Importance of on-site interaction in graphene.

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We use the Gutzwiller method to investigate the importance of the on-site Coulomb interaction in graphene. We apply it to Hubbard Hamiltonian to study the renormalization of the kinetic energy in graphene due to the on-site Coulomb interaction. We find that a reasonable strength of the interaction has a very weak effect in reducing the kinetic energy. Hence we predict that the Brinkmann-Rice metal-insulator transition in graphene is not possible. The effect is understood in terms of the high kinetic energy in graphene.

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Graphene is a two dimensional (2D) crystal of carbon atoms. It is an allotropy form of Carbon in which the atoms form a honeycomb lattice. The experimental success of creating the graphene[1, 2] has renewed the interest of studying the electronic properties of the two dimensional electron system. It is because the 2D crystals were predicted to be thermodynamically unstable at finite temperature.[3, 4] Graphene is stabilized by strong covalent bonding between carbon atoms and a small crumpling in the third dimension which increases the elastic energy. It was known theoretically that the low energy excitations of graphene behave as massless Dirac fermion [5]; which leads to different electronic properties in this system. In fact, the observation of the half integer quantum Hall effect in graphene is one of the examples.[2]

In graphene the nearest neighbor hopping, which sets a scale to the kinetic energy, is very high. In such case we need to understand how important the role of the Coulomb interaction will be in determining the electronic properties. Our previous study shows that the effect of the long range Coulomb interaction is not important in single layer graphene. We have shown that this system can not have charge inhomogeneous states ([6, 7]). It has also been shown that this system can not undergo a ferromagnetic transition([8]). Even if there is a consensus about the fact that the Coulomb interaction does not have a strong effect on the electronic properties of graphene, we do here an explicit calculation to benchmark this statement. We study the importance of the on-site Coulomb interaction using Hubbard model in Gutzwiller approach.[9, 10] In Gutzwiller frame work the Hubbard model leads to the possibility of a metal insulator transition at half filling, which is also known as the Brinkmann-Rice transition. The idea is to look at the effect of the on-site Coulomb repulsion on the renormalization factor of the kinetic energy which is a direct measure of the correlation effect. In graphene we find that the renormalization in the kinetic energy is very small. Hence we infer that the system can not be even close to the Brinkmann-Rice Metal-Insulator transition.

First, we introduce the Gutzwiller method briefly for which we closely follow Ref. [11]. Among numerous theoretical approaches, the Gutzwiller method provides a transparent physical interpretation in terms of the atomic configurations of a given site. Originally, it was applied to the one-band Hubbard model Hamiltonian. [12] In graphene also the electronic band close to the Fermi level is formed by the hybridization of neighboring p_z orbital. So introducing single Slater Koster [13] parameter $p_{\text{p}} \approx 3.0 \text{eV}$ it is straightforward to use the method in this system. We begin with the Hubbard Hamiltonian, 

$$H = H_{\text{kin}} + H_{\text{int}},$$

with,

$$H_{\text{kin}} = \sum_{i\neq j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma},$$

and,

$$H_{\text{int}} = U \sum_{i} n_{i\uparrow} n_{i\downarrow}.$$
an additional energy $U$ per site. Accordingly, the trial Gutzwiller wave function (GWF) $|\psi_G\rangle$ is built from the HWF $|\psi_0\rangle$,

$$|\psi_G\rangle = g^D|\psi_0\rangle. \tag{4}$$

The role of $g^D$ is to reduce the weight of the configurations with doubly occupied sites, where $D = \sum_i n_i^2 n_{-i}$ measures the number of double occupations and $g(<1)$ is a variational parameter. In fact, this method corrects the mean field (Hartree) approach for which up and down spin electrons are independent, and, some how, overestimates configurations with double occupied sites. Using the Rayleigh-Ritz principle, this parameter is determined by minimization of the energy in the Gutzwiller state $|\psi_G\rangle$, giving an upper bound to the true unknown ground state energy of $H$. Note that to enable this calculation to be tractable, it is necessary to use the Gutzwiller’s approximation which assumes that all configurations in the HWF have the same weight.

Nozieres \cite{14} proposed an alternative way which shows that the Gutzwiller approach is equivalent to the renormalization of the density matrix in the GWF. It can be formalized as

$$\rho_G = T^\dagger \rho_0 T. \tag{5}$$

The density matrices $\rho_G = |\psi_G\rangle \langle \psi_G|$ and $\rho_0 = |\psi_0\rangle \langle \psi_0|$ are projectors on the GWF and HWF respectively. $T$ is an operator which is diagonal in the configuration basis; $T = \prod_i T_i$ where $T_i$ is a diagonal operator acting on site $i$,

$$T_i|L_i, L'_i\rangle = \sqrt{\frac{p(L_i)}{p_0(L_i)}}|L_i, L'_i\rangle. \tag{6}$$

Here, $L_i$ is an atomic configuration of the site $i$, with probability $p(L_i)$ in the GWF and $p_0(L_i)$ in the HWF respectively, whereas $L'_i$ is a configuration of the remaining sites of the lattice. Note that this prescription does not change the phase of the wave function as the eigenvalues of the operators $T_i$ are real. The correlations are local, and the configuration probabilities for different sites are independent.

The expectation value of the Hamiltonian is given by,

$$\langle H \rangle_G = Tr(\rho_G H). \tag{7}$$

The mean value of the on-site operators is exactly calculated with the double occupancy probability, $d_i = \langle n_{i\uparrow} n_{i\downarrow}\rangle_G$. $d_i$ is the new variational parameters replacing $g$. Using Eqs. \tag{5,10}, the two-sites operator contribution of the kinetic energy can be written as,

$$\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_G = Tr(\rho_G c_{i\sigma}^\dagger c_{j\sigma}) = \langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0 \sum_{L_{-\sigma}} \frac{p(L'_{\sigma}, L_{-\sigma})}{p_0(L'_{\sigma})} \frac{p(L_{\sigma}, L_{-\sigma})}{p_0(L_{\sigma})}. \tag{8}$$

where $L'_{\sigma}$ and $L_{\sigma}$ are the only two configurations of spin $\sigma$ at sites $i$ and $j$ that give non-zero matrix element to the operator in the brackets. The summation is performed over the configurations of opposite spin $L_{-\sigma}$. The probabilities $p_0$ in the HWF depend only on the number of electrons, whereas the $p$ in the GWF also depends on $d_i$.

After some elementary algebra, one can show that the Gutzwiller mean value can be factorized into,

$$\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_G = \sqrt{q_{i\sigma}} \langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0 \sqrt{q_{j\sigma}}. \tag{9}$$

where these renormalization factors $q_{i\sigma}$ are local and can be expressed as,

$$\sqrt{q_{i\sigma}} = \frac{(1-n_{i\sigma}-n_{i-\sigma}+d_i+\sqrt{d_i})\sqrt{n_{i-\sigma}-d_i}}{\sqrt{n_{i\sigma}(1-n_{i\sigma})}}. \tag{10}$$

We used $n_{i\sigma}$ as a shorthand notation for $\langle n_{i\sigma}\rangle$, the average number of electrons on the considered “orbital-spin” in the HWF, which could be site and/or spin independent if the state is homogeneous and/or paramagnetic; this is the case we consider here.

As seen in Eq. \tag{9} the kinetic energy of the non-interacting electrons state, $\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0 = \varepsilon_{0\text{kin}}$, is renormalized by a factor of $q$ which is smaller than one in the correlated state, and equal to one in the HWF. This factor can be interpreted as a direct measure of the correlation effect. Indeed Vollhardt \cite{12} has shown that $1/q = m^*/m$ where $m^*$ is the effective mass and $m$ is the bare mass of the electron. Thus a $q$ close to 1 corresponds to less correlated electron system and smaller $q$ value reflects enhancement of the correlation effect. Eq. \tag{7} leads to the variational energy,

$$E(d) = \langle H \rangle_G = 2q\varepsilon_{0\text{kin}} + Ud, \tag{11}$$

which can be minimized with respect to the variational parameter $d$. In the case of half filling ($n=1/2$), we can show that the minimization condition is given by,

$$d = \frac{1}{4}(1 - \frac{U}{16\varepsilon_{0\text{kin}}}). \tag{12}$$
and,

\[ q = (1 - \frac{U^2}{(16c_{kin})^2}). \tag{13} \]

It implies that if the Coulomb repulsion \( U \) exceeds a critical value \( U_c = 16c_{kin} \), \( q \) is equal to zero, leading to an infinite quasiparticle mass with a Mott-Hubbard Metal-Insulator transition which is also known as "the Brinkmann-Rice transition" \[14\], as these authors first applied the Gutzwiller approximation to the Metal-Insulator transition.

To determine the magnitude of \( U_c \) we need to calculate the kinetic energy of the \( p_z \)-electrons in graphene. We use the recursion method to first calculate the local density of states (LDOS), i.e., projected on a given orbital:

\[ N_{\psi_1}(E) = \sum_n \delta(E - E_n)\langle \psi_1|n\rangle^2 \]

\[ = -\frac{1}{\pi} \lim_{\eta \to 0} \langle \psi_1 | \frac{1}{E + i\eta - H} | \psi_1 \rangle, \tag{14} \]

where \( |n\rangle \) are the eigenstates associated with eigenvalues \( E_n \), and using it we calculate the kinetic energy. Let us briefly remind the recursion method of finding the density of states. We follow Ref. \[17\] in describing the recursion method.

For a given normalized state \( |\psi_1\rangle \) in which we want to calculate the LDOS, we can always associate a recursion basis which is constructed by a Schmidt orthogonalization procedure starting from the set of states \( |\psi_1\rangle, H|\psi_1\rangle, H^2|\psi_1\rangle,...,H^{N-1}|\psi_1\rangle \). Let us consider \( H|\psi_1\rangle \). We can decompose it in a component parallel to \( |\psi_1\rangle \) and a component orthogonal to \( |\psi_1\rangle \). So we can write,

\[ H|\psi_1\rangle = a_1|\psi_1\rangle + b_1|\psi_2\rangle. \tag{15} \]

If the coefficient \( b_1 \) is chosen real and positive then \( |\psi_2\rangle \) can be defined in a unique way. Consider then \( H|\psi_2\rangle \), this vector can be decomposed in a component parallel to the space spanned by \( |\psi_1\rangle, |\psi_2\rangle \) and a component orthogonal to this space. Then we get,

\[ H|\psi_2\rangle = a_2|\psi_2\rangle + b'_1|\psi_1\rangle + b_2|\psi_3\rangle. \tag{16} \]

Furthermore, since \( H \) is a hermitian operator we deduce that \( b'_1 = b_1 \). If the coefficient \( b_2 \) is chosen real and positive then \( |\psi_3\rangle \) can also be defined in a unique way. We can repeat the process leading to the construction of a set of states \( |\psi_n\rangle \) which are orthonormal and satisfy,

\[ H|\psi_n\rangle = a_n|\psi_n\rangle + b_{n-1}|\psi_{n-1}\rangle + b_n|\psi_{n+1}\rangle. \tag{17} \]

In the basis of \( |\psi_n\rangle \) the Hamiltonian is tridiagonal. An important property of the states \( |\psi_n\rangle \) is that they spread progressively from the initial state. For example if \( |\psi_1\rangle \) is located on an atomic orbital \( p_z \) then the state \( |\psi_n\rangle \) can have non-zero components only on orbital that is reached by \( n - 1 \) applications of the Hamiltonian \( H \), i.e., \( n - 1 \) hopping from initial orbital.

The recursion basis establishes an order between states that are attained at shorter or longer times when the initial states is \( |\psi_1\rangle \). Thus, roughly speaking one expects that it is important to treat properly the states with smallest indices \( n \), and in general it will have smaller effect if states with larger indices are approximated or simply not considered.

From a technical point of view the interest of the recursion basis is that it can be used to calculate vectors like \( f(H)|\psi_1\rangle \) where \( f(H) \) is any operator that is a function of the Hamiltonian \( H \). This vector can be decomposed in the basis of the states \( |\psi_n\rangle \) as,

\[ f(H)|\psi_1\rangle = \sum_n |\psi_n\rangle \langle \psi_n|f(H)|\psi_1\rangle. \tag{18} \]

When one applies this method to a function, \( f(H) = (z - H)^{-1} \), one can show that,

\[ R(z) = \frac{1}{z - H}|\psi_1\rangle = \frac{1}{z - a_1 - \frac{b_1^2}{z - a_2 - \frac{b_2^2}{z - a_3 - \frac{b_3^2}{z - a_4 - \frac{b_4^2}{...}}}}. \tag{19} \]

In the simplest case where the spectrum does not have a gap, the coefficients \( a_n \) and \( b_n \) tend to a limit \( a_\infty \) and \( b_\infty \) respectively. If these limits are obtained to a good precision one can write

\[ R(z) = \frac{1}{z - a_1 - \frac{b_1^2}{z - a_2 - \frac{b_2^2}{z - a_3 - \frac{b_3^2}{z - a_4 - \frac{b_4^2}{...}}}}}, \tag{20} \]

where,

\[ R_T(z) = \frac{1}{z - a - \frac{b^2}{z - a - \frac{b^2}{z - a - \frac{b^2}{...}}}}. \tag{21} \]
is known as the terminator of the series. This infinite expansion means that $R_T(z)$ obeys a simple relation,

$$R_T(z) = \frac{1}{z - a - b^2 R_T(z)}, \quad (22)$$

from which one deduces,

$$R_T(z) = \frac{z - a \pm \sqrt{(z - a)^2 - 4b^2}}{2b^2}. \quad (23)$$

So $R_T(z)$ is the resolvent for a semi-elliptic density of states with energies in the range $a - 2b \leq E \leq a + 2b$. In the case of graphene, due to the the symmetry of the honeycomb lattice, all $a_n = 0$. On another hand the presence of the pseudo gap in the middle of the band leads to two alternating limits for $b_{\text{odd}}$ and $b_{\text{even}}$. Thus we use a second order terminator, which can be written as,

$$R_T(z) = \frac{1}{z - a_\infty - \frac{b_2}{z - a_\infty - b_\infty^2 R_T(z)}}, \quad (24)$$

which can be easily solved.

This continued fraction expansion of the diagonal element of the resolvent provides an efficient way of computing the LDOS using the relation,

$$N(E) = -\frac{1}{\pi} \text{Im} R(E). \quad (25)$$

Once we get the density of states as a function of filling factor, we can calculate the kinetic energy per spin using,

$$\varepsilon_{\text{kin}}^0 = \int_{a-2b}^{E} EN(E)dE. \quad (26)$$

The calculated density of states and kinetic energy as a function filling factor is presented in Fig. 1. The energy is measured in terms of $t = 3.0eV(=pp\pi)$, the nearest neighbor hopping energy. From the figure we can see that the kinetic energy per spin at half filling, $\varepsilon_{\text{kin}}^0 \approx 2.4eV$. So the critical on site repulsion required for the Brinkman-Rice transition is $U_C = 38.4eV$ which is far from being a plausible magnitude of the Coulomb interaction in graphene.

We also calculate the kinetic energy renormalization factor $q$ as a function of the on site Coulomb energy. The result is shown in Fig. 2. We can clearly see form the figure that the renormalization of the kinetic energy due to the on site Coulomb interaction is very small for practical values of the interaction. For example, even for the interaction as high as 10eV the kinetic energy is reduced by only about 5%.

In conclusion, we used Gutzwiller method to study the Brinkman-Rice transition in single layer graphene. We calculate the density of states and the kinetic energy of electrons at half filling using recursion method. We find that the kinetic energy of electrons in graphene is very high such that the potential energy required to have the metal insulator transition is unpractically high. The on-site Coulomb interaction has very small effect on the renormalization of the kinetic energy.

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