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Original article

Verification of continuum-based model of carbon materials

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ABSTRACT The continuous medium approximation to the description of a carbon material previously used to model the properties of spherical carbon shells of nanometer diameter. This approach is based on the transition from lattice operators to field operators. The present study verifies the given model evaluating the energy spectrum of electrons in a perfect flat carbon monolayer. An implementation of the Dirac cones within the continuous medium framework is demonstrated. Its are close to the positions of the vertices of the Brillouin zone for graphene. Increase of the Taylor series expansion order of field operators makes the result precise, and the approximate positions of the Dirac cones match the exact data for graphene.

KEYWORDS carbon lattice, continuum model, Dirac cone

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1. Introduction

It is necessary to know the key features of the energy spectrum of conduction electrons in the carbon layer to build a complete picture of the observed characteristics of carbon materials and the possibility of reliable prediction the properties of composites of various structures synthesized on their basis [1–3]. However, the known variety of carbon structures restricts the calculations effectiveness, since it requires an individual approach to each specific geometry. For example, it is implemented for carbon nanotubes and spherical shells [4–6].

A number of papers, e.g., [7–9], present a detailed analysis for carbon clusters, namely, fullerenes of a fixed dimension C_{24}, C_{60}, C_{70}. Such structures include relatively small number of atoms. Therefore, one can formulate a complete system of lattice equations based on the Hubbard model and analyze it. On the other hand, when synthesizing of larger size carbon structures like spherical shells, one can only control its characteristic average size. The specific diameter of a particular shell remains random. In addition, the amount of lattice sites reaches tens of thousands [10, 11]. Thus, it remains relevant to develop an efficient simplified model for description the energy spectrum of carbon structures of arbitrary dimensions.

Paper [12] presents the transformation from the lattice operators for electrons to the field operators and continuous medium limit. It potentially allows one to model the systems of complex geometry, including those with an irregular arrangement of atoms. The model was built in relation with high-dimensional spherical carbon shells, the synthesis technology, analysis of the growth kinetics and geometric parameters of which are described in papers [10, 11]. The optical and magnetic characteristics of a composite based on such shells are calculated, and theoretical results have a good agreement with the experimental data.

However, there is a question about the Dirac point implementation within the averaged framework. The present paper shows that it occurs at first when the terms of the third order are taken into account in the expansion of the electron field operators. The even terms in the Taylor series expansion determine the modulus of the wave number corresponding to the Dirac points, and the odd terms determine the structure and asymmetry of the Dirac cones, which, in contrast to the exact solution, turn out to be somewhat deformed within the approximations.

2. Continuum-based model of carbon lattice

The basic Hamiltonian for the considered model is the graphene monolayer in the tight-binding approximation [2,3]:

$$H = -\theta \sum_{j,\delta,\sigma} \left(a^\dagger_{j\sigma} b_{j+\delta,\sigma} + b^\dagger_{j\sigma} a_{j-\delta,\sigma} \right), \tag{1}$$

where a, b are the creation–annihilation fermionic operators of an electron with given spin σ at lattice site with number j. It is related to the carbon sublattice A and B, respectively. δ are radius-vectors from the node j to the nearest neighbours. In a flat lattice, these vectors are well-known (Fig. 1):

$$\delta_1 = (-1;0)a_0, \quad \delta_{2,3} = \left(\frac{1}{2}; \pm\frac{\sqrt{3}}{2}\right) a_0,$$

where a_0 is the interatomic bond length. The parameter θ is the hopping integral of transition between two lattice sites. The Coulomb repulsion of the electrons and impurities are not considered in the present study.

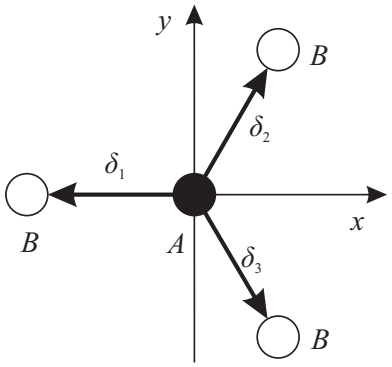

FIG. 1. The carbon–carbon bond vectors in a flat layer

The time-dependent Heisenberg equation

$$i\frac{dX}{dt} = [X, H]$$

allows one to build the evolution equations for the amplitudes of the electron wave functions at the lattice sites:

$$\begin{aligned} i\frac{da_{j\sigma}}{dt} &= -\theta\sum_{\delta} b_{j+\delta,\sigma}, \\ i\frac{db_{j\sigma}}{dt} &= -\theta\sum_{\delta} a_{j-\delta,\sigma}. \end{aligned} \tag{2}$$

In this system of equations, the geometry of a particular lattice is determined only by the δ vectors.

To pass to the continuous medium limit, lattice operators are considered as field operators which are the continuous functions of coordinates [13–16]:

$$a_{j\sigma} \to a_\sigma(\mathbf{r}_j),\ \ldots$$

This makes possible the application of the Taylor series expansion of the right-hand side operators:

$$\begin{aligned} b_{j+\delta,\sigma} \to b_\sigma(\mathbf{r}_j+\delta) &\approx \\ \approx b_\sigma(\mathbf{r}_j) &+ \delta\cdot\nabla b_\sigma(\mathbf{r}_j) + \frac{1}{2}\frac{\partial^2 b_\sigma(\mathbf{r}_j)}{\partial x^\mu \partial x^\nu}\delta^\mu\delta^\nu + \frac{1}{3!}\frac{\partial^3 b_\sigma(\mathbf{r}_j)}{\partial x^\mu \partial x^\nu \partial x^\lambda}\delta^\mu\delta^\nu\delta^\lambda + \ldots, \end{aligned} \tag{3}$$

The indices μ, ν and λ denote the spatial components of the two-dimensional vectors δ. There are sums over these indices. The lattice operators are considered as the finite-difference approximation of the field operators in that approach. The expansion is used to transform the sums of operators at the right hand sides of the equations (2). Finally, one rewrites the model as a system of linear partial differential equations.

When considering a flat layer or averaging over the electron momenta, the gradient terms in the expansion disappear. The final evolution equations include at least the second-order derivatives. E.g., the right-hand side of the first equation in (2) transforms as follows:

$$\begin{aligned} \sum_{\delta} b_{j+\delta,\sigma} &\to b(\mathbf{r}_j+\delta_1) + b(\mathbf{r}_j+\delta_2) + b(\mathbf{r}_j+\delta_2) = \\ = 3b &+ (\delta_{1;x}+\delta_{2;x}+\delta_{3;x})\frac{\partial b}{\partial x} + (\delta_{1;y}+\delta_{2;y}+\delta_{3;y})\frac{\partial b}{\partial y} + \\ &+ \frac{1}{2}\left(\left(\delta_{1;x}^2+\delta_{2;x}^2+\delta_{3;x}^2\right)\frac{\partial^2 b}{\partial x^2} + \left(\delta_{1;y}^2+\delta_{2;y}^2+\delta_{3;y}^2\right)\frac{\partial^2 b}{\partial y^2} + \right. \\ &+ \left. 2\left(\delta_{1;x}\delta_{1;y}+\delta_{2;x}\delta_{2;y}+\delta_{3;x}\delta_{3;y}\right)\frac{\partial^2 b}{\partial x \partial y}\right) + \ldots \end{aligned}$$

The first-order terms vanish exactly:

$$\delta_{1;x}+\delta_{2;x}+\delta_{3;x} = -1+\frac{1}{2}+\frac{1}{2} = 0, \quad \delta_{1;y}+\delta_{2;y}+\delta_{3;y} = \frac{\sqrt{3}}{2}-\frac{\sqrt{3}}{2} = 0,$$

while in the second-order term only xy-derivative vanishes:

$$\delta^2_{1;x} \quad + \quad \delta^2_{2;x} + \delta^2_{3;x} = 1 + \frac{1}{4} + \frac{1}{4} = \frac{3}{2}, \quad \delta^2_{1;y} + \delta^2_{2;y} + \delta^2_{3;y} = \frac{3}{4} + \frac{3}{4} = \frac{3}{2},$$

$$\delta_{1;x}\delta_{1;y} \quad + \quad \delta_{2;x}\delta_{2;y} + \delta_{3;x}\delta_{3;y} = 1 \cdot 0 + \frac{1}{2} \cdot \frac{\sqrt{3}}{2} - \frac{1}{2} \cdot \frac{\sqrt{3}}{2} = 0.$$

The xx- and yy-terms produce the two-dimensional Laplace operator. The high-order terms are transformed by the same way.

As a result, in the first non-zero approximation, the model is approximated by the following system:

$$i\frac{da_\sigma}{dt} = -\theta\left(3 + \frac{3a_0^2}{4}\nabla^2\right) b_\sigma, \qquad i\frac{db_\sigma}{dt} = -\theta\left(3 + \frac{3a_0^2}{4}\nabla^2\right) a_\sigma. \tag{4}$$

The description of specific geometric structures requires setting a suitable spatial basis for the wave functions. In particular, the basis of spherical harmonics is used for the shells described in [10–12]. The substitution of the basis reduces the problem to a system of linear ODEs, the eigenfrequencies of the solutions of which determine the energy spectrum of electron in the system.

As expected, substitution of the plane wave solution $\exp(i\mathbf{q}\cdot\mathbf{r})$ into (4) results in the isotropic energy spectrum:

$$\frac{\omega}{\theta} = \pm\left(3 - \frac{3}{4}q^2\right). \tag{5}$$

The particle energy vanishes on the entire circle $qa_0 = 2$, which is close to the inner-radius for the Brillouin zone of graphene. The dispersion relation becomes linear near this circle only under the condition $q_x = q_y$. Thus, the spectrum obtained in this approximation does not contain the Dirac points, and the applicability of the model to describe flat lattice is limited. However, with a high degree of irregularity due to defects and deviation of the lattice shape from the plane with a change in the angles between the bonds, one should expect better agreement between the proposed model and the characteristics of the material. If one takes into account the highest terms in expansion (3) it is possible to overcome this limitation with using the next order term only.

3. Approximate implementation of the Dirac points

If one takes into account the third derivatives in the Taylor series the dispersion relation has the following form

$$\frac{\omega}{\theta} = \pm\left(3 - \frac{3}{4}q^2 - \frac{iq_x}{8}\left(q_x^2 - 2q_y^2\right)\right). \tag{6}$$

That function has six zeros in the points, distributed uniformly over the circle with radius $2/a_0$ (Fig. 2):

$$\mathbf{Q}_{1,2} = \frac{1}{a_0}\left(0; \pm 2\right), \qquad \mathbf{Q}_{3,4,5,6} = \frac{1}{a_0}\left(\pm\frac{2}{\sqrt{3}}; \pm\frac{2\sqrt{2}}{\sqrt{3}}\right).$$

The expansion of the dispersion relation near the points $\mathbf{Q}_j$ confirms the approximate implementation of the deformed Dirac cones. For example, in the neighborhood of $\mathbf{Q}_1$, the energy spectrum takes the form of the elliptic cone:

$$\frac{\omega_1}{\theta} \approx 3\sqrt{\frac{k_x^2}{4} + k_y^2}, \tag{7}$$

where $\mathbf{k}$ is the deviation of the electron momentum vector from $\mathbf{Q}$: $\mathbf{q} = \mathbf{Q} + \mathbf{k}$. An increase in the expansion order leads to the consistent refinement of the location of the Dirac points, for which the even derivatives are responsible, and the shape of the cones, determined by the odd terms of the series. It can be seen from Fig. 2 that, within the accuracy of plotting of the graph, their positions in the model and in the exact calculation coincide, and the structure of the energy isolines around the valleys approaches locally isotropic when terms of 6–7th orders and higher are taken into account.

It is expected that when averaging over the directions of wave vectors in a deformed lattice, for example, in a spherical shell, which includes not only hexagonal cells, but also structural elements from a different number of atoms, the contribution of odd orders will decrease down to negligible values.

Of course, there exist a more standard and simple way to introduce the field operators within the flat carbon sheet. It uses the plane electron waves representing the two leading terms of the Fourier series near the Dirac points. It is well-described in literature [2]. That approach is applicable, at first, for flat regular structure.

In the present paper, the main goal of the described method is modeling of the complex shape of the carbon lattice with irregularity which should be strong enough to apply the averaging procedure. Here, the Fourier expansion by plane waves is inapplicable because of possibility of the large lattice curvature. Therefore, the proposed approach allows one to implement a more flexible approximation despite it has lower precision in the case of the flat layer (see [12]). To evaluate the Dirac points here, one should keep the relatively large number of expansion terms. The corresponding high-order equations can be difficult for analysis, but it is possible to use the perturbation theory.

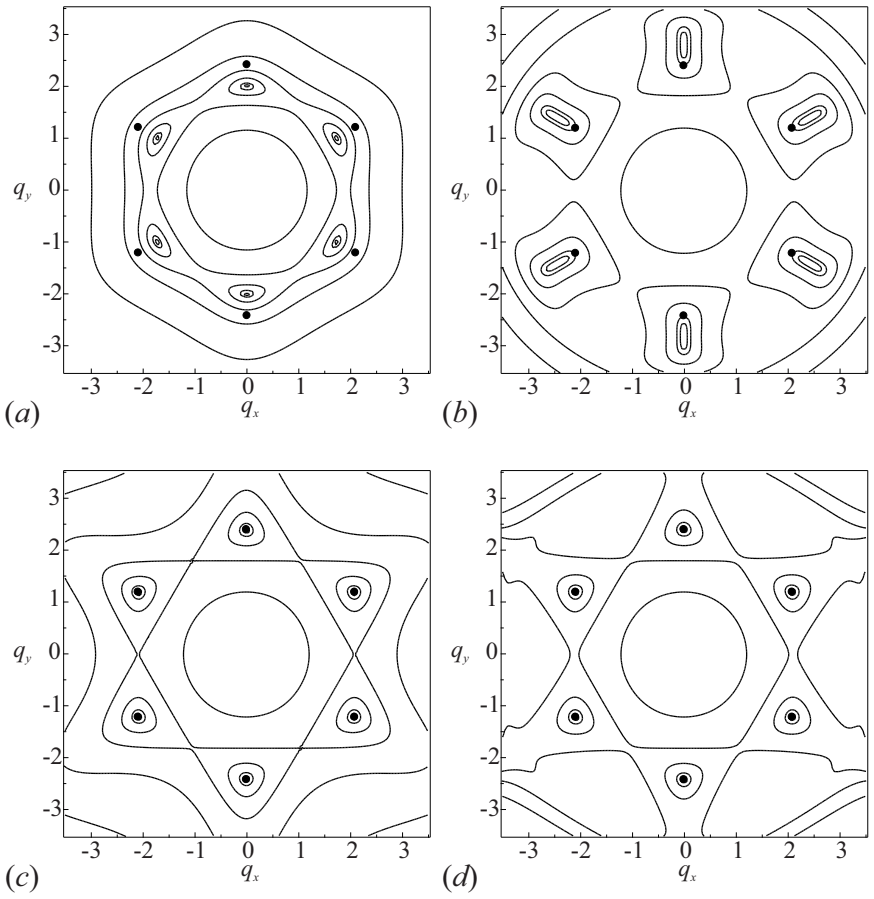

FIG. 2. Contour maps of the energy spectrum calculated within the framework of the continuum model using the expansion to terms of the following orders: (a) – 3rd, (b) – 5th, (c) – 7th, (d) – 9th order. The following energy levels are shown: 0, 0.1θ, 0.2θ, 0.5θ, 1.0θ, 2.0θ and 5.0θ. The dots indicate the positions of the Dirac cones of ideal graphene

4. Conclusion

The previously developed approach based on the continuum model produces the approximate energy spectrum of the plane electron waves in the carbon sheet with the approximate implementation of the Dirac cones. This result confirms the applicability of the developed model to the description of various carbon structures and ensures the reliability of the calculations performed for description of the properties of a spherical carbon shell.

It is expected that taking into account higher orders of decomposition makes it possible to refine the quantitative characteristics of the carbon composite based on nanospheres, however, even the first non-vanishing approximation provides reliable information about the features of the observed optical and magnetic properties of the material. In addition, the model, which is actually formulated as a pair of coupled Schrödinger equations for the wave functions of electron related to different carbon sublattices, can be easily adapted to structures of other geometries.

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