Analysis of optical transition rules in buckled and puckered bismuthene monolayers based on electron-photon dipole vectors

M J Prakoso¹, A B Cahaya¹, A R T Nugraha² and M A Majidi¹
¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok, Indonesia
²Research Center for Physics, Indonesian Institute of Sciences (LIPI), Tangerang Selatan, Indonesia

E-mail: aziz.majidi@sci.ui.ac.id

Abstract. When a material absorbs incident light, electrons can undergo an optical transition between valence and conduction bands depending on the frequency and polarization of light. In atomic-layered materials such as bismuthene, even a small change in its geometrical structure, e.g. from the buckled to puckered lattices, completely alters its electronic properties and, accordingly, its possible optical transitions. Since the strength and selection rule of optical transitions can be understood by analyzing the electron-photon dipole vectors, we calculate dipole vectors as a function of electronic wave vector between two quantum states in buckled and puckered bismuthene monolayers. We find that each of the bismuthene structures has its own, unique dipole vectors, implying a certain geometrical dependence of the dipole vectors. These materials are expected as a potential candidate for optoelectronics applications. Furthermore, one would consider applying various light polarization when the optical transition rules are well understood.

1. Introduction
In this century, we are living in an information and communication technology age, when we rely on electronic devices. Semiconductors and semimetals are useful to evolve electronic hardware, in which advanced semiconductors and semimetals can be utilized as an information carrier for multi-functional devices [1, 2].

It has been found in recent years that, two-dimensional (2D) materials in the Group IV of the periodic table, such as graphene, silicene, and germanene, have high carrier mobility and are potential for applications in both electronic and optical devices [3]. However, pristine monolayer graphene normally does not open a bandgap [4], which is required to be easily integrated with large scale optoelectronic applications. On the other hand, silicene and germanene are difficult to be synthesized and are unstable without substrate [3]. This situation triggered further research to explore other elemental 2D materials beyond the group IV members. A recent study, for example, showed that group V elements in their 2D forms, such as bismuthene, antimonene, and arsenene, may have
semiconducting properties and that they can be applied for electronics and computing devices \[2,5,6\]. A systematic study for their optical properties is unfortunately still lacking.

In this work, we investigate the selection rule of optical transition based on electron-photon dipole vectors of buckled and puckered bismuthene monolayers, which is part of the group V member, through the calculations of electronic band structure and electron-photon interaction. The electron-photon interaction will be described in terms of dipole vectors. The two different (buckled and puckered) geometrical structures of the bismuthene monolayers are considered to see the effect of the change in the crystal lattices on the electronic and optical properties on how significant it alters the transition rule of bismuthene \[5\].

2. Method
This section focuses on how to proceed with this work. One will first consider the analytical framework, to construct any physical interaction ideas. After that, these ideas are applied in a computational method.

2.1. Analytical Framework
To calculate the dipole vector, we start by defining the electron-photon interaction that emerges when the light incident to the material excites electrons from one band to another band. The electron-photon interaction gives a small perturbation to the system, under the Coulomb transverse gauge, and thus the total Hamiltonian, consisting of single-particle (electron) Hamiltonian \( H_0 \) and interaction Hamiltonian \( H_{\text{int}} \), can be written as

\[
H = \left\{ \frac{\mathbf{p}^2}{2m_e} + U(\mathbf{r}) \right\} + \left\{ \frac{i\hbar e}{m} \mathbf{A} \cdot \nabla \right\} = H_0 + H_{\text{int}},
\]

where \( \mathbf{p} \) is the electron momentum, \( m_e \) is the electron mass, \( U(\mathbf{r}) \) is the potential energy at a position \( \mathbf{r} \), \( \mathbf{A} \) is the vector potential, \( \nabla \) is the del operator, \( e \) is the electron charge, \( \hbar \) is the reduced Planck constant, and \( i \) is the imaginary number. The unperturbed Hamiltonian \( H_0 \) and the perturbed electron-photon interaction Hamiltonian \( H_{\text{int}} \) are, respectively, written as

\[
H_0 = \frac{\mathbf{p}^2}{2m_e} + U(\mathbf{r}), \\
H_{\text{int}} = -\frac{i\hbar e}{m_e} \mathbf{A} \cdot \nabla.
\]

Assuming that the electrons in the material interact with periodic perturbations from the electric field of light, the expression of the electric field at time \( t \) for light with frequency \( \omega \) is \( \mathbf{E} = E_0 \exp(i(\mathbf{k}_{\text{int}} \cdot \mathbf{r} \pm \omega t)) \mathbf{P} \), where \( \mathbf{P} \) is the polarization vector representing the unit vector of the electric field, \( E_0 \) is the magnitude of the field, and \( \mathbf{k}_{\text{int}} \) is the light wave vector. The vector potential \( \mathbf{A} \) will have the same frequency and wavenumber as the electric field. The light intensity can be expressed as \( I_0 = E_0^2 / \mu_0 c \) with \( \omega = c \mathbf{k}_{\text{int}} \) and \( c = 1/\sqrt{\mu_0 \varepsilon_0} \). Considering the Coulomb transverse gauge, where \( \nabla \cdot \mathbf{A} = 0 \), so that the vector potential can be written as

\[
\mathbf{A} = \frac{i}{\omega} \left( \frac{I_0}{c \varepsilon_0} \right) \exp(i(\mathbf{k}_{\text{int}} \cdot \mathbf{r} \pm \omega t)) \mathbf{P}. \tag{4}
\]

Under the dipole approximation, spatial variations of the electric field are neglected in the vicinity of the electron when the wavelength of light is much larger than the lattice constant that defines the crystal periodicity, where the wavelength of the polarized light is around 400-800 nm while the atomic
wave functions are less than 1 nm. This means that the vector potential of the polarized light can be left out from the integration. The dipole approximation implies that \( \mathbf{k}_{\text{int}} \cdot \mathbf{r} \ll 1 \) and thus the electron-photon interaction matrix element \( M_{if} \) for the optical transition from an initial state \( i \) to a final state \( f \) with an electron wave vector \( \mathbf{k} \) can be written as

\[
M_{if}(\mathbf{k}) = \langle f | H_{\text{int}} | i \rangle = -\frac{\hbar e}{m_e \omega} \sqrt{\frac{1}{c \varepsilon_0}} \exp\left(i(\omega_c - \omega \nu) t\right) \mathbf{P} \cdot \langle f | \mathbf{\nabla} | i \rangle
\]

\[
= -\frac{\hbar e}{m_e \omega} \sqrt{\frac{1}{c \varepsilon_0}} \exp\left(i(\omega_c - \omega \nu) t\right) \mathbf{P} \cdot \mathbf{D}_{if}.
\]

By defining \( \mathbf{D}_{if} \) as the dipole vector based on Eq. (5),

\[
\mathbf{D}_{if} \equiv \langle f | \mathbf{\nabla} | i \rangle.
\]

Then, by using the quantum states related to \( k \)-space, the dipole vector is more generally written as \( \mathbf{D}(\mathbf{k}_i, \mathbf{k}_f) \), where \( \mathbf{k}_i \) and \( \mathbf{k}_f \) represent the initial and final \( k \)-points according to the given wave functions. Therefore,

\[
\mathbf{D}(\mathbf{k}) \equiv \langle \psi^p(\mathbf{k}_i) | \mathbf{\nabla} | \psi^C(\mathbf{k}_f) \rangle.
\]

Besides that, we also calculate the oscillator strength as a function of the final wave vectors, the expression of the oscillator strength \( m_{if} \) is [7]

\[
m_{if} = \frac{m_e}{h^2} (E_f - E_i) \sum_{i,f} |\mathbf{D}(\mathbf{k}_i, \mathbf{k}_f)|^2.
\]

where \( E_i \) (\( E_f \)) is the initial (final) state energy. The dipole vectors are generally complex, while the oscillator strength is proportional to the absolute square of dipole vectors. Therefore, this quantity shows how light absorption can occur for a given optical transition.

2.2. Computational Method

From the dipole vector formula, in Eq. (7), it is clear that we need the information on the electronic band structure of the material to calculate the dipole vector. Hence, we perform the first-principles calculations based on the density functional theory (DFT) to obtain the electronic energy dispersion, density of states (DOS), and wave functions. The DFT numerical calculation is performed using the Quantum ESPRESSO package [8], which is useful to obtain the electronic energy bands and the wave functions of buckled and puckered bismuthene monolayers.

For buckled bismuthene, we adopt the projector augmented wave (KJPAW) pseudopotential including the spin-orbit interaction in the DFT calculation. The exchange-correlation effect is described by the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [9]. The cut-off energy is selected to be 40 Ry and we use a 16×16×1 grid for sampling the \( k \) points to calculate the optical absorption. We adopt a supercell to calculate the electronic band structure of buckled bismuthene in which the lattice parameter is 4.65 Å and the buckling height is 12.20 Å as shown in figure 1(a). The corresponding Brillouin zone is shown in figure 1(b).
Figure 1. Buckled bismuthene geometrical structure visualized using XCrysDen software [10]. (a) Buckled lattice in real space. (b) Corresponding Brillouin zone in reciprocal space showing a path from M, Γ, K, going back to the M point.

For puckered bismuthene, we again adopt the KJPAW pseudopotential in the DFT calculation. The exchange-correlation effect is described by the GGA-PBE functional. The cut-off energy is selected to be 45 Ry and we use a $12 \times 12 \times 1$ grid for sampling the k points. We adopt a supercell to calculate the electronic band structure of the puckered bismuthene in which the lattice constant of the puckered lattice is 4.50 Å. The real space and reciprocal space of the puckered bismuthene monolayer are shown in figures 1(a) and 1(b), respectively.

Figure 2. Puckered bismuthene geometrical structure visualized using XCrysDen software [10]. (a) Puckered lattice in real space. (b) Corresponding Brillouin zone in reciprocal space showing a path from M, X1, Γ, X2, M points.

After we obtained the electronic energy bands and the wave functions, we can use those data to compute the dipole vectors. This calculation can be done by modifying a computer program from Tatsumi et al. [11,12], which was originally intended to calculate Raman intensity. We integrate this program with the output of Quantum ESPRESSO packages to compute the dipole vectors. Finally, we can plot the dipole vector field from the processed data.
3. Result and Discussion
In this section, we show the calculated result based on DFT. We will compare the band structure and dipole vectors of buckled and puckered bismuthene monolayers. Dipole vectors work as a selection rule, which indicates only at a certain \( k \)-points optical transitions are possible. Dipole vectors are also dependent on the materials’ band structure since the band structure corresponds to the collective atomic wave functions when it is projected to the dipole vector operator. Meanwhile, the oscillator strength will describe the possible optical transition at some \( k \)-points. It can also indicate the intensity of optical absorption as a function of \( k \)-space.

3.1 Buckled bismuthene
In buckled bismuthene, putting spin-orbit coupling (SOC) into account, it turns out that the band structure at the \( \Gamma \) point in the Brillouin zone does not have an overlap between the valence and conduction band. In figure 3(a), a direct bandgap emerges at the \( \Gamma \) point. Apart from the band structure, one would also calculate the density of states (DOS) as shown in figure 3(b) because DOS also describes the characteristics of the material, complementary to the band structure calculation. The obtained band structure and DOS proves that buckled bismuthene is a direct-gap semiconductor, consistent with previous studies [5], but with a slight difference in the bandgap value of approximately 0.6 eV, which is acceptable due to numerical issues in every first-principles band structure calculation related to the choice of parameter. A direct-gap allows an electron to shift from the valence band to the conduction band while emitting a photon without changing the crystal momentum, which makes optical transition based on electron-photon dipole vectors possible.

![Figure 3](image-url)

**Figure 3.** (a) Band structure of buckled bismuthene with SOC. (b) Density of states of buckled bismuthene. The vertical dashed line represents the Fermi energy.

In figure 4, the plot shows that the dipole vectors of buckled bismuthene as a function of electronic wave vectors \( \mathbf{k} \). The red and blue arrows represent, respectively, the real and imaginary parts of the dipole vectors. The real and imaginary parts appear to be perpendicular to each other. The phases go accordingly with the reciprocal space of buckled bismuthene, which is comparable with figure 1. In figure 5, it appears that oscillator strength shows that the locations of \( k \) points for the possibly allowed optical transitions are indicated by bright colors. The plot shows that this material has very few bright
(yellow) colors for the allowed transitions. As a result, it is expected that the allowed optical transitions in buckled bismuthene are more localized at certain $k$ points [13, 14].

![Dipole vectors of buckled bismuthene monolayer.](image1)

**Figure 4.** Dipole vectors of buckled bismuthene monolayer.

![Oscillator strength of buckled bismuthene monolayer](image2)

**Figure 5.** Oscillator strength of buckled bismuthene monolayer

### 3.2 Puckered bismuthene

In figure 6(a), the band structure of puckered bismuthene has an overlap between the valence band and the conduction band. The obtained band structure appears as a Weyl fermion semimetal characteristics [6,14,15], where there are no bandgaps. A Weyl fermion semimetal is a semimetal system where Weyl fermion particles can be hosted. In this material, the inversion symmetry of a crystal structure can be broken and can form complex dipole vectors, due to its phase factor in the $k$ space. The DOS plot in figure 6(b), however, shows that the DOS value increases significantly at the Fermi energy. Therefore, puckered bismuthene also has the characteristics of a normal metal.
Figure 6. (a) Band structure of puckered bismuthene without SOC. (b) Density of states of buckled bismuthene. The vertical dashed line represents the Fermi energy.

In Figure 7, the dipole vectors of puckered bismuthene is a function of $k$. The blue and red arrows represent, respectively, the real and imaginary parts of the dipole vectors. The real and imaginary parts again appear to be perpendicular to each other and the phases go accordingly with the geometrical structure of the puckered bismuthene, in real and reciprocal space. In figure 8, the oscillator strength for puckered bismuthene has less dark (black) colors than buckled bismuthene. Henceforth, one could see that it indicates that the optical transitions in this material are allowed at quite a lot of $k$ points than in the buckled bismuthene [14, 15].

Figure 7. Dipole vectors of puckered bismuthene monolayer
4. Conclusion
We have calculated the electronic band structure, density of states, dipole vectors, and oscillator strength of a 2D buckled and puckered bismuthene monolayers by using the first-principles calculation. It appears that buckled bismuthene has a direct bandgap while puckered bismuthene resembles a Weyl fermionic system as well as having a normal metal feature. The dipole vectors and oscillator strength of the electron-photon interaction show that optical transitions are allowed in both buckled and puckered bismuthene at some specific electronic $k$ points when these materials absorb polarized light with a wavelength around 400-800 nm. The allowed $k$ points for optical transitions in puckered bismuthene are more spreading over the Brillouin zone rather than those in buckled bismuthene. These unique characteristics that depend on the geometrical structure of 2D bismuthene may be utilized for the additional degree of freedom as information carriers in the optoelectronic devices, as well as exploiting its dipole vectors and band structures to detect any valley polarization.

Acknowledgments
We acknowledge financial support from the Ministry of Research and Technology of the Republic of Indonesia through PDUPT Research Grant No NKB-217/UN2.RST/HKP.05.00/2020. A.R.T.N. acknowledges Mahameru Grid LIPI for their high-performance computing facilities.

References
[1] Schaibley, John R 2016 Valleytronics in 2D materials Nature Reviews Materials 1(16055). doi:10.1038/natrevmats.2016.55
[2] Zhou T, Zhang J, Jiang H, Žutić I, Yang Z 2018 Giant spin-valley polarization and multiple Hall effect in functionalized bismuth monolayers npj Quantum Materials 3(39) doi:10.1038/s41535-018-0113-4
[3] Roome N J, Carey J D 2014 Beyond Graphene: Stable Elemental Monolayers of Silicene and Germanene ACS Applied Materials & Interfaces 6(10) 7743-7750 doi:10.1021/am501022x
[4] Partoens B and Peeters F M 2006 From Graphene to Graphite: Electronic Structure around K point Physical Review B 74(075404) doi:10.1103/PhysRevB.74.075404
[5] Kecik D, Ozcelik V O, Durgun E and Ciraci S 2019 Structure Dependent Optoelectronic Properties of Monolayer Antimonene, Bismuthene, and their Binary Compound J. Chem.
Phys. 21(7907) doi:10.1039/c8cp07344a

[6] Yang S A 2016 Dirac and Weyl Materials: Fundamental Aspects and Some Spintronics Applications World Scientific 6(2) 1640003 doi:10.1142/s2010324716400038

[7] Chowdhury M T, Saito R and Dresselhaus M S 2012 Polarization dependence of x-ray absorption spectra in graphene Physical Review B 85 (115410) doi:10.1103/PhysRevB.85.115410

[8] Giannozzi P et al 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials J. Phys. Condens. Matter. 21(39)35502 doi:10.1088/0953-8984/21/39/395502

[9] Perdew J P, Burke K, Ernzerhof M 1996 Generalized Gradient Approximation Made Simple Physical Review Letters 77 3865-3868 doi:10.1103/PhysRevLett.77.3865

[10] Kokalj A, Mol A J 1999 Graphics Modelling 17(176-179) Code available from http://www.xcrysden.org/. doi:10.1016/S1093-3263(99)00028-5

[11] Tatsumi, Y., Ghalamkari, K., and Saito, R. 2016. Laser Energy Dependence of Valley Polarization in Transition-Metal Dichalcogenides. Physical Review B. 94(235408). doi:10.1103/PhysRevB.94.235408

[12] Tatsumi Y 2017 Polarization Dependence of Optical Absorption and Raman Spectra for Atomic Layer Materials. Ph.D.’s Thesis.

[13] Ghalamkari K, Tatsumi Y and Saito R 2018 Energy Band Gap Dependences of Valley Polarization of Hexagonal Lattice J. Phys. Soc. Jpn. 87(024710) doi:10.7566/JPSJ.87.024710

[14] Ghalamkari K 2017 Valley polarization in optical absorption of atomic layer materials. Master’s Thesis.

[15] Kowalczyk P J, Brown S A, Maerkl T, Lu Q, Chiu C-K, Liu Y, Bian G 2020 Realization of Symmetry Enforced Two-Dimensional Dirac Fermions in Nonsymmorphic α-Bismuthene ACS Nano 14 1888-1894. doi:10.1021/acsnano.9b08136

[16] Dini, Kevin, et al 2018 Optical valleytronics in gapped graphene arXiv 1807 01228.

[17] Han W, Kawakami R K, Gmitra M, Fabian J 2014 Graphene spintronics Nature nanotechnology. 9(10) 794-807 doi:10.1038/nnano.2014.214