Ab initio Study of the Excitonic Effects on the Optical Spectra of Single-layer, Double-layer, and Bulk MoS_2

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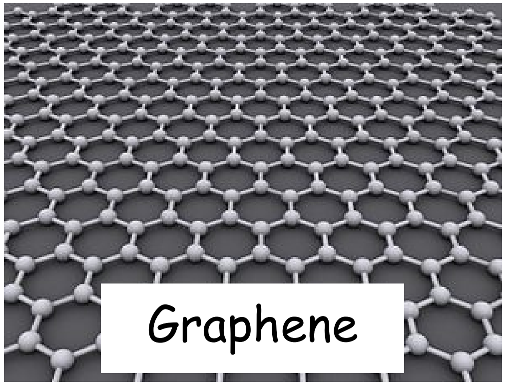
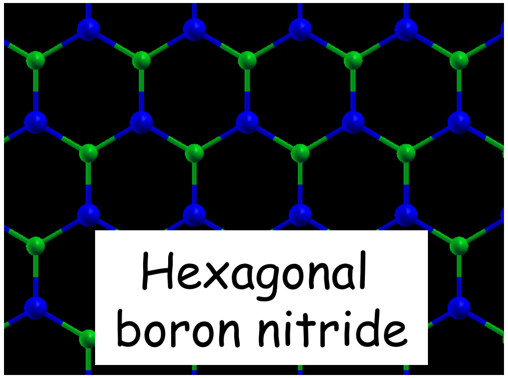
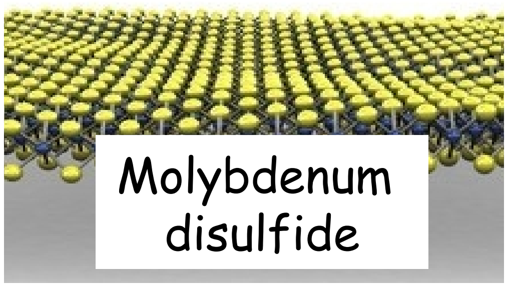
Physics and Material Sciences Research Unit (PHYMS)

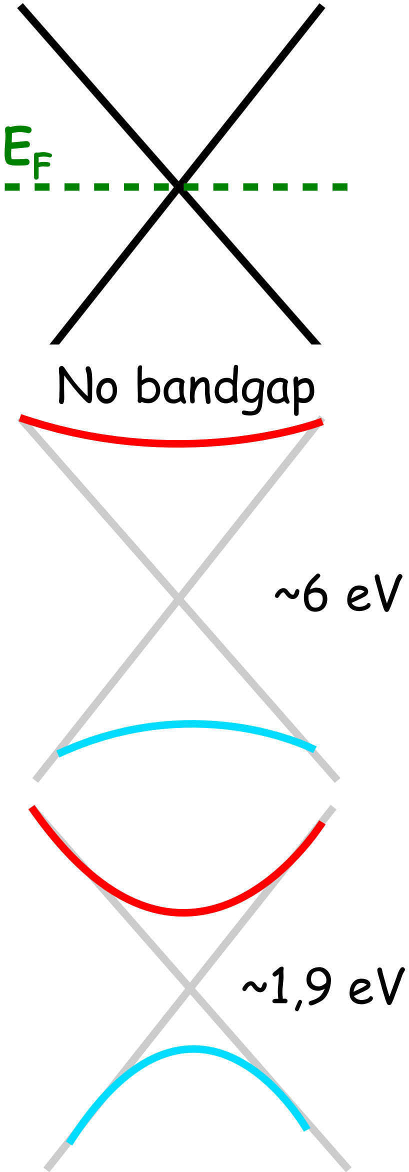
Single-layer semiconductors

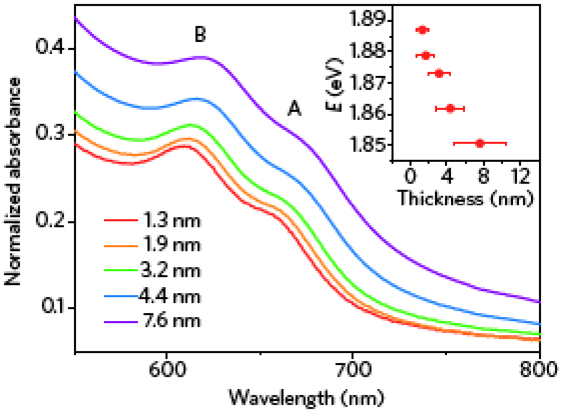
From graphene to a new *family* of materials





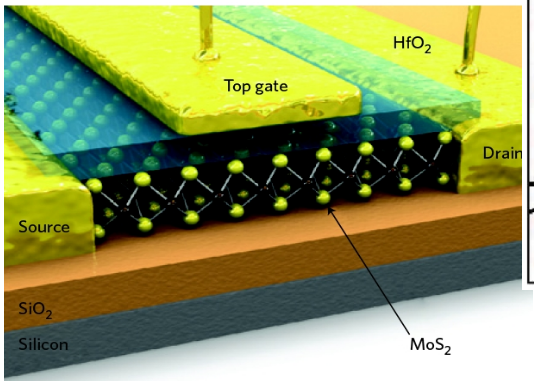


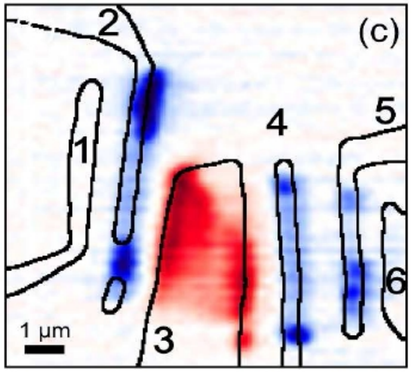




The bandgap and the high mobility makes MoS_2 a suitable alternative to graphene or carbon nanotubes.

Appealing for transistors, tunable photo-thermoelectric effect, field-effect transistors …





See review Nature Nanotechnology 7, 699 (2012)
A. Castellanos, Nano Lett.,
Phys. Rev. Lett. 108, 196802 (2012)

Transition metal dichalcogenides
Single-layer semiconductors

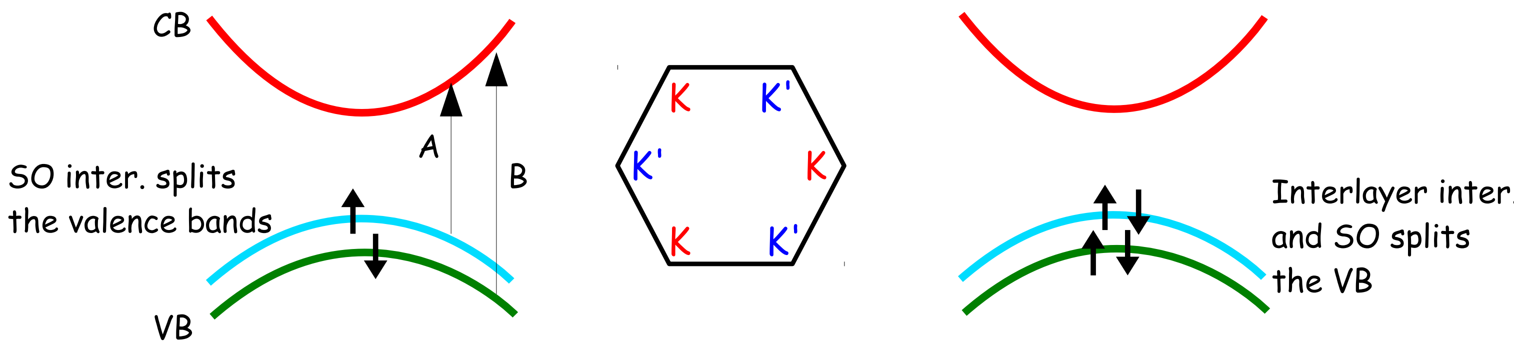
Crystal symmetry determines the electronic structure and optical properties

Single-layer (D_{3h})

No inversion symmetry

Double-layer and bulk (D_{6h})

Inversion symmetry



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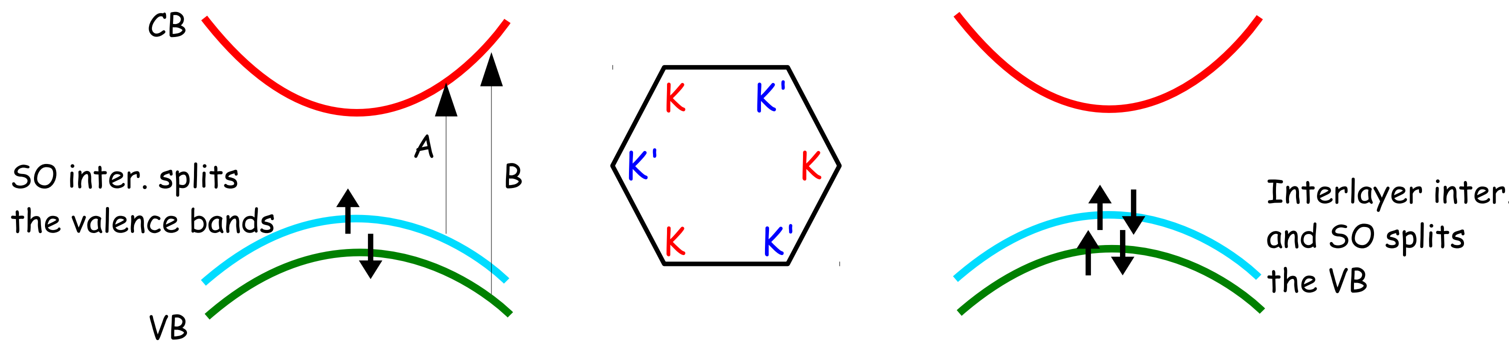
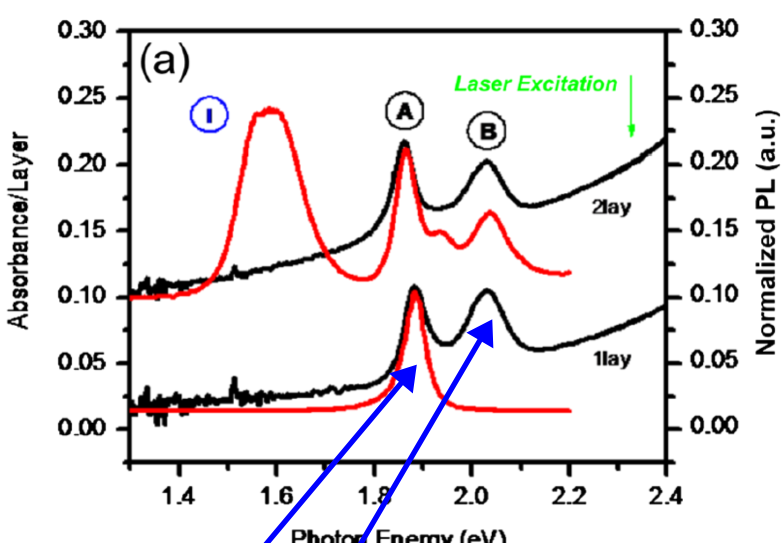
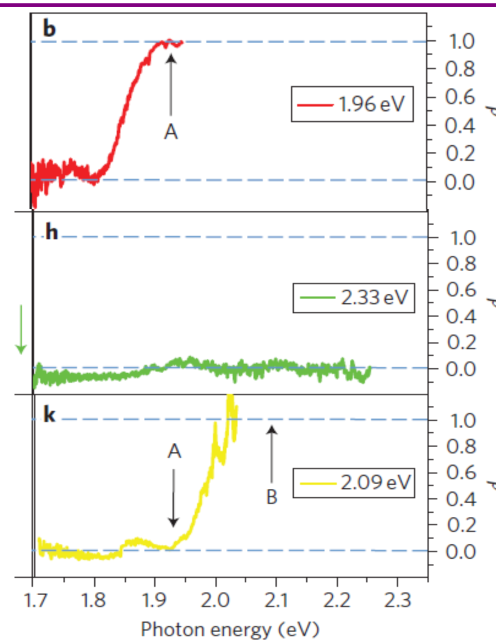




VB splitting is exhibited in the PL and absorption by a two peaks structure



Control of the light polarization helicity by tunning the excitation energy (valley physics).

MoS_2, SL, DL and BULK
- Electronic Structure: LDA and GW methods.
- Excitonic effects: Bethe-Salpeter equation with special attention in the convergence of the k-sampling.

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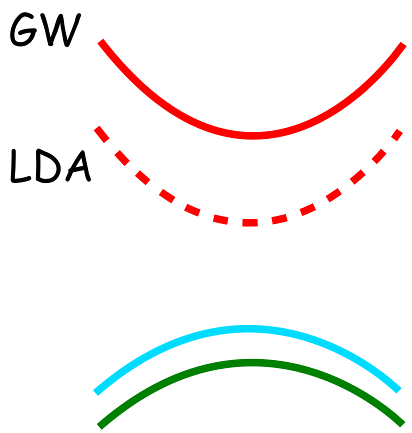
Phys. Rev. Lett. 105, 136805 (2010)

Nature Nanotechnology 7, 494 (2012)

MoS_2. Band Structure. LDA and GW method



Correction of LDA bandgap underestimation by means of the GW method (spin-orbit interaction is included).

LDA calculations made with ABINIT

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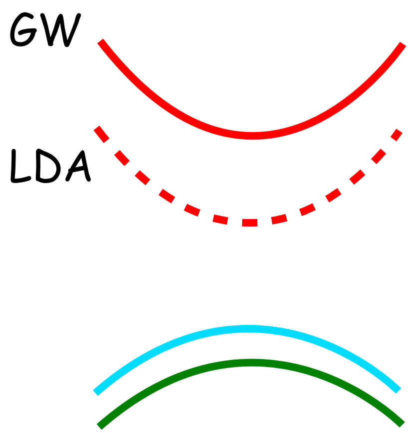

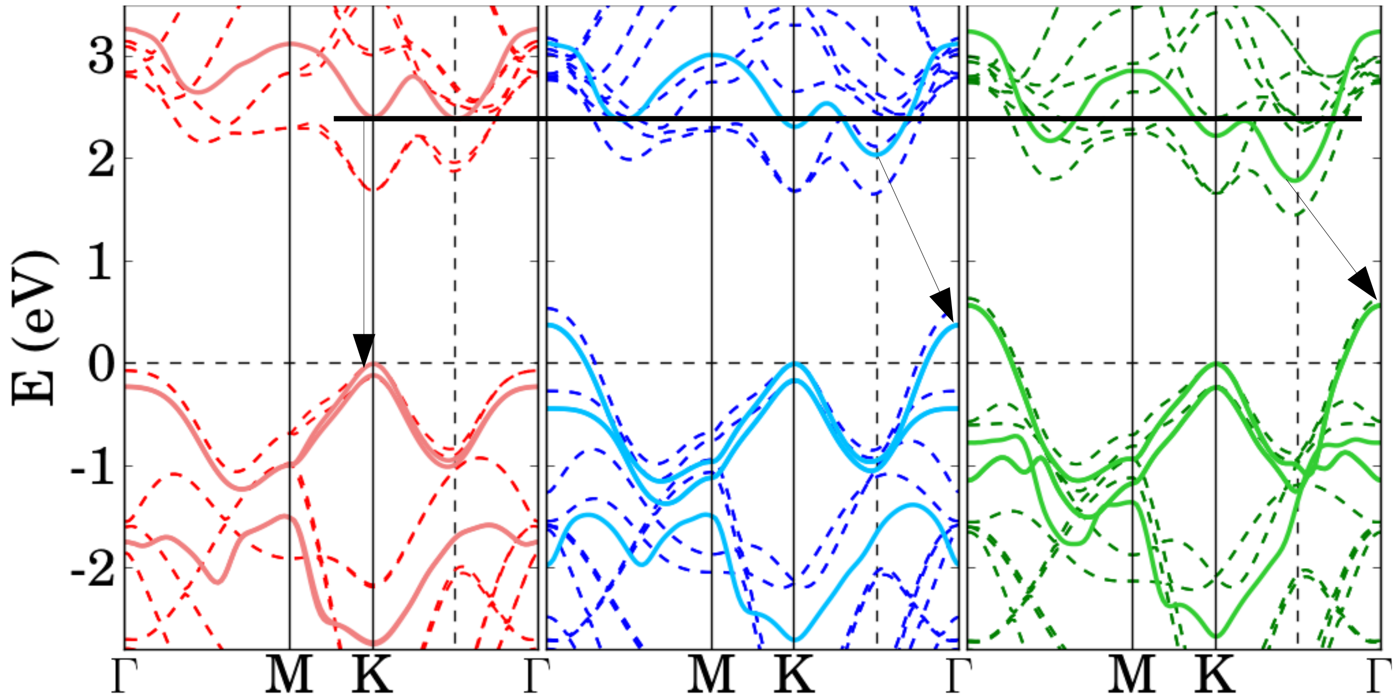

Correction of LDA bandgap underestimation by means of the GW method (spin-orbit interaction is included).

The addition of more layers changes the dielectric screening, the symmetry and the interlayer interaction.

Phys. Rev. B 84 , 155413 (2011). *LDA calculations made with ABINIT*

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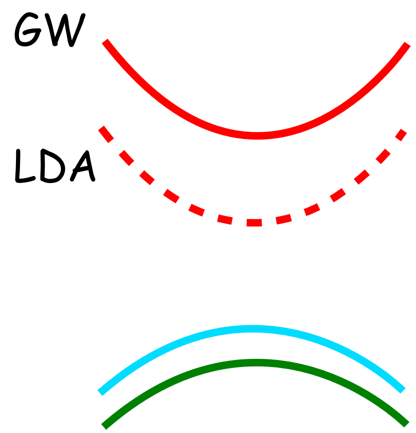
MoS$_2$. Band Structure. LDA and GW method



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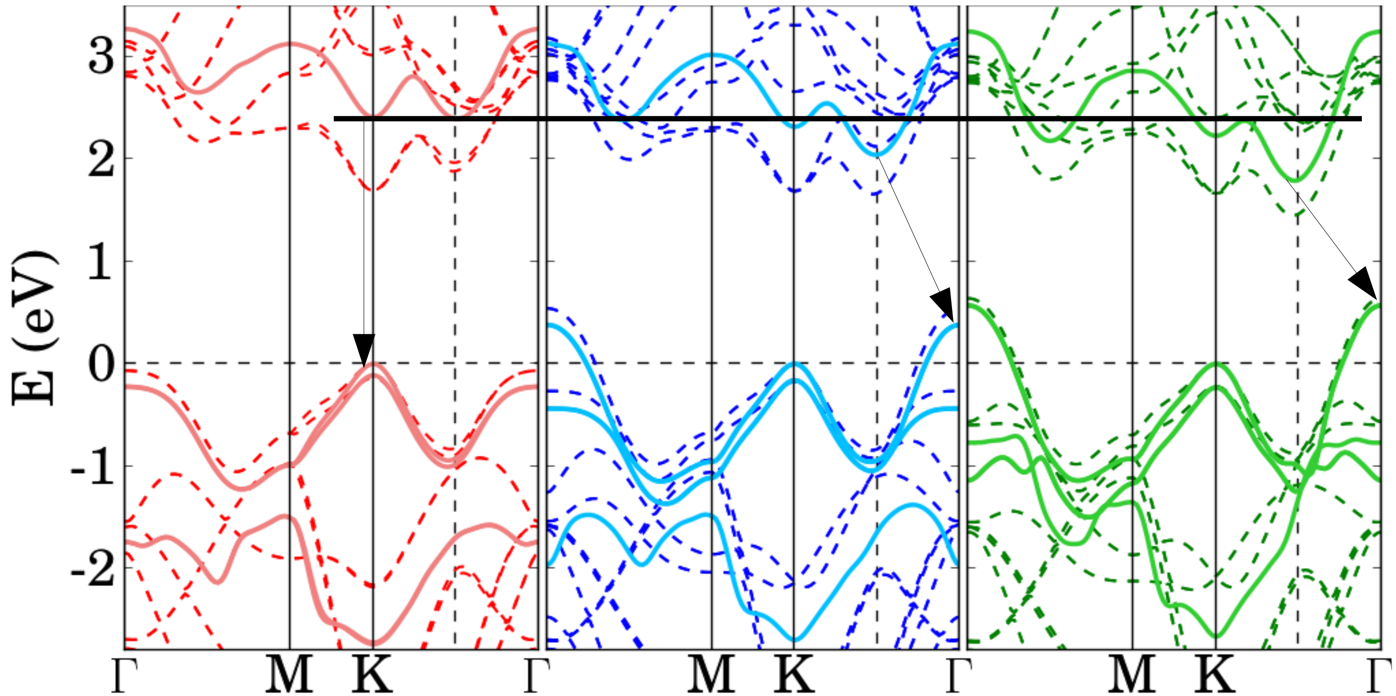

GW correction:

- Rigid shift of the conduction band
- Smaller correction for increasing number of layers

Bandgap extremely sensitive to lattice optimization

For multi-layers: Pushing of the valence band at Γ (indirect)

Excitonic effects are missing, strong influence on the optical spectra

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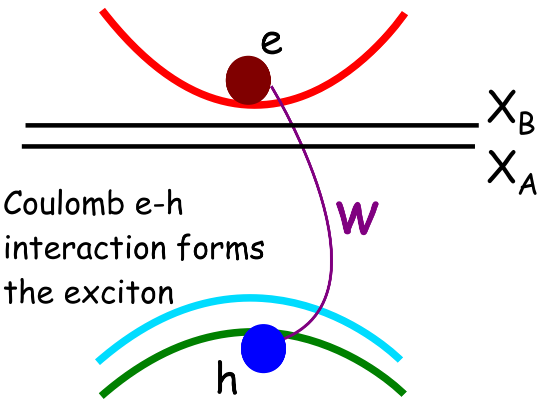
Phys. Rev. B 84 , 155413 (2011). *LDA calculations made with ABINIT*

MoS_2. Excitonic Effects. Bethe-Salpeter Equation



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

Energy difference — Bethe-Salpeter Kernel

$$\Xi_{\mathbf{K}_1\mathbf{K}_2} = -iV_{\mathbf{K}_1\mathbf{K}_2} + iW_{\mathbf{K}_1\mathbf{K}_2} \qquad \mathbf{K} \equiv (c, v, \mathbf{k})$$

Unscreended short ranged exchange interaction — Screened coulomb interaction

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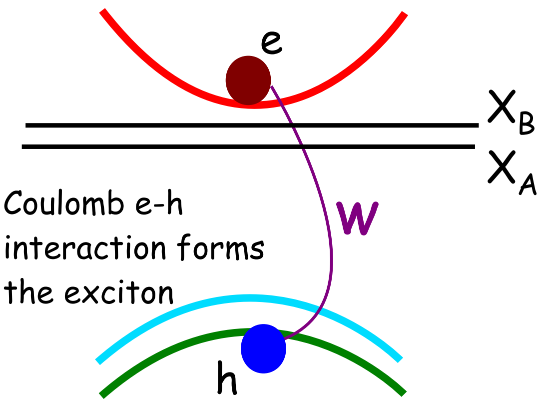

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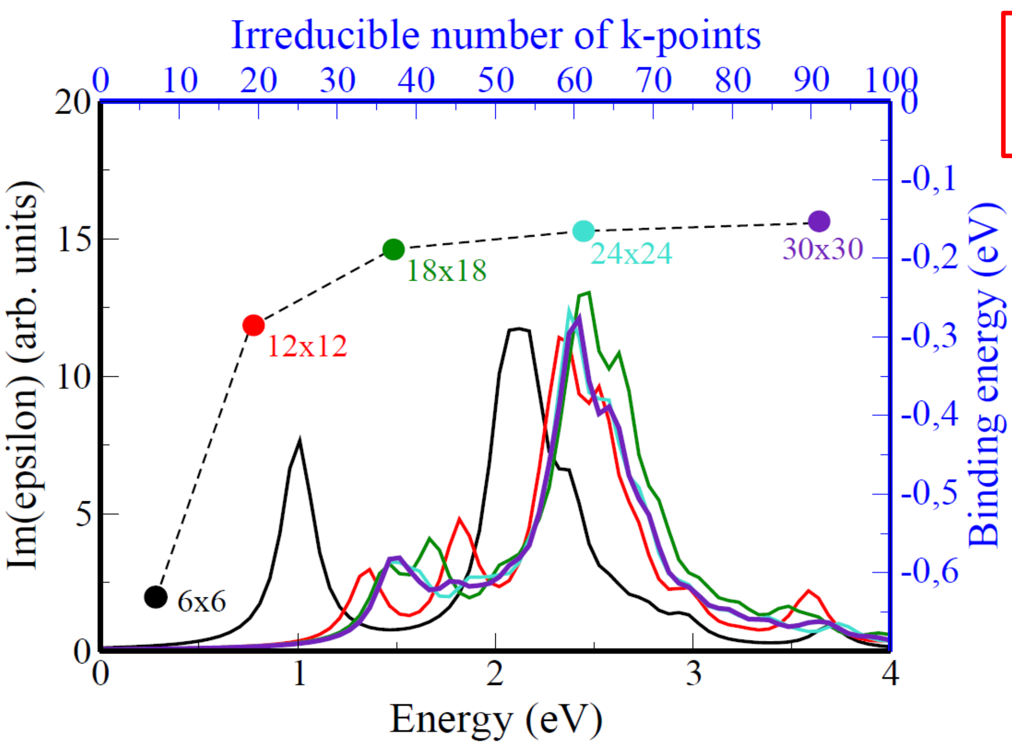

Key issue in reliable results: convergence in number of conduction and valence band states and k-points!

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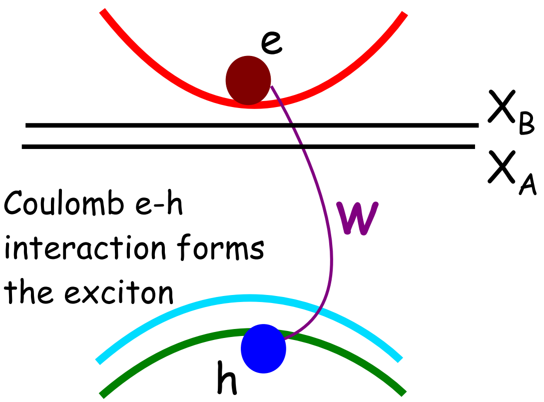
MoS_2. Excitonic Effects. Bethe-Salpeter Equation



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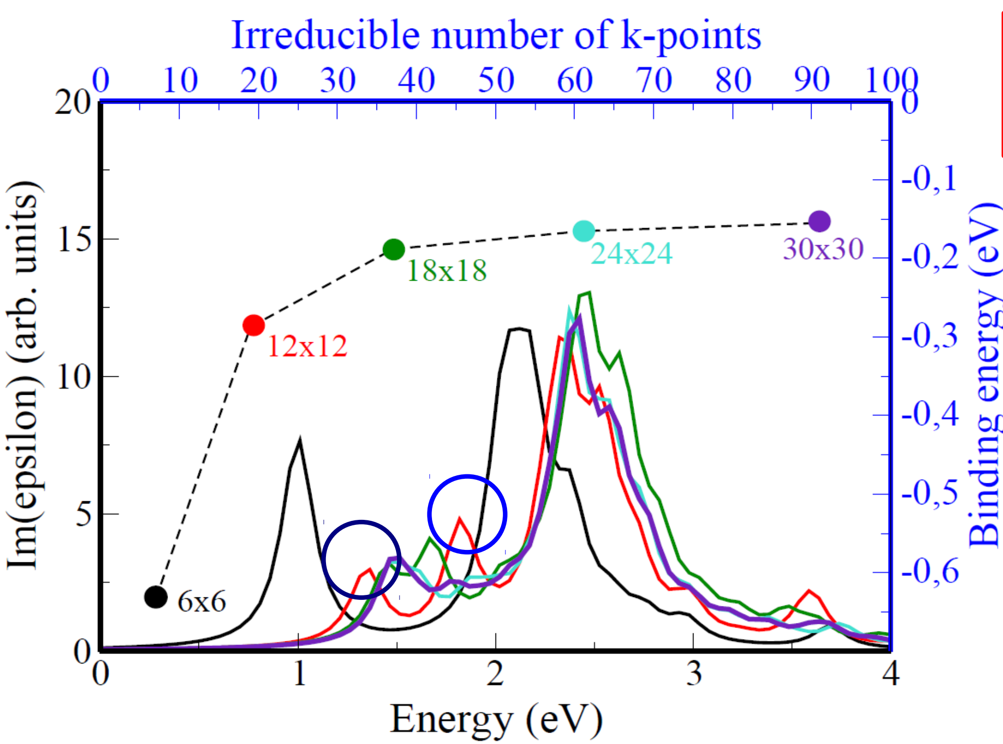
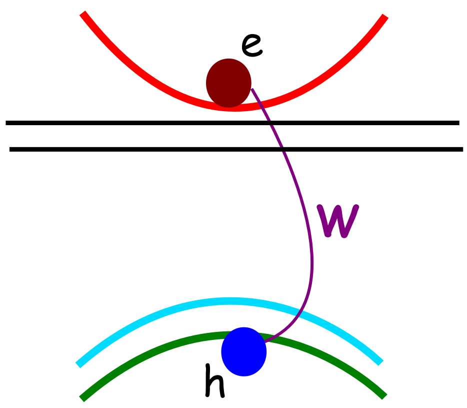
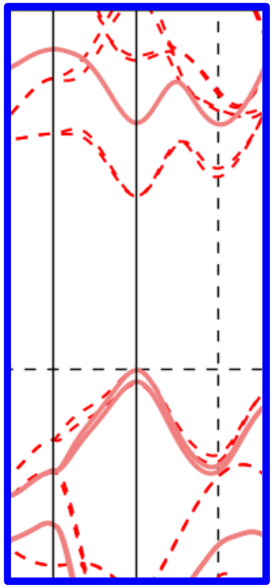


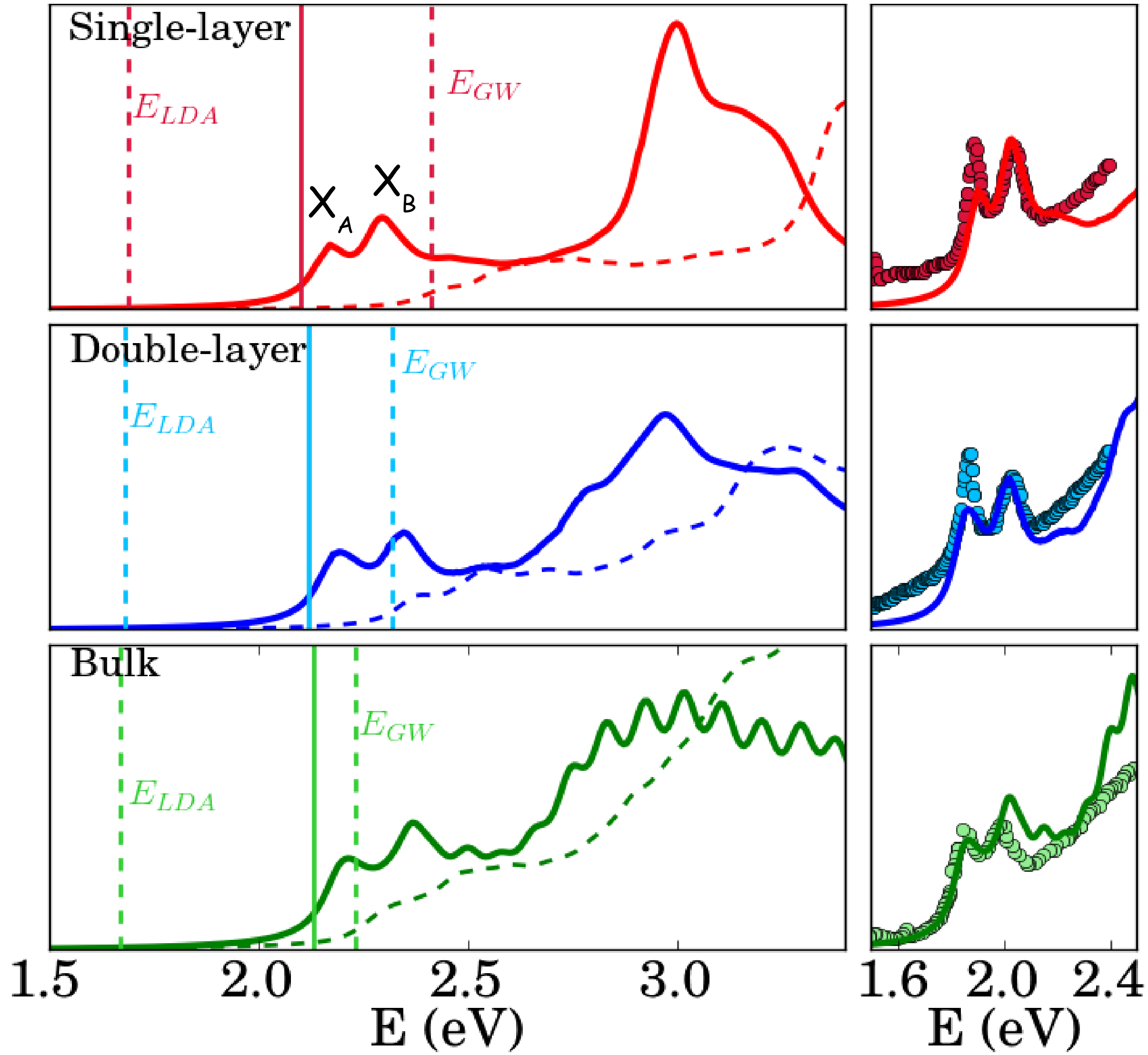
Key issue in reliable results: convergence in number of conduction and valence band states and k-points!

Lack of convergence in k-points overestimate the exciton binding energy.
The k-sampling is directly related to the numbers of unit cells employed to map the exciton wave functions.
Low k-sampling gives also artifacts in the optical absorption.

MoS_2. Excitonic Effects. Bethe-Salpeter Equation







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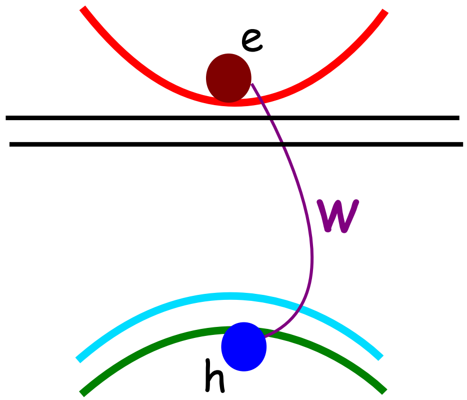
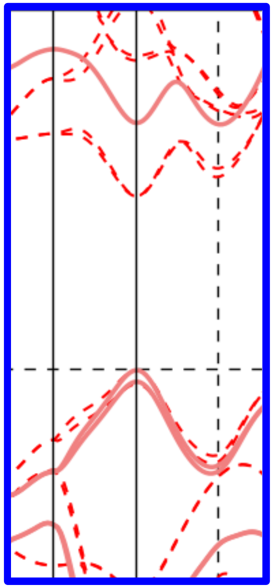
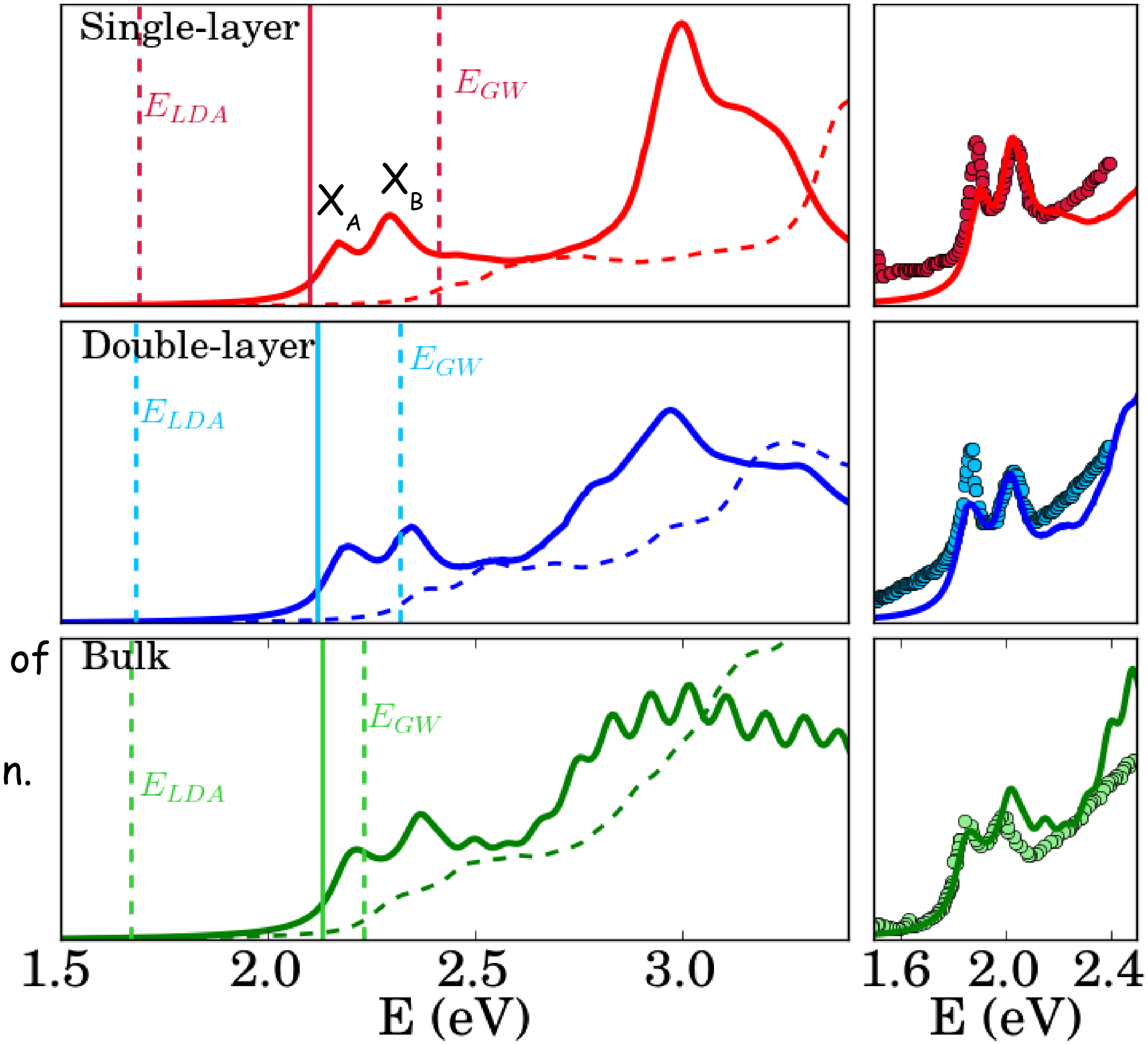
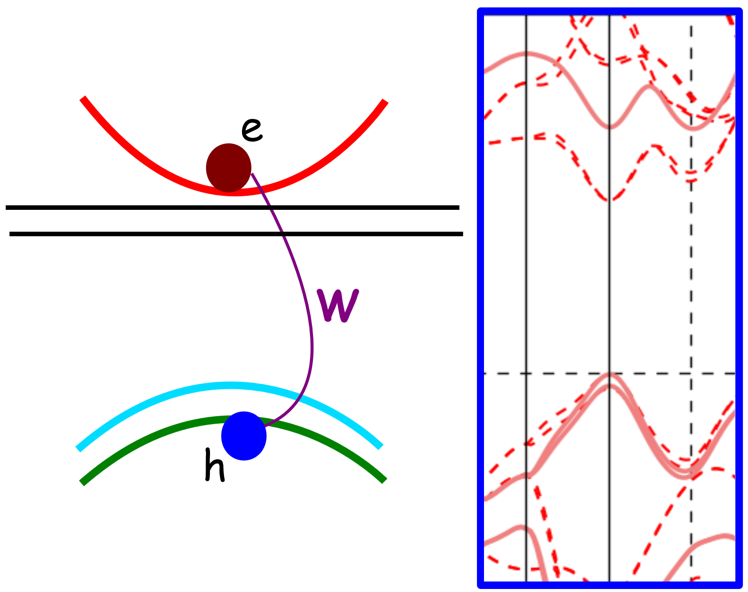


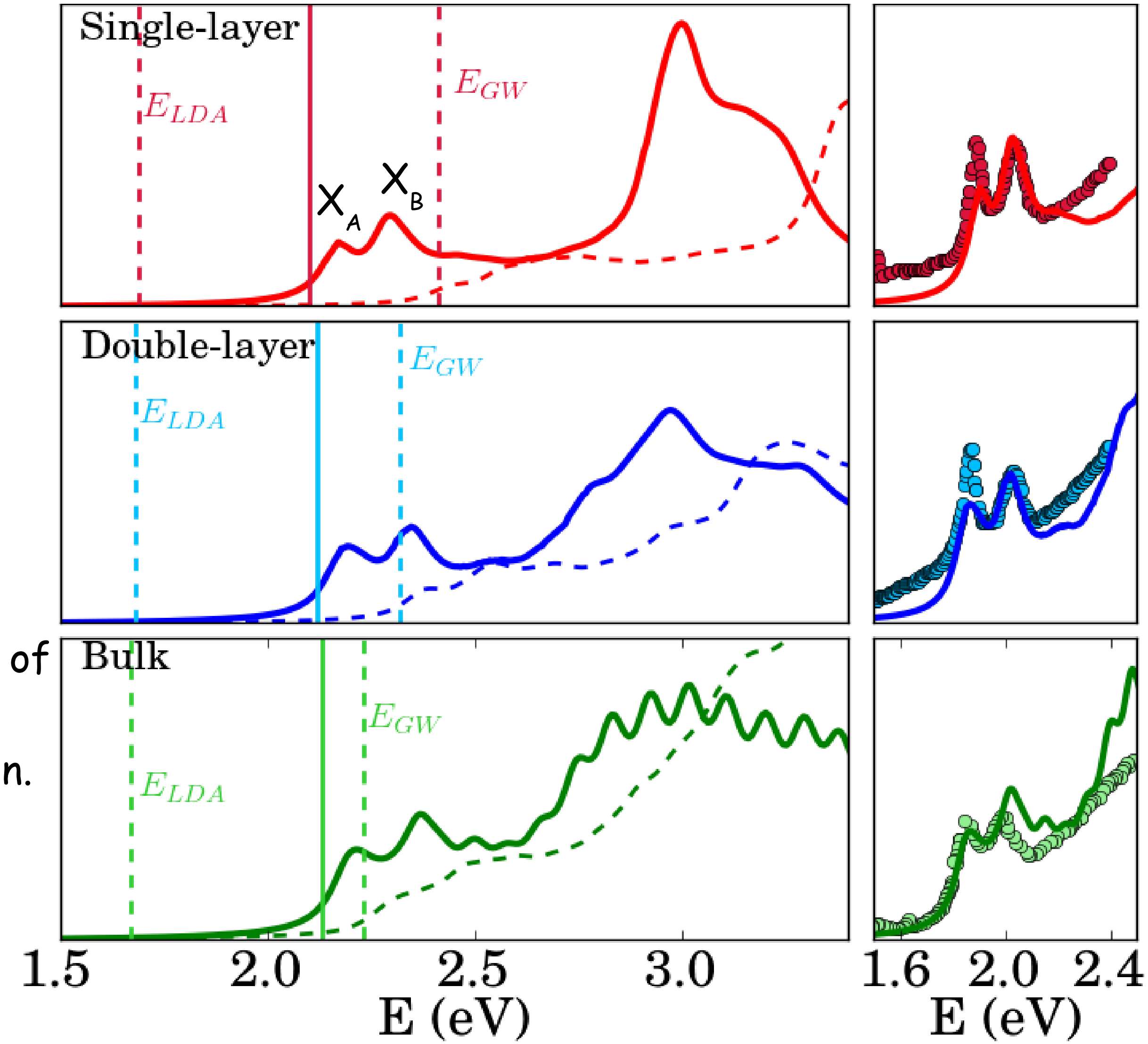




The exciton binding energy decreases with the number of layers. Consequence of larger dielectric screening. This compensates partially the GW correction.

MoS_2. Excitonic Effects. Bethe-Salpeter Equation



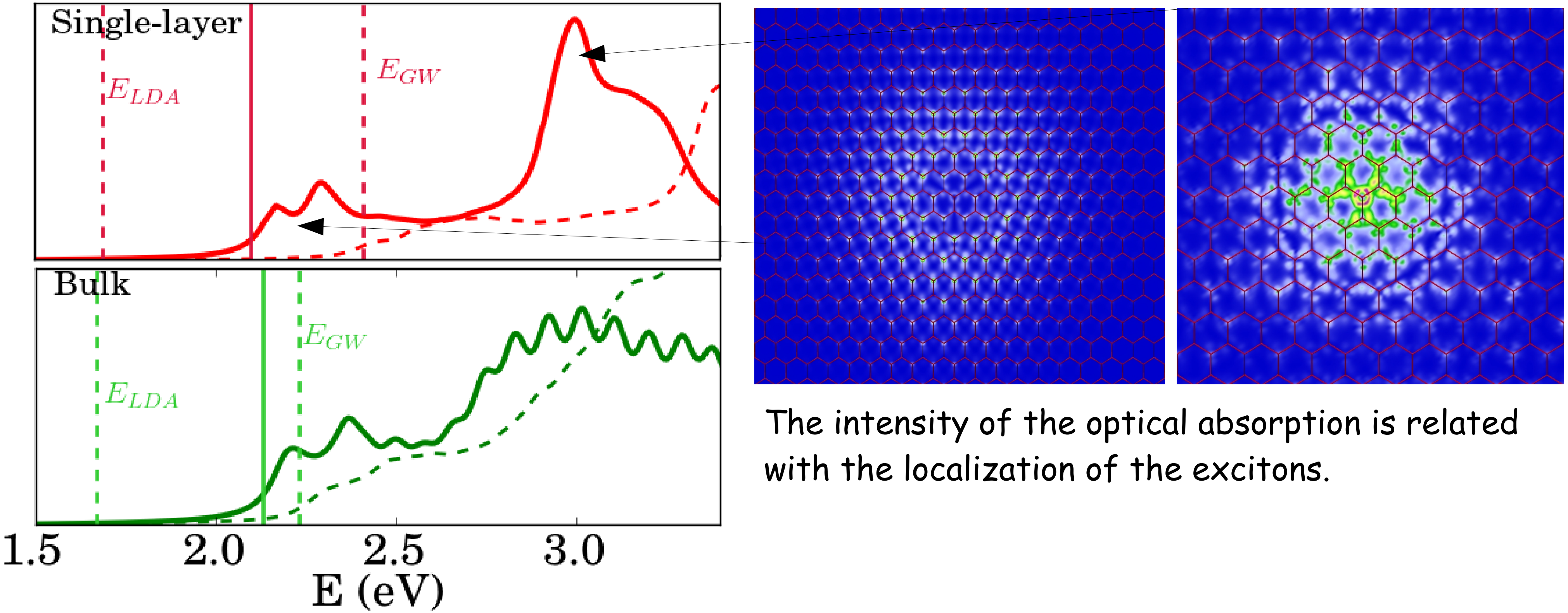


The exciton binding energy decreases with the number of layers. Consequence of larger dielectric screening. This compensates partially the GW correction.

For single-layers (around 3 eV) the absorption gains in efficiency (strongly bound exciton).

The theoretical spectra captures nicely the peaks separation for all the cases.

MoS_2. Excitonic Effects. Bethe-Salpeter Equation



The intensity of the optical absorption is related with the localization of the excitons.

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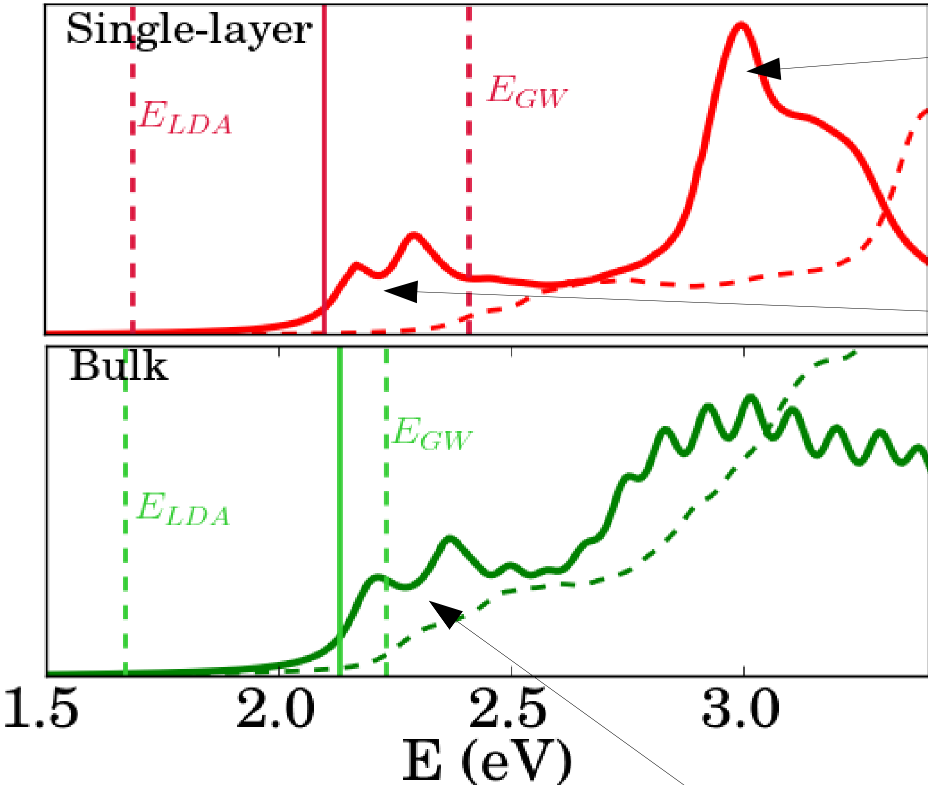
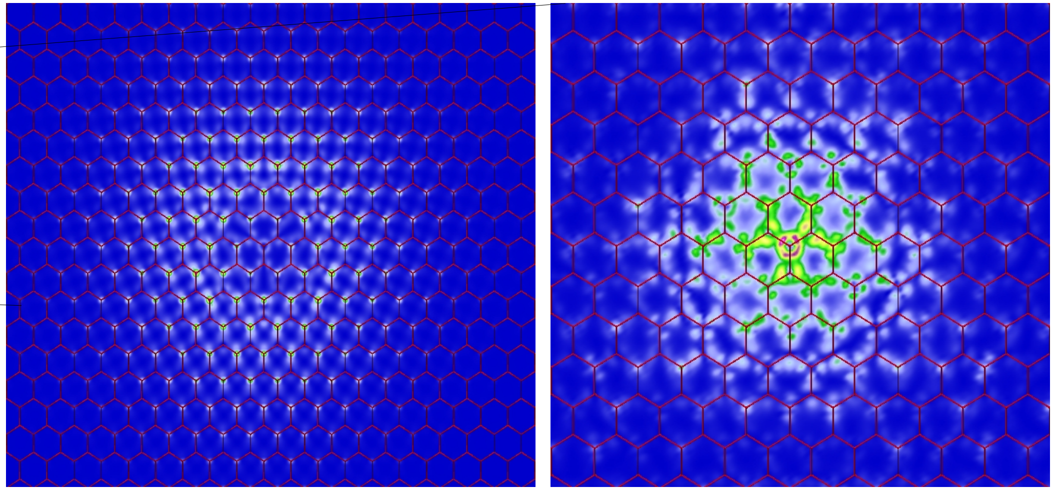
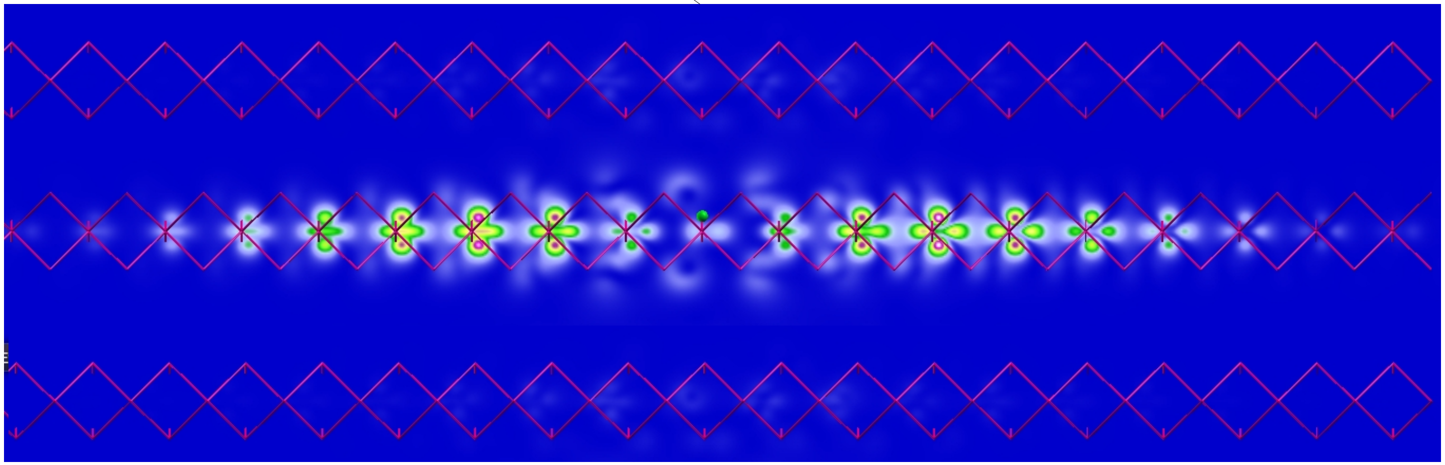




The intensity of the optical absorption is related with the localization of the excitons.

For bulk, the exciton is confined in only one layer, due to the large interlayer distance.



Excitonic wavefunction (d-orbitals)

Conclusions and ongoing work

- The bandgap (direct or indirect) depends critically on the number of layers and lattice optimization.
- Excitonic effects are stronger in enviroments with small dielectric constant (single-layers).
- Further studies will deal with strained layers and the influence on the optical response (tunability of the bandgap).

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Acknowledgements

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Thank you for your attention!

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