Three-particle Complexes in Two-Dimensional Semiconductors

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We map the three-body problem in two dimensions onto one particle in a three dimensional potential treatable by a purposely-developed boundary-matching-matrix method. We evaluate binding energies of trions $X^\pm$, excitons bound by a donor/acceptor charge $X^{D/A}$, and overcharged acceptors/donors in two-dimensional atomic crystals of transition metal dichalcogenides, where interaction between charges features logarithmic behavior at intermediate distances. We find that dissociation energy of $X^\pm$ is, typically, much larger than that of localised exciton complexes, so that trions are more resilient to heating, despite that their recombination line in optics is much less red-shifted from the exciton line, as compared to $X^{D/A}$.

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Atomic two-dimensional (2D) crystals, derived from layered materials, such as transition metal dichalcogenides [1–4], represent a new class of systems whose optical properties [4–10] attract a lot of interest. These monolayer crystals are direct band gap semiconductors [11–15], and their luminescence spectra contain distinct lines interpreted as the electron-hole recombination from neutral, X, and charged excitons (trions), $X^\pm$, [4, 16–24]. It was found [25] from investigation of energy levels of X, that the interaction between the charges is logarithmic up to the distance $r_*$ much larger than the excitonic Bohr radius [26]. This logarithmic interaction, caused by the polarisability of atomic orbitals, is also present in few-layer films and even in bulk layered crystals [27]. The excitons for such interaction has been studied before [25, 28, 29], whereas the three-particle states were never addressed theoretically.

In this Letter, we find energies of acceptor/donor-bound excitons ($X^{A/D}$), trions ($X^\pm$), and charged acceptors/donors ($A^+/D^-$), in atomic 2D crystals, using a method developed specifically to tackle three-body problem in two dimensions. Three 2D particles have six degrees of freedom, three of which correspond to a centre of mass motion and overall rotation. The quantum mechanics of the remaining degrees of freedom is equivalent to that of a particle moving in an effective three-dimensional potential, $U$. A relatively small dimensionality, together with a peculiar structure of $U$, enables us to develop an approach alternative to the Faddeev’s equations [30] or variational methods [31, 32] in three-body problems.

Wave function $\Psi(r_1, r_2, r_3)$ of three logarithmically interacting particles with masses $\mu_{1,2,3}$ and charges $q_i = e$, $q_1q_2 = e^2$; $q_3q_{1,2} = -e^2$, [see Table I] obeys the Schrödinger equation $\Psi$)

$$\left[ -\nabla_i^2 + \ln r + U(\theta, \phi) \right] \psi = \epsilon \psi;$$

$$\nabla_i^2 = -\frac{\partial^2}{\partial r_i^2} + \frac{3\partial}{r \partial r} + \frac{4\hat{L}_i^2}{r^2} + \frac{r^2 \sin^2 \theta}{\sin \theta} \frac{\partial}{\partial \theta};$$

$$U(\theta, \phi) = \frac{1}{2} \ln \frac{(1 - n \cdot n_1)(1 - n \cdot n_2)}{(1 - n_1 \cdot n_2)}.$$  

This transforms the three-body problem to a one-body problem in a higher-dimensional space, where $n$ is a position of a fictitious particle on a sphere, $\hat{L}$ is a 3-dimensional angular momentum operator, $\hat{L}_i^2 = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2};$ $\hat{L}^2 = -\frac{\partial^2}{\partial \phi^2} + 4 \cos \theta$ $\frac{\partial^2}{\partial \phi^2}$.

Vectors $n_1$ and $n_i$ ($i = (1, 2)$) characterize the direction of the maximal repulsion and attraction: respectively,

$$n_z = [0; 0; 1]; \quad n_i = [(-1)^i \sin \theta_i; 0; \cos \theta_i].$$

The color-scale visualization of $U$ is shown on the inset to Fig. 1. Classically, the particle collapses either to $n_1$ or $n_2$: this observation is useful for finding the large-distance asymptotic states.
Potential $U$ has a mirror reflection symmetry $U(\phi) = U(-\phi)$ (hereinafter we will omit coordinates invariant under transformations), which distinguishes the states into the groups of even ($e$) and odd ($o$) states

$$
\psi^e_j(\phi) = \psi^{e,J}_j(-\phi); \quad \psi^o_j(\phi) = -\psi^{o,J}_j(-\phi).
$$

(5c)

If two particles in the complex are identical, $\theta_1 = \theta_2$,

$$
U(\theta) = U(-\theta),
$$

(5d)

the states split into symmetric/anti-symmetric ($s/o$):

$$
\psi^s_j(-\theta) = \psi^s_j(\theta); \quad \psi^o_j(-\theta) = -\psi^o_j(\theta).
$$

(5e)

This symmetry determines spin/valley multiplets [27].

The ground state of any complex corresponds to even functions with $J = 0$, we shall focus on this case. We use the basis of spherical harmonics $Y_{l,m}(\theta, \phi)$, $|m| \leq l; l \geq 0$

$$
\psi^e_j = \sum_{l=0}^{L_{\text{max}}} \sum_{m=0}^{l} Y_{l,m}(\mathbf{n}) \psi_{l,m}(r), \quad \mathbf{L}^2 \psi^e = l(l+1) \psi^e;
$$

$$
Y^e_{l,0} = Y_{l,0}; \quad Y^e_{l,1 \leq m \leq l} = \frac{1}{\sqrt{2}} \left[ Y_{l,m} + (-1)^m Y_{l,-m} \right],
$$

(6)

where we use the convention of Ref. [33],

$$
Y_{l,m}(\theta, \phi) = (-1)^m \left[ Y_{l,m}(\theta, \phi) \right]^* = (-1)^m Y_{l,-m}(\theta, -\phi).
$$

These functions satisfy the gluing condition (5b) for $J = 0$. We will see that for the problems of interest the basis can be truncated without affecting physical answers.

In this basis, Schrödinger equation (3) becomes

$$
\left[ \frac{d^2}{dr^2} + \frac{3}{r} \frac{d}{dr} \right] \psi = \left( H(r) + \frac{\mathbf{L}^2}{R^2} \right) \psi,
$$

(7)

where $1/R^2 = -\epsilon$, vector $\psi$ is comprised by the components $\psi_{l,m}$, and the matrix $H(r)$ has elements
where $m = m_1 - m_2$, $l_{\min} = \text{max}(1, |l_1 - l_2|, |m|)$ and the $3j$ symbols follow Ref. 33, and $\mathbf{n}$ are from Eq. (4).

Numerically found eigenvalues of Hamiltonian (8) are shown in Fig. 1. At $r \gg 1$, the eigenfunctions are peaked near $\mathbf{n} = \mathbf{n}_{1,2}$ suggesting an adiabatic solution for Eq. (7) at $r \gg 1$. Consider an equation,

$$\frac{1}{\rho} \frac{d}{d\rho} \left( \frac{d}{\rho} + \frac{m^2}{\rho^2} + \ln \rho \right) \varphi_n^m(\rho) = \chi_n^m \varphi_n^m(\rho),$$

which determines the spectrum, of a two-dimensional exciton with the logarithmic interaction $e^2/r_2 \ln(\rho/r_2)$:

$$X_n^m = \frac{e^2}{r^2} \left[ \frac{1}{2} \ln \frac{\hbar^2(\mu_1 + \mu_3)}{2e^2 r_1^{\mu_1} \mu_3} + \chi_n^m \right].$$

(10)

Integer $m$ and $n \geq 0$ are the 2D angular momentum and radial quantum number, respectively. The inter-level distances [25, 29], determined by the numerically found eigenvalues listed in Table II, do not depend on the masses,

| $n$ | $m = 0$ | $m = 1$ | $m = 2$ |
|-----|---------|---------|---------|
| 0   | 0.5278  | 1.386   | 1.844   |
| 1   | 1.661   | 2.009   |         |
| 2   | 2.177   |         |         |

Table II. The numerical values for eigenvalues of Eq. (9).

The adiabatic wave function (closely bound electron-hole pair and the third particle far from the pair) is

$$\psi^{(1,2)}(r, \theta) = \varphi_0^m \left( r \sin(\hat{\theta}/2) \right) F^{(1,2)}_e \left( r \cos(\hat{\theta}/2) \right),$$

(11a)

where “local” coordinates near $\mathbf{n}_{1/2}$ on the unit sphere are introduced as $\mathbf{n}(\theta, \phi) = \cos \hat{\theta} \mathbf{n}_{1} + \sin \hat{\theta} \cos \hat{\phi} \mathbf{n}_{1}' + \sin \hat{\theta} \sin \hat{\phi} \mathbf{n}_{2}'$, with $\mathbf{n}_{1}'$, $\mathbf{n}_{2}'$ chosen as two unit vectors orthogonal to each other and to $\mathbf{n}$. Representation (11a) is valid if the tunneling between the two minima is weak. Substituting Eq. (11a) into Eq. (7), treating the singular logarithmic potential exactly and remainder in the second order perturbation theory we find

$$\left[ \frac{1}{x} \frac{d}{dx} + \frac{\gamma(x)}{x^2} \right] F^{(1,2)}_e(x) = e^{(1,2)} F^{(1,2)}_e(x);$$

(11b)

$$- e^{(1,2)} = \epsilon - \chi_0^m \left( \frac{2 \sin^2 \theta_1 + \theta_2}{2 \sin^2 \theta_2} \right),$$

where $\hat{\theta}$ is the binding energy of a complex and dimensionless strength of the van der Waals attraction is

$$\gamma_{1,2} = 1.23 \left[ \cot(\theta_{1,2}/2) - \cot((\theta_1 + \theta_2)/2) \right]^2 \equiv 1.23 \mu_{1,2}(\mu_{1,2} + \mu_3)^2/[\mu_1 \mu_2 \mu_3].$$

(11c)

The solution corresponding to the bound state is

$$F^{(1,2)} = K_{\gamma_{1,2}}(x \sqrt{e^{(1,2)}},$$

(11d)

where $K_{\gamma}(y)$ is the MacDonald function, $e^{(1,2)}$ is determined by matching Eq. (11d) with the solution of Eq. (7)

$$\psi_{l,m}(r) \propto r^{2l}, \quad r \ll 1.$$ (11e)

In the interaction region, $r \approx 1$, the problem can be handled only numerically. Numerical solution of Eq. (7) is not practical as many states in the interaction region are evanescent, see Fig 1, and the search for the bound state would require finding of $N = (L_{\text{max}} + 1)(L_{\text{max}} + 2)/2$ boundary conditions at $r \to 0$ with the exponential accuracy. Instead, we employ a procedure which does not suffer from the exponential dependence on $r$.

We notice that one can replace solving Eq. (7) for all $r$, with the solution on only $r > R$ (where $R > 0$ is an arbitrary distance) provided that the boundary condition matrix $\hat{\Lambda}$ defining the behavior $\psi(r \to R + 0)$

$$[r d\psi/dr + \hat{\Lambda}(R) \psi]_{r=R} = 0,$$ (12)

is known, (here $\hat{\Lambda}(R)$ is $N \times N$ matrix).

Requiring the invariance of solutions of Schrödinger equation Eq. (7) with respect to changing $R$, we find

$$Rd\hat{\Lambda}/dR = -R^2 \left[ 1/\hat{R}^2 + \hat{H}(R) \right] - 2\hat{\Lambda} + \hat{A}^2,$$ (13a)

where $1/\hat{R}^2 = -\epsilon$ is determined by the total energy of a complex and matrix multiplication is defined in the basis (6) as $\left[ \hat{A} \right]_{l,m} = \sum_{l' m'} \sum_{m=0} \left[ \hat{B} \right]_{l m} \left[ \hat{B} \right]_{l' m'}$. The initial condition follows from Eq. (11e),

$$\left[ \hat{\Lambda}(0) \right]_{l m'} = -2i \delta_{l m'} \delta_{mm'},$$ (13b)

and Eqs. (13a) and (8) give $\hat{\Lambda} = \hat{\Lambda}_* = \hat{\Lambda}^\dagger$ for all $R$. 


The asymptotic dependence of the highest eigenvalues \( \lambda_3 \) of matrix \( \hat{\Lambda}(R) \) corresponds to the asymptotic wave function in Eqs. (11a), (11d), so that at \( R \gg 1 \) and for the energy \( \epsilon \) corresponding to the bound state,

\[
-(\epsilon / F) dF / dx |_{x = R} = \lambda_3(R),
\]

(14)

(we omit superscript \((1, 2)\) as \( \gamma_1 = \gamma_2 \) for the symmetric case, otherwise the strongest potential minima has to be chosen). We use Eq. (14) to find energies of bound states numerically. First, we match tangentially the numerically calculated dependence of the highest eigenvalue \( \lambda_3(R) \) using Eq. (14) (as illustrated in Fig. 2), and find distance \( R^{(i)} \), and an overestimated binding energy \( \tilde{\epsilon}^{(i)} \). Next, we choose a distance \( R_{\text{max}} \), \( R^{(i)} < R_{\text{max}} < L_{\text{max}} \), to be used as a reference point in the rest of iterative procedure.

Then, using Eqs. (13a) with \( 1 / R^2 \) determined by the variable energy \( \epsilon < \tilde{\epsilon}^{(i)} \), we evaluate \( \hat{\Lambda}(R_{\text{max}}) \), and its highest eigenvalue \( \lambda_3(R_{\text{max}}) \), and find such energy \( \tilde{\epsilon} \) that

\[
\left[ x dF / (F dx) \right]_{x = R_{\text{max}}} + \lambda_3(R_{\text{max}})^2 \]

is minimal. The outcome of such matching is exemplified in Fig. 2 showing the eigenvalues of matrix \( \hat{\Lambda}(R) \) found for a trion, \( \theta_1 = \theta_2 \). The iterative procedure in this case can be repeated separately for symmetric (s) and anti-symmetric (a) states.

Figure 3 shows the calculated binding energies \( \tilde{\epsilon} \) of all charged three-particle complexes, which determine the activation energy needed to dissociate them into a neutral complex and a free carrier (\( X^\pm \rightarrow X + e / h; X^{D/A} \rightarrow D^0 / A^0 + h / e \)). It shows that, for \( 0.5 < \mu_e / \mu_h < 2 \), the dissociation of \( X^{D/A} \) into a neutral donor/acceptor and a hole/electron has a much smaller activation threshold than the dissociation of a trion.

Despite weaker binding (e.g., smaller dissociation energy), the line of \( X^{D/A} \) in recombination spectra, 

\[
\omega_{X^{D(A)}} = \omega_X - \frac{\epsilon}{\tau_e} \left( \tilde{\epsilon}_{X^{D(A)}} + \frac{1}{2} \ln \left[ 1 + \frac{\mu_e}{\mu_h} \right] \right),
\]

lies below (red-shifted) the line of a trion, \( \omega_X^\pm = \omega_X - \frac{\epsilon}{\tau_e} \tilde{\epsilon}_X^\pm \), because the two-particle binding energy of electron/hole in donor/acceptor is larger than the one of the exciton and overcompensates the difference between the three-particle binding energies. For comparable masses of electrons and holes, the exciton-trion splitting appears to be an order of magnitude smaller than splitting between the ground state of the exciton and its first optically active excited state \( X_1^{*} \), at \( \Delta_1 = \omega_X^* - \omega_X = 1.14 \frac{e}{\tau_e} \), whereas \( \omega_{X_{D(A)}} - \omega_X \approx 0.5 \Delta_1 \).

In conclusion, we developed a novel scheme for accurate finding the binding energies of three particles in two dimensions. The application of this method for the logarithmic interaction allows for the prediction of the relative energies of the optical transitions. We expect our results to be helpful in identifying the nature optical transitions in 2D crystals of transition metal dichalcogenides (TMDC). For instance, the analysis of the bound exciton \( X^{D/A} \) predicts that, in disordered TMDC the most red-shifted line is also the most sensitive to temperature, as it produced by complexes with lower dissociation energies.

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As shown in [27], \( r_* = a_z (\varepsilon_{||} - 1) / 2 \), where \( \varepsilon_{||} \) is the in-plane component of the dielectric permittivity tensor of the bulk layered material and \( a_z \) is the distance between layers in it.

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I. LOGARITHMIC ELECTRON-ELECTRON INTERACTION.

Below, we show how to relate parameters of the logarithmic interaction in 2D crystal to dielectric parameters of the corresponding layered materials. For a monolayer, the electrostatic interaction energy has the form

$$E_{\text{int}} = \frac{1}{2} \int \frac{d^2 \mathbf{r} d^2 \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \sigma(\mathbf{r})\sigma(\mathbf{r}') + \frac{1}{2\kappa} \int d^2 \mathbf{r} \mathbf{P}_\perp^2, \quad (S.1)$$

where $\rho(\mathbf{r})$ is a two-dimensional electron density, and $\mathbf{P}_\perp(\mathbf{r})$ is the vector of two-dimensional in-plane polarization. The latter includes both the polarization due to the lattice and to the virtual interband electron transition. The in-plane rigidity, $\kappa$, treated here as an independent parameter will be related to the in-plane component of the dielectric permittivity tensor of the multilayered material.

Integrating out polarization vector in the static approximation, we obtain

$$E_{\text{int}} = \frac{1}{2} \int \frac{d^2 \mathbf{q}}{(2\pi)^2} \frac{2\pi \epsilon^2}{q(1 + q r_*)} |\rho_{\mathbf{q}}|^2; \quad r_* \equiv 2\pi \kappa. \quad (S.2)$$

In the coordinate representation, Eq. (S.2) takes the form\(^1\)

$$E_{\text{int}} = \frac{1}{2} \int d^2 \mathbf{r} d^2 \mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}')V(|\mathbf{r} - \mathbf{r}'|); \quad (S.3)$$

\[V(\mathbf{r}) \approx \left\{ \begin{array}{ll}
\frac{e^2}{r_*} & |\ln \frac{r_*}{r_x}| \leq \frac{\pi}{\sqrt{2}}, \\
\frac{2}{r_*} & r \ll r_*; \\
\frac{2}{r_*} & r \gg r_*,
\end{array} \right.\]

where $C = 0.577 \ldots$ is Euler-Mascheroni constant. In the analysis of excitons and charged complexes, we study the physics on the scale shorter than $r_*$ at which the crossover from two- to three-dimensional (1/r) Coulomb interaction occurs. Omitting the constant shift in the interaction energy, we obtain Eq. (1) for three particle problem.

It is rather straightforward to generalize Eq. (S.1) to multilayer system. One finds

$$E_{\text{int}} = \sum_{n,n'} \int \frac{d^2 \mathbf{r} d^2 \mathbf{r}'}{2\Delta r} \sigma_n(\mathbf{r})\sigma_{n'}(\mathbf{r}') + \frac{1}{2\kappa_2} \sum_n \int d^2 \mathbf{r} \mathbf{P}_\perp^2, \quad \sigma_n(\mathbf{r}) = \epsilon \rho_n(\mathbf{r}) - \nabla \cdot \mathbf{P}_\perp(\mathbf{r}),$$

where $\rho_\perp(\mathbf{r})$ is the vector of two-dimensional in-plane polarization, $\kappa_2$ is the component of dielectric permittivity tensor in the direction perpendicular to the layers. The first line in Eq. (S.4) is the Coulomb interaction between charge densities of the electrons induced by electrons and in-plane polarization [compare with Eq. (S.1)], the second line is the Coulomb interaction between the dipole polarization $P_{\perp,n}$ perpendicular to the layers, $\kappa_2$ is the rigidity for such a polarization (in particular it includes the large Coulomb interaction on the atomic scale in the same layer which cannot be found from the continuous theory).

Performing the Fourier transforms and integrating out the polarizations, we obtain

$$E_{\text{int}} = \frac{1}{2} \int_{|q| \leq 2\pi/a_\perp} \frac{d^2 \mathbf{q}}{(2\pi)^2} V_{3D}(q, q_z)|\rho(q, q_z)|^2, \quad V_{3D} = 2\pi \frac{F_1}{F_2},$$

\[F_1 = \sinh q a_z / q - 2\pi \kappa q_z (\cosh q a_z + \cos q a_z), \quad (S.5)\]

\[F_2 = \cosh q a_z + \cos q a_z, \quad F_2 = 2\pi \frac{\kappa^2 a_z^2 q_z^2 (\cosh q a_z + \cos q a_z)}{(2\pi)^2} \sinh q a_z - (2\pi)^2 \kappa q_z^2 (\cosh q a_z + \cos q a_z); \]

$$\rho(\mathbf{r}, n) = \int_{|q| \leq 2\pi/a_\perp} \frac{d^2 q}{(2\pi)^2} e^{i\mathbf{q}_\perp \cdot \mathbf{r} + i q_z a_z n} \rho(q, q_z).$$

Taking the limit $q, q_z \to 0$ leads to

$$V_{3D} \approx \frac{4\pi}{(1 + 4\pi \kappa/a_\perp)^2} q^2 + (1 - 4\pi \kappa/a_\perp)^{-1} q_z^2. \quad (S.6)$$

This enables one to relate two model parameters, $\kappa$ and $\kappa_2$, to the component of dielectric permeability tensor in the direction perpendicular to the layers.
the bulk of the layered material,

\[ \varepsilon_{\parallel} = 1 + 4\pi \kappa \frac{a_z}{\varepsilon_{\parallel}}, \quad \varepsilon_z = \frac{1}{1 - 4\pi \kappa \frac{a_z}{\varepsilon_{\parallel}}} \tag{S.7} \]

This relation enables us to represent \( r_\ast = a_z(\varepsilon_{\parallel} - 1)/2 \).

Note that \( \kappa_z \) includes the short range Coulomb interaction within the same layer, so that the inequality \( 4\pi \kappa_z < a_z \) always holds.

To describe the interaction between two charges at the intermediate distances within the same 2D layer of the bulk crystal, one needs to use an effective 2D interaction,

\[ V = \int_{\pi/a}^{\pi/a} dq_3 V_{3D} q_a \ll 1, q_z \approx e^2/a\kappa q^2 = \frac{4\pi}{(\varepsilon_{\parallel} - 1)q^2}, \tag{S.8} \]

which results in that the logarithmic approximation, (S.3) is also applicable to the description of the Coulomb interaction in the bulk of layered material

\[ V(r) \approx \frac{e^2}{r_a} \ln \frac{r_a}{r} \quad ; \quad r < r_\ast / \sqrt{\varepsilon_z \varepsilon_{\parallel}}. \tag{S.9} \]

At larger \( r \) it matches the asymptotic tail \( e^2/r \sqrt{\varepsilon_z \varepsilon_{\parallel}} \) corresponding Eq. (S.6).

\section*{II. COORDINATES TRANSFORMATION.}

To perform the coordinate transformation leading to Eq. (3) in the main text, we rewrite the four-dimensional Laplacian in the covariant form

\[ \nabla_i^2 \equiv \nabla_i^2 + \nabla_\nu \equiv \frac{1}{\sqrt{g}} \nabla_i \sqrt{g} g^{ij} \nabla_j g = \det \hat{g}, \tag{S.10} \]

where \( g_{ij} \) is the metric tensor \( g_{ik} g^{kj} = \delta^i_j \), and in the original coordinates \( \hat{g} = 1 \).

Coordinates introduced in the main text

\[
\begin{pmatrix}
\tilde{r}_x \\
\tilde{r}_y \\
\tilde{r}_z
\end{pmatrix}
= r \begin{pmatrix}
\cos \frac{\varphi}{2} \cos \left( \Phi - \frac{\varphi}{2} \right) \\
\cos \frac{\varphi}{2} \sin \left( \Phi - \frac{\varphi}{2} \right) \\
\sin \frac{\varphi}{2} \cos \left( \Phi - \frac{\varphi}{2} \right)
\end{pmatrix},
\tag{S.11}
\]

associate to the metric tensor

\[
\hat{g} = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \frac{r^2}{4} & 0 & 0 \\
0 & 0 & \frac{r^2}{4} \cos \theta & \frac{r^2}{4} \cos \theta \\
0 & 0 & \frac{r^2}{4} \cos \theta & r^2
\end{pmatrix}.
\tag{S.12}
\]

Substitution of Eq. (S.12) into Eq. (S.10) gives Eq. (3) of the main text.

\section*{III. MATRIX ELEMENTS OF THE INTERACTION AND THE STRUCTURE OF ANGULAR HAMILTONIAN.}

The derivation of matrix elements of ’dimensionless potential’ \( U(n) \) consists in the evaluation of the integral

\[ \tilde{U}^{l_1 l_2}_{l_3 m_1 m_2} = \int_{0}^{\pi} d\theta \sin \theta \int_{0}^{2\pi} d\phi U(n) Y_{l_1 m_1}(n) Y_{l_2 m_2}(n), \tag{S.13} \]

where the spherical harmonics \( Y_{l_1 m_1}(n) \) are defined according to convention of Ref. 3, and the potential \( U \) is defined in Eq. (3) of the main text. Using the formula\(^2\),

\[ \ln(1 - n \cdot n_1) = -\sum_{l=1}^{\infty} \frac{2l + 1}{l(l + 1)} P_l(n \cdot n_1) + \ln 2 - 1, \tag{S.14} \]

applying addition theorem for the spherical harmonics

\[ P_l(n \cdot n_1) = \frac{4\pi}{2l + 1} \sum_{m=-l}^{l} Y_{l,m}(n_1) Y_{l,m}(n), \]

and the integral relation leading to 3j-symbols\(^3\),

\[ \int_{0}^{\pi} d\theta \sin \theta \int_{0}^{2\pi} d\phi Y_{l_1 m_1}(n) Y_{l_2 m_2}(n) Y_{l_3 m_3}(n) = \left[ \prod l_{1,2,3}(2l_i + 1) \right]^{1/2} \left( \begin{array}{ccc}
l_1 & l_2 & l_3 \\
m_1 & m_2 & m_3 \\
0 & 0 & 0
\end{array} \right) \left( \begin{array}{ccc}
l_1 & l_2 & l_3 \\
0 & 0 & 0
\end{array} \right), \tag{S.15} \]

where \( m_1 + m_2 + m_3 = 0 \) and \( l_{1,2,3} \) obey the triangular inequality, we arrive at
\[ \hat{U}_{12}^{m_1 m_2} = \frac{1}{2} \left( \ln 2 - 1 \right) \delta_{l_1 l_2, m_1 m_2} - \left[ \pi (2l_1 + 1)(2l_2 + 1) \right]^{1/2} (-1)^{m_1} \times \sum_{l = \max(1, |l_1 - l_2|, |m_1 - m_2|)}^{l_1 + l_2} \frac{\sqrt{2l_1 + 1} \left( l_1 \ l_2 \right)}{l (l + 1)} \left[ Y^{*}_{l_1, m_1 - m_2} (n_1) + Y^{*}_{l_2, m_2 - m_1} (n_2) - Y^{*}_{l_1, m_1 - m_2} (n_z) \right]. \] (S.16)

Here, unit vector \( n_{1,2,3} \) are defined in Eq. (4) of the main text. Symmetrizing matrix element according to Eq. (6) for \( Y^\ast \), we obtain Eq. (8) and the following non-numbered equation of the main text.

**IV. OPTICALLY ACTIVE TRION STATES**

In monolayers of transition metal dichalcogenides the absolute minima of conduction and and absolute maxima of the valence bands are at the two non-equivalent Brillouin zone corners \( K, K' \), known as valleys. The atomic spin-orbit interaction in transition metals introduces large spin-orbit splitting of the valence band (\( v \)) so that the low-energy excitons and trions involve only the lowest hole states,

\[ |+, \hbar \rangle = |K, \uparrow, v \rangle; \quad |-, \hbar \rangle = |K', \downarrow, v \rangle. \] (S.17)

In contrast, the spin orbit interaction for electrons is much smaller than the trion binding energy so that for each electron 4 states coming from the spin and valley degeneracy have to be taken into account.

**A. Negatively charged trion, \( X^- \)**

As we discussed in the main text, only symmetric orbital state is relevant (other bound states have exponentially small binding energy), so that we are left only with the six degenerate states anti-symmetric with respect to the permutations of the valley and spin indices (below, \( c \) denotes the conduction band):

\[
\begin{align*}
\sqrt{2} |+, ee \rangle &= |K', \downarrow, c \rangle |K, \uparrow, c \rangle - |K, \uparrow, c \rangle |K', \downarrow, c \rangle; \\
\sqrt{2} |-, ee \rangle &= |K, \downarrow, c \rangle |K', \uparrow, c \rangle - |K', \uparrow, c \rangle |K, \downarrow, c \rangle; \\
\sqrt{2} |1, ee \rangle &= |K, \downarrow, c \rangle |K', \uparrow, c \rangle - |K', \uparrow, c \rangle |K, \downarrow, c \rangle; \\
\sqrt{2} |2, ee \rangle &= |K', \downarrow, c \rangle |K', \uparrow, c \rangle - |K', \uparrow, c \rangle |K', \downarrow, c \rangle; \\
\sqrt{2} |3, ee \rangle &= |K, \uparrow, c \rangle |K', \uparrow, c \rangle - |K', \uparrow, c \rangle |K, \uparrow, c \rangle; \\
\sqrt{2} |4, ee \rangle &= |K, \downarrow, c \rangle |K', \downarrow, c \rangle - |K', \downarrow, c \rangle |K, \downarrow, c \rangle.
\end{align*}
\] (S.18)

Spin-orbit interaction splits single electron states into two Kramers doublets: \( E_{K, \uparrow} = E_{K', \downarrow} = \epsilon_{so}, \quad E_{K', \uparrow} = E_{K, \downarrow} = -\epsilon_{so} \). Accordingly, sextetuplet of two electron states (S.18) is split into two singlets \( E_{2, ee} = \pm 2\epsilon_{so} \) and a quadruplet \( E_{1,4, ee} = 0 \). The quadruplet may be further split due to the lattice effects (i.e. trigonal warping) which we neglect. Also, we neglect the electron-hole exchange. Then the spin-valley trion states are direct product of the two-electron (S.18) and hole states (S.17).

Because the optical transition conserves the spin and the quasi-momentum, the allowed optical transition by the circular left-handed polarized light are

\[
\begin{align*}
|+, ee \rangle |+, \hbar \rangle &\rightarrow |K, \uparrow, c \rangle; \\
|2, ee \rangle |+, \hbar \rangle &\rightarrow |K', \uparrow, c \rangle; \\
|4, ee \rangle |+, \hbar \rangle &\rightarrow |K, \downarrow, c \rangle; \\
|-, ee \rangle |-, \hbar \rangle &\rightarrow |K', \downarrow, c \rangle; \\
|1, ee \rangle |-, \hbar \rangle &\rightarrow |K, \downarrow, c \rangle; \\
|3, ee \rangle |-, \hbar \rangle &\rightarrow |K', \uparrow, c \rangle;
\end{align*}
\] (S.19)

and

\[
\begin{align*}
|+, ee \rangle |-, \hbar \rangle &\rightarrow |K, \uparrow, c \rangle; \\
|1, ee \rangle |-, \hbar \rangle &\rightarrow |K, \downarrow, c \rangle; \\
|3, ee \rangle |-, \hbar \rangle &\rightarrow |K', \uparrow, c \rangle;
\end{align*}
\] (S.20)

for the right-handed polarization. It is important to emphasize that even though the trion states and single-electron states are split by spin-orbit coupling, the optical line is not split, similarly to the exciton.

**B. Positively charged trion, \( X^+ \)**

As in the previous subsection, we are interested in the orbital symmetric state. The only allowed spin/valley part of the two-hole system is (see Eq. (S.17))

\[ \sqrt{2} |hh \rangle = |K', \downarrow, v \rangle |K, \uparrow, v \rangle - |K, \uparrow, v \rangle |K', \downarrow, v \rangle. \] (S.21)

The allowed optical transition by the circular left-handed polarized light are

\[ |hh \rangle |K, \uparrow, v \rangle \rightarrow |K, \uparrow, v \rangle, \] (S.22)

and

\[ |hh \rangle |K', \downarrow, v \rangle \rightarrow |K', \downarrow, v \rangle, \] (S.23)

for the right-handed polarization. Once again, these lines are not split by spin-orbit interaction.

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