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Anisotropic behavior and inhomogeneity of atomic local densities of states in graphene with vacancy groups

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ABSTRACT

The electron local density of states (LDOS) are calculated for graphene with isolated vacancies, divacancies and vacancy group of four nearest-neighbor vacancies. A strong anisotropy of behavior of LDOS near Fermi level is demonstrated for atoms near defect. Effect of next-to-nearest neighbor interaction on the properties of graphene with vacancies is established.

1. Introduction

The 2D graphene physics attracts a paramount interest for rather a long period due to its unique properties, basic and applied. The relativistic character of its electron spectrum near Fermi level ε_F, corresponding description of electron properties by Dirac equations, instead of Schrödinger, with a Fermi velocity instead of that of light has remained a challenge for half a century. Recent interest to different properties of graphene and related nano-arrangements is sufficiently aimed at controlled variation of electron density of states within energy range in close vicinity of ε_F. In particular, the search for possibilities to create either a finite semiconductor gap, or, in contrast, drastic increase of Fermi-level occupation in electron spectra of graphene and its nano-derivatives is in progress, as well as for possibilities of superconducting transition in such the structures [2–6].

It is well known [1], that graphene is a zero-gap semiconductor. Moreover, its effective electronic mass vanishes near Fermi-level with appearance of V-like (Dirac) singularity in electron spectrum. Eventually, electron spectrum of graphene becomes highly sensitive to some sorts of distortions. Therefore, it is promising to look for solution of tuning the electron spectrum of graphene near ε_F by a controlled production of both local and extended defects in carbon nanostructures [2–6].

Most fascinating properties are observed in graphene with vacancies [4,6–9]. As that, the calculated densities of states demonstrate most interesting peculiarities near the Dirac point, i.e. Fermi level, on the neighbors of single vacancy [4,6], with a behavior of local density of states on the sub-lattice of chosen site. The calculations [4,6–9], for simple models based on tight binding Hamiltonian are in good agreement with *ab initio* calculations both for single vacancies and their arrangements [10].

At the same time, it is not obvious, if the predicted peculiarities can be in fact observed, in particular, the strongly anisotropic local density of states (LDOS) in electron spectrum of graphene with vacancies [4,6]. As the work function of vacancy in graphene is about 18–20 eV [11], it can be produced by exposure to irradiation by either high-energy electrons (>86 keV), or ions in plasma. It is most probable then, a formation not only of isolated vacancy, but of some of their complexes. There is the question, if the predicted [4,6] qualitative difference in the LDOS of neighbor atoms will be conserved near ε_F? Moreover, the analytical solution [4] of the absence of resonances in LDOS of atoms from the same sub-lattice

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with vacancy is based on the tight-binding model with nearest-neighbors coupling only. What can be expected from a consideration of interaction with other neighbors, even much weaker? The response is to be given in present work.

In the next section, the effect of next-to-neighbor interactions on electron spectrum of graphene is analyzed using Jacoby matrix technique [12–14] for LDOS of atoms, which are distributed near an isolated vacancy. The Jacoby matrix technique was used in computations here for its efficiency in finding these characteristics, and because it does not use translational lattice symmetry explicitly, which is crucial for spectral calculations, when such symmetry is broken.

Further on, the analysis is presented for LDOS of the atoms near different types of divacancies and groups of four neighbor vacancies. The nearest and next-to nearest neighbors interactions are considered.

2. Effect of interaction with next-to-nearest neighbors on electron spectrum of pristine graphene and graphene with isolated vacancy

The elementary cell of graphene contains two atoms, which are physically equivalent, i.e their local Green functions and LDOS are the same for atoms from different sub-lattices. The structure of graphene and its 2D Brillouin zone with principal points are presented in Fig. 1.

The vectors of two-dimensional Bravais lattice are $\boldsymbol{a}_1 = \left(\frac{a}{2}, \frac{a\sqrt{3}}{2}\right)$ and $\boldsymbol{a_2} = \left(\frac{a}{2}, -\frac{a\sqrt{3}}{2}\right)$, while the special points of first Brillouin zone are $K = \left(0, \pm\frac{4\pi}{3a\sqrt{3}}\right) \cup \left(\pm\frac{2\pi}{3a}, \pm\frac{2\pi}{3a\sqrt{3}}\right)$ and $M = \left(\pm\frac{2\pi}{3a}, 0\right) \cup \left(\pm\frac{\pi}{3a}, \pm\frac{2\pi}{3a}\right)$, $\Gamma = (0,0)$.

Electron spectrum of graphene can be described in tight-binding approximation. A corresponding Hamiltonian in occupation-number representation is read (see, e.g., [14]) as

$$\widehat{H} = \sum_i \varepsilon_i |i\rangle\langle i| - \sum_{i,j} J_{ij} |i\rangle\langle j| \qquad (1)$$

It is assumed here, that electron hopping in the layer occur both between the nearest neighbors $J_{ij}(a) \equiv J \approx 2.8$ eV (see, e.g. [15]), and between the next-to-nearest neighbors $J_{ij}(a\sqrt{3}) \equiv J' \leq 0.1J$ (where $a \approx 1.415$ Å is the distance between the nearest neighbors in graphene layer). The Fermi energy corresponds to that in the K-point of first Brillouin zone, and the dispersion law can be written as

$$\varepsilon(\boldsymbol{k}) - \varepsilon_F = \varepsilon_0(\boldsymbol{k}) \cdot \left[1 \mp J' |\varepsilon_0(\boldsymbol{k})| \Big/ J^2\right], \qquad (2)$$

where $\varepsilon_0(\boldsymbol{k}) = \pm J\left[1 + 4\cos\frac{k_y a\sqrt{3}}{2} \cdot \left(\cos\frac{3k_x a}{2} + \cos\frac{k_y a\sqrt{3}}{2}\right)\right]$ is the well-known dispersion law of graphene, taking into account the interaction between the nearest neighbors (the sign «–» corresponds to the valence band, while «+» marks the conduction band. Consideration of next-to-neighbor then interactions in graphene expands then the valence band ($\Delta_v \equiv -\varepsilon_v(\Gamma) = 3J \cdot (1 + 3J'/J)$) and narrows the conduction band ($\Delta_c \equiv \varepsilon_c(\Gamma) = 3J \cdot (1 - 3J'/J)$).

In Fig. 2 the electron densities of states (DOS) are presented for pristine graphene for both the nearest neighbors interaction (curve 1), and with taking into account the next-to-neighbor interactions (curve 3 for $J' = 0.1J$). These dependences are presented for a comparison by dashed lines in the following figures (Figs. 3–6).

Both of the DOS are featured by V-like Dirac peculiarities at $\varepsilon = \varepsilon(K) = \varepsilon_F$, with the coincident tilt angles, and, consequently, Fermi velocities. Both of them demonstrate a behavior, typical of 2D structures: the steps at spectra boundaries, i.e. at $\varepsilon = \varepsilon(\Gamma) = \varepsilon_F \pm 3J \cdot (1 \mp 3J'/J)$, and logarithmic behavior at $\varepsilon = \varepsilon(M) = \varepsilon_F \pm J \cdot (1 \mp J'/J)$. While the curve 1 mirrors line $\varepsilon = \varepsilon_F$, the curve 2 is shifted to region of low energies with a «weight center» posed in a valence band.

In pristine graphene, LDOS of each atom coincides with a total DOS. A formation of single vacancy in graphene structure results, obviously, in a difference of LDOS of the near-to-vacancy atoms. In Fig. 3, there are presented LDOS of the first, second, seventhes and tenths neighbors of isolated vacancy.

In [16,17], it was shown for nearest-neighbor interaction, that at $\varepsilon = \varepsilon_F$ in the presence of vacancies, the sharp resonance appears in a total electron DOS of graphene. The Fig. 3 clearly demonstrates (curves 1), that sharp resonances of LDOS are observed at specific energy values only for the atoms pertained to sub-lattice with vacancies. For atoms in the same with vacancy lattice LDOS are vanished to zero at $\varepsilon = \varepsilon_F$. Moreover, the Dirac singularity of pristine material is remained for next-to-nearest neighbors of vacancy, while for slightly more distant atoms some micro-gap appears near the Fermi level. Farther apart from the vacancy, LDOS of all of the atoms tend, naturally, to the DOS of pristine graphene with a V-like Dirac singularity at $\varepsilon = \varepsilon_F$.

It can be proved using the relationship [18] obtained by means of Jacobi matrix technique [12–14], between an arbitrary matrix term of Green function $G_{mn}(\varepsilon) = \langle m|\varepsilon I - H|n\rangle$ c with its matrix term $G_{00}(\varepsilon) = \langle 0|\varepsilon I - H|0\rangle$. Here, H is Hamiltonian of the system Eq. (1); $|m\rangle$ and $|n\rangle$ stay for vectors of an orthogonally reduced basis $|n\rangle_0^\infty$, which is obtained by orthonormalization of sequence $\{H^n|0\rangle\}_0^\infty$; $|0\rangle$ is a generating vector in the space of electron excitations of the atom in a crystal structure of graphene, namely the nearest to vacancy neighbor for the case under consideration. This relationship is of the for:

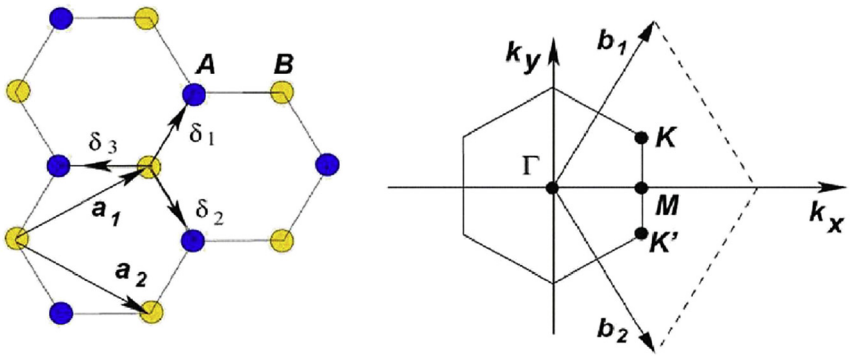

Fig. 1. Bravais lattice and first Brillouin zone of graphene.