Comment on "Orientation dependence of the optical spectra in graphene at high frequencies"

Huy-Viet Nguyen[1,3] and V. Hung Nguyen[2,3]

[1]*Institute of Research and Development, Duy Tan University, K7/25 Quang Trung, Da Nang, Vietnam*

[2]*Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Chemin des étoiles 8,*
B-1348 Louvain-la-Neuve, Belgium

[3]*Institute of Physics, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam*

Zhang *et al.* [Phys. Rev. B **77**, 241402(R) (2008)] reported a theoretical study of the optical spectra of monolayer graphene employing the Kubo formula within a tight-binding model. Their calculations predicted that at high frequencies the optical conductivity of graphene becomes strongly anisotropic. In particular, at frequencies comparable to the energy separation of the upper and lower bands at the Γ point, the optical conductivity is strongly suppressed if the field polarization is along the zigzag direction whereas it is significantly high for the armchair one. We find that, unfortunately, this result is just a consequence of the incorrect determination of the current operator in k space. Here, we present a standard scheme to obtain this operator correctly. As a result, we show that the optical conductivity of monolayer graphene is indeed isotropic, which is consistent with the results of other (both theoretical and experimental) studies in the literature.

The current operation is key ingredient in the calculation of optical spectra from the Kubo formula. For a periodic system, it is most convenient to evaluate this quantity using the k-space representation of the Hamiltonian and the corresponding Bloch wave functions. For graphene, the use of p_z-orbital tight-binding models has been shown to provide a good description of electronic states for many purposes. However, for monolayer graphene where C atoms are arranged in a honeycomb lattice with the unit cell containing two atoms, there are two tight-binding bases widely used in the literature. Because of this, care must be taken in order to avoid the use of inappropriate forms of certain operators which may lead to erroneous physical predictions as already noted in Ref. [1]. In particular, the momentum operator $\mathbf{p}$ for a periodic system has often been determined by [2]

$$\mathbf{p} = \frac{m_0}{\hbar} \nabla_\mathbf{k} H(\mathbf{k}), \tag{1}$$

where m_0 is the free-electron mass and $\nabla_\mathbf{k} H(\mathbf{k})$ is the gradient of the k-dependence representation of the Hamiltonian. Obviously, the form of $H(\mathbf{k})$ is not unique in that it depends on the tight-binding basis used [1] or even on the choice of unit cell [3]. Hence, one can get different results computing $\mathbf{p}$ from Eq. (1). One way to avoid this issue and to correctly achieve the k-dependence representation of operators is to use their original definitions and then represent them in k space as exemplified by the calculation of the current operator in graphene below.

We start from the standard formula of the current operator within an independent electron approximation,

$$\mathbf{j} = e\mathbf{v} = \frac{e}{m_0}\mathbf{p}, \tag{2}$$

$$\mathbf{p} = \frac{m_0}{i\hbar}[\mathbf{r}, H]. \tag{3}$$

The tight-binding Hamiltonian in the first nearest-neighbor approximation is written as

$$H = -t \sum_{\mathbf{R},\boldsymbol{\delta}} c_\mathbf{R}^\dagger c_{\mathbf{R}+\boldsymbol{\delta}}, \tag{4}$$

where $c_\mathbf{R}^\dagger$ and $c_{\mathbf{R}+\boldsymbol{\delta}}$ are creation and annihilation operators, respectively, for p_z electrons located at site $\mathbf{R}$ and its first nearest-neighbors $\mathbf{R} + \boldsymbol{\delta}$. Then, the current operator is

$$\mathbf{j} = -i\frac{et}{\hbar} \sum_{\mathbf{R},\boldsymbol{\delta}} \boldsymbol{\delta} c_\mathbf{R}^\dagger c_{\mathbf{R}+\boldsymbol{\delta}}. \tag{5}$$

Actually, this expression can also be obtained following another scheme by introducing the vector potential $\mathbf{A}$ in the tight-binding Hamiltonian in Eq. (4). Using the Peierls substitution,

$$t_{ij} \rightarrow t_{ij} e^{-i(e/\hbar)\mathbf{A}\cdot(\mathbf{r}_j - \mathbf{r}_i)}, \tag{6}$$

the current operator is then determined by

$$\mathbf{j} = -\frac{\partial H[\mathbf{A}]}{\partial \mathbf{A}}\bigg|_{\mathbf{A}\rightarrow 0}, \tag{7}$$

which leads to an identical formula as in Eq. (5).

In monolayer graphene with two atoms in its primitive cell, these operators can be rewritten in the following forms:

$$
\begin{aligned}
H &= \sum_{nm} \left(H_{nm} + H_{nm,\pm\mathbf{t}_1} + H_{nm,\pm\mathbf{t}_2} \right), \\
H_{nm} &= -t\left(a_{\mathbf{R}_{nm}}^\dagger b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3} + b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3}^\dagger a_{\mathbf{R}_{nm}} \right), \\
H_{nm,\mathbf{t}_{1,2}} &= -t b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3}^\dagger a_{\mathbf{R}_{nm}+\mathbf{t}_{1,2}}, \\
H_{nm,-\mathbf{t}_{1,2}} &= -t a_{\mathbf{R}_{nm}}^\dagger b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3-\mathbf{t}_{1,2}},
\end{aligned} \tag{8}
$$

and

$$
\begin{aligned}
\mathbf{j} &= \sum_{nm} \left(\mathbf{j}_{nm} + \mathbf{j}_{nm,\pm\mathbf{t}_1} + \mathbf{j}_{nm,\pm\mathbf{t}_2} \right), \\
\mathbf{j}_{nm} &= i\frac{et}{\hbar} \boldsymbol{\delta}_3 \left(a_{\mathbf{R}_{nm}}^\dagger b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3} - b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3}^\dagger a_{\mathbf{R}_{nm}} \right), \\
\mathbf{j}_{nm,\mathbf{t}_{1,2}} &= -i\frac{et}{\hbar} \boldsymbol{\delta}_{1,2} b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3}^\dagger a_{\mathbf{R}_{nm}+\mathbf{t}_{1,2}}, \\
\mathbf{j}_{nm,-\mathbf{t}_{1,2}} &= i\frac{et}{\hbar} \boldsymbol{\delta}_{1,2} a_{\mathbf{R}_{nm}}^\dagger b_{\mathbf{R}_{nm}-\boldsymbol{\delta}_3-\mathbf{t}_{1,2}},
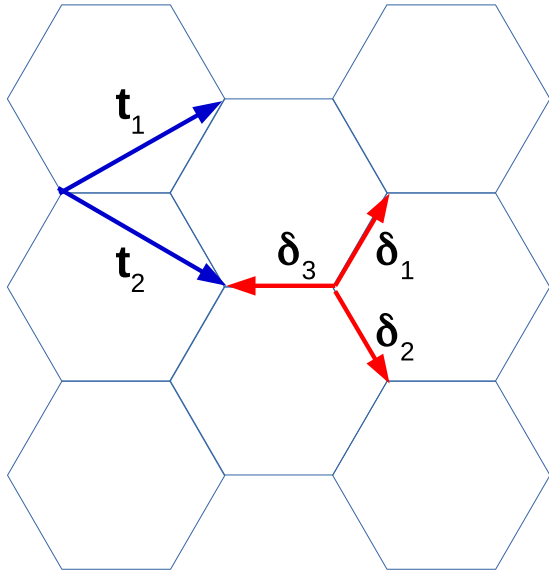\end{aligned} \tag{9}
$$

FIG. 1. Schematic of a graphene lattice with the conventions for vectors $\mathbf{t}_{1,2}$ and $\boldsymbol{\delta}_{1-3}$ used in the text.

where $\mathbf{R}_{nm} = n\mathbf{t}_1 + m\mathbf{t}_2$, $\boldsymbol{\delta}_3 = -(\mathbf{t}_1 + \mathbf{t}_2)/3$, and $\boldsymbol{\delta}_{1,2} = \mathbf{t}_{1,2} + \boldsymbol{\delta}_3$ and $\mathbf{t}_{1,2}$ are two primitive lattice vectors (see Fig. 1). Here we have distinguished two types of creation and annihilation operators: $a^\dagger, a$ for atoms in sublattice A and $b^\dagger, b$ for atoms in sublattice B.

As mentioned in Ref. [1], there are two tight-binding bases most commonly used to describe graphene in the literature. Accordingly, there are two forms of the Fourier transformation for a and b operators,

$$a_{nm} = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_{nm}+\mathbf{r}_a)}, \tag{10}$$

$$b_{nm} = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\mathbf{k}} b_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_{nm}+\mathbf{r}_b)}, \tag{11}$$

and

$$a_{nm} = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\mathbf{k}} \tilde{a}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_{nm}}, \tag{12}$$

$$b_{nm} = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\mathbf{k}} \tilde{b}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_{nm}}, \tag{13}$$

with N_{cell} being the number of periodic (primitive) cells. With these two Fourier transformations, the Hamiltonian (8) is rewritten in two different k-dependent forms, respectively,

$$H = -t \sum_{\mathbf{k}} [h(\mathbf{k}) b_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \text{H.c.}], \tag{14}$$

$$H = -t \sum_{\mathbf{k}} [\tilde{h}(\mathbf{k}) \tilde{b}_{\mathbf{k}}^\dagger \tilde{a}_{\mathbf{k}} + \text{H.c.}], \tag{15}$$

where $h(\mathbf{k}) = e^{i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3}$ and $\tilde{h}(\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{t}_1} + e^{i\mathbf{k}\cdot\mathbf{t}_2} + 1 \equiv e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_3} h(\mathbf{k})$. Similarly, the current operator (9) is

rewritten in two different forms, respectively,

$$\mathbf{j} = -\frac{et}{\hbar} \sum_{\mathbf{k}} [\mathbf{g}(\mathbf{k}) b_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \text{H.c.}], \tag{16}$$

$$\mathbf{j} = -\frac{et}{\hbar} \sum_{\mathbf{k}} [\tilde{\mathbf{g}}(\mathbf{k}) \tilde{b}_{\mathbf{k}}^\dagger \tilde{a}_{\mathbf{k}} + \text{H.c.}], \tag{17}$$

where $\mathbf{g}(\mathbf{k}) = i(\boldsymbol{\delta}_1 e^{i\mathbf{k}\cdot\boldsymbol{\delta}_1} + \boldsymbol{\delta}_2 e^{i\mathbf{k}\cdot\boldsymbol{\delta}_2} + \boldsymbol{\delta}_3 e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3})$ and $\tilde{\mathbf{g}}(\mathbf{k}) = i(\boldsymbol{\delta}_1 e^{i\mathbf{k}\cdot\mathbf{t}_1} + \boldsymbol{\delta}_2 e^{i\mathbf{k}\cdot\mathbf{t}_2} + \boldsymbol{\delta}_3) \equiv e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_3} \mathbf{g}(\mathbf{k})$.

Now, the Hamiltonians in Eqs. (14) and (15) are solved to compute their eigenvalues and eigenfunctions. In both cases, one obtains the same eigenvalue $\varepsilon_s(\mathbf{k}) = st|h(\mathbf{k})| \equiv st|\tilde{h}(\mathbf{k})|$ with $s = \pm 1$ for the conduction/valence bands, respectively. The corresponding eigenfunction has the form $\psi_s(\mathbf{k}) = \frac{1}{\sqrt{2}}\binom{-se^{i\theta_{\mathbf{k}}}}{1}$ where $e^{i\theta_{\mathbf{k}}} = h(\mathbf{k})/|h(\mathbf{k})|$ and $\tilde{h}(\mathbf{k})/|\tilde{h}(\mathbf{k})|$, respectively, for the Hamiltonians (14) and (15). Using these eigenfunctions, one can make a transformation to recast the Hamiltonians (14) and (15) and the current operators (16) and (17) to the following forms:

$$H = \sum_{\mathbf{k},s} \varepsilon_s(\mathbf{k}) c_{\mathbf{k},s}^\dagger c_{\mathbf{k},s}, \tag{18}$$

$$\mathbf{j} = \frac{et}{\hbar} \sum_{\mathbf{k},s} s \frac{\text{Re}\{h^*(\mathbf{k})\mathbf{g}(\mathbf{k})\}}{|h(\mathbf{k})|} c_{\mathbf{k},s}^\dagger c_{\mathbf{k},s}$$

$$+ i \frac{et}{\hbar} \sum_{\mathbf{k},s} s \frac{\text{Im}\{h^*(\mathbf{k})\mathbf{g}(\mathbf{k})\}}{|h(\mathbf{k})|} c_{\mathbf{k},s}^+ c_{\mathbf{k},-s}. \tag{19}$$

Note that, similar to the case of the Hamiltonian operator [Eq. (18)], one obtains the same formula for the current operator [Eq. (19)] regardless of the Fourier transformations used because $h^*(\mathbf{k})\mathbf{g}(\mathbf{k}) \equiv \tilde{h}^*(\mathbf{k})\tilde{\mathbf{g}}(\mathbf{k})$. This is consistent with the remarks in Ref. [1] that, if all operators are represented in the same basis, the expectation value of observable quantities is independent of the tight-binding basis. Since

$$h^*(\mathbf{k})\mathbf{g}(\mathbf{k}) = i\left\{ \boldsymbol{\delta}_1 + \boldsymbol{\delta}_2 + \boldsymbol{\delta}_3 + \boldsymbol{\delta}_1 e^{ik_y r_0} + \boldsymbol{\delta}_2 e^{-ik_y r_0} \right.$$

$$+ \left[\boldsymbol{\delta}_1 \exp\left(i\frac{k_y r_0}{2}\right) + \boldsymbol{\delta}_2 \exp\left(-i\frac{k_y r_0}{2}\right) \right]$$

$$\times \exp\left(i\frac{k_x r_0 \sqrt{3}}{2}\right)$$

$$\left. + 2\boldsymbol{\delta}_3 \cos\left(\frac{k_y r_0}{2}\right) \exp\left(-i\frac{k_x r_0 \sqrt{3}}{2}\right) \right\},$$

after some straightforward manipulations, one ends up with the following expressions for the current operator:

$$j_x = -2ev_F \sum_{\mathbf{k},s} s \frac{\cos\left(\frac{k_y r_0}{2}\right) \sin\left(\frac{k_x r_0 \sqrt{3}}{2}\right)}{|h(\mathbf{k})|} c_{\mathbf{k},s}^\dagger c_{\mathbf{k},s}$$

$$+ i\frac{2ev_F}{3} \sum_{\mathbf{k},s} s \frac{\cos(k_y r_0) - \cos\left(\frac{k_y r_0}{2}\right) \cos\left(\frac{k_x r_0 \sqrt{3}}{2}\right)}{|h(\mathbf{k})|}$$

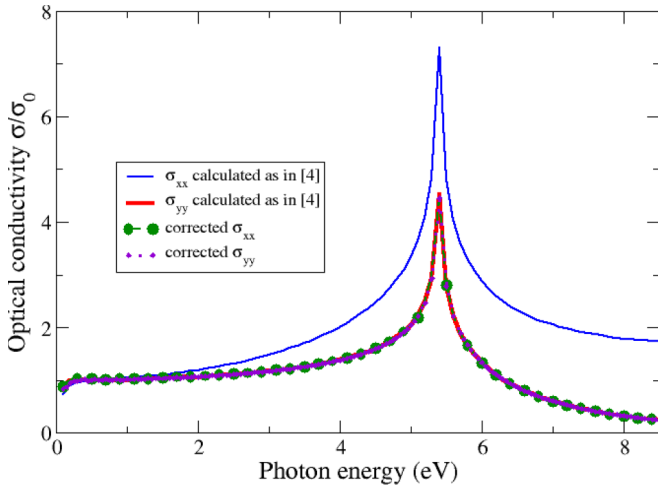$$\times c_{\mathbf{k},s}^\dagger c_{\mathbf{k},-s},$$

FIG. 2. Corrected optical conductivity in comparison with the calculations of Zhang *et al.* in Ref. [4] ($\sigma_0 = e^2/4\hbar$).

$$j_y = -\frac{2ev_F}{\sqrt{3}} \sum_{\mathbf{k},s} s \frac{\sin(k_y r_0) + \sin\left(\frac{k_y r_0}{2}\right)\cos\left(\frac{k_x r_0 \sqrt{3}}{2}\right)}{|h(\mathbf{k})|} c_{\mathbf{k},s}^\dagger c_{\mathbf{k},s}$$

$$- i\frac{2ev_F}{\sqrt{3}} \sum_{\mathbf{k},s} s \frac{\sin\left(\frac{k_y r_0}{2}\right)\sin\left(\frac{k_x r_0 \sqrt{3}}{2}\right)}{|h(\mathbf{k})|} c_{\mathbf{k},s}^\dagger c_{\mathbf{k},-s},$$

where r_0 denotes the C-C bond length in graphene.

Compared to the expressions for current operator presented by Zhang *et al.* in Ref. [4], the j_y component obtained here is identical to theirs, but it is not the case for the j_x component. We note that, even though the j_x and j_y components have different k dependences, the integral over the whole Brillouin zone in the Kubo formula [5,6] gives the same optical conductivities σ_{xx} and σ_{yy} as displayed in Fig. 2, i.e., *the optical spectra of graphene is indeed isotropic*, which is at variance with the anisotropic behavior shown in the calculations by Zhang *et al.* [4]. Additionally, the value of optical conductivity in the low-frequency limit reported in Ref. [4]

is $e^2/2\hbar$, which is twice the well-known value of $\sigma_0 = e^2/4\hbar$ for monolayer graphene [7]. Note that our obtained results are in good agreement with those reported (both theoretically with different methods [5,6,8,9] and experimentally [7]) in the literature. The anisotropy of optical spectra can be achieved only if the symmetry properties of the graphene lattice are broken, e.g., by strain effects as demonstrated in Ref. [6].

In Ref. [4], the authors provided no information on how the current operator was actually calculated. However, one could reproduce their expressions for $j_{x,y}$ when using the formula $j_\mu = \frac{e}{\hbar}\frac{\partial H}{\partial k_\mu}$—indeed used by Zhang *et al.* [4] in other studies [10,11]—with the Hamiltonian in Eq. (1) of Ref. [4] [i.e., Eq. (15) here]. Obviously, j_μ determined in this way is not correct because $\partial \tilde{h}(\mathbf{k})/\partial k_\mu$ is not identical to $\tilde{g}_\mu(\mathbf{k})$. The expression for the j_y component in Ref. [4] is fortuitously correct just because the y component of vectors $\boldsymbol{t}_{1,2}$ are identical to that of vectors $\boldsymbol{\delta}_{1,2}$, respectively, whereas $\delta_{3y} = 0$. Hence, we speculate that the use of the formula $j_\mu = \frac{e}{\hbar}\frac{\partial H}{\partial k_\mu}$ with the Hamiltonian in Eq. (15) is the origin of the erroneous results obtained by Zhang *et al.* [4]. We would like to note additionally that the use of this incorrect determination of the current operator results in the unit-cell dependence of optical matrix elements (see Fig. 3(a) and Ref. [3]). Basically, the calculations using supercells lead to the band folding compared to that of a primitive cell. Using the incorrect formulas of the current operators can allow for unphysical transitions between the folding bands and hence gives the wrong results at high energies [see Fig. 3(a)]. The authors in Ref. [3] tried to use group-theoretic arguments to demonstrate that one would obtain incorrect results if the unit cell chosen does not incorporate the symmetries of the bulk. Physically, these arguments do not sound reasonable to us as any change in the unit cell only leads to a change in the matrix representation of the operators and the calculated results should be, in principle, unchanged if the operators in the k space are correctly determined. This is actually confirmed by the data presented in Fig. 3(b) where our calculations were performed using the current operators determined from the original formula in Eq. (5).
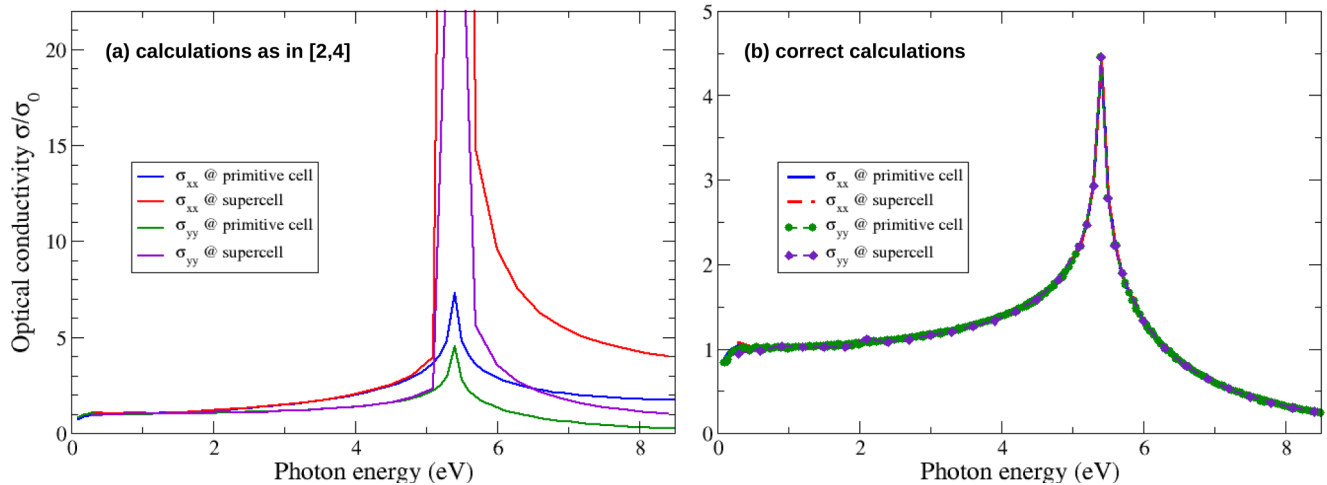

FIG. 3. (a) Incorrect unit-cell dependence of optical conductivity obtained using the scheme as in Refs. [3,4], in comparison with (b) the correct ones obtained using the scheme presented in this Comment ($\sigma_0 = e^2/4\hbar$).

Thus, in order to achieve the correct formula for the current operator in the k space, we recommend that one should perform the Fourier transform with its original formula in real space [i.e., Eq. (5)] or use the formula (7) with Peierls substitution in Eq. (6). In this way, the obtained results should depend neither on the tight-binding basis nor on the unit cell. This is because the use of another tight-binding basis or unit cell only leads to a change in the matrix representation of the operators and hence the expectation value of observable quantities should always be correctly achieved. However, there are some specific quantities determined directly from the Hamiltonian in the k space and the phase of the Bloch wave functions, e.g., the Berry connection and Berry curvature. In such cases, it has been demonstrated in Ref. [12] that only the Fourier transformation in Eqs. (10) and (11) gives the correct results. Similarly, the current operator in Eq. (16) can be also obtained correctly by using the formula $j_\mu = \frac{e}{\hbar} \frac{\partial H}{\partial k_\mu}$ with the Hamiltonian in Eq. (14), i.e., $\partial h(\mathbf{k})/\partial k_\mu$ is indeed identical to $g_\mu(\mathbf{k})$. In such cases, $\frac{e}{\hbar} \frac{\partial H}{\partial \mathbf{k}}$ is indeed identical to $-\frac{\partial H[\mathbf{A}]}{\partial \mathbf{A}}|_{\mathbf{A}\to 0}$.

To conclude, we have shown that the anisotropicity of the optical spectra reported by Zhang *et al.* in Ref. [4] is just a consequence of the incorrect determination of the current operator in the k space. Starting from the original definition of the current operator, we present a scheme to correctly obtain its formula in the k space, regardless of the tight-binding basis as well as the choice of unit cell used in the calculations. Our Comment thus emphasizes a simple but subtle and fundamental remark which will be of useful to researchers working with tight-binding calculations, particularly, in graphene and its derivatives.

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