Exciton g-factors of van der Waals heterostructures from first-principles calculations

Tomasz Woźniak[1] and Jens Kunstmann[2]

[1] Department of Semiconductor Materials Engineering, Wrocław University of Science and Technology, Poland, [2] Theoretical Chemistry, TU Dresden, Germany

ABSTRACT

We present how exciton g-factors and their sign can be determined by converged first principles calculations. We apply the method to monolayer excitons in transition metal dichalcogenides (TMDs) and to interlayer excitons in $MoSe_2/WSe_2$ heterobilayers. The precision of the method allows to assign measured g-factors of optical peaks to specific transitions in the band structure and also to specific regions of the samples. This revealed the nature of various, previously measured interlayer exciton peaks. We further show that, due to specific optical selection rules, g-factors in vdW heterostructures are strongly spin and stacking dependent. The presented approach can potentially be applied to a wide variety of semiconductors. [1] Recent measurements of individual bands g-factors in 1L TMDs additionally corroborate the validity and accuracy of our method. [2]

THEORY

Band structure Hamiltonian in external magnetic field:

$$H(\mathbf{B}) = H^0 + \mu_B \mathbf{B} \cdot \left(\mathbf{L} + \frac{g_0}{2}\mathbf{\Sigma}\right) + \frac{e_0^2}{8m_0}(\mathbf{B} \times \mathbf{r})^2$$

$\mu_B = \hbar e_0/2m_0$ – Bohr magneton, $\mathbf{L} = (\mathbf{r} \times \mathbf{p})/\hbar$ – angular momentum operator, $\mathbf{\Sigma} = (\Sigma^x, \Sigma^y, \Sigma^z)$ – Pauli matrices vector.

Bloch state energy in perpendicular magnetic field:

$$\varepsilon_{n\mathbf{k}}(\mathbf{B}) = \varepsilon^0_{n\mathbf{k}} + \mu_B B\,(L_{n\mathbf{k}} + \Sigma_{n\mathbf{k}}) + H^Q_{n\mathbf{k}}$$

where matrix elements $L_{n\mathbf{k}} = \langle n\mathbf{k}|L^z|n\mathbf{k}\rangle$, $\Sigma_{n\mathbf{k}} = \langle n\mathbf{k}|\Sigma^z|n\mathbf{k}\rangle$ and

$$H^Q_{n\mathbf{k}} = e_0^2 B^2/8m_0\,\langle n\mathbf{k}|(r^x)^2 + (r^y)^2|n\mathbf{k}\rangle$$

Effective g-factor of a Bloch state:

$$g_{n\mathbf{k}} = L_{n\mathbf{k}} + \Sigma_{n\mathbf{k}}$$

Orbital angular momentum matrix elements:

$$L_{n\mathbf{k}} = \frac{1}{im_0}\sum_{m=1,m\neq n}^{N} \frac{p^x_{nm\mathbf{k}}p^y_{mn\mathbf{k}} - p^y_{nm\mathbf{k}}p^x_{mn\mathbf{k}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}}}$$

where $r^\alpha_{nm\mathbf{k}} = \frac{\hbar}{im_0}\frac{p^\alpha_{nm\mathbf{k}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}}}$, $\varepsilon_{n\mathbf{k}} \neq \varepsilon_{m\mathbf{k}}$. The coupling of the SOC term to the vector potential is taken into account by replacing the momentum operator by $\boldsymbol{\pi} = \mathbf{p} + \frac{\hbar}{4m_0c^2}\mathbf{\Sigma} \times \mathbf{\nabla}V$

Exciton energy in perpendicular magnetic field:

$$E_\mathbf{k}(B) = \varepsilon_{c\mathbf{k}}(B) - \varepsilon_{v\mathbf{k}}(B) - E^{\text{bind}}_\mathbf{k} = E^0_\mathbf{k} + E^L_\mathbf{k}(B) + E^Q_\mathbf{k}(B)$$

Zeeman **shift** of exciton energy:

$$E^L_\mathbf{k}(B) = (g_{c\mathbf{k}} - g_{v\mathbf{k}})\mu_B B = g_\mathbf{k}\mu_B B$$

where $g_\mathbf{k}$ is ***intravalley* g-factor**.

Zeeman (valley) **splitting** of exciton energies:

$$\Delta E_Z = E_{\sigma+}(B) - E_{\sigma-}(B) = g\mu_B B$$

where g is ***intervalley* g-factor**.

MONOLAYER TMDs [1]

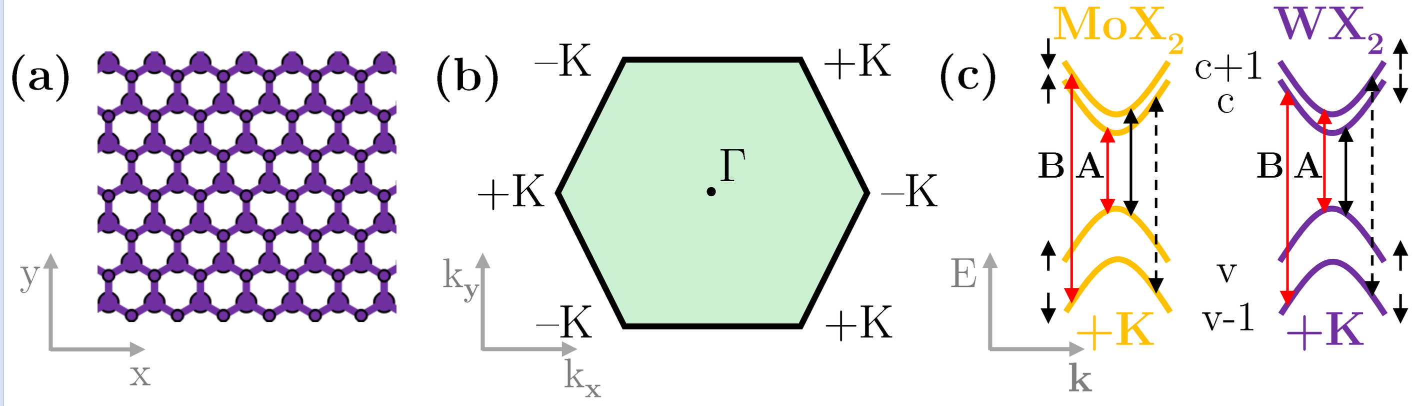


Fig. 1. (a) 1L TMDs, (b) Brillouin zone, (c) band edges and excitons.

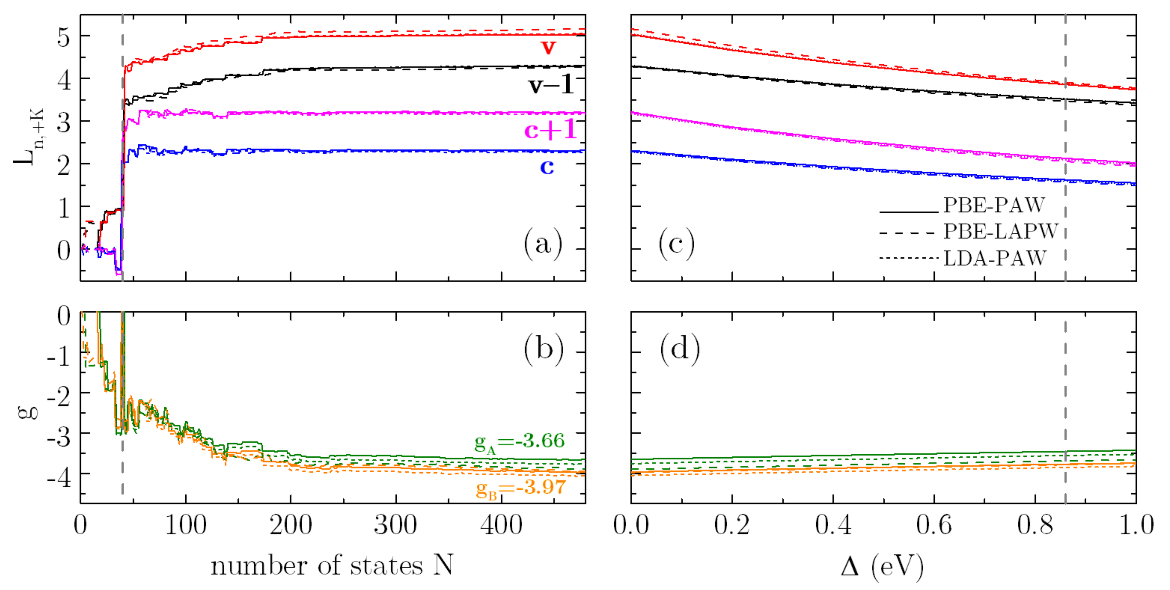


Fig. 2. WS_2: (a) orbital momenta and (b) g-factors vs number of states, and vs scissor correction (c), (d) for LDA/PBE and PAW/LAPW.

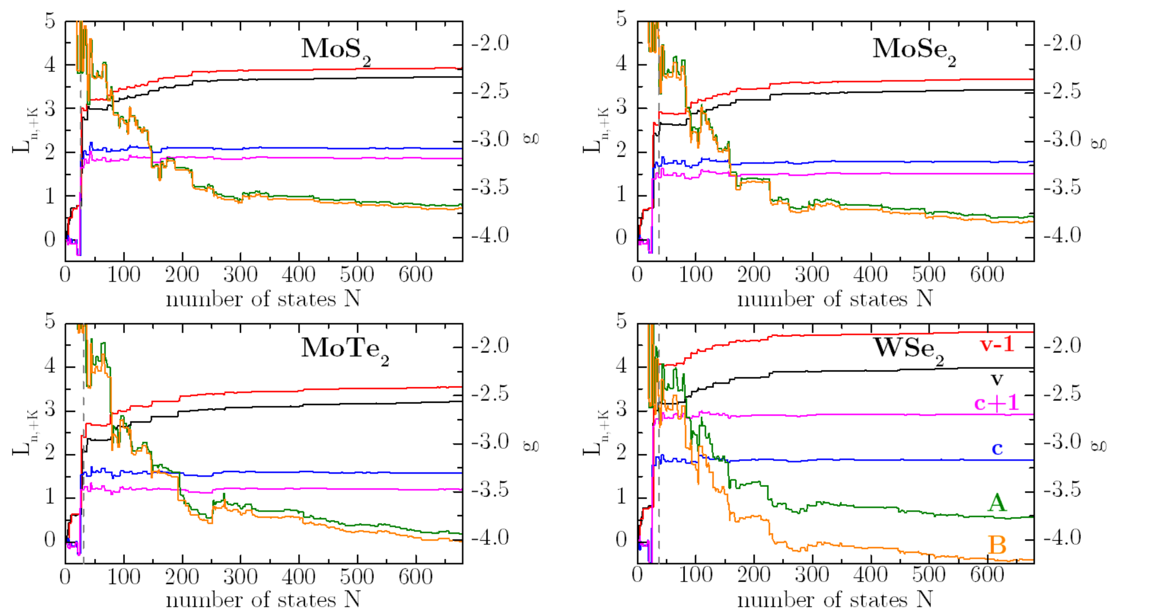


Fig. 3. Convergence of orbital momenta and g-factors for 1L TMDs.

	MoS_2	$MoSe_2$	$MoTe_2$	WS_2	WSe_2
g^{1L}_A	−3.68	−3.82	−3.96	−3.66	−3.80
g^{1L}_A (exp.)	−1.7,[a] −1.8,[s] −2.9,[b] −3.0,[b] −3.6,[b] −3.8,[b] −4.0,[c] −4.2,[p] −4.6[d]	−3.8[e,f], −4.0,[s] −4.1,[g] −4.2,[h] −4.3,[b] −4.4[d]	−4.3,[i] −4.7,[i] −4.8[i]	−3.7,[p] −3.94,[c] −4.0[b,p], −4.25,[j] −4.35[k]	−1.57,[l] −2.86,[l] −3.2,[q] −3.7,[f] −3.8,[h] −4.1[t] −4.25,[r] −4.3,[m] −4.37,[n] −4.38[o]
g^{1L}_B	−3.70	−3.88	−4.02	−3.96	−4.26
g^{1L}_B (exp.)	−4.3,[d] −4.65[c]	−4.2[p]	−3.8[h]	−3.99,[c] −4.9[p]	−3.9[p]
L_c/L_{c+1}	2.09/1.87	1.78/1.51	1.58/1.21	2.31/3.20	1.87/2.91
L_{v-1}/L_v	3.72/3.93	3.45/3.69	3.22/3.56	4.29/5.03	4.00/4.81
Intensity (A)	28.6	21.2	13.9	42.9	33.1

Tab. 1. Calc. and exp. g-factors, orbital momenta and intensities.

$MoSe_2/WSe_2$ HETEROBILAYER [1]

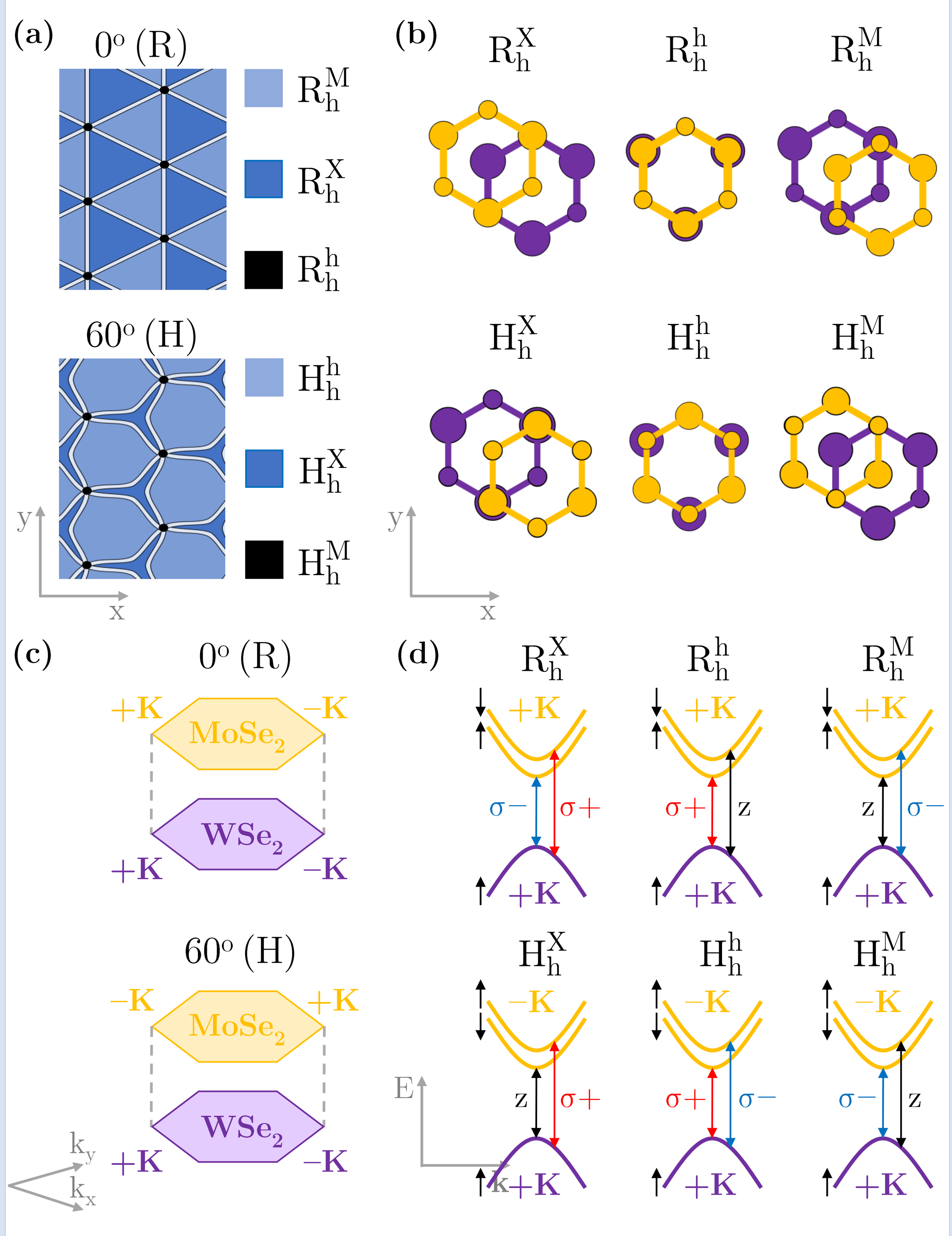


Fig. 4. $MoSe_2/WSe_2$: (a) atomic structures, (b) high symmetry stackings, (c) Brillouin zones, (d) optical selection rules for interlayer excitons.

	R^X_h		R^h_h	R^M_h	H^X_h	H^h_h		H^M_h
g^{HB}	**6.19**	−10.73	**−6.15**	10.42	−12.60	**−16.67**	12.15	16.31
g^{HB} (exp.)	6.72[a] 7.1[b] 6.99[e]	−10.6[f]	−8.5[b]			−15.89[a] −15.1[c] −15.2[d]	10.7[d]	
Transition	v → c	v → c+1	v → c	v → c+1	v → c+1	v → c	v → c+1	v → c
Intensity	0.08	0.05	0.12	10^{-7}	0.01	0.03	0.34	10^{-4}
Polarization	σ−	σ+	σ+	σ−	σ+	σ+	σ−	σ−
Spin	↑↑	↑↓	↑↑	↑↓	↑↑	↑↓	↑↑	↑↓
ΔΣ	0	−2	0	−2	0	−2	0	−2
$L_{c(+1)}$	1.80	1.53	1.79	1.53	−1.53	−1.79	−1.53	−1.78
L_v	4.90	4.90	4.86	4.74	4.77	4.54	4.54	4.37
ΔL	−3.10	−3.37	−3.08	−3.21	−6.30	−6.34	−6.07	−6.16

Tab. 2. Calc. and exp. g-factors, orbital momenta, sel. rules and intensities.

MONOLAYER WS_2 [2]

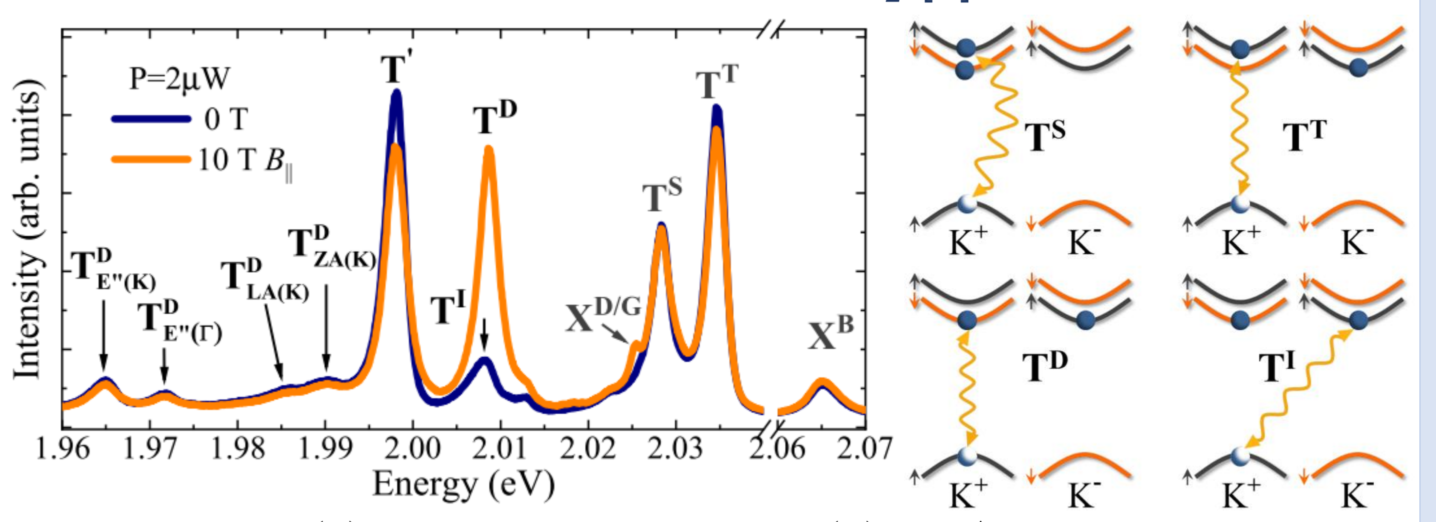


Fig. 5. 1L WS_2: (a) magneto-PL spectrum, (b) K+/- trions configurations.

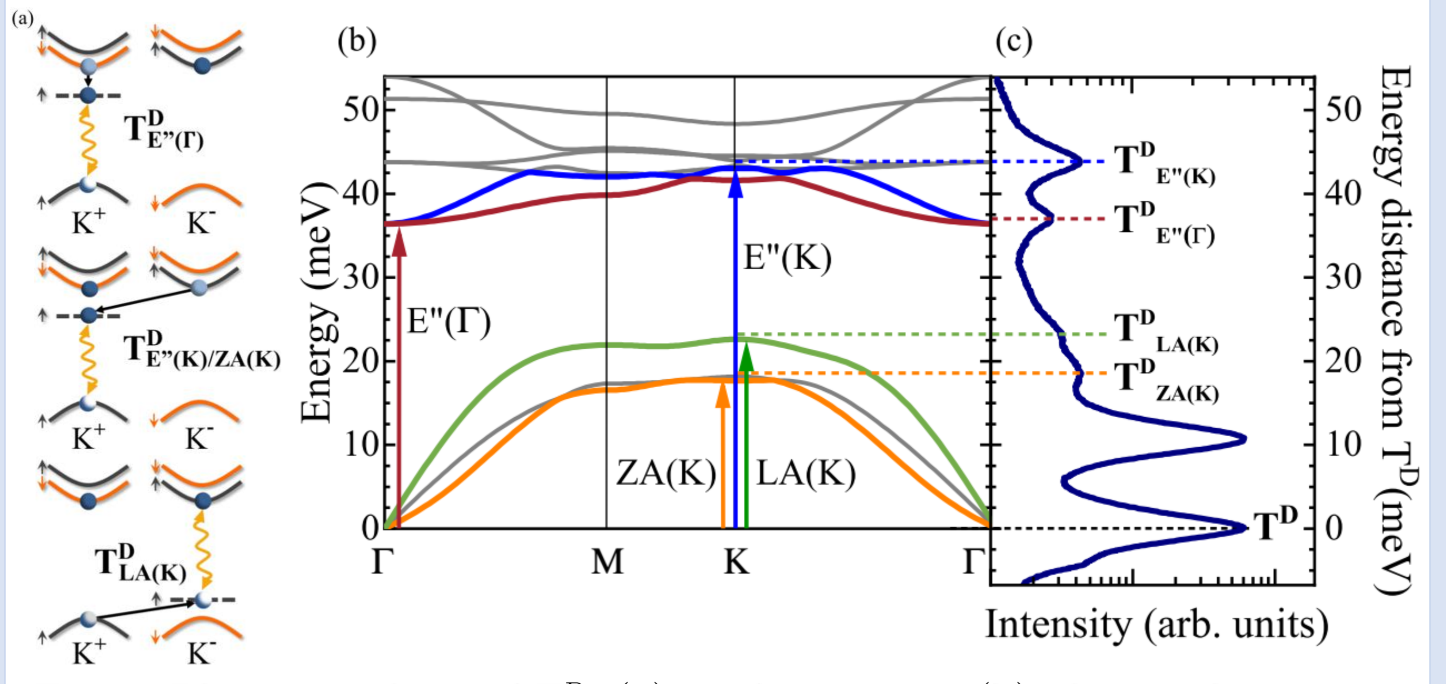


Fig. 6. Phonon replicas of T^D: (a) configurations, (b) phonon dispersion, (c) magneto-PL spectrum.

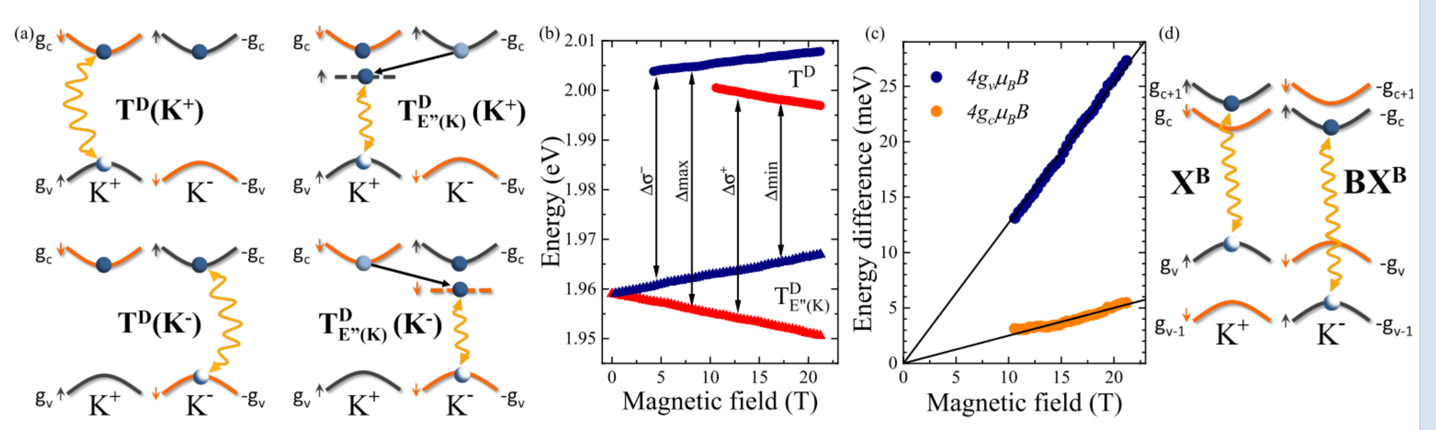
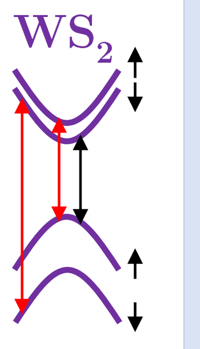


Fig. 7. Band g-factors: (a) T^D & $T^D_{E''(K)}$ configurations, (b) their Zeeman shifts and (c) splittings, (d) A & B excitons configurations.

	g^{exp}	g^{calc}	ΔL	$\Delta\Sigma$	P
X^B	-3.5				
T^S	-4.0				
T^T	-3.9	-3.56	-1.78	0	σ+
T'	-3.3				
XX^-_1	-4.1				
XX^-_2	-4.1				
T^D	-8.9	-8.73	-2.37	-2	σ+
$T^D_{E''(\Gamma)}$	-8.9				
T^I	-13.7				
$T^D_{E''(K)}$	-13.6	-12.20	-6.10	0	σ+
$T^D_{ZA(K)}$	-13.3				
$T^D_{LA(K)}$	+13.6	+12.20	-6.10	0	σ−

Tab 4. Calc. & exp. g-factors, orbital/spin contributions and polarizations.

n	g^{exp}_n	g^{calc}_n	L_n	Σ_n
v-1	2.81	2.79	3.79	-1
v	6.10	5.23	4.23	+1
c	0.86	0.87	1.87	-1
c+1	3.84	3.45	2.45	+1



Tab 5. Calc. & exp. band g-factors.

[2] M. Zinkiewicz, T. Woźniak, P. Kapuściński, T. Kazimierczuk, M. Potemski, M. Molas et al, Excitonic complexes in n-doped WS_2 monolayer, Nano Letters, 21, 6, 2519–2525 (2021).

[1] T. Woźniak, P. E. Faria Junior, G. Seifert, A. Chaves, J. Kunstmann, Exciton g factors of van der Waals heterostructures from first-principles calculations, PRB 101, 235408 (2020);

Computational resources were provided by ZIH Dresden, ICM Warsaw and PLGrid infrastructure.