Opening of a Gap in Graphene Due to Supercell Potential: Group Theory Point of View

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We analyze in the framework of the space group theory the change of the dispersion law in graphene in the vicinity of the Dirac points due to application of supercell potential with the \(\sqrt{3} \times \sqrt{3}\) space periodicity and the same point symmetry as graphene.

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Graphene is a two-dimensional crystal of carbon atoms, which form a honeycomb lattice with the point symmetry described by the group \(D_{6h}\). The first Brillouin zone (BZ) has a hexagonal form, and the conduction band touches the valence band in six BZ corners which form two non-equivalent triads of BZ corners, \(K\) and \(K'\). One of the routes toward tailoring the electronic properties of graphene is through the adsorption of atoms which form two non-equivalent triads of BZ corners, \(K\) and \(K'\) (these two points can be considered as the stars of the wave vector \(\mathbf{K}\), and designated \(*\mathbf{K}\) together, thus realizing a 4-dimensional representation of the \(D_{6h}\) group. Due to the identity

\[
D_{6h} = D_{3h} \cup C_3 \times D_{3h},
\]

any element of the group \(6h\) \(D\) can be presented as an element \(G\) of the group \(D_{3h}\), or as a product of \(C_2\) and such element. Representation of the point group \(D_{3h}\) \(E''\) realized at the point \(K\) (\(K'\)) defines representation of the space group realized at \(*K\). The matrix representing an element \(G\) is a super-matrix \(2 \times 2\)

\[
D^\ast \mathbf{K},E''(G) = \begin{pmatrix} D^{E''}(G) & 0 \\ 0 & D^{E''}(G) \end{pmatrix},
\]

super-indices 1 and 2 referring to the points \(K\) and \(K'\) respectively. The matrix representing an element \(C_2 \times G\) is

\[
D^\ast \mathbf{K},E''(C_2 \times G) = \begin{pmatrix} 0 & \cdots & \cdots \\ \cdots & 0 \\ \cdots & \cdots & 0 \end{pmatrix}.
\]

We will not need the exact form of the non-diagonal matrix elements in Eq. (3); what we need is the fact that the trace of the matrix \(D^\ast \mathbf{K},E''(C_2 \times G)\) is equal to zero. Naturally, when we consider dispersion in graphene as it is, space group symmetry point of view adds very little in comparison to point group symmetry point of view, because the Hamiltonian, which has the symmetry \(D_{3h}\), is block-diagonal. Now we apply the group theory to analyze what happens at the points \(K\), \(K'\) in graphene with a perfectly commensurate superlattice potential (which appears either because of the substrate or because of the absorbed atoms), which has the same point symmetry \(6h\) \(D\) as graphene. We consider explicitly a \(\sqrt{3} \times \sqrt{3}\) superlattice, known as the Kekule distortion of the honeycomb lattice\textsuperscript{8}. In this case we may consider the Brillouin zone (BZ) of the superlattice as the folding of the original\textsuperscript{9,10,11,12}. The folding leads to the identification of the corners of the original BZ (\(K\) and \(K'\)) with the center \(\Gamma\) of the new BZ. The Hamiltonian is no longer block diagonal and, because the points \(K\) and \(K'\) are now identical, has the full symmetry \(D_{6h}\). We thus observe a paradox situation: due to decrease of the translational symmetry the point symmetry of the Hamiltonian has increased. Because of the symmetry of the Hamiltonian, we need to decompose representation realized by matrices \textsuperscript{2} and \textsuperscript{3} with respect to the irreducible representations of the group \(6h\) \(D\). To obtain the decomposition, it is convenient to use equation

\[
a_\alpha = \frac{1}{g} \sum_G \chi(G) \chi^*_\alpha(G),
\]

which shows how many times a given irreducible representation \(\alpha\) is contained in a reducible one\textsuperscript{13}. In Eq. (4)
The specific form of the operator $\hat{V}(0)$ follows from the symmetry of the base functions realizing representations $E_{1g}$ and $E_{2u}$. By shifting origin of the energy axis these two constants can be chosen as

$$V_1 = -V_2 = V.$$  

Forming and solving the secular equation from these matrix elements, we obtain

$$\epsilon^{(0)}(k) = \pm \sqrt{v^2 k^2 + V^2},$$

the sign plus corresponding to an upper pair of bands, and the sign minus corresponding to a lower pair of bands. To resolve between the branches in each pair we should take into account $k$ corrections to the operator $\hat{V}(0)$. The first order in $k$ corrections is equal to zero because the symmetry group contains the center of inversion. To the second order in $k$ we have $(i,j = 1,2)$

$$\hat{V} = \hat{V}(0) + \hat{V}^{(2)} = \hat{V}(0) + \hat{\gamma}_{ij} k_i k_j,$$

where $\hat{\gamma}_{ij}$ is an Hermitian tensor operator (symmetrical in the suffixes $i$ and $j$). These include the corrections from the terms linear in $k$ in the Hamiltonian in the second-order perturbation theory and the corrections from the terms quadratic in $k$ in the first-order perturbation theory. Notice that $\hat{V}^{(2)}$ is small relative to both $\hat{V}^{(0)}$ and $\hat{H}_{K \cdot P}$ (because we consider the states in the vicinity of the point $\Gamma$). The relations exist between the matrix elements of
the operator because of the requirements of symmetry. As regards their transformation law under the symmetry operations, the wave functions which form the basis of the representation \( E_{2u} \) can be taken in the form

\[
\psi_1 \sim zx, \quad \psi_2 \sim zy,
\]

and the wave functions which form the basis of the representation \( E_{1g} \) can be taken in the form

\[
\psi_1 \sim z, \quad \psi_2 \sim zxy.
\]

From this, we easily conclude that in the first case the matrix elements of the \( \hat{\gamma}_{ij} \) reduce to three independent real constants

\[
<1|\gamma_{xx}|1> = <2|\gamma_{yy}|2> = A
\]
\[
<2|\gamma_{xx}|2> = <1|\gamma_{yy}|1> = B
\]
\[
<1|\gamma_{xy}|2> = <2|\gamma_{xy}|1> = C.
\]

The matrix elements of the operator \( \hat{V}^{(2)} \) are

\[
<1|\hat{V}^{(2)}|1> = <2|\hat{V}^{(2)}|2> = Ak_x^2 + Bk_y^2
\]
\[
<1|\hat{V}^{(2)}|2> = <2|\hat{V}^{(2)}|1> = 2Ck_xk_y.
\]

In the second case the matrix elements of the \( \hat{\gamma}_{ij} \) also reduce to three independent real constants

\[
<1|\gamma_{xx}|1> = <1|\gamma_{yy}|1> = D
\]
\[
<2|\gamma_{xx}|2> = <2|\gamma_{yy}|2> = E
\]
\[
<1|\gamma_{xy}|2> = <1|\gamma_{xy}|1> = F.
\]

The matrix elements of the operator \( \hat{V}^{(2)} \) are

\[
<1|\hat{V}^{(2)}|1> = Dk^2
\]
\[
<2|\hat{V}^{(2)}|2> = Ek^2
\]
\[
<1|\hat{V}^{(2)}|2> = 2Fk_xk_y.
\]

Forming and solving the secular equation from these matrix elements, we obtain for the \( E_{1g} \) branches of the spectrum

\[
\epsilon(k) = \epsilon^{(0)}(k) + Ak_x^2 + Bk_y^2 \pm 2Ck_xk_y.
\]

The formula for the \( E_{2u} \) branches of the spectrum can be obtained similarly.

The folding of the BZ, together with the destruction of previously existing gapless Dirac points, leads to appearance of the new ones. In fact, the new BZ is still a hexagon, and the same symmetry arguments used for graphene can be used to explain appearance of the gapless Dirac points at the corners of the new BZ (\( \tilde{K}, \tilde{K}' \)). However, these new Dirac points are situated deep below or high above the Fermi level and, hence, manifest themselves less than Dirac points of unreconstructed graphene.

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