

Existence of Mexican-hat dispersion and symmetry group of a layer

Vladimir Damljanović

*Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11000
Belgrade, Serbia*

**E-mail: damlja@ipb.ac.rs*

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Increased interest in physics of graphene and other two-dimensional materials boosted investigations of band structure near nodal points and lines. In contrast, group theoretical explanation of simple bands (that do not touch other bands), is sporadically present in the literature. This paper presents electronic dispersions up to forth order in momentum, near Brillouin zone (BZ) high symmetry points of all eighty layer groups. The method applies to non magnetic materials both with or without spin-orbit coupling. Particular attention is devoted to Mexican-hat dispersion, showing that it can appear only at BZ center of hexagonal layer groups. Presented symmetry adapted Taylor expansion of bands can be used to fit ab-initio or experimental band structures, or for analytical calculation of crystal properties. The results presented here might serve also as a guiding tool for design of new two-dimensional materials.
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1 Introduction

Discovery of electric field effect in atomically thin graphene increased investigations on two-dimensional (2D) materials. When placed in a vertical magnetic field topological properties of bands become physically measurable. In that sense, most attention is devoted to various type of band crossings, many of which are imposed by symmetry laws [1, 2].

On the other hand, simple bands (SB), *i.e.* parts of band structure that do not contain nodal points or lines, also lead to fascinating physics. Two dimensional materials having Mexican-hat dispersion (MHD) are predicted to be multiferroic due to presence of van Hove singularity of the $1/\sqrt{E}$ - type [3]. Furthermore, MHD gives that effective mass on two bands extrema changes sign so that originally repulsive electron-electron interaction becomes attractive, giving quasi-bound electron states [4, 5]. In addition, materials with MHD have large figure of merit, which makes them suitable for thermoelectric applications [6, 7]. For these reasons it would be useful if a general prescription on how to search materials with MHD would exist, and group theory is a powerful tool in this respect.

In 2D, no publications deal with exhaustive symmetry treatment of SB, to best of author knowledge, although two of them treat dispersions in the vicinity of nodal points and lines [8, 9]. On the other hand, encyclopedia type papers on dispersions in 3D [10–15] cannot be used easily for 2D in many cases. While it is straightforward task in crystals with axis of order three, four or six, going back from AA stacking to original layer can be complicated in orthorhombic crystals. Fortunately, recent upgrade in C2DB base [16] helps in solving this problem.

In this paper, we have used powerful group-theoretical tools to find dispersions of SB in the vicinity of high-symmetry points (HSPs) in the reciprocal space. We have adapted the Taylor expansion to the underlying symmetry up to polynomial of fourth degree. All HSPs of all eighty layer groups, both without and with spin-orbit coupling (SOC) are covered. The results are applicable to non-magnetic layers where the time-reversal (TRS) alone is symmetry of the system. We have illustrated our results using one-band tight-binding model on a structure having the same symmetry as graphene (which belongs to layer group 80).

2 Method

Let $\mathbf{k}_0$ be a HSP in the BZ. For $\mathbf{k} = \mathbf{k}_0 + \mathbf{q}$ ($|\mathbf{q}|$ is small), the electronic dispersion $E(\mathbf{q})$ has the following properties: $E(\hat{g}\mathbf{q}) = E(\mathbf{q})$ and, if $\mathbf{k}_0$ is time-reversal invariant momentum, $E(-\mathbf{q}) = E(\mathbf{q})$. Here $\hat{g}$ is rotation/improper rotation from the point group of the wave vector $G_0(\mathbf{k}_0)$ in two-dimensional reciprocal space. In that sense, *e.g.* spatial inversion is represented

by $-\hat{\sigma}_0$, while the Pauli matrix $\hat{\sigma}_3$, represents xz -(symmorphic or glide) reflection plane. TRS in the reciprocal space acts as spatial inversion $\hat{i}$, so that the effective little group is $\underline{G}_0(\mathbf{k}_0) + \hat{i}\underline{G}_0(\mathbf{k}_0)$, if $\underline{G}_0(\mathbf{k}_0)$ does not already contain $\hat{i}$. The groups obtained from $\underline{G}_0(\mathbf{k}_0)$ by adding $\hat{i}$ are given in Table 1.

Table 1 Correspondence between group $\underline{G}_0(\mathbf{k}_0)$ and the one with spatial inversion added.

$\underline{G}_0(\mathbf{k}_0)$	$\underline{G}_0(\mathbf{k}_0) \otimes \underline{C}_i$	$\underline{G}_0(\mathbf{k}_0)$	$\underline{G}_0(\mathbf{k}_0) \otimes \underline{C}_i$	$\underline{G}_0(\mathbf{k}_0)$	$\underline{G}_0(\mathbf{k}_0) \otimes \underline{C}_i$
$\underline{C}_1$	$\underline{C}_i$	$\underline{C}_4$	$\underline{C}_{4h}$	$\underline{D}_{2h}$	$\underline{D}_{2h}$
$\underline{C}_s$	$\underline{C}_{2h}$	$\underline{C}_6$	$\underline{C}_{6h}$	$\underline{D}_{4h}$	$\underline{D}_{4h}$
$\underline{C}_2$	$\underline{C}_{2h}$	$\underline{D}_2$	$\underline{D}_{2h}$	$\underline{D}_{6h}$	$\underline{D}_{6h}$
$\underline{C}_3$	$\underline{S}_6$	$\underline{D}_4$	$\underline{D}_{4h}$	$\underline{D}_{2d}$	$\underline{D}_{4h}$
$\underline{D}_3$	$\underline{D}_{3d}$	$\underline{D}_6$	$\underline{D}_{6h}$	$\underline{D}_{3d}$	$\underline{D}_{3d}$
$\underline{C}_{2v}$	$\underline{D}_{2h}$	$\underline{C}_{4v}$	$\underline{D}_{4h}$	$\underline{S}_4$	$\underline{C}_{4h}$
$\underline{C}_{3v}$	$\underline{D}_{3d}$	$\underline{C}_{6v}$	$\underline{D}_{6h}$	$\underline{S}_6$	$\underline{S}_6$
$\underline{C}_{3h}$	$\underline{C}_{6h}$	$\underline{C}_{2h}$	$\underline{C}_{2h}$	$\underline{C}_i$	$\underline{C}_i$
$\underline{D}_{3h}$	$\underline{D}_{6h}$	$\underline{C}_{4h}$	$\underline{C}_{4h}$	$\underline{C}_{6h}$	$\underline{C}_{6h}$

If $E(\mathbf{q})$ is simple band, one can expand $E(\mathbf{q})$ in Taylor series. The coefficients of the expansion (partial derivatives of E) are obtained by Wigner method of group projectors ($\otimes$ denotes the Kronecker product):

$$\hat{P}_n = \frac{1}{|\underline{G}_0(\mathbf{k}_0)|} \sum_{g \in \underline{G}_0(\mathbf{k}_0)} \underbrace{\hat{g} \otimes \dots \otimes \hat{g}}_n.$$

One acts with the projector $\hat{P}_n$ on trial vector of dimension 2^n ($n = 1, 2, 3, \dots$). The trial vector must be general but has to reflect symmetry under permutation of coordinates in partial derivatives. For example trial vector for second order derivatives is $|\text{trial2}\rangle = (\partial^2 E / \partial q_1^2, \partial^2 E / \partial q_1 \partial q_2, \partial^2 E / \partial q_2 \partial q_1, \partial^2 E / \partial q_2^2)^T = (u, v, v, w)^T$. We have applied this method for all HSPs of all eighty layer groups to find invariant Taylor polynomials up to fourth order in q_1, q_2 . The results are shown in the following section. The HSPs of layer groups hosting simple bands are derived by omitting nodal lines and points given in [8, 17].

3 Results

We found in total seven dispersion formulas. For little groups $\underline{C}_6$, $\underline{D}_6$, $\underline{C}_{6v}$, $\underline{C}_{6h}$, $\underline{D}_{6h}$, $\underline{S}_6$ and $\underline{D}_{3d}$ one gets the following dispersion (a, b, c, E_0 are real parameters):

$$E(\mathbf{q}) \approx E_0 + a\mathbf{q}^2 + b\mathbf{q}^4. \quad (1)$$

Groups $\underline{D}_{2d}$, $\underline{C}_{4v}$, $\underline{D}_4$ and $\underline{D}_{4h}$ give:

$$E(\mathbf{q}) \approx E_0 + a\mathbf{q}^2 + b_1(q_1^4 + q_2^4) + b_2q_1^2q_2^2, \quad (2)$$

groups $\underline{C}_4$, $\underline{C}_{4h}$ and $\underline{S}_4$ give:

$$E(\mathbf{q}) \approx E_0 + a\mathbf{q}^2 + b_1(q_1^4 + q_2^4) + b_2q_1^2q_2^2 + b_3(q_1^3q_2 - q_1q_2^3), \quad (3)$$

groups $\underline{D}_2$, $\underline{D}_{2h}$, $\underline{C}_{2v}^z$ and $\underline{C}_{2h}^{\text{horizontal}}$ give:

$$E(\mathbf{q}) \approx E_0 + a_1q_1^2 + a_2q_2^2 + b_1q_1^4 + b_3q_2^4 + b_2q_1^2q_2^2, \quad (4)$$

groups $\underline{C}_i$, $\underline{C}_2^z$ and $\underline{C}_{2h}^z$ give:

$$E(\mathbf{q}) \approx E_0 + \sum_{j,l=1}^2 a_{j,l}q_jq_l + \sum_{j,l,n,m=1}^2 b_{j,l,n,m}q_jq_lq_nq_m, \quad (5)$$

groups $\underline{C}_3$ and $\underline{C}_{3h}$ give:

$$E(\mathbf{q}) \approx E_0 + a\mathbf{q}^2 + c_1(q_1^3 - 3q_1q_2^2) + c_2(q_2^3 - 3q_1^2q_2) + b\mathbf{q}^4, \quad (6)$$

while groups $\underline{D}_3$, $\underline{C}_{3v}$ and $\underline{D}_{3h}$ give:

$$E(\mathbf{q}) \approx E_0 + a\mathbf{q}^2 + c_1(q_1^3 - 3q_1q_2^2) + b\mathbf{q}^4. \quad (7)$$

With these knowledge we obtain dispersions in all layer gray (single and double) groups. The results are shown in Figure 1, for SOC not included and Figure 2, for the case with SOC. The orientation of the basis vectors in the reciprocal space is the following: for all oblique and rectangular groups having fractional translations parallel to one direction, the vector $\mathbf{k}_1$ is orthogonal to that direction.

As an illustration we consider one site tight-binding model belonging to gray single layer group 80. The crystal structure is shown in the Figure 3 (visualization by use of VESTA [18]). The Hamiltonian is one dimensional and the band structure is:

$$E(\mathbf{k}) = E_0 + 2t \{ \cos(\mathbf{k} \cdot \mathbf{a}_1) + \cos(\mathbf{k} \cdot \mathbf{a}_2) + \cos[\mathbf{k} \cdot (\mathbf{a}_1 + \mathbf{a}_2)] \}. \quad (8)$$

Near BZ center we have $\mathbf{k} = 0 + \mathbf{q}$ so that the dispersion is:

$$E_{\Gamma}(\mathbf{q}) \approx E_0 + 6t - \frac{3}{2}ta^2\mathbf{q}^2 + \frac{3}{32}ta^4\mathbf{q}^4. \quad (9)$$

For $t > 0$ ($t < 0$) eq. (9) presents Mexican Hat dispersion (inverted Mexican Hat dispersion).

Around M-point we have $\mathbf{k} = \mathbf{b}_1/2 + \mathbf{q}$ so that:

$$E_M(\mathbf{q}) \approx E_0 - 2t + \frac{1}{2}ta^2(3q_1^2 - q_2^2) - \frac{1}{96}ta^4(9q_1^4 + 18q_1^2q_2^2 - 7q_2^4). \quad (10)$$

Around K-point we have $(\mathbf{k} = (\mathbf{b}_1 + \mathbf{b}_2)/3 + \mathbf{q})$:

$$E_K(\mathbf{q}) \approx E_0 - 3t + \frac{3}{4}ta^2\mathbf{q}^2 - \frac{\sqrt{3}}{8}ta^3(q_1^3 - 3q_1q_2^2) - \frac{3}{64}ta^4\mathbf{q}^4. \quad (11)$$

The equations (9), (10) and (11) are another confirmations of the theory presented here.

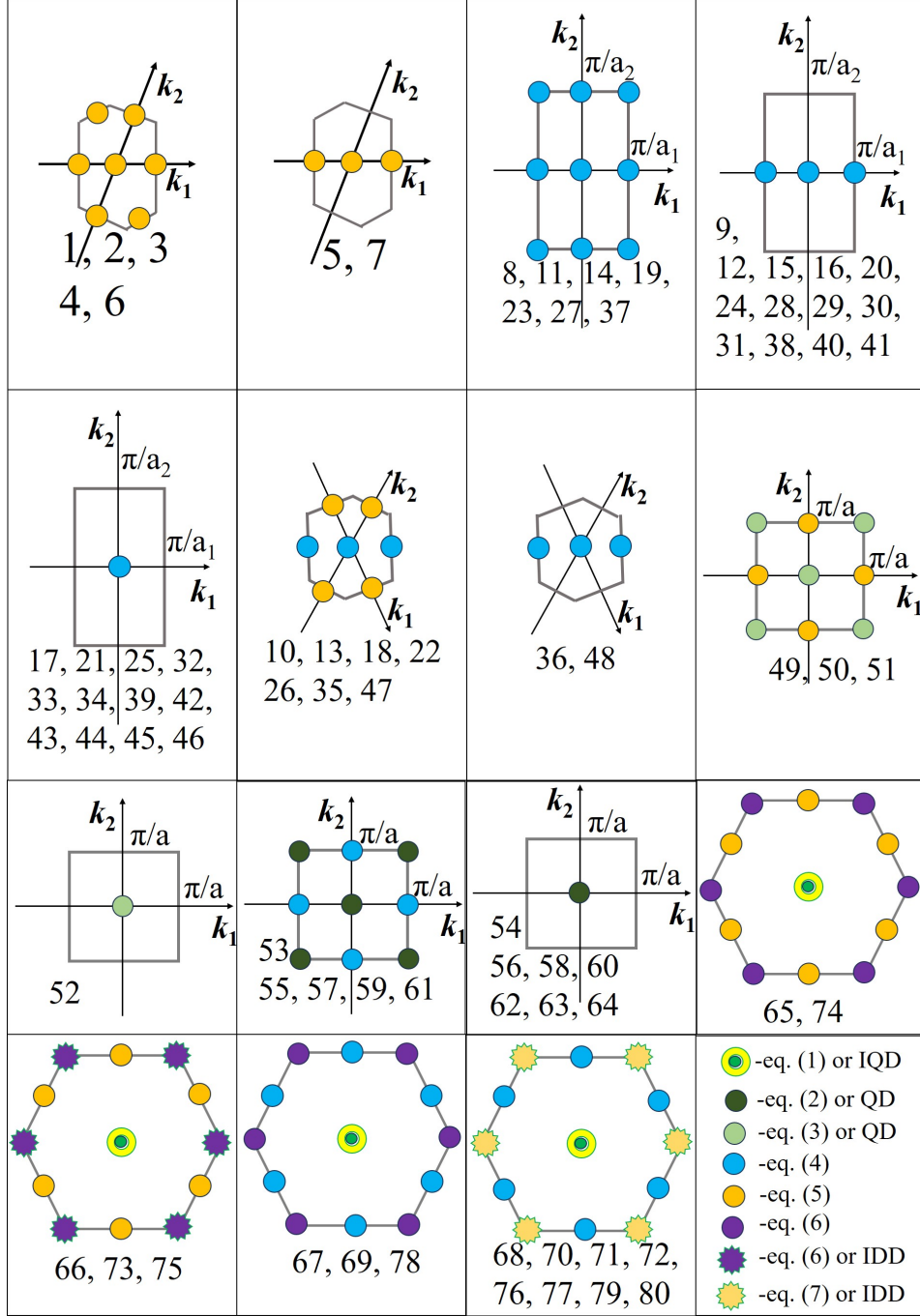


Fig. 1 Positions of simple bands in k -space for all gray layer groups without SOC. IDD - isotropic Dirac dispersion: $E_{1,2,3,4}(\mathbf{q}) = E_0 \pm a|\mathbf{q}|$, QD - quadratic dispersion: $E_{1,2,3,4}(\mathbf{q}) = E_0 + a\mathbf{q}^2 \pm \left\{ [b_3(q_1^2 - q_2^2) + b_1q_1q_2]^2 + [b_4(q_1^2 - q_2^2) + b_2q_1q_2]^2 \right\}^{1/2}$, IQD - isotropic quadratic dispersion: $E_{1,2,3,4}(\mathbf{q}) = E_0 + (a \pm b)\mathbf{q}^2$.

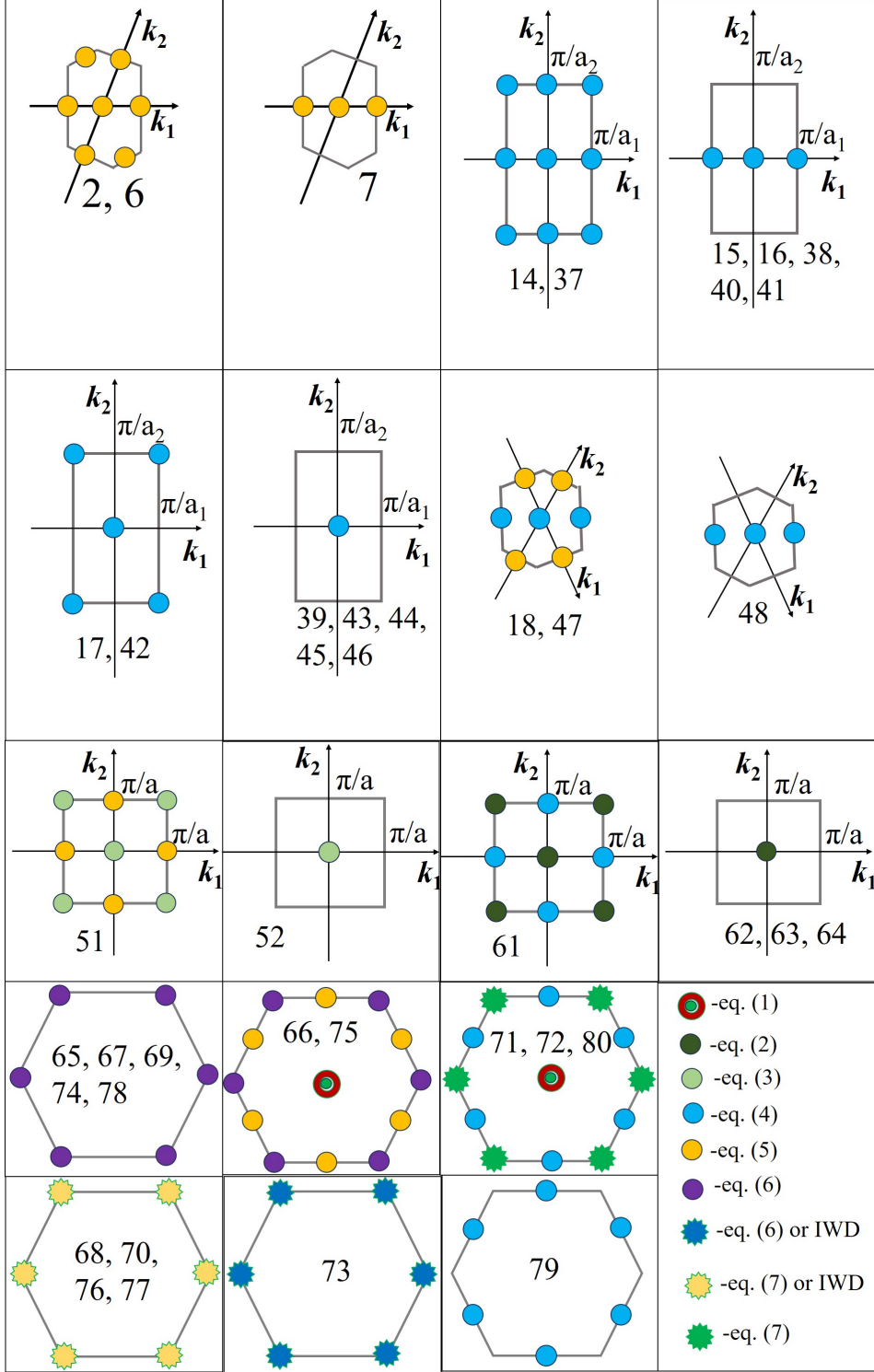


Fig. 2 Positions of simple bands in k -space for all gray layer groups with SOC. Superscript D for double groups is omitted. IWD - isotropic Weyl dispersion: $E_{1,2} = E_0 \pm a|\mathbf{q}|$.

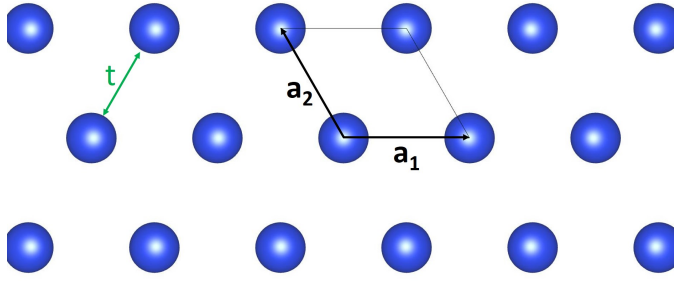


Fig. 3 Lattice structure for the tight-binding model. Black parallelogram denotes primitive unit cell. Hopping parameter t between nearest neighbors is indicated in green color.

4 Discussion

The signs of parameters in formulas (1) - (7) can not be determined using group theory alone, so *e.g.* in formula (1) it is not guaranteed that $ab < 0$, the necessary condition for MHD/inverted MHD. However, in multiband cases, for the lowest lying band, the second order perturbation theory gives $a < 0$, which is the first prerequisite for MHD. In addition, Figures 1 and 2 show that the symmetry forbids appearance of MHD outside of BZ centers of hexagonal groups. Existence of MHD at the Γ -point is experimentally confirmed in hexagonal GaSe grown on GaAs by molecular beam epitaxy [19]. The MHD and high electron mobility are numerically predicted in single layers of γ -SnX (X = O, S, Se, Te), which are also hexagonal materials, by first principles investigation [20]. Similarly, hexagonal lattices of group-VA elements, having symmetry of graphene, are shown analytically to exhibit MHD with magnetic instability and unique thermoelectric properties [21]. First principle calculations show inverted MHD at BZ center in Janus γ -Ge₂XY (X/Y = S, Se, Te) monolayers having symmetry $p3m1$ (layer group 69) [22]. The inverted MHD remains feature in the band structure also when vertical electric field is applied. This effect can be explained having in mind that group $p3m1$ is also a wallpaper group, so it does not contain elements that flip the surface of 2D material. When homogenous electric field is applied perpendicularly to the sample, the symmetry group remains the same.

Formulas other than (1) are also used in the literature for fitting. Penta-graphene belongs to layer group $p\bar{4}2_1m$ (layer group 58), so that its isogonal group is $\underline{D}_{2d}$ which is non-centrosymmetric [23]. After adding spatial inversion the group becomes $\underline{D}_{4h}$, which requires eq. (2) for fitting bands around BZ center. This exact equation is used in [23] under the name tetragonal MHD.

Sometimes it is necessary to go beyond fourth order invariant polynomials. Hexagonal gallium chalcogenides belong to layer group 78 ($p\bar{6}m2$) and the band structure is

fitted with polynomial of order six in [24]. Instead of giving full polynomial of order six, for comparison with the results of [24] here we only calculate the number of real coefficients. Using general formula for symmetrized n -th power of a representation [25], we get: $[\Gamma^{\otimes 6}] = 2A_{1g} + A_{2g} + 2E_{2g}$ in the group $\underline{D}_{6h}$. The number of parameters is equal to two, which is in accordance with formula for fitting in [24]. On the other hand, the formula four in [26], used for fitting of hexagonal GaS band structure around Γ -point, can not be justified by symmetry since it contains two coefficients in second order polynomial instead of one. Deviations from completely isotropic dispersion in the vicinity of BZ center are due to higher order terms in the Taylor expansion of electronic energy, as already suggested by [24].

5 Conclusion

In summary we have determined dispersions of simple bands in the vicinity of special points in the reciprocal space for non-magnetic two-dimensional materials without and with spin-orbit coupling. Further research is necessary to clarify cases when TRS alone is broken. This can be the case of magnetic layers, where extension of spin group concepts from *e.g.* quasi one-dimensional materials [27–29], would be appropriate.

Our results are presented in graphical form, not in encyclopedia manner, which might ensure easier usage. The problem of finding new materials is reduced, in this particular case of simple bands, to problem of synthesis of 2D materials with prescribed symmetry. In that sense, available data bases of numerically stable and real materials might be useful [30–32]. The last point for crystal growers would be the right placement of the Fermi level, which can not be addressed using symmetry alone, although electron filling conditions for symmetry groups of insulating systems can be helpful [33–35].

Acknowledgment

Author acknowledges funding by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia provided by the Institute of Physics Belgrade.

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