03,08

Short-range impurity center in a monolayer of transition metal dichalcogenides

© R.Z. Vitlina, L.I. Magarill, A.V. Chaplik

Rzhanov Institute of Semiconductor Physics, SB RAS
Novosibirsk, Russia

E-mail: ritta@isp.nsc.ru; chaplik@isp.nsc.ru

Received July 23, 2025
Revised July 24, 2025
Accepted July 24, 2025

Electronic characteristics of a short-range impurity center in a monolayer of transition metal dichalcogenides (TMDC) are theoretically investigated. The bound states energy, electron scattering cross-section and photoionization probability are found. The valley selectivity coefficient for the impurity-to-band transitions is calculated.

Keywords: transition metal dichalcogenides, short-range impurity, transport cross-section, photoionization.

DOI: 10.61011/PSS.2025.08.62255.210-25

1. Introduction

A two-dimensional electron system, which is a TMDC monolayer, is interesting for a specific feature of its band structure. Presence of two nonequivalent valleys, wherein each of them has a nonzero total moment of momentum, generates a number of unusual physical effects, which were studied in many theoretical and experimental studies [1–6]. Significantly less attention is paid in the literature to the influence of the mentioned specific features of a band spectrum of the TMDC monolayers on processes, which are related to presence of impurities in the system. Meanwhile, these processes are also distinguished from similar phenomena in ordinary semiconductors and these differences can be experimentally detected.

In the proposed article, we consider a spectrum impurity states on a short-range center, photoionization of this center, i.e. impurity−band transitions, as well as electron scattering on the impurity, which determines a contribution by the impurities to resistance of the monolayer. We describe electrons in the TMDC monolayer by a two-band model accepted in the literature [7] with taking into account spin-orbit (SO) band splitting:

$$\hat{H} = \begin{vmatrix} \Delta/2 + \lambda_c \sigma\tau & \gamma(\tau\hat{k}_x - i\hat{k}_y) \\ \gamma(\tau\hat{k}_x + i\hat{k}_y) & -\frac{\Delta}{2} + \lambda_v \sigma\tau \end{vmatrix}, \qquad (1)$$

where $\hat{\mathbf{k}}$ — the operator of the 2D momentum of electron, $\sigma = \pm 1$ — the spin number, $\tau = \pm 1$ — the valley number, $2\lambda_v$, $2\lambda_c$ — the spin splittings in a valence band and a conduction band, γ — the interband velocity, Δ — the band gap width within taking into account SO (hereinafter $\hbar = 1$).

All the things below belong to an exactly solvable model of the potential $U(r)$ of the impurity center — a round potential well of the radius a and the depth V_0. In the cylindrical coordinates, components of a spinor wave function of the Hamiltonian (1) are written as $\psi_1 = R_1(r)e^{im\varphi}$, $\psi_2 = R_2(r)e^{i(m+\tau)\varphi}$, where the radial functions satisfy the system of equations:

$$R_1(r)\big[dc - E + U(r)\big] - i\gamma\left[\frac{m+\tau}{r}R_2(r) + \tau R_2'(r)\right] = 0,$$

$$i\gamma\left[\frac{m}{r}R_1(r) - \tau R_1'\right] - R_2(r)\big[dv + E - U(r)\big] = 0. \qquad (2)$$

Here, $d = \Delta/2$, a prime means differentiating with respect to r. For the spinors ($R = (R_1, R_2)$) bound in a well of states, we have:

$$R(r) = \left(J_m(qr),\ \frac{i\gamma q J_{m+\tau}(qr)}{dv + E + V_0}\right) \quad (r < a)$$

$$R(r) = \left(K_m(r\kappa_0),\ K_{m+\tau}(r\kappa_0)\frac{i\gamma\kappa_0\tau K_{m+\tau}(r\kappa_0)}{dv + E}\right) \quad (r > a), \qquad (3)$$

where J_m and K_m are the Bessel and Macdonald functions. The following notations are introduced in (2) and (3):

$$dc = d + \lambda_c\nu, \quad dv = d - \lambda_v\nu; \quad \nu = \pm 1;$$

$$(\gamma q)^2 = (E - dc + V_0)(E + dv + V_0);$$

$$(\gamma\kappa_0)^2 = (dc - E)(dv + E).$$

By stitching the spinors in the point $r = a$, we find a dispersion equation for energies of bound levels $E_m(\sigma, \tau)$:

$$\frac{J_m(qa)(E + dv + V_0)}{qJ_{m+\tau}(qa)} = \frac{K_m(\kappa_0 a)(E + dv)}{\tau\kappa_0 K_{m+\tau}(\kappa_0 a)}. \qquad (4)$$

It follows from properties of the cylindrical functions that the spectrum of the bound states is characterized by a symmetry $E_m(\sigma, \tau) = E_{-m}(-\sigma, -\tau)$, i.e. all the levels are doubly degenerate.

Numerical calculation for MoS_2 when $a = 5$ Å, $V_0 = 0.5$ eV gives two levels with a moment $m = 0$ in each

valley, which differ by a spin projection (of the quantum number σ). The binding energies of these levels are 72 meV and 83 meV. Spin splitting in each valley at the specified τ is equal to splitting by the valley index τ for each value of the spin projection σ.

All the foregoing belongs to an electric-type impurity, which attracts electrons and repels holes. In a two-band situation, another-type impurity is possible, for example, a structural defect or a deep trap that attracts both electrons and holes (a recombination center). In this case, the impurity potential in the form of $U(r)\sigma_z$ is included in the Hamiltonian. Calculation for MoS_2 shows a slight difference of the binding energy from the above-considered case: 53 meV and 63 meV.

2. Elastic scattering

In order to find a scattering section, it is necessary to have a solution of the system of equations (2), which in infinity consists of a flat wave with a spinor amplitude (falling particles) and a superposition of diverging cylindrical waves with the different moments m. As in the case of a common Schrödinger scattering problem, superposition coefficients are selected so that all terms with the converging waves are cancelled in the difference of the exact solution and the spinor flat wave. If selecting the spinor flat wave normalized to a unit flux (the current operator in the considered problem is $\hat{\mathbf{v}} = \gamma\boldsymbol{\sigma}_\tau = \gamma(\tau\sigma_x, \sigma_y)$), then a squared module of the spinor scattering amplitude $\hat{f}(\phi)$ will at once provide a differential scattering section along the direction ϕ. By omitting a long, but quit obvious computation, we provide a result:

$$\hat{f} = \begin{vmatrix} f_1 \\ f_2 \end{vmatrix} = \sum_m \left(\frac{e^{-i\pi/4}}{2\sqrt{\pi\gamma\kappa}} (e^{2i\Phi_m} - 1) \begin{vmatrix} G\, e^{im\phi} \\ (\tau/G)\, e^{i(m+\tau)\phi} \end{vmatrix} \right), \tag{5}$$

where

$$\kappa = \sqrt{(E - dc)(E + dv)}/\gamma;$$

$$G = \left(\frac{E + dv}{E - dc}\right)^{1/4}; \quad e^{2i\Phi_m} = \frac{D_{1,m}}{D_{2,m}}. \tag{6}$$

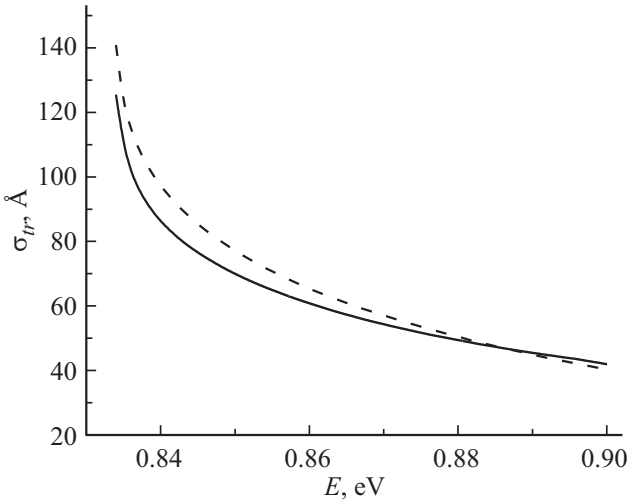
For $D_{1,m}$ and $D_{2,m}$ we have:

$$D_{1,m} = -\frac{i\gamma\kappa}{E + dv} J_m(qa) H^{(2)}_{m+\tau}(\kappa a) - \frac{i\gamma q}{E + dv + V_0} J_{m+\tau}(qa) H^{(2)}_m(\kappa a); \tag{7}$$

$$D_{2,m} = D^*_{1,m}. \tag{8}$$

The bilinear combinations $f_1 f_2^*$ and $f_1^* f_2$ now have no dependence on the index τ explicitly included in the formulas, so that the section depends on the valley only via a combination $\tau\sigma$ included in the parameters dc and dv. When calculating the full transport section, a multiplier $(1 - \cos(\phi))$ after angle integration leaves only 3 terms in the double sum on m and m': $m = m'$, $m = m' - 1$ and $m = m' + 1$, wherein the third contribution is reduced to the second one by shifting a summing index. Finally we obtain:

$$\sigma_{tr} = \frac{2}{\kappa} \sum_{m=-\infty}^{m=\infty} \sin^2(\Phi_m - \Phi_{m-1}) \tag{9}$$



Dependence of the transport section on the energy. The solid curve corresponds to the electric-type impurity potential, while the dotted line corresponds to the structural defect.

The formula (9) written in this form coincides with the result obtained in the study [8] and [9] for the ordinary semiconductor described by the Schrödinger equation, but determination of the phases Φ_m is of course different from the TMDC case.

The twice as large coefficient in front of the sum is explained in the studies [8,9] by the fact that we relate (9) to this valley and this value of the spin index σ, whereas the authors [8,9] neglected spin splitting and just made a spin summation.

In the same way as in the above-considered issue of the bound-state energy, replacement of the electric impurity potential with a deep trap potential does not result in crucial changes in the scattering pattern as long as the amplitude V_0 is still less than a half-width of the band gap.

Results of numerical calculation of the dependence of the transport section on the energy in MoS_2 for the well with the parameters $V_0 = 0.5$ eV, $a = 5$ Å are given in the figure. The curves show the dependence $\sigma_{tr}(E)$ for both the types of the potential when $\nu = +1$ (in this case the threshold energy is $d + \lambda_c$).

We note an interesting specific feature of the energy dependence of the singularity section for the two types of the impurity. In case of the electric-type potential, its matrix element of the undisturbed wave functions is provided by a sum of integrals, wherein one of them includes upper components of the spinors of the initial and final states and the second one includes the lower components thereof. And for the impurity of the structural-defect type there is a difference of such integrals, therefore, the module of the

matrix element is smaller in the latter case. It results in two competing factors. First of all, at the same parameters of the well this potential „holds" the particles more weakly than the electric-type potential and the energy level in it is more shallow. Secondly, the smaller value of the matrix element decreases perturbation of the wave function of a bombarding particle, thereby resulting in attenuation of scattering. With the low energies, the more shallow level enhances a resonance effect in scattering and this effects turns out to be stronger than reduction of the module of the matrix element. With the increase of the energy, a role of the resonance effect decreases and a section of scattering by the structural defect becomes less than in the case of the electric-type impurity. The described competition results in intersection of the curves in the figure at a certain value of the energy E_c. In our example, E_c is spaced away from a bottom of the conduction band by ~ 53 meV.

3. Photoionization of the impurity center

Let us consider the impurity–band under effect of circularly polarized emission with the polarization vector $\mathbf{e} = (1, i\xi)/\sqrt{2}$ ($\xi = \pm 1$ is the polarization index). An operator of interaction with radiation in the system with the Hamiltonian (1) is provided by an expression

$$\hat{H}_{int} = e\gamma \mathscr{A}_0 \hat{h}_{\tau,\xi} \mathrm{e}^{-i\omega t} + h.c.;$$

$$\hat{h}_{\tau,\xi} = \frac{1}{2}\left(\tau\sigma_x + i\xi\sigma_y\right) = \frac{1}{2}\begin{bmatrix} 0 & \tau+\xi \\ \tau-\xi & 0 \end{bmatrix}, \qquad (10)$$

where $\mathscr{A}_0$ — the amplitude of the light-wave vector-potential, $\xi = \pm 1$ for right (left) polarization of light.

Transitions between states with a definite value of the moment under effect of circularly polarized emission from the state (E_0, m) into the state (E, m') follow the rule selection by the number m, which is determined only by an angular part of the wave function and therefore does not depend on details of a behavior of the axially symmetrical potential. At any τ we have $m' = m + \xi$. The numbers τ and σ are preserved during the optical transition. But in case of photoionization of the bound state the finite wave function shall in infinity have a form of the flat wave with a certain momentum. By constructing the spinor of the final state according to the known rules, we obtain superposition of the wave functions with all the moments m. Integration with the wave function of the bound level $(m = 0)$ in the matrix element of the transition selects only a term with $m' = \xi$ from the entire superposition. The wave function of the state (E, m') shall asymptotically at large distances from the center transform into superposition of the flat wave and the converging spherical wave, wherein the moduli of momenta of both the waves correspond to the energy of the final state $E = E_0 + \omega$ (ω — the frequency of incident radiation).

Probability of the process W is equal to a sum of the two contributions:

$$W = \frac{(1+\xi\tau)}{2} W_+ + \frac{(1-\xi\tau)}{2} W_-. \qquad (11)$$

Although all the integrals that determine W_+ and W_- are taken in a closed form, appearing expressions are rather cumbersome. In (11), we have explicitly parenthesized multipliers than carry the dependence on radiation polarization.

Of interest is a threshold behavior of probability of the process with the energy of a photon close to the minimum possible one ω_c, where $\omega_c = d - E_0$. This behavior is described by the formulas:

$$W_+ = C_+(\omega - \omega_c), \quad W_- = C_-(\omega - \omega_c). \qquad (12)$$

The constants C_+ and C_- are provided by the following expressions:

$$C_+ = \left\{ \frac{\sqrt{d}(2V_0 + d)[q_0\bar{q}a^2 J_0(\bar{q}a)J_1(q_0a) - q_0^2 a^2 J_0(q_0a)J_1(\bar{q}a)]}{\sqrt{2}(q_0^2 - \bar{q}^2)(d + E_0 + V_0) \times [d\bar{q}aJ_0(\bar{q}a)J_1(q_0a) + V_0 J_1(\bar{q}a)]} + \frac{\sqrt{d}\,K_2(\kappa_0 a)}{(d+E_0)\sqrt{2}} \right\}^2; \qquad (13)$$

$$C_- = \left\{ \frac{a\bar{q}J_0(q_0a)J_1(\bar{q}a) - J_0(\bar{q}a)J_1(q_0a)}{\sqrt{2d}(q_0^2 - \bar{q}^2)J_0(\bar{q}a)} + \frac{a}{\sqrt{2d}\kappa_0 J_0(\bar{q}a)} K_1(\kappa_0 a) \right\}^2. \qquad (14)$$

The notation is introduced here:

$$q_0 = \sqrt{(E_0 + V_0)^2 - d^2}/\gamma, \quad \kappa_0 = \sqrt{(d^2 - E_0^2)}/\gamma,$$

$$\bar{q} = \sqrt{(2V_0 + d)V_0}/\gamma.$$

Inequality of these constants means selectivity of probability of photoionization, wherein its energy dependence is qualitatively different from the similar dependence of the band–band transition for the free electron. The latter is determined by a ratio $s = W_+/W_-$ and in the symmetrical model ($\Delta_c = \Delta_v = \Delta$) $s = [(\omega - \Delta)/(\omega + \Delta)]^2$, where ω — the frequency of the absorbed photon. Thus, in one of the valleys absorption tends to zero at the threshold of the process. In our case, when approaching the threshold $\omega = \omega_c$ the ratio W_+/W_- tends to a constant value, which is for the symmetrical model turns out to be quite close to unity. Let us provide the values of the selectivity parameter $s(V_0, a)$ for MoS_2 at several values of the parameters of the potential well (V_0 in electron-volts, a in angstroms): $s(0.5, 2.5) = 1.0009$; $s(0.5, 3) = 1.0102$; $s(0.5, 4) = 1.0776$; $s(0.5, 5) = 1.0918$; $s(0.4, 5) = 1.0917$; $s(0.3, 5) = 1.0544$; $s(0.2, 5) = 1.0127$.

We see that the photo-induced band−band transitions, in which the momentum of the electron is preserved (the transitions are vertical), result in much more pronounced valley selectivity of the process than the transitions from the state, in which the particle has not a certain momentum, but has a certain moment.

Thus, on the example of the TMDC monolayer we have shown that in the two-valley band structure the two-dimensional electron system with a Dirac spectrum interacts with the impurity qualitatively similarly to the ordinary single-valley situation, if we talk about the bound states on the impurity or about scattering of the electrons on it. However, the optical effects related to the impurity significantly differ from the ordinary situation: photoionization of the impurity center has valley selectivity, whose value depends on the parameters of the impurity potential. It is shown that in the impurity-band transitions selectivity is much less than in the interband transitions, in which the momentum of the electron is preserved.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A. Kormanyos, G. Burkard, M. Gmitra, J. Fabian, V. Zolyomi, N.D. Drummond, V. Falko. 2D Materials **2**, 022001 (2015).
[2] Felix Rose, M.O. Goerbig. Frederic Piechon. Phys. Rev. B **88**, 125438 (2013).
[3] G. Catarina, J. Have, Fernandez-Rossier, N.M.R. Peres. Phys. Rev. B **99**, 125405 (2019).
[4] V.V. Enaldiev. Phys.Rev. B, **96**, 235429 (2017).
[5] D. Oliveira, J. Fu, L.V. Lelovsky, A.C. Dias, F. Qu. Phys. Rev. B, **93**, 205422 (2016).
[6] F. Qu, A.C. Dias, J. Fu, L. Villegas-Lelovsky, D.L. Azevedo. Scientific Reports. **7**, 41044 (2017).
[7] Di Xiao, Gui-Bin Liu, Wanxiang Feng, Xiaodong Xu, Wang Yao. Phys. Rev. Lett. **108**, 196802 (2012).
[8] F. Stern, W.E. Howard. Phys. Rev. **163**, p. 816 (1967).
[9] M.E. Portnoi. Pis'ma v ZhTF, **14**, 1252 (1988). (in Russian).

Translated by M.Shevelev