using YAMBO code. An affordable supercell including 32 carbon atoms is adopted. Norm conserving pseudopotentials [204] are adopted in plane-wave basis with a 60 Ry cut-off energy. We choose a $64 \times 1 \times 1$ k point sampling. We compared the DFT and GW quasiparticle results for our CEBG models close to the Dirac point as shown in Fig.4.5. As expected, for AA stacking there is still no gap though GW self-energy corrections usually enlarge the gap. For AB stacking the quasiparticle band structure has a significantly larger band gap (0.7eV) instead of DFT value of 0.3 eV, which is compared with bulk Ge (0.67 eV). As a comparison of CEBG, we also performed GW calculations for bilayer graphene nanoribbons in Fig.4.6(c) and (d). Clearly, for the CEBGs in Fig.4.6(a) and (b), we obtained the above conclusion. For bilayer graphene nanoribbons, the situation remains the same even after including GW self-energy corrections: they are always metallic for AA and AB stacking cases. Note that though the supercell studied here is quite small, the conclusion for bigger case is still held. Therefore, our previous finding, independently of the level of sophistication, is arguably convincing and sheds new light on graphene research.

It is worth noting that band gap opening for AB stacking CEBG originates from a new mechanism which is not suit for pristine open-edge bilayer graphene or graphite. As for open-edge bilayer graphene or graphite, the phases of pseudospins in different layers are not phase correlated and do not carry the exclusive chirality. This point can be seen from Berry phase which is closely attached to pseudospin. The Berry phase for a standing wave near zigzag is trivial whether single layer or bilayer zigzag ribbons [205, 206, 207]. After closing the edges, a nontrivial Berry phase of π appears for CEBG structures, different from the 2π phase of bilayer grapheme [208, 209]. This variation from bilayer graphene to CEBG will significantly influence the Hall conductance and deserve a direct evidence

Figure 4.6: GW quasiparticle (Red circle) correction to LDA eigenvalues (black cube) of CEBG for AA stacking (a) and AB stacking (b), as well as bilayer zigzag graphene nanoribbons for AA stacking (c) and AB stacking (d). The corresponding atomic configurations are shown theatrically by floating the band structures.

for the quantum Hall effect experiments.

Our theory is valid for these three systems: bilayer graphene (with two open boundaries), folded graphene [210] (with one closed boundary), CEBGs or collapsed nanotubes [211] (no open boundaries). For bilayer graphene, the phases of pseudospin in different layers are not phase correlated and do not carry the exclusive chirality. After a single layer graphene is folded or edges are closed, one can travel from the top layer to the bottom layer and thus leads to interlayer interaction from opposite pseudospin chirality. The mechanism for metal-to-semiconductor transition in collapsed metallic armchair tubes is the physical distinction of the two sublattices [212, 213], which is invalid for other two systems [214]. Actually, this mechanism is just a special case of our theory. More generally, based on our theory, any bilayers with different pseudospin chirality will present a gap. Indeed, gaps appear in bilayer graphene even without external magnetic and electric fields due to electron-electron interactions [215, 216, 217, 218, 219, 220]. Compared with the gap caused by pseudospin interaction, this spontaneous gap that estimated to be of order 1 meV is trivial. Therefore, the features of our finding still remain the same.

Figure 4.7: DFT calculated wavefunction square of the CBM electrons and VBM holes of AA and AB stacking CEBG from top to bottom. The isosurface level set to 0.0003. Red, yellow, purple, and blue colors indicate electron density from higher to lower.

We also plot the density distribution of holes at VBM and electrons at CBM of CEBGs in Fig.4.7. The LE states of AA stacking CEBG distribute symmetrically with higher density around the center due to the interlayer coupling. However, for AB stacking CEBG, the symmetric distributions of densities destroy, showing the VBM states on the top left wing and bottom right wing (\style) and the CBM states on the top right wing and bottom left wing (/ style). Obviously, such asymmetric charge profiles are energetically favored over the symmetric cases due to the geometrical asymmetry in AB stacking CEBG. This spatial separation of electrons and holes effectively forms a type-II junction without impurity doping and provide the possibility of new charge separation mechanisms, as proposed by Wu *et. al.* in tapered or strained silicon nanowires [221, 222]. Over many years of development of semiconductor electronics, realizing charge separation has always been the critical requirement for application in electronic or optoelectronic devices by p - n homojunctions or type II heterojunctions. Here, AB stacking CEBG, which also can be referred to “type-II homojunction”, will remove the technical hurdles of doping in the p - n homojunctions and also eliminate deficiencies caused by lattice mismatch at the interfaces in type II heterojunctions. In addition, compared to the

tapered or strained silicon nanowires, our CEBG models have more remarkable charms owing to its high carrier mobility and high transparency in graphene. While having the geometrically separated charges and the opened band gap, the AB stacking CEBG can be used as bricks for developing the future graphene-functionalized electronic devices, such as solar cell.

Figure 4.8: The band structures of twist bilayer graphene with closed edges. Insert: Geometry of the commensuration cell for bilayers faulted at 21.79° .

We examined the electronic properties of twisted bilayer graphene when the edges are closed. According to our theoretical predictions, the AA stacking case is special situation which presents a gapless feature. For other general case where there are some misorientations between the top layer and bottom layer, its band gap should exist an intermediate value between that of the AA stacking (0 eV) and AB stacking case (~ 0.1 eV). As shown in Fig.4.8, the commensurate cell for bilayer twisted at 21.79° was adopted. For twist bilayer graphene at 21.79° , it has proved to be gapless [223, 224, 225, 226, 227, 228, 229, 230]. However, when the edges are closed, the calculated band structure shows a small gap (about 50 meV). On the other hand, as a collapsed carbon nanotube its prototype, i.e. the chiral (12, 6) nanotube, is also metallic and thus such band gap opening origins from pseudospin chirality.

The role of ribbon width in the band gap opening in our CEBG models has been also

examined. The calculated band gap, as shown in Fig.4.9, shows the decreasing trend by increasing the length of central region of the unit cell along the in-plane direction, which can be attributed to the confinement effect. Thus, by tuning the ribbon width, the band gap of CEBG can be varied from 0.27 eV to 0.04 eV, even a lower value.

Figure 4.9: Variation of the energy gap with the length of central region (Red region) along the in-plane direction. No. of unitcell is the number of carbon ring in central region.

4.4 Summary

In summary, we have shown that AB stacking CEBG exhibit appealing features such as the band gap opening and spatial charge separation. The former originates from the pseudospin interaction, while the latter arises from geometrical asymmetry. Concerning the daunting obstacles to opening the band gap in graphene, the present findings could boost electronic properties of graphene-based devices and pave a novel way towards future pseudospin electronics for harvesting the distinct transport properties of graphene.

Chapter 5

Electronic and optical properties of MoO_3

5.1 Introduction

Molybdenum trioxide, $\alpha\text{-MoO}_3$, has received considerable attention due to its wide band gap nature and exhibits a variety of potential applications, such as catalysis [26, 27, 28], Li-ion batteries [29, 30], gas sensors [34, 35], recording materials [40, 41], solar cells [42, 43, 44], photochromic and electrochromic devices [45, 46, 47]. Despite the spectacular prospect and progress, the properties of MoO_3 are by far less well known than its sulfide counterpart (MoO_2) [53, 54, 55, 56] and a corresponding deep understanding is still lacking.

Experimentally, the electronic properties of MoO_3 have been studied using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), X-ray emission spectroscopy (XES), and valence electron energy-loss spectroscopy (VEELS). Firment *et al.* [231] performed a pioneer study to examine the electronic properties of the MoO_3 (010) surfaces by means of EELS, XPS, UPS. They reported that the valence bandwidth for MoO_3 is around 7 eV and three main peaks at 1.5, 3.6, and 5.6 eV present in DOS below VBM. Through the photocurrent measurement, S. K. Deb [232] reported the value of band gap for single crystal (3.59 eV) and thin film (3.56 eV) at the room

temperature. A recent study by O.Yu. Khyzhun [233] compared the electronic properties of the cubic phase, as well as the usual orthorhombic form using XES, XPS and NEXAFS methods. Their results indicate that the valence bands mainly origin from O $2p$ -like states. Later, T. Learmonth [234] measured the electronic structure of MoO_3 by means of XES, XAS, and O K-edge RIXS. They found that the band gap locates between the O $2p$ nonbonding bands and π^* bands, which is around 3~4 eV in magnitude. The XAS and XES experiments were then carried out by H. Sato [235] to study the anisotropic electronic structure of MoO_3 single crystal. According to their results, the obtained bandwidth of the occupied O $2p$ states by XES (~ 7 eV) is in accordance with the previous experimental results. As concerns the conduction bands, they gave a value of 4 eV band gap between the nonbonding O $2p$ states and π^* antibonding states. Very recently, L. Lajaunie [236] performed VEELS to investigate the dielectric properties of α - MoO_3 and obtained the features containing plasmons, interband transitions, surface effects, and relativistic losses. From experimental VEELS spectrum, the band gap of α - MoO_3 (~ 3 eV) is obtained as the onset of the signal.

To gain information on the band gap, the other strategy in experiment is to record the absorption spectrum. Near the absorption edge, the relation of the absorption coefficient α and photon energy $h\nu$ can be given by the following equation: $\alpha h\nu \sim (h\nu - E_g)^n$ where the exponent n associates with the different type of optical transition: $n = 1/2, 3/2, 2$ for transitions being direct allowed, direct forbidden, and indirect allowed, respectively. Through extrapolating the linear part in the plot of $\alpha h\nu \sim (h\nu - E_g)^n$, the optical band gap E_g can be thus derived. The value of E_g varies with the morphologies and structural order-disorder of MoO_3 , as well as the temperature, i.e. 3.66 eV for single crystal [232], 3.25 eV for MoO_3 flakes [237, 238], 4.1 eV for MoO_3 crystals at 6 K [239], 3.05 eV for α - MoO_3 lamellas [240], from 3.19 to 3.62 eV at the annealing temperature from 300K to 673 K for MoO_3 nanoparticles [241], 3.75 eV for MoO_3 nanobelts [242], 3.1-3.4 eV annealed at 400 °C and 500 °C for thin films [243], 3.24 eV for thin film at room temperature [244]. As mentioned before, the value of E_g is affected by the amount of structural defects (i.e. oxygen vacancy) and dangling bonds in the samples, as well as

electron-phonon interactions.

From theory's level, MoO_3 has been attracted a number of theoretical studies. Over a decade ago, Rozzi *et al.* [245] have carried out a tight binding calculation for both the stoichiometric and oxygen-reduced MoO_3 based on linear muffin tin orbital approach within LDA. They observed a small 0.5 eV band gap for the stoichiometric samples, which may be attributed to the underestimation in the LDA. By *ab initio* linearized augmented plane-wave (LAPW) approach, A.D. Sayede *et al.* [52] obtained a more reasonable gap of 2.23 eV within GGA. Recently, several research groups have performed the first-principles DFT calculations within GGA to investigate the electronic structures of MoO_3 and their obtained values are not of the same magnitude: 1.9 eV by Xianwei Sha [246], 1.95 eV by David O. Scanlon [51], 2.0 eV by L. Lajaunie [236], 1.79 eV by Alexis T. Bell [247], 1.71 eV by Fengyu Li [248], 2.0 eV by Matteo Baldoni [249]. Such large discrepancy between DFT calculations and the experimental results are common to underestimate the band gap of MoO_3 because the related states are not appropriately depicted. Theorists attempted to address more precise on-site Coulomb interactions for strongly correlated systems involving of *d*- or *f*-orbitals by introducing an extra inter-electron repulsion term (U_{eff}). Such DFT+U methods have been successfully applied to various transition metal oxides and significantly improved the DFT results compared with experiments. As for the case of MoO_3 , even large values of U_{eff} slightly widen the calculated band gap by ~ 0.1 eV, the obtained band gap of MoO_3 remains short of the experimental value [247, 250]. The poor performance of DFT calculations calls for a new recipe to remedy or eliminate this discrepancy, though uncertain experimental data, and this is the first purpose of this chapter.

As for the optical properties of MoO_3 , several investigations on single crystals of MoO_3 have been carried out. Deb *et al.* [232] have measured the absorption spectra in the temperature range 150 K to 340 K by using polarized light with the electric vector parallel to the long axis ($E \perp c$) and to the short axis ($E \perp a$). Then Minoru Itoh *et al.* [251] have carried out a series of optical measurements on single crystals of MoO_3 with polarized light at 6 K and confirmed the strong anisotropy of the optical response. On the

other hand, DFT calculations attempted to reproduce the absorption spectra following the experiments but the performance is barely satisfactory compared with experimental optical data [249]. Such discrepancy arises from the limitation of DFT calculations for the excited states, i.e. DFT calculations are only based on the independent-particle scheme for the ground states. It is well-known that many-body effects including e - e and e - h interactions will play a critical role in low-dimensional nanostructures [252, 253, 254]. For example, enhanced e - e interactions will result in huge QP corrections to the band gap. Bound excitons with large binding energies are formed with a reduced screening among e - h pairs. In MoO_2 case, both *ab initio* calculations and experiments have indicated that many-body effects (e - e and e - h interactions) remarkably modify their electrical and optical properties [255, 256, 257]. Therefore, it is of crucial importance for considering many-body effects to study the optical properties of MoO_3 and this is the second goal for this chapter.

5.2 Models and computational details

Similar to its sulfide counterpart MoS_2 , α - MoO_3 possesses the desired orthorhombic layered structure with $Pbnm$ symmetry ($a=3.963$ Å, $b=13.86$ Å, $c=3.696$ Å) [258], which is determined first by Brakken [259] and Wooster [260] in 1931. As illustrated in Fig.5.1, the structure consists of dual layers of distorted MoO_6 octahedrons that are oriented along the $[010]$ axis through a weak van der Waals interaction. Each layer can be viewed as edge sharing zigzag chains of MoO_6 along the $[001]$, while the chains are mutually linked by corner O sites along the $[100]$ directions. Three inequivalent oxygens are involved in the structure: terminated O(1), two-coordinated O(2), and three-coordinated O(3), respectively in Fig.5.1(b). O(1) connects singly with each Mo atom at the axial position between the layers forming the shortest Mo-O bonds of 1.67 Å. O(2) atoms are asymmetrically coordinated with two Mo atoms along the $[100]$ axis with one shorter bond (1.73 Å) and one longer bond (2.25 Å), respectively. O(3) atoms form symmetrically two Mo-O bonds in one layer (1.94 Å) and one longer Mo-O bond (2.33 Å) in the other

sublayer. These three inequivalent oxygens are chemically distinct and thus induce the large geometric distortion of the MoO_6 octahedral.

Figure 5.1: Atomic structure of $\alpha\text{-MoO}_3$. (a) Structural representation of orthorhombic MoO_3 with the layered structure along the b axis. (b) Edge shared MoO_6 -distorted octahedra with three types of oxygen atoms are illustrated [51, 250].

Generally, many-body calculations beyond DFT need start from the wave functions of the ground states and thus it is critical to construct proper Kohn-Sham results for further QP calculations. In this chapter, we first carried out the ground states of MoO_3 using *ab initio* calculations implemented in the QUANTUM ESPRESSO (QE) code [261]. We adopted the norm-conserving pseudopotentials [262] for the ion-electron interactions. An orthorhombic unitcell including 16 atoms (four Mo atoms and twelve O atoms) was used for the bulk case (Fig.5.1). We used a vacuum spacing of 10 Å to avoid periodic interactions for the single layer case. A plane-wave energy cut-off of 35 Ry and a $6 \times 6 \times 1$ Monkhorst-Pack k -point mesh were used. The Perdew-Burke-Ernzerhof exchange correlation functional [197] was adopted. The cell and atomic sites were optimized till forces on atoms down to 0.01 eV/Å were achieved. Both GW and BSE calculations are carried out by using the YAMBO code [263]. For the optical absorption spectra, fifteen valence bands and fifteen conduction bands were considered.

The optimized parameters of MoO_3 are summarized in Table 5.1. Relaxed lattice constants and bond lengths match well with experimental results [264, 265] and previous theoretical calculations using GGA [250], LDA [254] and HF [266]. For the interlayer

distance, our GGA calculations give an overestimated lattice vector. This can be understood by the fact of poor performance of DFT methods in dealing with van der Waals forces. In Ref. [196] and Ref [199], the authors fixed the b lattice parameter using the experimental value (13.855 Å).

Table 5.1: Optimized lattice constants and Mo–O Bond length of $\alpha\text{-MoO}_3$

	This work	GGA[196]	GGA[199]	LDA[215]	HF[216]	Exp.[213]	Exp.[214]
a	4.04	4.02	4.02	3.73	3.91	3.96	3.96
b	16.56	13.86	13.86	13.04	14.27	13.86	13.86
c	3.70	3.76	3.75	3.48	3.68	3.70	3.70
$d_{\text{Mo-O}_1}$	1.70	1.70	1.70	1.67	1.64	1.71	1.67
$d_{\text{Mo-O}_2}$	1.76	1.76	1.75	1.75	1.69	1.96	1.73
$d_{\text{Mo-O}_{2'}}$	2.29	2.28	2.29	2.24	2.24	2.03	2.25
$d_{\text{Mo-O}_3}$	1.97	1.98	1.97	1.94	1.94	1.90	1.95
$d_{\text{Mo-O}_{3'}}$	2.47	2.34	2.34	2.32	2.21	2.47	2.25

5.3 Electrical properties of MoO_3

As shown in Fig.5.2, we have calculated the band structures of MoO_3 within DFT-PBE and GW along the high-symmetry lines for the bulk and single layer, respectively. In bulk MoO_3 , based on the DFT calculations, we reported that MoO_3 is indirect semiconductor with the gap of 2.04 eV, where the electrons transition occurs from the CBM at the G point to the VBM near S point. Our reported value is in accordance with previous DFT-PBE calculations [236, 246, 249]. As expected, the obtained value of the gap still is lower than that reported experimentally. However, when introducing the effect of e - h interactions, the value of the band gap increased from 2.04 eV (DFT) to 3.96 eV (GW). In the case of single layer, the quasiparticle corrections boost the gap value from 2.1 eV to 4.25 eV, which can be easily understood by an outcome of much Coulomb interactions in low dimensional systems. Our GW results for the bulk MoO_3 correspond to the experimental measurement by T. Learmonth [234] using XES, and XAS, but still vary a certain amount from other experiments, especially the absorption spectrum. Here, we should clarify the difference between “electric gap” and “optical gap”. The former is linked with the photoemission and inverse-photoemission spectroscopies, while the

absorption spectra account for the latter. In other words, the discrepancy between the two is ascribed to the binding energy of excitons involved in optical excitations beyond the single-particle picture, as discussed later.

Figure 5.2: GW corrections (open circles) to DFT band structures (thin solid lines) for bulk (a) and single layer (b) $\alpha\text{-MoO}_3$.

5.4 Optical properties of MoO_3

In this section, we turn to investigate the optical absorption spectrum of MoO_3 through solving the Bethe-Salpeter equations. The calculated absorption spectra of MoO_3 including excitonic effects are compared with the experimental data [239] for the in-plane polarized light along a (Fig.5.3a) and c axis (Fig.5.3b). It worth noting that here we

only consider the polarization for the in-plane light instead of the perpendicular light polarization, because of its weak absorption strength. For both $[100]$ and $[001]$ cases, the calculated optical spectra at the GW+BSE level including excitonic effects (thick solid line) are significantly comparable with experimental results [239]. For $[100]$ case, two split peaks occur at 4.35 eV and 4.75 eV for calculated spectra while a prominent peak near 4.5 eV appeared in the experiment. For $[001]$ case, the calculated spectra presents complex multi-peaks and we can just conclude its trend is on par with that of experiment. Note that though we have obtained the converged results, the calculated spectrum only conforms to the experimental results for low frequencies. A general issue emerges: it is difficult to obtain the global converge for the whole spectrum in BSE calculations. In other words, we can discuss the low energy part with confidence while more k -point and, possibly, more bands need to be involved in the converged spectrum at higher frequencies. In our study thirty bands are included, which is much more than the common demand (no more than ten bands).

Figure 5.3: Calculated absorption spectra for bulk $\alpha\text{-MoO}_3$ with (red line) excitonic effects for light polarized along $[100]$ direction (a) and $[001]$ direction (b) versus photon energy compared with the experimental data (grey area).

We now examine the fine structure of the excitons ascribed to the low-energy peaks in our calculated absorption spectrum for both the bulk and single layer cases, as shown in Fig.5.4. We label “D” to denote the lowest-energy dark exciton and adopt “I” to denote distinct series of bright excitons. Along $[100]$ direction, the first two bright excitons emerges at 3.68 eV (I^1) and 3.92 eV (I^2) for the bulk case. The first bright exciton I^1 at

3.68 eV ascribed to one exciton with the binding energy of 1.26 eV, which arise from the transitions from the VBM to the CBM near $1/3$ of the way from K point, as shown in Fig.5.2(a). The second absorption peak I^2 at 3.92 eV can be attributed to another exciton with the binding energy of 1.48 eV, which come from the multi-transitions at S point as illustrated in Fig.5.2(a). As for along $[001]$ direction, many optically inactive excitons, i.e. dark excitons, are distributed below the first bright exciton, which are dipole forbidden. The lowest one (D^1) located at 3.58 eV. In the case of $[001]$, the first two optically active excitons I^1 and I^2 locate at 4.39 eV and 4.48 eV, respectively, which dominantly composed of transitions from the top valence band to the bottom conduction band at the S point. The binding energies of I^1 and I^2 in $[001]$ are 0.32 and 0.23 eV, respectively. Such a broad divergence our found between the excitonic binding energy along $[100]$ direction and $[001]$ direction reveal the strong anisotropy of the optical response for bulk MoO_3 . Compared with the bulk case, we also list the results obtained in the single case, as shown in Table 5.2. Due to the quantum confinement in single layer, the corresponding excitonic binding energies increase by ~ 0.2 eV as a consequence of less efficient screening.

Table 5.2: Energies (eV) of first two lowest bright excitons along $[100]$ and $[001]$ direction in bulk and single layer MoO_3 .

	Along $[100]$		Along $[010]$	
	I_1	I_2	I_1	I_2
Bulk	1.26	1.48	0.32	0.23
Monolayer	1.46	1.69	0.55	0.41

In order to understand this strong anisotropy of excitonic binding energies, we depict the electron probability distributions $\left| \Psi^\lambda(\vec{r}_h, \vec{r}_e) \right|^2$ relative to the paired hole by fixing the hole position for the first bright exciton (I^1) at 4.39 eV, taking the single layer as an example. Such distributions for a hole fixed upon an O atom (black dot) as shown in Fig.5.5. The electron amplitudes are tightly localized within an extent of a short interatomic length with the root-mean-square size of 3.67 Å along $[100]$ axis (see the left panel), while the electron distribution is extended over the width of the ribbon with the root-mean-square size of 8.59 Å along $[001]$ axis (see the right panel). Such a huge anisotropy in behavior is due to weaker coulomb screening among e - h wave functions

Figure 5.4: Compared excitation binding energy (E_b) of the first bright exciton for bulk (red line) and single layer (dark line) MoO_3 . The absorption threshold and GW band gap are marked with vertical solid and dashed lines, respectively.

along $[100]$, which manifests larger binding energy in the case of $[100]$ rather than that of $[001]$.

Figure 5.5: Three-dimensional exciton probability distributions in real space when the hole position (blue dot) is fixed on an O atom for the first bright exciton in single layer MoO_3 along $[100]$ (a) and $[001]$ (b) axis.

5.5 Summary

Although α - MoO_3 has been found widespread use in solid state microbatteries and heterogeneous catalysis, its electronic and particularly optical properties still have not been well established. The resulting computed in-plane polarized optical spectrum, obtained by solving the Bethe-Salpeter equation for many-body Green function, is in excellent agreement with experiment and has a strong anisotropy. A detailed analysis of the excitonic structures within the band gap shows strong excitonic effects with a significantly large binding energy assigned to the bound excitons. This provides an explanation for the observed “optical gap” contradictions between experiments and theories.

Chapter 6

Spin-orbit splitting in single layer MoS₂

6.1 Introduction

Due to its low coefficient of friction, molybdenum disulfide, MoS₂ exhibits excellent lubricating properties and has been widely used as a "dry lubricant" as well as graphite in decades [267, 268, 269]. MoS₂ crystallizes in a layered 2H prototype structure with the $P6_3/mmc$ symmetry, which is composed of weakly coupled S-Mo-S sandwich layers [270]. (See Fig.6.1(a,c)) In each sandwich layer, hexagonally arranged Mo atoms are bonded to six S atoms in trigonal prismatic coordination. The S-Mo-S sandwich layers are stacked together by weak Van der Waals interactions, resulting in its lubricating properties.

Inspired by the mechanical exfoliation of graphene from graphite, monolayer MoS₂ can be extracted from its bulk crystal through the similar approach [271]. The trigonal prismatic arrangement is reserved, whereas the symmetry of monolayer MoS₂ is reduced to $P6m2$ due to the breaking of inversion symmetry. Unlike semimetallic graphene, single layer MoS₂ is found, from both experiments [272] and theories [87], be to a direct-gapped semiconductor with a band gap of 1.8 eV (Fig.6.1(b)). Such a moderate band gap is desirable and has been recently attracted extensive research interest as field effect transistors (FETs) [273], light emitting diodes (LEDs) [274], complex electronic circuits

[275] and solar cells [276]. The mobility of carries in monolayer MoS_2 with HfO_2 as a gate insulator can be dramatically enhanced to $200 \text{ cm}^2/\text{Vs}$, which is comparable to that of thin silicon films. The monolayer MoS_2 transistor exhibits an on/off ratio exceeding 1×10^8 at the room temperature [60]. More interesting, MoS_2 has been verified to exhibit an indirect-direct band gap transition from multilayer to monolayer due to a missing interlayer interaction.

Another important discrepancy to graphene is the presence of transition-metal d orbitals in monolayer MoS_2 , which is not encountered in graphene with a trivial spin-orbit coupling (SOC) [277, 278]. Both the highest valence bands and the lowest conduction bands are formed primarily from the Mo d -orbitals (Fig.6.1(d)). In single layer MoS_2 , the strong SOC due to the absence of inversion symmetry splits the highest valence bands at the K points by around 150 meV [279], as illustrated in Fig.6.1(b). Moreover, the signs of split spins in K and K' valleys are reversed due to the time-reversal symmetry, leading to an intriguing relation of the spins and the valley degrees of freedom. Optical selection rules for interband transitions allow valley population by optical pumping by means of circularly polarized lasers as predicted by the theory [280] and observed by the experiments [281]. The splitting at the VBM induced by SOC give rise to two low-energy exciton peaks (A and B excitons) in the absorption spectra, which are linked to the direct transitions from two split valence bands to a doubly degenerate CBM at the valley, as shown in Fig.6.1(b). Therefore, such spin-valley coupling provides promising possibilities of manipulating carriers towards the next generation of spintronics or valleytronics [282].

The effects of mechanical strain is crucial in MoS_2 research field from the fundamental understanding and practical applications. In practice, CVD grown MoS_2 inevitably encounter the introduced strain due to the lattice mismatch between MoS_2 and the substrates. Particularly, given the potential applications in flexible electronics, MoS_2 on flexible substrates will subject to high elastic strains. From the theatrical viewpoint, mechanical strain can have profound effects upon the band structure of MoS_2 , which can be viewed as a common method to modify the performance of electronic devices. For strains exceeding 1%, single layer MoS_2 becomes indirect-gapped from the direct semiconductors

[283, 284]. Moreover, the strain-induced band gap modification will increase its carrier mobility [276] and improve the collection efficiency for solar cells. The presence of local strain can even engineer the magnetic properties in MoS_2 [285]. As two-dimensional material, single layer MoS_2 is predicted to sustain elastic tensile strain up to 25% before the breaking [286, 287]. Such high elastic strain limit allows exceptional room for strain modification and has stimulated a surge of theoretical studies [288, 289, 290, 291, 292, 293] on strain induced changes in the band structures of MoS_2 . The focus of previous works on the strain engineering of the band structure without considering SOC. As well known, the valley and spins are closely connected to the crystal symmetry and are expected to be modified through the application of mechanical strain. Hence, it is of both fundamental and practical interests to examine the role of strain on the electronic properties of MoS_2 including the spin-orbit interactions.

Figure 6.1: (a,c) Schematic of monolayer MoS_2 from the top and side view. The unit cell is cased by dashed lines. (b) DFT calculated band structure of monolayer MoS_2 . Due to spin-orbit coupling, the valence-band maximum is split to two spin polarized bands, spin-up $\uparrow$ and spin-down $\downarrow$. (d) The partial density of states for MoS_2 phase. The Fermi level is shift to be zero.

Recently, our experimental collaborator S. L. Sun compared Raman spectra of MoS_2 samples with the different layers excited by various excitation lasers. As shown in Fig.6.2, obviously, the intensities of three high-order modes excited by 325 nm laser are enhanced dramatically. These three Raman peaks with prominent intensities are observed in the range from 750 to 840 cm^{-1} , which have been assigned as the second order and combination modes of E_{2g}^1 and A_{1g} [294, 295]. In addition, the comparable intensities of the high-order modes with their first-order counterparts for few layer MoS_2 hints a phonon energy dependent resonant Raman mechanism. We attribute this intensity enhancement of the second-order modes observed to the electron-two-phonon involved triply resonant Raman scattering process [296, 297, 298]. As illustrated in Fig.6.2(b): (1) an electron is excited resonantly from ν_2 band to c_i band by absorbing a photon; (2) the hole in ν_2 band is scattered by a phonon with momentum q to ν_1 band by interband transition; (3) another phonon with momentum $-q$ scatters the hole to the top of ν_1 band by intraband transition; (4) the electron-hole pair recombines at the top of ν_1 band and a photon emits during this recombination process. Within this triply resonant process, the key factor to fulfill the conditions is that the energy difference between the two split bands (ν_1 and ν_2) matches the twice energy of involved first-order phonons well. As for MoS_2 , we need to address one question: what is the link between energy difference of two bands and the selected excitation laser?

Figure 6.2: (a) The Raman spectra of MoS_2 samples with different layer number excited by 325 nm laser. The first order E_{2g}^1 and A_{1g} modes, as well as their overtone and combination modes are shown. (b) Schematic diagram for triply resonant process in MoS_2 .

6.2 Theoretical results

The calculated electronic band structures in the absence of SOC for different layered MoS_2 nanoflakes are shown in Fig.6.3(a-d), using Vienna *ab initio* Simulation Package (VASP) within the local-density approximation (LDA)[199, 299]. The cut-off energy for the basis set was 400 eV. The Brillouin-zone integration was performed within Monkhorst-Pack scheme using a $36 \times 36 \times 1$ mesh and the Methfessel-Paxton smearing with a width of 0.1 eV. The energy relaxation for each strain step is continued until the forces on all the atoms are converged to less than 0.01 eV/Å. The calculations considering spin-orbit coupling effects have been performed in the non-collinear mode implemented in VASP by Kresse and Lebacq [300]. As expected, the highest valence bands at K point splits into two, three, and four bands respectively for bi-, tri-, and quad-layer MoS_2 due to the interlayer interactions. However, when SOC is considered, the splitting pattern is completely changed as shown in Fig.6.4(a-d). The highest valence bands split into two degenerate manifolds (marked as ν_1 and ν_2 bands) with a splitting magnitude regardless of the layer numbers for few layer MoS_2 . For 1L MoS_2 , as mentioned above (see Fig.6.1(b)), it possesses a crystal structure with inversion symmetry broken which leads to a giant SOS value[301]. For 2L and bulk MoS_2 , the electronic bands ν_1 and ν_2 are also split due to SOC and interlayer interaction effects as shown in Fig. 6.4(a-d) [302]. Furthermore, from the band structure in Fig.6.1(b), it is noted that the energy difference between $c_{5(6)}$ bands and ν_2 band is ~ 3.8 eV. Thus, the energy band structures of MoS_2 samples can fulfill the first step of the triply resonant Raman scattering (RRS) when the excitation laser energy is ~ 3.81 eV (325nm), as shown by the red arrow in Fig.6.1(b) (from ν_2 to $c_{5(6)}$). Meanwhile, the energy matching between SOS and high order phonons gives rise to the resonant Raman enhancement. The detailed mechanism for this triply resonant Raman process in MoS_2 can be explained well following Fig.6.2(b).

To get an insight into the resonant electronic transition between ν_2 and $c_{5(6)}$ bands, we have calculated the real-space partial charge density for these four electronic bands. Fig.6.5(a-d) show the three dimensional-partial charge density (PCD) of the electronic bands $\nu_{1(2)}$ and $c_{5(6)}$ for 1L MoS_2 , respectively. It shows clearly that the PCD of ν_2 bands

Figure 6.3: (a-d) Band structures without spin-orbit coupling for MoS_2 systems.

Figure 6.4: (a-d) Band structures with spin-orbit coupling for MoS_2 systems.

are mainly contributed by d orbits of Mo atoms; while the c_6 bands are mainly originated from p orbits of S atom with a low concentration of d orbital of Mo atoms. The origination for these electronic bands can also be reflected clearly by 2D PCD images as shown in Fig.6.5(e-h). Thus it is allowable for electronic transition (step (1)) from d orbitals of ν_2 band to p orbitals of c_6 bands as the difference of angular quantum number between d and p orbits is 1. Compared to the c_5 band, the c_6 band should be the dominant final state of electronic transition in step (1) due to the high concentration of p orbitals of S atoms.

Figure 6.5: (a-d) 3D partial charge density for electronic bands (a) ν_1 , (b) ν_2 , (c) c_5 and (d) c_6 of single layer MoS_2 , respectively. (e-h) 2D partial charge density graphs corresponding to the four electronic bands in (a-d).

6.3 Strain effects on the spin-orbit induced splitting

Now we turn to investigate the effects of strain on the electrical properties of single layer MoS_2 considering spin-orbit coupling. We apply the isotropic strain from -9.6% to 12.8% on single layer MoS_2 to modify the electronic structures. Then we harvest the interesting results when trying to figure out the physical pictures behind the variation of the band structures of monolayer MoS_2 under bi-axial elastic strains (i.e. under tensile and compressive conditions) by implementing detailed calculations and they are shown in Fig.6.6. From (a) and (b), we can see that the direct band gap energy of MoS_2 is smaller

Figure 6.6: The band structures under the (a) tensile and (b) compressive strain, respectively. (c) The value of spin-orbit splitting *versus* isotropic strain. (d) The evolution of the direct (Red dot) and indirect (Black square) band gap with the isotropic strain from -9.6% (Red region) to 12.8% (Blue region)

than the indirect band gap energy under the condition of no external tensions, so it is direct-gapped semiconductor material now with both valence band maximum (VBM) and conduction band minimum (CBM) locating at the K point in the first Brillouin zone. With the increasing of the bi-axial tensile strain (*e.g.* up to 9%), the VBM of monolayer MoS_2 moves to Γ point gradually and it becomes an indirect band gap semiconductor. While with enhancing the bi-axial compression on MoS_2 (*e.g.* up to -9%), its CBM is shifted to between K and Γ , meanwhile, MoS_2 turns into an indirect band gap semiconductor. The transition from direct semiconductor to indirect semiconductor can be attributed to that the bi-axial strain changes the distance between Mo atom and S atom. Hence, the changes of lattice constants cause the variations of band structures. Since the band gaps are sensitive to bi-axial strains, we plot both the direct and indirect band gap energy curves in two colors under different bi-axial strains (see Fig.6.6(d)), and it can be divided into three regions. Apparently: (1) monolayer MoS_2 retains its direct band gap in the central region, *i.e.* the small strain regardless of the strain direction. (2) In the left region, the direct band gap energy increases while the indirect band gap energy decreases when monolayer MoS_2 is compressed along the given crystal axes. (3) In the right region, the energy of the indirect band gap reduces faster than the direct band gap when MoS_2 suffering from bi-axial tensile strain. So monolayer MoS_2 will transform into an indirect semiconductor out of the central region.

To gain further insights, we also keep an eye on the effects of isotropic strain on the value of spin-orbital splitting. It seems that the evolution of the value of SOC takes a monotonic relation with the bi-axial strain. Our finding proposed a new route to manipulate the strength of SOC through a mechanical strain, which reflect the feasibility of intrinsic spin-flip for intravalley spin relaxation. In unstrained MoS_2 , spin and valley relaxation are suppressed at the highest valence bands as a large energy barrier (~ 160 meV) need to be overcome for spin flip. We then can reduce the energy barrier by applying a compressive stress to monolayer MoS_2 . More importantly in valleytronics and spintronics, MoS_2 under tensile strain exhibit long lived spin and valley because the flip of each index is forbidden.

6.4 Summary

In previous reported results, GW approximation, Heyd-Scuseria-Ernzerhof (HSE), and Perdew-Burke-Ernzerhof (PBE) have been performed to calculate the spin-orbit splitting in 1L MoS_2 , but the value has not been unified [303]. Thus the exact value of the SOC induced energy splitting at K point is still in debate which cannot be confirmed solidly [304]. In our experiment, as the second order and combination modes fulfill the triply RRS due to the spin-orbit splitting, both phonon energies of $2E_{2g}^1(0.093\text{eV})$ and $2A_{1g}(0.102\text{eV})$ should be close to the energy of splitting due to SOC for 1L MoS_2 , which means that the value is ~ 0.1 eV. This value is also in the range of reported theoretical value within the allowable error range [301]. Furthermore, the intensities of the second order and combination Raman modes are very sensitive to the energy splitting between ν_1 and ν_2 , because it determines resonant degree for the triply RRS (steps (2) and (3) shown in Fig.6.2(b)). Thus, in terms of the Raman intensities of the second order and combination modes of different layered MoS_2 samples shown in Fig.6.2(a), we can infer that the energy splitting between ν_1 and ν_2 should be also close to ~ 0.1 eV for few-layer MoS_2 samples (2L and 4L), but far away from ~ 0.1 eV for bulk MoS_2 sample (much weaker intensities of overtone and combination modes compared to that of 1L MoS_2). It is reasonable that, as shown in Fig.6.4(d), bulk MoS_2 possesses much larger energy splitting compared to ultrathin MoS_2 flakes, which means that the probability of triply RRS is reduced. Therefore, the probing of spin-orbit splitting energy for single layer MoS_2 by UV laser excited RRS is reliable.

By means of the first-principles calculation including SOC effects, we proved that the experimental resonant phenomenon for the second order and combination modes is attributed to electron-two-phonon triply resonant process, and the spin-orbit splitting at the top of valence bands play an important role for fulfillment of high order modes resonance. Particularly, by studying the electrical structures respect to applied strain, we revealed the tunable band gap of monolayer MoS_2 . Furthermore, due to the monotonic spin-orbit splitting with the change of lattice parameters, it has strong implications for the potential applications of MoS_2 in spin physics and spintronics. Hence, our studies on the

SOC in MoS_2 reveal the mechanism behind the observed Raman intensity enhancement excited by 325 nm laser and our calculations about the effects of strain for single layer MoS_2 opens a new and convenient way to probe the spin-orbit splitting-based spintronics and quantum valley Hall effects [305, 306].

Chapter 7

Crystal structure prediction

7.1 Molybdenum oxide

7.1.1 Introduction

Molybdenum oxide, as one typical transition metal oxides, have attracted much interest because of their various crystalline polymorphs and intrinsic chromogenic properties [307, 308, 309, 310, 311, 312]. As well known, the novel properties have close inner link with their particular crystalline phases or structures [313, 314]. Previous attempts to synthesize molybdenum oxide have been performed by improving recipes and synthetic routes for both molybdenum trioxide [315, 316, 317, 318] and molybdenum dioxide [319, 320, 321]. Up to date, three crystalline polymorphs phases of MoO_3 have been fabricated: the well-known stable orthorhombic α - MoO_3 , metastable monoclinic β - MoO_3 and hexagonal h - MoO_3 . As mentioned in Chapter 1, these three phases are basically built up of MoO_6 octahedra in various ways. Among other polymorphs, h - MoO_3 shows an tunnel structure as shown in Fig.1.6(c). With such salient structural feature, h - MoO_3 offers versatile conduits and intercalation sites for mobile ions [322], which is useful in Li^+ batteries, chromic and sensor devices [323, 324, 325]. Based on XRD data its lattice constant is given as $a = b = 10.53 \text{ \AA}$, and $c = 14.87 \text{ \AA}$. It is worthy noting that the ideal h - MoO_3 phases have been not realized yet in spite of various attempts [326, 327, 328]. The practical h - MoO_3 phase is synthesized only if m -units of NH_4 and n -units of H_2O

exist. The practical formula for hexagonal MoO_3 should be $h\text{-MoO}_3 \cdot m\text{NH}_4n\text{H}_2\text{O}$ instead of $h\text{-MoO}_3$, where the NH_4^+ stay inside the tunnel while the H_2O^+ are found between the octahedron layers. As the reduction of MoO_3 , MoO_2 has been used in gas sensors, catalysts, Li-ion batteries [329]. Especially, the pronounced ferromagnetism in MoO_2 without doping recently paved a new way to the research area of spintronics [330]. In spite of such potential applications, MoO_2 has received less attention in theory compared with MoO_3 . Recently, S.H. Han and his co-workers [331] studied the origin of ferromagnetism in undoped MoO_2 using DFT calculations using both the GGA and GGA+U approaches and they found that the magnetism in undoped MoO_2 ought to mainly derived from the type-I O vacancies. Then D. S. L. Law [51] compared the calculated cross-section weighted densities of states with the XPS spectra. Their results show that MoO_2 is a metallic material with Fermi level crossing over the conduction bands.

7.1.2 Methods and computational details

Our objective in this chapter is to explore possible new phases of molybdenum oxide through particle swarm optimization (PSO) algorithm [332], which is one of the most powerful tools for crystal structure prediction by the swarm intelligence and self-improving structures. Such algorithm has been integrated into CALYPSO code [333]. The scheme of our method is shown in Fig.7.1. An ensemble of structures is initially built up randomly and the symmetry operations of all space groups are also considering. Once the initial structures are produced, their geometries can be optimized by employing the DFT calculations based on first principle. Meanwhile, their total energies are worked out. The structures then evolve towards to the lower-energy configurations by self- and swarm-structure learning. Typically, each generation creates a mutable amount of random structures about 20%–40% during the process.

Our structure predictions for molybdenum oxide were performed with variable-cell using CALYPSO code. The first-principles DFT calculations for structural relaxations have been implemented by the plane wave basis Vienna *ab initio* simulation pack (VASP) code [334]. The electron-ion interaction was explained by employing a projector augmented

wave method [335, 336] and the exchange correlation potential was described with the aid of the local density approximation (LDA). We choose a cut-off energy of 400 eV. The Brillouin zone was sampled using a $6 \times 6 \times 1$ Monkhorst–Pack k-point mesh. In our calculations, we maximize the optimization of geometries till the forces on atoms are less than 0.01 eV/Å.

Figure 7.1: Schematic program chart of CALYPSO for searching structures.

7.1.3 Computational results on MoO₃

By applying the developed PSO method on MoO₃, the experimentally observed orthorhombic and monoclinic structures were successfully reproduced. The properties of

orthorhombic α -MoO₃ have been investigated as a wide indirect band-gap semiconductor [51, 52]. A.D. Sayede [52] reported that monoclinic β -MoO₃ should present a moderate bandwidth of 1.67 eV based on the LAPW calculations. Besides, in our study, of great interest is one energetically competitive low-energy h -MoO₃ because it has different crystalline phases with open structures, where the prime is used to distinguish with experimental h -MoO₃ phase. Note that we did not obtain the h -MoO₃ phase due to its complex morphology. Similar to h -MoO₃ phase, our predicted h -MoO₃ phase possesses 1D open tunnel structure, where MoO₆ octahedra are alternately linked to form interlocking hexagonal rings, as shown in Fig.7.2. It crystallizes with lattice constants: $a = b = 5.105$ Å, and $c = 3.149$ Å and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ with the space group $P6_3/m$. h' -MoO₃ phase is energetically less stable than h -MoO₃ phase by 0.849 eV/unit cell and thus is considered to be one metastable phase.

Figure 7.2: Schematic representation of h' -MoO₃ from the top view (a) and side view (b). The red atom is O, and the purple atom is Mo. The energy difference of various phases relative to the experimental orthorhombic α -MoO₃ phase per unit cell is indicated.

Calculated band structures and partial density of states (DOS) of h' -MoO₃ phase are present in Fig.7.3, to illustrate its electronic properties. Clearly, the CBM situated at M point. For VBM, the situation seems ambiguous: the energy difference between Γ and M points is merely 0.01 eV, resulting in a direct bangap of 1.87 eV and an indirect band gap of 1.86 eV. We believe that such slight energy difference will not influence the direct band-to-band photoluminescence. The unique band structure feature need to be examined by other advanced functionals or approximations, such as HSE hybrid

functional or GW approximation. Similar to α - MoO_3 phase, VBM states for h' - MoO_3 phase is manipulated by O $2p$ states, while CBM states origin mainly from Mo($4d\ t_{2g}$) and Mo($4d\ e_g$) states with some hybridization with O p states in Fig.7.3(b), which is a general feature of the electronic structure for $4d$ binary oxides with the wide band gap [337, 338].

Figure 7.3: (a) Calculated band structure for h' - MoO_3 along high-symmetry lines. The horizontal dashed line is the Fermi level. (b) The partial density of states for h' - MoO_3 . The contributions of the Mo $4d\ e_g$ and Mo $4d\ t_{2g}$ states are shown for comparison. The vertical dashed line is the Fermi level.

Next, we examine the effects of vacancy on the electrical properties for h' - MoO_3 by removal one O atom or Mo atom in the $2 \times 2 \times 1$ supercell, resulting in a vacancy concentration of 3.226%. Fig.7.4 shows the calculated band structures for h' - MoO_3 with one O vacancy (V_o) and one Mo vacancy (V_{Mo}). For V_o case, the band states for spin

up and spin down are degenerate. The Fermi level lies in the conduction bands and can be considered as an n-doping semiconductor. For V_{Mo} case, the behavior of spin up and spin down states are distinct: the Fermi level situated at the valance bands for spin-down states, while the spin-up states possess a moderate band gap of 1.96 eV. This may imply that Mo-vacancy in h' - MoO_3 will induce the half-metallic behavior. To further confirm this point, we plotted the corresponding PDOS for above models, as shown in Fig.7.5. Observably, the presence of O-vacancy will induce the defects states within the band gap, which mainly arises from O 2p orbitals, and thus the Fermi level is lifted up towards the conduction bands, resulting in a smaller band gap of 0.43 eV. Moreover, no magnetic-moment forms for V_o case and PDOS shows the symmetric characteristics for spin up and spin down states in Fig.7.5(a). Unlike that of h' - MoO_3 with O vacancy, the half-metallic features emerge in Fig.7.5(b): the spin-down states exhibit a metallic behavior cross the Fermi level, while the spin-up states possess the semiconducting properties. The total magnetic moment for the system equals to $5.0 \mu_B$, which origins from the p states of the neighbor O atoms adjacent the vacancy. Such conclusion can also be inferred from the calculated spin charge density for h' - MoO_3 with one Mo vacancy in Fig.7.6. As inferred, the p orbitals of O atoms contribute to the magnetic moment.

As a short summary, by using PSO simulation, we have successfully predicted one hitherto unexpected phase of molybdenum trioxide, h' - MoO_3 , with a moderate band gap. By generating one vacancy in h' - MoO_3 phase, we then investigated the electrical properties of two systems: V_o and V_{Mo} . For the former case, the system still exhibit semiconducting properties but with a smaller band gap of 0.43 eV. For the latter case, the system show half-metallic behavior. The total magnetic moment for the system is $5.0 \mu_B$ and arises from the p orbitals of surrounding O atoms. We believe that our finding will not only play critical roles in nanoelectronics, but also present the potential for next generation spintronics.

Figure 7.4: Calculated band structures for h' -MoO₃ with (a) one O vacancy and (b) one Mo vacancy for both spin-up (black solid line) and spin down states (red solid line). The horizontal dashed line represents the Fermi level.

7.1.4 Computational results on MoO₂

In the case of MoO₂, we found several energetically competitive low-energy structures compared with the experimental monoclinic phase (named as MoO₂-I, MoO₂-II and MoO₂-III in Fig.7.7). The corresponding structure parameters and formation energies are summarized in Table .7.1. Surprising, the formation energies of MoO₂-I and MoO₂-II are found to be lower than the monoclinic phase. Unlike other 3D phases, MoO₂-I possesses the 2D layered structure similar with its sulfide counterpart-MoO₂. It is noteworthy that the analogous structure in the case of MoO₂ is named as 3R structure not the lowest-energy 2H phase. We also calculated the energy of 2H phase for bulk MoO₂ and found the formation energy would be lower 0.179 eV/cell than 3H phase. Our finding of MoO₂-I phase and its variants may pave a new path in 2D materials filed. Given the lower formation energies than the monoclinic phase, the fabrications of such 2D phases become accessible in experiment. MoO₂-II phase is the lowest-energy configuration from our PSO simulations and the metastable phase MoO₂-III actually can be adopted from the experimental monoclinic phase.

Next, we turn to investigate the electrical properties of above new phases starting from the monoclinic MoO₂. As shown in Fig.7.8(a), the monoclinic MoO₂ shows metallic behaviors because the Fermi level lies within the bands, which is consistent with previous calculations. Furthermore, PDOS in Fig.7.9(a) shows that the Mo 4*d* states ranging

Figure 7.5: The partial density of states for h' -MoO₃ with (a) one O vacancy and (b) one Mo vacancy. The vertical dashed line represents the Fermi level.

Figure 7.6: Calculated spin charge density for h' -MoO₃ with one Mo vacancy.

Table 7.1: Optimized structure parameters and formation energies of MoO₂. Notations: N_c — number of unitcells in the model; a , b , c — the lattice constants; α , β , γ — angles between the basis vectors. ΔE — the energy difference relative to the monoclinic phase per unit cell (units are meV/cell).

Structure	Symmetry	N_c	a	b	c	α	β	γ	ΔE
MoO ₂	$P2_1/c$	4	5.611	4.856	5.629	90	120.95	90	0
MoO ₂ -I	$R3m$	3	2.815	2.815	15.209	90	90	120	98
MoO ₂ -II	$C2/m$	6	14.923	2.559	5.008	90	84.09	90	280
MoO ₂ -III	$P-3_1m$	3	4.814	4.814	4.810	90	90	120	-20

Figure 7.7: The predicted low-energy structures of MoO_2 . The red atom is O, and the purple atom is Mo. The energy difference of various phases relative to the experimental monoclinic phase per unitcell is indicated. Left and right panels are from the side and top views.

Figure 7.8: Calculated band structures for (a) monoclinic MoO_2 and (b) MoO_2 -I phase along high-symmetry lines. The horizontal dashed line is the Fermi level.

Figure 7.9: The partial density of states for (a) monoclinic MoO₂ and (b) MoO₂-I phase. The vertical dashed line is the Fermi level.

Figure 7.10: The partial density of states for (a) MoO₂-II phase and (b) MoO₂-III phase. The vertical dashed line is the Fermi level.

from -2 to +2 eV can account for the metallic nature of MoO₂. Unlike monoclinic MoO₂, MoO₂-I phase exhibit semiconducting properties with an indirect band gap of 1.74 eV, which is comparable with MoO₂. As in MoO₂, the VBM states possess a strong hybridization among O 2*p* and Mo 4*d* orbitals, while the CBM states at the upper part mainly arises from the Mo *d* orbitals. For other new phases MoO₂-II and MoO₂-III), we also show that the Fermi level is located within the bands dominated by Mo 4*d* orbitals. Therefore, the MoO₂ systems all exhibit a noticeable metallic behavior, especially MoO₂-I phase. Due to the demand for low-dimensional semiconductors, our findings introduce one new member into two-dimensional molybdenum compounds class, which comprises of molybdenum trioxide (MoO₃), disulphide (MoS₂), diselenide (MoSe₂) and ditelluride (MoTe₂). Given the nature of thickness dependent properties for these materials, the corresponding properties of MoO₂-I phase are yet to be investigated. Our results strongly suggest further experimental realizations by through Oxygen plasma treatment of MoO₂.

7.2 Carbon allotrope

7.2.1 Introduction

Owing to its broad *sp*, *sp*² and *sp*³ hybridizing flexibility, carbon is capable of forming numerous allotropes such as graphite, diamond, graphene and their derivatives [88]. The size of the building blocks, the bonding characters between the building blocks and the stacking patterns endow different carbon allotropes with diverse electronic properties and superior mechanical performances.

Motivated by the potential applications and intriguing properties of those carbon structures, decades of research have focused on searching for new carbon allotropes, in which theoretical studies are indispensable. For instance, the body-centered tetragonal bct-C₄ carbon was investigated theoretically about its structural, vibrational, and electronic properties in 2010 [98]. The monoclinic polymorph M-carbon which is viewed as a possible candidate for cold-compressed graphite, has been proposed by *ab initio* evolutionary algorithm [97]; soon thereafter, several groups reported independently one novel

allotrope with $Cmmm$ symmetry using the different methods, which is named as Z-carbon in ref. [102], Cco-C₈ in ref. [101] and oC16II in ref. [100]. Besides, numerous other carbon phases including W-carbon [99], R-carbon [103], X-carbon [105] and O-carbon [106] have been predicted by various methods. Despite these findings, many new allotropes with fascinating properties remain unexplored, which largely arises from the incomprehensive understanding of the atomistic mechanisms of cold compression graphite [93, 94, 95, 96]. Scientists attempted to identify the observed superhard phase in cold-compressed graphite among above predicted allotropes, but none of them can match the experimental XRD data satisfactorily. Frankly, the simulated XRD for all above potential candidates can merely fit the experimental data to some extent [97, 99, 100, 101, 102, 103, 106]. In other words, up to now, identified structure for the cold-compressed graphite have not been revealed. This motivated us to explore likely carbon phases to shed light on above issues.

7.2.2 Methods and computational details

In this chapter, the CALYPSO [332, 333] code designed to predict stable and metastable structures for a given compound has been employed. The structural relaxations using the first-principles DFT simulations were carried out using the plane wave basis Vienna *ab initio* simulation pack (VASP) [199, 334] code within the local-density approximation (LDA). The kinetic energy cut-off was adopted at 600 eV and the Brillouin-zone integrations were used by an Monkhorst-Pack $36 \times 36 \times 1$ grid. The structural optimization for each step stopped till the forces are less than 0.01 eV/Å. The phonon dispersion for U-carbon using the density functional theory (DFT) was performed using Quantum ESPRESSO [261] (QE) codes within LDA. We used the Troullier-Martin (TM) norm-conserving pseudopotentials [204].

7.2.3 Computational results on U-carbon

A novel P2₁/c structure with 16 atoms/unit cell (Fig.7.11) was predicted in our study, which is named as U-carbon hereafter. As shown in Fig.7.11, the U-carbon allotrope is formed by the stacking of distorted 5- and 6-member carbon rings. Unlike in our

Figure 7.11: Crystal structure of U carbon from the top view (a) and (b) the side view.

U-carbon model, Bct- C_4 has 4 + 8 rings and Z-carbon was built on 4 + 8 rings with one additional 6 ring layer; while M-carbon and W-carbon both consist of 5+7 rings. Its lattice constants are $a = 6.399 \text{ \AA}$, $b = 5.729 \text{ \AA}$, $c = 4.783 \text{ \AA}$, and $\beta = 148.83^\circ$. We have compared the enthalpy per atom for U-carbon with five other representative carbon allotropes in Fig. 7.14. At 0 GPa, U-carbon is more stable than Bct- C_4 . At high pressure, U-carbon becomes even more stable than both graphite and bct- C_4 above 16.2 GPa as shown in Fig.7.12. We also calculated the phonon dispersion spectra as shown in Fig.7.13(a), the dynamic stability of U-carbon was confirmed as we found no imaginary frequencies along the high-symmetry points.

The cold-compressed graphite are transparent with high electric resistivity, resulting in an insulator phase. The band structure of U-carbon is present in Fig.7.13(b). It reveals that U-carbon is an indirect band gap insulator (4.41eV), as listed in Table .7.2. The VBM is located at the middle of Z point and Gamma point; the CBM is near the point U along U $\rightarrow$ X direction. Compare with other allotropes, the band gap of U-carbon is larger than bct C_4 (2.56 eV) [98] and M-carbon (3.60 eV) [97]; as well larger than that of diamond (4.19 eV) [101]. Hence, U-carbon is considered to be consistent with the experimental observations of optical transparence [94].

To further confirm the validity of the U-carbon allotrope, we compared the simulated XRD for U-carbon with the experimental data, as shown in Fig.7.14. The x-ray wavelength for the simulation was set to be $0.3329 \text{ \AA}$. The coexistence of U-carbon and

Figure 7.12: The enthalpy per atom for U-carbon compared with other five representative carbon allotropes.

Figure 7.13: Calculated (a) phonon dispersion and (b) electronic band structure of U-carbon.

Table 7.2: Calculated equilibrium volume (V_0 in $\text{\AA}^3/\text{atom}$), band gaps (E_g in eV), bulk modulus (B_0 in GPa) for diamond, bct C_4 , Cco- C_8 and U-carbon.

Structure	Method	V_0	E_g	B_0
Diamond	This work	5.52	4.23	464.9
	LDA [101]	5.52	4.19	466.8
	LDA [99]	5.52	4.20	466.3
	Exp. [339]	5.67	5.47	446
bct C_4	This work	5.82	2.25	431.7
	LDA [101]	5.83	2.62	431.2
Cco- C_8	This work	5.67	3.57	446.1
	LDA [101]	5.68	3.12	444.1
U-carbon	This work	5.75	4.41	433.3

Figure 7.14: Comparison between simulated and experimental XRD patterns of the mixture of graphite and U-carbon at (a) 18.4 GPa and (b) 23.9 GPa.

graphite seems to account for the observed broadenings of the 100 ($\sim 9^\circ$) and 110 ($\sim 15.5^\circ$) peaks well. In previous research work, the coexistence of several theoretically predicted carbon allotropes and graphite can agree with most peaks from 8.5° – 10.5° and 15° – 17° , as well as U-carbon. Unfortunately, any of them cannot identify the main peak between 6° and 7° , some people believed that this peak might reflect the sp^2 bonding environment as in graphite [340] while J. T. Wang tried to assign this peak to the combined graphite and W-carbon [99]. Here, this emphasized peak as shown in Fig.7.14 for U-carbon gives the prominent match with cold-compressed graphite unprecedentedly. Moreover, another unassigned peak at $\sim 5.3^\circ$ now can be fitted excellent in U-carbon. In view of the mechanical and thermodynamic stability, transparency, bulk modulus and especially the similarity of XRD patterns between U-carbon and cold-compressed graphite, U-carbon is an excellent candidate for the cold-compressed graphite.

In summary, a novel superhard carbon allotrope U-carbon has been successfully found to give a better accordance with the XRD data for cold-compressed graphite than all previous proposed carbon allotropes, by employing the PSO algorithm combined with the first principles DFT calculations. Besides, U-carbon can account for experimental observations on bulk modulus, optical transparence and density of the undetermined superhard carbon phase, and is more stable than graphite above 16.2 GPa. Therefore, U-carbon can be viewed as one promising candidate for the phase of cold-compressed graphite.

Chapter 8

Conclusions

In this thesis we present a systematic study of two-dimensional (2D) materials, such as few layer graphene and molybdenum trioxide, using the first-principles calculations. Firstly, we systematically explore the mechanism of the stacking order transformation from ABC- to ABA-stacking orders in trilayer graphene by evaporating organic molecules onto its surface. Secondly, we reveal the novel properties of AB-stacking bilayer graphene by closing the edges along the zigzag direction, such as the band gap opening and spatial charge separation. Thirdly, we investigate the electronic and optical properties of molybdenum trioxide, α -MoO₃. Our finding provides an explanation for the observed “optical gap” contradictions between experiments and theories. Fourthly, we illuminate the mechanism for the enhancement of intensities of overtone peaks excited by 325 nm laser in MoS₂, which attribute to the energy match between the phonon energy and SOS. Finally, we explore new phases of molybdenum oxide (including MoO₂ and MoO₃) and carbon allotropes employing the particle swarm optimization (PSO) algorithm combined with the first principles calculations.

The further theoretical step would be investigate the effects of defects in such 2D materials. Here, the defects include the point defects (such as vacancies or impurities), line defects (such as dislocations) and planar defects (such as grain boundaries). For graphene systems, it has involves some defects in our current projects. For example, the grain boundaries between graphene domains can be formed by Stone-Wales defects

containing 5- and 8-membered carbon rings. In the case of MoO_3 , its catalytic properties depend sensitively on the presence and nature of defects. Such studies would be more interesting due to the various types and important role of defects in guiding the properties.

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Appendices

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