Comment on “*Ab initio* calculation of the shift photocurrent by Wannier interpolation”

Jae-Mo Lihlm*

Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea

(Dated: June 1, 2021)

In a recent paper, Ibañez-Azpiroz et al. [Phys. Rev. B 97. 245143 (2018)] derive a band-truncation-error-free formula for calculating the generalized derivative of the interband dipole matrix using Wannier interpolation. In practice, the denominators involving intermediate states are regularized by introducing a finite broadening parameter. In this Comment, I show that when a finite broadening parameter is used, a correction term must be added to the generalized derivative to obtain results that are independent of the phase convention for the Bloch sums.

Ibañez-Azpiroz et al. [1] derive a truncation-error-free formula for the Wannier interpolation of the generalized derivative of the interband dipole matrix. This result enables an efficient and accurate calculation of the shift-current response.

In practice, to avoid numerical problems due to near-degenerate states, the energy denominator involving intermediate states is regularized by introducing a broadening parameter \( \eta \) (see Eq. (38) of Ibañez-Azpiroz et al. [1]). Within the Wannier-interpolation scheme, the regularized version of the generalized derivative of the interband dipole matrix element is given from Eqs. (36) and (38) of Ibañez-Azpiroz et al. [1] by

\[
\bar{\tau}^{a; b}_{nm}(\eta) = \bar{\tau}^{a; b}_{nm}(0) + \frac{i}{\omega_{nm}} + \frac{\eta}{\omega_{nm}} \frac{\tau^{a; b}_{nm}}{\omega_{nm}} + i \omega_{nm} \delta_{nm} \bar{\tau}^{a; b}_{nm},
\]

where \( M \) is the number of Wannier functions. Here, \( \bar{\tau}^{a; b}_{nm}(0) \) refers to the case without regularization, which equals to \( \tau^{a; b}_{nm} \) in Eq. (36) of Ibañez-Azpiroz et al. [1]. I use tilde to distinguish the quantity obtained from the Wannier interpolation scheme of Ibañez-Azpiroz et al. [1] from a direct calculation using Kohn-Sham wavefunctions.

In this Comment, I show that when \( \eta \) is nonzero, \( \bar{\tau}^{a; b}_{nm}(\eta) \) defined in Eq. (1), as well as the corresponding shift-current spectrum, depends on the phase convention for the Bloch sums. I derive a correction term that should be added to Eq. (1) to obtain a phase-convention-independent result.

I consider two phase conventions, the tight-binding (TB) convention [Eq. (14) of Ibañez-Azpiroz et al. [1]]

\[
\bar{\tau}^{a; b}_{ij}^{(W, TB)} = \sum_{R} e^{-i k \cdot (R + \tau_{j} - \tau_{i})} \bar{\tau}^{a; b}_{ij}(R),
\]

and the Wannier90 (W90) convention

\[
\bar{\tau}^{a; b}_{ij}^{(W, W90)} = \sum_{R} e^{-i k \cdot (R + \tau_{j})} \bar{\tau}^{a; b}_{ij}(R).
\]

Here, \( \tau_{j} \) is the position of the \( j \)-th atom of the unit cell. The “internal” matrix elements that appear in Eq. (1) such as \( \bar{\tau} \) and \( \bar{\tau} \) depend on the phase convention. In the tight-binding (TB) convention, one finds

\[
\partial^{a} H_{ij}^{(W, TB)} = \sum_{R} e^{i k \cdot (R + \tau_{j} - \tau_{i})} \bar{\tau}^{a; b}_{ij}(R),
\]

and

\[
A_{ij}^{a(W, TB)} = \sum_{R} e^{i k \cdot (R + \tau_{j} - \tau_{i})} \bar{\tau}^{a; b}_{ij}(R).
\]

In the W90 convention, one finds

\[
\partial^{a} H_{ij}^{(W, W90)} = \sum_{R} e^{i k \cdot (R + \tau_{j} - \tau_{i})} \bar{\tau}^{a; b}_{ij}(R),
\]

\[
A_{ij}^{a(W, W90)} = \sum_{R} e^{i k \cdot (R + \tau_{j} - \tau_{i})} \bar{\tau}^{a; b}_{ij}(R).
\]

The unitary matrices that diagonalize the Hamiltonians in the two conventions can be related as

\[
U_{in}^{(TB)} = e^{-i k \cdot \tau_{in}^{(W90)}}.
\]

Comparing Eqs. (6, 7) with Eqs. (4, 5), one can show that the internal matrix elements in the two conventions are related as

\[
\bar{\tau}^{a; b}_{nm}^{(TB)} = \bar{\tau}^{a; b}_{nm}^{(W90)} + i \omega_{nm} \delta_{nm}
\]

and

\[
\bar{\tau}^{a; b}_{nm}^{(TB)} = \bar{\tau}^{a; b}_{nm}^{(W90)} - i \omega_{nm} \delta_{nm}
\]

where

\[
\delta_{nm}^{(TB)} \equiv \sum_{i} U_{in}^{(TB)} \bar{\tau}^{a; b}_{im} U_{in}^{(TB)}.
\]

Thus, if there is an atom that is not at the origin of the unit cell, the two phase conventions give different internal matrix elements. Ibañez-Azpiroz et al. [1] showed that when \( \eta = 0 \), the additional terms involving \( \tau \) cancel out so that the two conventions give identical shift-current spectrum. Here, I show that such cancellation is incomplete when \( \eta \neq 0 \).
First, let us define the generalized derivative with finite broadening $\eta$ based on Bloch wavefunctions as follows:

$$\eta_{nm}(\eta) = \frac{i}{\omega_{nm}} \left\{ \frac{v_{nm}^a A_{nm}^b + v_{nm}^b A_{nm}^a}{\omega_{nm}} - w_{nm}^b \right\} + \sum_{p \neq n,m}^{\infty} \left[ \text{Re} \left( \frac{1}{\omega_{np} + i\eta} \right) v_{np}^a v_{pm}^b - \text{Re} \left( \frac{1}{\omega_{np} + i\eta} \right) v_{np}^b v_{pm}^a \right].$$

(12)

When $\eta = 0$, $\eta_{nm}(\eta)$ reduces to Eq. (12) of Ibañez-Azpiroz et al. [1]. Our goal is to obtain a Wannier interpolation formula for $\eta_{nm}(\eta)$ which holds true at finite $\eta$.

We find

$$\eta_{nm}(\eta) - \eta_{nm}(0) = \frac{i}{\omega_{nm}} \sum_{p \neq n,m}^{\infty} A_{nm,p}^a b(\eta)$$

(13)

where we defined

$$A_{nm,p}^a b(\eta) = \text{Re} \left( \frac{1}{\omega_{pm} + i\eta} - \frac{1}{\omega_{pm}} \right) v_{np}^a v_{pm}^b - \text{Re} \left( \frac{1}{\omega_{np} + i\eta} - \frac{1}{\omega_{np}} \right) v_{np}^b v_{pm}^a.$$

(14)

In principle, Eq. (13) requires a sum over an infinite number of unoccupied bands and thus cannot be computed using Wannier interpolation. However, note that

$$\text{Re} \left( \frac{1}{\omega_{pm} + i\eta} - \frac{1}{\omega_{pm} + i\eta} \right) = \text{Re} \left[ \frac{-i\eta}{\omega_{pm} + i\eta} \right]$$

(15)

is very small as long as $|\omega_{pm}|$ is much larger than $\eta$. Also, when computing the shift-current response, $\eta_{nm}(\eta)$ is computed only for the low-energy states $n$ and $m$ which are a pair of occupied and unoccupied states that can be resonantly excited by an external electric field. Thus, Eq. (13) converges rapidly with the number of states included in the sum. We exploit this rapid convergence to approximate the infinite sum in Eq. (13) by a finite sum over Wannier-interpolated bands

$$\eta_{nm}(\eta) - \eta_{nm}(0) \approx \frac{i}{\omega_{nm}} \sum_{p \neq n,m}^{M} A_{nm,p}^a b(\eta),$$

(16)

where $A_{nm,p}^a b(\eta)$ [Eq. (14)] is calculated using the Wannier interpolation of energy and velocity matrix elements. Later, I demonstrate the validity of this approximation using numerical calculation (see Fig. 3).

Now, let us study the relation between Eq. (1) and Eq. (12). The velocity matrix element can be written as

$$v_{nm}^a = v_{nm}^a + i\omega_{mn} s_{nm}^a.$$

(17)

This expression can be obtained from Eqs. (9, 10), and (23) of Ibañez-Azpiroz et al. [1]. From Eqs. (9, 10), one can easily show that $v_{nm}^a$ does not depend on the phase convention. By using Eqs. (1, 14), we find

$$\frac{i}{\omega_{nm}} \sum_{p \neq n,m}^{M} A_{nm,p}^a b(\eta) = \tilde{\eta}_{nm}(\eta) - \tilde{\eta}_{nm}(0) + \frac{i}{\omega_{nm}} \sum_{p \neq n,m}^{M} \text{Re} \left[ \frac{-i\eta}{\omega_{pm} + i\eta} \right] \left[ v_{np}^a v_{pm}^b \right] - \frac{i}{\omega_{nm}} \sum_{p \neq n,m}^{M} \text{Re} \left[ \frac{-i\eta}{\omega_{np} + i\eta} \right] \left[ v_{np}^b v_{pm}^a \right].$$

(18)
Using Eqs. (16, 18) and \( r_{nm}^{a,b}(0) = r_{nm}^{b,a}(0) \) which is proven in Ibañez-Azpiroz et al. [1], we find

\[
r_{nm}^{a,b}(\eta) \approx \tilde{r}_{nm}^{b,a}(\eta) \frac{1}{\omega_{nm}} \sum_{p \neq n,m} \frac{\eta^2}{\omega_{pm}^2 + \eta^2} \left[ \epsilon_{np}^{a} \psi_{pm}^{b} - (\psi_{np}^{a} + i\omega_{np} \epsilon_{np}^{a}) a_{pm}^{b} \right] \\
+ \frac{1}{\omega_{nm}} \sum_{p \neq n,m} \frac{\eta^2}{\omega_{np}^2 + \eta^2} \left[ \epsilon_{np}^{b} a_{pm}^{a} - \omega_{np}(\psi_{pm}^{a} + i\omega_{pm} a_{pm}^{a}) \right].
\]

(19)

The right-hand side of Eq. (19) is the desired phase-convention-independent Wannier interpolation formula for the generalized derivative of the interband dipole matrix element at finite \( \eta \). This expression is independent of the phase convention. The reason is as follows. Equation (18) is phase-convention independent because \( A^{a,b}_{nm,p}(\eta) \) [Eq. (14)] is defined only in terms of phase-convention independent matrix elements. Also, \( \tilde{r}_{nm}^{a,b}(0) \) is phase-convention independent because it equals \( r_{nm}^{a,b}(0) \) which is defined in terms of Kohn-Sham wavefunctions. Since the right-hand side of Eq. (19) is the sum of Eq. (18) and \( r_{nm}^{a,b}(0) \), it is also independent of the phase convention.

When \( \eta = 0 \), the correction terms in Eq. (19) vanish as expected. When \( \eta \) is nonzero, the correction terms are finite. Also, we find that these correction terms depend on the phase convention used for the Bloch sums. Thus, if this correction is not applied, the calculated \( r_{nm}^{a,b}(\eta) \) matrix elements, as well as the shift-current spectrum, becomes dependent on the phase convention.

Now, I demonstrate these findings with numerical calculations. I implemented the correction formula Eq. (19) in WANNIER90 and calculated the shift-current spectrum of monolayer GeS. For the density functional theory calculation, I used fully relativistic ONCV pseudopotentials [2] taken from the PseudoDojo library (v0.4) [3] and a wavefunction kinetic energy cutoff of 80 Ry. Other computational parameters are the same as in Ibañez-Azpiroz et al. [1] unless otherwise noted.

Figure 1 shows the difference between the shift-current spectrum calculated using the two conventions. Without the correction term, there is a small but nonzero discrepancy between the two spectra. The discrepancy increases with \( \eta \). When the correction term is added, the shift-current spectra calculated using the TB and the W90 conventions perfectly agree for all values of \( \eta \). This result demonstrates the phase-convention independence of Eq. (19).

Figure 2 shows the change in the shift-current spectrum due to the correction term. For \( \eta = 40 \) meV, which is used in Ibañez-Azpiroz et al. [1], the change in the shift-current spectrum due to the correction is below \( 0.3 \mu A/V^2 \). This correction is nonzero but will have little effect on the calculated shift-current spectrum [Fig. 5(a) of Ibañez-Azpiroz et al. [1]] whose magnitude is around \( 50 \mu A/V^2 \).

Finally, I test the validity of approximating the infinite sum over bands in Eq. (16) by a finite sum over Wannier-interpolated bands as Eq. (16). Let us define the following approximant of Eq. (13):

\[
s_{nm,p}^{a,b}(E_{\text{cutoff}}; \eta) = \frac{i}{\omega_{nm}} \sum_{p \neq n,m} A_{nm,p}^{a,b}(\eta).
\]

(20)

Here, I replaced the infinite sum over \( p \) in Eq. (13) with a finite sum for states with \( \epsilon_p \leq E_{\text{cutoff}} \). Equation (13) is recovered in the limit \( E_{\text{cutoff}} \to \infty \). In a Wannier interpolation, only the bands inside the frozen window for Wannierization are accurately interpolated. So, to use Wannier interpolation, we choose \( E_{\text{cutoff}} \) to be \( E_{\text{froz}} \), the upper bound of the frozen window for Wannierization.
Then, the truncation error in evaluating Eq. (13) is

$$\delta r_{nm}^{ab}(\eta) = f_{n,m}(\infty; \eta) - f_{n,m}(E_{froz}; \eta). \quad (21)$$

To study the magnitude of the error in the shift-current spectra due to this truncation, I calculated the shift-current spectrum with \( r_{nm}^{ab} \) in the shift-current formula [Eqs. (5, 8) of [1]] replaced with \( \delta r_{nm}^{ab}(\eta) \) [Eq. (21)]. Since the high-energy bands need to be explicitly included, I performed the calculation at the DFT level. The infinity in Eq. (21) was replaced with the conduction band minimum energy plus 20 eV, as the contribution from bands with even higher energies was found to be negligible. Due to the high computational cost, I used \( k \)-point grids coarser than the 1000×1000×1 grid used in the calculation of the shift-current spectra. Figure 3 shows the truncation error of the shift-current spectra. The results indicate that the magnitude of the truncation error is almost converged at a 200×200×1 \( k \)-point grid.

To summarize, I showed that when using a finite broadening parameter \( \eta \) to calculate the generalized derivative of the interband dipole matrix, one needs to add a correction term [Eq. (19)] to Eq. (36) of Ibañez-Azpiroz et al. [1]. Without this change, the exact agreement between the two phase conventions was not reached. All results in this Comment were obtained after this change.

Note that the use of \( \eta \) is necessary to avoid numerical problems due to near-degenerate states. As one uses smaller \( \eta \), a larger number of \( k \) points need to be used to converge the calculated shift-current spectrum. In other words, the number of \( k \) points used gives the lower bound of \( \eta \) for the calculated spectrum to remain stable.

I also note that I fixed a small inconsistency between the shift-current implementation of WANNIER90 and the formalism of Ibañez-Azpiroz et al. [1]. In the WANNIER90 implementation, the broadening \( \eta \) was included in denominators that do not contain any intermediate states, such as \( 1/\omega_{nm} \) in Eq. (1), while the formalism [1] does not include \( \eta \) in such cases. I changed the WANNIER90 code so that it is consistent with Ibañez-Azpiroz et al. [1].

Computational resources were provided by KISTI Supercomputing Center (KSC-2020-INO-0078).

* jaemo.lihm@gmail.com

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