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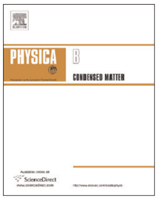

Model study of the effect of Coulomb interaction on band gap of graphene-on-substrates

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Graphene develops modulated gap, when it is placed on different substrates. In order to study the effect of Coulomb interaction on the gaps, we propose here a tight-binding model taking nearest-neighbor hopping integrals in the presence of Coulomb interactions on two inequivalent sublattices of honeycomb lattice of graphene. Here Coulomb interaction is treated within a Hartree–Fock mean-field approximation and difference in electron occupation numbers is computed numerically and self-consistently. It is observed that the system develops ferromagnetism at A-site atoms as well as B-site atoms. However this ferromagnetisms in two sub-lattices are antiferromagnetically ordered. The Coulomb interaction develops a gap near 'K' point in reciprocal space. The evolution of this gap is investigated in the electron density of states, energy band dispersion and electron specific heat of graphene.

1. Introduction

Graphene has attracted an enormous research interest [1] because of its intriguing physical properties [2] such as ultrahigh electron mobility and very low resistivity, mass less Dirac fermion [3] and abnormal Hall effect [4]. The unit cell of a monolayer graphene consists of two carbon atoms at the A and B sublattices. The band structure of graphene shows that two bands in reciprocal space intersect at two inequivalent points K and K' called Dirac points. The valence and conduction bands are degenerate at Dirac points and hence graphene is an intrinsic zero band gap semiconductor. Various methods of engineering of a band gap in graphene have been studied to induce band gap for its application in making devices. A gap can be induced in graphene by growing graphene epitaxially on SiO_2/SiC sublattice. The interaction between the substrate and graphene layer can break the A and B sublattice symmetry and open a band gap. Small band gaps have been observed, when graphene is grown on substrates SiC, i.e. 0.260 eV [5] and 0.250 eV [6] and gold on ruthenium (200 meV) [7]. Besides graphene on substrates, large band gaps can be generated in graphene of the order of several eV by chemical modifications with hydrogen (graphane) [8] and fluorine (fluorographene) [9,10]. Alternatively the band gap in bilayer graphene has been observed experimentally by Ohta et al. [11] using angle resolved photo-emission spectroscopy (ARPES) and by Zhang et al. [12] using infrared spectroscopy. By applying electric field perpendicularly to the bilayer graphene a tunable band gap of 70–250 meV [11–15] has been reported in both experimental and theoretical calculation. This is in agreement with the experimental observations which show that the external potential difference is strongly screened with a maximum energy gap of ~300 meV [16]. It is essential that a technique should be developed for enhancing these gaps upto the order of 1 eV seen in silicon for application in digital electronics.

The role of Coulomb interaction in graphene and related systems provides a long standing problem. The two dimensional graphene [17,18], systems with a number of adatoms on semiconductor surfaces such as Si : X (Si, C, Sn, Pb) [19], Bechgard Salts [20] polymers [21,22] display strong local as well as nonlocal Coulomb interactions. It is observed that in graphene the on-site Coulomb interaction is $U/t_1 \sim 3.3$ and the near-neighbor Coulomb interactions is $V/t_1 \sim 2$ where t_1 is the nearest neighbor hopping $t_1 = 2.8$ eV [17]. The effective on-site (Hubbard) interaction is $U = 3.3t_1$ in graphene in the close vicinity of the critical value separating conducting graphene from an insulating phase [23]. In defect free graphene the possibility of magnetisation has been predicted theoretically. An antiferromagnetic insulating ground state has been predicted for local Coulomb interaction for $U_{AFM} \geq 4.5t_1$ in Monte Carlo calculation [24–26] and $U_{AFM} \geq 2.2t_1$ in Hartree–Fork theory [24,25]. The nonlocal Coulomb interactions can enrich the phase diagram leading to topologically nontrivial phases [27] arising due to a competition between charge and spin

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density wave phases [28,29]. The Coulomb interaction between massless fermions in pristine graphene remains long ranged and unscreened. It is currently unclear whether this would lead to strongly correlated electronic phases like an insulator [28,30] or whether graphene is rather weakly correlated. The unscreened long-range Coulomb interaction is shown to be responsible for many unusual behaviours in graphene [2,31]. The local Coulomb interaction is crucial for the theory to understand the defect induced magnetism [32] and Mott transitions on the surfaces like Si:X.

It is important to estimate the effective strength of Coulomb interaction acting on the carbon π electrons. The bare on-site Coulomb interaction in benzene was estimated long ago to be 16.93 eV from the atomic carbon p_z orbitals [32]. The weak coupling perturbation theory yields an effective on-site Coulomb repulsion of 10 eV for the analysis of optical spectroscopy experiments of poly-acetylene [33,34]. The coupling constant for Coulomb interaction in graphene is described by $\alpha = e^2/\epsilon\hbar v_F$ with dielectric constant ϵ arising due to screening by the Fermi velocity v_F. It is observed that for pristine graphene $\alpha = 2.14$ and for graphene placed on a SiO_2 substrate, the corresponding $\alpha = 1.02$ [35]. The inelastic X-ray scattering experiments for free standing graphene suggest a fully screened dielectric constant of $\epsilon = 15$ corresponding to the base value $\alpha = 2.2$. Cudazzo et al. [36] have reported a theoretical study of the implications of dielectric screening for excitonic and impurity states in graphene. Upto now, the strength of Coulomb interactions in graphene and related materials remains unclear and controversial – both theoretically and experimentally.

Earlier we have reported the study of band gap opening in graphene by a single impurity taking the tight binding model upto the third nearest-neighbor hopping in the absence of Coulomb interaction [37]. In the present communication, we study the effect of Coulomb interaction on the band gap present in the graphene on substrates. We propose a tight-binding model Hamiltonian consisting of the site energy of the carbon atoms and nearest- neighbor hopping of π electrons of carbon atoms taking into account the substrates and Coulomb interaction effects in graphene. We solve the model Hamiltonian by Zubarev's Green's function technique in Section 2. We calculate the band dispersion, the difference in occupation numbers and density of states in Section 3. We discuss the effect of Coulomb interaction on the band gap near Dirac point in Section 4 and finally give conclusions in Section 5.

2. Theoretical model

Single layer graphene is formed by carbon atoms arranged in a two-dimensional non-Bravais honeycomb lattice. The distance between nearest-neighbor carbon atoms is $a_0 \simeq 1.42$ Å, while the lattice constant is $a = \sqrt{3}a_0$. The geometry and the 2D-character of the lattice do not allow the overlap of the p_z orbitals of a given carbon atom and the s, p_x, p_y orbitals of its neighbors. The s, p_x, p_y orbitals hybridize to create sp^2 bonds and form high energy σ bands. The π band is created by the overlap of p_z orbitals in graphene and this band is responsible for electronic properties. A simple tight-binding model incorporating only the nearest-neighbor hopping between adjacent distinct A and B sublattices provides a good approximation for studying the low energy electronic excitations and doping in pristine graphene.

Assuming that the electron can hop to both the nearest and next-nearest-neighbor atoms, the tight binding Hamiltonian for electron in graphene can be written as

$$\begin{aligned} H_0 = &\sum_{i,\sigma}(\epsilon_a a^\dagger_{i,\sigma}a_{i,\sigma} + \epsilon_b b^\dagger_{j,\sigma}b_{j,\sigma}) - t_1\sum_{\langle i,j\rangle,\sigma}(a^\dagger_{i,\sigma}b_{j,\sigma} + b^\dagger_{j,\sigma}a_{i,\sigma}) \\ &- t_2\sum_{\langle\langle i,j\rangle\rangle,\sigma}(a^\dagger_{i,\sigma}a_{j,\sigma} + b^\dagger_{j,\sigma}b_{i,\sigma} + H.\,C) \\ &- t_3\sum_{\langle\langle\langle i,j\rangle\rangle\rangle,\sigma}(a^\dagger_{i,\sigma}b_{j,\sigma} + b^\dagger_{j,\sigma}a_{i,\sigma}) \end{aligned} \tag{1}$$

where $a^\dagger_{i,\sigma}$ $(a_{i,\sigma})$ creates (annihilates) an electron with spin σ $(\sigma = \uparrow, \downarrow)$ on site $\overrightarrow{R_i}$ on sublattices A. Similarly $b^\dagger_{i,\sigma}$ $(b_{i,\sigma})$ creates (annihilates) an electron on sublattices B. Here $t_1(=2.5$ to 3.0 eV) is the nearest-neighbor hopping energy, t_2 with $0.02t_1 \le t_2 \le 0.2t_1$ [37,38] is the next-nearest-neighbor hopping energy and $\epsilon_a(\epsilon_b)$ is the site energy at the sublattice site A(B). Further $\langle i, j\rangle$, $\langle\langle i, j\rangle\rangle$ and $\langle\langle\langle i, j\rangle\rangle\rangle$ stand for nearest, next-nearest and next-to-next–nearest-neighbor hoppings from site $\overrightarrow{R_i}$ to $\overrightarrow{R_j}$. The Fourier transformed dispersion $\gamma_1(k)$ for the nearest neighbor hopping is

$$\gamma_1(k) = e^{ik_xa_0} + 2e^{-i(1/2)k_xa_0}.\cos\frac{\sqrt{3}}{2}k_ya_0 \tag{2}$$

and the dispersions $\gamma_2(k)$, $\gamma_3(k)$ for the second and third nearest neighbor hoppings are $\gamma_2(k) = \sum_{\delta_2}e^{i\vec{k}.\vec{\delta}_2}$, $\gamma_3(k) = \sum_{\delta_3}e^{i\vec{k}.\vec{\delta}_3}$. where $\overrightarrow{\delta_2}$, $\overrightarrow{\delta_3}$ are corresponding lattice vectors. Gharekhanlau et al. [39] have reported the theoretical calculation of electronic band structure of patterned graphene taking tight-binding approximation for the dispersion of π and π^* electronic bands including upto five nearest-neighbor hopping integrals. They have patterned the graphene layers in such a way that carbon atoms are periodically replaced by vacancies. This type of symmetry breaking has resulted in opening of gap at Dirac point in graphene. Graphene deposited on SiO_2 is well described by the 2D massless Dirac equation [3]. Graphene grown on SiC can be described in terms of massive 2D Dirac electron [5]. Substrate induced potential can break the symmetries of the honeycomb lattice and generate gaps in the electronic system. In a graphene-on-substrate system, the electron interacts with the static potential induced by the substrate. As a result, a modulated potential, where A site have energy $+\Delta$ and B sites with energy $-\Delta$, leads to the breaking of the symmetry between A and B sites and gives rise to a gap. Such a symmetry breaking Hamiltonian is written as

$$H_{sub} = \Delta\sum_{i,\sigma}a^\dagger_{i,\sigma}a_{i,\sigma} - \Delta\sum_{i,\sigma}b^\dagger_{i,\sigma}b_{i,\sigma} \tag{3}$$

This system exhibits a band gap 2 Δ and if undoped, has an insulating ground state with the Fermi level lying in the gap.

The effect of Coulomb repulsion is to stop both electrons occupying the same site. The Hamiltonian describing the Coulomb interaction with an effective Coulomb energy U is written as

$$H_U = U\sum_i[n^a_{i\uparrow}n^a_{i\downarrow} + n^b_{i\uparrow}n^b_{i\downarrow}] \tag{4}$$

where $n^\alpha_{i\uparrow}(n^\alpha_{i\downarrow})$ with $\alpha \in A, B$ sublattices, represents the occupation number operator of up(down) spin. For weak coupling, the Hamiltonian can be decoupled by Hartree–Fock mean-field decoupling scheme, i.e. $Un^\alpha_{i\uparrow}n^\alpha_{i\downarrow} \approx U\langle n^\alpha_{i\uparrow}\rangle n^\alpha_{i\downarrow} + U\langle n^\alpha_{i\downarrow}\rangle n^\alpha_{i\uparrow} - U\langle n^\alpha_{i\uparrow}\rangle\langle n^\alpha_{i\downarrow}\rangle$ where $\alpha \equiv a, b$ corresponding to A and B site interactions. The mean-field solutions are taken as $(n^a_{i\uparrow} + n^b_{i\uparrow})/2 = n$ and $(n^a_{i\uparrow} - n^b_{i\uparrow})/2 = d$ and this leads to the condition, $\langle n^a_{i\uparrow}\rangle = n + d$ and $\langle n^b_{i\uparrow}\rangle = n - d$ where n represents the mean electron occupation and d the deviation from the mean occupation. Similar expression can be formed for the down spin electron. The difference (d) and the electron occupation number (n) are computed self-consistently. After Fourier transformation in momentum space, the total Hamiltonian is given by