Auger recombination of dark excitons and trions in WX_2 2D transition metal dichalcogenides

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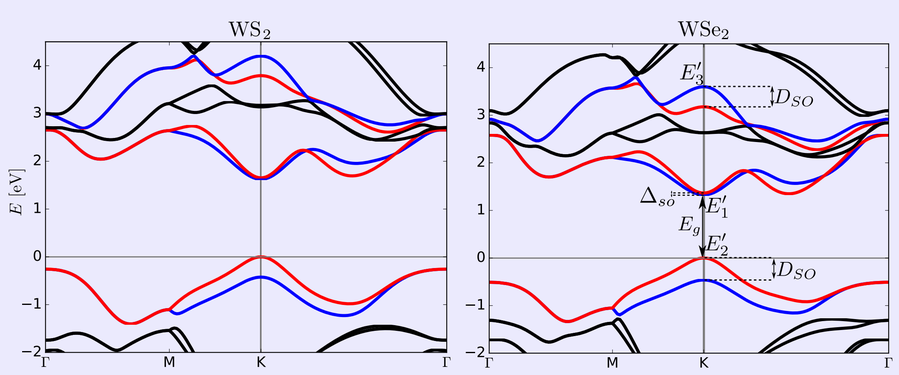
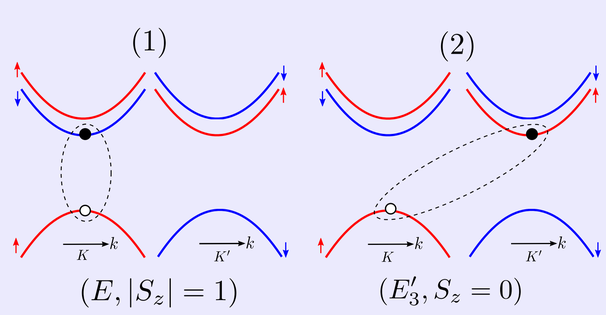
Introduction

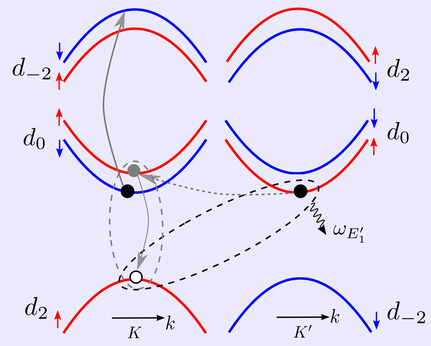
Monolayer transition metal dichalcogenides (TMDCs) have attracted wide attention for their potential in optoelectronic applications. In contrast to bulk TMDC crystals, the monolayers of MoS_2, $MoSe_2$, WS_2, and WSe_2 are direct band semiconductors, with the conduction (c) and valence (v) bands edges at the K/K' points of the Brillouin zone (BZ). Several experiments have already demonstrated a strong light-matter interaction in these 2D crystals. Potentially practical implementations of these TMDC atomic crystals in optoelectronic devices require high quantum efficiency of the optical process. However, despite the recent progress in improving the quality of 2D TMDCs, the quantum efficiency observed in photoluminescence experiments [1] never exceeded 1%. Such systematically low quantum efficiency calls for finding the mechanism responsible for the non-radiative recombination of electron-hole pairs, excitons, or trions.



DFT calculated band structure of WS_2 and WSe_2. The spin split v, c, and c+2 bands are labelled according to the irreps of C_{3v}'' and colored according to the S_z spin component (red-up, blue-down)



Sketch of WX_2 band structure at the K/K' points, and the two exciton ground states (1) completley dark $|S_z|$=1 exciton, and (2) S_z=0 dark exciton due to momentum mismatch.



Schematics of the phonon assisted Auger process. Dashed gray line corresponds to the virtual transition.

Symmetry analysis

Character table for the irreducible representations of the extended point group [2] 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	Ψ_{c+2}
D_{xy}	12	0	0	0	-3	-3	phonons
D_z	3	0	0	1	3	0	b

$$C''_{3v} = C_{3v} + tC_{3v} + t^2C_{3v}$$

Excitons representations: $E'_1 \otimes E'_2 = E \oplus E'_3$

Auger

Initial state: $E'_1 \otimes E'_3 = E \oplus E'_2$

Final electron state (c+2): E'_3

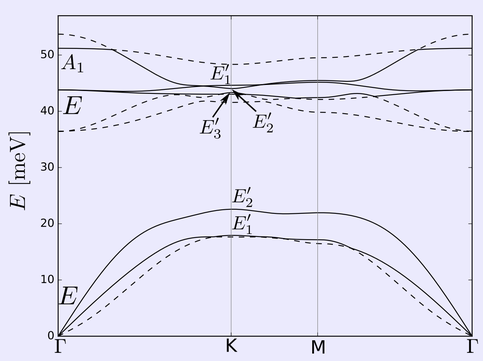
Required phonon modes: $E \otimes E'_3 = \overline{E'_1 \oplus E'_2}$

Radiative

Initial state exciton: E'_3

Final state light: E

Required phonon modes: $E \otimes E'_3 = \overline{E'_1 \oplus E'_2}$



WS_2 phonon spectrum
(Solid lines are σ_h symmetric modes)

The E_2' phonon mode couples to the hole, resulting in a large denominator due to the large v band spin plitting, and will be neglected.

Model and interactions

Electron band structure near the K/K' points:

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

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

Light-matter interaction:

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

Auger contact interaction:

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

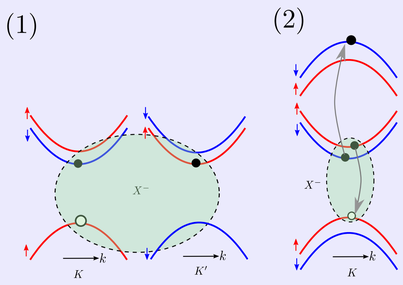
Phonon spectrum and electron-phonon interaction:

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

	$\frac{m_c}{m}$ [a]	$\frac{m_v}{m}$ [a]	$\frac{m_{c+2}}{m}$ [a]	Δ_{SO} [meV]	D_{SO} [eV]	E_g [b] [eV]	Υ [eV]	$\frac{v}{c}$ [a]	α
WS_2	0.26	−0.35	0.39	30	0.42	2.0	0.6	1.7×10^{-3}	1.3
WSe_2	0.28	−0.36	0.35	38	0.46	1.7	0.6	1.6×10^{-3}	1.7

[a] Ref. [3]
[b] Ref. [4]

Results - trions



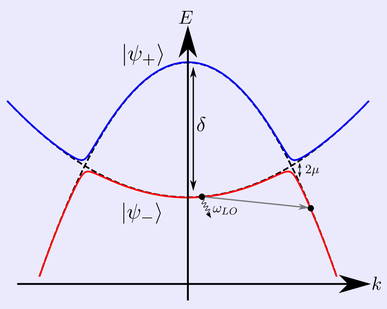
(1) ground state trion (2) Auger process for phonon activated trion.

For the phonon-activated ground state trion with resulting line at $\hbar\omega_\gamma = E_t - \hbar\omega$:

$$\frac{\tau_r}{\tau_A} = \frac{3}{4}\frac{\hbar c}{e^2}\left(\frac{c}{v}\right)^2\frac{m_{c+2}}{m}\frac{\hbar^2}{mE_g}\frac{\alpha^2}{\left(1+\frac{\Upsilon}{\Delta_{SO}+\hbar\omega}\right)^2}\frac{|\psi(0,0)|^2}{\int d^2\vec{\rho}|\psi(\rho,0)|^2} \sim 0.01$$

Auger dominates

In the case of resonant activation of the ground state trion, the Auger process mixes the trion and electron states, from which the trion can decay by emitting a phonon.



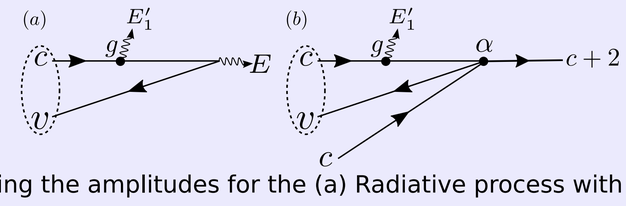
$$\tau_A^{-1} = \frac{2\pi^2}{\hbar}\frac{Z^2E_B}{(1+q_*r_*)^2}\frac{E_B}{\hbar\omega_{LO}}\frac{a_B^2}{A}\frac{m_{c+2}}{M_r}[1+n(\hbar\omega_{LO})]\left|1+\frac{\gamma(q_*)}{\frac{\hbar\omega_{LO}}{\delta}\left(1+\frac{m_{c+2}}{2m_c+|m_v|}\right)+\frac{m_{c+2}}{2m_c+|m_v|}}\right|^2\frac{\mu^2}{\delta^2};$$

$$q_* = \frac{1}{\hbar}\sqrt{2m_{c+2}(\delta+\hbar\omega_{LO})}$$

$$\tau_r^{-1} = \frac{4E_*}{3\hbar}\frac{e^2}{\hbar c}\left(\frac{v}{c}\right)^2\left|\int d^2\vec{\rho}\,\psi(\vec{\rho},0)\right|^2$$

In this case the radiative process dominates over the Auger process (factor 10-10^2), however the thermal activation results in reduced intensity by a factor $e^{-\frac{\Delta_{SO}}{k_BT}}$ for the line at $\hbar\omega_\gamma = E_t + \Delta_{SO}$.

Results - excitons



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

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

Taking the ratio:

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

Required carrier densities for Auger process to dominate radiative process:

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

References

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