Scanning tunneling spectroscopy of a magnetic atom on graphene in the Kondo regime

Huai-Bin Zhuang\(^1\), Qing-feng Sun\(^{(a)}\) and X. C. Xie\(^{1,2}\)

\(^1\) Beijing National Lab for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences
Beijing 100190, China
\(^2\) Department of Physics, Oklahoma State University - Stillwater, OK 74078, USA

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Abstract – The Kondo effect in the system consisting of a magnetic adatom on the graphene is studied. By using the non-equilibrium Green function method with the slave-boson mean-field approximation, the local density of state (LDOS) and the conductance are calculated. For a doped graphene, the Kondo phase is present at all time. Surprisingly, two kinds of Kondo regimes are revealed. But for the undoped graphene, the Kondo phase only exists if the adatom’s energy level is beyond a critical value. The conductance is similar to the LDOS, thus, the Kondo peak in the LDOS can be observed with the scanning tunneling spectroscopy. In addition, in the presence of a direct coupling between the STM tip and the graphene, the conductance may be dramatically enhanced, depending on the coupling site.

Graphene, a single-layer hexagonal lattice of carbon atoms, has recently attracted a great deal of attention due to its unique properties and potential applications \([1,2]\). The graphene has a unique band structure with a linear dispersion near the Dirac points, such that its quasi-particles obey the two-dimensional Dirac equation and have the relativistic-like behaviors. For a neutral graphene, the Fermi level passes through the Dirac points and the density of states (DOS) at the Fermi surface vanishes, so that its transport properties are greatly deviated from that of a normal metal.

The Kondo effect has been paid great attention in condensed-matter community over the years \([3–5]\). It is a prototypical many-body correlation effect involving the interaction between a localized spin and free electrons. The Kondo effect occurs in the system of a magnetic impurity embedded in a metal \([3–5]\) or a quantum dot coupled to the leads \([6–8]\), in which the magnetic impurity or the quantum dot acts as a localized spin. At low temperature, the localized spin is screened by the free electrons, resulting a spin singlet and a very narrow Kondo peak located near the Fermi surface in the local DOS (LDOS).

For a conventional metal, it has a finite DOS at the Fermi surface, thus, at zero temperature the Kondo effect can occur with any weak exchange interaction \(J_{ex}\) between the magnetic impurity and the free electrons. But in certain special systems, such as the nodal \(d\)-wave superconductors or the Luttinger liquids, the DOS vanishes at the Fermi surface with power law behavior. In these systems, there exists a critical exchange coupling \(J_c\), and the Kondo effect only occurs when the exchange interaction \(J_{ex} > J_c\) \([9]\).

The graphene, which was successfully fabricated in recent years, has a unique band structure \([1]\). For the undoped neutral graphene, its DOS is directly proportional to the energy \(|\epsilon|\) and the DOS vanishes at the Fermi surface, so it has an unconventional Kondo effect.

Very recently, some studies have investigated the Kondo effect in the graphene and a finite critical Kondo coupling strength was revealed \([10,11]\). By varying the gate voltage, the charge carriers of graphene can be easily tuned experimentally. Then the Fermi level can be above or below the Dirac points, and the DOS depends on the energy \(\epsilon\) in the form \(|\epsilon - \epsilon_0|\), with the Dirac-point energy denoted by \(\epsilon_0\). In this situation, the DOS is quite small but finite at the Fermi surface. In addition, there exists a zero point in DOS that is very close to the Fermi surface. How is the Kondo effect affected by this unique energy band structure?

In this letter, we study the Kondo effect in the graphene. We consider the model of a magnetic adatom on the graphene and to investigate its scanning tunneling spectroscopy of a magnetic atom on graphene in the Kondo regime.
spectroscopy by attaching a STM tip near the magnetic adatom (see fig. 1). Taking the slave-boson (SB) mean-field approximation and using the non-equilibrium Green function method, the expressions of the LDOS and conductance are obtained. Our results exhibit that for the doped graphene the Kondo phase always exists; however, two kinds of Kondo regimes emerge. For the undoped neutral graphene, the Kondo phase only exists when the energy level \( \epsilon_d \) of the adatom is larger than a critical value \( \epsilon_{dc} \).

The above-mentioned system can be described by the Anderson Hamiltonian. Here the magnetic atom is modeled by a single level \( \epsilon_d \) with the spin index \( \sigma = \uparrow, \downarrow \) and a constant on-site Coulomb interaction \( U \). In the limit \( U \to \infty \), the double occupancy is forbidden. Then the SB representation can be applied, and the Hamiltonian of the Anderson model describing the system is transformed to the following form [12]:

\[
H = \sum_{\sigma} \epsilon_d n_{\sigma} + \sum_{i,\sigma} \epsilon_0 a_{i,\sigma}^\dagger a_{i,\sigma} + \frac{t}{2} \sum_{\langle j,\sigma \rangle} a_{j,\sigma}^\dagger a_{j,\sigma} + \sum_{k,\sigma} \epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,\sigma} (t_L c_{k,\sigma}^\dagger f_{\sigma} b_{\sigma}^\dagger + t_{LR} c_{k,\sigma}^\dagger a_{\sigma} + H. c.) + \sum_{\sigma} (t_R f_{\sigma}^\dagger b a_{0,\sigma} + H. c.) + \lambda \left( b^\dagger b + \sum_{\sigma} n_{\sigma} - 1 \right),
\]

(1)

where \( n_{\sigma} = f_{\sigma}^\dagger f_{\sigma} \). \( a_{i,\sigma} \) and \( c_{k,\sigma} \) are the annihilation operators at the discrete site \( i \) of the graphene and the tip of STM, respectively. Here the graphene is assumed to be two dimensional and without disorder. In Hamiltonian (1), the graphene is described by the tight-binding model and only the nearest-neighbor hopping \( t \) is considered. \( f_\sigma \) and \( b_\sigma \) are the pseudofermion operator and SB operator of the magnetic atom. The last term represents the single-occupancy constraint \( b^\dagger b + \sum_{\sigma} n_{\sigma} = 1 \) with Lagrange multiplier \( \lambda \). The magnetic atom couples to the graphene at the lattice site 0 with the coupling coefficient \( t_R \). The STM tip couples to both of the magnetic atom and graphene, and \( t_L \) and \( t_{LR} \) are their coupling coefficients. Here we consider that the STM tip only contacts to a lattice site \( J \) of the graphene. Following, we take the standard SB mean-field approximation in which the operator \( b \) is replaced by the \( c \)-number \( \langle b \rangle \). This approximation is qualitatively correct for describing the Kondo regime at zero temperature [12]. For convenience, we also introduce the renormalized energy \( \epsilon_{d} \equiv \epsilon_d + \lambda \) and hopping elements \( t_L \equiv tl \langle b \rangle \) and \( t_{LR} \equiv tr \langle b \rangle \).

Next, we consider that a bias \( V \) is applied between the STM tip and the graphene to obtain the current \( I \) flowing from STM to the graphene and the LDOS around the magnetic atom. By using the non-equilibrium Green function method, the current \( I \) and LDOS are [13]:

\[
I = \frac{4e}{h} \int d\omega \text{Re} \left[ t_L G_{JJ}^< (\omega) + t_{LR} G_{JJ}^< (\omega) \right],
\]

(2)

\[
\text{LDOS}(\omega) = -(1/\pi) \text{Im} G_{JJ}^r (\omega),
\]

(3)

where \( G^< \) and \( G^r \) are the standard lesser and retarded Green’s functions, and \( G_{JJ}^</r \) in eq. (2) and eq. (3) are the elements of the matrix \( G^</r \). Under the SB mean-field approximation, \( G^< \) \ and \( G^r \) \ can be solved from the Keldysh and Dyson equations: \( G^< = (1 + G^r \Sigma^r)G^< (1 + \Sigma^r G^<) \) \ and \( G^r = (G^< - \Sigma^r)^{-1} \), where \( \Sigma^r, \Sigma^r \) \ are the self-energies. \( \Sigma^r_{JJ} = \Sigma^r_{LJ} = \Sigma^r_{LR} \) \ and other elements of \( \Sigma^r \) \ are zero. \( G^r < \) are the Green’s functions of the isolated STM tip, magnetic atom, and graphene \( i.e. \) while \( t_L = t_R = t_{LR} = 0 \). They can easily be obtained: \( g_{JJ}^< (\omega) = \sum_k g_k^< = -i\pi \rho_L \) \ and \( g_{JJ}^r (\omega) = 1/(\omega - i\pi) \) \ and \( g_{JJ}^r (\omega) = \sum_k g_k^r = 2i\pi \rho_L f_L (\omega) \), \( g_{JJ}^r (\omega) = -f_L (\omega)(\langle g_{JJ}^r \rangle - \langle g_{JJ}^r \rangle) \), and

\[
g_{JJ}^r (\omega) = \int d\lambda [t_{a,\lambda} d_{a,\lambda} \epsilon_{a,\lambda} (\langle x, y \rangle_{a,\lambda} + \langle y, x \rangle_{a,\lambda}) g_{a,\lambda}^r (\omega) d_{a,\lambda}^\dagger (\omega) ,
\]

(4)

where \( \rho_L \) \ is the DOS of the STM tip, \( f_L (\omega) \) \ and \( f_R (\omega) \) \ are the Fermi-Dirac distribution functions in the isolated STM tip and graphene, respectively. \( g_{JJ}^r < (\omega) \) \ are the Green’s functions of the isolated graphene, and \( i = (x, y) \) \ and \( j = (x, y) \) \ are the indices of the unit cell. Since there are two carbon atoms per unit cell, \( g_{JJ}^r < (\omega) \) \ is a \( 2 \times 2 \) matrix. In eq. (4) and eq. (5), \( a \) \ is the lattice constant of the graphene. The integral \( d\lambda d_{a,\lambda} \) \ runs over the Brillouin zone, and \( \phi = t(1 + e^{-iak_x} + e^{-iak_x} + iak_y) \).

At the end we need to self-consistently calculate two unknowns \( \langle b \rangle \) \ and \( \lambda \) \ with the self-consistent equations:

\[
\langle b \rangle^2 + n_t + n_j = 1,
\]

(6)

\[
2 \text{Im} \int \frac{d\omega}{2\pi} \left( t_L G_{JJ}^r (\omega) + t_{LR} G_{JJ}^r (\omega) \right) + \lambda \langle b \rangle^2 = 0,
\]

(7)

where \( n_t = \int (d\omega/2\pi) \text{Im} G_{JJ}^r (\omega) \) \ is the electron occupation number in the spin state \( \sigma \) of the magnetic atom. In the
From the position $\omega_1$ and half-width $\Gamma_R$ of the Kondo peak, we can estimate the Kondo temperature by [4] $T_k = \sqrt{\omega_1^2 + \Gamma_R^2(\omega_1)}$, where the peak position $\omega_1$ is obtained from the equation $\omega - \tilde{\epsilon}_d - \text{Re}[\Gamma_R g_{00}(\omega)] = 0$ and the peak half-width $\Gamma_R = -2\text{Re} \ln|g_{00}(\omega)|$. Figure 3a shows the Kondo temperature $T_k$ vs. the level $\epsilon_d$ at a fixed $t_R$ for different energy $\epsilon_0$. $T_k$ possesses the following characteristics: i) $T_k$ decreases monotonically with reducing of $\epsilon_d$. When $\epsilon_d$ is approaching $-\infty$, $T_k$ goes to zero. ii) For $\epsilon_d \neq 0$, there exist two different Kondo regimes. When $\epsilon_d$ is larger than a critical value $\epsilon_{dc}$, $T_k$ is almost linearly dependent on $\epsilon_d - \epsilon_{dc}$, so that $T_k$ drops rapidly while $\epsilon_d$ is near $\epsilon_{dc}$ (see fig. 3a). This characteristic is very different comparing to the conventional Kondo effect, and it originates from the linear DOS of the graphene and the vanishing of the DOS at the Dirac point. On the other hand, when $\epsilon_d < \epsilon_{dc}$, $T_k \propto e^{\epsilon_d}$ (i.e. ln $T_k \propto \epsilon_d$ as shown in fig. 3a). In this case the system's behavior is similar to that of the conventional Kondo effect. Since $k_BT_k \ll |\epsilon_0 - \mu_L|$ in this regime, the DOS at the Fermi surface is approximatively constant on the energy scale $k_BT_k$. So it recovers the conventional Kondo behavior. iii) The behavior of $T_k$ for $\epsilon_d < 0$ (i.e. the electron-doped graphene) and $\epsilon_0 > 0$ (i.e. the hole-doped graphene) is similar.

Figure 3b shows the renormalized level $\tilde{\epsilon}_d$ which determines the position of the Kondo peak. While $\epsilon_0 < 0$, the renormalized level $\tilde{\epsilon}_d$ is always positive and it decreases monotonically with reducing of $\epsilon_d$. $\tilde{\epsilon}_d$ approaches zero as $\epsilon_d \rightarrow \infty$. On the other hand, while $\epsilon_0 > 0$, $\tilde{\epsilon}_d$ can be negative. The curve of $\tilde{\epsilon}_d$ has a negative minimum. But $\tilde{\epsilon}_d \rightarrow 0$ is still true as $\epsilon_d \rightarrow -\infty$.

Now we focus on the case of $\epsilon_0 = 0$. When the Dirac-point energy $\epsilon_0$ approaches 0, the zero-DOS point
approaches the Fermi surface, then both of the Kondo temperature $T_k$ and the renormalized level $\epsilon_d$ go to zero in the whole region of $\epsilon_d < \epsilon_{dc}$. At $\epsilon_d = 0$ (i.e., for the undoped neutral graphene), $T_k$ and $\epsilon_d$ reach zero at $\epsilon_d = \epsilon_{dc}$. On the $\epsilon_d < \epsilon_{dc}$ side, the self-consistent equations (6) and (7) do not have a solution. In other words, the system cannot be in the Kondo phase for $\epsilon_d < \epsilon_{dc}$. On the other side with $\epsilon_d > \epsilon_{dc}$, the Kondo phase does exist. The Kondo temperature $T_k$ is roughly proportional to $\epsilon_d - \epsilon_{dc}$ (see fig. 3c). The critical value $\epsilon_{dc}$ depends on the coupling strength $t_R$ between the magnetic atom and the graphene. The larger $t_R$ is, the larger $|\epsilon_{dc}|$ is (see fig. 3c).

From $T_k = 0$ or $\epsilon_d = 0$ at $\epsilon_d = \epsilon_{dc}$ and with the aid of eq. (7), the critical value $\epsilon_{dc}$ can be analytically obtained:

$$\epsilon_{dc} = -\frac{2}{\pi} t_R^2 \int_{-\infty}^{0} d\omega \text{Im} \left( g_{60}(\omega) \right) \frac{1}{\omega}.$$  

The above integral over $\omega$ is about 1.408, hence $\epsilon_{dc} \approx -0.896 t_R^2/t$. Figure 3d shows the phase diagram in the parameter space of $(\epsilon_d, t_R)$. The curve gives the critical value $\epsilon_{dc}$ vs. the coupling strength $t_R$. In the top right region, the Kondo phase emerges at low temperature. But in the bottom left region, the system cannot enter into the Kondo state even at zero temperature.

Finally, we investigate the conductance $G$ ($G \equiv dI/dV$) while the STM tip is coupled. The coupling between the STM tip and the adatom is normally much weak compared to that between the graphene to the adatom, so we set $t_J$ and $t_{LR}$ on the order of 0.01$t$. Figure 4 shows the conductance $G$ vs. the bias $V$ in the Kondo regime. While without the direct coupling ($t_{LR} = 0$), the curve of $G$-$V$ is very similar to the curve of LDOS-$\omega$ (see figs. 4a and 2c) since for the weak-coupled STM tip, the conductance $G$ is proportional to the LDOS of the adatom [14]. When the direct coupling is present ($t_{LR} \neq 0$), the coherence between the direct path and the path passing the magnetic adatom occurs, which usually leads to the Fano resonance [15]. But in the present graphene system, the Fano resonance does not appear anywhere, the reason is that the transmission coefficient of the direct path also depends on the energy of the incident electron. In figs. 4b, c, and d, $J$ of the contact point of the STM tip to the graphene is 0 (same contact point with the adatom), 1 (the nearest-neighbor site), and 2 (the next-nearest-neighbor site), respectively. For the same and the next-nearest-neighbor contact points, the conductance $G$ is almost unaffected by the opening of the direct path, although $t_{LR} = 0.03t$ is much larger than $t_J = 0.002t$. Because that in the Kondo regime, a high Kondo peak emerges in the LDOS of the adatom, so the path passing the adatom is large and plays the dominant role. However, when the contact point is at the nearest-neighbor site, the conductance is greatly enhanced by the opening of the direct path (see fig. 4c, note the different scale comparing with the other plots in fig. 4) since the Kondo singlet state is quite extensive. For the graphene system, the sharp Kondo peak not only appears in the LDOS of the adatom, but also in the LDOS of all odd-neighboring sites. The large LDOS in the odd-neighboring sites and $t_{LR} > t_J$ lead that the direct path is dominant, and the conductance $G$ is enhanced.

In summary, the Kondo effect in the system of a magnetic adatom on the graphene and its scanning tunneling spectroscopy are theoretically studied. For a doped graphene, the Kondo phase always exists at zero temperature regardless of n-type or p-type doping, and it exhibits two Kondo regimes: the conventional and the unconventional regimes. For the undoped neutral graphene, the Kondo phase only exists while the adatom’s energy level is above a critical value. These Kondo characteristics can be observed from scanning tunneling spectroscopy since the conductance vs. the bias is similar to the LDOS of the adatom. In addition, if a direct coupling between the STM tip and the graphene is present, the conductance may be greatly enhanced, depending on the coupling site.

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