Electronic and optical properties of monolayer tin diselenide: The effect of doping, magnetic field, and defects

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A parametrized tight-binding (TB) model based on the first-principles calculations is developed for monolayer tin diselenide (SnSe2). The truncated model is derived from six maximally localized Wannier orbitals, which accurately describe the quasiparticle electronic states of SnSe2 over a wide energy range. Based on this TB model, we investigate the effects of doping, magnetic field, and point defects on the electronic and optical properties of SnSe2. Our numerical calculation shows that the ambipolar optical absorption can be effectively modulated by the type of injected carriers. The plasmonic spectrum of doped SnSe2 consists of standard intraband two-dimensional excitation and interband transition modes, which damp into electron-hole pairs with different speed. In the presence of perpendicular magnetic field, monolayer SnSe2 behaves like traditional two-dimensional electron gas with equally spaced Landau-level spectrums and magneto-optical conductivity. Moreover, the appearance of point defects in the sample would generate sharp midgap states, activating new transitions in the optical spectrum. Our proposed TB model can be used for further exploring the electronic and optical properties of large-scale SnSe2 with complex structures beyond the first-principles calculations.

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I. INTRODUCTION

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have been receiving continuous interest in the last few years because of their potential applications in electronic and optical devices [1–3]. More interestingly, their metastable 1T phases are reported to have some exotic properties [4,5]. Thus, the main group metal dichalcogenide (MDC) family, whose ground state holds the same atomic configuration of 1T TMDCs, has attracted much attention recently [6–9]. These layered MDCs are highly abundant in earth, environment-friendly, and of low toxicity [10–12]. Particularly, the 1T structure endows them with unique anisotropic thermal transport properties [13,14]. One typical example is tin diselenide (SnSe2), whose figure of merit (ZT) value reaches 2.95 (0.68) along a (c) axis, much higher than that in 2H- and 1T-TMDCs [15,16]. In addition to the high thermoelectric performance, they also exhibit excellent electronic and optical properties. Field effect transistor made of few-layer SnSe2 is reported to have high current on/off ratio $(10^5)$ and mobility $(85 \text{ cm}^2\text{V}^{-1}\text{s}^{-1})$ [17,18]. When it is combined with other 2D materials like WSe2 and black phosphorus to form van der Waals (vdW) heterostructures [19–21], negative differential resistance and good subthreshold swing phenomenon are observed. The large work function and band-gap alignment with WSe2 make it an ideal candidate as intercalation in 2D heterojunctions for high efficient tunneling field effect transistors (TFETs) [20]. Very recently, gate-induced superconductivity is demonstrated in 1T SnSe2 through the ionic liquid gating technique [22]. Thanks to its high specific surface area, ultrathin SnSe2 is widely investigated as a photocatalyst and light-harvesting material absorber for photochemical reactions and optoelectronic devices as well [23,24]. Impressively, the SnSe2-based photodetector has a high responsivity of $1.1 \times 10^3 \text{ A W}^{-1}$ and a high external quantum efficiency (EQE) of $2.61 \times 10^5\%$ [23]. Most of these exciting results are concluded from high-quality layered SnSe2, which now can be obtained by chemical vapor deposition (CVD) [23] and physical mechanical exfoliation from the bulk crystals [24] in experiments. However, how to better describe the physical phenomena of realistic SnSe2 system comparable to experimental samples is still under exploring.

Theoretically, the physical properties of pristine monolayer SnSe2 have been investigated by first-principles calculations [16,25,26]. Motivated by a recent work on the conductor-insulator-superconductor transition in twisted bilayer graphene with doping [27], we are eager to know the effect of external environment on the physical properties of realistic SnSe2. However, it is not feasible to perform first-principles calculations, as a result of the high computational cost. On the other hand, many-body effects are crucial for 2D SnSe2 due to the depressed screening and reduced dimensionality of suspended 2D semiconductors [28,29]. It is thus helpful to develop an effective Hamiltonian for monolayer SnSe2 based on the quasiparticle energy, to further study its physical properties with doping, external magnetic field, and disorder.

In this paper, we derive a tractable tight-binding (TB) model for monolayer SnSe2 within the $GW$ approximation,
The model describes the quasiparticle electronic states over a wide spectrum region, which is validated by good consistency with the band structure and density of states from first-principles calculations. Based on the proposed TB model, we study the ambipolar optical conductivity and plasmon spectrum properties of monolayer SnSe$_2$. Then, we investigate the effects of perpendicular magnetic field and disorder on the density of states and optical conductivity. Our proposed TB model paves a way to consider real SnSe$_2$ systems with disorder and external magnetic field.

The remainder of this paper is organized as follows: In Sec. II, the atomic structure and quasiparticle electronic properties of monolayer SnSe$_2$ are calculated by first-principles method. In Sec. III, we propose our simple TB model and analyze the fitting results. In Sec. IV, we study the ambipolar optical conductivity and rich plasmon spectrum of doped monolayer SnSe$_2$. In Sec. V, we investigate the perpendicular magnetic field effects on the density of states and optical conductivity of SnSe$_2$. In Sec. VI, we discuss the effects of point defects on monolayer SnSe$_2$. Finally, we give a summary of this work in Sec. VII.

II. FIRST-PRINCIPLES RESULTS

Unlike traditional TMDCs with $D_{3d}$ space group, monolayer SnSe$_2$ crystallizes in a $1T$-phase structure with $D_{3d}$ point group, as presented in Figs. 1(a) and 1(b). It includes a threefold rotation symmetry axis $C_{3v}$ and a vertical mirror plane $\delta_d$. The optimized lattice parameter $a$ is 3.87 Å, the bond length of Sn-Se is 2.75 Å, and the distance between two Se planes is 3.19 Å. They are in line with previous results [25,30]. The projected band structures of Sn and Se atoms in monolayer SnSe$_2$ are displayed in Figs. 1(d) and 1(e). Monolayer SnSe$_2$ is an indirect-gap semiconductor; the conduction band minimum (CBM) is located at the $M$ point, while the valence band maximum (VBM) is slightly away from the $\Gamma$ point (energy difference $\sim$85 meV). The Perdew, Burke, and Ernzerhof (PBE) calculated indirect band gap between the $\Gamma$ and $M$ points is about 0.78 eV. Our result shows that the presented six bands in low-energy window mainly involve the $s$ and $p$ orbitals of Sn and Se atoms. The first and second valence bands at the $\Gamma$ point are doubly degenerate, with orbital decomposition of the corresponding wave function $|\psi_{\text{VBM}}(\Gamma)\rangle = 0.31 |s_{\text{Se}}\rangle + 0.95 |p_{y}\rangle_{\text{Se}}$. And the wave function of the CBM is $|\psi_{\text{CBM}}(M)\rangle = 0.79 |s_{\text{Sn}}\rangle + 0.54 |p_{y}\rangle_{\text{Se}} + 0.18 |p_{x}\rangle_{\text{Se}} + 0.24 |p_{z}\rangle_{\text{Se}}$.

Considering that density functional theory (DFT) usually underestimates the band gap of semiconductor, we further perform the $GW$ calculation to get a reliable quasiparticle band gap of monolayer SnSe$_2$. Similar to those found in other monolayer 2D semiconductors, such as monolayer hexagonal TMDCs [28] and phosphorene [31], significant self-energy enhancements are observed in SnSe$_2$; at the “single-shot” $G_0W_0$ level, the quasiparticle band gap at $\Gamma$ point of monolayer SnSe$_2$ is increased to be 2.75 eV. Self-consistent $GW$ ($sc-GW$) scheme beyond single-shot calculations has been verified to be necessary for some 2D semiconductors [28]. Hence, we execute one self-consistent update to the Green’s function $G$; the quasiparticle band gap is further increased to be 3.07 eV. More self-consistent steps only slightly change the band gap ($\sim$0.1 eV) and we stop at the sc-$G_1W_0$ level. Finally, the enhanced many-electron effects enlarge the band gaps, but do not alter the dispersion shape. And the energy between the VBM and $\Gamma$ point is shifted by $\sim$77 meV, which is nearly the same as the PBE calculated value. In the following, all our discussions are based on the finalized sc-$G_1W_0$ results.

III. TIGHT-BINDING MODEL

Given that the valence and conduction bands are dominated by $s$ and $p$ orbitals, and that they are separated from other states, it is possible to provide an accurate description of those states in terms of a tractable TB model in the low-energy region. Our parametrization procedure used in this work is based on the formalism of maximally localized Wannier functions (MLWFs), and six orbitals are obtained as the basis for the TB model. A real-space distribution of the MLWFs is shown in Fig. 2, where a combination of three hybrid $sp$-like orbitals localized around Sn and Se atoms, giving rise to six MLWFs per cell on two sublattices. The three orbitals are equivalent with a rotational symmetry of $2\pi/3$, effectively reducing the independent TB parameters.

The resulting nonrelativistic TB model is given by a $6 \times 6$ effective Hamiltonian. The matrix elements of the
The orbitals are represented by the negative part of the Wannier SnSe$_2$ corresponding to the basis of the TB Hamiltonian presented in this work. For clarity, orbitals are shown for one sublattice with one orbital per atom only. The orbitals in the second sublattice are symmetric with respect to the inversion center.

Hamiltonian in real space are

$$H_{\alpha\beta} = \langle \alpha, \mathbf{k} | H | \beta, \mathbf{k} \rangle = \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot \mathbf{R}} \langle \alpha, 0 | H | \beta, \mathbf{R} \rangle = t_{\alpha\beta}(\mathbf{R}) \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot \mathbf{R}},$$

(1)

where $t_{\alpha\beta}$ is the effective hopping parameter describing the interaction between $\alpha$ and $\beta$ orbitals residing at central and neighbor atoms, respectively. To make the model more tractable yet accurate enough, we first discard the hoppings with an interatomic distance larger than 11.62 Å, then ignore hopping parameters with amplitudes $|t| < 20$ meV. The residual hopping parameters are further reoptimized by minimizing the following least-square function:

$$\delta(t) = \sum_{n,k} \frac{\left[ E_{n,k}^{\mathrm{G}_1 W_0}(\{t\}) \right]^2 - \left[ E_{n,k}^{\mathrm{TB}}(\{t\}) \right]^2}{\exp \left[ \left( E_{n,k}^{\mathrm{TB}}(\{t\}) - E_{n,k}^{\mathrm{G}_1 W_0}(\{t\}) \right)^2 \right]},$$

(2)

where $\{t\}$ is the hopping set from Eq. (1), $E_{n,k}^{\mathrm{G}_1 W_0}(\{t\})$ ($E_{n,k}^{\mathrm{TB}}(\{t\})$) corresponds to the eigenvalues of $G_1 W_0$ (TB) Hamiltonian with $n$ and $k$ being the band index and momenta along the high-symmetry lines in the first Brillouin zone, respectively. In order to get much more reliable results near the band edge, we add a Gaussian function $\exp \left[ \left( E_{n,k}^{\mathrm{TB}}(\{t\}) - E_{n,k}^{\mathrm{G}_1 W_0}(\{t\}) \right)^2 \right]$ here, in which $E_{n,k}^{\mathrm{G}_1 W_0}(\{t\})$ is the energy of VBM/CBM from $G_1 W_0$ approximation. The remaining orbitals and relevant hopping parameters are schematically shown in Fig. 3 and Table I.

The band structure and density of states (DOS) obtained from the given TB model are shown in Fig. 4. The quasiparticle energy within $G_1 W_0$ is plotted for comparison. One can see a good match between the TB and original first-principles calculations, especially for the band edges. This can be further quantified by the band gaps and effective masses analysis, which are accurately reproduced by the given TB model as shown in Table II. The indirect (direct) band gap obtained from TB model is 2.33 (3.07) eV, in good agreement with the value of 2.30 (3.07) eV in $G_1 W_0$ calculation. This consistence is also remarkable in the effective masses of carriers in monolayer SnSe$_2$. The anisotropic effective masses of electrons along the $K$-$M$ and $\Gamma$-$M$ directions are 0.56$\,m_0$ and 0.20$\,m_0$ in the proposed TB model, and the corresponding values from $G_1 W_0$ are 0.65$\,m_0$ and 0.20$\,m_0$, respectively. Thus, our proposed TB model can be used effectively in describing the electronic, optical, and transport properties of monolayer SnSe$_2$.

**IV. DOPING EFFECTS**

In experiments, doping is the most common way in tuning the physical properties of 2D materials. It can be easily

### Table I. Hopping parameters $t_i$ (in eV) assigned to the simple TB Hamiltonian of monolayer SnSe$_2$. $d$ is the distance between the atomic sites on which the interacting orbitals are centered. The hoppings are schematically shown in Fig. 3.

<table>
<thead>
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<th>$i$</th>
<th>$t_i$ (eV)</th>
<th>$d$ (Å)</th>
<th>$i$</th>
<th>$t_i$ (eV)</th>
<th>$d$ (Å)</th>
</tr>
</thead>
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<td>5.49</td>
<td>7</td>
<td>0.09</td>
<td>3.90</td>
</tr>
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<tr>
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</tr>
<tr>
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<td>0.30</td>
<td>3.87</td>
<td>11</td>
<td>0.06</td>
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</tr>
<tr>
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<td>0.29</td>
<td>3.87</td>
<td>12</td>
<td>0.05</td>
<td>7.74</td>
</tr>
</tbody>
</table>

**FIG. 3.** Hopping diagram in the TB model of monolayer SnSe$_2$. The orbitals are represented by the negative part of the Wannier orbitals as indicated by the green ellipses.

**FIG. 4.** Comparison of the band structure and density of states for monolayer SnSe$_2$ obtained from $G_1 W_0$ (red line) and TB (blue line) calculations, respectively.
realized by carrier injection through substrate [32], gating, and p-n junction construction [33,34]. In numerical simulations, it is usually represented by a rigid shift of the Fermi level, thus, the effect on electronic structure is obvious. However, how the photon and plasmon in SnSe2 is affected by doping is still unknown. In this section, we will focus on the optical and plasmonic properties of monolayer SnSe2 with doping.

### A. Optical conductivity

Based on the the tight-binding Hamiltonian in Sec. III, we obtain the optical conductivity $\sigma_{\alpha\beta}$ of monolayer SnSe2 using the Kubo formula

$$
\text{Re} \sigma_{\alpha\beta}(\omega) = \lim_{\epsilon \to 0^+} \frac{e^{-\beta \mu} - 1}{\hbar \omega \Omega} \int_0^\infty \left( e^{-\epsilon t} \sin \omega t \right) e^{-\beta \hbar \epsilon} d\epsilon,
$$

(3)

where $\beta = 1/k_B T$, $\Omega$ is the sample area, $f(H) = (e^{\beta(H-\mu)} + 1)^{-1}$ is the Fermi-Dirac distribution operator, $\mu$ is the chemical potential, and the time-dependent current operator in the $\alpha$ (x or y) direction $J_{\alpha}(t) = e^{iHt/\hbar} J_{\alpha} e^{-iHt/\hbar}$. Figure 5 presents the optical conductivity spectrum of undoped and doped monolayer SnSe2. For the case of undoped SnSe2 in Fig. 5(a), our results show that a sharp increase appears at around 2.69 eV, corresponding to the direct optical transition from the highest valence band to the lowest conduction band at $M$ point (2.63 eV). We label this transition $T$ in Fig. 5(c). This correspondence coincides with our $GW_0$ calculation, suggesting the reliability of our proposed TB model. Different from the optical conductivity spectrum of semimetallic graphene [35] and semiconducting black phosphorus [36], the optical conductivity spectrum of monolayer SnSe2 has a flat plateau from 2.69 to 3.06 eV, which can be attributed to the transitions along $M$-$\Gamma$ lines. There are two sharp peaks 1 and 2 in low-energy window, which are located on 3.58 and 4.13 eV, respectively. The magnitude of the peak corresponds to the density of states at the transition point. The peak 1 is caused by the transition $T_1$ at van Hove singularity of the highest valence band, as shown in Fig. 5(c). Obviously, the largest possible DOS is realized in the cases of van Hove singularity and flat bands, enhancing the electron-hole transitions. The peak 2 corresponds to the transition $T_2$ in Fig. 5(c), which is in the local flat conduction band.

When electron or hole is introduced by changing the chemical potential $\mu$ in Eq. (3), the optical conductivity will change dramatically. To be compatible with a real experimental setup by gating or p-n junction, three typical values of $\mu$ are set to be $1.25, -1.17$, and $-1.35$ eV, corresponding to the electron doping of $3.27 \times 10^{13}$ cm$^{-2}$, hole doping of $2.85 \times 10^{13}$ cm$^{-2}$ and $1.68 \times 10^{14}$ cm$^{-2}$, respectively. Upon electron doping, the lowest conduction band at the $M$ point is occupied. Thus, direct optical transition at the $M$ point in undoped SnSe2 is forbidden. Accordingly, the optical spectrum shows blueshift around the optical gap. While for hole doping, it is much more complicated. In the low-energy region ($\omega < 0.5$ eV), two main peaks appear in the optical gap around 0.20 and 0.45 eV. Our analysis on the optical transition in Fig. 5 shows that for $\mu = -1.35$ eV, the first peak originates from the interband transition $T_3$ near the $\Gamma$ point, and the second peak is caused by the transition $T_4$ at the $\Gamma$ point, as labeled in Fig. 5(c). These strong absorption at very low energy can be applied in far-infrared optical devices. In the high-energy window $\omega > 2.5$ eV, the spectrum shows similar behavior with that of the undoped SnSe2. This is because the highest valence band at the $M$ point retains the same after hole doping. When we

![FIG. 5. The optical conductivity spectrum of undoped (a) and doped (b) monolayer SnSe2. The undoped case is also presented in (b) for comparison. The chemical potentials discussed in (a) and (b) are labeled by dotted lines within the band structure in (c), demonstrating the shift of Fermi level. We label some main transitions $T$, $T_1$, $T_2$, $T_3$, and $T_4$ in (c). The sample used in the numerical calculations contains $2 \times 1500 \times 1500$ atomic sites, and we use the periodic boundary conditions in the plane of SnSe2 layers. $\sigma_0 = e^2/4\hbar$ is the universal graphene optical conductivity.](125430-4)
change the hole-doping level, taking \( \mu = -1.17 \text{ eV} \) as example, the optical conductivity spectrum resembles that for the case of \( \mu = -1.35 \text{ eV} \) with a decreasing amplitude. Thus, the switch between electron and hole doping can be used to design the ambipolar monolayer SnSe\(_2\)-based optical transistor.

Spin-orbit coupling (SOC) effects could affect the band structure of monolayer SnSe\(_2\). We compare the band structures with and without the inclusion of SOC effects for monolayer SnSe\(_2\) at PBE level in Fig. 11. With the inclusion of SOC effects, the band dispersions of monolayer SnSe\(_2\) remain fairly consistent but with reduced gap. This reduced gap will lead to a redshift in the optical spectrum of SnSe\(_2\). Moreover, the first and second degenerate valence bands at the \( \Gamma \) point will split into two untouched bands, which may cause new peaks corresponding to the transition T4 for hole-doped SnSe\(_2\). Apart from SOC effects, excitonic effects also could impact the optical spectrum of 2D materials. The excitonic effects in monolayer SnSe\(_2\) will induce new peaks at low-energy window in the optical spectrum. The details of excitonic optical conductivity are beyond our TB study, which needs further investigation in the future.

### B. Plasmon spectrum

Next, we turn to the effect of doping on the plasmonic properties of monolayer SnSe\(_2\). The dynamical polarization \( \Pi(\mathbf{q}, \omega) \) and dielectric function \( \varepsilon(\mathbf{q}, \omega) \) are calculated via the Lindhard function

\[
\Pi(\mathbf{q}, \omega) = -\frac{g_s}{(2\pi)^3} \int_{\text{BZ}} d^2k d\omega \sum_{l,l'} n_{l'}(E_{kl}) \delta(E_{kl} - E_{kl'} - \hbar\omega + ik) \\
\times |\langle \mathbf{k}'| e^{i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}\rangle|^2, \tag{4}
\]

where \( l \) is the band index, \( \mathbf{k}' = \mathbf{k} + \mathbf{q} \), \( n_{l'}(E) = (e^{\beta(E-E_{l'})} + 1)^{-1} \) is the Fermi-Dirac distribution for chemical potential \( \mu \), \( |\mathbf{k}| \) and \( E_{kl} \) are the eigenstates and eigenvalues of the TB Hamiltonian, respectively. The integral is calculated in the first Brillouin zone (BZ) including both interband and intraband transitions. The dielectric function is calculated using the dynamical polarization within the random phase approximation (RPA)

\[
\varepsilon(\mathbf{q}, \omega) = 1 - V(q)\Pi(\mathbf{q}, \omega), \tag{5}
\]

where \( V(q) = \frac{2e^2}{\varepsilon_0 m^*} \) is the Coulomb interaction for an effective dielectric medium with static dielectric constant \( \varepsilon_0 \). Here, we take \( \varepsilon_0 = 7.0 \) to represent the environment of mica substrates in experiments [23]. We present the imaginary part of the dynamical polarization function at \( q = 1 \text{ nm}^{-1} \) on the \( \Gamma-M \) line for different chemical potentials in Fig. 6(a). Owing to the wide energy window within TB Hamiltonian, the spectrum is rich in features with contributions from many interband excitations. For pristine monolayer tin diselenide, the spectrum starts at 2.36 eV, corresponding to the indirect band gap 2.33 eV, as only interband transitions are allowed in this case. When doped with electron or hole, the polarization function \( \Pi(\mathbf{q}, \omega) \) beyond band-gap energy is almost undisturbed by different chemical potentials since it is merely caused by interband transitions between lower hole bands and higher electron bands. On the other hand, some extra low-energy peaks appear in the dynamic polarization, as a result of additional interband and intraband electron-hole excitations. Moreover, the intraband transitions dominate the polarization spectrum in low-energy window \( \omega < 2.36 \), concluded from the band transition analysis.

The corresponding dielectric functions \( \varepsilon(\mathbf{q}, \omega) \) at \( q = 1 \text{ nm}^{-1} \) on the \( \Gamma-M \) line are in Fig. 6(b). Generally, the plasmons exist at zeros of the real part of the dielectric function, while its damping speed is determined by imaginary part of the dielectric function when plasmon appears. The larger value means that the plasmon modes damp faster. There is a well-defined high-energy plasmon mode at around \( \omega = 7.5 \text{ eV} \) with \( \text{Im}[\varepsilon(\mathbf{q}, \omega)] = 0 \). This mode is independent on the chemical potential, but relies on the wave vector \( \mathbf{q} \). For example, this high-energy plasmon mode will disappear at small \( q = 0.1 \text{ nm}^{-1} \). In the presence of doping, there is another distinct region where \( \text{Re}[\varepsilon(\mathbf{q}, \omega)] \) locates at the low-energy window. In contrast to the high-energy plasmon mode, this

![Graphs showing the imaginary part of the polarization function and dielectric function for different chemical potentials.](125430-5)
low-energy plasmon mode is chemical-potential dependent, with energy increasing from 0.5 to 1.1 eV. However, the mode is Landau damped, whose dispersion lies inside the continuum of electron-hole excitations with \( \text{Im}[\varepsilon(q, \omega)] > 0 \). Nevertheless, both the high- and low-energy plasmon modes can be measured by electron energy-loss spectroscopy (EELS) and nanoinfrared imaging in experiments [37], respectively. Considering that doping usually has a notable effect on low-energy window, we further discuss the dielectric function of monolayer tin diselenide in the long wavelength window, we further discuss the dielectric function of monolayer tin diselenide in the long wavelength \( q = 0.1 \text{nm}^{-1} \) for different chemical potentials. Our result shows that the plasmon exist in the energy window from 0.11 to 0.27 eV.

The damped low-energy plasmon mode at \( q = 1 \text{nm}^{-1} \) damps slowly at \( q = 0.1 \text{nm}^{-1} \) because of the smaller \( \text{Im}[\varepsilon(q, \omega)] \) at the energy of \( \text{Re}[\varepsilon(q, \omega)] = 0 \). For large doping of \( \mu = -1.37 \text{eV} \), there are three \( \omega \) values of 0.15, 0.18, and 0.27 eV, respectively, with \( \text{Re}[\varepsilon(q, \omega)] = 0 \). We will focus on the low-energy window of the plasmon spectrum in the following discussion, which is more relevant to experimental probes with potential applications.

The energy-loss function is calculated by \( S(q, \omega) = -\text{Im} \varepsilon^{-1}(q, \omega) \). A proper undamped plasmon, also defined by \( \text{Im} \varepsilon(q, \omega) = 0 \), corresponds to a delta peak in \( S(q, \omega) \). Thus, a sharp peak in \( S(q, \omega) \) demonstrates a long-lived plasmon at that frequency and momentum. Figure 7 shows the density plot for the energy-loss function for electron- and hole-doped monolayer tin diselenide with \( \omega \leq 1 \text{eV} \) and \( q \leq 1 \text{nm}^{-1} \) at three chemical potentials. For the electron injection in Fig. 7(a), there is only one well-defined intraband plasmon branch, showing a standard 2D electron gas \( \sqrt{q} \)-dispersion behavior. It decays into uncoupled electron-hole pairs at large \( q \). The damped regions are identified by the imaginary part of the polarization function \( \text{Im} \Pi(q, \omega) \) for different chemical potentials.

\[
\text{Im}[\varepsilon(q, \omega)] = \frac{2\pi |q|}{\varepsilon_B \omega} \text{Re}[\sigma(\omega)],
\]

where \( \varepsilon_B \) is the background dielectric constant, and \( \text{Re}[\sigma(\omega)] \) is the optical conductivity only containing direct interband transition. For a given \( q = 0.1 \text{nm}^{-1} \), \( \text{Re}[\sigma(\omega)] \) has two peaks at \( \omega = 0.19 \) and 0.44 eV, when \( \mu = -1.17 \text{eV} \) in Fig. 7(b), indicating that the plasmon mode decays into interband electron-hole pairs, leading to the minigap in the dispersion relation. Furthermore, \( \text{Im}[\varepsilon(q, \omega)] \) increases with the increasing \( q \), which suggests that the plasmon mode will damp quickly with the increasing \( q \) values. The gapped plasmon feature is similar to the plasmon-phonon coupled modes in graphene [39]. On the other hand, the dispersion of this mode at low energies can be expressed as

\[
\omega_{pl}(q) = \sum_i \sqrt{\frac{n_i}{m_i}} q.
\]
SnSe$_2$. For high magnetic field, the Landau level has a blueshift and touches the band-edge parts of (a) and (b) in the insets, respectively. (c) Original (circles) and numerical fitting (line) of Landau levels in monolayer plasmon mode at $\varepsilon_0$, thus only present the Landau levels in low-energy window. The sample used in the numerical calculations contains 2 x 1500 x 1500 atomic sites, and we use the periodic boundary conditions (XY) in the plane of SnSe$_2$ layers.

where $n_i$ and $m_i$ are the carrier density and effective mass in pocket $i$.

The gapped plasmon feature also exists at $q = 0.1$ nm$^{-1}$ in Fig. 7(c), caused by the strong interband transitions around $\omega = 0.20$ and 0.45 eV, for $\mu = -1.35$ eV in Fig. 5(b). Compared with the hole doping $\mu = -1.17$ eV in Fig. 7(b), the damped plasmon modes in Fig. 7(c) damp more quickly because of larger $\text{Re}[\sigma(\omega)]$ at the corresponding damping energy for $\mu = -1.35$ eV. The damping mode is in line with that the $\text{Im}[\varepsilon(\omega = 0.15)]$ and $\text{Im}[\varepsilon(\omega = 0.27)]$ are larger than $\text{Im}[\varepsilon(\omega = 0.27)]$ at $q = 0.1$ nm$^{-1}$ in Fig. 6(c). Thus, the plasmon mode at $\omega = 0.27$ eV is still well defined, but the modes at $\omega = 0.15$ and 0.18 eV are damped. These damping modes can be clearly seen by the polarization function in Fig. 7(f), showing large negative values of $\text{Im}(\Pi)$. Furthermore, the intensity of the plasmon mode depends on the DOS at the corresponding energy, which are enhanced by the flat pockets $i$.

Considering that the environment affects the plasmon mode significantly, we change the mica substrate to vacuum environment, and find that the low-energy plasmon pole is environment independent. Since SOC effects cause splitting of top valence band at the $\Gamma$ point, the SOC effects are anticipated to modify the exact location of the plasmon modes, which can be further investigated in the future.

V. MAGNETIC FIELD

Landau quantization was reported in many 2D materials when external magnetic field is applied. Next, we will study the electronic and optical properties of monolayer SnSe$_2$ with external magnetic field, which is still a challenge in DFT calculation. In the case of a perpendicular magnetic field $B$, the hopping term between two sites $t_{\alpha\beta}$ in Eq. (1) is replaced by

$$t_{\alpha\beta} \rightarrow t_{\alpha\beta} \exp \left( \frac{\epsilon}{\hbar c} \int_{R_{\beta}} A \cdot dl \right),$$

(8)

where $A = (-By, 0, 0)$ is the vector potential in the Landau gauge. The quantifying magnetic field leads to discrete DOS as the Landau-level (LL) peaks, which are presented in Fig. 8. The geometrical broadening in the LLs is owing to the energy resolution and total number of time steps in the tight-binding propagation method, which is limited by the calculated sample size (number of atoms). Figures 8(a) and 8(b) show the quantized DOS in a wide energy window. We zoom in the band-edge parts in the insets, in which the LL peaks can be seen clearly. Because the electrons and holes are not symmetric in monolayer SnSe$_2$, the obtained LL spectrum consists of two sets of equidistant LLs, which can be simply described as [36,40]

$$\varepsilon_{n,s}^{kp} = E_f + \frac{s e B h}{m_e} \left( n + \frac{1}{2} \right) w_z,$$

(9)

where $s = \pm 1$ denotes the conduction and valence bands, $E_{+/-}$ is the energy at the conduction and valence band edge, $n$ is the Landau index, and $w_z = m_e/m^*_e$ is the relative ratio between free electron and the average effective masses at the band edges. For all investigated magnetic field, the LL spectrum follows well linear dependence on $n$ in Eq. (9) with fitting values of $E_{+/-} = 1.15(-1.09)$ eV and $w_{+/-} = 3.00(1.38)$, respectively, as shown in Fig. 8(c). On the other hand, the LL spectrum also exhibits linear dependence with $B$, which is similar to a typical 2D electron gas. Unlike the $\sqrt{n}$ in massive Dirac system [sgn$(n)\sqrt{\frac{\sqrt{2\epsilon B} + |n|}{\hbar c}}$], the Landau index in Eq. (9) resembles that of Schrödinger fermions [sgn$(n + 1/2)]$, in agreement with the parabolic dispersion of band edge in Fig. 4.

In the presence of magnetic field, the continuous optical conductivity becomes quantized with discrete values in Fig. 9, however, which are not very sharp as the cases for graphene and arsenene [41,42]. This is because the highest valence band at the $M$ point is not discrete, clearly shown in the high-energy part at -1.50 eV in the black window in Fig. 8(b).
FIG. 9. The optical and magneto-optical conductivity spectrum of monolayer SnSe\(_2\) is calculated with \(B = 0\), 50, and 100 T, respectively. We zoom in the low-energy parts in the inset. Here, \(\sigma_0 = e^2/4\hbar\) is the universal graphene optical conductivity. The sample used here is the same as in Fig. 8.

Thus, the magneto-optical spectrum can be classified into two categories: one is the direct-gap semiconductors like arsenene with absolutely discrete peaks, and the other is indirect-gap semiconductors in this study with no sharp discrete values. Furthermore, the discrete peaks in monolayer SnSe\(_2\) exhibit blueshifts with increasing magnetic field. For example, when the magnetic field varies from 50 to 100 T, the first and second peaks of the magneto-optical conductivity shift from 2.68 and 2.71 eV to 2.69 and 2.74 eV, respectively.

VI. EFFECT OF POINT DEFECTS

During the synthesis of SnSe\(_2\), defects like vacancy or adsorption are observed in experiments [15,23]. As an extension of our tight-binding model, we further study the effects of point defect on the electronic and optical properties of monolayer SnSe\(_2\). The point defects in our TB model are introduced by elimination of atoms which are randomly distributed over the sample. This way allows us to study point defects such as unreconstructed vacancies, chemically bonded atoms, or molecules and strong substitutional defects, which prevent the electronic hopping to the neighbors. The effects of point defects at different concentrations on the DOS of monolayer SnSe\(_2\) are plotted in Fig. 10(a). Our result shows that such defects in the samples result in several peaks in the gapped region of the DOS, which are strongly correlated to the creation of midgap states around the defects. These gapped states are in contrast to the results in previous DFT calculations on bulk SnSe\(_2\), where no midgap states are induced by intrinsic vacancies [43]. Limited by the computational resources, DFT calculations usually adopt a finite cell and patterned defects, leading to high-defect concentration in the single-particle frame. Therefore, the DFT method could not describe the realistic disordered samples with a random distribution of defects at low concentration in experiments.

For the main impurity peaks, the defect concentration does not change its position, but enhances its strength, when the defect concentration increases from 0.1% to 1%. At high-defect concentration, the emerging peaks become dispersive and hybridized with the conduction bands. Meanwhile, the

FIG. 10. DOS (a) and optical conductivity (b) of monolayer SnSe\(_2\) for different concentrations of single-point defects. The sample used here is the same as in Fig. 8.

FIG. 11. Comparison of the band structure for monolayer SnSe\(_2\) without (red line) and with (blue line) SOC effects at PBE level, respectively.
strong-defect interaction creates some ministates at $-3.75 \text{ eV}$ within the gap, which may be caused by bidefects at high-defect concentration. In general, our numerical simulations show that defected monolayer SnSe$_2$ is a typical $n$-type semiconductor, which has been verified by the transport studies of heavily $n$-doped SnSe$_2$ [43].

The impurity states affect the optical conductivity of monolayer SnSe$_2$ as well. As shown in Fig. 10(b), the existence of defects in the sample results in flat midgap states, activating new transitions with lower excitation energy. Consequently, these new optical transitions give rise to a background contribution to the low-energy regions of optical spectrum. Moreover, the new optical transitions also modify the spectrum at the high-energy part when the defect concentration reaches 1%. This is in agreement with the modified band-edge part at defect concentration of 1% in the DOS Fig. 10(a). It has to be noted that the defects could have available contribution to the optical spectrum of MoS$_2$ [44].

**APPENDIX A: COMPUTATIONAL METHODS**

In order to get a reliable TB model, the geometrical optimization and electronic properties of monolayer SnSe$_2$ are performed by first-principles calculations. We fully relax the atomic structures according to the force and stress performed by density functional theory (DFT) using the Vienna ab initio simulation package (VASP) code [45,46]. The generalized gradient approximation (GGA) functional of the PBE form [47] and the projected augmented-wave (PAW) method [48] are adopted. The cutoff energy is set to 500 eV after convergence tests. An equivalent Monkhorst-Pack $k$-points [49,50] grid $15 \times 15 \times 1$ is chosen for relaxation and $40 \times 40 \times 1$ for the static calculations. In our current simulations, the total energy is converged to less than $10^{-3}$ eV, and the maximum force is less than 0.02 eV/Å during the optimization. A vacuum layer of 30 Å is fixed to avoid spurious interactions. The quasiparticle energies and band gaps are calculated by the GW approximation within the general plasmon pole model [51]. The unoccupied conduction band number for calculating the dielectric function and self-energy is about 10 times the involved occupied valence band number, and the vacuum layer is still 30 Å after converge tests. Because of the lack of truncation of the Coulomb interaction along the nonperiodic axis [52] for 2D materials, the GW calculations in the VASP code have to be checked carefully on the $k$ grid, empty bands, and vacuum thickness to get reliable results. We increase $k$ grids of $20 \times 20 \times 1$ for relaxation and $60 \times 60 \times 1$ for static calculations, empty bands of 200, and vacuum thickness of 50 Å, and find that the GW gap changes slightly ($\sim 0.1$ eV). Thus, our final calculated parameters are based on converge result.

The construction of the Wannier functions and TB parametrization of the DFT Hamiltonian is done with the WANNIER90 code [53]. The electronic density of states and the optical conductivity are calculated by the tight-binding propagation method (TBPM) [41,54,55]. This numerical method is based on the Chebyshev polynomial algorithm without the diagonalization of the Hamiltonian matrix. It is an efficient numerical method in large-scale calculations of quantum systems with more than millions of atoms.

**APPENDIX B: HAMILTONIAN MATRIX IN RECIPROCAL SPACE**

Considering the inversion symmetry of atomic structure, our reciprocal-space Hamiltonian matrix in Eq. (1) can be represented as

$$H(k) = \begin{pmatrix} E(k) & T(k) \\ T^\dagger(k) & E(k) \end{pmatrix},$$

where $E(k)$ and $T(k)$ are $3 \times 3$ matrices describing the intrasublattice and intersublattice interactions, respectively. The subscript $r$ in $U(k_r)$ indicates rotation in the opposite direction, resulting from the vertical mirror symmetry $\delta_z$. Because the three basic orbitals have threefold rotation symmetry $C_{3v}$ [56], the corresponding matrices have the
form

\[
E(\mathbf{k}) = \begin{pmatrix}
A(\mathbf{k}) & B(\mathbf{k}) & B^* (\mathbf{k}) \\
B^* (\mathbf{k}) & A(\mathbf{\overline{k}}) & B(\mathbf{\overline{k}}) \\
B(\mathbf{\overline{k}}) & B^* (\mathbf{\overline{k}}) & A(\mathbf{\overline{k}})
\end{pmatrix}
\]  
(E2)

and

\[
T(\mathbf{k}) = \begin{pmatrix}
C(\mathbf{k}) & D(\mathbf{k}) & C(\mathbf{\overline{k}}) \\
D(\mathbf{k}) & C(\mathbf{k}) & D(\mathbf{\overline{k}}) \\
C(\mathbf{\overline{k}}) & D(\mathbf{\overline{k}}) & C(\mathbf{\overline{k}})
\end{pmatrix}
\]  
(E3)

where \(\mathbf{k}\) and \(\mathbf{\overline{k}}\) are the \(\mathbf{k}\) vector rotated by \(2\pi/3\) and \(4\pi/3\), respectively. The matrix elements in Eqs. (E2) and (E3) are

\[
A(\mathbf{k}) = 2t_6 \cos \left( \frac{\sqrt{3}}{2}ak_x - \frac{1}{2}ak_y \right) + 2t_6 \cos \left( \frac{\sqrt{3}}{2}ak_x + \frac{1}{2}ak_y \right) + 2t_{10} \cos(ak_y) + 2t_{12} \cos(\sqrt{3}ak_x),
\]  
(E4)

\[
B(\mathbf{k}) = t_{12} e^{i(\frac{\sqrt{3}}{2}ak_x - \frac{1}{2}ak_y)} + t_{15} e^{-i(\frac{\sqrt{3}}{2}ak_x + \frac{1}{2}ak_y)}
\]  
(E5)

\[
C(\mathbf{k}) = t_{13} e^{-iak_y} + t_{14} e^{i(\frac{\pi}{6}ak_x + \frac{1}{2}ak_y)} + t_{14} e^{-i(\frac{\pi}{3}ak_x - ak_y)}
\]  
(E6)

\[
D(\mathbf{k}) = t_{14} e^{i(\frac{\pi}{6}ak_x - \frac{1}{2}ak_y)} + t_{15} (1 + e^{-iak_y})
\]  
(E7)

**APPENDIX C**

Since Sn atoms are heavy atomic species, we thus take into account SOC in Fig. 11. Compared with the band structures without SOC, the SOC slightly reduces the band gap of monolayer SnSe₂, but nearly does not change the band dispersions of SnSe₂. Furthermore, the first and second degenerate valence bands at the Γ point will split into two untouched bands with the inclusion of SOC effects.


