Effects of spin-orbit coupling on the optical response of a material

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(Dated: July 19, 2018)

We investigate the effects of spin-orbit coupling on the optical response of materials. In particular, we study the effects of the commutator between the spin-orbit coupling part of the potential and the position operator on the optical matrix elements. Using a formalism that separates a fully-relativistic Kleinman-Bylander pseudopotential into the scalar-relativistic and spin-orbit-coupling parts, we calculate the contribution of the commutator arising from spin-orbit coupling to the squared optical matrix elements of isolated atoms, monolayer transition metal dichalcogenides, and topological insulators. In the case of isolated atoms from H (Z = 1) to Bi (Z = 83), the contribution of spin-orbit coupling to the squared matrix elements can be as large as 14%. On the other hand, in the cases of monolayer transition metal dichalcogenides and topological insulators, we find that this contribution is less than 1% and that it is sufficient to calculate the optical matrix elements and subsequent physical quantities without considering the commutator arising from spin-orbit coupling.

I. INTRODUCTION

The electronic structure of materials containing heavy elements can be significantly affected by spin-orbit coupling (SOC). Due to the recent advances in the investigation of materials having strong SOC effects such as transition metal dichalcogenides (TMDCs), topological insulators, or Weyl semimetals to name a few, it becomes important to accurately simulate the effects of SOC using first-principles density functional theory (DFT) calculations. Because SOC allows the manipulation of the spin degrees of freedom in materials by using light, understanding the effects of SOC on the optical response of materials is a matter of importance.

Consider a system described by an effective Hamiltonian

\[ \hat{H} = \frac{\hat{p}^2}{2m} + V_{\text{loc}}(\hat{\mathbf{r}}) + \hat{V}_{\text{NL}}, \]  

where \( m \) is the mass of an electron, \( \hat{p} \) is the momentum operator, \( \hat{\mathbf{r}} \) is the position operator, and \( V_{\text{loc}}(\hat{\mathbf{r}}) \) and \( \hat{V}_{\text{NL}} \) are the local and non-local parts of the potential, respectively. The optical matrix elements of the system are given by the matrix elements of the velocity operator

\[ \hat{\mathbf{v}} = \frac{\hat{p}}{m} + \frac{i}{\hbar} \left[ \hat{V}_{\text{NL}}, \hat{\mathbf{r}} \right]. \]  

(2)

In many DFT calculations, the pseudopotential method is used because of its computational efficiency. Within the non-relativistic and scalar-relativistic pseudopotential methods, the effects of the commutator in Eq. (2) on the optical matrix elements and absorption spectra have been investigated for various types of systems including isolated atoms, semiconductors, and metals. It was reported that the contribution of the commutator can be large, e.g., in the cases of carbon and bulk copper.

SOC is proportional to \( \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \), where \( \hat{\mathbf{L}} \) and \( \hat{\mathbf{S}} \) are the orbital and spin angular momentum operators, respectively. Because the orbital angular momentum operator does not commute with the position operator, SOC results in an additional contribution to the velocity operator via the commutator and to the optical matrix elements.

It has not been well established whether the effects of the commutator arising from the SOC part of the potential are important or not in a system where the influence of SOC on the electronic structure is known to be strong. For example, in some previous studies on the optical response of Bi₂Se₃, a topological insulator that has been extensively investigated, the contribution of the commutator arising from SOC was neglected and \( \hat{p}/m \) as an approximation to \( \hat{\mathbf{v}} \) [Eq. (2)] was used to calculate the optical matrix elements. On the other hand, the authors of a recent study claimed that the SOC contribution to the velocity operator plays a crucial role in explaining the results of their photoemission experiments.

In this study, we investigate the effects of SOC on the optical matrix elements and absorption spectra in various types of systems: isolated atoms, monolayer TMDCs, and topological insulators. The method used in this study allows for the calculation of the optical matrix elements with and without inclusion of the commutator arising from the intrinsic non-locality of SOC while using the same (fully-relativistic) pseudopotential, from which we can directly assess the importance of the effects of SOC in evaluating the optical matrix elements and optical properties of materials.

II. METHODS

The non-local part of a fully-relativistic pseudopotential in semi-local form can be written as

\[ \hat{V}_{\text{SL}} = \sum_{l=0}^{l_{\text{max}}} \sum_{j=-\frac{l}{2}}^{\frac{l}{2}} \sum_{m_j=-j}^{j} |l, j, m_j \rangle V_{l,j}(r) \langle l, j, m_j |, \]  

(3)
where \( V_{l,j}(r) \) is the radial potential of \( \hat{V}_{SL} \) for a given pair of the orbital angular momentum quantum number \( l \) and the total angular momentum \( j \) and \( |l,j,m_j\rangle \) is the spin-angular function \(^{14,15} \) satisfying \( \mathbf{J}^2 |l,j,m_j\rangle = j(j+1)\hbar^2 |l,j,m_j\rangle \) and \( \hat{J}_z |l,j,m_j\rangle = m_j \hbar |l,j,m_j\rangle \) \((\mathbf{J} = \mathbf{L} + \mathbf{S})\).

The spin-angular function can be explicitly written in terms of the orbital angular momentum eigenstates \( |l,m_l\rangle \) satisfying \( \mathbf{L}^2 |l,m_l\rangle = l(l+1)\hbar^2 |l,m_l\rangle \) and \( \hat{L}_z |l,m_l\rangle = m_l \hbar |l,m_l\rangle \) \((m_l = -l, \cdots, l)\) and the spin angular momentum eigenstates \(|\uparrow\rangle\) and \(|\downarrow\rangle\): for \( j = l+1/2, \)

\[
|l,j,m_j\rangle = \sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}} |l,m_j-\frac{1}{2}\rangle |\uparrow\rangle + \sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}} |l,m_j+\frac{1}{2}\rangle |\downarrow\rangle ,
\]
and for \( j = l-1/2, \)

\[
|l,j,m_j\rangle = \sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}} |l,m_j-\frac{1}{2}\rangle |\uparrow\rangle - \sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}} |l,m_j+\frac{1}{2}\rangle |\downarrow\rangle .
\]

Using the fact that the spin-angular function is an eigenstate of \( \mathbf{L} \cdot \mathbf{S} \), \( \hat{V}_{SL} \) can be rewritten as the sum of the scalar-relativistic and SOC parts \(^{13,15} \)

\[
\hat{V}_{SL} = \sum_{l=0}^{l_{\text{max}}} |l\rangle \hat{V}_{l}^{\text{SR}} (r) |l\rangle + \sum_{l=1}^{l_{\text{max}}} |l\rangle \hat{V}_{l}^{\text{SO}} (r) \mathbf{L} \cdot \mathbf{S} |l\rangle ,
\]

where \(|l\rangle |l\rangle \) is the orbital angular momentum projector for a given \( l \), which is the sum of \(|l,m_l\rangle |l,m_l\rangle \) over all \( m_l \). In Eq. (6), the radial potentials of the scalar-relativistic and SOC parts of \( \hat{V}_{SL} \) are given as

\[
\hat{V}_{l}^{\text{SR}} (r) = \frac{l+1}{2l+1} \hat{V}_{l,l+\frac{1}{2}} (r) + \frac{l}{2l+1} \hat{V}_{l,l-\frac{1}{2}} (r) ,
\]
and

\[
\hat{V}_{l}^{\text{SO}} (r) = \frac{2}{2l+1} \left( \hat{V}_{l,l+\frac{1}{2}} (r) - \hat{V}_{l,l-\frac{1}{2}} (r) \right) ,
\]
respectively. The scalar-relativistic potential, \( \hat{V}_{l}^{\text{SR}} (r) \), includes the effects of the Darwin term and the mass-velocity term. Hybertsen and Louie\(^{16,17} \) considered the effects of the SOC potential, \( \hat{V}_{l}^{\text{SO}} (r) \), on the spin-orbit splittings in the band structure of semiconductors within first-order perturbation theory and found good agreement with experiments.

For computational efficiency, pseudopotentials of the fully-separable Kleinman-Bylander (KB) form \(^{18-20} \) are commonly used instead of those of the semi-local form. The non-local part of a fully-relativistic KB pseudopotential can be written as

\[
\hat{V}_{KB} = \sum_{l=0}^{l_{\text{max}}} \sum_{j=|l-1/2|}^{j} \sum_{m_j=-j}^{j} |l,j,m_j\rangle \langle \beta_{l,j} | \hat{V}_{l,j} (r) |l,j,m_j\rangle ,
\]

where the radially non-local projector \( |\beta_{l,j}\rangle \langle \beta_{l,j}| \) is used instead of the radial potential \( V_{l,j} (r) \).

Similarly to the case of the semi-local pseudopotential, a fully-relativistic KB pseudopotential can be rewritten as the sum of the scalar-relativistic and SOC parts:

\[
\hat{V}_{KB} = \sum_{l=0}^{l_{\text{max}}} |l\rangle \hat{V}_{l}^{\text{SR}} (r) |l\rangle + \sum_{l=1}^{l_{\text{max}}} |l\rangle \hat{V}_{l}^{\text{SO}} (r) \mathbf{L} \cdot \mathbf{S} |l\rangle ,
\]

where the non-local potentials of the scalar-relativistic and SOC parts of \( \hat{V}_{KB} \) are defined as

\[
\hat{V}_{l}^{\text{SR}} = \frac{l+1}{2l+1} \langle \beta_{l,l+\frac{1}{2}} | \hat{V}_{l,l+\frac{1}{2}} (r) |\beta_{l,l+\frac{1}{2}}\rangle + \frac{l}{2l+1} \langle \beta_{l,l-\frac{1}{2}} | \hat{V}_{l,l-\frac{1}{2}} (r) |\beta_{l,l-\frac{1}{2}}\rangle ,
\]

and

\[
\hat{V}_{l}^{\text{SO}} = \frac{2}{2l+1} \left( \langle \beta_{l,l+\frac{1}{2}} | \hat{V}_{l,l+\frac{1}{2}} (r) |\beta_{l,l+\frac{1}{2}}\rangle - \langle \beta_{l,l-\frac{1}{2}} | \hat{V}_{l,l-\frac{1}{2}} (r) |\beta_{l,l-\frac{1}{2}}\rangle \right) ,
\]

respectively.

The fully-relativistic velocity operator that includes all the non-local effects of the fully-relativistic KB pseudopotential is written as

\[
\hat{\mathbf{v}}^{(\text{FR})} = \hat{\mathbf{v}}^{(\text{P})} + \frac{i}{\hbar} \left[ \hat{\mathbf{V}}_{KB}, \mathbf{\bar{r}} \right] ,
\]

where \( \hat{\mathbf{v}}^{(\text{P})} = \mathbf{p}/m \) is introduced for notational convenience. The commutator on the right-hand side of Eq. (13) can be separated into scalar-relativistic and SOC parts. By using the expressions in Eqs. (10), (11), and (12), we define the scalar-relativistic velocity operator that includes only the effects arising from the scalar-relativistic part of \( \hat{V}_{KB} \):

\[
\hat{\mathbf{v}}^{(\text{SR})} = \hat{\mathbf{v}}^{(\text{P})} + \frac{i}{\hbar} \sum_{l=0}^{l_{\text{max}}} \langle l\rangle \hat{\mathbf{v}}_{l}^{(\text{SR})} (l) \frac{\mathbf{\bar{r}}}{\hbar} ,
\]

Within this formalism, the non-local effects of SOC on the velocity operator arise from the difference between \( \hat{\mathbf{v}}^{(\text{FR})} \) and \( \hat{\mathbf{v}}^{(\text{SR})} \) which can be written as the sum of the commutators arising from \( \hat{V}_{l}^{(\text{SO})} \):

\[
\hat{\mathbf{v}}^{(\text{SO})} = \hat{\mathbf{v}}^{(\text{FR})} - \hat{\mathbf{v}}^{(\text{SR})} = \sum_{l=1}^{l_{\text{max}}} \hat{\mathbf{v}}_{l}^{(\text{SO})} ,
\]

where

\[
\hat{\mathbf{v}}_{l}^{(\text{SO})} = i/\hbar \left[ \langle l\rangle \hat{\mathbf{v}}_{l}^{(\text{SO})} \mathbf{L} \cdot \mathbf{S} \frac{\mathbf{\bar{r}}}{\hbar} \right] .
\]
The optical matrix elements of our interest are $\langle f e \cdot \mathbf{v}^{(SR/FR)} | i \rangle$, where $|i\rangle$ and $|f\rangle$ are the initial and final electronic states, respectively, and $e$ is the polarization vector of the incident light. We investigate the difference between the matrix elements of $\mathbf{v}^{(SR)}$ and $\mathbf{v}^{(FR)}$ in several systems having heavy elements such as W and Bi. In the case of an isolated atom, the initial and final states are the eigenstates of angular momentum operators $|n,l,j,m_j\rangle$ where $n$ is the principal quantum number. In periodic systems, the initial and final states are the Bloch states in the valence band $|v,k\rangle$ and those in the conduction band $|c,k\rangle$, respectively, where $k$ is the crystal momentum, and $v$ and $c$ are the indices of the valence and conduction bands, respectively.

The imaginary part of the dielectric function is calculated within the independent-particle random-phase approximation:

$$\text{Im} \varepsilon^{(p/FR/FR)}(\omega) = \frac{4\pi}{\omega^2 \Omega N_k} \sum_{c,v} \left| \langle c,k | e \cdot \mathbf{v}^{(p/FR)} | v,k \rangle \right|^2 \times \delta \left( E_{c,k} - E_{v,k} - \hbar \omega \right),$$  \hspace{1cm} (17)

where $\omega$ is the frequency of the incident light, $\Omega$ is the volume of the unit cell, $N_k$ is the number of $k$ points in the Brillouin zone, and $E_{c,k}$ and $E_{v,k}$ are the Kohn-Sham energy eigenvalues of $|c,k\rangle$ and $|v,k\rangle$, respectively.

From Eq. (17), we can see that SOC affects the absorption spectra of materials in two different ways: (i) SOC changes the Kohn-Sham energy eigenvalues, $E_{c,k}$ and $E_{v,k}$, and eigenstates, $|c,k\rangle$ and $|v,k\rangle$, and (ii) SOC gives an additional contribution, $\mathbf{v}^{(SO)}$ in Eq. (17), to the (fully-relativistic) velocity operator. The focus of our work is on the second contribution.

In this work, we performed fully-relativistic DFT calculations within the generalized gradient approximation using the Quantum ESPRESSO package. The optical matrix elements and the imaginary part of the dielectric function were calculated by using the Yambo code. We modified the program so that we can construct both the scalar-relativistic and fully-relativistic velocity operators using the same set of fully-relativistic KB pseudopotentials. All the fully-relativistic KB pseudopotentials used in this work were generated by using the ONCVPSP code. The generating parameters for the pseudopotentials were taken from the work of Schlipf and Gygi, while slight modifications were made to get the fully-relativistic pseudopotential of Bi.

### III. RESULTS AND DISCUSSION

#### A. Isolated atomic systems

We study the effects of SOC on the optical matrix elements of isolated W and Bi atoms which are heavy elements and have an electronic structure strongly affected by SOC. We calculated the squared optical matrix elements of the form $\langle f e^+ \cdot \mathbf{v}^{(SR/FR)} | i \rangle^2$, where the initial and final states are chosen to be the total angular momentum eigenstates, $|n,l,j,m_j\rangle$, and $e^+$ is the polarization vector of the left-circularly polarized light propagating along the $z$ direction. By comparing the squared matrix elements of $\mathbf{v}^{(SR)}$ and $\mathbf{v}^{(FR)}$ for a given pair of initial and final states, we calculated the effects of SOC on the individual optical matrix element.

Figures 1(a) and 1(b) show the squared matrix elements of $\mathbf{v}^{(FR)}$, $\mathbf{v}^{(SR)}$, and $\mathbf{v}^{(p)}$. In the case of a W atom, the difference between the squared matrix elements of $\mathbf{v}^{(SR)}$ and $\mathbf{v}^{(FR)}$ is not very large. In the case of a Bi atom, however, the squared matrix elements of $\mathbf{v}^{(SR)}$ significantly differ from those of $\mathbf{v}^{(FR)}$, especially for the 5$d$ to 6$p$ transitions. It is known that such non-local effects arising from the scalar-relativistic part of $\mathbf{V}_{KB}$ can be significant if there is a large difference between the $l$-orbital components of the scalar-relativistic potential, $\mathbf{v}^{(SR)}_{l,l+1}$. On the other hand, the difference between the squared matrix elements of $\mathbf{v}^{(FR)}$ and $\mathbf{v}^{(SR)}$ is relatively small for all the optical transitions.

Figures 1(c) and 1(d) show the difference between the squared matrix elements of $\mathbf{v}^{(SR)}$ and $\mathbf{v}^{(FR)}$. In the case of a W atom, the difference between the squared matrix elements of $\mathbf{v}^{(FR)}$ and $\mathbf{v}^{(SR)}$ can be as large as 4.3% of the squared matrix elements of $\mathbf{v}^{(FR)}$. This difference is even more significant for a Bi atom and can reach 14% (in the case of 6$s$ to 6$p$ transitions). Although the effects of SOC on the optical matrix elements strongly depend upon the characters of the initial and final states, we find that the non-local effects of SOC on the optical matrix elements are not negligible in W and Bi atoms.

The relatively large effects of SOC on the optical matrix elements in the case of a Bi atom can be qualitatively understood by looking at the SOC potentials of the W and Bi pseudopotentials in the semi-local form [Eq. (8)]. Figure 2 shows $V_{S^{(SO)}}^{(p)}(r)$ of the W and Bi pseudopotentials used in our calculations (their generating parameters are shown in Tab. 1). Because $V_{S^{(SO)}}^{(p)}(r)$ is defined as the difference between $V_{l,l+1/2}(r)$ and $V_{l,l-1/2}(r)$, $V_{l,l+1/2}^{(SO)}(r)$ is localized within the pseudization radii of $V_{l,l-1/2}(r)$ and $V_{l,l+1/2}(r)$. Because the pseudization radii of the W pseudopotential are smaller than those of the Bi pseudopotential (see Tab. 1), $V_{S^{(SO)}}^{(p)}(r)$ of the W pseudopoten-
The incident light is left-circularly polarized. The matrix elements obtained by using the fully-relativistic scalar-relativistic velocity operator, and the scalar-relativistic velocity operator.

The largest four squared matrix elements of the fully-relativistic optical matrix elements are in Hartree. We note that for both atoms the p-orbital part of the SOC potential, \( V_{l=2}^{SO}(r) \), is much larger than the \( d \)- and \( f \)-orbital parts, \( V_{l=3}^{SO}(r) \) and \( V_{l=3}^{SO}(r) \).

The matrix elements of \( \hat{\psi}^{(SO)}_l \) [Eq. (10)] can be explicitly written as

\[
\langle f | \hat{\psi}^{(SO)}_l | i \rangle = \frac{i}{\hbar} \sum_{\sigma, \sigma'} \int dr V^{SO}_l(r) \times \\
\psi^*_i(r, \sigma) \left[ \mathbf{L} \cdot \mathbf{S}_{\sigma, \sigma'} |l\rangle \langle l| \right] \psi_j(r, \sigma'),
\]

where \( \sigma \) and \( \sigma' \) are the spin indices, \( \psi_i(r, \sigma) \) and \( \psi_j(r, \sigma) \) are the \( (r, \sigma) \) component of \( |i\rangle \) and \( |f\rangle \). Because Eq. (18) contains the volume integration of \( V^{SO}_l(r) \), not only the value of \( V^{SO}_l(r) \) near the core region \( (r \sim 0) \) but also the spatial extent of \( V^{SO}_l(r) \) is an important factor that affects the magnitude of \( \langle f | \hat{\psi}^{(SO)}_l | i \rangle \).

To sketch the influence of \( V^{SO}_l(r) \) on the matrix elements of \( \hat{\psi}^{(SO)}_l \), we evaluate the volume integration of \( |V^{SO}_l(r)| \) for the atoms in the periodic table from H \((Z=1)\) to Bi \((Z=83)\) except those in the Lanthanide series (Fig. 3). Roughly speaking, the volume integration of \( |V^{SO}_l(r)| \) increases with the atomic number \( Z \), or with the atomic mass. For example, the volume integration of \( |V^{SO}_{l=1}(r)| \) of the Bi \((Z=83)\) pseudopotential is 0.78 Hartree, while the same quantity of the W \((Z=74)\) pseudopotential is 0.3. The result is consistent with our observation in Fig. 4 that the effects of SOC on the optical matrix elements increase with the atomic mass (4.3 % and 14 % of the squared matrix elements of \( \hat{\psi}^{(FR)} \) for W and Bi atoms, respectively).

For most atoms in Fig. 3, we find that the p-orbital component of the SOC potential, \( |V^{SO}_{l=1}(r)| \), is the largest, the \( d \)-orbital component, \( |V^{SO}_{l=2}(r)| \), is the second largest, and the \( f \)-orbital component, \( |V^{SO}_{l=3}(r)| \), is the smallest. Therefore, it is natural to expect that the contribution of \( V^{SO}_{l=1}(r) \) to the optical matrix elements is the most important one and that the contribution of \( V^{SO}_{l=2}(r) \) becomes smaller as \( l \) increases. To investigate the contribution of \( V^{SO}_{l=1}(r) \) to the squared matrix elements of \( \hat{\psi}^{(FR)} \), we calculated the squared matrix elements of \( \hat{\psi}^{(FR)} \) and \( \hat{\psi}^{(FR)}_l - \hat{\psi}^{(SO)}_l \).

Figure 3 shows the difference between the squared matrix elements of \( \hat{\psi}^{(FR)} \) and \( \hat{\psi}^{(FR)}_l - \hat{\psi}^{(SO)}_l \) in the cases of W and Bi atoms. In both cases, the contribution of \( \hat{\psi}^{(SO)}_{l=1} \) to the squared matrix elements of \( \hat{\psi}^{(FR)} \) is the largest among the contributions of \( \hat{\psi}^{(SO)}_l \). The contribution of \( \hat{\psi}^{(SO)}_{l=2} \) is the second largest and that of \( \hat{\psi}^{(SO)}_{l=3} \) is the smallest and negligible. In the case of a W atom, there is a case where the contribution of \( \hat{\psi}^{(SO)}_{l=2} \) is almost half of the contribution of \( \hat{\psi}^{(SO)}_{l=1} \). In the case of a Bi atom, the contributions of \( \hat{\psi}^{(SO)}_{l=2} \) and \( \hat{\psi}^{(SO)}_{l=3} \) are very small.

Because \( \hat{\psi}^{(SO)}_l \) contains the orbital angular momentum projector, \( |l\rangle \langle l| \), the matrix elements of \( \hat{\psi}_l^{(SO)} \) are finite.

**FIG. 1.** (a) and (b) The squared optical matrix elements of W and Bi atoms obtained by using the fully-relativistic velocity operator, the scalar-relativistic velocity operator, and the momentum operator for the optical transitions between the total angular momentum eigenstates. Only the cases of the largest four squared matrix elements of the fully-relativistic velocity operator among \( 5p \to 5d \) transitions in a W atom and those among \( 5d \to 6p \) and \( 6s \to 6p \) transitions in a Bi atom are shown. (c) and (d) The difference between the squared optical matrix elements obtained by using the fully-relativistic velocity operator and the scalar-relativistic velocity operator. The incident light is left-circularly polarized. The matrix elements are in Hartree.

**FIG. 2.** The spin-orbit coupling potential [Eq. (3)] of the fully-relativistic pseudopotentials of W [W(2) pseudopotential in Tab. II] and Bi atoms.
Therefore, the matrix elements of $\hat{v}$ are finite only if the difference between the $l$’s of $|i\rangle$ and $|f\rangle$ is $\pm 1$. Therefore, the matrix elements of $\hat{v}^{(SO)}_{l=3}$ are finite only for the transitions between the states that have $d$- and $f$-orbital angular momentum characters. In our calculations, the contribution of $\hat{v}^{(SO)}_{l=3}$ to the squared matrix elements of $\hat{v}^{(PR)}$ is usually very small for such transitions.

It is known that the effects of SOC on the energy levels and wavefunctions of atomic systems are the largest for $p$-orbitals and become smaller for $d$- and $f$-orbitals. In fact, if we recall the fine structure of a hydrogen atom, we easily see that the energy splittings induced by SOC show the same $l$-dependent behavior ($p > d > f$). Our results are in line with these relativistic effects on atomic systems.

B. Monolayer transition metal dichalcogenides

We calculate the optical matrix elements and absorption spectra of a monolayer of four 2H-type semiconducting TMDCs (MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$). Figure 4(a) shows the structure of the two-dimensional crystal. The TMDC monolayer of 2H-type consists of a transition metal layer (Mo or W) which is sandwiched by two chalcogen layers (S or Se). Figure 4(b) shows the two-dimensional Brillouin zone.

In our DFT calculations using fully-relativistic pseudopotentials, we set the kinetic energy cutoff of the plane-
and Im $\epsilon$ are the imaginary part of the dielectric function and the commutator arising from the scalar-relativistic and SOC parts of the pseudopotential, respectively. In the high energy regime ($\hbar\omega > 2$ eV), we see step-function-like behaviors of Im $\epsilon^{(\text{FR})}(\omega)$ which mainly result from the optical transitions between the band-edge states at K and K', i.e. the two highest-energy valence and the two lowest-energy conduction bands. These band-edge states mostly consist of the d orbitals of transition metal atoms and the p orbitals of chalcogen atoms. In the high energy regime ($\hbar\omega > 2$ eV), additional sharp features arise as the states other than the band-edge states make contributions to Im $\epsilon^{(\text{FR})}(\omega)$.

Figures 6(c)-(f) show the difference between Im $\epsilon^{(\text{FR})}(\omega)$ and Im $\epsilon^{(\text{SR})}(\omega)$. In the low energy regime ($\hbar\omega < 2$ eV), the difference between Im $\epsilon^{(\text{FR})}(\omega)$ and Im $\epsilon^{(\text{SR})}(\omega)$ is three orders of magnitudes smaller than Im $\epsilon^{(\text{FR})}(\omega)$ itself, which indicates that the non-local effects of SOC on Im $\epsilon^{(\text{FR})}(\omega)$ are negligibly small in this range of energy. The effects of SOC become larger at higher energies ($\hbar\omega > 2$ eV). However, the difference between Im $\epsilon^{(\text{FR})}(\omega)$ and Im $\epsilon^{(\text{SR})}(\omega)$ remains smaller than 1% of Im $\epsilon^{(\text{FR})}(\omega)$.

In general, the non-local part of a pseudopotential strongly depends on its generating parameters such as valence (and core) configurations, pseudization radii, and the local part of the pseudopotential. Therefore, the effects of the commutator on the optical matrix elements and absorption spectra of a material (including the contributions from the scalar-relativistic and SOC parts of the pseudopotential) can change significantly by the non-local character of the pseudopotential used in the calculations.

In Fig. 7, we plot the imaginary part of the dielectric function of monolayer WSe$_2$ obtained by using two different fully-relativistic KB pseudopotentials of W (for comparison, we fixed the pseudopotential of Se). We checked that the two different pseudopotentials of W yield almost the same band structure within the energy range of our interest ($\hbar\omega = 0-4$ eV). The absorption spectra in Figs. 7(a) and 7(c) were obtained by using a W pseudopotential that includes 4f electrons in the valence (see W(1) in Tab. 1), while those in Fig. 7(b) and 7(d) were obtained by using a W pseudopotential that includes 4f electrons in the core (see W(2) in Tab. 1).

By comparing Im $\epsilon^{(\text{P})}(\omega)$ in Figs. 7(a) and 7(b), we find that the absorption spectrum strongly depends on the pseudopotential of W, if we neglect all the effects arising from the non-local part of the pseudopotential and use $\psi^p$ as the velocity operator. In the case of the W(1) pseudopotential, Im $\epsilon^{(\text{P})}(\omega)$ is much smaller than Im $\epsilon^{(\text{SR})}(\omega)$. The result shows that the commutator arising from the scalar-relativistic part of the W(1) pseudopotential affects strongly the absorption spectrum. The large difference between Im $\epsilon^{(\text{SR})}(\omega)$ and Im $\epsilon^{(\text{P})}(\omega)$ is attributed to the presence of 4f electrons in the valence which makes the W(1) pseudopotential strongly non-local. On the other hand, in the case of the W(2) pseudopotential, Im $\epsilon^{(\text{P})}(\omega)$ is quite similar to Im $\epsilon^{(\text{SR})}(\omega)$. The effects of the commutator arising from the scalar-relativistic part of the pseudopotential are much smaller for the W(2) pseudopotential where 4f electrons are treated as core electrons. We note that in both cases, Im $\epsilon^{(\text{SR})}(\omega)$ is almost identical to Im $\epsilon^{(\text{FR})}(\omega)$.

Figures 7(c) and 7(d) show the difference between Im $\epsilon^{(\text{FR})}(\omega)$ and Im $\epsilon^{(\text{SR})}(\omega)$. We find that the contributions of SOC to Im $\epsilon^{(\text{FR})}(\omega)$ for the two different pseudopotentials of W are very similar to each other in the whole energy range. The result shows that the effects of the commutator arising from SOC on the absorption spectra do not depend much on the pseudopotential.

It is possible that even if the non-local effects of SOC on the individual optical matrix element are large, the effects on the absorption spectrum are small as we sum over the contributions from many optical matrix ele-
FIG. 6. (a)-(d) The imaginary part of the dielectric function of monolayer transition metal dichalcogenides obtained by using the fully-relativistic velocity operator. (e)-(h) The difference between the imaginary part of the dielectric functions of monolayer transition metal dichalcogenides obtained by using the fully-relativistic velocity operator and the scalar-relativistic velocity operator.

FIG. 7. (a) and (b) The imaginary part of the dielectric function of monolayer WSe$_2$ obtained by using two different pseudopotentials of W, which were generated from two different valence configurations (see Tab. I for details). Im$\varepsilon$(FR), Im$\varepsilon$(SR), and Im$\varepsilon$(p) are the imaginary part of the dielectric function obtained by using the momentum operator, the scalar-relativistic velocity operator, and the fully-relativistic velocity operator, respectively. (c) and (d) The difference between the imaginary part of the dielectric function obtained by using the fully-relativistic and the scalar-relativistic velocity operators.

Next, we further investigate the dependence of the squared matrix elements of $\hat{v}^{(FR)}$, $\hat{v}^{(SR)}$, and $\hat{v}^{(p)}$ on

ments with different momenta and band indices. To check this possibility, we calculated the squared matrix elements $|\langle c_i, k | e^{+} \cdot \hat{v}^{(SR/FR)} | v_j, k \rangle |^2$, where $i$ and $j$ are 1 or 2, $v_1$ and $v_2$ are the band indices of the highest-energy and second-highest-energy states in the valence band, respectively, $c_1$ and $c_2$ are the band indices of the lowest-energy and second-lowest-energy states in the conduction band, respectively, and $k$ is on the path $-M \rightarrow -K \rightarrow \Gamma \rightarrow K \rightarrow M$ [Fig. 5(b)].

Figures 8(a)-(d) show the squared matrix elements of $\hat{v}^{(FR)}$. Here, we see that the squared matrix elements of $\hat{v}^{(FR)}$ near K are larger in magnitude than those near $-K$. Because we assumed the incident light to be left-circularly polarized, the result can be explained by the valley-selective circular dichroism of monolayer TMDCs.

Figures 8(e)-(h) show the difference between the squared matrix elements of $\hat{v}^{(FR)}$ and $\hat{v}^{(SR)}$. Although the contribution of the commutator arising from SOC to the squared matrix elements of $\hat{v}^{(FR)}$ becomes larger in the case of having heavier transition metal atoms (WS$_2$ and WSe$_2$), even in those cases the contribution from SOC remains smaller than 1 % of the squared matrix elements of $\hat{v}^{(FR)}$. If we compare this result with the previous result of an isolated W atom, the influence of the commutator arising from SOC on the optical matrix elements is much suppressed: In the case of a W atom, the effects of SOC on the squared optical matrix elements can be as large as 4.3 % of the squared matrix elements of $\hat{v}^{(FR)}$ [Figs. 1(a) and 1(c)].

Next, we further investigate the dependence of the squared matrix elements of $\hat{v}^{(FR)}$, $\hat{v}^{(SR)}$, and $\hat{v}^{(p)}$ on
FIG. 8. (a)-(d) The squared optical matrix elements obtained by using the fully-relativistic velocity operator of monolayer transition metal dichalcogenides for the optical transitions involving the highest-energy and second-highest-energy states in the valence band, \( v_1 \) and \( v_2 \), respectively, and the lowest-energy and second-lowest-energy states in the conduction band, \( c_1 \) and \( c_2 \), respectively. The squared optical matrix elements were calculated along the path in the momentum space, \(-M \rightarrow -K \rightarrow \Gamma \rightarrow K \rightarrow M\). (e)-(h) The difference between the squared optical matrix elements obtained by using the fully-relativistic velocity operator and those obtained by using the scalar-relativistic velocity operator. In all cases, the incident light is left-circularly polarized.

The initial and final states in the case of monolayer WSe\(_2\). We calculated the squared matrix elements at \( K \), \( |\langle K, K \Gamma K M | e^+ \cdot \hat{v}^{(SR)} | v, K \rangle|^2 \), where \( v \) and \( c \) are the band indices of the initial and final states, respectively. The band indices are in increasing order of energy (the band indices of the initial and final states, respectively. The effects of SOC on the optical transitions having \([3, K]\), \([18, K]\), and \([26, K]\) as initial states are much more delocalized than the initial state

The result of \(|\langle K, K \Gamma K M | e^+ \cdot \hat{v}^{(SR)} | v, K \rangle|^2\) is as large as 6.8\% while in the case of \([26, K]\), the effects are much smaller, less than 1.1\%.  The result of \([18, K]\) falls somewhere between the results of \([3, K]\) and \([26, K]\).

Figure 10(b) and 10(c) show that \(\tilde{\psi}_{i=1}^{(SO)}\) is relatively less important in the cases of \([18, K]\) and \([26, K]\) than in the case of \([3, K]\). The result can be qualitatively understood by looking at the \(p\)- and \(d\)-orbital characters of the initial states. As we move from \([3, K]\) to \([18, K]\) and \([26, K]\), the proportion of the \(W\) \(5p\)-orbital component in the initial state decreases while that of the \(W\) \(4d\)-orbital component increases. In the case of \([26, K]\), because the initial state mostly consists of the \(W\) \(4d\) orbitals, the matrix elements of \(\tilde{\psi}_{i=1}^{(SO)}\) are not only for the final states having \(W\) \(6p\)-orbital character (\(\Delta l = \pm 1\)). Such final states are much more delocalized than the initial state and the matrix elements of \(\tilde{\psi}_{i=1}^{(SO)}\) are small.

Figures 10(a)-(c) show the differences between the squared matrix elements of \(\tilde{\psi}^{(FR)}\) and \(\tilde{\psi}^{(FR)} - \hat{v}_i^{(SO)}\) for the optical transitions having \([3, K]\), \([18, K]\), and \([26, K]\) as the initial states. In the case of \([3, K]\), we find that among \(\tilde{\psi}_i^{(SO)}\)’s, \(\tilde{\psi}_i^{(SO)}\) gives the largest contribution to the squared matrix elements of \(\tilde{\psi}^{(FR)}\). The \(d\)-orbital part \(\tilde{\psi}_{i=2}^{(SO)}\) gives the second largest contribution and the contribution from the \(f\)-orbital part \(\tilde{\psi}_{i=3}^{(SO)}\) is negligible. This result is similar to the result of an isolated \(W\) atom [Fig. 10(a)].
FIG. 9. (a)-(c) The squared optical matrix elements of monolayer WSe$_2$ obtained by using the fully-relativistic velocity operator, the scalar-relativistic operator, and the momentum operator for the optical transitions at K in the momentum space. (d)-(f) The difference between the squared optical matrix elements obtained by using the fully-relativistic velocity operator and the scalar-relativistic operator. In all cases, left-circularly polarized light was considered.

FIG. 10. (a)-(c) The difference between the squared matrix elements of monolayer WSe$_2$ obtained by using the fully-relativistic velocity operator and $\hat{v}_{\text{FR}} - \hat{v}_{\text{SO}}$ [see Eqs. (13) and (15)] for the optical transitions at K in the momentum space. In all cases, left-circularly polarized light was considered.
elements are usually the largest and the effects of the matrix elements of \(\hat{V}^{(FR)}\) on 5-quintuple-layer slabs of Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\). In this way, we can obtain the surface states localized at the top and bottom sides of Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\) slabs. In the calculation of the optical matrix elements, we chose the surface state with momentum \(k' = 0.05\Gamma K\) as our initial state [in blue dots in Figs. 11(a) and 11(b)]. Also here, we consider all the final states that satisfy \(E_{c,k'} - E_{v,k'} < 1\) Ry. We set the kinetic energy cutoff of the plane-wave basis to 80 Ry and use a 6\(\times\)6\(\times\)1 Monkhorst-Pack grid for \(k\)-point sampling. Figures 12(a) and (b) show the squared matrix elements of \(\hat{V}^{(FR)}\), \(\hat{V}^{(SR)}\), and \(\hat{V}^{(p)}\). We find that the difference between the squared matrix elements of \(\hat{V}^{(FR)}\) and \(\hat{V}^{(SR)}\) is very small, while the difference between the squared matrix elements of \(\hat{V}^{(SR)}\) and \(\hat{V}^{(p)}\) is large in some cases of Bi\(_2\)Te\(_3\). Figures 12(c) and (d) show the differences between the squared matrix elements of \(\hat{V}^{(FR)}\) and \(\hat{V}^{(SR)}\) in a different scale. As in the case of the transitions from the valence-band maximum of monolayer WSe\(_2\) [Figs. 9(c) and (f)], the effects of SOC on the optical matrix elements of Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\) slabs are very small (less than 1% of the squared matrix elements of \(\hat{V}^{(FR)}\)).

Figure 13 shows the difference between the squared matrix elements of \(\hat{V}^{(FR)}\) and \(\hat{V}^{(FR)} - \hat{V}^{(SO)}\) for the same optical transitions presented in Fig. 12. We find that the effects of the \(p\)-orbital part \(\hat{V}^{(SO)}\) on the optical matrix elements are usually the largest and the effects of the \(d\)- and \(f\)-orbital parts, \(\hat{V}^{(SO)}\) and \(\hat{V}^{(SO)}\), are much smaller. This is because (i) the \(p\)-orbital component of the SOC potential \(\hat{V}^{(SO)}(r)\) of Bi is much larger than the \(d\)- and \(f\)-orbital components \(\hat{V}^{(SO)}(r)\) (see Figs. 2 and 3) and (ii) in particular, the surface states of Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\) mostly consist of the \(6\)\(p\) orbitals of Bi atoms.

The circular dichroism is defined as the relative difference between the squared optical matrix elements for left- and right-circularly polarized light (see the top of Fig. 14). We calculated the circular dichroism by using \(\hat{V}^{(FR)}\) and \(\hat{V}^{(SR)}\) and investigated whether the effects of the commutator arising from SOC cannot change the circular dichroism of Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\) slabs.

In Fig. 14, we see that the difference between the circular dichroisms obtained by using \(\hat{V}^{(FR)}\) and \(\hat{V}^{(SR)}\) is negligible. Contrary to the arguments in Ref. 12, the effects of the commutator arising from SOC cannot change the circular dichroism of Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\) slabs, which means that the methods used in Refs. 5, 6, and 11 will give correct results. Although we did not find the correct final states (satisfying the proper boundary condition) in the calculations of the optical matrix elements, because the effects of SOC on the optical matrix elements are negli-
In conclusion, we confirm that while the effects of the commutator arising from spin-orbit coupling on the optical matrix elements are not negligible in atomic systems, the effects are much suppressed in the cases of monolayer transition metal dichalcogenides and topological insulators where the effects of spin-orbit coupling on the optical transitions from the valence band edge states.

In the case of five-quintuple layer slabs of Bi$_2$Se$_3$ and Bi$_2$Te$_3$, the effects of spin-orbit coupling on the optical matrix elements are again very small as in the case of monolayer transition metal dichalcogenides. We find that the non-local effects of spin-orbit coupling on the optical matrix elements are so small that the effects do not change the circular dichroism of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ slabs.

In conclusion, we confirm that while the effects of the commutator arising from spin-orbit coupling on the optical matrix elements are not negligible in atomic systems, the effects are much suppressed in the cases of monolayer transition metal dichalcogenides and topological insulators where the effects of spin-orbit coupling on the electronic structure are considered to be important.

Our calculation results show that in studying the optical response of a material with heavy elements, it is sufficient to calculate the optical matrix elements neglecting the commutator arising from spin-orbit coupling in the velocity operator if one has obtained well the electronic structure of the system, i.e. the energy eigenvalues and eigenstates, from fully-relativistic first-principles calculations.

T.Y.K. and C.-H.P. were supported by Korean NRF No-2016R1A1A1A05919979 and by the Creative-Pioneering Research Program through Seoul National University. AF acknowledges financial support from the EU Centre of Excellence “MaX - Materials Design at the Exascale” (Horizon 2020 EINFRA-5, Grant No. 676598). Computational resources were provided by KISTI Supercomputing Center (KSC-2018-C2-0002).
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