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LOCAL DENSITY OF STATES OF ELECTRONS IN GRAPHEN

The local density of states of electrons in a graphen calculation provided based on a Green's function method for Bethe lattice approximation.

A rapid development of nanotechnologies requires at least qualitative theoretical research of physical properties of newly synthesized materials. Precise mathematical description of energy and oscillatory specters of such materials is well enough problematic due to multiplicity of their structure and composition. That is why, in a recent time theoretical interpretation of experimental data can only be made on a base of highly simplified model calculation, which, though, must correctly represent main features of these data.

Among the shared concepts in the theory of electron structure in a disordered materials, the preferences should be given to approximations based on a Green's functions calculation, as these functions are directly related with the density of states and doesn't require introduction of long-range order concepts.

For determination of local density of states of electron (LDSE) in hexagonal monolayer (graphen) we'll use Green's function method with semi-empirical single-electron tight-binding Hamiltonian included all important two center interactions between nearest atoms. Structure of graphen is being modeled with a Bethe lattice, holding hexagonal arrangement of neighboring atoms. As the basis for tight-binding Hamiltonian we'll chose one s- and two p_x, p_y – atomic orbitals.

According to Sletter-Coster notation [1], parameters of interaction in a two center approximation have a look:

$$E_s = \left\langle S_0 \left| \widehat{H} \right| S_0 \right\rangle; \quad E_p = \left\langle P_0 \left| \widehat{H} \right| P_0 \right\rangle$$

$$; \quad U = \left\langle S_0 \left| \widehat{H} \right| S_i \right\rangle;$$

$$V = \left\langle P_{0x} \left| \widehat{H} \right| P_i \right\rangle; \quad X = \left\langle S_0 \left| \widehat{H} \right| P_i \right\rangle;$$

$$W = \left\langle P_{0y} \left| \widehat{H} \right| P_i \right\rangle \tag{1}$$

here subscript 0 related with the central atom, i – with its nearest neighbors. In a nodal representation the Hamiltonian's matrix has block structure. Each block of 3x3 dimensionality (according to number of basis functions), represents a matrix of interactions of nearby atoms. According to accepted notations (1) it can be written as

$$\underline{H}_0 = \begin{bmatrix} E_s & 0 & 0 \\ 0 & E_p & 0 \\ 0 & 0 & E_p \end{bmatrix};$$

$$\underline{H}_0 = \begin{bmatrix} U & X & 0 \\ -X & V & 0 \\ 0 & 0 & W \end{bmatrix} \tag{2}$$

It is easily can be shown that other matrices of interaction can be gained from (2) with the help of symmetry transformations

$$H_{0i} = L_j^{-1} H_{0j} L_j , \qquad (3)$$

where

$$L_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -\cos\theta & \sin\theta \\ 0 & -\sin\theta & -\cos\theta \end{bmatrix} ; \qquad (4)$$

$$L_3 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -\cos\theta & -\sin\theta \\ 0 & \sin\theta & -\cos\theta \end{bmatrix}$$

here q – a valence angle.

It is obviously that:

$$L_{ij} = L_j^{-1}; \quad L_j L_j = -L_k ; \qquad (5)$$

$$i, j, k, l = 1, \dots, 3$$

The Green's function for ith node can be calculated from the Dyson's equation:

$$(E_i - H_i) G_j = I_j + \sum_{k=1}^{3} H_k G_k \qquad (6)$$

where I_{ij} – identity matrix, and the summing provided for nearest neighbors. Let us interested in a density of states for central, 0th, atom. Then, (6) will represent an infinite sequence of equations:

$$(E - H_0) G_o = I + \sum_k H_{0k} G_{k0} \qquad (7)$$

$$(E - H_0) G_{k0} = H_{0k}^T G_0 + \sum_{k' \neq k} H_{0k'} G_{k'0}$$

This sequence can be closed only if we'll use two basic properties of the Bethe lattice: first, each node of the lattice can be transformed into another by a finite number of transformations; secondly, any two nearest nodes are bonded only with each other. This fact allows us to introduce so-called transfer matrices:

$$\Phi_{L(\nu)} = G_0 G_0^{-1} ; \quad \Phi_{L(\mu)} = G_0 G_0^{-1} ; \qquad (8)$$

$$L(\nu) \; L(\mu) = 1,2,3$$

Substituting (8) in to system (7), for 0th atom we'll have:

$$G_0 = [E - H_0 - \Sigma]^{-1}, \qquad (9)$$

where, a self-energy part is:

$$\Sigma = \sum_\nu H_{0\nu} \Phi_{L(\nu)} \qquad (10)$$

and the transfer matrices can be determined from the equations:

$$\Phi_{L(\nu)} = \left[E_\nu - H_\nu - \widetilde{\Sigma} + H_\mu^T \Phi_{L(\nu)} \right]^{-1} H_\mu^T \qquad (11)$$

$$\widetilde{\Phi}_{L(\mu)} = \left[E_\mu - H_\mu - \Sigma + H_\mu \Phi_{L(\nu)} \right]^{-1} H_\mu \qquad (12)$$

here $\widetilde{\Sigma} = \sum_\lambda H_\lambda^T \widetilde{\Phi}_{L(\lambda)}$. For homopolar Bethe lattice the transfer matrices $\Phi_{L(\nu)}$ and $\widetilde{\Phi}_{L(\mu)}$ are related with each other by the transposition operation. Thus it will be sufficient to solve only one of these two matrix equations. We chose the second one. For different bonds the transfer matrices can be transformed into each other by the same symmetry operations as for the interaction matrices, so:

$$\Phi_1 = \begin{bmatrix} u & x & 0 \\ -x & v & 0 \\ 0 & 0 & w \end{bmatrix} ; \qquad (13)$$

$$\Phi_2 = L_2^{-1} \Phi_1 L_2 ; \quad \Phi_3 = L_3^{-1} \Phi_1 L_{143} .$$

Equation (12) can be rearranged as

$$[E - H_0 - \Sigma + H_0 \Phi_1] \widetilde{\Phi}_1 = H_0 \qquad (14)$$

or, multiplying (14) from the right on H_0^T, we'll obtain a matrix equation for determination of transfer matrix:

$$Z_1 = H_0 \Phi_1 \qquad (15)$$

$$(\varepsilon - \Sigma + Z_A)Z_A^T = H_0 H_0^T$$

here $\varepsilon = \boldsymbol{E} - H_0$.

In a common case it is a quite difficult to solve equations (15). Analytical solution can be found if we neglect ppπ interaction between p-orbitals of neighboring atoms:

$$G_0^s = \frac{1}{\Sigma_s} \qquad \text{and} \qquad G_0^p = \frac{1}{\Sigma_p} \qquad (16)$$

$$\Sigma_s = \frac{\varepsilon_s \pm \sqrt{\varepsilon_s^2 - 4(9(U^2 + X^2) - \varepsilon_s^2)(2 - 9\varphi^2)}}{2(2 - 9\varphi^2)} \qquad (17)$$

$$\Sigma_p = \frac{-\varepsilon_p \pm \sqrt{\varepsilon_p^2 - (9(V^2 + X^2) - \varepsilon_p^2)(2 - 9\varphi^2)}}{2 - 9\varphi^2} \qquad (18)$$

where

$$= \delta^2 \frac{\varepsilon_s^2 \varepsilon_p^2 - \gamma \pm \sqrt{(\varepsilon_s^2 \varepsilon_p^2 - 2\gamma)^2 - 4\delta^2}}{\Delta} \qquad (19)$$

and used the notations

$$\gamma = \varepsilon_s^2 (9(X^2 + V^2) - \varepsilon_p^2) +$$
$$+ \varepsilon_p^2 (9(9(X^2 + U^2) - \varepsilon_s^2) - 9\delta,$$
$$\delta = 3X(U - V),$$
$$\Delta = \gamma^2 - 16\varepsilon_s^2 \varepsilon_p^2 (9(X^2 + V^2) - \qquad (20)$$
$$- 4\varepsilon_p^2)(9(X^2 + U^2) - \varepsilon_s^2,$$
$$\varepsilon_s = E - E_s, \ \varepsilon_p = E - E_p$$

It is easy to ensure that function j²(E) approaches zero if sps (X=0) –interactions can be neglected. In this case we obtain known solution for Bethe lattice with single-parametric tight-binding Hamiltonian, set in basis of single s-orbital function per each atom.

Let us remind that partial density of states determined as imaginary parts of Green's function

G_0^s and G_0^p and the total local density of states of electron is the sum of these partials.

On a figure 1 represented LDSE of hexagonal monolayer (solid curve) calculated by equations (16) – (20) and tetrahedrally coordinated structure (dashed curve)[2].

It is well enough seen that energy spectrum of hexagonal structure, unlike the tetrahedral, doesn't have forbidden gap, i.e. the graphite monolayer has a metallic type of conductivity. Consequently, as it was mentioned in [3], the most significant properties of electron sub-system of solids are determined by the short-range order. Note that represented graphs have qualitative character. All calculations are provided to establish the influence of geometry of nearest atomic arrangement on an electron energy spectrum.
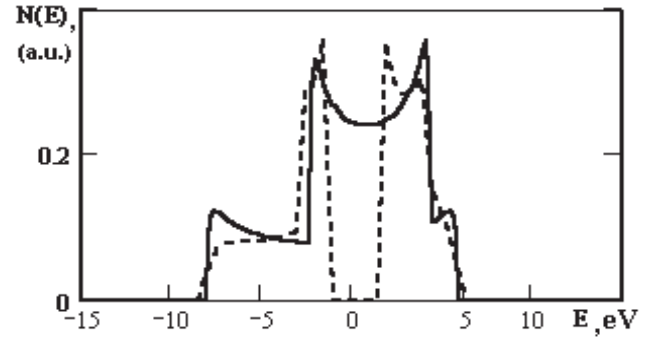

Figure 1 — LDSE of tetrahedral [2](dashed) and hexagonal (solid line) structures

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Abstract

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Key word: density of states, Green function, graphen.

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ЛОКАЛЬНАЯ ПЛОТНОСТЬ ЭЛЕКТРОННЫХ СОСТОЯНИЙ ГРАФЕНА

Резюме

В данной работе рассчитана локальная плотность электронных состояний графена методом функций Грина на основе приближения решетки Бете.Ж

Ключевые слова: плотность состояния, функция Грина, графен.

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ЛОКАЛЬНА ГУСТИНА ЕЛЕКТРОННИХ СТАНІВ ГРАФЕНУ

Резюме

У данній роботі розрахована густина електронних станів графену методом функцій Гріна на основі наближення гратки Бете.

Ключові слова: густина стану, функія Гріна, графен.