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Structure-Interaction Effects In Novel Nanostructured Materials

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Structure-Interaction Effects In Novel Nanostructured Materials

by

Nam B. Le

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Applied Physics
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Dedication

To my wife, Hoa Le, and my two sons, Vinh Le and Phong Le!
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I had started from scratch with computational physics in USF. It was very challenging at first but, thankfully, I have done significant jobs with the help of people around me.

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Abstract

Recent advances in experimental and computational methods have opened up new directions in graphene fundamental studies. In addition to understanding the basic properties of this material and its quasi-one dimensional structures, significant efforts are devoted to describing their long ranged dispersive interactions. Other two-dimensional materials, such as silicene, germanene, and transition metal dichalcogenides, are also being investigated aiming at finding complementary to graphene systems with other "wonder" properties. The focus of this work is to utilize first principles simulations methods to build our basic knowledge of structure-interaction relations in two-dimensional materials and design their properties. In particular, mechanical folding and extended defects in zigzag and armchair graphene nanoribbons can be used to modulate their electronic and spin polarization characteristics and achieve different stacking patterns. Our simulations concerning zigzag silicene nanoribbons show width-dependent antiferromagnetic-ferromagnetic transitions unlike the case of zigzag graphene nanoribbons, which are always antiferromagnetic. Heterostructures, build by stacking graphene, silicene, and MoS$_2$, are also investigated. It is found that hybridization alters the electronic properties of the individual layers and new flexural and breathing phonon modes display unique behaviors in the heterostructure compositions. Anchored to SiC substrate graphene nanoribbons are also proposed as possible systems to be used in graphene electronics. Our findings are of importance not only for fundamental science, but they could also be used for future experimental developments.
Chapter 1

Introductions

Materials at the nano-meter scale have drawn much attention as they served as templates to discover novel effects and fundamental principles as well as the construction of devices with functions unattainable at larger scales. There are many examples in science and technology, where specific nanostructures or devices help define a separate direction. For example, semiconducting quantum dots, systems in which the confinement of carriers in a material on the order of $5 - 100 \text{ nm}$, allow unprecedented possibilities for electronic and optical tuning\cite{5}. Another example is nanoelectromechanical systems (NEMS), a class of hybrid devices in nano-to-micrometer scale that can attain extremely high resonance frequencies and ultrasensitive mechanical sensitivity\cite{6,7}.

The discovery of graphene\cite{8} has opened up a new direction for surface materials. Graphene is an atomically thin sheet of carbon atoms arranged in an $sp^2$ bonded honeycomb lattice. Despite its atomic thickness, graphene is stable under ambient conditions. This material has high carrier mobility and possesses exceptional mechanical, transport and optical properties. With tensile strength of 130 GPa\cite{9}, graphene is stiffer than diamond. It has the electrical conductivity of copper and conducts heat better than any other known material\cite{8,10–13}. It is almost completely transparent with only 2.3\% of incident visible light being absorbed\cite{14}. With these extraordinary properties, graphene is highly expected to be the material of novel technological devices.
Its transport characteristics allow it to be used for high-frequency electronics, such as field-effect printed graphene circuits\cite{15}, top-gated transistors with epitaxial graphene on SiC\cite{16}, field-effect transistors\cite{17-22}, single molecule detection\cite{23,24}, and spin injection\cite{25-28}. In addition, self-aligned graphene transistor with transferred gate stacks can operate at cut-off frequency up to 427 GHz\cite{29}. Graphene can also be used in high modulation speed optical devices\cite{30} and many more\cite{11,31,32}.

Progress in experimental research has enabled the synthesis of graphene derivative systems. Specifically, graphene nanoribbons (GNRs) are quasi-one dimensional (quasi-1D) strips obtained via lithography, where single graphene layers have been mechanically extracted from graphite onto a SiO$_2$/Si substrate\cite{33}, then patterned to form an etched mask defining nanoribbons of 10 $\div$ 100 nm in width and 1 $\div$ 2 $\mu$m in length\cite{34}. GNRs of similar width but larger length (20 $\div$ 30 $\mu$m) have been achieved by chemical vapour deposition process\cite{35}. Narrower GNRs with less than 10 nm in width have been synthesized via chemical and sono-chemical methods\cite{36} or bottom-up fabrication approach\cite{37}. They can also be achieved by plasma etching and solution-based oxidative processes of unzipping multi-walled carbon nanotubes\cite{38,39} or the metal-catalysed cage-opening of C$_{60}$ fullerenes\cite{40}. More recently, GNRs with predefined shapes and dimensions have been done by the so-called nanotomy method, in which nanoribbons are exfoliated from highly oriented pyrolytic graphite\cite{41}.

Beside sharing intriguing properties with graphene, GNRs have their own characteristics. One of the most remarkable features is that GNR properties are highly sensitive to the width\cite{42-47}. Another factor, which is not only important for the GNR electronic structure, but it is also of great relevance to the magnetic properties, is the type of edges present: armchair or zigzag\cite{42-48}. Although the energy gap and resistivity of both types of GNRs generally increase with decreasing of the width\cite{46,49}, armchair ribbons exhibit an oscillatory bandgap as a function of number of armchair carbon lines\cite{46}. Whereas, zigzag GNRs are characterized by local magnetic ordering at the edges, which have been explained by the so-called flat-band ferromagnetism\cite{48}.

With its special electronic and magnetic properties, this type of quasi-1D derivative
of graphene is promising for electronic and spintronic applications. In the miniaturization of electronic devices, it is important to have materials with high permittivity and low loss at radio and low microwave frequencies, which can be fabricated by incorporating GNRs into dielectric polymers\textsuperscript{[50,51]}. GNRs can be combined with graphene and wrapped-MnS\(_2\) to form desired materials for lithium-ion batteries and super-capacitors\textsuperscript{[52]}. They can also be used together with polyaniline, a conducting polymer of the semi-flexible rod polymer family, to achieve a nano-composite with a high inhibition in gas permeation\textsuperscript{[52]}, which is useful for applications in food packaging and mobile gas storage containers.

The fabrication of graphene has been acclaimed as significant breakthrough in material science and modern physics. The research interest in this material and its quasi-1D nanostructures has been exploded in the past few years. However, there have been several challenges that make it difficult to use graphene in practical technological applications. Since pristine graphene has no bandgap, it is not probable to use it for logical circuits operating at room temperature. Inducing a bandgap in the band structure has had limited success. This is typically done by chemical or mechanical modifications, which leads to loosing some of the attractive transport properties of the pure graphene. Thus much work has been devoted to the search of other 2D materials.

The search for other layered materials has also been motivated by other practical applications as well as the possibilities for the discovery of new properties. In particular, 2D layers of honeycomb Si atoms, forming silicene, have been proposed\textsuperscript{[53,54]} and synthesized\textsuperscript{[55–57]}. Germanene (made of Ge atoms)\textsuperscript{[58,59]} and stanene (made of Sn atoms)\textsuperscript{[60–62]} are also possible. Although silicene, germanene, and stanene have similar properties to graphene, their slightly staggered lattices and large spin orbit coupling result in their unique characteristics. Silicene is also quite attractive from a technological point of view. Its compatibility with the existing silicon technology promises a better suitability than graphene for miniaturized devices.

Since its theoretical prediction, silicene and its quasi-1D nanoribbons have been studied from experimental and theoretical aspects\textsuperscript{[53–58,63–71]}. Theoretical works and
density functional theory (DFT) calculations have shown that silicene and silicene nanoribbons (SiNRs) possess not only properties similar to graphene and GNRs but also unique characteristics\cite{58,63-65,67,71}. Recent experimental advances towards synthesis\cite{55-57,66,68-70} have opened up new perspectives for applications. In spite of the fact that energy bands in silicene and graphene have similar linear dispersions at characteristic points of the Brillouin zone (BZ), the large spin orbit coupling has made silicene suitable for realizing quantum Hall spin effects and topological insulator features\cite{67,71,72}.

Silicene has been successfully grown on Ag substrates by depositing Si atoms onto Ag(110)\cite{55,66,68} and Ag(111)\cite{56,69,70} surfaces. It can also be formed through surface segregation on ZrB$_2$ thin films grown on Si wafers\cite{57}. The honeycomb structure of silicene was identified using scanning tunneling microscopy\cite{55,56,66}, in combination with low-energy electron diffraction\cite{70} or angular-resolved photoemission spectroscopy\cite{69}. Experimentally, freestanding form of silicene has not been realized yet, although this may be possible in the near future given the rapid progress in experimental techniques.

Besides hexagonal 2D surface systems, there are other layered materials, which have also attracted much interest. These include transition metal dichalcogenides (TMDC)\cite{73}, such as MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$, MoTe$_2$, and WTe$_2$. These 2D-TMDCs have nearly identical primitive cells in the form of a noncentrosymmetric crystal structure, where their symmetric point groups do not have center inversion. It is also remarkable that the electronic band structures of these atomically thin semiconductors are very similar, revealing direct energy bandgaps\cite{73-76}.

The freestanding monolayer d-electron TMDCs have recently drawn great scientific interest because of their exceptional electronic and optical properties\cite{74-79}. As an example, MoS$_2$ has tunable bandgap with a transition from indirect gap in bulk and few-layer crystals to a direct gap in monolayer nanosheets. This indirect-to-direct bandgap transition has been confirmed theoretically via DFT calculation\cite{74} and experimentally via optical spectroscopy\cite{74,75} showing that the monolayer MoS$_2$ has a photoluminescence quantum efficiency as strong as more than $10^4$ times than that of
the bulk counterpart. It is likely that MoS$_2$ and similar TMDCs, with the advantage of having significant bandgaps and strong photoluminescence, hold even more promise for actual applications than graphene. For example, monolayer MoS$_2$ can be used for manufacturing atomically thin transistors$^{[79]}$. They can also be used as light emitters in optoelectronic devices$^{[80,81]}$.

Without a doubt, the discovery of graphene$^{[8]}$ has been a stepping-stone in the evolution of materials science. Graphene and other honeycomb materials have revealed unprecedented physical properties, giving superior grounds for the future technological applications. The next essential step of development has been to realize systems by combining monolayers of different kinds to build various heterostructures stacked in a vertical manner. Scientific interest toward these Lego-like constructions was initiated by the fabrications of the combination of graphene and hexagonal boron nitride (hBN). By doping carbon atoms in hBN sheets one can obtain domains of graphene$^{[82]}$ or, inversely, monolayer hBN can be obtained by doping boron and nitrogen atoms in graphene$^{[83]}$. Graphene-hBN heterostructure can also be made laterally by low-pressure chemical vapour deposition$^{[84-86]}$.

In heterostructures, while strong chemical bonds are responsible for the in-plane stability of each layer, the relatively weak van der Waals (vdW) interaction keeps the layers together. It is expected that any set of different chemically inert 2D materials can be combined as a group and, therefore, one can have numerous types of heterostructures. Beside graphene-hBN as mentioned above, there are several other structures which have been synthesized, including combinations of graphene and TMDCs$^{[87-91]}$ and systems consisting of different types of TMDCs$^{[92]}$.

In addition to investigating the inherent properties of 2D and quasi-1D materials and how they interact, much effort is devoted to understanding how external modifications can be used to tailor their properties. Several reports have focused on mechanical and structural modifications. Making origami-like structures by mechanically manipulating 2D crystals can produce new physical properties$^{[93-97]}$. Modifying the structures by creating vacancies$^{[98-101]}$, defects$^{[102-104]}$ or horizontal heterostructures$^{[105,106]}$
can also lead to desired characteristics.

With high in-plane Young’s modulus\cite{107}, graphene and GNRs can be easily wrapped in the out-of-plane direction to form stable folded structures with one or more closed edges\cite{94,96,97}. Much effort has been devoted in the past several years to achieve such graphene nanostructures. Specifically, folded GNRs (FGNRs) have been thermally treated and studied by high-resolution transmission electron microscope (TEM)\cite{94}, surprisingly exhibited the dominance of AA stacking. They have also been synthesized by plasma-enhanced chemical vapor deposition\cite{108}, and studied by nanoarea electron diffraction (NED) together with TEM imaging\cite{96}.

Graphene has the ability to reconstruct by forming disorders within the hexagonal network\cite{12,109}. For example, the pentagon/heptagon Stone-Wales defect\cite{110}, a topological disorder where the number of atoms is unchanged, can be formed when a bond is rotated by 90° in the plane. By using DFT and quantum Monte Carlo simulations, researchers have shown that Stone-Wales defect in graphene results in out-of-plane wavelike defect structures that extend over several nanometers\cite{103}. Pentagon/heptagon defect can also be obtained at grain boundaries composed of a periodic array of dislocations in graphene. In the boundaries, two distinct transport behaviors, either high transparency or perfect reflection of charge carriers have been found\cite{111}. Another interesting example is the pentagon/octagon defect, which can be extended in a line to form a metallic wire imbedded in a graphene sheet\cite{104}.

**Outline:** The focus of my PhD dissertation is to explore structure-property-interaction relations for graphene and its related systems. By using first principles simulations based on Density Functional Theory, simulations of graphene and graphene nanoribbons are performed to investigate how "soft" mechanical deformations and structural defects affect their electronic structure. A particular attention is devoted to the role of vdW interactions. It is shown that such dispersive long ranged forces are key ingredients for the stability of graphene folds as well as vertically stacked heterostructures. Patterned anchored graphene nanoribbons with zigzag edges into a SiC substrate are also simulated. Such composite materials maybe of relevance to
electronic applications. My investigations on silicene and its nanoribbons show that such structures have properties similar to graphene, however they also possess distinct characteristics due to their significant spin orbit coupling.
Chapter 2

Characteristic Properties and Mechanisms

The fundamental understanding of graphene and its derivatives as well as their utilization for many technological applications relies on the basic science of their structural and electronic properties. Specifically, the unique energy band structure is a key component for their transport. In addition, structural modifications affect the electronic structure in profound ways, which in turn provides means to modulate the transport. Furthermore, the weak vdW interactions may also induce changes in the properties giving additional "knobs" for modulations. In this Chapter, we review basic properties of graphene systems that are of relevance of the subsequent work described in what follows.

2.1 Electronic structure properties

Even though graphene was synthesized only recently, the theory of its basic energy band structure has been available for several decades before that. P. R. Wallace\textsuperscript{[112]} was the first to consider via a tight binding model a single layer of hexagonal C atoms as a building block for graphite. He noted not only its atomic thickness, but also its unusual semiconducting behavior due to the linear bands at the Fermi level. In the following years, the electronic and magnetic properties of graphite and its monolayer
was studied by J. E. Hove\cite{113}, J. W. McClure\cite{114,115}, and J. C. Slonczewski and P. R. Weiss\cite{116}. In 1984, the 2D massless Dirac equation was first used to describe a mono-

layer of graphite by G. W. Semenoff\cite{117} and D. P. DiVincenzo and E. J. Mele\cite{118}. G. W. Semenoff pointed out in his work that it is possible to fabricate a graphite mono-

layer\cite{117}.

To summarize the basic electronic structure properties, we consider a hexagonal lattice of graphene whose primitive cell consists of two inequivalent atoms, A and B [fig. 2.1-(a)]. The 2D lattice vectors are also shown with coordinates

\[
a_1 = c \left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \right) \quad \text{and} \quad a_2 = c \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right),
\]

(2.1)

where \( c = \sqrt{3}a \approx 2.46\, \text{Å} \) is the lattice parameter (length of the lattice vectors) with \( a \approx 1.42\, \text{Å} \) being the nearest neighbor distance. The two unit vectors of the reciprocal (momentum) space can also be derived using the relation \( a_i \cdot b_j = 2\pi \delta_{ij} \) with \( i, j = 1, 2, \)

\[
b_1 = \frac{2\pi}{c} \left( \frac{1}{\sqrt{3}}, -1 \right) \quad \text{and} \quad b_2 = \frac{2\pi}{c} \left( \frac{1}{\sqrt{3}}, 1 \right).
\]

(2.2)

By using (2.1) and (2.2) one finds that the first BZ of graphene is a hexagon [fig. 2.1-(b)]. High symmetric k-points are \( \Gamma \) at the center of the first BZ, \( K \) and \( K' \) at the corners, and \( M \) in the middle of each side. Of particular interest are the graphene Dirac points.
K and K’,

\[ \mathbf{K} = \frac{1}{3} \mathbf{b}_1 + \frac{2}{3} \mathbf{b}_2 = \frac{2\pi}{c} \left( \frac{1}{\sqrt{3}}, \frac{1}{3} \right), \quad \mathbf{K} = \frac{2}{3} \mathbf{b}_1 + \frac{1}{3} \mathbf{b}_2 = \frac{2\pi}{c} \left( \frac{1}{\sqrt{3}}, -\frac{1}{3} \right). \] (2.3)

Utilizing the nearest neighbor approximation, Wallace derived the energy band structure of graphene within the tight binding approximation\[112]\,

\[ E_{\pm}(\mathbf{k}) = \pm t \sqrt{3 + 2 \cos(ck_y) + 4 \cos\left(\frac{ck_y}{2}\right) \cos\left(\frac{\sqrt{3}ck_x}{2}\right)}, \] (2.4)

where plus and minus signs refer to \(\pi^*\) and \(\pi\) bands, respectively, and \(t \approx 2.8\) eV is the nearest-neighbor hoping energy. By expanding (2.4) in the vicinity of \(\mathbf{K}\) (or \(\mathbf{K}'\)), it is found that\[11\]

\[ E_{\pm}(\mathbf{q}) \approx \pm v_F |\mathbf{q}|, \quad (\mathbf{q} = \mathbf{k} - \mathbf{K}, \ |\mathbf{q}| \ll |\mathbf{K}|), \] (2.5)

where \(v_F\) (\(v_F \approx 10^6\) m/s \(\approx c/300\)) is the Fermi velocity in graphene.

The electronic bandstructure of graphene from DFT calculations is shown in \textbf{fig. 2.2}. It shows that the DFT bandstructure agrees with the predictions from the tight-binding model in the vicinity of the Dirac point. Both theories exhibit a linear dependence of energy on momentum around \(\mathbf{K}\). That results in a momentum-independent Fermi velocity and zero effective mass for graphene\[119\]. Therefore, electrons and holes in
graphene behave like Dirac fermions which satisfy the Dirac equation for a massless particle,

\[-i v_F \sigma \cdot \nabla \psi(r) = E \psi(r).\]  \hspace{1cm} (2.6)

Here, \(\sigma = (\sigma_x, \sigma_y)\) are the Pauli matrices and \(\psi(r)\) is the two-component wave function\(^{[11]}\).

One of the extraordinary features of graphene is that it is a zero-overlap semimetal with very high electrical conductivity. For each carbon atom in graphene, the two \(s\) electrons and two \(p\) electrons in the outer shell hybridize to create three \(sp^2\) orbitals which are responsible for the in-plane bonding. The remaining \(pz\) orbital (also termed \(\pi\) orbital) is perpendicular to the plane. The bonding and anti-bonding of the \(\pi\) orbitals (correspond to valance and conduction bands, respectively) determine the electronic properties of graphene. This is illustrated by the density of states (DOS) in fig. 2.2, showing that the contribution around the Fermi level is determined by \(pz\). The concentration of charge carriers in graphene is found to be as high as \(10^{13} \text{ cm}^{-2}\)\(^{[8,120]}\) and their mobilities can be up to \(10^6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\)\(^{[120]}\). These charge carriers can travel thousands of interatomic distances without scattering, a phenomenon known as ballistic transport\(^{[8,10,33,120,121]}\).

The energy band structure of GNRs can also be derived using a nearest neighbor tight binding model\(^{[122]}\) by requiring that the wave function vanish at the edges, or by DFT calculations\(^{[1,2,46]}\). Different types of edges, armchair or zigzag [fig. 2.3-(b,c)],

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2_3.png}
\caption{(a) Flat graphene lattice; Hydrogen-saturated GNRs with (b) zigzag and (c) armchair edges; (d) Staggered silicene lattice.}
\end{figure}
have different consequences on the electronic structure. Armchair GNRs are classified into three families based on the number of armchair-lines, $N_a = 3p$, $N_a = 3p + 1$, and $N_a = 3p + 2$, where $p$ is a positive integer. The classification is dictated by the fact that the Fermi wavelength of $\pi$ orbitals approximates the distance between four atomic sites along the width of the AGNR$^{[1]}$. Using nearest neighbor tight binding model, it is found that the first two families are semiconductors with energy bandgaps decreasing in almost the same way vs. the width, while the third one exhibits metallic behavior for all $p$. In contrast, DFT calculations show that all the three families are semiconductors, as can be seen from fig. 2.4-(a).

Nevertheless, such classification does not apply for ribbons with zigzag edges. Results from first-principles calculations show that zigzag GNRs (ZGNRs) have direct bandgaps which decrease smoothly as a function of increasing width, as can be seen in fig. 2.4-(b)$^{[2,46]}$. Several theoretical and experimental studies have shown that ZGNRs have flat bands near the Fermi level $E_F$, which result in very large density of states (DOS)$^{[2,42,46,48,106]}$. In addition, it was shown that for number of zigzag lines $N_z \geq 8$, the relation$^{[46]} E_g = 9.33/ (W + 15)$ between energy gaps ($E_g$ in eV) and the width ($W$ in Å) of ZGNRs holds. For both armchair and zigzag GNRs, the energy gaps decreases as the width of the system increases. It has been experimentally confirmed$^{[34,123]}$. 

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Fig. 2.4 Energy gaps of (a) AGNRs and (b) ZGNRs; Electronic bandstructures of (c) 30 armchair-lines AGNR and (d) 20 zigzag-lines ZGNR.
2.2 Zigzag edges and spin polarization

One of the most interesting properties of GNRs is the possibility of spin polarization of the zigzag edge, despite the fact that carbon is not a ferromagnetic element. It has been shown that each zigzag edge, with successive edge segments at opposite angles which are responsible for holding highly localized states, is ferromagnetic. Whereas, the spins at the two edges of a ZGNR are oppositely oriented making the overall ribbon antiferromagnetic\textsuperscript{[2,42,43,46,48,106,123–125]}. That spin polarization can be interpreted by Hubbard model\textsuperscript{[126–128]}, in which it is related to the flat-band ferromagnetism\textsuperscript{[129–131]} and the associated infinitely large DOS around the Fermi level\textsuperscript{[132]}. In the fig. 2.4-(d), a flat energy band of the 20 zigzag-lines GNR is present at the large k-point region above the Fermi level. While, a typical example of bandstructures of AGNRs is given in fig. 2.4-(c), showing that it does not have flat bands and, therefore, does not have spin polarizations.

The spin polarization of ribbons with zigzag edges is not specific to carbon-atom sheets. Boron nitride nanoribbons with normal zigzag edges or zigzag edges in the form of pentagon-heptagon defective lines can also have such feature\textsuperscript{[133,134]}. Other structures containing zigzag edges have also been reported to exhibit magnetic ordering. In specific, hybrid lateral composites consisting of alternating hBN and carbon zigzag ribbons joined together have been shown to be be ferromagnets\textsuperscript{[105,106]}.

The ferromagnetic ordering of a single zigzag edge is present in any system composed of hexagonally arranged species despite their atomic nature. We have shown that zigzag silicene nanoribbons not only possess this feature, but they also exhibit antiferromagnetic to ferromagnetic transition as a function of the width\textsuperscript{[3]}. The origin of the tunable spin polarization in this case has also been interpreted in terms of the balance between the exchange correlation and kinetic energy contributions from the total energy of the system. For ZSiNRs with small width, the balance is such that antiferromagnetic state is preferable, similar to what happens in ZGNRs. When the width becomes larger the interference between the two edges decreases and much more kinetic energy is sacrificed towards exchange correlation for the ferromagnetic state.
2.3 Spin-orbit coupling in graphene and silicene

In quantum physics, spin-orbit (SO) coupling is a relativistic effect which describes the interaction between spin and angular momentum of a particle. It is well known that the coupling between spin and orbital degrees of freedom of electrons in an atom causes the shifting of energy levels and splits the spectrum lines of the atom. In a tight-binding model, the Hamiltonian for the SO interaction has the form

\[ H_{SO} = \frac{\hbar}{4m_e^2c^2} - (\nabla V \times p) \cdot s, \tag{2.7} \]

where \( V \) is the electrostatic potential, \( p \) is the momentum and \( s \) is the spin of the electron.

A structure with significant SO coupling can be used to generate and control spin currents without an applied magnetic field. This phenomenon, predicted by M. I. Dyakonov and V. I. Perel in 1971\[^{137,138}\], is called the spin Hall effect (SHE)\[^{139,140}\]. When a spin current is injected into a large sheet of pure graphene at low temperature, SO coupling exhibits the so-called quantum SHE (QSHE), in which the spin currents are conducted by surface states and are protected by topological order that destroys all small perturbations\[^{136}\]. To have SO effect and QSHE in graphene without external spin currents, one needs to introduce impurities in order to create \( sp^3 \) bonds\[^{141–143}\]. It is clear that the \( sp^3 \) distortion strongly enhances the coupling between spin and orbital degrees of freedom in 2D hexagonal crystals. In any case, while it is possible to observe SO effect in graphene, it is not an easy task.

Silicene, as mentioned in chapter 1, has available \( sp^3 \) hybrid bonds from its low-buckled structure due to the large ionic radius of silicon\[^{53,57,58,63,70,72,144}\]. This is a clear advantage of silicene as compared to graphene for the existence of SO coupling. By using first-principles calculations, it was shown that the bandgap of silicene corresponds to SO coupling is 1.55 meV\[^{67}\], which is much higher than the value 24 \( \mu \)eV of graphene\[^{145,146}\]. That makes QSHE and topological insulator, the quantum state with insulating gap in the bulk and zero gap edges which are topologically protected\[^{147,148}\],
in silicene be experimentally accessible. With strong SO coupling, the topological state in silicene is tunable by an applied electric field. Under the action of a perpendicular electric field, silicene sustains a topological phase transition from topological insulator to a band insulator\cite{72,149} or, when the field is appropriately polarized, another insulator which has an opened Dirac valley and a closed one, at $K'$ and $K$ in the first BZ, respectively\cite{71}.

### 2.4 Roles of van der Waals interactions

In addition to their basic internal properties, understanding graphene and related systems interact with the environment or other materials is also important. Due to the chemical inertness of these layered materials the vdW interaction becomes prominent.

The vdW force is induced by electromagnetic fluctuations\cite{150}. It is relatively weak compared to other chemical interactions and is often ignored in electronic structure calculations. However, the vdW interaction has crucial roles in systems of neutral objects and in many cases, it decides the formations of composites and systems, which in turn affect their characteristics.

There are several approximation methods for vdW interactions\cite{151–153}. The simplest one is the Lennard Jones (LJ) model\cite{154}, in which the vdW potential comes from the pairwise summation of interatomic potentials. For two sheets of 2D or quasi-1D materials, the interaction potential is integrated over the surfaces of the sheets,

\[ V = \sigma^2 \int \left( -\frac{A}{\zeta^6} + \frac{B}{\zeta^{12}} \right) \mathrm{d}S_1 \mathrm{d}S_2, \tag{2.8} \]

where $\sigma$ is the surface density, $A$ and $B$ are Hamaker constants\cite{155}, and $\zeta$ is the distance between two surface elements $\mathrm{d}S_1$ and $\mathrm{d}S_2$. We note that the vdW term corresponds to the first term in (2.8), while the second one reflects the repulsion due to other quantum mechanical processes at small $\zeta$. In spite of its simplicity, this semi-empirical method gives acceptable results for many systems, including carbon nanotubes\cite{156–158}.

Eq. (2.8) is the continuous version of the pair-wise Lennard-Jones approximation
for finite atomic and molecular systems. It provides a straightforward way to estimate the interaction energy and equilibrium distances, which will depend on the Hamaker constants. The vdW interaction, however, is a many-body phenomena due to its long-ranged electronic correlations. It is precisely the collective nature that has made it difficult to compute the interaction from first principles for extended systems up until recently\textsuperscript{[159]}.

When the separation of the interacting objects is larger than several angstroms, the overlap of their electronic distributions can be neglected meaning that each object can be treated independently and the mutual Coulomb potential can be taken as perturbation. In such cases, computational methods are not required to calculate the vdW interaction and one can turn to the use of more appropriate analytical methods. Perhaps the most popular approach has been the Lifshitz theory, which uses the macroscopic dielectric response of each object mediated by the Coulomb interaction. This approach is supplemented by the fluctuation dissipation theorem, which shows that such long-ranged interactions are due to virtual fluctuating dipoles\textsuperscript{[153,160]}.

The regime of small distances (less than several angstroms) signals that the atomistic nature of the interacting objects and the overlap of their electronic distributions must be taken into account. The computational task is formidable in such situations and only recently progress has been made in solving this problem. The vdW approximations available in DFT calculations are reviewed in the next Chapter.
Chapter 3

Methodology

3.1 Ab initio simulations

In computational physics, ab initio simulations refer to methods of calculations which start from theoretical principles (first-principles), with no empirical parameters or experimentally-derived information. The primary goal of the methods is to solve the Schrödinger equation of quantum theory taking into account the explicit atomic structure. However, it is almost impossible to computationally obtain the exact solutions for even systems of several atoms. Therefore, mathematical approximations have been used to lighten the calculations. Within various methods in first-principles calculations, density functional theory (DFT) has been utilized in countless types of systems and composites in modern science. It is considered an important step in contemporary computational physics. The development of DFT has befitted by several, simpler approximations, which are briefly discussed below.

The first example is the Born-Oppenheimer (BO) approximation method\cite{161,162}. This is a two-step procedure which approximately solves Schrödinger equations for a molecule, where motions of electrons and nuclei are treated separately under the assumption that nuclei are much heavier than electrons. In the first step, nuclei are considered as "fixed" entities, i.e. they are clamped at certain positions in space and their kinetic energy is neglected. The electronic wavefunction depends upon positions
of nuclei but not on their velocities. These assumptions mathematically break up the total wavefunction of the molecule into electronic and nuclear parts,

$$\Psi_{\text{tot}}(r, R) = \Psi_e(r, R)\Psi_n(R), \quad (3.1)$$

where $r$ and $R$ are the compact notations for positions of electrons and nuclei, respectively. Within this step, $R$ is infinitesimally changed for numerous times, and the Schrödinger equation for electrons,

$$H_e\Psi_e(r, R) = E_e\Psi_e(r, R), \quad (3.2)$$

is solved for each small step of $R$. This equation, however, can be solved exactly for the simplest case of hydrogen atom. For any decent size systems, even an accurate numerical solution is a formidable task. In these cases, we need to invoke other methods to numerically solve it.

In the second step, the resulting electronic eigenvalue $E_e$ from (3.2), which changes with $R$ to form an energy surface, is used as the potential term of the total Hamiltonian. The Schrödinger equation for the whole molecule,

$$[T_n + E_e(R)]\Psi_{\text{tot}}(r, R) = E\Psi_{\text{tot}}(r, R), \quad (3.3)$$

will be solved to get the total energy $E$ and derive the physical properties of the molecule. Here, the nuclear kinetic energy $T_n$ consists of rotational, translational and vibrational movements of the nuclei. This equation is not easy to solve, too, since the external (rotational and translational) and internal (vibrational) terms cannot be fully separated. In the usual case of a semi-rigid molecule with a potential energy surface which has a well-defined minimum, the Eckart conditions\textsuperscript{[163]} (also called the Sayvetz conditions\textsuperscript{[164]}) is utilized in order to minimize the coupling between the two terms.

Even though the BO approximation significantly simplifies the calculations, it is quite crude and has some limitations that need to be improved. Moreover, this method
may fail when two or more different electronic states have closed energy at particular nuclear geometries. All degeneracies of electronic motion for clamped nuclei are highly forbidden\cite{162}. This is not possible for real systems. Therefore, BO approximation cannot be used as a standalone method. However, the situation changes if another approximation, such as Hartree-Fock (HF) method, is embedded in it.

HF theory\cite{165} was developed to solve the electronic Schrödinger equation of the form (3.2), which was derived in the first step of the BO approximation. Consider an atom of \(N\) electrons, it is assumed that the electrons do not directly interact each other. Instead, each electron approximately feels the Coulomb repulsion due to the average position of all electrons. By that assumption, the electronic wavefunction can be written in terms of products of single-electron orbitals. Furthermore, with the help of the Slater determinant\cite{166}, it can be written in an antisymmetric form (required by the Pauli exclusion principle),

\[
\Psi_e(1, 2, \ldots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_{1}^{(in)}(\mathbf{r}_1) & \cdots & \phi_{N}^{(in)}(\mathbf{r}_1) \\
\vdots & \ddots & \vdots \\
\phi_{1}^{(in)}(\mathbf{r}_N) & \cdots & \phi_{N}^{(in)}(\mathbf{r}_N)
\end{vmatrix},
\]

(3.4)

where \(\phi_{i}^{(in)}(\mathbf{r}_j)\) denotes for the \(i^{th}\) (input) orbital when it is occupied by the \(j^{th}\) electron. Initially, an appropriate basis set of orthonormal functions is chosen, base on the type of the molecule in studying, to be the input single-electron states\cite{167}. Then, the chosen basis set is used for constructing the single-electron and total densities,

\[
\rho_{i}^{(in)}(\mathbf{r}) = |\phi_{i}^{(in)}(\mathbf{r})|^2 \quad \text{and} \quad \rho^{(in)}(\mathbf{r}) = \sum_{i=1}^{N} \rho_{i}^{(in)},
\]

(3.5)

respectively.

In the next step, the equation (3.2) is solved for \(\Psi_e\) in (3.4). The solutions (output) \(E_e\) and \(\phi_{i}^{(out)}(\mathbf{r}_j)\) are written in terms of the input densities \(\rho_{i}^{(in)}\) and \(\rho^{(in)}\). Output densities \(\rho_{i}^{(out)}\) and \(\rho^{(out)}\) are calculated by using formulas similar to (3.5). If the output is closed enough to the input then it can be used for calculating properties of the system.
Construct $\rho^{(in)}_i(r) = |\phi^{(in)}_i(r)|^2$, $\rho^{(in)}(r) = \sum_{i=1}^{N} \rho^{(in)}_i$

Choose $\phi^{(in)}_i$

Solve $H_e \Psi_e(r, R) = E_e \Psi_e(r, R) \Rightarrow E_e$ and $\phi^{(out)}_i(r)$

Construct $\rho^{(out)}_i(r) = |\phi^{(out)}_i(r)|^2$

$|\rho^{(out)}_i(r) - \rho^{(in)}_i(r)| < \delta$

No

Yes

Calculate properties

End!

Fig. 3.1 Hartree-Fock algorithm.

Otherwise, (3.2) needs to be solved again with $\rho^{(out)}_i$ and $\rho^{(out)}$ now become new input parameters. The procedure is repeated until the difference between output and input is small enough.

The method discussed above is a self-consistent field method, whose algorithm is summarized in fig. 3.1. More detail of the HF method can be found in Refs. The method, however, have disadvantages since it ignores the direct interactions between electrons and, therefore, part of the electron correlation would be missed.

3.2 Density functional theory

The DFT was born in the 1960s by P. Hohenberg, W. Kohn and L. J. Sham. It has widely been used in physics since the 1970s. With about 15,000 world-wide publications per year within the last five years, it has become very popular not only in physics but also in chemistry, biology and many others. This method allows one to replace the complicated many-body electronic wavefunction and its associated Schrödinger equation by a set of independent orbitals described by the so-called Kohn-Sham equation using the electronic density of the system. It derives, in principle, that any physical property of a many-body system can be viewed as a functional of the ground state density. The theory, therefore, drastically simplifies the many-body prob-
lems and it lowers the computational costs as compared to the traditional methods, including the HF theory discussed earlier.

The platform of DFT is the two theorems stated by P. Hohenberg and W. Kohn in their 1964 paper\cite{hohenberg1964}. Consider a system of interacting electrons in an external potential \( v(r) \). The Hamiltonian of the system has the form

\[
\mathcal{H} = \mathcal{T} + \mathcal{U} + \mathcal{V},
\]

(3.6)

where \( \mathcal{T}, \mathcal{U} \) and \( \mathcal{V} \) are the kinetic, Coulomb interaction and external potential parts, respectively. Here,

\[
\mathcal{V} = \langle \Psi | v | \Psi \rangle \equiv \int v(r)\Psi^*(r)\Psi(r)dr = \int v(r)n(r)dr,
\]

(3.7)

where \( \Psi(r) \) is the many-body electronic wavefunction and \( n(r) = |\Psi(r)|^2 \) is the electronic density of the system.

We assume that the ground state of the system is nondegenerate for any external potential. That is to say there is one and only one ground state \( \Psi_0(r) \) corresponds to the lowest energy \( E_0 \) which satisfies

\[
\mathcal{H} |\Psi_0\rangle \equiv (\mathcal{T} + \mathcal{U} + \mathcal{V}) |\Psi_0\rangle = E_0 |\Psi_0\rangle.
\]

(3.8)

Clearly, \( v(r) \) (or \( \mathcal{V} \)) determines \( \Psi_0(r) \) and, therefore, is a functional of the ground state density \( n_0(r) = |\Psi_0(r)|^2 \). There is, however, a question raised up. Can a different external potential give the same ground state density?

Let us consider a new potential \( v'(r) \) which gives ground state \( \Psi_0'(r) \) and energy \( E_0' \),

\[
\mathcal{H}' |\Psi_0\rangle \equiv (\mathcal{T} + \mathcal{U} + \mathcal{V}') |\Psi_0\rangle = E_0' |\Psi_0\rangle.
\]

(3.9)

From the degeneracy of the ground state \( \Psi_0'(r) \) must be different from \( \Psi_0(r) \) (except for the trivial case of \( v'(r) - v(r) = \text{constant} \)). In other words \( \Psi_0'(r) \) must be an excited
state in the old external field \( v(r) \). Therefore,

\[
E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_o \rangle < \langle \Psi'_0 | \mathcal{H} + V - V' | \Psi'_0 \rangle
\]

or, by using (3.7),

\[
E_0 < E'_0 + \int [v(r) - v'(r)] n'_0(r) dr. \tag{3.10}
\]

Similarly, since \( \Psi_0(r) \) is an excited state in the new external field \( v'(r) \),

\[
E'_0 < E_0 + \int [v'(r) - v(r)] n_0(r) dr. \tag{3.11}
\]

It turns out that if \( n'_0(r) = n_0(r) \) then (3.10) and (3.11) lead to the inconsistency

\[
E_0 + E'_0 < E_0 + E'_0. \tag{3.12}
\]

A conclusion, which is the first theorem of the DFT, can be made from that.

**Hohenberg-Kohn Theorem I.** *For a system of interacting electrons moving under the influence of an external potential \( v(r) \), the external potential is (to within a constant) a unique functional of the electronic density \( n_0(r) \) in the ground state of the system.*

Since most of the many-body systems encountered in physics have nondegenerate ground states, this theorem can be applied with no need of an extension. However, it has been generalized to the situations which have degenerate ground states by several authors, including W. Kohn[174-177].

According to the theorem, \( n_0(r) \) uniquely determines \( v(r) \) and, therefore, uniquely determines \( \mathcal{H} \) (to within a constant shift of the energy). It follows that the electronic wavefunctions and energies for all (ground and excited) states, the sources of all physical properties, can be specified given only \( n_0(r) \). That leads to an important corollary.

**Corollary I.** *All properties of an interacting electronic system can be completely determined by the ground-state density.*
The kinetic and Coulomb energies are functionals of the electronic density. At the current time we do not know the explicit forms of these terms. However, we can define a universal functional \( F[n] \) which plays the role as \( \langle \Psi | T + U | \Psi \rangle \) in the theory,

\[
F[n(r)] \equiv \langle \Psi | T + U | \Psi \rangle.
\]  

(3.13)

When \( F[n] \) is chosen, an energy functional can be defined, base on the form of \( H \) in (3.6), as

\[
E[n(r)] \equiv F[n(r)] + \int v(r)n(r)dr.
\]  

(3.14)

By minimizing this functional in the variation of \( n(r) \) one can get the ground state energy. That is summarized in the second theorem of DFT.

**Hohenberg-Kohn Theorem II.** For a system of electrons, a universal functional for the energy in term of the electronic density, \( E[n(r)] \), can be defined, valid for any external potential and any number of particles. For a particular functional, the exact ground state energy of the system is the global minimum of this functional, and the density that minimizes the functional is the exact ground state density \( n_0(r) \):

\[
E_0 = E[n_0(r)] = \min E[n(r)],
\]  

(3.15)

\[
\frac{\delta E[n(r)]}{\delta n(r)} \bigg|_{n(r)=n_0(r)} = 0.
\]  

(3.16)

Following is an immediate corollary of this theorem.

**Corollary II.** The energy functional \( E[n(r)] \) alone is sufficient to determine the exact ground state energy and density.

For the convenience, \( F[n] \) is separated as

\[
F[n] = \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} drdr' + G[n],
\]  

(3.17)

where the first term is the classical Coulomb energy and the second term, \( G[n] \), is a
universal functional. The energy functional is rewritten as

\[ E[n] = \int v(r)n(r)dr + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|}drdr' + G[n]. \] (3.18)

To this point, no approximation has been applied and the external potential is still present explicitly as can be seen in the first term of \( E[n] \).

In the paper of W. Kohn and L. J. Sham\(^{[171]}\), they proceeded one more step by separating

\[ G[n] = T_s[n] + E_{xc}[n], \] (3.19)

where \( T_s[n] \) is the kinetic energy of a fictitious system of noninteracting electrons with the same density \( n(r) \) and \( E_{xc}[n] \) is the exchange-correlation energy of the interacting system. If \( n(r) \) varies slowly then the exchange-correlation energy can be written as\(^{[170]}\)

\[ E_{xc}[n] = \int n(r)\epsilon_{xc}(n(r))dr, \] (3.20)

where \( \epsilon_{xc}(n) \) is the exchange-correlation energy per electron of a uniform electron gas with the same density, which is regarded as a known quantity.

By using the Hohenberg-Kohn Theorem II for the energy functional (3.18), the variation of \( n(r) \) when the total number \( N \) of electrons is unchanged leads to

\[ \int \delta n(r) \left\{ \frac{\delta T_s[n]}{\delta r} + v_{KS}(r) \right\} dr = 0, \] (3.21)

where

\[ v_{KS}(r) = v(r) + \int \frac{n(r')}{|r-r'|}dr' + \frac{d(n\epsilon_{xc}(n))}{dn} \] (3.22)

is the Kohn-Sham potential. It can be seen from (3.21) that the given system, with density \( n(r) \) and moving in the external potential \( v(r) \), is equivalent to a fictitious noninteracting system, which has the same density and moves in the effective potential \( v_{KS}(r) \).

For a noninteracting system, we simply solve a set one-particle Schrödinger equa-
Assume \( n^\text{in}(\mathbf{r}) \) in (3.22) to construct \( v_{\text{KS}}(\mathbf{r}) \) from (3.22), solve (3.23) and construct new \( n(\mathbf{r}) \) using (3.24). The algorithm of this method is illustrated in the fig. 3.2.

3.3 Van der Waals

One of the challenges of DFT calculations is the lack of electronic correlations due to Coulomb interactions. This is a significant shortfall of this popular computational scheme since many systems have prominent vDW interactions. Only in the last several years, significant steps forward in taking into account vDW interactions have been
achieved. Researchers have reported several types of approaches to account for long-ranged electronic correlations, utilizing different approximations.

Recently, a semi-empirical method based on the Lennard-Jones pairwise type of vdW interaction was implemented in DFT. This DFT-D scheme was first proposed by S. Grimme in 2004\textsuperscript{178}, in which the vdW dispersion energy is calculated as

\[
E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_{6,ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij}),
\]

where \(s_6\) is a global scaling factor (its value depends on which functional is used in DFT), \(C_{6,ij}\) is the dispersion coefficient for the atom pair \(ij\), and \(R_{ij}\) is the interatomic distance. Here, unlike the LJ method, the near-singularities are eliminated by a special form of the damping function

\[
f_{\text{dmp}}(R) = \frac{1}{1 - \exp \left[ -\alpha \left( R/R_0 - 1 \right) \right]},
\]

where \(\alpha\) is a constant and \(R_0\) is the sum of atomic vdW radii. The method has been developed in the following years by Grimme and his coworkers\textsuperscript{179,180}. It works well for systems of light elements, including carbon.

A more advanced scheme is the DFT-TS method, which was proposed by A. Tkatchenko and M. Scheffler in 2009\textsuperscript{181} and developed by their team in 2012\textsuperscript{182}. The formula for dispersion energy in this method is formally identical to that in DFT-D. However, it involves a self-consistent screening calculation of the frequency-dependent atomic dipole polarizability\textsuperscript{182},

\[
\alpha_p^{\text{SCS}}(i\omega) = \alpha_p^{\text{T}_{\text{S}}}(i\omega) - \alpha_p^{\text{T}_{\text{S}}}(i\omega) \sum_{q \neq p}^{N} \tau_{pq} \alpha_q^{\text{SCS}}(i\omega),
\]

where \(\tau_{pq}\) is the dipole interaction tensor. In this method, it is also important that the dispersion coefficients and damping function are charge-density dependent.

A different way to take into account dispersion correlations relies on a vdW density functional (vdW-DF) method developed by M. Dion and coauthors\textsuperscript{183,184}. This is a
seamless functional method since it starts from the correlation-energy part due to the nonlocal response of the density,

\[ E_{\text{c}}^{\text{nl}}[n] = \frac{1}{2} \int d^3r d^3r' n(r) \phi(r, r') n(r'), \]

(3.28)

where \( n(r) \) is the electron density at \( r \) and \( \phi(r, r') \) is a function that depends on \( r - r' \) and the densities in the vicinities of \( r \) and \( r' \). This energy is included in the total exchange-correlation energy. Therefore, the vdW correction part is self-consistently calculated as the DFT energy is. It is computationally more expensive than the previous semi-empirical methods, but is more reliable, especially for systems of gases and benzene dimers.
Chapter 4

Graphene Nanoribbons$^{[1,2]}$

The general properties and potential applications of graphene and GNRs were discussed in the previous chapters, showing that they are highly expected to be the materials of the future technology, especially for high-speed electronic devices. This chapter is devoted to studying GNRs under deformations, including folded structures and structures with defective lines. The obtained results for folded armchair and zigzag GNRs (FAGNRs and FZGNRs, respectively, for short) will be presented in section 4.3 and section 4.4.

4.1 Motivation

As mentioned in chapter 1, mechanical manipulations can result in altering the properties and functionalities of graphene and GNRs. Of particular interest is wrapping in out-of-plane direction yielding various folded structures. Folded GNRs (FGNRs) can be viewed as two flat sheets connected by a curved edge. They are also referred to as fractional nanotubes because the curved edge has a nanotube-like structure. Graphene folds have been observed experimentally$^{[108]}$, and they can also be achieved by mechanical stimulations$^{[94,96]}$ or by high temperature annealing$^{[185]}$. Recently a variety of different forms of graphene pleats have also been demonstrated$^{[97,186]}$. The majority of natural graphite occurs in the Bernal (AB) stacking sequence, and only a small portion appears in the rhombohedral ABC form$^{[187]}$. However, scanning tunneling microscopy
studies have shown that FGNRs can occur not only in AB but also in AA or other patterns\cite{97,185}. Thus folding can offer the possibility to generate other registry dependent configurations.

The existence of interlayer coupling together with the edges at the open ends and bending energy at the closed edge influence the stability and electronic and transport characteristics in a profound way. Recent studies have developed a coarse-grained model showing that the balance between the bending and adhesion determines self-folding\cite{188}. Nearest-neighbor tight binding reports have calculated the conductance of FGNRs showing that the electronic structure can be changed significantly by assuming different values of the adhesion between the flat portions\cite{189}. Electronic structure calculations have revealed that FGNRs have permanent electric dipoles\cite{190}.

Here we investigate folded structures of AGNRs with single and double closed edges. The open sides of the studied structures have H-saturated armchair ends. The folded configurations are found to have a variety of unusual stacking patterns. Our \textit{ab initio} calculations reveal the evolution of the geometries as a function of the width of the ribbons. Particular emphasis is placed on the role of the van der Waals (vdW) dispersion and its role in terms of the stability of the various formations. The electronic structure is also obtained showing that single and double folds can have much different properties as compared to those of their planar counterparts.

Creating organized extended defects is another promising way for tailoring properties of ZGNRs. For instance, a defective line consisting of $sp^2$ C pentagons and octagons, which behaves as a metallic wire in graphene\cite{104}, is expected to greatly influence on properties of ZGNRs if embedded. A topic of considerable interest is to study the interplay between the particular types of GNRs, the presence of extended defects and folding concurrently in order to find new ways to further change the properties of these functional materials.
4.2 Methods

Our calculations are performed using self-consistent density functional theory (DFT) implemented in the Vienna Ab-Initio Simulation Package (VASP)\cite{191,192}, where the Kohn-Sham equations are solved using the projector-augmented-wave (PAW) method of Blochl\cite{193,194}, with a plane-wave basis set and periodic boundary conditions. The exchange-correlation energy is described by the Perdew-Burke-Ernzerhof (PBE) functional\cite{195}.

In the study of AGNRs, \((1 \times 1 \times 7)\) Monkhorst-Pack k-grid sampling of the Brillouin zone was taken for the self-consistent calculations with an energy cutoff of 430 eV. The structures are allowed to relax with \(10^{-5}\) eV total energy and \(0.02\) eV·Å\(^{-1}\) force convergence criteria. Each supercell is constructed so that the distance between the nearest neighbors in each direction is about 10 Å so that the self-interaction (interaction between a supercell with its images) is negligible. For ZGNRs we use the same k-grid sampling total energy criterion. However, due to the fact that properties of the zigzag edge are more sensitively influenced by the surrounding environment, we increase the force criterion to \(0.01\) eV·Å\(^{-1}\). The closest distance between supercells is also increased, to 20 Å in every direction. To avoid chemical self-interaction, the ends of the ribbons are always saturated by hydrogen atoms, which do not have any effect on the electronic structure and magnetic ordering of the ribbons.

The long-ranged van der Waals (vdW) interaction plays a determining role in the formation and stability of the folded structures. The vdW coupling is taken into account via the DFT-D2 approach\cite{196,197} implemented in VASP, with the parametrization given by Grimme et al.\cite{178,179}. In this method, a semiempirical dispersion potential is added to the conventional Kohn-Sham energy, and the vdW correlations are calculated self-consistently through a pairwise force field optimized for DFT functionals. Despite its two-body nature, the DFT-D2 implementation is an efficient way enabling first principles calculations to take into account vdW dispersive interactions.
4.3 FAGNRs and electronic structure modifications

Folded structures of AGNRs with single and double closed edges are studied in this section. The geometrical phases of these structures are obtained, showing interesting phase transition in the case of single folded ribbon. The electronic structure in terms of energy needed for the folding process, van der Waals contribution, energy bandgaps, and band structures are also calculated. The results are interpreted in terms of peculiarities of the structures and dispersion interactions. It is shown that significant modifications in the electronic structure can be achieved as a result of folding.

4.3.1 Energy and geometric structure

Flat AGNRs, which are nonmagnetic and of semiconducting nature with energy bandgaps decrease in the increasing of the ribbon width, will be used to construct single and double folded structures for this study. Each AGNR can be represented via the number of C atomic lines $N$ along its axis, as shown in fig. 4.1-(a). A single FAGNR is prepared by bending the flat ribbon onto itself creating a symmetric structure with two parallel graphene portions lying on top of each other. A double FAGNR is done in a similar manner but folding the ribbon twice with three graphene portions on top of each other.

Each fold is relaxed within the criteria specified in section 4.2. The obtained structures of some of the single folded ribbons are shown in fig. 4.1-(b). We find that when $17 \leq N \leq 27$, the single fold takes a shape that looks like a racket without a handle. The distance between the furthest points on the curved side increases as the width of the ribbon becomes larger with a maximum value of 8.7 Å, achieved for $N = 27$ [fig. 4.1-(b)]. When $N = 28$, the folded structure experiences a geometrical phase transition, resulting in a reduced curved region and forming two flat GNR-like strips. When $N \geq 28$, the geometrical form becomes racket-like. Interestingly, the shape of the curvature is almost unchanged except the length of the flat regions becomes larger for larger value of $N$, as can be seen from fig. 4.1-(b). The distance between the flat
regions is similar to the interplane separation in graphite. It is \( \sim 3.2 \, \text{Å} \) for even \( N \) and \( \sim 3.5 \, \text{Å} \) for odd \( N \) number of Carbon lines.

The type of open edges determines the stacking patterns of the folded ribbons. It is realized that \( AA \) stacking is geometrically compatible with armchair GNRs, while \( AB \) stacking is geometrically compatible with zigzag GNRs. Fig. 4.1-(c) and Fig. 4.1-(d) show the side and top views of the studied single folds. It turns out that all ribbons with odd \( N \) take \( AA \)-stacking patterns. The folded ribbons with even \( N \) occur in an orthorombic \( AB' \) orientation characterized with a CC bond symmetrically situated above the center of each hexagon. We point out that \( AB' \) stacking is highly unusual in regular graphite. It is one of the intermediate phases that may exist if very high pressure is applied\(^{[198]}\), and yet here it occurs relatively easy by simple folding.

Fig. 4.2 shows some of the studied cases of the double folded structure. No pronounced geometrical phase transition is found here. However, as the GNR increases, the flat-like portions become larger, while the curved regions experience little change. The distance between the flat regions is always \( \sim 9 \, \text{Å} \), which is almost triple the distance between the flat sides of the single folded ribbons with \( N > 28 \). Considering the top view, the stackings for the different ribbons are resolved. It is obtained that they fall into categories distinguished by the number of carbon lines: for \( N = 3p \) (\( p \) is
integer), the pattern is $AAA$; for $N = 3p + 1$, the pattern is $AB'A'$; and for $N = 3p + 2$, it is $AA'A''$. The last geometrical phase is described by having two CC bonds symmetrically positioned in the Carbon hexagon (top view).

The graphene folding is a process that involves a balance between the elastic bending and the vdW interaction. The vdW attraction seeks to make a loop and it decreases the overall energy of the structure, while the bending tries to resist that tendency and it increases the total energy. The balance between these two effects determines the size and form of the loop as well as the flat-like regions. We find that the smallest ribbon for which single folding can occur is $N = 17$ ($W = 19.7\,\text{Å}$), while the smallest double folded ribbon has $N = 28$ Carbon lines ($W = 33.3\,\text{Å}$). Our calculations show that if the vdW potential is not taken into account, the single folded $N = 17$ and double folded $N = 28$ ribbons are not stable, indicating the importance of dispersion for the stability of the folds.

Further, we calculate the energy needed to achieve folding via the relation

$$\Delta E_{1,2} = E_{1,2}^{\text{tot}} - E_0^{\text{tot}}. \quad (4.1)$$

where $E_{0,1,2}^{\text{tot}}$ are the total energies for the unfolded, single folded, and double folded GNRs, respectively. Results from the calculations are shown in fig. 4.3. It is seen that in general, the energy decreases rather smoothly as the width becomes larger (larger $N$).
Fig. 4.3 (a) Total energy per atom needed to create single (1fold) and double (2fold) FGNRs as a function of C atomic lines \( N \); (b) vdW energy per atom for single and double FGNRs as a function of C atomic lines \( N \).

We compare these results with the vdW energy obtained via the \( D_2 \) Grimme approach [fig. 4.3-(b)]. The vdW interaction is stronger when graphenes or GNRs are parallel and at a distance \( \sim 3 \, \text{Å} \). Thus \( E_{vdW} \) becomes larger as the width of the ribbon increases reducing \( \Delta E \). At the same time, the loop is smaller, thus less energy is needed for bending.

For the single FGNR with \( N = 27 \), \( E_{vdW} \) is smaller in magnitude as compared to the others, which reflects the lack of parallel flat-like portions since the geometrical phase transition occurs for \( N = 28 \). It is interesting to note that in practically all of the other cases \( |E_{vdW}| \) is in \( 62 \div 72 \, \text{eV} \) range. The oscillatory-like behavior as a function of \( N \) is attributed to the strong geometrical influence originating from the registry dependence of the C atoms for the different stackings. This effect has been previously realized in other graphitic nanostructures and it has also been attributed to the geometrical dependence in such dispersive interactions\[159\]. One notes that for single FGNRs with even \( N \) (\( AB' \)), \( E_{vdW} \) is always lower than that of the closest odd \( N \) (\( AA \)). The vdW energy for the double FGNR with \( AB'A \) stacking also appears as local minima, however this trend is not pronounced as well.

### 4.3.2 Electronic structure

The electronic structure of the different ribbons is also calculated within VASP. The resulting energy bandgaps are given in fig. 4.4, while the energy bandstructure for three
GNRs is shown in Fig. 4.5. All unfolded GNRs are found to be semiconductors which is directly related to the wave vector quantization along the finite width of the ribbon and the shorter H-C bond lengths at the ends. We find that the end H-C bonds are about 23% shorter than the C-C bonds in the middle of the ribbon (∼ 1.42 Å). This is particularly important for the $N = 3p + 2$ cases, which are predicted to be metals within a nearest neighbor tight binding model\cite{97}. If the tight binding model is modified to account for this difference in bond length, $E_g$ is non-zero in agreement with DFT calculations. The oscillatory and generally decreasing $E_g$ as a function of $N$ is in accordance with previously reported \textit{ab initio} simulations of graphene ribbons\cite{45}. The periodicity of 3 for these bandgap oscillations are in the same classes as outlined above - $N = 3p$, $3p + 1$, $3p + 2$. These are directly related to the $\pi$ nature of the ribbon orbitals having Fermi wavelength approximately four atomic sites along the width of the ribbon. Therefore, every time a C line is added, the Fermi wavelength changes in a 3-fold periodic pattern. Although the folded structures have reduced energy gaps as compared to the ones for the unfolded ribbons, the oscillatory-like behavior is preserved for the single FGNRs. Fig. 4.4 shows that local maxima ($N = 3p + 1$) and minima ($3p + 2$) in $E_g$ for single folds generally coincide with local maxima and minima for the unfolds. This behavior, however, is not preserved for the double folded structures. This is expected since additional stacking patterns occur in the 2fold GNRs.

The unfolded $N = 28$ GNR is a semiconductor with relatively large bandgap
$E_g = 0.461 \text{ eV}$ at the $\Gamma$ point as seen in fig. 4.5-(a). Folding the ribbon once results in moving the highest valence and lowest conduction bands closer [fig. 4.5-(b)]. The energy bands of the double folded ribbon around the Fermi level are found to be almost touching away from the $\Gamma$ point, indicating that the system becomes semimetal. Similar behaviour is found for the single folded $N = 35$ ribbon [fig. 4.5-(e)]. The $N = 40$ ribbon does not experience a semiconductor-semimetal transition due to the folding process. Folding it once and twice reduces the gap which is always at $\Gamma$ [fig. 4.5-(g,h,i)]. Perhaps the most interesting transition is found for the double folded $N = 35$ GNR. The system is a metal with a band crossing the Fermi level near $\Gamma$ [fig. 4.5-(f)].

Our calculations show that the vdW interaction is quite important for the magnitude of $E_g$ of the studied structures. If the vdW dispersion is not taken into account, the separation between the parallel portions is larger and consequently the coupling is weaker. For the $N = 28$ 1fold GNR, for instance, the distance between the ends is 3.356 Å without vdW and 3.156 Å with vdW interaction, while for the $N = 40$ 1fold GNR, the corresponding separations are 4.043 Å and 3.568 Å. Comparing the energy gaps, we find that the vdW coupling reduces the bandgaps. For example, for $N = 39$ $E_g = 0.138 \text{ eV}$ (single fold) and $E_g = 0.035 \text{ eV}$ (double fold) without the vdW interaction, while $E_g = 0.125 \text{ eV}$ (single fold) and $E_g = 0.0086 \text{ eV}$ (double fold) when the vdW interaction is taken into account. Similarly, for $N = 40$ $E_g = 0.362 \text{ eV}$ (single fold) and $E_g = 0.246 \text{ eV}$ (double fold) without vdW, while $E_g = 0.301 \text{ eV}$ (single fold) and $E_g = 0.060 \text{ eV}$ (double fold) with vdW interaction.

Analyzing the electronic structure shows that the energy bands around $E_F$ are mainly determined by the $p$ orbitals from the edge atoms which are perpendicular to GNR axis. These can be considered as edge $\pi$ states. Upon folding, the interaction between the flat parallel-like portions lifts all degeneracies causing the energy bands to move closer. If the vdW dispersion is taken into account, the interlayer coupling is stronger leading to more distorted edge $\pi$ states, more prominent band splitting and thus smaller gaps. In addition, relatively small $\sigma-\pi$ hybridization from the orbitals located on the curved regions is found to contribute to the energy bands around $E_F$ due
to the folding process. The smaller distance between the flat-like regions upon inclusion of the vdW dispersion in the simulations leads to slightly stronger bond changes at the curvature and the $\sigma - \pi$ hybridization is somewhat increased, although the dominant effect is still the interlayer interaction. The curved regions also have smaller influence on the electronic structure of larger ribbons. Their energy bandstructure is mainly determined by the parallel regions. The number of parallel layers further influences the bandstructure. If there are more such layers, the band splitting further increases due to the interlayer interaction and further reducing the bandgap. Additional bands may also appear around $E_F$, which is the case in Fig. 4.5-(f), for example. Thus, in general, double folded GNRs have smaller $E_g$. For the double folded structures with smaller $N$, however, there are no significant flat regions since the widths of ribbons are relatively small. As a result, for several $N$ $E_g$ for 2fold is actually larger than $E_g$ for 1fold [Fig. 4.4].

These results illustrate how diverse the physical and energy band structures can be when effects due curvature, dispersive interlayer coupling, registry dependence, and structure size influence the system simultaneously. The stacking patterns and bandstructure characteristics functionalities are complex. The shift in registry can result in transforming an armchair GNR from a semiconductor to another semiconductor, a semimetal, or even a metal. Folded ribbons with $AA$ and $AB'$ stackings can exist as semiconductors or semimetals depending on the number of C lines in each case. Tak-
ing into account the vdW dispersion is also important since it influences the energy band splitting and the resulting energy bandgaps.

4.4 FZGNRs, extended defects and spin polarization

In this section, geometric, electronic and magnetic properties of single and double folded ZGNRs are studied using DFT methods. Some asymmetric folded structures and structures with an octagon/hexagonal defective line are also considered. The geometrical and magnetic phases of the studied structures are obtained, showing that the magnetic states of the folds depend strongly on their stacking patterns. Significant changes in the electronic structure as a result of folding and adding line defects are also achieved.

4.4.1 Energy, geometric structures and magnetic ordering

Each ZGNR can be specified by the number \( N \) of zigzag lines or by the width \( W \) as shown in fig. 4.6-(a). We study single and double folded symmetric zigzag ribbons which are illustrated in fig. 4.6-(b,d) and asymmetric single folds as can be seen in fig. 4.6-(c). Line defects comprised of rotated CC bonds and forming an ordered extension of two pentagons followed by an octagon are also created in the center of a zigzag GNRs [fig. 4.7-(a)]. Consequently, single and double folded defective GNRs, as shown in fig. 4.7-(b,c), are also investigated.

In our study zigzag GNRs with \( 10 \leq N \leq 27 \) are found to be stable with single folded structures. Double folds, however, exist for \( N \geq 18 \) and here we investigate structures with \( 18 \leq N \leq 27 \). The studied systems are relaxed with the criteria specified section 4.2 and some representatives are shown in fig. 4.6 after relaxation. The folded structures are found to be stable due to the balance between the elastic bending from the curved regions and the vdW force from the flat-like portions. The elastic bending resists the curving, while the vdW attraction favors it. The shape of the single
Fig. 4.6 Top and side views of the GNR structures: (a) unfolded ribbon with $N = 10$ zigzag C lines; (b) single folded ribbons with $N = 21$ C lines; (c) asymmetrically single folded ribbon with $N = 26$; (d) double folded ribbon with $N = 27$ Carbon lines. The magnetic moments for each structure are shown as arrows on the corresponding atoms.

Folds looks like a racket, but for $N < 21$ ($W < 43 \text{ Å}$) the racket does not have a "handle", which is its flat-like portion. For larger ribbons, the flat portions are bigger and the curved regions are slightly reduced, which causes the configurations to be more stable.

We note that for the cases of armchair single folds, there is an abrupt geometrical transition at $N = 28$ carbon lines ($W = 33 \text{ Å}$), where the folded ribbon experiences a significant reduction of the curved region (by $\sim 1/2$) and increase in the "handle" (by $\sim 2$) as compared to $N = 27$. For the zigzag single folds, however, there is a gradual transition as the shape of the curved region remains practically constant, but the size of the parallel parts increase gradually.

Of particular interest is the variety of stacking patterns one achieves by such fractional nanotubes. For example, AA stacking is found for all even $N$ 1folds, while the pattern for all odd $N$ is the one shown in fig. 4.6-(b), which is called AB’. Other variations can be found in the 2folds. We point out that achieving different CC ring orientations in layered graphene systems maybe difficult to obtain experimentally, however, folding seems to provide many possible ways of obtaining layered registry dependence. For the asymmetric 1folds, by changing the size of the overlap region we can also obtain various types of stacking patterns. The natural form of bilayer graphene
and graphite is the Bernal (AB) stacking. However, other patterns have been seen in scanning tunneling microscopy imaging due to misaligned or twisted graphene layers\textsuperscript{[199]}. Different patterns in such graphene layered systems can lead to modifications in their electronic and optical properties\textsuperscript{[200,201]}.

We also simulate unfolded, single and double folded structures for a GNR with $N = 20$ zigzag lines and with an extended linear defect comprised by octagon/pentagons patterns positioned in the center. This line defect breaks the CC hexagonal symmetry and the curvature is reduced as compared to the defect free case. However, the double fold geometrical form is practically unchanged since the line defect is in the center of the ribbon [fig. 4.7].

The energetics for the studied zigzag GNRs is further investigated. In fig. 4.8-(a), we show $\Delta E = E_{AFM} - E_{NM}$, which is the difference between the total energies for the antiferromagnetic (AFM) and nonmagnetic (NM) ground states for the 0, 1, and 2folded structures. The figure shows that the ground state for all unfolded and double folded GNRs is AFM. The C atoms at the very ends are found to have magnetic moments with magnitude $m = 0.16\mu_B$ ($\mu_B$ is the Bohr magneton). The magnetic moment strength quickly decreases towards the middle of the ribbon [fig. 4.6]. The value of $m$ here is compatible with the value found by M. Fujita et al. ($m = 0.19\mu_B$) in 1996 us-
Fig. 4.8 (a) Difference in energy between an AFM ($E_{\text{AFM}}$) and nonmagnetic ($E_{\text{NM}}$) ground states for 0fold, 1fold, 2fold zigzag GNRs as a function of $N$; (b) vdW energy $E_{\text{vdW}}$ as a function of $N$ for 1fold and 2fold GNRs; (c) Energy gap $E_g$ as a function of $N$. 

The Hubbard model within the mean-field approximation\cite{48}. For the 1folded ribbons with even $N$, however, the ground state is always found to be nonmagnetic. We note that for such 1folded ribbons, the AA stacking pattern causes the edge C atoms from the two sublattices residing on the two flat portions to be directly above each other, while for odd $N$ the AB’ stacking is realized [fig. 4.6-(b)]. Consequently, the first type of registry dependence destroys the AFM ordering, while the second one does not. We further note that the symmetric ribbons with a line defect experience the same magnetic ordering as the corresponding defect-free ones do. Since $N$ is even, the 1folded defective ribbon is nonmagnetic, while the 0 and 2folded ribbons maintain their edge AFM moments. This indicates that the defect line in the center does not influence the edge magnetism of the graphene nanostructures. The asymmetric single folded structures preserve the localized edge moments for all $N$, since the edge atoms from the opposite sublattices/flat regions are never above each other.

Fig. 4.8-(b) shows how the vdW energy for each folded GNR changes as the width becomes larger. $E_{\text{vdW}}$ increases as $N$ grows, which is a consequence of the increase of overlap between the flat-like portions of each fold. The saw-tooth-like behavior of $|E_{\text{vdW}}|$ vs. $N$ indicates a strong influence from the geometrical dependence of the interacting atoms\cite{159}. Generally, we find that $|E_{\text{vdW}}|$ is smaller for even $N$ as compared to the closest odd $N$ cases for the single folds. For the double folds, the oscillatory-like pattern is characterized by a period of $N = 2$ separating the lowest and highest points.
of this functional behavior.

### 4.4.2 Electronic structure

We also investigate the electronic structure for the different folded structures of ZGNRs by examining their energy gaps. Fig. 4.8-(c) shows that all studied unfolded ribbons are semiconductors with gradually decreasing energy gaps $E_g$ as the width of the ribbons increases. All the double folds are also semiconductors, however, their energy gaps differ significantly for some $N$ from the smooth $E_g$ decrease for the unfolded ribbons. For single folds, only the ones with odd $N$ are semiconductors. Interestingly, most of the nonmagnetic 1folds of even $N$ have been found to be semimetals. We note that some of the armchair 1folds, which are nonmagnetic, are also semimetal, but no such clear pattern as the one for the zigzag 1folds was established. Fig. 4.8-(c) reveals an oscillatory-like behavior following the pattern for the vdW energy. For example, 1fold GNRs have larger gaps for odd $N$ (corresponding to smaller $|E_{vdW}|$) as compared to the cases of even $N$ (corresponding to larger $|E_{vdW}|$).
The characteristic energy bandstructure for some structures is given in Fig. 4.9. The energy gaps appear at the $K$ point of the GNR Brillouin zone. The two parallel-like energy levels which are closest to the Fermi level are determined by the edge $\pi$ states. Upon folding, the interaction between the flat portions causes these energy bands to move closer in some cases or farther apart in others from the Fermi level, while the bending from the curved regions has only a secondary effect. Taking into account the vdW interaction can influence the overall interlayer coupling. This can have quite a profound effect on the energy gaps and the characteristic behavior of the low lying energy states for 0fold, 1fold, 2fold, or asymmetrically folded ribbons. The vdW correction is taken into account self-consistently, therefore the relaxation of the structures.
will be affected at each step and it may contribute to changes in the bond-lengths, curvature of the folded parts and equilibrium distances. By comparing these results to the energy bandstructure for the folded armchairled GNRs shown in section 4.3, we can see that no metal-semiconductor transition are found for the zigzag folds. For the armchair folds, however, a rich picture of several such transition was uncovered. This includes closing the energy gaps at different locations, and lifting the degeneracy of several bands.

Finally, we investigate the electronic structure of the unfolded, single and double folded GNRs for the particular case of a ribbon with \( N = 20 \) zigzag lines and with an octagon/pentagon topological defect line in the middle. The energy bandstructures and corresponding densities of states are calculated and shown in fig. 4.10. We find that the magnetic ordering is not influenced by the line defect, as the magnetic edge states maintain the pattern found for nondefective structures. However, other researchers have shown that various locations of the line defect with respect to the edges and/or the presence of strain can lead to half-metallic or ferromagnetic behavior\(^{[202,203]}\).

The defect line destroys the particle-hole symmetry for the perfect \( N = 20 \) ribbon and lifts the degeneracy of the bands around the Fermi level, as seen in fig. 4.10-(a). The lowest valence and highest conduction dispersionless bands are due to the localized states at the octagon/heptagon line, while the next closest to \( E_F \) bands are due to the states localized at the edges. Very similar characteristics are found for the double folded ribbon [fig. 4.10-(c)] with the small difference that the flat bands now reside on the Fermi level. The interaction between the flat portions in the single folded structure, however, affects the bandstructure in a profound way. The dispersionless bands are pushed above the \( E_F \). The energy levels around the Fermi level are still composed of the localized states at the defect line, but they cross at \( k = 0.33\pi/c \), where \( c \) is the length of the lattice vector. In fact, the bandstructure for the single folded defective ribbon is very similar to the one found in single walled armchairled carbon nanotubes (see\(^{[204]}\), for example). Although, the energy bands in both cases have similar behav-
ior, the crossing at $k = 0.33 \pi / c$ for the armchair nanotubes is due to the zone folding due to the cylindrical boundary conditions. For the single forded ribbons, this is due to the topological defect line in the center of the ribbon together with the interaction between the parallel-like regions.

\section*{4.5 Summary}

In this chapter we have studied folded armchair and zigzag GNRs with single and double closed edges. The DFT approach is augmented self-consistently via the DFT-D2 dispersion correction, a semiempirical correction, in order to take into account the van der Waals interactions. Some asymmetric and topological line defective structures are also considered. We obtain geometrical phases of the studied structures in terms of various characteristic distances and stacking patterns, which are generally not found in open ended layered graphene or GNRs. We find that the folded ribbons have a variety of stacking patterns, which strongly affect the dispersive vdW contribution to the total energy. These registry dependent effects are also important for the energy bandgap and electronic structure modifications as a result of the folding process.

Electronic and magnetic properties of the studied folded GNRs are interpreted in terms of the calculated band structures, energy bandgaps, electronic densities of states and localized magnetic moments. It has been shown that modifications in the electronic structure can be obtained from the folding and/or adding extended defect octagon/heptagon lines. Our studies present a comprehensive description of the interplay between mechanical alterations and electronic structure modifications in graphene nanoribbon structures. The results here can be of interest to researchers searching for ways to engineer graphene/GNR properties taking advantage of the out of plane flexibility of these nanostructured systems.
Chapter 5

Silicene Nanoribbons\textsuperscript{[31]}

Silicene is a newly invented allotrope of silicon which is structurally similar to graphene. The only difference in the geometries of the two materials is that the structure of silicene is staggered, which makes it suitable for observing quantum spin Hall effect and topological insulator phases. Because of its compatibility with the current silicon-based electronics, more effort needs to be invested on this graphene-like system.

5.1 Motivation

We have discussed in chapter 1 that despite of having extraordinary characteristics, graphene and and its quasi-1D derivatives have been challenging for the integration into the current silicon based electronics. Within the analogous materials, silicene is possibly the best substitution due to its similarity to graphene, not only in geometry but also in electronic structure, and its suitability with the existing electronic devices. Although the free-standing form of silicene has not been realized yet, it has been synthesized on substrates of Ag\textsuperscript{[55,56,66,68–70]} and ZrB\textsubscript{2}\textsuperscript{[57]}. 

In graphene, C atoms are bonded by $sp^2$ orbital hybridization to form a flat 2D configuration. Whereas, due to the strong electron correlation, Si atoms in silicene prefer a low-buckled honey-comb structure\textsuperscript{[53,57,58,63,70,72,144]}. The bonding in that low-buckled structure has been shown to be a combination between $sp^2$ and $sp^3$ hybridiza-
Theoretical study using DFT calculations have revealed that the π and π* states around the Fermi level of silicene are similar to those of graphene. Namely, their energy bands are linear nearby the Fermi level and form Dirac points in the hexagonal BZ. However, due to the relatively large atomic number of Si and the staggered lattice structure, spin-orbit coupling in silicene is not negligible as in the case of graphene. That causes silicene Dirac electrons to be massive and leads to unique properties comparing to graphene. As an example, large SOC in silicene makes the mass of Dirac electrons be controllable by an applied electric field which is perpendicular to the silicene sheet, produces a prominent topological phase transitions.

Despite the predictions for many exotic features in silicene systems, their structure-property relationships are not fully known and understood yet. The quasi-1D nature, edges, and strong SOC are of particular interest. Here, we present computational studies using DFT methods for zigzag SiNRs exploring how their characteristics are influenced by the size of the width, magnetic orientation, and the presence of extended topological defects. It turns out that the SOC plays a critical role for the electronic structure and that there is a width dependent antiferromagnetic-ferromagnetic transition. In addition, extended topological defects, containing pentagonal and octagonal rings embedded in the hexagonal low-buckled structure result in novel spin polarized properties.

5.2 Methods

To investigate the SiNR properties, first principles simulations using the the PAW-PBE potential embedded in the VASP code are performed. The SOC has a relatively large contribution to the electronic structure due to the buckled structure and it is responsible for the massive Dirac carriers at the $K, K'$ points. For the systems considered here, the SOC is taken into account via non-collinear magnetic calculations. The implementation in VASP uses valence electrons taken into account through second-variation method and scalar-relativistic eigenfunctions. Although this
brings a substantial additional computational cost, the SOC is necessary to properly describe the electronic structure properties of the nanoribbons.

Due to the specific characteristics of silicene systems and the addition of the SOC effect, better values of energy cutoff, k-grid sampling and convergent criteria as compared to those in the calculation for graphene systems in chapter 4, are used. In the ionic relaxation of all studied structures, the energy cutoff and k-points sampling are increased to 500 eV and \((1 \times 1 \times 11)\) automatic-mesh, respectively. The relaxed structures are obtained with force and total energy difference criteria of \(5 \times 10^{-3} \text{ eV} \cdot \text{Å}^{-1}\) and \(10^{-6} \text{ eV}\), respectively.

### 5.3 Structure of silicene nanoribbons

SiNRs with widths in the \(24 - 112\) Å range \((N = 8 - 32\) zigzag lines\), and hydrogen saturated zigzag edges are studied. The hydrogen ends have a small effect on the intrinsic properties of the ribbons, which makes it useful to study the intrinsic properties of the silicene zigzag edge. However, other compounds can also be used to passivate the highly reactive Si nanoribbon ends, as past research for graphene nanoribbons has shown\[205\]. The supercells are constructed to have \(20\) Å vacuum separation between ribbons in neighboring cells. Similar to the nomenclature used for GNRs, the width of each SiNR corresponds to a specific number of zigzag Si lines as shown in fig. 5.1-(a). SiNRs with extended topological defects composed of alternating pentagon-octagon pairs are also investigated. Such defects can appear in different locations with respect to the edges. Here we study \(N = 8 - 30\) SiNRs with a defect line located in the middle of the ribbons [fig. 5.1-(b)], and a \(N = 20\) SiNR with an asymmetrically positioned defect line specified by different \(N_1, N_2\) zigzag lines [fig. 5.1-(c)].

The buckled lattice of SiNRs have been confirmed by comparing the total ground state energy of each structure with that of the corresponding flat-like one. For example, we investigate that the energy difference for the ground state is \(\sim 0.39 \text{ eV}\) for \(N = 8\) and \(\sim 1.57 \text{ eV}\) for \(N = 32\) ribbons in favor of the buckled lattice. After relaxation, the
Fig. 5.1 Relaxed SiNR with \( N = 20 \) zigzag lines and (a) no defect present; (b) extended defect positioned in the center; (c) extended defect located asymmetrically. Characteristic Si-Si distances and degrees of buckling are denoted. Atoms residing on the defect line are denoted in yellow. Zigzag edges are saturated with H atoms (denoted in red). The infinite axial direction is denoted as \( y \).

degree of buckling of 0.47 Å above the plane is found to be the same for all studied nanoribbons. However, the Si atoms located on the defect line are protruded by 0.53 Å above the plane. Comparing perfect and defective SiNRs with the same number of zigzag lines shows that the topological defect results in an approximately 2 Å larger width due to the extra Si line at the defect.

For all structures we performed nonmagnetic (NM), antiferromagnetic (AFM), and ferromagnetic (FM) calculations. It turns out that all ribbons are magnetically ordered and the width is crucial for the particular magnetic state. For thinner ribbons \((N \leq 23)\) the AFM state is the most stable one, while for thicker ones the ground state is FM. Fig. 5.2-(a) shows that similar to zigzag GNRs\(^{[2,48]}\), the edge atoms bear the largest spin.
polarization and the magnitude of the atomic magnetic moments decreases quickly towards the center of the ribbon. All SiNRs with extended topological defects are found to be ferromagnets with majority edge spins and minority spins at the zigzag lines surrounding the defect [Fig. 5.2-(b,c)]. The total magnetization is $M \sim 0.78 \mu_B$ for all defect-free SiNR, and $M \sim 0.83 \mu_B$ for defective ribbons ($\mu_B$ is the Bohr magneton).

The origin of the spin polarization in zigzag nanoribbons has been attributed to localized edge states and their effect on the electronic structure\cite{105,106}. The existence of a flat-band in some of the Brillouin zone and associated electronic correlations leads to a FM polarization of each edge. It has been suggested that the flat-band magnetism is not specific to C atoms. It also occurs in edges with B and N atoms. Our calculations also show the existence of localized edge states in SiNRs, which is a testament that zigzag magnetism can exist even in a staggered honeycomb lattice with significant SOC.

The overall magnetic state of the ribbons can be understood by investigating the energy difference $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$\cite{206–208} and the contributions making up $E_{\text{AFM,FM}}$. For the DFT calculations here, the kinetic and exchange-correlation contributions to
Fig. 5.3 (a) Total energy difference $\Delta E = E_{AFM} - E_{FM}$; the inset shows $E_{FM} - E_{NM}$ (green) and $E_{AFM} - E_{NM}$ (blue). (b) Kinetic $\Delta T = \Delta T_{AFM} - \Delta T_{FM}$ and exchange-correlation $\Delta E_{xc} = \Delta E_{xc}^{AFM} - \Delta E_{xc}^{FM}$ differences. (c) Energy gap $E_g$. (d) Majority and minority energy gaps as a function of $N$ for defect-free SiNRs.

the AFM and FM energies are determining factors for $\Delta E$.

Let us first study $\Delta E$ as a function of the SiNR width. Fig. 5.3-(a) shows that $|\Delta E|$ decreases nonlinearly as $N$ is increased and for $N = 23$ the total AFM energy is $\sim 1$ meV lower than the total FM energy. Although this difference is small, the results did not change by increasing the Brillouin zone sampling, energy cutoff, or other precision-related criteria. For the ribbon with $N = 24$, $\Delta E \sim 41$ meV signaling the AFM-to-FM transition, with $\Delta E$ being almost constant for all $N > 24$ ribbons. The inset of fig. 5.3-(a) shows that for $N \leq 23$, the NM state is the least preferred as it has the highest total energy, while for $N \geq 24$, the AFM and NM total energies become practically the same.
The energy difference $\Delta E$ shown in fig. 5.3-(a) is a key component in understanding the spin polarization of the nanoribbons. It is directly related to the interedge interaction, which determines the spin alignment at the edges\cite{207}. The DFT calculations imply that $\Delta E = \Delta T + \Delta E_{xc}$, where $\Delta T$ is the kinetic (band) energy and $\Delta E_{xc}$ is the exchange-correlation contributions. The electrostatic energies, which also contribute to $E_{AFM,FM}$, are canceled in $\Delta E$ since they are identical. Both AFM and FM states sacrifice kinetic energy to gain interaction energy. Fig. 5.3-(b) shows that both $\Delta T$ and $\Delta E_{xc}$ are small and oscillatory-like functions centered at zero for $14 \leq N \leq 23$. Nevertheless, the balance is such that the preferred state is AFM. This $\Delta E$ vs $N$ behavior is very similar to that reported for graphene nanoribbons. $\Delta E$ decreasing as the width is increased but still favoring the AFM state has been obtained by mean field Hubbard model theory and \textit{ab initio} calculations for graphene nanoribbons\cite{206–208}. Comparing our results with the ones for the graphene systems shows the decisive role of the exchange correlation for the AFM.

As $N$ is increased, the interedge interference decreases and much more kinetic energy is sacrificed towards exchange correlation for the FM state [fig. 5.3-(b)]. The majority of this energy corresponds to the $k > 0.3\pi/c$ ($c$ - lattice vector length) region in the Brillouin zone as we further show. It is interesting to see that the oscillatory behavior is still present for $N > 24$, but $\Delta T > 0$ and $\Delta E_{xc} < 0$. The competition is such that the FM alignment is preferred with a rather large $\Delta E \sim 40$ meV indicating that the FM state is quite stable for wider SiNRs. The dominance of exchange-correlation for the FM orientation is unlike the case of graphene nanoribbons. For these systems no AFM-FM transition as a function of the width is found since the exchange-interaction dominates the AFM orientation for all ribbons.

5.4 Edges and extended defects in SiNRs

We also calculate the energy bandstructure to further understand the magnetic edge states. Fig. 5.3-(c) shows that the energy gap between the highest valence and lowest
conduction bands smoothly decreases as $N$ is increased for the AFM SiNRs ($N \leq 23$). Looking at the energy bandstructure, displayed in fig. 5.4, one finds that for $N = 8$ and $N = 23$ (AFM) $E_g$ is located at $k = 0.36\pi/c$, between double degenerate bands for each spin. The highest valence and the lowest conduction bands are of $\pi$ bonding and $\pi^*$ antibonding character, respectively. Flat bands appear in $k > 0.36\pi/c$, but they are far away from $E_F$ because of the significant interedge interference due to the small width.

For $N = 24$, an AFM-FM transition occurs. The flat bands are brought closer to $E_F$ and much more kinetic energy is sacrificed for exchange-correlation for the FM state [fig. 5.3-(b)]. In contrast to the AFM state, the SOC is found to impact the energy bands significantly for $N \geq 24$. Fig. 5.4 displays the bands for the $N = 24$ ribbon with and without SOC (SOC-off). If the spin-orbit interaction is not taken into account, the $\pi$ and $\pi^*$ bands cross at $E_F$ as they are partly occupied and partly unoccupied. The inclusion of the SOC results in opening of a small gap. This transforms the majority (minority) band into a fully unoccupied (occupied) state. Similar results are found for all studied FM ribbons.

The ferromagnetism and the SiNR width determine not only the position of the minority and majority bands at $E_F$, but also those of the next levels. The energy gap between the majority highest valence and majority lowest conduction bands is different as compared to the one for the minority highest valence and minority lowest conduction bands. Fig. 5.3-(d) shows that $E_g^{\text{mino}} = 61.5$ meV ($E_g^{\text{majo}} = 99.2$ meV) is the highest (lowest) for $N = 30$. Actually, for ribbons with $N \geq 29$, these energy gaps within each spin species become indirect as can be seen from fig. 5.4.

The SOC contribution to the total energy is calculated via

$$\Delta E_{\text{SOC}} = |E_{\text{DFT+SOC}}^{\text{tot}} - E_{\text{DFT}}^{\text{tot}}|, \quad (5.1)$$

where $E_{\text{DFT+SOC}}^{\text{tot}}$ and $E_{\text{DFT}}^{\text{tot}}$ are the total energies with and without the SOC, respectively. We find that $\Delta E_{\text{SOC}}$ is nearly unchanged for the different ribbon. $\Delta E_{\text{SOC}} = 0.17$ meV per atom for the defect-free structures. Once the extended defect is embedded, the
Fig. 5.4 Energy bandstructure for several perfect and defective SiNRs. Energy bands for both spin orientations are shown. $N_1$ and $N_2$ denote the number of zigzag lines present on both sides of the extended defect.

The strength of the SOC energy is doubled, $\Delta E_{\text{SOC}} = 0.35 \text{ meV per atom}$. The doubling of the SOC magnitude is related to the geometrical role of the extended line defect, which essentially joins two nanoribbons with intact zigzag edges. If two defect lines are introduced in the ribbon, one obtains magnitude of the SOC for three ribbons.

The energy band structure of the SiNRs exhibits further interesting properties directly influenced by the magnitude of the width, the edges, and the extended topological defects. As discussed earlier, all defective ribbons are ferromagnets regardless of the location of the defect. Several cases are shown in the fig. 5.4. It turns out that there is always a majority band crossing the Fermi level, which is indicative of the metallic transport behavior of the majority spins. At the same time, large flat portions of the
minority bands are found in the vicinity of \( E_F \). In some cases, these flat levels lie exactly on \( E_F \) \((N_1 = N_2 = 4)\). In other cases they are above and below the Fermi level \((N_1 = N_2 = 10; N_1 = 6, N_2 = 14)\) open a finite indirect gap between the highest valence and lowest conduction minority bands. For example, the calculated minority gap is \( 56.8 \text{ meV} \) for \( N_1 = N_2 = 10 \) and \( 54.0 \text{ meV} \) for \( N_1 = 6, N_2 = 14 \). That is the indication for a possibility to obtain half-metallic characteristics in SiNRs with extended topological defects, in which the majority carriers are conductors, while the minority carriers are semiconducting.

The nature of the electronic structure can further be analyzed by considering the density of states (DOS). In fig. 5.5, we show the orbital and site projected DOS when the defect line is symmetrically located with respect to edges \((N_1 = N_2 = 4)\). One notes that the majority DOS is much larger as compared to the minority DOS for the displayed region. The contribution at the Fermi level for the majority DOS is attributed to the metallic dispersive band crossing \( E_F \) [fig. 5.4-(a)]. The minority DOS experiences a dip almost touching \( E_F \), which is due to the small flat portion of the highest valence band close to the \( X \) point. The flat region of the lowest conduction minority band for \( 0 < k < 0.19\pi/c \) is \( 8 \text{ meV} \) contributing to the peaked DOS above \( E_F \).

Fig. 5.5-(a) also indicates that the \( p_z \) orbitals have a significant contribution to the majority DOS at \( E_F \). The role of the other orbitals is small, but not negligible. One
finds that while the $p_z$ contribution is large for $E \in (-3, -2)$ eV, the $p_x$ and $p_y$ are more prominent in the deeper valence region of $E \in (-5, -1)$ eV. The $s$ states are characteristic for energies below $-5$ eV. All states contribute significantly in the conduction region for $E > 1$ eV. We further note that the minority DOS is almost completely determined by the $p_z$ states and the $sp^3$ hybridization around $E_F$ happens entirely for the majority carriers. Also, due to the much larger DOS around $E_F$, the transport in these systems will mainly be due to the majority carriers.

Since the spin polarization is rather localized around the edges and extended defect line, it is important to examine the site-projected DOS to determine the contribution from individual atoms. Fig. 5.5-(b) shows the site-projected DOS for those atoms that have the most contribution. It is found that the majority DOS is composed mainly of the zigzag edge atoms (1) and the atoms forming the defect line (8) and (9). One notes that although atoms (8) are in the middle they have the same geometrical (zigzag) disposition as atoms (1). The minority DOS is much smaller and the peak at $E_F$ is attributed to atoms (8), while the edge atoms (1) are responsible for the two peaks in the valence and conduction regions.

### 5.5 Summary

By comparing these results for ZSiNRs with the previous studies for ZGNRs chapter 4 it shows that, besides the common properties, SiNRs exhibit unique structure-property relations. While all ZGNRs are found to be AFM with monotonously decreasing energy gap as a function of the increasing width$^{[2,46]}$, ZSiNRs experience an AFM-FM transition, which has a dramatic effect on the energy gap. The AFM state of the silicene ribbons is very similar to the one for GNRs, although the SiNR $E_g$ decays faster as the ribbons become wider. It turns out that the SOC does not affect the electronic structure properties of the graphene ribbons, however, this relativistic effect is much more pronounced for the staggered silicene lattice giving the massive nature of the Dirac electrons. The SOC is responsible for a spin-dependent energy gap for the FM
SiNRs. Differences and similarities in the properties are found when an extended topological defect is included in the zigzag graphene and silicene nanoribbons. While such a defect does not change the AFM ordering in ZGNRs, it makes all ZSiNRs be ferromagnets. In some cases it is also possible to obtain half-metallic behavior depending on the location of the defect. Furthermore, the composition of DOS for both types of ribbons is similar but with more pronounced spin-dependent $sp^3$ hybridization for the SiNRs.

The systematic *ab initio* studies of the structure-property relations show that in order to understand and describe silicene nanoribbons one needs to take into account not only the staggered hexagonal lattice, but also the SOC and magnetic orientation. The SiNRs unique properties indicate that such nanoribbons may find applications in spintronics or for topological insulator transitions, where SOC in Dirac electrons is necessary.
Chapter 6

Two-Dimensional Heterostructures\cite{4}

Graphene, silicene and other atomically thin two-dimensional structures have been widely and intensively studied from the beginning of the new century and are still the most attractive materials in scientific research at the current time. In addition, single-layered crystals of different types can be reassembled to form van der Waals heterostructures in Lego-like constructions. These combinations are promising for rich physics and are likely to develop in their own direction.

6.1 Motivation

The first synthesis of a heterostructure had been made very recently, in 2011\cite{82}. Since then, it has drawn much scientific interest in both experimental and theoretical aspects. Up-to-the-minute techniques have been applied in fabrication of this type of materials and many two layered heterostructures have already been synthesized\cite{83–92,209–212}, showing that experimental advances of various stacking patterns can be used to achieve a system with an array of different characteristics. Recent computational studies of 2D vdW heterostructures have also been reported\cite{213–216}. These investigations are typically concerned with the energetic stability of the system and mainly with the electronic band structures around the Fermi level, where the energy bands are additive. Theoretical studies uncovering the evolution of the higher conduction and lower valence regions are lacking, however. The influence of interlayer hybridization in vdW
heterostructures is of much interest not only from a fundamental point of view, but also for practical applications in view of control and design of desired properties.

Furthermore, interlayer optical coupling involving 2D transition metal dichalcogenides (TMDCs) has been demonstrated already\cite{217}. Such interactions are inevitably connected with the understanding of changes in the electronic structure due to the interlayer coupling. Thus addressing the roles of the dispersive vdW interactions and the orbital overlap is necessary in order to provide effective ways of tuning capabilities. Along these lines, determining universal and material specific hybridization features would be much desirable. The vibrational properties of vdW heterostructures are also of great interest. Studies of phonon excitations of homogeneous vdW systems (composed of graphene only or MoX2 layers only with X being the chalcogen atom) as a function of number of layers have shown there is a delicate balance between surface vs. bulk effects\cite{218–221}. The evolution of acoustic and other low-frequency modes, such as shear and breathing modes, for a given 2D vdW HS can hardly be overestimated as such issues are of primary relevance to thermal conduction.

6.2 Methods

Long-ranged vdW interaction, which is unfortunately not included in the original Kohn-Sham equation of DFT\cite{170,171}, is naturally the driving force for the stability of 2D heterostructures. Therefore, the choosing correction method for vdW interaction must be a good one to best describe this newly invented type of materials. In this work we use the vdW-DF2 functional of D. C. Langreth and B. I. Lundqvist groups\cite{222}, one of the developed versions of the vdW density functional of M. Dion et al.\cite{183,184} which had been introduced in section 3.3 of chapter 3. In this method, the vdW energy is calculated self-consistently together with the total exchange-correlation energy. The calculation therefore becomes much heavier but is indispensable for the studying of heterostructures.

We have performed the VASP code\cite{191,192} for our studied structures using PBE
functional\cite{195} for the exchange-correlation energy with vdW-DF2 functional embedded in it. We use the same plane wave cutoff energy of 600 eV for all calculations. Whereas, different Brillouin zone samplings have been used depend upon the types of calculations: \((15 \times 15 \times 1)\) k-mesh for relaxation and DOS calculations and \((25 \times 25 \times 1)\) k-mesh for obtaining the energy band structures. The global break condition for the electronic self-consistent loop is set to \(10^{-5}\) eV and the break condition for the ionic relaxation loop is \(10^{-3}\) eV\(\cdot\)\(\text{Å}^{-1}\).

Phonon frequency spectra of the examined structures are obtained using the PHONOPY package\cite{223,224}. With a sufficiently large relaxed supercell, finite atomic displacements with an amplitude of 0.01 Å are introduced. The atomic forces within the supercell are calculated using VASP followed by phonon frequency calculations from the dynamical matrix represented in terms of the force constants.

We have also performed bandstructure unfolding using the BandUP package\cite{225,226}. This is a state of the art code which enables obtaining a primitive cell representation of a system simulated via the DFT supercell approach. Being able to generate an unfolded band structure projected on the particular primitive cell for each layered component of the vdW HS is an important advantage. It provides common ground when comparisons with experimental data obtained via angle-resolved photoemission spectroscopy (ARPES), for example.

### 6.3 Geometric structures

In this study, we use first principles simulations to investigate the interface properties of the following 2D heterostructures: graphene/silicene (GR/SIL), graphene/MoS\(_2\) (GR/MoS\(_2\)), and silicene/MoS\(_2\) (SIL/MoS\(_2\)). It turns out that the vdW interaction is of primary importance for the electronic and vibrational properties of the studied systems. On one hand, the vdW interaction together with the orbital overlap leads to non-trivial changes in the deeper valence and higher conduction regions in terms of hybridization energy gap. On the other hand, the vdW coupling is found to be necessary
for the vibrational stability of the HS meaning that real phonon dispersion relations are achieved. The calculations are performed by constructing supercells with periodic boundary conditions. For this purpose several unit cells from each constituent are utilized, which however, leads to artificially folded bands in the band structure\[227\]. Such artificial folding inhibits the discovery of important features in the electronic properties and make the comparison with experimental data difficult. Here we present the unfolded band structures for each HS projected on the individual primitive Brillouin zone (BZ). The obtained emerging energy gaps in the conduction and valence regions are found are explained in terms of interlayer hybridization and vdW effects. The interface phonon properties are also investigated with acoustic, shear and breathing modes analyzed in terms of the interlayer interactions and comparisons with the phonon properties of the individual constituents.

The calculations are performed using periodic boundary conditions by constructing a supercell for each considered system. Since the layered constituents have different bond lengths and lattice parameters, the supercells consist of several unit cells of the individual layer. Specifically, the GR/SIL structure is formed by 9 graphene and 4 silicene unit cells, the GR/MoS\(_2\) is formed by 25 graphene and 16 MoS\(_2\) unit cells, and the SIL/MoS\(_2\) is formed by 16 silicene and 25 MoS\(_2\) unit cells. The particular stacking configurations after relaxation with respect to the atomic positions and lattice parameters are shown in fig. 6.1.

<table>
<thead>
<tr>
<th>Heterostructure</th>
<th>GR/SIL</th>
<th>GR/MoS(_2)</th>
<th>SIL/MoS(_2)</th>
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</thead>
<tbody>
<tr>
<td>Strain (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No DF2</td>
<td>+0.8/-3.5</td>
<td>+1.0/-2.1</td>
<td>+1.8/-1.0</td>
</tr>
<tr>
<td>DF2</td>
<td>+1.0/-3.8</td>
<td>+1.9/-4.0</td>
<td>+3.5/-1.6</td>
</tr>
<tr>
<td>(d) (nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No DF2</td>
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<td>0.432</td>
<td>0.398</td>
</tr>
<tr>
<td>DF2</td>
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<td>0.354</td>
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</tr>
<tr>
<td>(\Delta E) (meV)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>No DF2</td>
<td>1.28</td>
<td>0.82</td>
<td>2.43</td>
</tr>
<tr>
<td>DF2</td>
<td>28.07</td>
<td>24.67</td>
<td>34.57</td>
</tr>
</tbody>
</table>

**Tab. 6.1** Structural parameters obtained after relaxation. The strain values correspond to lattice expansion (+) or shrinking (-) with respect to the corresponding free layers. \(\Delta E = E_{\text{HS}} - (E_1 + E_2)\) is the energy/atom \((E_{\text{HS}}\) total energy for the HS; \(E_{1,2}\) total energy for each layer).

The formation of each vdW HS introduces slight strains in the 2D layers when compared with the individual, free standing constituent. These relative lattice strains
are calculated via \((a_{SH} - a)/a\) (\(a_{SH}\) - lattice constant of the HS; \(a\) lattice constant of the corresponding layer) and they are shown in tab. 6.1 with and without taking into account the vdW interaction. For example, the graphene layer in the GR/SIL structure is expanded by 0.8\%, while the silicene is shrunk by 3.5\% when compared with their free standing counterparts. If DF2 is included in the simulations, we find that after relaxation the graphene expansion is slightly higher (1.0\%), while the silicene shrink is slightly less (–3.8\%). The respective values for the other two heterostructures can also be found in tab. 6.1. We note that slight straining in order to achieve a composite structure with different individual lattices is found in other systems, such as graphene on Au, Ag, and SiC substrates[^228-230]. Our subsequent calculations indicate that comparing the properties of the slightly strained individual layers with the properties of the fully relaxed ones does not show significant differences, therefore one concludes that such small lattice parameters modifications have little effect on the vdW HS characteristics.

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>GR/SIL</th>
<th>GR/MoS2</th>
<th>SIL/MoS2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No DF2</td>
<td>DF2</td>
<td>No DF2</td>
</tr>
<tr>
<td>SIL</td>
<td>0.449</td>
<td>0.497</td>
<td>0.589</td>
</tr>
</tbody>
</table>

**Tab. 6.2** Thickness \(h\) (Å) of each layer (except for graphene) obtained after relaxation.
It is further found that the separation between the layers is affected significantly by the vdW interactions. This distance is reduced upon taking into account the DF2 functional; the largest reduction of 0.078 nm occurs for the GR/MoS$_2$ system. The buckling of silicene as well as the thickness of MoS$_2$ are affected not only by the vdW interaction, but also by the specific HS, as can be seen in tab. 6.2. The DF2 correction generally enhances the silicene buckling and the MoS$_2$ thickness. Graphene also makes a big difference in $h$ when forming the particular HS, such that $h$ of silicene is increased by 0.112 Å, while $h$ for MoS$_2$ is increased by 0.086 Å when compared with their free counterparts (DF2 included in both cases). Interestingly, the buckling of silicene in its HS with MoS$_2$ is reduced by 0.036 Å. The role of the vdW interaction is also significant when considering the energetic stability of each structure. Our results in tab. 6.1 show that each vdW HS is much more stable upon the inclusion of the DF2 functional as the corresponding energy is increased by at least an order of magnitude. The case of SIL/MoS$_2$ is particularly noteworthy. The calculations indicate that the vdW interaction results in $\Delta E$ higher than 32.14 eV as compared to the case of no DF2. We conclude that such long range corrections play an important role for the stability of the layered HS and must be included in the subsequent analysis.

### 6.4 Electronic and phonon properties

The electronic structure properties of the different heterostructures are also calculated. The different number of unit cells for each layer used to construct the supercell result in two BZ-s with different sizes, as shown in fig. 6.1-(d) for GR/SIL. The resulting artificially folded bands must be untangled and projected on the primitive BZ-s of the individual components as shown in fig. 6.2. Considering fig. 6.2-(a), we see distinct Dirac-like bands crossing the Fermi level, such that the linear bands at the K-points belong to silicene, while the linear bands at the M-point belong to graphene. Another set of linear bands for graphene crossing at the Γ-point (barely visible in the graph) is also present. Comparing with the density of state results in fig. 6.3-(a,b), it is de-
determined that the electronic structure around $E_F$ is essentially a superposition of the graphene and silicene individual contributions [fig. 6.4-(d)] from their out of plane $\pi$ orbitals. Thus the Dirac cones for each layer are intact with well-preserved characteristic linear dispersion.

The electronic structure, however, is significantly altered in the deeper valence and higher conduction regions. First, one notes that while the vdW interaction does not affect the properties close to the Fermi level, its role away from $E_F$ is much more pronounced. The inclusion of DF2 results in shifting of several of the characteristic peaks including those around $-4$, $-2$ and $2$ eV regions [fig. 6.3-(a)]. In addition, the band structure projected on the primitive silicene cell [fig. 6.2-(a)] shows that there are several energy gaps of rather significant magnitude, opened in the conduction region around 2 eV. These energy gaps, which are on the order of $0.005 \div 0.3$ eV, occur when
strong hybridization between the $\pi$-states of C and Si happens, as evident in fig. 6.3-(b). Similar hybridization occurs in the $-2$ eV and $-4$ eV regions, although the energy gaps are smaller and they are visible on the GR/SIL band structure projected on the primitive cell of the graphene BZ [fig. 6.4].

The electronic structure of the other two heterostructures exhibits similar features. Fig. 6.2-(b-d) and fig. 6.3-(c-f) show that again the energy bands and DOS are a superposition of the contributions from the graphene (silicene) and MoS$_2$ contributions.
While the corresponding Dirac bands cross $E_F$, MoS$_2$ is a conventional semiconductor with parabolic dispersion and no states around $E_F$. We find that the MoS$_2$ in the GR/MoS$_2$ HS is an indirect gap semiconductor with a gap of 1.6 eV along the K-$\Gamma$ path. MoS$_2$ from SIL/MoS$_2$ has a direct gap of the same magnitude at the K point. Although the magnitude of the energy gap of the free MoS$_2$ layer (a direct gap semiconductor) is not affected due to the particular HS ($\sim 1.6$ eV for all the cases), it is concluded that the role of the graphene is more prominent as compared to silicene. Specifically GR/MoS$_2$ resembles the situation of two-layer MoS$_2$ system, which also exhibits similar transition to an indirect semiconductor when compared to the individual layer\cite{74}.

The vdW interaction is also important for the GR/MoS$_2$ and SIL/MoS$_2$ systems. The inclusion of the DF2 function leads to shifting of the DOS peaks towards the Fermi level when compared to the DOS peaks with no DF2 corrections [fig. 6.3-(c,e)]. These shifts are more pronounced for the deeper valence and higher conduction regions. Further inspection of the electronic structure shows that significant hybridization due
to the out of plane overlapping orbitals leads to strong modifications farther away from $E_F$. Fig. 6.2-(b-d) show the opening of several energy gaps as large as 0.3 eV along several directions of the graphene and silicene bands in the ($-4, -2$) eV region. Similar situation is observed for the conduction range around 2 eV. These effects are due to hybridization of the p-orbitals (graphene or silicene) and the d-orbitals (MoS$_2$) as indicated from the DOS results [Fig. 6.3-(d,f)]. The strong out-of-plane character is quite prominent in these heterostructures similar to the case of GR/SIL.

Understanding the vibrational properties is also important in building a complete picture of the unique interface characteristics of the vdW heterostructures. Recent studies have investigated graphene/h-BN systems; stacked 2D transition metal dichalcogenides; and few layer graphene structures$^{[231–235]}$. Much of the emphasis in these reports has been on the layer breathing modes, since such vibrations are specific to a structure with two or more stacked layers. It has been shown that breathing mode vibrations have relatively low frequencies and they can be Raman or Infrared active$^{[232,233]}$. Characteristic energetic shifts of these breathing modes in terms of number of layers comprising the system have also been reported$^{[232]}$.

In this study, we focus on the vibrational properties of GR/SIL and GR/MoS$_2$ structures. Fig. 6.5 summarizes our results for the phonon bands and associated total and atomically resolved phonon DOS for each case. It turns out that the vdW interaction is quite prominent here. Specifically, without taking into account the DF2 functional, there are imaginary frequency branches which indicate that the GR/SIL and GR/MoS$_2$ systems are unstable. Taking into account the vdW coupling leads to removing the imaginary frequency branches [Fig. 6.5] stabilizing each HS.

The three lowest frequency modes starting at the $\Gamma$-point constitute the acoustic branches, which are compared to the corresponding acoustic branches of the individual layers [Fig. 6.6]. It is noted that unlike bulk materials, flexural modes are particularly important for surface systems as they have the lowest frequency dispersion and they are non-linear with respect to the wave vector. The role of such vibrations in single graphene, silicene, and MoS$_2$ has been recognized in many reports with theo-
Fig. 6.5 Phonon dispersion and density of states (total and atomically resolved) for (a) GR/SIL and (b) GR/MoS$_2$. (c) - Schematics of the shear and breathing modes.

Theoretical and experimental consequences$^{[236–238]}$. Flexural modes have a large contribution to the phonon DOS and they are responsible for the thermal conduction (even up to room temperature) for the individual graphene, silicene, and MoS$_2$. Such vibrations are dominated mainly by boundary scattering as the phonon-phonon scattering is relatively weak. The transport due to flexural excitations is almost ballistic with a characteristic frequency dispersion $f = Dq^2$. Our simulations show that for graphene $D = 3.45 \times 10^{-6}$ m$^2$/s, for silicene $D = 2.77 \times 10^{-6}$ m$^2$/s, and for MoS$_2$ $D = 4.68 \times 10^{-6}$ m$^2$/s along the $\Gamma$-M direction.

The transverse and longitudinal acoustic modes have linear dispersion with characteristic group velocities displayed in tab. 6.3. Comparing the phonon band structure for the individual layers helps understand the thermal conduction properties of the individual 2D systems. Phonon modes for graphene are higher than those of MoS$_2$ and silicene (by a factor of $\sim 2$ or $3$) indicating that the corresponding graphene vibrations carry more energy. This is an important factor contributing to the graphene large thermal conductivity. On the other hand, the frequency gap between the acoustic and optical regions in silicene and MoS$_2$ forbids many phonon scattering mechanisms indicating that the acoustic vibrations are protected. Further examination of the dispersion shows that the GR/MoS$_2$ flexural modes have departed from the quadratic wave vec-
Fig. 6.6 Phonon dispersion of (a) single graphene; (b) single silicene; (c) single MoS$_2$; (d) GR/SIL; (e) GRA/MoS$_2$.

Torsion dispersion and the frequency is $f \sim q^x$, where $x = 1.45$. At the same time, this type of vibrations for the GR/SIL system display a linear $q$-dependence along Γ-M ($q$-small). It is interesting to compare with other studied vdW structures. For example, for $\leq 5$ stacked graphenes the flexural modes are $f \sim q^x$ where $1 \leq x \leq 2$ ($x = 1$ for $N = 5$)\textsuperscript{233}. While GR/MoS$_2$ exhibits this intermediate flexural dispersion ($x = 1.45$), the flexural mode has acquired linear dispersion in GR/SIL.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$v_{TA}$ (m/s)</th>
<th>$v_{LA}$ (m/s)</th>
<th>$v_{S1}$ (m/s)</th>
<th>$v_{S2}$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR/SIL</td>
<td>3,706</td>
<td>7,854</td>
<td>13,162</td>
<td>20,093</td>
</tr>
<tr>
<td>GR/MoS$_2$</td>
<td>4,385</td>
<td>7,053</td>
<td>11,075</td>
<td>16,189</td>
</tr>
<tr>
<td>Graphene</td>
<td>12,192</td>
<td>20,612</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silicene</td>
<td>4,891</td>
<td>8,561</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>3,726</td>
<td>6,150</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3 Velocities of transverse acoustic (TA), longitudinal acoustic (LA), and shear (S1, S2) branches.

The results for the transverse and longitudinal acoustic modes in terms of their group velocities are also given in Table 6.3. Comparing the obtained values, one finds...
that \( v_{TA,LA} \) for the GR/SIL and GR/MoS\(_2\) heterostructures are significantly lower (by an order of magnitude) than the corresponding values of the free graphene. At the same time, while \( v_{TA} \) for the considered heterostructures is larger than \( v_{TA} \) for the free silicene and MoS\(_2\) components. The opposite trend is found for \( v_{LA} \) for the heterostructures, which are slightly larger than \( v_{TA} \) for the individual silicene and MoS\(_2\). Nevertheless, there is a general phonon softening in the GR/SIL and GR/MoS\(_2\) systems which contributes to the decrease of the thermal conductivity. In addition, the phonon modes density distribution for the heterostructures increases when compared to the individual components, which means that the probabilities for scattering processes is also increased. As a result, the scattering phonon time is going to be reduced resulting in a decreased thermal conductivity.

Besides the acoustic vibrations, there are other low lying frequency modes specific for stacking heterostructures. The two linear-like modes starting at \( f = 0.085 \) THz for GR/MoS\(_2\) are the shear modes [fig. 6.5] with velocities shown in tab. 6.3. The corresponding shear modes for GR/SIL start at two different frequencies, 0.117 THz and 0.135 THz, at \( \Gamma \) with linear velocities in tab. 6.3. In both cases, \( v_{S1,S2} \) have similar values to \( v_{TA,LA} \) of single graphene. The next branch of the heterostructures constitutes the breathing mode vibrations, characterized as an optical mode, where the two layers move along a perpendicular to the layers direction. Fig. 6.5 shows that the breathing starts starts at 2.11 THz frequency for the GR/SIL systems, while the same type of branch is found at 0.51 THz at the \( \Gamma \)-point for the GR/MoS\(_2\) system.

The calculated phonon dispersion properties show that graphene exhibits superior thermal transport since their low energy acoustic modes can carry much more energy as compared to the ones for free silicene or MoS\(_2\). The thermal conduction capabilities, when compared with free graphene, are also worsened when considering graphene vdW heterostructures and the acoustic phonon softening is of importance here. The transformation of the flexural modes and the appearance of shear and breathing modes, however, may be useful for probing other fundamental characteristics of the heterostructures.
6.5 Summary

Our investigation clearly demonstrates that the graphene and silicene Dirac-like electronic properties of the vdW heterostructures around the Fermi level are preserved, while MoS$_2$ may exhibit direct to indirect semiconducting behavior. At the same time, the interlayer hybridization results in the opening of several gaps in the higher conduction and lower valence regions. Such gaps may have a common behavior as they occur for all studied systems but for different energy ranges. This diversity suggests an approach for tuning optical transitions in a particular layer by simply choosing a suitable component for the HS. Furthermore, the vdW interaction determines the vibrational stability of the heterostructures. The flexural modes depart from the characteristic $q^2$ dependence for the individual layers and the emergence of shear and breathing modes is demonstrated. By showing how the vibrational properties evolve, one can potentially control the heat transfer in 2D systems.
Chapter 7

Anchored Graphene Nanoribbons

Investigating the internal properties of graphene sheets and related structures is an important component not only for basic understanding but also for device applications. Elements in electronic devices require the utilization of proper substrates as well as various types of processing and patterning. Therefore, research is needed to investigate such factors for graphene systems property modifications.

7.1 Motivation

Epitaxial graphene\cite{239-241} is of particular interest for electronic applications, since single or few graphene layers grown on top of substrates are found to be useful for post-CMOS (complementary metal-oxide-semiconductor) devices\cite{242}. Structurally, epitaxial graphene is the same as its free-standing counterpart with hexagonal lattice of $sp^2$ bonded carbon atoms. However, its properties can be altered by the interactions with the substrate, which also depends on the type of the selected material for the substrate. It has been shown by DFT calculations that an appropriate number of graphene layers grown on SiC can electrically behave like an isolated graphene sheet and the behavior is slightly changed with different (Si- or C-) anchored faces\cite{230}.

GNRs have also been grown successfully on SiC\cite{243-245}. Utilizing the highly reactive unsaturated edges of the ribbons, their sidewall growth on SiC nanofacets has been reported. The achieved structures contain chemically connected edges to the
substrate, while the rest of the GNRs are free, as shown by scanning tunneling spectroscopy and local point probe transport measurements\cite{244}. Such anchored ribbons are especially attractive for field-effect transistors. Taking advantage of the mid-size energy gaps of the GNRs combined with their relatively good carrier mobilities is quite desirable for such devices. In this work, we focus on the electronic and spin polarized properties of patterned anchored GNRs with zigzag edges on SiC substrates.

### 7.2 Methods and structures

In an anchored structure, while the ribbon’s edges chemically connect with atoms in the substrate, its main body interacts with the substrate via long-ranged vdW coupling. Here, in order to examine how vdW interaction influence the structure and characteristics of the system, we perform self-consistent calculations using the vdW-DF2 functional\cite{183,184,222}. The chemical interaction at the edges of the ribbon are also expected to give a large impact on the localized magnetic states of the zigzag edges. The impact is studied in comparison with the corresponding states of the flat GNR. All three possible cases of NM, AFM and FM states are considered.

The first principles calculations are performed using VASP code\cite{191,192} with PBE exchange-correlation energy functional\cite{195}. The studied structures are relaxed with $10^{-6}$ eV in the global break condition for the electronic self-consistent loop, $10^{-3}$ eV·Å$^{-1}$ in the break condition for the ionic relaxation loop, 600 eV in the kinetic energy cutoff, and $(9 \times 9 \times 1)$ in k-grid sampling. The DOS calculations are performed with self-consistent breaking condition of $10^{-7}$ eV, energy cutoff of 650 eV, and k-grid sampling of $(25 \times 25 \times 1)$.

The system under consideration is shown in fig. 7.1. To simulate the patterned anchored ribbons, the SiC substrate is represented to have 3 layers [fig. 7.1-(a)]. The ends are saturated by H-atoms except those connections positioned below the unsaturated zigzag GNR. The nanoribbon contains 8 zigzag C lines with width $\sim$ 16 Å. The separation between the neighboring edges of two adjacent ribbons is $\sim$ 10 Å. The separation
between the so-constructed supercells in vertical (z) direction is \( \sim 20 \, \text{Å} \). In addition to the ribbon being exposed to the unsaturated Si atoms in the substrate, exposure to the C unsaturated ends from the substrate is also calculated.

Relaxed structures of the anchored GNRs attached to the Si or C atoms are shown in Fig. 7.1-(d,e). A top view of Fig. 7.1-(c) shows the stacking orientation of the ribbon with respect to the substrate. The relaxation procedure was performed with the above specified criteria.

The most energetically stable configuration was obtained after optimization of the lattice parameters. Fig. 7.2 displays one of the results from the optimization procedure, which shows that the most stable structure has lattice structure parameter \( c_{\text{min}} = 3.0636 \, \text{Å} \) \( (c^{\text{SiC}} = c_{\text{min}} \text{ and } c^{\text{GR}} \equiv 3d^{\text{SiC}}/2 = \sqrt{3}c_{\text{min}}/2) \). The displayed results correspond to the anchored to the Si side of the substrate with AFM orientation since this is the most stable spin polarized state, as shown in what follows.

Comparison between the lattice parameters of the free GNR and free substrate with respect to the ones from the anchored structures is shown in Tab. 7.1. It should be noticed that the lattice constant of the attached ribbons is larger than that of the free
one, while the lattice constant for the substrate with the attached ribbons is smaller
than the one for the free substrate. In addition, the DF2 inclusion for vdW interaction
typically enhances the lattice parameters when compared to the results with no such
correction.

<table>
<thead>
<tr>
<th></th>
<th>$d$ (Å)</th>
<th>$c_{GR}$ (Å)</th>
<th>$c_{SiC}$ (Å)</th>
<th>$\frac{c_{GR}^{SiC} - c_{GR}^{SiC}}{c_{GR}^{SiC}}$</th>
<th>$\frac{c_{SiC}^{SiC} - c_{SiC}^{SiC}}{c_{SiC}^{SiC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-anchored</td>
<td>No DF2</td>
<td>4.555</td>
<td>2.6322</td>
<td>3.0394</td>
<td>6.96%</td>
</tr>
<tr>
<td></td>
<td>DF2</td>
<td>4.438</td>
<td>2.6531</td>
<td>3.0636</td>
<td>7.81%</td>
</tr>
<tr>
<td>C-anchored</td>
<td>No DF2</td>
<td>4.040</td>
<td>2.6298</td>
<td>3.0367</td>
<td>6.86%</td>
</tr>
<tr>
<td></td>
<td>DF2</td>
<td>3.900</td>
<td>2.6514</td>
<td>3.0616</td>
<td>7.74%</td>
</tr>
</tbody>
</table>

**Tab. 7.1** Optimized lattice parameters. Here, $c_{GR}^{SiC} = 2.461$ Å and $c_{SiC}^{SiC} = 3.085$ Å.

### 7.3 Spin polarization and electronic structure

The most stable spin polarized state is resolved by comparing the total energies ob-
tained from the calculations after the optimization and relaxation procedures. The
obtained results are shown in **tab. 7.2**, where one finds that the preferred state is the
one with an AFM spin polarization. The inclusion of the DF2 functional does not
change this qualitative outcome. It appears that the AFM state for a planar ribbon is
preserved if the ribbon now is attached to the SiC substrate. **Tab. 7.2** further shows
that the GNR attached to the Si side is more stable (by $\sim 2$ eV) than the one attached to the C side, which is similar to the experimental results.

Our calculations in the presence of spin polarizations also show that the magnetic moments of all the atoms in the substrate are zero except for small contributions from the ones in the close vicinities at the ends of the ribbon. The spins are therefore primarily located at the ribbon. More specifically, the polarization is localized at the anchored edges. This compares well with a free ZGNR, in which the magnetic moments are also localized at the two edges as its strength decays quickly towards the middle of the ribbon\[2\]. However, it is significant that the SiC substrate plays an important role in defining the magnitude $m$ of the magnetic moment for the atoms at the ends of the ribbon. Our result for the free ZGNR with 8 zigzag-C lines is $m = 0.150 \, \mu_B$ ($\mu_B$ is the Bohr magneton). When the ribbon is anchored on the SiC substrate, it remarkably increases to $m = 0.183 \, \mu_B$ (22.0%) for Si-anchored and $m = 0.182 \, \mu_B$ (21.3%) for C-anchored cases.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{AFM}}$ (eV)</th>
<th>$E_{\text{FM}}$ (eV)</th>
<th>$E_{\text{NM}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-anchored</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No DF2</td>
<td>-1101.2565</td>
<td>-1101.2362</td>
<td>-1101.1397</td>
</tr>
<tr>
<td>DF2</td>
<td>-1146.0265</td>
<td>-1146.0044</td>
<td>-1145.8981</td>
</tr>
<tr>
<td>C-anchored</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No DF2</td>
<td>-1099.1514</td>
<td>-1099.1354</td>
<td>-1099.0409</td>
</tr>
<tr>
<td>DF2</td>
<td>-1144.0157</td>
<td>-1143.9993</td>
<td>-1143.8730</td>
</tr>
</tbody>
</table>

Tab. 7.2 Total energies obtained after relaxation for the Si- and C-anchored structures with and without DF2.
To study electronic structure of the studied systems, we have calculated the DOSs using VASP. The DF2 functional is taken into account in this process and since the AFM polarization is the most preferable, we have performed the calculations for this state only. The results are plotted in fig. 7.3. For the free GNR, fig. 7.3-(a) shows strongly localized peaks at the top of the valence and bottom of the conduction regions with an energy gap of $\sim 0.45$ eV. These peaks are primarily composed of contributions from the zigzag edges.

Fig. 7.3-(b,c) show DOS for the anchored nanoribbon to the Si and C ends in the substrate. In both cases, one finds that the main contribution to DOS around the Fermi level comes from the nanoribbon itself, and the energy gap at $E_F$ is preserved from the free ribbon ($\sim 0.45$ eV). We further note that beside the semiconducting gap, additional gapped regions become possible for the anchored ribbon. For example, a gap $\sim 0.17$ eV is found in the $(1.10, 1.27)$ eV region for the Si-anchored nanoribbon. For the C-anchored ribbon, there is a gapped region $(-0.54, -0.39)$ eV in the valence and another gapped region $(0.87, 1.04)$ eV in the conduction ranges. It is interesting that an asymmetry in the DOSs can be seen, for example, clearly around $E_F$ in fig. 7.3-(b). The asymmetry is also observed in the charge density plots [fig. 7.4]. We believe the vdW interaction between the ribbon and the substrate and the unequal chemical anchored bonds at the ends of the ribbon are related to the asymmetric characteristic of
the studied systems. However, this feature deserves further investigation.

7.4 Summary

Our DFT calculations have shown that a GNR can be anchored on both C- and Si-terminated sides of a SiC substrate, although the ribbon attached to the Si side is energetically preferable. We have shown that the SiC substrate significantly influences the atomic magnetic moments of anchored ribbon. The interaction between the ribbon and the substrate alters the electronic structure by creating new energy gaps in the valence and conduction regions closed to the Fermi level. We suggest that such patterned by GNR substrates may be suitable for electronic applications at the nanoscale.
Chapter 8

Conclusion And Future Outlook

Graphene with $sp^2$-bonded carbon atoms arranged in a hexagonal lattice has been the leading material in research for several years. The linear energy bands with zero gap at the Dirac points of the first BZ allow charge carriers in graphene to have very high mobility. That is the driving force for its unique characteristics, which cannot be found in 3D materials. Whereas, strips of graphene, i.e. GNRs, have electronic and magnetic properties which strongly depend on the types of the edges and the magnitude of the width.

It is remarkable that properties of GNRs can be easily controlled by mechanical manipulations, such as folding to create closed edges or adding defective lines. Our investigations using DFT calculations with DFT-D2 dispersion correction for the van der Waals interactions revealed geometrical phases of the folded GNRs in terms of various characteristic distances and stacking patterns, which are distinguished from opened ends in layered graphene or GNRs. The closed edges and defective lines result in electronic structure and magnetic ordering modifications of the studied systems.

It is natural to extend the study of graphene to similar 2D structures, such as silicene, which may be better suited with the current silicon based electronics. Besides sharing some extraordinary properties with graphene, silicene has its own characteristics due to its staggered structure. For example, it has significant spin-orbit coupling which leads to noticeable quantum spin Hall effect and topological insulating phases.
Our study showed that, unlike the graphene counterpart, ZSiNR experience an AFM-FM transition as a function of the width. FM states are available in ZSiNRs, especially in the presence of extended topological defects, and in many cases the DOS of the minority spin is much smaller than that of the majority spin. ZSiNR is, therefore, a candidate for spintronic applications.

Vertical assemblies of monolayers of graphene, silicene and MoS\textsubscript{2} have also been studied. For these Lego-like heterostructures, the vdW interaction plays a crucial role since it is the force to stabilize the structures. We consider it by using vdW-DF2 functional\textsuperscript{[183,184,222]}, an advanced method where the vdW energy is self-consistently calculated. As a result of the interlayer hybridization, several electronic bands are broken to open local energy gaps in different energy regions. Those openings make it possible to use heterostructures for tuning optical transitions. The vdW interaction also determines the vibrational stability of the heterostructures. The flexural modes, which are typical for surface elastic media, depart from the characteristic $q^2$ dependence for the individual layers. New modes, such as shear and breathing vibrations, also occur. By showing how the vibrational properties evolve, one can potentially control the heat transfer in 2D systems.

Finally, we have considered an anchored structure of a ZGNR on a SiC substrate. Although this study has not been completed yet, we have gotten some important results. Both cases of the GNR anchored on the C and Si atoms of the substrate have been shown to be stable. The SiC substrate significantly influences the characteristics of the anchored ribbon, originating from the van der Waals interaction as well as the chemical anchored bonding. Significant altering has been found in the electronic and magnetic properties of the anchored ribbon as compared to the free one.

Materials from the graphene family present new direction for research exploration, as this body of work has shown. However, there are many unexplored areas for which \textit{ab initio} simulations methods are especially suitable to utilize. My vision for the immediate future is to understand better the origin of the asymmetry in the electronic structure of the anchored ribbons as well as to simulate armchair GNRs to a SiC sub-
strate. For the anchored armchair ribbons, the zigzag edge now appears in the sub-
strate itself, therefore it would be important to see if there is spin polarized states and
if the electronic structure around the Fermi level will change.

However, new ideas originating from the creation of various derivatives from sil-
icene, germanene, and stanene, the construction of various heterostructures, or com-
posite systems are especially worthy to pursue further using first principles methods.
Bibliography


