Dark excitons and semi-dark trions and biexcitons in WS_2 and WSe_2

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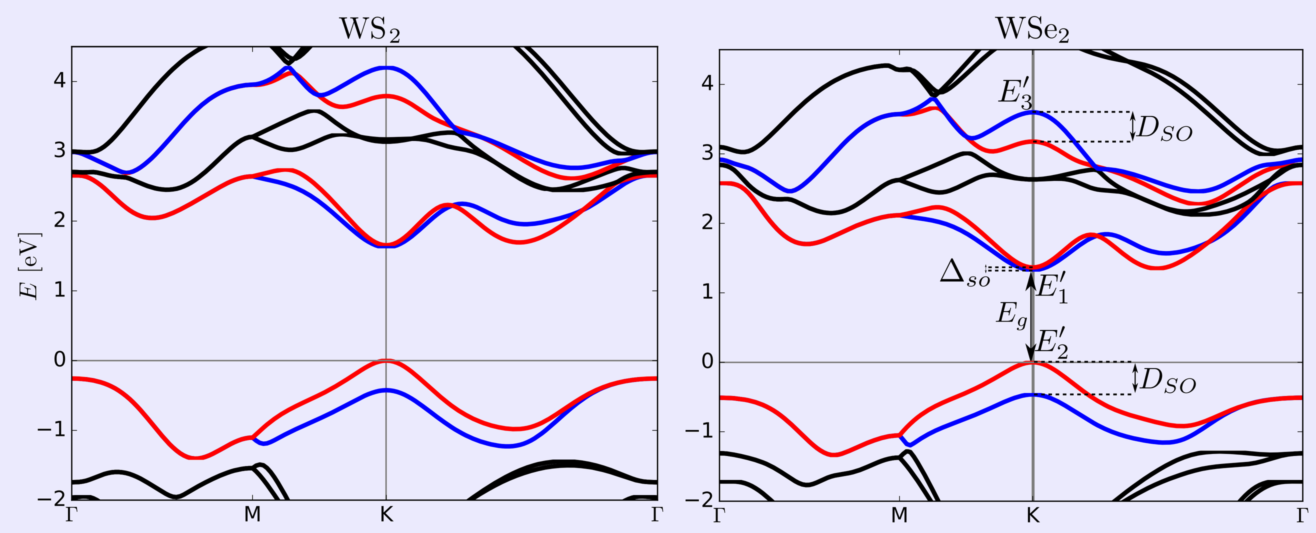
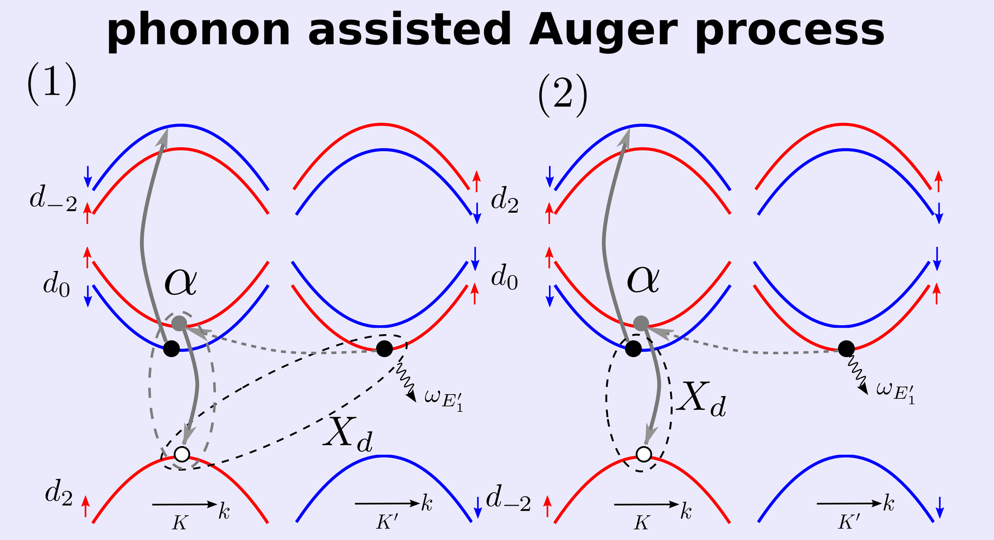
Introduction

The direct band gap character and large spin-orbit splitting of the valence band edges (at the K and K' valleys) in monolayer transition metal dichalcogenides (TMDCs) have put these two-dimensional materials under the spot-light of intense experimental and theoretical studies. In particular, for the Tungsten based dichalcogenides it has been found [1] that the sign of the spin splitting of the conduction band edges makes the ground state excitons, trions and biexcitons optically inactive (dark) due to spin and momentum mismatch.
Utilizing the unique band structure of monolayers of WS_2 and WSe_2, we reveal new pathways for the non-radiative recombination of the dark excitons [2] aiming at explaining the low quantum efficiencies observed [3] in these materials, as well as a novel mechanism for the radiative recombination of the dark ground state trions and biexcitons through intervalley electron-electron scattering.



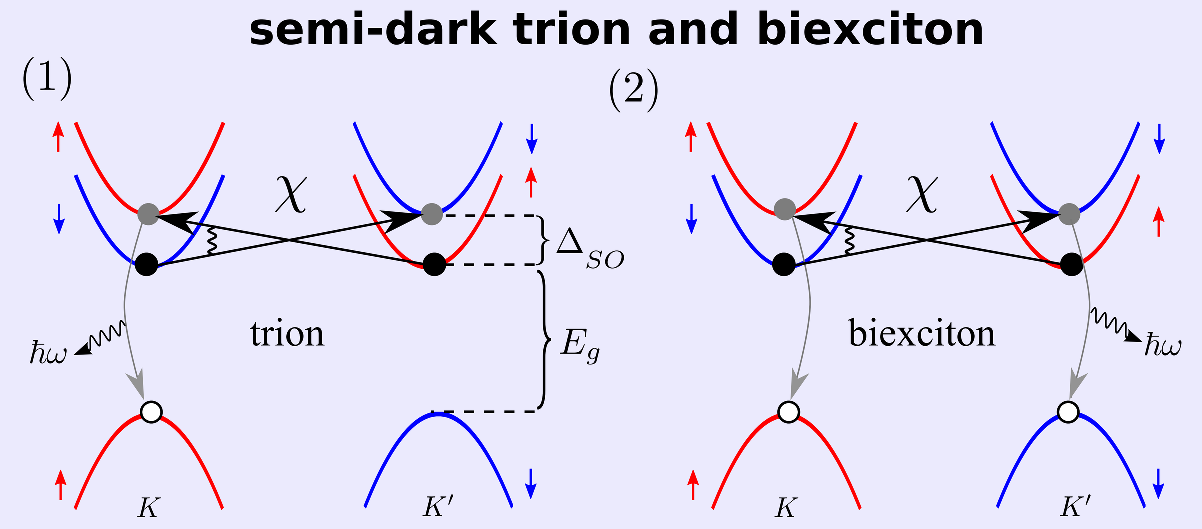
DFT calculated band structure of WS_2 and WSe_2. The spin split v, c, and c' bands are labelled according to the irreps of C_{3v}'' and colored according to the S_z spin component (red-up, blue-down)

phonon assisted Auger process



(E_3',$|S_z|$=0) dark exciton (E,$|S_z|$=1) dark exciton

semi-dark trion and biexciton



dark-bright trion mixing dark-bright biexciton mixing

Symmetry analysis

Character table for the irreducible representations of the extended point group C_{3v}'', and the correspondence to the relevant fermionic and bosonic fields.

C_{3v}''	E	t,t^2	$2C_3$	$9\sigma_v$	$2tC_3$	$2t^2C_3$	
A_1	1	1	1	1	1	1	
A_2	1	1	1	-1	1	1	
E	2	2	-1	0	-1	-1	$(\mathcal{E}_x,\mathcal{E}_y)$
E_1'	2	-1	-1	0	2	-1	Ψ_c
E_2'	2	-1	2	0	-1	-1	Ψ_v
E_3'	2	-1	-1	0	-1	2	$\Psi_{c'}$
D_{xy}	12	0	0	0	-3	-3	phonons
D_z	3	0	0	1	3	0	b

Excitons $E_1'\otimes E_2' = E\oplus E_3'$

Auger

Initial state: $E_1'\otimes E_3' = E\oplus E_2'$

Final electron state (c'): E_3'

Required phonon modes: $E\otimes E_3' = E_1'\oplus E_2'$

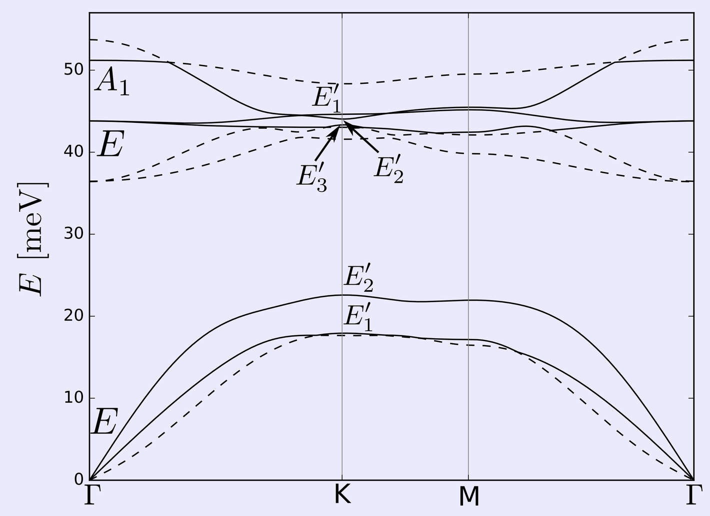
Radiative

Initial state exciton: E_3'

Final state light: E

Required phonon modes: $E\otimes E_3' = E_1'\oplus E_2'$

same phonon modes



WS_2 phonon spectrum
(Solid lines are σ_h symmetric modes)

Trions/Biexcitons

Two electrons representaion: $E_1'\otimes E_1' = A_1 \oplus A_2 \oplus E_1'$

opposite valleys same valley

Trions: $A_1\otimes E_2' = E_2'$

Biexcitons: A_1

The bright and dark singlet (trion/biexciton) states belong to the same irrep and can be mixed.

Model and interactions

Electron band structure near the K/K' points:

$$\epsilon_\nu = E_{\nu\sigma\tau} + \frac{\hbar^2k^2}{2m_\nu};\quad \nu = v,c,c',\quad \sigma=\pm(\uparrow,\downarrow),\quad \tau=\pm(K/K').$$

$$E_v = -\frac{D_{SO}}{2}(1-\tau\sigma),\quad E_c = E_g + \frac{\Delta_{SO}}{2}(1+\tau\sigma),\quad E_{c'} = 2E_g + \Upsilon - \frac{D_{SO}}{2}(1+\tau\sigma)$$

Light-matter interaction:

$$H_r = \frac{e\hbar v}{E_g}\sum_{\sigma,\tau}\int d^2\vec{r}\,\Psi^\dagger_{c\sigma\tau}\Psi_{v\sigma\tau}(\mathcal{E}_x + i\tau\mathcal{E}_y) + h.c.$$

Auger contact interaction:

$$H_c = \frac{\hbar^2\alpha}{m_{c'}}\sum_{\sigma,\tau}\int d^2\vec{r}\left(\Psi^\dagger_{v\sigma}\Psi^\dagger_{c'-\sigma}\Psi_{c-\sigma}\Psi_{c\sigma}\right)_{\vec{r},\tau} + h.c.$$

Phonon spectrum and electron-phonon interaction:

$$H_{ph} = \hbar\omega\sum_\tau\int d^2\vec{r}\,b^\dagger_\tau(\vec{r})b_\tau(\vec{r}) + g\sum_{\sigma,\tau}\int d^2\vec{r}\left(\Psi^\dagger_{c\sigma\tau}\Psi_{c\sigma-\tau}b^\dagger_\tau + h.c.\right)$$

Intervalley scattering contact interaction:

$$H_{iv} = \frac{\hbar^2\chi}{2m_c}\sum_{\sigma,\tau}\int d^2\vec{r}\,\Psi^\dagger_{c,\sigma,-\tau}(\vec{r})\Psi^\dagger_{c,-\sigma,\tau}(\vec{r})\Psi_{c,-\sigma,-\tau}(r)\Psi_{c,\sigma,\tau}(\vec{r}).$$

Material parameters [4], [5]

	$\frac{m_c}{m}$	$\frac{m_v}{m}$	$\frac{m_{c'}}{m}$	Δ_{SO} [meV]	D_{SO} [eV]	E_{X_b} [eV]	Υ [eV]	$\frac{v}{c}$	α
WS_2	0.26	−0.35	−0.39	30	0.42	2.0	0.6	1.7×10^{-3}	0.5
WSe_2	0.28	−0.36	−0.35	38	0.46	1.7	0.6	1.6×10^{-3}	0.6

Semi-dark trions and biexcitons

Effective H for dark (d) and bright (b) trion/biexciton states with mixing:

$$H = \begin{pmatrix} E_b^{T/B} & \mu_{T/B} \\ \mu^*_{T/B} & E_d^{T/B}\end{pmatrix},\quad \mu_T = \frac{\hbar^2\chi}{m_c}\underbrace{g_T}_{\text{e-e contact pair-density}},\quad \mu_B = \frac{\hbar^2\chi}{m_c}g_B$$

Intervalley e-e scattering matrix element parameter:

$$\chi = \frac{m_c}{m}\frac{A}{a_B}\underbrace{|C|^4}_{\text{Tight binding orbital amplitude}}\sum_{\vec{R}}e^{i\vec{K}\cdot\vec{R}}\int d^3\vec{r}_1 d^3\vec{r}_2\frac{\overbrace{|\phi(\vec{r}_1)|^2}^{\text{metal d-orbital}}|\phi(\vec{r}_2)|^2}{|\vec{r}_2-\vec{r}_1+\vec{R}|}$$

Radiative rates

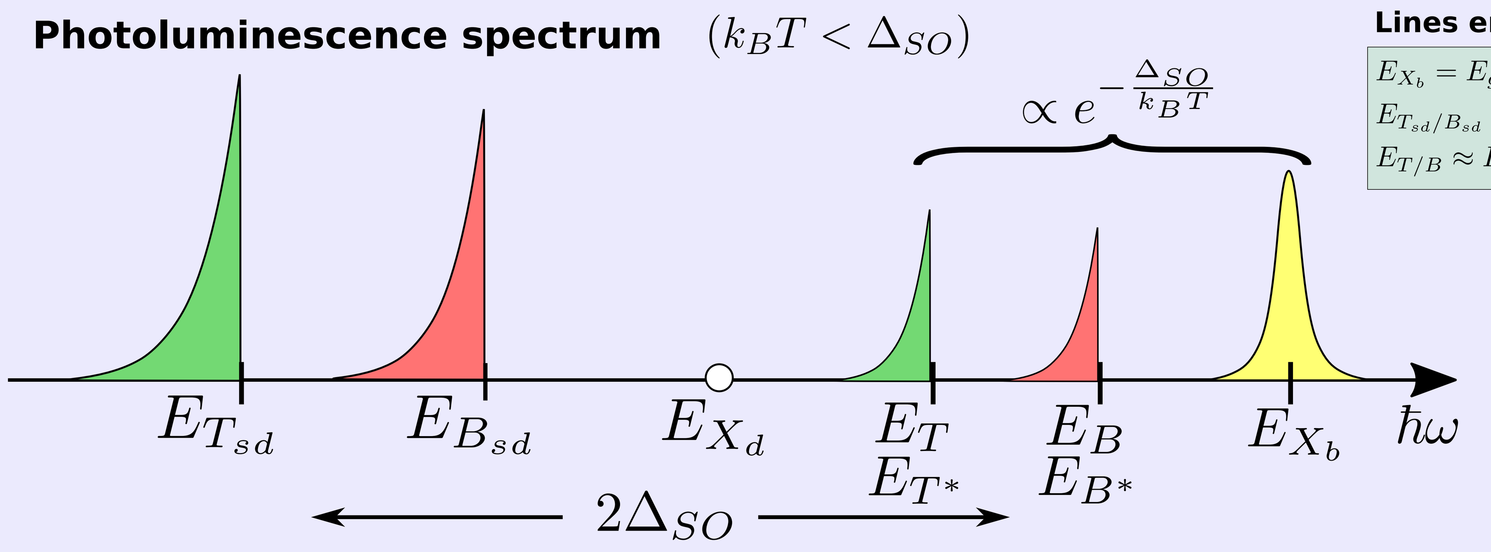
$$\frac{1}{\tau_{sd}} \approx \left(1 - \frac{1}{\sqrt{1+\left(\frac{\mu_{T/B}}{\Delta_{SO}}\right)^2}}\right)\overbrace{\frac{\alpha_{T/B}}{2}}^{\text{Oscillator strength parameter}}\tau_X^{-1},$$

$$\frac{1}{\tau_X} = \frac{8\pi}{\hbar}\frac{e^2}{\hbar c}\frac{\hbar^2v^2}{E_{X_b}}|\underbrace{\Phi_X(0)}_{\text{Exciton wave function}}|^2$$

Radiative lifetimes of semi-dark trion/biexciton

	χ_{DFT}	χ_{TB}	μ_T [meV]	μ_B [meV]	τ_X [ps]	$\tau_{sd}(T)$ [ps]	$\tau_{sd}(B)$ [ps]
WS_2	1.0	1.6	18 [29]	13 [21]	0.25	7.7 [3.9]	10 [4.5]
WSe_2	1.3	2.0	19 [30]	14 [22]	0.26	9.1 [4.7]	12 [5.7]

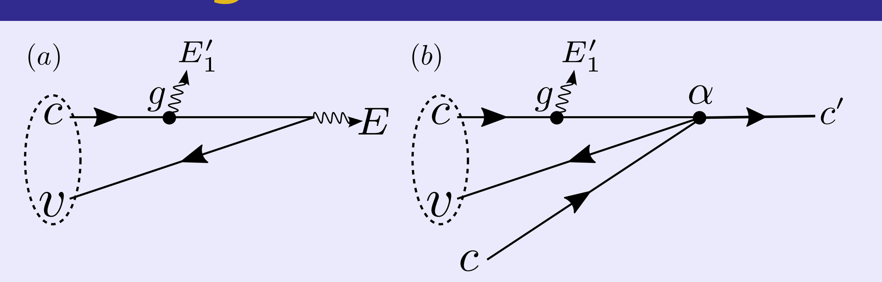
Photoluminescence spectrum $(k_BT < \Delta_{SO})$



Lines energies

$$E_{X_b} = E_g + \Delta_{SO} - \epsilon_X,$$
$$E_{T_{sd}/B_{sd}} \approx E_{X_b} - \epsilon_{T/B} - 2\Delta_{SO},$$
$$E_{T/B} \approx E_{X_b} - \epsilon_{T/B}$$

Dark excitons - Auger vs. radiative



Diagrams describing the amplitudes for the (a) radiative process with a line at $\hbar\omega_\gamma = E_x - \hbar\omega$ and (b) Auger process.

$$\frac{1}{\tau_r} = \frac{8E_g}{3\hbar}\frac{e^2}{\hbar c}\left(\frac{v}{c}\right)^2\frac{|\phi(0)|^2g^2}{(\Delta_{SO}+\hbar\omega)^2};\qquad \frac{1}{\tau_A} = \frac{E_g}{\hbar}\frac{\hbar^2n_e}{|m_c'|E_g}\frac{\alpha^2|\phi(0)|^2g^2}{[\Delta_{SO}+\hbar\omega+\frac{|m_{c'}|}{|m_v|+m_c}\Upsilon]^2}$$

Critical density for Auger process to dominate radiative process:

$$\frac{\tau_r}{\tau_A} = \frac{n_e}{n_e^*}\quad\rightarrow\quad n_e^* = \frac{8|m_c'|E_g}{3\hbar^2}\left(\frac{v}{\alpha c}\right)^2\left(\frac{e^2}{\hbar c}\right)\left(1+\frac{\frac{|m_{c'}|}{|m_v|+m_c}\Upsilon}{\Delta_{SO}+\hbar\omega}\right)^2$$

$$n_e^*(WS_2)\sim 10^{10}\ \text{cm}^{-2}$$
$$n_e^*(WSe_2)\sim 4\times10^{9}\ \text{cm}^{-2}$$

Estimated phonon-assisted exciton-exciton annihilation rate:

$$\tau^{-1}\sim 0.003\ n_X\ \text{cm}^2\text{s}^{-1}$$

References

[1] X. Zhang, Y. You, S. Yang, F. Zhao, and T. F. Heinz, *Phys. Rev. Lett.* 115 (2015) 257403.
[2] M. Danovich, V. Zólyomi, I. L. Aleiner, V. I. Falko, *2D Materials*, 3, 035011 (2016).
[3] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim,G. Galli, and F. Wang, *Nano Letters*, 10, 1271(2010)
[4] A. Kormnyos, G. Burkard, M. Gmitra, J. Fabian, V. Zólyomi, N. D. Drummond, and V. Fal'ko, *2D Materials*, 2, 022001 (2015).
[5] M. Palummo, M. Bernardi, and J. C. Grossman, *Nano Letters*, 15, 2794 (2015).