Nonlinear Optical Properties of Transition Metal Dichalcogenide MX$_2$ (M = Mo, W; X = S, Se) Monolayers and Trilayers from First-principles Calculations

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Due to the absence of interlayer coupling and inversion symmetry, transition metal dichalcogenide (MX$_2$) semiconductor monolayers exhibit novel properties that are distinctly different from their bulk crystals such as direct optical band gaps, large band spin splittings, spin-valley coupling, piezoelectric and nonlinear optical responses, and thus have promising applications in, e.g., optoelectronic and spintronic devices. Here we have performed a systematic first-principles study of the second-order nonlinear optical properties of MX$_2$ (M = Mo, W; X = S, Se) monolayers and trilayers within the density functional theory with the generalized gradient approximation plus scissors correction. We find that all the four MX$_2$ monolayers possess large second-order optical susceptibility $\chi^{(2)}$ in the optical frequency range and significant linear electro-optical coefficients in low frequency limit, thus indicating their potential applications in non-linear optical devices and electric optical switches. The $\chi^{(2)}$ spectra of the MX$_2$ trilayers are overall similar to the corresponding MX$_2$ monolayers, albeit with the magnitude reduced by roughly a factor of 3. The prominent features in the $\chi^{(2)}$ spectra of the MX$_2$ multilayers are analyzed in terms of the underlying band structures and optical dielectric function, and also compared with available experiments.

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I. INTRODUCTION

Structurally, layered transition metal dichalcogenides of general formula MX$_2$ form a coherent family of compounds, where the metal (M) atoms are each coordinated by six chalcogen (X) atoms and each layer (monolayer) of the crystal is made up of a two-dimensional (2D) hexagonal array of M atoms sandwiched between the similar arrays of X atoms. The MX$_2$ sandwich monolayers are bound together by the weak van der Waals forces. They are highly anisotropic and have been known as quasi-2D materials. Mechanically, therefore, they could be easily cleaved to prepare thin films, similar to graphite. Physically, however, the compounds have widely different electrical and optical properties and also host a number of interesting phenomena such as charge density wave and superconductivity phase transitions (see, e.g., Refs. 1-4 and references therein). Chemically, the layered materials may be intercalated by Lewis bases such as alkali metals and organic molecules (see, e.g., Refs. 5 and 6 and references therein), often resulting in pronounced changes in their physical properties. Therefore, the compounds had been under intensive investigations for nearly three decades since early 1960’s.

In a recent optical experiment, a MoS$_2$ crystal was found to exhibit an indirect to direct band gap transition when it is thinned down to a monolayer (ML). This discovery has triggered a growing renewed interest in the MX$_2$ semiconductors, albeit in their ML forms, because these MX$_2$ semiconductor MLs exhibit fascinating properties that their bulk crystals do not have. Structurally, the MX$_2$ MLs have two distinct differences from the MX$_2$ crystals, namely, lack of interlayer interaction and broken spatial inversion symmetry. The former causes the MX$_2$ MLs to become semiconductors with a direct band gap of $\sim 2.0$ eV. Therefore, the MX$_2$ MLs are promising materials for, e.g., electro-optical devices with efficient light emission$^7$ and field effect transistors with high on-off ratios$^8$. The broken inversion symmetry, on the other hand, makes the MLs to exhibit novel properties of fundamental and technological interest such as band spin-splitting$^{11}$, spin-valley coupling$^{12}$ and piezoelectric property$^{13}$.

Being direct band gap semiconductors with noncentrosymmetry, the MX$_2$ MLs are also expected to show significant second-order nonlinear optical susceptibility [$\chi^{(2)}$], and thus to provide novel applications in optoelectronics such as coherent control of valley- and spin-polarized currents$^{14}$. Indeed, second-harmonic (SH) generation in the MoS$_2$ MLs has been observed in recent experiments$^{15-17}$, although the reported $\chi^{(2)}$ modulus under 810 nm laser illumination varies as much as three orders of magnitude. To interpret the measured $\chi^{(2)}(\omega)$ spectra and also to help search and design new MX$_2$ MLs with better nonlinear optical properties, ab initio material specific calculations of the $\chi^{(2)}$ would be needed. However, in contrast to the recent extensive theoretical investigations of the electronic, transport and linear optical properties of the MX$_2$ MLs, only theoretical calculations of $\chi^{(2)}$ for the MoS$_2$ ML$^{18,19}$ have been reported.

In this work, we systematically investigate the second-order nonlinear optical susceptibility and also the linear electro-optical coefficient of all the four MX$_2$ (M = Mo, W; X = S, Se) MLs and trilayers (TLs). Our main goal is to find out the features and magnitude of the SH generation and linear electro-optical coefficients of the MX$_2$ MLs in order to foresee their potential applications in nonlinear optical and electro-optical devices such as...
TABLE I. Experimental structural parameters for the MX$_2$ monolayers: In-plane lattice constant $a$, $z$-coordinate ($z$) of the X atoms, and effective thickness $h$ of one MX$_2$ ML. $h$ is simply taken as half of the lattice constant $c$ of the corresponding bulk MX$_2$.

| MX$_2$ | MoS$_2$$^a$ | MoSe$_2$$^a$ | WS$_2$$^b$ | WSe$_2$$^b$ |
|--------|-------------|-------------|-----------|-------------|
| $a$ (Å) | 3.160       | 3.299       | 3.152     | 3.282       |
| $2z$ (Å) | 3.172       | 3.338       | 3.142     | 3.341       |
| $h$ (Å)  | 6.147       | 6.469       | 6.162     | 6.481       |

$^a$ Reference 20.
$^b$ Reference 21.

II. THEORY AND COMPUTATIONAL METHOD

The crystal structure of the MX$_2$ MLs is illustrated in Fig. 1(a). The transition metal M atom sits on $(a/3, 2a/3, 0)$ in the central plane, sandwiched by the chalcogen X atoms on $(2a/3, a/3, \pm z)$. Here $a$ is the in-plane lattice constant and $z$ is the distance between the X and M atomic planes (Fig. 1). To examine the effect of the interlayer interaction on the electronic and optical properties of the MX$_2$ multilayers, we also consider the MX$_2$ TLs [see Fig. 1(b)]. Note that the MX$_2$ bilayers and indeed all the even number MX$_2$ multilayers do not exhibit the second-order nonlinear optical response because they possess the spatial inversion symmetry. In the MX$_2$ TLs, the three M atoms are located at $(a/3, 2a/3, 0)$ and $(2a/3, a/3, \pm h)$ while the six X atoms sit on $(a/3, 2a/3, -h \pm z)$, $(2a/3, a/3, \pm z)$, and $(a/3, 2a/3, h \pm z)$. In the present calculations, the slab-supercell approach is adopted and a large vacuum slab of more than 18 Å that separate the neighboring slabs is added in the direction perpendicular to the atomic planes. The experimental structural parameters of the corresponding bulk crystals$^{20,21}$ (see Table I) are used in the present calculations. The effective thickness $h$ of one MX$_2$ ML is simply taken as half of the lattice constant $c$ of the MX$_2$ crystal. The effective thickness of the MX$_2$ trilayers is $3h$.

SH generation, sum-frequency generation, electro-optical switch, and electro-optical modulator. We also investigate the effects of the interlayer interaction on the second-order nonlinear optical properties by performing the \textit{ab initio} calculations for the MX$_2$ TLs.

The rest of this paper is organized as follows. In Sec. II, the theoretical approach and computational details are briefly described. In Sec. III, the calculated band structure, density of states and second-order nonlinear optical susceptibility of the MX$_2$ MLs and TLs are presented. Finally, a summary is given in Sec. IV.

A. Band structure calculation

The present first-principles calculations are based on the density functional theory with the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhoff$^{22}$. The accurate full-potential projector-augmented wave (PAW) method$^{23}$, as implemented in the VASP package$^{24}$, is used. A large plane-wave cut-off energy of 400 eV is used throughout. The self-consistent band structure calculations are performed with a dense $k$-point grid of $20 \times 20 \times 1$. For comparison, we also perform the same first-principles calculations for bulk MX$_2$ crystals. A $k$-point grid of $20 \times 20 \times 5$ is used for the bulk calculations.

B. Calculation of the optical properties

In this work, the linear optical dielectric function and nonlinear optical susceptibility are calculated based on the linear response formalism with the independent-particle approximation, as described before$^{25,26}$. The imaginary part $[\varepsilon''(\omega)]$ of the dielectric function due to direct interband transitions is calculated from the final self-consistent electronic band structure by using the Fermi golden rule$^{25,26}$. The real part $[\varepsilon'(\omega)]$ of the dielectric function is obtained from $\varepsilon''(\omega)$ by a Kramer-Kronig transformation

$$\varepsilon'(\omega) = 1 + \frac{2}{\pi} \text{P} \int_0^{\infty} d\omega' \frac{\omega'^2 \varepsilon''(\omega')}{\omega'^2 - \omega^2}.$$  \hspace{1cm} (1)

Given the complex dielectric function $(\varepsilon' + i\varepsilon'')$, all other linear optical properties such as reflective index, reflectivity and absorption spectrum can be calculated.

Following previous nonlinear optical calculations$^{25,27}$, the imaginary part $[\chi_{abc}^{(2)}(-2\omega, \omega, \omega)]$ of the second-order optical susceptibility due to direct interband transitions is obtained from the self-consistent electronic band
structure by using the expressions already given elsewhere\textsuperscript{25,27}. The real part of the second-order optical susceptibility is then obtained from $\chi'^{(2)}_{abc}$ by a Kramer-Kronig transformation

$$\chi'^{(2)}(-2\omega, \omega, \omega) = \frac{2}{\pi} \text{P} \int_0^\infty d\omega' \omega' \chi'^{(2)}(2\omega', \omega', \omega') \omega'^2 - \omega^2. \quad (2)$$

The linear electro-optic coefficient $r_{abc}(\omega)$ is connected to the second-order optical susceptibility $\chi'^{(2)}_{abc}(-\omega, \omega, 0)$ through the relation\textsuperscript{28}

$$\chi'^{(2)}_{abc}(-\omega, \omega, 0) = -\frac{1}{2} n_0^2(\omega) n_0^2(\omega) r_{abc}(\omega) \quad (3)$$

where $n_0(\omega)$ is the refraction index in the $a$-direction. Therefore, in the zero frequency limit,

$$r_{abc}(0) = -\frac{2}{n_0^2(0) n_0^2(0)} \lim_{\omega \to 0} \chi'^{(2)}_{abc}(-2\omega, \omega, \omega) \quad (4)$$

Furthermore, for the photon energy $\hbar \omega$ well below the band gap the linear electro-optic coefficient $r_{abc}(\omega) \approx r_{abc}(0)$ because $\chi'^{(2)}_{abc}(-2\omega, \omega, \omega)$ and $n(\omega)$ are nearly constant in the very low frequency region\textsuperscript{25,27}.

In the present calculations, the $\delta$-function in the Fermi golden rule formulas\textsuperscript{25,27} is approximated by a Gaussian function

$$\delta(x) \approx \frac{1}{\sqrt{\pi} \Gamma} e^{-x^2/\Gamma^2}, \quad (5)$$

with $\Gamma = 0.1 \text{ eV}$. To obtain accurate optical properties, the $k$-point grid used is much denser than that used in the self-consistent band structure calculations (Sec. II.A). We use a $k$-point grid of $130 \times 130 \times 1$ for the MX$_2$ MLs and of $100 \times 100 \times 1$ for the MX$_2$ TLs. Furthermore, to ensure that $\epsilon'$ and also $\chi'^{(2)}$ calculated via Kramer-Kronig transformation are accurate, at least twenty five energy bands per atom are included in the present optical calculations. The unit cell volume $\Omega$ of the MX$_2$ MLs and TLs in the slab-supercell approach is not well defined. Here we use an effective unit cell volume $\Omega$ that is given by the area of the in-plane unit cell times the effective thickness of the MX$_2$ ML ($h$) or TL ($3h$) (Fig. 1).

In this work, the linear and nonlinear optical properties are calculated based on the independent-particle approximation (IPA), i.e., the quasi-particle self-energy corrections and excitonic effects were neglected. However, these many-body effects on the linear optical properties of 2D systems such as SiC, MoS$_2$ and WSe$_2$ MLs\textsuperscript{29-31} are especially pronounced due to quantum confinement. Nevertheless, accurate \textit{ab initio} calculations of the optical properties including the excitonic effect are usually extremely demanding computationally. Indeed, it was recently demonstrated that a convincing agreement between experimental and theoretical absorption spectra could be achieved in the Bethe-Salpeter exciton approach only when several thousand $k$-points and tens of bands were included in the calculations\textsuperscript{32}. Furthermore, \textit{ab initio} calculations of nonlinear optical properties face another challenge which comes from the complexity of the expression for the correlated nonlinear susceptibility in terms of the electronic band structure, and this makes the full \textit{ab initio} calculations within many-body perturbation theory impractical. Consequently, much simpler approaches such as the real-time propagation\textsuperscript{18} and semiepipirical tight-binding-based model potentials\textsuperscript{26} were adopted in recent calculations of the second-order nonlinear optical susceptibility for the MoS$_2$ ML. In this work, instead, we introduce the so-called scissors correction (SCI) to reduce the errors caused by the neglected many-body effects. This simple approach allows us to carry out a systematic investigation of the nonlinear optical properties of all the four MX$_2$ materials in both the ML and TL structures, using large numbers of $k$-points and conduction bands which are needed to ensure that the theoretical results are numerically reliable. In Fig. 2, we display the $|\chi'^{(2)}|$ of the single BN sheet calculated within the IPA\textsuperscript{18,27}, and also the real-time approach to the excitonic effect\textsuperscript{18}. It is clear from Fig. 2 that all the principal features in the $|\chi'^{(2)}|$ spectrum from the real-time approach\textsuperscript{27} are more or less reproduced by the IPA calculation\textsuperscript{26} except the red-shift of the peak energy positions. Furthermore, away from the excitonic resonances, the values of $|\chi'^{(2)}|$ from both approaches are rather close. For example, the $|\chi'^{(2)}(0)|$ values from Refs. 27 and 18 are 40.7 and 41.2 pm/V, respectively. A scissors correction to the IPA with an energy shift of 1.34 eV brings the two spectra in good agreement, \textit{albeit}, with the $|\chi'^{(2)}|$ magnitude from the present IPA+SCI being less than half of that from the real-time approach (see Fig. 2). Note that the recent experimental estimation\textsuperscript{16} of $|\chi'^{(2)}|$ of $\sim$20.8 pm/V at 1.53 eV is nearly identical to that of $\sim$20.7 pm/V from the present IPA+SCI calculation, while, in contrast, it is much smaller than that from the real-time
approach (∼92 pm/V)\cite{18} and the IPA calculation\cite{27} (68 pm/V).

III. RESULTS AND DISCUSSION

A. Band structures of MX\textsubscript{2} Monolayers

The calculated band structures as well as total and site-decomposed densities of states of the four MX\textsubscript{2} MLs studied here are displayed in Fig. 3, and the corresponding band gaps are listed in Table II. Figure 3 shows that all the four MX\textsubscript{2} MLs are semiconductors with a direct band gap at the K symmetry point, as found in previous optical experiments on the MoS\textsubscript{2} MLs\cite{27}. Furthermore, Table II suggests that the magnitude of the band gaps are in the visible light wavelengths and thus the direct band gaps can be observed in photoluminescence experiments\cite{32,33}. Therefore, all these four MX\textsubscript{2} MLs have promising potentials for electronic, optical and electro-optical devices. We note that the calculated band structures of the MX\textsubscript{2} MLs (Fig. 3) are in good agreement with previous GGA and local density approximation (LDA) calculations\cite{8,9}.

Since all the MX\textsubscript{2} MLs have the same crystalline structure and are isoelectronic, their electronic band structures are rather similar, as Fig. 3 shows. In particular, the left panels in Fig. 3 show that all of them have the M\textit{d}\textsubscript{z}\textsuperscript{2}-dominated top valence band with certain X\textit{p}\textsubscript{z} component and also the strongly X\textit{p}-orbital and M\textit{d}-orbital hybridized lower valence bands. Thus the bonding of these compounds is mainly of covalent type. The lower conduction bands of the MX\textsubscript{2} MLs are M\textit{d}-dominant bands with significant X\textit{p}-orbital contributions. Therefore, the optical transitions would be dominated by the transitions from the valence states of chalcogen\textit{p}-orbital and metal\textit{d}-orbital hybrid to the conduction states of metal\textit{d} character.

Nonetheless, there are minor differences among the band structures of the MX\textsubscript{2} MLs. Table II shows that the band gap decreases as the S atoms are replaced by the Se atoms. On the other hand, when the chalcogen atoms are kept, the band gap becomes slightly larger if the Mo atoms are substituted by the W atoms. Furthermore, for the MoS\textsubscript{2} and MoSe\textsubscript{2} MLs, there is a gap in the conduction band at around 5 eV while this gap is absent in the WS\textsubscript{2} and WSe\textsubscript{2} MLs (Fig. 3). Finally, the WS\textsubscript{2} ML has the largest band gap while the MoSe\textsubscript{2} ML has the smallest one.

B. Second-order nonlinear optical susceptibility of MX\textsubscript{2} Monolayers

Bulk MX\textsubscript{2} crystals have zero second-order nonlinear susceptibility since their symmetry class is D\textsubscript{6h} with the spatial inversion symmetry. However, the MX\textsubscript{2} MLs have the D\textsubscript{3h} symmetry without the inversion symmetry.

Therefore, the MX\textsubscript{2} MLs would exhibit the second-order nonlinear optical response with nonzero susceptibility elements of $\chi^{(2)}_{xxy} = \chi^{(2)}_{yxx} = \chi^{(2)}_{yxy} = -\chi^{(2)}_{xyy}$, as dictated by the D\textsubscript{3h} symmetry. Here subscripts $x$ and $y$ denote the two Cartesian coordinates in the MX\textsubscript{2} ML plane. Our theoretical results are consistent with this symmetry consideration, demonstrating that our numerical method and calculations are qualitatively correct. The calculated real and imaginary parts as well as the modulus of the imaginary part of $\chi^{(2)}_{xxy}(-2\omega, \omega, \omega)$ are shown in Fig. 4.
It is well known that the band gaps from both the LDA and GGA calculations are usually smaller than that measured in optical experiments. For example, Table II shows that the calculated band gaps of bulk MX$_2$ are smaller than the measured values by about 20~30%. It is clear from the Fermi golden rule formulas that the smaller the size of the energy gap between the initial and final states on each $k$-point in the Brillouin zone, the larger the magnitude of the second-order nonlinear susceptibility and dielectric function. In other words, the optical calculations using a GGA band structure may overestimate the second-order nonlinear susceptibility and dielectric function. To reduce this overestimation, we repeat the optical calculations using the scissors corrected band structures. In the present scissors corrections, we use the energy differences ($\Delta E_{k}^{\text{bulk}}$) between the measured (by optical absorption) direct band gaps of bulk MX$_2$ crystals and calculated energy gaps of the MX$_2$ MLs at the $k$-point (see Table II) to shift the conduction bands upwards. The optical band gap of some MX$_2$ MLs has been measured by photoluminescence (PL) experiments. However, the PL measurement usually underestimates the band gap. On the other hand, a recent optical absorption experiment showed that the band gap of the MoS$_2$ ML is the same as the direct band gap of bulk MoS$_2$ (1.88 eV). Therefore, we expect that the band gaps of the MX$_2$ MLs are close to the direct band gaps of the corresponding bulk MX$_2$ crystals. The real and imaginary parts as well as the absolute value of the
TABLE III. Calculated static refraction index ($n_x$), second-order optical susceptibility \(\chi^{(2)}(0)\), \(\chi^{(2)}(1.53\text{ eV})\) and linear electro-optical coefficient \(r_{xx}^{(1)}\) of the MX\(_2\) MLs (a) and TLs (b) using the band structures without (IPA) and with (SCI) scissors correction. The available experimental values (exp.) are also listed.

|          | MoS\(_2\) | MoSe\(_2\) | WS\(_2\) | WSe\(_2\) |
|----------|-----------|-----------|----------|-----------|
| (a) MLs  |           |           |          |           |
| \(n_x\)  | 3.92      | 3.91      | 3.76     | 3.75      |
| \(\chi^{(2)}(0)\) (pm/V) | IPA 3.65  | 3.64      | 3.48     | 3.51      |
| SCI      | 109       | 128       | 93       | 132       |
| \(|\chi^{(2)}(1.53)\) (pm/V) | IPA 847   | 558       | 819      | 227       |
| SCI      | 573       | 449       | 712      | 163       |
| \(r_{xx}^{(0)}/n\) (0)(pm/V) | exp. 322 | exp. 10\(^3\) | 5000 | exp. 4 | 322 | 16 \(\times 10^3\) |
| (b) TLs  |           |           |          |           |
| \(n_x\)  | 3.96      | 3.93      | 3.79     | 3.78      |
| \(\chi^{(2)}(0)\) (pm/V) | IPA 3.69  | 3.55      | 3.51     | 3.54      |
| SCI      | 49        | 58        | 43       | 58        |
| \(|\chi^{(2)}(1.53)\) (pm/V) | IPA 257   | 158       | 257      | 144       |
| SCI      | 164       | 180       | 267      | 166       |
| \(r_{xx}^{(0)}(0)/n\) (pm/V) | exp. 80   | 17 \(\times 10^3\) | exp. 322 | 16 \(\times 10^3\) | 16 \(\times 10^3\) |
| (c) TLs vs. MLs |           |           |          |           |
| \(\chi^{(2)}_{TL}/\chi^{(2)}_{ML}(0)\) | IPA 0.35  | 0.34      | 0.34     | 0.33      |
| SCI      | 0.35      | 0.34      | 0.34     | 0.33      |
| \(\chi^{(2)}_{TL}/\chi^{(2)}_{ML}(1.53)\) | IPA 0.30  | 0.28      | 0.31     | 0.63      |
| SCI      | 0.28      | 0.40      | 0.39     | 1.02      |
| exp.     | 0.25 \(\times 10^3\) | 0.21 \(\times 10^3\) | 0.60 \(\times 10^3\) | 0.92 \(\times 10^3\) |

\(a\) Experimental value from Ref. 16.
\(b\) Experimental value from Ref. 35.
\(c\) Experimental value from Ref. 16.
\(d\) Experimental value from Ref. 35.

imaginary part of \(\chi^{(2)}_{xx}(-2\omega, \omega, \omega)\) of the MX\(_2\) MLs calculated from the scissors corrected band structures, are displayed in Fig. 5. Figures 4 and 5 show that although the line shapes of the SH generation coefficient and dielectric function from the two calculations are nearly identical, the magnitude of these optical quantities from the scissors correction calculations gets reduced by about 25\% and the peak positions is shifted upwards by about \(\Delta E_{\text{bulk}}\) (see also Table III). In the rest of this paper, we will concentrate mainly on the optical properties calculated with scissors corrections which should give rise to more accurate optical quantities.

Figure 5 indicates that the \(\chi^{(2)}_{xx}(-2\omega, \omega, \omega)\) of the MX\(_2\) MLs are large in the entire range of optical photon energy, in the sense that they are comparable to that of GaAs\(\text{As}\), an archetypical nonlinear optical semiconductor. We note that these SH susceptibilities are several times larger than that of the graphitic BN sheet\(\text{BN}\). Furthermore, \(\chi^{(2)}_{xx}(-2\omega, \omega, \omega)\) of the MX\(_2\) MLs is purely dispersive for photon energy being smaller than half of the direct band gap, because the absorptive part of \(\chi^{(2)}_{xx}\) becomes nonzero only for photon energy larger than half of the band gap [see Table II, Figs. 4(a) and 5(a)]. Table III also indicates that low frequency linear electro-optic coefficients of these monolayers are also large. All these suggest that the MX\(_2\) MLs may have application potentials in second order nonlinear optical devices and linear electro-optic modulators.

In general, the static SH susceptibility is small for a MX\(_2\) ML with a large band gap. Table III shows that this is indeed the case, except that the WSe\(_2\) ML has the largest SH generation coefficient but does not have the smallest band gap. This may be explained by the fact that the fifth conduction band of the WSe\(_2\) ML is lower than the MoSe\(_2\) ML, and this may give rise to a larger static value via the Kramers-Kronig transformation.

To analyze the prominent features in the calculated \(\chi^{(2)}(\omega)\) spectrum in a MX\(_2\) ML, it is helpful to compare the magnitude of the imaginary part of \(\chi^{(2)}(\omega)\) with the absorptive part of the corresponding dielectric function \(\varepsilon'(\omega)\). Figures 4 and 5 show that the peaks in the \([\varepsilon''(\omega)/\varepsilon'(\omega)]\) in the energy range from the absorption edge of \(\varepsilon'\omega/2\) to the absorption edge of \(\varepsilon''\omega/2\) can be correlated with the features in the \(\varepsilon''\omega/2\) spectra, indicating that they are due to two-photon resonances. The peaks above the absorption edge of \(\varepsilon''\omega/2\), on the other hand, can be related to the features in either the \(\varepsilon''\omega/2\) or \(\varepsilon''\omega/2\) or both, suggesting that they can be caused by both double-photon and single-photon resonances. Due to the contributions from both one and two photon resonances, the spectra oscillate rapidly in this region and diminish gradually at higher photon energies.

C. Band structures of MX\(_2\) Trilayers

In order to investigate the effects of the interlayer interaction on the optical properties of the MX\(_2\) multilayers, we also calculate the electronic structure as well as linear and nonlinear optical properties of the MX\(_2\) TLs. The calculated band structures of the MX\(_2\) TLs are shown in Fig. 6. If there were no interlayer interaction, the band structure of a MX\(_2\) TL should be identical to that of the corresponding ML, except that the energy bands are now three fold degenerate. Nevertheless, the degenerated energy bands in the MX\(_2\) TL are split due to the weak interlayer interaction. Overall, the band structure of the MX\(_2\) TL is similar to that of the MX\(_2\) ML except that the number of bands is tripled (see Figs. 3 and 6), because the band splittings due to the interlayer interaction are generally not large (Fig. 6). This similarity is especially clear in the calculated density of states for the MX\(_2\) ML and TL (see Figs. 3 and 6). Significantly, however, these band splittings due to the interlayer interaction lower the conduction bands near the \(\Sigma\) point along the K-\(\Gamma\) sym-
FIG. 5. (a) Real and imaginary parts as well as (b) the absolute value of the imaginary part of the second-order susceptibility $\chi^{(2)}_{xxy}$ of the MX$_2$ MLs calculated from the scissors corrected band structures. (c) Imaginary part $\varepsilon''$ of the corresponding dielectric function of the MX$_2$ MLs.

metry line to below the bottom of the conduction band at the K point, and also raise the top valence band at the Γ point to above the top of the valence bands at the K point (see Fig. 6). Therefore, all the four MX$_2$ TLs are semiconductors with an indirect band gap. And the band gaps in the MX$_2$ TLs are smaller than those of the MX$_2$ MLs by as much as 0.7 eV (see Table II). Interestingly, the direct energy gap at the K point is hardly affected by the interlayer interaction, and it decreases only slightly (within 0.1 eV) from the MLs to TLs (Table II). We note that the band structures of the MX$_2$ TLs shown in Fig. 6 are very similar to the band structures of the MX$_2$ multilayers reported before. The features that distinguish the MoX$_2$ MLs from the WX$_2$ MLs are still present in the MX$_2$ TLs. For example, there is a small energy gap at about 5 eV in the MoX$_2$ TLs which is absent in the WX$_2$ TLs (Fig. 6).

D. Second-order nonlinear optical susceptibility of MX$_2$ Trilayers

As for the MX$_2$ MLs, we calculate the linear and nonlinear optical properties of the MX$_2$ TLs by using both the GGA and scissors corrected band structures. Since there is no reported measurement on the direct energy gap ($E_K$) at the K point of the MX$_2$ TLs and also the calculated $E_K$ for bulk MX$_2$ and the MX$_2$ TLs are close (Table II), we simply use the differences ($\Delta E_{\text{bulk}}^K$) between the measured and calculated $E_K$ for bulk MX$_2$ for the scissors corrections. As mentioned before, the line shapes of the SHG susceptibility and dielectric function from the two types of calculations are nearly identical, although the magnitude of these optical quantities from the scissors correction calculations is reduced by about 25% (see Table III) and the peak positions are shifted upwards by about $\Delta E_{\text{bulk}}^K$. Therefore, here we display only the spectra of the SH susceptibilities and dielectric functions obtained from the scissors corrected band structures in Fig. 7.

All the MX$_2$ multilayers with an odd number of MLs belong to the D$_{3h}$ symmetry class. Therefore, their nonzero elements of the SH susceptibility tensor are the same as that of the MX$_2$ MLs. The results of our nonlinear optical calculations are consistent with this symmetry consideration. Figure 6 shows that the SH generation coefficients $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ are still significant in the entire optical frequency range. Figure 6 also indicates that, as in the case of the MX$_2$ MLs, the absorption edge of $\chi^{(2)}_{xxy}(\omega)$ and $\varepsilon''(\omega/2)$ is at half of the energy gap at the K point for the MX$_2$ TLs, due to the two photon inter-band transitions at the K point. Therefore, the $\chi^{(2)}_{xxy}(\omega)$ of the MX$_2$ TLs are purely dispersive (i.e., lossless) for photon energy below half of the energy gap at the K point. We also find that the absorption edge of the imaginary part of the $\varepsilon''(\omega)$ is equal to the energy gap at the K point.
due to one photon inter-band transition. Both single and double photon resonances occur above the energy gap at the K point in the MX$_2$ trilayers, resulting in rapid oscillations in the $\chi^{(2)}$ spectra which gradually diminish in the high photon energy region.

Figures 5 and 7 clearly show that the SH susceptibilities of the MX$_2$ TLs are generally smaller than that of the MX$_2$ MLs, although their line shapes look rather similar. In fact, if there were no interlayer interaction, the SH susceptibility of a MX$_2$ TL would be 1/3 of that of the corresponding MX$_2$ ML. This is because the contributions from two MLs in the TL would cancel each other but the effective unit cell volume were tripled. Table III shows that the ratio of the static values of the SH generation coefficients between the TLs and MLs varies in the range of 0.28–0.35, being indeed close to 1/3. The slight deviations from 1/3 are due to the weak interlayer interaction. For the incident laser beams with a wavelength of 810 nm wavelength (or 1.532 eV photon energy), the ratio can deviate more significantly from 1/3 and it is especially so for the WSe$_2$ ML and TL (Table III). This may be expected because 1.532 eV falls within the regime of mixed single and double photon resonances where not only the magnitude of the SH susceptibility gets reduced but also the energy positions of the peaks shift as one moves from the ML to TL (see Figs. 5 and 7).

E. Comparison with previous theoretical calculations and experiments

Theoretical calculations of SH generation in the MoS$_2$ ML using an ab initio real-time approach and also a semi-empirical tight-binding method have been reported recently. The $|\chi^{(2)}|$ spectra calculated previously within the IPA are reproduced in Fig. 8(a) for comparison with the present calculation. Figure 8(a) indicates that the $|\chi^{(2)}|$ spectra from the previous and present ab initio IPA calculations agree quite well especially for the photon energy above 1.8 eV. Below 1.8 eV, the $|\chi^{(2)}|$ spectrum from the present calculation has a much larger magnitude and also have an additional peak located at $\sim$ 1.7 eV. The much broad features in the $|\chi^{(2)}|$ spectrum from the previous ab initio calculations could be caused by much fewer k-points (a k-point mesh of $21 \times 21 \times 1$) and a larger broadening of 0.2 eV used in Ref. The $|\chi^{(2)}|$ spectrum from the previous tight-binding calculation also agrees rather with the present calculation except that below 1.3 eV. The much sharper features in this previous calculation could be due to a much smaller broadening of 0.03 eV used there. The $|\chi^{(2)}|$ spectra for the MoS$_2$ ML calculated previously with electron-hole interaction taken into account are reproduced in Fig. 8(b). Figure 8(b) shows that the $|\chi^{(2)}|$ spectra from the previous real-time approach and present IPA+SCI calculations agree rather well in both shape and magnitude except that below 1.4 eV. Note that the $|\chi^{(2)}|$ spectra from the previous ab initio calculations without and with inclusion of electron-hole interaction look quite similar [see Figs. 8(a) and 8(b)]. This suggests that the pronounced excitonic peaks in the linear optical spectra such as optical absorption might have largely been washed out in the second-order nonlinear optical susceptibility, being consistent with the result in Ref. The $|\chi^{(2)}|$ spectrum from the previous tight-binding calculation with the excitonic effect included would also look quite similar to the present IPA+SCI calculation if the present $|\chi^{(2)}|$ spec-
FIG. 7. (a) Real and imaginary parts as well as (b) the absolute value of the imaginary part of the second-order susceptibility $\chi^{(2)}_{xy}$ of the MX$_2$ trilayers calculated from the scissors corrected band structures. (c) Imaginary part $\varepsilon''$ of the corresponding dielectric function of the MX$_2$ trilayers.

Trum is blue-shifted by about 0.2 eV. However, the magnitudes of the two spectra differ by about five times. Nevertheless, this five-fold increase in the magnitude of $|\chi^{(2)}|$ due to the inclusion of electron-hole interaction is not seen in the previous ab initio real-time approach.

Three groups recently reported observation of SH generation in the MoS$_2$ multilayers. SH generation in WS$_2$ and WSe$_2$ multilayers were also reported. One of the experiments reported that, at 810 nm wavelength of Ti:sapphire laser, the $|\chi^{(2)}|$ of mechanically exfoliated MoS$_2$ ML is as large as $\sim 10^5$ pm/V and for triangular flakes of the MoS$_2$ ML fabricated by chemical vapor deposition is $5 \times 10^4$ pm/V. The former value is about 170 times larger than the SCI theoretical $|\chi^{(2)}|$ value of $\sim 573$ pm/V and the latter value is also about 9 times larger than our SCI value (Table III). In contrast, in another recent experiment, the $|\chi^{(2)}|$ value of the MoS$_2$ ML measured at 810 nm wavelength is about 320 pm/V, being about half of our SCI value (Table III). In a more recent experiment, the SH generations of the MoS$_2$ ML and TL were measured for a range of photon energy, and these experimental spectra are plotted in Fig. 8, together with the theoretical results. Figure 8(a) indicates that the experimental $|\chi^{(2)}|$ spectrum for the MoS$_2$ ML has a line shape that agrees rather well with all three IPA theoretical $|\chi^{(2)}|$ spectra, albeit with a much smaller magnitude. The experimental $|\chi^{(2)}|$ spectrum also agrees well in shape with the result of the tight-binding calculation that included the electron-hole interaction, although the peak in the experimental spectrum appears to be red-shifted by 0.1 eV relative to the present SCI calculation and also previous ab initio real-time approach to the excitonic effect. However, again, the experimental $|\chi^{(2)}|$ spectrum has a much smaller magnitude. For example, the experimental $|\chi^{(2)}|$ value at 1.532 eV is $\sim 82$ pm/V, being about seven (ten) times smaller than our theoretical SCI (IPA) value (Table III). Finally, Fig. 8(c) indicates that the experimental $|\chi^{(2)}|$ spectrum for the MoS$_2$ TL roughly agrees in shape the present SCI spectrum.

The fact that the measured $|\chi^{(2)}|$ values at 1.532 eV photon energy vary as much as three orders of magnitude, indicates the difficulties in accurate experimental deductions of SH generation coefficients of the MX$_2$ MLs which depend on a number of experimental parameters. On the other hand, we note that 1.532 eV photon energy falls in the energy range of mixed single and double photon resonances, as mentioned before, and the magnitude of $|\chi^{(2)}|$ can change as much as two orders of magnitude in this region (Fig. 8). Worse still, 1.532 eV photon energy is close to the energy position of a sharp peak in the $|\chi^{(2)}|$ spectra (Fig. 8). Consequently, the peak position of different samples prepared by different methods could vary, and this variation of the peak position could give rise to very different measured $|\chi^{(2)}|$ values at 810 nm wavelength. Obviously, it would be helpful if the $|\chi^{(2)}|$
spectra are measured over a range of photon energy and then are compared with each other and also with the theoretical results. These large discrepancies between the experiments and also between the experiments and theoretical results suggest that further experiments on these interesting ML materials would be desirable.

As mentioned before, the SH susceptibility of the MX₂ TLs is generally reduced with respect to that of the MX₂ MLs. This reduction factor should be 1/3 if there were no interlayer interaction. At 810 nm wavelength, the calculated ratio of the SH susceptibility of the MoS₂ TL to the ML (0.28) deviates slightly from 1/3 but agrees rather well with the experimental values of 0.25 and 0.21 (Table III). The pronounced deviation of the ratio from 1/3 is predicted to occur in the WSe₂ ML and TL and is consistent with the experimental results (see Table III). However, the measured ratio (0.60) between the WS₂ TL and the ML is significantly larger than the theoretical result (0.39) (Table III). Nonetheless, given that the experimental χ⁽²⁾ values at this wavelength could vary a couple of orders of magnitude (Table III), we believe that this level of the agreement in the χ⁽²⁾ ratio between the experiments and our theoretical results is rather satisfactory.

IV. SUMMARY

We have carried a systematic ab initio investigation of the second-order nonlinear optical properties of the MX₂ (M=Mo,W and X=S, Se) MLs and TLs within the GGA plus scissors correction. We have used the accurate full-potential PAW method. We find that the second-order nonlinear optical susceptibility [χ⁽²⁾] of the MX₂ MLs in the entire optical photon energy range are large, being comparable to that of GaAs. The calculated linear electro-optical coefficients in the low photon energy limit are also significant. This shows that the four two-dimensional MX₂ semiconductors have promising potentials in, e.g., ultrathin second-harmonic and sum frequency generation devices, electro-optical switches and light signal modulators. The χ⁽²⁾ spectra of the MX₂ TLs are similar to the corresponding MX₂ MLs, albeit with the magnitude reduced roughly by a factor of 3. The minor deviations from the 1/3 ratio are caused by the weak interlayer coupling of the electronic states. The prominent features in the calculated χ⁽²⁾ spectra of the MX₂ multilayers have been successfully correlated with the peaks in the imaginary part of the corresponding optical dielectric function ε(ω) in terms of single and double photon resonances. The theoretical χ⁽²⁾ spectra of the MX₂ multilayers are compared with the available experimental data, and the large discrepancies of as much as three orders of magnitude among the measured χ⁽²⁾ data are analyzed in terms of the present theoretical results. We hope that this work will stimulate further experimental investigations into the second-order nonlinear optical responses and related properties of these fascinating few-layer MX₂ ultrathin films.

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