

STRUCTURE- AND ADATOM-ENRICHED ESSENTIAL PROPERTIES OF GRAPHENE NANORIBBONS

Shih-Yang Lin Ngoc Thanh Thuy Tran Sheng-Lin Chang Wu-Pei Su Ming-Fa Lin





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Shih-Yang Lin Department of Physics, University of Houston Ngoc Thanh Thuy Tran Department of Physics, National Cheng Kung University, Taiwan Sheng-Lin Chang Department of Physics, National Chiao Tung University, Taiwan

> Wu-Pei Su Department of Physics, University of Houston

Ming-Fa Lin Quantum Topology Center, National Cheng Kung University, Taiwan



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Authors

Shih-Yang Lin received his PhD in physics in 2015 from the National Cheng Kung University (NCKU), Taiwan. Since 2015, he has been a postdoctoral researcher at NCKU. Recently, he is a visitor scholar in University of Houston. His research interests include low-dimensional group IV materials and first-principle calculations.

Ngoc Thanh Thuy Tran obtained her PhD in physics in January 2017 from the National Cheng Kung University (NCKU), Taiwan. Since 2017, she has been a postdoctoral researcher at NCKU. She is currently working at Hierarchical Green-Energy Materials (Hi-GEM) Research Center, NCKU. Her scientific interests are focused on the functionalization of graphene and its derivatives using firstprinciple calculations.





Shen-Lin Chang obtained his PhD in 2014 in physics from the National Cheng Kung University (NCKU), Taiwan. Since 2014, he has been a postdoctoral researcher at NCKU and NCTU. His main scientific interests are in the field of condensed matter physics. Most of his research is focused on the electronic and magnetic properties of one-dimensional nanomaterials.

Wu-Pei Su is a professor in the Department of Physics, University of Houston. His research interest has been focusing on solving the X-ray phase problem in protein crystallography. It is a problem encountered in constructing threedimensional molecular images of proteins from the X-ray diffraction data of protein crystals. For protein crystals with high solvent content, Su's team has discovered a solution to the problem. He is currently extending the solution to a more general crystal.

Ming-Fa Lin is a distinguished professor in the Department of Physics, National Cheng Kung University, Taiwan. He received his PhD in physics in 1993 from the National Tsing-Hua University, Taiwan. His main scientific interests focus on essential properties of carbon related materials and low-dimensional systems. He is a member of American Physical Society, American Chemical Society, and the Physical Society of Republic of China (Taiwan).







Preface

This book aims to provide a systematic review of the feature-rich essential properties in emergent graphene nanoribbons, covering both up-to-date main-stream theoretical and experimental researche. It includes a wide range of 1D systems, namely, armchair and zigzag graphene nanoribbons without/with hydrogen terminations, curved and zipped graphene nanoribbons, folded graphene nanoribbons, carbon nanoscrolls, bilayer graphene nanoribbons, edge-decorated graphene nanoribbons, and alkali-, halogen-, Al-, Ti, and Bi-absorbed graphene nanoribbons. The first-principles calculations are successfully developed to thoroughly explore the physical, chemical, and material phenomena; furthermore, the concise pictures are proposed to explain the fundamental properties. The systematic studies on the various effects, which are due to edge structure, quantum confinement, curing, zipping, scrolling, folding, stacking, layer, orbital, spin, and adatom chemisorption, can greatly promote the basic and applied sciences. They could attract much attention from researchers in the scientific community, not only for the study of emergent 1D materials, but also for the exploration of other 0D, 2D, and 3D systems.

The content presents the reliable and complete calculation results, the other theoretical models, and the various experimental measurements and applications. The optimal geometric structures, electronic properties, and magnetic configurations are investigated in detail by the first-principle density functional theory using the Vienna ab initio simulation package (VASP). The exchange-correlation energy due to the electron-electron interactions is evaluated from the Perdew-Burke-Ernzerhof functional under the generalized gradient approximation. The projector-augmented wave pseudopotentials are employed to evaluate the electron-ion interactions. The spin configurations are taken into account for any graphene nanoribbons, especially for the adatomadsorbed systems. Moreover, the van der Waals force is employed to correctly describe the interactions between two graphene layers. The calculated results cover the ground state energy, binding energy, non-uniform honeycomb lattice, planar/non-planar structure, interlayer distance, bond length, bond angle, position and height of adatom, adatom nanostructure, band structure, width-dependent band gap, adatom-induced energy gap and free carriers, charge distribution, spin configuration, magnetic moment, and orbital- and spin-decomposed DOSs.

Specifically, the critical orbital hybridizations are accurately examined from the atom-dominated energy bands, the spatial charge density and the difference after chemisorption/bonding, and atom- and orbital-projected DOSs. Furthermore, the diverse magnetic configurations are delicately identified from the strong competition between zigzag edge carbons and adatoms, the spinsplit/spin-degenerate band structure, the spin-induced net magnetic moment, and the spatial spin distributions around host atoms and guest adatoms. Such theoretical framework is absent in the published books and papers of other research groups, and it could be generalized to emergent 0D-3D materials. A detailed comparison with the other theoretical studies and the experimental measurements is made. The high potentials in various materials applications are also discussed.

Contributors

Shih-Yang Lin

Department of Physics University of Houston, USA Department of Physics National Chung Cheng University, Taiwan

Ngoc Thanh Thuy Tran Hi-GEM

National Cheng Kung University, Taiwan Department of Physics National Cheng Kung University, Taiwan **Sheng-Lin Chang** Department of Physics National Chiao Tung University, Taiwan

Wu-Pei Su Department of Physics University of Houston, USA

Ming-Fa Lin Quantum Topology Center National Cheng Kung University, Taiwan Hi-GEM National Cheng Kung University, Taiwan



1

Introduction

Carbon atoms, which possess four active valence electrons, can create the dimension- and curve-related condensed-matter systems, such as, graphite [26, 342], graphene [255, 103], graphene nanoribbon (GNR) [193, 117], carbon nanotube [139, 140], carbon toroid [220, 300], and fullerene [170, 169]. The carbon-related materials, with the diverse chemical bondings $(sp^3, sp^2, and$ sp bondings), have attracted a lot of theoretical and experimental researche since the successful syntheses of C_{60} in 1985 [170], multi-walled carbon nanotubes in 1991 [139], carbon tori in 1998 [220], and few-layer graphenes in 2004 [255]. They are very suitable for studying the novel physical, chemical, and material phenomena, especially for the emergent low-dimensional systems. GNRs are one of the main stream nanomaterials, because the essential properties are greatly diversified by the complex relations among honeycomb lattice, one-atom thickness, finite-size quantum confinement, edge structure, planar/non-planar geometry, stacking configuration, adatom decoration, and chemical doping. Each GNR could be regarded as a finite-width graphene or an unzipped carbon nanotube. Up to now, GNRs have been successfully synthesized by the various experimental methods under the top-down and bottom-up schemes. The direct cutting of graphene layers covers the lithographic patterning and etching [117, 17], sonochemical breaking [193, 355], metal-catalyzed cutting [81, 76], and oxidization reaction [238, 100]. The unzipping of multi-walled carbon nanotubes is achieved by the chemical attack [166, 51], laser irradiation[171], plasma etching [147, 146], metal-catalyzed treatment [93, 264], hydrogen treatment and annealing [332], scanning tunneling microscope (STM) tip [261], transmission electron microscopy (TEM) [155], intercalation and exfoliation [47, 167], and electrochemical [310] and sonochemical processes [145, 369]. Moreover, other strategies involve chemical vapor deposition [45, 361, 325] and chemical synthesis [377, 44, 33], being able to produce macroscopic quantities of graphene nanoribbons. This systematic work is focused on the width-, layer number-, stacking-, curving-, folding-, scrolling-, decorating-, and doping-dependent geometric structures, electronic properties, and magnetic configurations which are mainly investigated by using the first-principles calculations. Monolayer and bilayer GNRs, curved GNRs, carbon nanotubes, folded GNRs, carbon nanoscrolls, adatompassivated GNRs, and alkali-, halogen-, and (Al,Bi,Ti)-doped GNRs are taken into account. We propose physical and chemical pictures to fully comprehend the rich and unique phenomena. The single- and multi-orbital hybridizations

between the same or distinct atoms, and the edge- and adatom-enriched spin configurations are thoroughly analyzed from the calculated results. Detailed comparisons with the other theoretical predictions and the experimental measurements are made. The high potentials of various materials applications are also discussed.

Graphene nanoribbons, with one-dimensional quantum confinement effects, can greatly diversify the essential properties, shedding light on potential applications in nanodevices, and thus attracting numerous theoretical studies. Monolaver graphene is a zero-gap semiconductor with zero density of states (DOS) at the Fermi level, and the other layered graphenes are semi-metals because of the interlayer atomic interactions. It should be noticed that the vanishing energy gaps have induced high barriers in certain important applications. However, electronic and magnetic properties of graphene nanoribbons are strongly affected by the ribbon widths [323], crystallographic orientations [21], and edge saturations [180]. Energy gaps, which are created by the finitesize effects, are confirmed in both armchair and zigzag GNRs. That is, they are found to be very sensitive to the change in edge structure. In addition to the parabolic energy bands, a pair of partially flat valence and conduction bands crossing the Fermi level is predicted to only exist in zigzag nanoribbons. The tunable electronic properties have further stimulated a lot of researche on magnetic properties [324, 91], optical excitations [376, 136], and transport properties [197, 350]. Experimentally, the width dependent energy gaps are verified by the measurements of electrical conductance [117]. The atomic structures, 1D parabolic energy dispersions, and low-lying asymmetric/symmetric peaks of the density of states are verified by STM [336], angle-resolved photoemission spectroscopy (ARPES) [294], and scanning tunneling spectroscopy (STS) [160], respectively. On the application side, GNRs have been explored and utilized in semiconductor industry, environmental engineering, and biochemistry. GNRs with width below 10 nm can serve as field-effect transistors (FETs) at room temperature [193, 355]. GNR arrays down to 5 nm width exhibit an exceptional NO_2 sensing performance [1]. A GNR transistor integrated with solid-state nanopore becomes a sensor for DNA translocation [341]. How many kinds of energy gaps with/without edge passivations and their origination are the core topics of this systematic study.

The changes in geometric structures of pristine graphene nanoribbons can modify and enrich the essential properties. The curved systems are directly synthesized from the cylindrical carbon nanotubes using physical and chemical methods [166, 51, 171, 147, 146, 93, 264, 332, 261, 155, 47, 167, 310, 145, 369]. The unzipping of multi-walled carbon nanotubes offers an efficient way in producing graphene nanoribbons with controlled structure and quality. The unzipped and zipped graphene structures have been observed under the measurements of atomic force microscopy (AFM), TEM, and scanning electron microscopy (SEM). The curved surfaces and dangling bonds are an ideal chemical environment for modulating the geometric structure and electronic properties. A planar graphene nanoribbon presents a typical sp^2 bonding, being determined by the π bonding of the parallel $2p_z$ orbitals and the σ bonding of the in-plane $(2s, 2p_x, 2p_y)$ orbitals. On the other hand, a perfect cylindrical surface in a carbon nanotube can create the coexistent sp^2 and sp^3 hybridizations, as verified by theoretical calculations [150, 314] and experimental measurements [260]. Apparently, graphene nanoribbons and carbon nanotubes sharply contrast with each other in the curvature and boundary condition, and so do the other essential properties. A cylindrical system has a periodical boundary condition along the azimuthal direction, so that the angular momentum serves as a good quantum number in addition to the axial wave vector. The transferred longitudinal momentum and transverse angular momentum are conserved in various scattering mechanisms, e.g., optical excitations [4, 210, 313] and Coulomb interactions [226, 209, 208]. However, an open boundary condition in a finite-width nanoribbon cannot create the transverse quantum number, leading to the absence of its conservation law in the excitation processes [75, 303, 304, 41]. These two critical factors, being responsible for the essential properties of the curved systems, are explored in details, such as the effects on the ground state energy, the effective interac-

tion distance, the bond length, orbital hybridization, the dominance of edge

carbon atoms, and the semi-conducting/metallic behavior. The folding of a honeycomb lattice may induce new and distinct properties in graphene-related systems. The folded graphene nanoribbons have been produced in experimental laboratories [193, 224, 387, 219, 135], and have been confirmed by the direct mapping of the open and closed edges using the high-resolution TEM (HRTEM). Transport measurements show that they could act as high-performance FETs [193] and electrode materials [60], Each unique geometric structure is composed of a chiral/non-chiral open boundary, a bilayer-like graphene, and a half carbon nanotube; that is, it consists of three distinct carbon honeycomb regions. For example, two zigzag/armchair graphene nanoribbons are connected by a fraction of armchair/zigzag carbon nanotube, in which the former are stacked in the manner of AA, AB or other configurations. The folded systems can provide rich physical and chemical environments in terms of edge structure, finite size, curvature, and orbital bonding. They are predicted to exhibit unusual phenomena, such as the magnetic quantization of highly degenerate Landau levels [278, 97], the semiconductor-metal transition under a structural transformation [60], the complex width dependences of energy gaps, and the diverse spin configurations. The combined effects, which arise from the quantum confinement, the spin arrangement near the specific edges, the edge-edge interactions, the van der Waals interactions between two planes, and the mechanical bending of a curved surface, will play critical roles in the optimal geometries, electronic properties, and magnetic configurations. This is worthy of a systematic investigation by the first-principles calculations.

Carbon nanoscrolls, with the spiral cross-sections, were first reported by Bacon in 1960 using the arc-discharge of graphite [16]. The distinct synthesis methods are further developed to fabricate high-quality carbon nanoscrolls more efficiently [189, 345, 305, 311, 315, 370]. They present tube-like structures under the disclosed surfaces. Each nanoscroll is an open-ended spirally wrapped graphene nanoribbon. The main features cover the inner and outer edges, the non-uniform curved surfaces, and the multi-walled structures with tunable interlayer distances. The formation and structure stability could be simulated by the molecular dynamics method [40]. As a result of the unusual structures, the essential properties are easily modulated by chemical doings, external fields, and mechanical strains. Carbon nanoscrolls are expected to have high potentials in applications, such as hydrogen storages [246], electromechanical nanoactuators [295], FETs, and microcircuit interconnect components [370]. First-principles calculations on energy bands shows strong dependence on edge structure and ribbon width [69, 172], as revealed in planar systems. However, the optimal structures, the multi-orbital hybridizations, and the spin arrangements need to be taken into consideration to fully understand the unusual geometric, electronic, and magnetic properties, e.g., the critical configuration parameters, the diverse width dependences of energy gaps, and the specific spin configurations (Chapter 6). Apparently, the structureinduced combined effects are quite different from among the scrolled, folded, curved, and planar graphene nanoribbons. This means that the geometric structures will result in diverse essential properties.

Few-layer graphene nanoribbons are frequently produced in various experimental syntheses [17, 193, 166, 147, 361]. The stacking symmetries of layered systems play critical roles in diversifying the essential properties, as confirmed by many theoretical [202, 340, 357, 71, 165, 265] and experimental [258, 257, 316, 38, 327, 107, 77, 37, 329] studies on 2D few-layer graphenes. For example, the trilayer graphenes, with AAA, ABA, ABC, and AAB stackings, present the linear, parabolic, sombrero-shape, and oscillatory for the first pair of energy bands measured from the Fermi level. The dramatic transitions will come to exist by modulating the stacking configurations between two layers, such as the metal-semiconductor transition and the generation/destruction of magnetism [58]. The shift-dependent variation of stacking symmetries could be achieved by electrostatic manipulation of STM, as done for graphene-related systems [373, 98, 225, 282]. Specifically, bilayer zigzag graphene nanoribbon could serve as a model system in revealing the combined effects due to the edge-edge interactions, the stacking configurations, and the intralver and interlayer spin arrangements. Previous theoretical calculations on typical AA and AB stackings predict the planar/non-planar profiles and the magnetic/nonmagnetic configurations [111, 301, 201, 266]. More complete calculated results are required to clearly identify the stacking-induced diverse behaviors. The shift-dependent optimal geometries, relatively stable stacking configurations, magnetic moments, spin distributions, spin degeneracies, low-lying energy dispersions, band gaps/free carrier densities, spatial charge densities near two open edges, and van Hove singularities are worthy of further detailed examinations. Furthermore, theoretical studies on the sliding bilayer graphene can fully explain the confinement-induced effects and the dimensional crossover.

How to dramatically change the essential properties is one of the mainstream topics in materials science and application. The chemical functionalization is one of the most effective ways. Pristine graphene nanoribbons, without passivation, possess a honeycomb lattice and two open edges, provide a reactive chemical environment. The intrinsic dangling bonds associated with edge carbon atoms are highly unstable, so that the dopants could be applied to passivate the active boundary. The dopant-created chemical bonding will play a critical role in determining the most stable configuration and thus other essential properties. Up to now, the H- [330], Cl- [333], and Oterminated [166] graphene nanoribbons have been produced by chemical synthesis methods, as examined by the measurements of STM, X-ray diffraction, and XPS. The first and the second adatom-decorated systems are, respectively, identified to present the planar and distorted edge structures with an open boundary. According to the theoretical calculations, the active edges tend to adsorb atoms [234, 133, 228, 131, 268, 105, 302, 14, 356, 317, 348, 217], molecules [52, 307, 80] or radical groups [52, 307]. The predicted decoration effects cover the edge reconstructions, the adatom-dominated energy bands, the greatly reduced energy gaps, and the semiconductor-metal transitions. They are closely related to the strong competitions between the edge passivation and the finite-size confinement. How many types of edge structures and width-dependent energy gaps can exist needs to be thoroughly clarified from detailed calculations and discussions. Specially, the adatom/molecule decorations might happen during the unzipping of carbon nanotubes through strong chemical reactions. The edge passivation and curvature are expected to have strong effects on the geometric, electronic, and magnetic properties [57], such as the adatom- and curvature-dominated planar/curved/tubular structures, the metallic/semiconducting behaviors, and the anti-ferromagnetic/ferromagnetic/non-magnetic configurations.

Adatom adsorptions on honeycomb surfaces can greatly modify the essential properties of graphene nanoribbons. Alkali, halogen, and metal atoms (Chapters 9–11), which possess the unique chemical and physical features, are very suitable for exploring the adsorption-induced dramatic changes, e.g., the semiconductor-metal transition, the n- or p-type doping (the creation of free electrons or holes), and the transformation between different spin arrangements. Up to now, alkali atoms have been successfully synthesized in carbon-related systems, such as graphite [360], fullerene [267], carbon nanotube [39], and graphene [128]. The alkali-doped systems are verified to present metallic behavior as a result of the high-density conduction electrons. They have displayed potential applications, e.g., the Li-ion batteries based on graphene [191]. There are many theoretical studies on the n-type doping effects [104, 271]. The alkali-adsorbed graphene and graphene nanoribbon are predicted to exhibit the blue-shift Fermi level [218]. The former is confirmed by the ARPES measurements [398]. It is well known that each alkali atom has one very active s-orbital, leading to significant chemical bonding with carbon atom. The critical orbital hybridization, which is determined by the delicate energy bands, spatial charge distribution, and DOS (discussed later in Section 2.1), is expected to dominate the diversified electronic properties and magnetic configurations. Determination of the number of conduction electrons due to the outmost s-orbitals and fine tuning of the spin magnetism are the main focuses under systematic investigations.

Halogen atoms are very good candidates for chemical modifications, mainly owing to the rather strong electron affinities. They have five electrons in the outmost (p_x, p_y, p_z) orbitals; furthermore, the adatom-induced spin states might come to exist after chemical adsorptions. The halogenated graphene nanoribbons are expected to exhibit complicated orbital hybridizations in chemical bonds and the adatom- and edge-C-created magnetic configurations. The diverse electronic and magnetic properties will be present in the variations of concentrations, distributions, and edge structures. How to identify the charge- and spin-dependent mechanisms is a critical issue and needs to be examined from the various physical quantities. Recently, there are many experimental [277, 292, 185] and theoretical [240] studies on the halogenation effects of graphene-related systems. Fluorinated [292], chlorinated [185], brominated [194] and iodinated [389] graphene systems have been successfully synthesized by various chemical methods. The important differences between fluorinated and other halogenated graphene systems in the semiconducting or metallic behavior are confirmed by the transport [365], optical [61], and ARPES measurements [352]. However, only very few studies are conducted on 1D halogenated graphene nanoribbons. Theoretical calculations predict very strong fluorination effects, such as the multi-orbital hybridizations in F-C, C-C, and F-F bonds, the irregular relations between energy gaps (valence hole densities) and adatom-adsorption cases, and five kinds of electronic and magnetic properties [253]. All the halogenation effects arising from the distinct kinds of adatoms are included in this work, especially the adsorption conditions/mechanisms in determining the feature-rich energy bands, free carrier densities, magnetic/NM configurations, and significant differences of the F-C and (Cl,Br,I,At)-C bonds.

Metal atoms, including aluminum, titanium, bismuth, and iron/cobalt/ nickel could provide effective dopings in conduction electrons (the *n*-type dopings) [216, 66, 64, 63], as revealed in alkali ones. After adsorption on graphene nanoribbon surfaces, they are expected to induce more complicated multi-orbital hybridizations in the significant carbon-metal bonds, compared with the $2p_z$ orbital and the outermost *s* orbital in the carbon-alkali bonds. Based on detailed first-principles calculations on the Al-, Ti/Fe/Co/Ni-, and Bi-adsorbed graphenes, the critical bondings are identified to arise from the $(3s, 3p_x, 3p_y)$, $(3d_{z^2}, 3d_{xy}, 3d_{x^2-y^2})$, and the $(6s, 6p_x, 6p_y, 6p_z)$ orbital, respectively. The theoretical predictions could highly promote further understanding of experimental measurements. For example, the aluminum-based batteries have been developed quickly to greatly enhance the charging and discharging reactions and to reduce the cost of the metallic anode [206]. The Al-adsorbed graphene is predicted to create as many free carriers as the alkali adatoms do, while the concentration of the former has an upper limit of 25% [216]. When the low-coverage titanium adatoms are adsorbed on monolayer graphene supported by 4H-SiC(0001) substrate, the high-density free electrons are verified from the high-resolution ARPES measurements [66]. The theoretical calculations suggest that the Ti adsorptions could exhibit the high-concentration adsorptions. The measured results agree with the calculated ones under the very strong orbital hybridizations in the Ti-C bonds. Specially, a large-scale hexagonal array of Bi adatoms on graphene surface is clearly revealed at room temperature using the STM measurements [64, 63]. It becomes three- and four-member nanostructures under the annealing process. The six-layer SiC substrate, the buffer graphene layer, and the slightly deformed monolayer graphene in the first-principles model are proposed to explain the most and meta-stable optimal structures [213]. The critical orbital hybridizations in generating free conduction electrons are also examined in detail [213]. Four different stable structures have been observed on Fe adsorbed graphene, and the corresponding DFT calculations shows that these structures all possess magnetic moments of either 2.00 or 4.00 μB [120]. The adsorption site, magnetic ground state, and anisotropy of single Co adatoms on 2D graphene are determined by experiments [88]. The different adatom concentration, the metal-induced free carrier density, and the magnetic properties are focuses of the metal-adsorbed graphene nanoribbons.

A thorough and systematic study is conducted on the essential properties of the structure-enriched and adatom-doped graphene nanoribbons. It covers a lot of critical mechanisms, lattice symmetries, boundary conditions, quantum confinements, edge structures, stacking-dependent interlayer interactions, curvature effects, edge-edge interactions, distributions and concentrations of adatoms, charge transfers, orbital hybridizations, magnetic environments, and adatom-created moments/spin configurations. The optimal geometric structures are related to the most/relatively stable configurations, various nonplanar profiles, interlayer and edge-edge distances, stacking configurations, critical curvatures, minimum widths/inner diameters, saturated nanotube diameters, bond lengths, bond angles; positions and heights of adatoms. Energy bands are characterized by the dominances of carbon, adatom and (carbon, adatom), linear, parabolic, partially flat and oscillatory energy dispersions, symmetry or asymmetry about the Fermi level, energy gaps due to the combined effects, free electron/hole densities, state degeneracy, and spinrelated splitting. The 1D critical points in energy bands reveal as the special van Hove singularities, including plateaus, asymmetric peaks, and symmetric peaks. Specifically, the delicate atom- and orbital-projected DOSs, the atom-dominated energy bands and the spatial charge densities, provide much information about the dominating chemical bondings. They could be used to identify the orbital hybridizations in C-C, C-X, and X-X bonds (X adatom). Furthermore, the magnetic configurations, the ferro-magnetic, antiferro-magnetic, and non-magnetic ones (FM, AFM, and NM) are examined from the net magnetic moment, the spin-dependent energy bands, the spatial spin distribution, and the spin-decomposed DOSs. According to the rich and unique essential properties, materials functionalities and potential applications are further discussed.

This book is organized as follows. Chapter 2 includes a detailed discussion of the computational methods and experimental tools, as well as important progresses achieved recently. The geometric, electronic, and magnetic properties are studied for monolayer systems in Chapter 3, especially for the finitesize and boundary effects. Chapter 4 focuses on the zipped/unzipped variations of curved systems, in which the critical arc angles, the edge-induced chemical bondings and energy bands, and the semiconductor-metal transitions are explored thoroughly. A detailed comparison is made between curved nanoribbons and carbon nanotubes. In Chapter 5, eight typical types of high-symmetry folded graphene nanoribbons are considered for studying the bilayer- and tuble-like composite structures, the unusual low-lying energy dispersions, the semiconductor-metal transitions, the diversified width dependences of band gaps, and the distinct magnetic environments, being based on the complex combined effects. How to sustain a stable carbon nanoscroll with an optimal spiral profile is discussed in Chapter 6, especially for the sufficiently large ribbon width and inner diameter. The edge-, width-, and spin-created diverse properties are investigated. Furthermore, the important differences among the planar, curved, folded, and scrolled graphene nanoribbons are fully clarified. Chapter 7 presents the dramatic transformations of the essential properties in bilayer zigzag graphene nanoribbon caused by the relative displacement between two layers. Also discussed is sliding bilayer graphene to illustrate the dimension-dominated behaviors. How to modify the boundary structure with the chemical edge passivation is the focus of Chapter 8. The decoration and curvature effects are examined for a lot of symmetric configurations and various adatoms to explore the diversified essential properties, especially for the types of geometric structures and the metallic/semiconducting behaviors.

The surface adatom adsorptions are investigated for graphene nanoribbons with hydrogen edge passivation. The critical chemical bondings and the adatom-induced spin states are proposed to explain the diversified properties. Chapter 9 explores the alkalization effects on the geometric, electronic, and magnetic properties. Whether there exists a specific relation between the alkali concentration and the 1D conduction electron density is examined for any absorption configurations. Furthermore, the spin arrangements at zigzag edges are delicately tuned by changing the position and concentration of alkali adatoms. The fluorination and chlorination-related effects are investigated in Chapter 10, especially for the significant mechanisms. The focus is on how to achieve the planar/buckled honeycomb structure, the high/low binding energy, the destruction/existence of the π -electronic band structure, the halogen-dependent energy bands, and the metallic or semi-conducting behavior through the multi-/single-orbital hybridizations in X-C bonds. Furthermore, the adsorption-dominated spin configuration and their strong competition with the zigzag-edge one are expected to create different types of magnetic configurations. Chapter 11 thoroughly discusses the main features of the Al-, Ti-, and Bi-adsorbed graphene nanoribbons and the significant differences among such systems. It includes the complicated orbital hybridizations arising from the distinct (s,p,d) orbitals, the metal-dominated low-lying conduction and valence bands, the adatom-induced free electron densities, and the adatom-dependent spin distributions. Finally, Chapter 12 includes concluding remarks and future studies.



The first-principles method and experimental instruments

The details of numerical evaluations and experimental measurements are discussed in the following two sections.

2.1 Theoretical calculations

2

A typical condensed-matter crystal consists of a periodic atomic arrangement, in which each atom might have several valence electrons distributed around an ionic core. Any system presents the complicated many-body effects due to the electron-electron Coulomb interactions and the electron-ion crystal potential. Apparently, it is rather difficult to accurately deal with the many-particle Schrödinger equation. The evaluation difficulties will be greatly enhanced when the unusual geometric structures and the strong chemical adsorptions need to be taken into consideration, e.g., the folded/scrolled and adatomdoped graphene nanoribbons. Some approximation methods have been developed to obtain the reliable electronic states. Up to now, the first-principles calculations become a dominant method in getting the quantum states of periodic systems. Such numerical calculations are very efficient for studying the essential physical properties. Specifically, Vienna *ab initio* simulation package (VASP) [168] evaluates an approximate solution within the density functional theory by solving the Kohn-Sham equations. [163] Electron charge density is responsible for all the interactions of a periodic condensed-matter system; that is, it can determine the ground state energy and the essential properties. The spatial charge density will be solved by the numerical self-consistent scheme, as indicated in a flow chart of calculation (Figure 2.1). Compared to this numerical method, the tight-binding model, with the atomic interaction parameters, cannot not be utilized to investigate the optimal geometric structures and the complicated orbital hybridizations in various chemical bonds. However, this model is efficient in studying the essential properties under the external fields, e.g., the quantized Landau levels [109, 232, 173, 75, 203], magneto-optical excitations [112, 113, 126], magnetoplasmons [24, 384], Hall quantum transports [151, 368]. and transverse electric-field-induced semiconductor-meta transitions [239]. In addition, the direct experimental verifications on the Landau wave functions of layered graphene systems are absent up to date, while they could be identified from the STM/STS examinations for few-layer graphene nanoribbons (the well-behaved quasi-Landau levels with the oscillatory and localized spatial probability distributions under the specific number of zero points).

The geometric structures, electronic properties, and magnetic configurations are thoroughly studied for 1D GNR-related systems using VASP [168]. The spin-polarized density functional theory is used to realize the magnetic configurations arising from the edge structures and adatom adsorptions [270]. The Perdew-Burke-Ernzerhof functional under the generalized gradient approximation can characterize the many-body Coulomb interactions, the exchange and correlation energies [270]. The projector-augmented wave pseudopotentials account for the electron-ion interactions [35]. In solving the manyparticle Schrodinger equation, plane waves, with a maximum energy cutoff of 400 eV, are the bases in building the Bloch wave functions. The 1D periodic boundary condition is along \hat{x} , and the vacuum spacing associated with \hat{y} and \hat{z} is larger than 15 Å to avoid the interactions between two neighboring nanoribbons. The Brillouin zone is sampled by $15 \times 1 \times 1$ and $600 \times 1 \times 1$ k point meshes within the Monkhorst–Pack scheme for geometric optimizations and further calculations on electronic structures, respectively. The convergence of energy is set to be 10^{-5} eV between two simulation steps, and the maximum Hellmann–Feynman force acting on each atom is less than 0.01 eV/Å during the ionic relaxations. Specifically, to correctly describe the significant atomic interactions between two neighboring graphene nanoribbons, the van der Waals force is included in the calculations by the semi-empirical DFT-D2 correction of Grimme [106].

For the structure-enriched and adatom-doped GNRs, the theoretical calculations cover the ground state energy, binding energy, interlayer distance, bond length, bond angle, planar/curved/buckled/scrolled/folded/stacked honeycomb lattice, hexagonal/non-hexagonal edge decoration, position and height of adatom, atom-dependent band structure, adatom-induced carrier density and energy gap, spatial charge distribution, spin arrangement, magnetic moment, and orbital- and spin-projected DOSs. The detailed analyses on the calculated results can get the concise physical and chemical pictures and thus fully comprehend the cooperative/competitive relations among the honeycomb lattice, the finite-size quantum confinement, the edge structure, the interlayer atomic interaction, the non-planar curvature effect, and the critical orbital hybridizations in carbon-adatom bonds, and the spin configurations. Whether there exist the diverse electronic properties (semiconductors or metals) and magnetic configurations (non-magnetism, ferromagnetism, or anti-ferromagnetism) is explored thoroughly. The theoretical predictions are compared with the up-to-date experimental measurements, especially for those from ARPES, STM, and STS. The complete and reliable results are very useful in the development of potential applications. Moreover, the first-principles cal-



FIGURE 2.1 The TEM instrument in measuring electron diffraction pattern.

culations are available to determine the important hopping integrals (atomic interactions; the important parameters) in the tight-binding model [10].

The critical orbitals of carbons and adatoms are fully considered in the numerical calculations. The single- or multi-orbital hybridizations in chemical bondings, which dominate the feature-rich essential properties, are clearly identified from the atom dominance of energy band, the orbital-dependent charge distribution, and the orbital-projected DOSs. For pristine graphene nanoribbons, they can comprehend the dramatic changes of chemical bondings on the non-planar surfaces, e.g., the curvature effects related to the misorientation of $2p_z$ orbitals and the sp^3 hybridization of $(2s, 2p_x, 2p_y, 2p_z)$ orbitals [214]. Moreover, there exist the rich and unique orbital hybridizations in the various X-C and X-X bonds. They are responsible for the optimal geometric structure, the unusual electronic properties, and even diversify the magnetic configurations. As to the edge-carbon- and/or adatom-induced spin states, they are thoroughly examined from the magnetic moment, the atom-dominated spin degeneracy, the spatial spin distribution, and the spindecomposed DOSs, being sensitive to the edge structures, the non-planar structures, the stacking configurations, the edge decoration, the kind of adsorption atatoms, the strength of X-C and X-X bonds, and the distribution and concentration of adatoms. In short, both orbital hybridizations and spin distributions will play critical roles in creating the diverse electronic properties and magnetic configurations, the FM/AFM/NM metals and semiconductors. The developed theoretical framework is very useful in the further studies on the emergent 1D and 2D materials, such as the essential properties of silicene-, germanene-, tinene-, and phosphorene-related systems.

2.2 Experimental instruments

Experimental measurements can directly identify the main characteristics of the essential properties; furthermore, the detailed comparisons with the theoretical predictions will provide the concise physical and chemical pictures to establish the basic concepts. Four main instruments throughout this work are TEM, STM, STS, and ARPES, in which the latter three also cover the spin-polarized measurements. They are very powerful in determining lattice symmetry, bond lengths, stacking configurations, spin distribution, local nanostructures, adatom positions, van Hove singularities (special structures) in DOS, spin-split states, energy dispersions of valence bands, band-edge states, and energy gap. A brief introduction to each characterization tool and the recent experimental progress is presented as follows.

Transmission electron microscopy is a microscopy technique in which an electron beam with a uniform current density is transmitted through an ultra thin specimen to form an image, owing to the interactions between incident charges and sample. The TEM was first demonstrated by Ernst Ruska and Max Knoll in 1931. Ruska was later awarded the Nobel Prize in physics for the development of TEM. TEMs can achieve a higher resolution than light microscopes, as a result of the smaller de Broglie wavelength of electrons. A TEM instrument, as shown in Figure 2.1, consists of an electron source, the first and second condenser lenses with aperture, specimen, an objective lens with aperture, intermediate and projector lenses, and a fluorescent screen. A set of condenser lenses helps to focus the beam on the sample. And then, an objective lens collects all the electrons after interactions, forms an image of the sample, and determines the limit of structure resolution. Moreover, a set of intermediate lenses magnifies this image and projects it on a fluorescent screen, a layer of photographic film, or a sensor. Compared to other microscopes, the main advantage of TEM measurements is to simultaneously provide accurate information in the real space (from the imaging mode) and reciprocal space (from the diffraction mode). The de Broglie wavelength of electrons of TEM is much smaller than atomic separations in the solids; therefore, it is achievable to observe crystal details below the atomic sizes. The resolution for TEM measurements is about 1-2 Å [183].

TEM is the powerful experimental technique for directly visualizing the crystal structure, locating and identifying the type of defects, and studying structural phase transitions. It has a very strong electrons' atomic scattering factor, being $\sim 10,000$ times that from the X-ray diffraction. This provides electron diffraction an advantage to detect even the weakest diffracted spot. However, the resolution of TEM is limited by spherical and chromatic aberrations of the lenses. More delicate techniques for improving the diffraction resolution become indispensable. By applying a monochromator and a Cs corrector into TEM, which is called high resolution TEM (HRTEM), the structural resolution can reach less than 0.5 Å [158]. HRTEM has been successfully and extensively used for analyzing crystal structures and lattice imperfections in various kinds of nanomaterials [286, 259]. The TEM/HRTEM measurements on graphene-related systems are very suitable in identifying the various nanoscaled geometric structures, such as the multi-walled cylindrical structures of carbon nanotubes [139, 166], the curved [166, 51, 171], folded [224, 387], and scrolled [345, 305, 311] profiles of graphene nanoribbons, as well as the stacking configurations and the interlayer distances of graphenes [45, 359, 181].

STM has become the most important experimental technique in resolving the surface structure since the first invention by Binnig and Rohrer in 1982 [29, 30]. This instrument is able to image the topographies of surfaces in real space with both lateral and vertical atomic resolution, such as the nanoscale bond lengths, crystal orientations, planar/non-planar structures, step edges, local vacancies, dislocations, adsorbed adatoms/molecules, and clusters/islands. The STM instrument, as shown Figure 2.2, consists of a conducting (semi-conducting) solid surface and a sharp metal tip, in which the distance of several angstroms is modulated by piezoelectric feedback devices. A weak current is built by the quantum tunneling effect in the presence of a bias voltage between surface and tip. It has a strong relation with distance, being assumed to present the exponential decay form. This current flows from the occupied electronic states of tip into the unoccupied ones of surface under the positive bias voltage V > 0, or vice versa. In general, the quantum tunneling current is chosen to serve as a feedback signal. The most commonly used mode, a constant tunneling one (current and voltage), will be operated to resolve surface structure very accurately by applying a piezoelectric device. By combining a probe of metal tip and a precise scanning device, the full spectroscopic information of surface morphology is obtained at the preselected positions under the well-defined conditions. The structural response is hardly affected by the background effects, being attributes to an ultra-high vacuum environment. Up to now, the spatial resolution of STM measurements can reach 0.1 Å. In addition to STM, other experimental techniques are available in characterizing the geometric properties of low-dimensional systems, covering transmission electron microscopy (TEM) [325, 221], scanning transmission electron microscope (STEM) [45], atomic force microscopy (AFM) [237], and low-energy electron diffraction (LEED) [86]. It should be noticed that STM is very sensitive to electron spin by using a ferromagnetic/antiferromagnetic probe tip. This spin-dependent spectroscopic mode was first proposed by Pierce in 1988 and realized by Wiesendanger et al. in 1990 [273, 363]. The up-to-date spin-polarized STM (SP-STM) can provide detailed information of magnetic phenomena with atomic resolution, such as spin polarizations of individual adatoms on magnetic surfaces [379], and domain structures of magnetic elements [276, 296].

STM is a powerful experimental technique in revealing the spatially atomic distributions with the nanoscale precisions. The very accurate measurements on the carbon-related systems have confirmed the rich and unique geometric structures, illustrating the complex relations among the hexagonal lattice, the finite-size confinement, the flexible feature, and the diverse chemical bondings of carbon atoms. From the up-to-date STS observations, graphene nanoribbons present the nanoscale-width planar honeycomb lattice, accompanied with the non-chiral (armchair and zigzag) and chiral edge structures [294, 335, 233]. Furthermore, they could also be formed in the curved [335], folded [193], scrolled [345], and stacked lattice structures [148]. Carbon nanotubes possess the achiral and chiral arrangements of the hexagons on cylindrical surfaces [364, 256]. The atomic-scale measurements directly identify the AB, ABC, and AAB stacking configurations of few-layer graphenes [181, 293], the corrugated substrate and buffer graphene layer [64, 63], the rippled structures of graphene islands [241, 18, 87], and the adatom distributions on graphene surface [262, 19]. The layered graphite could exhibit the 2D networks of local defects on surface [53]; the pyridinic-nitrogen and graphitic-N structures [164]. In addition, the folded graphene nanoribbons are also confirmed by high-resolution TEM measurements [193].

STS, as shown in Figure 2.3, is an extension of STM by using more delicate



FIGURE 2.2

The schematic illustration of STM in observing surface configuration by controlling the tip height under a specific tunneling current.