Calculation of shift current tensors in two-dimensional transition metal dichalcogenides

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Abstract. We investigate the shift current induced by optical excitation in two-dimensional transition metal dichalcogenides. Our approach is based on a second-order perturbation expansion of the semiconductor Bloch equations which are formulated in the basis of a three-band tight-binding model. From that, shift current tensors have been calculated for several different materials and their dependence on photon energy has been investigated and discussed.

Keywords: Nonlinear optics, Photovoltaic effect, Transition metal dichalcogenides.

1 Introduction

The interaction of light with a noncentrosymmetric crystal can produce an electric current [1–6]. This phenomenon is known as the bulk photovoltaic effect (BPVE) and is a second-order response in the light-matter interaction. Microscopic analysis shows that BPVE consists of different contributions such as shift current, rectification current, and ballistic current. The shift and rectification currents result from the asymmetric displacement of electrons in real space when they are excited resonantly and nonresonantly, respectiverly. While the above two currents originate from single-particle properties, i.e. determined by the band structure and single-particle wave function, the ballistic current is a many-body effect, caused by asymmetric scattering processes.

Two-dimensional transition metal dichalcogenides (TMDs) have recently received much attention due to their interesting properties for applications [7–11]. In monolayer form these materials are semiconductors with a direct band gap. Thanks to the huge spin-orbit coupling and the absence of an inverse symmetry center in the crystal, TMDs belongs to the group of materials with a large photovoltaic effect [12–14].

In this work we focus on the shift current in two-dimensional TMDs. From the perturbation solution of the semiconductor Bloch equations, we derive the analytical expression for the shift current tensor. We next perform numerical calculations using the band structure and wave functions obtained from the three-band tight-binding model for monolayers of TMDs [15].

2 Theoretical approach

To calculate the band structrure and single-electron wave functions for monolayers of TMDs, we employ the three-band tight-binding model with spin-orbit coupling proposed in Ref. [15].

The tight-binding wave function has the form

$$|\psi_{\lambda\mathbf{k}}(\mathbf{r})\rangle = \sum_{\alpha} c_{\lambda\alpha}(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{\alpha}(\mathbf{r}-\mathbf{R})\rangle \tag{1}$$

and the matrix elements of the tight-binding Hamiltonian are given by

$$H^{\mathrm{TB}}_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \langle\phi_{\alpha}(\mathbf{r})|\hat{H}|\phi_{\beta}(\mathbf{r}-\mathbf{R})\rangle, \tag{2}$$

where λ denotes the band index, $\mathbf{k}$ is the two-dimensional wave vector, $\mathbf{R}$ is the lattice vector, $\hat{H}$ is the single-particle Hamintonian, and $|\phi_{\alpha}\rangle$ and $|\phi_{\beta}\rangle$ are the basic atomic orbital functions. By numerically diagonalizing the tight-binding Hamiltonian for each value of $\mathbf{k}$, one obtains the band structure $\varepsilon_{\lambda}(\mathbf{k})$ and expansion coefficients $c_{\lambda\alpha}(\mathbf{k})$ of eigenstates $|\psi_{\lambda\mathbf{k}}(\mathbf{r})\rangle$.

In the basis of the above tight-binding eigenstates the second-quantized Hamiltonian that describes electrons interacting with a light field is written in velocity gauge as

$$H = \sum_{\lambda,\mathbf{k}} \varepsilon_{\lambda}(\mathbf{k}) a^{+}_{\lambda\mathbf{k}} a_{\lambda\mathbf{k}} + \frac{e}{m} \sum_{\lambda,\lambda',\mathbf{k}} \mathbf{A}(t)\cdot\mathbf{p}_{\lambda\lambda'}(\mathbf{k}) a^{+}_{\lambda\mathbf{k}} a_{\lambda'\mathbf{k}}, \tag{3}$$

where $a^{+}_{\lambda\mathbf{k}}$ ($a_{\lambda\mathbf{k}}$) is the creation (annihilation) operator of an electron with wave vector $\mathbf{k}$ in band λ, $\mathbf{A}(t)$ is the vector potential of the light field, e is the elementary charge, m is the mass of free electron, and $\mathbf{p}_{\lambda\lambda'}(\mathbf{k})$ are the matrix elements of canonical momentum. Neglecting the intra-atomic contribution, the momentum matrix elements are approximately given by [16]

$$\mathbf{p}_{\lambda\lambda'}(\mathbf{k}) = \frac{m}{\hbar} \sum_{\alpha,\beta} c^{*}_{\lambda\alpha}(\mathbf{k}) \nabla_{\mathbf{k}} H^{\mathrm{TB}}_{\alpha\beta}(\mathbf{k}) c_{\lambda'\beta}(\mathbf{k}). \tag{4}$$

The optoelectronic response is described by the quations of motion for the reduced density matrix elements $\rho_{\lambda\lambda'}(\mathbf{k}) = \langle a^{+}_{\lambda'\mathbf{k}} a_{\lambda\mathbf{k}}\rangle$, which are also known as the semiconductor Bloch equations [17–20]

$$\begin{aligned} \frac{d}{dt}\rho_{\lambda\lambda'}(\mathbf{k}) = &-\frac{i}{\hbar}\left(\varepsilon_{\lambda}(\mathbf{k}) - \varepsilon_{\lambda'}(\mathbf{k})\right)\rho_{\lambda\lambda'}(\mathbf{k}) \\ &- \frac{ie}{\hbar m}\mathbf{A}(t)\cdot\sum_{\mu}\left(\mathbf{p}_{\lambda\mu}(\mathbf{k})\rho_{\mu\lambda'}(\mathbf{k}) - \rho_{\lambda\mu}(\mathbf{k})\mathbf{p}_{\mu\lambda'}(\mathbf{k})\right). \end{aligned} \tag{5}$$

From the reduced density matrix, it is posible to calculate the current density

$$\mathbf{J}(t) = \frac{e}{L^2 m} \sum_{\lambda,\lambda',\mathbf{k}} \left(\mathbf{p}_{\lambda\lambda'}(\mathbf{k}) + e\mathbf{A}(t)\right)\rho_{\lambda'\lambda}(\mathbf{k}). \tag{6}$$

In the case of weak fields, we can use a perturbation approximation for the light-matter interaction. Expanding the density matrix as a power series of the field amplitude, $\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + ...$, where $\rho^{(n)} \propto A^n$, we obtain the equations of motion for the density matrix component of arbitrary order

$$\frac{d}{dt}\rho^{(n)}_{\lambda\lambda'}(\mathbf{k}) = -i\omega_{\lambda\lambda'}(\mathbf{k})\rho^{(n)}_{\lambda\lambda'}(\mathbf{k}) - \frac{ie}{\hbar m}\mathbf{A}(t)\cdot\sum_{\mu}\left(\mathbf{p}_{\lambda\mu}(\mathbf{k})\rho^{(n-1)}_{\mu\lambda'}(\mathbf{k}) - \rho^{(n-1)}_{\lambda\mu}(\mathbf{k})\mathbf{p}_{\mu\lambda'}(\mathbf{k})\right), \tag{7}$$

where $n \geq 1$ and $\hbar\omega_{\lambda\lambda'}(\mathbf{k}) = \varepsilon_{\lambda}(\mathbf{k}) - \varepsilon_{\lambda'}(\mathbf{k})$. After solving Eq. (7) up to second order ($n = 2$) we obtain the second-order current response from

$$\mathbf{J}^{(2)}(t) = \frac{e}{L^2 m} \sum_{\lambda,\lambda',\mathbf{k}} \mathbf{p}_{\lambda\lambda'}(\mathbf{k})\rho^{(2)}_{\lambda'\lambda}(\mathbf{k}). \tag{8}$$

For the vector potential of the light field in the form

$$\mathbf{A}(t) = \mathbf{A}_\omega e^{-i\omega t} + c.c., \tag{9}$$

the steady current component of (8) which is known as the shift current has the analytical form as follows

$$J_i^{\text{shift}} = \sum_{j,k} \sigma_{ijk}^{\text{shift}}(\omega) A_\omega^{j*} A_\omega^k + c.c., \tag{10}$$

where

$$\sigma_{ijk}^{\text{shift}}(\omega) = \frac{e^3}{L^2\hbar^2 m^3} \sum_{c,v,\mathbf{k}} \frac{p_{cv}^k(\mathbf{k})}{\omega_{cv}(\mathbf{k}) - \omega - i\gamma} \left[\sum_{\lambda \neq c} \frac{p_{v\lambda}^j(\mathbf{k}) p_{\lambda c}^i(\mathbf{k})}{\omega_{c\lambda}(\mathbf{k}) - i\gamma} - \sum_{\lambda \neq v} \frac{p_{v\lambda}^i(\mathbf{k}) p_{\lambda c}^j(\mathbf{k})}{\omega_{\lambda v}(\mathbf{k}) - i\gamma} \right] \tag{11}$$

is the shift current tensor, and i, j, k are Cartesian coordinate indices.

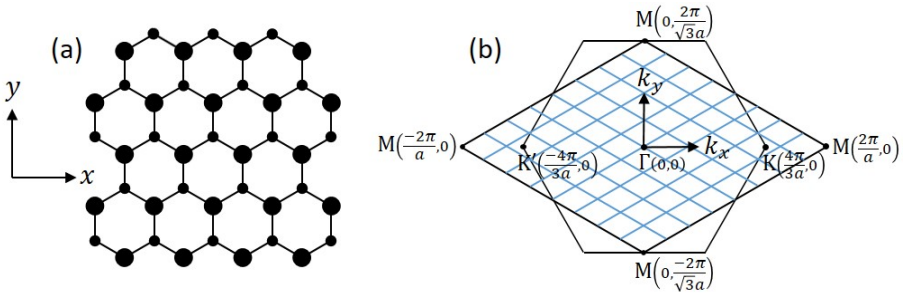

Fig. 1. (a) Top view of TMD monolayer in real space. (b) The primitive cell of the reciprocal lattice and the k-grid used in the calculation.

3 Numerical results and discussion

To calculate the sum over $\mathbf{k}$ states we use the approximate integration

$$\sum_{\mathbf{k}} ... \longrightarrow \frac{L^2}{4\pi^2} \iint_{\text{BZ}} dk_x dk_y ...$$

Fig. 1 shows (a) the TMD crystal structure in two dimensional real space and (b) its Brillouin zone (BZ) in k-space. For convenience, we choose the primitive cell of the reciprocal lattice and the grid of $\mathbf{k}$ points to be rhombus-shaped as shown in Fig. 1(b). The number of $\mathbf{k}$ points in the numerical calculation is up to $N_k = 200^2 = 40000$. The band structure and wave functions for several materials are numerically computed using the three-band tight-binding model [15].

We calculate shift current tensors using Eq. (11) with a damping coefficient of $\hbar\gamma = 0.1$ eV. Since monolayer TMD has the symmetry of D_{3h} point group, there are the following non-zero second-order tensors: $-\sigma_{yyy}^{\text{shift}} = \sigma_{yxx}^{\text{shift}} = \sigma_{xxy}^{\text{shift}} = \sigma_{xyx}^{\text{shift}}$. In Figs. 2(a) and 2(b) we plot the real part and the imaginary part of shift current tentor $\sigma_{yxx}^{\text{shift}}$ as a function of photon energy $\hbar\omega$ for several monolayer TMDs. From Fig. 2 we see that the shift current is absent when the photon energy is smaller than the bandgap. As the photon energy increases near and above the bandgap the shift current appears and changes in a complex and non-monotonous way. The sign change of the current tensor at a certain photon energy means that the current

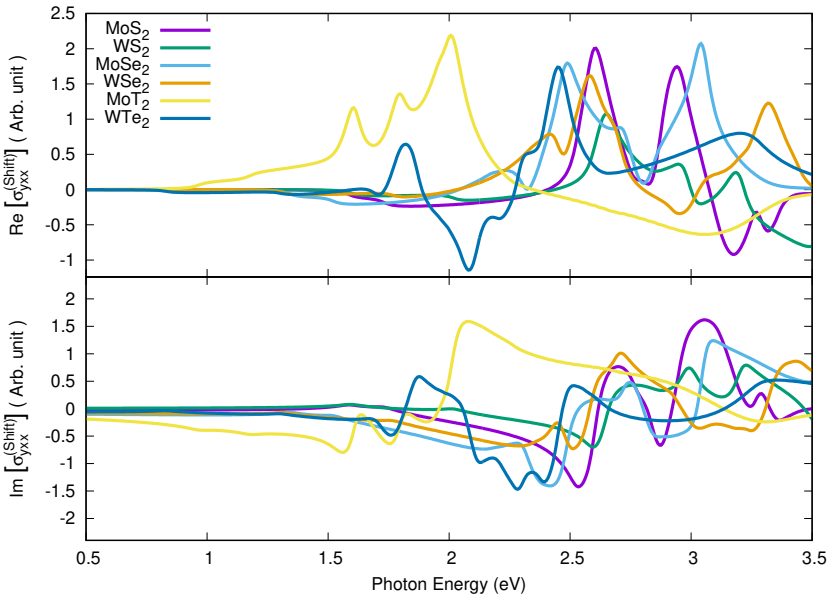

Fig. 2. (a) The real and (b) imaginary parts of the shift current tensor as a function of photon energy $\hbar\omega$ for several different materials. The bandgaps of MoS_2, WS_2, $MoSe_2$, WSe_2, $MoTe_2$, WTe_2 are 1.585, 1.596, 1.339, 1.314, 0.965, 0.83, respectively.

reverses its direction and this can be useful in applications of controlling the direction of photovoltaic current by changing the frequency of the excitation light.

In this study, we however ignored many-body effects such as the Coulomb interaction between carriers and the interaction between carriers and phonons. Many-body interactions in a spatial asymmetric medium can produce an asymmetric distribution of carriers in k-space and thus generate a ballistic current. Unlike the shift current obtained from off-diagonal contributions ($\lambda \neq \lambda'$) of the density matrix in Eq. (8), the ballistic current is given by the diagonal contributions ($\lambda = \lambda'$). Our recent work on GaAs showed that Coulomb interaction between electron and hole leads to a ballistic current that is even larger than the shift current for excitonic resonance excitations [20].

4 Conclusions

Based on the three-band tight-binding model and the perturbative solutions of the semiconductor Bloch equations, we have calculated the shift current tensor for several monolayer TMDs. We obtain a complex non-monotonic dependence of the shift current tensor on the photon energy. Work on calculating many-body interactions, in particular, the electron-hole Coulomb interaction to describe ballistic currents, is in progress.

Acknowledgement

This work is supported by the Vietnam Academy of Science and Technology through the project CSCL14.03/23-24.

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