Journal of Science: Advanced Materials and Devices 1 (2016) 167–173

Contents lists available at ScienceDirect

Journal of Science: Advanced Materials and Devices

journal homepage: www.elsevier.com/locate/jsamd

Original article

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

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ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form
13 June 2016
Accepted 13 June 2016
Available online 18 June 2016

Keywords:
Electron spectrum
Two-dimensional crystals
Graphene
Vacancy

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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Peer review under responsibility of Vietnam National University, Hanoi.

http://dx.doi.org/10.1016/j.jsamd.2016.06.011

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:

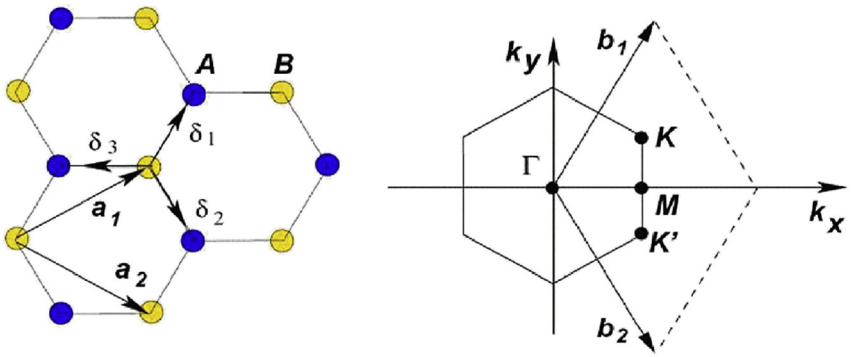

Fig. 1. Bravais lattice and first Brillouin zone of graphene.

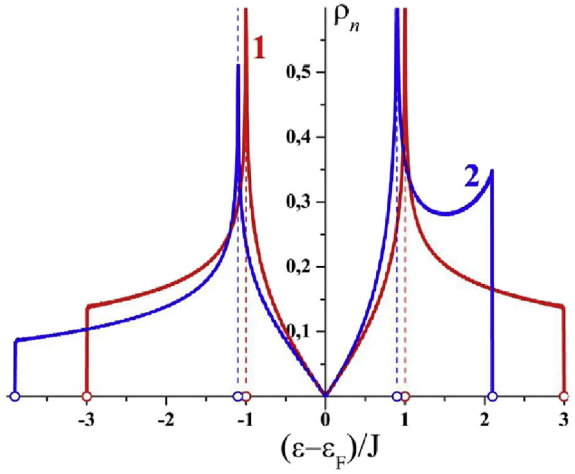

Fig. 2. Electron DOS of graphene for varied next-to-neighbor interactions: curve 1 corresponds to $J' = 0$, and curve 2 to $J' = 0.1\,J$.

$$G_{mn}(\varepsilon) = -P_{\alpha}(\varepsilon)Q_{\beta}(\varepsilon) + P_m(\varepsilon)\,P_n(\varepsilon)\cdot G_{00}(\varepsilon); \quad \alpha = \min\{m,n\}; \quad \beta = \max\{m,n\}. \tag{3}$$

In (3) the polynomials are obtained from recurrent equations.

$$b_n\{P,Q\}_{n+1}(\varepsilon) = (\varepsilon - a_n)\{P,Q\}_n(\varepsilon) - b_{n-1}\{P,Q\}_{n-1}(\varepsilon) \tag{4}$$

Under assumption $P_{-1}(\varepsilon) = Q_0(\varepsilon) = 0$ and $P_0(\varepsilon) = 1$, $Q_1(\varepsilon) = b_0^{-1}$. The values a_n and b_n are the diagonal and non-diagonal element of Jacobi matrix, in respect, in which the Hamiltonian (1) is represented in orthonormalized basis $|n\rangle_0^{\infty}$. Eq. (3) yields, that LDOS is

$$\rho_n(\varepsilon) = \pi^{-1}\mathrm{Im}\lim_{\gamma\to 0} G_{nn}(\varepsilon + i\gamma) = P_n^2(\varepsilon)\cdot\rho_0(\varepsilon), \tag{5}$$

where $\rho_0(\varepsilon) = \pi^{-1}\mathrm{Im}\lim_{\gamma\to+0} G_{00}(\varepsilon + i\gamma)$ is LDOS nearest to vacancy neighbor.

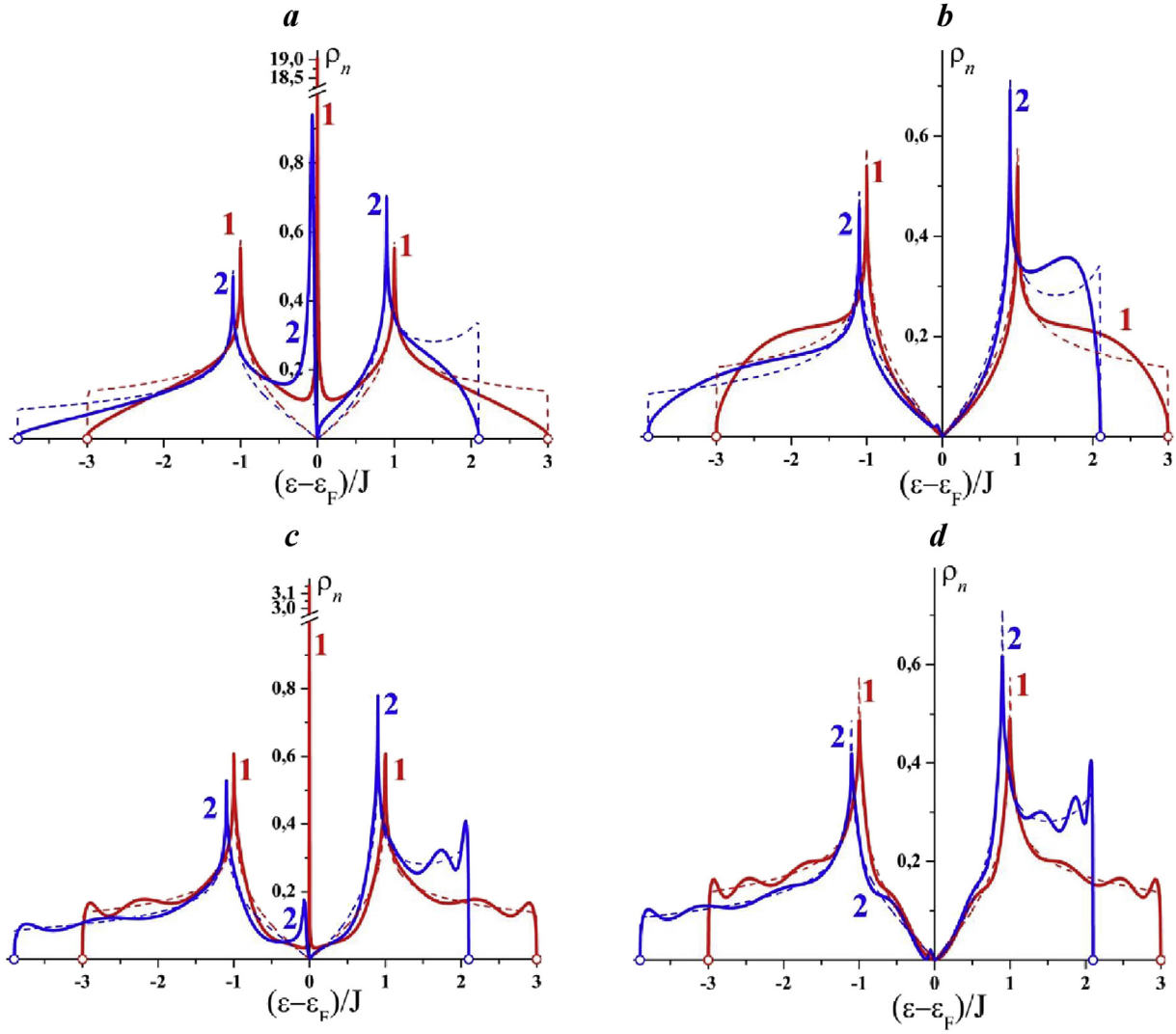

Fig. 3. LDOS of nearest (***a***); second (***b***); sevenths (***c***) and tenths (***d***) neighbors of isolated vacancy in graphene. Curves 1 correspond to the value $J' = 0$, and curves 2 to $J' = 0.1\,J$.

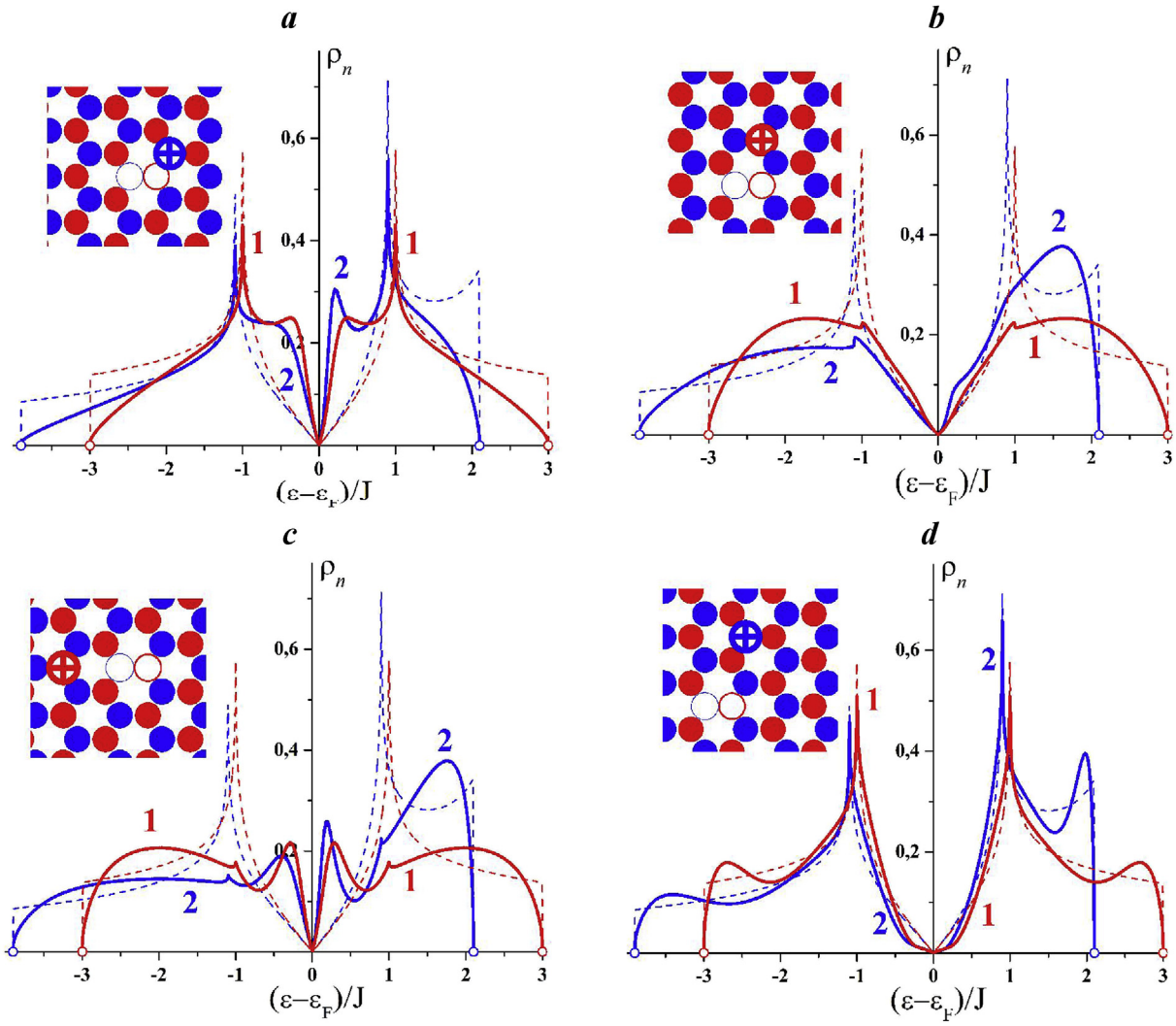

Fig. 4. LDOS for neighbors of vacancy produced by two closely distributed vacancies. Insets of each fragment illustrate position of corresponding atom. Curves 1 and curves 2 correspond to $J' = 0$, and to $J' = 0.1\,J$ respectively.

In the case $J' = 0$ all diagonal elements of Jacobi matrix are zero with respect to the Fermi level. The polynomials $P_n(0)$ are then zero at all odd n and, otherwise, are non-zero:

$$P_{2k}(0) = \prod_{l=0}^{k} \frac{b_{2l}}{b_{2l+1}} \tag{6}$$

The construction of Jacobi matrix, i.e. the sequence $|n\rangle_0^\infty$ yields, that even n at $J' = 0$ correspond to excitations of atoms from vacancy-frie sublattice and the odd ones to excitations of atoms in sublattice with vacancy.

Concideration of next-to-neighbor interactions results in different values of diagonal matrix elements a_n (at $n \to \infty$ $a_n \to [\varepsilon_v(\Gamma) + \varepsilon_c(\Gamma)]/2 < 0$). For the even n (atomic excitations in vacancy-free sublattice) the difference of elements a_n makes n to broadaning of the peak in LDOS, and their negative vakues shift resonance towards the valence band. For odd n (sublattice with vacancy) the values of $P_n(0)$ are finite, and corresponding LDOS demonstrate a formation of minute peaks near upper boundary of valence band (see. curves 2 in Fig. 3).

Hence, consideration of next-to-nearest neighbor interactions does not remove, but slightly modify, stron anisotropy of electron spectra of the atoms from different sublattices due to formation of single vacancy in graphene.

3. Electron spectra of graphene with vacancy arrangements

The presence of several closely distributed vacancies in the system can affect sufficiently the pattern of electron LDOS of the neighboring atoms, as well as their inhomogeneities, the occupation of Fermi level vicinity, in particular, for which the single isolated vacancy is responsible. In this section the LDOS are presented for neighbor-to-divacancy, the latter being produced both by nearest neighbor vacancies (Fig. 4), and by two next to nearest neighbor vacancies (Fig. 5).

In the former case, the vacancies occupy both sub-lattices of graphene and each atom belong to a lattice with vacancy. Then, in contrast to the above considered case of isolated vacancy, in the total DOS, as well as in all of the LDOS near $\varepsilon = \varepsilon_F$ resonances are absent (see Fig. 4). This result is in close agreement with the data of work [19].

Inhomogeneity of behavior of electron LDOS is not qualitative, though we should note a sequence of atoms with LDOS characterized by a pronounced V-like Dirac singularity near Fermi level (Fig. 4a and c), and atoms with LDOS, which are similar to local densities of electronic states of conventional extremely narrow-band semiconductors, described by a common non-relativistic, square dispersion law (Fig. 4 b and d).

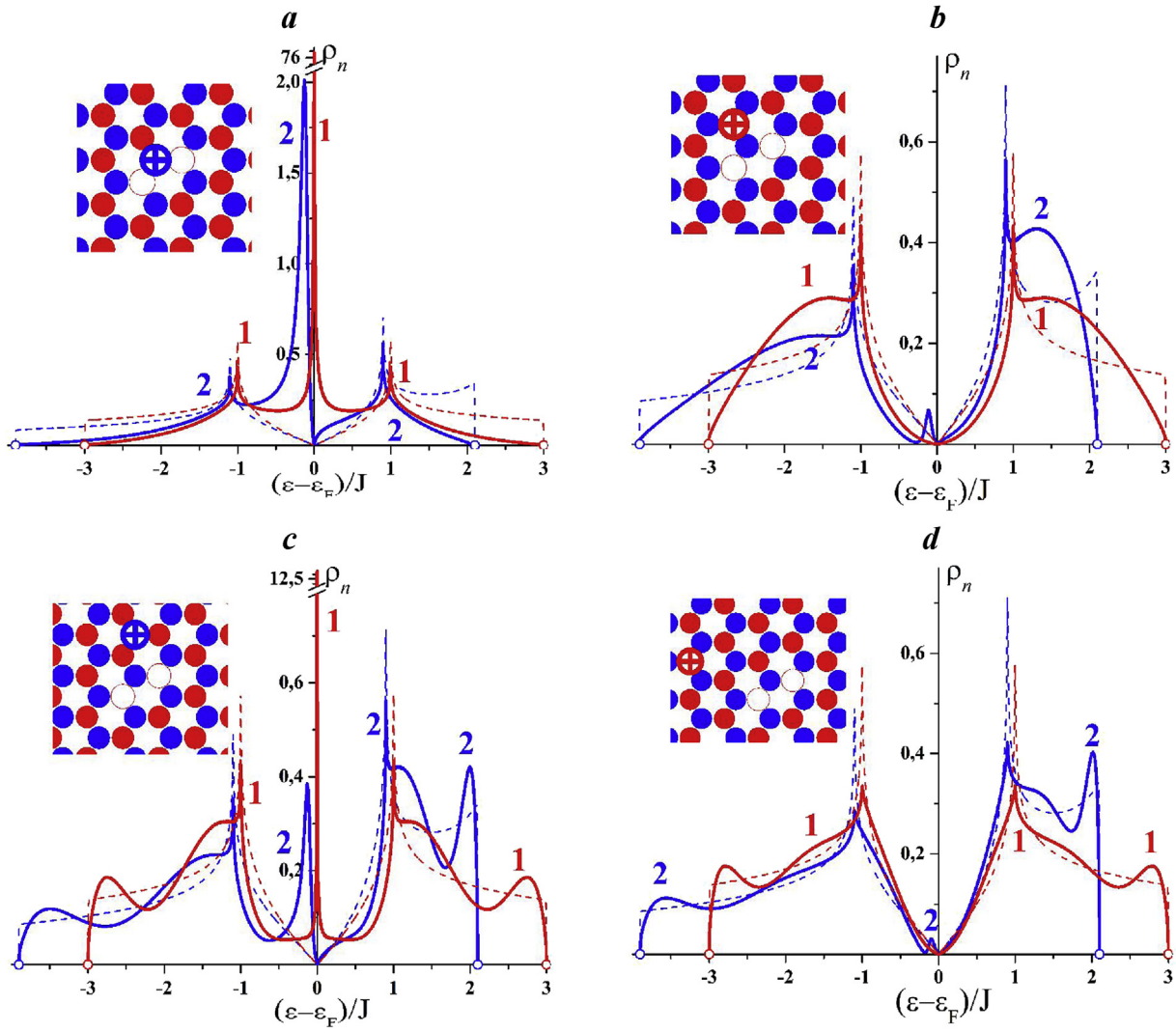

Fig. 5. LDOS for divacancy, formed by two next-to-nearest neighbor vacancies. The labels correspond to those in Fig. 4.

Consideration of next-to nearest neighbors interaction does not affect significantly the behavior of electron densities near Fermi level, but giving rise to slight asymmetry of corresponding curves.

In the case of divacancy, formed by two next-to-nearest neighbor vacancies, i.e. those in the same sub-lattice, a behavior of LDOS is similar to isolated vacancy, though much more pronounce due to enhancement of defect (Fig. 5a and c). In the LDOS of atoms, pertained to the vacancy-free sub-lattice, the sharp resonances appear near $\varepsilon = \varepsilon_F$. Their height exceeds those in Fig. 3 for more than two orders of magnitude.

Similar to the case of isolated vacancy (see Fig. 3), the account of second neighbors yields broadening of the peak and its shift towards energy range of valence band, while occupation of Fermi level itself is sufficiently decreased. Note, for this type of vacancy, it is clearly seen, that despite weak occupation of Fermi level, the corresponding LDOS show a behavior, typical of metal, moreover its dispersion is described by non-relativistic, square law.

Atoms of the same lattice with vacancies, similar to the case of isolated vacancy do note reveal such the peak in their LDOS near $\varepsilon = \varepsilon_F$ (Fig. 5b and d). It is proved for $J' = 0$ in the same way as in above section. Interaction of second neighbors, which smears this peak with a its shift from Fermi level, results in a formation on corresponding LDOS of slight peak, which is more pronounced in the case of such divacancy, compared to isolated vacancy, but remains two orders of magnitude weaker, than peak on LDOS of atoms from another lattice, which are distributed at approximately the same distance from defect.

It is worth noting, that near Fermi level a non-relativistic, square dispersion law, typical of semiconductor, is more obvious for behavior LDOS of the atoms from sub-lattice with such the vacancy, both at $J' = 0$, and at consideration of second neighbors.

Finally, a defect formed by a group of four vacancies is considered. An arbitrary “central” atom is knocked out together with its three nearest neighbors. A behavior of LDOS of diverse atoms (Fig. 6) qualitatively resembles the case of divacancy, formed by two vacancies in the same sub-lattice. For atoms of the same sub-lattice with «center», i.e. with the nearest to defect neighbors, the considered characteristics reveal at $J' = 0$ sharp resonances near Fermi level, which broaden with increase of J' and shift to valence band. Behavior of LDOS of these atoms is typical of the metals with a low concentration of carriers and square dispersion of electrons (Fig. 6a and c).

Local density of states of the atoms, pertained to sub-lattice with three edge vacancies from this group, manifest a behavior typical of extremely narrow-gap semiconductor. Interaction with next-to-nearest neighbors results then in a formation of minute peak on

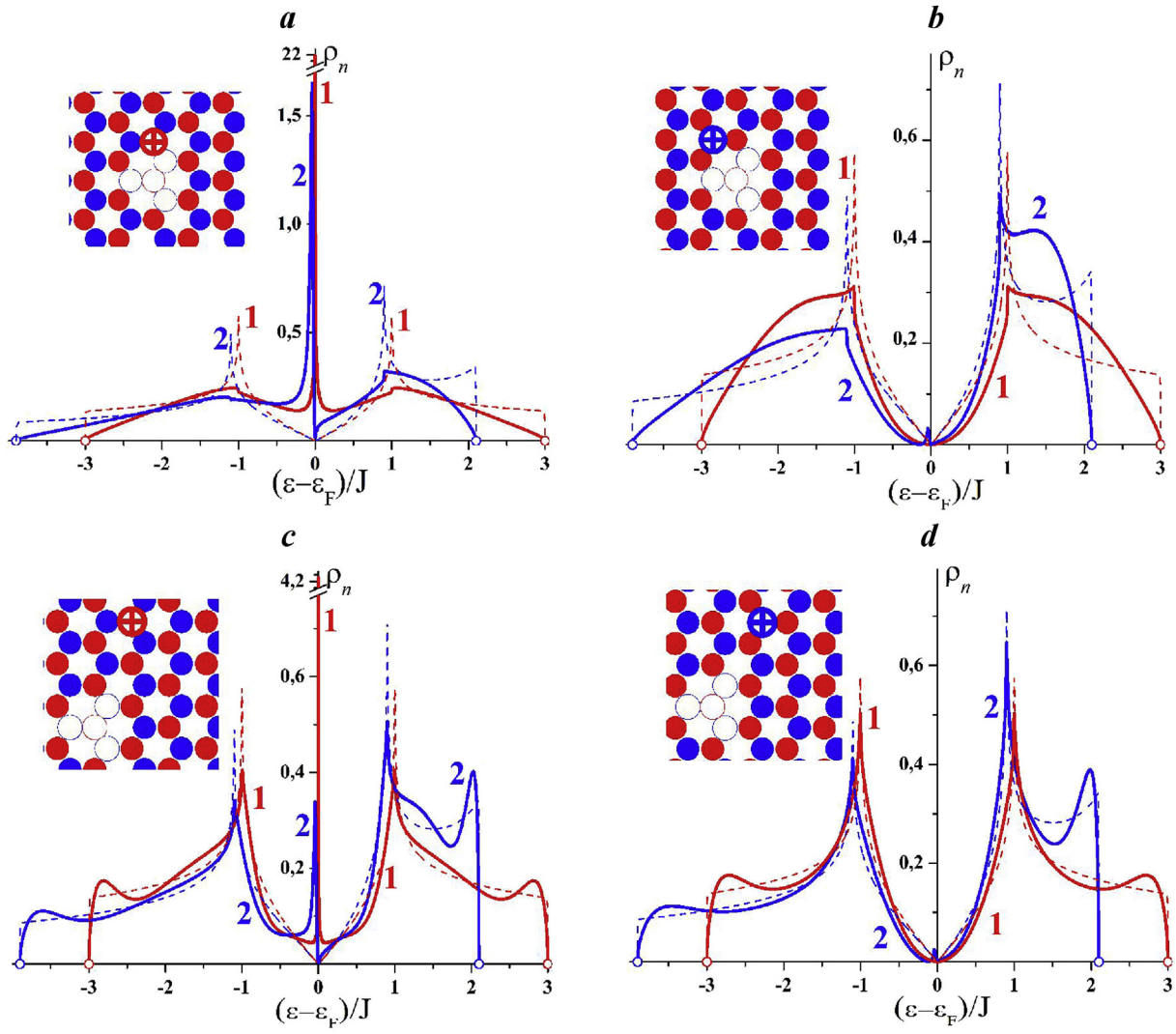

Fig. 6. LDOS of neighbors of the vacancy group, formed by four vacancies, when there are knocked "central" atom together with its three nearest neighbors. All labels are the same as in Fig. 4.

LDOS in a valence band near Fermi level, which is several orders of magnitude weaker, than those on LDOS of atoms from another sublattice.

4. Conclusion

It is shown here that interaction with next-to-nearest neighbor interaction does not remove a pronounced qualitative inhomogeneities in behavior of local density of electronic states and and in occupation of Fermi level, stemmed in graphene with vacancy.

The presence of several vacancies in the system favors both a significant decrease of such inhomogeneity, e.g. for divacancy, formed by two nearest vacancies, and its enhancement.

It should be noted, that in the case of a formation by some vacancy group of resonance in total LDOS near Fermi level, such the resonance will feature LDOS of each of the atoms. This system will necessarily contain atoms with LDOS typical of electron density of states of narrow-band semiconductors. We argue, that atoms with such electron density of states must be present in the structures of works [16,17], and that consideration of interaction with next-to-nearest neighbors does not remove such inhomogeneity.

Similar inhomogeneity of local densities of electron states was noticed in thin carbon nano-films with defects of "step edge" type in work [5], and should be present in graphene nano-ribbons which gained recently a broad study.

Acknowledgement

The works of Prof. Peter Brommer have contributed much to understanding the influence of structural features of complex systems on their physical properties, quasi-particle spectra, in particular. Fruitful communications with him have inspired our activity. This contribution is dedicated to the memory of Prof. Peter Brommer, the outstanding scientist and personality.

The support of grant of NAS of Ukraine # 4/16 –H is acknowledged.

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