Symmetry classification of energy bands in graphene

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We present the results of the first principle calculations of the energy bands in graphene and their symmetry classification. The valence bands and four lowest conduction bands are classified according to their symmetry at the points $\Gamma$ and $K$. Merging of the bands is interpreted in the framework of the group theory.

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INTRODUCTION

Since graphene was first isolated experimentally \cite{1}, it is in the focus of attention of both theorists and experimentalists. Obviously, our understanding of graphene starts from the knowledge of its energy bands. It is common knowledge that the highest valence ($\pi$) band and the lowest lying conduction ($\pi^*$) band merge at the Fermi level at point $K$ (the corner of the Brillouin zone). The dispersion law of these two bands (obtained in the tight-binding approximation) is also well known since the seminal paper by Wallace \cite{2,3}. The other bands in graphene were also studied previously, although in a much less detailed way than the above mentioned two. In particular, there were performed first principle calculations of the band structure of graphene \cite{4–6,15}.

However, a crucial element in our understanding of the band structure of graphene is still missing, that is the symmetry analysis of the bands. Such analysis (for any periodic crystal Hamiltonian) is most easily performed with the help of elementary group theory \cite{9,10}. The symmetry of crystal is characterized by a point group $R$. Any operation of this group (save the unit transformation) takes a general wavevector $k$ into a distinct one. However, for some special choices of $k$ some of the operations of the crystal symmetry group will take $k$ into itself rather than into a distinct wavevector. These particular operations are called the group of $k$: it is a subgroup of the full symmetry group of the crystal. Lines in the Brillouin zone for which the group of the wavevector contains elements other than the unit element are called symmetry lines. At special points in the Brillouin zone the group of the wavevector may be larger than that on symmetry lines which thread it; these are called symmetry points. We may use a state (states) corresponding to such a special wavevector to generate a representation for the group of $k$ \cite{9,10}. (For an arbitrary wavevector, of course, the group of the wavevector is simply $E$, and the only irreducible representation which may be realized by the states corresponding to such a wavevector is the unit representation.)

We may classify states at a wavevector corresponding to a symmetry point according to the irreducible representation of the group of the wavevector at that point. As the wavevector then moves away from the point, the group of the wavevector becomes smaller and some of the degeneracies will be split. We may determine the irreducible representations into which the original representation will split. Conditions relating the irreducible representations of adjoining points and lines are called compatibility relations and were discussed for the first time in Ref. 11. The early classical papers in the field are reprinted in Ref. 12. The energy band calculations are most commonly carried out along symmetry lines in the Brillouin zone.

SYMMETRY CLASSIFICATION OF THE ENERGY BANDS

We have calculated the band-structure of graphene along the $\Gamma$–$K$–$M$–$\Gamma$ line with the code Elk \cite{13} which implements the full potential linearized plane wave method (FP-LAPW) \cite{14} and the local-density approximation (LDA) exchange-correlation (xc) potential. The k-vector grid was unshifted with 64 × 64 × 1 points with all the symmetries applied. The separation $d$ between the periodically repeated in the perpendicular direction graphene layers was chosen at 200 bohr. With this, the elimination of the inter-layer interaction has been ensured.

The results of the calculation are presented in Fig. \ref{fig:fig1}. The curves marked have been found well converged with respect to the further increase of $d$ and they represent the intrinsic nine lowest-lying valence and conduction bands of graphene. While the overall agreement with previous pseudopotential-based band-structure calculations \cite{4,5,15} is found, one important point warrants a special noting: In Ref. 15, the two low-lying (at $\Gamma$ point) bands were attributed to image-potential states. Since, in contrast to Ref. 15, we do not impose an additional image potential, and since LDA for xc potential does not account for the latter \cite{16}, we conclude that the two bands
in question are ordinary Kohn-Sham LDA energy bands rather than the image-state bands.

The gray background in Fig. 1 represents the continuous spectrum which is extrapolated in the $d \to \infty$ limit from the quasi-continuous one obtained from the calculations. The edge of the continuum is at approximately 4.6 eV at the $\Gamma$ point which gives the vacuum level in this calculation. The bands entering continuum (red lines inside the gray background) turn into resonances, i.e., the corresponding wave-functions leak out from the graphene plane into vacuum. However, this leakage is apparently weak as indicated by the stability of the corresponding bands with respect to the $d$ increase. The studies of the width of the resonances, including those corresponding to the higher bands, will be submitted for publication separately.

![Figure 1: (Color online) Graphene band-structure evaluated with use of the FP-LAPW method. The red-marked lines are well-converged single graphene layer bands, while gray background corresponds to continuous spectrum.](image)

The symmetry points in graphene are point $\Gamma$, the center of the Brillouin zone, points $K$, which are corners of the Brillouin zone, and points $M$, which are the centers of the edges of the Brillouin zone. The symmetry lines are $\Gamma-K$, $\Gamma-M$ and $K-M$ lines. The small group of vector $k$ at point $\Gamma$ is $D_{6h}$. The small group of vector $k$ at point $K$ is $D_{3h}$. The small group of vector $k$ at lines $\Gamma-K$ is $C_{2v}$.

The representation of the group $D_{6h}$ we can obtain noticing that

$$ D_{6h} = D_6 \times C_i. \quad (1) $$

Thus representation, say, $A_1$ of group $D_6$ begets two representations of the group $D_{6h}$: $A_{1g}$ and $A_{1u}$, where the letter $g$ or $u$ means that the representation is even or odd with respect to inversion respectively. The $z$-axis is always chosen perpendicular to the graphene plane. When considering the $\Gamma-K$ line, the $x$ axis is chosen in the direction of the line.

### Table I: Character tables

| $C_{2v}$ | $E$ | $C_{2v}$ | $C_{1v}$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | -1 | -1 |
| $B_2$ | 1 | -1 | -1 |

### Table II: Character tables; $\epsilon = e^{2\pi i/3}$

| $C_{3v}$ | $E$ | $C_{3v}$ | $C_{3v}$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | -1 | -1 |
| $B_1$ | 1 | 1 | -1 |
| $B_2$ | 1 | -1 | 1 |
| $B_3$ | 1 | -1 | -1 |

The compatibility relations of the groups are obtained by taking into account that irreducible representations of the groups $D_{6h}$ and $D_{3h}$ become reducible when we consider them as the representations of the group $C_{2v}$.

The expansion of these representations with respect to irreducible representations of the group $C_{2v}$ can be easily done using the tables of characters (Tables I and II). Equation

$$ a^{(\alpha)} = \frac{1}{g} \sum_G \chi(G)\chi^{(\alpha)}(G) \quad (2) $$

shows how many times a given irreducible representation is contained in a reducible one. All the relevant compatibility relations are presented in Table III.

Now let us come directly to the classification of the energy bands. We assume that the representation realized by the lowest valence band at point $\Gamma$ is the maximum symmetry representation $A_{1g}$. From Table III we immediately come to the conclusion that the band at the line $\Gamma-K$ is characterized by the representation $A_1$. The representation $A_1$ is compatible with one-dimensional representation $A'_1$ and two-dimensional representation $E'$ at the point $K$. But because of degeneracy in this point we come to the conclusion that the lowest valence band realizes the representation $E'$ at point $K$, and the other band, merging with it at point $K$, at line $\Gamma-K$ realizes

### Table III: Compatibility relations for the honeycomb lattice ($\Gamma-K$ line)

| Rep | $D_{6h}$ | $D_{3h}$ | $D_{2h}$ |
|---|---|---|---|
| $A_1$ | $A_{1g}, B_{1u}, E_{1u}, E_{2g}$ | $A'_1, E'$ | $A_2, B_{1g}, B_{2u}, B_{3u}$ |
| $A_2$ | $A_{1u}, B_{1g}, E_{1g}, E_{2u}$ | $A'_1, E'$ | $A_2, B_{1g}, B_{2u}, B_{3u}$ |
| $B_1$ | $A_{2g}, B_{2u}, E_{1u}, E_{2g}$ | $A'_2, E'$ | $A_2, B_{1g}, B_{2u}, B_{3u}$ |
| $B_2$ | $A_{2u}, B_{2g}, E_{1g}, E_{2u}$ | $A'_2, E'$ | $A_2, B_{1g}, B_{2u}, B_{3u}$ |
the representation $B_1$. Hence the third band, merging with the second one at the point $K$, at line $\Gamma-K$ realizes the representation $A_1$. The second and the third band realize at point $\Gamma$ either the representation $E_{1u}$ or $E_{2g}$. Assuming that these two bands produce a bonding (that is symmetric) orbital, we come to the conclusion that they realize at the point $\Gamma$ representation $E_{1u}$. Taking into account that $\sigma_h = IC_2$, we deduce that these valence bands are even with respect to the $\sigma_h$ operation.

Let us come to two bands which merge at the Fermi level at the point $K$. It is common knowledge that they are antisymmetric with respect to reflection in the graphene plane, the latter are characterized by the representations $A_2$ and $B_2$ respectively, and at point $K$ they are characterized by the representation $E''_{1u}$ (antibonding and, hence, antisymmetric orbital). At line $\Gamma-K$ they are characterized by the representations $A_2$ and $B_2$ respectively, and at point $K$ they are characterized by the representation $E''_{1u}$ (antibonding and, hence, antisymmetric orbital). At line $\Gamma-K$ they are characterized by the representations $A_2$ and $B_2$ respectively, and at point $K$ they are characterized by the representation $E''_{1u}$ (antibonding and, hence, antisymmetric orbital).

The most prominent features in the band structure presented in Fig. 1 is the merging of the bands. In the next Section we will interpret merging of the $\pi$ and $\pi^*$ bands at point $K$ and merging of the $\sigma$ bands at point $\Gamma$ using the tight binding model. In the Section after the next one we will interpret merging of the bands at point $K$ using the quasi-free electrons model.

**TIGHT–BINDING HAMILTONIAN + GROUP THEORY**

It is interesting to look at the proposed symmetry classification of the bands in general and at their merging in particular from the point of view of the tight–binding model. In isolated form, carbon has six electrons in the orbital configuration $1s^22s^22p^2$. When arranged in the honeycomb crystal, two electrons remain in the core 1s orbital, and are traditionally ignored in band calculations. The remaining four electrons occupy four valence bands; there are also conduction bands, of which a few lowest ones are of interest. The tight–binding Hamiltonian for $sp$-bonded systems includes four orbitals per atom: $s, p_x, p_y, p_z$. The Hamiltonian being symmetric with respect to reflection in the graphene plane, the bands built from the $p_z$ orbitals decouple from those built from $s, p_x, p_y$ orbitals. The former are odd with respect to reflection in the graphene plane, the latter are even. The classification with respect to reflection in the graphene plane already done, we can talk about $C_{6v}$ and $C_{3v}$ groups instead of $D_{6h}$ and $D_{3h}$.

The $\pi$ bands

The structure of graphene can be seen as a triangular lattice with a basis of two atoms per unit cell, displaced from each other by any one (fixed) vector connecting two sites of different sub-lattices, say $\delta = -a (1,0)$. The general Hamiltonian for the $\pi$ bands is

$$ H = -\left( \sum_a t'(a) e^{i \mathbf{k} \cdot \mathbf{a}} - \sum_a t(a + \delta) e^{-i \mathbf{k} \cdot (\mathbf{a} + \delta)} \right) \sum_a t'(a) e^{i \mathbf{k} \cdot \mathbf{a}} $$

where $\mathbf{a}$ is an arbitrary lattice vector, that is a linear combination of $\mathbf{a}_1 = \frac{a}{2} (3, \sqrt{3})$, $\mathbf{a}_2 = \frac{a}{2} (3, -\sqrt{3})$.

The selection rule for matrix elements gives

$$ \sum_a t(a + \delta) e^{i \mathbf{K} \cdot (\mathbf{a} + \delta)} = 0, $$

where $\mathbf{K}$ is a corner of the Brillouin zone. In fact, we are dealing with the product of two functions: $t(a + \delta)$ realizes the unit representation of the point symmetry group $C_3$ (the full symmetry group of the inter–sublattice hopping is $C_{3v}$, but the restricted symmetry $C_3$ will be enough to prove the cancellation). As far as the function $e^{i \mathbf{K} \cdot (\mathbf{a} + \delta)}$ is concerned, rotation of the lattice by the angle $2\pi/3$, say anticlockwise, is equivalent to rotation of the vector $\mathbf{K}$ in the opposite direction, that is to substitution of the three equivalent corners of the Brillouin zone: $\mathbf{K}_1 \rightarrow \mathbf{K}_2 \rightarrow \mathbf{K}_3 \rightarrow \mathbf{K}_1$, where $\mathbf{K}_1 = \left( \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right)$, $\mathbf{K}_2 = \left( 0, -\frac{4\pi}{3\sqrt{3}a} \right)$ and $\mathbf{K}_3 = \left( -\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right)$. Thus due to the rotation $e^{i \mathbf{K} \cdot (\mathbf{a} + \delta)}$ is multiplied by the factor $e^2$ and realizes $x-iy$ representation of the group $C_3$. Because each of the multipliers in Eq. 1 realizes different irreducible representation of the symmetry group, the matrix element is equal to zero. Simply speaking, at a point $\mathbf{K}$ the sublattices become decoupled, and this explains the degeneracy of the electron states in this point (these points) or, in other words, merging of the two branches of the single Brillouin zone.

On the other hand, generally

$$ \sum_a t'(a) e^{i \mathbf{K} \cdot \mathbf{a}} \neq 0. $$

To understand this statement consider the maximum symmetry group of the intra–lattice hopping: $C_{6v}$. The function $t'(a)$ realizes the $A_1$ representation of the group. Applying Eq. 2 we see that reducible representation of the group $C_{6v}$, realized by the two functions $e^{i \mathbf{K} \cdot \mathbf{a}}$ and $e^{i \mathbf{K} \cdot \mathbf{a}}$ can be decomposed as $A_1 + B_2$. 

\[ \text{(3)} \]

\[ \text{(4)} \]
In addition, the tight-binding model provides us with a simple explanation of why the dispersion law in the vicinity of the merging points is linear, that is why these points are Dirac points. The dispersion law for the Hamiltonian is given by equation

$$F(E, k) = 0,$$  \hspace{1cm} (6)

where

$$F(E, k) = \left| \frac{E + \sum_a t'(a) e^{i k \cdot a}}{\sum_a t'(a) e^{i k \cdot a}} \sum_a t(a + \delta) e^{-i k \cdot (a + \delta)} \right| E + \sum_a t'(a) e^{i k \cdot a}.$$  \hspace{1cm} (7)

In mathematics the Dirac points, we are dealing with, are called conical points of the surface; if the surface is given by equation (3) is given by equation (4) guaranties that the conditions (8) for $k = K$. This explains linearity of the spectrum in the vicinity of the points $K(K')$.

The $\sigma$ bands

We will concentrate upon the dispersion law of the $\sigma$ bands along the $\Gamma-K$ line. Mirror reflection in this line exchanges the graphene sublattices, changes $y$ to $-y$, and does not change the wave vector. It means that the valence bands labeled by $A_1$ are constructed from sub-lattice symmetric combinations of $s$ and $p_x$ orbitals and from sub-lattice antisymmetric combinations of $p_y$ orbitals. The valence band labeled by $B_1$ is constructed from sub-lattice antisymmetric combinations of $s$ and $p_x$ orbitals and from sub-lattice symmetric combinations of $p_y$ orbitals.

We can be more specific speaking about the valence states at points $\Gamma$ and $K$. The states with the symmetry $A_{1g}$ and $A'_{1g}$ are the sub-lattice symmetric combinations of $s$ orbitals. The states with the symmetry $E_{2g}$ and $E'_{2g}$ are the (degenerate) sub-lattice symmetric combinations of $p_x$ and $p_y$ orbitals.

Looking at the conduction bands we realize that the two bands which merge at the point $\Gamma$ with the symmetry $E_{2g}$ are probably of the same nature as the two valence bands which merge at the point $\Gamma$ with the symmetry $E_{1u}$, and the states with the symmetry $E_{2g}$ are the (degenerate) sub-lattice antisymmetric combinations of $p_x$ and $p_y$ orbitals. (In the language of quantum chemistry sub-lattice symmetric and antisymmetric combinations are bonding and antibonding orbitals respectively.)

\[ C_{3v} \begin{array}{ccc} E & 2C_3 & 3\sigma_v \end{array} \]
\[ R \begin{array}{ccc} 3 & 0 & 1 \end{array} \]

Table IV: Characters of natural representation

QUASI–FREE ELECTRONS + GROUP THEORY

If we consider separately $\sigma$ and $\pi$ states we can ignore the third dimension and treat graphene as purely two dimensional. The Hamiltonian of the electrons is

$$H = H_0 + V,$$  \hspace{1cm} (9)

where $H_0$ is the Hamiltonian of the free electrons and $V$ is the crystalline potential. The following reasoning uses the extended Brillouin zone scheme and is the application of group theory to quantum mechanics.

All the eigenstates of the Hamiltonian $H_0$ with the same $|k|$ are degenerate. The potential $V$ having lower symmetry partially (nearly completely) removes the degeneracy. To find the maximum splitting we should find among the continuum of the vectors with the given value of $|k|$ those which realize an irreducible representation of this or that sub–group of the space group of the crystal. For arbitrary value of $|k|$ each state is symmetric only with respect to the sub–group of translations and realizes a one–dimensional representation of this sub–group.

However, the states with the wavevector $K + b$, where $b$ is an arbitrary vector of the inverse lattice (corners of the Brillouin zones) have higher symmetry. They realize a representation (infinite dimensional) of the group which includes in addition to translations the point group $C_{3v}$. We will expand this representation into the irreducible ones in two stages.

First we will divide all the vectors $K + b$ into the sets such, that elements of a given set are connected with each other by the operations of the group $C_{3v}$. Such sets turn out to be triplets. For example, the states with the wavevectors $K_1, K_1 - b_1, K_1 - b_2$, where $b_1 = \frac{2\pi}{3\alpha}(1, \sqrt{3})$ and $b_2 = \frac{2\pi}{3\alpha}(1, -\sqrt{3})$ are the elementary reciprocal-lattice vectors. Another example is the states having wavevectors $K_1 - b_2, K_1 + b_2, K_1 - 2b_1 - b_2$. Still another example is two triplets having the same energy: $K_1 - 2b_1 - 2b, K_1 + b_1, K_1 - b_1 + b_2$ and $K_1 - b_1 - 2b_2, K_1 - 2b_1, K_1 + b_1 + b_2$.

At the second stage, applying Eq.\. 11 we decompose the reducible representation $R$ of the symmetry group $C_{3v}$, generated by a triplet into the irreducible representations. The triplet generates natural representation of the group $C_{3v}$. Applying Eq.\. 11 we obtain

$$R = A_1 + E.$$  \hspace{1cm} (10)

It should be noted that the result does not depend on $V$ being in any sense small.

Recalling the symmetry of the states relative to reflection in the plane of graphene, Eq.\. 11 can be rewritten
as
\[ R = A' + E' \]
for \( \sigma \) states, and as
\[ R = A'' + E'' \]
for \( \pi \) states.

A picture that emerges becomes clear in the extended Brillouin zone scheme, where the Brillouin zones fill the whole plane. Each Brillouin zone being a hexagon, three zones meet at their corners; two of them merge.

To find the dispersion law in the vicinity of the merging point we may consider a reduced Hamiltonian,
\[ H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}, \]
where each element is a linear function of \( k_x, k_y \) (\( k \) is the deviation of the wavevector from the merging point), and we have shifted the energy axis, such that the energy in the merging point is now zero. The dispersion law for the Hamiltonian (13) is given by equation
\[ E = c_i k_i + \sqrt{d_{ij} k_i k_j}, \]
describing two cones, which is a general situation for levels crossing \[23\]. However, in the case considered, we can be more specific about these cones. Because any vector in the \( k_x, k_y \) plane compatible with the symmetry \( C_3v \) is identically equal to zero, and any tensor of rank two compatible with the symmetry is proportional to the unity tensor, the dispersion law is just
\[ E \sim \pm|k|, \]
and the cones are circular, with the axis perpendicular to the \( k_x, k_y \) plane.

The important role played by discrete symmetries in protecting a \( k \)-linear dispersion in graphene was pointed out in Ref. \[24\]. Ref. \[25\] was an important precedent in applying group theory methods to graphene. The appearance of massless Dirac fermions under conditions of hexagonal symmetry was considered in Ref. \[26\]. Group theory was used to derive an invariant expansion of the Hamiltonian for electron states near the K points of the graphene Brillouin zone in Ref. \[27\]. The influence of stress on the bands merging was analyzed in Refs. \[28\], \[29\]. The influence of spin-orbit interactions on the band structure of graphene was studied in Ref. \[30\].

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