# Supporting information

# Interlayer trions in the $MoS_2/WS_2$ van der Waals heterostructure

Thorsten Deilmann[1,*] and Kristian Sommer Thygesen[1,2]

[1] *Center for Atomic-Scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark*

[2] *Center for Nanostructured Graphene (CNG), Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark*

[*] thorsten.deilmann@wwu.de, +45 45 25 31 88

## THEORETICAL METHODS

The results presented in the main text are obtained within the framework of many-body perturbation theory (MBPT). This allows for an ab initio description of electronic and optical properties including excitons (1), (2) and trions (3).

Therefore we apply a hierarchy of methods starting with a density functional theory (DFT) calculation within the local density approximation (LDA) including spin-orbit coupling. On top of this we apply the $GW$ approach within the $GdW$ approximation to obtain a reliable quasiparticle band structure (4)

$$\hat{H}^{\mathrm{QP}}_{GdW} = \hat{H}^{\mathrm{DFT}} + iGW - \underbrace{iGW_{\mathrm{metal}}}_{\approx V_{\mathrm{xc}}} = \hat{H}^{\mathrm{DFT}} + iGdW.$$

In the next step the optical properties are investigated using the $GW$/BSE approach (1, 2, and 5). The excitons (in the Tamm-Dancoff approximation) are described by the eigenstates of the Hamiltonian with matrix elements

$$\begin{aligned}\langle \mathbf{vc}|\hat{H}^{(eh)}|\mathbf{v'c'}\rangle =& (\epsilon_{\mathbf{c}} - \epsilon_{\mathbf{v}})\delta_{\mathbf{cc'}}\delta_{\mathbf{vv'}} && (\hat{H}_{\mathrm{BS}})\\ &- (W_{\mathbf{v'c},\mathbf{vc'}} - V_{\mathbf{v'c},\mathbf{c'v}}) \ , && (\hat{H}_{eh})\end{aligned}$$

where $|\mathbf{vc}\rangle$ denotes electron-hole pair excitations from the ground state $|0\rangle$, $\epsilon_{\mathbf{i}}$ the quasiparticle energies, and $W$ ($V$) the screened coulomb (bare exchange) interaction. Finally the coupled electron-hole excitations of the system can be evaluated by

$$|S\rangle = \sum_{\mathbf{vc}} B^S_{\mathbf{vc}}|\mathbf{vc}\rangle \tag{1}$$

with the coefficients $B^S_{\mathbf{vc}}$ and corresponding eigenvalues $\Omega^S$. To describe the trions we apply the recently developed method, work done in part by one of the present authors, described in detail in Ref. (3) and its supplement. This results in the diagonalization of the eigenproblem, e.g. for negative trions

$$\begin{aligned}&\langle \mathbf{vc}_1\mathbf{c}_2|\hat{H}^{(eeh)}|\mathbf{v'c}'_1\mathbf{c}'_2\rangle = && (2)\\ &\quad (\epsilon_{\mathbf{c}_1} + \epsilon_{\mathbf{c}_2} - \epsilon_{\mathbf{v}})\delta_{\mathbf{c}_1,\mathbf{c}'_1}\delta_{\mathbf{c}_2,\mathbf{c}'_2}\delta_{\mathbf{v},\mathbf{v'}} && (\hat{H}_{\mathrm{BS}})\\ &+(W_{\mathbf{c}_1\mathbf{c}_2,\mathbf{c}'_1\mathbf{c}'_2} - W_{\mathbf{c}_1\mathbf{c}_2,\mathbf{c}'_2\mathbf{c}'_1})\delta_{\mathbf{v},\mathbf{v'}} && (\hat{H}_{ee})\\ &-(W_{\mathbf{v'c}_1,\mathbf{vc}'_1} - V_{\mathbf{v'c}_1,\mathbf{c}'_1\mathbf{v}})\delta_{\mathbf{c}_2,\mathbf{c}'_2} && (\hat{H}_{eh,1})\\ &-(W_{\mathbf{v'c}_2,\mathbf{vc}'_2} - V_{\mathbf{v'c}_2,\mathbf{c}'_2\mathbf{v}})\delta_{\mathbf{c}_1,\mathbf{c}'_1} \ . && (\hat{H}_{eh,2})\end{aligned}$$

In addition to the band structure term $\hat{H}_{\mathrm{BS}}$ and the electron-hole interactions $\hat{H}_{eh,1/2}$ the electron-electron (hole-hole) repulsion $\hat{H}_{ee}$ is taken into account. Eventually we end up with the correlated trion states

$$|T,\mathbf{K}\rangle = \sum_{\mathbf{vc_1c_2}} A^{(T,\mathbf{K})}_{\mathbf{vc_1c_2}} |\mathbf{vc_1c_2}\rangle \ , \tag{3}$$

and the position in the spectrum

$$\Omega(|T,\mathbf{K}\rangle \leftrightarrow |c\mathbf{K}\rangle) = E^{(T,\mathbf{K})} - \epsilon_{c\mathbf{K}} \ , \tag{4}$$

which is given by the energy of the trions compared to the final electron (hole) $|c\mathbf{K}\rangle$.

## NUMERICAL DETAILS

Numerical details of trion calculations in carbon nanotubes (3) and intralayer excitations in monolayer TMDCs (6) have been discussed previously. At this stage we mostly elaborate on the convergence of interlayer states.

In our calculation for excitons we employ 4 valence and 8 conduction bands. This is sufficient to describe the lower energy part of the spectrum we are interested in this study. The convergence with respect to the **k**-mesh is shown in Figure S1, The dependence on the mesh is small and linearly extrapolated to an infinite mesh.

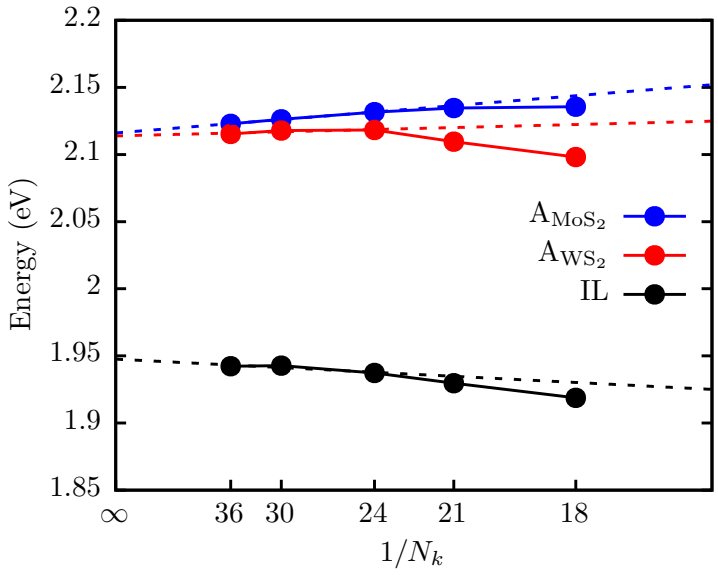


Figure S1. Convergence of interlayer and intralayer excitons in respect to the **k**-mesh. The values are extrapolated to an infinite mesh.

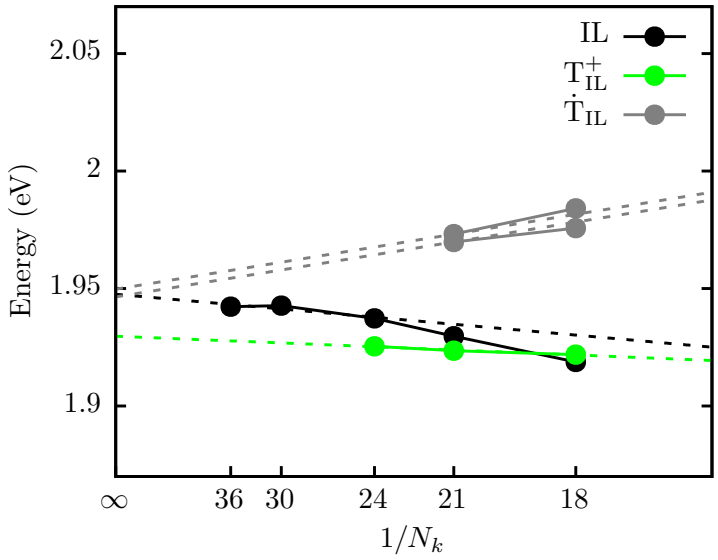


Figure S2. Convergence of interlayer trions in respect to the **k**-mesh. The values are extrapolated to an infinite mesh.

For the description of bound interlayer trions $T^+_{IL}$ (see Figure S2) similar good convergence in respect to the **k** mesh as previously for intralayer states (6). On the other hand the resonant states $\dot{T}^+_{IL}$ depend slightly stronger on the mesh. Here, we interpolate them in parallel to an infinite mesh. We note that the energies of $\dot{T}^+_{IL,(1/2)}$ are distinctly larger than for $T^+_{IL}$ (see Eq. (4)) and the diagonalization of significant more eigenstates is required.

## REFERENCES


(1) Onida, G.; Reining, L.; Rubio, A. *Rev. Mod. Phys.* **2002**, *74*, 601–659.

(2) Rohlfing, M.; Louie, S. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, 4927–4944.

(3) Deilmann, T.; Drüppel, M.; Rohlfing, M. *Phys. Rev. Lett.* **2016**, *116*, 196804.

(4) Rohlfing, M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 205127.

(5) Strinati, G. *Phys. Rev. Lett.* **1982**, *49*, 1519–1522.

(6) Drüppel, M.; Deilmann, T.; Krüger, P.; Rohlfing, M. *Nat. Commun.* **2017**, *8*, 2117.