RKKY interaction in heavily vacant graphene

Alireza Habibi\(^1\) and S A Jafari\(^{1,2,3}\)

\(^1\) Department of Physics, Sharif University of Technology, Tehran 11155-9161, Iran
\(^2\) Center of excellence for Complex Systems and Condensed Matter (CSCM), Sharif University of Technology, Tehran 1458889694, Iran
\(^3\) School of Physics, Institute for Research in Fundamental Sciences (IPM), Tehran 19395-5531, Iran

E-mail: akbar.jafari@gmail.com

Received 8 April 2013, in final form 16 July 2013
Published 21 August 2013
Online at stacks.iop.org/JPhysCM/25/375501

Abstract

Dirac electrons in clean graphene can mediate the interactions between two localized magnetic moments. The functional form of the RKKY interaction in pristine graphene is specified by two main features: (i) an atomic-scale oscillatory part determined by a wavevector \(\vec{Q}\) connecting the two valleys; with doping another longer range oscillation appears which arises from the existence of an extended Fermi surface characterized by a momentum scale \(k_F\); (ii) an algebraic \(R^{-\alpha}\) decay in large distances where the exponent \(\alpha = -3\) is a distinct feature of undoped Dirac sea in two dimensions. In this work, we investigate the effect of a few per cent vacancies on the above properties. Depending on the doping level, if the chemical potential lies on the linear part of the density of states, the exponent \(\alpha\) remains at \(-3\) even in vacant graphene. Otherwise \(\alpha\) reduces towards more negative values. Presence of vacancies washes out both atomic-scale and Friedel oscillations of the RKKY interaction. The absence of atomic-scale oscillations indicates the destruction of two-valley structure of the parent graphene material. However, the absence of Friedel oscillations upon ‘alloying’ with vacancies indicates that a quantum ground state of heavily vacant doped graphene is not given by a unique \(k_F\) momentum scale.

(Some figures may appear in colour only in the online journal)

1. Introduction

The two-dimensional nature of graphene, along with the Dirac nature of charge carriers [1]—as contrasted to the Schroedinger nature of the carriers in ordinary conductors—makes graphene a spectacular platform for condensed matter realization of many exciting ideas of low-dimensionality and relativistic physics [2, 3]. Among the properties of interest in materials is the nature of effective interaction between external agents mediated by the carriers of the host materials. An important example of this would be the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction which is the exchange interaction between two magnetic impurities mediated via the propagators of the host. The RKKY interaction in graphene was studied first by Saremi [4] who found a generic ‘atomic scale’ oscillatory behavior where the sign of the interaction alternates between the two sub-lattices of the bipartite honeycomb structure. The wavevector characterizing these oscillations is \(\vec{Q} = \vec{K}^+ - \vec{K}^-\) where \(\vec{K}^\pm\) denote the momenta associated with two Dirac cones. The oscillations decay as \(R^{-3}\) in long distances, where the exponent \(\alpha = -3\) comes from the linear Dirac cone dispersion in two dimensions. The investigation of Saremi was extended by Sherafati and Satpathy in two directions. First for the undoped graphene they extended the results to a model of full \(\pi\)-bands [5]. Secondly for the low-energy Dirac cone model, they considered the effect of non-zero doping [6], and as in ordinary two-dimensional conductors additional \(k_F\)-related oscillations with a \(R^{-2}\) decay at large distances appeared [7]. Such long-wavelength oscillations are due to an underlying sharp Fermi surface and disappear when the limit of undoped graphene (\(k_F \to 0\)) is approached in pristine graphene.

The above line of research was also extended to the case of disordered graphene by Lee and co-workers who considered the effect of diagonal and hopping disorder on the
RKKY interaction in undoped [8] and doped graphene [9]. They found that for strong enough on-site disorder where Anderson localization takes place, the RKKY interaction exponentially decays with distance which is consistent with the picture based on the localized spectrum [10]. For the doped graphene and weak disorder they found that the Friedel oscillations due to the Fermi surface co-exist with the atomic-scale oscillations due to interference between the two Dirac cones. Various forms of defects are ubiquitous in the surface of graphene [11]. In this work motivated by the fact that vacancies are the most likely form of defects which can be introduced in a controlled way, instead of a generic Anderson model, we consider a specific model for vacancies and investigate the RKKY interaction in the presence of randomly distributed vacancies. The presence of defects modifies electronic, magnetic and mechanical properties of materials. For example vacancies generated by ion irradiation of graphene give rise to magnetic moments [12, 13] and the most probable form of defects produced by irradiation are single vacancies [14]. Moreover coherence exchange of spin between such magnetic moments and the spectrum of fermions of the host graphene leads to unconventional Kondo effect in graphene [15, 16].

In this work we find that the randomness caused by randomly positioned vacancies has a different physics from the Anderson model studied in [8]; we find that propagation of electron waves in a defective environment reduces the exponent $\alpha$ in $R^\alpha$ distance dependence of the RKKY interaction from $\alpha = -3$ to below $-4$ when the defective sample is away from half-filling. The exponent $\alpha$ will not differ from $-3$ when the chemical potential lies around energies where the density of states is linear in energy. We find that $\alpha$ is controlled by the concentration of vacancies and the chemical potential, but not much dependent on the energy level of the localized orbitals bound to vacancy location. At higher concentrations of vacancies, they are expected to form their own impurity band and, based on Mott’s argument [17], such a band is expected to cause a metallic type transport in neutral vacancies when the concentration goes beyond $\sim$1% [17, 18] or so. Therefore we expect Friedel oscillations to appear as a signature of metallic state. But surprisingly we find that not only the atomic-scale oscillations, but also the Friedel oscillations due to the Fermi surface disappear.

2. Model and method

Modeling disorder in graphene has been extensively discussed in the literature [19]. In most cases the ‘disorder’ refers to a dilute mixture of some forms of defects co-existing with the host material. In this work we are interested in a very specific form of disorder, namely vacancies at very high concentrations on the scale of $\sim$1%. For this we use a specific model which takes into account Jahn–Teller distortion and the fact that each vacancy contributes a localized orbital to the whole Hilbert space of the system. Kanao and co-workers proposed a simple and conceivable model for a localized orbital and its hybridization with the adjacent $p_z$ orbitals needed to understand the physics of local magnetic moments and their interaction with the Dirac electrons of graphene [20]. They considered a Jahn–Teller distorted geometry of a single atom point defect shown in figure 1 where the $sp^2$ orbital of one of the atoms, e.g. 1, is hybridized with $p_z$ orbitals of the two remaining atoms 2, 3 surrounding the vacancy. Then the effective Hamiltonian for the defective graphene becomes

$$H = H_g + H_{\text{def}} + H_{\text{hyb}},$$

where $H_g$ is the tight-binding Hamiltonian of graphene with nearest-neighbor hopping, given by

$$H_g = -t \sum_{\langle ij \rangle \sigma} (d_{i \sigma}^\dagger b_{j \sigma} + \text{h.c.}) - \mu N,$$

where $-t < 0$ is the hopping integral and $\mu$ is the chemical potential which can be conveniently controlled by a gate voltage. $H_{\text{def}}$ is the effective Hamiltonian for $sp^2$ orbitals at sites of type 1:

$$H_{\text{def}} = \sum_v \sum_{\sigma} (E_{sp^2} - \mu) d_{1 \sigma}^\dagger d_{1 \sigma},$$

where $E_{sp^2} < 0$ is the energy level of the $sp^2$ orbital, sum over $v$ stands for summation over vacancies and the notation $d_{1 \sigma}^\dagger$ is adopted for the creation operator at this site to emphasize its localized nature in analogy with the situation where the localized orbital arises from a transition metal ad-atom. Note that in fact $d_{1 \sigma}^\dagger$ creates an electron in a localized orbital cooperatively constructed in the three-dimensional sub-space of $sp^2$ orbitals of atoms 1, 2, 3. The Jahn–Teller distortion piles the wavefunction of such orbital around atom 1 and hence it has been given a subscript 1. Since in this paper we are interested in the physics of RKKY interaction, we assume that the local moments are formed, and concentrate on their exchange interaction mediated by the electronic states of the defective host. Therefore we do not include the on-site Coulomb repulsion between the electrons in this localized orbital. Finally $H_{\text{hyb}}$ is the hybridization which is given for each defect by

$$H_{\text{hyb}} = V \sum_v \sum_{\sigma=\uparrow,\downarrow} [(a_{2 \sigma}^\dagger + a_{3 \sigma}^\dagger) d_{1 \sigma} + \text{h.c.}].$$

Figure 1. Schematic picture of the electronic state around the defect in graphene. The symbol at site 1 shows the active sp$^2$ orbital and the circles at sites 2 and 3 the $\pi$ orbitals. Two of the three sp$^2$ orbitals ($i = 2, 3$) form a covalent bond. $V$ is the amplitude of the hybridization between the active $sp^2$ orbital and the two $\pi$ orbitals.
Here $a_{i\sigma}$ for $i = 2, 3$ is an annihilation operator of a $p_z$ electron at site $i$ around the vacancy with spin $\sigma = \uparrow, \downarrow$ and $V$ is the amplitude of hybridization. The $\sum_i$ indicates summation over all vacant sites. Note that there is no hopping between the $2p_z$ orbitals of atoms 2, 3. The missing carbon atom can belong to both sub-lattices. The Jahn–Teller distortion preferring atom 1 over the other two can take place in any direction. In this paper we take all three possibilities with equal probability. In equation (4), we set $V = -0.2t$ for the amplitude of hybridization between $p_z$ and $s^\pi$ orbitals [21] and $E_{2p_z} = -0.5t$, unless otherwise specified. Note that compared to [20] we have not included the on-site Coulomb repulsion $U$ as we are not interested in the Kondo physics here. The presence of a large $U$ prevents double occupancy of the impurity states and hence yields higher values of $\mu$ for a given concentration of charge carriers.

To get a feeling for what happens to the density of states (DOS) of the vacancy alloyed graphene, in figure 2 the DOS of clean graphene is compared to that of highly vacant graphene. By increasing the concentration of defects, two peaks to the left and right of the Dirac point develop. The chemical potential can be tuned with a gate voltage. In the absence of a gate voltage and for neutral vacancies we have the half-filled situation corresponding to one $2p_z$ electron per existing carbon atom. Because of the major peak appearing at $E_{2p_z}$ the chemical potential corresponding to half-filled vacant graphene deviates to the left of zero. Therefore the $\mu = 0$ in the vacant graphene corresponds to electron doping as the area under DOS corresponding to negative energies is more than the area corresponding to positive energies.

The general perturbative expression for the RKKY exchange interaction is given by [22, 23]

$$J_{\text{RKKY}} = \frac{J^2 S (S + 1)}{4 \pi S^2} \int d\omega f(\omega) \times \text{Im} \left[ G(\tilde{r}, \tilde{r}, \omega) G(\tilde{r}, \tilde{r}, \omega) \right],$$

where $S$ is the magnitude of the impurity spin, $J$ is the interaction between the localized moments and the spin of the itinerant electrons, $i$ and $j$ are the site index of magnetic impurities which are located at position $\tilde{r}_i$ and $\tilde{r}_j$ and $f(\omega)$ is the Fermi–Dirac distribution function. Ignoring the constants appearing before the integral, the integral appearing in this equation for our purposes can be simplified to

$$\text{Im} \int d\omega f(\omega) \sum_{n,m} \frac{F_{nm}^i}{(E_n - \omega + i\delta)(E_m - \omega + i\delta)},$$

where $F_{nm}^i = \psi_n^i(\tilde{r}_i)\psi_m^i(\tilde{r}_i)\psi_n^i(\tilde{r}_j)\psi_m^i(\tilde{r}_j)$, with $\psi_n^i(\tilde{r}_i)$ denoting the eigenvector corresponding to the eigenvalue $E_n$ of the Hamiltonian. The lattice constant $a$ and $h$ are set to unit in all calculations. We assume that temperature is zero ($T = 0$) so that the Lehman representation of the above integral in terms of appropriate spectral functions becomes

$$J_{\text{RKKY}} = -\int_{\epsilon_{\text{F}}}^{\epsilon_{\text{F}}} d\epsilon \int_{\epsilon_{\text{F}}}^{\epsilon_{\text{F}}} d\epsilon' \frac{F(\epsilon, \epsilon')}{\epsilon - \epsilon'},$$

where $F(\epsilon, \epsilon') = \text{Re}[A_{ij}(\epsilon)A_{ij}(\epsilon')]$ and the ‘spectral function’ matrix is given by $A_{ij}(\epsilon) = \langle \psi_i | \delta(\epsilon - H) | \psi_j \rangle$. The kernel polynomial method (KPM) can be conveniently used to evaluate various spectral functions including $A_{ij}(\epsilon)$ [8, 10, 24]. In this method, $A_{ij}(\epsilon)$ can be expressed as a series in Chebyshev (or any other complete set of orthogonal) polynomials and the expansion coefficients—the so-called moments—are evaluated by repeated operation with powers of the appropriately re-scaled Hamiltonian in such a way that a $T_m(H)$ is generated via their recursive relations. In appendix B we briefly summarize the KPM method. The defects considered here are on the scale of few per cent and their positions in the lattice as well as the preferred direction due to Jahn–Teller distortion is drawn from a uniform random distribution. Typical averages are obtained by geometric averages of the form $J_{\text{RKKY}} = \exp((1/2)\ln(J_{\text{RKKY}}^2)_{\text{ave}})$. The geometric averages of the above type are known to better represent the propagating nature of waves, and when they become zero indicate the transition to insulating state [8, 9]. To ensure that the same holds for our particular form of disorder, in appendix A we have compared the statistics of geometric and arithmetic averages.

3. Numerical results for the RKKY exchange

3.1. RKKY interaction in clean graphene

Let us first discuss the performance of KPM in addressing the RKKY interaction. In [5], the authors used a lattice Green’s function method to calculate the RKKY interaction for pristine graphene beyond the low-energy model of Dirac fermions. Their result agrees with other authors [4, 25]. They obtain the following analytical results for the clean honeycomb lattice:

$$f_{AB}^0 = 3CJ^2 \frac{1 + \cos(\hat{Q} \cdot \hat{R} + \pi - 2\theta R)}{(R/a)^3},$$

$$f_{AA}^0 = -CJ^2 \frac{1 + \cos(\hat{Q} \cdot \hat{R})}{(R/a)^3}.$$
where $C = 9\lambda^2 \hbar^2 / (256\pi t)$ is a positive quantity, $\lambda$ is the lattice constant, $K^\pm = (\pm 2\pi / (3\sqrt{3}a), 2\pi / (3a))$ are the Dirac points in the momentum space, $\vec{R} = \vec{R}_i - \vec{R}_j$ and angle $\theta_{R}$ is the polar angle between $\vec{R}$ and $\vec{Q} = K^+ - K^-$. These equations indicating ferromagnetic (anti-ferromagnetic) correlation on the same (different) sub-lattice were numerically confirmed with the KPM method [8, 9]. We have also checked that the KPM results obtained in the clean limit (see figure 3) agree with the numerically exact method of Green’s functions for the pristine graphene [5, 8]. The advantage of the KPM method is that it can handle clean and disordered systems on the same footing. For the disordered case only an averaging method is that it can handle clean and disordered systems on the same footing. For the disordered case only an averaging method is that it can handle clean and disordered systems on the same footing.

3.2. RKKY interactions in heavily vacant graphene

We create evenly distributed vacancies on the graphene in order to measure their effect on the mediation of RKKY interactions. The energies are measured in units of the hopping amplitude, i.e. we have set $t = 1$. We used a graphene sheet with periodic boundary condition and $2.5 \times 10^8$ lattice points are used. We generate $1.5 \times 10^6$ different random configurations for the distribution of vacancies. The number of Chebyshev moments is in the range 3000–4500. The hybridization parameter is fixed at $V = -0.2t$, and $E_{sp^2} = -0.5t$.

In figure 3 we have plotted the distance dependence of the RKKY interaction for both pristine sample and a sample with 1% vacancies. The inset shows the DOS and the integrated DOS (electron number) for clean and 1% vacant sample. The results are reported for the armchair direction. The first important feature in pristine graphene is the presence of atomic-scale oscillations which are due to the interference between two valleys. The second feature which has become more manifest in the log–log plot is that the atomic-scale oscillations diminish at long distances for both half-filled and electron-doped ($\mu = 0$) cases. This means that the Brillouin zone scale wavevector connecting the two Dirac cones of the pristine graphene no longer exists in the 1% vacant sample.

Another feature seen in the two plots corresponding to the vacant sample is that the slope of the log–log plot which determines the exponent $\alpha$ characterizing the overall power-law decay of RKKY interaction stays at $\alpha = -3$ for the half-filled situation, while it is below $\alpha = -3$ for the electron-doped case ($\mu = 0$). To further explore this observation, we check that when the chemical potential falls in the $\rho(E) \propto |E|$ region (which is naturally inherited from the DOS of graphene parent) the exponent remains at $\alpha = -3$ in agreement with another KPM study [9]. To understand this, we note that a linear average DOS in two dimensions corresponds to a linear dispersion relation, which by dimensional analysis is expected to give rise to $R^{-3}$ dependence in the particle–hole bubble. With this point in mind, we now proceed to study the variations in the exponent $\alpha$ in vacant graphene at $\mu = 0$.

3.3. Doping dependence

Based on the discussion in section 3.2, at $\mu = 0$ which corresponds to electron doping in vacant graphene and the chemical potential falling in the region of DOS which is strongly nonlinear, we expect significant variations in the exponent $\alpha$ which can be attributed to hindered motion of electron waves inside the vacant graphene medium. For this purpose, in figure 4 we plot the dependence of RKKY interaction to distance in a log–log scale for the armchair direction. To extract the exponent $\alpha$ in the clean and vacant systems, first we discard the length scales below $R = 10a$, as the power-law is meant for long distances. Second, slight oscillations surviving the presence of disorder are removed in order to focus on the power-law part of the dependence. We will return to the question of oscillations in the sequel.

The clear change in the exponent $\alpha$ indicates that the propagation of electrons in heavily vacant graphene is harder than in the clean sample, which is conceivable as the disorder is expected to make the propagation of both single-particle and particle–hole excitations more difficult. Based on dimensional arguments, the change in $\alpha$ could be effectively ascribed to a change in the average dispersion relation of the electronic states characterizing the vacant sample. Along the zigzag direction a similar conclusion holds, with a minor difference that for a given concentration, the value of the exponent $\alpha$ for the zigzag direction slightly differs from the armchair direction. The qualitative distinction between the armchair and zigzag directions of the pristine graphene does not prevail in the realm of high concentration of vacancies and the qualitative behavior along the two directions.
Figure 4. (a) Plot of $J_{RKKY}$ as a function as $R$ at $\mu = 0$ in clean graphene (black squares), 0.2% (red circles), 0.5% (blue up-triangles), 1% (pink down-triangles) and 2% (green diamonds) vacancy concentrations. The inset shows the exponent $\alpha$ as a function of vacancy concentration. By increasing distance between two magnetic impurities in the armchair direction, $J_{RKKY}$ still decreases according to a power law. The data in the inset are obtained from the distance dependence in the armchair direction. By increasing vacancy concentration, $\alpha$ will decrease. For the zigzag direction the trend is similar, with slightly different exponents at a given concentration.

is not expected to be much different when a few per cent vacancies are introduced.

At the $\mu = 0$ situation we also examine the dependence of $\alpha$ on the energy level $E_{sp^2}$ of the vacancy for a sample with 1% vacancy. As can be seen in figure 5 this exponent is not sensitive to the precise value of the impurity level as long as it is not deep enough to allow for the formation of localized bound states which totally changes the nature of propagation of electronic waves.

3.4. The fate of Fermi surface oscillations

When the pristine graphene is doped, in addition to atomic scale oscillations in the RKKY interaction which merely

arise from the wavevector $\vec{Q}$ connecting the two Dirac cone valleys, another longer-range oscillation appears due to the presence of extended Fermi surface with characteristic wavevector $k_F$ [6]. When the disorder is introduced within the Anderson model, both atomic-scale oscillations and the Friedel oscillations due to Fermi surface survive [9]. Note that the Dirac picture remains quite robust against the weak disorder [10] within the generic Anderson model approach. Therefore, given the dimensional consistency, the overall physics of the RKKY interaction is expected to survive in the weak disorders considered in [9]. As we show in the following, for the model of vacant graphene considered here, even the Fermi surface oscillations are washed out. To begin with, note that since the functional dependence of the oscillatory part of the RKKY interaction on distance $R$ always comes through the combination $k_F R$, it could be viewed as an oscillatory function of $k_F$ instead. With this in mind, in figure 6 we have plotted the $\mu$-dependence of the pristine and vacant graphene with 1% and 6% vacancies at a fixed distance

Figure 5. Plot of $J_{RKKY}$ as a function as distance for (a) armchair and (b) zigzag directions at $\mu = 0$ for different values of $E_{sp^2}$ in a 1% vacant system. As can be seen, the exponent $\alpha$ is not much sensitive to the precise value of $E_{sp^2}$.

Figure 6. Plot of $J_{RKKY}$ as a function as $\mu$ for two points at a fixed distance $R = 32\alpha$ in the armchair direction. Vacancies tend to wash out Friedel oscillations. Concentration of vacancies is indicated in the legend.
For the clean graphene a perfect particle–hole symmetry is seen in the RKKY interaction which is a symmetry of the Hamiltonian. Also, an oscillatory dependence on $\mu$ is seen which implies oscillatory dependence on $k_F$ and hence on $k_F R$ on dimensional grounds. By adding vacancies to the system note that the particle–hole symmetry is lost as the presence of vacancies breaks such symmetry. At 0.01 vacancy concentration there are no Friedel oscillations up to $\mu$ values where the pristine graphene would complete one cycle of oscillations. Some oscillations with reduced amplitude can be seen below $\mu \approx -0.3$. When the vacancy concentration is increased up to 0.06 no Friedel oscillations can be found.

To compare the real-space profile of the oscillations more clearly, in figure 7 we have plotted $R^3 J_{\text{RKKY}}$ as a function of $R$ along the armchair direction for various values of $\mu$ at vacancy concentration 0.01. The plots are contrasted to the case of pristine graphene. As can be seen for the pristine graphene, when the chemical potential is at $\mu = 0$ which corresponds to the undoped case, the function $R^3 J_{\text{RKKY}}$ only shows atomic-scale oscillations at large $R$ (black, filled-square plot). When the chemical potential is tuned away from the Dirac point in pristine graphene (the red, filled-circle plot) it can be clearly seen that in addition to the atomic-scale oscillations, Friedel-type oscillations due to the presence of a Fermi surface with a definite characteristic scale $k_F$ appear and are superimposed onto the atomic-scale oscillations in agreement with analytical results for clean graphene [6]. However, the striking observation is made when 1% vacancies are introduced. In such case, not only are the atomic-scale oscillations diminished, but also there is no sign of oscillations due to ‘Fermi surface’ at chemical potentials corresponding to half-filling and $\mu = 0.1$. At $\mu = 0.3$ it seems that some tiny atomic scale oscillations are present, while longer-range Fermi surface oscillations are still absent. The absence of Friedel-type oscillations in vacant graphene indicates that in the presence of such amount of vacancies the picture of a Fermi surface with a sharp length scale $k_F^{-1}$ no longer holds. This is reminiscent of the disorder-driven non-Fermi-liquid behavior in Kondo alloys [26] where the creation of vacancies plays a role akin to alloying. Therefore it is likely that in such case the Fermi surface is characterized with a multitude of length scales arising from local Fermi surfaces, the disorder averaging over, which washes out the oscillations corresponding to the presence of a sharp single Fermi wavevector scale of clean metallic state. It should also be noted that in figure 7 in the case of pristine graphene the amplitude of long-range oscillations in the function $R^3 J_{\text{RKKY}}$ increases which indicates that the decay power in this type of term is weaker than the $R^{-3}$ behavior [6]. The same argument for the vacant system at $\mu = 0.3$ indicates that the decay power of $J_{\text{RKKY}}$ is not as strong as the $R^{-3}$ behavior.

The absence of Fermi surface oscillations in our model compared to the disordered graphene studied within the Anderson model in [9] is rooted in the basic difference between the model employed here and the generic Anderson model. The Anderson model addresses situations where very low concentration of random impurities (on the scale of one part per million or so) gives rise to spatial inhomogeneities, while our model deals with a situation where the concentration of impurities is so high that the impurities may even form their own (narrow) band [17]. This should be contrasted to the case of the Anderson model.

To summarize, we find that when vacancies on the scale of one per cent are introduced to graphene, the nature of RKKY interaction changes as follows: when the doping level is such that the chemical potential falls in the energy region where DOS is linear, the exponent $\alpha$ in $R^\alpha$ remains at $\alpha = -3$; otherwise the presence of vacancies pushes $\alpha$ to more negative values. Regarding the oscillatory nature of the RKKY interaction in pristine graphene, a few per cent vacancies wash out both atomic-scale oscillations and the Friedel oscillations due to the Fermi surface for a remarkable range of chemical potential values.

**Figure 7.** Plot of $R^3 J_{\text{RKKY}}$ as a function of $R$ for the armchair direction. The clean limit is compared with 1% vacancy situation at different doping levels. Adding the 1% vacancy kills both type of short-ranged and long-ranged oscillations for the considered chemical potentials.

**Appendix A. Statistics of geometric averages**

In this appendix we present the statistics of our geometric averaging process. We evaluate the probability distributions for both $x = (1/2) \ln(J_{\text{RKKY}})$ (corresponding to geometrical averaging) and $J_{\text{RKKY}}$ (corresponding to arithmetic averaging) in figure A.1 panels (a) and (b) respectively. As can be seen, the distribution in $x$ is a Gaussian, 

$$P(x) = \frac{N}{\sqrt{2\pi}\sigma^2} \exp \left[ -\frac{(x-x_0)^2}{2\sigma^2} \right].$$  \hspace{1cm} (9)

By fitting the Gaussian to the distribution data in panel (a), we find the corresponding width $\sigma$ of the distribution, which is plotted in figure A.1(c) as a function of the impurity concentration. It is interesting to compare the behavior in figure A.1(b) with the linear behavior reported in [9] for the Anderson model disorder.
Appendix B. Adjusting the chemical potential in KPM

In this appendix we derive a simple relation that enables us to find the chemical potential corresponding to a given number of electrons in the system. To be self-contained, we briefly review the kernel polynomial method (KPM) as well [24].

Consider a quadratic Hamiltonian $H$ whose energy eigenvalues $E$ are limited to a bandwidth $[E_{\text{min}}, E_{\text{max}}]$. Rescaling the Hamiltonian from $H(E)$ to $\hat{H}(\varepsilon)$ where $\hat{H} = (H-b)/a$ and $\varepsilon = (E-b)/a$ where $b = (E_{\text{max}} + E_{\text{min}})/2$ and $a = (E_{\text{max}} - E_{\text{min}})/2$, one can expand spectral functions such as the DOS in a complete set of e.g. Chebyshev polynomials defined in the range $\varepsilon \in [-1, 1]$ as

$$\hat{\rho}(\varepsilon) = \frac{1}{\pi \sqrt{1 - \varepsilon^2}} \left( \mu_0 g_0 + 2 \sum_{m=1}^{N_c} \mu_m g_m T_m(\varepsilon) \right)$$

(10)

where $T_m(\varepsilon) = \cos(m \arccos(\varepsilon))$ are the $m$th Chebyshev polynomials, $\mu_m$ are Chebyshev moments and $g_m$ are appropriate attenuation factors to minimize the Gibbs oscillations. The moments are traces of polynomials of the Hamiltonian and can be statistically calculated as a trace, $\mu_m = 1/r \sum_{n=1}^{r} \langle \phi_n | T_m(\hat{H}) | \phi_n \rangle$, where $\phi_n$ are random single-particle states, $r$ is the number of random realizations used in numerical calculations and $N_c$ is a large number where the expansion is cut off. To obtain the effect of $T_m(\hat{H})$ on a given ket, the recurrence relation of Chebyshev polynomials, $T_m(\hat{H}) = 2HT_{m-1}(\hat{H}) - T_{m-2}(\hat{H})$ with initial conditions $T_1(\hat{H}) = \hat{H}$ and $T_0(\hat{H}) = 1$, is used. At the end the DOS in the original bandwidth scale is obtained as $\rho(E) = \hat{\rho}(\varepsilon)/a$.

The spectral functions corresponding to space non-diagonal propagation can also be similarly calculated between any two points $i$ and $j$ in the lattice,

$$\hat{\rho}_{ij}(\varepsilon) = \frac{1}{\pi \sqrt{1 - \varepsilon^2}} \left( \mu_0^i g_0^i + 2 \sum_{m=1}^{M} \mu_m^i g_m^i T_m(\varepsilon) \right),$$

(11)

where the non-local moment $\mu_m^{ij}$ is given by the matrix element $\langle i | T_m(\hat{H}) | j \rangle$.

When we add vacancies in a graphene sheet, the particle–hole symmetry is lost, and the half-filling will no longer correspond to $\mu = 0$. Therefore within the KPM we need to find a formula to give a relation between the particle number density $n$ and the chemical potential $\mu$. The filling factor is given by

$$n(\mu) = \int_{-1}^{+1} \theta(\varepsilon - \mu) \hat{\rho}(\varepsilon) d\varepsilon,$$

(12)

where $\theta(\varepsilon - \mu)$ is a Heaviside function and $\mu$ is the (scaled) Fermi level. Expanding the integral in Chebyshev polynomials and using the trigonometric representation of Chebyshev polynomials one can easily perform the integration to get

$$n = \frac{\mu_0 g_0}{\pi} \arccos(-\mu) - 2 \sum_{m=1}^{N_c} \frac{\mu_m g_m}{m \pi} \sin(m \arccos \mu).$$

(13)

For a given $n$ one needs to adjust $\mu$ to satisfy this equation. Then the physical $\mu$ is obtained by undoing the rescaling. For example it can be checked that in clean graphene, the solution of the above equation with $n(\mu) = 0.5$ will be given by $\mu = 0$.

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666
[2] For a concise review, see e.g. Ando T 2007 Physica E 40 213
[3] Katsnelson M I 2007 Mater. Today 10 20
[4] Saremi S 2007 Phys. Rev. B 76 184430
[5] Sherafati M and Satpathy S 2011 Phys. Rev. B 83 165425
[6] Sherafati M and Satpathy S 2011 Phys. Rev. B 84 125416
[7] Kogan E 2011 Phys. Rev. B 84 115119
[8] Kogan E 2012 arxiv:1211.5775
[9] Lee H, Kim J, Mucciolo E R, Bouzerar G and Kettemann S 2012 Phys. Rev. B 85 075420
[9] Lee H, Kim J, Mucciolo E R, Bouzerar G and Kettemann S 2012 Phys. Rev. B 86 205427

[10] Amini M, Jafari S A and Shahbazi F 2009 Europhys. Lett. 87 37002

[11] Hashimoto A, Suenaga K, Gloter A, Urita K and Iijima S 2004 Nature 430 870

[12] Nair R R, Sepioni M, Tsai I-L, Lehtinen O, Keinonen J, Krasheninnikov A V, Thomson T, Geim A K and Grigorieva I V 2012 Nature Phys. 8 199

[13] Yazyev O and Helm L 2007 Phys. Rev. B 75 125408

[14] Ugeda M M, Brihuega I, Guinea F and Gomez-Rodriguez J M 2010 Phys. Rev. Lett. 104 096804

[15] Chen J-H, Cullen W G, Jang C, Fuhrer M S and Williams E D 2009 Phys. Rev. Lett. 102 236805

[16] Chen J-H, Cullen W G, Williams E D and Fuhrer M S 2011 Nature Phys. 7 535

[17] Haberer D et al 2011 Phys. Rev. B 83 165433

[18] Allaei M, Jafari S A and Akbarzadeh H 2008 J. Phys. Chem. Solids 69 3283

[19] Pereira V M et al 2006 Phys. Rev. Lett. 96 036801

[20] Kanao T, Matsuura H and Ogata M 2012 J. Phys. Soc. Japan 81 063709

[21] Perezag D, Frauenheim Th, Köhler Th, Seifert G and Kaschner R 1995 Phys. Rev. B 51 12947

[22] Sólyom J 2010 Fundamentals of the Physics of Solids vol 3 (Berlin: Springer)

[23] White R M 1970 Quantum Theory of Magnetism (New York: McGraw-Hill)

[24] Weiße A, Wellein G, Alvermann A and Fehske G 2006 Rev. Mod. Phys. 78 275

[25] Black-Schaffer M 2010 Phys. Rev. B 81 205416

[26] Miranda E, Dobrosavljevic V and Kotliar G 1997 Phys. Rev. Lett. 78 290