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# Internal mobility edge in doped graphene: Frustration in a renormalized lattice

Gerardo G. Naumis
*Departamento de Física-Química, Instituto de Física, Universidad Nacional Autónoma de México (UNAM),*
*Apartado Postal 20-364, 01000 México, Distrito Federal, Mexico*

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We show that a localization mobility edge can appear around the Fermi energy in graphene by introducing impurities or by producing vacancies in the lattice. The edge appears at the center of the spectrum and not at the band edges, in contrast with the usual picture of localization. Such result is explained by showing that the bipartite nature of the lattice allows one to renormalize the Hamiltonian, and this internal edge appears because of frustration effects in the renormalized lattice. The size in energy of the spectral region with localized states is similar in value to that observed in narrow gap semiconductors.

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Only very recently, a two dimensional form of carbon was obtained.[1] This material, known as graphene, has attracted a lot of research due to its amazing electrical and mechanical properties.[2–4] For example, electrons in graphene behave as massless relativistic fermions that satisfy the Dirac equation.[5] Such property is a consequence of the bipartite crystal structure,[6] in which a linear dispersion relationship appears at the center of the electronic spectrum. Also, one can cite the high mobility of its charge carriers that remains higher even at high electric-field-induced concentration, which translates into ballistic transport on a submicron scale[7] at 300 K. These and other unusual electronic properties of graphene make it a promising material for building electronic devices. However, from the point of view of applications, the use of pure graphene poses some problems. The transmission probability of electrons across a potential barrier is always unity, irrespective of the height and width of the barrier. This behavior is related to the Klein paradox in relativistic quantum mechanics.[2] As a result, conductivity cannot be changed by an external gate voltage, a feature required to build a field effect transistor, although a quantum dot has been used to perform the required task.[8] In a previous work, the density of states of graphene with Anderson type of disorder revealed that the linear dispersion relationship was affected,[9] and recently, many electrical properties of graphene with disorder have been obtained.[10–14] Here, we show that graphene doped with impurities or with vacancies presents a very unusual property; instead of having a localization mobility edge (defined as the energy at which the states change from extended to localized[15]) at the band limits as in the usual Anderson localization, the localized states appear at the center of the spectrum, around the Fermi energy. As we will show, this is a simple consequence of the bipartite crystal structure, which produces a frustration effect in a renormalized Hamiltonian that removes the bipartite symmetry.

Let us start by considering the tight-binding Hamiltonian of graphene with disorder, which can be written as $H=H_0+H_1$, where $H_0$ is the pure graphene Hamiltonian,[16]

$$H_0 = E_0\sum_{i} |i\rangle\langle i| + \gamma_0\sum_{\langle i,j\rangle} |i\rangle\langle j|. \tag{1}$$

$E_0$ is the on-site energy of carbon and $\gamma_0$ is the carbon-carbon resonance integral, as given in Ref. 16. $H_1$ is the Hamiltonian due to defects,

$$H_1 = \delta E\sum_{i} |i\rangle\langle i| + \delta\gamma_0\sum_{\langle i,j\rangle} |i\rangle\langle j|, \tag{2}$$

where we define $\delta E \equiv E_I - E_0$ and $\delta\gamma_0 \equiv \gamma_I - \gamma_0$. Here, $E_I$ is the on-site energy of the defects, and $\gamma_I$ the transfer integral between impurities. When $\delta E \gg E_0$, the spectrum is divided in two parts; one centered around $E_0$ and the other at $E_0+\delta E$. The states in the subband around the carbon on-site energy $E_0$, which we call the C band, are strongly confined on carbon atoms. Furthermore, in the limit $\delta E \gg E_0$, it has been shown that impurity atoms can be formally removed in a tight-binding Hamiltonian,[17] and thus, the C band can be studied by using a Hamiltonian restricted to C sites only,

$$H_{\mathrm{CC}} = E_0\sum_{i\in \mathrm{C}} |i\rangle\langle i| + \gamma_0\sum_{i,j\in \mathrm{C}} |i\rangle\langle j|. \tag{3}$$

This Hamiltonian describes an electron that can hop from one site to its neighbors only if both are carbon atoms (C). Furthermore, the problem for the C subband is similar to a lattice with vacancies[17] and, thus, the results presented here are also valid for such a case.

Now let us study the spectrum of $H_{\mathrm{CC}}$. We will work on a renormalized Hamiltonian which takes advantage of the bipartite nature of the C lattice, once the $I$ atoms are removed. The bipartite character means that it can be separated in two interpenetrating sublattices, $A$ and $B$. We define two orthogonal operators that project the wave functions into these sublattices,

$$P_A = \sum_{i\in A} |i\rangle\langle i| \quad \text{and } P_B = \sum_{j\in B} |j\rangle\langle j|. \tag{4}$$

To simplify the renormalization process, we shift the energy scale in such a way that $E_0$ corresponds to zero energy. Therefore, any eigenvector $|\phi\rangle$ of $H_{\mathrm{CC}}$ can be written in terms of these projectors,

$$H_{\mathrm{CC}}(P_A+P_B)|\phi\rangle = E(P_A+P_B)|\phi\rangle. \tag{5}$$

Since $H_{\mathrm{CC}}$ produces a hopping between the $A$ and $B$ sublattices, we have

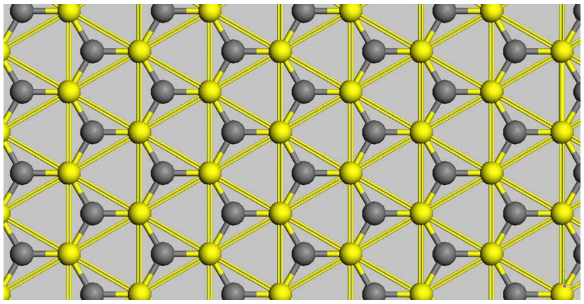

FIG. 1. (Color online) Renormalization of the graphene lattice. Atoms in the $A$ sublattice are shown with a different color than those in the $B$ sublattice. The new lattice that appears after renormalizing $B$ is represented with double bonds.

$$H_{\mathrm{CC}}P_A|\phi\rangle = EP_B|\phi\rangle \quad \text{and } H_{\mathrm{CC}}P_B|\phi\rangle = EP_A|\phi\rangle. \tag{6}$$

From these equations, one can see that the spectrum is symmetric around $E=0$ (which means symmetric around $E_0$, when $E_0$ is not set to zero), since if $(P_A+P_B)|\phi\rangle$ is an eigenvector with eigenvalue $E$, $(P_A-P_B)|\phi\rangle$ is also an eigenvector with eigenvalue $-E$. We can decouple the sublattices by further applying $H_{\mathrm{CC}}$ to Eqs. (6),

$$H_{\mathrm{CC}}(H_{\mathrm{CC}}(P_i|\phi\rangle)) = H_{\mathrm{CC}}^2(P_i|\phi\rangle) = E^2(P_i|\phi\rangle), \tag{7}$$

where $i=A,B$. Thus, the projection of an eigenvector in each sublattice is a solution of the squared Hamiltonian. Observe that the eigenvalues of $H_{\mathrm{CC}}^2$ are positive definite, and their eigenstates are, at least, doubly degenerate. This spectrum can be regarded as the folding of the original spectrum of $H_{\mathrm{CC}}$ around $E=0$, in such a way that the two band edges of $H_{\mathrm{CC}}$ are mapped into the highest eigenvalue of $H_{\mathrm{CC}}^2$, while the states at the center of the original band are now at the minimum eigenvalue of the squared Hamiltonian. The important property of the renormalized Hamiltonian $H_{\mathrm{CC}}^2$ is that the states at the bottom of the spectrum have an antibonding nature (the phase difference between neighbors is maximal), and we can expect that the frustration of the wave function can prevent the spectrum from reaching its minimum eigenvalue in a continuous form.[18,19] This leads to localization since the wave function tends to avoid regions of higher frustration. The mobility edge appears when the energy cost in localization is less than that of having amplitude in frustrated bonds. As we will show next, frustration augments with disorder. To do this, we observe that the Hamiltonian $H_{\mathrm{CC}}^2$ is equivalent to a renormalization of sites $B$ in the lattice, which leads to a triangular lattice with an effective interaction, as shown in Fig. 1. The new lattice contains odd rings, and when impurities are present, there are vacancies, as indicated in Fig. 1(b). The corresponding Schrödinger equation derived from $H_{\mathrm{CC}}^2$ after returning to the original energy scale, is

$$[(E-E_0)^2 - Z_i\gamma_0^2]c_i(E) = \gamma_0^2 \sum_{(j,i)\epsilon A} c_j(E), \tag{8}$$

where $c_i(E)$ is the amplitude of the wave function at site $i$ for an eigenenergy $E$. The notation $(j,i)\epsilon A$ means that the sum is taken only for C atoms which are first neighbors in the new triangular lattice, i.e., those atoms that were second neighbors in the original hexagonal lattice. Finally, $Z_i$ is the coordination number at site $i$. This number ranges from 0, when a C atom is surrounded by impurities, to 3 when it is surrounded by three C atoms. Then we perform a variational procedure to estimate the ground state of Eq. (8). After multiplying Eq. (8) by $c_i^*(E)$ and summing over $i$, we get

$$(E-E_0)^2 = \sum_i Z_i\gamma_0^2|c_i(E)|^2 + \gamma_0^2\sum_i \sum_{(j,i)\epsilon A} c_i^*(E)c_j(E), \tag{9}$$

The first contribution is an effective on-site energy, while the second depends on the number of bonds and on the amplitude and phase of the wave function. For example, in pure carbon, $Z_i=3$ and $c_j(E)=e^{i\phi_j}/\sqrt{N}$, where $\phi_j$ is a phase and $N$ the number of atoms. The minimal eigenvalue is obtained from Eq. (8) when the phase difference between sites is $2\pi/3$. Thus, the ground state has nearly an antibonding nature since for each bond we have $c_i^*(E)c_j(E)+c_j^*(E)c_i(E) = 2\cos(2\pi/3)/\sqrt{N} = -1/\sqrt{N}$. Then it follows that $E=E_0$. As a consequence, there is no gap for pure graphene, as expected. The graphene case reveals an interesting fact; the zero gap is due to the exact balance between the positive renormalized on-site energy $Z_i$ and the antibonding contribution.

Now consider the case of a finite concentration $x$ of impurities or vacancies. Since an impurity belongs to a given bipartite sublattice, there are two effects. The first is a reduction in the coordination number, and the second is that some bonds are deleted. The coordination effect can be estimated as follows. We write the first term of Eq. (9) as an average term plus a correlation of amplitude-coordination,

$$\sum_i Z_i\gamma_0^2|c_i(E)|^2 = \langle Z\rangle\gamma_0^2 + V\gamma_0^2\sum_i \delta Z_i \delta c_i^2(E), \tag{10}$$

where it was used that $Z_i$ can be written as an average $\langle Z\rangle$ plus a fluctuation part $\delta Z_i$. A similar procedure can be made for $|c_i(E)|^2 \equiv \langle c^2(E)\rangle + \delta c_i^2(E)$. The average $Z$ can be obtained by observing that around a given carbon atom, there are four possible configurations: it can be surrounded by one, two, and three impurities, or it can be completely surrounded by carbon atoms. For each configuration, there is a different coordination number $Z$, since impurities act as vacancies. As a result, $Z$ has a binomial probability distribution $P(Z)$

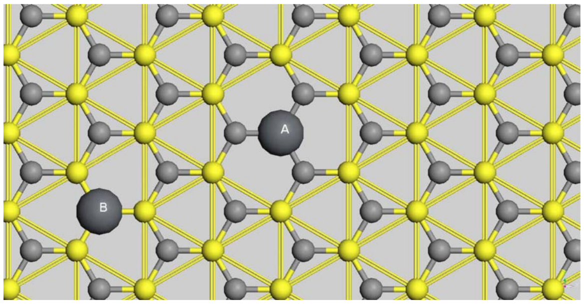

FIG. 2. (Color online) Renormalization of the lattice with defects. The impurities are shown with dark color. There are two cases: the impurities can fall in sublattice $A$ or in $B$, as indicated in the figure. In the first case, six bonds are deleted in the renormalized sublattice, while only three bonds disapear in the other case.

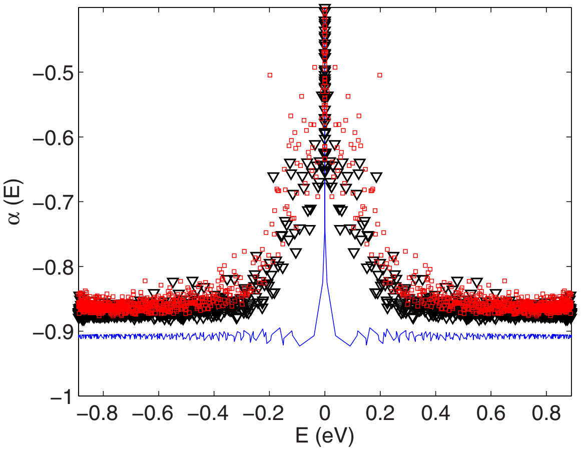

FIG. 3. (Color online) Logarithm of the inverse participation ratio as a function of the energy for pure graphene (line) compared with the doped cases with $x=0.01$ (triangles) and $x=0.02$ (squares) around the center of the spectrum of the carbon subband, for a lattice with 5184 sites. Observe the rise at the center of the spectrum for the doped case. A band of degenerate states is also observed for pure graphene. The zero corresponds to the Fermi energy.

$=C_Z^3 x^Z(1-x)^{3-Z}$, where $C_Z^3$ is a combinatorial factor. It follows that $\langle Z\rangle$ is the first moment of the binomial distribution: $\langle Z\rangle=\Sigma_{Z=0}^{Z=3}ZP(Z)=3(1-x)$. Notice that the contribution of the last term in Eq. (10) leads to the production of localized states, since it is the correlation between amplitude and on-site energy fluctuations. Thus, the system has a mobility edge when this term lowers the energy compared with the energy required for having an extended state with amplitude in frustrated bonds.

The other effect is the removal of bonds that changes the second term of Eq. (9). We can estimate this effect as follows. Impurities are isolated for low doping ($x \ll 1$), since the probability of having two impurities as neighbors goes as $x^2$. Then we will consider that impurities are isolated. Two situations are possible. Either an impurity belongs to the renormalized sublattice, or it can remain as shown in Fig. 2. For each impurity site that is renormalized, three bonds are lost. In the other case, six bonds are lost for each impurity. Since they are randomly distributed in sublattices $A$ and $B$, the concentration of impurities is $x$ on each sublattice. As a result, the number of missing bonds is $(6+3)xN$, from a previous total of $3N$. Using this count in Eq. (9), and assuming no on-site energy amplitude correlation in Eq. (10) for an antibonding trial state, we obtain the approximate position of the mobility edge ($E_d$),

$$(E_d-E_0)^2 \approx 3\gamma_0^2(1-x)-\gamma_0^2(3-9x)=6\gamma_0^2 x,$$

which leads to a symmetric mobility edge separated an energy $\Delta$ from the center of the band,

$$\Delta \approx \pm\sqrt{6x}\gamma_0. \quad (11)$$

As a check of these ideas, in Fig. 3, we present the normalized logarithm of the inverse participation ratio,

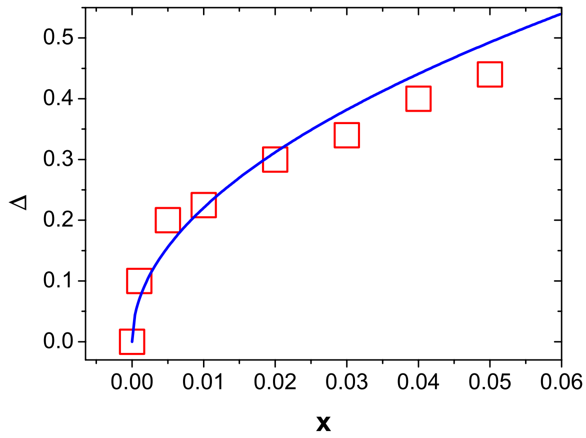

FIG. 4. (Color online) Theoretical value of the mobility edge predicted from Eq. (11), indicated with a solid line, and the value obtained from a direct diagonalization of the Hamiltonian (squares). The numerical results were obtained from an average of ten lattices with $N=5184$ sites

$$\alpha(E)=\frac{\log \mathrm{IP}(E)}{\log N}, \quad (12)$$

where IP($E$) is the inverse participation ratio, defined as $\mathrm{IP}(E)=\Sigma_{i=1}^N\|c_i(E)\|^4$, which is a well-known measure of localization. For extended states, $\alpha(E)\approx -1$, while it tends to be bigger values when localization is present. Figure 3 shows a comparison between a pure graphene case and the doped cases, for a tight-binding simulation using an average of ten lattices with $N=5184$ sites. It is worthwhile mentioning that few degenerated states appear in the center of pure graphene. They are a consequence of the local topology of the lattice,[20] as also happens in other lattices.[17,19] Figure 3 shows that the $\alpha(E)$ is, in general, bigger for the doped case, but at the center of the spectrum, there is a clear rise in its value, indicating a greater degree of localization. In Fig. 4, we compare Eq. (11) with the numerical value of $\Delta$ obtained from the localization plot, which shows good agreement with the predicted value.

The value of $\gamma_0$ is around[16] 0.9 eV or $\gamma_0=20$ kcal/mol. For 1% doping, the size of the whole localized region is around $2\Delta \approx 0.44$ eV. Since light is absorbed when the band-gap energy is in the limit of the visible spectrum 1.77 eV (700 nm), the localized region in doped graphene can be considered as similar in size to the energy gap in narrow-band-gap semiconductors.

In conclusion, we have shown that doped graphene presents a mobility edge at the center of the spectrum, and this can be useful for many devices since the position of the edge can be controlled by doping.

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