Ferrimagnetism and single-particle excitations in a periodic Anderson model on the honeycomb lattice

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Abstract. By using the variational cluster approximation and cluster perturbation theory, we investigate the magnetism and single-particle excitations of a periodic Anderson model on the honeycomb lattice as an effective model for the single-side hydrogenated graphene, namely, graphone. We calculate the magnetic moment as a function of $U$ (Coulomb interaction on impurity sites) with showing that the ground state is ferrimagnetic for any $U > 0$. We then calculate the single-particle excitations and show that the single-particle excitations are gapless and exhibit quadratic dispersion relation near the Fermi energy.

1. Introduction

Recently, a series of hydrogenated graphene [1, 2] attracts increasing attention because of its potential rich physics. A first-principles calculation based on density functional theory (DFT) has predicted that the single-side hydrogenated graphene, called graphone, becomes a ferromagnetic semiconductor with a small indirect gap [3]. Other DFT based study has suggested that the single-side hydrogenated and fluorinated graphenes can be a quantum spin liquid [4]. Possible increase of the spin-orbit coupling due to the $sp^3$ lattice distortion has been also discussed [5, 6]. However, electron correlation effects on the hydrogenated graphene beyond the DFT based calculations have not been investigated so far.

Here, we employ the variational cluster approximation (VCA) [7] and the cluster perturbation theory (CPT) [8] to investigate electron correlation effects on graphone by modeling it as a half-filled periodic Anderson model on the honeycomb lattice. We find that the ground state is ferrimagnetic (FM). The calculation of the magnetic moment as a function of electron correlation $U$ at zero temperature shows that the magnetic moment in the weak-coupling region is naturally related to the flat-band FM. We also calculate the single-particle excitations and show that the low-energy excitations display the gapless quadratic dispersion.

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Figure 1. The periodic Anderson model on the honeycomb lattice. Carbon sites on $A$- and $B$-sublattices are denoted as green and red circles, respectively, and hydrogen sites are denoted as yellow circles. The shaded regions represent the 4-site (6-orbital) clusters used in the VCA and the CPT calculations. The arrows indicate primitive translational vectors for the cluster. The primitive translational vectors of the honeycomb lattice are also denoted by $d_1$ and $d_2$.

Figure 2. The Brillouin zone of the honeycomb lattice. $\Gamma$, $M$, $K$, and $K'$ points are denoted as dots. Here $\Gamma = (0, 0)$ and $M = 4\pi/3(0, \sqrt{3}/2)$. The thick triangle connecting $\Gamma$, $M$, and $K$ points represents the momentum path used in Figs. 3(a) and (b).

2. Model
2.1. Periodic Anderson model
We consider a periodic Anderson model on the honeycomb lattice defined as

$$\mathcal{H} = \mathcal{H}_0 + \epsilon_H \sum_{i,\sigma} n_i \sigma H + U \sum_i n_{i+1} \sigma H n_i \sigma H,$$

where

$$\mathcal{H}_0 = -t \sum_{\langle i,j \rangle, \sigma} c_{i \sigma A} c_{j \sigma B} - t \sum_{i, \sigma} c_{i \sigma A} c_{i \sigma B} + t_{sp} \sum_{i, \sigma} c_{i \sigma B} c_{i \sigma H} + \text{H.c.},$$

(1)
$c^\dagger_{i\sigma\alpha}$ is the electron creation operator with spin $\sigma$ (=$\uparrow, \downarrow$) and orbital $\alpha$ (= $A, B, H$) in the $i$-th unit cell, and $n_{i\sigma\alpha} = c^\dagger_{i\sigma\alpha}c_{i\sigma\alpha}$. Here, orbital $A (B)$ denotes carbon $p_z$ orbital on $A (B)$-sublattice of the honeycomb lattice and orbital $H$ indicates hydrogen $s$ orbital [see Fig. 1(a)]. The sum in the first term of Eq. (2), indicated by $(i, j)$, runs over all pairs of nearest-neighboring unit cells. The first and second terms represent the hopping between the nearest-neighboring carbon sites with the hopping integral $t$, forming the conduction bands. $t_{sp}$ is the hybridization between the hydrogen “impurity” site and the carbon site on $B$-sublattice. $\epsilon_H$ is the on-site potential energy and $U$ is the on-site Coulomb repulsion of the hydrogen sites. This is the simplest model for graphene by implicitly assuming the hopping integral $t$ in Eq. (2) as the renormalized one due to electron correlations in carbon sites [9, 10]. We consider the particle-hole symmetric case with $\epsilon_H = -U/2$, in which the electron density $n$ is exactly 1 for any $U$ values. We also set $t = t_{sp} = 1$ and $\hbar = k_B = 1$.

### 2.2. Non-interacting limit

In the non-interacting case with $\epsilon_H = 0$, the Hamiltonian in the momentum space can be written as

$$\mathcal{H}_0 = \sum_{\mathbf{k}, \sigma} \left( c^\dagger_{i\kappa A}c^\dagger_{i\kappa B}c^\dagger_{i\kappa H} \right) \begin{pmatrix} 0 & \gamma_{\mathbf{k}} & 0 \\ \gamma_{\mathbf{k}}^* & 0 & t_{sp} \\ 0 & t_{sp} & 0 \end{pmatrix} \begin{pmatrix} c_{i\kappa A} \\ c_{i\kappa B} \\ c_{i\kappa H} \end{pmatrix},$$

where $c^\dagger_{i\kappa\alpha}$ is the Fourier transform of the real-space creation operator and

$$\gamma_{\mathbf{k}} = -t \left( 1 + e^{i\mathbf{k}\cdot\mathbf{d}_1} + e^{i\mathbf{k}\cdot\mathbf{d}_2} \right)$$

is the matrix element between carbon $p_z$ orbitals on $A$ and $B$ sublattices. Here,

$$\mathbf{d}_1 = \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right), \quad \mathbf{d}_2 = \left( -\frac{1}{2}, \frac{\sqrt{3}}{2} \right),$$

Figure 3. (a) The non-interacting tight-binding dispersion relations $E_{\mathbf{k}}^-$, $E_{\mathbf{k}}^{\text{flat}}$, and $E_{\mathbf{k}}^+$ with $t_{sp}/t = 1$ (red solid lines). The non-interacting tight-binding dispersion relations for pure graphene model are also shown (blue dashed lines). (b) The orbital-resolved spectral weights $w_{\mathbf{k}A}^{\text{flat}}$, $w_{\mathbf{k}B}^{\text{flat}}$, and $w_{\mathbf{k}H}^{\text{flat}}$ for the flat band $E_{\mathbf{k}}^{\text{flat}}$ in the non-interacting limit with $t_{sp}/t = 1$. The results are shown along the path in the momentum space given in Fig. 2.
are primitive translational vectors of the honeycomb lattice (Fig. 1). Notice that, at \( k = K \) and \( K' \) points defined as (see also Fig. 2)

\[
K = \frac{4\pi}{3} \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right), \quad K' = \frac{4\pi}{3} \left( -\frac{1}{2}, \frac{\sqrt{3}}{2} \right),
\]

(6)

\( \gamma_k \) becomes zero, i.e., \( \gamma_K = \gamma_K' = -t(1 + e^{2\pi i/3} + e^{4\pi i/3}) = 0 \). The non-interacting tight-binding band dispersion relations are given as

\[
E^\text{flat}_k = 0,
\]

(7)

\[
E^\pm_k = \pm \sqrt{|\gamma_k|^2 + t_{sp}^2}.
\]

(8)

We thus find that \( \mathcal{H}_0 \) has a flat band just at the Fermi energy \( E_F = 0 \). It also should be noted that the massless Dirac electronic dispersion is absent in the non-interacting limit [see Fig. 3(a)]. The orbital-resolved spectral weights for the flat band are given as

\[
\omega^\text{flat}_{kA} = \langle \psi^\text{flat}_k \mid c^\dagger_{kA\sigma} c_{kA\sigma} \mid \psi^\text{flat}_k \rangle = \frac{t_{sp}^2}{|\gamma_k|^2 + t_{sp}^2},
\]

(9)

\[
\omega^\text{flat}_{kB} = \langle \psi^\text{flat}_k \mid c^\dagger_{kB\sigma} c_{kB\sigma} \mid \psi^\text{flat}_k \rangle = 0
\]

(10)

\[
\omega^\text{flat}_{kH} = \langle \psi^\text{flat}_k \mid c^\dagger_{kH\sigma} c_{kH\sigma} \mid \psi^\text{flat}_k \rangle = \frac{|\gamma_k|^2}{|\gamma_k|^2 + t_{sp}^2},
\]

(11)

where \( \mid \psi^\text{flat}_k \rangle \) is the eigenstate of the flat band. Equations (9)-(11) indicate that the flat band consists of \( A \) and \( H \) orbitals, but not \( B \) orbital. In particular, the flat band at \( K \) (and \( K' \)) point is solely consists of \( A \) orbital [see Fig. 3(b)].

The existence of the flat band Eq. (7) can be understood by recalling the Lieb’s argument on bipartite lattices [11]. Namely, because of the imbalance of the number of sublattices, \( \mathcal{H}_0 \) has \( |A| + |H| - |B| \) (\( |\alpha| \): the number of \( \alpha \) orbitals) zero eigenvalues, forming the flat band. This also explains why the wave functions with zero eigenvalues are contributed only from \( A \) and \( H \) orbitals, but not from \( B \) orbital. It should be also noted here that the tight-binding model considered here captures the characteristic features of the band structures for graphene obtained by a spin-unpolarized DFT calculation [4].

3. Methods

3.1. Variational cluster approximation

In order to investigate a possible symmetry breaking state, we employ the VCA [7] which is a cluster method formulated based on the self-energy-functional theory [12]. In the VCA, the original lattice is divided into disconnected finite-size clusters, and then variational parameters are introduced to examine possible symmetry breaking states. Here the two-body interaction term must be the same as the original one, whereas the one-body term can be changed [12]. The collection of these disconnected clusters is called “reference system” and its self-energy is used as a trial function for the grand-potential functional to be optimized based on the self-energy functional theory.

Here, we introduce, as a variational parameter, a uniform field \( h' \) on the hydrogen (impurity) sites [13] described as

\[
\mathcal{H}_{h'} = h' \sum_i (n_{i\uparrow H} - n_{i\downarrow H}).
\]

(12)
The reference system $H_{\text{ref}}$ considered is thus composed of a collection of disconnected finite size clusters as shown in Fig. 1(a), each cluster being described by $\mathcal{H}$ with no hopping terms between clusters (denoted as $H_c$), and $H_{\text{h'}}$, i.e., $H_{\text{ref}} = H_c + H_{\text{h'}}$.

In the VCA, the grand-potential functional per unit cell at zero temperature is given as [14]

$$
\Omega = \frac{1}{L_c} \Omega' - \frac{1}{NL_c \pi} \int_0^\infty dx \sum_{\sigma} \sum_{k} \ln \left| \det \left( I - V_\sigma(k) G_{\sigma}(ix) \right) \right|,
$$

(13)

where $\Omega'$ is the exact grand potential of the single cluster, $\mathbf{k}$ is the wave vector defined in the reduced Brillouin zone of the reference system, $N$ is the number of clusters and $L_c$ is the number of unit cells in a cluster. The exact single-particle Green’s function of $H_{\text{ref}}$ is denoted as $G_{\sigma}(ix)$ and $V_\sigma \equiv G_{\sigma}^{-1} - G_{\sigma}^{-1}_0$ represents the difference between the one-body terms of $\mathcal{H}$ and $H_{\text{ref}}$. We employ the exact diagonalization technique to calculate $G_{\sigma}(ix)$ and $\Omega'$. The FM state is obtained when a saddle point $\partial \Omega / \partial h' |_{h'=-h^*} = 0$ with the lowest $\Omega$ is at $h^* \neq 0$. Notice that in this paper we focus on the physics at zero temperature.

3.2. Cluster perturbation theory

The CPT [8] is employed to obtain the translational invariant Green’s function of the infinite systems. In the CPT, the single-particle Green’s function $G_{\sigma}^{D}(\mathbf{k}, \omega)$ is given as

$$
G_{\sigma}^{D}(\mathbf{k}, \omega) = \frac{1}{3L_c} \sum_{i,j} \left( G_{\sigma}^{-1}(\omega) - V_\sigma(\mathbf{k}) \right)^{-1}_{i\alpha,j\beta} e^{-i \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)},
$$

(14)

where $\mathbf{r}_i$ denotes the location of the $i$-th unit cell in the cluster. Here, the momentum $\mathbf{k}$ can take arbitrary value in the momentum space, and the frequency $\omega$ can only be taken by the complex-frequency space. The single-particle spectral function for $\alpha$ orbital with spin $\sigma$ is given as

$$
A_{\sigma}^{\alpha}(\mathbf{k}, \omega) = \frac{1}{\pi} \Im G_{\sigma}^{\alpha\alpha}(\mathbf{k}, \omega + i\eta),
$$

(15)

where $\eta$ gives the Lorentzian broadening of the spectra.

4. Results

4.1. Ferrimagnetism

By calculating the grand-potential functional $\Omega$ as a function of $h'$, we find that the FM state is stabilized for $U > 0$. We then calculate the magnetic moment per unit cell defined as

$$
m_z = \sum_\alpha m_{z\alpha}
$$

(16)

where $m_{z\alpha}$ is the magnetic moment of $\alpha$ orbital per unit cell which is given as [14]

$$
m_{z\alpha} = \frac{1}{NL_c \pi} \int_0^\infty dx \sum_{\sigma} \sum_{k} \sum_i \sigma_z \Re \left[ \left( G_{\sigma}^{-1}(ix) - V_\sigma(\mathbf{k}) \right)^{-1} \right]_{i\alpha,i\alpha}
$$

(17)

with $\sigma_z$ being the $z$ component of the Pauli matrices, i.e., $\sigma_z = 1(-1)$ for $\sigma = \uparrow (\downarrow)$. Figure 4 shows the calculated results of $m_{zA}, m_{zB}, m_{zH}$, and $m_z$ as a function of $U/t$ at zero temperature. We find that $m_z = 1$ within the numerical accuracy for any $U$. We also find that $m_{zA} > 0$, $m_{zB} < 0$, and $m_{zH} > 0$ as expected from the bipartite structure of the lattice. In the small $U$ region, $m_{zB}$ approaches to zero, whereas $m_{zA}$ and $m_{zH}$ approach finite values in the non-interacting limit. Now let us consider the magnetic moment in the non-interacting limit. Since
there exists the flat band at $E_F$, the system is unstable against the FM long-range order for any $U > 0$. Assuming that the flat band is fully polarized in the non-interacting limit, the magnetic moments in the non-interacting limit can be calculated as [see Eqs. (9), (10), and (11)]

$$\lim_{U \to 0} m_{zA} = \frac{1}{L} \sum_k \frac{t_{sp}^2}{|\gamma_k|^2 + t_{sp}^2} \simeq 0.362,$$

$$\lim_{U \to 0} m_{zB} = 0,$$

$$\lim_{U \to 0} m_{zH} = \frac{1}{L} \sum_k \frac{|\gamma_k|^2}{|\gamma_k|^2 + t_{sp}^2} \simeq 0.638,$$

where $L$ is the number of unit cells and the numerical values are for $t = t_{sp} = 1$. The magnetic moments calculated by the VCA indeed approach to those values with decreasing $U$. Notice that a similar model on the square lattices has been recently studied in Ref. [15].

In the large $U$ region, the magnetic moment becomes dominated by $H$ orbital. Note that, in the strong coupling limit, an electron in each hydrogen site is completely localized and the RKKY interaction [16, 17, 18] between these localized spins is ferromagnetic [19], which naturally induces the FM ground state.

4.2. Single-particle excitations

Figures 5(a)-(d) show the single-particle excitation spectra $A_{\sigma \alpha}^a(k, \omega)$ for momentum $k$ around $K$ point at $U/t = 4$. The low-energy single-particle excitations show quadratic dispersion relation around $K$ point, indicating massive Dirac quasi-particle excitations. Although the dispersion
relation is massive, the single-particle gap is absent at $K$ point. We also find that the $A$-orbital spectral weight at $K$ point at $E_F$ is finite even there exists the electron correlation $U$ in $H$ orbital, which also forms the flat band in the non-interacting limit. This is because the $A$ orbital is completely decoupled from the $H$ orbital at $K$ point in the non-interacting limit [see Fig. 3(b)], thereby the electron correlation $U$ on $H$ orbital does not affect the spectrum of $A$ orbital at $K$ point. Therefore, the single-particle gap is absent at $K$ point even at finite $U$. The same discussion holds for $K'$ point. The single-particle excitation spectra in the FM state thus exhibit point-contact massive Dirac dispersion.

5. Summary
Using the VCA and the CPT, we have studied the magnetism and single-particle excitations of a half-filled periodic Anderson model at zero temperature. We have calculated the spontaneous magnetization as a function of electron correlation $U$. In the small $U$ region, the calculated magnetic moments approach to those estimated from the flat-band ferrimagnetism. In the large $U$ region, the $H$ orbital gives the dominant contribution to the magnetic moment. Interestingly, the single-particle excitations in the FM state show a point-contact quadratic dispersion relation around the $K$ and $K'$ points. So far our study has been done at zero temperature in the magnetic state. Further study at finite temperatures in which the magnetic long-range order is destabilized will be reported elsewhere [20].
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