Large bulk photovoltaic effect and second-harmonic generation in few-layer pentagonal semiconductors $\text{PdS}_2$ and $\text{PdSe}_2$

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Abstract

Recently, atomically thin $\text{PdSe}_2$ semiconductors with rare pentagonal $\text{Se–Pd–Se}$ monolayers were synthesized and were also found to possess superior properties such as ultrahigh air stability, tunable band gap and high carrier mobility, thus offering a new family of two-dimensional (2D) materials for exploration of 2D semiconductor physics and for applications in advanced opto-electronic and nonlinear photonic devices. In this work, we systematically study the nonlinear optical (NLO) responses [namely, bulk photovoltaic effect (BPVE), second-harmonic generation (SHG) and linear electric-optic (LEO) effect] of noncentrosymmetric bilayer (BL) and four-layer $\text{PdS}_2$ and $\text{PdSe}_2$ by applying the first-principles density functional theory with the generalized gradient approximation plus scissors-correction. First of all, we find that these few-layer $\text{PdX}_2$ ($X = \text{S and Se}$) exhibit prominent BPVE. In particular, the calculated shift current conductivity is in the order of $130 \mu \text{A V}^{-2}$, being very high compared to known BPVE materials. Similarly, their injection current susceptibilities are in the order of $100 \times 10^8 \text{A V}^{-2} \text{s}^{-1}$, again being large. Secondly, the calculated SHG coefficients ($\chi^{(2)}$) of these materials are also large, being one order higher than that of the best-known few-layer group 6B transition metal dichalcogenides. For example, the maximum magnitude of $\chi^{(2)}$ can reach $1.4 \times 10^3 \text{pm V}^{-1}$ for BL $\text{PdSe}_2$ at 1.9 eV and $1.2 \times 10^3 \text{pm V}^{-1}$ at 3.1 eV for BL $\text{PdS}_2$. Thirdly we find significant LEO coefficients for these structures in the low photon energy. All these indicate that 2D $\text{PdX}_2$ semiconductors will find promising NLO applications in light signal modulators, frequency converters, electro-optical switches and photovoltaic solar cells. Fourthly, we find that the large BPVE and SHG of the few-layer $\text{PdX}_2$ structures are due to strong intralayer directional covalent bonding and also 2D quantum confinement. Finally, we also discuss the prominent features of these NLO spectra of these materials in terms of their electronic structure and optical dielectric functions.

1. Introduction

Because of their extraordinary electronic and optical properties, two-dimensional (2D) materials such as graphene, atomically thin (few-layer) transition metal dichalcogenides (TMDCs) and black phosphorus, have attracted an enormous amount of interest in recent years, finding diverse applications in electronic, opto-electronic and nonlinear photonic devices with superior performances. Among them, group 6B TMDC semiconductors with chemical formula $\text{MX}_2$ ($M = \text{Mo, W}; X = \text{S, Se}$) and each layer made up of a 2D hexagonal array of $M$ atoms sandwiched between the similar arrays of $X$ atoms, constitute a particularly interesting family of 2D materials. In particular, they were found to exhibit an indirect to direct band gap transition when they were thinned down to a monolayer (ML) [1]. This makes the $\text{MX}_2$ MLs semiconductors with a direct band gap, thus becoming promising materials for, e.g. electro-optical devices with efficient light emission [1] and field effect transistors with high on-off ratios [2]. Furthermore, these
hexagonal 2D MX$_2$ materials with an odd layer-number lack the spatial inversion symmetry, although their bulk crystals are centrosymmetric. This broken inversion symmetry makes them exhibit novel properties of fundamental and technological interests, especially second-order nonlinear optical (NLO) responses such as second-harmonic generation (SHG) [3–7] and bulk photovoltaic effect (BPVE) [8].

Stimulated by the recent fabrications of few-layer PdSe$_2$ via molecular beam epitaxy, chemical vapor deposition and mechanical exfoliation [9–11], palladium-based TMDC 2D materials have also attracted much attention in the past five years [12]. Indeed, these few-layer Pd-based TMDC materials were found to exhibit some desired properties for applications, such as tunable band gap, high carrier mobility, anisotropy, enhanced thermoelectric property and ultrahigh air stability [9, 12–16]. There are several distinct differences between group 6B TMDC and Pd-based TMDC 2D materials. In particular, compared with Mo and W atoms, Pd atoms have a nearly filled d-shell and thus there are stronger hybridization between Pd d-orbitals and chalcogen p-orbitals in Pd-based TMDC 2D materials. This result in stronger covalent bonding within each PdX$_2$ (X = S and Se) layer as well as stronger interlayer binding. The latter gives rise to layer-number dependent properties especially band gap size [9, 12, 16]. In contrast to groups 5B and 6B TMDCs, bulk PdS$_2$ and PdSe$_2$ crystallize in the orthorhombic layered structure (see figure 1(a)) with the centrosymmetric Pnma space group [17, 18]. Furthermore, in each PdX$_2$ layer, a Pd atom bonds with four chalcogen atoms, and Pd and chalcogen atoms form a buckled pentagonal layered structure (see figure 1(c)) [9, 14]. Depending on their thickness (i.e. layer-number), few-layer PdX$_2$ structures have different symmetries compared with their bulk crystals. Interestingly, 2D PdX$_2$ materials with an even layer-number crystallizes in a noncentrosymmetric structure with space group Pnma and point group symmetry of C$_{2v}$ (or mm2), while 2D PdX$_2$ materials with an odd layer-number form a centrosymmetric structure of space group P2$_1$/c [9, 12, 19]. Note that 2D group 6B TMDC structures with an odd-layer number are noncentrosymmetric, while that with an even layer-number have the inversion symmetry. Therefore, as for few-layer group 6B TMDC materials with an odd layer-number, 2D PdX$_2$ structures with an even layer-number are expected to show second-order NLO properties. Indeed, strong angle-dependent SHG signals in bilayer (BL) and four-layer (FL) PdSe$_2$ were observed recently [20], although the precise SHG susceptibility was not determined. Motivated by these exciting developments, in this work we perform a systematic theoretical study of the NLO responses of BL and FL PdX$_2$, based on first-principles density functional theory (DFT) calculations.

In this paper, we focus on three principal second-order NLO responses of few-layer PdX$_2$ materials, namely, SHG, linear electric-optical (LEO) effect and BPVE. The SHG, one of the best-known second-order
NLO effects, converts the two photons of the same-frequency into a new photon with a doubled photon energy [3, 4]. Noncentrosymmetric materials with a large SHG susceptibility $\chi^{(2)}(-2\omega; \omega, \omega)$ have many applications in nonlinear photonic devices such as frequency conversion. The SHG is also a powerful probe of the symmetry of surfaces and interfaces [3]. Here we find that all Pd$_2$X$_2$ structures possess large $\chi^{(2)}$ in the visible frequency spectrum and BL PdSe$_2$ has the largest $\chi^{(2)}$ value of $1.4 \times 10^3$ pm V$^{-1}$ at 1.9 eV. The LEO effect refers to the linear refractive index change ($\Delta n$) with the applied electric field strength ($E$), $\Delta n = n' \varepsilon_0 E^2 / 2$, where $n$ is the refraction index and $r$ is the LEO coefficient [4]. The LEO effect thus allows one to use an electrical signal to control the amplitude, phase or direction of a light beam in the NLO material, and leads to a widely used means for high-speed optical modulation and sensing devices (see, e.g. reference [21] and references therein). We find that the LEO coefficients of BL Pd$_2$S and BL PdSe$_2$ are significant and comparable to that of trilayer group 6B TMDC semiconductors [5]. The BPVE (also known as photogalvanic effect) refers to the generation of dc photocurrents in noncentrosymmetric materials [8]. In a nonmagnetic semiconductor, there are two main contributions to the BPVE, namely, the circular injection current and linear shift current [8, 22–24]. Materials having large BPVE are crucial for applications in photovoltaic solar cells and high sensitive photodetectors. Here we predict that the BPVE in the considered few-layer Pd$_2$X$_2$ structures is generally strong, with a large shift current conductivity of up to 130 $\mu$A V$^{-2}$ and injection current susceptibility of up to $100 \times 10^3$ A V$^{-2}$ s$^{-1}$ in the visible frequency range. These superior NLO responses of the BL and FL Pd$_2$X$_2$ structures will make them valuable for technological applications in NLO and electro-optic devices such as light signal modulators, frequency converters, electro-optical switches, photovoltaics and photodetector applications.

2. Computational methods

Bulk Pd$_2$X$_2$ crystallize in a layered orthorhombic structure with space group $Pbca$ (see figure 1), as mentioned above. The experimental lattice constants are $a = 5.460$ Å, $b = 5.541$ Å and $c = 7.531$ Å for PdS$_2$ [17] and $a = 5.7457$ Å, $b = 5.8679$ Å and $c = 7.6976$ Å for PdSe$_2$ [18]. The bulk unit cell contains two $X$–Pd–$X$ MLs stacked along the $c$-axis and each nearly square unit cell contains two chemical formulas (f.u.) (i.e. six atoms) (see figure 1). In each $X$–Pd–$X$ layer, interestingly, a Pd atom bonds with four chalcogen atoms, and Pd and chalcogen atoms form a rare pentagonal structure (see figure 1(c)) [9, 14]. In the present calculations, a BL (FL) structure is constructed by cutting two (four) $X$–Pd–$X$ layers out of the bulk crystal. The slab-superlattice approach is adopted with the separations of neighboring slabs being at least 15 Å. We notice that a number of the structural optimization calculations for bulk PdSe$_2$ using more than ten exchange-correlation functionals have been carried out [9, 11, 19, 25]. The discrepancies between the experimental and theoretical lattice constants are large, varying from 2% all the way up to 20% depending strongly on the exchange-correlation functional used [9, 25]. On the other hand, the experimental inplane lattice constants of BL PdSe$_2$ are only slightly larger than the corresponding lattice constants of bulk PdSe$_2$ [11]. Thus, we use the experimental bulk structural parameters in the present calculations. We believe that using the experimental structural parameters of atomically thin PdX$_2$ would not significantly change the calculated electronic and optical properties of BL and FL Pd$_2$X$_2$ to be presented below.

The electronic structure calculations are performed using the accurate projector augmented wave method [26] as implemented in the Vienna $ab$-initio simulation package (VASP) [27, 28]. For the exchange-correlation potential, we adopt the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof parametrization [29]. A large plane-wave energy cutoff of 400 eV is used throughout the calculations. The valence configuration of Pd atom is taken as 4d$^9$ 5s$^1$, S atom is 3s$^2$ 3p$^4$ and for Se atom it is 4s$^2$ 4p$^4$. A $k$-point mesh of $18 \times 18 \times 1$ is used in the Brillouin zone (BZ) integrations for few-layer PdX$_2$ structures. All the calculations are performed within the scalar-relativistic projector augmented potentials, with the energy convergence up to $10^{-6}$ eV between the successive iterations.

All the linear and NLO properties of the 2D PdX$_2$ structures are calculated from the self-consistent electronic band structures within the linear response formalism with the independent-particle approximation (IPA). Specifically, we first calculate the imaginary part ($\varepsilon''(\omega)$) of the dielectric function due to direct interband transitions by using the Fermi golden rule [30]. The obtained $\varepsilon''(\omega)$ is used to get the real part ($\varepsilon'(\omega)$) of the dielectric function by a Kramer–Kronig transformation [30]. Given the complex dielectric function ($\varepsilon' + i\varepsilon''$), all other linear optical properties can be calculated. For example, complex refraction index $(n + i\kappa) = \sqrt{\varepsilon' + i\varepsilon''}$ and absorption coefficient $\alpha = \omega\varepsilon''/(nc)$ where $n$ is the refraction index, $\kappa$ is the extinction coefficient and $c$ is the speed of light.
For the BPVE, the dc photocurrent density along the a-axis in a noncentrosymmetric material under the applied optical electric fields $E_b$ and $E_c$ may be written as [22, 23, 32]

$$J_a(0) = \sum_{k} \sigma_{abc}(0; \omega, -\omega) E_b(\omega) E_c(-\omega),$$  

where the photocurrent conductivity $\sigma_{abc}$ is a third-rank tensor [22]. For a nonmagnetic semiconductor, the dc photocurrent contains two main contributions, namely, the linear shift current [22] and also the circular injection current [32]. That is, $\sigma_{abc} = \sigma_{abc}^{ib} + \sigma_{abc}^{0ib}$. Within the length gauge formalism, the shift current conductivity $\sigma_{abc}^{ib}$ can be written in terms of the interband position matrix element $r_{ij}^b$ and its momentum derivative $\partial r_{ij}^b / \partial k_{\parallel}[22]$. By replacing $r_{ij}^b$ with $p_{ij}^b / i\epsilon_j$ where $p_{ij}^b = (k_j p_j a_i)$ is the a-component of the momentum matrix element, $\epsilon_j = (\epsilon_k - \epsilon_i)$ and $\epsilon_k$ is the energy of the $|k\rangle$ band state, one may obtain [33]

$$\sigma_{abc}^{ib}(\omega) = \frac{\pi}{\Omega N_k} \sum_k \sum_{i\in VB+C} \sum_{j\neq i} \sum_{\gamma} \sum_{l \neq \gamma} \text{Im}\left\{ \frac{p_{ij}^b(p_{ij}^b p_{ij}^a + p_{ij}^a p_{ij}^a)}{2\epsilon_j} \right\} \delta(\epsilon_j - \omega),$$  

where $(p_{ij}^a p_{ij}^a) = \frac{1}{2}(p_{ij}^a p_{ij}^a + p_{ij}^a p_{ij}^a)$, $\Omega$ is the unit cell volume and $N_k$ is the number of $k$-points used. The injection current conductivity $\sigma_{abc}^{0ib} = \tau \eta_{abc}$ where $\tau$ is the relaxation time of photoexcited carriers and $\eta_{abc}$ is the injection current susceptibility, which can also be written in terms of $r_{ij}^b$ and $\partial r_{ij}^b / \partial k_{\parallel}$ (see equation (31) in reference [32]). Again, by substituting $r_{ij}^b$ with $p_{ij}^b / i\epsilon_j$, one would get

$$\eta_{abc}^{ij}(\omega) = \frac{2\pi}{\Omega} \sum_k \sum_{i\in VB+C} \sum_{j\neq i} \Delta_{ij}^b \text{Im}\left[p_{ij}^a p_{ij}^a\right] \delta(\epsilon_j - \omega),$$  

where $\Delta_{ij}^b = (p_{ij}^a - p_{ij}^a)$. Note that the atomic unit is adopted here and hence $\hbar = m_e = 1$.

The imaginary part $[\chi_{abc}^{m(2)}(-2\omega, \omega, \omega)]$ of the SHG susceptibility is obtained from the self-consistent electronic band structure by using the expression already reported elsewhere [30, 34]. The real part $[\chi_{abc}^{m(2)}(-2\omega, \omega, \omega)]$ of the SHG susceptibility is then obtained from $\chi_{abc}^{m(2)}$ by the Kramer–Kronig transformation [30, 34]. We also calculate the low-frequency LEO coefficients of the considered materials using the obtained static dielectric constants and SHG susceptibility. The LEO coefficients in the zero frequency limit are given by

$$r_{abc}(0) = -\frac{2}{\epsilon_{\infty}(0) \epsilon_2(0)} \lim_{\omega \to 0} \chi_{abc}^{m(2)}(-2\omega, \omega, \omega).$$  

To ensure the accuracy of the calculated optical properties we use denser $k$-point meshes of $110 \times 110 \times 1$ for BL structures and $60 \times 60 \times 1$ for FL structures. Furthermore, to ensure that $\epsilon'(\omega)$ and $\chi^{m(2)}$ calculated via Kramer–Kronig transformation are reliable, at least 150 and 300 energy bands are included in the present optical calculations for BL and FL structures, respectively. The unit-cell volume is not well-defined for low-dimensional systems. Therefore, similar to the previous calculations [5, 30, 34], we use the effective unit-cell volume (i.e. $a \times b \times nh$, where $n$ is the layer-number and $h$ is the effective layer thickness) of the 2D material rather than the volume of the supercell which is arbitrary. Since each unit cell of bulk PdX$_2$ contains two layers, the effective layer thickness $h$ is 3.766 Å for few-layer PdS$_2$ and 3.849 Å for few-layer PdSe$_2$.

Correct band gaps would be important for obtaining accurate optical properties. However, in general the GGA functional is known to underestimate the band gaps because some many-body effects especially the quasiparticle self-energy corrections are neglected. Therefore, we perform the band-structure calculations using the hybrid Heyd–Scuseria–Ernzerhof (HSE) functional, which is known to produce much improved band gaps for semiconductors [37, 38]. We then use the HSE band gaps and calculate all the optical properties with the well-known scissors-correction (SC) [35]. In the SC calculations, the conduction bands are uniformly up-shifted so that the band gap would match the HSE gap together with the renormalized transition matrix elements [35]. All the optical properties presented in this paper are obtained with this SC scheme.

3. Results and discussion

3.1. Electronic structure

The calculated GGA band structures of BL PdX$_2$ and FL PdX$_2$ are presented, respectively, in figure 2 and figure S1 of the supplementary information (SI) (https://stacks.iop.org/NJP/23/093028/mmedia). All the four structures are an indirect band gap semiconductor. The valence band maximum (VBM) is located at...
Figure 2. Band structures of (a) BL PdS₂ and (b) BL PdSe₂. The horizontal dashed line denotes the top of valance bands.

Table 1. Band gaps (in eV) of BL and FL PdX₂ calculated with GGA and HSE functional. The available experimental band gap values are in parentheses for comparison.

|     | PdS₂ GGA | HSE | PdSe₂ GGA | HSE |
|-----|---------|-----|-----------|-----|
| BL  | 0.78    | 1.90| 0.74      | 1.62| (1.15 [11]) |
| FL  | 0.40    | 1.47| 0.27      | 1.11| (1.06 [9])  |

The Γ point and the conduction band minimum (CBM) is located on the M–Γ line in the 2D Brillouin zone (see figure 1(d)) for both BL and FL PdS₂ structures (figure 2(a) and figure S1(a)). In the PdSe₂ structures, the VBM is located in the Γ–X direction and the CBM is located on the M–Γ line (figure 2(b) and figure S1(b)). The present band structure of BL PdSe₂ agrees rather well with that reported in references [9, 11, 19]. Table 1 shows that the band gap decreases significantly as the S atoms are replaced by the Se atoms in PdX₂ and also as we move from the BL to FL PdX₂ structure, indicating the tunability of the band gap by chalcogen substitution and also by layer-number variation.

The calculated total- and orbital-projected density of states (DOS) for BL PdX₂ and FL PdX₂ are presented in figure 3 and in figure S3 of the SI, respectively. Figure 3 shows that the upper valence band edge and lower conduction band edge are contributed almost equally by the Pd d orbitals and chalcogen (X) p orbitals (see figures 3(a) and (b)). This indicates a strong covalent bonding in the PdX₂ structures (see also [36]), being in rather strong contrast to group 6B TMDCs (e.g. MoS₂) which may be called charge-transfer semiconductors [5]. This is due to the nearly filled Pd d states in the PdX₂ structures while in MoS₂ the Mo d states are less than half-filled [5]. Furthermore, orbital-projected DOS spectra show that the contribution at the upper valence band edge comes predominantly from Pd dₓ₂−ᵧ₂ and chalcogen pₓ,ᵧ with minor contribution from pₓᵧ states while the contribution at the lower conduction band edge comes from Pd dₓᵧ and chalcogen pₓ,ᵧ and pₓ states. Thus, the optical transitions in PdX₂ take place from the valence states of the hybridized Pd d and chalcogen p states to the conduction band states of Pd d orbitals.

Table 1 shows that the GGA band gaps for BL and FL PdSe₂ are significantly smaller than the corresponding experimental values [9, 11], indicating that the GGA functional generally underestimates the band gaps of semiconductors, as mentioned in the preceding section. Therefore, we also perform the band-structure calculations using the HSE functional [37, 38] and the HSE band structures are presented in figure S2 in the SI. Although the dispersions of the HSE band structures are similar to that of the corresponding GGA band structures, the band gaps from the HSE functional are significantly larger than that of the GGA ones (table 1). Furthermore, the HSE band gaps of BL and FL PdSe₂ are in better agreement with the experimental values than the GGA band gaps (table 1). Therefore, all the optical properties presented in the following sections are calculated within the SC scheme [35] by using the
HSE band gaps (table 1). Nevertheless, we notice that the experimental band gap for BL PdSe$_2$ is significantly smaller than that of the HSE calculation (table 1). This discrepancy could be due to the effect of the graphene substrate [11] because the environment can significantly affect the electronic properties of 2D materials [39, 40]. For example, the graphene substrate can introduce extra screening, thus reducing the band gap [39, 40]. In particular, putting a BN sheet on graphene would reduce the band gap of BN ML by as much as $\sim 1.0$ eV (14%) [39].

3.2. Linear optical properties

The calculated dielectric functions of all the four Pd$_X$$_2$ structures are plotted in figure 4. As can be expected of a 2D material, there are huge differences between the out-of-plane and in-plane components of the dielectric functions (see figure 4). For example, the real part of the z-polarized dielectric function $\varepsilon''_{zz}$ is only about half of that for the in-plane polarized dielectric function $\varepsilon''_{xx}$ and $\varepsilon''_{yy}$ below 3 eV. The imaginary part of the z-polarized dielectric function $\varepsilon''_{zz}$ is about four times smaller than that of the in-plane dielectric functions $\varepsilon''_{xx}$ and $\varepsilon''_{yy}$. There are also discernible differences between the two in-plane components of the dielectric functions, namely, $\varepsilon''_{xx}$ and $\varepsilon''_{yy}$ (see figure 4). In particular, the real dielectric constant of $\varepsilon''_{xx}$ is slightly higher than $\varepsilon''_{yy}$ in the energy range of 2.5–3.0 (2.0–2.5) eV and 4.3–5.6 (4.0–5.0) eV, whereas $\varepsilon''_{yy}$ in the energy range of 3.0–4.3 (2.5–4.0) eV and also in 5.6–6.0 (5.0–5.7) eV is higher than $\varepsilon''_{xx}$ for BL PdS$_2$ (PdSe$_2$) (see figures 4(a) and (c)). In FL PdS$_2$ (PdSe$_2$) structure, the real dielectric constant $\varepsilon''_{xx}$ is higher than $\varepsilon''_{yy}$ in the energy range of 2.2–2.7 (1.9–2.5) eV and 4.3–5.6 (4.0–5.6) eV, whereas $\varepsilon''_{yy}$ in the energy range of 2.7–4.3 (2.5–4.0) eV and also in 5.6–6.00 (5.0–6.0) eV is slightly higher than $\varepsilon''_{xx}$ (see figures 4(e) and (g)). Similar profile is found in the imaginary part of the dielectric constant, where $\varepsilon''_{xx}$ is higher than $\varepsilon''_{yy}$ in the energy range of 2.6–3.1 eV (2.5–3.4 eV) and 3.9–5.0 eV (5.0–6.0 eV) for BL (FL) PdS$_2$ and 2.2–2.9 eV (2.1–3.0 eV) and 4.5–5.4 eV (4.5–5.3 eV) for FL (BL) PdSe$_2$, whereas in the other energy windows $\varepsilon''_{yy}$ is higher than $\varepsilon''_{xx}$ for both BL (FL) PdS$_2$ and PdSe$_2$ structures, see figures 4(b) and (d) (figures 4(f) and (h)). It is worth mentioning that the large imaginary part of the dielectric function of all the Pd$_X$$_2$ structures spans over a wide range of the visible frequency range. This suggests that these 2D Pd$_X$$_2$ structures will be useful for opto-electronic applications such as high solar-absorption efficiency solar cells [41].

3.3. Shift and injection currents

As mentioned before, the point symmetry group of BL and FL Pd$_X$$_2$ is $C_{2v}$, with the $C_2$ rotation axis along the y-axis. Therefore, there are only five inequivalent nonzero shift current tensor elements [42], namely,
η may be attributed to the fact that the absorptive part of the out-of-plane polarized dielectric function ε and the absorption edge. In BL PdS2, the calculated injection conductivity σ−inj with the peak value being about 580 μA V−2 at 2.9 eV (see figure 5(b)). In both BL structures, the magnitudes of the injection conductivity elements are zero below the absorption edge but increase rapidly above the absorption edge. Notably, the injection conductivity element xxy of BL PdS2 has a second peak with the reduced maximum of 65 μA V−2 at 3.9 eV (see figure 5(a)). For BL PdSe2, these two prominent peaks in the σxxy spectrum become comparable with the maximum values of ~115 μA V−2 and ~126 μA V−2 at 2.6 eV and 3.6 eV, respectively (see figure 5(b)). In both BL structures, the magnitudes of the injection conductivity elements are also pronounced in the photon energy range from the absorption edge to ~5.0 eV. For example, the σxxy of BL PdS2 has a negative peak at ~3.9 eV with the maximum value of ~90 μA V−2. Figure 5 also indicates that the magnitude of the σyzz spectra from all the four structures is much smaller than all the other shift conductivity elements. This may be attributed to the fact that the absorptive part of the out-of-plane polarized dielectric function element εyy is much smaller than that of the in-plane polarized dielectric function elements εxx and εyy (see figure 4). In the FL structure, the maximum shift current conductivity is from σsh(xxy) of the order of ~97 (~90) μA V−2 at a photon energy of 2.9 (2.5) eV for PdS2 (PdSe2) (see figures 5(c) and (d), respectively). Similar to the BL structures, FL PdX2 also have contributions of ~50 μA V−2 from other elements such as σsh(yyy) for FL PdS2 and σsh(xyy, yxx, yzz) for FL PdSe2 in the energy range of 3–4 eV (see figures 5(c) and (d)).

The calculated nonzero injection current susceptibility element ηxxy is displayed as a function of photon energy for both BL and FL PdX2 in figure 6. Using the typical relaxation time τ = 0.04 ps for 2D PdX2 materials [13], we obtain the injection photocurrent conductivity σxxy inj = τηxxy, as shown in figure 6. For all of the PdX2 structures, both ηxxy and σxxy inj are zero below the absorption edge but they increase rapidly above the absorption edge. In BL PdS2, the calculated injection conductivity σxxy inj has two negative prominent peaks with the maximum values of ~240 and 360 μA V−2 at 2.7 and 4.7 eV, respectively (see figure 6(b)). Similarly, in BL PdSe2, we also find two pronounced peaks with larger maximum values of ~400 and ~580 μA V−2 at 3.1 and 4.0 eV, respectively (see figure 6(d)). In the FL structures, the magnitudes of both ηxxy and σxxy inj spectra are smaller compared with that from the BL structures (figure 6). In particular, the magnitudes of the ηxxy and σxxy inj of FL PdSe2 are generally less than half of that from BL PdSe2 (see figures 6(c) and (d)). Nonetheless, FL PdS2 and FL PdSe2 do have a rather pronounced peak in the σxxy inj spectrum with the peak value being about –200 μA V−2 at 3.1 and 2.8 eV, respectively.
Let us now compare the BPVE in the present structures with the well-known BPVE materials to access their application potentials in photovoltaic solar cells and opto-electronic devices. The theoretically predicted shift current conductivity for the archetypal ferroelectrics PbTiO3 and BaTiO3 [43], have a value within 10 μA V⁻² in the visible frequency range, which is in agreement with the earlier experiments [44]. These values are several times smaller than the present predictions for the 2D PdX₂ materials, as shown in figure 7(a). Recently, the shift current conductivity of some chiral materials was predicted to be rather large, being in the range of 20 ~ 80 μA V⁻² in the visible frequency range [45]. Furthermore, ML group-IV monochalcogenides were found to exhibit large shift current conductivity of about 100 μA V⁻² in the visible frequency range. Nevertheless, these values are smaller or at best comparable to the present predictions for the 2D PdX₂ structures (see figure 7). Interestingly, the calculated injection current susceptibility of the present PdX₂ structures is two-orders larger than the experimental values of 1.5 × 10⁸ A V⁻² s⁻¹ and 4 × 10⁸ A V⁻² s⁻¹ for semiconductors CdSe and CdS [46], respectively, which are in the same order of magnitude with the theoretical predictions reported in reference [32]. Among the 2D materials, as figure 7(b) shows, the injection current susceptibility of ML group-IV chalcogenides was reported to be one-order larger compared to the present PdX₂ structures [51, 54].

Nevertheless, 2D PdX₂ structures are atomically thin with thickness being about two-orders of magnitude smaller than visible light wavelength. One may wonder whether such atomically thin films would absorb sufficient light and generate significant photocurrent. In figure 8, we display the absorbance spectra of 2D PdX₂ structures. It is clear from figure 8 that although atomically thin, BL and FL PdX₂ can absorb around 10% and 20% of incident light above the absorption edge, respectively. Now we evaluate the photocurrent due to the BPVE in 2D PdX₂ structures. Let us consider the normal incidence of linearly polarized light of intensity I₀. The shift current is then given by

\[ J_{sh}^{abb} = w \sigma_{sh}^{abb} \int_0^d |E_b(z)|^2 dz = w \sigma_{sh}^{abb} \frac{2I_0(0)}{\varepsilon_0 c} \int_0^d e^{-\alpha d} dz \]

\[ = w \sigma_{sh}^{abb} \frac{2I_0(0)}{\varepsilon_0 c \alpha d} (1 - e^{-\alpha d}), \]

(5)

where \( w \) is the width of the sample, \( d = nh \) is the effective film thickness, \( I_0(z) = \varepsilon_0 |E_b(z)|^2/2, \varepsilon_0 \) is the vacuum permittivity and \( c \) the speed of light. Here we choose the same experimental parameters \( w = 0.15 \) cm and \( I_0(0) = 0.5 \) mW cm⁻¹ as in the experiment on BaTiO₃ [44]. The calculated shift current spectra are plotted in figure 8. Strikingly, the shift currents due to the BPVE in the atomically thin PdX₂
semiconductors are comparable to the measured one in bulk ferroelectric BaTiO$_3$ [44] (see figure 2 in reference [43]). This clearly indicates that 2D PdX$_2$ semiconductors would find promising applications in, e.g. solar cells.

### 3.4. Second-harmonic generation

For a noncentrosymmetric material, the nonzero elements of its SHG susceptibility tensor are the same as that of its shift current conductivity tensor. Therefore, as for the shift current conductivity, the SHG susceptibility tensor of the BL and FL PdX$_2$ has five independent nonzero elements, i.e. $\chi^{(2)}_{xx} = \chi^{(2)}_{yy} = \chi^{(2)}_{zz} = \chi^{(2)}_{xy} = \chi^{(2)}_{yx}$. The real and imaginary parts as well as the absolute of these nonzero elements for BL PdX$_2$ and FL PdX$_2$ are presented in figures 9 and 10, respectively. Figures 9 and 10 show that the imaginary (absorptive) parts of the SHG susceptibility for both BL and FL PdX$_2$ are zero for photon energy being smaller than half of the band gaps but they increase rapidly above half of the band gaps. Furthermore, below half of the band gaps, the real (dispersive) parts of the SHG susceptibility are small and remain almost constant. These nonzero dispersive parts of the SHG susceptibility below half of
Figure 8. Absorbance and shift current ($J_{sh}$) of BL PdS$_2$ and PdSe$_2$ as well as FL PdS$_2$ and PdSe$_2$. Absorbance is given by absorption coefficient ($\alpha$) times film thickness ($d$). Shift current is calculated by using the parameters for the experiment on BaTiO$_3$ [44], namely, incident light intensity $I_{bb}(0) = 0.5$ mW cm$^{-2}$ and sample width $w = 0.15$ cm.

Figure 9. Real (upper panels) and imaginary (middle panels) parts as well as absolute (lower panels) of the SHG susceptibility of BL PdS$_2$ and BL PdSe$_2$.

the band gaps give rise to the low-frequency LEO effect in the PdX$_2$ structures, which will be discussed in the next section. As for the imaginary parts, they increase rapidly above half of the band gaps.

Among the nonzero SHG susceptibility elements, $\chi^{(2)}_{yy}$ and $\chi^{(2)}_{yxx}$ generally exhibit larger magnitudes in the visible frequency range for all the PdX$_2$ structures (see figures 9(c) and (f) as well as figures 10(c) and (f)). In BL PdS$_2$, both $\chi^{(2)}_{yy}$ and $\chi^{(2)}_{yxx}$ spectra show a pronounced peak with almost the same maximum value of $\sim 1.2 \times 10^3$ pm V$^{-1}$ at slightly different photon energies of 3.1 and 3.3 eV, respectively (see figure 9(c)).
They come from the negative peak in the real and imaginary parts of the $\chi^{(2)}_{yyy}$ and $\chi^{(2)}_{yxx}$ spectra at 3.1 and 3.3 eV, respectively (see figures 9(a) and (b)). The $\chi^{(2)}_{yyy}$ spectrum of BL PdS$_2$ exhibits the second maximum of $0.9 \times 10^3$ pm V$^{-1}$ at 1.6 eV (see figure 9(c)). It originates from the negative peak near 1.6 eV in both real and imaginary parts of the $\chi^{(2)}_{yyy}$ spectrum (see figures 9(a) and (b)). Remarkably, the $\chi^{(2)}_{yyy}$ absolute spectrum of BL PdSe$_2$ has two gigantic peaks of heights of $1.1 \times 10^3$ pm V$^{-1}$ at 1.4 and 1.9 eV, respectively (see figure 9(f)) and they stem from the negative and positive peaks at 1.4 and 1.9 eV in the real and imaginary parts of the spectrum (see figures 9(d) and (e)). The $\chi^{(2)}_{yxx}$ spectrum of BL PdSe$_2$ has a broad twin peak of magnitude of $1.1 \times 10^3$ pm V$^{-1}$ centered at $\sim$1.9 eV (see figure 9(f)). Nonetheless, below the band gap, the magnitudes of the $\chi^{(2)}_{xxy}$ and $\chi^{(2)}_{yzz}$ spectra of the PdX$_2$ structures are generally comparable or even larger than that of the $\chi^{(2)}_{yyy}$ and $\chi^{(2)}_{yxx}$ spectra. For example, both BL PdS$_2$ and BL PdSe$_2$ have a rather broad peak of $\sim 0.8 \times 10^3$ pm V$^{-1}$ at 1.5 and 1.3 eV, respectively (see figures 9(c) and (f)). All the $\chi^{(2)}_{abc}$ spectra from the FL PdX$_2$ structures are generally smaller than the corresponding spectra of the BL PdX$_2$ structures. Nonetheless, the magnitudes of the $\chi^{(2)}_{yyy}$ and $\chi^{(2)}_{yxx}$ spectra of FL PdSe$_2$ do peak at 1.2 and 1.7 eV with the large maximum values of $0.94 \times 10^3$ and $1.2 \times 10^3$ pm V$^{-1}$, respectively (see figure 10(f)).

As shown before (see, e.g. reference [5] and references therein), the prominent features in the SHG susceptibility are generally caused by either single ($\omega$) and double ($2\omega$) photon resonances or both. Thus, to help understand the origins of the prominent features in the calculated SHG spectra, we plot the absolute values of the imaginary parts of the nonzero SHG elements of BL PdX$_2$ and FL PdX$_2$ in figures 11 and 12, respectively, along with the absorptive parts of the corresponding dielectric functions $\varepsilon''(\omega)$ and $\varepsilon''(2\omega)$. Figures 11(a) and (b) (figures 12(a) and (b)) show that the prominent features in the $|\chi^{(2)}_{yyy}|$ and $|\chi^{(2)}_{yxx}|$ spectra above the band gap of 2.5 eV ($2\omega$), have a shape similar to that in the $\varepsilon''(\omega)$, suggesting that they are caused primarily by single-photon resonances. Similarly the pronounced features in the $|\chi^{(2)}_{xxy}|$ and $|\chi^{(2)}_{yzz}|$ spectra above the band gap of 2.5 eV ($2\omega$) have a much reduced amplitude and also are rather oscillatory, being rather similar to the $\varepsilon''(2\omega)$ spectra in this regime. This indicates that they stem mainly from the double ($2\omega$) photon resonances.
We now compare the calculated SHG susceptibility of BL and FL PdX₂ with that reported for other NLO materials. ML group 6B TMDC semiconductors such as MoS₂, are considered to be the most promising 2D NLO materials because of their direct band gaps and large SHG susceptibility (see reference [5] and references therein). Remarkably, figure 7(c) shows that the maximum values of the SHG susceptibility of BL PdX₂ are comparable or even larger than that of ML group 6B TMDCs [5]. Similarly, FL PdX₂ generally have the SHG susceptibility that are comparable or even larger than that of TL group 6B TMDCs [5]. Interestingly, ReS₂ is another rare TMDC that exhibits second-order NLO responses only when the number of layers is even. The measured SHG susceptibility of BL ReS₂ is large, being about 900 pm V⁻¹ at 0.8 eV [55]. Nevertheless, this is smaller than that of BL PdS₂ and BL PdSe₂.

### 3.5. Linear electro-optical coefficient

Here we estimate the LEO coefficients of BL and FL PdX₂ structures, based on the obtained SHG susceptibility at low-frequency limit and static dielectric constant. Note that the LEO coefficients we present here represent only the electronic contribution. There are other contributions to the LEO coefficient such as ionic and piezoelectric contributions, which are beyond of the scope of the present work. The calculated LEO coefficients $r_{abc}(0)$ at zero frequency along with the static dielectric constants and SHG susceptibilities $\chi^{(2)}(0,0,0)$ are listed in table 2. It is clear from table 2 that BL PdS₂ and BL PdSe₂ have much larger LEO values than FL PdS₂ and FL PdSe₂. BL PdS₂ and BL PdSe₂ also exhibit a rather strong anisotropy in the LEO effect. Semiconductor GaAs was reported to have an LEO coefficient of $r_{xyz}(0) = -1.5$ pm V⁻¹ [57]. Recent calculations [5] predicted that the magnitudes of the LEO coefficients of ML group 6B TMDC semiconductors are about 1.5 pm V⁻¹, being close to that of GaAs. Table 2 indicates that the LEO coefficients for BL PdS₂ and BL PdSe₂ are many times smaller than that of GaAs [57] and also ML group 6B TMDC semiconductors [5]. Nevertheless, they are in the same order of magnitude as that of trilayer group 6B TMDC semiconductors [5].

### 4. Discussion and conclusions

It was recently pointed out [58] that the size of the band gap of a semiconductor is a principal factor that determines the strength of its second-order NLO responses. To understand other origins of the large NLO responses in the 2D PdX₂ structures compared with other NLO materials of similar band gaps, we calculate the deformation charge density, which is defined as the difference between the valence charge density and
the superposition of the free atomic charge densities. The calculated deformation charge density distributions for the four 2D PdX$_2$ structures look very similar. Thus, here we focus only on the deformation charge density of BL PdSe$_2$, which is displayed in figure 13. Clearly, there is a significant buildup of the electron charge in the vicinity of the Pd–Se bond center by depleting the charge around the Pd atoms along the bond directions. This is caused by the strong directional covalent bonding in BL PdSe$_2$, and can lead to an enhanced optical responses due to large spatial overlap between the wavefunctions of the initial and final states, and high anisotropy which would result in large NLO response values [58–60].

We notice that the NLO responses of FL PdX$_2$ are generally weaker than that of BL PdX$_2$ (see figures 5–7, 9 and 10). In particular, figure 6(c) shows that the injection current susceptibility of FL PdSe$_2$ is about half of that of BL PdSe$_2$. This can be roughly explained as follows. As mentioned earlier, 2D PdX$_2$ materials with an odd layer-number is centrosymmetric, i.e. they have no second-order NLO response. On the other hand, a 2D PdX$_2$ material with an even layer-number, which can be considered as a 2D PdX$_2$ material with an odd layer-number plus one PdX$_2$ ML, is noncentrosymmetric. In other words, in either BL or FL PdX$_2$, effectively, only one PdX$_2$ ML is second-order NLO active. Consequently, since the effective unit cell volume for FL PdX$_2$ is a factor of 2 larger than that of BL PdX$_2$, the magnitude of the NLO responses of FL PdX$_2$ would be only half of that for BL PdX$_2$ if both structures had a similar band gap and

|        | $\varepsilon_x$ | $\varepsilon_y$ | $\varepsilon_z$ | $\chi^{(2)}_x(0)$ (pm V$^{-1}$) | $\chi^{(2)}_y(0)$ (pm V$^{-1}$) | $\chi^{(2)}_z(0)$ (pm V$^{-1}$) | $r_{yx}$ (pm V$^{-1}$) | $r_{xy}$ (pm V$^{-1}$) | $r_{yz}$ (pm V$^{-1}$) | $r_{yz}$ (pm V$^{-1}$) |
|--------|-----------------|-----------------|-----------------|-------------------------------|-------------------------------|-------------------------------|------------------|------------------|------------------|------------------|
| BL-PdS$_2$ | 12.95           | 12.73           | 5.97            | $-$11                        | $-$8.80                       | $-$13                        | 0.13             | 0.11             | 0.16             | 0.09             |
| BL-PdSe$_2$ | 13.84           | 13.90           | 6.68            | $-$28                        | $-$22                         | $-$24                        | 0.29             | 0.23             | 0.25             | 0.19             |
| FL-PdS$_2$ | 12.09           | 11.92           | 5.40            | $-$6.75                      | 1.39                          | $-$5.41                      | 0.09             | 0.02             | 0.08             | 0.01             |
| FL-PdSe$_2$ | 14.84           | 14.64           | 8.46            | $-$0.96                      | 12                            | 4.90                         | 0.01             | 0.11             | 0.05             | 0.05             |

Figure 12. (a) and (c) Absolute value of the imaginary part of the SHG susceptibility and (b) and (d) imaginary dielectric constant of FL PdS$_2$ [PdSe$_2$].
also interlayer interaction is negligible (see equations (2) and (3)). Nevertheless, FL PdX$_2$ generally has a smaller band gap than BL PdX$_2$. Also interlayer interaction is not negligibly small. Therefore, the strength of the second-order NLO responses of FL PdX$_2$ generally falls between half and one of that for BL PdX$_2$. This is quite similar to 2D group 6B TMDC semiconductors (MX$_2$) where the magnitude of SHG for TL MX$_2$ is about 1/3 of that of ML MX$_2$ [3].

In conclusion, we have systematically studied the second-order NLO responses of BL and FL PdX$_2$ structures using first-principles DFT calculations. First of all, we predict that the BPVE in the considered 2D PdX$_2$ structures is generally strong, with a large shift current conductivity of up to 130 $\mu$A V$^{-2}$ and injection current susceptibility of up to $100 \times 10^8$ A V$^{-2}$ s$^{-1}$ in the visible frequency range. Indeed, the calculated shift currents in these atomically thin PdX$_2$ semiconductors (figure 8) are comparable to that observed in bulk ferroelectric BaTiO$_3$ [44]. Secondly, we find that all PdX$_2$ structures possess large SHG susceptibility $\chi^{(2)}$ in the visible frequency spectrum and BL PdSe$_2$ has the largest $\chi^{(2)}$ value of $1.4 \times 10^3$ pm V$^{-1}$ at 1.9 eV. Thirdly, we find that the LEO coefficients of BL PdS$_2$ and BL PdSe$_2$ are significant. These superior NLO responses of the BL and FL PdX$_2$ structures will make them valuable for technological applications in NLO and electro-optic devices such as light signal modulators, frequency converters, electro-optical switches, photovoltaics and photodetector applications. Finally, the strong NLO responses of BL and FL structures of PdX$_2$ are attributed to strong intralayer directional covalent bonding and also 2D quantum confinement.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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