

# Comparison of radiative and Auger recombination of free trions in $WX_2$ TMDCs

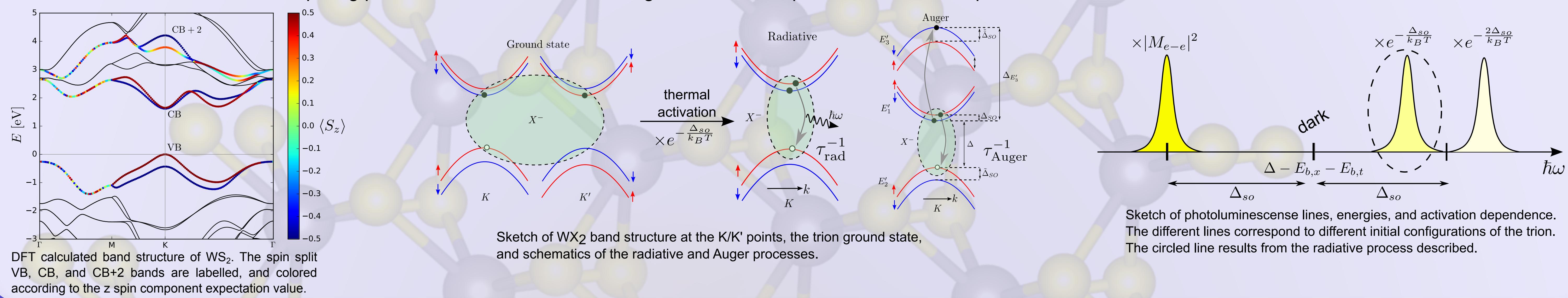
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## Introduction

Monolayer transition metal dichalcogenides (TMDCs) have attracted wide attention for their potential in optoelectronic applications. This is attributed to their direct band gap in the optical range at the corners of the Brillouine zone (BZ), the strong excitonic effects due to the two dimensional (2D) confinement, and large spin splittings in the valence and conduction bands. The efficiency of semiconductor devices for optoelectronic applications is limited by non-radiative processes competing with the radiative processes. Tungsten based TMDCs ( $WS_2$ ,  $WSe_2$ ) have the unique property of opposite spin split bands in the conduction (CB) and valence (VB) bands, resulting in a semi-dark trion ground state which cannot recombine radiatively due to spin and momentum conservation. The negatively charged trion ( $X^-$ ), with a binding energy  $\sim 30$  meV [2], can become bright if the electron is transferred to the correct valley where it can radiatively recombine with the hole, emitting light. However, in the bright state, due to the presence of a secondary high energy (comparable to the trion energy) conduction band (CB+2), a novel phonon assisted Auger process can take place, in which the two electrons scatter from each other into the VB and CB+2 bands. The two competing processes can affect the resulting line in the trion photoluminescence spectrum.



## Auger and radiative recombination rates

**Trion**  
 $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_h) = \frac{1}{A^{3/2}} e^{i\vec{k}_t \cdot \vec{R}} \psi(\vec{p}_1, \vec{p}_2); \quad \psi(\vec{p}_1, \vec{p}_2) \propto e^{-\frac{p_1}{a} - \frac{p_2}{b}} + e^{-\frac{p_1}{b} - \frac{p_2}{a}}$   
center of mass motion  
relative motion (symmetrical-singlet ground state)

Trion radii [2]  
 $a \sim a_{exciton} \approx 1$  nm  
 $b \sim 2a$

### Auger Matrix element

Character table of  $D_3'' = D_3 + iD_3 + i^2 D_3$ , tripled unit cell

$D_3''$	$E$	$t, t^2$	$2C_3$	$9\sigma_v$	$2tC_3$	$2t^2C_3$
$A_1$	1	1	1	1	1	1
$A_2$	1	1	1	-1	1	1
$E$	2	2	-1	0	-1	-1
$E'_1$ (CB)	2	-1	-1	0	2	-1
$E'_2$ (VB)	2	-1	2	0	-1	-1
$E'_3$ (CB+2)	2	-1	-1	0	-1	2
$E'_1 \otimes E'_1$	4	1	1	0	4	1
$E'_2 \otimes E'_3$	4	1	-1	0	-2	= $E \otimes E'_1$

initial state      final state      common irreducible representation, process allowed by symmetry

$H_{Auger} = \frac{\alpha}{A} \sum_{\vec{k}_1, \sigma, \sigma'} b_{\vec{k}_3 - \vec{k}_2 - \vec{k}_1, \sigma}^\dagger d_{\vec{k}_3, \sigma'}^\dagger c_{\vec{k}_2, \sigma'}^\dagger c_{\vec{k}_1, \sigma}^\dagger$

$\alpha$  was calculated using DFT, and confirmed (within factor 2) using a simplified Coulomb scattering of Bloch states

### Trion-electron mixed states

The Auger process mixes the trion and CB+2 electron states, which have opposite curvature dispersions:

Trion and electron dispersions:  
 $E_t(k) = E_x - E_t + \Delta_{SO} + \frac{\hbar^2 k^2}{2m_t}$   
 $E_e(k) = \Delta E'_3 - \frac{\hbar^2 k^2}{2m_e}$

Trion-electron effective Hamiltonian:  
 $H = \begin{pmatrix} E_t(k) & \mu \\ \mu^* & E_e(k) \end{pmatrix}$   
 $\mu = \langle \psi | H_{Auger} | \psi \rangle = \alpha \psi(0,0)$

mixing parameter

Lower energy eigenstate:  
 $|\psi_{-}(k)\rangle = \frac{1}{\sqrt{1+\nu^2}} \begin{pmatrix} \nu \\ 1 \end{pmatrix} = \frac{\nu(t) + |e|}{\sqrt{1+\nu^2}}$   
 $\nu = -x(k) - \sqrt{1+x(k)^2}; \quad x(k) = \frac{E_x(k) - E_t(k)}{2\mu}$

### Phonon scattering

The phonon scattering rate:  $\tau_{LO}^{-1} = \frac{2\pi}{\hbar} \sum_f \langle \psi_{-,f} | H_{e-ph,LO} | \psi_{-,i} \rangle \langle (1 + n(\hbar\omega_{LO})) \delta(E_f - E_i + \hbar\omega_{LO}) + n(\hbar\omega_{LO}) \delta(E_f - E_i - \hbar\omega_{LO}) \rangle$

electron part      trion part  
 $\xi = \langle \psi_{-,f} | H_{e-ph,LO} | \psi_{-,i} \rangle = \frac{g_{LO}(q) + \nu(k_i) \nu(k_f) g_{LO}(q) \gamma(q)}{\sqrt{(1 + \nu^2(k_i))(1 + \nu^2(k_f))}}$

electron-phonon coupling coefficient:  
 $|g_{LO}| = \sqrt{\frac{\hbar}{2M_r \omega_{LO}}} \frac{1}{A} \frac{2\pi Z e^2}{1 + qr_*}$

Trion form factor  $\gamma(q)$ :

$$\gamma(\vec{q}) = \int d^2\vec{p}_1 d^2\vec{p}_2 |\psi(\vec{p}_1, \vec{p}_2)|^2 \left[ e^{-i\vec{q}[(\eta-1)\vec{p}_1 + \eta\vec{p}_2]} + e^{-i\vec{q}[\eta\vec{p}_1 + (\eta-1)\vec{p}_2]} - e^{-i\eta\vec{q}(\vec{p}_1 + \vec{p}_2)} \right]; \quad \eta = \frac{m_e}{m_t}$$

### Auger recombination rate

We expand the phonon scattering matrix element  $\xi$ , to leading order in  $\frac{\mu}{\delta}$ , and the scattering rate to fourth order (for high T) in the trion's wavevector  $k_i/q_*$ ,  $k_i = \sqrt{2m_t k_B T / \hbar}$ :

$$\tau_{Auger}^{-1} = \tau_0^{-1} \left[ 1 + I_2(q_*) \left( \frac{k_i}{q_*} \right)^2 + I_4(q_*) \left( \frac{k_i}{q_*} \right)^4 \right] \left\{ 1 + n(\hbar\omega_{LO}) \right\};$$

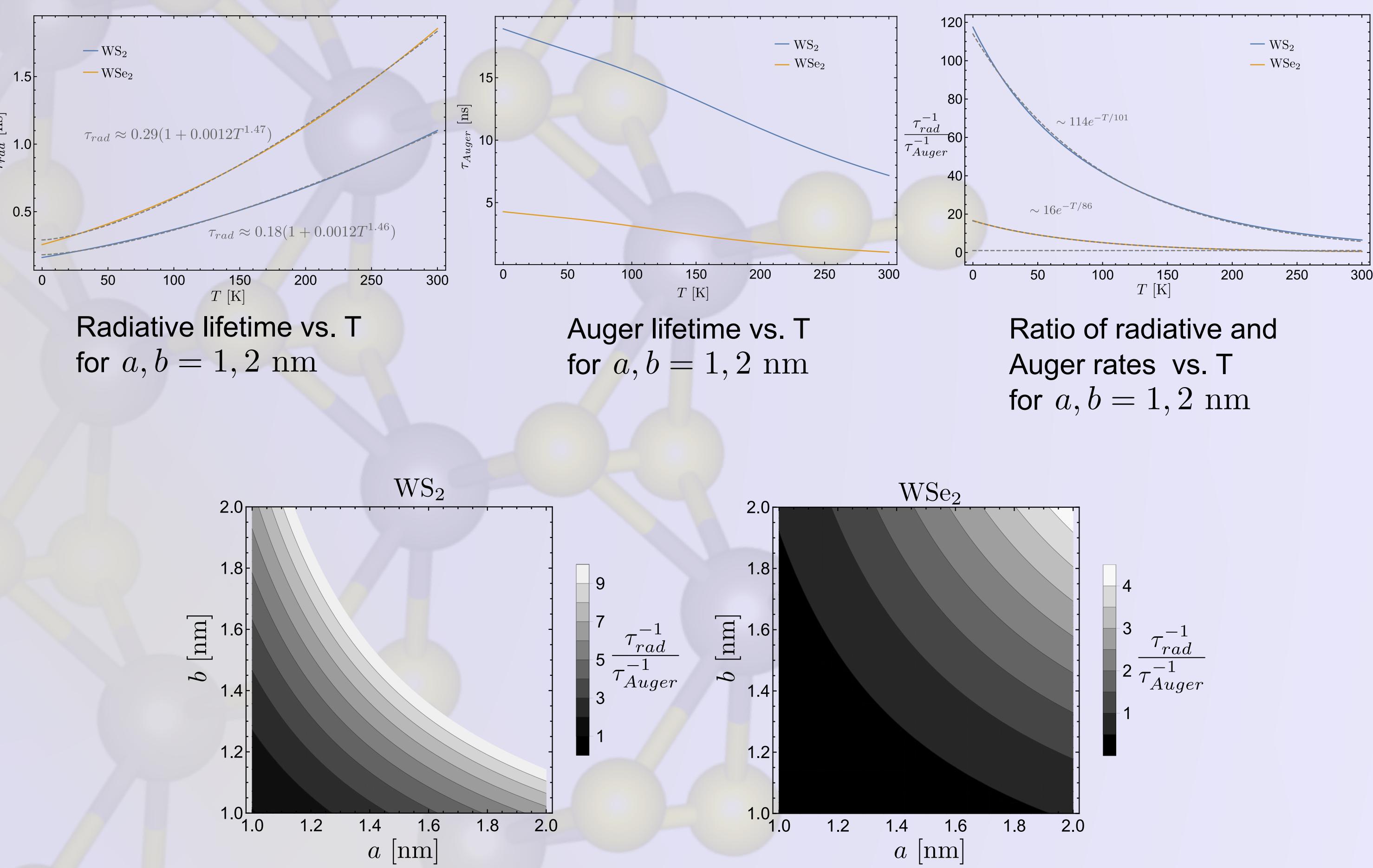
$$\tau_0^{-1} = \frac{m'_e A}{\hbar^3} |g_{LO}(q_*)|^2 \left| 1 - \frac{\gamma(q_*)}{1 - \frac{\hbar^2 q_*^2 (m'_e + m_t)}{2\delta m'_e m_t}} \right|^2 \frac{\mu^2}{\delta^2}; \quad q_* = \frac{1}{\hbar} \sqrt{2m'_e (\delta \pm \hbar\omega_{LO})}$$

### Radiative recombination rate

The radiative recombination of a trion leaves one free electron which takes the initial momentum of the trion, and the photon's energy is determined by the trion's initial energy.

$$\tau_{rad}^{-1} = \frac{4c^2 |P_{vc}|^2 q_\gamma}{3\hbar m_0^2 c^2} \left| \int d^2\vec{p} e^{-i\frac{m_e}{m_t} \vec{p} \cdot \vec{k}_t} \psi(\vec{p}, 0) \right|^2; \quad q_\gamma = \frac{1}{\hbar c} \left( E_x - E_t - \frac{\hbar^2 k_t^2}{2m_e} \frac{m_x}{m_t} \right)$$

## Results



### Material parameters used in the calculations [1]

$\delta$ [meV]	$q_*$ [nm $^{-1}$ ]	$k_*$ [nm $^{-1}$ ]	$\alpha$ [ $\frac{2\pi e^2}{\hbar} \text{Å}$ ]	$\Delta E'_3$ [eV]	$\Delta_{SO}$ [meV]	$\tilde{\Delta}_{SO}$ [meV]	$\frac{m'_e}{m_0}$	$\frac{m_t}{m_0}$	$E_x$ [eV]	$E_t$ [meV]	$ P_{vc} $ [eV]	
$WS_2$	646	2.66	2.17	0.11	2.65	38	-429	0.39	0.87	2	34	1410
$WSe_2$	655	2.51	2.12	0.14	2.37	46	-437	0.35	0.92	1.7	31	1212

## Summary

- The radiative recombination with a typical life time of  $\sim 1$  ns, dominates over the Auger process for temperatures up to room temperature for both materials, and for typical trion radii.
- The stronger LO phonon coupling in  $WSe_2$ , attributed to the larger Born effective charge, results in a higher Auger rate which becomes comparable to the radiative rate at room temperature.
- The calculated rates are restricted to the particular trion configuration, which may be differentiated from other configurations through fine splittings in the trion's spectrum.
- The calculated Auger rates due to LO phonon scattering set a lower bound. Additional phonon modes scattering will further increase the calculated Auger rates.

## References

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- [2] Timothy C. Berkelbach, Mark S. Hybertsen, and David R. Reichman, *Phys. Rev. B*, 88, (2013), 045318
- [3] Axel Esser, Erich Runge, Roland Zimmermann, and Wolfgang Langbein, *Phys. Rev. B*, 62, (2000), 8232-8239

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