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Magnetic susceptibility and heat capacity of graphene in two-band Harrison model

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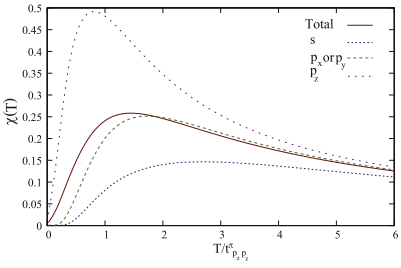
HIGHLIGHTS

- The Pauli paramagnetic susceptibility and electronic heat capacity of graphene are investigated in two-band model.
- Green's function formalism is implemented.
- Contributions of *s* and *p* orbitals in the valence band are considered.

GRAPHICAL ABSTRACT



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ABSTRACT

Using a two-band tight-binding Harrison model and Green's function technique, the influences of both localized σ and delocalized π electrons on the density of states, the Pauli paramagnetic susceptibility, and the heat capacity of a graphene sheet are investigated. We witness an extension in the bandwidth and an increase in the number of Van-Hove singularities as well. As a notable point, besides the magnetic nature which includes diamagnetism in graphene-based nanosystems, a paramagnetic behavior associated with the itinerant π electrons could be occurred. Further, we report a Schottky anomaly in the heat capacity. This study asserts that the contribution of both σ and π electrons play dominant roles in the mentioned physical quantities.

1. Introduction

Graphene [1] is constructed by covalent chemical bonding of valence electrons of carbon atoms, localized at atomic positions of a two-dimensional (2D) hexagonal lattice. Structurally, the π bands are related to the chemical π bondings of the transversely non-hybridized p_z orbitals out-of-plane, while the remaining valence orbitals, i.e. *s*, p_x and p_y, create σ bonds lying in the graphene plane with bond angle of 120°. The electronic properties of graphene could be explained by π bondings in a tight-binding (TB) model [2] but to explore its full band structure all relevant atomic orbitals have to be taken into account [3–7].

During last decades, the magnetic susceptibility of diverse carbon allotropes, particularly the graphene sheet as a newly synthesized case, has widely been studied [8–16]. The orbital magnetism in graphene-based systems was first studied for a graphene monolayer as a simple model to explain the large diamagnetism of graphite [12,13]. For instance, qualitative and quantitative results of the orbital magnetization in graphene and graphene nanoribbons were obtained by Liu et al. [14]. The temperature dependency of the magnetic susceptibility of graphene has also been investigated by Peres et al. [15]. A theoretical study on the orbital magnetism in multilayer graphene has been

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presented through the effective mass approximation by Koshino and Ando [16]. They found that the monolayer-type sub-band exists only in odd layers while the bilayer-type sub-band appears in every layer number. Remarkably, the magnetic susceptibility of the nanostructured graphene-based systems has been studied by the authors of Ref. [17].

The electronic contribution of magnetization and specific heat depend directly on the electronic structure. Basically, the heat capacity is a quantity which directly reflects the details of the excitation spectrum. In recent years, the extraordinary thermal transport properties of low-dimensional systems compared with macro scales have attracted great attention [18–22]. For example, the low-energy electronic structure and the heat capacity of graphene strips versus temperature have been investigated by Yi et al. [18]. They found that its heat capacity is similar to a two-level system due to the finite width of the conduction and valence bands. The thermal conductivity of isotopically modified graphene has experimentally been measured by Chen et al. [21] via the optothermal Raman technique.

In this theoretical effort, the density of states (DOS), paramagnetic (PM) susceptibility, and electronic heat capacity of graphene are investigated through σ and π bands of TB Harrison model. In Section 2, our model is introduced and Green's function formalism is followed in Section 3. Section 4 involves a comparison between the temperature behavior of the remarked quantities of the system for various contributions of s and p orbitals. The results, discussion, and conclusion are presented in the last two sections.

2. Hamiltonian model

We start with the following Harrison's two-center TB Hamiltonian model [3–7] for a 2D honeycomb graphene lattice (Fig. 1):

$$\hat{\mathcal{H}} = \sum_{i,j}^{N_c}\sum_{\alpha,\beta}^{N_a}\sum_{\mu,\nu}^{N_o} t_{i\mu j\nu}^{\alpha\beta}\,\hat{c}_{i\mu}^{\alpha\dagger}\hat{c}_{j\nu}^{\beta} + \sum_{i}^{N_c}\sum_{\alpha}^{N_a}\sum_{\mu}^{N_o}\varepsilon_{i\mu}^{\alpha}\hat{c}_{i\mu}^{\alpha\dagger}\hat{c}_{i\mu}^{\alpha}, \tag{1}$$

where i and j denote the position of the cells, α and β point to the A or B sub-sites inside the Bravais lattice unit cell (Fig. 1), N_c is the number of unit cells or equivalently the number of modes in the first Brillouin zone (FBZ), N_o displays the number of orbitals at each atomic site of the graphene plane, $t_{i\mu j\nu}^{\alpha\beta}$ represents the amplitude for an electron to hop from orbital μ of sub-site α in the unit cell i to the orbital ν of sub-site β in the nearest-neighbor (NN) cell j, $\hat{c}_{i\mu}^{\alpha\dagger}$ ($\hat{c}_{i\mu}^{\alpha}$) indicates the creation (annihilation) operator of an electron on sub-site α in orbital μ of the unit cell i, and $\varepsilon_{i\mu}^{\alpha}$ refers to the on-site energy corresponding to the electronic state with quantum numbers $\{i, \alpha, \mu\}$. The spherical symmetry of s orbitals requires the overlap between the NN orbitals of this kind to be negative, while according to the arrangement of positive and negative lobes of $\{p_x, p_y, p_z\}$ orbitals, the sign of the overlap of p orbitals with the NN s or p ones could appropriately be positive or negative [3–7]. Besides, we have fitted the origin of energy to the on-site energy of orbital p, i.e. $\varepsilon_{p_x} = \varepsilon_{p_y} = \varepsilon_{p_z} = 0$, so the on-site energy of the orbital s would be a negative quantity [6,7]. It should be noted that since every graphene's Bravais lattice unit cell includes $N_a = 2$ nonequivalent atomic sites A and B, each with one s and three p orbitals in the valence levels, each cell incorporates $N_aN_o = 8$ orbitals. Conclusively, the Hamiltonian is represented by an 8×8 matrix constructed on the following set of orthogonal orbital basis kets of the Hilbert space:

$$\{|\Phi_{is}^{A}\rangle, |\Phi_{ip_x}^{A}\rangle, |\Phi_{ip_y}^{A}\rangle, |\Phi_{ip_z}^{A}\rangle, |\Phi_{is}^{B}\rangle, |\Phi_{ip_x}^{B}\rangle, |\Phi_{ip_y}^{B}\rangle, |\Phi_{ip_z}^{B}\rangle\}. \tag{2}$$

Just for simplicity, we have used such system of units that all physical constants (like $\hbar$) are equal to one.

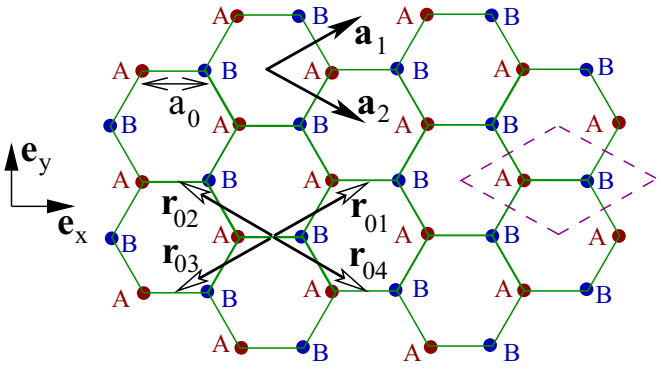

Fig. 1. Geometry of graphene lattice with interatomic distance a_0 and $\{\mathbf{a}_1, \mathbf{a}_2\}$ as primitive vectors. Dashed lines illustrate the Bravais lattice unit cell including A and B sub-sites. The vectors $\mathbf{r}_{01}$, $\mathbf{r}_{02}$, $\mathbf{r}_{03}$ and $\mathbf{r}_{04}$ connect a cell to its NNs.

3. Green's function approach

According to the Hamiltonian and the basis kets introduced in (2), Green's function of graphene for σ and π bands takes the form of

$$\begin{pmatrix} (\mathcal{G}_{\mu\nu}^{\mathbf{AA}}(i,j;\tau))_{4\times4} & (\mathcal{G}_{\mu\nu}^{\mathbf{AB}}(i,j;\tau))_{4\times4} \\ (\mathcal{G}_{\mu\nu}^{\mathbf{BA}}(i,j;\tau))_{4\times4} & (\mathcal{G}_{\mu\nu}^{\mathbf{BB}}(i,j;\tau))_{4\times4} \end{pmatrix}, \tag{3}$$

in which $\tau = \imath t$ denotes the imaginary time, and the arrays are 4×4 sub-matrices. Typically, $\mathcal{G}_{\mu\nu}^{\mathbf{AA}}(i,j;\tau)$ could be expressed as

$$\mathcal{G}_{\mu\nu}^{\mathbf{AA}}(i,j;\tau) = \begin{pmatrix} G_{ss}^{AA}(i,j;\tau) & G_{sp_x}^{AA}(i,j;\tau) & G_{sp_y}^{AA}(i,j;\tau) & G_{sp_z}^{AA}(i,j;\tau) \\ G_{p_xs}^{AA}(i,j;\tau) & G_{p_xp_x}^{AA}(i,j;\tau) & G_{p_xp_y}^{AA}(i,j;\tau) & G_{p_xp_z}^{AA}(i,j;\tau) \\ G_{p_ys}^{AA}(i,j;\tau) & G_{p_yp_x}^{AA}(i,j;\tau) & G_{p_yp_y}^{AA}(i,j;\tau) & G_{p_yp_z}^{AA}(i,j;\tau) \\ G_{p_zs}^{AA}(i,j;\tau) & G_{p_zp_x}^{AA}(i,j;\tau) & G_{p_zp_y}^{AA}(i,j;\tau) & G_{p_zp_z}^{AA}(i,j;\tau) \end{pmatrix}, \tag{4}$$

with $G_{\mu\nu}^{\alpha\beta}(i,j;\tau) = -\langle\mathcal{T}\hat{c}_{i\mu}^{\alpha}(\tau)\hat{c}_{j\nu}^{\beta\dagger}(0)\rangle$ wherein $\mathcal{T}$ stands for the time ordering operator. Using the Heisenberg equation and Green's function method [23,24], the equation of motion for the electrons in valence bands of graphene sheet would be exploited:

$$\sum_{\ell}\left[\left(-\mathbf{I}\frac{\partial}{\partial\tau} + \boldsymbol{\varepsilon}_i\right)\delta_{i\ell} + \mathbf{t}_{i\ell}\right]\mathbf{G}(\ell,j;\tau) = \delta(\tau)\delta_{ij}\mathbf{I}, \tag{5}$$

where $\mathbf{I}$ is an 8×8 identity matrix, $\delta_{i\ell}$ (δ_{ij}) indicates the Kronecker symbol while $\delta(\tau)$ refers to the Dirac δ-function. Applying the imaginary time Fourier transformation,

$$\mathbf{G}(\ell,j;\tau) = \frac{1}{\beta}\sum_{n} e^{-\imath\omega_n\tau}\mathbf{G}(\ell,j;\imath\omega_n), \tag{6}$$

to Eq. (5) yields

$$\sum_{\ell}[(\imath\omega_n\mathbf{I} + \boldsymbol{\varepsilon}_i)\delta_{i\ell} + \mathbf{t}_{i\ell}]\mathbf{G}(\ell,j;\imath\omega_n) = \delta_{ij}\mathbf{I}, \tag{7}$$

with $\beta = T^{-1}$ being the inverse of temperature and $\omega_n = \pi(2n+1)/\beta$ being the fermionic Matsubara frequencies with integer numbers n. The analytical continuation of Eq. (7) by $\imath\omega_n \to E = \mathcal{E} + \imath\eta$ (η is an infinitesimal positive value) leads to the following equation:

$$\sum_{\ell}[(E\mathbf{I} + \boldsymbol{\varepsilon}_i)\delta_{i\ell} + \mathbf{t}_{i\ell}]\mathbf{G}(\ell,j;E) = \delta_{ij}\mathbf{I}. \tag{8}$$