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Conductivity of graphene with resonant adsorbates: beyond the nearest neighbor hopping model

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Abstract

Adsorbates on graphene can create resonances that lead to efficient electron scattering and strongly affect the electronic conductivity. Therefore, a proper description of these resonances is important to gain a good insight into their effect on conductivity. The characteristics of the resonance and in particular its *T*-matrix depend on the adsorbate itself but also on the electronic structure of graphene. Here we show that a proper tight-binding model of graphene which includes hopping beyond the nearest-neighbor leads to sizable modifications of the scattering properties with respect to the mostly used nearest neighbor hopping model. We compare results obtained with hopping beyond the nearest-neighbor to those of our recent work (2013 *Phys. Rev. Lett.* **113** 146601). We conclude that the universal properties discussed in our recent work are unchanged but that a detailed comparison with experiments requires a sufficiently precise tight-binding model of the graphene layer.

Keywords: graphene, adsorbate, conductivity, Anderson localization, quantum transport calculation

Classification numbers: 3.00, 3.02, 5.15

1. Introduction

Electronic transport in graphene is sensitive in particular to local defects such as vacancies or adsorbates [1-5]. These defects are interesting in the context of functionalization which aims at controlling the electronic properties by attaching groups of atoms to graphene [6-13]. Therefore, a theoretical understanding of conductivity in the presence of such defects is needed. So far, the case of resonant local defects has attracted much attention because these defects strongly scatter electrons and therefore profoundly affect the electronic transport properties. Yet most of the studies are done in the standard nearest neighbor hopping model of graphene. In particular, in a recent work [12] we detailed some universal regimes of transport close to the Dirac point. The aim of the present study is to analyze the effect of

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. hopping beyond nearest neighbors in the graphene plane. As we show, the universal regimes presented in the previous work [12] still exist but their domain of existence in terms of electron concentration for example is affected, which may be important for precise comparison with experiments.

2. Modelization

We have developed a simple tight-binding (TB) scheme that reproduces *ab initio* electronic structure in the energy range $\pm 2 \text{ eV}$ around the Dirac energy E_D [14, 15]. Only p_z orbitals are taken into account since we are interested in electronic properties at the Fermi energy E_F . The Hamiltonian is

$$\hat{H} = \sum_{\langle i;j \rangle} t_{ij} \left(c_i^* c_j + c_j^* c_i \right), \tag{1}$$

where the coupling element matrix t_{ij} depends on the distance r_{ij} between orbital *i* and orbital *j*,

$$t_{ij} = -\gamma_0 \exp\left(q\left(1 - \frac{r_{ij}}{a}\right)\right) \tag{2}$$



Figure 1. Density of states (DOS) n versus energy E, for concentration c of resonant adsorbates (vacancies): (dashed line) first neighbor coupling only, (solid line) beyond first neighbor coupling.

with the first neighbor distance, a = 0.142 nm, and the first neighbors interaction in a graphene plane, $\gamma_0 = 2.7$ eV. The constant q is fixed to have a second neighbors interaction equal to $0.1\gamma_0$ [10, 13]. We consider that resonant adsobates (such as H, OH, CH₃, etc) can create a covalent bond with some carbon atoms of the graphene sheet. Then a generic model is obtained by removing the p_z orbital of the carbon that is just below the adsorbate [6, 13].

In our calculations resonant adsorbates (mono-vacancies) are distributed at random with a finite concentration *c*. Preliminary results of quantum diffusion for these models have been published in [10]. The conductivity is computed by the Mayou–Khanna–Roche–Triozon (MKRT) method [16–19]. This method allows very efficient numerical calculations by recursion in real-space. Our calculations are performed on a sample containing up to 10^8 atoms. That corresponds to typical size of about $1 \,\mu \text{m}^2$ which allows studying systems with inelastic mean-free length of the order of a few hundreds of nanometers. MKRT method has also been used to study other kinds of defects in graphene sheet [9, 11, 20, 21].

In the relaxation time approximation, we introduce an inelastic scattering time τ_i beyond which the propagation becomes diffusive due to the destruction of coherence by inelastic process (see [12] and references therein). One finally gets the conductivity

$$\sigma(E_F, \tau_i) = e^2 n(E_F) D(E_F, \tau_i)$$
(3)

and the diffusivity

$$D(E_{\rm F},\tau_{\rm i}) = \frac{L_{\rm i}^2(E_{\rm F},\tau_{\rm i})}{2\tau_{\rm i}},\qquad(4)$$

where *n* is the density of states (DOS) and L_i is the inelastic mean-free path. $L_i(E, \tau_i)$ is the typical distance of propagation during the time interval τ_i for electrons at energy *E*.

3. Results and discussion

The total density of states (DOS) for concentrations c = 1, 2 and 3% is shown in figure 1. With only first neighboring



Figure 2. Conductivity σ (solid line) and inelastic scattering length L_i (dashed line) versus inelastic scattering time τ_i for concentration c = 2% of resonant adsorbates (vacancies), for three energy values and with coupling beyond first neighbor. $G_0 = 2e^2/h$.



Figure 3. Microscopic conductivity σ_M versus energy *E* for concentration c = 1, 2 and 3% with same symbols than figure 1: (dashed line) first neighbor coupling only, (solid line) beyond first neighbor coupling. $G_0 = 2e^2/h$.

coupling a resonance of the DOS is found at the Dirac energy (E = 0). This is reminiscent of the midgap state produced by just one missing orbital [6, 13]. With coupling beyond nearest neighbors, the resonance of the density of states is enlarged and displaced by the effect of the hopping beyond nearest neighbors [13, 10]. This changes of course the relation between the density of states, the electronic mean-free path L_e and the Fermi energy or the filling factor (electron density) of the band.

The conductivity σ and the inelastic scattering length L_i are shown in figure 2. At short times the propagation is ballistic and the conductivity increases when τ_i increases. For large τ_i , the conductivity decreases with increasing τ_i due to quantum interference effects, and it goes to zero due to Anderson localization in two-dimension (2D) [22]. We defined the microscopic conductivity σ_M as the maximum value of $\sigma(\tau_i)$ values (figure 2). The microscopic conductivity is shown in figure 3 for different values concentration *c*. According to the renormalization theory [22] this value is obtained when the inelastic mean free path L_i and the elastic mean free path L_e are comparable. Here we compute L_e by

$$L_{\rm e}(E) = \frac{2D_{\rm M}(E)}{V},\tag{5}$$



Figure 4. Elastic mean free path $L_e(E)$, versus energy E, for concentration c: (dashed line) first neighbor coupling only, (solid line) beyond first neighbor coupling.



Figure 5. Conductivity $\sigma(L_i)$ versus the inelastic scattering length L_i for concentration c (%) and different energies E (eV) in the plateau of σ_M (E): (dashed line) first neighbor coupling only, (solid line) beyond first neighbor coupling. $G_0 = 2e^2/h$.

where $D_{\rm M}(E)$ is the maximum value of the diffusivity and *V* is the velocity of electrons at energy *E*. $L_{\rm e}$ versus *E* is shown figure 4. Finally we define the localization length ξ as the value for which the extrapolated conductivity (see below) cancels, i.e. $\sigma(L_{\rm i} \simeq \xi) = 0$ (figure 5).

For Fermi energy $E_{\rm F}$ very close to the Dirac energy $E_{\rm D}$ a strong fine peak in the microscopic conductivity is found for the model with nearest-neighbor coupling only (inset of figure 3) [11, 12, 23]. This particular behavior, which is a consequence of the resonance in the DOS, is specific to this model and it is not found when hopping beyond nearest neighbors is included. Indeed in the last case, the microscopic conductivity is slightly higher but still close to the universal plateau [9-12, 20, 21] of microscopic conductivity (figure 3), $\sigma_{\rm M} \simeq 4e^2/(\pi h)$. Thus, our results with hopping beyond nearest neighbors show that the plateau of the microscopic conductivity near the Dirac energy is robust. In contrast, the high central peak of the conductivity and the anomalous behavior at the Dirac energy (see [12]) are not robust and are specific to the model with nearest neighbor hoping only.

For $L_{\rm e} < L_{\rm i} < \xi$, the conductivity is not equal to the microscopic conductivity and quantum interference have to

be taken into account. As shown in figure 5, $\sigma(L_i)$ follows the linear variation with the logarithm of the inelastic mean free path L_i that was found in our previous work for smaller concentration of adsorbates [12]

$$\sigma(L_{\rm i}) = G_0 \left(2 - \alpha \log \left(L_{\rm i}/L_{\rm e}\right)\right) \text{ with } G_0 = 2e^2/h \quad (6)$$

and $\alpha \simeq 0.25$, which is close to the result of the perturbation theory of 2D Anderson localization for which $\alpha = 1/\pi$ [22]. As discussed in [12, 24] this could be tested through magneto-conductance measurements.

4. Conclusion

We propose a unified description of transport in graphene with resonant adsorbates simulated by simple vacancies [12]. Sufficiently far from the Dirac energy and at sufficiently small concentration of adsorbates, the semi-classical theory is a good approximation. For Fermi energy $E_{\rm F}$ close to the Dirac energy $E_{\rm D}$ different quantum regimes are found.

Some universal aspects of the conductivity are present with or without the hoping beyond nearest neighbors. For small inelastic scattering length L_i such as $L_i \simeq L_e$, the conductivity σ is almost equal to the universal minimum (plateau) of microscopic conductivity $\sigma_{\rm M} \simeq 4e^2/(\pi h)$, except for $E_{\rm F} \simeq E_{\rm D}$ when the model only takes into account nearest neighbor hopping. For larger L_i , $L_e < L_i$, the conductivity follows a linear variation with the logarithm of L_i [12] for both models, with nearest neighbor hopping only and with hopping beyond nearest neighbors. In contrast, the high central peak of the conductivity and the anomalous behavior at the Dirac energy (see [12]) are not robust and are specific to the model with nearest neighbor hoping only. Therefore, we conclude that a precise comparison of conductivity with experiments requires a detailed description of the electronic structure and in particular of that of graphene [25].

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References

- Berger C et al 2004 J. Phys. Chem. B 108 19912
 Berger C et al 2006 Science 312 1191
- [2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197
- [3] Zhang Y, Tan Y W, Stormer H L and Kim P 2005 Nature 438 201
- [4] Wu X, Li X, Song Z, Berger C and de Heer W A 2007 Phys. Rev. Lett. 98 136801
 - Wu X, Sprinkle M, Li X, Ming F, Berger C and de Heer W A 2008 *Phys. Rev. Lett.* **101** 026801
- [5] Nakaharai S, Iijima T, Ogawa S, Suzuki S, Li S L, Tsukagoshi K, Sato S and Yokoyama N 2013 ACS Nano 7 5694
- [6] Peres N M R, Guinea F and Castro Neto A H 2006 Phys. Rev. B 73 125411

- [7] Bostwick A, McChesney J L, Emtsev K V, Seyller T, Horn K, Kevan S D and Rotenberg E 2009 *Phys. Rev. Lett.* 103 056404
- [8] Chen J H, Cullen W G, Jang C, Fuhrer M S and Williams E D 2009 Phys. Rev. Lett. 102 236805
- [9] Leconte N, Moser J, Ordejon P, Tao H, Lherbier A, Bachtold A, Alsina F, Sotomayor Torres C M, Charlier J C and Roche S 2010 ACS Nano 4 4033
- [10] Trambly de Laissardière G and Mayou D 2011 Mod. Phys. Lett. B 25 1019
- [11] Cresti A, Ortmann F, Louvet T, Van Tuan D and Roche S 2013 Phys. Rev. Lett. 110 196601
- [12] Trambly de Laissardière G and Mayou D 2013 Phys. Rev. Lett. 111 146601
- [13] Pereira V M, Lopes dos Santos J M B and Castro Neto A H 2008 Phys. Rev. B 77 115109
- [14] Trambly de Laissardière G, Mayou D and Magaud L 2010 Nano Lett. 10 804
- [15] Trambly de Laissardière G, Mayou D and Magaud L 2012 Phys. Rev. B 86 125413

- G Trambly de Laissardière and D Mayou
- [16] Mayou D 1988 Europhys. Lett. 6 549
- [17] Mayou D and Khanna S N 1995 J. Phys. I Paris 5 1199
- [18] Roche S and Mayou D 1997 *Phys. Rev. Lett.* **79** 2518
 Roche S and Mayou D 1999 *Phys. Rev.* B **60** 322
- [19] Triozon F, Vidal J, Mosseri R and Mayou D 2002 Phys. Rev. B 65 220202
- [20] Lherbier A, Blase X, Niquet Y M, Triozon F and Roche S 2008 Phys. Rev. Lett. 101 036808
 Lherbier A, Dubois S M M, Declerck X, Roche S, Niquet Y M
- and Charlier J C 2011 *Phys. Rev. Lett.* **106** 046803 [21] Leconte N, Soriano D, Roche S, Ordejon P, Charlier J C and
- Palacios J J 2011 ACS Nano 5 3987
- [22] Lee P A and Ramakrishnan T V 1985 *Rev. Mod. Phys.* **57** 287
- [23] Ostrovsky P M, Titov M, Bera S, Gornyi I V and Mirlin A D 2010 Phys. Rev. Lett. 105 266803
- [24] McCann E, Kechedzhi K, Fal'ko V I, Suzuura H, Ando T and Altshuler B L 2006 Phys. Rev. Lett. 97 146805
- [25] Ducastelle F 2013 Phys. Rev. B 88 075413