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Fermi velocity renormalization in doped graphene

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We present an *ab initio* study of the graphene quasi-particle band structure within *GW* approximation. In particular we studied the renormalization of the Fermi velocity v_F as function of the electrostatic doping. We show that within local density approximation (LDA) the Fermi velocity is substantially renormalized by correlation effects and that this renormalization rapidly decreases with doping. We discuss our results in the light of recent experiments on graphene and intercalate graphite.

1 Introduction Since its discovery [1–3] graphene raised a great interest in the scientific community for the possibility to use it as new material with tunable properties [4] in electronic devices and to probe open quantum mechanics questions. Electron–electron interaction in graphene, and related compounds, is expected to play an important role due to its low dimensionality. Lately the quasi-particle dynamics of graphene, graphite, and its intercalate compounds have been addressed by high-resolution angle resolved photoemission spectroscopy (ARPES) [5–7] experiments. It has been found that conical bands are distorted due to many-body interactions, which renormalize the Fermi velocity. The self-energy corrections to the bare band structure are crucial to determine transport, optics, Raman spectroscopy, [8] and other properties of graphene-based materials.

Moreover, recent experiments on doped graphene [9] report variation of the Fermi velocity and Fermi surface topology induced by doping. Minor changes are definitely due to the small variation of the lattice constant [10] with doping but mainly larger differences are expected to be due to correlation effects in doped graphene [11, 12]. In this paper, we study the quasi-particle band structure of extrinsic graphene (doped graphene) as function of the doping, gated or electrostatic. Correlation effects are evaluated using *ab initio* many-body self-energy calculated in *GW* approximation, where the polarization needed to evaluate W is calculated within the random phase approximation (RPA). The validity of the RPA in the calculation of graphene self-energy has been recently questioned [13] but successively turned out to be a valid and controlled approximation in doped graphene for any sufficient small doping [11]. Therefore, in all our calculations we always introduce a Fermi distribution for the electrons even in the undoped case in order to guarantee the validity of our approximations and to be closer to the experimental results where a finite doping is always present, due to impurities or substrate interaction.

2 Methods In order to simulate isolated graphene we used a slab-geometry, i.e., bulk geometry with large distance between the layers, and an elementary 2D graphene cell with two atoms with a lattice constant $a = 2.46$ Å. All density functional theory (DFT) calculations were performed in local density approximation (LDA) with the plane wave-code ABINIT [14], using a cutoff of 60 Ry for the wave-function, a $60 \times 60 \times 1$ Monkhorst-Pack grid for the density and Troullier Martins pseudo-potentials [15] for the carbon atom. The quasi-particle band structure were successively obtained from the self-energy $\Sigma(E)$ evaluated in the *GW* approximation [16, 17]. *GW* calculations were performed with the code *Yambo* [18] starting from DFT–LDA wave-functions. Because we are not interested in the total energy but only in spectral properties, we did not perform a self-consistent calculation but we stop this approximation at the

first order $\Sigma = G_0 W_0$ [19]. The quasi-particle band structure is then obtained as:

$$E_{nk} = \varepsilon_{nk} + Z_{nk}\,\mathrm{Re}\,\Delta\Sigma_{nk}(\varepsilon_{nk}) \quad (1)$$

where $\Delta\Sigma = \Sigma - V^{xc}$, V^{xc} is the LDA exchange–correlation functional, ε_{nk} are the Kohn–Sham eigenvalues, and Z is the renormalization factor $Z_{nk} = [1 - \partial\,\mathrm{Re}\,\Delta\Sigma/\partial w]^{-1}$. The screened electron–electron interaction W have been calculated in RPA in term of the dielectric constants $\varepsilon_{G,G'}(q,\omega)$ using a plasmon-pole model [20]. Bands up to 60 eV in energy have been employed both for W and for the expansion of the Green Function G, that corresponds roughly to 60 bands in the case of 20 a.u. distance between the graphene sheets. A k-point grid $36 \times 36 \times 1$ has been employed for each calculation and convergence in the size of the dielectric function $\varepsilon_{G,G'}(q,\omega)$ has been carefully checked. In all the GW calculations a small Fermi–Dirac broadening 0.002 Ry was used.

3 Quasi-particle band structure of graphene In Fig. 1, we report the quasi-particle band structure of graphene for the π and π* bands along the symmetry lines Γ K M Γ in LDA and GW approximation. It is clear that the bandwidth is increased in GW and consequently the Fermi velocity v_F is renormalized.

Very close to K we found a nonlinear behavior of the π bands similar to the one obtained by Trevisanutto et al. [21] (see Fig. 2 panel b). Therefore, in order to estimate v_F we performed a linear fit of the bands just in the zone close to K where nonlinear effects disappear, the same procedure was used by Trevisanutto et al. (see Fig. 2 of Ref. [21]). In Table 1, we report the value of v_F at zero doping $12.5(5) \times 10^6$ m/s, to be compared with the LDA one $8.46(1) \times 10^6$ m/s, this result shows the strong renormalization effects at zero doping.

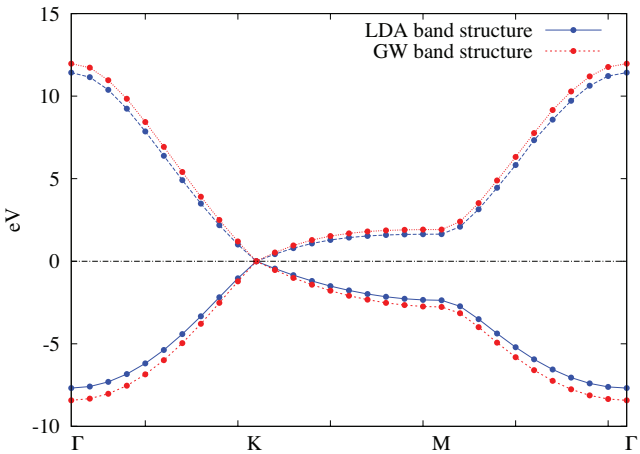

Figure 1 (online color at: www.pss-b.com) Band structure of graphene in LDA and GW approximation, using 20 a.u. slab geometry and $36 \times 36 \times 1$ k-points sampling.

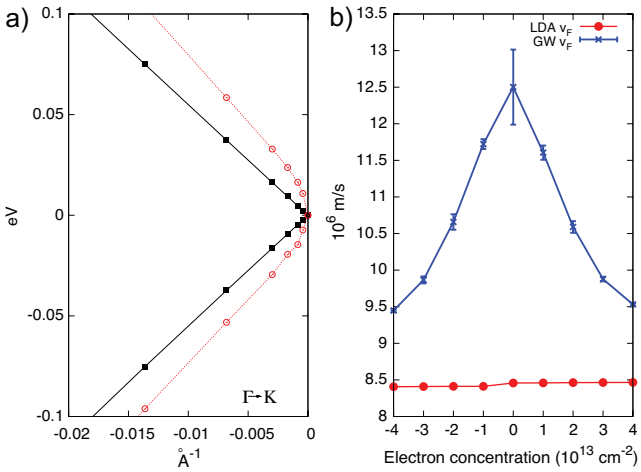

Figure 2 (online color at: www.pss-b.com) In panel a we report the quasi-particle band structure close to K for the undoped case, in panel b we report the Fermi velocity v_F as function of the doping.

4 The effect of doping Doped graphene is simulated changing the number of electrons in the unit cell and then compensating the negative charge with an uniform positive background. When we start doping graphene the system evolves from a semi-metal to a real metal, and the effective interaction felt by the electrons starts to be weaker because of the stronger screening. This causes a smaller renormalization of the band structure and a consequent decrease of the Fermi velocity. In Fig. 2, we report v_F *versus* the electrostatic doping. As one can see while in LDA v_F slightly changes with doping, while the situation is completely different in GW. In fact the strong renormalization, present at zero doping, rapidly decreases in a symmetric way for positive or negative doping. This effect can be qualitative understood in a transparent way using a massless Dirac-fermion (MDF) model with chiral quasi-particles, that is, a good description of graphene at low energies (Ref. [22]). This model can be studied at Hartree–Fock level, and one can expect that correlations play an essential quantitative but not qualitative role. For weakly doped graphene, following Refs.

Table 1 Fermi velocity of graphene as function of the electron concentration, the large error bar at zero doping is due to the nonlinear shape of the bands close to K.

charge (10^{13}/cm^2)	GW v_f (10^6 m/s)
−4.0	9.44(1)
−3.0	9.86(4)
−2.0	10.6(1)
−1.0	11.72(6)
0.0	12.5(5)
1.0	11.60(9)
2.0	10.59(7)
3.0	9.87(3)
4.0	9.53(1)

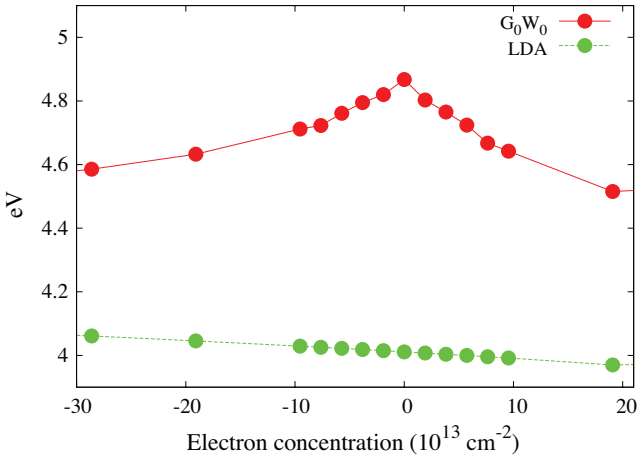

Figure 3 (online color at: www.pss-b.com) Band gap of graphene at the M point in *GW* and LDA as function of the doping.

[23, 24], the leading contribution to the velocity renormalization can be written as:

$$v \to v_0 \left[1 + \frac{f}{4g} \ln(\Lambda)\right] \tag{2}$$

where $\Lambda = k_c/k_F$ is the ratio between the ultraviolet cutoff $k_c \simeq 1/a$ with $a = 2.46$ Å and k_F and f is a dimensionless coupling constant $f = g/(\varepsilon v \hbar^2)$. For zero doping $\Lambda \to \infty$ one expects a logarithmic divergence of the Fermi velocity, however in our calculation we expect that Λ will behaves as $\Lambda = k_c/(k_F + c)$ where the constant c is due to the Fermi–Dirac broadening introduced in all calculations. We found that this behavior is well reproduced from our results (see Fig. 2, panel *a*). Moreover, to be more consistent we report also the gap at the M point for a broader doping range, where there are not error bars due to the fitting procedure (Fig. 3). Also in this case the behavior is the same of v_F one confirming that the qualitative change of v_F with doping is due to exchange effects. In order to highlight the logarithmic divergence of the Fermi velocity close to the K point we performed a calculation with the smallest broadening compatible with our *k*-point grid, and report the results in Fig. 2 panel *a*. As it is shown in this figure the logarithmic divergence is present only very close to the K point and just a bit beyond the bands recover the linear behavior. The presence of this divergence causes the large error bar in the determination of v_F in the undoped case (Fig. 2 panel *b*). Notice however that this divergence rapidly disappears with doping.

5 Conclusion We have studied the quasi-particle band structure of graphene as function of doping. The bands dispersion is obtained by the real part of the self-energy calculated in G_0W_0 approximation, that is, generally considered accurate for a broad range of materials, including graphene. We found a strong renormalization for intrinsic graphene, that rapidly decreases as function of doping. This result can be used as new reference for future experiments on doped graphene and intercalate graphite because it provides for the first time an estimation of the Fermi velocity change with doping. We report also the gap at M as function of doping, a quantity that can be easily compared with optics experiments on doped graphene where transition at M point are measured. Moreover, close the K we found that the bands are distorted and the Fermi velocity diverges for doping that goes to zero. This finding opens the possibility to a different interpretation of the experimental results on the gap opening in graphene [5, 25, 26], in fact even recent calculations by Kim et al. [27], predicted a gap opening at the Dirac point in epitaxial graphene on SiC, our result shows that the size of this gap could be underestimated in ARPES experiments due to nonlinear shape of the bands close to K. Hopefully new experiments on suspended graphene, Ref. [28], will be able to highlight the space of the π bands close to the Dirac point without the substrate effects.

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