Applications of Double Group Theory in 2D Materials

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***Abstract*—Group theory is a fundamental mathematical framework valuable for analyzing the band structures in materials science. The hexagonal structures have unique electronic structures, especially in 2D materials in group-IV, where the system is observed as the topological insulator. Meanwhile, in the case of group-V, it is semiconductors. This paper analyzes group-IV and group-V band structures based on group theory and proposes a method to identify the irreducible representation (IR) in symmorphic systems. It is found that all materials in group-IV are topological insulators. The evaluation of Z_2 invariant *v* in group-V found that the phosphorene and bismuthene cases are $v = 0$ and $v = 1$, respectively, and belong to trivial and topological insulator materials for phosphorene and bismuthene, respectively.**

***Index Terms*—Group Theory, 2D Materials, Group IV, Group V**

I. INTRODUCTION

Group theory is a branch of mathematics that uses powerful tools to describe the symmetry and structure of physical systems. In materials science, the symmetry and transformations of a crystal lattice or a molecular structure reflect the arrangement and organization of atoms or ions in an orderly spatial lattice. Those directly correlate with the materials' optical, electronic, and mechanical properties.

The crystal symmetry have depends on the rotation, translation, reflection and inversion that affect physical properties. The ground state of physical systems is measured by maximum symmetry due to attraction between its components, and thus, the ground state of the crystals should be invariant and respected to all operations of the group. The symmetry corresponds to conserved quantities and allows the classification of quantum mechanical state, including the representation theory and degeneracy or level splittings. The wave functions or operators determine the state; the set of the spectrum of an operator (eigenvalues) is discrete. Those means to measure the quantization phenomenon of the operators in discrete[1].

In the cases of 2D materials, group IV and group V have been attracting scientific interest due to their novelty[2], [3], [4], [5], [6]. Group IV forms hexagonal symmetries, which rotate $2\pi/3$ at the z-axis. The hexagonal structure is found in Group V when the thickness is large[7], [8], [9], [10], [11]. The electronic structure characteristics of group IV have a Dirac cone; meanwhile, group V is semiconductors[2], [3], [12], [13], [14], [15], [16]. At the Dirac cone, the spin-orbit coupling splits the stick bands that affect to induces a topological insulator. The materials containing heavy elements have large SOC and this materials is one of the candidates for topological materials[17], [18]. Furthermore, both groups are observed as topological insulators at different conditions.

To understand the electronic properties of 2D materials group IV and group-V, the band structure is analyzed based on double group theory. Identifying the irreducible representation (IR) of symmetric systems, including SOC, requires analyzing double group theory.

This research uses double group theory to analyze the IR band in order to study the 2D materials of group IV and group V. For consideration, the materials are graphene, silicene, germanene and stanene as group IV and phosphorene and bismuthene as group V, respectively. The proposed method to identify IR in non-SOC and SOC bands is discussed. The Z_2 invariants are evaluated to observe the materials, including topological or trivial insulators.

II. METHOD

The previous studies used the method to identify IR when non-SOC calculations are applied[15], [16], [19], [20], [21], [22]. It also reported that the technique for SOC calculations was used in the cases of symmorphic and non-symmorphic systems[23], [24]. Since the symmetry is hexagonal symmetry, the system belongs to symmorphic system.

First, introduced a method to identify the IR of the wavefunctions, $\psi^{\gamma}_{k,n}$. γ is two component of spinor Bloch wavefunctions. The band index in the ascending sequence of energy is *n*, and the wavevector in the first Brillouin zone is *k*. When the wavefunctions have the *m*-th degeneracy [3,4], we evaluate $Q^{\beta} = \frac{1}{p}\sum_{a=n}^{n+m-1}\sum_{i}\chi^{\beta}(\hat{R}_i)^{*}\left\langle \psi^{a}_{\mathbf{k}} \mid \hat{R}_i \mid \psi^{a}_{\mathbf{k}} \right\rangle$, where *p* is the order of the group and $\chi^{\beta}(\hat{R}_i)$ is the character of the IR β. i runs over the symmetry operations R_i. The wavefunctions belong (do not belong) to the β-th IR when Q^{β} = 1 (Q^{β} = 0). The detailed explanation of the group theory in the non-SOC and SOC systems was observed in the previous papers[20], [23], [24].

The above methods are implemented to identify IR in the First-principles calculation `PHASE/0` code[25]. First, the self-consistent calculation of the electronic structure of the crystal is calculated based on density functional theory using `PHASE/0` code until the ground state occurs in both cases (non-SOC and SOC calculations). Then, calculate the band structure by considering the first Brillouin zone. Analyze the band structure results computed from `PHASE/0` with `Band_Symm` using group theory to identify the IRs to which the state belongs. `TSPACE` package is used to indices the IR

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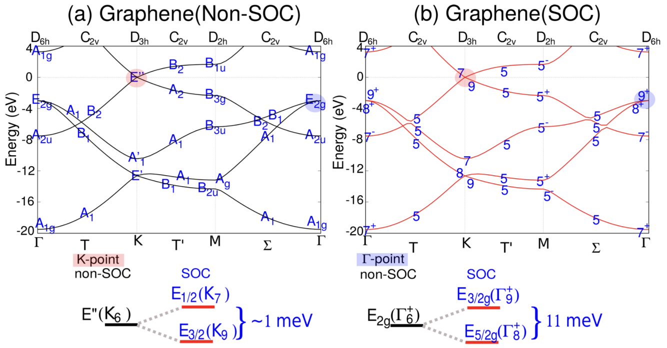

Fig. 1. Band structures of graphene obtained from (a) non-SOC and (b) SOC calculations.

of the *k*-group and the symmetry operations, etc, during the calculation[26].

III. Result and Discussion

Graphene forms flat hexagonal structure and belong to D^1_{6h} (P6/mmm) space group. The calculate lattice constant in the ground state is 2.485Å and this result is close to the previous studies. The bond angle and bond length for non-SOC calculation are 119.2Å and 1.428Å, respectively. SOC bond length and bond angle are 119.6Å and 1.425Å. Those geometry parameters show that the structure are stable in both cases; the calculation vary 0.001Å and 0.01° for bond length and bond angle, respectively. Our results of geometry parameters are close to the previous studies[19], [23].

In the cases of silicene, germanene, and stanene, the structure are stable in buckled structure and those belong to D^3_{3d} (P$\bar{3}$m1). The lattice constant is calculated 3.83Å for silicene, 4.06Å for germanene, and 4.68Å for stanene. The ground state of the bond length is 2.23Å, 2.34Å, and 2.69Å for silicene, germanene, and stanene, respectively. Those geometry structures are close to the previous study[23].

The SOC calculation splits the Dirac cone in the graphene case. Band E" (K_6) level split into the $E_{1/2}$ (K_7) and $E_{3/2}$ (K_9) levels, which the two bands $E_{1/2}$ and $E_{3/2}$ are the product of double group. It is found that $E_{3/2}$ (K_9) level have lower energy than $E_{1/2}$ (K_7) level. It is found that the lower level (K_9) is occupied by two electrons. Graphene becomes an insulator because of the small energy splitting (0.5 meV). On the other hand, the SOC splits the highest occupied E_{2g} (Γ_6^+) level of non-SOC into the $E_{3/2g}$ (Γ_9^+) and $E_{5/2g}$ (Γ_8^+) levels at the Γ point; Γ_9^+ level is higher 11 meV than Γ_8^+ as shown in Fig. 1.

2D materials of Silicene, germanene and stanene have the ground state structure buckled, and the Dirac cone belongs to the two-dimensional E level. The E level splits into two parts. The two bands belong to two different one-dimensional IR, $e_{3/2(1)}$ (K_4) and $e_{3/2(2)}$ (K_5), the time-reversal symmetry pairs these bands. On the other hand, the higher two levels belong to the two-dimensional IR, $E_{1/2}$ (K_6). The non-SOC highest occupied level at the Γ point belong to E_g (Γ_3^+). and the SOC splits the level into two parts. The lower two levels belong to the two-dimensional IR $E_{1/2g}$ (Γ_6^+) and the higher two levels belong to two different one-dimensional IR, $e_{3/2g}$ (1) (Γ_4^+) and $e_{3/2g}$ (2) (Γ_5^+), which are paired.

We find that the above mentioned split due to the SOC becomes large as the atom becomes heavy. The splits at the K (Γ) point are 0.5 meV (11 meV), 2 meV (50 meV), 40 meV (200 meV) and 135 meV (400 meV) for graphene, silicene, germanene and stanene, respectively.

In the case of group-V, phosphorene and bismuthene have hexagonal structure with buckling structure as group-IV silicene, germanene and stanene which is called β structure. This symmetry belong to D^3_{3d} (P$\bar{3}$m1) and it is found that the optimize lattice constant is 4.267Å for bismuthene and 3.271Å for phosphorene.

In phosphorene case, the two bands of non-SOC from top to bottom in order occupied state belong to A_{2u} and E_g, respectively. In SOC case, A_{2u} (Γ_2^-) band become $E_{1/2u}$ (Γ_6^-) band and E_g band split become $e_{3/2g}(1)(2)\Gamma_4^+ + \Gamma_5^+$ and $E_{1/2g}$ (Γ_6^+) bands. $e_{3/2g}(1)(2)\Gamma_4^+ + \Gamma_5^+$ band have higher energy than $E_{1/2g}$ (Γ_6^+) band. The split energy of $e_{3/2g}(1)(2)\Gamma_4^+ + \Gamma_5^+$ and $E_{1/2g}$ (Γ_6^+) bands is small (47 meV).

In Bismuthene case, the non-SOC band is the similar as phosphorene case. Contrary in SOC case, the E_g (Γ_6^+) band have large split energy (800 meV). Thus, the $e_{3/2g}(1)(2)\Gamma_4^+ + \Gamma_5^+$ become unoccupied state and $E_{1/2u}$ (Γ_6^-) moving down to occupied state. Because the inversion symmetry of the energetically order at the Γ-point, the lowest unoccupied belong to $e_{3/2g}(1)(2)\Gamma_4^+ + \Gamma_5^+$ and $E_{1/2u}$ (Γ_6^-) become the highest occupied band.

A. Z_2 invariant

To evaluate the materials have topological insulator properties, it is necessary to calculate the Z_2 invariant v of group-IV and group-V systems having the inversion symmetry[27], [28], [29], [30]:

$$(-1)^v = \prod_j \Delta_j. \tag{1}$$

In Eq. 1, i runs over the time-reversal invariant momenta at the *k*-points, which is in hexagonal FBZ is Γ and three M points. Δ_j is calculated as follows:

$$\Delta_j = \prod_{b=1}^{M_{occ.}/2} \xi_{2b}(\mathbf{k}_j). \tag{2}$$

$\xi_{2b}(\mathbf{k}_i)$ and $M_{occ.}$ are the parity of the $2b$-th band at the point $\mathbf{k}_j$ and the number of the occupied bands, respectively. Group-IV and Group-V system are identified as a topological insulator when the calculated result of $v = 1$.

In the band structure analysis, the Bethe symbols are used. The sign + and - according to parities of even and odd, respectively, whereas in Mulliken symbols of g is even and u is odd. This sign was previously used in the theoretical studies[23], [24].

To identify IR of the bands, the evaluation of the Z_2 invariant v necessary. It confirms that v = 1 for 2D materials group-IV[27], [28], [31]. Since phosphorene is semiconductors with band gap 2.08 eV, the SOC calculations are shown that this system is remain semiconductor due to small split (47 meV) at Γ-point[24]. The calculate *v*=0 consider to trivial insulator. On the contrary, the calculation of Z_2 invariant in the case of bismuthene is $v = 1$. This is due to the large split band which is reversed the lowest unoccupied and highest occupied bands. Therefore, the Z_2 invariant of 1 is because the strong SOC in heavy materials of group-V.

IV. CONCLUSION

To identify IR of the SOC wavefunctions using computers, a method based on double group theory succeeded in implementing it to analyze the band structures of two-dimensional systems group-IV and group-V. In the cases of group-IV, the two-dimensional IR are found in the Dirac cone of planar E" and buckled structures E. The SOC split those bands in planar graphene into $E_{1/2}$ and $E_{3/2}$ and $E_{3/2}$ have lower energy than $E_{1/2}$. The SOC calculation of buckled structure group-IV split the Dirac cone into lower levels of $e_{3/2}(1)$ and $e_{3/2}(2)$ and $E_{1/2}$. The two levels, $e_{3/2}(1)$ and $e_{3/2}(2)$, have the same energy due to time-reversal symmetry. On the other hand, the SOC split the E_g level of group-V into $e_{3/2g}(1)$ and $e_{3/2g}(2)$ and $E_{1/2}$ which is the former has high energy than the latter. The large split energy in bismuthene case is shown to reverse the E_g level and $e_{3/2g}(1)$ and $e_{3/2g}(2)$ become unoccupied state. The evaluation of Z_2 invariant *v* of group-IV is found that all materials are topological insulators. In the case of group-V, the trivial and topological insulators are detected in phosphorene and bismuthene cases, respectively. The topological insulator in group-V is observed that the large SOC affect the reverse band and the calculation of *v=1* as a topological insulator..

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