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Electron spin resonance in presence of a magnetic impurity in graphene

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ABSTRACT

The ESR of a magnetic probe sited at a distance R from an adatom in graphene, interacting via a RKKY interaction, is studied. The spin relaxation rate of the magnetic probe in the case of pristine graphene satisfies a T^3 dependence for all temperatures at the Dirac point. However, away from the Dirac point a T^3 dependence is observed only for high temperatures unlike the Korringa behavior at low temperatures. Moreover, the zero-temperature relaxation rate of the pristine graphene demonstrates a quadratic dependence on the chemical potential. In the presence of the magnetic adatom hybridized with one site of the graphene sublattice we observe a dip in the relaxation rate away from the Dirac point. At the Dirac point a deviation from the T^3 dependence is observed. The presence of the Coulomb interaction U also modifies the zero-temperature relaxation rate when compared to that of pristine graphene. The transition from the magnetic state to the non-magnetic state is also characterized by a minimum in the relaxation rate.

1. Introduction

The pioneering experimental work of Andre Geim and Kostya Novoselov, at the University of Manchester in 2004 [1–4], has triggered a huge interest in the scientific community to study graphene, mainly motivated by their unusual electronic properties, such as the behavior of non-massive chiral Dirac fermion at low excitation energies, as well the possibility of its application in nanoscience and nanotechnology as a possible candidate to replace the silicon-based electronics devices [5].

Graphene is truly a two-dimensional material, consisting of carbon atoms in the sp^2 hybridization state, distributed in a hexagonal lattice formed by two interpenetrating triangular sublattices, A and B. In the lattice plane the s and p orbitals of the carbon atom form covalent bonds, which give a high mechanical strength to graphene. The remaining p orbitals of the carbon atoms in each sublattice, in the direction perpendicular to the plane of the lattice, hybridize, forming a conduction and a valence energy bands, known as π^* and π bands, respectively. The hexagonal distribution of the carbon atoms results in two bands that touch each other at two points of high symmetry in the Brillouin zone, K and K', known as Dirac points, reason due to which graphene is considered as a zero gap semiconductor. Around these points the dispersion relation takes a conical shape, with the energy varying linearly as a function of the moment $\vec{k}$, obeying the relation $E = \pm\hbar v_F \mid \vec{k} \mid$, where $\hbar$ is the reduced Planck constant and v_F is the Fermi velocity, that is similar to the dispersion relation of the photon, with the speed of light c playing the role of the velocity of the electrons in the Fermi level of graphene. As a two-dimensional Dirac fermion system, graphene presents unusual and interesting behavior. For instance, graphene shows a minimum conductivity about of e^2/h, an anomalous quantum Hall effect and a nonzero cyclotron mass m_c described by $E = m_c v_F^2$, although from the linear spectrum of fermion in graphene it would be zero. This similarity with Dirac fermions enables the prediction of the properties of the charge carriers in graphene from the relativistic Dirac equation, such as tunneling through a potential barrier without any reflection, which is known as Klein's paradox.

In the last few years there has been an increased attention to study the effect of magnetic adatom in a pristine graphene due to its potential use in spintronics. Studies have been performed to characterize the necessary conditions under which the transition metal adatom on graphene can form localized magnetic moment. Using density-functional-theory, a systematic first-principles study of transition metals from Sc to Zn, including nonmagnetic adatoms Cu and Au, embedded in graphene has been performed [6]. It has revealed remarkable behavior of these adatoms in graphene. For example, the absence of magnetic moment when a Fe or a Ni adatom is adsorbed, otherwise well known as magnetic elements. On the other hand there is magnetic moment when the adatom is one of V, Cr or Mn. The even more surprising is that Cu and Au, which are nonmagnetic elements, become magnetic when substituting a carbon atom in graphene.

One of the experimental techniques that can be used to analyze the dynamic susceptibility of magnetic adatom in graphene is the

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electron spin resonance (ESR). It has proved to be an important method in identifying the ground state of strongly correlated electron systems. This technique measures the linewidth ΔH at resonance absorption of a well-defined magnetic moment. ESR measurements on graphene, a novel member of carbon nanostructure family, is yet very few. The work [7] reports ESR signal and spin susceptibility with temperature for mechanically exfoliated graphene for itinerant electron. However, one important question continues to persist whether the ESR signal of the itinerant electrons can be observed or not. For example, in the cases of Fe or Ni adsorbed to the carbon atom in graphene, probably no detectable signal will be measured. For this reason we suggest the introduction of an additional ESR probe ion in graphene. The probe, such as Gd^{3+}, will detect indirectly the effect of the dynamic susceptibility of the adatom via RKKY exchange interactions transmitted through the conduction electrons. The ESR linewidth of a probe with a stable magnetic moment is given by the transversal spin relaxation rate $(1/T_2)$, which in graphene equals the longitudinal relaxation rate $(1/T_1)$. The ESR of a magnetic probe has already been studied in metals [8–10]. Moreover, recently ESR signal in graphene has been studied including intrinsic Bychkov-Rashba and ripple spin orbit coupling [11] which has shown that a large density of states (DOS) and narrow line width are prerequisites to observe ESR on graphene. Large DOS is possible by having chemical potential away from the Dirac point or by introducing impurities.

Magnetic adatom introduced in a metal has been successfully studied in the light of the single adatom Anderson model [12], which recently has been applied also to study adatom in graphene [13,14]. Depending on the relation between the constitutive parameters of this model, the adatom orbital can be empty, single or doubly occupied. In particular, for temperatures higher than the Kondo temperature [15], there is a formation of local magnetic moment when the adatom and the conduction electrons are weakly hybridized and the Coulomb interaction between the electrons in the adatom orbital is greater than their binding energy. Moreover, for hybridization energy higher than the electron binding energy the orbital presents the valence fluctuation regime [15]. It has been observed that the coupling of an adatom to a graphene sublattice results in a much easier formation of magnetic moment due to the anomalous broadening of the electronic levels of the adatom [15]. In the present work we study the ESR of a magnetic probe in graphene sited at a distance R from an adatom with which interacts via a RKKY interaction. Using analytic arguments, very recently it has been shown that the RKKY interaction between localized magnetic moments in doped graphene becomes more long-ranged than in pristine graphene once the moments are set in motion with a finite excitation frequency [16]. In addition it suggests a way to overcome the difficulty to probe the RKKY interaction in graphene, by exciting the magnetization of the magnetic object in contact to it, which can be achieved using the method of inelastic scanning tunneling spectroscopy (ISTS).

2. The model

The model Hamiltonian of graphene with an adatom hybridized with a graphene sublattice and a probe interacting via a contact interaction with the conduction electrons represented schematically in Fig. 1. is written as

$$H = H_{TB} + H_f + H_V + H_{\text{probe}} \tag{1}$$

where H_{TB} is the tight binding Hamiltonian of the graphene, H_f is the adatom Hamiltonian, H_V is the hybridization of the adatom localized states with the graphene conduction electrons and H_{probe} is the contact interaction between the probe and the conduction electrons.

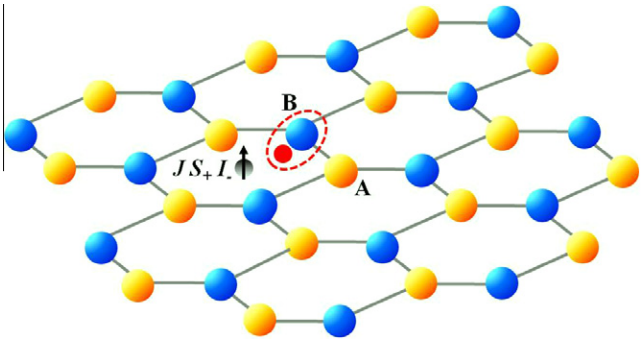

Fig. 1. Schematic diagram of the lattice structure of graphene with an impurity atom and the probe.

The tight binding Hamiltonian is given by

$$H_{TB} = -t\sum_{\langle i,j\rangle\sigma,l}\left[a^\dagger_\sigma(R_i)b_\sigma(R_j) + H.c.\right] \tag{2}$$

where the operator $a_\sigma(R_i)$ $(b_\sigma(R_j))$ annihilates a state with spin σ at the position $R_i(R_j)$ on the sublattice A (B), $\langle i,j\rangle$ stands for summation over nearest neighbors and the parameter t is the nearest neighbor hopping energy. In momentum space, we have

$$H_{TB} = -t\sum_{\mathbf{k},\sigma}\left[\phi(\mathbf{k})a^\dagger_{\mathbf{k},\sigma}b_{\mathbf{k},\sigma} + \phi(\mathbf{k})b^\dagger_{\mathbf{k},\sigma}a_{\mathbf{k},\sigma}\right] \tag{3}$$

where $\phi(\mathbf{k}) = \sum_\delta e^{i\mathbf{k}.\bar{\delta}_i}$ with $\bar{\delta}_1 = a(\hat{x}/2 + \sqrt{3}/2\hat{y})$, $\bar{\delta}_2 = a(\hat{x}/2 - \sqrt{3}/2\hat{y})$ and $\bar{\delta}_3 = -a\hat{x}$ as the nearest neighbor vectors. Diagonalizing the Hamiltonian (3) one generates two bands $\epsilon_\pm(\mathbf{k}) = \pm t|\phi(\mathbf{k})|$, which can be linearized around the Dirac points $\mathbf{K}$ at the corners of the Brillouin zone: $\epsilon_\pm(\mathbf{K}+\mathbf{q}) \sim \pm v_F|\mathbf{q}|$, where $v_F = 3ta/2$ is the Fermi velocity of the Dirac electrons. Hence the Hamiltonian H_{TB} can be written as

$$H_{TB} = \sum_{\mathbf{k},\sigma}\left[\epsilon_+(\mathbf{k})c^\dagger_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma} + \epsilon_-(\mathbf{k})d^\dagger_{\mathbf{k},\sigma}d_{\mathbf{k},\sigma}\right] \tag{4}$$

where $c_{\mathbf{k},\sigma}$ and $d_{\mathbf{k},\sigma}$ can be written in the basis $\{a_{\mathbf{k},\sigma}, b_{\mathbf{k},\sigma}\}$ as

$$c_{\mathbf{k},\sigma} = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{\phi(\mathbf{k}^*)}{\phi(\mathbf{k})}}a_{\mathbf{k},\sigma} + b_{\mathbf{k},\sigma}\right)$$

$$d_{\mathbf{k},\sigma} = \frac{1}{\sqrt{2}}\left(-\sqrt{\frac{\phi(\mathbf{k}^*)}{\phi(\mathbf{k})}}a_{\mathbf{k},\sigma} + b_{\mathbf{k},\sigma}\right)$$

The adatom Hamiltonian is described by

$$H_f = \sum_\sigma \epsilon_f f^\dagger_\sigma f_\sigma + U n_\uparrow n_\downarrow, \tag{5}$$

where $f_\sigma(f^\dagger_\sigma)$ is the annihilation (creation) operator of a state with a spin $\sigma = \uparrow, \downarrow$ of the adatom, $n_\sigma = f^\dagger_\sigma f_\sigma$ is the adatom occupation number operator, ϵ_f is the energy of the adatom electron, and U is the Coulomb interaction due to the double occupancy of an energy level in the adatom. For simplicity we adopt a mean-field approximation to the electronic correlations at the adatom, $Un_\uparrow n_\downarrow = U\sum_\sigma\langle n_{-\sigma}\rangle f^\dagger_\sigma f_\sigma - U\langle n_\uparrow\rangle\langle n_\downarrow\rangle$. Hence, the adatom Hamiltonian can be rewritten as $H_f = \sum_\sigma \epsilon_{f\sigma} f^\dagger_\sigma f_\sigma$ where $\epsilon_{f\sigma} = \epsilon_f + U\langle n_{-\sigma}\rangle$. The adatom orbital is sited at the origin of the sublattice B and is hybridized with a hybridization strength V represented by the Hamiltonian

$$H_V = V\sum_\sigma [f^\dagger_\sigma b_\sigma(0) + H.c] \tag{6}$$

In the basis $c_{\mathbf{k},\sigma}$ and $d_{\mathbf{k},\sigma}$ we can write the hybridization Hamiltonian as

$$H_V = \frac{V}{\sqrt{2}}\sum_\sigma [f^\dagger_\sigma c_{\mathbf{k},\sigma} + f^\dagger_\sigma d_{\mathbf{k},\sigma} + H.c] \tag{7}$$