Screening of Coulomb Impurities in Graphene

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We calculate exactly the vacuum polarization charge density in the field of a subcritical Coulomb impurity, $Z|e|/r$, in graphene. Our analysis is based on the exact electron Green's function, obtained by using the operator method, and leads to results that are exact in the parameter $Z\alpha$, where α is the "fine-structure constant" of graphene. Taking into account also electron-electron interactions in the Hartree approximation, we solve the problem self-consistently in the subcritical regime, where the impurity has an effective charge $Z_{\rm eff}$, determined by the localized induced charge. We find that an impurity with bare charge $Z = 1$ remains subcritical, $Z_{\rm eff}\alpha < 1/2$, for any α, while impurities with $Z = 2$, 3 and higher can become supercritical at certain values of α.

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It has been known for a long time that the single electron dynamics in a monolayer of graphite (graphene) is described by a massless two-component Dirac equation [1–3]. A surge of interest in the problem was caused by the recent successful fabrication of graphene [4] and measurements of transport properties [5–10], including an unconventional form of the quantum Hall effect. Because of the Coulomb interaction between electrons, graphene represents a peculiar two-dimensional (2D) version of massless quantum electrodynamics (QED) [2]. It appears to be much simpler than conventional QED because the interaction is described by the instantaneous $1/r$ Coulomb's law. On the other hand the Fermi velocity $v_F \approx 10^6$ m/s $\approx c/300$ (c is the velocity of light), and therefore the "fine-structure constant" $\alpha = e^2/\hbar v_F \sim 1$, leading to a strong-coupling version of QED. Below we set $\hbar = v_F = 1$. Screening of a charged nucleus due to vacuum polarization is an effect of fundamental importance in QED. This problem was investigated in detail both in the subcritical and supercritical regimes [11–14]. The problem of charged impurity screening in graphene, which also can be treated in terms of vacuum polarization, has recently received a lot of attention [15–23], due to the importance of the problem for transport properties involving charged impurities, as well as for our general understanding of the theory of graphene.

To leading order in the weak coupling expansion, $Z\alpha \ll 1$, the induced charge is negative and localized at the impurity position, $\rho_{\rm ind} = -|e|\frac{\pi}{2}(Z\alpha)\delta(\mathbf{r})$, which leads to screening of the impurity potential [20–22,24]. We denote by $Z|e|$ the impurity charge, and $e = -|e|$ is the effective electron charge; from now on we refer to Z as the impurity charge with the understanding that it is measured in units of $|e|$. In graphene, the strong-coupling problem $Z\alpha \sim 1$ was recently addressed [20], and it was argued that the supercritical regime occurs for $Z\alpha > 1/2$, where a $1/r^2$ tail appears in the induced charge density, while in the subcritical regime $Z\alpha < 1/2$, the induced charge is always localized at the impurity site. Analytical results were also supplemented by numerical lattice calculations [21], leading to similar conclusions. The induced charge behavior for small $Z\alpha$ was first emphasized in a different context in Ref. [24], and it is in agreement with a recent perturbative calculation of nonlinear vacuum polarization at order $(Z\alpha)^3$ [22]. It was also pointed out [22] that a power law tail can appear even in the subcritical regime due to interaction effects (at order $Z\alpha^2$).

In the present Letter we investigate analytically the induced charge density in graphene in the subcritical regime. We use the method of calculation suggested in Ref. [13], where the induced charge density in a strong Coulomb field was obtained in coordinate space in three-dimensional (3D) QED. We express the induced charge density via the exact Green's function in a Coulomb field, calculated within the operator technique [25]. Our main result is an exact expression for the polarization charge, nonperturbative in the parameter $Z\alpha$, and we explore its physical consequences. The exact result allows us to determine the effective impurity charge $Z_{\rm eff}$ in a self-consistent way. Perhaps most surprisingly, we find that an impurity with bare charge $Z = 1$ can never become supercritical, i.e., $Z_{\rm eff}\alpha < 1/2$. In spite of this, screening can be very substantial, i.e., one can have $Z_{\rm eff} \ll 1$ for large enough α.

Electron Green's function in a Coulomb field.—It is convenient, for technical reasons, to introduce a small "electron mass" M which we set to zero at the end of our calculations. This will allow us to avoid some difficulties which appear in the calculation of the induced charge in massless QED [12], and will serve the renormalization purpose. Physically the mass describes a small energy splitting between carbon atoms in the unit cell. We will consider only the half-filled case of graphene, i.e., we set the chemical potential to zero.

The electron Green's function $G(\mathbf{r}, \mathbf{r}'|\epsilon)$ in a Coulomb field satisfies the two-component equation

$$\left(\epsilon + \frac{Z\alpha}{r} - (\boldsymbol{\sigma}\cdot\mathbf{p}) - \sigma_3 M\right)G(\mathbf{r},\mathbf{r}'|\epsilon) = \delta(\mathbf{r}-\mathbf{r}'). \tag{1}$$

Here $\boldsymbol{\sigma} = (\sigma_1, \sigma_2)$, and $\sigma_{1,2,3}$ are the Pauli matrices; $\mathbf{p} = (p_x, p_y)$ is the momentum operator. Following Ref. [25] we represent the solution of Eq. (1) in the form

$$G(\mathbf{r},\mathbf{r}'|\epsilon) = -i\left(\epsilon + \frac{Z\alpha}{r} + (\boldsymbol{\sigma}\cdot\mathbf{p}) + \sigma_3 M\right)\int_0^\infty ds e^{2is\epsilon Z\alpha}\exp\left(is\left[r\Delta_r + \frac{\hat{K}}{r} + r(\epsilon^2 - M^2)\right]\right)\sqrt{\frac{r}{r'}}\delta(r-r')\delta(\phi-\phi'), \tag{2}$$

where Δ_r is the radial part of the Laplace operator and $\hat{K} = \partial^2/\partial\phi^2 + (Z\alpha)^2 - iZ\alpha(\boldsymbol{\sigma}\cdot\mathbf{n})$, $\mathbf{n} = \mathbf{r}/r$. Then we express $\delta(\phi-\phi')$ via the projectors P_λ that are eigenfunctions of the operator $\hat{K}$, $\hat{K}P_\lambda = -\lambda^2 P_\lambda$:

$$\delta(\phi-\phi') = \sum_\lambda P_\lambda(\phi,\phi'), \qquad \lambda = \gamma \mp 1/2, \qquad \gamma = \sqrt{\varkappa^2 - (Z\alpha)^2}, \qquad \varkappa = m + 1/2, \tag{3}$$

and $m = 0, 1, 2, \ldots$. The explicit form of P_λ for $\lambda = \gamma - \frac{1}{2}$ is

$$\begin{gathered} P_\lambda(\phi,\phi') = \frac{1}{4\pi\gamma}\begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22}\end{pmatrix}, \qquad P_{11} = (\gamma+\varkappa)e^{im(\phi-\phi')} + (\gamma-\varkappa)e^{-i(m+1)(\phi-\phi')}, \\ P_{12} = -iZ\alpha(e^{-i(m+1)\phi}e^{im\phi'} + e^{im\phi}e^{-i(m+1)\phi'}), \qquad P_{11} = P_{22}^*, \qquad P_{12} = -P_{21}^*. \end{gathered} \tag{4}$$

The projector with eigenvalue $\lambda = \gamma + 1/2$ is obtained from (4) by replacing $\gamma \to -\gamma$. After substitution of the expansion (3) into Eq. (2), the problem is reduced to calculation of the action of the operator $\exp(-2is[A_1 + k^2\frac{A_3}{2}])$ on $\sqrt{\frac{r}{r'}}\delta(r-r')$. Here $k^2 = M^2 - \epsilon^2$ and the operators are defined as: $A_1 = \frac{1}{2}(-\frac{\partial}{\partial r}r\frac{\partial}{\partial r} + \frac{\lambda^2}{r})$, $A_3 = r$. Along with $A_2 = -i(r\partial/\partial r + 1/2)$, these operators generate an $O(2,1)$ algebra, which was considered in Ref. [25] in relation to the 3D Green's function for the Dirac equation of an electron in a Coulomb field. Therefore we can directly use the operator transformation of that work. As a result we find the following integral representation for the solution of Eq. (1):

$$G(\mathbf{r},\mathbf{r}'|\epsilon) = -\left(\epsilon + \frac{Z\alpha}{r} + (\boldsymbol{\sigma}\cdot\mathbf{p}) + \sigma_3 M\right)\sum_\lambda P_\lambda(\phi,\phi')\int_0^\infty ds\frac{k}{\sin(ks)}e^{2is\epsilon Z\alpha}\exp[ik(r+r')\cot(ks) - i\pi\lambda]J_{2\lambda}\left(\frac{2k\sqrt{rr'}}{\sin(ks)}\right). \tag{5}$$

Here $J_\nu(x)$ is the Bessel function.

*Induced charge.—*The induced charge density in the vacuum is

$$\rho_{\text{ind}}(\mathbf{r}) = -ieN\int_C \frac{d\epsilon}{2\pi}\mathrm{Tr}\{G(\mathbf{r},\mathbf{r}|\epsilon)\}, \tag{6}$$

where G is the Green's function calculated above, and $N = 4$ reflects the spin and valley degeneracies. The contour of integration C goes below the real axis in the left half-plane and above the real axis in the right half-plane of the complex ϵ plane. Taking into account the analytical properties of the Green's function, the contour of integration with respect to ϵ can be deformed to coincide with the imaginary axis. The integration contour with respect to s in Eq. (5) can then also be rotated to coincide with the imaginary axis so that it extends from zero to $-i\infty$ for $\mathrm{Im}\epsilon > 0$, and from zero to $i\infty$ for $\mathrm{Im}\epsilon < 0$. After these transformations and obvious change of variables, we obtain

$$\begin{aligned} \rho_{\text{ind}}(r) = {}& -N\frac{e}{\pi^2 r} \\ & \times \sum_{m=0}^\infty \int_0^\infty \int_0^\infty d\epsilon ds e^{-y\cosh s}\Big(2Z\alpha\cos(\mu s) \\ & \times \coth s I_{2\gamma}(y) - \sin(\mu s)\frac{\epsilon}{k}yI'_{2\gamma}(y)\Big), \end{aligned} \tag{7}$$

where $k = \sqrt{\epsilon^2 + M^2}$, $y = 2rk/\sinh s$, $\mu = 2Z\alpha\epsilon/k$, $I_\gamma(x)$ is the modified Bessel function of the first kind, and $I'_{2\gamma} = dI_{2\gamma}(y)/dy$. We note that $\rho_{\text{ind}}(r)$, Eq. (7), is an odd function of $Z\alpha$.

In fact, the expression (7) is not well defined and the answer depends on the order of integration over ϵ and s. To overcome this problem we follow the usual procedure of QED. We perform the regularization of the integrals introducing a finite upper limit of integration for ϵ, and a lower limit of integration for s. Then we carry out the renormalization using the obvious physical requirement of zero total induced charge. We can satisfy this requirement due to the nonzero mass M because the induced charge density diminishes rapidly at distances $r \gg 1/M$. After renormalization the result is independent of the cutoff parameters and the order of integration. It is technically convenient to do the renormalization in momentum space. All details of calculations which we need to perform are similar to those described in detail in Ref. [13] for the problem of 3D vacuum polarization in QED. Finally, we obtain the renormalized induced charge density in momentum representation $\rho_{\text{ind}}^R(q/M)$. The leading term of the asymptotics of this function at $M \to 0$ (or $q/M \to \infty$) is a constant, Q_{ind}. Therefore the induced charge density in coordinate space has the form

$$\rho_{\rm ind}(\mathbf{r}) = Q_{\rm ind}\delta(\mathbf{r}) + \rho_{\rm distr}. \tag{8}$$

For the induced charge $Q_{\rm ind}$ we find

$$Q_{\rm ind} = eN\left[\frac{\pi}{8}Z\alpha + \Lambda(Z\alpha)\right] \equiv -|e|A(Z\alpha),$$
$$\Lambda(Z\alpha) = \frac{2}{\pi}\sum_{m=0}^{\infty}{\rm Im}\left[\ln\Gamma(\gamma - iZ\alpha) + \frac{1}{2}\ln(\gamma - iZ\alpha) - (\gamma - iZ\alpha)\psi(\gamma - iZ\alpha) + \frac{iZ\alpha}{2\varkappa} - iZ\alpha\varkappa\psi'(\varkappa)\right], \tag{9}$$

where $\Gamma(x)$ is the gamma function and $\psi(x) = d\ln\Gamma(x)/dx$. The induced charge $Q_{\rm ind}$ is negative [the function $A(Z\alpha)$ is positive, see below]. The distributed charge density $\rho_{\rm distr}$ in Eq. (8) is positive and at distances $r \ll 1/M$, $\rho_{\rm distr} \propto M^2\ln(1/Mr)$. The density vanishes in the limit $M \to 0$, however the total distributed charge is $-Q_{\rm ind}$. We comment that in conventional 3D QED, the induced charge density also consists of local and distributed parts. In that case the distributed density $\rho_{\rm distr} \propto -|e|Z\alpha/r^3$ at $r \ll 1/M$ [26]. Interestingly, the signs of the local and distributed charges in 3D QED are different from those in Eq. (8). The difference is in the leading (linear in $Z\alpha$) contribution, while the signs of the next-to-leading contributions (nonlinear vacuum polarization) are the same in both cases. Physically this difference is related to the fact that the effective charge e^2 is renormalized (increases at short distances) in conventional QED, while in graphene the charge is not renormalized [2].

The series expansion of the function $A(Z\alpha) = (\pi/2)Z\alpha + 4\Lambda(Z\alpha)$, for small $Z\alpha$ reads

$$A(Z\alpha) = \frac{\pi}{2}(Z\alpha) + 0.783(Z\alpha)^3 + 1.398(Z\alpha)^5 + \ldots. \tag{10}$$

The first term of the expansion in Eq. (10) reflects the linear one-loop polarization contribution [20,22]. The coefficient of the $(Z\alpha)^3$ term was also found recently in perturbation theory [22].

The coefficients in the nonlinear terms are not small and grow as the order increases; this is in contrast with conventional QED where they are very small and decrease rapidly [12]. The exact function $A(Z\alpha)$ is shown in Fig. 1. For $Z\alpha > 0.3$ our exact result starts to deviate substantially from the linear order and this deviation is particularly strong as the critical value $Z\alpha = 1/2$ is approached. The exact $A(Z\alpha)$ behavior is also stronger than the one found in a recent numerical calculation [20], which also exhibits lattice size dependence. Around the critical value $Z\alpha \sim 1/2$ the function $A(Z\alpha)$ has the following expansion

$$A(Z\alpha) = 1.12 - 1.19\sqrt{\frac{1}{2} - Z\alpha} - 0.29\left(\frac{1}{2} - Z\alpha\right) + \ldots \tag{11}$$

Notice that the induced charge $Q_{\rm ind} = -|e|A < 0$ has a screening sign, leading to a decrease of the effective impurity charge: $Z_{\rm eff} = Z - A(Z\alpha)$. In fact complete screening seems possible for $Z = 1$ and $\alpha \approx 1/2$, where $Z_{\rm eff} = 0$. However we will show that the self-consistent treatment of the problem (within the Hartree approximation) can drastically change this behavior.

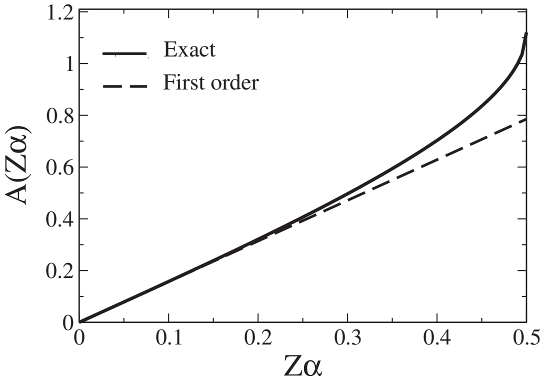

FIG. 1. The induced charge $Q_{\rm ind}/e \equiv A$ as a function of $Z\alpha$. The solid line is the exact result from Eq. (9) and the dashed line is the one-loop result $A^{(1)} = \pi(Z\alpha)/2$.

Self-consistent screening.—Since the induced charge is fully concentrated at the origin, one can easily take into account electron-electron interactions in the Hartree approximation. The Hartree contribution is expected to dominate over the Fock (exchange) contribution for $N \gg 1$ ($N = 4$, from the spin and valley degeneracy in graphene). To find the effective charge $Z_{\rm eff}$ in the Hartree approximation, it is sufficient to solve the following self-consistent equation:

$$Z_{\rm eff}\alpha = Z\alpha - \alpha A(Z_{\rm eff}\alpha). \tag{12}$$

If one uses the function $A(Z\alpha) = A^{(1)} = \pi(Z\alpha)/2$ calculated in the one-loop approximation, then this equation is equivalent to the usual random phase approximation (RPA). However, since the exact $A(Z\alpha)$ accounts for all orders in $Z\alpha$, Eq. (12) is more accurate than the RPA. In particular, for the case $Z = 1$, the self-consistent RPA and the full nonlinear theory lead to qualitatively different results (see below).

The solution $Z_{\rm eff}$ of Eq. (12) is a function of Z and α. The function $Z_{\rm eff}\alpha$ versus $Z\alpha$ is shown in Fig. 2 for different values of the bare charge Z. An impurity with charge $Z = 1$ represents the most important practical case. Interestingly, the impurity with $Z = 1$ remains subcritical for all values of α, i.e., $Z_{\rm eff}\alpha < 1/2$. The subcritical behavior is enforced by the strongly nonlinear variation of $A(Z\alpha)$, found in our exact calculation. Notice that the RPA alone would predict a transition to a supercritical regime at $\alpha \approx 2.25$. Impurities with $Z = 2$ and higher can become critical even in the exact theory. For $Z = 2$, 3 the critical points are $\alpha_c^{Z=2} = 0.568$ and $\alpha_c^{Z=3} = 0.266$, as shown in Fig. 2. The present technique is not applicable in the supercritical regime, although we expect (see below) that $Z_{\rm eff}\alpha$ will continue to grow continuously and slowly for $\alpha \geq \alpha_c$.

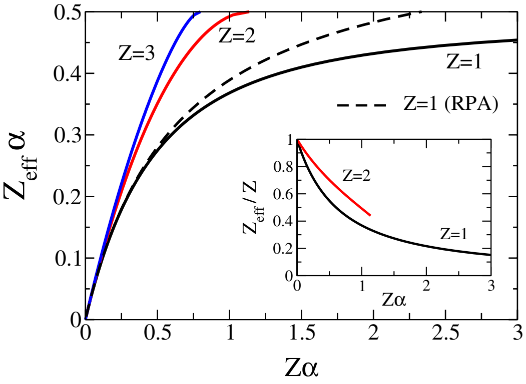

FIG. 2 (color online). The effective coupling $Z_{\rm eff}\alpha$ from Eq. (12) as a function of $Z\alpha$ for $Z = 1$ (black line), $Z = 2$ (red line), and $Z = 3$ (blue line). For comparison, the RPA result is also shown for $Z = 1$ (dashed line). Inset: Reduction of the impurity effective charge relative to its initial value, $Z_{\rm eff}/Z$.

Even though the supercritical regime is never reached for $Z = 1$, the screening is very substantial, as shown in the inset of Fig. 2. For example, for $\alpha = 0.5$, $Z = 1$, we find $Z_{\rm eff}/Z = 0.55$. In the case $Z = 2$, the effective charge $Z_{\rm eff}$ cannot be computed by our technique beyond $Z\alpha_c = 1.136$, when the impurity becomes supercritical. The ratio $Z_{\rm eff}/Z$, where $Z_{\rm eff}$ is defined as the effective point charge, will most likely continue to decrease continuously as a function of $Z\alpha$ beyond the critical point. This is expected because the relevant physics in the supercritical regime occurs at large length-scales [14,20], and thus the local behavior is presumably not strongly affected. It is well known from conventional QED that the supercritical problem requires a different technique [14], and therefore we leave this problem for a separate study.

The $Z = 1$ case is the most relevant experimentally, since alkali atoms, such as potassium [10], typically serve as charged scatterers in graphene. For graphene on SiO_2 substrate with typical dielectric constant $\varepsilon \approx 4$, the value of α is $\alpha \approx 0.9$ (using $e^2 \to 2e^2/(1 + \varepsilon)$). For such large α the vacuum polarization effect is very strong and could be important for interpretation of experiments [10].

In the present work we have considered half-filled graphene, exactly at the Dirac point (zero Fermi energy). However our results are also applicable for a finite small Fermi energy, and both cases are relevant experimentally [3]. The main observation is that the induced charge density is proportional to a δ-function, meaning that it is localized within one lattice spacing. As long as the Thomas-Fermi screening length, $\lambda \propto (\alpha k_F)^{-1} = v_F/(\alpha\epsilon_F)$, is large compared to the lattice spacing, the finite doping does not influence the short-range physics considered here. (On the other hand the Coulomb potential is affected at large distances, $r \gtrsim \lambda$, where it decreases faster than $1/r$.)

To summarize, we have presented an exact solution of the Coulomb impurity screening problem in graphene in the subcritical regime. The explicit result for the induced vacuum polarization charge, Eq. (9), is valid to all orders in the potential strength $Z\alpha$. The exact solution, when combined with the Hartree approximation, leads to a self-consistent solution of the impurity problem. An impurity with charge $Z = 1$ is found to be always in the subcritical regime, where the induced charge is localized at the impurity site. In this regime vacuum polarization screening is very strong and weakens substantially the impurity potential. However, impurities with $Z = 2$, 3 and higher can become supercritical.

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