Effect of inter-site Coulomb correlation on Band gap of Graphene-on-Substrates

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Abstract. The pristine graphene has zero band gap at Dirac points. However small band gaps have been observed, when graphene is placed on substrates such as silicon carbide (SiC), silicon dioxide (SiO_2) and Gold (Au) on Ruthenium. In order to study the effect of inter-site Coulomb correlation   as well as on-site Coulomb correlation on these gaps, we propose here a tight binding model taking into account of electrons hoppings upto third nearest- neighbor hoppings in honeycomb lattice of graphene in presence of on-site and inter-site Coulomb interactions on both sites. Here Coulomb interactions are treated within a mean-field approximation and the difference in electron occupation numbers is computed numerically and self- consistently. Then the effect of Coulomb interaction on the band gap of the graphene is investigated by varying the on-site and inter-site Coulomb interaction Potentials. Finally Results are discussed with respect to experimental observations.

Keywords. Graphene, Coulomb potential , Occupation number

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1.   Introduction

Graphene [1] is a single layer, two dimensional (2D) crystal of carbon atoms arranged on a hexagonal honeycomb crystal lattice that has two atoms per unit cell. It has become the most attractive carbon based material and one of the hot topics in the condensed matter physics [2]. The 2D electronic properties of graphene are well described by π- band tight binding (TB) model [3]. The valence and conduction bands touch at the six corner points K (Dirac Point) of the 2D Brillouin zone (BZ). At low energies, the electronic dispersions are linear

in momentum and the tip of the two cones associated with valence and conduction bands respectively meet at a single Dirac point in pristine graphene. The Coulomb interaction remains a long standing problem for the graphene physics. The long ranged Coulomb interaction in pristine graphene may lead to insulating state due to strongly correlated electrons and may lead to metal-insulator transition or magnetisms due to weak correlation. Due to repulsive Coulomb interactions, there exists the evidence for modification of bare dispersions due to formation of plasmarons. Experimentally angle resolved photoemission spectroscopy (ARPES) spectra show that the Dirac point associated with the point of coincidence of valence and conduction bands is splitted into two and an extended plasmaron region is observed between these two points[4]. We have reported earlier the study of band gap opening in graphene by impurity effect taking in account of the third nearest-neighbor hopping electron hoppings in absence of Coulomb interaction [5] and in the presence of on-site Coulomb interaction [6]. In the present communication, we investigate the effect of inter-site Coulomb interaction on the charge gap and electronic energy dispersion in mono-layer graphene. We describe the model Hamiltonian in section 2 and calculation of electron Green's functions and band gap equation in section 3.We present the results and discussion in section 4 and conclusion in section 5.

2. Model Hamiltonian

The tight-binding Hamiltonian of a monolayer graphene containing repulsive Coulomb interactions of electrons is given by

$$H_0 = \sum_{i,\sigma} \epsilon_a \, a_{i,\sigma}^\dagger \, a_{i,\sigma} + \sum_{j,\sigma} \epsilon_b \, b_{i,\sigma}^\dagger \, b_{j,\sigma} \tag{1}$$

$$H_1 = -t_1 \sum_{<i,j>,\sigma} [\, a_{i,\sigma}^\dagger \, b_{j,\sigma} + \, b_{j,\sigma}^\dagger \, a_{i,\sigma}] \tag{2}$$

$$H_2 = -t_2 \sum_{<<i,j>>,\sigma} [\, a_{i,\sigma}^\dagger \, a_{j,\sigma} + \, b_{j,\sigma}^\dagger \, b_{i,\sigma} + h.p\,] \tag{3}$$

$$H_3 = -t_3 \sum_{\ll i,j \gg,\sigma} [\, a_{i,\sigma}^\dagger \, b_{j,\sigma} + \, b_{j,\sigma}^\dagger \, a_{i,\sigma}] \tag{4}$$

$$H_{sub} = \sum_{i,j,\sigma} \Delta \left(\, a_{i,\sigma}^\dagger \, a_{i,\sigma} - b_{j,\sigma}^\dagger \, b_{j,\sigma} \right) \tag{5}$$

$$H_{imp} = \sum_{i,j,\sigma} V_0 \left(\, x_a \, a_{i,\sigma}^\dagger \, a_{i,\sigma} + \, x_b \, b_{j,\sigma}^\dagger \, b_{j,\sigma} \right) \tag{6}$$

$$H_U = U \sum_i \left(n_{i\uparrow}^a \ n_{i\downarrow}^a + n_{i\uparrow}^b \ n_{i\downarrow}^b \right) + U_1 \sum_{i,j} \left(n_{i,\uparrow}^a \ n_{j,\downarrow}^b + n_{i,\uparrow}^b \ n_{j,\downarrow}^a \right) \qquad (7)$$

The Hamiltonian H_0, H_1, H_2 and H_3 represent the on-site and first-to-third nearest-neighbor hopping of electrons inside the carbon atoms having t_1, t_2, and t_3 as the hopping integrals. Here $a_{i,\sigma}^\dagger (a_{i,\sigma})$ and $b_{j,\sigma}^\dagger (b_{j,\sigma})$ are the respective creation (annihilation) operators of electrons at A and B sublattice atoms with site energies ϵ_a and ϵ_b. The Hamiltonian H_{sub} represents the substrate effect on graphene where the orbital's on A-sites are shifted in energy by Δ and decreased in energy by $-\Delta$ on B producing a gap 2Δ. The Hamiltonian H_U represents the effect of Coulomb repulsive interactions in graphene. The U and U_1 represent the on-site and inter-site Coulomb potentials with $n_{i\uparrow}^a$ ($n_{i\downarrow}^a$) is the occupation number of up spin (downspin) at A sub-lattices and $n_{i\uparrow}^b$ ($n_{i\downarrow}^b$) is the occupation number of upspin (downspin) occupation number at B sub lattices respectively. For weak coupling, the interacting Hamiltonian (H_U) may be decoupled using Hartree-Fock approximation i.e. $U\, n_{i\uparrow}^\alpha \ n_{i\downarrow}^\alpha \approx U < n_{i\uparrow}^\alpha > n_{i\downarrow}^\alpha + U\ n_{i\uparrow}^\alpha < n_{i\downarrow}^\alpha > - U < n_{i\uparrow}^\alpha > < n_{i\downarrow}^\alpha >$ where $\alpha \equiv a, b$ corresponding to A and B sites and $U_1 n_{i,\uparrow}^a \ n_{j,\downarrow}^b \approx U_1 < n_{i,\uparrow}^a > n_{j,\downarrow}^b + U_1 < n_{j\downarrow}^b > n_{i\uparrow}^a - U_1 < n_{i\uparrow}^a > < n_{j\downarrow}^b >$ The mean-field solutions are taken as $(n_{i\uparrow}^a + n_{i\uparrow}^b) = n$ and $(n_{i\uparrow}^a - n_{i\uparrow}^b) = d$ and this leads to the condition, $< n_{i\uparrow}^a > = \frac{(n+d)}{2}$ and $< n_{i\uparrow}^b > = \frac{(n-d)}{2}$, where 'n' represents the mean electron occupation and 'd' the deviation from the mean occupation. The total Hamiltonian is given by $H = H_0 + H_1 + H_2 + H_3 + H_{sub} + H_{imp} + H_U$

3. Calculation of Green's functions and gap equation

In order to calculate the physical parameters, we calculate the two coupled electron Green's functions using Zubarev's technique for A site carbon atom, defined as

$$A_1(k, \omega) = \ll a_{k,\sigma}; a_{k,\sigma}{}^\dagger \gg_\omega , \qquad A_2(k, \omega) = \ll b_{k,\sigma}; a_{k,\sigma}{}^\dagger \gg_\omega \qquad (8)$$

Similarly the Green's functions for electron at B site are defined as

$$B_1(k, \omega) = \ll b_{k,\sigma}; b_{k,\sigma}{}^\dagger \gg_\omega , \qquad B_2(k, \omega) = \ll a_{k,\sigma}; b_{k,\sigma}{}^\dagger \gg_\omega \qquad (9)$$

The above coupled electron Green's functions are solved and the electron correlation functions, the occupation numbers $n_\sigma^a = 1/N \sum_k < a_{k,\sigma} a_{k,\sigma}{}^\dagger >$ and $n_\sigma^b = 1/N \sum_k < b_{k,\sigma} b_{k,\sigma}{}^\dagger >$ are calculated for A and B sites respectively. Hence,

the temperature dependent gap equation for the difference in occupation numbers $d(t)$ is derived

$$d(t) = \sum_{k,\sigma} \frac{[\tilde{\varepsilon}_{a,\sigma}(k) - \tilde{\varepsilon}_{b,\sigma}(k)] \, [f(\beta\omega_{1k,\sigma}) - f(\beta\omega_{2k,\sigma})]}{(\omega_{1k,\sigma} - \omega_{2k,\sigma})} \tag{10}$$

The quasi-particle band dispersions are written as

$$\omega_{1k,\sigma}, \omega_{2k,\sigma} = \frac{1}{2}\left[(\tilde{\varepsilon}_{a,\sigma}(k) + \tilde{\varepsilon}_{b,\sigma}(k)) \right.$$
$$\left. \pm \sqrt{\left(\tilde{\varepsilon}_{a,\sigma}(k) - \tilde{\varepsilon}_{b,\sigma}(k)\right)^2 + 4\,|\varepsilon_{13}(k)|^2} \,\right] \tag{11}$$

where $\tilde{\varepsilon}_{a,\sigma}(k) = \epsilon_a - t_2\gamma_2(k) + \Delta + V_0 x_a + U < n^a_{-\sigma} > + U_1 < n^b_{-\sigma} >$ and $\tilde{\varepsilon}_{b,\sigma}(k) = \epsilon_b - t_2\gamma_2(k) - \Delta + V_0 x_b + U < n^b_{-\sigma} > + U_1 < n^a_{-\sigma} >$, the modified gap is $\bar{\Delta} = \frac{(\epsilon_a - \epsilon_b)}{2} + (\Delta + U\,^d/_2)$ and $f(\beta\omega)$ is the Fermi function. The difference in occupation numbers $d(t)$ at $t = 0$ is discussed by Hague [7,8]. The electron energy dispersion $\omega_{1k,\sigma}$ and $\omega_{2k,\sigma}$ are computed numerically for appropriate momentum limits in Brillouin Zone. All the calculations are done by shifting the momenta to Dirac points lying on the Fermi level. All the physical parameters are scaled by nearest neighbor hopping integral t_1.

4. Results and Discussion

The temperature dependent difference $d(t)$ in electron occupancies for up spins is given in equation (10) is computed numerically for different values of on-site coulomb interaction $u = 1.5 - 5.0$ in absence of inter-site Coulomb potential ($u_1 = 0$) as shown in figure 1(a). The $d(t = 0)$ exhibits its maximum value $d_{max} \cong 0.092$ at temperature $t = 0$. It is observed that the difference $d(t)$ is suppressed continuously with increase of on-site Coulomb interactions. In other words, the A-site electron occupancy for up spins is suppressed, while the B-site electron occupancy is enhanced. As a result, the $d(t) = n^a_\uparrow - n^b_\uparrow$ is suppressed with increase of u. Finally $d(t) = n^a_\uparrow - n^b_\uparrow$ becomes zero at temperature $t = 0$ for given Coulomb potential $= 5.0$. Under this condition, $d(t)$ gradually increases with temperature, then attains a peak value with $d(t) = 0.02$ and then slowly decreases with further increase of temperature. It is to note further that the temperature at which $d(t)$ attains its peak value shifts to lower temperatures with decrease of Coulomb interactions.
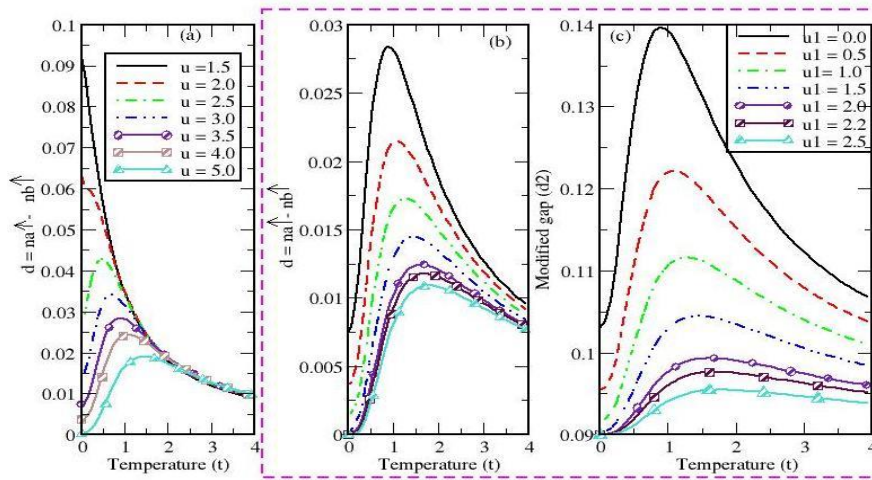
Fig. 1(a). The plot of charge gap $d(t)$ vs. temperature (t) for different on-site Coulomb potential u = 1.5 − 5.0 at fixed substrate induced gap $d_1 = 0.090$ in the absence of inter site Coulomb potential. **Fig. 1(b)** shows the plot of $d(t)$ vs. temperature (t) for inter-site Coulomb potential $u_1 = 0 − 2.5$ for fixed $u = 3.5$ and **Fig. 1(c)** shows the plot of modified gap d_2 vs. temperature for on-site Coulomb potential u and inter-site Coulomb potential u_1.

Figure1(b) shows the effect of nearest-neighbor spin-spin interaction with Coulomb potential $u_1 = 0 − 2.5$ for given values of on-site Coulomb potential $u = 3.5$ for graphene-on-substrate. For $u = 3.5$, in the absence of inter-site Coulomb potential $u_1 = 0$, the temperature dependent difference in electron occupancies $(d(t))$ increases from $d = 0.0075$ at $t = 0$ to a maximum value $d \cong 0.028$ and then gradually decreases with temperature. The magnitude $d(t)$ is suppressed rapidly with further increase of inter-site Coulomb potential (u_1). However, the suppression of $d(t)$ becomes slower for higher inter-site coulomb potentials $(i.e.\, u_1 = 2.0 − 2.5)$. It is to note that the peak maxima in $d(t)$ shift gradually to higher temperatures with increase of nearest-neighbor coulomb potential. This indicates that the nearest-neighbor Coulomb potential is less than the on-site Coulomb potential i.e. $u_1 < u$. Further, the contribution of nearest-neighbor Coulomb interaction is significantly higher to $d(t)$ and it cannot be neglected .The contribution of only on-site Coulomb potential in the calculation over estimates the results. Under this circumstances, our calculation for the contribution of the next-nearest neighbor Coulomb interaction is in progress [9]. Wehling et.al. have estimated the Coulomb potential $U = 3.5 * t_1$ and $u_1 = 2.2 * t_1$ and $u_2 = 0.5 * t_1$ [10].

The temperature dependent modified substrate induced gap $\bar{\Delta} = \Delta + \frac{u\,d(t)}{2}$, which in dimensional form appears at $d_2 = d_1 + u\frac{d(t)}{2}$. This indicates that the substrate induced gap $d_1 = 0.090$ is modified by the Coulomb interaction (u) and difference in electron occupancy ($d(t)$). The plot of $d_2 \sim t$ is shown in figure 1(c) for different values of NN Coulomb potential u_1. For a given $u = 3.5$, in the absence of NN Coulomb interaction, the modified gap is $d_2 = 0.103$ at $t = 0$ and attains its maximum value $(d_2)_{max} = 0.14$. The modified gap d_2 is suppressed continuously with increase of NN coulomb interaction. Finally the modified gap becomes nearly equal to the substrate induced gap alone i.e. $d_2 = d_1 = 0.09$ at $t = 0$ for $u_1 = 2.0 - 2.5$. However, the modified gap d_2 becomes higher than the substrate induced gap ($i.e.\ d_2 > d_1$) at higher temperatures. Again, this result indicates that the contribution of the NN Coulomb interaction cannot be neglected.

5. Conclusions

The present tight-binding model calculation shows the significant contribution of on-site and N-N Coulomb potentials to the electronic properties of the graphene-on-substrate. The only contribution of on-site Coulomb interaction over estimates the results of electron occupancies. However, the inter-site Coulomb Interaction is significant which cannot be neglected.

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