Atomic Collapse and Quasi-Rydberg States in Graphene

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Charge impurities in graphene can host an infinite family of Rydberg-like resonance states of massless Dirac particles. These states, appearing for supercritical charge, are described by Bohr-Sommerfeld quantization of collapsing classical trajectories that descend on point charge, in analogy to Rydberg states relation with planetary orbits. We argue that divalent and trivalent charge impurities in graphene is an ideal system for realization of this atomic collapse regime. Strong coupling of these states to the Dirac continuum via Klein tunneling leads to striking resonance effects with direct signatures in transport, local properties, and enhancement of the Kondo effect.

The discovery of massless Dirac excitations in graphene 1 triggered new interest in solid-state realization of quantum electrodynamics (QED) 2,3,4. Transport phenomena in this system 2,3 can be used to probe classic concepts of QED, such as chiral dynamics 5, flavor degrees of freedom 6 and particle/hole co-existence 7. Here we demonstrate that graphene opens a way to investigate in the laboratory a fundamental quantum relativistic phenomenon, that is, atomic collapse in a strong Coulomb electric field 8,9,10, long sought for but still inaccessible in high-energy experiments 11.

Bohr’s theory of an atom has explained that, while an electron is irresistibly pulled to the nucleus by the Coulomb force, it is prevented from falling on it by the quantum mechanical zero-point motion. This balance, however, becomes more delicate in the relativistic theory. The effects undermining the stability of matter arise already in classical dynamics, where electron trajectory can spiral around the nucleus and eventually fall down on it 12 (see Fig.1a,b), provided that electron angular momentum is small enough: \( M < M_c = \frac{Ze^2}{c} \), where \( Z \) is nuclear charge. Quantum mechanics partially saves matter from collapse by imposing the angular momentum quantization \( M = n\hbar \), which makes the relativistic fall-down possible only for heavy \( Z > \frac{\hbar c}{e^2} \approx 137 \).

Early work on the Dirac-Kepler problem has revealed bizarre properties of atoms with nuclear charge in excess of \( Z = 137 \), posing as a fundamental bound on the periodic table of elements extent at large \( Z \). The breakdown at \( Z > 137 \) of the low-Z solution of the Dirac equation requires accounting for a finite nuclear radius 22. The resulting electron states dive into the hole continuum at \( Z > 170 \) and decay by positron emission 17,10,11. These phenomena, never observed in the laboratory due to the difficulty of producing heavy nuclei, should be more readily accessible in graphene owing to its large “fine structure constant,” \( \alpha = \frac{e^2}{\hbar c v_F} \approx 2.5 \), where \( v_F = 10^6 \text{ m/s} \) is the velocity of Dirac excitations.

Charge impurities are an essential ingredient of our current understanding of transport in graphene. Scattering on charge impurities explains 13,14,15 the linear density dependence of conductivity in this material 16, and is thus regarded as one of the main factors limiting carrier mobility. Recent investigations of screening of impurity potential 17,18,19,20,21 have only reinforced these conclusions, making graphene an ideal test system for the theory of Coulomb scattering 18,22 of massless Dirac particles.

In this work we show that, although massless particles cannot form bound states, an infinite family of quasi-bound states appears abruptly when the Coulomb potential strength exceeds a certain critical value \( \beta = \frac{1}{2} \). These states are obtained from Bohr-Sommerfeld quantization of collapsing orbits which descend on the point charge, similar to how the hydrogenic Rydberg states are
found from circular orbits. The energies of these states converge on zero, $\varepsilon_n \to 0$ at large $n$, whereas their radii diverge, similar to the Rydberg states. These results are corroborated by an exact solution of the 2D Dirac-Kepler problem. In graphene, the effective Coulomb potential strength is given by $\beta = Ze^2/\hbar v_F^2$ with intrinsic dielectric constant $\kappa \approx 5$, and therefore the critical value $\beta = 1/2$ can be reached already for the impurity charge $Z \gtrsim 1$. This is a lot more convenient from the experimental point of view than $Z > 170$ in heavy atoms.

Coupling of quasi-Rydberg states to the Dirac continuum, mediated by Klein tunneling, leads to strong resonances in the scattering cross-section, manifest in the radial dynamics separated from non-falling trajectories by a centrifugal barrier. This is implied in the radial dynamics $p_r^2 = v_F^2 \left( \varepsilon + \frac{Ze^2}{r} \right)^2 - \frac{M^2}{r^2}$, where $p_r$ is the radial momentum. This defines a classically forbidden region, the annulus $r_1 < r < r_2$, $r_{1,2} = (Ze^2 + M v_F)/\varepsilon$, where 1 is negative. The quasi-bound states trapped by this barrier can be found from the Bohr-Sommerfeld quantization condition $\int_{r_1}^{r_2} p_r \, dr = \pi n$, where $r_0$ is the lattice cutoff (cf. Refs. [24, 25]). Evaluating the integral with logarithmic accuracy, we obtain $\gamma \ln \frac{Ze^2}{r_0} = \pi n$, where $\gamma \equiv \left( M^2 - M^2 \right)^{1/2}$, which gives the quasi-Rydberg states

$$\varepsilon_n \approx \frac{Ze^2}{r_0} e^{-\pi n/\gamma}, \quad n > 0. \quad (2)$$

The energies (2) are equally spaced on the log scale with the separation diverging as $1/\gamma$ at the threshold $M_c \approx M$.

To find the transparency of the barrier, we integrate $\Im p_r$ to obtain the tunneling action

$$S = \int_{r_1}^{r_2} r \left[ \frac{M^2}{r^2} - \left( \frac{\varepsilon}{v_F} + \frac{M_c}{r} \right)^2 \right] = \pi (M_c - \gamma). \quad (3)$$

Taken near the threshold $\gamma \approx 0$, the transparency $e^{-2S/\hbar}$ gives the width $\Gamma_n \sim |\varepsilon_n| \exp(-2\pi Ze^2/\hbar v_F)$. Notably, since $S$ has no energy dependence, all the states (2) feature the same width-to-energy ratio.

It is instructive to compare these results to the exact solution of the Coulomb scattering problem. For that, we consider the Dirac equation for a massless electron in a potential $V(r) = \frac{Ze^2}{r}$, where $\beta \equiv -Ze^2/\hbar v_F$. (It will be convenient to include the minus sign in $\beta$ to explicitly account for attraction.) Performing standard angular decomposition and solving the radial equation separately in each angular momentum channel, one finds the scattering phases $\delta_m(k)$ that behave differently in the three regimes: (i) $\beta > \beta_m$, (ii) $-\beta_m < \beta < \beta_m$ and (iii) $\beta < -\beta_m$ ($\beta_m = |m + 1/2|$). As illustrated in Fig. [24], $\delta_m(k)$ are energy-independent in case (ii) and have a logarithmic dependence $\delta_m(k) \sim -\gamma \ln kr_0$ in case (i), where $\gamma = \sqrt{\beta^2 - \beta_m^2}$. In the case (iii) the dependence is described by kinks of height $\pi$ equally spaced on a log scale:

$$e^{i2\delta_m(k)} = e^{i\pi/\beta_m} \frac{z + e^{i\chi(k)}}{1 + e^{i\chi(k)} z^*}. \quad (4)$$

(see 18, Eq. (20)) where $z = \frac{e^{\pi/\eta} \Gamma(1+2i\gamma) \Gamma(-i\gamma+i\beta)}{\eta \Gamma(1-i\gamma) \Gamma(1+i\gamma+i\beta)}$, and

$$\chi(k) = 2\gamma \ln 2kr_0 + 2\arctan \frac{1+\eta}{\eta}, \quad \eta = \sqrt{\frac{\beta^2 - \beta_m^2}{\beta^2}}. \quad (5)$$

The average winding rate of the phase in case (iii), $\delta_m(k) \sim \gamma \ln kr_0$, is the same as in case (i) up to a sign (see Fig. [2]). The kinks signal the appearance of quasi-bound states at negative energies.

To find the quasi-bound states, we seek a scattering state with complex energy in which there is no incoming wave. This implies vanishing of the numerator (denominator) of (4) at $\varepsilon < 0$ ($\varepsilon > 0$). In the $\varepsilon < 0$ case we obtain an equation for $k$: $\varepsilon e^{i\chi(k)} = -z$. The right-hand
obtained quasiclassically, Eq. (2). The threshold \( \beta \) plays a role in the solutions similar to our quasiclassical result (2), which makes it impossible to satisfy it by a real \( k \). In contrast, \( \arg k \) is negative semi-axis. Thus there are no long-lived states upon \( \beta > \beta^0 \). For near-critical negative values \( \beta < -\frac{1}{2} \) we have \( \arg k \approx n \pi \), as illustrated in Fig. 1. (B) Transport cross-section (10) vs. potential strength. Fano resonances corresponding to quasi-bound states occur at \( \beta < -\frac{1}{2} \). The oscillatory behavior at \( \beta > \frac{1}{2} \) results from the energy dependence \( \delta_m(k) \sim -\gamma_m \) in \( kr_0 \). The cross-section asymmetry upon \( \beta \rightarrow -\beta \), with the values at \( \beta < 0 \) typically lower than at \( \beta > 0 \), reflects that the Klein barrier prevents particles from reaching the region of strong scattering \( r \sim 0 \).

This case all \( k_n \)'s are found near the negative real semi-axis (\( \varepsilon > 0 \)). This is in agreement with particle/hole symmetry.

Before discussing manifestations in graphene, where at finite carrier density the 1/r potential is screened, we note that the essential physics will be unaffected by screening as long as the quasi-bound states persist. At finite density, the RPA screening length is comparable to the Fermi wavelength \( \lambda_F = \hbar v_F/\varepsilon_F \) [13, 14, 15], whereas our quasiclassical estimate of the state radius gives \( r_1 \approx (M - M_F) v_F/|\varepsilon| \). The latter is much smaller than \( \lambda_F \) near \( \beta = \frac{1}{2} \), which means that RPA screening is non-detrimental for these states. Similarly, estimates for nonlinear screening [18] indicate that its effect is insessional at weak coupling, leaving enough room for quasi-bound states.

Resonance scattering on the quasi-bound states will manifest itself in the dependence of transport properties on the carrier density. Here we analyze electrical conductivity described by the Drude-like model (see Ref. [13]):

\[
\sigma = \frac{e^2}{\hbar} 2 \varepsilon_F \tau, \quad \tau^{-1} = v_F n_{imp} \sigma_{tr},
\]

where \( \varepsilon_F \) is the Fermi energy, \( n_{imp} \) is the concentration of charge impurities and \( \sigma_{tr} \) is the transport scattering cross-section for one impurity. We use the 2D scattering amplitude partial wave decomposition

\[
f(\varphi) = \frac{2i}{\sqrt{2\pi k}} \sum_{m=0}^{\infty} (e^{2im\pi} - 1) \cos(m + \frac{1}{2})\varphi,
\]
peaks at the densities for which the Fermi energy \( \varepsilon \) enters at \( \delta_m \approx \delta_{m+1} \), with the phases \( \delta_m \) given by (1) for overcritical channels (see Ref. [22] for subcritical channels).

For subcritical potential strength the phases are energy-independent and thus \( \sigma_t \) scales as \( 1/|\varepsilon| \), giving conductivity \( \sigma \) linear in the carrier density \( 14, 14, 15 \).

For \( |\beta| > \frac{1}{2} \) the contribution of the subcritical channels still scales as \( 1/|\varepsilon| \), while the overcritical channels, because of energy-dependent \( \delta(m) \), give an oscillatory contribution (cf. Fig. 2B). These oscillations, shown in Fig. 3 inset, have a characteristic form of Fano resonances centered at \( \varepsilon_n \). In this regime the conductivity \( \sigma \) exhibits peaks at the densities for which the Fermi energy \( \varepsilon_F \) aligns with \( \varepsilon_n \). As evident from Fig. 3 the peak position is highly sensitive to the potential strength \( \beta \), changing by an order of magnitude when \( \beta \) varies from \(-1.0 \) to \(-1.3 \), which is a combined effect of \( \varepsilon_F \) quadratic dependence on density and of the exponential dependence in \( |\theta| \).

Another striking feature in the conductivity vs. density plots in Fig. 3 is the \( n \to -n \) asymmetry, which results from the scattering cross-section being typically lower at \( \varepsilon < 0 \) than at \( \varepsilon > 0 \). Such asymmetry, noted already in the subcritical regime \([22]\), becomes more prominent in the supercritical regime because of the Klein barrier preventing particles with negative energies from reaching the strong scattering region \( r \sim 0 \).

The signatures of quasi-bound states, similar to those in conductivity, will be featured by other transport coefficients. In particular, they will be strong in the thermoelectric response because it is proportional to the energy derivative of \( \sigma_t \). Yet the most direct way to observe these states is via the local density of states (LDOS) \( \nu(\varepsilon, r) = \frac{4}{\pi \hbar v_F} \sum_m |\psi(k, r)|^2, \quad k_x = -\frac{\varepsilon}{\hbar v_F} \), (11)

where \( \psi \) is the two-component Dirac wave function (5) \([18]\). This quantity can be readily measured and scanned using tunneling spectroscopy probes. Evolving the sum over \( m \) in (11), we obtain LDOS map shown in Fig. 4.

Several quasi-bound states are seen in LDOS maps (Fig. 4) as local resonances at \( \varepsilon < 0 \). The values of \( \beta \) were chosen to illustrate that the width \( \Gamma \) of each resonance scales with \( \varepsilon \), while its spatial extent scales as \( 1/|\varepsilon| \), in agreement with our quasiclassical analysis and Eq. (7).

A distinct advantage of local probes, as opposed to transport, is that the supercritical impurities do not need to be a majority. In fact, it suffices to locate just one non-univalent impurity and perform STM imaging in vicinity. Alternatively, one can identify groups of two or three univalent impurities that together will act as one supercritical impurity, or even deliberately create such a group by inducing local charge by voltage applied to STM tip.

The resonances (10) also give rise to anomalously strong Kondo-like effects. The striking property of the linewidth (7), namely, its proportionality to the energy (see Fig. 4), indicates that the dwell time diverges at \( \varepsilon \to 0 \). This divergence compensates the suppression of Kondo temperature \( T_F \) by the Dirac \( |\varepsilon| \) density of states. Standard estimates \([31]\) for the Anderson model with the localized spin state associated with one of our resonant levels yield the Kondo temperature exponent that exhibits no suppression at \( \varepsilon_F \to 0 \). This is in contrast to the Kondo problem with extraneous spin impurities \([32, 33]\).

In summary, although massless particles are incapable of forming discrete states, an infinite family of quasi-Rydberg states can appear in a Coulomb potential of supercritical strength. These quasi-bound states manifest themselves in a variety of physical properties, in particular in resonant scattering and local resonances, providing a striking signature of the atomic collapse regime that can be modeled using charge impurities in graphene.

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FIG. 4: Spatial map of the local density of states (LDOS) near a charge impurity. The signatures of the quasi-bound states are resonances appearing at \( \beta < -\frac{1}{2} \) at \( r \sim 0 \) and \( \varepsilon < 0 \) (marked by arrows). Note the localization length that scales inversely with \( \varepsilon \), and the linewidth proportional to \( \varepsilon \), as predicted by Eq. (7). The intensity of the resonances is well in excess of the asymptotic value \( \nu(\varepsilon) \propto |\varepsilon| \) at large \( r \). Periodic modulation at \( |\varepsilon| > 0 \) with maxima at \( kr \approx \pi n \) is the standing wave oscillation \( 18, (k = \varepsilon/\hbar v_F, \varepsilon_0 = 10^{-3} \hbar v_F/r_0) \).

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