Electronic Properties of Two-Dimensional Carbon

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We present a theoretical description of the electronic properties of graphene in the presence of disorder, electron-electron interactions, and particle-hole symmetry breaking. We show that while particle-hole asymmetry, long-range Coulomb interactions, and extended defects lead to the phenomenon of self-doping, local defects determine the transport and spectroscopic properties. Our results explain recent experiments in graphitic devices and predict new electronic behavior.

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Carbon with sp^2 bonding has many allotropic forms with different dimensionality: three-dimensional graphite [1], one-dimensional nanotubes [2], zero-dimensional fullerenes [3], and two-dimensional Carbon, also known as graphene. Graphene can be considered the *materia* prima for the other forms of Carbon that can be obtained from it either by stacking (graphite), wrapping (nanotubes), or creation of topological defects (fullerenes). Hence, the electronic response of many Carbon based systems depends fundamentally on the basic physics of graphene. Recent experiments in graphene-based devices have shown that it is possible to control their electrical properties, such as carrier type (particle or hole), by the application of external gate voltage [4, 5]. These experiments not only have opened doors to carbon-based nanoelectronics but also pose new questions on the nature of the electronic properties in these systems.

Being two-dimensional, true long range positional order of the Carbon atoms is not possible at any finite temperature, since thermal fluctuations introduce topological lattice defects such as dislocations (the Hohenberg-Mermim-Wagner theorem). Furthermore, because of the particular structure of the honeycomb lattice, the dynamics of lattice defects in graphene belongs to the generic class of kinetically constrained models [6, 7], where defects are never completely annealed since their number is only weakly dependent on the annealing time [6]. Indeed, defects are ubiquitous in carbon allotropes with sp^2 coordination, as confirmed by recent experiments [8]. Furthermore, lattice defects induced by proton bombardment have been correlated to the appearance of magnetism in graphitic samples [9], indicating the interplay between electron-electron interactions and disorder.

Besides dislocations, graphene can sustain other types of extended defects such as disclinations, edges, and micro-cracks. It is known that certain edges (such as the zig-zag edge) lead to the appearance of localized states at the Fermi level [10, 11]. Other defects such as pentagons and heptagons (lattice disclinations) also admit localized states [12]. Furthermore, tight-binding calculations show that a combination of a five-fold and seven-fold ring (a lattice dislocation) or a Stone-Wales defect (made up of two pentagons and two heptagons) also lead to a finite density of states at the Fermi level[13, 14, 15]. The presence of states at the Fermi level generated by defects can be tracked down to the particular electronic structure of graphene. Each π -orbital contributes with one electron (a half-filled band) and the low-energy physics is described by a two-dimensional Dirac equation with a vanishing electronic density of states at the Fermi level. The vanishing of the density of states has two very important consequences: the enhancement of the electron-electron interactions because of the absence of electronic screening, and the formation of defect states at the Fermi level. In this respect, our work complements the extensive literature on defects on electronic systems described by the two dimensional Dirac equation[16].

In the present work, we show that unscreened Coulomb interactions, particle-hole symmetry breaking and defects play a fundamental role in the electronic properties of graphene. In particular, graphene presents the phenomenon of *self-doping*, that is, charge transfer between extended defects and the bulk. In this case, depending on particle-hole symmetry breaking, graphene samples can either have electron or hole pockets. While selfdoping derives from extended defects and controls the number and type of charge carriers, transport properties also depend on point-like defects such as vacancies, and surface ad-atoms. As we show in what follows, magnetotransport properties, such as Shubnikov-de Hass oscillations and quantum Hall effect (QHE), as well as spectroscopic quantities, such as quasiparticle lifetimes and infrared reflectivity, can be completely explained within this framework. Besides explaining published experimental data, we also make new experimental predictions that can be used as tests of our theory.

The bulk Hamiltonian of graphene can be written as: $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_V + \mathcal{H}_U$, where,

$$\mathcal{H}_{0} = -t \sum_{\sigma;\langle i,j \rangle} c^{\dagger}_{i,\sigma} c_{j,\sigma} + t' \sum_{\sigma;\langle\langle i,j \rangle\rangle} c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c.$$
(1)

where $c_{i,\sigma}$ $(c_{i,\sigma}^{\dagger})$ annihilates (creates) electrons at the site \mathbf{R}_i with spin σ $(\sigma = \uparrow, \downarrow)$, t and t' are the near-

est neighbor and next-nearest neighbor hopping energies, respectively. For $\mathbf{k} \to 0$ the electronic dispersion is $\epsilon_{\mathbf{k}} \approx 3t' + v_{\mathrm{F}}|\mathbf{k}| + (9t'a^2|\mathbf{k}|^2)/4$. Notice that t' does not change the structure of the extended electronic wavefunctions, that remain described by the two-dimensional Dirac equation with a Fermi-Dirac velocity $v_{\mathrm{F}} = (3ta)/2$ (a is the lattice spacing). \mathcal{H}_V describes the disorder,

$$\mathcal{H}_V = \sum_j V_j n_j \,, \tag{2}$$

where V_j is the potential strength (for vacancies, $V_j \rightarrow \infty$ at the vacant site and is zero, otherwise), and $n_j = \sum_{\sigma} c_{j,\sigma}^{\dagger} c_{j,\sigma}$. The electron interactions read,

$$\mathcal{H}_U = (e^2/\epsilon_0) \sum_{i,j \ (i \neq j)} n_i n_j / |\mathbf{R}_i - \mathbf{R}_j|, \qquad (3)$$

e is the electric charge, and ϵ_0 is the dielectric constant.

Standard derivations of localized states near defects assume electron-hole symmetry, that is, t' = 0. In this case, the localized states lie exactly at the Fermi level. In order to ensure charge neutrality, these states are half filled, and there is no charge transfer between extended and localized states. Electron-hole symmetry is broken by terms in the Hamiltonian that allow for hopping between sites in the same sublattice, that is, when $t' \neq 0$. In this case the band of localized states near an extended defect acquires a bandwidth of order t' and is shifted from Fermi energy. Using (1) and (3), we have studied in the Hartree approximation the induced charge transfer between the edge and the bulk in a long graphene ribbon of width W. In Fig.[1] we present the results for the induced electrostatic potential, charge density, and charge transferred from a zigzag edge to (delocalized) bulk states. We have studied zig-zag edges as long as 0.1μ m in graphene ribbons with up to 10^5 atoms. As one can clearly see in Fig.[1], selfdoping effects are suppressed as the width of the edge increases. The Coulomb energy at the edge induced by a constant doping δ per Carbon atom is approximately $\sim (\delta e^2/a)(W/a)$. The charge transfer is arrested when the potential shifts the band of localized states to the Fermi energy, that is, when $t' \approx (e^2/a)(W/a)\delta$. Hence the self-doping is $\delta \sim (t'a^2)/(e^2W)$. The numerical results are consistent with this estimate. Note that the sign of the induced charge depends on the sign of t'. The extended defects lead to a scattering rate, $\tau_{\text{elastic}}^{-1} \sim v_{\text{F}}/W$. The pocket induced by the self-doping has a Fermi energy of $\epsilon_{\rm F} \sim (\hbar v_{\rm F} \sqrt{\delta})/a \sim t \sqrt{(t'a^2)/(e^2W)}$ and thus, $\hbar \tau_{\rm elastic}^{-1} \ll \epsilon_{\rm F}$ in wide ribbons. Hence, disorder due to extended defects does not smooth out the details of the small Fermi surface induced by the self-doping. For $t = 2.7 \text{ eV} [1], t' = 0.2t \approx 0.54 \text{ eV}$ (see below), and a = 1.42Å, we get $\delta \sim 10^{-5} - 10^{-4}$ per Carbon atom in a system with domains of typical dimensions $W \sim 0.1 - 1 \ \mu$ m, consistent with experiments [4].



FIG. 1: Top: Electrostatic potential (dashed line) and electronic charge (continuous line) as a function of position along a long graphene ribbon terminating on a zig-zag edge. Energies are given in units t, and distances in units of a. We have used t' = 0.2t, and $e^2/(\epsilon_0 ta) = 0.5$. The inset shows the details of the electronic density near the edge. Bottom: Total additional charge per C atom in extended states as function of the ribbon width, W.

We can use the ribbon geometry described above to analyze the properties of graphene in the integer QHE. A magnetic field B changes the phases of the hopping terms in the Hamiltonian (1), leading to the appearance of bands of degenerate Landau levels. In the continuum limit the Landau levels have energy $\epsilon_n = \pm v_{\rm F} l_{\rm B}^{-1} \sqrt{n}$, where n is a positive integer, $l_{\rm B} = \sqrt{\Phi_0/B}$ is the cyclotron radius, and $\Phi_0 = h/e$ is flux quanta. The Hall conductance can be obtained from the number of bulk states that cross the Fermi level due to the presence of an edge [17]. The calculated energy levels of a graphene ribbon in a magnetic field are shown in Fig. [2]. Notice that the momentum along the ribbon fixes the position of the levels. When the position approaches the edges, the positive energy levels rise in energy as for electron-like Landau levels in the 2D electron gas, while the negative energy levels behave in a hole-like fashion. There is a zero energy mode that splits into a set of electron and hole-like levels. Finally, the localized states at the edges are quite insensitive to the applied magnetic field. If we fix the chemical potential above (below) the zero mode energy, all bulk electron-like (hole-like) levels of lower energy give rise to crossings, and contribute to the Hall conductance. Each Landau level is doubly degenerated since the honeycomb lattice gives rise to two inequivalent sets of Dirac fermions [18]. Hence, the Hall conductance arising from the bulk modes is:

$$\sigma_{\text{Hall}} = 2(2N+1)e^2/h$$
, (4)

and thus the Hall conductivity is quantized in odd number of $2e^2/h$ (the factor of 2 comes from the spin degeneracy since cyclotron energy, $\hbar\omega_c = \sqrt{2}v_{\rm F}\hbar/l_{\rm B}$, is much larger than the Zeeman energy, $g\mu_B B$, where $g \approx 2$ and μ_B the Bohr magneton). This analysis neglects corrections due to the additional band of localized states at the edges induced by the structure of the ribbon.



FIG. 2: Energy levels of a graphene ribbon of width 600 *a* with zig-zag edges as function of the momentum parallel to the edges. Energy in units of *t*, and t' = 0.2t. Momentum in units of $1/(2\sqrt{3}a)$. Top: zero magnetic field; Centre: a magnetic flux per C atom of $\Phi = 0.00025 \Phi_0$; Bottom: $\Phi = 0.0005 \Phi_0$.



FIG. 3: (a): Density of states as function of vacancy concentration (*D* is a high energy cut-off); (b): As in (a), in the presence of an applied field. Dashed lines mark the positions of the Landau levels in the absence of disorder; (c) and (d): $\sigma(\mu)$ as function of the Fermi energy μ . t' = 0 in all cases.

While extended defects induce self-doping they do not change significantly the electronic properties. However, point defects such as vacancies or ad-atoms can change the transport properties even if they do not lead to selfdoping. It is known that weaker types of disorder do not change the semi-metallic nature of a system described by the Dirac equation [16]. Nevertheless, point defects in the unitary limit can lead to a sharp resonance at the Fermi energy [16]. We describe the effect of vacancies in the transport properties using the Coherent Phase Approximation (CPA), that gives a good description of the spectral and transport properties of graphene, except perhaps within a small region near Fermi energy where electronic localization becomes important [20]. Within CPA, the one-particle spectral function is written as:

$$A(\mathbf{k},\omega) = \operatorname{Im} \left[\omega - \Sigma_{CPA}(\omega) - \epsilon_{\mathbf{k}}\right]^{-1}$$
(5)

where electron self-energy, $\Sigma_{CPA}(\omega)$, has to be determined self-consistently from (1) and (2). The electronic density of states, $\rho(\omega) = \sum_{\mathbf{k}} A(\mathbf{k}, \omega)$, as function of applied magnetic field and impurity concentration, in the continuum limit, is shown in Fig.[3](a)-(b). Unlike for weaker forms of disorder, vacancies induce a finite density of states at the Fermi level. Furthermore, $\text{Im}\Sigma_{\text{CPA}}(\omega)$ is finite at the Fermi level, and is monotonically *increasing* as $\omega \to 0$ indicating that vacancies have a strong effect on the Dirac fermions. This function can be considered an intrinsic linewidth as measured in ARPES. Besides the effect of disorder, the lifetime of quasiparticles has also an intrinsic contribution from interaction effects associated with eq. (3) giving a contribution $e^2/v_{\rm F} |\omega|[19]$, which is monotonically decreasing as $\omega \to 0$. Therefore, the final result, as shown in Fig.[4], predicts that that the total linewidth of quasiparticles shows a minimum.



FIG. 4: $|\Sigma''(\omega)|$, as a function of energy ω . Inset: $A(\mathbf{k}, \omega)$.

The frequency dependent conductivity can be written as:

$$\sigma(\omega, T) = 2e^2/(\hbar\pi) \int_{-\infty}^{\infty} d\epsilon K(\epsilon, \omega) [f(\epsilon, T) - f(\epsilon + \omega, T)]/\omega$$
(6)

where $K(\epsilon, \omega)$ is a conductivity kernel, and $f(\epsilon, T)$ is the Fermi-Dirac distribution function. At low temperatures, the d.c. conductivity, $\sigma(\mu) = \sigma(\omega = 0, T)$, is approximately proportional to $K(\mu, \omega = 0)$, and can be experimentally measured by the application of a gate voltage, V, to a graphene plane (in the presence of a voltage Vthe chemical potential shifts from μ to $\mu + eV$). In Fig. [3] (c)-(d) we show $\sigma(\mu)$. A non-conventional μ dependence is found when compared to other 2D electronic systems, in agreement with experiments [4]. As the temperature rises, the d.c. conductivity is found to increase with temperature, as the thermally excited carriers contribute (as in the case of a narrow gap semiconductor) and is also in agreement with the experimental data [4]. When $\mu + eV = 0$ the low temperature conductance per plane has a universal value, independent of disorder and magnetic field [21], $\sigma_{\rm dc} = 4e^2/(\pi h)$. A similar universal behavior was predicted for d-wave superconductors [22]. Because of particle-hole symmetry breaking, $t' \neq 0$, we expect an asymmetry in the Shubnikov-de Haas oscillations as function of gate voltage. We can quantify this asymmetry by looking at Landau levels j^* and $-j^*-1$ with $j^* \gg 1$. It is possible to show [23] that:

$$|t'/t| \approx \sqrt{2}/12(j^*+3/2)^{-1}(j^*+1)^{-1/2}(\ell_{\rm B}/a).$$
 (7)

For $j^* \approx 6$ for B = 12 T ($\ell_{\rm B} = 52$ Å) [4], we find $|t'/t| \approx 0.2$, which is the value used in this work.

In Fig.[5] we show $\sigma(\omega)$ in the presence of impurities and finite magnetic field. The existence oscillations in the conductivity at low temperatures is clearly seen. An analysis of the transitions to the different peaks shows that those involving the j = 0 Landau level are suppressed and that the energy of the lowest Landau levels is significantly shifted by the disorder.



FIG. 5: $\sigma(\omega)$ for different magnetic fields and $n_i = 0.001$, using the parameters given in the text. The lower right graph shows a scaling of the curves as function of ω/\sqrt{B} .

We have analyzed the influence of lattice defects on the electronic properties of graphene. Our results show that: (i) Extended defects lead to the existence of localized states, or resonances, near the Fermi level of the pure system. In the absence of electron-hole symmetry, these states lead to self-doping, and to the existence of electron or hole Fermi pockets with $10^{-4} - 10^{-5}$ electrons per unit cell for domains of sizes $0.1 - 1\mu$ m. (*ii*) An integer QHE with a quantized Hall conductivity in odd values of $2e^2/h$. (*iii*) Point defects lead to a finite inverse scattering time in undoped graphene, which decreases with increasing energy. As the inelastic contribution rises linearly with temperature, a minimum in the lifetime observed in ARPES experiments is predicted. (*iv*) The d.c. conductivity in undoped graphene has a universal value at low doping and temperatures. In undoped samples, it rises with temperature, as the number of thermally activated carriers increases. (*v*) The optical conductivity in a magnetic field is modulated due to Landau levels.

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