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# Power-law singularity in the local density of states due to the point defect in graphene

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Defects in graphene give rise to zero modes that are often related to the sharp peak in the local density of states near the defect site. Here we solved all zero modes induced by a single defect in the finite-size graphene and show that their contributions to the local density of states vanish in the thermodynamic limit. Instead, lots of resonant states emerge at low energies and eventually lead to a power-law singularity in the local density of states. Our findings show that the impurity problem in graphene should be treated as a collective phenomenon rather than a single impurity state.

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Graphene, a single-layer graphite composed of carbon atoms arranged in two-dimensional honeycomb lattice, is recently fabricated in laboratory and attracts intense attentions from both experimental and theoretical aspects.[1–4] One of the striking features of graphene is its relativistic description, described by a pair of massless Dirac fermions in the low-energy regime.[5,6] The relativistic spectrum gives rise to interesting phenomena such as half-integer quantum Hall effect,[7] Klein paradox,[8] edge magnetism,[9,10] and others.[11–13]

In a two-dimensional Dirac system a peculiar quasilocalized state can be induced by a point defect.[14] Such a state can be seen in graphene as a pronounced peak in the local density of states (LDOS) at zero energy.[15–17] Density-functional studies[18,19] suggest that point defects can be created by chemisorption of hydrogen atoms.[20] Furthermore, there exists quantized magnetic moment associated with each defect.[18,21,22]

Is the peak in the LDOS near the defect site caused by the zero modes in graphene? It is tempting to say yes. However, we revisit this problem and find the origin of the peak is not from the zero modes. We start from the finite-size graphene in nanotorus geometry and investigate how the system evolves toward the thermodynamic limit. At finite system size $N$, we can solve the zero modes due to a single defect analytically, contributing a zero-energy peak in LDOS as expected.[23] However, its spectral weight decays as $1/\ln N$ or $1/N$ (depending on whether the nanotorus is semiconducting or metallic) and eventually vanishes in two dimensions. Therefore, even though the defect gives rise to zero modes, they do not contribute to the pronounced peak in LDOS for two-dimensional graphene.

The pronounced peak in LDOS found in previous studies can be explained in two steps. First of all, our numerics show that the defect in graphene induces enormous resonant peaks in the LDOS at energies close to zero. Then, as the system size grows to infinity, these peaks crowd into zero energy and become singular. Both numerical and analytic approaches give $1/|E|$ power-law singularity with weak logarithmic corrections. That is to say, the peak in the LDOS is not from a single impurity state. Instead, it is a power-law singularity from collective resonance induced by the defect. It is rather amusing that the impurity state in graphene dissolve into a power-law singularity as the single-particle state disappears in one-dimensional interacting electron gas.[24] The emergence of the power-law singularity resembles the quantum criticality found in many two-dimensional systems[25,26] and suggest that graphene is a quantum critical system[27,28] as well. As a result, introducing a point defect reshuffles the LDOS leading to a power-law singularity rather than a delta-function (or broadened Lorentzian) peak.

Now we walk through the details which lead to the conclusions sketched in above. Because the band structure of graphene obtained by the first-principles calculations is well approximated by the nearest-neighbor hopping for the active $\pi$ orbitals,[29,30] it is sufficient to start from a tight-binding Hamiltonian and add a single defect at the origin,

$$H = -t\sum_{\langle \mathbf{r},\mathbf{r}'\rangle}[c^{\dagger}(\mathbf{r})c(\mathbf{r}') + c^{\dagger}(\mathbf{r}')c(\mathbf{r})] + V_0 c^{\dagger}(\mathbf{0})c(\mathbf{0}), \quad (1)$$

where $t$ is the nearest-neighbor hopping amplitude, and $V_0$ is the strength of the impurity potential. In the remaining part of the calculations, we mainly focus on the unitary limit $V_0 \to \infty$. Though the impurity state in the unitary limit has been solved analytically in a recent paper,[15] it is insightful to rederive it with cares so that the evolution of the impurity state with the system size $N$ is clarified. For simplicity, we apply periodic boundary conditions in both directions, wrapping the finite-size graphene into a nanotorus. The number of unit cells along the $x$ and $y$ axes is $N_x$ and $N_y$ and the lattice sites are labeled by the coordinates $x$ and $y=n+x/2$ with $x=0,\pm 1,\ldots,(\pm)N_x/2$ and $n=0,1,\ldots,N_y-1$ as shown in Fig. 1.

Let us consider the carbon nanotube limit first by taking $N_x \to \infty$ but keeping $N_y$ finite. Because the honeycomb lattice is bipartite, the wave function of the zero modes only show up in one of the sublattices[31] as shown in Fig. 1. The wave function for the left and right sectors can be written as the linear combinations of all evanescent modes,

$$\Psi_l(x,y) = \sum_l C_l e^{ik_l y}(z_l)^{-x},$$

$$\Psi_r(x,y) = \sum_r C_r e^{ik_r y}(z_r)^{x}, \quad (2)$$

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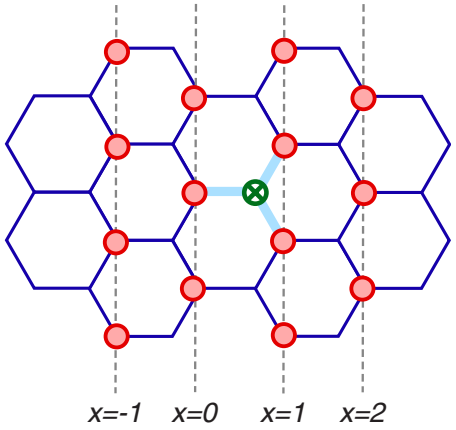


FIG. 1. (Color online) Schematic figure for the nanorotus. Only the part near the defect site is shown for clarity. Note that the wave function of the zero mode only shows up in one of the sublattices shown as the filled circles.

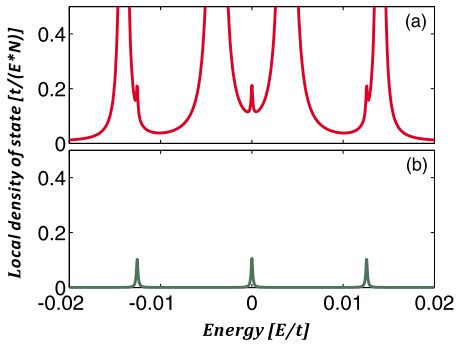


FIG. 2. (Color online) The LDOS for a nanotorus of the size $N=300\times144$ (a) with and (b) without a point defect evaluated at its nearest-neighbor site.

where the quantized momenta $k_l=2\pi l/N_y$ and $k_r=2\pi r/N_y$ are in the ranges $2\pi/3\leq k_l\leq 4\pi/3$ and $-2\pi/3\leq k_r\leq 2\pi/3$ to ensure both $z_l=-2\cos(k_l/2)$ and $z_r=-1/2\cos(k_r/2)$ have modulus less than unity.

The total number of evanescent modes at the left (right) of the defect is denoted as $N_L(N_R)$. Construct a $(N_L+N_R)$-dimensional vector to represent the solution, $\boldsymbol{C}=[C_l,C_r]$. Meanwhile, we can also introduce $(N_y-1)$ vectors in the same space $\boldsymbol{B}_j=[e^{ik_lj},e^{ik_rj}]$, where $j=1,2,\ldots,N_y-1$. The boundary conditions[15] then take the simple form $\boldsymbol{B}_j\cdot\boldsymbol{C}=0$, i.e., we are looking for all linearly independent vectors $\boldsymbol{C}$ which is orthogonal to the subspace expanded by the $N_y-1$ vectors $\boldsymbol{B}_j$.

For semiconducting nanotubes $(N_y\neq 3m)$, the quantized momentum does not cut through the Dirac points at $k=2\pi/3,4\pi/3$. Thus, counting all localized states within $2\pi/3<k_l<4\pi/3$ gives $N_L=[(N_y+1)/3]$, where $[x]$ denotes the Gauss symbol. Similarly, it is straightforward to obtain $N_R=[(2N_y+1)/3]$. Since the combination of $k_l$ and $k_r$ exhausts all quantized momenta in the Brillouin zone, $N_L+N_R=N_y$. The boundary conditions nail down the symmetric solution,

$$\boldsymbol{C}=[1,1,\ldots,1]. \tag{3}$$

It is easy to verify that $\boldsymbol{C}\cdot\boldsymbol{B}_j=\Sigma_{n=1}^{N_y}e^{i2\pi nj/N_y}=N_y\delta_{j,0}=0$, satisfying all orthogonal criteria. Furthermore, because $\boldsymbol{B}_j$ expand a subspace of dimension $N_y-1$ in the $N_y$ dimensional space, only one solution is allowed. Normalization of the above solution involves a summation over all evanescent modes, $(1/N_y)\Sigma_l 1/(1-z_l^2)\sim\ln N_y$. As a result, the spectral weight at zero energy scales as $1/\ln N_y$ in the thermodynamic limit.

For metallic nanotubes $(N_y=3m)$, there are two additional extended states at the Dirac points with the nodal structure. These extended states can hybridize with the localized states and should be included on both sides. Thus, $N_L=(N_y/3)+1$ and $N_R=(2N_y/3)+1$. The dimension of the vector space is larger $N_L+N_R=N_y+2$ here. Let us count the number of independent solutions first. Subtracting the dimension of the vector space $N_y+2$ by the dimension $N_y-1$ expanded by $\boldsymbol{B}_j$, we expect *three* independent solutions. Let us start with the simple ones which do not involve the localized states,

$$\boldsymbol{C}_{D1}=[1,0,\ 0,\ldots,0,\ -1,0,\ 0,\ldots,0],$$

$$\boldsymbol{C}_{D2}=[0,1,\ 0,\ldots,0,\ 0,-1,\ 0,\ldots,0]. \tag{4}$$

For clarity, the components corresponding to the Dirac points are in italics while those for localized states are in roman. The orthogonal criteria are trivially satisfied. In fact, these two solutions are just the extended states at the Dirac points. The third solution is

$$\boldsymbol{C}_m=\left[\frac{1}{2},\frac{1}{2},\ 1,\ldots,1,\ \frac{1}{2},\frac{1}{2},\ 1,\ldots,1\right]. \tag{5}$$

Although the solution is similar to that in Eq. (3), its hybridization with the extended state at the Dirac points makes it an extended state as well. Thus, despite the superficial resemblance, its contribution to the spectral weight at zero energy is dramatically different and scales down much faster as $1/N_y$.

The above analytic solutions exclude the zero modes as the cause for the pronounced peak in the LDOS. We also perform numerical diagonalization (not shown here) to confirm the different trends for semiconducting and metallic cases toward the two-dimensional limit. So, what causes the peak in LDOS then? Note that, in addition to the impurity state, the defect in graphene also generates resonant states near zero energy, inaccessible by analytic approach. We employ numerical diagonalization for the nanotorus to address this issue. For comparison, we computed the LDOS for a metallic nanotorus with and without a point defect as shown in Fig. 2. The change of the LDOS *right at* zero energy caused by the defect is almost invisible. But, the induced resonant peaks *close to* the zero energy are enormous and largely change the profile of the LDOS. It is reasonable to expect that the resonant peaks are far more important than the impurity state at zero energy in the thermodynamic limit.

The remaining task is to understand how these resonant peaks crowd into the zero-energy regime as the system size goes to infinity. The numerical results are shown in Fig. 3. In

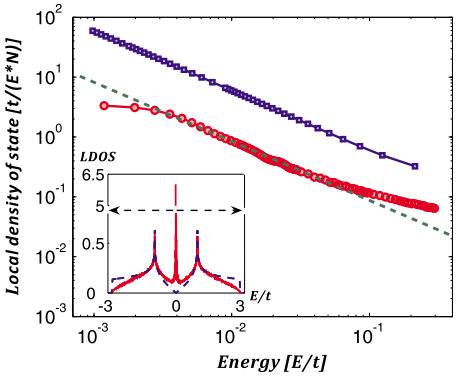


FIG. 3. (Color online) The LDOS at the nearest-neighbor site of the defect for a nanotorus of the size $N=564\times564$ with a broadening factor 0.004 (red circles) and in the two-dimensional limit with a broadening factor $10^{-5}$ (blue squares). The green dashed line of $1/|E|$ is the guide to the eyes. The deviation from the power law near $E=0$ arises from the finite broadening factor. In the inset, the LDOS at the nearest-neighbor site (shown in red solid line) is compared to that deep inside the bulk (shown in blue dashed line). The zero-energy peak is high and thus chopped off by the double-arrow dashed line for clarity.

the inset, we compare the LDOS near the defect and in the bulk. As in previous studies, the most noticeable difference is the sharp peak at zero energy. However, one may also observe that there exists large spectral weight transfer from the higher-energy regime to the lower energy. This is an indirect hint that the sharp peak at zero energy may not attribute to a single impurity state. To illustrate this point, the LDOS shown in the log-log plot reveals the $1/|E|$ power-law dependence. The deviation from the power-law singularity at extremely small energy where it is rounded off comes from the Lorentzian energy broadening factor introduced in the numerical calculations. We emphasize that, even for a rather small nanotorus with $N_x=N_y\sim10^2$, the resonant states coarse grain into the power-law singularity. In consequence, the peak in LDOS should be treated as a collective phenomenon involving many resonant states and cannot be described as a single impurity state.

To further strengthen our numerical findings for finite-size graphene, it is inspiring to compare the answer in two dimensions. The change of the LDOS due to a point defect can be expressed in terms of the noninteracting retarded Green's functions, $G_0^{\pm}(\mathbf{k},E)=1/(E\pm|h(\mathbf{k})|+i\eta)$, representing the propagation of particles and holes with the dispersion $h(\mathbf{k})=t+2t\cos(k_x/2)e^{i\sqrt{3}k_y/2}$ from the tight-binding model. Following standard Green's function techniques, the change of the LDOS at the first-nearest-neighbor sites ($B$) of the defect (located at the $A$ site) is

$$\Delta\rho(E)=-\frac{1}{\pi}\mathrm{Im}\left[\frac{V_0G_{AB}G_{BA}}{1-V_0G_{AA}}\right], \tag{6}$$

where $G_{\Lambda\Lambda'}$ with $\Lambda,\Lambda'=A,B$ are the Green's functions between sites $\Lambda$ and $\Lambda'$. In the unitary limit $V_0\to\infty$, the change of the LDOS no longer depends on the strength of the impurity potential as expected.

For graphene, it is straightforward to show that symmetries between these Green's functions lead to the relations, $G_{AA}=G_{BB}$ and $G_{AB}=G_{BA}$,

$$G_{AA}(E)=\int\frac{d^2\mathbf{k}}{8\pi^2}[G_0^-(\mathbf{k},E)+G_0^+(\mathbf{k},E)], \tag{7}$$

$$G_{AB}(E)=\int\frac{d^2\mathbf{k}}{8\pi^2}\frac{h(\mathbf{k})}{|h(\mathbf{k})|}[G_0^-(\mathbf{k},E)-G_0^+(\mathbf{k},E)]. \tag{8}$$

These Green's functions can be solved numerically to compute the LDOS. The results are shown as blue squares in Fig. 3. It delivers the same power-law singularity in the LDOS. It is also interesting to notice that, though with the same exponent, the absolute values of the LDOS for the large nanotorus with $N=564\times564$ and the two-dimensional graphene are different–another hint for the collective phenomena rather than a single impurity state for the zero-bias anomaly.

The power-law singularity comes from the linear dispersion near the Dirac cones. Carrying out the angular part of the integral near the Dirac points with linear dispersion, the Green's functions are approximately

$$G_{AA}(E)\sim E\ln(E^2/\Lambda^2)+i|E|, \tag{9}$$

$$G_{AB}(E)\sim\Lambda^2-E^2\ln(E^2/\Lambda^2)+i\,\mathrm{sign}(E)E^2, \tag{10}$$

where $\Lambda$ is a momentum cutoff introduced for linearizing the spectrum. Since $G_{AB}(E)$ appears in the numerator, it can be treated as a constant in low-energy limit. Therefore, the change of the LDOS is $\Delta\rho(E)\sim\mathrm{Im}[G_{AA}]/(\mathrm{Re}[G_{AA}]^2+\mathrm{Im}[G_{AA}]^2)$ and the singularity near $E=0$ emerges,

$$\Delta\rho(E)\sim\frac{1}{|E|(\ln|E|)^2}. \tag{11}$$

Because the logarithmic correction is very weak (beyond the resolution of our numerical results), the singularity is essentially a power-law $1/|E|$ and agrees with our previous numerical findings.

The above calculations are readily generalized to other systems with gapless dispersion $h(\mathbf{k})\sim|\mathbf{k}|^{\alpha}$. Following the same steps, it is straightforward to show that the imaginary of the Green's function follows the energy dependence, $\mathrm{Im}[G_{AA}]\sim|E|^{(2/\alpha)-1}$. Ignoring the logarithmic correction, the real part of the Green's function shares the same energy dependence. Thus, the change of the LDOS exhibits the power-law $\Delta\rho(E)\propto|E|^{1-(2/\alpha)}$. For double-layer graphene with bernal stacking, the local energy dispersion is linear ($\alpha=1$) at the sites directly connected to the neighboring layer, but is quadratic ($\alpha=2$) at the sites that are not directly connected. The latter gives a constant $\Delta\rho(E)$ at zero energy, in contrast to the former and to the single-layer graphene.

Though it is generally believed that the mutual interactions between electrons are likely to be irrelevant in graphene, there are evidences that the correlation effects may be significant near defects or open boundaries. Further in-depth investigations are necessary to explore how the power-law singularity evolves with the inclusion of electronic correlations. However, it is worth mentioning how the exponent changes in the analogous one-dimensional interacting

system.[24] Upon the inclusion of interaction, the delta function for the quasiparticle changes into $1/|E|$ power-law singularity. Increasing the strength of the interaction suppresses the density of states near the zero energy and gradually changes the exponent from the negative $\gamma=-1$ to positive values, exhibiting the so-called "pseudogap" behavior. We may expect that similar trend happens for defect in grapheme, but it needs further investigations. In conclusions, we revisit the defect problem in graphene and find the sharp peak in the LDOS is not a single impurity state but a power-law singularity.

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