Symmetry of Electron Bands in Graphene: (Nearly) Free Electron Versus Tight-Binding

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1. Introduction

The electronic band structure of graphite and a graphite monolayer, called graphene, was a subject of intense study since analytic calculation of Wallace using a tight-binding model (TBM).[1] In particular, understanding of the symmetries of the electronic energy bands in graphene was of crucial importance. First, symmetry classification of them in graphene was presented by Lomer in his seminal article.[2] Later on, the subject was developed in numerous publications.[3-7] Despite this, band theory and group-theoretical analysis of 2D hexagonal materials in general, and graphene in particular, continues to attract attention in the very recent years.[8-21]

The symmetry labeling of all electron bands in graphene obtained by combining numerical band calculations and analytical analysis based on group theory is presented. The latter is performed both in the framework of the (nearly) free electron model, or in the framework of the tight-binding model. The predictions about relative positions of the bands which can be made on the basis of each of the models just using the group theory (and additional simple qualitative arguments, if necessary) are complimentary.

In our studies of electronic bands in graphene, we combined numerical band calculations with the analytical symmetry analysis of the bands.[22-24] In Figure 1, we reproduce the results of the band structure calculations with symmetry labeling following our previous articles[22,24] where the details can be found. Here, we just remind about the distinction between the \( \sigma \) and the \( \pi \) bands (the former being even with respect to reflection in the plane of graphene, the latter—odd.) Attention is traditionally attracted to the \( \pi \) bands merging at the Fermi level.[25] However, we are interested in all the bands (and even in the lowest scattering resonances).

By the analytical symmetry analysis we mean reproduction of the electron band symmetry without solving any differential or even algebraic equations, but just using the group theory (and additional simple qualitative arguments, if necessary). To make such analysis possible, one must choose a model as simple as possible.

There are two alternative approaches to the analysis, both presented, for example, in the book by Kittel.[26] One can use either TBM, or the (nearly) free electron model (FEM); note that in spite being just opposite to each other, as a rule, these two approaches give the same result for the bands symmetry.[26,27]

The minimalistic TBM, with four orbitals on each atom (\( \langle 2s, 2p \rangle \)), correctly describes the symmetry of all the occupied bands and the unoccupied \( \pi \) band touching the Fermi level. We call these bands the TBM bands.

However, the minimalistic TBM does not describe correctly the other unoccupied bands. The latter are also differ from the TBM bands in their dispersion law and localization with respect to the graphene plane. This is why we called them the FEM bands.[23,24] To describe the symmetry of all the bands, we used a hybrid approach, combining TBM and FEM.[24] For a very recent review, see Ref. [28].

In the present article, we want now to draw attention to the fact, that symmetry analysis of all the bands can be performed alternatively within each of the models—either FEM or TBM (for the latter at the price of extending the basis of atomic orbitals). We compare the predictions (and the predictive power) of the models.

To understand the symmetry classification of the bands, one should remember that the group of wave vector \( \mathbf{k} \) at the \( \Gamma \) point is \( D_{6h} \); at the \( K \) point – \( D_{3h} \); at the point \( M = D_{3h} \). The group of wave vector \( \mathbf{k} \) at each of the lines constituting triangle \( \Gamma – K – M \) is \( C_{2v} \).[29,30] Representations of the groups can be found in the book by Landau and Lifshitz.[31] One of rotations \( U_2 \) for the \( D_{6h} \) group is about the direction \( \Gamma – K \). Rotation \( C_2 \) for the \( D_{3h} \) group is

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about the normal to graphene plane, rotation $C^3$—about the $\Gamma - M$ line. Reflection $\sigma_v$ for the $C_{2v}$ groups is relative to the plane of graphene.

2. (Nearly) Free Electron Model

For the sake of the symmetry analysis, we present the wave functions of all the bands in the factorized form

$$\psi_k(x, y, z) = f_k(z)\varphi_k(x, y),$$

(1)

where $\varphi_k(x, y)$ are linear combinations of appropriate plane waves, and the functions $f(z)$ are determined by the boundary conditions $\lim_{z \to \pm \infty} f_k(z) = 0$. For the $\sigma$ band $f(z)$ is an even function, and for the $\pi$ band—an odd one. Analysis of the representations of the groups realized by the plane waves is presented in our previous publications.$^{[23,24]}$ Notice that the model can equally well incorporate both the TBM bands, localized in graphene, and the FEM bands, having long vacuum tails. The distinction between the two kinds of bands will be reflected in difference between the corresponding functions $f(z)$.

The model potential which would correspond to our choice of the wave functions for the FEM is the sum of two potentials: $x, y$ independent and $z$-dependent strong potential $V_1(z)$ which localizes the electron states near the graphene plane, and weak potentials $V_2(x, y, z)$ which have graphene lattice symmetry in the $x, y$ plane. Probably, to consider the existence of carbon ion cores, it would be more correct to consider $\psi$ (and $\varphi$) as a kind of orthogonalized plane wave, and $V_2(x, y, z)$ as pseudo potentials. If we compare the two lowest $\sigma$ bands with the two lowest $\pi$ ones on Figure 1, the idea to treat the same way both classes of bands looks quite natural.

Extended reciprocal lattice for the honeycomb lattice, we will use, is presented in Figure 2.

Wave functions $\varphi$ of the lowest energy states inside the Brillouin zone (BZ) are just plane waves, at the boundaries of the zone—combinations of two plane waves, and at the band vertexes—of three plane waves.$^{[26]}$ Weak lattice potential should lead to small splitting within a doublet or triplet. Figure 1, with its the lowest singlet at the $\Gamma$ point, lowest doublet at the $K - M$ line and lowest triplet at the $K$ point, certainly speaks in favor of the applicability of the approach.

More specifically, a single point (or line) in the reduced scheme corresponds to infinitesimal number of points (or lines) in the extended scheme. Thus to a single point $\Gamma$ in the reduced scheme, in the extended scheme there correspond the $\{\Gamma, \Gamma_1, \ldots, \Gamma_6\}$, etc., to the $K$ point—the points $\{K, K_4, K_3\}$, $\{K_4, K_6, K_5\}$, etc., to the $M$ point—the points $\{M, M_4\}$, $\{M_4, M_5\}$, $\{M_5, M_6\}$, etc. To a single line $K_M$ in the reduced scheme, in the extended scheme there correspond the lines $\{K - M, K_2 - M_2\}$, $\{K_1 - M_1, K_4 - M_4\}$, $\{K_5 - M_2, K_6 - M_6\}$, etc.

At the $\Gamma$ point, the plane wave $\varphi_\Gamma(x, y)$ equal identically to 1 realizes representation $A_{1g}$ for even $f(z)$ and representation $A_{2u}$ for odd $f(z)$. At the line $\Gamma - K$, the only basis plane wave $\varphi_\Gamma(x, y)$ realizes representation $A_1$ for even $f(z)$ and representation $B_1$ for odd $f(z)$.

At the $K$ point, $\varphi_K(x, y)$ is a linear combination of three plane waves $e^{ikx}$ with the wave vectors corresponding to the three equivalent vertices of the hexagon $K = \{2\pi, 2\pi\}$, $K_2 = (0, \frac{2\pi}{3})$, $K_4 = (2\pi, 0)$. For even $f(z)$ the functions $f(z) \times \{e^{ik_1x}, e^{ik_2x}, e^{ik_3x}\}$ realize $A_1 + E'$ representations of $D_{3h}$. For odd $f(z)$ the functions realize $A_{2g} + E'$ representations. The $\pi$ triplet can be substantially higher than the $\sigma$ triplet corresponding to the same plane waves due to the difference between the energy of odd and even states in the strong $V(z)$ potential.

To find explicitly splitting of the bands at the $K$ point, we should solve the secular equation, which, considering the symmetry and shifting energy by the diagonal matrix element of the potential, we may write down in the form
where \( V_2 \) is the matrix element of the potential \( V_2(x, y, z) \) between some pair of different states from \( K, K_2, K_3 \). Using Cardano’s formula, we may write down the roots as

\[
E = 2\text{Re} \left( \sqrt[3]{V^3} \right)
\]

where \( \text{Re} \) means real part. From the fact that one of the roots should be doubly degenerate, we come to the conclusion that \( V \) is real. (Of course, this can be obtained in a more direct way, on the basis of potential’s symmetry.) Anyhow, the roots are \( E_{1,2} = -V, \ E_3 = 2V \). We understand that relative positions of the singlet and the doublet depend upon sign of \( V \). If we assume that the matrix element \( V_2 \) is positive, we obtain that in each triplet the doublet should be lower than the singlet.

At the \( M \) point, \( \phi_5(x, y) \) is a linear combination of two plane waves with the wave vectors \( \mathbf{M} = (\pm \frac{2\pi}{a}, 0) \). For even \( f(z) \), the function \( f(z) \times (\text{sum or difference of the exponents}) \) realizes \( A_2 \) and \( B_{2u} \) representations of \( D_{2h} \), respectively. For odd \( f(z) \), the function \( f(z) \times (\text{sum or difference of the exponents}) \) realizes \( B_{1u} \) and \( B_{2g} \) representation of \( D_{2h} \), respectively.

The wave functions of the bands at the \( K \) point, higher than the lowest triplets, are combinations of the plane waves with the wave vectors \( K_4 = (0, \frac{2\pi}{\sqrt{3}a}, \frac{4\pi}{\sqrt{3}a}) \), \( K_5 = (\frac{4\pi}{3a}, -\frac{4\pi}{3a}, -\frac{4\pi}{3a}) \), \( K_6 = (\frac{4\pi}{3a}, -\frac{4\pi}{3a}, -\frac{4\pi}{3a}) \), which realizes representations identical to those realized by the plane waves with the wave vectors \( K, K_2, K_3 \). This explains the second copy of the representations \( A_1 + E \) we observe at the \( K \) point on Figure 1.

The wave functions of the bands at the \( M \) point, higher than the lowest ones, are combinations of two plane waves with the wave vectors \( M_1, 2 = (0, \pm \frac{2\pi}{\sqrt{3}a}) \). For even \( f(z) \), the function \( f(z) \times (\text{sum or difference of the exponents}) \) realizes \( A_2 \) and \( B_{2u} \) representation of \( D_{2h} \), respectively. The bands with these symmetries we see in Figure 1. For odd \( f(z) \), the function \( f(z) \times (\text{sum or difference of the exponents}) \) realizes \( B_{1u} \) and \( B_{2g} \) representation of \( D_{2h} \), respectively.

To describe still higher bands at the \( M \) point, we consider four additional plane waves \( e^{i\mathbf{M} \cdot \mathbf{r}} \), with the wave vectors \( M_3, \ldots, 8 = (\pm \frac{2\pi}{a}, \pm \frac{2\pi}{3a}) \). These four plane waves, multiplied by even function \( f(z) \), realize \( A_2 + B_{1g} + B_{2u} + B_{1u} \) representation of the group \( D_{2h} \).

The wave functions of the bands at the \( \Gamma \) point, with numbers higher than two lowest ones, correspond to combinations of six plane waves with the wave vectors \( \Gamma_1, \ldots, \Gamma_6 \), presented in Figure 2, and corresponding to \( (\pm \frac{2\pi}{a}, \pm \frac{2\pi}{3a}, 0) \). For even \( f(z) \), the functions \( \{ \} \) realize \( A_{1g} + B_{1u} + E_{2g} + E_{1u} \) representations of the group \( D_{2h} \). To find explicitly splitting of the bands at the \( \Gamma \) point, we should diagonalize the Hamiltonian, which in the representation \( \Gamma_1, \ldots, \Gamma_6 \) is a circulant \( 6 \times 6 \) matrix with the matrix elements

\[
\hat{H} = \begin{pmatrix}
0 & V_2^{(a)} & V_2^{(b)} & V_2^{(c)} & V_2^{(a)} & V_2^{(a)} \\
V_2^{(a)} & 0 & V_2^{(a)} & V_2^{(b)} & V_2^{(c)} & V_2^{(b)} \\
V_2^{(b)} & V_2^{(a)} & 0 & V_2^{(a)} & V_2^{(c)} & V_2^{(c)} \\
V_2^{(c)} & V_2^{(b)} & V_2^{(a)} & 0 & V_2^{(a)} & V_2^{(b)} \\
V_2^{(a)} & V_2^{(c)} & V_2^{(c)} & V_2^{(a)} & 0 & V_2^{(a)} \\
V_2^{(a)} & V_2^{(b)} & V_2^{(c)} & V_2^{(b)} & V_2^{(a)} & 0
\end{pmatrix}
\]

(4)

Note that due to the symmetry of the problem, there are only three different matrix element of \( V_{1}(x, y, z) \): \( V_{\Gamma_1, \Gamma_2} \equiv V_2^{(a)}, V_{\Gamma_1, \Gamma_2} \equiv V_2^{(b)}, \) and \( V_{\Gamma_1, \Gamma_2} \equiv V_2^{(c)} \) (we again shifted energy by the diagonal matrix element of the potential). The eigenvalues of the matrix (4) are

\[
E_1 = V_2^{(a)} r_1 + V_2^{(b)} r_1^2 + V_2^{(c)} r_1^3 + V_2^{(b)} r_1^4 + V_2^{(a)} r_1^5
\]

(5)

where \( r_1 \) is one of the distinct solutions of \( r^6 = 1 \). After simple algebra, we obtain

\[
E_1 = 2V_2^{(a)} + 2V_2^{(b)} + V_2^{(c)} E_{1,2} = V_2^{(a)} - V_2^{(b)} - V_2^{(c)} E_{4,5}
\]

\[
- V_2^{(a)} - V_2^{(b)} + V_2^{(c)} E_6 = -2V_2^{(a)} + 2V_2^{(b)} - V_2^{(c)}
\]

(6)

Considering only \( \sigma \) bands, we may say that the eigenfunction corresponding to \( E_1 \) realizes \( A_{1g} \) representation, the eigenfunctions corresponding to \( E_{2,3} \) realize \( E_{1u} \) representation, the eigenfunctions corresponding to \( E_{3,4} \) realize \( E_{2g} \) representation, and the eigenfunction corresponding to \( E_6 \) realizes \( B_{1u} \) representation of the group \( D_{2h} \).

If we assume that the largest, by absolute value, matrix elements of the potential \( V(x, y, z) \) are between the states, with the opposite wave vectors, and negative, we obtain that the three lowest bands are even with respect to rotations by an angle \( \pi \) about the \( z \) axis, perpendicular to the graphene plane, and the three others are odd. That is sextuplet is divided into two triplets: the lower one—\( A_{1g} + E_{2g} \) and the higher one—\( B_{1u} + E_{1u} \).

On the line \( K \rightarrow M \) in the reduced scheme, the lowest doublet would corresponds to two plane waves with the wave vectors on the lines \( K \rightarrow M \) and \( K_2 \rightarrow M_2 \). For even \( f(z) \), the function \( f(z) \times (\text{sum of the exponents}) \) realizes \( A_1 \) representations, and the function \( f(z) \times (\text{difference of the exponents}) \) realizes \( B_1 \) representation of \( C_{2v} \). For odd \( f(z) \), the function \( f(z) \times (\text{sum of the exponents}) \) realizes \( B_2 \) representation, and the function \( f(z) \times (\text{difference of the exponents}) \) realizes \( A_2 \) representation of the group.

The third band corresponds to the single plane waves with the wave vectors on the lines \( K_3 \rightarrow M_1 \) and the fourth band corresponds to the single plane waves with the wave vectors on the lines \( K_4 \rightarrow M_4 \). Both realize representation \( A_1 \).

Then comes doublet corresponding to the plane waves with the wave vectors on the line \( K_5 \rightarrow M_7 \) and \( K_6 \rightarrow M_8 \). From the point of symmetry it should be identical to the first doublet.

### 3. Tight-Binding Model

In the frame of the TBM, we look for the solution of the Schrödinger equation as a linear combination of the functions
\[ \psi_{j\mathbf{k}} = \sum_{\mathbf{R}_j} e^{i\mathbf{R}_j \cdot \mathbf{r}} \psi_j(\mathbf{r} - \mathbf{R}_j) \quad (7) \]

where \( \psi_{j\mathbf{k}} \) are atomic orbitals, \( j = A, B \) labels the sub-lattices, and \( \mathbf{R}_j \) is the radius vector of an atom in the sublattice \( j \). (Notice that we assume only symmetry of the basis functions with respect to rotations and reflections; the question how these functions are related to the atomic functions of the isolated atom is irrelevant.)

A symmetry transformation of the functions \( \psi_{j\mathbf{k}} \) is a direct product of two transformations: the transformation of the sub-lattice functions \( \phi^\mathbf{A}_k \), where

\[ \phi^\mathbf{A}_k = \sum_{\mathbf{R}_j} e^{i\mathbf{R}_j \cdot \mathbf{r}} \]

and the transformation of the orbitals \( \psi_j \). Thus the representations realized by the functions (7) will be the direct product of two representations. One should pay attention that the wave vector \( \mathbf{k} \) in Equation (7) and (8) is reduced to the first BZ, whereas the wave vector in Equation (1) was considered as belonging to the infinite plane (extended zone scheme).

We will start from summing up the results of the symmetry analysis in the framework of the TBM obtained in our previous publications, when the basis included only four atomic orbitals: \( [s, p] \). \cite{22-24} The \( \sigma \) bands are constructed from the \( [2s, 2p_{z\sigma}] \) orbitals, and the \( \pi \) bands are constructed from the \( [p_{\pi}] \) orbitals. At the \( \Gamma \) point, the representations realized by the \( \sigma \) bands are \( A_{1g} + B_{1u} \) (constructed from the \( [s] \) orbitals) and \( E_{1u} + E_{2g} \) (constructed from the \( [p_{\pi}] \) orbitals); the representations realized by the \( \pi \) bands are \( A_{2u} + B_{1g} \). At the \( \Gamma \) point, the representations realized by the \( \sigma \) bands are \( A_{1g} + A_{1g} \) (constructed from the \( [s, p_{\pi}] \) orbitals) and \( E' \) (constructed from the \( [s, p_{\pi}] \) orbitals); the representation realized by the \( \pi \) bands is \( E' \). At the \( \Gamma \) point, the representations realized by the \( \sigma \) bands are \( A_{2g} + B_{1u} \) (constructed from the \( [s] \) orbitals, same representations constructed from the \( [p_{\pi}] \) orbitals, and \( B_{1g} + B_{1u} \) (constructed from the \( [p_{\pi}] \) orbitals); the representations realized by the \( \pi \) bands are \( B_{1u} + B_{2g} \).

Just by counting the number of bands on Figure 1, we realize that the basis of atomic orbitals should be expanded to describe additional bands. Actually, the necessity to extend the basis for accurate description of the occupied bands, comparable to the result of calculations based on plane waves is well known (traditionally one chooses two sets of \( s, p \) and one set of \( d \) atom-centered basis functions based on the atomic orbitals. However, this choice yields a wrong description of the first unoccupied bands, which start about 3.25 eV above the Fermi level and are parabolic around the BZ center, \( E_{\mathbf{k}} \). \cite{22-24} These bands have long expansion into the vacuum, and are strongly influenced by the image-potential tail \cite{34} with even and odd mirror symmetry in the graphene plane. Moreover, they can be easily influenced by applied electric field, \cite{35,35a} and adsorbate deposition, \cite{36-38} or transformed upon variation of the graphene sheet shape. \cite{39} Notice that the first two unoccupied states are important for, e.g., the description of interlayer states, reactivity, intercalation, \cite{40,41} and tunneling into graphene, where the inelastic phonon scattering plays a dominant role. \cite{42,43} To overcome this defect, there was presented an interesting idea to add long-range orbitals to the minimalistic \( [2s, 2p] \) basis. \cite{44} Notice that the main dynamical effect defining the long tail bands proposed by Papior et al. is precisely the image potential experienced by an electron due to its image charge in the graphene sheet. \cite{13,45-46}

Our article is mostly devoted to FEM, and in the spirit of our emphasis of simple models, we decided, while considering the TBM for comparison, just to add to the minimalistic basis atomic orbitals one by one, to understand which minimal additions are necessary to describe the symmetry of all calculated bands. Analysis of the TBM with the aforementioned long-range orbitals will be the subject of our next publication.

The first choice is clear—\( |3\sigma \rangle \) atomic orbital, to describe redundant \( \sigma \) band, and \( |3p_{\pi} \rangle \) atomic orbital, to describe redundant \( \pi \) band. As far as the symmetry is concerned, the orbitals give copies of the bands constructed from \( |2s \rangle \) and \( |2p_{\pi} \rangle \) atomic orbitals. The fact, that the symmetry of the two lowest unoccupied bands at the \( \Gamma \) point is identical to the symmetry of the two lowest occupied ones, speaks in favor of such choice.

However, there is a problem with the unoccupied \( z \) band at the \( K \) point. The \( |3p_{\pi} \rangle \) atomic orbitals, like \( |2p_{\pi} \rangle \) orbitals, give doubly degenerate band at the point. To solve the problem, we have to introduce \( |3d \rangle \) orbitals. In fact, expanding the \( D^2 \) representation of the rotations group, the orbitals realize, with respect to irreducible representations of the group \( D_{3h} \), \cite{31} we obtain

\[ D^2 = A_1' + E' + E'' \]

We can choose the bases of the representations respectively as

\[ |d_{z^2} \rangle, |d_{x^2−y^2} \rangle, |d_{xy} \rangle, |d_{xz} \rangle, |d_{yz} \rangle \]

The \( \pi \) band should be constructed from the last two orbitals. The functions \( \phi^\mathbf{A}_k \) realize \( E' \) representation of the group \( D_{3h} \). Thus \( \pi \) bands at the \( K \) point realize the following representations

\[ E' \times E' = A_{2v} + A_{1v} + E'' \]

Thus the calculated \( A_{2v} \) band is accounted for.

4. Comparison Between the Band Calculations and the Predictions of the Models

The symmetry of each band can be obtained from inspection of the wave function describing the band (at a given value of wave vector) obtained as the result of band calculations. Such analysis was performed in our previous publication for all bands apart from four highest bands at the \( M \) point. \cite{34} In the present publication, we fill this void. In Figure 3–8, we present the results of the calculations of the density and wave functions of the bands with numbers from the six to the eight (counting from below) at the \( M \) point. Inspection of the \( z \)-dependence of the density shows that these are \( \sigma \) bands. The wave functions of the \( \sigma \) bands are plotted at the plane \( z = 0 \). For the \( \pi \) bands, the wave function is identically equal to zero at the \( z = 0 \) plane, so we plotted the wave function at the plane \( z = 1 \) au.

For the seventh band, the wave function is equal to zero along the \( y \)-axis, which corresponds to the representation \( B_{1u} \). (Because the wave function is antisymmetric with respect to reflection, it should be equal to zero at the axis of reflection.) The wave
functions of the sixth and eighth band are different from zero everywhere at the plane, which is consistent with the representation $A_g$.

In Figure 9 and 10, we present the results of the calculations of the density of the ninth and tenth bands. The wave function is identically equal to zero at the $z = 0$ plane, so it is $\pi$ band. To find
the symmetry of these bands, we plot in Figure 11 and 12 their wave functions at the plane \( z = 1 \text{ au} \). The wave function of the ninth band is different from zero everywhere at the plane, which is consistent with the representation \( B_{1u} \). For the tenth band, the
Let us start our analysis from \( \sigma \) bands. At the \( \Gamma \) point, the TBM with the \( |2s,2p_{x,y}\rangle \) basis gives \( A_{1g} + E_{2g} + B_{1u} + E_{1u} \) bands. The position of the three last bands relative to the three first ones can be understood recalling the distinction between binding and antibinding orbitals. Addition to the basis of the \( |3s\rangle \) orbital gives additionally \( A_{1g} \) and \( B_{1u} \) bands. We have to assume that the \( B_{1u} \) band is swallowed by the continuum.

The FEM gives at the \( \Gamma \) point the lowest band (\( A_{1g} \)), then the sextuplet \( A_{1g} + E_{2g} + B_{1u} + E_{1u} \). The large energy difference is explained by the fact that the former corresponds to the plane wave with \( k = 0 \), and the latter is constructed from plane waves corresponding to the points \( \Gamma_1, \ldots, \Gamma_6 \). The order of the bands in the sextuplet was discussed in Section 2. The order within the sextuplet observed on Figure 1 can be explained in the framework of the FEM by making plausible assumptions about the lattice (pseudo) potential (see Section 2).

At the \( M \) point, the TBM gives three times \( A_{1g} + B_{3u} \) bands, constructed from \( |2s\rangle, |2p_z\rangle \) and \( |3p_z\rangle \) orbitals respectively, and \( B_{1g} + B_{2u} \) bands, constructed from \( |2p_y\rangle \) orbitals. We have to assume that \( B_{1g} \) and \( B_{2u} \) bands are swallowed by the continuum. The counterintuitive fact is that the band \( B_{1g} \) of the \( |2p_f\rangle \) origin is swallowed, whereas one of the bands of the \( |3p_x\rangle \) origin is not.

The FEM gives at the \( M \) point the lowest doublet (\( A_{1g} + B_{3u} \)), then the higher doublet (\( A_{1g} + B_{2u} \)), and then four still higher bands (\( A_{1g} + B_{2g} + B_{2u} + B_{3u} \)). We have to assume that the bands \( B_{1g} \) and \( B_{2u} \) from the highest quadruplet are swallowed by the continuum. The distances between the multiplets is explained in the FEM by the fact that the lowest doublet is constructed from the plane waves with the wave vectors corresponding to the points \( M \) and \( M_2 \), the second one—\( M_3 \) and \( M_4 \), and the quartet—\( M_5, \ldots, M_8 \). The weak the potential \( V(x,y) \) should lead to weak splitting within each multiplet, and also to weak splitting of the lowest doublet along the whole \( K - M \) line. The weak splitting of the lowest doublet along the whole \( K - M \) line (including the \( M \) point), and the weak splitting of the highest doublet at the \( M \) point is what we see on Figure 1. To be honest, we must notice that strong splitting of the second doublet at the \( M \) point does not agree well with the idea of weak (pseudo) potential \( V(x,y) \).

At the K point, the TBM gives \( A_{1g} + A_{3g} \) bands of \( |2s\rangle \) origin, the bands with the same symmetry of \( |3s\rangle \) origin, and twice \( E' \) bands of of \( |p_{x,y}\rangle \) origin. To be in line with the band calculations, we have to assume that one of the \( |2s\rangle \) bands is swallowed by the continuum, whereas one of the \( |3s\rangle \) bands is not.

The FEM gives at the K point two triplets with identical symmetry (\( A_{1g} + E' \)). Large distance between the triplets is explained by the fact that the first triplet is constructed from the plane waves corresponding to the points \( K, K_2, K_1 \), and the second triplet is constructed from the plane waves corresponding to the points \( K_4, K_3, K_5 \). The assumption of weak \( V(x,y) \) potential leads to prediction that the bands within each triplet will be only weakly split.

The FEM predicts relative positions of the bands at the line \( K - M \): close doublet, higher a single band, still higher the next single band, and then still higher another close doublet. This prediction corresponds to what we see on Figure 1.

Now let us come to \( \pi \) bands. At the \( \Gamma \) point, the TBM gives \( A_{2g} + B_{2g} \) bands constructed from \( |2p_y\rangle \) orbitals and bands with the same symmetry constructed from \( |3p_y\rangle \) orbitals. We have to...
assume that $B_{2g}$ bands is swallowed by the continuum. The FEM gives $A_{2u}$ band and sextuplet $A_{2u} + B_{2g} + E_{1u} + E_{2g}$. We have to assume that $E_{1u}$ and $E_{2g}$ bands are swallowed by the continuum.

At the $M$ point, the TBM gives $B_{1u} + B_{2g}$ bands, constructed from $|2p_x\rangle$ orbitals, and bands with the same symmetry constructed from $|3p_z\rangle$ orbitals. We have to assume that $B_{2g} |3p_z\rangle$ band is swallowed by the continuum. The FEM gives lower doublet $B_{1u} + B_{2g}$ and the second doublet $B_{1u} + B_{3g}$.

The $K$ point is especially problematic to TBM. More specifically, the two bands merging at the Fermi level and realizing representation $E^\prime$ are well described as constructed from the $|2p_z\rangle$ orbitals. The problem is with the higher $\pi$ band. Like it was shown in Section 3, to describe the nondegenerate $\pi$ band at the $K$ point in the framework of the TBM, we need $|3d_{xz}\rangle, |3d_{yz}\rangle$ orbitals. But this choice leaves unanswered the question: Why, $\pi$ band constructed from $|3d\rangle$ orbitals turns out to be lower than that constructed from $|3p_z\rangle$ orbitals? Probably, it can be explained by its hybridization with the scattering resonances predicted\[47\] and observed\[48–50\] recently in graphene. It would be interesting to clarify this point in the future.

On the other hand, the FEM predicts at the $K$ point the triplet $E'' + A_2$, which we clearly see in Figure 1. To be honest, we must notice that strong splitting of between the $A_2$ and $E''$ bands does not agree well with the idea of weak (pseudo) potential $V(x, y)$.

Looking at the bands at the line $K – M$ in Figure 1, one sees similarity between $\pi$ bands and four lowest $\sigma$ ones. The higher $\pi$ bands are swallowed by the continuum. Comparing the two alternative approaches to the symmetry classification of the electron bands, we must say that their predictions are complimentary.

5. Conclusion

We presented the symmetry labeling of all electron bands in graphene obtained by combining numerical band calculations and analytical analysis based on group theory. The emphasis was on the comparison of the predictions of the tight-binding
and (nearly) free electron models. The predictions of these two models were found to be complimentary to each others and agreeing well with the results of numerical band calculations.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

band calculations, graphene, group theory, image states, tight-binding approximation

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