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Tight binding model study of the effect of doping on the charge gap in paramagnetic state of graphene-on-substrate

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Abstract. We report here a microscopic study of the hole/electron doping on the charge gap in graphene grown on a substrate. The Hamiltonian consists of electron hoppings between nearest neighbors, impurity and the effect of on-site Coulomb interaction paramagnetic limit. The Hamiltonian is solved by Zubarav's Green's function technique and hence the electron occupancies of the two sub-lattices are calculated and solved numerically and self-consistently. Finally the temperature dependent charge gap is computed by varying the model parameters of the system.

Keywords: Graphene, Paramagnetism, Tight-binding.

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1. Introduction

Very recently the magnetic behavior of graphene has become the main focus of intensive studies because of its possible potential applications in spintronics. The room temperature ferromagnetism in graphene samples obtained from graphene oxide was observed by Wang et.al. [1]. Diamagnetism at room temperature and paramagnetism at low temperature are reported recently by Sepioni et al. [2]. The paramagnetic orbital susceptibilities are theoretically predicted for electrons in doped graphene, when many particle Coulomb interactions and lattice effects are taken into consideration for calculation. Substrate induced asymmetry appears in electron densities in two sub-lattices at low temperatures. Sahu et. al. have reported a tight binding model study of

ferromagnetic and anti-ferromagnetic properties of graphene on substrate[3,4]. More recently, we have considered a tight binding model calculation taking substrate effect, electron-electron interaction effect and have reported the important role played by the band filling on charge gap in paramagnetic limit in graphene [5]. Again we have also studied the evolution of charge gap in graphene at Dirac point [6, 7] and enhancement of metallic behaviour of graphene in paramagnetic state of graphene-on-substrate due to Coulomb interaction [8]. The effect of different substrates on electron specific heat in graphene in paramagnetic limit has been also studied [9]. In continuation of this work, we present, in this communication, the role played by the electron doping and Coulomb interaction on charge gap and electron density of states (DOS). The formalism is presented in section 2 and the calculation of charge gap and electron DOS in section 3. Finally, the results are given in section 4 and conclusion in section 5.

1. Model Hamiltonian and charge gap calculation

The tight binding Hamiltonian for electron in graphene can be written as

$$H_0=\sum_{k,\sigma}(\epsilon_a\, a^{\dagger}_{k,\sigma}\, a_{k,\sigma}+\epsilon_b\, b^{\dagger}_{k,\sigma}\, b_{k,\sigma})+\sum_{k,\sigma}\left(\epsilon_{1k}\, a^{\dagger}_{k,\sigma}\, b_{k,\sigma}+\epsilon^{*}_{1k}\, b^{\dagger}_{k,\sigma}\, a_{k,\sigma}\right) \quad (1)$$

where, $a^{\dagger}_{k\sigma}$ ($a_{k\sigma}$)and $b^{\dagger}_{k\sigma}$ ($b_{k\sigma}$) are the creation (annihilation) electron operators with spins ($\sigma=\uparrow,\downarrow$) on sublattices A and B respectively. Here ϵ_a and ϵ_b are the sight energies at A and B sublattices. The impurity effect Hamiltonian is given as

$$H_{imp}=V\sum_{i,\sigma}(x_a\, a^{\dagger}_{i,\sigma}\, a_{i,\sigma}+x_b\, b^{\dagger}_{i,\sigma} b_{i,\sigma}) \quad (2)$$

where, V, x_a, x_b are respectively the impurity potential and impurity concentrations at A and B sites. The total Hamiltonian is written as $H=H_0+H_{imp}+H_U$. The Coulomb interaction with an effective Coulomb energy U is written as

$$H_U=U\sum_i\left[n^a_{i\uparrow}n^a_{i\downarrow}+n^b_{i\uparrow}n^b_{i\downarrow}\right] \quad (3)$$

where, $n^a_{i\uparrow}(n^a_{i\downarrow})$ represents the occupation number of electron of up(down) spin at A sub-lattice. For weak coupling, the Hamiltonian can be decoupled by Hartree–Fock mean-field decoupling scheme, i.e.

$$Un^a_{i\uparrow}n^a_{i\downarrow}\approx U\langle n^a_{i\uparrow}\rangle n^a_{i\downarrow}+U\langle n^a_{i\downarrow}\rangle n^a_{i\uparrow}-U\langle n^a_{i\uparrow}\rangle\langle n^a_{i\downarrow}\rangle \quad (4)$$

2. Calculation of charge gap and DOS

The Green's functions for A and B site electron operator can be defined as,

$$G_1(k,\omega) = \ll a_{k,\sigma}; a_{k,\sigma}^{\dagger} \gg_{\omega} \; ; \; G_2(k,\omega) = \ll b_{k,\sigma}; b_{k,\sigma}^{\dagger} \gg_{\omega} \tag{5}$$

By using Zubarev's Green's function technique, the final expressions of the above Green's functions are

$$\mathrm{G_1(k,\omega)} = \frac{1}{2\pi}\,\frac{(\omega - \epsilon_{\mathrm{b,k}})}{(\omega-\omega_{1\mathrm{k}\sigma})(\omega-\omega_{2\mathrm{k}\sigma})};\; G_2(\mathrm{k},\omega) = \frac{1}{2\pi}\,\frac{(\omega-\epsilon_{\mathrm{a,k}})}{(\omega-\omega_{1\mathrm{k}\sigma})(\omega-\omega_{2\mathrm{k}\sigma})} \tag{6}$$

The two quasiparticle bands namely $\omega_{1\mathrm{k}\sigma}$ for conduction band and $\omega_{2\mathrm{k}\sigma}$ for valence band are given by,

$$\omega_{1\mathrm{k}\sigma} = \frac{(\varepsilon_{\mathrm{a,k}}+\varepsilon_{\mathrm{b,k}}) + \sqrt{(\varepsilon_{\mathrm{a,k}} - \varepsilon_{\mathrm{b,k}})^2 + 4|\varepsilon_1(\mathrm{k})|^2}}{2} \tag{7}$$

$$\omega_{2\mathrm{k}\sigma} = \frac{(\varepsilon_{\mathrm{a,k}}+\varepsilon_{\mathrm{b,k}}) - \sqrt{(\varepsilon_{\mathrm{a,k}} - \varepsilon_{\mathrm{b,k}})^2 + 4|\varepsilon_1(\mathrm{k})|^2}}{2} \tag{8}$$

where, $\varepsilon_{\mathrm{a,k}} = \varepsilon_{\mathrm{a}} + \Delta + \mathrm{v_{xa}} + \mathrm{U}\langle \mathrm{n^a}\rangle$ and $\varepsilon_{\mathrm{b,k}} = \varepsilon_{\mathrm{b}} - \Delta + \mathrm{v_{xb}} + \mathrm{U}\langle \mathrm{n^b}\rangle$. The electron densities at A and B sites are calculated from the correlation functions obtained from the Green's functions. Taking the difference between the electron densities we finally get the expression for charge gap below with $\alpha = 1,2$.

$$\Delta_{\mathrm{c}} = -\mathrm{U}\sum_{\mathrm{k},\sigma}\left[\frac{(-1)^{\alpha}(2\omega_{\alpha\mathrm{k}\alpha} - \epsilon_{\mathrm{ak}} - \epsilon_{\mathrm{bk}})\,\mathrm{f}(\beta\omega_{\alpha\mathrm{k}})}{(\omega_{1\mathrm{k}} - \omega_{2\mathrm{k}})}\right] \tag{9}$$

The electron DOS is calculated from the imaginary part of the Green's functions at A and B sb-lattices as given in equation (6) by using the relation,

$$\mathrm{DOS} = -2\pi\sum_{\mathrm{k},\sigma}\mathrm{Im}[\mathrm{G_1(k\omega + i\eta) + G_2(k\omega + i\eta)}] \tag{10}$$

where, η represents the spectral width. The DOS describes the electronic states near the Fermi level describing the charge gap effect. The different physical parameters of the system are scaled by the nearest neighbour hopping integral t_1 and are given as, the Coulomb energy $\mathrm{u} = \frac{\mathrm{U}}{\mathrm{t_1}}$, substrate induced gap $\mathrm{d_1} = \frac{\Delta}{\mathrm{t_1}}$, temperature $\mathrm{t} = \frac{\mathrm{k_B T}}{\mathrm{t_1}}$, hopping integral $\mathrm{t_1} = 2.78$ eV and band energy $\mathrm{C_1} = \frac{\omega}{\mathrm{t_1}}$.

3. Results and Discussion

The charge gap in equation (9) is solved self-consistently as shown in figure 1. The temperature dependent charge gap increases with temperature, attains its maximum value and then decreases with temperature to attain its zero value at higher temperatures. The charge gap is reduced with electron doping at A site throughout the temperature range. Since carbon is a tetravalent atom, the pentavalent atom like nitrogen is doped at carbon atom sites located at A-site. The impurity potential developed is an attractive potential i.e. $\mathbf{v = -3 (V = vt_1 \approx 8.34\ eV)}$ in the present calculation. Increasing the impurity concentration from $\mathbf{x_a = 0}$ **to** $\mathbf{x_a = 0.15}$, we observe that the charge gap is much reduced at lower temperatures and becomes zero at higher temperatures. However for $\mathbf{x_a = 0.20}$, the charge gap completely vanishes and becomes negative. The charge gap completely vanishes for impurity concentration $\mathbf{x_a = 0.18}$. This implies that the charge gap developed due to substrate effect and Coulomb interaction effect is neutralized at $\mathbf{x_a = 0.18}$.

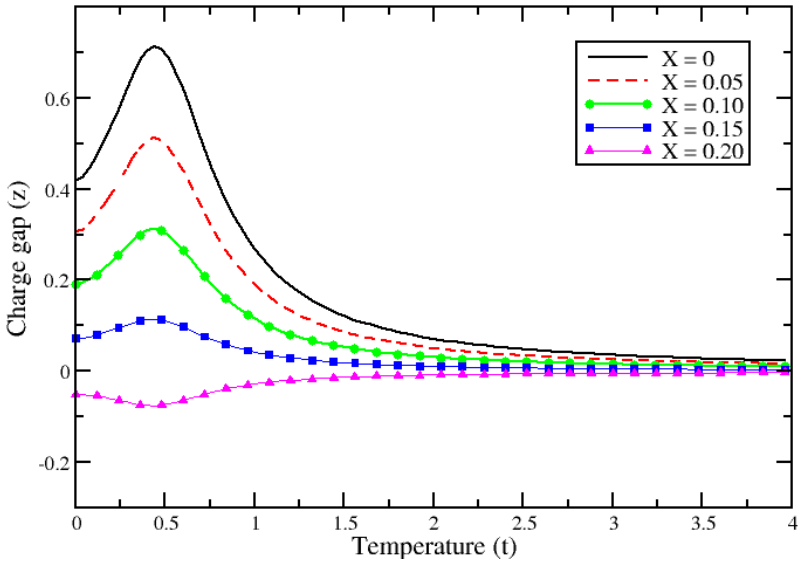

Figure 1. The variation charge gap (z) with temperature (t) for different values of hole doping for fixed substrate induced band gap $d_1 = 0.090$, Coulomb potential $u = 2.30$ and imputity potential $v = -3$.

The electron DOS written in equation (10) is computed numerically for different values of Coulomb interaction i.e. $\mathbf{u = 1.00, 2.00, 2.30, 2.40}$ as shown in figure 2. For Coulomb potential energy $\mathbf{u = 1.00}$, the DOS shown in

figure 2 shows two sharp peaks at Van-Hoff singularities, where the electron DOS becomes maximum at the middle of the valence band for energy $\mathbf{C_1 < 0}$ and in the middle of the conduction band for energy $\mathbf{C_1 > 0}$. The valence band is filled up to Fermi level lying at energy $\mathbf{C_1 = 0}$, since the carbon atom contains one $\mathbf{2P_z}$ electron per atom responsible for valence band, while the conduction band is vacant. Further, we observe a band gap of energy nearly one (2.78 eV) by increasing the Coulomb energy. Again the electron DOS shifts to higher energy states lying above the Fermi level ($\mathbf{C_1 = 0}$), while electron DOS in the conduction band shifts to higher energies with a very small amount. As a result, the band gap is much reduced to a lower value of magnitude 0.3 corresponding to Coulomb energy $\mathbf{u = 2.40}$.

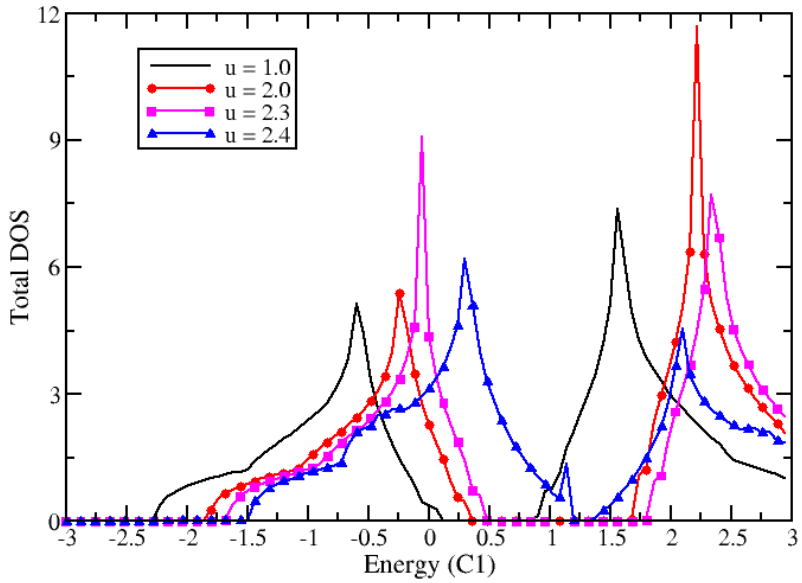

Figure 2. The plot of density of states (DOS) vs. band energy (C1) for different values of Coulomb energy, $u = 2.0, 2.3, 2.4$ for fixed substrate induced gap $d_1 = 0.09$, electron band filling, $n = 1$, temperature, $t = 0.04$ in absence of doping.

4. Conclusions

We have proposed a tight binding model Hamiltonian for graphene taking into account the effect of electron doping and attractive Coulomb interaction. The charge gap and the electron DOS are calculated by Zubarev's Green's function technique and are computed numerically. It is observed that the charge gap is suppressed throughout the temperature range with the introduction of electron

doping by adding pentavalent atom like Nitrogen. The Coulomb interaction shifts the electron DOS above the Fermi level and reduces the gap for higher Coulomb interaction effects. The higher Coulomb interaction can develop in monolayer graphene by synthesizing it on highly polarized substrates like SiC and SiO_2.

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