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**Gas Nanosensing In Armchair Graphene Nanoribbon
and Investigation of Physical Properties of
Nanostructure Semiconducting**

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

با تشکر فراوان از :

کمیته حمایت از پروژه های نانو وابسته به ریاست جمهوری .
استاد راهنمای عزیزم جناب آقای دکتر رستم مرادیان که همواره با راهنمایی و
مساعده علمی بسیار، باعث امیدواری من برای ادامه راه بودند.
پدر و مادر مهربان و بزرگواری که هر آنچه دارم نتیجه زحمات دیروز آنهاست.
پدر و مادر همسر که همواره مشوق و تکیه گاه محکمی برایم بوده اند.
همسر مهربانم و دخترم هیلا که همچون شمعی خالصانه در این سالهای پر تلاطم
به زندگیم نور تاباندند.
برادر و خواهرهای خود و همسر که همیشه دلسوزانه مشوقم بودند.

To my dear wife Gity,

and my daughter Hilla

Abstract

In this thesis, the works are divided in two categories, theoretical and experimental works. A theoretical approach based on a tight-binding model is developed for studying the effects of finite concentration gas adsorption (for what are known as diatomic, triatomic and quadratomic gas molecules in the general forms denoted by XY , XY_2 and XY_3 , respectively) on electronic properties of armchair graphene nanoribbons (AGNRs). To consider the edge effects on electronic properties of pure AGNRs for the first time, two hopping parameters, for hydrogen-carbon and carbon-carbon nearest neighbor hopping, are considered. We found, for some specified values of hopping integrals and random on-site energies, that adsorbed molecule AGNRs act as donors or acceptors, which is consistent with reported experimental results for CO, NO₂, O₂, N₂, CO₂ and NH₃ adsorption on graphene.

In experimental work, The cadmium selenide nanoparticle films have been deposited by chemical bath deposition method (CBD). Effects of deposition time, pH and annealing operation on the optical, structural and electrical properties of CdSe nanoparticles films are studied. The structural and morphological of the samples are investigated by X-ray diffraction (XRD), UV-Visible spectrometer and scanning electron microscope (SEM). We found, the optical gap, nanoparticles size and density of states near the Fermi level are vary by changing pH, increasing deposition time and annealing operation. Our measured conductivities data are consistent with the theoretical hopping model for the electrical transport description.

Table of contents	Page
Chapter 1 a trip into very small spaces	
1.1 Introduction to nanotechnology.....	1
1.2 Nanomaterials	1
1.2.1 Theoretical Aspect	4
1.2.2 Effective Mass Approximation	5
1.3 Graphene “Mother of all graphitic forms”	8
1.4 Graphene Nanoribbons	13
1.5 Gas Nanosensors	15
Chapter 2 Equation of motion and Random Green function matrix for a diatomic gas adsorbed Armchair Graphene Nanoribbon	
2.1 Introduction.....	21
2.2 Equation of motion.....	21
2.3 Random Green function matrix for a diatomic gas adsorbed Armchair Graphene Nanoribbon	32
Chapter 3 Electrical and Optical properties of the disorder material	
3.1 Introduction.....	37
3.2 Low electric field conductivity	37
3.2.1 DC Electrical conductivity	37
3.2.1.1 Extended state conduction	37
3.2.1.2 Conduction in band tails.....	40
3.2.1.3 Conduction in localized states at the Fermi energy.....	41
3.3 Optical Absorption.....	42
3.3.1 Linear Optical Properties Of Semiconductors.....	44
3.3.1.1 Direct Transition (direct gap semiconductors).....	48
3.3.1.2 Indirect Transition (indirect gap semiconductors).....	50
3.4 X-ray Diffraction	55
Chapter 4 Experimental and measurements	
4.1 Introduction	58
4.2 SOLUTION CHEMISTRY	58

4.2.1 Basic Terminolog	58
4.2.2 Hydrolysis of Metal Ions	58
4.2.3 Solubility Product.....	59
4.2.4 Crystal growth.....	60
4.3 Sample preparation.....	62
4.4 UV-Vis Absorption.....	63
4.5 X-Ray Diffraction patterns.....	64
4.6 Electrical measurements.....	66
4.7 Scanning electron microscopy.....	66
4.8 Atomic Force Microscopy	68
Chapter 5 Results and Discussins	
5.1 Introduction	70
5.2 Results of Optical absorption	71
5.3 Results of data electrical data.....	78
5.4. X-ray diffraction (XRD) analyzing of samples.....	85
5.5 Results and discussion on gas absorbed in Armchair Graphene Nanoribbon.....	86

1.1 Introduction to Nanotechnology

A technological journey is underway a trip into very small spaces. The journey is led by an eclectic band of engineers and scientists from all disciplines biology, chemistry, physics and mathematics who are pooling their talents to create a new field called “nanotechnology”. The destination of this journey is not yet entirely clear. Are these nanotech pioneers leading us into a new world of bountiful productivity, or into a dangerous ravaged landscape?

One focus of the Nanotech Pioneers is clear: they are out to change the way that we build things now with bulk materials, whittling them down or molding them, to a model that is more like that used by living things, creating objects with defined features that extend to the molecular level. Nanotech seeks to “...rebuild the world one molecule (or even one atom) a time”, or so the slogan goes. But is the world really in need of rebuilding?

In 1959, the great physicist of our time Professor Richard Feynman gave the first illuminating talk on nanotechnology, which was entitled as: **There’s Plenty of Room at the Bottom**. He consciously explored the possibility of “direct manipulation” of the individual atoms to be effective as a more powerful form of ‘synthetic chemistry’. Feynman talked about a number of interesting ramifications of a ‘general ability’ to manipulate matter on an atomic scale. He was particularly interested in the possibility of denser computer circuitry and microscopes that could see things much smaller than is possible with ‘scanning electron microscope’. The IBM research scientists created today’s ‘atomic force microscope’ and ‘scanning tunneling microscope’, and there are other important examples [1].

1.2 Nanomaterials

The changing in material properties with size was already reported in the nineteenth century by Michael Faraday. In the early twentieth century, work on glasses containing CdS showed that there was a red-shift in the absorption threshold with the growth of CdS particle size. [2] However, it was not until 1982 that this effect was related to the change of

the band gap with size in materials [3, 4]. In the past two decades, research on materials with sizes in the nanometer regime has gained enormous momentum. This can be gauged by the number of books and review articles (for example, see references [5-6]) that have been published in recent years on nanoscale materials, and also by the fact that now an entire ten volume encyclopedia exists, dedicated to this research area. [7]. The interest in nanomaterials is due to the fact that they have many interesting optical, electronic and chemical properties that are size-dependent. These materials have potential applications in developing new catalysts, [8, 9] nanosensors, [10, 11] and optoelectronic nanodevices [12-14]. Another important area of application of nanomaterials is in computer chips. Already chips are lithographed with patterns that are ~ 100 nm. Even smaller structures (roughly 20 nm) will be required to realize higher speeds and storage capacities. One can define nanomaterials as fragments of solids that have dimensions in the range of 1-50 nm. Solids and molecules have been studied for many years now and their properties are fairly well understood. However, nanomaterials that lie in the domain that is in between these two extremes, exhibit properties that are entirely different from either of them. The reason for such a difference in behavior stems partly from the fact that in case of nanomaterials the surface to volume ratio is extremely high. It ranges from about 90% for a 10 \AA particle to $\sim 10\%$ for a 100 \AA particle; in bulk materials the surface effects can usually be neglected. Surface atoms, thus, play an important role in governing the electronic, optical and thermodynamic properties in these nanomaterials. For example, bulk cadmium sulfide melts at about $1600 \text{ }^\circ\text{C}$, whereas a 25 \AA nanocrystal of the same material has a melting temperature of about $400 \text{ }^\circ\text{C}$ [15]. Such effects are observed because of the higher surface energy of the nanomaterials. Another effect of the higher surface to volume ratio is the elevation of pressure required for a phase transformation in nanomaterials [16]. High pressure X-ray diffraction in a number of semiconductors such as CdS [17] and CdSe [18-20] has revealed that the pressure required to induce a transformation to a more dense phase increases with a decrease in the nanocrystal size. Another reason for such a marked difference in the behavior of nanomaterials is that the wavelength of the electron wavefunctions in these materials is comparable to the size of the particle. The density of states changes as one goes from the bulk to quantum films that are confined in one dimension to quantum wires confined in two dimensions and finally, the nanocrystals or quantum dots that are confined in all three dimensions. This variation is shown schematically in Fig. 1.1. The variation of density of states versus energy for confined

systems does not follow the typical $E^{-\frac{1}{2}}$ dependence, as in the case of an infinite solid. In the present thesis, we focus on materials that are confined in all the three dimensions, namely the quantum dots, also known as nanocrystals (when they are crystalline) or nanoparticles (a general term that includes noncrystalline quantum dots as well).

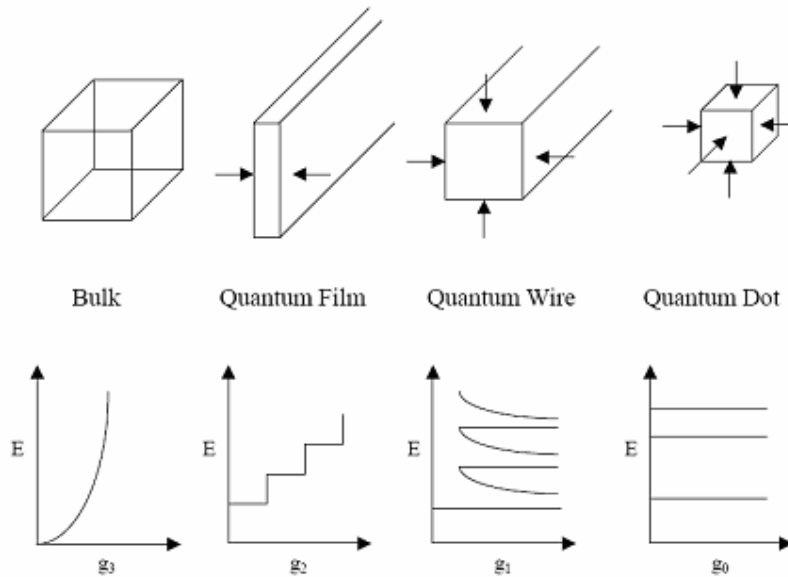


Figure 1.1: Evolution of the density of states with dimensionality showing the variation of density of states with energy for the infinite bulk solid, a quantum film, a quantum wire and a quantum dot. (Adapted from Ref. [21])

Based on their electronic structure, nanomaterials can be divided into two broad classes: metals and semiconductors. An important difference between metals and semiconductors is the possibility of tuning the band gap in semiconductors by changing their size in the nanometer regime. In case of metals, since there is no band gap, one needs to go down to very low sizes in order to open up a gap between the electronic states; this is the situation in the case of molecules or small clusters. In the band dispersions, the curvature of the bands at the external points is high compared to the curvature at the center of the bands. The changes in band structure with size depend on the band curvatures, and the change is more rapid where the band curvature is high. For semiconductors, the valence and conduction band edges decide the electronic properties and they vary rapidly with changing the size due to the higher curvature. The evolution of the density of states on going from the bulk semiconductor crystal to the nanocrystal is shown in Fig. 1.2 The continuum of states in the bulk semiconductor gives rise to the valence and the conduction bands separated by a band gap. On reducing the size of the particles of the semiconductor material, the band edges shift giving rise to an increase in the band gap and the energy

levels close to the edges become discrete as shown in Fig. 1.2. The reason for the band edges to become discrete before the band center is the fact that the density of states is very low near the band edges and it decreases further as one reduces the size, thus making these edges discrete before affecting the center of the band where the density of states is considerably higher. This is also known as the top-down approach since one approaches the nanocrystals starting from the bulk material. In the bottom-up approach, the evolution of the cluster can also be thought of as a number of individual molecules adding up together and forming bands starting from the single molecule as shown in Fig. 1.2.

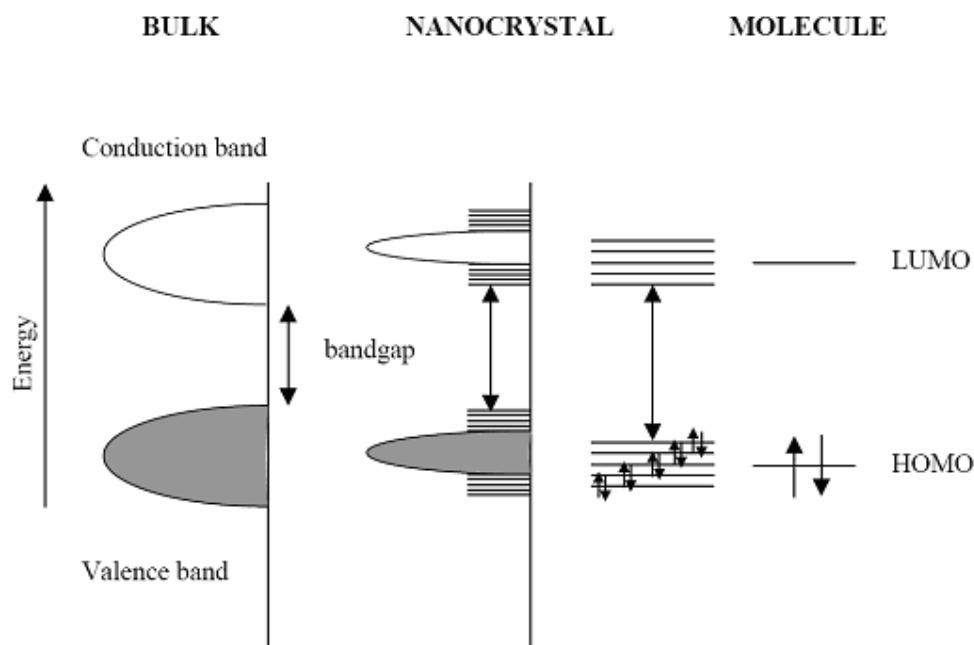


Figure 1.2: Schematic changes in the density of states on going from a bulk crystal to a nanocrystal to molecule.

1.2.1 Theoretical Aspects

In a bulk semiconductor, an electron and a hole are formed upon excitation across the band gap. As the wavefunctions of electrons and holes are delocalized over a number of ions or molecules that make the material and also because of the large dielectric constant of the material, the binding energy of the electron and the hole forming an exciton is relatively small. The average separation between the electron and the hole in the exciton is known as the Bohr exciton radius, a_B . It is typically of the order of a few nanometers in most semiconductors. Such a weakly bound electron-hole pair is also known as a Wannier exciton, which is transported through the semiconductor crystal until it is trapped by defect sites, annihilated by collision with another exciton, or relaxed by radiative recombination

of the electron and the hole. What happens when the size of the semiconductor material is reduced so that it is comparable to a_B ? We can view this as the simple particle-in-a-box problem. The solution of the Schrodinger equation gives the eigenfunctions

$$\psi_n(x) = \sqrt{\frac{1}{2L}} \text{Sin}(kx) \quad , \quad k_n = \frac{n\pi}{L} \quad (1.1)$$

Whose corresponding energy eigenvalues are given by:

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (1.2)$$

As the size of the box is reduced, the energy level spacing increases since it is inversely proportional to L^2 , the square of the length of the box. Thus, the kinetic energy, E_n , and the excitation energy, separation between two energy levels ($E_n - E_m$), of this particle increases upon confinement. This simple picture however does not give a quantitative measure of the change in band gap with size. There are various methods to quantitatively estimate the electronic properties of nanocrystals which we discuss in brief in the following subsection.

1.2.2 Effective Mass Approximation

In crystalline materials, the energy-momentum relationship is defined by a complex set of equations. This relationship is known as the band dispersion of the crystal [22]. Semiconductors or insulators differ from metals in exhibiting an energy gap between the valence band and the conduction band. If the charge carrier has a small amount of kinetic energy then the simplified description in Fig. 1.3 is often applicable for a single particle picture.

At low energies, near the band edges, delocalized electron (or hole) waves follow a quadratic equation describing the wave vector, k dependence of energy, E

$$E = \frac{\hbar^2 k^2}{2m^*} \quad (1.3)$$

Where m^* is the effective mass of the charge carrier (electron or hole). The motion of single charge carriers under the influence of external fields is described by this relation. Within the effective mass approximation (EMA), one can also describe the motion of a coupled electron-hole pair, the exciton. To use the effective mass approximation for describing the band gap variation with size for nanoparticles, one needs to solve the Schrodinger equation for the envelope function ψ :

$$\left[-\frac{\hbar^2 \nabla_e^2}{2m_e} - \frac{\hbar^2 \nabla_h^2}{2m_h} - \frac{e^2}{4\pi\epsilon_0\epsilon r_{eh}} + V_0 \right] \psi(r_e, r_h) = E \psi(r_e, r_h) \quad (1.4)$$

Where the subscripts e and h refer to the electron and the hole with r and m being the position vector and mass, respectively, and $r_{eh} = |r_e - r_h|$. ϵ_0 and ϵ are the permittivity in vacuum and the relative dielectric constant of the material. The potential V_0 is assumed to be zero inside the nanoparticle and infinite outside for the EMA calculation corresponding to an infinite barrier height. Using a trial wave function the above equation can be solved by approximate methods.

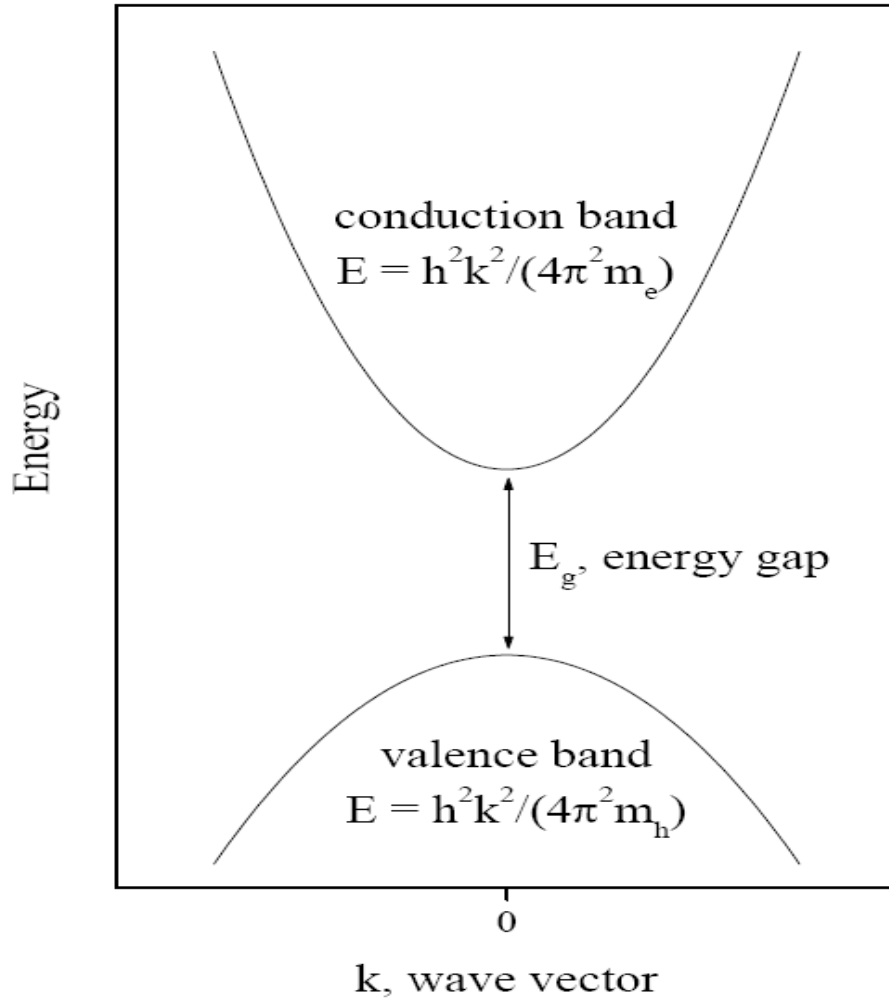


Figure 1.3: Schematic band dispersion: energy-momentum relation for a direct band gap semiconductor.

Brus [23-25] considered a model for the particles that incorporates (a) the effective mass approximation for the kinetic energy of the electron and the hole, (b) an electrostatic potential term from classical continuum polarizability theory and (c) tunneling of electrons

and holes out of the crystallite at the surface in the case of a finite barrier height. For an infinite barrier height the model yields the following expression for the band gap, E_R , of the quantum dot,

$$E_R = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon R} - 0.248 E_{Ry}^* \quad (1.5)$$

Where E_g is the bulk band gap, and R is the radius of the quantum dot. The third term arises due to the Coulomb attraction, and the fourth term due to the spatial correlation between the electron and the hole is negligible. The effective energy Rydberg E_{Ry}^* , in meV is defined as:

$$E_{Ry}^* = 13605.8 \frac{1}{\epsilon^2} \left(\frac{m_0}{m_e} + \frac{m_0}{m_h} \right)^{-1} \quad (1.6)$$

Kayanuma [26] has identified two limiting cases depending upon the ratio of the radius, R , of the quantum dot to the Bohr exciton radius, a_B of the bulk solid. For $\frac{R}{a_B} \gg 1$ the

exciton can be pictured as a particle moving inside the quantum dot with only little increment in energy due to the confinement. This is the weak confinement regime. In the strong confinement regime where $\frac{R}{a_B} \ll 1$, confinement effects obviously dominate. It

was pointed out that in this regime, the electron and hole should be viewed as individual particles in their respective single particle ground states with little spatial correlation between them. Kayanuma further found that the strong confinement regime is not only limited to $\frac{R}{a_B} \ll 1$ but the effects are seen up to $R = 2a_B$. This is the regime where the

effective mass approximation as given by Brus can be applied; however, we point out in this thesis that Eq.1.5 overestimates the band gap for all sizes, with the mismatch between the experiments and the calculated results increasing progressively for decreasing particle size.

Some improvement over the EMA with an infinite barrier was made when Schmidt and Weller [27] used a configuration interaction approach for the electron and the hole, treating it like a two-electron atom. They also used the Hylleraas functions and a perturbation expansion in R to obtain band gap energies slightly better than those described by the single particle EMA [28].

1.3 Graphene “Mother of all graphitic forms”

Graphene is a rapidly rising star on the horizon of materials science and condensed matter physics. This strictly two-dimensional material exhibits exceptionally high crystal and electronic quality, and, despite its short history, has already revealed a cornucopia of new physics.

Carbon is the materia prima for life and the basis of all organic chemistry. Because of the flexibility of its bonding, carbon-based systems show an unlimited number of different structures with an equally large variety of physical properties.

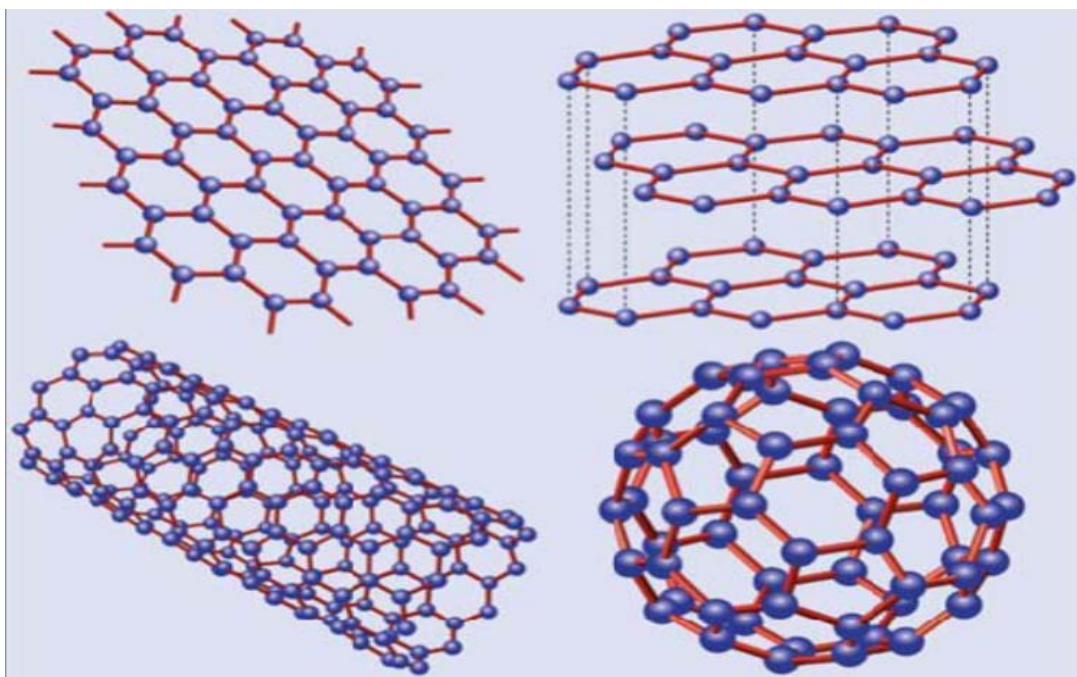


Figure 1.4: (Color online) Graphene (top left) is a honeycomb lattice of carbon atoms. Graphite (top right) can be viewed as a stack of graphene layers. Carbon nanotubes are rolled-up cylinders of graphene (bottom left). Fullerenes (C_{60}) are molecules consisting of wrapped graphene by the introduction of pentagons on the hexagonal lattice. .

These physical properties are, in great part, the result of the dimensionality of these structures. Among systems with only carbon atoms, graphene a two dimensional (2D) allotrope of carbon plays an important role since it is the basis for the understanding of the electronic properties in other allotropes. Graphene is made out of carbon atoms arranged on a honeycomb structure made out of hexagons (see Fig. 1.4), and can be thought of as composed of benzene rings stripped out from their hydrogen atoms (Pauling, 1972). Fullerenes (Andreoni, 2000) are molecules where carbon atoms are arranged spherically, and hence, from the physical point of view, are zero dimensional objects with discrete

energy states. Fullerenes can be obtained from graphene with the introduction of pentagons (that create positive curvature defects), and hence, fullerenes can be thought as wrapped-up graphene. Carbon nanotubes (Saito *et al.*, 1998; Charlier *et al.*, 2007) are obtained by rolling graphene along a given direction and reconnecting the carbon bonds. Hence carbon nanotubes have only hexagons and can be thought of as one-dimensional (1D) objects. Graphite, a three dimensional (3D) allotrope of carbon, became widely known after the invention of the pencil in 1564 (Petroski, 1989), and its usefulness as an instrument for writing comes from the fact that graphite is made out of stacks of graphene layers that are weakly coupled by van der Waals forces. Hence, when one presses a pencil against a sheet of paper, one is actually producing graphene stacks and, somewhere among them, there could be individual graphene layers. Although graphene is the mother for all these different allotropes and has been presumably produced every time someone writes with a pencil, it was only isolated 440 years after its invention (Novoselov *et al.*, 2004). The reason is that, first, no one actually expected graphene to exist in the Free State and, second, even with the benefit of hindsight, no experimental tools existed to search for one-atom thick flakes among the pencil debris covering macroscopic areas (Geim and MacDonald, 2007). Graphene was eventually spotted due to the subtle optical effect it creates on top of a chosen SiO₂ substrate (Novoselov *et al.*, 2004) that allows its observation with an ordinary optical microscope (Abergel *et al.*, 2007; Blake *et al.*, 2007; Casiraghi *et al.*, 2007). Hence, graphene is relatively straightforward to make, but not so easy to find.

The structural flexibility of graphene is reflected in its electronic properties. The Sp_2 hybridization between one s -orbital and two p -orbitals leads to a trigonal planar structure with a formation of a δ -bond between carbon atoms that are separated by 1.42 Å. The δ -band is responsible for the robustness of the lattice structure in all allotropes. Due to the Pauli principle, these bands have a filled shell and, hence, form a deep valence band. The unaffected p -orbital, which is perpendicular to the planar structure, can bind covalently with neighboring carbon atoms, leading to the formation of a π -band. Since each p -orbital has one extra electron, the π -band is half filled. Half-filled bands in transition elements have played an important role in the physics of strongly correlated systems since, due to their strong tight-binding character, the Coulomb energies are very large, leading to strong collective effects, magnetism, and insulating behavior due to correlation gaps or Mottness (Phillips, 2006). In fact, Linus Pauling proposed in the 1950s

that, on the basis of the electronic properties of benzene, graphene should be a resonant valence bond (RVB) structure (Pauling, 1972). RVB states have become popular in the literature of transition metal oxides, and particularly in studies of cuprate oxide superconductors (Maple, 1998). This point of view should be contrasted with contemporaneous band structure studies of graphene (Wallace, 1947) that found it to be a semimetal with unusual linearly dispersing electronic excitations called Dirac electrons. While most current experimental data in graphene support the band structure point of view, the role of electron-electron interactions in graphene is a subject of intense research. It was P. R. Wallace who in 1946 wrote the first paper on the band structure of graphene and showed the unusual semi-metallic behavior in this material (Wallace, 1947). At that time, the thought of a purely 2D structure was not reality and Wallace's studies of graphene served him as a starting point to study graphite, an important material for nuclear reactors in the post World War II era. During the following years, the study of graphite culminated with the Slonczewski-Weiss-McClure (SWM) band structure of graphite, which provided a description of the electronic properties in this material (McClure, 1957; Slonczewski and Weiss, 1958) and was successful in describing the experimental data (Boyle and Nozières 1958; McClure, 1958; Spry and Scherer, 1960; Soule *et al.*, 1964; Williamson *et al.*, 1965; Dillon *et al.*, 1977). From 1957 to 1968, the assignment of the electron and hole states within the SWM model were opposite to what is accepted today. In 1968, (Schroeder *et al.*, 1968) established the currently accepted location of electron and hole pockets (McClure, 1971). The SWM model has been revisited in recent years because of its inability to describe the van der Waals-like interactions between graphene planes, a problem that requires the understanding of many-body effects that go beyond the band-structure description (Rydberg *et al.*, 2003). These issues, however, do not arise in the context of a single graphene crystal but they show up when graphene layers are stacked on top of each other, as in the case, for instance, of the bilayer graphene. Stacking can change the electronic properties considerably and the layering structure can be used in order to control the electronic properties. One of the most interesting aspects of the graphene problem is that its low energy excitations are massless, chiral, Dirac fermions. In neutral graphene, the chemical potential crosses exactly the Dirac point. This particular dispersion, that is only valid at low energies, mimics the physics of quantum electrodynamics (QED) for massless fermions except for the fact that in graphene the Dirac fermions move with a speed V_F , which is 300 times smaller than the speed of light c . Hence, many of the unusual

properties of QED can show up in graphene but at much smaller speeds (Castro Neto *et al.*, 2006a; Katsnelson *et al.*, 2006; Katsnelson and Novoselov, 2007). Dirac fermions behave in unusual ways when compared to ordinary electrons if subjected to magnetic fields, leading to new physical phenomena (Gusynin and Sharapov, 2005; Peres, Guinea, and Castro Neto, 2006a) such as the anomalous integer quantum Hall effect (IQHE) measured experimentally (Novoselov, Geim, Morozov, *et al.*, 2005a; Zhang *et al.*, 2005). Besides being qualitatively different from the IQHE observed in Si and GaAlAs (heterostructures) device (tone, 1992), the IQHE in graphene can be observed at room temperature because of the large cyclotron energies for “relativistic” electrons (Novoselov *et al.*, 2007). In fact, the anomalous IQHE is the trademark of Dirac fermion behavior. Another interesting feature of Dirac fermions is their insensitivity to external electrostatic potentials due to the so called Klein paradox, that is, the fact that Dirac fermions can be transmitted with probability 1 through a classically forbidden region (Calogeracos and Dombey, 1999; Itzykson and Zuber, 2006). In fact, Dirac fermions behave in an unusual way in the presence of confining potentials, leading to the phenomenon of Zitterbewegung, or jittery motion of the wave function (Itzykson and Zuber, 2006). In graphene, these electrostatic potentials can be easily generated by disorder. Since disorder is unavoidable in any material, there has been a great deal of interest in trying to understand how disorder affects the physics of electrons in graphene and its transport properties. In fact, under certain conditions, Dirac fermions are immune to localization effects observed in ordinary electrons (Lee and Ramakrishnan, 1985) and it has been established experimentally that electrons can propagate without scattering over large distances of the order of micrometers in graphene (Novoselov *et al.*, 2004). The sources of disorder in graphene are many and can vary from ordinary effects commonly found in semiconductors, such as ionized impurities in the Si substrate, to adatoms and various molecules adsorbed in the graphene surface, to more unusual defects such as ripples associated with the soft structure of graphene (Meyer, Geim, Katsnelson, Novoselov, Booth, *et al.*, 2007a). In fact, graphene is unique in the sense that it shares properties of soft membranes (Nelson *et al.*, 2004) and at the same time it behaves in a metallic way, so that the Dirac fermions propagate on a locally curved space. Here analogies with problems of quantum gravity become apparent (Fauser *et al.*, 2007). The softness of graphene is related with the fact that it has out of plane vibrational modes (phonons) that cannot be found in 3D solids. These flexural modes, responsible for the bending properties of graphene, also account for the lack of long range structural order in soft membranes leading to the phenomenon of crumpling

(Nelson *et al.*, 2004). Nevertheless, the presence of a substrate or scaffolds that hold graphene in place can stabilize a certain degree of order in graphene but leaves behind the so called ripples (which can be viewed as frozen flexural modes). It was realized early on that graphene should also present unusual mesoscopic effects (Peres, Castro Neto, and Guinea, 2006a; Katsnelson, 2007a0). These effects have their origin in the boundary conditions required for the wave functions in mesoscopic samples with various types of edges graphene can have (Nakada *et al.*, 1996; Wakabayashi *et al.*, 1999; Peres, Guinea, and Castro Neto, 2006a; Akhmerov and Beenakker, 2008). The most studied edges, zigzag and armchair, have drastically different electronic properties. Zigzag edges can sustain edge (surface) states and resonances that are not present in the armchair case. Moreover, when coupled to conducting leads, the boundary conditions for a graphene ribbon strongly affect its conductance, and the chiral Dirac nature of fermions in graphene can be used for applications where one can control the valley flavor of the electrons besides its charge, the so-called valleytronics (Rycerz *et al.*, 2007). Furthermore, when superconducting contacts are attached to graphene, they lead to the development of supercurrent flow and Andreev processes characteristic of the superconducting proximity effect (Heersche *et al.*, 2007). The fact that Cooper pairs can propagate so well in graphene attests to the robust electronic coherence in this material. In fact, quantum interference phenomena such as weak localization, universal conductance fluctuations (Morozov *et al.*, 2006), and the Aharonov-Bohm effect in graphene rings have already been observed experimentally (Recher *et al.*, 2007; Russo, 2007). The ballistic electronic propagation in graphene can be used for field-effect devices such as p - n (Cheianov and Fal'ko, 2006; Cheianov, Fal'ko, and Altshuler, 2007; Huard *et al.*, 2007; Lemme *et al.*, 2007; Tworzydło *et al.*, 2007; Williams *et al.*, 2007; Fogler, Glazman, Novikov, *et al.*, 2008; Zhang and Fogler, 2008) and p - n - p (Ossipov *et al.*, 2007) junctions, and as “neutrino” billiards (Berry and Modragon, 1987; Miao *et al.*, 2007). It has also been suggested that Coulomb interactions are considerably enhanced in smaller geometries, such as graphene quantum dots (Milton Pereira *et al.*, 2007), leading to unusual Coulomb blockade effects (Geim and Novoselov, 2007) and perhaps to magnetic phenomena such as the Kondo effect. The transport properties of graphene allow for their use in a plethora of applications ranging from single molecule detection (Schedin *et al.*, 2007; Wehling *et al.*, 2008) to spin injection (Cho *et al.*, 2007; Hill *et al.*, 2007; Ohishi *et al.*, 2007; Tombros *et al.*, 2007). Because of its unusual structural and electronic flexibility, graphene can be tailored chemically and/or structurally in many different ways: deposition of metal atoms (Calandra and Mauri, 2007; Uchoa *et al.*, 2008) or molecules (Schedin *et*

et al., 2007; Leenaerts *et al.*, 2008; Wehling *et al.*, 2008) on top; intercalation [as done in graphite intercalated compounds) Dresselhaus *et al.*, 1983; Tanuma and Kamimura, 1985; Dresselhaus and Dresselhaus, 2002]; incorporation of nitrogen and/or boron in its structure (Martins *et al.*, 2007; Peres, Klironomos, Tsai, *et al.*, 2007) [in analogy with what has been done in nanotubes Stephan *et al.*, 1994]; and using different substrates that modify the electronic structure (Calizo *et al.*, 2007; Giovannetti *et al.*, 2007; Varchon *et al.*, 2007; Zhou *et al.*, 2007; Das *et al.*, 2008; Faugeras *et al.*, 2008). The control of graphene properties can be extended in new directions allowing for the creation of graphene-based systems with magnetic and superconducting properties (Uchoa and Castro Neto, 2007) that are unique in their 2D properties. Although the graphene field is still in its infancy, the scientific and technological possibilities of this new material seem to be unlimited. The understanding and control of this material's properties can open doors for a new frontier in electronics. As the current status of the experiment and potential applications have recently been reviewed (Geim and Novoselov, 2007), in this paper we concentrate on the theory and more technical aspects of electronic properties with this exciting new material [29].

1.4 Graphene Nanoribbons

The carbon atoms on the edge of Graphene Nanoribbons have two typical topological shapes, namely armchair and zigzag. The analytical wave function and energy dispersion of zigzag nanoribbons have been derived by several research groups [30, 31]. For armchair GNRs, the analytical forms of wave functions within the low-energy range have been worked out based on the effective-mass approximation. It is predicted that all zigzag GNRs are metallic with localized states on the edges [30-33] while armchair GNRs are either metallic or insulating, depending on their widths[30-34]. To date, there is no general expression of the wave function in armchair GNRs. In this paper, we derive a general analytical expression of wave function and eigenenergy in armchair GNRs applicable to various energy ranges. Due to the quantum confinement, the spectrum breaks into a set of subbands and the wave vector along the confined direction becomes discretized, which is similar to the case of carbon nanotubes[35, 36]. We observe that the electronic structure of perfect armchair GNRs strongly depends on the width of the ribbon. The system, for instance, is metallic when $n=3m+2$ and is insulating otherwise, where m is an integer [30-34]. Furthermore, we study the low energy electronic structure. The linear dispersion relation is observed in armchair GNRs. Calculation results based on the derived analytical