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 grapenein the vicinity of the (former) Dirac points due to application of supercell potential with the $\sqrt{3} \times \sqrt{3}$ space periodicity and the same point symmetry as graphene.

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 metals[1,2]. Recently, several types of adatoms were used to dope graphene in attempts to tailor properties of graphenebased devices[3–7]. The gap opening in the high symmetry points for the hexagonal lattices due to interaction with the interface was considered in Ref. 8. In Ref. 9 was shown, using ab initio density functional calculations, that the adsorption of an alkali-metal submonolayer on graphene occupying every third hexagon of the honeycomb lattice in a commensurate $(\sqrt{3}\times\sqrt{3})R30°$ arrangement induces an energy gap in the spectrum of graphene. We decided to analyze this opening of the gapin the framework of the group theory. In our previous publications[10–12] we summed up the classification of the energy bands in graphene on the basis of the point group analysis. The only fact from that analysis we need in the present work, is the fact that the little group at the point K and is D_{3h} and the bands π and π^* realize E'' representation of the group. The same can be said about the point K'. This fact by itself means that the bands π and π^* touch each other at the points K and K', and the electron states in the vicinity of these points are described by massless Dirac equation[11].

For the purpose of the present paper we should put the abovementioned fact into the framework of the theory of the space group symmetry[13,14], from which we will need only a few basic ideas. According to the theory of the space group symmetry, the bands π and π^* should be considered at the points K and K' (these two points can be considered as the stars of the wave vector **K**, and designated ∗**K** together, thus realizing a 4-dimensional representation of the D_{6h} group. Due to the identity

$$D_{6h} = D_{3h} \cup C_c \times D_{3h}, \qquad (1)$$

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 2×2

$$D^{*\mathbf{K},E''}(G) = \left(\begin{array}{c|c} D^{E''}(G) & 0 \\ \hline 0 & D^{E''}(G) \end{array} \right), \qquad (2)$$

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

$$D^{*\mathbf{K},E''}(C_2 \times G) = \left(\begin{array}{c|c} 0 & \dots \\ \hline \dots & 0 \end{array} \right). \qquad (3)$$

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 $D^{*\mathbf{K},E''}(C_2 \times G)$ is equal to zero. Naturally, when we consider dispersion in grapheme 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 grapheme 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[9]. In this case we may consider the Brillouine zone (BZ) of the superlattice as the folding of the original[9,15]. The folding leads to the identification of the corners of the original BZ (K and K') with the center $\tilde{\Gamma}$ 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 (2) and (3) with respect to the irreducible representations of the group 6h D .To obtain the decomposition, it is convenient to use equation

$$a_\alpha = \frac{1}{g} \sum_G \chi(G)\chi_\alpha^*(G), \qquad (4)$$

which shows how many times a given irreducible representation α is contained in a reducible one[16].In Eq. (4)

D_6		E	C_2	$2C_3$	$2C_6$	$3U_2$	$3U_2'$
	D_{3h}	E	σ	$2C_3$	$2S_3$	$3U_2$	$3\sigma_v$
A_1	A_1'	1	1	1	1	1	1
A_2	A_2'	1	1	1	1	-1	-1
B_1	A_1''	1	-1	1	-1	1	-1
B_2	A_2''	1	-1	1	-1	-1	1
E_2	E'	2	2	-1	-1	0	0
E_1	E''	2	-2	-1	1	0	0

TABLE I: Character table for irreducible representations of D_6 and D_{3h} point groups

g is the number of elements in the group, $\chi_\alpha(G)$ is the character of an operator G in the irreducible representation α and $\chi(G)$ is the character of the operator G in the representation being decomposed. Actually, even without using Equation (4), just by inspection of the two lowest line of Table 1 we obtain the decomposition

$$R = E_{1g} + E_{2u}. \qquad (5)$$

We see that due to supercell potential two degenerate Dirac points disappear. At the point $\tilde{\Gamma}$ we have two merging bands realizing representation E_{1g} and another two merging bands realizing representation E_{2u}. We may expect that representation E_{1g} , as being more symmetrical, is realized at the top of the valence band, and the representation E_{2u} is realized at the bottom of the conduction band.

To get the form of the energy spectrum of the electrons in the vicinity of the point $\tilde{\Gamma}$ let us consider both the $\mathbf{k} \cdot \mathbf{p}$ term[17] and the supercell potential as a perturbation. The effective Hamoltonian is

$$\hat{H}_{eff} = \hat{V} + \hat{H}_{\mathbf{k} \cdot \mathbf{p}}, \qquad (6)$$

where

$$\hat{H}_{\mathbf{k} \cdot \mathbf{p}} = \begin{pmatrix} 0 & v(k_x - ik_y) & 0 & 0 \\ v(k_x + ik_y) & 0 & 0 & 0 \\ 0 & 0 & 0 & v(k_x + ik_y) \\ 0 & 0 & v(k_x - ik_y) & 0 \end{pmatrix}, \qquad (7)$$

and $\hat{V} = \hat{V}^{(0)}$ reduces to two independent real constants

$$\hat{V}^{(0)} = \begin{pmatrix} 0 & 0 & V_1 & 0 \\ 0 & 0 & 0 & V_2 \\ V_1 & 0 & 0 & 0 \\ 0 & V_2 & 0 & 0 \end{pmatrix} \qquad (8)$$

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

$$V_1 = -V_2 = V. \qquad (9)$$

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

$$\epsilon^{(0)}(k) = \pm\sqrt{v^2 k^2 + V^2}, \qquad (10)$$

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 $\mathbf{k}$ corrections to the operator $\hat{V}^{(0)}$. The first order in $\mathbf{k}$ corrections is equal to zero because the symmetry group contains the center of inversion. To the second order in $\mathbf{k}$ we have $(i, j = 1, 2)$

$$\hat{V} = \hat{V}^{(0)} + \hat{V}^{(2)} = \hat{V}^{(0)} + \hat{\gamma}_{ij} k_i k_j, \qquad (11)$$

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 $\mathbf{k}$ in the Hamiltonian in the second-order perturbation theory and the corrections from the terms quadratic in $\mathbf{k}$ in the first-order perturbation theory[17]. Notice that $\hat{V}^{(2)}$ is small relative to both $\hat{V}^{(0)}$ and $\hat{H}_{\mathbf{k} \cdot \mathbf{p}}$ (because we consider the states in the vicinity of the point $\tilde{\Gamma}$). 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

$$\psi_1 \sim zx, \quad \psi_2 \sim zy, \tag{12}$$

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

$$\psi_1 \sim z, \quad \psi_2 \sim zxy. \tag{13}$$

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

$$
\begin{aligned}
&< 1|\gamma_{xx}|1 >=< 2|\gamma_{yy}|2 >= A \\
&< 2|\gamma_{xx}|2 >=< 1|\gamma_{yy}|1 >= B \\
&< 1|\gamma_{xy}|2 >=< 2|\gamma_{xy}|1 >= C.
\end{aligned}
\tag{14}
$$

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

$$
\begin{aligned}
&< 1|\hat{V}^{(2)}|1 >=< 2|\hat{V}^{(2)}|2 >= Ak_x^2 + Bk_y^2 \\
&< 1|\hat{V}^{(2)}|2 >=< 2|\hat{V}^{(2)}|1 >= 2Ck_xk_y.
\end{aligned}
\tag{15}
$$

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

$$
\begin{aligned}
&< 1|\gamma_{xx}|1 >=< 1|\gamma_{yy}|1 >= D \\
&< 2|\gamma_{xx}|2 >=< 2|\gamma_{yy}|2 >= E \\
&< 1|\gamma_{xx}|2 >=< 1|\gamma_{yy}|2 >= F.
\end{aligned}
\tag{16}
$$

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

$$
\begin{aligned}
< 1|\hat{V}^{(2)}|1 > &= Dk^2 \\
< 2|\hat{V}^{(2)}|2 > &= Ek^2 \\
< 1|\hat{V}^{(2)}|2 > &= 2Fk_xk_y.
\end{aligned}
\tag{17}
$$

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

$$\epsilon(\mathbf{k}) = \epsilon^{(0)}(k) + Ak_x^2 + Bk_y^2 \pm 2Ck_xk_y. \tag{18}$$

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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[1] B. Uchoa, C.-Y. Lin, and A. H. Castro Neto, Phys. Rev. B **77**, 035420 (2008).

[2] G. Giovannetti, P. A. Khomyakov, G. V. Brocks, M. Karpan, J. van den Brink, and P. J. Kelly, Phys. Rev. Lett. **101**, 026803 (2008) .

[3] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, Science **323**, 610 (2009)

[4] J.-H. Chen, C. Jang, S. Adam, M. S. Fuhrer, E. D. Williams, and M. Ishigami, Nature Phys. **4**, 377 (2008).

[5] S. Y. Zhou, D. A. Siegel, A. V. Fedorov, and A. Lanzara, Phys. Rev. Lett. **101**, 086402 (2008).

[6] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, Nature Mat. **6**, 652 (2013).

[7] D. Lamoen and B.N.J. Persson, J. of Chem. Phys. **108**, 3332 (1998)

[8] G. Vasseur, Y. Fagot-Revurat, B. Kierren, M. Sicot and D. Malterre, Symmetry **5**, 344 (2013).

[9] M. Farjam and H. Rafii-Tabar, Phys. Rev. B **79**, 045417 (2009).

[10] E. Kogan and V. U. Nazarov, Phys. Rev. B **85**, 115418 (2012)

[11] E. Kogan, Graphene **2**, N 2, 74 (2013).

[12] E. Kogan, V. U. Nazarov, V. M. Silkin, and M. Kaveh, M. Phys. Rev. B, accepted for Publication.

[13] C. J. Bradley and A. P. Cracknell, *The mathematical Theory of Symmetry in Solids*, (Clarendon Press, Oxford 1972).

[14] M. I. Aroyo, C. Capillas, G. De la Flor, A. K. Kirov, D. Orobengoa, J.. Perez-Mato, and H. Wondraschek, *Representations of Cristallographic Groups*, `http://www.crystallography.fr/mathcryst/ pdf/nancy2010/Aroyo_reps2010.pdf.`

[15] V. V. Cheianov, V. I. Falko, O. Syljyuasen, and B. L. Altshuler, Solid State Commun. **149**, 1499 (2009).

[16] L. D. Landau and E. M. Lifshitz, *Landau and Lifshitz Course of Theoretical Physics: Vol. 3 Quantum Mechanics*, (Pergamon Press, Oxford, 1991).

[17] E. M. Lifshitz and L. P. Pitaevskii, *Landau and Lissitz: Course of Theoretical Physics on Statistical Physics* (Pergamon Press, Oxford, 1991).