Tuning Kondo physics in Graphene with gate voltage

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We show theoretically that graphene, which exhibits a massless Dirac like spectrum for its electrons, can exhibit unconventional Kondo effect that can be tuned by an experimentally controllable applied gate voltage. We demonstrate the presence of a finite critical Kondo coupling strength in neutral graphene. We discuss the possibility of multichannel Kondo effect in this system which might lead to a non-Fermi liquid like ground state and provide a discussion of possible experimental realization of Kondo phenomenon in graphene.

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Graphene, a two-dimensional single layer of graphite, has been recently fabricated by Novoselov *et. al.* [1]. In graphene, the energy bands touch the Fermi energy at six discrete points at the edges of the hexagonal Brillouin zone. Out of these six Fermi points, only two are inequivalent; they are commonly referred to as K and K' points [2]. The quasiparticle excitations about these K and K' points obey linear Dirac-like energy dispersion. The presence of such Dirac-like quasiparticles is expected to lead to a number of unusual electronic properties in graphene including relativistic quantum hall effect with unusual structure of Hall plateaus [3]. Recently, experimental observation of the unusual plateau structure of the Hall conductivity has confirmed this theoretical prediction [4]. Further, the presence of Dirac-like quasiparticles in graphene provides us with an experimental test bed for Klein paradox [4], transmission resonance [5] and Lorenz-boost [6] type phenomena.

An extremely interesting phenomenon in conventional metal systems is the Kondo effect which occurs in the presence of dilute concentration of localized quantum spins coupled to the spin-degenerate Fermi sea of metal electrons [7]. The impurity spin-electron interaction then results in perfect or partial screening of the impurity spin leading to an apparently divergent resistance, as one approaches zero temperature. It also results in a sharp 'Kondo Resonance' in electron spectral functions. Recent developments in quantum dots and nano devices have given new ways in which various theoretical results in Kondo physics, which are not easily testable otherwise, can be tested and confirmed experimentally [8]. Most of the early studies in Kondo effect were carried on for conventional metallic systems with constant density of states (DOS) at the Fermi surface [9]. Some studies on Kondo effect in possible flux phases [10], nodal quasiparticles in d-wave superconductors [11], Luttinger liquids [12], and hexagonal Kondo lattice [13], for which the DOS of the associated Fermions vanishes as some power law at the Fermi surface, has also been undertaken. However, although effect of non-magnetic impurities has been studied [14], there has been no theoretical study till date on the nature of Kondo effect in graphene.

In this letter we present a large N analysis for a generic local moment coupled to Dirac electrons in graphene to show that Kondo effect in graphene is unconventional can be tuned by gate voltage. We demonstrate the presence of a finite critical Kondo coupling strength in neutral graphene. We point out that local moments in graphene can lead to non Fermi-liquid ground state via multi channel Kondo effect. We also suggest possible experimental realization of such Kondo scatterers in graphene.

The crucial requirement for occurrence of Kondo effect is that the embedded impurities should retain their magnetic moment in the presence of conduction of electrons of graphene. We will not quantitatively address the problem of local moment formation in the presence of Dirac sea of electrons in graphene in the present paper. We expect that large band width and small linearly vanishing density of states at the fermi level in graphene should make survival of impurity magnetic moment easier than in the conventional 3D metallic matrix. A qualitative estimate of the resultant Kondo coupling can be easily made considering hybridization of electrons in π band in graphene with d orbitals of transition metals. Typical hopping matrix elements for electrons in π band is $t \sim 2$eV and effective Hubbard U in transition metals is 8eV. So the Kondo exchange $J \sim 4t^2/U$, estimated via standard Schrieffer-Wolf transformation, can be as large as 2 eV which is close to one of the largest $J \simeq 2.5$ eV for Mn in Zn. In the rest of this work, we shall therefore use the Kondo Hamiltonian [15] as our staring point.

Our analysis begins with the Hamiltonian for non-interacting Dirac electron in graphene. In the presence of a gate voltage V, the Hamiltonian can be expressed in terms of electron annihilation operators $\Psi^s_{A(B)\alpha}$ at sublattice $A(B)$ and Dirac point $s = K, K$ with spin $\alpha = \uparrow, \downarrow$ as

$$H = \int \frac{d^2k}{(2\pi)^2} \left(\Psi^{s\dagger}_{A\alpha}(\mathbf{k}), \Psi^{s\dagger}_{B\alpha}(\mathbf{k})\right) \times \begin{pmatrix} eV & \hbar v_F(k_x - i\mathrm{sgn}(s)k_y) \\ \hbar v_F(k_x + i\mathrm{sgn}(s)k_y) & eV \end{pmatrix} \begin{pmatrix} \Psi^s_{A\alpha}(\mathbf{k}) \\ \Psi^s_{B\alpha}(\mathbf{k}) \end{pmatrix} \quad (1)$$

where $\mathrm{sgn}(s) = 1(-1)$ for $s = K(K')$, v_F is the Fermi velocity of graphene, and all repeated indices are summed over. In Eq. 1 and in rest of the work, we shall use an upper momentum cutoff $k_c = \Lambda/(\hbar v_F)$, where $\Lambda \simeq$ 2eV corresponds to energy up to which the linear Dirac dispersion is valid, for all momenta integrals.

Eq. 1 can be easily diagonalized to obtain the eigenvalues and eigenfunctions of the Dirac electrons: $E_\pm = eV \pm \hbar v_F k$ where $\mathbf{k} = (k_x, k_y) = (k, \theta)$ denote momenta in graphene and $(u_A^{s\pm}, u_B^{s\pm}) = 1/\sqrt{2}\,(1, \pm \exp(i\mathrm{sgn}(s)\theta))$. Following Ref. [10], we now introduce the ξ fields, which represents low energy excitations with energies $E_\pm$, and write

$$\begin{aligned}\Psi^s_{A\alpha}(\mathbf{k}) &= \sum_{j=\pm} u_A^{sj}\xi^s_{j\alpha} = 1/\sqrt{2}(\xi^s_{+\alpha}(\mathbf{k}) + \xi^s_{-\alpha}(\mathbf{k})),\\ \Psi^s_{B\alpha}(\mathbf{k}) &= \exp(i\theta)/\sqrt{2}(\xi^s_{+\alpha}(\mathbf{k}) - \xi^s_{-\alpha}(\mathbf{k})). \qquad (2)\end{aligned}$$

In what follows, we shall consider a single impurity to be centered around $\mathbf{x} = 0$. Thus to obtain an expression for the coupling term between the local moment and the conduction electrons, we shall need to obtain an expression for $\Psi(\mathbf{x} = 0) \equiv \Psi(0)$. To this end, we expand the ξ fields in angular momentum channels $\xi^s_{+\alpha}(\mathbf{k}) = \sum_{m=-\infty}^{\infty} e^{im\theta}\xi^{ms}_{+\alpha}(k)$, where we have written $\mathbf{k} = (k, \theta)$. After some straightforward algebra, one obtains

$$\begin{aligned}\Psi^s_{B\alpha}(0) &= \frac{1}{\sqrt{2}}\int_0^{k_c}\frac{kdk}{2\pi}\left(\xi^{-\mathrm{sgn}(s)s}_{+\alpha}(k) - \xi^{-\mathrm{sgn}(s)s}_{-\alpha}(k)\right),\\ \Psi^s_{A\alpha}(0) &= \frac{1}{\sqrt{2}}\int_0^{k_c}\frac{kdk}{2\pi}\left(\xi^{0s}_{+\alpha}(k) + \xi^{0s}_{-\alpha}(k)\right). \qquad (3)\end{aligned}$$

Note that $\Psi_B(0)$ receives contribution from $m = \pm 1$ channel while for $\Psi_A(0)$, the $m = 0$ channel contributes. The Kondo coupling of the electrons with the impurity spin is given by

$$H_K = \frac{g}{2k_c^2}\sum_{s=1}^{N_s}\sum_{l=1}^{N_f}\sum_{\alpha,\beta=1}^{N_c}\sum_{a=1}^{N_c^2-1}\Psi^{s\,\dagger}_{l\alpha}(0)\tau^a_{\alpha\beta}\Psi^s_{l\beta}(0)S^a, \qquad (4)$$

where g is the effective Kondo coupling for energy scales up to the cutoff Λ, $\mathbf{S}$ denotes the spin at the impurity site, τ are the generators of the SU(N_c) spin group, and we have now generalized the fermions, in the spirit of large N analysis, to have N_s flavors (valley indices) N_f colors (sublattice indices) and N_c spin. For realistic systems $N_f = N_c = N_s = 2$. Here we have chosen Kondo coupling g to be independent of sublattice and valley indices. This is not a necessary assumption. However, we shall avoid extension of our analysis to flavor and/or color dependent coupling term for simplicity. Also, the Dirac nature of the graphene conduction electrons necessitates the Kondo Hamiltonian to mix $m = \pm 1$ and $m = 0$ channels (Eqs. 3 and 4). This is in complete contrast to the conventional Kondo systems where the Kondo coupling involves only $m = 0$ angular momentum channel.

The kinetic energy of the Dirac electrons can also be expressed in terms of the ξ fields: $H_0 = \int_0^\infty \frac{kdk}{2\pi}\sum_{m=-\infty}^{\infty}\sum_{s,\alpha}\left(E_+(k)\xi^{ms\,\dagger}_{+\alpha}\xi^{ms}_{+\alpha} + E_-(k)\xi^{ms\,\dagger}_{-\alpha}\xi^{ms}_{-\alpha}\right)$. Typically such a term involves all angular momenta channels. For our purpose here, it will be enough to consider the contribution from electrons in the $m = 0, \pm 1$ channels which contribute to scattering from the impurity (Eqs. 3 and 4). To make further analytical progress, we now unfold the range of momenta k from $(0, \infty)$ to $(-\infty, \infty)$ by defining the fields $c^s_{1(2)\alpha}$

$$\begin{aligned}c^s_{1(2)\alpha}(k) &= \sqrt{|k|}\xi^{0(-\mathrm{sgn}(s))s}_{+\alpha}(|k|), \quad k > 0,\\ c^s_{1(2)\alpha}(k) &= +(-)\sqrt{|k|}\xi^{0(-\mathrm{sgn}(s))s}_{-\alpha}(|k|), \quad k < 0, \qquad (5)\end{aligned}$$

so that one can express the Ψ fields as $\Psi^s_{A(B)\alpha}(0) = \int_{-\infty}^{\infty}\frac{dk}{2\pi}\sqrt{|k|}c^s_{1(2)\alpha}(k)$. In terms of the $c^s_{1(2)\alpha}$ fields, the kinetic energy (in the $m = 0, \pm 1$ channels) and the Kondo terms in the Hamiltonian can therefore be written as

$$\begin{aligned}H_0 &= \int_{-k_c}^{k_c} dk/(2\pi)E_k c^{s\,\dagger}_{l\alpha}c^s_{l\alpha}\\ H_K &= g/(8\pi^2k_c^2)\int_{-k_c}^{k_c}\int_{-k_c}^{k_c}\sqrt{|k|}\sqrt{|k'|}dkdk'\\ &\quad\times\left(c^{s\,\dagger}_{l\alpha}(k)\,\tau^a_{\alpha\beta}\,c^s_{l\beta}(k')\,S^a\right), \qquad (6)\end{aligned}$$

where $E_k = eV + \hbar v_F k$ and summation over all repeated indices are assumed.

Next we follow standard procedure [16] of representing the local spin by SU(N_c)Fermionic fields f_α and write the partition function of the system in terms of the f and c fields

$$\begin{aligned}Z &= \int \mathcal{D}c\mathcal{D}c^\dagger\mathcal{D}f\mathcal{D}f^\dagger\mathcal{D}\epsilon\, e^{-S/\hbar}, \quad S = S_0 + S_1 + S_2\\ S_0 &= \int_0^{\beta\hbar}d\tau\int_{-k_c}^{k_c}dk/(2\pi)\left(c^{s\,\dagger}_{l\alpha}(k,\tau)G_0^{-1}c^s_{l\alpha}(k,\tau)\right),\\ S_1 &= J/(4\pi^2N_ck_c^2)\int_0^{\beta\hbar}d\tau\int_{-k_c}^{k_c}\int_{-k_c}^{k_c}\sqrt{|k|}\sqrt{|k'|}dkdk'\\ &\quad\times\left[c^{s\,\dagger}_{l\alpha}(k,\tau)\,\tau^a_{\alpha\beta}\,c^s_{l\beta}(k',\tau)f^\dagger_\gamma(\tau)\tau^a_{\gamma\delta}f_\delta(\tau)\right]\\ S_2 &= \int_0^{\beta\hbar}d\tau\left[\left(f^\dagger_\alpha(\tau)\left[\hbar\partial_\tau + \epsilon(\tau)\right]f_\alpha(\tau)\right) - \epsilon(\tau)Q\right], \qquad (7)\end{aligned}$$

where $G_0^{-1} = \hbar\partial_\tau + E_k$ is the propagator for c fields, $J = gN_c/2$ is the renormalized Kondo coupling, we have imposed the impurity site occupancy constraint $\sum_\alpha f^\dagger_\alpha f_\alpha = Q$ using a Lagrange multiplier field $\epsilon(\tau)$.

We now use the identity $\tau^a_{\alpha\beta}\tau^a_{\gamma\delta} = N_c\delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta}$ [16] and decouple S_1 using a Hubbard-Stratonovitch field ϕ^s_l. In the large N_c limit one has $S = S_0 + S_2 + S_3 + S_4$,

where

$$S_3 = \int_0^{\beta\hbar} d\tau \int_{-k_c}^{k_c} \frac{\sqrt{|k|}dk}{(2\pi)} \left(\phi_l^{*\,s}(\tau) c_{l\alpha}^{s\,\dagger}(k,\tau) f_\alpha(\tau) + \text{h.c}\right)$$
$$S_4 = N_c k_c^2/J \int_0^{\beta\hbar} d\tau \phi_l^{*\,s}(\tau)\phi_l^s(\tau). \quad (8)$$

Note that at the saddle point level $\langle\phi_l^s\rangle \sim \left\langle \sum_\alpha c_{l\alpha}^{s\,\dagger} f_\alpha \right\rangle$ so that a non-zero value of ϕ_l^s indicates the Kondo phase. In what follows, we are going to look for the static saddle point solution with $\phi_l^s(\tau) \equiv \phi_0$ and $\epsilon(\tau) \equiv \epsilon_0$ [16]. In this case, it is easy to integrate out the c and f fields, and obtain an effective action in terms of ϕ_0 and ϵ_0 and one gets $S' = S_5 + S_6$ with

$$S_5 = -\beta\hbar N_c \text{Tr}\left[\ln\left(i\hbar\omega_n - \epsilon_0 - N_s N_f \phi_0^* G_0'(i\omega, V)\phi_0\right)\right],$$
$$S_6 = \beta\hbar\left(N_s N_c N_f k_c^2 \left|\phi_0\right|^2/J - \epsilon_0 Q\right), \quad (9)$$

where Tr denotes Matsubara frequency sum as well as trace over all matrices and the Fermion Green function $G_0'(ip_n, q) \equiv G_0'$ is given by [10]

$$G_0' = \frac{-\Lambda}{2\pi(\hbar v_F)^2}(ip_n - q)\ln\left[1/\left|ip_n - q\right|^2\right], \quad (10)$$

where, in the last line we have switched to dimensionless variables $p_n = \hbar\omega_n/\Lambda$ and $q = eV/\Lambda$.

One can now obtain the saddle point equations from Eq. 9 which are given by $\delta S'/\delta\phi_0 = 0$ and $\delta S'/\delta\epsilon_0 = 0$. Using Eqs. 9 and 10, one gets (after continuing to real frequencies and for $T = 0$)

$$1/J = -\Lambda/(\pi\hbar v_F k_c^2)^2 \int_{-1}^{0} dp\, G_0(p - \nu - \Delta_0 G_0/2)^{-1},$$
$$Q/N_c = 1/(2\pi)\int_{-1}^{0} dp\, \nu(p - \nu - \Delta_0 G_0/2)^{-1}, \quad (11)$$

where we have defined the dimensionless variable $\Delta_0 = N_f N_s |\phi_0|^2/(\pi\hbar^2 v_F^2)$, $p = \hbar\omega/\Lambda$, $G_0 = 2\pi(\hbar v_F)^2 G_0'/\Lambda$, $\nu = \epsilon_0/\Lambda \geq 0$, and have used the energy cutoff Λ for all frequency integrals. At the critical value of the coupling strength, putting $\nu = 0$ and $\Delta_0 = 0$, we finally obtain the expression for $J_c(q,T)$

$$J_c(q,T) = J_c(0)\left[1 - 2q\ln\left(1/q^2\right)\ln\left(k_B T/\Lambda\right)\right]^{-1} \quad (12)$$

where the temperature $k_B T$ is the infrared cutoff, $J_c(0) = (\pi\hbar v_F k_c^2)^2/\Lambda = \pi^2\Lambda$ is the critical coupling in the absence of the gate voltage, and we have omitted all subleading non-divergent term which are not important for our purpose. For $V = 0 = q$, we thus have, analogous to the Kondo effect in flux phase systems [10], a finite critical Kondo coupling $J_c(0) = \pi^2\Lambda \simeq 20$eV which is a consequence of vanishing density of states at the Fermi energy for Dirac electrons in graphene. Of course, the mean-field theory overestimates J_c. A quantitatively accurate estimate of J_c requires a more sophisticated analysis which we have not attempted here.

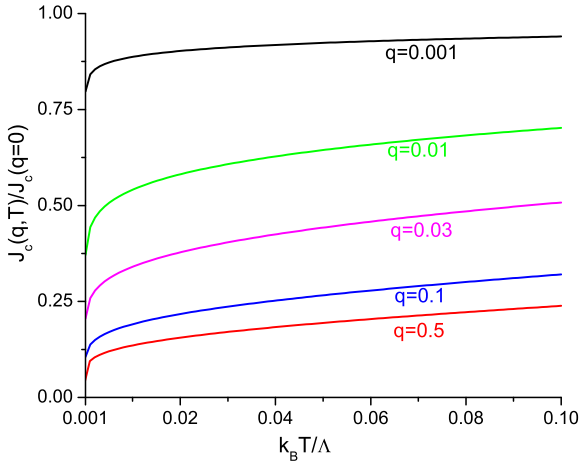

FIG. 1: Sketch of the critical Kondo coupling $J_c(q,T)$ as a function of temperature for several applied voltages $q = eV/\Lambda$. The Kondo phase exists for $J > J_c$.

The presence of a gate voltage leads to a Fermi surface and consequently $J_c(q,T) \to 0$ as $T \to 0$. For a given experimental coupling $J < J_c(0)$ and temperature T, one can tune the gate voltage to enter a Kondo phase. Fig. 1, which shows a plot of $J_c(q,T)$ as a function of T for several gate voltages q illustrates this point. The temperature $T^*(q)$ below which the system enters the Kondo phase for a physical coupling J can be obtained using $J_c(q,T^*) = J$ which yields

$$k_B T^* = \Lambda \exp\left[(1 - J_c(0)/J)/(2q\ln[1/q^2])\right] \quad (13)$$

For a typical $J \simeq 2$eV and voltage $eV \simeq 0.5$eV, $T^* \simeq 35$K [17]. We stress that even with overestimated J_c, physically reasonable J leads to experimentally achievable T^* for a wide range of experimentally tunable gate voltages.

We now discuss the possible ground state in the Kondo phase qualitatively. In the absence of the gate voltage a finite J_c implies that the ground state will be non-Fermi liquid as also noted in Ref. [10] for flux phase systems. In view of the large J_c estimated above, it might be hard to realize such a state in undoped graphene. However, in the presence of the gate voltage, if the impurity atom generates a spin half moment and the Kondo coupling is independent of the valley(flavor) index, we shall have a realization of two-channel Kondo effect in graphene owing to the valley degeneracy of the Dirac electrons. This would again lead to overscreening and thus a non Fermi-liquid like ground state [9]. The study of details of such a ground state necessitates an analysis beyond our large N mean-field theory. To our knowledge, such an analysis

has not been undertaken for Kondo systems with angular momentum mixing. In this work, we shall be content with pointing out the possibility of such a multichannel Kondo effect in graphene and leave a more detailed analysis as an open problem for future work.

Next, we discuss experimental observability of the Kondo phenomena in graphene. The main problem in this respect is creation of local moment in graphene. There are several routes to solving this problem. i) Substitution of a carbon atom by a transition metal atom. This might in principle frustrate the strong sp^2 bonding and thus locally disturb the integrity of graphene atomic net. However, nature has found imaginative ways of incorporating transition metal atoms in p-π bonded planar molecular systems such as porphyrin [18]. Similar transition metal atom incorporation in extended graphene, with the help of suitable bridging atoms, might be possible. ii) One can try chemisorption of transition metal atoms such as Fe on graphene surface through sp-d hybridization in a similar way as in intercalated graphite [19]. iii) It might be possible to chemically bond molecules or free radicals with magnetic moment on graphene surface as recently done with cobalt pthalocyanene (CoPc) molecule on AU(111) surface [20]. This might result in a strong coupling between graphene and impurity atom leading to high Kondo temperatures as seen for CoPc on AU(111) surface ($T_K \simeq 280K$). iv) Recently ferromagnetic cobalt atom clusters with sub nanometer size, deposited on carbon nanotube, have exhibited Kondo resonance[21]. Similar clusters deposition in graphene might be a good candidate for realization of Kondo systems in graphene. v) From quantum chemistry arguments, a carbon vacancy, or substitution of a carbon atom by a boron or nitrogen might lead to a spin-half local moment formation. In particular, it has been shown that generation of local defects by proton irradiation can create local moments in graphite [22]. Similar irradiation technique may also work for graphene.

For spin one local moments and in the presence of sufficiently large voltage and low temperature, one can have a conventional Kondo effect in graphene. The Kondo temperature for this can be easily estimated using $k_B T_K \sim D\exp(-1/\rho J)$ where the band cutoff $D \simeq 10$eV, $J \simeq 2-3$eV and DOS per site in graphene $\rho \simeq 1/20$ per eV. This yield $T_K \simeq 6-150$K. The estimated value of T_K has rather large variation due to exponential dependence on J. However, we note that Kondo effect due to Cobalt nano-particle in graphitic systems such as carbon nanotube leads to a high $T_K \approx 50K$ which means that a large J may not be uncommon in these systems.

Finally, we note that recent experiments have shown a striking conductance changes in carbon nanotubes and graphene, to the extent of being able to detect single paramagnetic spin-half NO_2 molecule [23]. This has been ascribed to conductance increase arising from hole doping (one electron transfer from graphene to NO_2). Although Kondo effect can also lead to conductance changes, in view of the fact that a similar effect has been also seen for diamagnetic NH_3 molecules, the physics in these experiments is likely to be that of charge transfer and not local moment formation.

In conclusion, we have shown that the Kondo effect in graphene is unconventional and can be tuned by an applied gate voltage. We have shown that it is possible to have multichannel Kondo effect in graphene and discussed experimental possibilities of its realization.

After submission of the first version of this manuscript in the arXiv (arXiv:0705.0257, v1), we became aware of Ref. [24] with similar conclusion regarding existence of finite critical Kondo coupling in neutral graphene.

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