The elementary electronic properties of graphene

Qinlong Luo
qluo@utk.edu
Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996, USA
(Dated: April 8, 2010)

In this paper, the elementary electronic properties of graphene are generally introduced. This paper mainly focus on the energy-momentum dispersion of graphene, investigated by a tight-binding model theoretically and Shubnikov-de Haas oscillations experimentally. It shows that the carriers in graphene are massless Dirac fermions, which should be described by Dirac's relativistic equation.

PACS numbers:

I. INTRODUCTION

Quantum electrodynamics (QED) has made a clear understanding of phenomena from particle physics to astrophysics (high energy). But these phenomena have never observed in condensed matter system (low energy), until the discovery of graphene six years ago [1, 2]. The electron transport in graphene is essentially described by Dirac's relativistic equation, not the non-relativistic Schrödinger equation.

Graphene is made of carbon atoms arranged on a honeycomb lattice with lattice constant $a = 1.42\mathring{A}$ [6]. It can be also considered as composed of benzene rings stripped out from their hydrogen atoms. This two-dimensional (2D) material plays a key role since it is the basis of all the graphitic forms (see Fig. 1): graphene can be wrapped up into 0D Fullerenes [9], rolled along a given direction into 1D carbon nanotubes [10], and stacked layer by layer into 3D graphite which exists in pencil. The reasons for discovering graphene so late are mainly [6]: (1) graphene was expected to be unstable in the free state before its discovery; (2) no experimental tools existed to detect the one-atom-thick graphene. Graphene was eventually spotted due to the subtle optical effect it creates on top of a chosen SiO_2 substrate, which allows its obeservation with an ordinary optical microscope.

The structure flexibility of graphene and its two-dimensionality provide a lot of unexpected electronic properties. The most interesting property is that its low-energy excitations are massless Dirac fermions with speed $v_F \simeq 1.0 \times 10^6 m/s$ [3]. These unusual Dirac fermions in the magnetic fields lead to the anomalous integer quantum Hall effect [3]. Another interesting property is the Klein paradox, describing that the Dirac fermions can be transmitted with probability 1 through a classically forbidden region [8]. And the disorder in graphene results in some interesting properties [6], such as ripples, localized states near edges, impurity states and topological lattice defects. All these presented and unpresented interesting properties make graphene a hot topic in the condensed matter physics community.

This paper is organized as follows: the crystal structure of graphene is discussed in Sec. II. And Sec. III focuses on the band dispersion calculation theoretically. Sec. IV provides some experiments,especially the Shubnikov-de Haas oscillations (SdHO) which is consist with the calculation above. And the conclusions will be found in Sec. V.

II. THE CRYSTAL STRUCTURE AND THE sp^2 HYBRIDIZATION IN GRAPHENE

The crystal structure of graphene in Fig. 2 shows that graphene is made of carbon atoms arranged in hexagonal honeycomb-like structure. It can be imaged as a triangular lattice with a basis of two atoms which are shown as yellow and blue solid dots. The two lattice vectors can be written as:

$$a_1 = \frac{a}{2}(3, \sqrt{3}), \qquad a_2 = \frac{a}{2}(3, -\sqrt{3}) \tag{1}$$

where $a \simeq 1.42\mathring{A}$ is the carbon-carbon distance.

In the Brillouin zone (BZ), the Dirac cones are located at two corners K and K', which are of particular importance. Their positions in the reciprocal space are:

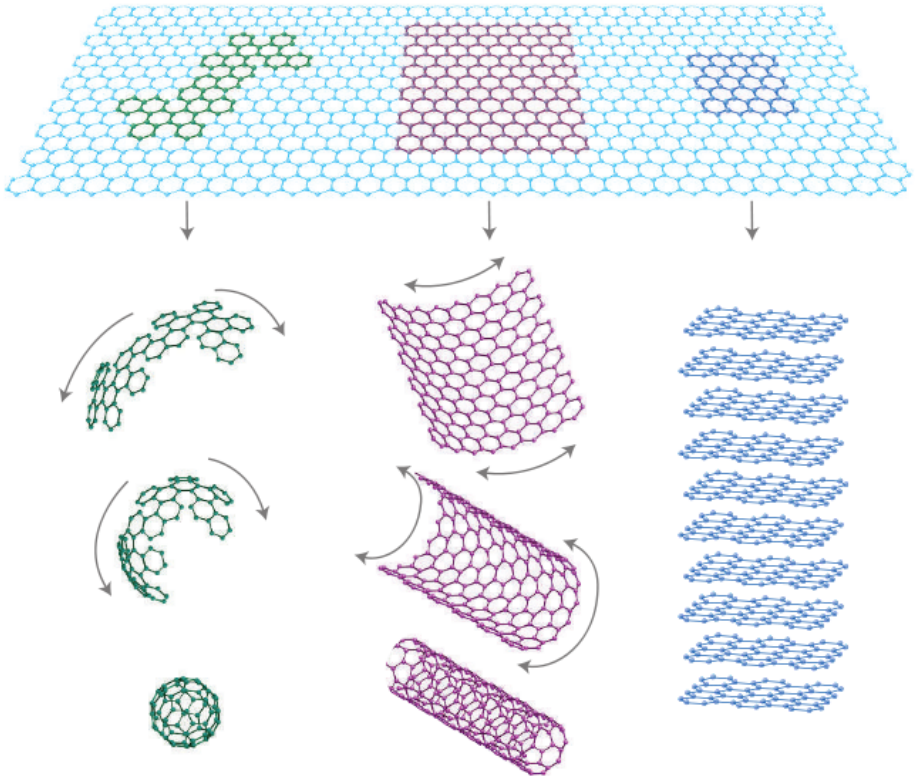

FIG. 1: Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D Fullerenes, rolled into 1D nanotubes or stacked into 3D graphite. Taken from Ref. [5]

$$K = (\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}), \qquad K' = (\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}) \tag{2}$$

And the three nearest-neighbor (NN) vectors in real space read:

$$\delta_1 = \frac{a}{2}(1, \sqrt{3}), \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}), \quad \delta_3 = -a(1, 0) \tag{3}$$

While the six next nearest-neighbor (NNN) vectors read:

$$\delta_1' = \pm a_1, \quad \delta_2' = \pm a_2, \quad \delta_3' = \pm(a_2 - a_1). \tag{4}$$

The sp^2 hybridization in carbon atoms is of great importance. The hybridization between one s orbital and two p orbitals forms a σ band which makes the lattice structure robust, and leads to a hexagonal planar structure. These bands have a filled shell due to the Pauli principle. The other p orbital is perpendicular to the planar. This p orbitals can bind with the neighboring carbon atoms, which forms a π band. It is half-filled because this p orbital has one extra electron.

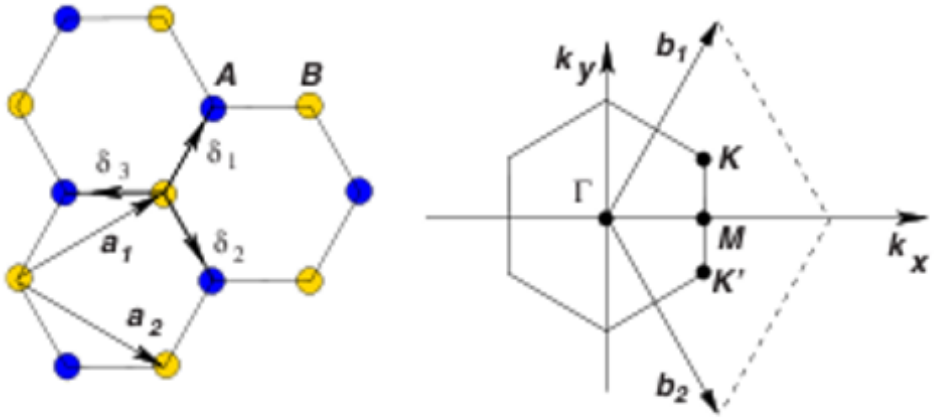

FIG. 2: Honeycomb lattice and its Brillouin zone. Left: lattice structure of graphene, made out of two interpendetrating triangular lattices (a_1 and a_2 are the lattice unit vectors, and δ_i, i=1,2,3 are the nearest-neighbor vectors). Right: corresponding Brillouin zone. The Dirac cones are located at the K and K' points. Taken from Ref. [6]

III. BAND DISPERSION CALCULATION

It was P. R. Wallace who first calculate the band dispersion of graphene using a tight-binding model. The Hamiltonian in second quantization language reads:

$$H = -t_1 \sum_{<i,j>,\sigma} (a^\dagger_{i,\sigma} b_{j,\sigma} + h.c.) - t_2 \sum_{<<i,j>>,\sigma} (a^\dagger_{i,\sigma} a_{j,\sigma} + b^\dagger_{i,\sigma} b_{j,\sigma} + h.c.) \tag{5}$$

where $a_{i,\sigma}$ ($a^\dagger_{i,\sigma}$) annihilates (creates) an electron with spin σ on site R_i on sublattice A, while $b_{i,\sigma}$ ($b^\dagger_{i,\sigma}$) annihilates (creates) an electron with spin σ on site R_i on sublattice B. And t_1 is the NN hopping amplitude while t_2 is the NNN hopping amplitude.

Making a Fourier transformation of H results in the Hamiltonian in momentum space [12], which is given by:

$$H = \sum_{\vec{k},\sigma} (T_1 a^\dagger_{\vec{k},\sigma} b_{\vec{k},\sigma} + T_2 b^\dagger_{\vec{k},\sigma} a_{\vec{k},\sigma} + T_3 (a^\dagger_{\vec{k},\sigma} a_{\vec{k},\sigma} + b^\dagger_{\vec{k},\sigma} b_{\vec{k},\sigma})) \tag{6}$$

where the coefficients reads:

$$T_1 = -t_1 (2e^{i\frac{a}{2}k_x} \cos(\frac{\sqrt{3}}{2} a k_y) + e^{-iak_x}) \tag{7}$$

$$T_2 = -t_1 (2e^{-i\frac{a}{2}k_x} \cos(\frac{\sqrt{3}}{2} a k_y) + e^{iak_x}) \tag{8}$$

$$T_3 = -t_2 (4\cos(\frac{3}{2} a k_x) \cos(\frac{\sqrt{3}}{2} a k_y) + 2\cos(\sqrt{3} a k_y)) \tag{9}$$

$$\tag{10}$$

This Hamiltonian can be represented by a 2×2 matrix and the diagonalization of this matrix gives the band dispersion as:

$$E_{\pm}(\vec{k}) = \pm t_1\sqrt{3 + f(\vec{k})} - t_2 f(\vec{k}), \tag{11}$$

$$f(\vec{k}) = 2\cos(\sqrt{3}ak_y) + 4\cos(\frac{\sqrt{3}}{2}ak_y)\cos(\frac{\sqrt{3}}{2}ak_y) \tag{12}$$

where "+" applies to the upper band while "−" the lower band. From Eq.(11), the band structure is symmetric around zero energy if $t_2 = 0$. But the electron-hole symmetry is broken and the upper and lower bands become asymmetric for finite t_2. The whole band dispersion of graphene is shown in Fig.(3) with finite t_1 and t_2. And the bands near one of the Dirac cones is also shown in the zoom in figure in Fig.(3). This dispersion can be obtained by expanding Eq.(11) aound the K point, as $\vec{k} = \vec{K} + \vec{q}$ (the vector K is given by Eq.(2)) with $|\vec{q}| \ll \vec{K}$, and ignoring the t_2 term since t_2 is small enough. This approximation gives the results as:

$$E_{\pm}(\vec{q}) \approx \pm t_1\sqrt{(\frac{3a}{2}q_x)^2 + (\frac{3a}{2}q_x)^2 + O(q_x^3) + O(q_y^3)} \tag{13}$$

$$= \pm v_F|\vec{q}| + O[q^2] \tag{14}$$

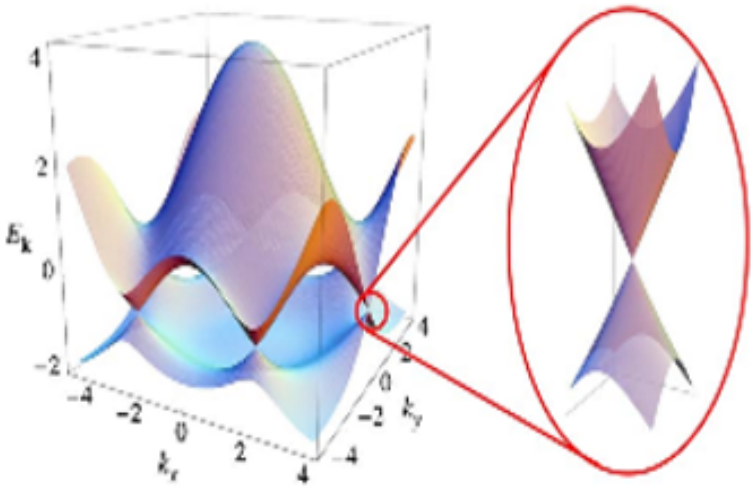

FIG. 3: Electronic dispersion in the honeycomb lattice. Left: energy spectrum (in units of t) for finite values of t_1 and t_2, with $t_1 = 2.7eV$ and $t_2 = -0.2t$. Right: zoom in of the energy bands close to one of the Dirac points. Taken from Ref. [6].

This equation gives the Fermi velocity of the carriers in graphene with a value $v_F = \frac{3at_1}{2} \simeq 1 \times 10^6 m/s$. And this dispersion relation shows that the carriers in graphene is Dirac fermions which should be described by Dirac relativistic equation. And the description of Dirac fermions in graphene is specified in Ref. [6] which is not shown here.

IV. ELECTRIC FIELD EFFECT AND THE SHUBNIKOV-DE HAAS OSCILLATIONS

The massless Dirac fermions in graphene was first discovered by K.S. Novoselov [3], who also first found graphene in 2004 [1]. In his electric field effect experiment (shown in Fig. 4), it was found that the conductivity σ is linear

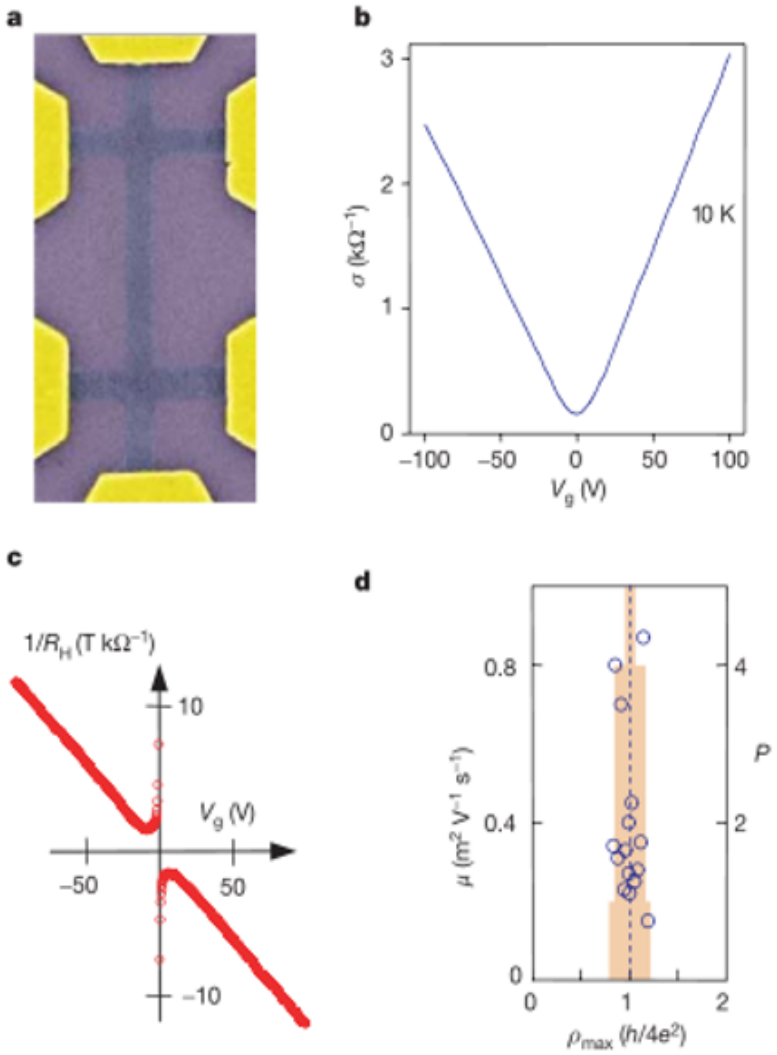

FIG. 4: Electric field effect in graphene. a, Scanning electron microscope image of graphene. b,c, Changes in graphene's conductivity σ (b) and Hall coefficient R_H (c). d, Maximum values of resisitivity $\rho = 1/\sigma$ (circles) exhibited by devices with different mobilities μ. Taken from Ref. [3]

with the gate voltage V_g for both polarities. The Hall coefficient measurement suggests that the concentrations of electrons (holes) are induced by positive (negative) gate voltages, which is called electrical (hole) doping. In Fig. 4c, the linear dependence $\frac{1}{R_H} \propto V_g$ yields $n = \alpha V_g$ with $\alpha \approx 7.3 \times 10^10 cm^{-2} V^{-1}$, which is consistent with the theoretical calculation $\frac{n}{V_g} \approx 7.2 \times 10^10 cm^{-2} V^{-1}$.

Fig. 5 shows the Shubnikov-de Haas oscillations (SdHOs) in graphene for different magnetic fields B, gate voltage and temperatures. From these results, the relation between fundamental SdHO frequency B_F and the gate voltage V_g can be determined by using standard fan diagrams. This results in the linear dependence $B_F = \beta n$ with $\beta \approx 1.04 \times 10^{-15} Tm^2$ in Fig. 6a. Fig. 6d shows square-root denpedence between the cyclotron mass m_c and the concentrations

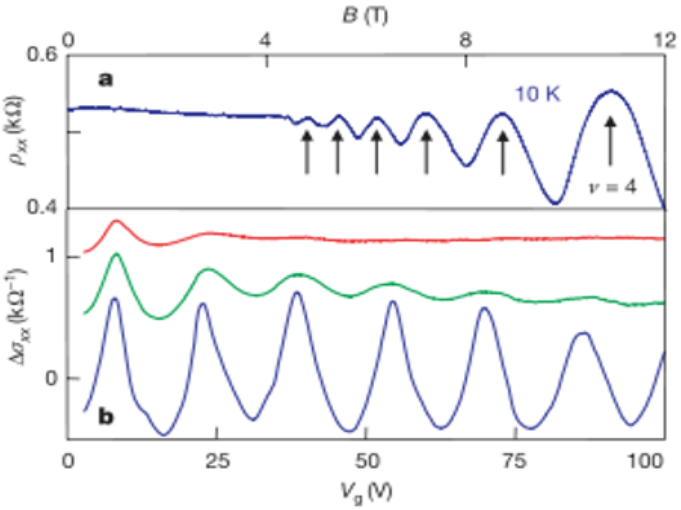

FIG. 5: Quantum oscillations in graphene. SdHO at constant gate voltage $V_g = 60eV$ as a function of magnetic field B (a) and at constant $B = 12T$ as a function of V_g (b). Taken from Ref. [3].

n of the carriers in graphene, which is $m_c \propto n^{1/2}$. Within the semiclassical approximation [11], the cyclotron mass is defined as:

$$m_c = \frac{\hbar^2}{2\pi}\frac{\partial S(E)}{\partial E} \tag{15}$$

where $S(E) = \pi k^2$ is the area in k-space of the orbits at the Fermi energy $E(k)$. And the fundamental SdHO frequency is defined as :

$$B_F = \frac{\hbar}{2\pi e}S(E) \tag{16}$$

Combined with the experimentally found dependences $m_c = \alpha n^{1/2}$ and $B_F = (h/4e)n$, we can obtain:

$$S(E) = \frac{2\pi e}{\hbar}\frac{h}{4e}n = \pi^2 n \tag{17}$$

$$\frac{\partial S(E)}{\partial E} = \frac{2\pi}{\hbar^2}\alpha n^{1/2} \tag{18}$$

$$\tag{19}$$

Then we can obtain $\frac{\partial S(E)}{\partial E} \propto S^{1/2}$, which means $S(E) \propto E^2$. Combining this relation with $S(E) = \pi k^2$ yields the linear dispersion $E = v_F k$ and the best fit to the experimental data yields $v_F \approx 10^6 m/s$, in perfect agreement with the band dispersion calculation in Sec. III. This shows the Dirac fermions in graphene from experimental aspect.

V. CONCLUSIONS

In conclusion, some electronic properties of graphene are introduced. All these interesting properties make graphene a key material in condensed matter physics. A tight-binding Hamiltonian is investigated to calculate the band dispersion of graphene. And quantum oscillation and electric field effect experiments are introduced as well. Both

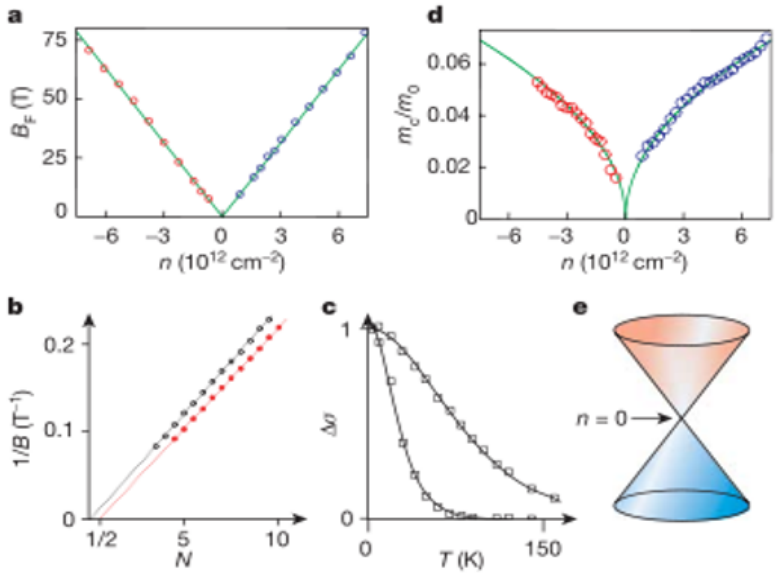

FIG. 6: Dirac fermions of graphene. a, Dependence of B_F on carrier concentration n (positive n corresponds to electrons; negative to holes). b, Examples of fan diagrames used in the analysis to find B_F. Taken from Ref. [3]

calculation and the experiments lead to a linear band dispersion $E = v_F k$ with the same Fermi velocity $v_F = 10^6 m/s$. Therefore, we can demonstrate the exist of Dirac Fermions in graphene.

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science **306**, 5696 (2004).
[2] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov and A.K. Geim, PNAS **102**, 10451-10453 (2005).
[3] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos and A.A. Firsov, Nature **438**, 197-200 (2005).
[4] P.R. Wallace, Physical Review **71**, 622-634 (1947).
[5] A.K. Geim and K.S. Novoselov, Nature Materials **6**, 183-191 (2007) .
[6] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov and A.K. Geim, Rev. Mod. Phys **81**, 109-162 (2009).
[7] A. Fasolino, J.H. Los and M.I. Katsnelson, Nature Materials **6**, 858-861 (2007).
[8] M.I. Katsnelson, K.S. Novoselov, Solid State Communications **143**, 3-13 (2007).
[9] W. Andreoni, The Physics of Fullerene-Based and Fullerene-Related Materials (Springer, Berlin).
[10] R. Saito, G. Dresselhaus and M.S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, London)
[11] Ashcroft and Mermin, Solid State Physics, (Thomson Learning, 1976) 257003 (2008).
[12] notes from Dr. Dagotto's class: Solid State Physics II.