CONDENSED MATTER IN PARIS 2014

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Université PARIS DESCARTES

Optical properties of MoS_2
Excitons beyond the bandgap

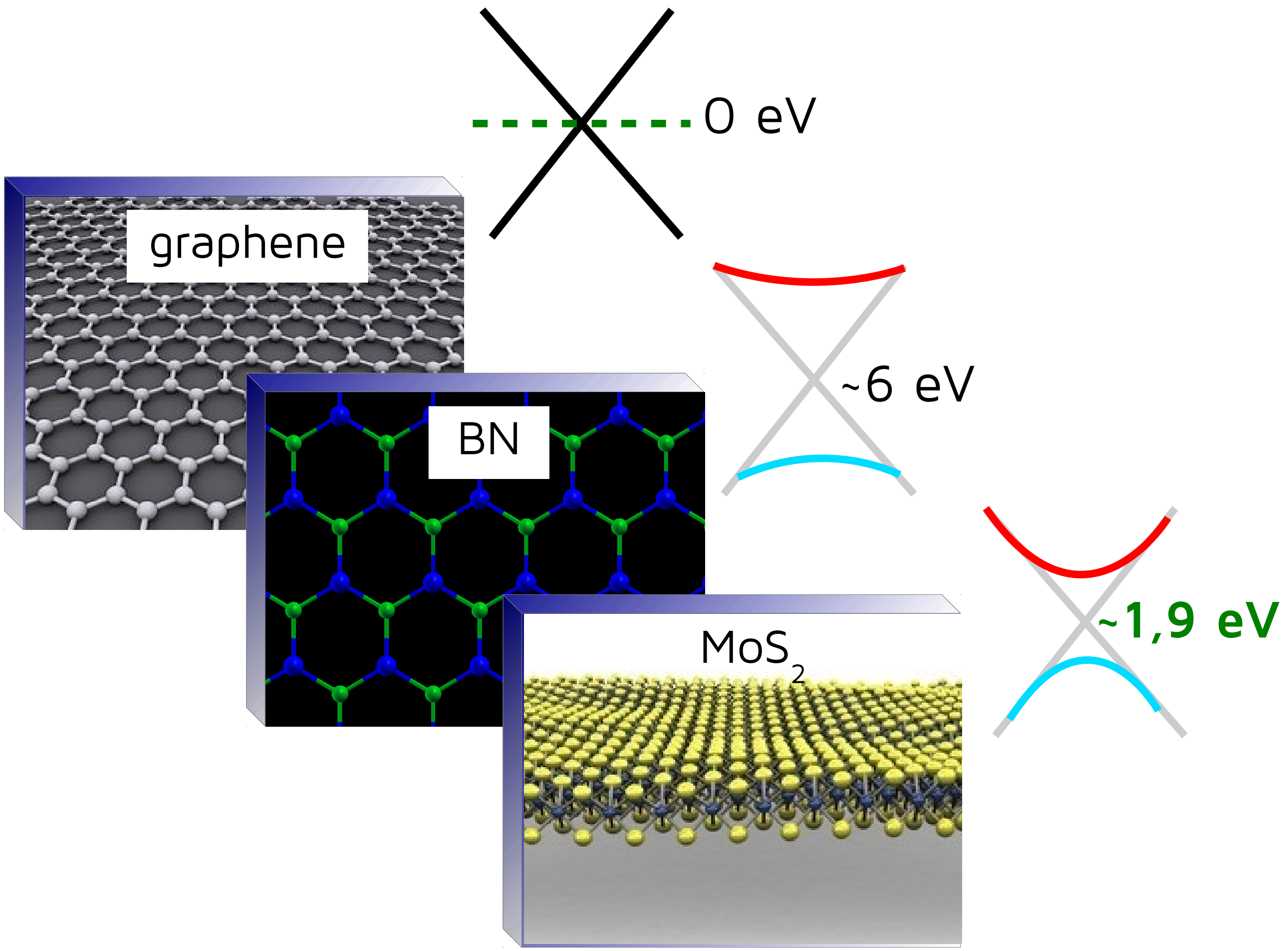
Alejandro Molina-Sánchez

University of Luxembourg

Paris, 26-8-2014

uni.lu

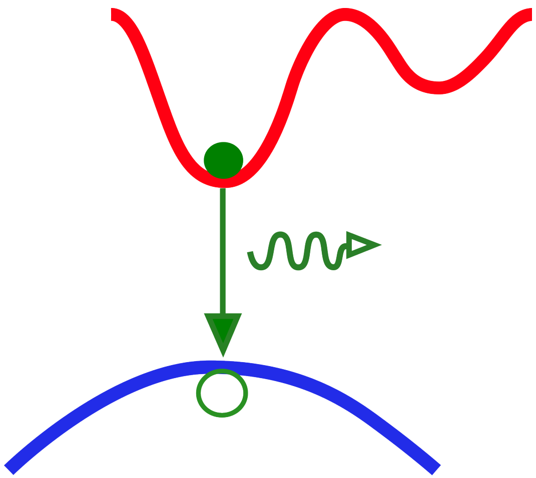
MoS_2 semiconducting alternative to graphene...

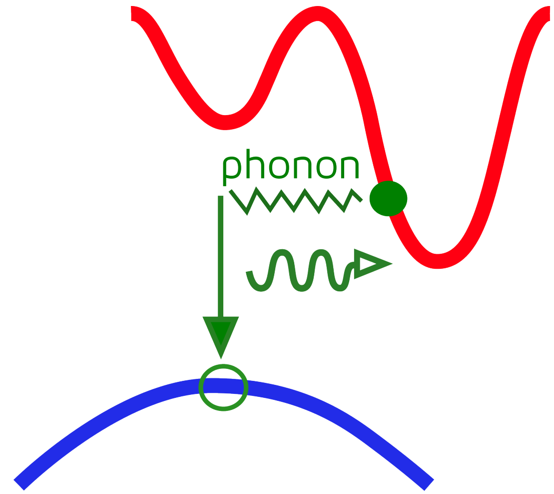


… Bandgap engineering and transistors

Single-layer MoS_2

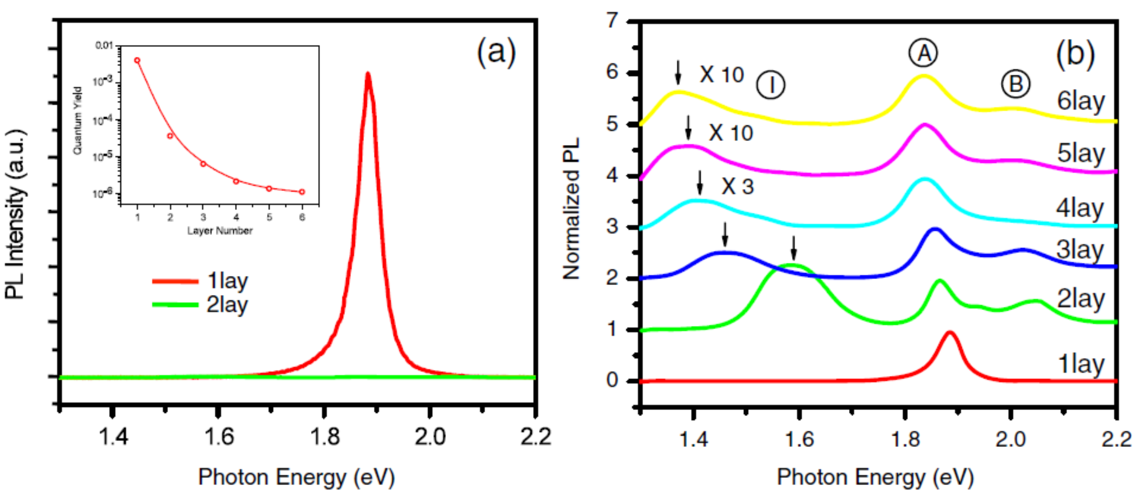
N-layers and bulk MoS_2



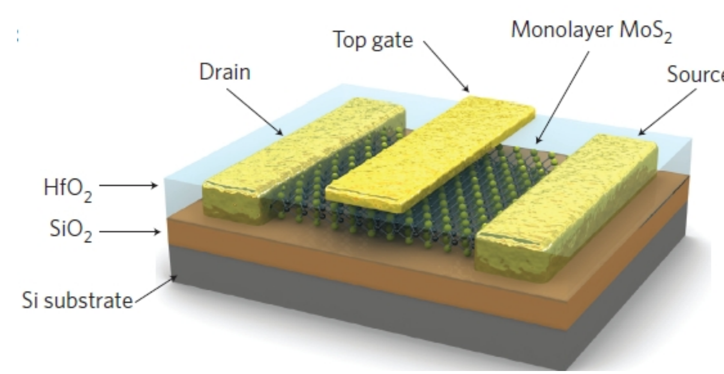


Direct/indirect bandgap depending on number of layers and strain

Higher efficiency of photoluminescence in single-layers

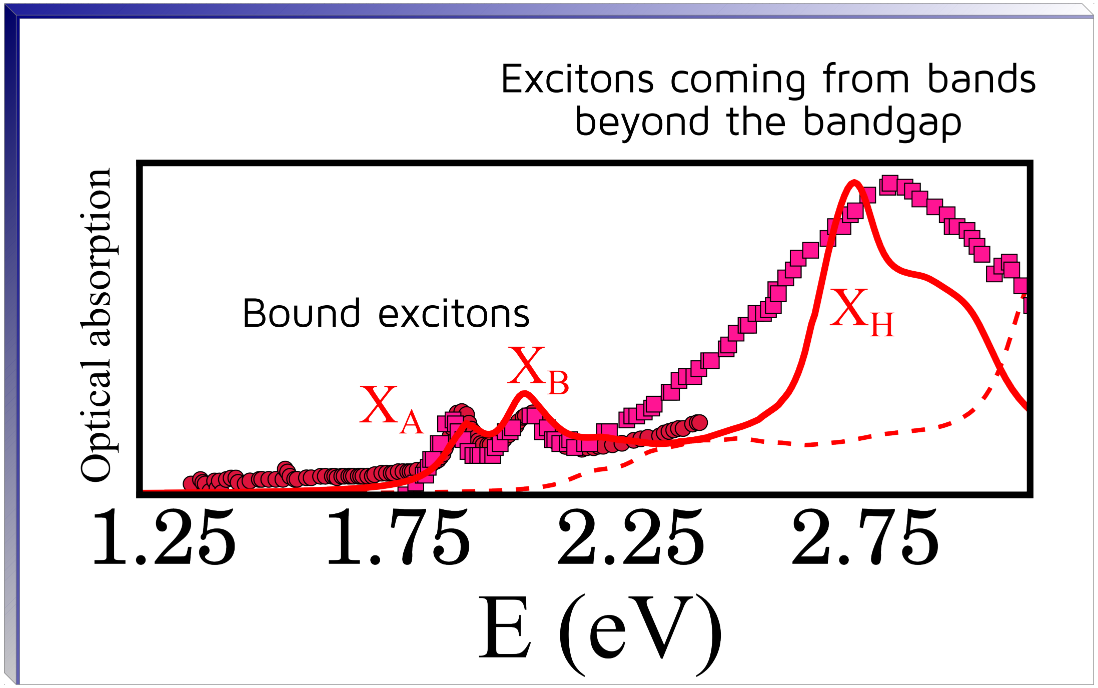


T. Heinz group, Phys. Rev. Lett. 105, 136805 (2010)



A. Kis group, Nat. Nano 6, 147 (2011)

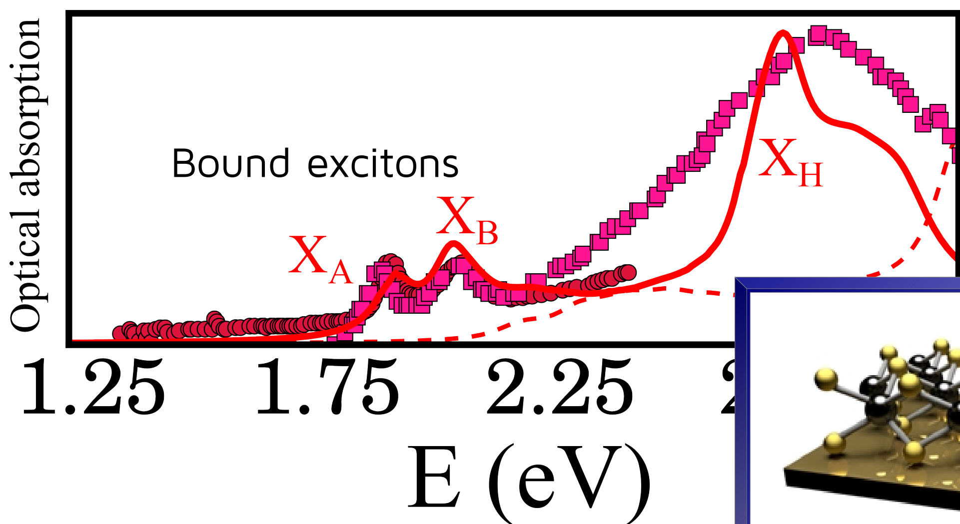
... a rich phenomenology in optical properties

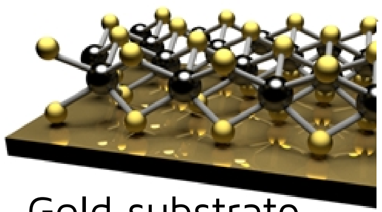


Intrinsic MoS_2: AMS *et. al.*, *Phys. Rev. B* **88**, 045412 (2013).
MoS_2 on metals: J. Mertens, Y. Shi, AMS, L. Wirtz, H. Y. Yang, and J. J. Baumberg, *Appl. Phys. Lett.* **104**, 191105 (2014).

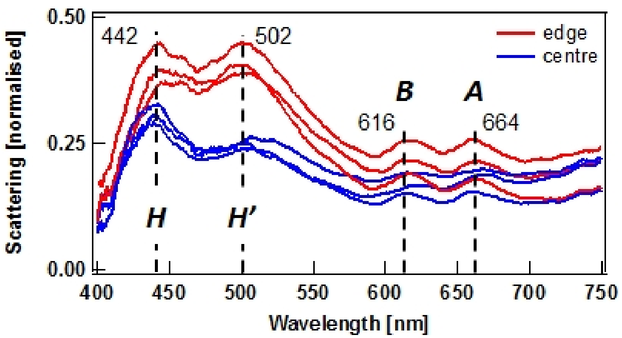
... a rich phenomenology in optical properties

Excitons coming from bands beyond the bandgap





Dark field optical spec.



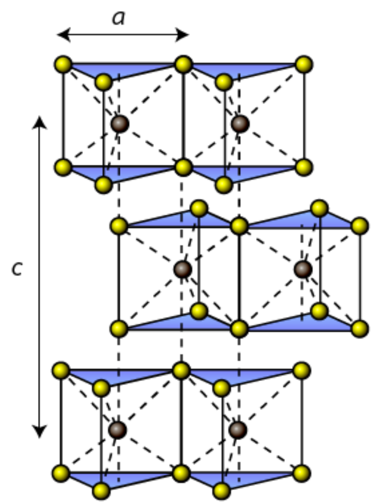
Different behaviour of bound (A,B) and high-energy (H,H') excitons

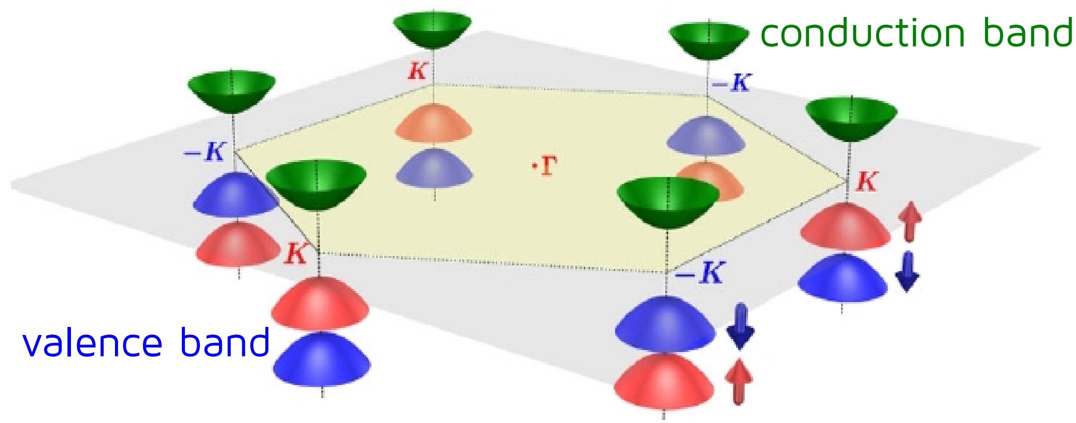
Tuning optical props. with thin metallic coatings

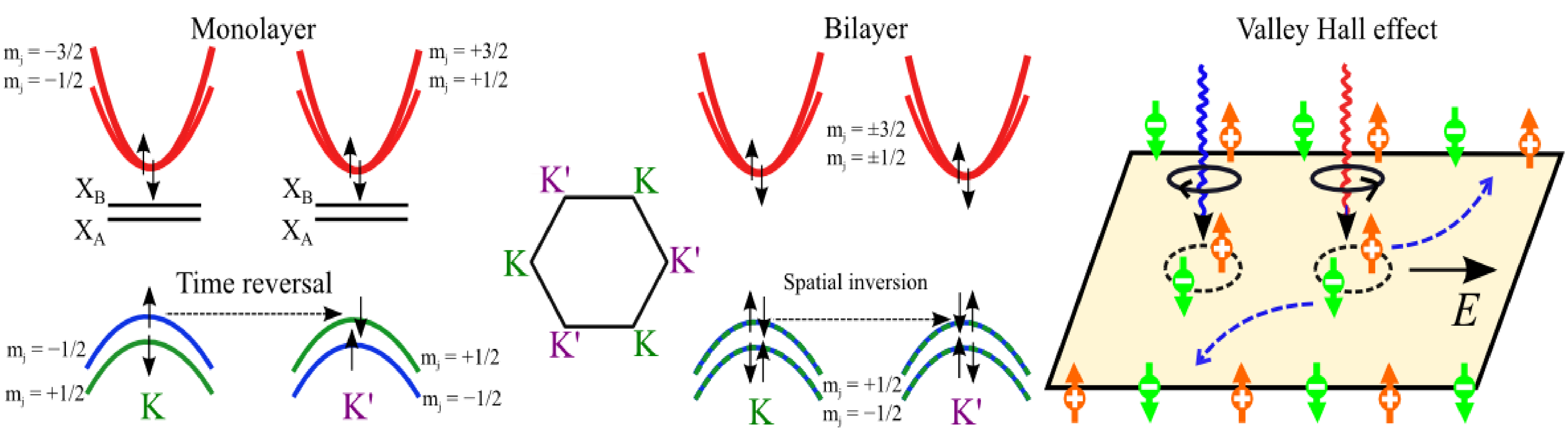
Intrinsic MoS_2: AMS *et. al.*, *Phys. Rev. B* **88**, 045412 (2013).
MoS_2 on metals: J. Mertens, Y. Shi, AMS, L. Wirtz, H. Y. Yang, and J. J. Baumberg, *Appl. Phys. Lett.* **104**, 191105 (2014).

… spin- and valley-physics

Spin-orbit interaction + breaking inversion symmetry

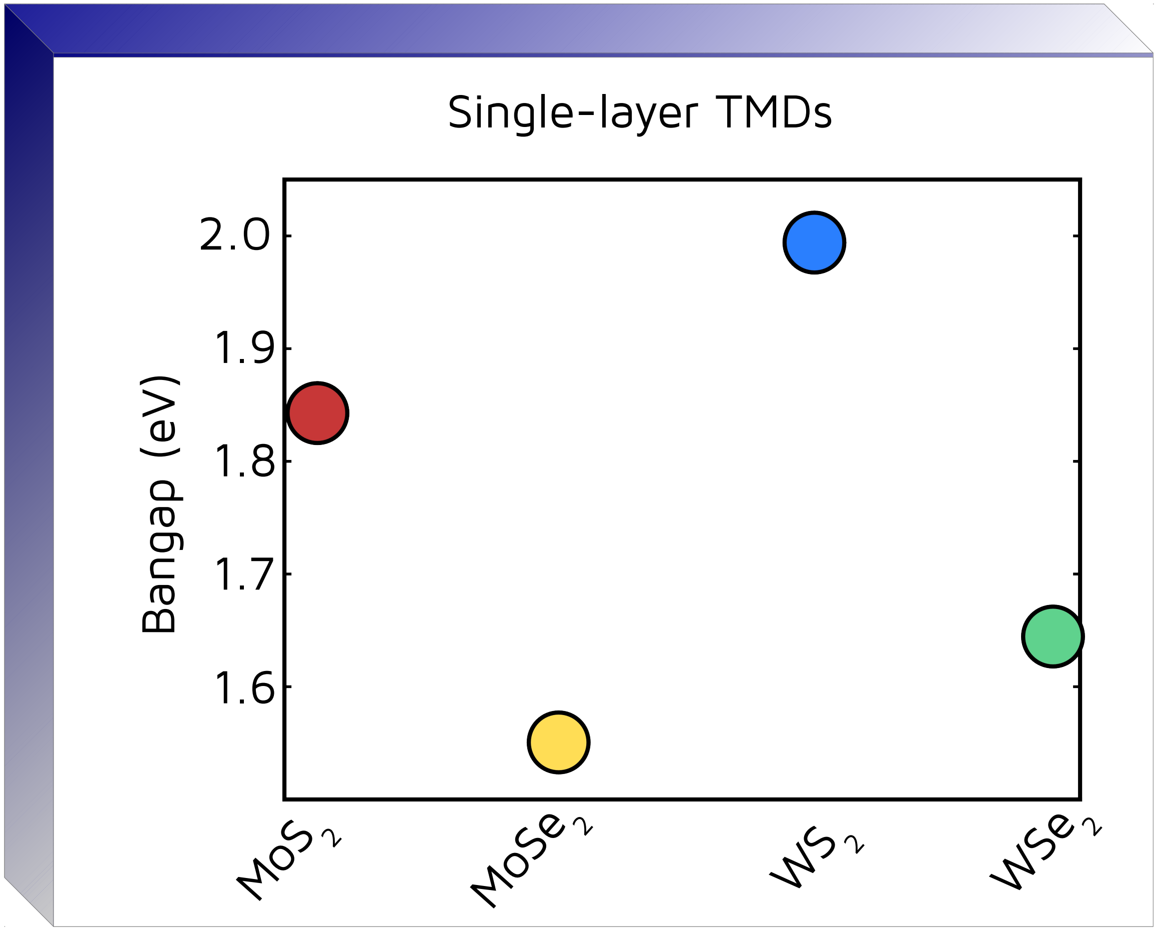


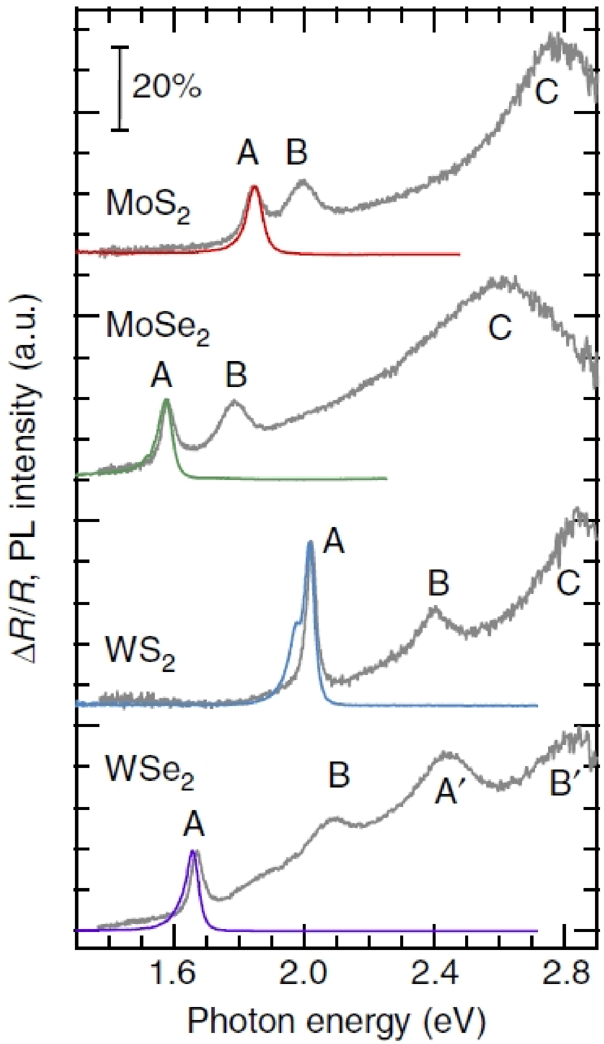




Valley-physics: PRL 108, 196802 (2012), Nat. Nano 7, 494 (2012), Nat. Nano 7, 490 (2012),.

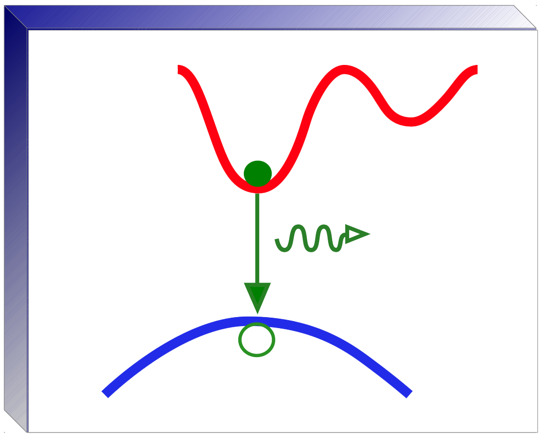
… an increasing family of materials





Kozawa *et al.*, Nature Communications **5**, 4543 (2014)

MoS_2 semiconducting alternative to graphene…



Electronic properties (band structure)

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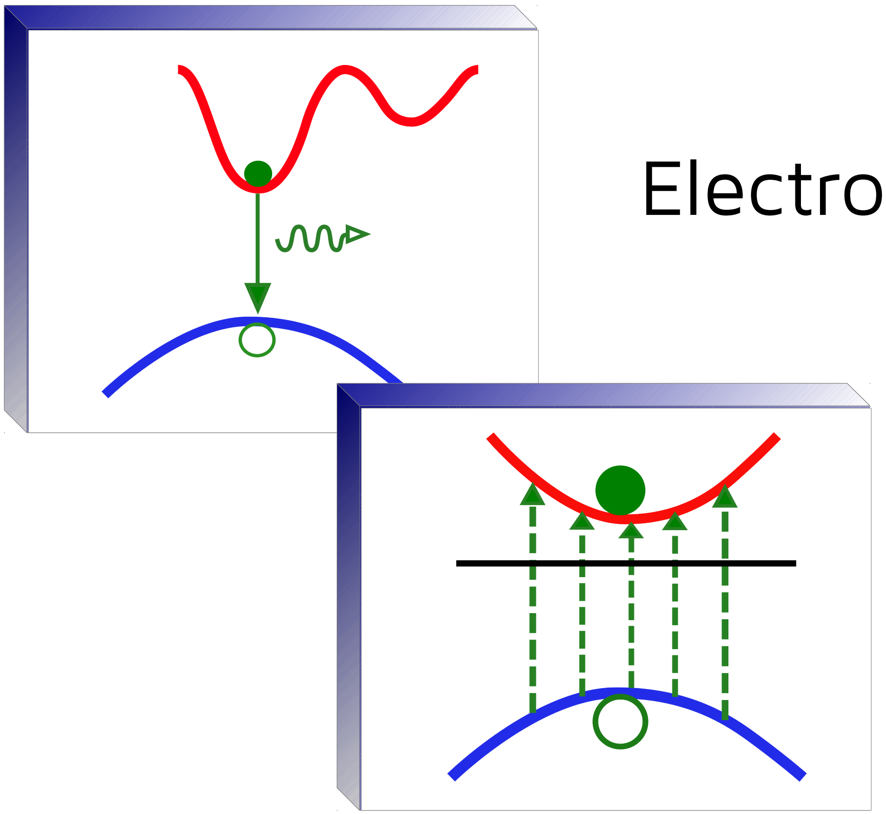
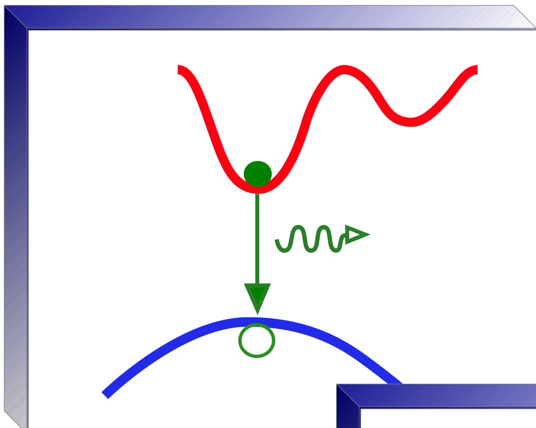
MoS_2 semiconducting alternative to graphene...



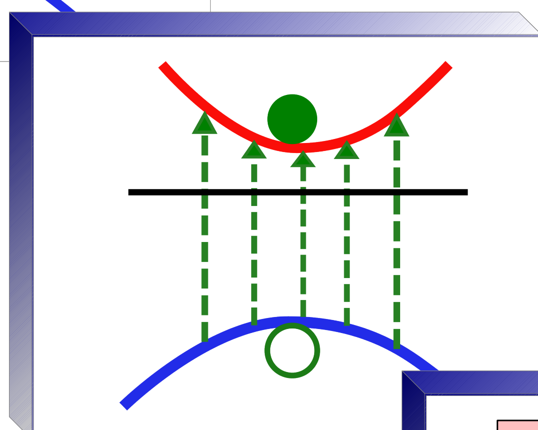
Electronic properties (band structure)

Optical Properties (excitons)

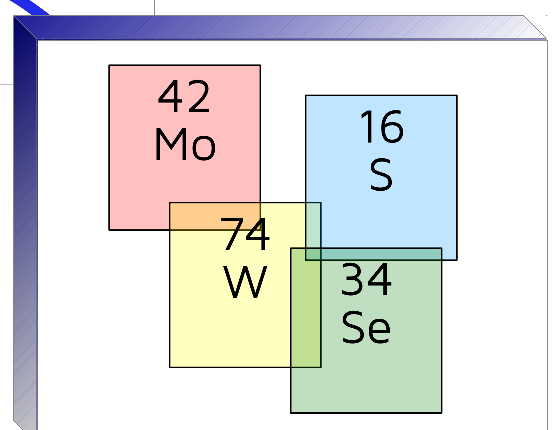
MoS_2 semiconducting alternative to graphene...



Electronic properties (band structure)



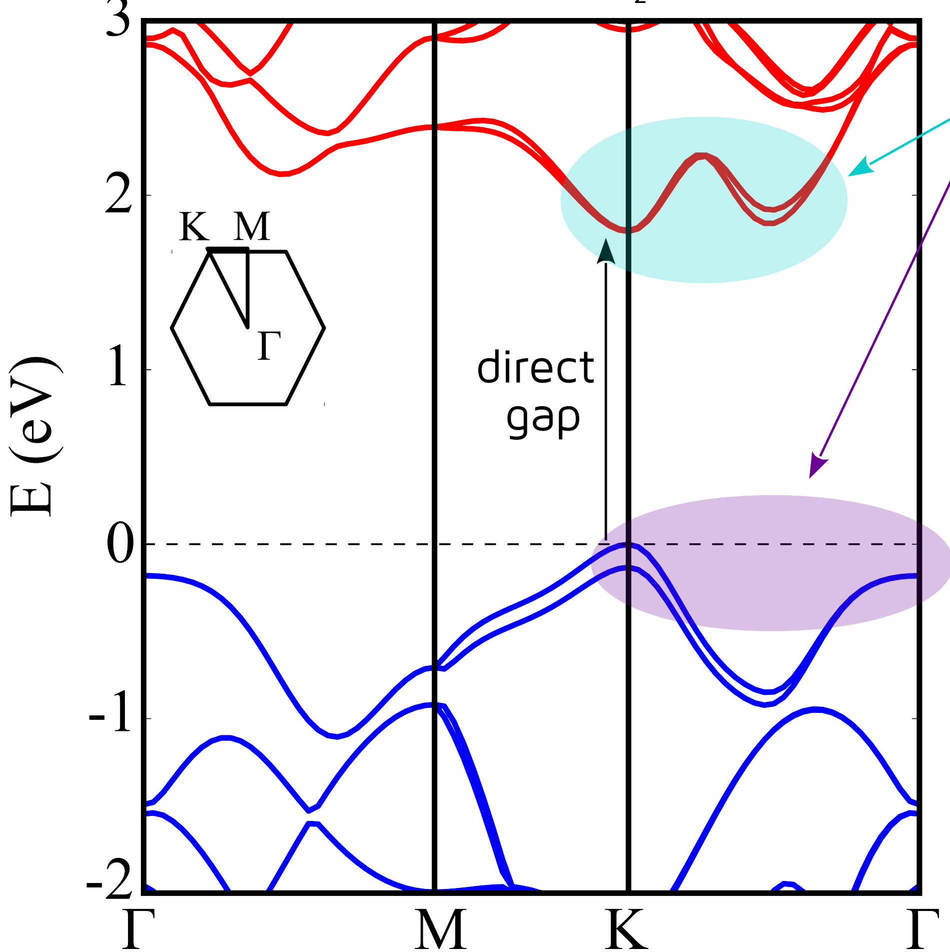
Optical Properties (excitons)



Other TMDs /
Interaction
with substrate

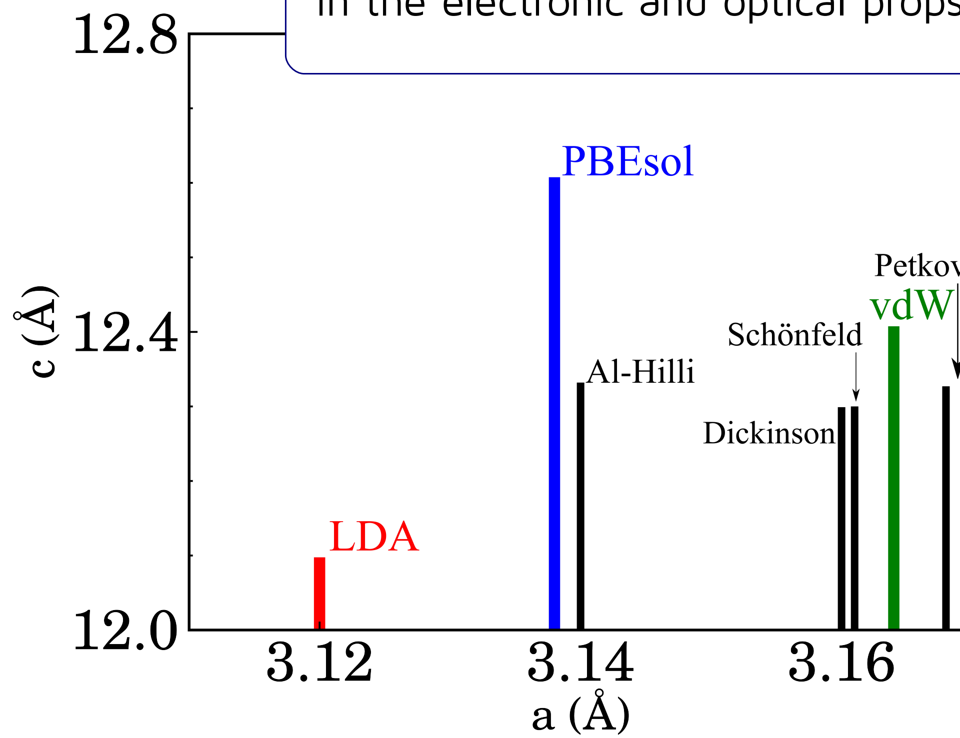
Electronic structure

Single-layer MoS_2 (LDA)



Valley's position determine the "directness" of the material. Strong dependence in the lattice parameters.

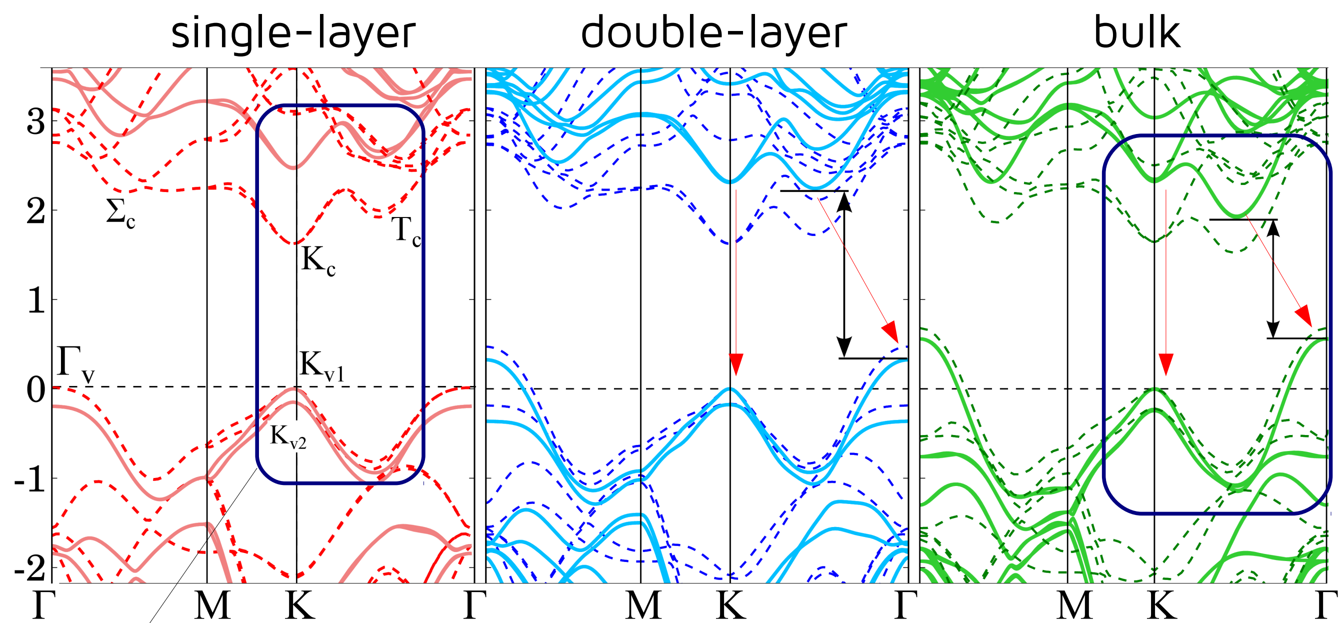
Functional choice plays an important role for reliable results in the electronic and optical props.



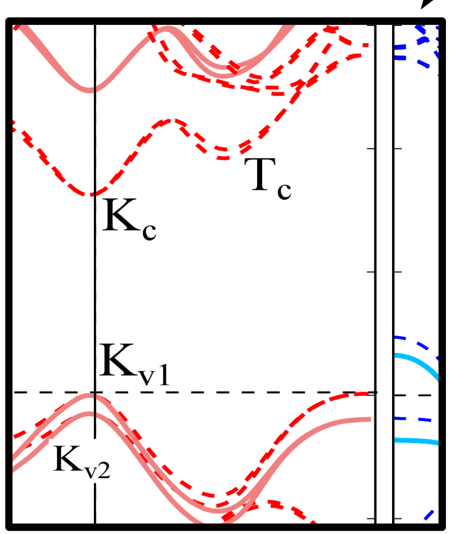
See Refs. in review, AMS, K. Hummer and L. Wirtz, *Surface Science Reports*

Electronic structure

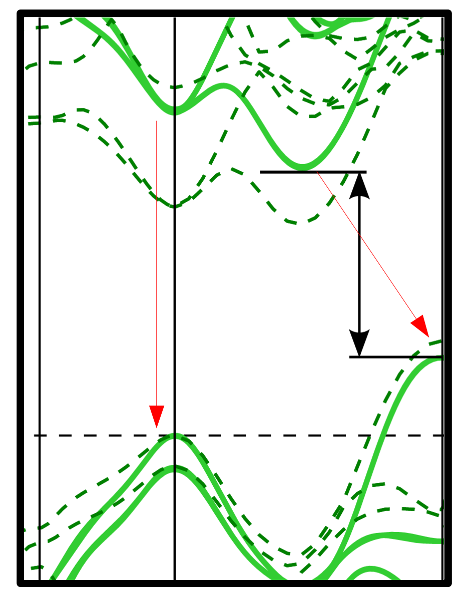
- Beyond LDA. ScGW-method
- Spinor fully described
- Semi-core d-orbitals
- On top of van der Waals lattice optimization



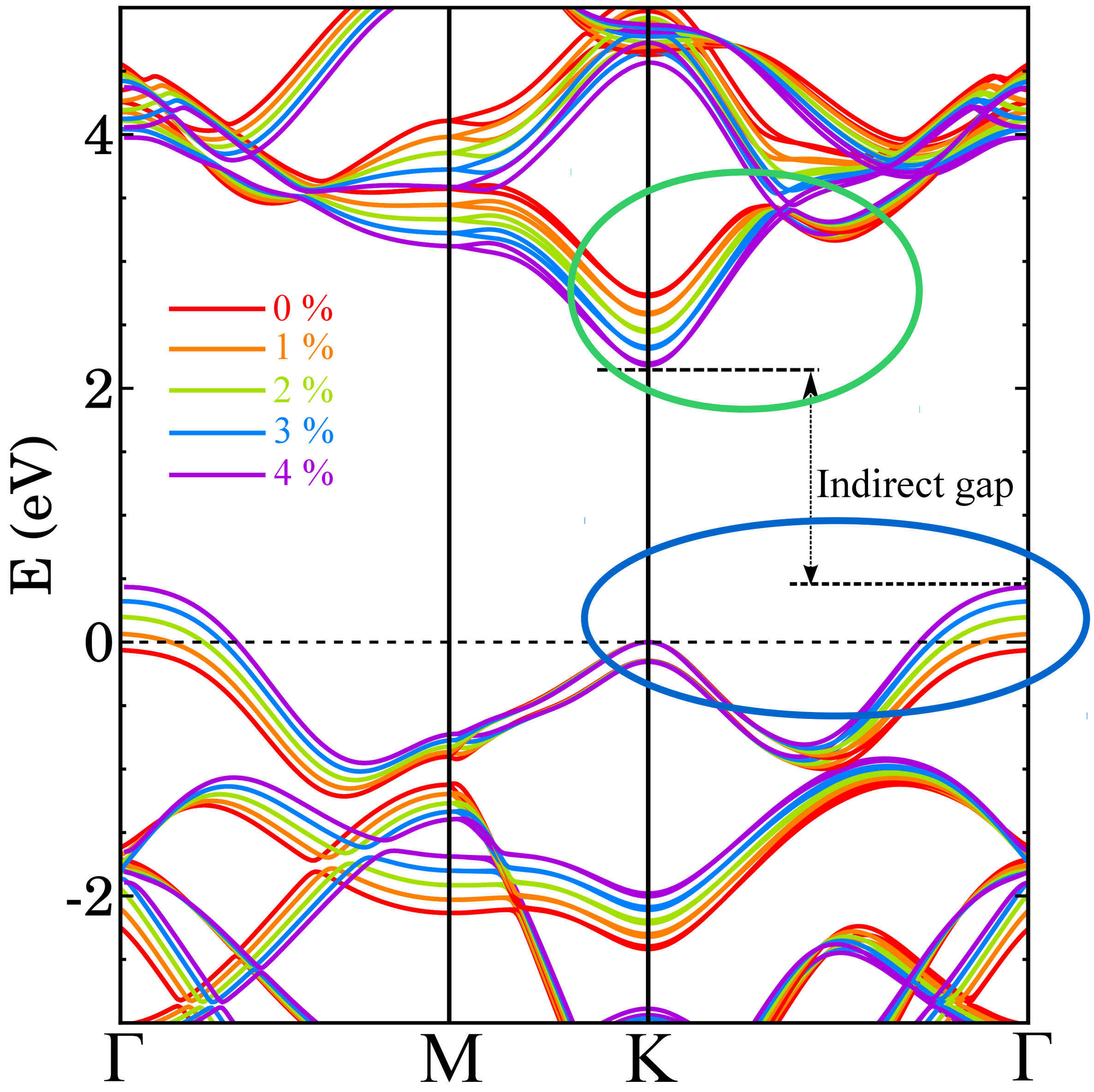
Results critically depends on scGW "flavour", structural starting point, etc.



For n-layer systems, interlayer interaction changes valleys position



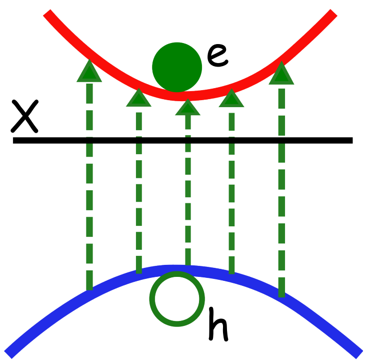
Electronic structure



Bandgap engineering can be performed with external strain.

Not only the bandgap value changes, the character direct/indirect is reversed depending on the sign and strength of the applied strain.

Optical properties



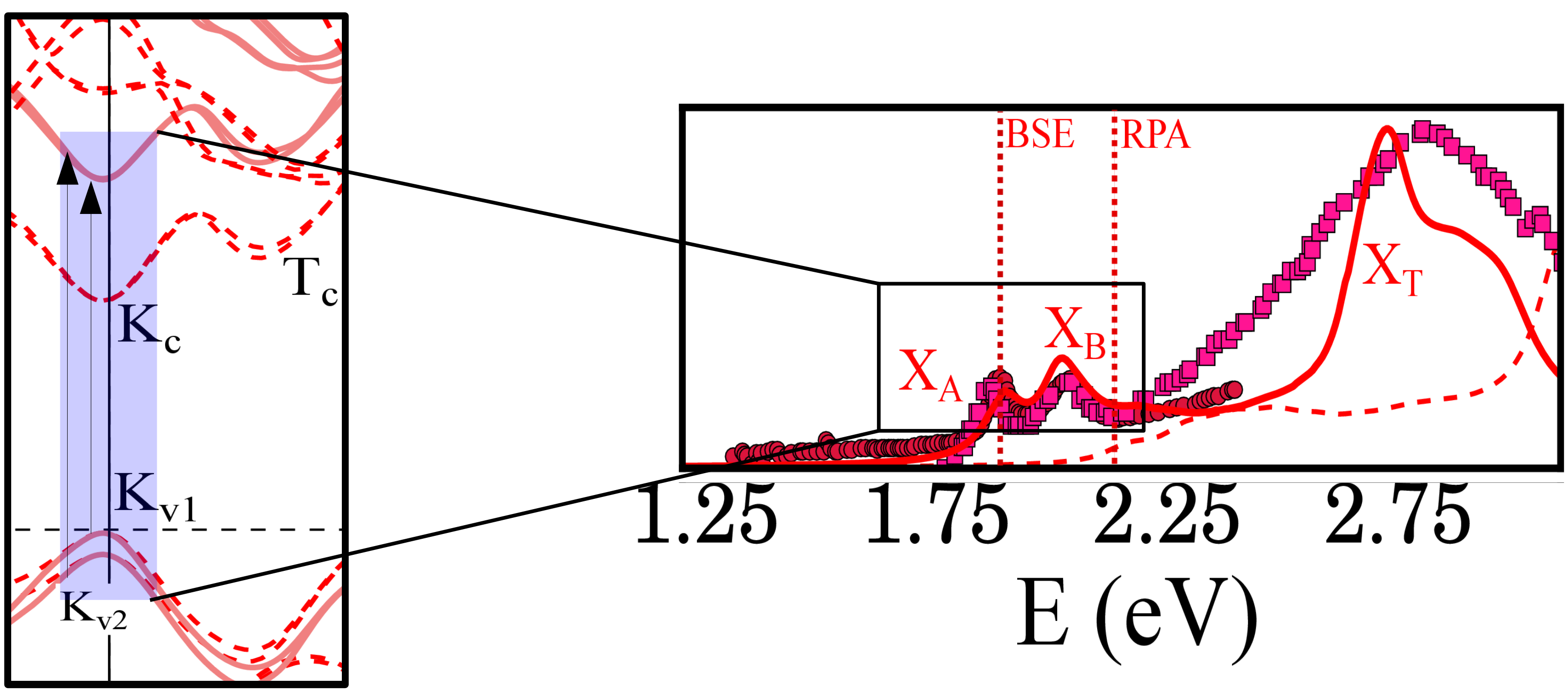
e-h pairs interact and form the exciton

$$H^X_{(n_1,n_2),(n_3,n_4)} = \left(E_{n_2} - E_{n_1}\right)\delta_{n_1,n_3}\delta_{n_2,n_4} + i\left(f_{n_2} - f_{n_1}\right)\Xi_{(n_1,n_2),(n_3,n_4)}$$

Energy difference — Bethe-Salpeter Kernel

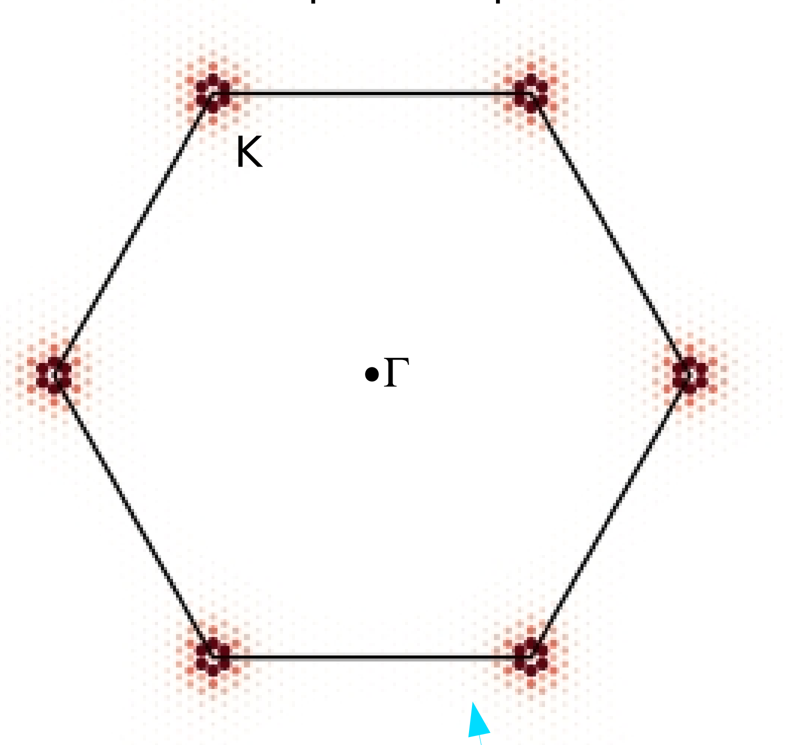
$$\Psi(\mathbf{r}_e,\mathbf{r}_h) = \sum_{i,j} A_{i,j,\mathbf{k}}\phi_i(\mathbf{r}_e)\phi_j(\mathbf{r}_h)$$

X_A and X_B excitons come from the interband transitions at **K**



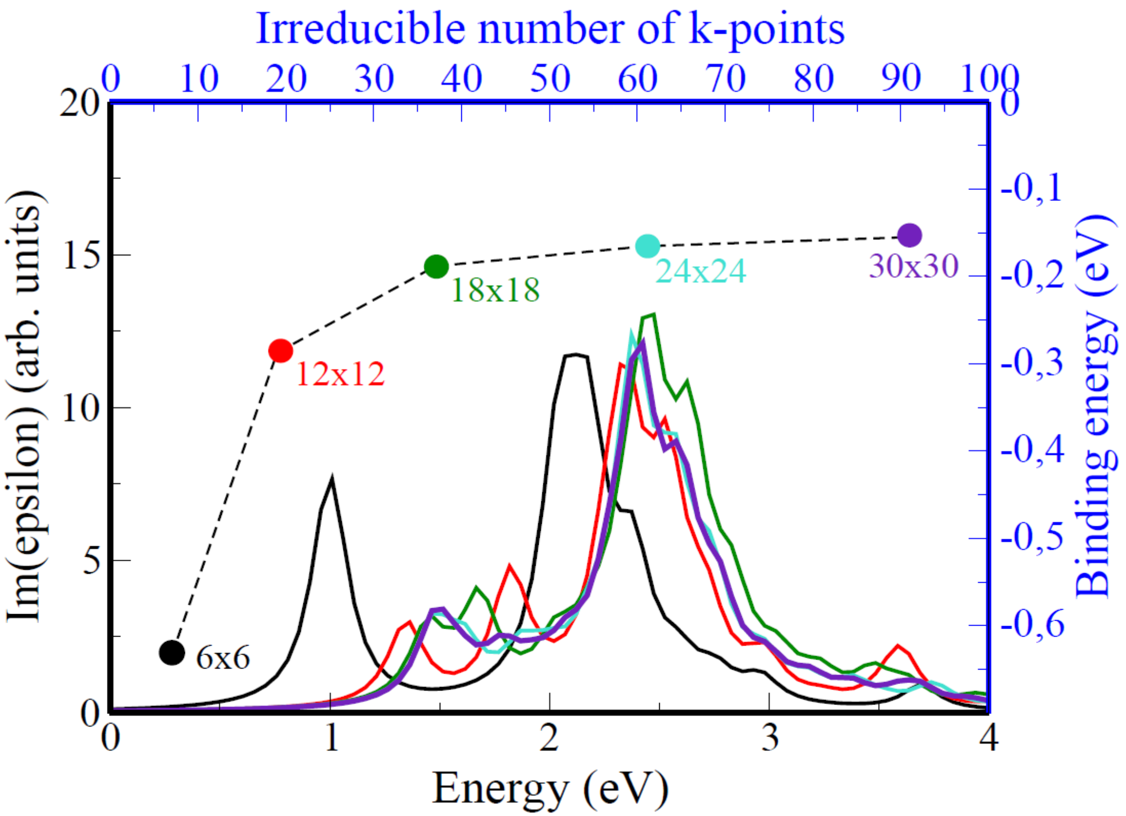
Optical properties

X_A exciton wavefunction in reciprocal space



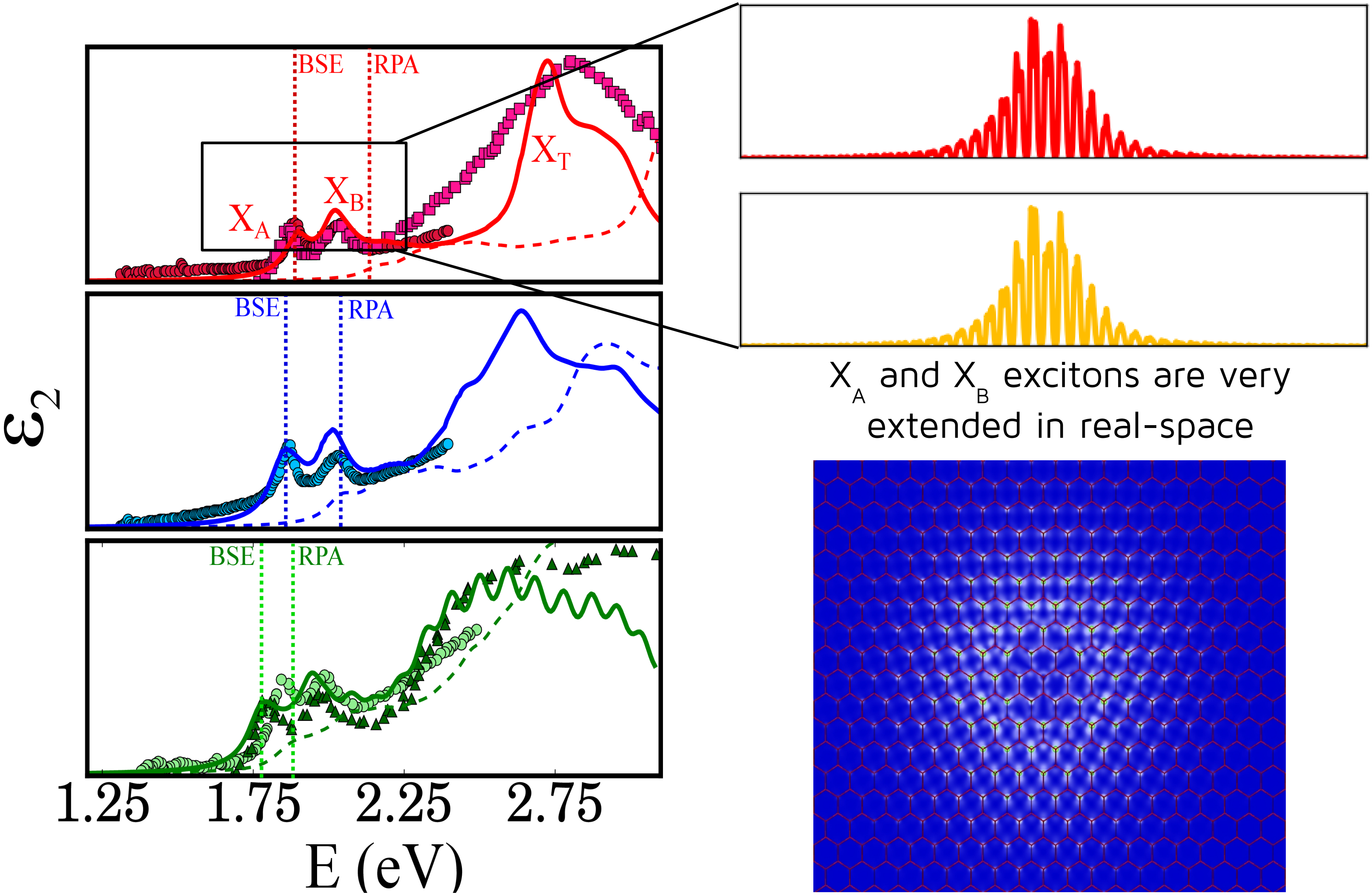
$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{i,j} A_{i,j,\mathbf{k}} \phi_i(\mathbf{r}_e) \phi_j(\mathbf{r}_h)$$

We represent these coefficients summing over all the transitions (i,j index)



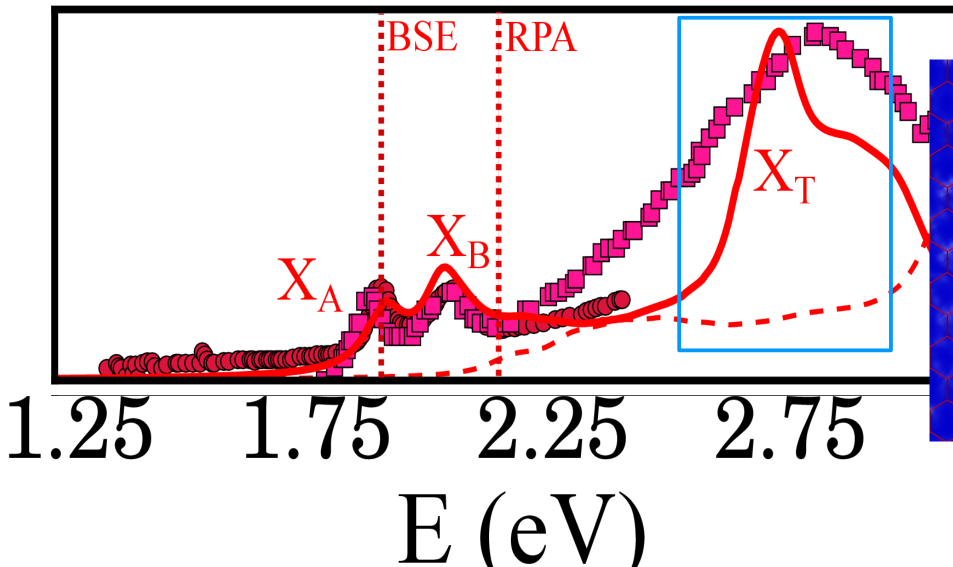
Convergence depends strongly on k-sampling of the Brillouin zone

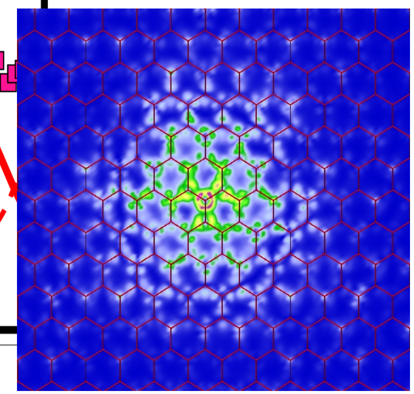
Optical properties



X_A and X_B excitons are very extended in real-space

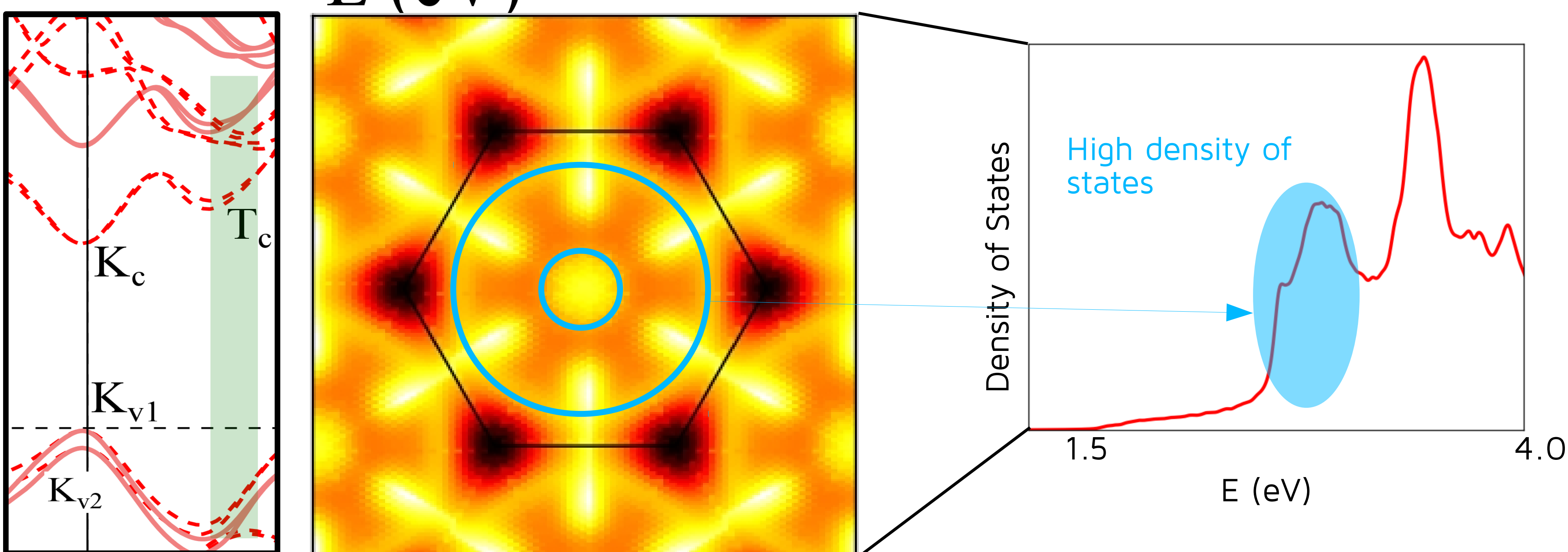
Optical properties





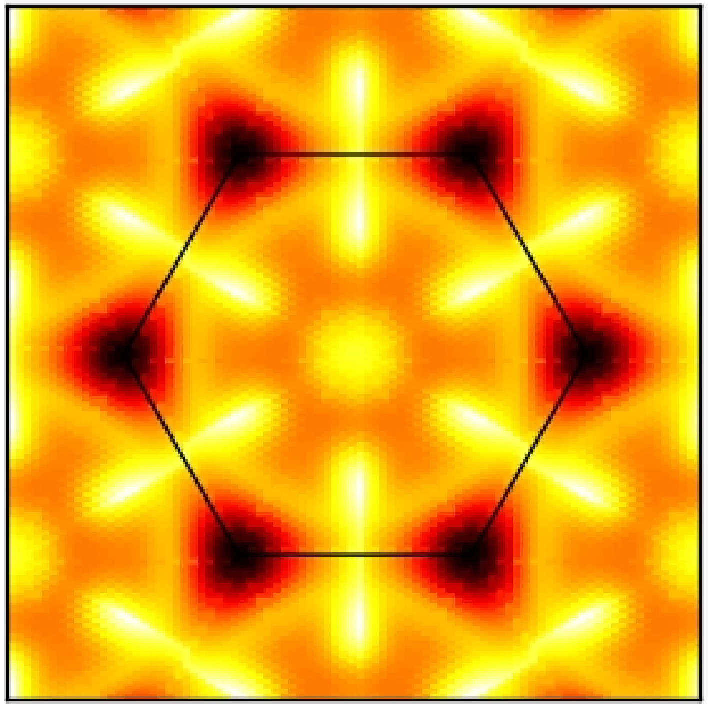
Another interesting feature is the large peak at high energy…

What is the origin?

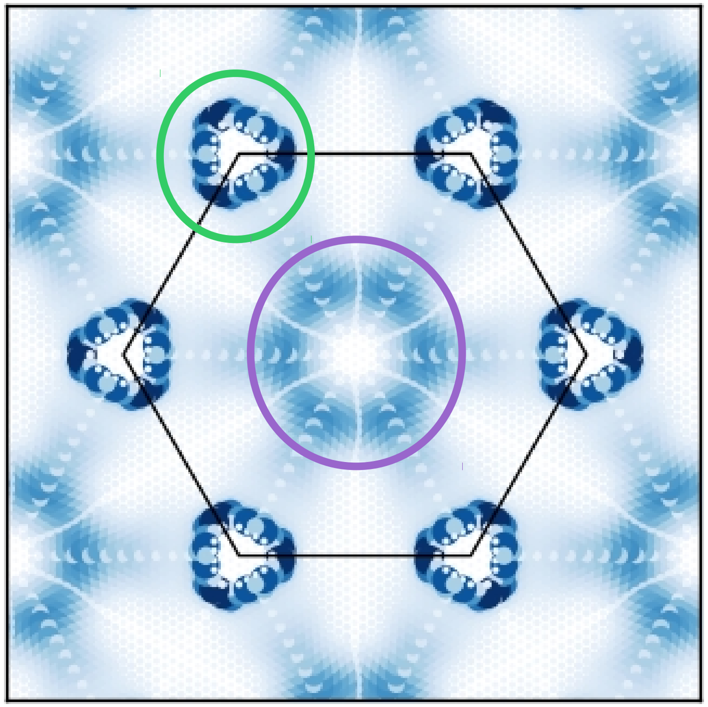


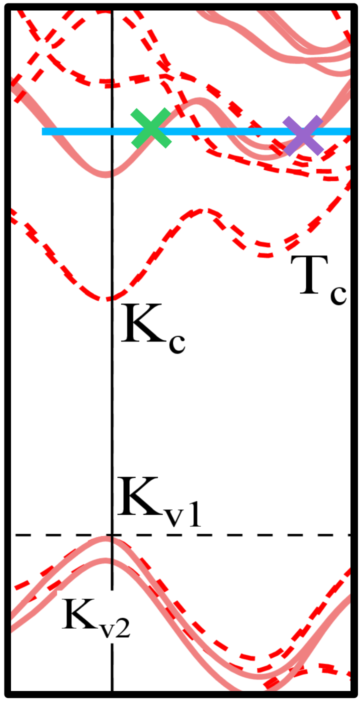
Optical properties

Density of states



Exciton in k-space





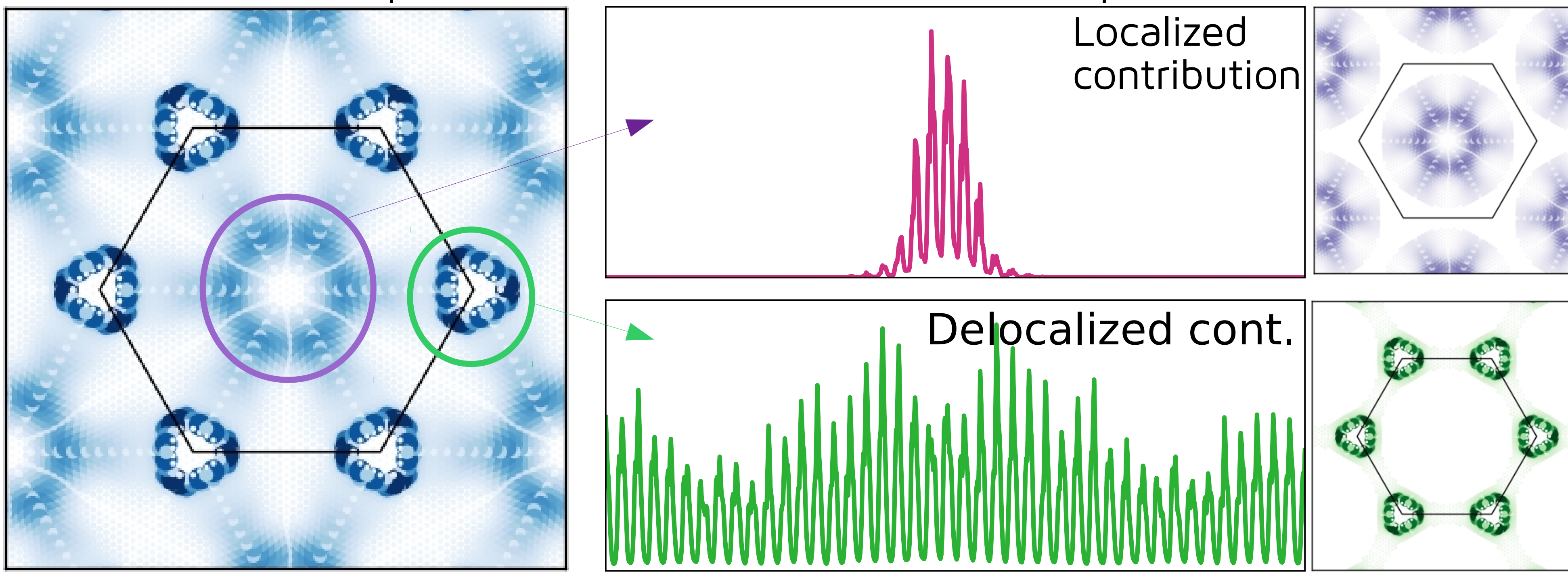
The wave function of this exciton has two contributions

Around **K** and around **G**

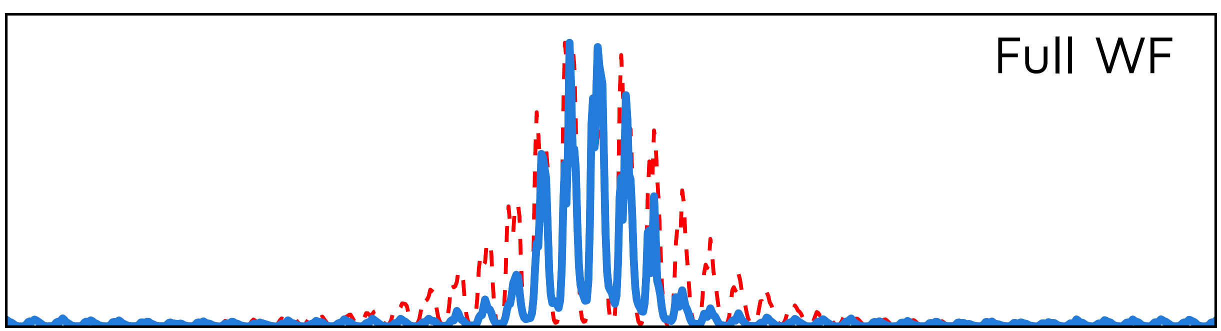
Optical properties

Exciton in k-space

Exciton in real-space



Only the localized part contributes to the total WF. Much more confined than XA and XB excitons



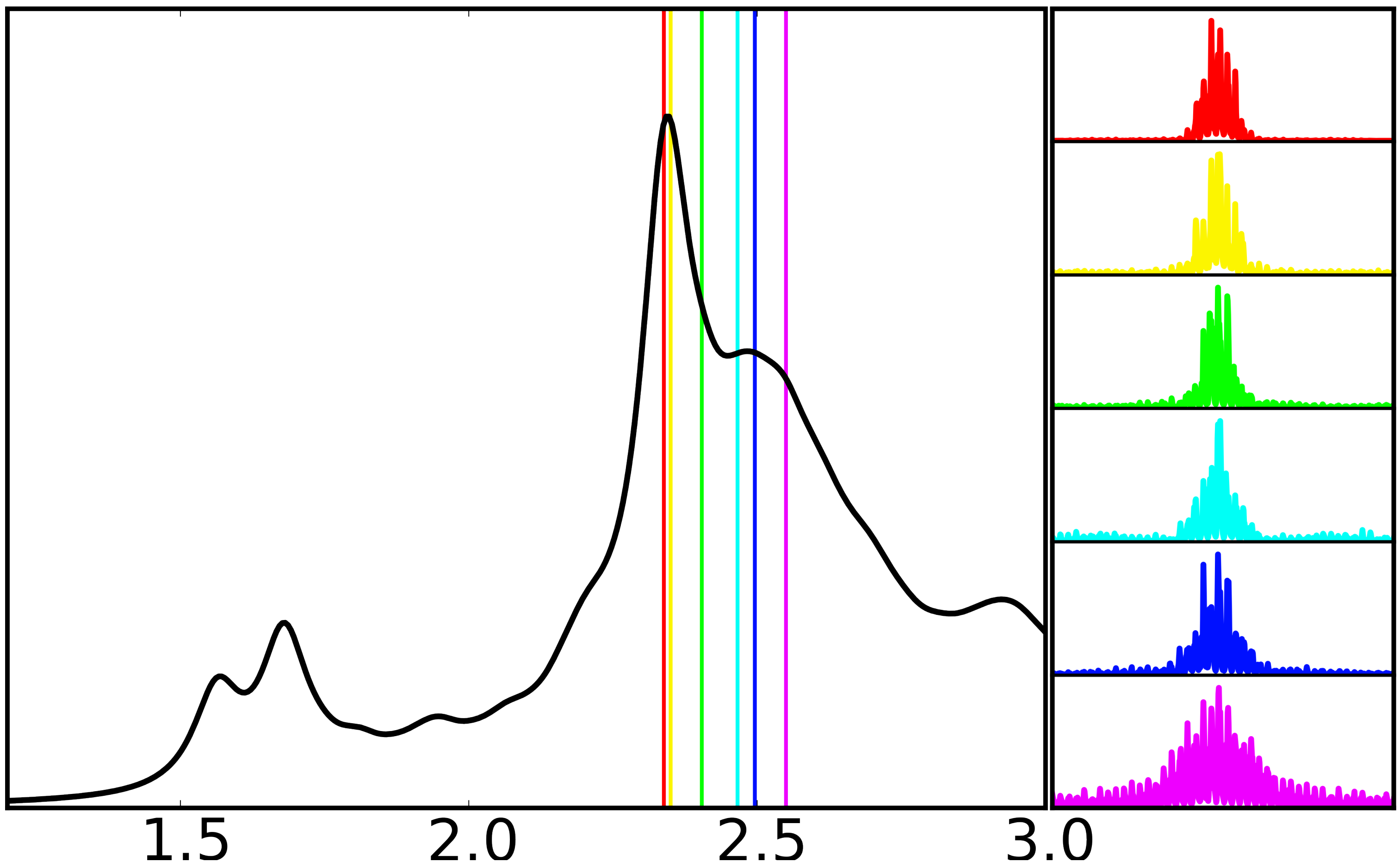
Excitons in a mirror: Formation of "optical bilayers" using MoS2 monolayers on gold substrates. J. Mertens, Y. Shi, AMS, L. Wirtz, H. Y. Yang, and J. J. Baumberg, *Appl. Phys. Lett.* **104**, 191105 (2014).

Observed also in experiments of photocurrent spectroscopy and second harmonic generation (A. R. Klots et. al, arXiv:1403.6455; PRB 87, 201401(R) (2013))

Optical properties

H exciton is not a single peak

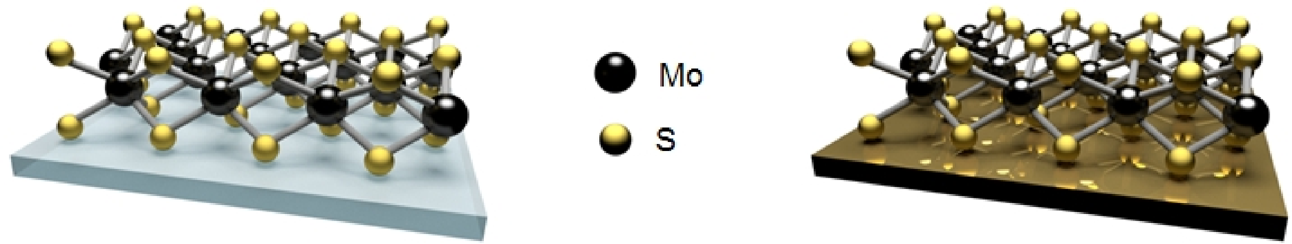
We find localized excitons in a range of 0.1 eV



Interaction with metallic substrates

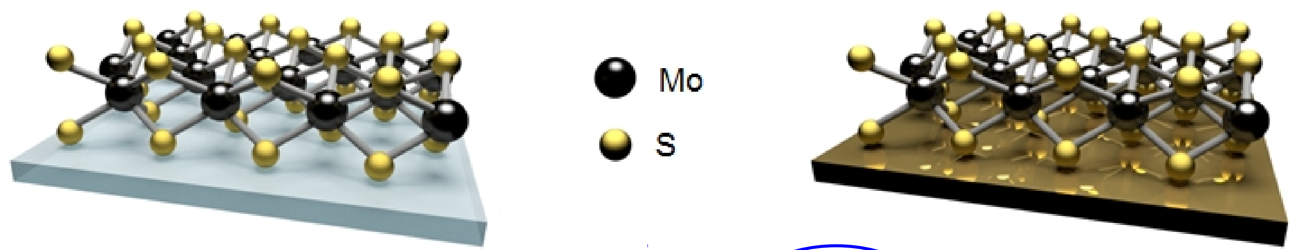
Quartz substrate

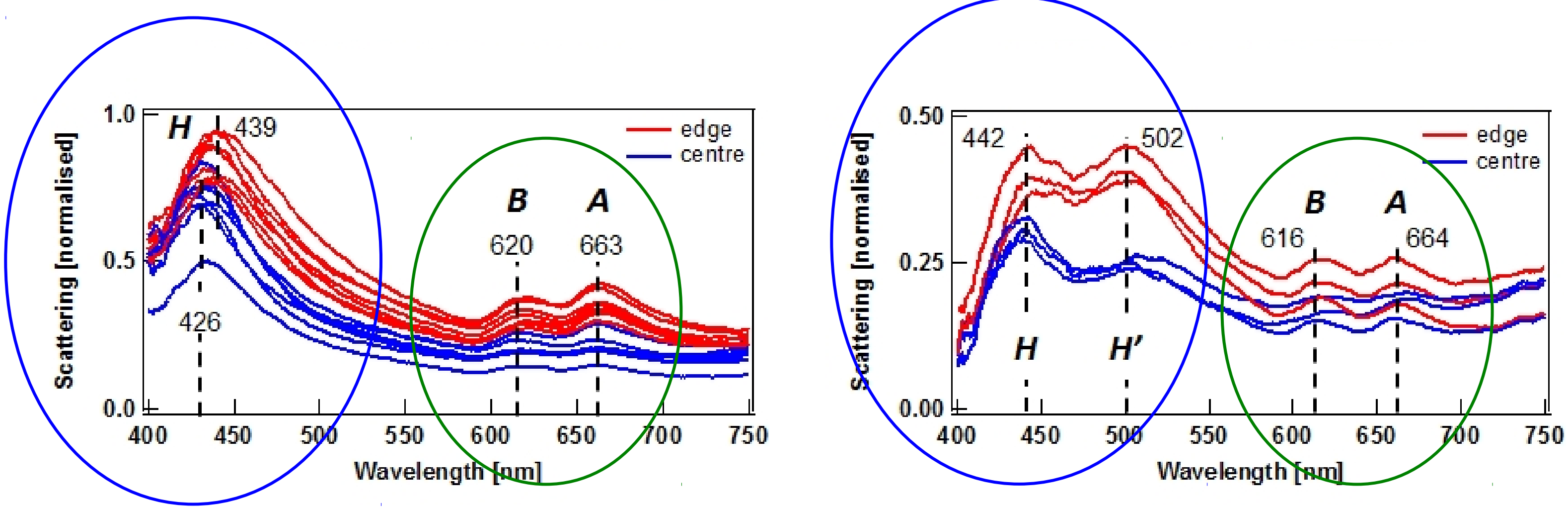
Gold substrate



Interaction with metallic substrates

Quartz substrate | Gold substrate



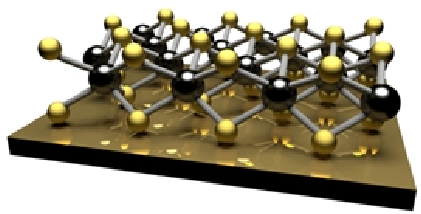


Splitting the H-peak in gold substrate

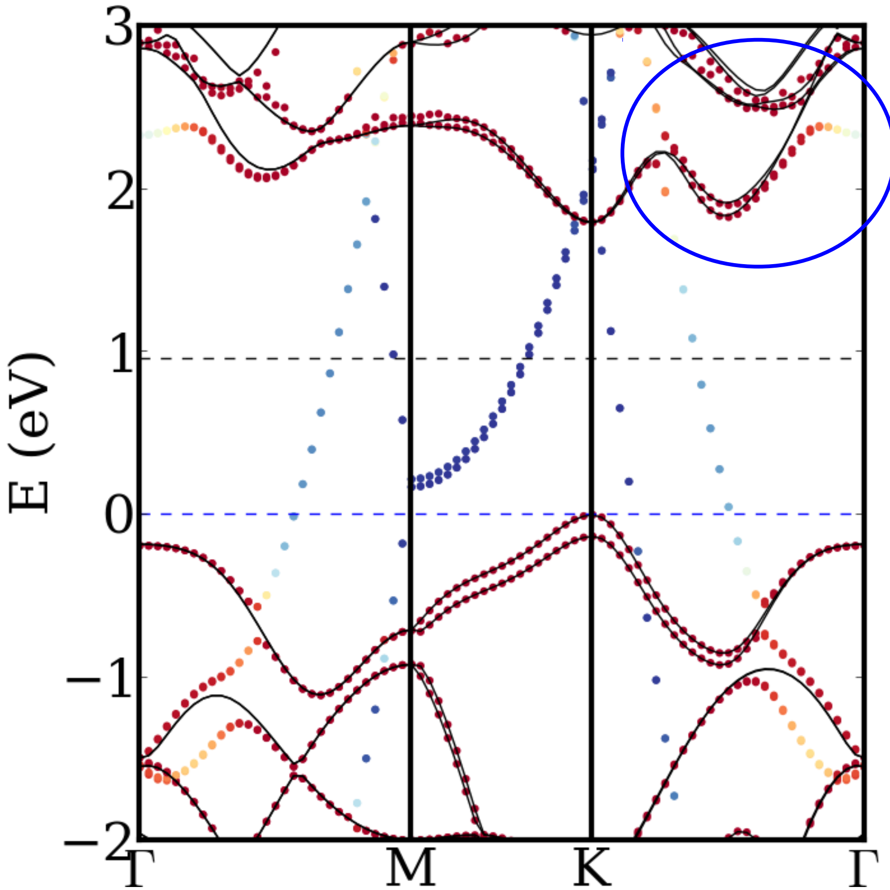
A- and B-excitons are scarcerly affected

Excitons in a mirror: Formation of "optical bilayers" using MoS2 monolayers on gold substrates. J. Mertens, Y. Shi, AMS, L. Wirtz, H. Y. Yang, and J. J. Baumberg, *Appl. Phys. Lett.* **104**, 191105 (2014).

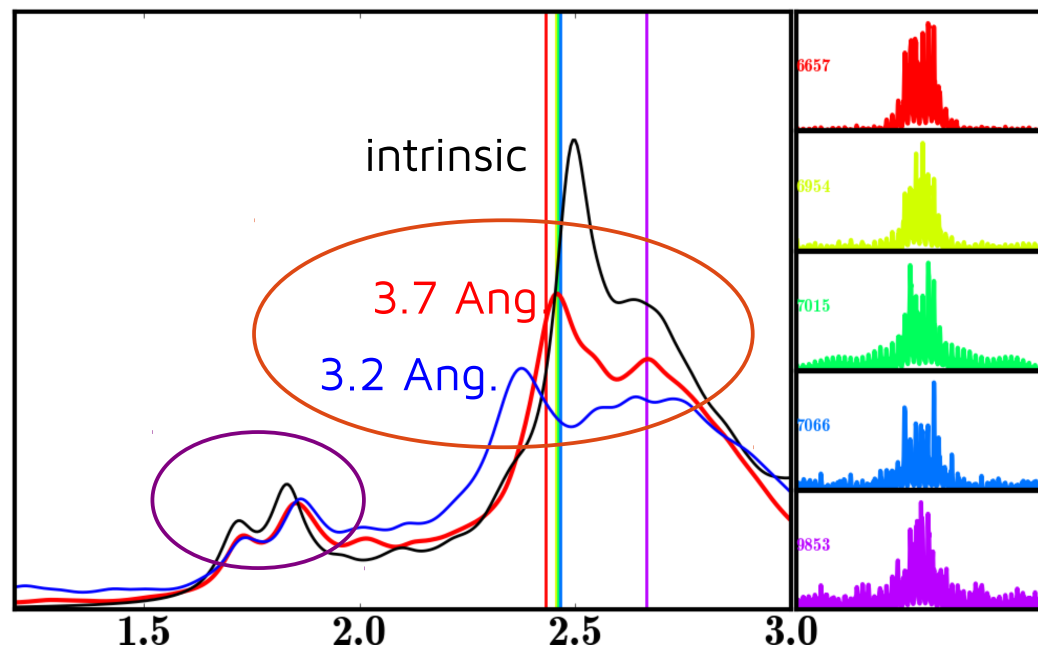
Interaction with metallic substrates



Cupper substrate

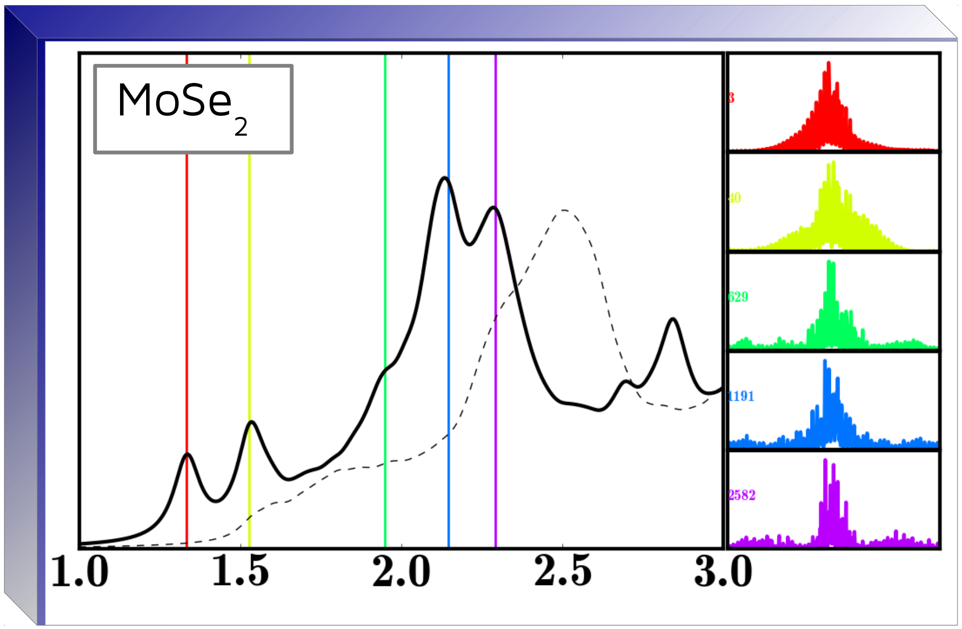


Splitting due to substrate and spin-orbit interaction

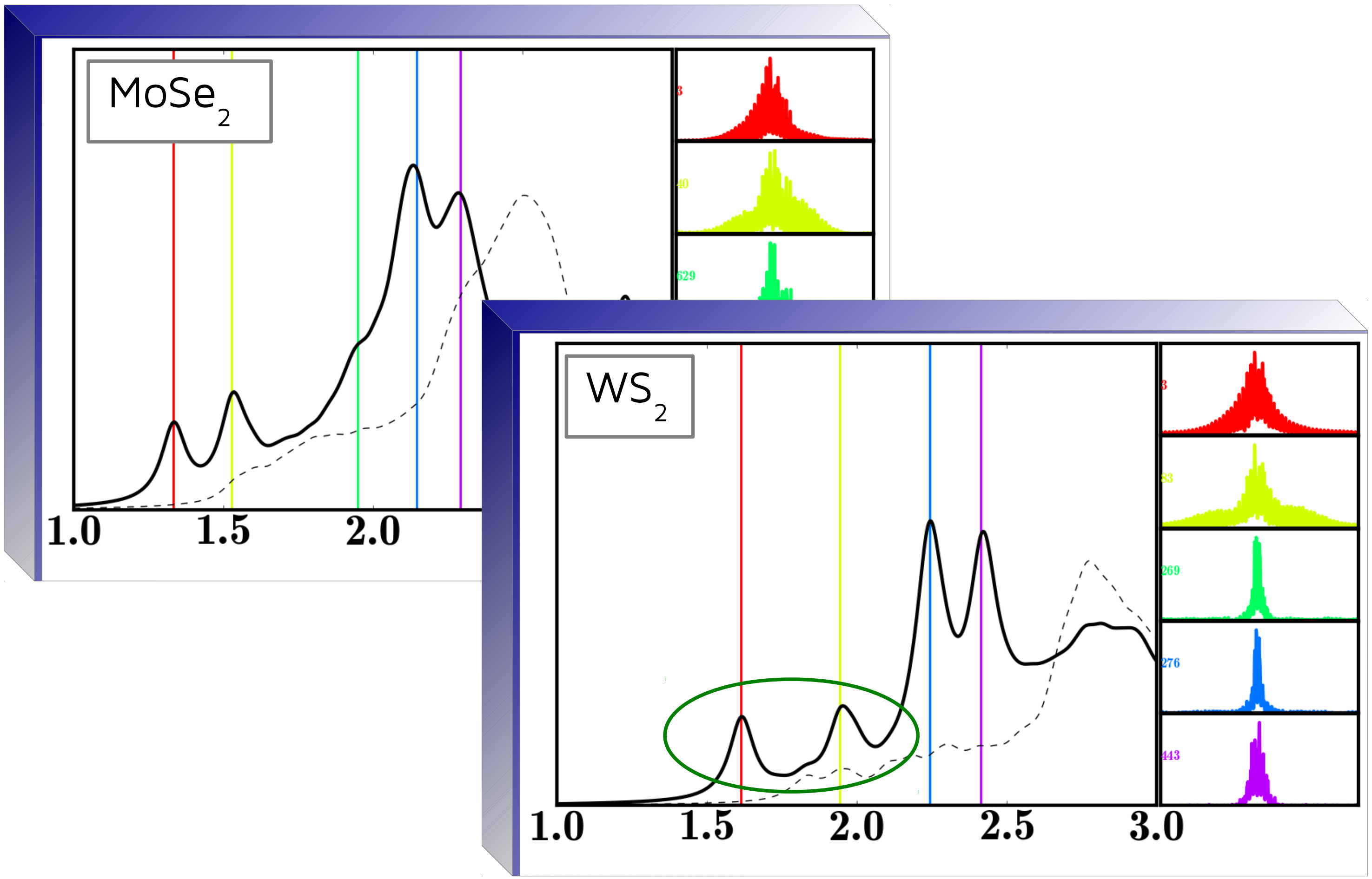


A and B excitons
are unchanged

Other TMDs ($MoSe_2$, WS_2, WSe_2)



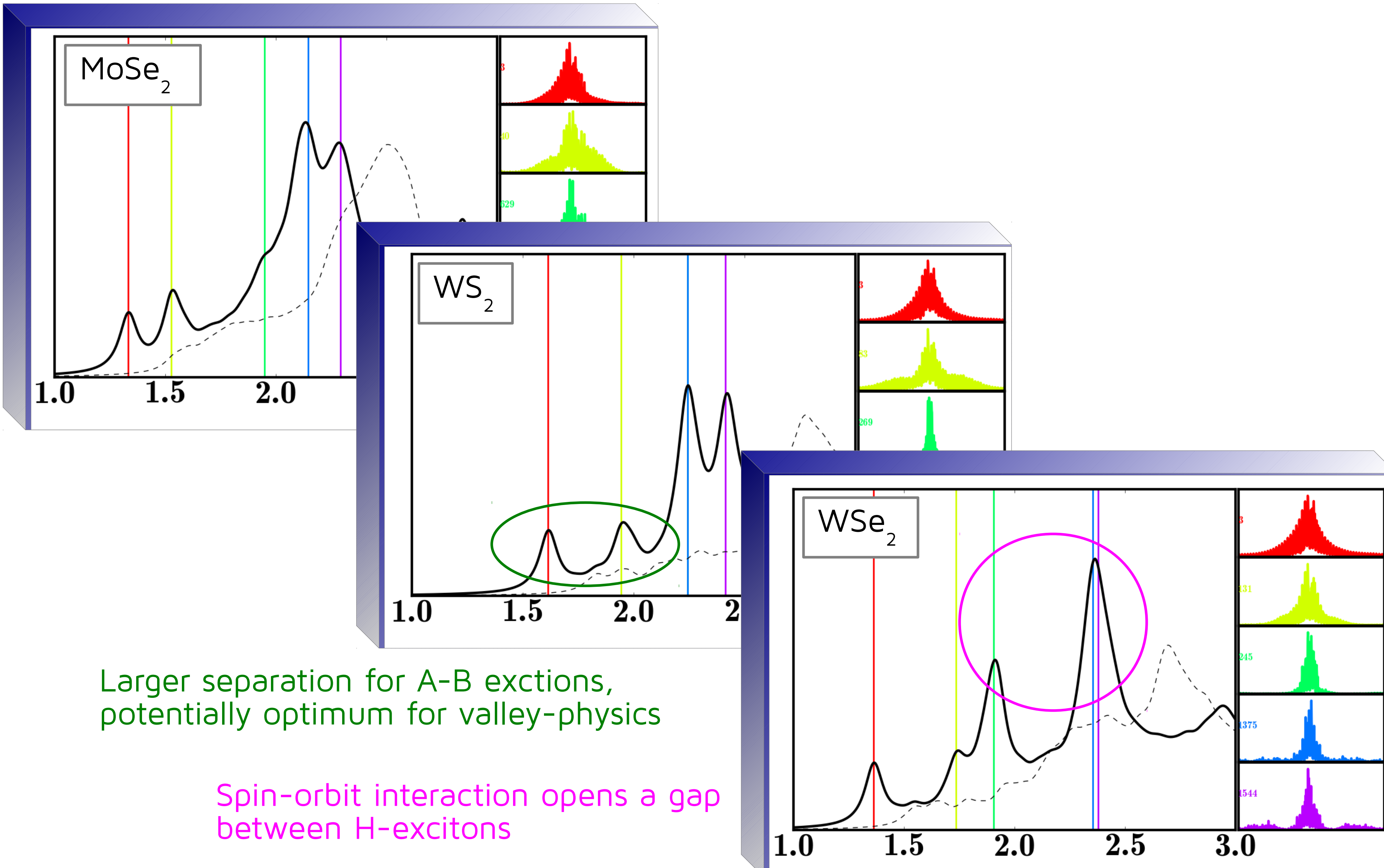
Other TMDs ($MoSe_2$, WS_2, WSe_2)



Larger separation for A-B exctions,
potentially optimum for valley-physics

Spin-orbit interaction opens a gap
between H-excitons

Other TMDs ($MoSe_2$, WS_2, WSe_2)



Larger separation for A-B exctions, potentially optimum for valley-physics

Spin-orbit interaction opens a gap between H-excitons

Conclusions and ongoing work

- Bandgap engineering by applying strain
- A and B peak can be modelled by interband transitions between parabolic bands
- H peak arise from a high density of states. “Van-Hove” exciton?
- A and H excitons have different response to interaction with the substrate
- Metals as Cu and Au seem to affect only the H-excitons

- Role of different substrates
- Role of the electron-phonon interaction
- Valley physics (relaxation processes after optical excitation)

References and acknowledgements

- **Phonons**: A. Molina-Sánchez and L. Wirtz, *Phys. Rev. B* **84**, 155413 (2011).
- **Band structure and excitons**: A. Molina-Sánchez, D. Sangalli, K. Hummer, A. Marini, and L. Wirtz, *Phys. Rev. B* **88**, 045412 (2013).
- **Interaction of MoS_2 with gold substrate**: J. Mertens, Y. Shi, A. Molina-Sánchez, L. Wirtz, H. Y. Yang, and J. J. Baumberg, *Appl. Phys. Lett.* **104**, 191105 (2014).
- **Review**: A. Molina-Sánchez, K. Hummer, and L. Wirtz, Surface Science Reports, coming soon.

- **Yambo team**. Davide Sangalli and Andrea Marini. CNR Roma.
- **GW calculations**. Kerstin Hummer, University of Vienna.
- **Experiments**. Jeremy J. Baumberg, University of Cambridge.
- **Theoretical Solid State Physics**. Ludger Wirtz.

THANKS FOR YOUR ATTENTION!