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Impurity effects in a two-dimensional system with the Dirac spectrum

Yu. V. Skrypnyk[1] and V. M. Loktev[2]
[1]*G. V. Kurdyumov Institute of Metal Physics, National Academy of Sciences of Ukraine, Vernadskogo Avenue 36, Kyiv 03142, Ukraine*
[2]*Bogolyubov Institute for Theoretical Physics, National Academy of Sciences of Ukraine, Metrolohichna Street 14-b, Kyiv 03143, Ukraine*

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It is demonstrated that in a two-band two-dimensional system resonance state is manifested close to the energy of the Dirac point in the electron spectrum for a sufficiently large impurity perturbation. With increasing impurity concentration, the electron spectrum undergoes a rearrangement, which is characterized by the opening of a broad quasigap in the vicinity of the nodal point. If the critical concentration for the spectrum rearrangement is not reached, the domain of localized states remains exponentially small compared to the bandwidth.

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The effect of impurities on quasiparticle spectra in disordered systems is qualitatively determined by the ratio of the dimensionality of the disordered system to the exponent in the respective dispersion relation. The disordered system exhibits low-dimensional behavior when this ratio is less than unity. In general, impurity effects are more pronounced in low-dimensional systems. Materials like graphene are certainly two-dimensional (2D) objects.[1,2] However, electrons in graphene feature the linear dispersion close to the Fermi level. A number of experiments evidently demonstrate that graphene is highly tolerant to impurity-induced perturbations. This fact can be attributed to the increased effective dimensionality of the electron subsystem in graphene. With respect to the ordinary quadratic dispersion graphene could be regarded as a four-dimensional system. This high effective dimensionality should be beneficial for the reduction of localization effects that occur due to impurities, which are inevitably present (or intentionally introduced) in corresponding materials.

The importance of impurity effects for the physics of graphene had been frequently emphasized. Notwithstanding, the effects of disorder were studied only in both weak-scattering[3] and unitary[4,5] limits, or for a kind of interpolation between such extreme cases.[6] When impurity states of single defects are located in the vicinity of the van Hove singularities of the host system, an increase in the impurity concentration yields a substantial spectrum rearrangement (SR), albeit the relative impurity concentration remains quite low.[7,8] This transition between two qualitatively different regimes of impurity scattering takes place only for a finite magnitude of the single-impurity perturbation. The type of the state that is produced by the single impurity is usually reflected in the passage of the SR. Below we are attempting to examine a possibility for impurity states to appear close to the Dirac point of the electron spectrum in a 2D system with linear dispersion for an arbitrary strength (unitary limit included) of the single-impurity perturbation, and to outline a scenario of SR with varying impurity concentration. Similar issues were raised in Ref. 9 but the problem was not solved correctly.

In order to model a system with a Dirac spectrum, one can choose the host tight-binding Hamiltonian in the most basic form,[10]

$$\hat{H}_0=\sum_{\boldsymbol{k}}[f(\boldsymbol{k})c_1^{\dagger}(\boldsymbol{k})c_2(\boldsymbol{k})+f^{*}(\boldsymbol{k})c_2^{\dagger}(\boldsymbol{k})c_1(\boldsymbol{k})], \tag{1}$$

where $c_{\alpha}^{\dagger}(\boldsymbol{k})$ and $c_{\alpha}(\boldsymbol{k})$ are creation and annihilation operators on the two sublattices, and $\boldsymbol{k}$ is a 2D wave vector. Since only the close vicinity of the nodal point will be of concern, it is sufficient to put $f(\boldsymbol{k})=ta(k_x+ik_y)$, $t>0$, where t is the hopping parameter, and a is the lattice constant. Then, the dispersion relation $\epsilon(\boldsymbol{k})=\pm tak$ does possess a Dirac point at the zero energy, which separates two bands that are touching each other.

We also assume that our system can be reasonably well described as a substitutional binary alloy with a diagonal disorder (the so-called Lifshits model). It is supposed that impurities are distributed absolutely at random on both sublattices, so that on-site potentials can take one of two values, say V_L and 0, with probabilities c and $1-c$, respectively. The full Hamiltonian of the disordered system is then represented by the sum of the translationally invariant host part (1) and the perturbation,

$$\hat{H}=\hat{H}_0+\frac{V_L}{N}\sum_{\boldsymbol{k},\boldsymbol{k}',\langle\alpha,p\rangle}e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{r}_p}c_{\alpha}^{\dagger}(\boldsymbol{k})c_{\alpha}(\boldsymbol{k}'), \tag{2}$$

where $\langle\alpha,p\rangle$ ranges over those sites on the lattice that are occupied by impurities.

Let only the zeroth site on one of the sublattices be occupied by an impurity. Then, the diagonal element of the Green's function (GF) $\hat{G}=(\epsilon-\hat{H})^{-1}$ on this site,

$$G_0=g_0/(1-V_L g_0), \tag{3}$$

where g_0 is the diagonal element of the GF in the host, $\hat{g}=(\epsilon-\hat{H}_0)^{-1}$. The site-diagonal elements g_0 are equal on both sublattices and can be easily obtained by approximating the Brillouin zone with a circle,

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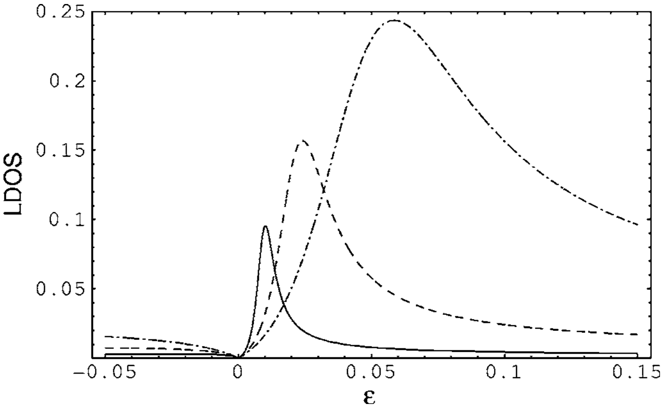

FIG. 1. LDOS at the impurity site for $v=-10,-5,-2.5$ is shown by solid, dashed, and dot-dashed curves, respectively.

$$g_0 = \frac{1}{N}\sum_{\boldsymbol{k}} \frac{\epsilon}{\epsilon^2-\epsilon(\boldsymbol{k})^2} = \frac{a^2}{2\pi}\int_0^{2\sqrt{\pi}/a} \frac{\epsilon k\,dk}{\epsilon^2 - t^2a^2k^2}$$
$$= \frac{\epsilon}{4\pi t^2}\ln\left(\frac{\epsilon^2}{4\pi t^2-\epsilon^2}\right) - i\frac{|\epsilon|}{4t^2}, \quad |\epsilon|\le 2\sqrt{\pi}t. \qquad (4)$$

It is convenient to choose the energy unit in such a way that the bandwidth $2\sqrt{\pi}t=1$. Thus, for (4) one obtains

$$g_0 = \epsilon \ln[\epsilon^2/(1-\epsilon^2)] - i\pi|\epsilon|. \qquad (5)$$

The local density of states (LDOS) at the impurity site (see Fig. 1) is given by the imaginary part of the diagonal element of the GF (3),

$$\rho_0 = -\frac{1}{\pi}\mathrm{Im}\, G_0 = \frac{|\epsilon|}{\{1 - v\epsilon\ln[\epsilon^2/(1-\epsilon^2)]\}^2 + (v\pi\epsilon)^2}, \qquad (6)$$

where v is the dimensionless single-impurity perturbation. For sufficiently large $|v|$, a prominent peak is manifested in the LDOS (6) close to the Dirac point in the spectrum, indicating the presence of a resonance state. Its energy ϵ_r is defined by the Lifshits equation

$$1 \approx 2v\epsilon_r \ln|\epsilon_r|. \qquad (7)$$

It should be emphasized that for the attractive impurity potential $v<0$ the energy ϵ_r is located above the nodal point ($\epsilon_r>0$), and, vice versa, it is located below this point ($\epsilon_r<0$) for the repulsive impurity potential $v>0$. In contrast to 3D systems, the resonance state is accompanied by a deep local level outside both adjacent bands. Thus, the total number of states near the nodal point is gradually diminishing with increasing $|v|$.

When the resonance peak is relatively narrow, the denominator in Eq. (6) can be expanded about ϵ_r,

$$\rho_0 \approx \frac{|\epsilon|\Gamma^2}{(v\pi\epsilon_r)^2[(\epsilon-\epsilon_r)^2+\Gamma^2]},$$

$$\Gamma = \pi|\epsilon_r||\ln[\epsilon_r^2/(1-\epsilon_r^2)] + 2/(1-\epsilon_r^2)|^{-1}. \qquad (8)$$

The resonance state is well defined when the effective damping (8) is much less than its separation from the closest van Hove singularity,

$$\Gamma/|\epsilon_r| \approx \pi/[2|\ln|\epsilon_r| + 1|] \ll 1. \qquad (9)$$

The inequality is satisfied only when the resonance energy ϵ_r is located fairly close to the Dirac point and is strengthening with decreasing $|\epsilon_r|$. Thus, the resonance presence in the unitary limit[4,5] is justified. It is worth mentioning that well-defined resonances cannot appear in the vicinity of the band edge in a single-band 2D or 3D system within the Lifshits model (2).

It is not difficult to calculate also the change $\Delta\rho$ in the total DOS in the system that is caused by the single impurity center,[8]

$$\Delta\rho = \frac{v}{N\pi}\mathrm{Im}\left(\frac{dg_0}{d\epsilon}\frac{1}{1-vg_0}\right)$$
$$= \frac{-v\,\mathrm{sgn}(\epsilon)(1-\epsilon^2+2v\epsilon)}{N(1-\epsilon^2)\left\{\left[1 - v\epsilon\ln\left(\frac{\epsilon^2}{1-\epsilon^2}\right)\right]^2 + (v\pi\epsilon)^2\right\}}. \qquad (10)$$

It can be verified that bare states are redistributed within the bands. For the case $v<0$, states are removed from the domain of the continuous spectrum in the lower band to the split-off local level, and in the upper band states are pushed toward ϵ_r. However, there is a notable negative dip in $\Delta\rho$ at the nodal point, where the host DOS is zero [see Eq. (5)]. Therefore, the close vicinity of the nodal point cannot be described properly by direct expansion in the impurity concentration even at a negligibly small concentration of impurities.

Commonly, renormalized methods, such as the coherent-potential approximation (CPA), are most effective inside the continuous spectrum. The one-electron GF of the disordered system can be expressed by the corresponding self-energy $\hat{\Sigma}(\boldsymbol{k})$. Since the translational invariance is restored by configurational averaging over impurity distributions,

$$\hat{G}(\boldsymbol{k})^{-1} = \hat{g}(\boldsymbol{k})^{-1} - \hat{\Sigma}(\boldsymbol{k}), \qquad (11)$$

where the operators $\hat{G}(\boldsymbol{k})$, $\hat{g}(\boldsymbol{k})$, and $\hat{\Sigma}(\boldsymbol{k})$ are acting in the sublattice space. For the model system under consideration, the self-energy within the CPA is site diagonal and identical on both sublattices. According to the conventional procedure, it should be determined in a self-consistent manner from the equation

$$\sigma = cv/[1-(v-\sigma)g_0(\epsilon-\sigma)]. \qquad (12)$$

In the effective medium constructed by the CPA, the self-energy can be expanded into a series in impurity clusters,[7,8]

$$\Sigma^{\alpha\beta}(\boldsymbol{k}) = \delta^{\alpha\beta}\sigma + \sigma_2^{\alpha\beta}(\boldsymbol{k}) + \cdots, \qquad (13)$$

where $\hat{\sigma}_2(\boldsymbol{k})$ represents the contribution from pair diagrams,

$$\sigma_2^{\alpha\beta}(\boldsymbol{k}) = \delta^{\alpha\beta} \sum_{m,n,l\gamma\neq 0\alpha} \xi_m \xi_n \frac{\tau_m^3 \tau_n^2 (\mathfrak{G}_{0l}^{\alpha\gamma})^2 (\mathfrak{G}_{l0}^{\gamma\alpha})^2}{1 - \tau_m \tau_n \mathfrak{G}_{0l}^{\alpha\gamma} \mathfrak{G}_{l0}^{\gamma\alpha}} + \sum_{m,n,l\beta\neq 0\alpha} \xi_m \xi_n \frac{\tau_m^2 \tau_n^2 (\mathfrak{G}_{0l}^{\alpha\beta})^2 \mathfrak{G}_{l0}^{\beta\alpha} \exp(i\boldsymbol{k}\boldsymbol{r}_l)}{1 - \tau_m \tau_n \mathfrak{G}_{0l}^{\alpha\beta} \mathfrak{G}_{l0}^{\beta\alpha}}. \tag{14}$$

In Eq. (14) l and the indices α, β, and γ enumerate lattice cells and sublattices, respectively,

$$\mathfrak{G}_{0l}^{\alpha\beta} = \frac{1}{N} \sum_{\boldsymbol{k}} g^{\alpha\beta}(\epsilon - \sigma, \boldsymbol{k}) \exp(-i\boldsymbol{k}\boldsymbol{r}_l), \tag{15}$$

the single-site T matrix is denoted by

$$\tau_m = (\upsilon_m - \sigma)/[1 - (\upsilon_m - \sigma) g_0(\epsilon - \sigma)], \tag{16}$$

while the indices m and n enumerate atom types (impurity or host), so that ξ_m attains values c or $1-c$ depending on the value of these indices, and the variable υ_m is υ or 0, respectively.

The relative magnitude of contributions from scatterings on impurity clusters is increasing on approaching any van Hove singularity in the spectrum, so that the CPA becomes unreliable in their vicinity. The necessity to implement a relevant applicability criterion for the CPA and other approximate methods based on the partial summation of the series for the GF has been overlooked in some recent papers devoted to the impurity effects in graphene.[5] The analysis of the series expansion for $\hat{\Sigma}(\boldsymbol{k})$ shows that the series does have a small parameter,

$$R(\epsilon) = \sum_m \xi_m (\tau_m)^2 \sum_{l\beta\neq 0\alpha} (\mathfrak{G}_{0l}^{\alpha\beta})^2. \tag{17}$$

Cluster diagrams can be omitted on $|R(\epsilon)| \leqslant 1/2$. Inside the energy domains, where this inequality holds, only the first term can be retained in the series and the resulting approximate expression for the self-energy does not depend on $\boldsymbol{k}$. If the relative impurity concentration is kept low, multiple-occupancy corrections that are included in the derivation of the CPA can be neglected too, so it is reduced to the so-called method of the modified propagator,

$$\sigma = c\upsilon/[1 - \upsilon g_0(\epsilon - \sigma)]. \tag{18}$$

Since our interest is restricted to the narrow vicinity of the nodal point in the spectrum, it is possible to make an obvious approximation for the diagonal element of the host GF,

$$g_0 \approx 2\epsilon \ln|\epsilon| - i\pi|\epsilon|, \quad |\epsilon| \ll 1. \tag{19}$$

By making a substitution $\epsilon - \sigma = \varkappa \exp(i\varphi)$, $0 < \varphi < \pi$, the imaginary part of Eq. (18) can be rewritten as follows

$$c\upsilon^2[2\ln\varkappa + (2\varphi - \pi)\cot\varphi] + \{1 - \upsilon\varkappa[2\ln\varkappa\cos\varphi - (2\varphi - \pi)\sin\varphi]\}^2 + \{\upsilon\varkappa[2\ln\varkappa\sin\varphi + (2\varphi - \pi)\cos\varphi]\}^2 = 0. \tag{20}$$

Starting from some threshold magnitude of $\varkappa$, there are two solutions of Eq. (20) for the phase φ at the given concentration of impurities, which correspond to the two existing bands. The corresponding values of ϵ are then provided by the real part of Eq. (18), which closes the parametric solution of the problem. Correspondingly, the validity criterion for the CPA assumes the form

$$|R(\epsilon)| \approx \left| \frac{\ln\varkappa + 1 + i(\varphi - \pi/2)}{\ln\varkappa + (\varphi - \pi/2)\cot\varphi} \right| \leqslant \frac{1}{2}. \tag{21}$$

As usual, for the renormalized wave vector in both bands one has $\tilde{k}a = 2\sqrt{\pi}\varkappa|\cos\varphi|$. The spatial behavior of the host GF on one of the sublattices at large intercell distances is given by

$$g_{0l} = \frac{a^2}{(2\pi)^2} \int_0^{2\sqrt{\pi}/a} \frac{\epsilon k\, dk}{\epsilon^2 - (ak)^2/(4\pi)} \int_0^{2\pi} e^{ikr_l \cos\phi} d\phi \approx 2\epsilon \int_0^{\infty} \frac{J_0(ur_l/a) u du}{4\pi\epsilon^2 - u^2} = \pi\epsilon[Y_0(2\sqrt{\pi}|\epsilon| r_l/a) - i\,\mathrm{sgn}(\epsilon) J_0(2\sqrt{\pi}|\epsilon| r_l/a)], \tag{22}$$

where J_0 and Y_0 are the Bessel functions of the first and second kind, respectively. It follows from Eq. (22) that the mean free path should be written as $\ell = a/(4\sqrt{\pi}\varkappa\sin\varphi)$. Thus, the localization parameter from the Ioffe-Regel criterion[11] takes the simple form $\tilde{k}\ell = |\cot\varphi|/2$.

An overview of the SR scenario can be provided based on simple estimations. It may seem that $\epsilon = \sigma = c\upsilon$ is an appropriate solution of Eq. (18). However, this is not the case. Formally, this equation is satisfied, but an analytical solution for the GF that is passing through this point cannot be constructed. On the other hand, there should be always an energy at which $\mathrm{Re}(\epsilon - \sigma) = 0$. As follows from Eq. (20), a certain amount of damping ($\mathrm{Im}\,\sigma \neq 0$) is always present at this energy

$$-2c\upsilon^2 \ln\varkappa_0 = 1 + (2\upsilon\varkappa_0 \ln\varkappa_0)^2. \tag{23}$$

When the impurity concentration is sufficiently small, $\varkappa_0 \approx \exp[-1/(2c\upsilon^2)]$. It is not difficult to see from the real part of Eq. (18) that $\mathrm{Re}\,\sigma \approx c\upsilon$ in this case. In other words, the energy at which two bands coincide is shifted approximately by $c\upsilon$ from zero toward the impurity local level. The width of the concentration smearing area around $\epsilon \approx c\upsilon$, where states are highly localized according to the Ioffe-Regel criterion, should be proportional to $\varkappa_0$, while the guess value for the mean free path inside this area remains exponentially large. For small $\varkappa$, Eq. (20) is reduced to

$$c\upsilon^2[\ln\varkappa + (\pi - 2\varphi)\cot\varphi] \approx -1. \tag{24}$$

In the same approximation, it follows from the real part of Eq. (18) that

$$\epsilon - c\upsilon \approx c\upsilon^2(\pi - 2\varphi)\varkappa/\sin\varphi. \tag{25}$$

Although the threshold magnitude of the localization parameter that separates states that can be described by the wave vector can be argued to some extent, it seems reasonable to choose it from the thoroughly tested method of the potential-well analogy,[12–14] $|\cot\varphi| > \sqrt{3}$. Then, the width of the concentration smearing area is

$$\Delta_{IR} \approx (8\pi/3)\exp(\pi/\sqrt{3})cv^2 \exp[-1/(2cv^2)]. \qquad (26)$$

In the narrow vicinity of $\epsilon \approx cv$, contributions from scatterings on impurity clusters are becoming significant. According to the applicability criterion Eq. (21), the electron spectrum obtained by the CPA cannot be justified inside an area with the width of $\Delta_R \approx \exp[-1/(4cv^2)]/e$, which is wider than Δ_{IR} that follows from the Ioffe-Regel criterion. It has been shown that in 3D systems the small parameter of the series expansion Eq. (17) and the localization parameter $\tilde{k}\ell$ can be expressed through each other[15] and depend on the phase φ only. However, in the system under consideration the cutoff phase for the CPA applicability criterion depends on the disorder parameter cv^2 at the small impurity concentration. The reason for this discrepancy is the subject of a more detailed study.

With an increase in the impurity concentration, the absolute values of the shift $|cv|$ and the width of the concentration smearing area are also gradually increasing in magnitude. It is obvious from the expression for $\varkappa_0$, which can be rewritten as $\varkappa_0 \approx -c|v|(2|v|\varkappa_0 \ln \varkappa_0)$, that parametrically $|cv|$ and $\varkappa_0$ simultaneously become of the order of the resonance energy $|\epsilon_r|$. The second area of concentration smearing opens in the vicinity of the resonance energy and, finally, both areas of concentration smearing are merged together. This is indicative of the spectrum rearrangement. Both criteria are coinciding in this regime ($\Delta_R \approx \Delta_{IR}$). An expression for the critical concentration of the SR can be obtained by comparing the two main parameters of the problem by their magnitude,

$$cv^2 \exp[-1/(2cv^2)] = \zeta c|v|, \qquad (27)$$

where ζ is a certain constant to be determined. This immediately yields

$$c_r = -1/[2v^2 \ln(\zeta/|v|)].$$

This expression fits well the calculated critical concentrations of the SR with $\zeta \sim 10^{-5}$.

At an impurity concentration that is far exceeding this critical value (i.e., $c \gg c_r$), it follows from Eq. (23) that in the first approximation $\varkappa_0$ does not depend on the magnitude of the impurity perturbation v. Both criteria give similar results for the width of the broad concentration smearing area, $\Delta_R \sim \Delta_{IR} \sim \sqrt{-(c)/\ln(\sqrt{c})}$, which is nearly symmetric about the Dirac point of the host system. As was mentioned above, an analogous approach to the description of the impurity effects in graphene has been undertaken in Ref. 9, in which some miscalculations were committed in the course of the theoretical analysis of the problem. Nevertheless, the width of the concentration smearing area for $c \gg c_r$ was estimated correctly.

While the passage of the SR in a system with linear dispersion deserves closer attention, some conclusions can be made at this stage. When the change in the on-site potential caused by the impurity atom is noticeably larger than the bandwidth, a well-defined resonance state can appear in a system with a Dirac spectrum. However, this resonance is not very sharp for a reasonable amount of the impurity perturbation. As a rule, the presence of the well-defined resonance state leads to SR of the cross type with an increase in the impurity concentration. Yet there are some exceptions from this rule, and the system under consideration belongs to them.[16] Despite the resonance, the SR is of the anomalous type that is common in low-dimensional systems. This anomalous SR is characterized by the opening of a quasigap, in which any adequate cluster expansion cannot be constructed and states are highly localized. The electron spectrum is not much distorted outside of the concentration smearing area, and there are no prominent features in it close to the resonance energy.

When the change in the on-site potential on the impurity site is not extremely large, the SR does not occur at all, and the width of the quasigap remains exponentially small. Indeed, from the practical point of view, such an exponentially small quasi-gap will remain unnoticed in most situations, and virtually does not affect the carrier mobility. In the case of a large change in the on-site potential disorder effects are not significant until a critical concentration of the impurities is reached. The obtained results also apply to systems with a gap in the host quasiparticle spectrum when this gap is less than the width of the concentration smearing area.

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