

Hybridization and Charge transfer in Graphene– Nickel nano System: a Tight-Binding model Study

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Received: 15.6.2017 ; Revised : 3.7.2017 ; Accepted :25.7. 2017

Abstract. We have investigated the electronic and magnetic properties of graphene–nickel system by tight-binding mean-field method. Here monolayer graphene is placed over one layer of ferromagnetically ordered metal Ni (111). Due to the close matching of lattice constant between graphene and nickel, the hybridization between graphene $2p_z$ and Ni $3d_{z^2}$ orbitals are very strong. This hybridization greatly affects the electronic and magnetic properties of this bilayer system, resulting in a significantly reduced local magnetic moment of the nickel layer and an induced spin polarization on the graphene layer. We have calculated the intrinsic magnetization in nickel (111) and induced magnetization on the graphene layer by Zubrev's double time Green's function techniques and results are interpreted with experimental observations.

Keywords. Graphene-nickel system, Green's function, Magnetization, Tight-binding method

PACS No. : 73.22.Pr, 74.20.Pq, 71.28. +d

1. Introduction

Single-layer of carbon material, graphene has unique electronic properties due to its out-of-plane bonding and also has opened a new space for basic research as well as nano device applications [1]. The intra-plane sp_2 bonding is mainly responsible for structural stability and the out-of-plane $p - \pi$ states control the transport as well as interfacing properties. When graphene is placed on layered materials or substrates, the $2p_z$ orbitals may hybridize with electronic states of the substrate, which greatly affects the electronic as well as transport properties of the interface. These face-to-face interactions bring additional

controls to the intrinsic properties of graphene and may even lead to interesting properties that has not shown in pristine form.

Due to slightly lattice mismatch $\sim 1\%$ and structural resemblance with graphene, the close-packed structure of the Ni(111) has been commonly used for making graphene-metal system [2]. Recently, the increasing interest of theoretical and experimental work in graphene-metal system resulting the exploration for new novel functional materials for magnetic tunnel junction (MTJ) applications[3]. The observations of induced magnetization in the graphene layer [4] and charge transfer from metal to graphene have been reported[5]. In order to exploit the complete potential of graphene in these applications, it is very important to have detail understanding of the graphene-metal interfacial physics, especially the interplay of charge transfer, $2p_z - 3d_{z^2}$ hybridization, and magnetic properties at the interface.

In the present Communication, we report here about intrinsic magnetization in nickel monolayer and its effect on induced magnetization in graphene by tight-binding mean- field approach. We present the formalism of the graphene-nickel (111) system in section 2, the calculation of the Green's function and the induced magnetization in section 3, results and discussion in section 4 and finally conclusion in section 5.

2. A minimal tight-binding model Hamiltonian

The graphene-nickel (111) system consists of single layer of graphene over one layer of nickel (111). The single particle Hamiltonian for upper layer graphene is given by

$$H_1 = \sum_{k,\sigma} [\varepsilon_a(k) a_{k,\sigma}^\dagger a_{k,\sigma} + \varepsilon_b(k) b_{k,\sigma}^\dagger b_{k,\sigma}] + \sum_{\alpha,k} [\varepsilon_{13}(k) a_{k,\sigma}^\dagger b_{k,\sigma} + \varepsilon_{13}^*(k) b_{k,\sigma}^\dagger a_{k,\sigma}] \quad (1)$$

Here the first part of Hamiltonian H_1 contains site energies $\varepsilon_a(k) = \varepsilon_a + \varepsilon_{2k}$ and $\varepsilon_b(k) = \varepsilon_b + \varepsilon_{2k}$ for both site of carbon atoms in graphene. The electron operators $a_{k,\sigma}^\dagger(a_{k,\sigma})$ and $b_{k,\sigma}^\dagger(b_{k,\sigma})$ are the creation (annihilation) operators at two in equivalent sub-lattices A and B. The second part of Hamiltonian H_1 consists of hopping of electrons to inter site sub-lattices having site energies

$\varepsilon_{13}(k) = \varepsilon_{1k} + \varepsilon_{3k}$. The Hamiltonian for monolayer nickel (111) can be written as

$$H_{Ni} = \sum_{k,\sigma} \left[E(k) + \frac{U}{4} \sigma m \right] c_{k,\sigma}^\dagger c_{k,\sigma} \quad (2)$$

Here H_{Ni} represents the Hamiltonian for nickel (111) having band dispersion energy $E(k)$. U , m and σ are the onsite Coulomb potential, intrinsic magnetization for both the spins within mean-field approximation. When graphene is placed over nickel (111), there may be charge transfer and p-d hybridization between graphene-metal interfaces. Then the interlayer Hamiltonian for graphene-metal system is given by

$$H_{\perp} = \sum_{k,\sigma} \left[\varepsilon_{pa}(k) a_{k,\sigma}^\dagger c_{k,\sigma} + \varepsilon_{pa}^*(k) c_{k,\sigma}^\dagger a_{k,\sigma} \right] \\ \sum_{k,\sigma} \left[\varepsilon_{pb}(k) b_{k,\sigma}^\dagger c_{k,\sigma} + \varepsilon_{pb}^*(k) c_{k,\sigma}^\dagger b_{k,\sigma} \right] \quad (3)$$

The Hamiltonian H_{\perp} represents the hopping of electrons from first layer to second layer and vice-versa with interlayer hopping energy $\varepsilon_{pa(b)}(k)$. The total Hamiltonian is given by $H = H_1 + H_{Ni} + H_{\perp}$

3. Calculation of Green's functions and magnetization graphene-nickel system

In order to calculate the physical parameters, we calculate the three coupled electron Green's functions involving electrons of graphene at A-site are defined as $A_1(k, \omega) = \langle\langle a_{k,\sigma}; a_{k,\sigma}^\dagger \rangle\rangle_{\omega}$, $A_2(k, \omega) = \langle\langle b_{k,\sigma}; a_{k,\sigma}^\dagger \rangle\rangle_{\omega}$ and $A_3(k, \omega) = \langle\langle c_{k,\sigma}; a_{k,\sigma}^\dagger \rangle\rangle_{\omega}$. Similarly we can define the Green's functions involving electrons at B site of graphene and Ni (111) which are not shown explicitly. The coupled Green's functions are solved by Zubarev's technique[6] and we found $A_1(k, \omega) = \frac{a_{11}}{2\pi|D(\omega)|}$ and $B_1(k, \omega) = \frac{b_{11}}{2\pi|D(\omega)|}$ for graphene and $C_1(k, \omega) = \frac{c_{11}}{2\pi|D(\omega)|}$ for nickel. Here a_{11} , b_{11} and c_{11} are not given explicitly and $|D(\omega)|$ is written as $|D(\omega)| = a\omega^3 + b\omega^2 + c\omega + d$. As the equation is a cubic in ω , which is solved numerically by equating the denominator term to zero i.e. $|D(\omega)| = 0$, we can obtain the quasi-particle band dispersion energies $\omega_{\alpha,k,\sigma}$ by taking 500×500 grid points of the electron momentum in XY plane. Here $a = 1$, $b = -[\varepsilon_a(k) + \varepsilon_b(k) + (E(k) + \frac{U}{4} \sigma m)]$, $C = (\varepsilon_a(k) + \varepsilon_b(k)) \left(E(k) + \frac{U}{4} \sigma m \right) + \varepsilon_a(k)\varepsilon_b(k) - |\varepsilon_{pa}(k)|^2 - |\varepsilon_{13}(k)|^2$, $d = \varepsilon_b(k)|\varepsilon_{pa}(k)|^2 +$

$\left(E(k) + \frac{U}{4}\sigma m\right) |\varepsilon_{13}(k)|^2 - \varepsilon_a(k)\varepsilon_b(k) \left(E(k) + \frac{U}{4}\sigma m\right)$. We have obtained three electron bands w_{1k}, w_{2k} and w_{3k} for bilayer graphene-nickel system. The intrinsic magnetization is given as $m = -(n_{\uparrow}^{Ni} - n_{\downarrow}^{Ni})$, where $n_{\sigma}^{Ni} = \sum_{\alpha=1-3} f(\beta\omega_{\alpha,k,\sigma})k_{\alpha}(\omega_{\alpha,k,\sigma})p_{\alpha}$. The expression of p_{α} is not shown explicitly.

4. Results and Discussion

The tight-binding calculation on graphene-nickel bilayer system leads to the band dispersion which appears in cubic form. Therefore we have solved numerically the cubic equation to find the three band dispersion energies. Using these band dispersion energies, we have computed numerically the temperature dependent ferro-magnetization (\mathbf{m}) of nickel layer as shown in figure 1(a). It is observed that for given Coulomb energy, $U = 3.99 \text{ eV}$, the magnetization exhibits a small peak at low temperature and decreases with temperature to attains its minimum value i.e. $m_{min} \cong 0.1287$ at temperature $\sim 0.006 \text{ eV} (T_c \cong 60^{\circ}\text{K})$ corresponding to Coulomb energy $U = 3.99 \text{ eV}$ and then increases with further increase of temperature. For monolayer nickel, we assume that this temperature $T_c \cong 60^{\circ}\text{K}$ is the Curie temperature of the monolayer nickel which is much reduced compared to its bulk counter part 630°K [7]. It has been reported by Baberschke [7,8] experimentally that the Curie temperature of nickel bilayer is $T_c \cong 46^{\circ}\text{K}$. Our results come out to be same order. It is to note further that the ferromagnetic materials in their low dimensional form exhibit much reduced magnetic moments associated with very low Curie temperature due to instability of the magnetic order. It is to mention further that monolayer nickel exhibits lower stability compared to bilayer and tri-layer nickel systems. Therefore the magnetization is not exactly zero at the Curie temperature for the monolayer system as observed in our tight-binding calculation. In the present work, we have considered only the on-site Coulomb interaction energy within mean-field approach to find the expression for ferromagnetic magnetization. The nearest- neighbor and next-nearest neighbor Coulomb interactions are expected to stabilize more the system. The two and three layers of nickel may stabilize further the graphene-nickel system. The calculations of these aspects are in progress for the above system. It is observed that the ferromagnetic magnetization is suppressed with increase of Coulomb interaction energy accompanied by very small enhancement of Curie temperature (see fig. 1(a)). The suppression of magnetization with increase of Coulomb interaction indicates that there is charge transfer from bottom nickel layer to top

graphene layer. Therefore there appears induced magnetization in graphene layer. Therefore the magnetic order develops in non-magnetic graphene monolayer which can be used as nano-electronic spintronics devices. This type of induced magnetization in graphene opens flood gates of intense research activities in graphene system both experimentally and theoretically.

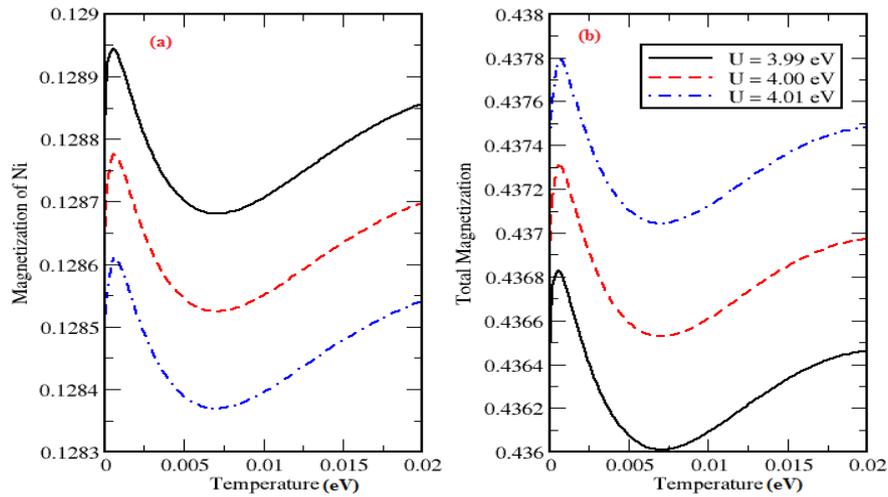


Figure 1. Plot of magnetization of vs. temperature for different values of on-site Coulomb potential $U = 3.99eV, 4.00eV, 4.01eV$ (a) monolayer nickel (b) graphene-nickel system

We have calculated the induced ferromagnetic magnetization at A and B sub-lattices of graphene and finally computed the total temperature dependent induced magnetization in graphene for different values of Coulomb interaction energy as shown in fig 1(b). It is observed that the nature of temperature dependent induced magnetization in graphene is similar to that of nickel layer with same Curie temperature $T_c \cong 60^0K$ corresponding to the Coulomb energy $U = 3.99 eV$. It is to note further that the induced magnetization in graphene layer is much higher (more than three times) as compared to the corresponding magnetization in nickel layer. This signifies that there is substantial charge transfer from nickel layer to graphene layer. There are several experimental reports of charge transfer in graphene-nickel system [9]. It is further observed that the mean-field Coulomb interaction enhances the induced magnetization in graphene layer leading to the enhancement of induced magnetization with increase of Coulomb interaction. It is to note further that the magnetization in nickel layer is suppressed with increase of Coulomb potential, while the induced

magnetization is enhanced with Coulomb potential. This indicates that there is substantial charge and spin transfer from bottom nickel to top graphene layer. It has been reported that coulomb interaction in graphene- Cobalt layer system is of the order of 4 eV based on the density functional theory calculation[10].

1. Conclusion

We have reported here a tight-binding model study of charge transfer effect in graphene on monolayer nickel, where A-site carbon atom lies above the nickel atom of the bottom layer, while the B-site carbon atom lies above the center of the honeycomb lattice of nickel layer. The ferromagnetic magnetization in bottom layer nickel is considered within Hatree-Fock type mean-field approach of the on-site Coulomb interaction at nickel site. The total Hamiltonian is solved by Zubarev's Green's function technique leading to the cubic form of dispersion relation of the system. The dispersion and hence the magnetization in nickel layer are computed self consistently and finally the temperature dependent induced magnetization in non-magnetic graphene layer is computed. Our results clearly show a substantial charge transfer from nickel layer to graphene layer.

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