Orthogonality catastrophe and Kondo effect in graphene.

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Anderson’s orthogonality catastrophe in graphene, at energies close to the Dirac point, is analyzed. It is shown that, in clean systems, the orthogonality catastrophe is suppressed due to the vanishing density of states at the Dirac point. In the presence of preexisting localized states at the Dirac energy, the orthogonality catastrophe shows similar features to those found in normal metals with a finite density of states at the Fermi level. The implications for the Kondo effect induced by magnetic impurities, and for the Fermi edge singularities in tunneling processes are also discussed.

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INTRODUCTION.

Graphene has attracted a great deal of attention recently, due to its novel fundamental properties and potential applications. It is by now well established that its electronic properties at low energies are well described by the two dimensional Dirac equation. At half filling graphene should be a semimetal, with a vanishing density of states. This fact implies that many properties of a metal, which are parametrized by the density of states at the Fermi level, are different in a clean graphene sample. The description of the electronic bands in graphene based on the Dirac equation also leads to localized states in samples with edges or lattice defects. These states change the density of states near the Dirac energy, as they induce a peak at this energy. Hence, the density of states of graphene at the Dirac energy can either vanish, in a clean sample, or diverge, if localized states are induced.

We study here Anderson’s orthogonality catastrophe (AOC) in clean and dirty graphene. The AOC can be considered the simplest non trivial feature in the response of a metal, and it is dependent on the value of the density of states at the Fermi level. The AOC directly leads to many singularities in experiments which probe the dynamical response of a metal, like the Fermi edge singularity in X-ray absorption, and singularities in the transport properties of quantum dots and metallic grains. In graphene, the interplay between the AOC and Coulomb blockade may be relevant for the analysis of transport experiments on small quantum dots.

The Kondo effect induced by magnetic impurities in metals can be seen as a direct consequence of Anderson’s orthogonality catastrophe. The coupling between the impurity spin and the conduction electrons can be divided into a transverse term, \( J_\perp \), which leads to spin-flip processes, and a longitudinal term, \( J_\parallel \), which induces an AOC associated to the same spin flips. This AOC leads to a strong suppression of spin fluctuations, although the effects of \( J_\perp \) prevail at the lowest temperatures. These two competing processes can be defined, in a very transparent way, in the dissipative two level system, which is equivalent to the Kondo Hamiltonian. The Kondo temperature, \( T_K \), can be seen as the scale at which spin flip processes ultimately cut off the AOC.

The AOC is modified in disordered metals and ballistic mesoscopic systems, due to the changes in the electronic wavefunctions. We will analyze the AOC in graphene using the numerical methods explained in, and also a phaseshift analysis similar to that in.

We analyze first the phaseshifts induced by a local potential, first in clean graphene, and then in graphene in the presence of preexisting localized levels. The next section presents a numerical study of the full overlap between the electronic ground state before and after the potential is switched on can be written as:

\[
S \leq N \sum_l \frac{2 \pi}{l^2} \sin^2(\delta_l) \tag{1}
\]

where \( N \) is the number of electrons, and \( \delta_l \) is the phaseshift induced by the potential in the scattered waves at the Fermi level with angular momentum \( l \). In a typical metal, a weak local potential of strength \( \epsilon_0 \ll \epsilon_F \) induces a phaseshift in the \( s \) channel which can be approximated by \( \delta_0 \approx \epsilon_0 N(\epsilon_F) \ll 1 \), where \( N(\epsilon_F) \) is the density of states at the Fermi level.
This analysis can be extended in a straightforward way to graphene, where the electronic wavefunctions can be approximated by the two dimensional Dirac equation (see below):

\[
\mathcal{H} = v_F \begin{pmatrix}
0 & \pm k_x + i k_y \\
\mp k_x + i k_y & 0
\end{pmatrix}
\]  

(2)

where the two signs correspond to the two inequivalent corners of the Brillouin Zone of the honeycomb lattice.

We use eq. (2) in order to describe the dependence of the overlap on the number of electrons, by computing analytically the phaseshifts induced by different types of potentials. In the following, we use energy and momentum units such that \(v_F = 1\).

\[
\mathcal{H} = \begin{pmatrix}
0 & k & i e^{-i \phi} \partial_r - \frac{i e^{-i \phi}}{r} \partial_\phi \\
-k & 0 & 0 \\
i e^{i \phi} \partial_r + \frac{i e^{i \phi}}{r} \partial_\phi & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]  

(3)

where the two first entries correspond to the \(K\) point, and the two last ones to the \(K'\) point.

We add a constant perturbation in the region \(r \leq R_0\):

\[
V = \begin{pmatrix}
\epsilon_0 & 0 & 0 & \Delta \\
0 & \epsilon_0 & \Delta & 0 \\
0 & \Delta & \epsilon_0 & 0 \\
\Delta & 0 & 0 & \epsilon_0
\end{pmatrix}
\]  

(4)

where \(\epsilon_0\) is a constant energy shift, and \(\Delta\) is a potential which induces scattering between the two valleys, and it is compatible with the symmetries of the honeycomb lattice\([24]\).

We analyze the scattering of an incident \(s\) wave with incoming energy \(k\):

\[
\Psi_{\text{inc}}(r, \phi) = \begin{pmatrix}
J_0(kr) \\
-i J_1(kr) e^{i \phi} \\
0 \\
0
\end{pmatrix}
\]  

(5)

where \(J_0(x)\) and \(J_1(x)\) are Bessel functions of the first kind. They satisfy: \(\lim_{x \to 0} J_0(x) \approx 1\), and \(\lim_{x \to 0} J_1(x) \approx x/2\).

The reflected waves outside the well can be written as:

\[
\Psi_{\text{ref}}(r, \phi) = R_1 \begin{pmatrix}
Y_0(kr) \\
-i Y_1(kr) e^{i \phi} \\
0 \\
0
\end{pmatrix} + R_2 \begin{pmatrix}
0 \\
0 \\
i Y_1(kr) e^{i \phi} \\
Y_0(kr)
\end{pmatrix}
\]  

(6)

\(Y_0(x)\) and \(Y_1(x)\) are Bessel functions of the second kind. They satisfy: \(\lim_{x \to 0} Y_0(x) \approx 2/\pi (\log(x/2) + \gamma)\), and \(\lim_{x \to 0} Y_1(x) \approx -2/(\pi x)\). The first contribution on the right hand side of eq. (6) is a reflected wave in the same valley, and the second term is a wave in the opposite valley as the incident wave.

Inside the potential well, the spectrum has a gap for energies \(\epsilon_0 - \Delta \leq \epsilon \leq \epsilon_0 + \Delta\). Within this range of energies, the wavefunction inside the well can be written as:

\[
\Psi_{\text{trans}}(r, \phi) \equiv T_1 \begin{pmatrix}
\frac{\sqrt{x^2 - \Delta^2}}{2 \Delta} I_0(k'r) \\
\frac{\sqrt{x^2 - \Delta^2}}{2 \Delta} I_1(k'r) e^{i \phi} \\
0 \\
\frac{1}{\sqrt{2}} I_0(k'r)
\end{pmatrix} + T_2 \begin{pmatrix}
\frac{\sqrt{x^2 - \Delta^2}}{2 \Delta} i k'r I_0(k'r) \\
\frac{\sqrt{x^2 - \Delta^2}}{2 \Delta} i k'r I_1(k'r) e^{i \phi} \\
i \frac{1}{\sqrt{2}} I_0(k'r) \\
0
\end{pmatrix}
\]  

(7)
\(I_0(x)\) and \(I_1(x)\) are modified Bessel functions of the first kind. They satisfy: \(\lim_{x \to 0} I_0(x) \approx 1\), and \(\lim_{x \to 0} I_1(x) \approx x/2\). The value of \(k'\) in eq. (1) is given by: \(\epsilon = \sqrt{\Delta^2 - k'^2}\). As \(k = \epsilon + \epsilon_0\), we have \(k' = \sqrt{\Delta^2 - (k - \epsilon_0)^2}\).

For \(|\epsilon - \epsilon_0| \geq \Delta\), we have:

\[
\Psi_{\text{trans}}(r, \phi) = T_1 \begin{pmatrix}
-\frac{1}{\sqrt{2}} J_0(k'r) \\
\frac{\sqrt{2}}{2} J_1(k'r) e^{i\phi}
\end{pmatrix} + T_2 \begin{pmatrix}
\frac{i\Delta}{\sqrt{2\Delta^2 + k'^2}} J_0(k'r) \\
\frac{i\Delta}{\sqrt{2\Delta^2 + k'^2}} J_1(k'r) e^{i\phi}
\end{pmatrix}
\]

and \(\epsilon = \sqrt{\Delta^2 + k'^2}\), and \(k' = \sqrt{(k - \epsilon_0)^2 - \Delta^2}\).

The scattering phaseshifts are determined by the reflection coefficients \(R_1\) and \(R_2\) defined in eq. (9). The boundary conditions at \(r = R_0\) are simply the continuity of the spinors, which define a set of four equations for the four variables \(R_1, R_2, T_1\) and \(T_2\).

For \(\Delta = 0\) we have \(R_2 = T_2 = 0\) and \(R_1 = \bar{R}\). As \(\lim_{x \to -\infty} J_0(x) \approx \sqrt{2/(\pi x)} \cos(x - \pi/4)\), and \(\lim_{x \to \infty} J_0(x) \approx \sqrt{2/(\pi x)} \sin(x - \pi/4)\), the phaseshift \(\delta\) is \(\tan(\delta) = \bar{R}\). We find:

\[
\tan(\delta) = \bar{R}(kR_0) = -\frac{J_1[(k - \epsilon_0)R_0]J_0(kR_0) - J_0[(k - \epsilon_0)R_0]J_1(kR_0)}{J_1[(k - \epsilon_0)R_0]Y_0(kR_0) - J_0[(k - \epsilon_0)R_0]Y_1(kR_0)}
\]

The phaseshift vanishes linearly at the Dirac point implies that the overlap between the Slater determinants before and after the potential is switched on does not scale like some power of the number electrons, and the AOC does not take place at this energy.

**Phaseshift analysis in the presence of a localized state.**

We will neglect here possible intervalley scattering terms. We study the phaseshifts induced by a weak potential near the edges of a circular void which supports surface states. A sketch of the model is shown in Fig. 2.

We write the wavefunction as:

\[
\Psi(\tilde{r}) \equiv \begin{pmatrix}
\psi_1(\tilde{r}) \\
\psi_2(\tilde{r})
\end{pmatrix}
\]

The edge of a crack, or extended vacancy is modeled by the boundary condition:

\[
\psi_1(\tilde{r}) = 0, \quad \tilde{r} \in \Omega
\]

where \(\Omega\) is the boundary of the void.

We analyze a circular void, of radius \(R'\). The boundary condition, eq. (12), allows for solutions at zero energy of the type:

\[
\Psi(\tilde{r}) \equiv \begin{pmatrix}
0 \\
\frac{\alpha_0 J_0(kR') + \beta_0 Y_0(kR')}{\rho^\pm}
\end{pmatrix}
\]

where the two signs correspond to the two inequivalent corners of the Brillouin zone.

Eq. (12) implies, for s-wave scattering:

\[
\alpha_0 J_0(kR') + \beta_0 Y_0(kR') = 0
\]
with boundary conditions:

\[
\begin{align*}
\alpha' J_0[(k + \epsilon_0)R] + \beta' Y_0[(k + \epsilon_0)R] &= 0 \\
\alpha' J_0[(k + \epsilon_0)R] + \beta' Y_0[(k + \epsilon_0)R] &= \alpha J_0(kR) + \beta Y_0(kR) \\
\alpha' J_1[(k + \epsilon_0)R] + \beta' Y_1[(k + \epsilon_0)R] &= \alpha J_1(kR) + \beta Y_1(kR)
\end{align*}
\] (17)

These equations allow us to obtain the phasishift of the combined system, void and circular impurity, as \( \delta = \arctan(\beta/\alpha) \). The overlap between the Slater determinants before and after the impurity potential is switched on, is determined by the phase difference, \( \delta - \delta_0 \), where \( \delta_0 \) is given in eq. (15).

Results for the individual phasishifts \( \delta \) and \( \delta_0 \), as well as their difference are shown in Fig. 3 for \( \epsilon_0 = 0.1 \), \( R' = 0.9 \) and \( R = 1 \). In this regime of energies much lower than \( \epsilon_0 \), the phasishift \( \delta \) seems to approach \( \delta_0 \) from below, indicating that the repulsive character of the void is weakened by the additional constant potential. For the small energies close to the Dirac point focused on here, the relative phasishift, \( \delta - \delta_0 \), is always finite and seems to approach a constant. This behavior differs strikingly from our findings for clean graphene where the vanishing of the phasishift at the Dirac point (cf. Fig. 1) indicates the suppression of AOC. In the presence of voids, the small dependence of the phasishift induced by an additional external potential on energy near the Dirac point implies that the overlap between Slater determinants is determined by the phase difference, \( \delta - \delta_0 \), before the potential whose effect we want to calculate is turned on, is:

\[
\delta_0(k) = \arctan \left( \frac{\beta_0}{\alpha_0} \right) = -\arctan \left( \frac{J_0(kR')}{Y_0(kR')} \right)
\]

Next, we model a weak impurity near the void as an isotropic perturbation of depth \( \epsilon_0 \), defined in the region \( R' \leq |\bar{r}| \leq R \). Following eqs. (5,6) and neglecting intervalley scattering, the wavefunction can be written as:

\[
\Psi(\bar{r}) = \begin{cases} 
\alpha' J_0[(k + \epsilon_0)R] + \beta' Y_0[(k + \epsilon_0)R] & R' \leq r \leq R \\
\alpha' J_1[(k + \epsilon_0)R] + \beta' Y_1[(k + \epsilon_0)R] & R \leq r
\end{cases}
\]

with boundary conditions:

\[
\begin{align*}
\alpha' J_0[(k + \epsilon_0)R] + \beta' Y_0[(k + \epsilon_0)R] &= 0 \\
\alpha' J_0[(k + \epsilon_0)R] + \beta' Y_0[(k + \epsilon_0)R] &= \alpha J_0(kR) + \beta Y_0(kR) \\
\alpha' J_1[(k + \epsilon_0)R] + \beta' Y_1[(k + \epsilon_0)R] &= \alpha J_1(kR) + \beta Y_1(kR)
\end{align*}
\] (16)
nants should scale with the number of electrons in a similar fashion to that in a normal metal with a finite density of states. We shall see in the remainder of this paper that there are indeed considerable differences between clean graphene vs. graphene with localized states, that are visible, e.g., in the behavior of the AOC overlap.

**CALCULATION OF THE OVERLAP.**

**Clean graphene.**

The overlap between the unperturbed and perturbed Slater determinants for clean graphene clusters of different sizes has been calculated using the methods described in [21, 22, 23]. The perturbation is a local potential at a given site, $\Delta = \epsilon_0$. Its strength is measured in terms of the scaled perturbation strength $\propto \Delta / d$ with $d$ being the mean level spacing $6/\sqrt{N(N+1)-2}$. Periodic boundary conditions are used in systems with $N \times N$ unit cells, up to $N = 80$; the vertical stripes visible in Fig.[4] are an artefact of the periodic boundary conditions. The results for the overlap for $N = 12$ and different potential strengths (ranging from weak to strong for repulsive as well as attractive perturbations) are shown in Fig.[4]. An effective phaseshift can be defined by dividing the energy shift of the level closest to the Fermi energy by the average level spacing in that energy range. This phaseshift is also shown in Fig.[4].

**Graphene with localized states.**

The method described in [23] assumes that the wavefunctions of all eigenstates of the unperturbed system have the same weight on the site where the perturbation is turned on. This leads to a considerable simplification of the calculation of the overlap between Slater determinants. Generalization of this method generalized to chaotic mesoscopic systems [21, 22] was done based on...
FIG. 6: (Color online). Dependence of the overlap on perturbation strength when the perturbation is turned on near an existing vacancy (empty circles, black), and in clean graphene (filled circles, red). Calculations are done for $12 \times 12$ clusters. Circles correspond to one hole in the cluster (Dirac energy, $\epsilon_F = 0$), whereas diamonds characterize a cluster with five holes (corresponding to $\epsilon_F = -0.5$, or a filling of $\sim 0.47$).

FIG. 7: (Color online). Dependence of the overlap on perturbation strength, at the Dirac energy, when the perturbation is turned on near an existing vacancy (circles, black), and in clean graphene (diamonds, red). Large symbols correspond to a $12 \times 12$ cluster and small symbols correspond to a $15 \times 15$ cluster.

CONCLUSIONS.

The results presented here show the existence of two regimes for Anderson’s orthogonality catastrophe in graphene at low fillings, depending on whether there are localized states at the Dirac energy or not. In the absence of localized states the AOC is suppressed near the Dirac point, in agreement with the vanishing of the density of states at this energy. When localized states are present, the AOC is qualitatively similar to that found in metals with a finite density of states. The latter behavior is a consequence of the fact that, when localized states are sufficiently near the Fermi surface, they contribute to the non adiabatic response of the electron gas. This situation is unique to graphene, as, in most metallic systems, localized states appear at energies well below the Fermi level.

The features discussed above imply that the Kondo effect in graphene also depends on the strength of the scalar potential induced by the magnetic impurity. If the potential induced on the graphene electrons is weak, as when the magnetic impurity is at some distance of the graphene plane, we expect the formation of a Kondo resonance to be suppressed, and the magnetic impurity will give rise to a free magnetic moment. On the other hand, if the magnetic impurity lies within the graphene plane, it will give rise to a strong scalar potential, and possibly to localized states at the Dirac energy. Then, the Kondo effect will not be suppressed, despite the low density of states in graphene near the Dirac energy.
Similar effects can be expected for the Fermi edge singularities induced by electrons tunneling into or out of graphene quantum dots. The strength of the Fermi edge singularities depend on the existence of localized states in the quantum dot. These states will be induced in graphene dots with sharp and rough edges, where, in addition to Coulomb blockade, the AOC associated to electron tunneling will further suppress the conductance at low voltages.

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