Interface dark excitons at sharp lateral two-dimensional heterostructures

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Keywords: 2D materials, Lateral Heterostructure, Exciton, Binding energy, geometrical effects

Abstract
We study the dark excitons at the interface of a sharp lateral heterostructure of two-dimensional transition metal dichalcogenides (TMDs). By introducing a low-energy effective Hamiltonian model, we find the energy dispersion relation of exciton and show how it depends on the onsite energy of composed materials and their spin–orbit coupling strengths. It is shown that the effect of the geometrical structure of the interface, as a deformation gauge field (pseudo-spin–orbit coupling), should be considered in calculating the binding energy of exciton. By discretization of the real-space version of the dispersion relation on a triangular lattice, we show that the binding energy of exciton depends on its distance from the interface line. For exciton near the interface, the binding energy is equal to 0.36 eV, while for the exciton far enough from the interface, it is equal to 0.26 eV. Also, it has been shown that for a zigzag interface the binding energy increases by 0.34 meV compared to an armchair interface due to the pseudo-spin–orbit interaction (gauge field). The results can be used for designing 2D-dimensional-lateral-heterostructure-based optoelectronic devices to improve their characteristics.

1. Introduction
The direct-band semiconductors are the most widely used materials in optoelectronic devices. When an electron absorbs a photon with energy equal to or greater than the semiconductor bandgap energy, the electron is excited to the conduction band. If the excited electron falls to the valence band, a photon will be emitted. When an electron is excited by absorbing photon energy, leaves behind a positively charged electron-hole in the valence band. The electron is attracted to the hole by electrostatic Columb force, which creates an electrically neutral quasiparticle called exciton. The electron and hole in an exciton can have either parallel or anti-parallel spin, which forms a bright or dark exciton, respectively. Exciton generation, like doping an impurity, forms new energy levels in the semiconductor band gap.

A homojunction can be created by doping an impurity in a semiconductor material. The interface of two dissimilar semiconductors forms a heterojunction. If photon absorption occurs at the depletion region of the junction, or one diffusion length away from it, the electric field inside the depletion region sweeps away the carriers, which results in a photocurrent. A heterostructure device is composed of multiple heterojunctions that connected together. The semiconductors band alignment in heterojunctions can be categorized into three different types. In type I (straddling gap), the conduction band minima (CBM) of one material is contained (nested) inside the bandgap of the other material. If the bandgap of the first material is rested inside the bandgap of the other material, the type II alignment (staggered gap) is formed. In type III (broken gap), the CBM of one material is equal to the valence band maxima (VBM) of the other one. By bandgap engineering in heterostructures, characteristics of optoelectronic devices can be tuned for the desired application.

Recently, two dimensional materials (2DMs) have been considered as the new candidate for manufacturing heterostructures. Different two-dimensional materials with honeycomb structures including hexagonal boron nitride (h-BN) [1, 2], transition metal dichalcogenides (TMDs) [3, 4], black phosphorus (BP) [5, 6], and silicene...
[7] have been studied for electronic and optoelectronic device development. By vertical (vertical heterostructures (VHSs)) or lateral (lateral heterostructures (LHSs)) integration of 2DMs, an artificial heterostructured 2D layer can be fabricated. The single-, double-, and multi-step chemical vapor deposition (CVD) approaches have been used to grow large-area, sharp 2D heterostructures [8–11]. Also, using the techniques, researchers could grow hetero-triangles composed of a central TMD and an outer triangular ring of another TMD [8, 12, 13]. The other structures such as truncated triangles, hexagons, hexagrams [14] and more complex patterned structures have also been reported [15].

The built-in potential in p–n-junction and its increasing rate under the reversed bias condition are important parameters in designing the homojunction-based optoelectronic devices. Similarly, the band alignment (or band offset) across the junction is an important parameter in material design. The band offset in VHSs [16, 17] and in LHSs [18] have been studied by using the density functional theory (DFT). Ozcelik et al., have introduced the periodic table of heterostructures (HSs) based on the band offset between them [19]. For studying the properties of HSs the tight-binding approach has been used for not only commensurate HSs [20, 21] but also for incommensurate types [22].

Different types of devices can be designed and manufactured after acquisition of design and manufacturing technologies of two dimensional Heterostures (2DHSs). For example, by using monolayer WSe2–WS2 HS, high mobility field-effect transistors (FETs), complementary metal-oxide semiconductor (CMOS) and superior photovoltaic devices have been demonstrated [23]. A light-emitting device (LED) with large conversion efficiency has been built by using the lateral WSe2–MoS2 HS [24]. It has been shown that one can manufacture a photodiode with high photodetectivity of 1013 Jones and short response time of sub-100μs by using the LHS of graphene and thin amorphous carbon [25]. Amani et al., have reported near-unity photon quantum yield in TMD monolayer, which led to the development of highly efficient optoelectronic devices [26]. It has been shown that Mo- and W-based TMDs have bright and dark exciton ground states, respectively, due to the reversal of exciton spin Hall effect in van der Waals HSs [27, 28].

As it has been mentioned above, exciton energy level is placed inside the energy band gap region. Therefore, the creation of exciton in 2DHSs is important from the 2DHS-based optoelectronic devices point of view. The long-lived interlayer excitons in monolayer MoSe2–WSe2 HS have been reported [29], and the light-induced exciton spin Hall effect in van der Waals HSs has been studied [30]. Latini et al., have studied the role of the dielectric screening on the properties of excitons in van der Waals HSs [31]. Lau et al., have studied the interface excitons at lateral heterojunctions in monolayer semiconductors and shown that the competition between the lattice and Coulomb potentials implies the properties of exciton at the interface [32].

One of the important properties of 2DMs is the effect of its boundary on the electronic properties of the nanoribbons composed by the materials. Therefore, it is expected that by changing the electronic property of the nanoribbons, due to the change in their boundaries, the photon absorption and emission by the nanoribbons change, too. It means that in addition to the previous important parameters, the boundary condition or the geometry of two-dimensional nanoribbons be another important parameter in designing and manufacturing the 2DHS-basde optoelectronic devices. For example, it has been shown that the plane integrated modal wave functions of the VBM and CBM for different LHSs with long armchair and zigzag interfaces are localized on Mo-side and W-side, respectively [33]. Also, it has been shown that the wave function behavior is quite different in LHSs with zigzag interface compared to armchair interface [33]. For studying the effect of geometry on the wave function, the normal derivative is substituted by the covariant derivative. It is done by introducing a deformation gauge filed $\tilde{A}$ which is subtracted from the momentum operate in the Hamiltonian of the system [33].

The above short review shows that band gap energy, band offset voltage, type of alignment, interface structure, and the type of chalcogenide in the lateral MX₂–MX₂M (M = transition metal, X = chalcogenide) heterostructures are important in designing an exciton-based optoelectronic devices. The importance of these factors motivated us to study the relationship between the energy of exciton, its binding energy, and the mentioned parameters in the LHSs.

In this paper, we consider monolayer LHSs of transition metal dichalcogenide with armchair and zigzag interfaces. By introducing a low-energy effective Hamiltonian model, we find the energy dispersion relation of dark exciton and show how it depends on the onsite energy of composed materials and their spin–orbit coupling strengths. Using the real-space version of exciton dispersion energy relation and its discretizing on a triangular lattice we find the binding energy of exciton. It is shown that the binding energy depends on the distance of the exciton from the interface line which is governed by the competition between lattice and Coulomb potentials. We show that the effect of the geometrical structure of the interface appears as a deformation gauge field and increases the binding energy of exciton in the zigzag interface. The structure of the article is as follows: section 2 includes the Hamiltonian model. The numerical calculations are provided in section 3. The results and discussion and summary are provided in sections 4 and 5, respectively.
2. Hamiltonian model

Let us consider a lateral heterostructure of MoX$_2$–WX$_2$ with an armchair interface. Since the plane integrated modular wave function of VBM and CBM are localized on W-side and Mo-side, respectively [33], near K ($K'$)-point we can consider the low-energy two-band Hamiltonian model (appendix A) in both sides for studying the behavior of electrons and holes. If the wave functions of Mo (W)-side are called $\phi^M(W)$ and $\phi^M(W)$, a new base function $\psi = (\phi^M(W), \phi^M(W), \phi^M(W), \phi^M(W))^T$ can be defined such that

$$
\begin{pmatrix}
H_{c1}^{Mo} - H_{c1}^{W} \\
-H_{c1}^{W} & H_{c1}^{Mo} - H_{c1}^{W} & 0 \\
0 & H_{c2}^{Mo} - H_{c2}^{W} & 0 \\
0 & 0 & H_{c1}^{Mo} - H_{c1}^{W}
\end{pmatrix}
\times
\begin{pmatrix}
\phi^M(W) \\
\phi^M(W) \\
\phi^M(W) \\
\phi^M(W)
\end{pmatrix}
= (E^{Mo} - E^{W})
$$

(1)

where, $H_{c1}^{Mo} = \begin{pmatrix} H_{c1}^{Mo} & H_{c1}^{W} \\ H_{c1}^{W} & H_{c1}^{Mo} \end{pmatrix}$ and $H_{c1}^{W} = \begin{pmatrix} H_{c1}^{W} & H_{c1}^{Mo} \\ H_{c1}^{Mo} & H_{c1}^{W} \end{pmatrix}$. It should be noted that the Hamiltonian of spin-down hole in W-side is given by $H_{c1}^{W} = -H_{c1}^{W}$. Since, the spin of electron is up and the spin of the hole is down the total spin of the exciton is zero. It means that the exciton is dark. Now, we introduce four eigenfunctions as below

$$
\psi_1 = (\cos(\theta_1/2)\cos(\theta_2/2), \cos(\theta_1/2)e^{i\varphi_1}\sin(\theta_2/2), e^{i\varphi_2}\sin(\theta_1/2)\cos(\theta_2/2), e^{i\varphi_2}\sin(\theta_1/2)e^{i\varphi_2}\sin(\theta_2/2))^T
$$

(2)

$$
\psi_2 = \left( e^{-i\varphi_1}\sin(\theta_1/2) e^{-i\varphi_2}\sin(\theta_2/2), -e^{i\varphi_1}\sin(\theta_1/2)\cos(\theta_2/2), -e^{i\varphi_2}\sin(\theta_1/2)e^{-i\varphi_2}\sin(\theta_2/2), e^{i\varphi_2}\sin(\theta_1/2)\cos(\theta_2/2))^T
$$

(3)

$$
\psi_3 = (\cos(\theta_1/2)e^{i\varphi_1}\sin(\theta_2/2), -\cos(\theta_1/2)\cos(\theta_2/2), e^{i\varphi_2}\sin(\theta_1/2)e^{-i\varphi_2}\sin(\theta_2/2), -e^{i\varphi_2}\sin(\theta_1/2)\cos(\theta_2/2))^T
$$

(4)

$$
\psi_4 = \left( e^{-i\varphi_1}\sin(\theta_1/2) e^{-i\varphi_2}\sin(\theta_2/2), e^{i\varphi_2}\sin(\theta_1/2)/2 e^{i\varphi_2}\sin(\theta_2/2), -\cos(\theta_1/2)\cos(\theta_2/2), -\cos(\theta_1/2)e^{i\varphi_2}\sin(\theta_2/2))^T
$$

(5)

Here, $\theta_1 (\theta_2)$ and $\varphi_1 (\varphi_2)$ are attributed to Mo (W)-side and their definitions are provided in appendix A.

Using the results of appendix A, the low-energy Hamiltonian of lateral heterostructure can be written as

$$
H = \begin{pmatrix}
\frac{\Delta_1 + \Delta_2}{2} & -a_2t_2k_2e^{-i\varphi_2} & a_1t_1k_1e^{i\varphi_1} & 0 \\
-a_1t_2k_2e^{-i\varphi_2} & \frac{\Delta_1 + \Delta_2}{2} - \lambda_2 & 0 & a_1t_1k_1e^{-i\varphi_1} \\
a_1t_1k_1e^{i\varphi_1} & 0 & \frac{\Delta_1 - \Delta_2}{2} + \lambda_1 & -a_1t_2k_2e^{-i\varphi_2} \\
0 & -a_1t_1k_1e^{i\varphi_1} & -a_1t_2k_2e^{-i\varphi_2} & \frac{\Delta_1 - \Delta_2}{2} + \lambda_1 - \lambda_2
\end{pmatrix}
$$

(6)

where, the subscript 1 (2) is attributed to Mo (W)-side. Therefore, it can be easily shown that

$$
H\psi_1 = (E_1 - E_2)\psi_1
$$

(7)

$$
H\psi_2 = (-E_1 + E_2 + \lambda_1 - \lambda_2)\psi_2
$$

(8)

$$
H\psi_3 = (E_1 + E_2 - \lambda_2)\psi_3
$$

(9)

$$
H\psi_4 = (-E_1 - E_2 + \lambda_1)\psi_4
$$

(10)

It is obvious that the Hamiltonian matrix, $H$, can be diagonalized by using the matrix $P = (\psi_1, \psi_2, \psi_3, \psi_4)$ i.e.,

$$
P = \begin{pmatrix}
\cos(\theta_1/2)\cos(\theta_2/2) & e^{-i\varphi_1}\sin(\theta_1/2) & e^{-i\varphi_2}\sin(\theta_2/2) & e^{i\varphi_1}\sin(\theta_1/2) \\
\cos(\theta_1/2)e^{i\varphi_1}\sin(\theta_2/2) & -\cos(\theta_1/2)\cos(\theta_2/2) & e^{i\varphi_2}\sin(\theta_1/2) & -\cos(\theta_1/2)e^{i\varphi_2}\sin(\theta_2/2) \\
e^{i\varphi_1}\sin(\theta_1/2)\cos(\theta_2/2) & -\cos(\theta_1/2)e^{i\varphi_2}\sin(\theta_2/2) & -\cos(\theta_1/2)e^{-i\varphi_2}\sin(\theta_2/2) & -\cos(\theta_1/2)\cos(\theta_2/2) \\
e^{i\varphi_2}\sin(\theta_1/2)e^{i\varphi_2}\sin(\theta_2/2) & \cos(\theta_1/2)e^{-i\varphi_2}\sin(\theta_2/2) & -\cos(\theta_1/2)\cos(\theta_2/2) & -\cos(\theta_1/2)e^{i\varphi_2}\sin(\theta_2/2)
\end{pmatrix}
$$

(11)

However, the eigenfunction $\psi_3$ includes the eigenfunction of electrons which belongs to Mo-side with energy $E_1$, and the eigenfunction of electrons which belongs to W-side with energy $(-E_2 + \lambda_2)$. The eigenvalue related to $\psi_3$ is $(E_1 - (-E_2 + \lambda_2))$.

Up to now, we assumed that the electrons and holes moves freely in the conduction and valence band, respectively. But the electron and hole of exciton are coupled to each other. In the other words, the coupling and
the lattice potentials should be added to the total Hamiltonian matrix at the beginning of the calculation. After adding the all potential terms, the $4 \times 4$ Hamiltonian matrix of equation (6) can be divided to four $2 \times 2$ matrices. It has been shown that if the non-diagonal elements of the $2 \times 2$ matrix, which is placed at the down right corner of $4 \times 4$ Hamiltonian matrix, be equal to zero and the low momentum behavior are only considered the next calculations can be simplified[30]. Under these assumptions, they have shown that equation (13) is satisfied. Instead of using the assumptions, we use a mathematical trick i.e., we consider the free electrons and holes and found the eigenvalue of the eigenfunction $\psi_0$. Now, if we add the lattice potential $V_l = V_e + V_h$ and Coulomb potential $V_C$ to the eigenvalue of $\psi_0$ we will find the energy equation of the exciton as below

$$E_{exc} = E_{h_M}^{h_0} - E_{v_W}^{v_0} + V_l + V_C = E_{h_M}^{h_0} + E_{v_W}^{v_0} + V_l + V_C$$

We can fit a parabola to the energy dispersion curve of Mo-side and W-side near $K$ ($K'$)-point and show (appendix A) $E_{h_M}^{h_0} \approx \frac{h^2 k_x^2}{2 m_1} + \frac{\Delta_1}{2}$ and $E_{v_W}^{v_0} \approx -\frac{h^2 k_x^2}{2 m_2} - \frac{\Delta_2}{2} + \lambda_2$. Therefore, the energy dispersion relation of exciton is as below

$$E_{exc} = \frac{h^2 k_x^2}{2 m_1} + \frac{h^2 k_x^2}{2 m_2} + \frac{\Delta_1 + \Delta_2}{2} - \lambda_2 + V_l + V_C$$

(13)

It means that the final result of our mathematical trick is equal to the final result of Li et al[30]. In the other words, we used a simpler method and showed that the final results are same.

Now a question can be asked. How it would be in other kinds of interfaces? The effect of interface structure can be understood by adding a deformation gauge field to the Hamiltonian[33]. An in-plane gauge field, $\vec{A} = (A_x(x, y), A_y(x, y))$, creates a magnetic filed $\vec{B} = B_y \hat{z}$ which acts as a pseudo-spin–orbit coupling and splits the CBM and VBM and creates the surface states (appendix A). For example, if $\vec{A} = (A_x(y), 0)$ for a zigzag interface, then $B_y = 0$ and the energy of the surface states located in the vicinity of the interface reads [33, 34]:

$$E = \frac{v_F p_x}{\cosh(\frac{1}{g} \int dy A_x(y))}$$

(14)

Therefore, The eigenvalues of zigzag interface differ from armchair interface due to the existence of the surface states. It means that, as it is shown in appendix A, by changing the geometrical structure of the interface, the eigenvalues of the Hamiltonian, $H$, changes, and it is expected that the exciton binding energy changes, too (appendix A). It should be noted that the above results can be used for studying the excitons in van der Waals heterostructures of TMDs because the electrons are localized on the top (bottom) layer while the holes are localized on the bottom (top) layer. Of course, the suitable $V_l$ and $V_C$ should be used[31]. Also, for studying the bright exciton, one should only use the Hamiltonian $E_{w}^{v} = -E_{w}^{v}$ instead of $E_{w}^{h} = -E_{w}^{h}$.

3. Numerical calculations

By using the Fourier transformation, one can find the real-space version of equation (10). Since, the center-of-mass and relative space coordinates are

$$\vec{R}(X, Y) = \frac{1}{M}(m_e \vec{x} + m_h \vec{r}_h)$$

(15)

$$\vec{r}(x, y) = \vec{x} - \vec{r}_h$$

(16)

the Hamiltonian of exciton in real space will be equal to

$$H = -\frac{\hbar^2}{2M} \nabla^2 \vec{R} - \frac{\hbar^2}{2\mu} \nabla^2 \vec{r} + V_C(\vec{R}, \vec{r}) + V_l(\vec{R}, \vec{r})$$

(17)

where, $M = m_e + m_h$ and $\mu = \frac{m_e m_h}{m_e + m_h}$.

Since, the total mass $M$ is at least four times greater than the reduced mass $\mu$, we can apply the Born-Oppenheimer approximation (BOA) and write the eigenfunction as below

$$\Phi(\vec{R}, \vec{r}) = \Psi(\vec{R}) \Theta(\vec{R}, \vec{r})$$

(18)

where $\Psi$ and $\Theta$ are the center of mass and relative motion eigenfunctions, respectively. However, the potential $V_l$ has translational symmetry along the width of the device. Therefore, it is independent of $Y$, and in consequence, $\Psi$ and $\Theta$ can be written as $\Psi = \Psi(X) e^{i\beta Y}$ and $\Theta = \Theta(X, \vec{r})$, where for the ground state of type-II interface exciton $P_y = 0$. Therefore, the corresponding Schrodinger’s equations for the relative motion and center-of-mass motion read [32]
where, $E_{gx}$ is the minimum energy within the exciton band, and $E(X)$ is the energy of exciton. By discretizing equation (18), one can find the minimum eigenvalue $E(X)$ under open boundary conditions for both directions. By using the minimum value, the exciton energy, $E_{gx}$ can be found by solving the equation (19). The binding energy will be found by using the relation $E_{bi} = E_f - E_{gx}$ where $E_f$ is the energy of a noninteracting electron-hole pair at the interface.

How can one discretize equation (18)? Liu et al., introduced a three-band tight-binding model for describing the low-energy physics in a monolayer of TMDs [35]. They showed that the conduction and valence bands are accurately described by $d$ orbitals of metal atoms. Their model involving up to the third-nearest-neighbor hoppings can well reproduce the energy band in the entire Brillouin zone [35]. Therefore, we can assume that the electrons and holes hop between metal atoms that construct a triangular lattice structure. It means that the relative coordinate, $\vec{r}$, moves on a triangular lattice structure when the electron (hole) the hop and hole (electron) is fixed. Therefore, we consider the triangular lattice of metal atoms and discretize the equation (18). It can be shown that the hopping integral on triangular lattice is equal to $\frac{\hbar^2}{3mu}$, where $a$ is the lattice constant (appendix B). It shoul be noted that a nanoribbon can be constructed by repeating a supercell. In electron-side and hole-side of the nanoribbon, we consider a supercell. The geometry and the number of atoms in each supercell change by changing the geometry of the interface. In consequence, in tight-binding method, the elements of the Hamiltonian matrix changes by changing the geometry of the interface and the boundary conditions are implemented.

It is expected that the excitons are created in the vicinity of the interface line by competition between Coulomb and band offset potentials [32, 33]. Therefore, we can consider $\Psi(X) \propto e^{-\alpha|x|}$, where $\alpha = \frac{\sqrt{5M(E(X) - E_g)}}{b}$ > 0 and $X$ is the distance from the interface line in $\hat{x}$-direction. It means that $E_g < E(X)$ because $E(X) < 0$. But, $E(X)$ depends on the competition between $V_f$ and $V_C$, and in consequence, the broadening of $\Psi(X)$ and its value depend on the competition. Hence, the values $V_f$ and $V_C$ are very important for calculating $E(X)$ and $\Psi(X)$.

However, what are the suitable formulas of $V_f$ and $V_C$ for the numerical calculations? The Coulomb potential and its usage for studying the Hydrogen-like atoms and the dielectric properties of two-dimensional materials have been widely studied [31, 36–44]. Felbacq et al., have used the below formula for studying the dielectric properties of two-dimensional materials [42] (appendix C):

$$V_C = \frac{1}{\sqrt{r^2 + \tau^2}} + \frac{\tau}{r}$$

where, $\tau = \left(\frac{2}{5}\right) \times 10^{-4}$. Also, they showed that their results are in a good agreement with the results of others [3]. Therefore, we use the above equation in the following numerical calculations and, for $r = 0$ we set $V_C = U_0 = cte$. The assumption $V_C(r = 0) = U_0 = cte$ have been used by Ref.32 and Ref.42 in order to make the calculation convergent.

The lattice potential $V_f$ possesses the translational symmetry along the width of the nanoribbon and changes along its length in type II lateral heterostructure of TMDs. Also, the conduction and valence band edges as functions of position are regarded as the step functions [32]. Lau et al., has numerically modeled the interface potential as $V_f = \frac{V_0 + \delta}{2} (1 - \tanh(\frac{x}{w}))$ and $V_h = \frac{V_0 - \delta}{2} (1 - \tanh(\frac{x}{w}))$ [32]. Here, $w$ is the width of the interface which is very small in sharp interface and $\delta$ characterizes the difference of the band offsets for electron and hole. they have considered the symmetric heterostructures with $\delta = 0$ and $w = 0.1a$ where $a$ is the lattice constant [32]. We use a model such that it covers all the length of the nanoribbon. Therefore by assuming a symmetric heterostructure with type- II interface and finite width, we will use the below formula for lattice potential in the next calculations. 

$$V_f = \frac{V_0}{2Max(V_f)} \left(1 - \tanh\left(\frac{x}{w}\right)\right)$$

where, $w$ is the width of the interface, $x$ is $\hat{x}$-coordinate on triangular lattice, $V_0$ is the band offset voltage, and $Max(V_f)$ is the maximum value of $V_f$. It should be noted that for sharp interfaces, $w$ is very small.
4. Results and discussion

Theoretically, in equation (13) for $k_1 = k_2 = 0$, if $E_g = \frac{\Delta_0 + \Delta_x}{2} - \lambda_x$, we can write

$$E_g - E_{exc} = -(V_f + V_C)$$  \hspace{1cm} (23)

where, $(E_g - E_{exc})$ is the binding energy of exciton. The Coulomb potential attempts to bind the electron and hole while the lattice potential at interface attempts to separate them and prefers to place them on the complementary sides of the interface. Therefore, the properties of the exciton depend on the competition between these potentials, especially at the interface. But, the plane integrated modular square wave function of VBM and CBM for different LHSs are localized on W-side and Mo-side, respectively [33]. Hence, as the Coulomb potential decays rapidly from the interface line, it is expected that the excitons are created in the vicinity of the interface. Of course, Kang et al., investigated the band offsets and heterostructures of monolayer and few-layer transition-metal dichalcogenides MX$_2$ (M=Mo, W; X=S, Se, Te) and showed that $V_0 \approx 0.26$ eV [18]. A tight-binding model has been introduced for studying the properties of the lateral heterostructures of two-dimensional materials [45]. They demonstrated that the onsite energy $\Delta_2 \rightarrow \Delta_2 + 0.26$ in the presence of $\Delta_1$. So, $E_g = 1.77$ (1.57) eV for MoS$_2$-WS$_2$ (MoSe$_2$-WSe$_2$) lateral heterostructure because, $\Delta_{MoS_2} = 1.66$ eV, $\Delta_{MoS_2} = 1.79$ eV, $\Delta_{MoSe_2} = 1.47$ eV, $\Delta_{WSe_2} = 1.60$ eV, $\lambda_{WS_2} = 0.215$ eV, and $\lambda_{WSe_2} = 0.23$ eV [45].

Now let us find the binding energy of exciton numerically. Figure 1 shows the triangular grid of a lateral heterostructure of 2D-TMDs with an armchair interface. If the scale of $x(y)$-axis is multiplied by $\sqrt{3}$ (0/$\sqrt{3}$), the structure of the zigzag interface will be found (appendix D).

First, we consider the armchair interface. Here, the hopping integral $\frac{\hbar v}{\sqrt{2}\mu a}$ is equal to 0.0218 eV because $m_{e/h} = 0.32 m_0$ and $a=3.325$ Angstrom (Å) [32]. In the type-II heterostructures, the interface is atomically sharp, and in consequence, we can set $w = 0.003$ Å in equation (21). Because, for $r = 0$ the value of $V_C$ from equation (20) will be at the order of $10^4$, we set $V_C(r = 0) = -1.5$ eV and will show how its effects on the final results can be compensated by a suitable choice of band offset energy, $V_0$. Figure 2 shows a typical comparison between $V_f$ and $V_C$. It should be noted that in each supercell, there are eight atoms, and four of them have the same x-coordinate, and consequently, the same lattice potential $V_f$.

As figure 2 shows the Coulomb potential has a significant value only at the interface and couples the electrons and holes at the region. For studying the effect of $V_C$, we should obtain $E(X)$ for different values of $V_C$ by attention to the value of the band offset voltage. It has been shown that there are two characteristic behaviors, the regime of small band offset ($V_0 < 0.1$ eV) and large band offset ($V_0 > 0.4$ eV) [32]. For sufficiently large $V_0$, the electron and hole are well separated into opposite regions, while for small and intermediate $V_0$, the separation is weak, and in consequence, on-site Coulomb interaction plays the main role. For example, it has been shown that for $V_0 = 0.2$ eV, the binding energy of the interface exciton is about 0.22 eV which is about 0.1 eV smaller than that of the 2D exciton [32]. The effect of Coulomb potential on the energy of excitons ($E(X)$) is shown in figure 3, for $V_0 = 0.26$ eV. It can be seen that the exciton energy depends on $V_C(r = 0)$ because $|V_C| > |V_f|$ at some atomic sites near the interface (figure 2(a)). However, for $V_0 = 0.4$ eV, as figure 4 shows, the second minimum eigenvalue does not change when the value of $V_C(r = 0)$ changes. Under this condition, $|V_C| < |V_f|$ and lattice
Figure 2. Lattice and Coulomb potentials for (a) $V_0 = 0.26$ eV, and (b) $V_0 = 0.4$ eV. $V_C(r = 0) = -1.5$ eV (not shown).

Figure 3. The effect of Coulomb potential on the energy of exciton when $V_0 = 0.26$ eV.
potential dominates (figure 2(b)), and therefore, the effect of $V_c(r = 0)$ on the second minimum of eigenvalue is negligible. We consider $V_0 = 0.4$ eV and the second minimum eigenvalue as $E(X)$ in the next calculations and will show that under these conditions the correct binding energy can be calculated for MoX$_2$–WX$_2$ LHSs. Also, as figure 4 shows, the Coulomb potential decreases the second minimum of $E(X)$ energy by 0.26 eV. It means that the system is more stable now. As the first approximation, we can consider the difference as the binding energy of exciton which is of the same order as a two-dimensional exciton in TMDs. In what follows, we will show that under which conditions the approximation is satisfied.

Our guess for the wave function of center-of-mass was
\[ \Psi(X) = e^{-\alpha|X|} \] where $\alpha = \frac{2M(E(X) - E_0)}{\hbar^2} > 0$. As electron and hole are well separated into opposite regions for $V_0 = 0.4$ eV even for very long nanoribbon [1, 5] and considering the behavior and value of the Coulomb potential compared to the lattice potential (figure 2(b)), it is expected that $\Psi(X)$ decays to $1/e$ of its maximum value for a specific value of $X$ (called $X_b$). For $X = X_b$ we have $\frac{2M(E(X) - E_0)}{\hbar^2} = \frac{1}{X_b}$ and in consequence:

\[ E_{gr} = E(X) - \frac{\hbar^2}{2MX_b^2} \] (24)

Therefore, by increasing $X_b$ (well separation of electron and hole) the term $\frac{\hbar^2}{2MX_b^2}$ decreases rapidly and $E_{gr} \rightarrow E(X)$.

But, the minimum value of $X_b$ is equal to $2\sqrt{2M} = \frac{a}{2} = 0.83$ Angstrom when one electron is at interface ($x = 0$) and one hole is at ($x = a/2$). So, the maximum value of $\frac{\hbar^2}{2MX_b^2} = 0.08$ eV and $E_{gr} = E(X) - 0.08$. Under this condition, $E_{bi} = 0.34$ eV which is equal to the binding energy of 2D exciton, approximately [32]. As a result, it can be concluded that near the interface $E_{bi} = 0.34$ eV and far from it $E_{bi} = 0.26$ eV. It means that the binding energy of exciton depends on its distance from the interface.

Now let us, study the effect of the interface structure on binding energy. Figure 5 shows the comparison between the binding energy of zigzag and armchair interfaces. As it shows, the difference is $\Delta E_{min}(X) = 0.34$ meV. $\Delta E_{min}(X)$ is created by the deformation gauge field which is a pseudo spin–orbit coupling. Its value is small due to its nature.

### 5. Summary

We studied the dark exciton in two–dimensional dichalcogenide LHSs with a sharp interface. We introduced a low–energy effective Hamiltonian model and found the energy dispersion relation of exciton and showed how it depends on the onsite energy of composed materials and their spin–orbit coupling strengths. It was shown that the balance between the Coulomb and offset potential implies the behavior of exciton, especially at the interface. Also, by assigning a deformation gauge field to the geometrical structure of the interface, we could find the effect of the geometry on the binding energy of exciton. By discretization of the real–space version of dispersion relation on a triangular lattice, the exciton binding energy calculated as 0.36 eV (0.26 eV) near (far enough from) the interface i.e., the binding energy of exciton depends on its distance from the interface line. Finally, we could
show that the binding energy of a zigzag interface increases by 0.34 meV in comparison with an armchair interface due to the pseudo-spin–orbit coupling term (deformation gauge field). The results can be useful in the design of new optoelectronic devices with improved performance and characteristics.

Data availability statement

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

Appendix A

The low-energy two-band effective Hamiltonian of spin-up electrons near the K-point is given by [45]

$$ H = \begin{pmatrix} \frac{\Delta}{2} & atk_- \\ atk_+ & -\Delta \frac{a}{2} + \lambda \end{pmatrix} $$

where, $k_x = k_y = k_x$, and $\Delta, a$, and $t$ are the energy band gap, lattice constant, and hopping integral, respectively. Here, $2\lambda$ is the spin–orbit coupling (SOC) strength. It can be shown that the eigenvalues are given by

$$ E = \frac{\lambda}{2} \pm \sqrt{\left(\frac{\Delta}{2} - \frac{\lambda}{2}\right)^2 + a^2t^2k^2} $$

Figure 5. Comparison between binding energy of (a) zigzag and (b) armchair interfaces. $V_0 = 0.4$ eV.
By defining \( \cos\frac{\theta}{2} = \frac{\lambda}{\Delta} \sqrt{E - \frac{\Delta}{2}(2E - \lambda)} \) and \( \tan^{-1}\frac{\lambda}{\Delta} \), one can easily diagonalize the Hamiltonian, \( H \), by using the matrix

\[
P = \begin{pmatrix}
\cos\frac{\theta}{2} & e^{-i\phi} \sin\frac{\theta}{2} \\
e^{-i\phi} \sin\frac{\theta}{2} & -\cos\frac{\theta}{2}
\end{pmatrix}
\]

and shows

\[
P^{-1}HP = \begin{pmatrix}
E & 0 \\
0 & -E + \lambda
\end{pmatrix}
\]

(A3)

For \( k = 0 \), the energy eigenvalues are \( E = \frac{\lambda}{2} \pm \frac{\Delta}{2} - \frac{\lambda}{2} \) and in consequence the conduction band minimum (CBM) and valence band maximum (VBM) are equal to \( \frac{\Delta}{2} \) and \( -\frac{\Delta}{2} + \lambda \), respectively. For spin-down electrons, CBM and VBM are \( \frac{\Delta}{2} \) and \( -\frac{\Delta}{2} - \lambda \), respectively. So, the band splitting happens at VBM by the SOC.

If the eigenfunctions \( \phi_1 = \begin{pmatrix} \cos\left(\frac{\theta}{2}\right) e^{-i\phi} \sin\left(\frac{\theta}{2}\right) \end{pmatrix} \) and \( \phi_2 = \begin{pmatrix} e^{-i\phi} \sin\left(\frac{\theta}{2}\right) - \cos\left(\frac{\theta}{2}\right) \end{pmatrix} \) are used it can be shown that

\[
H\phi_1 = E\phi_1 \quad \text{(A4)}
\]

\[
H\phi_2 = (-E + \lambda)\phi_2. \quad \text{(A5)}
\]

For adding a gauge field, \( A \), to the Hamiltonian, we should use the covariant derivatives. It means that we should replace \( p \) by \( p - A \) in the Hamiltonian matrix. If we consider the equation \( H\psi = E\psi \), it can be shown that

\[
E = \frac{\lambda}{2} \pm \sqrt{\left(\frac{\Delta}{2} - \frac{\lambda}{2}\right)^2 + v_F^2 (p - A)^2} \pm hv_F^2 B_z
\]

(A6)

where, \( v_F \) is Fermi velocity, \( p = h k \), \( A = (A_x(x, y), A_y(x, y)) \), and \( B = \nabla \times A \). If \( k = 0 \), and by neglecting the term \( A^2 \), it can be shown that

\[
E = \frac{\lambda}{2} \pm \sqrt{\left(\frac{\Delta}{2} - \frac{\lambda}{2}\right)^2} \pm hv_F^2 B_z
\]

(A7)

If \( \frac{\Delta - \lambda}{2} \gg hv_F^2 B_z \) then

\[
E_{(h)} = \frac{\Delta}{2} + (-) \frac{hv_F^2 B_z}{2}
\]

(A8)

and

\[
E_{(s)} = -\frac{\Delta}{2} + \lambda + (-) \frac{hv_F^2 B_z}{2}.
\]

(A9)

Therefore, the term \( hv_F^2 B_z \) is pseudo-spin–orbit coupling and splits not only VBM but also CBM. Because for \( E = 0 \) the equation (A-6) has a non-trivial solution, the surface states exist.

Appendix B

In \( xy \)-plane, one can define three vectors \( u = (u_x, 0) \), \( \nu = (v \cos \alpha, v \sin \alpha) \), and \( \omega = (w \cos \beta, w \sin \beta) \) and shows that

\[
\partial_{u_x} = \partial_{x}, \quad \partial_{\nu} = (\cos^2 \alpha) \partial_x + (\sin^2 \alpha) \partial_y + 2(\sin \alpha)(\cos \alpha) \partial_{xy}
\]

(B2)

\[
\partial_{u_y} = (\cos^2 \beta) \partial_x + (\sin^2 \beta) \partial_y + 2(\sin \beta)(\cos \beta) \partial_{xy}
\]

(B3)

In a triangular lattice, \( \alpha = 60 \) and \( \beta = 120 \) and in consequence \( [46] \)

\[
\partial_x^2 + \partial_y^2 = \frac{2}{3} (\partial_x^2 + \partial_y^2 + \partial_z^2)
\]

(B4)

Now by discretizing the right-hand side of the equation (B-4), the below equation can be derived \([46]\)

\[
-\frac{h^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) = -\frac{h^2}{3ma^2} (-6\psi_{i,j,k} + \psi_{i+1,j,k} + \psi_{i-1,j,k} + \psi_{i,j+1,k} + \psi_{i,j-1,k} + \psi_{i,j,k+1} + \psi_{i,j,k-1})
\]

(B5)
where, \( i, j, \) and \( k \) are in \( \mathbf{u}, \mathbf{v}, \) and \( \mathbf{w} \) directions. Therefore, the hopping integral is equal to \(-\frac{\hbar^2}{3ma^2}\) where, \( a \) is the lattice constant.

**Appendix C**

It is assumed that two electric charges \( e \) and \( e' \) are located at positions \((\rho_0, z_0)\) and \((0, z'_0)\), respectively in a slab of dielectric constant \( \epsilon_f \). The slab width is \( d \) and is surrounded by a medium of dielectric constant \( \epsilon_1 (z \leq -d/2) \) and a medium of dielectric constant \( \epsilon_2 (z \geq d/2) \). Felbacq et al, have shown that the electrostatic energy between both charges is given by \([42]\):

\[
V(\rho, z_0, z'_0) = \frac{e}{2\pi\epsilon_f d} I(r, x, y)
\]

where, \( \epsilon_f \) is the dielectric constant of slab, \( r = \frac{\rho}{a}, x = \frac{\rho_0}{a}, y = \frac{\rho'_0}{a}, \) and \( u = \frac{1}{a} \). Here,

\[
I(r, x, y) = \int_a^b f(u, x, y)J_0(r, u)du + \frac{1}{2\sqrt{r^2 + |x - y|^2}}
\]

where \( f(u, x, y) = W(u, x, y) - \frac{1}{2} \exp(-u|x - y|) \) and \( J_0(r, u) \) is Bessel function. By proofing a theorem, they have shown that the kernel of the first integral tends exponentially fast toward zero and it defines a function that regular near the origin \( x = y = 0 \). It means that the screened electrostatic potential in a dielectric slab can be considered as the usual Coulomb potential plus a correction term \([42]\). If the slab width is large compared to the relative distance between the two electric charges the correction term is exponentially small. Also, if the height \( z \) approaches zero, the expression does not present any divergence \([42]\). The expression is suitable for further numerical calculations aiming to compute the binding energy of excitons in quasi-2D materials \([42]\).

**Appendix D**

Figures D1(A) and (B) show the monolayer lateral heterostructure of MoS\(_2\) – WS\(_2\) with zigzag and armchair interfaces, respectively. If one looks at the figures from side (figure D1(C)), he/she is able to recognize the difference between zigzag and armchair interfaces. For finding the Cartesian coordinates of each atom, we should calculate \( b, c, d, \) and \( e \) in terms of \( a \). It is easy to show that \( b = a\sqrt{3}/2, c = a/2, e = a/2, \) and \( d = a\sqrt{3}/2 \).

![Figure D1. (A) zigzag interface, (B) armchair interface, and (C) the direction of recognizing the difference between interfaces. Bulu, green, and yellow circles stand for Mo, W, and S atoms, respectively.](image)

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