Valley Trions in Monolayer Transition Metal Dichalcogenides in the Framework of the Method of Hyperspherical Harmonics

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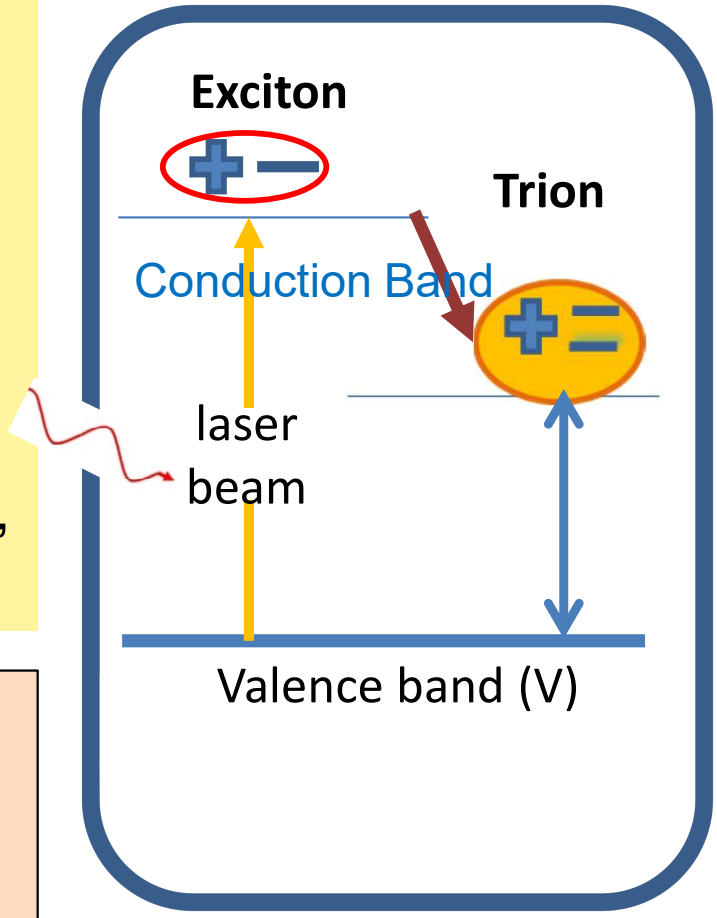
Objectives

- Develop the theoretical formalism and study the formation of valleytrions in transition metal dichalcogenides monolayers within the framework of a nonrelativistic potential model using the method of hyperspherical harmonics (HH) in four-dimensional space.
- Present and discuss the origin of the binding energy difference between X^- and X^+ trions.

Exciton, Trion

- An exciton - a bound electron–hole pair fundamental optical excitation found in semiconductors
- Coulomb attraction between the two oppositely charged quasiparticles.
- When the exciton density is increased with the intensity of the exciting light, excitonic complexes trions and biextions , are expected to form.



Excitons and trions in monolayer TMDs are stable at room temperature due to their remarkably large binding energies in the range of a few hundred meV.

Exciton-history

- Excitons - bound complexes of an electron and a hole in solids-was predicted by Frenkel in 1931 (J Phys. Rev. 37 17 (1931)
- In most semiconductors can form hydrogen-like electron-hole complexes, also called Wannier-Mott excitons (1937) (Phys. Rev. 52 191 (1937) ;Proc. R. Soc. Lond. A 167 384 (1938))

Trion-history

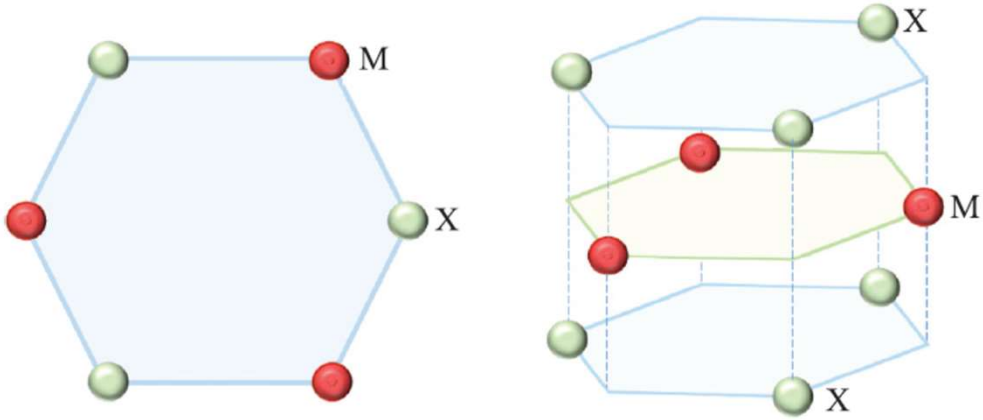
- The possibility of the existence of bound three-particle electron-hole complexes in semiconductors was predicted in 1958 by Lampert (Phys. Rev. Lett. 1, 450)
- Similar quantum mechanical systems made of two identical particles and a third particle with a different mass and opposite electric charge are the hydrogen ion H- and the molecular ion H2+

Trion

- The difference between trions and the H-and H2+ ions is that the mass ratio of an electron and a hole is no longer a small.
- We can’t separate the coordinates of the electron and hole subsystems.
- The calculations much more complicated.

The structure of a TMDC monolayer.

Atomic layers of hexagonal transition metal dichalcogenides (TMDCs) represent a new class of systems.

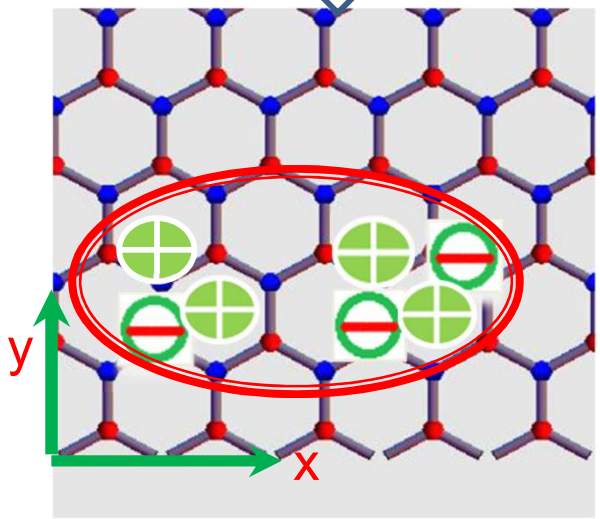


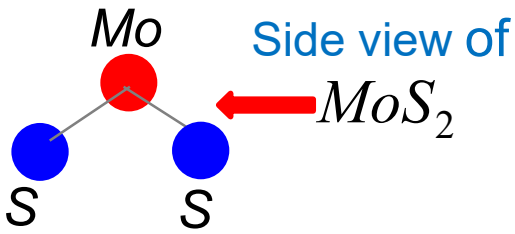
These two-dimensional (2D) crystals are the direct band gap semiconductors.

Luminescence spectra contain discrete lines understood as the electron-hole recombination from neutral X and charged excitons (X^+, X^-) and neutral biexcitons

Two Dimensional (2D) TMDs

Top view on the hexagonal lattice of MoS_2 lying in the *xy* plane





Side view of MoS_2

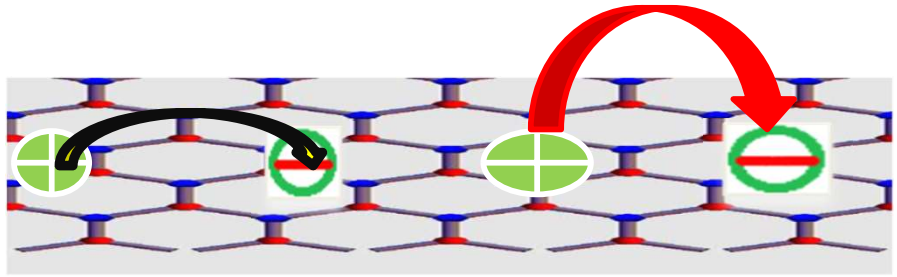
2D TMD

22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961		16 S Sulfur 32.066	MoS_2
40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	→	34 Se Selenium 78.96	$MoSe_2$
72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84		52 Te Tellurium 127.60	$MoTe_2$
					WS_2
					WSe_2
					WTe_2

Band Gap. Coulomb Interaction

The optical band gaps are 1.9 eV (MoS_2), 1.65 eV ($MoSe_2$), 2 eV (WS_2), and 1.7 eV (WSe_2)

- A noticeable properties of 2D TMDs is the dielectric confinement- the strength of dielectric screening is distance dependent.



The electric field lines between two distant charges go outside of the 2D TMD , when $r>r_0$

r_0 –screening length of the medium

When $r<r_0$, most of the electric field lines are confined within the 2D TMD- the Coulomb potential becomes logarithmic.

The electron-hole interaction potential

The electron-hole interaction potential V in momentum (q) space is found by solving the Poisson equation:

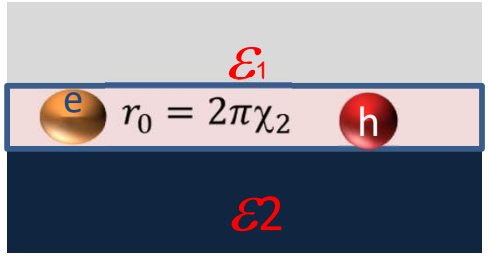
$$V(q) = \frac{-2\pi}{q(k + r_0 q)}$$

k- is the average dielectric constant, $r_0 = 2\pi\chi$, χ –the polarizability of the 2D materials

The 2D screened electrostatic interaction potential

The Rytova-Keldysh (RK) potential is a better description in TMD

$$V(r) = \frac{\pi q^2}{(\varepsilon_1 + \varepsilon_2) r_0} \left[H_0\left(\frac{r}{r_0}\right) - Y_0\left(\frac{r}{r_0}\right) \right]$$



V. Keldysh, JETP Lett. **29**, 658 (1979). N.S.Rytova, Proc. MSU, Phys Astron, .30, (1967)

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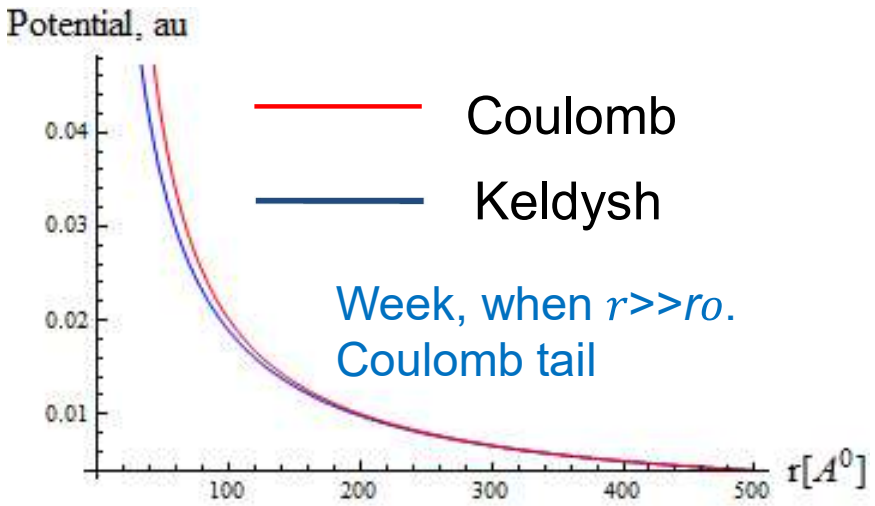
Phys Rev. Phys Rev B98, 125308, (2018

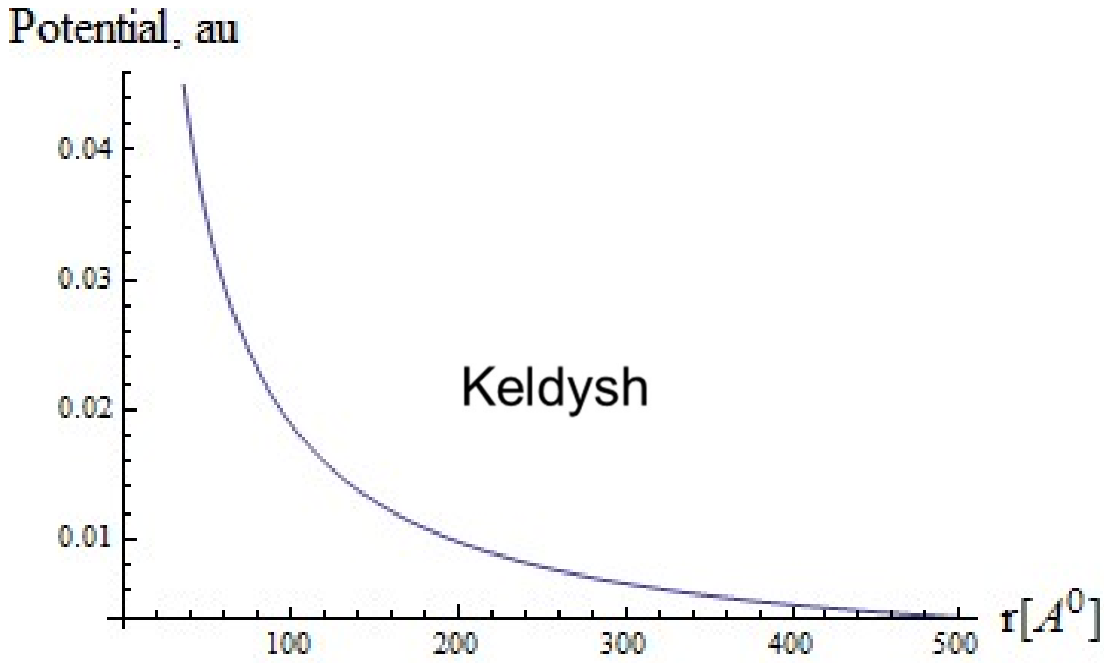
Exhibiting nonlocal macroscopic screening which arises in 2D systems Cudazzo, I. V. Tokatly, and A. Rubio, Phys. Rev. B 84, 085406 (2011).

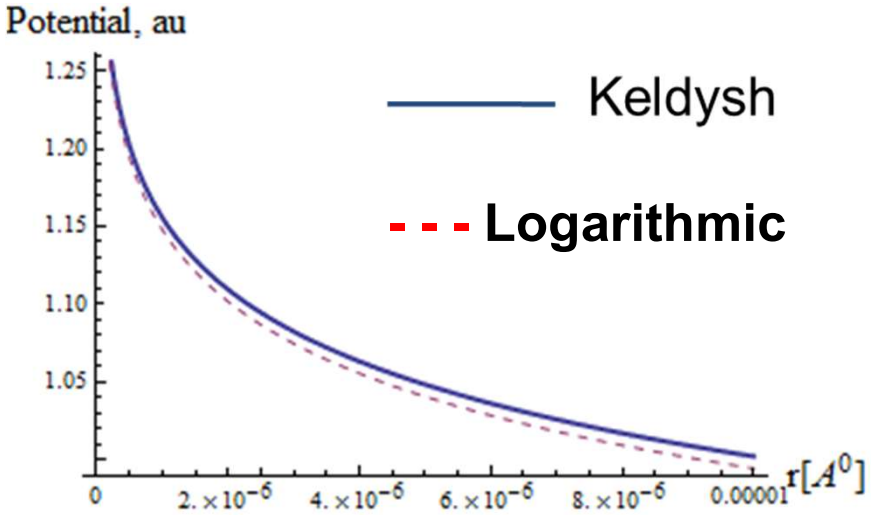
The 2D screened electrostatic interaction potential

$r>>ro$ and $r \ll r_o$



Week, when $r>>ro$.
Coulomb tail





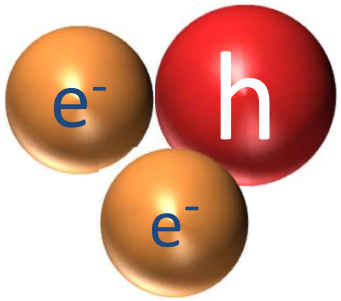
The input model parameters

The table shows electron and hole effective mass in units $\mathbf{m_e}$ and screening length - $\rho_0 = 2\pi\chi_{2D}$

Mono-layer TMD	m_n	m_h	Screening Length ρ_0 , A^0
MoS2	0.35	0.43	38.62
MoSe2	0.38	0.44	51.7
WS2	0.27	0.32	38
WSe2	0.29	0.34	45

Liu, et al. PRB 88,(2013).
Liu et al. IEEE Trans. Electron Devices 58, (2011),

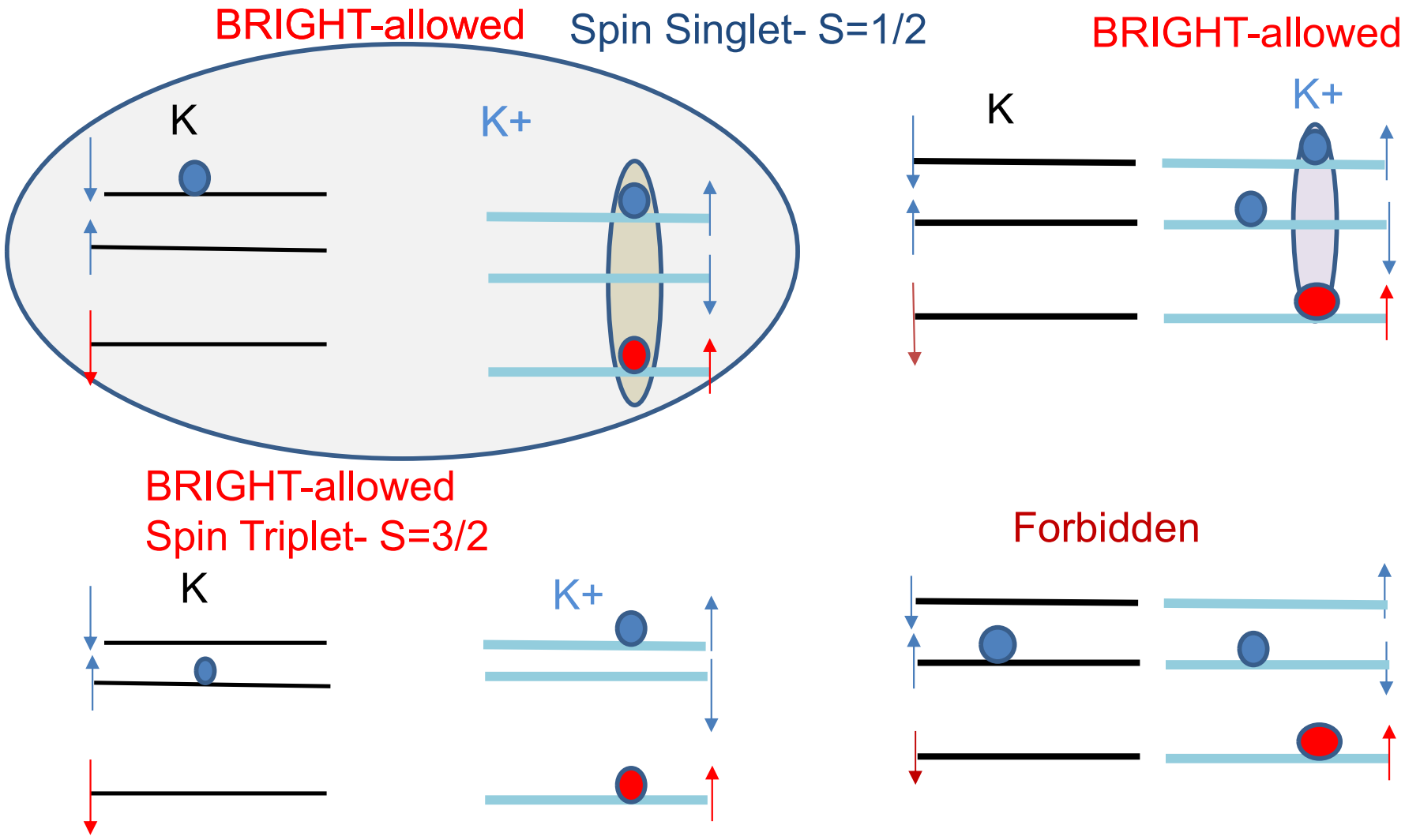
Trions have been of significant interest for the fundamental studies of many-body interactions:



- carrier multiplication
- Wigner crystallization (Wigner, E. *Phys. Rev.* **46**, (1934)
- Spin manipulation [a trion is a charged exciton with nonzero spin, Xu et al, Spin. *Nat. Phys.* **10**, (2014)]

The theoretical technique – the Hyperspherical Function Method is applied to negative and positive trions.

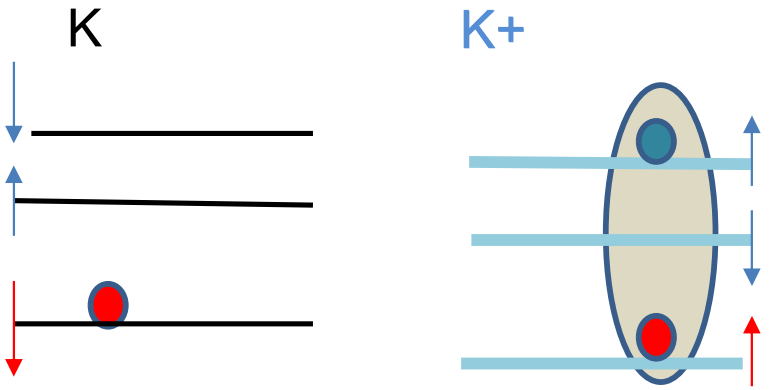
Examples of symmetric negative X-trions



Symmetric positive X+ trion:

Spin Singlet- S=1/2

BRIGHT-allowed



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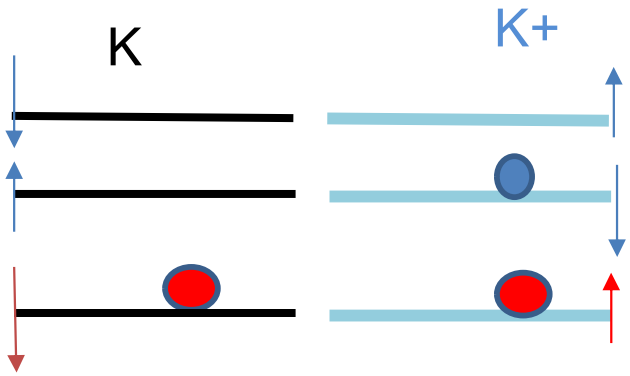


The input model parameters WSe_2–based compound

Electrons have different masses, where one electrons from the top spin –split valley of the conduction band , second from the bottom.

H. Dery and Y. Song, Phys. Rev. B 92, 125431 (2018).

E. Courtade, at all Phys. Rev. B 96, 085302 (2017).

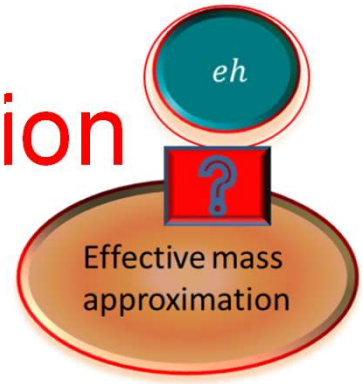
Mono-layer TMD	m_e	m_h	m'e	m'h
MoSe2	0.55	0.64	0.55	0.64
WSe2	0.29	0.36	0.4	0.36

$e^- e^- h$ (T-),

m'e >me

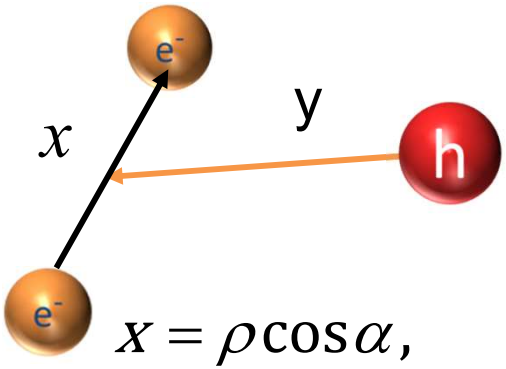
Kormanyos, at all, 2D Mater. 2, 022001, (2015).

The nonrelativistic Hamiltonian of a trion



$$H = -\frac{\hbar^2}{2}\sum_{i<j}^{3}\frac{1}{m_i}\nabla_i^2 + \sum_{i<j}^{3}V_{ij}\left(\frac{r_{ij}}{r_0}\right)$$

where m_i, r_i, and q_i are respectively the 2D position vector, effective mass, and charge of the i - th particle.



$$x = \rho\cos\alpha,$$

$$y = \rho\sin\alpha$$

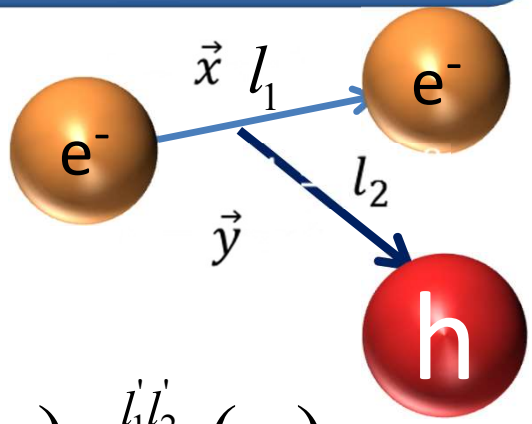
$$\rho = \sqrt{x^2 + y^2}$$

$$\Psi(\rho,\Omega_i) = \rho^{-3/2}\sum_{K\lambda} u_{K\lambda}^{L}(\rho)\Phi_{K\lambda}^{LM}(\Omega)\chi_s\phi_\tau.$$

The function χs is the spin function for X trion, and ϕ is the valley band wave function at the two valleys where index τ = +1,-1 corresponds to the electron being in the K or K0 valley, respectively

Hyperspherical Function Formalizm: Three Body e^-e^-h Cluster

The relative three-body Schrodinger's equation in hyperspherical coordinates can be written as:



$$\left(\frac{\partial^2}{\partial\rho^2}-\left[\chi^2+\frac{(K+1)^2-1/4}{\rho^2}\right]\right)\varphi_{KL}^{l_1l_2}(\rho)=$$
$$=\sum_{K'l_1'l_2'M'}W_{KK'LL'MM'}^{l_1l_2l_1'l_2'}(\rho)\varphi_{K'L'}^{l_1'l_2'}(\rho)$$

$$W_{KK'LL'MM'}^{l_1l_2l_1'l_2'}(\rho)=\frac{2\mu}{\hbar^2}\int\Phi_{KLM}^{l_1l_2}(\Omega_i)U_{123}(\rho,\alpha)\Phi_{K'L'M'}^{l_1'l_2'}(\Omega_i)d\Omega_i$$

Kezerashvili R Ya, Tsiklauri S M Few-Body Syst. 58 18 (2017

Kezerashvili, Tsiklauri, at all J. Phys. G: Nucl. Part. Phys. 43 (2016).; EPJ Web of Conference 113, (2016).

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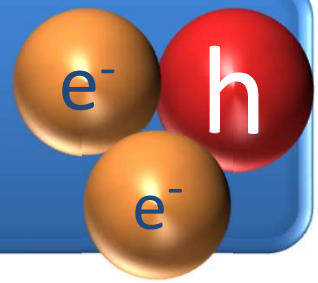
Kezerashvili,. Tsiklauri, EPJ Web of Conference 81, (2014).

Berman,. Kezerashvili, and Tsiklauri Int. J.Mod. Phys B28, (2014).

Kezerashvili, Tsiklauri, " Few-Body Syst. 54, (2013)

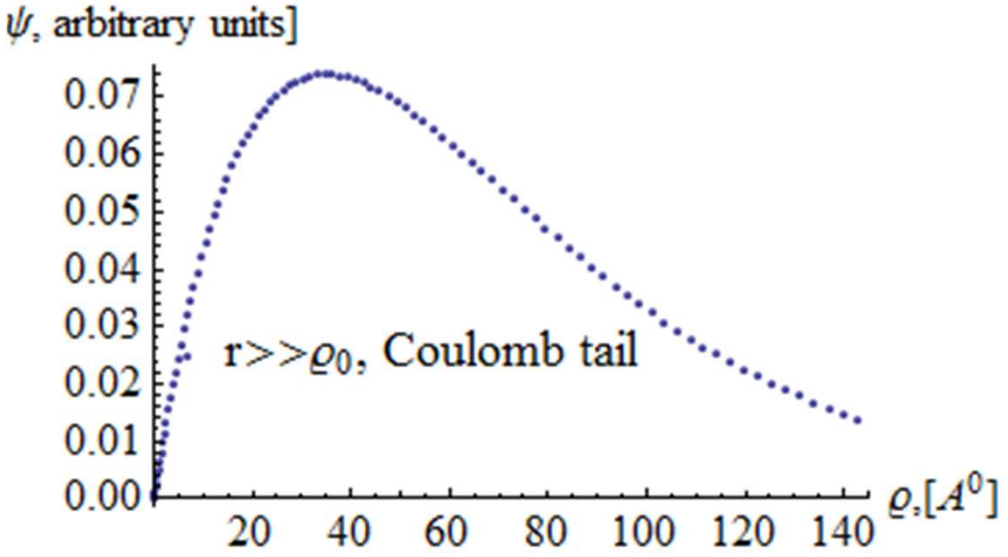
Binding Energy for Trion in TMD: Coulomb Potential



$$W^{l_1 l_2 l_1' l_2'}_{KK'LL'MM'}(\rho)$$

Week, when $r>>ro$. Coulomb Potential

TMD	E, meV (K=0)	E, meV (K=0,2,4,6,8)
MoS_2	21.1	22.5
$MoSe_2$	21.3	22.4
WS_2	22.5	23.7
WSe_2	21.8	22.9



$$E = -\frac{2\mu W^2_{123}[(l),(l'),K,K']}{\hbar^2(2N+2K+3)^2}$$

Binding Energy for Biexciton: Logarithmic Potential

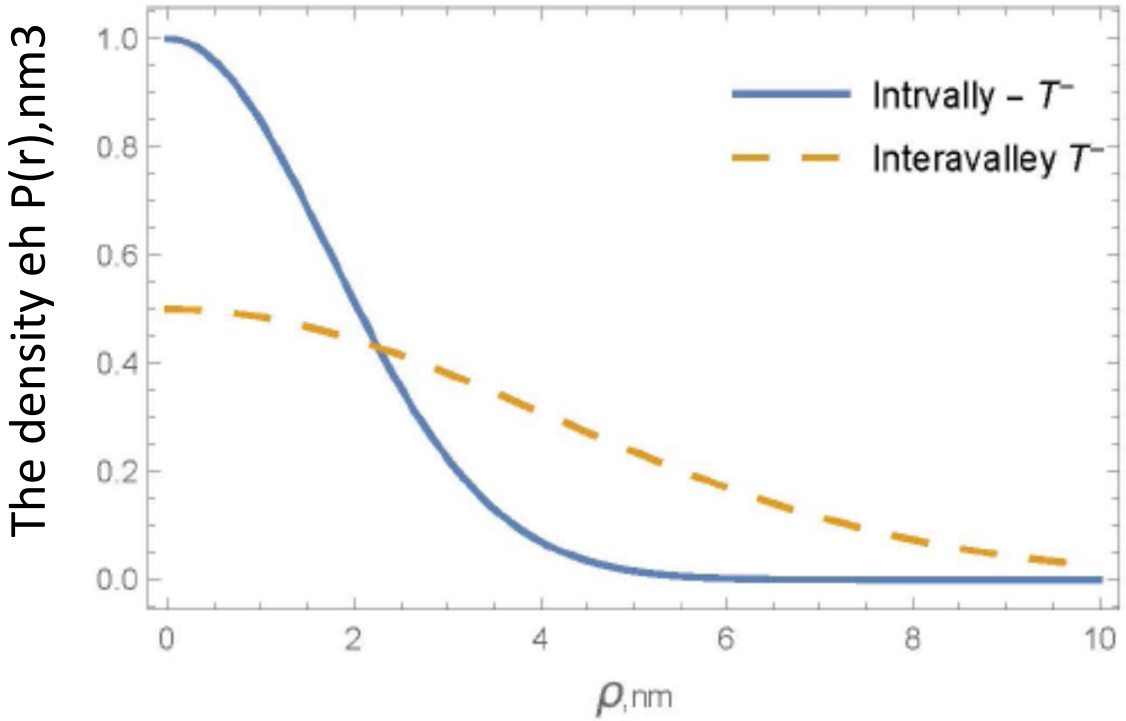
$$W^{l_1 l_2 l_1' l_2'}_{KK'LL'MM'}(\rho)$$

Strong regime, when $r << ro$. Logarithmic Potential

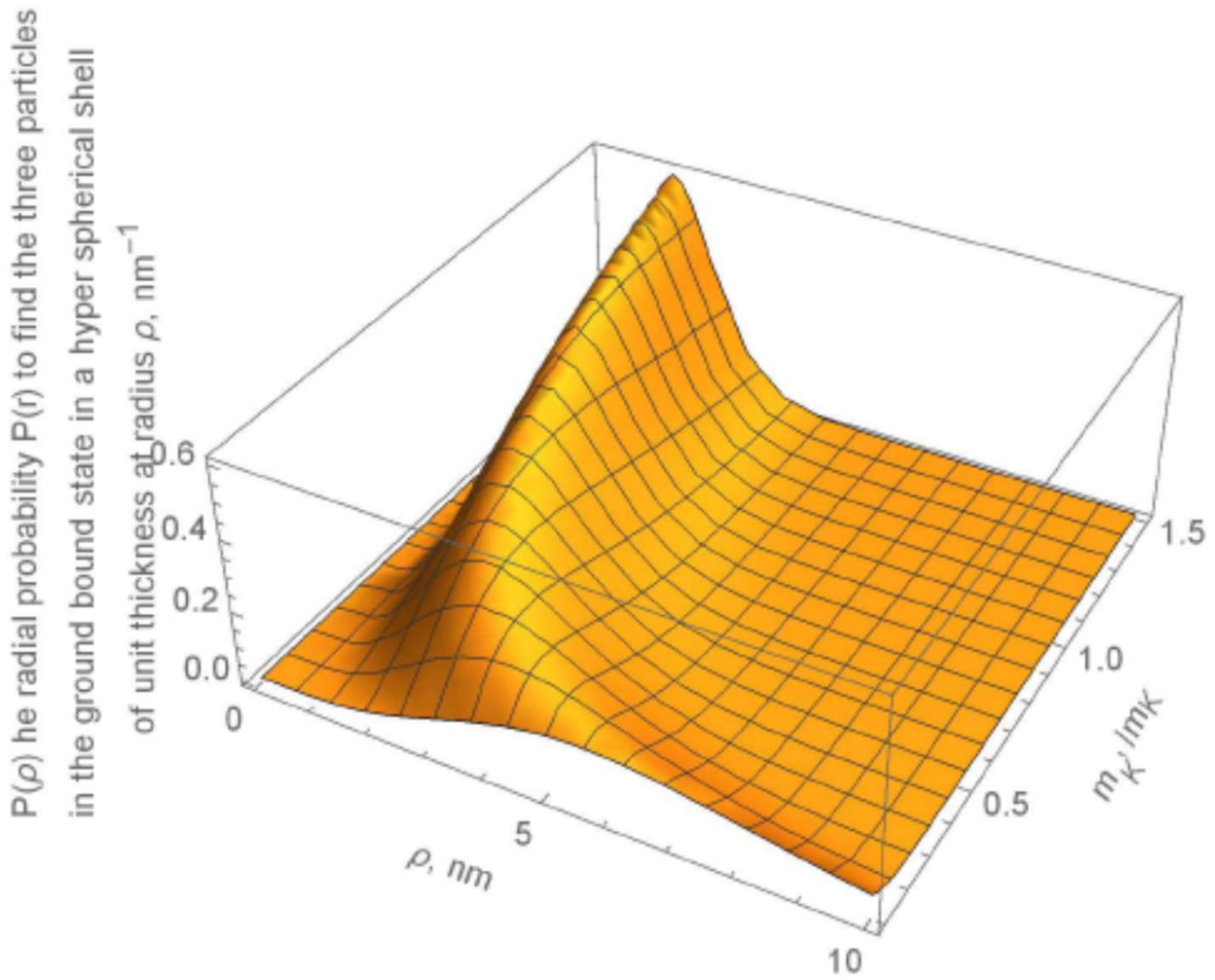
In the diagonal approximation there is an approximate analytical solution

TMD	E, meV (K=0)	EXP. (mev)
MoS_2	34.3	18, 30,32
$MoSe_2$	30.4	30
WS_2	33.9	30
WSe_2	31.8	30

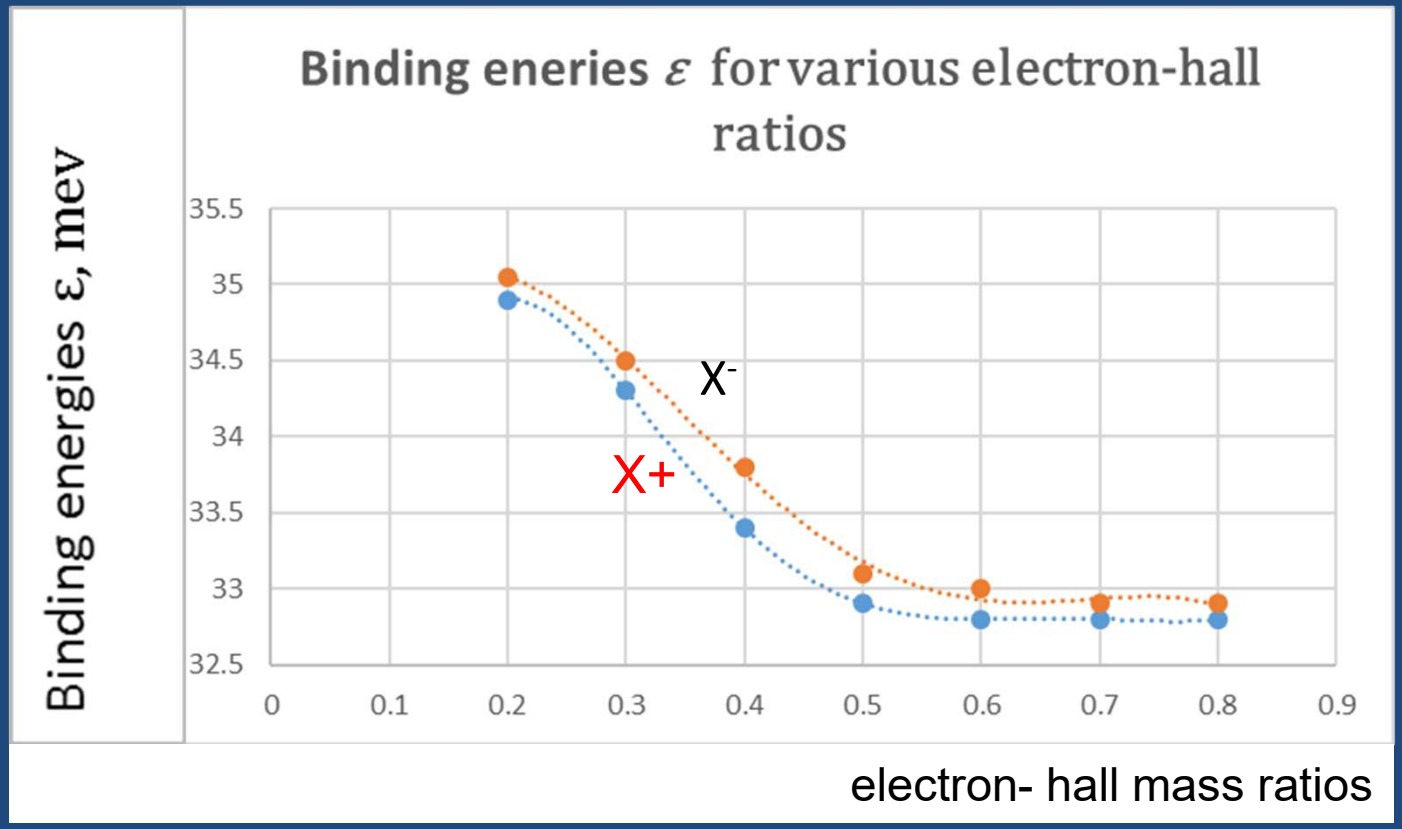
- Few theoretical calculations
- **What is the biding energy and density?**



The difference in the probability distribution is related to the difference of the effective masses of electrons in K and K

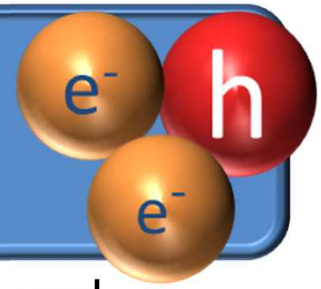


Binding Energy of Trions for various electron- hall mass ratios



Ganchev at al., PRL **114**, (2015)

Results and Discussion



We used the effective Keldysh potential for calculations of the ground state binding energy for the e^-e^-h system. The solution of the system of coupled differential equations with Keldysh potential allows to find the binding energies and corresponding wave functions

Binding energy of X^- and X^+ trions in WSe_2, mev			
	Freestanding	Supported	Encapsulated
Intravalley, singlet state, $L = 0$, $S = 1/2$			
X^-, K valley electrons	38.7	34.6	29.4
X^-, K' valley electrons	28.6	21.4	18.2
Intervalley, singlet state, $L = 0$, $S = 1/2$			
X^+, K valley electron	29.4	24.5	21.6
X^+, K' valley electron	28.9	22.9	19.8
Intervalley, triplet state, $L = 1$, $S = 3/2$			
X^-, K, $K^{'}$ valley electrons	26.3	20.1	18.7

Summary

- We develop the theoretical formalism and study the formation of valleytrions in transition metal dichalcogenides monolayers within the framework of a nonrelativistic potential model using the method of hyperspherical harmonics (HH) in four-dimensional space .
- We solve the three-body Schrödinger equations with the Rytova-Keldysh potential by expanding the wave functions of a trion in terms of the antisymmetrized HH. The antisymmetrization is based on the electron and hole spins and valley indexes

Summary

- Our approach yields the analytical solution for binding energies of trions in diagonal approximation for these two limiting cases - the Coulomb and logarithmic potentials. We obtained exact analytical expressions for energy eigenvalues and eigenfunctions for X^- and X^+ trions. The corresponding energy eigenvalues can be considered as the lower and upper limits for the trions binding energies