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Pseudo-gap opening and Dirac point confined states in doped graphene

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ABSTRACT

The appearance of a pseudo-gap and the build up of states around the Dirac point for doped graphene can be elucidated by an analysis of the density of states spectral moments. Such moments are calculated by using the Cyrot-Lackmann theorem, which highlights the importance of the network local topology. Using this approach, we sum over all disorder realizations up to a certain radius to show how the spectral moments change. As a result, the spectrum becomes unimodal, however, strictly localized states appears at the Dirac point. Such states are important for the magnetic properties of graphene, and are calculated as a function of the doping concentration. By removing these states in the count of the spectral moments, it is finally seen that the density of states increases its bimodal character and the tendency for a pseudo-gap opening. This result is important to understand the trends in the magnetic and electronic properties of doped graphene. In graphene with vacancies, the same ideas can also be useful to isolate in a rough way which effects are due solely to topology.

Graphene is currently a 'rising star' in condensed-matter physics [1]. Mainly, because it is the first truly two-dimensional crystal [2], and has a high electrical [3] and thermal conductivity [4]. These properties place graphene as an ideal candidate for a new electronic, based in carbon, to replace silicon. The problem is that graphene is not a semiconductor. However, it has been shown that graphene can present a change from metal to insulator when it is doped by adsorbed H [5], as was also predicted by using arguments on frustration due to the graphene's underlying triangular symmetry [6,7]. It is important to remark that such theoretical results, were performed under the supposition that hydrogen is bonded to graphene covalently with the $2p_z$ orbital, and very roughly, it confines the wave function spatially like a vacancy [8,9]. Although this approach may seems too simplistic, it has been useful to predict localization tendencies and the size of a pseudo-gap [6], in good agreement with experimental data [5]. More recent detailed calculations show that in fact, vacancies and impurities are different, both requiring a fine tuning of the tight-binding Hamiltonian [10,11], instead of using an infinite self-energy at impurity sites. For example, nitrogen and boron have a scattering potential with a extension larger than 10 shells of neighbors [10]. However, the exercise of considering impurity sites with infinite self-energy is interesting because it allows to understand which effects are due solely to the honeycomb lattice topology. For low concentration of impurities, this procedure leads to resonant states near the Dirac energy [12], E_D, which coincides with the Fermi energy for a zero bias potential. For higher concentrations, a region of localized and critical states appears [6,13]. Such critical states are believed to be multifractal [13]. Numerical simulations suggest that a pseudo-gap is open at the Dirac point [6]. On the other hand, in the middle of the pseudo-gap, states appears as the impurity concentration raises. Such states are important to understand the diamagnetic properties of graphene [14]. Some of these features are robust against the specific parameters of disorder since they only depend on general symmetry arguments [15]. So for example, more detailed calculations will shift the pseudo-gap or its size, but the basic mechanism is provided by topology [6,7]. More refined results can be obtained by performing a systematic series expansion for finite impurity self-energy. Here we present only the first and dominant term of such serie, others are corrections to it. Also, renormalization techniques can be used to treat local disorder in non-diagonal elements [6,13].

In the same spirit, here we show that the appearance of the pseudo-gap and the build up of states around E_D can be elucidated by an analysis of the spectral moments [16] which highlights the importance of the network local topology. Furthermore, this method allows to count the number of states at E_D as a function of the concentration, and explain them, above the percolation threshold, as strictly confined states in local clusters.

As a model, consider the graphene's honeycomb lattice with substitutional impurities placed at random with a uniform distribution. The corresponding tight-binding Hamiltonian for the electron in the π orbital is given by [17],

$$\mathcal{H} = -t\sum_{\langle \boldsymbol{i},\boldsymbol{j}\rangle} |\boldsymbol{i}\rangle\langle\boldsymbol{j}| + \varepsilon\sum_{\ell}|\ell\rangle\langle\ell|, \quad (1)$$

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where the first sum is over nearest neighbors, $t=2.79$ eV is the hopping energy [18], and the second is over every impurity sites with self-energy ε. The number of impurities sites, N_{imp}, is determined by the concentration $C=N_{\mathrm{imp}}/N$, where N is the total sites on the honeycomb lattice. It is well known that for pure graphene ($\varepsilon=0$), the density of states (DOS) is bimodal, i.e., the two Van Hove singularities dominate in the DOS. We will show that the bimodal behavior tends to increase when the concentration is increased, although one must be careful since states at the middle of the spectrum (at E_{D}) have a weight that needs to be removed first.

To prove this, we will consider here the moments of the DOS function $\rho(E)$. The spectral moments are defined as

$$\mu_{\boldsymbol{i}}^{(n)}=\int_{-\infty}^{\infty}(E-\mathcal{H}_{\boldsymbol{ii}})^{n}\rho_{\boldsymbol{i}}(E)\,dE. \tag{2}$$

These moments can be calculated by counting closed paths that start and return at the same lattice site $\boldsymbol{i}$, as was shown by Cyrot-Lackman [19],

$$\mu_{\boldsymbol{i}}^{(n)}=\langle\boldsymbol{i}|(\mathcal{H}-\mathcal{H}_{\boldsymbol{ii}})^{n}|\boldsymbol{i}\rangle, \tag{3}$$

since the right hand term of the equation corresponds to the number of paths with n steps that return to the original site $\boldsymbol{i}$.

There is a dimensionless parameter to measure the tendency of the local DOS (LDOS) to open a pseudo-gap at its center [19],

$$s_{\boldsymbol{i}}=\frac{\mu_{\boldsymbol{i}}^{(4)}\mu_{\boldsymbol{i}}^{(2)}-(\mu_{\boldsymbol{i}}^{(2)})^{3}-(\mu_{\boldsymbol{i}}^{(3)})^{2}}{(\mu_{\boldsymbol{i}}^{(2)})^{3}} \tag{4}$$

If $s_{\boldsymbol{i}}\geq 1$ the LDOS is unimodal; meanwhile, if $s_{\boldsymbol{i}}<1$ the LDOS is bimodal, and has a tendency for a pseudo-gap opening at the center [19].

Also, it is important to remark that here, no self-energy $\mathcal{H}_{\boldsymbol{ii}}$ was considered for carbon atoms in the unperturbed Hamiltonian. Thus, the zero energy has been chosen to coincide with the vertices of the Dirac cone at E_{D}. As a result, the spectrum is symmetric around $E=0$. The real spectrum can be readily obtained by an energy shifting, as usually done in all works concerning graphene.

Let us now consider first the case of pure graphene. The sites are undistinguished, i.e. DOS = LDOS, and therefore we can toggle off the site index $\boldsymbol{i}$ and calculate the moments. It is easy to see that

- $\mu^{(0)}=1$ due to the normalization condition.
- $\mu^{(1)}=0$.
- $\mu^{(2)}=3t^{2}$ and is proportional to the coordination of each site, Z=3 (Fig. 1).
- $\mu^{(3)}=0$, because the electron can not return to the original site with 3 steps. The same holds for any odd spectral moment. Thus, any bipartite lattice always has a symmetric spectrum, as for example, in the Penrose lattice (vertex model) [20].
- $\mu^{(4)}=15t^{4}$ after counting the four steps paths (Fig. 1), that revisit and not revisit the original site.

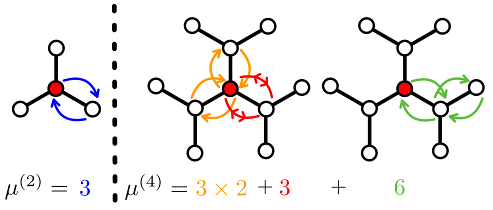

Fig. 1. (Color online) Sketch of the path counting for the honeycomb lattice. Left panel, a two step path that returns to the original site. Right panel, four step paths are divided in revisiting (red and orange), and no revisiting (green) to the original site. The red paths go from the origin to a neighboring site and come back and visit the same site neighbor. The orange paths go from the origin to a neighboring site, come back and visit another neighbor.

From the previous considerations, $s=2/3$ for pure graphene, and this value corresponds to a bimodal DOS.

If there is a concentration of impurities, C, the problem is much more difficult. However, here we are interested in impurities which take one electron from the π orbital leaving almost a hole. We will model this case assuming $t/\varepsilon\ll 1$. It is important to remark that more detailed calculations show that impurities or vacancies present a more complex behavior. For example, nitrogen and boron involve a significant modification of the diagonal elements of the matrix only, while a vacancy can be modeled [10] using $\varepsilon=10$ eV and $t_{\mathrm{IJ}}=1.9$ eV (compared with $t=2.7$ eV for pristine graphene). Here we will consider the case $t/\varepsilon\ll 1$. In spite of this, one can include in a natural way a smaller ε by performing a series expansion in powers of t/ε using the same techniques [21]. Thus, here we are computing the lowest order term of the serie. This case corresponds to the split band limit, and bands are suitable to be studied in a separate way [21]. The reason is that the wavefunctions of the graphene band do not have amplitude on impurities, while for the impurity band the opposite is true. This can be proved in general, and corrections are easy to find using a t/ε expansion of the wavefunction [21]. Here, we will restrict our calculations to the graphene band, using a restricted Hamitonian,

$$\mathcal{H}_{\mathbf{cc}}=-t\sum_{\langle\boldsymbol{i},\boldsymbol{j}\rangle\in\mathbf{cc}}|\boldsymbol{i}\rangle\langle\boldsymbol{j}|, \tag{5}$$

where the sum over $\boldsymbol{i}$ and $\boldsymbol{j}$ is carried only over carbon sites (indicated by the subindex **cc**), with DOS $\rho_{\mathbf{cc}}(E)$. A similar Hamiltonian can be written for the impurity band, $\mathcal{H}_{\mathbf{ib}}$ with DOS given by $\rho_{\mathbf{ib}}(E)$. The total DOS is $\rho(E)=\rho_{\mathbf{cc}}(E)+\rho_{\mathbf{ib}}(E)$. In what follows, we will consider only the DOS and spectral moments of $\mathcal{H}_{\mathbf{cc}}$, so for simplicity, we drop any subindex **cc**. The impurity band can be easily obtained from $\mathcal{H}_{\mathbf{cc}}$ by considering the behavior for concentrations $1-C$ and a shift of the spectrum by ε.

Now we define the moments averages over all disorder realizations, i.e., for all the possible combinations of impurities sites (ℓ) and carbon sites as

$$\langle\mu^{(n)}\rangle=\sum_{\boldsymbol{j}_{1},\ldots\boldsymbol{j}_{n-1}\neq\ell}P(\boldsymbol{i}\boldsymbol{j}_{1},\ldots\boldsymbol{j}_{n-1})\times\mathcal{H}_{\boldsymbol{i}\boldsymbol{j}_{1}}\mathcal{H}_{\boldsymbol{j}_{1}\boldsymbol{j}_{2}}\ldots\mathcal{H}_{\boldsymbol{j}_{n-1},\boldsymbol{i}} \tag{6}$$

where $P(\boldsymbol{i}\boldsymbol{j}_{1},\ldots\boldsymbol{j}_{n-1})$ is the probability of each path made only from carbon atoms.

In order to obtain $\langle s\rangle$, we need to calculate $\langle\mu^{(2)}\rangle$ and $\langle\mu^{(4)}\rangle$. Again $\langle\mu^{(3)}\rangle=0$ since the lattice defined on pure carbon sites is bipartite. Notice that this property only holds for $t/\varepsilon\ll 1$. Now we perform the calculation of the first moments by summing over all statistical realizations of disorder.

The second moment, $\langle\mu^{(2)}\rangle$, can be counted by noting that there are four possible configurations with impurities and non-impurities for nearest neighbors (Fig. 2). Following the diagram in the figure, it is easy to see that the statistical distribution of configurations is a binomial. It follows that the second moment is just the average coordination of the network ($\langle Z\rangle$), obtained from the binomial distribution:

$$\langle\mu^{(2)}\rangle=t^{2}\sum_{Z=0}^{3}\binom{3}{Z}C^{3-Z}(1-C)^{Z}Z=3t^{2}(1-C). \tag{7}$$

where Z denote the coordination of a site. This value gives an excellent approximation to the graphene band width.

For the fourth moment, we chose a Carbon site and again we divide our count on paths which revisit the original site and those which do not revisit. Fig. 3 shows schematically the possible