Direct/indirect band gap and exciton dispersion: Monolayer and bulk hexagonal boron nitride

L. Sponza, L. Schué, H. Amara, C. Attaccalite, F. Ducastelle, A. Loiseau, J. Barjon

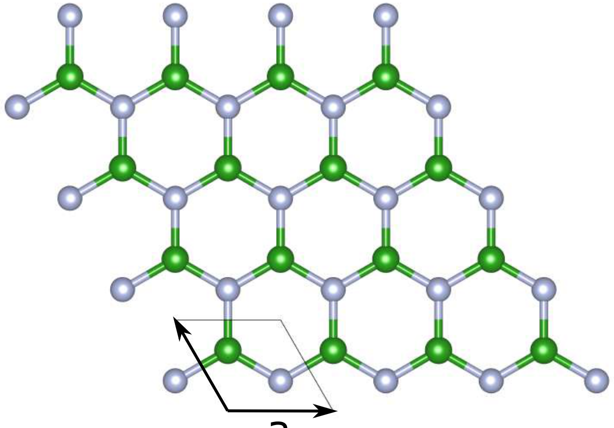
Graphene 2018 26-29/06 Dresden

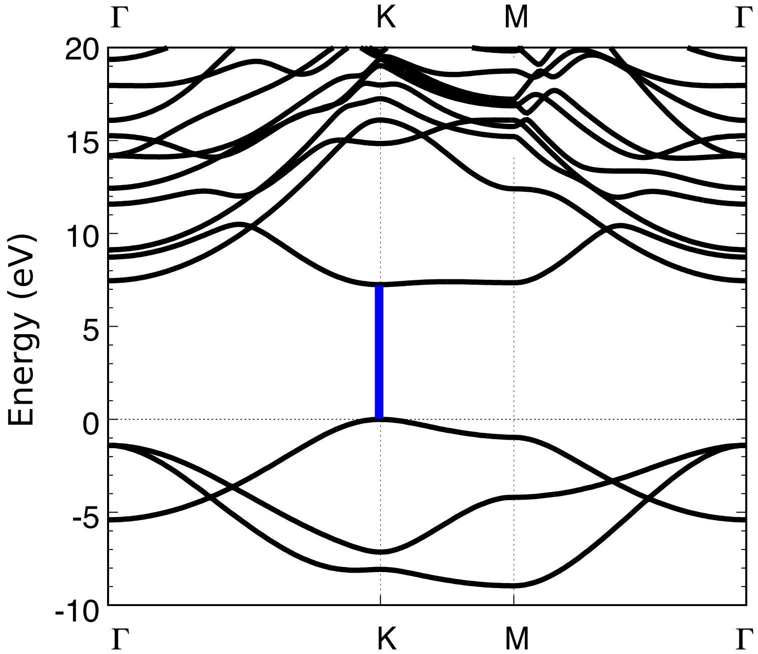
Outlook

- **The curious spectra of hexagonal boron nitride (hBN)**
  - contradiction between electronic and optical properties
  - modeling free carriers and excitons
- **Tight-binding model of the exciton**
  - validation of the model in the monolayer
  - insight from the monolayer to the bulk
- **Ab initio exciton dispersion in bulk hBN**
  - conciliation of the contraddictions (theory)
  - experimental evidences
- **Predictions about the Bernal stacking**

Hexagonal boron nitride: electronic structure

Monolayer





quasiparticle gap

GGA + 2.75 eV

direct K	7.25 eV
indirect KM	7.35 eV

L. Sponza et al., arXiv:1806.06201 (2018)

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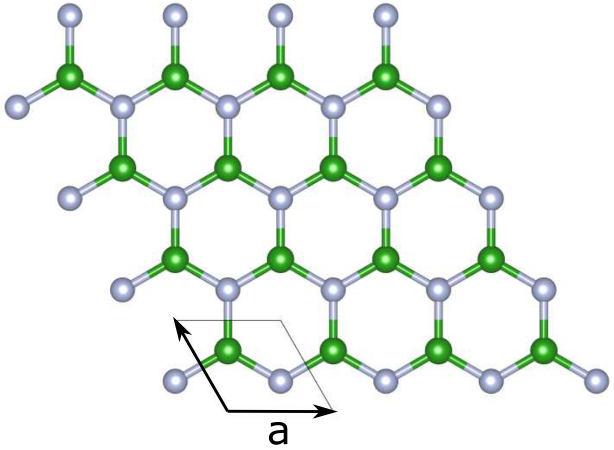

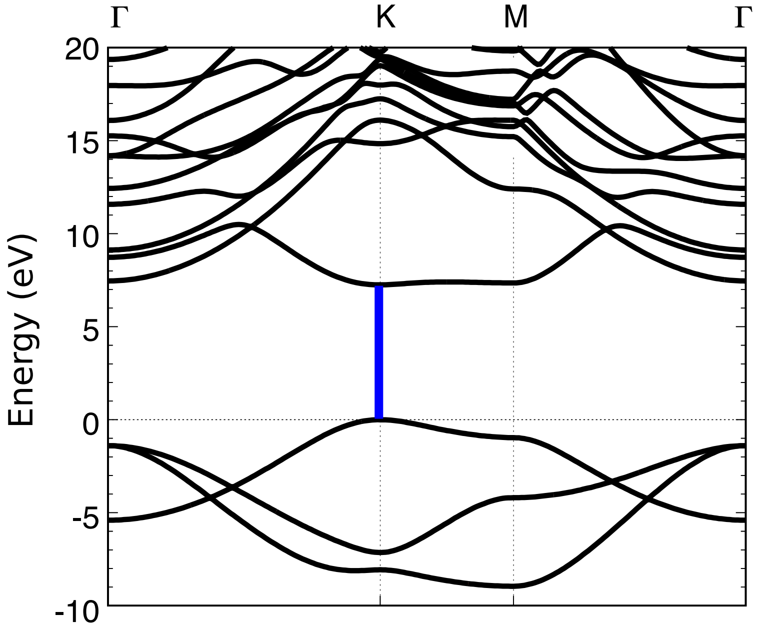

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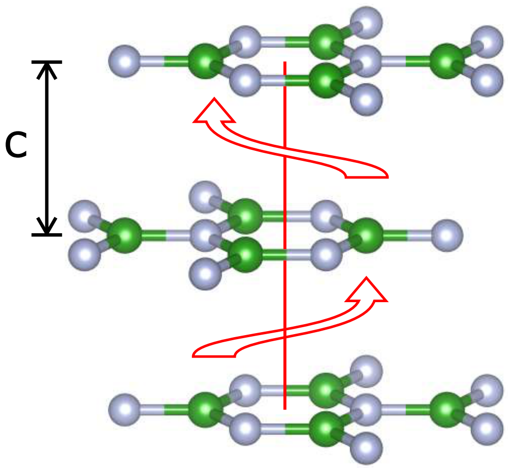
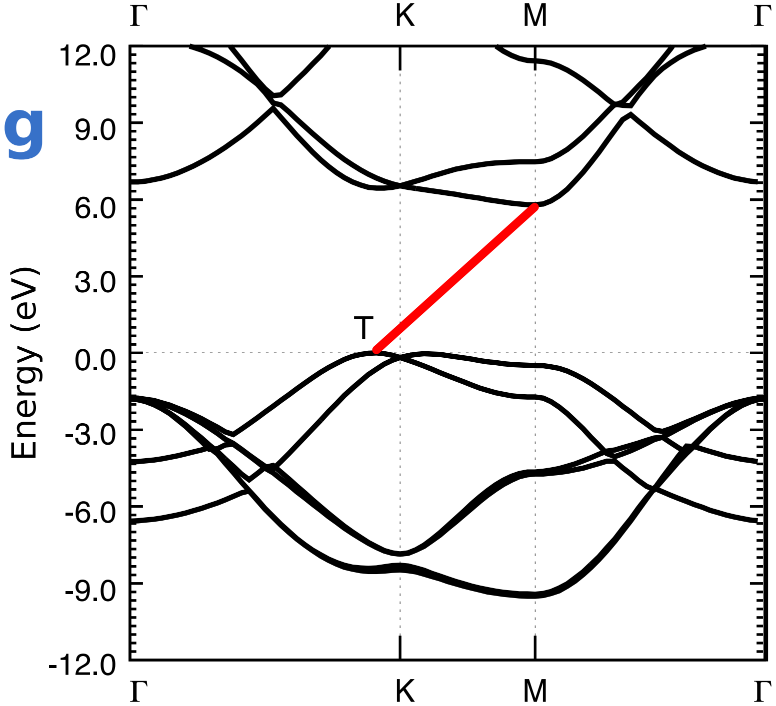
Bulk: AA' stacking





quasiparticle gap

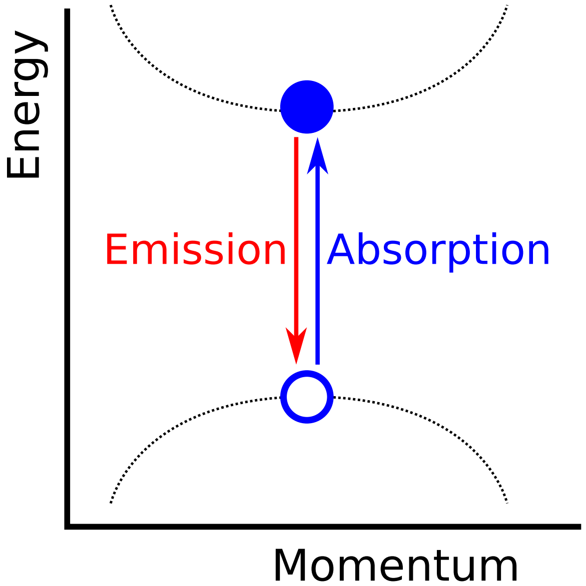
LDA + G_0W_0

direct T	6.45 eV
direct M	6.28 eV
indirect TM	5.80 eV

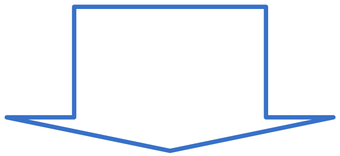
L. Sponza et al., arXiv:1806.06201 (2018)

Expectations from direct and indirect gaps

Direct gap



coupling only
to **photons (q=0)**



- High probability
- High efficiency

Expectations from direct and indirect gaps

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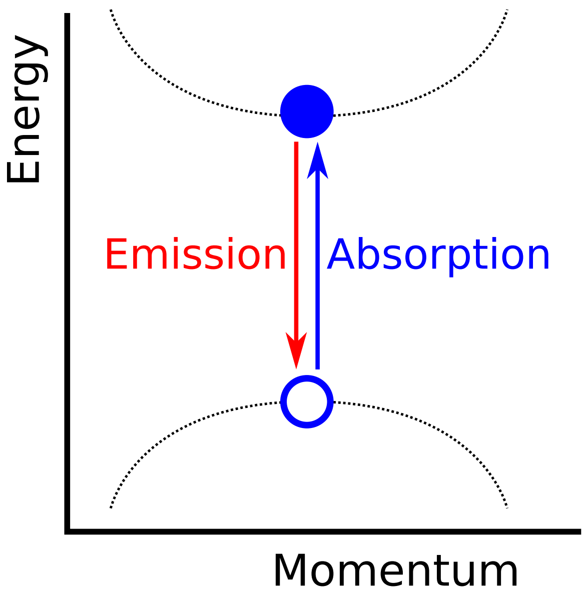

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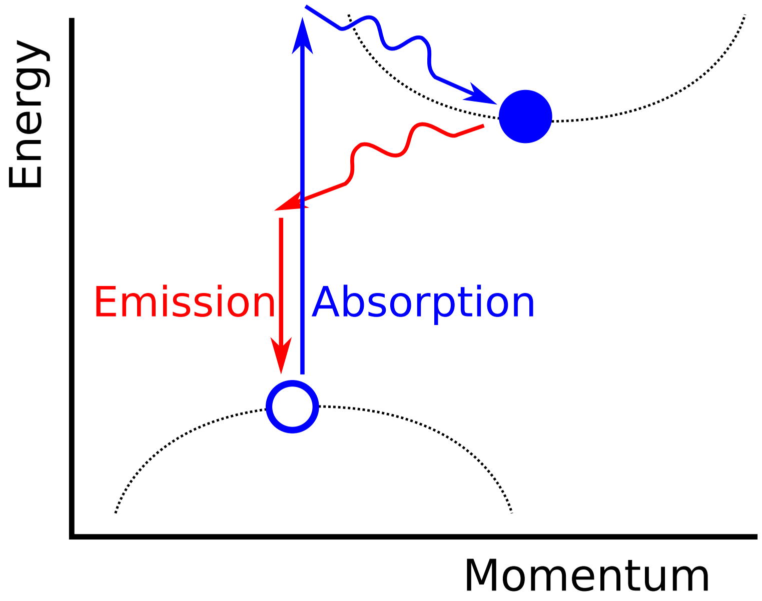
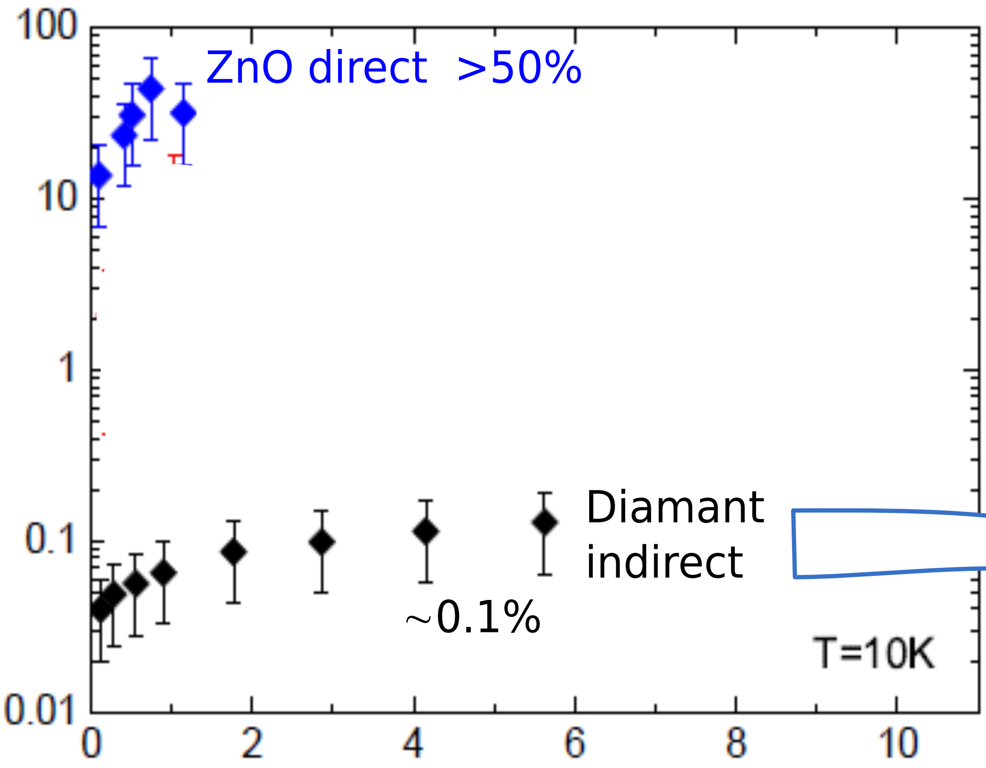
Indirect gap

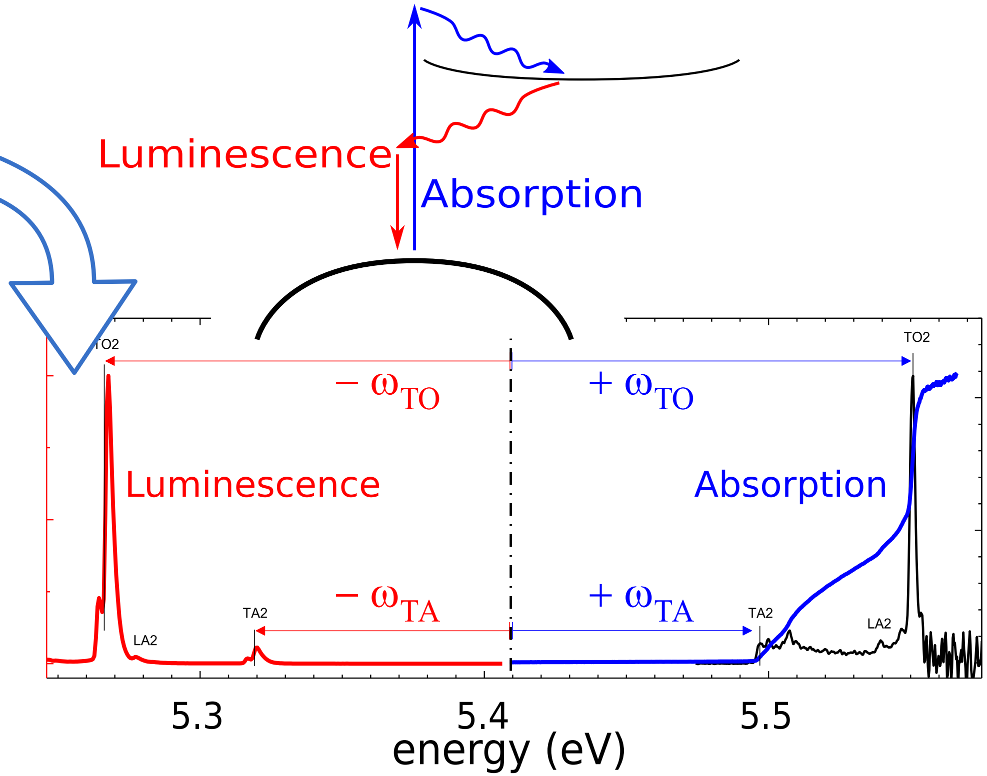


coupling
to **photons (q=0)**
and **phonons (q≠0)**

- Low probability
- Low efficiency

Experimental luminescence of bulk hBN





Paradigmatic indirect gap material (diamond) has **low luminescence efficiency** and **abs/lum mirror symmetry** holds for spectra.

L. Schué et. al., arXiv:1803.03766 (2018)

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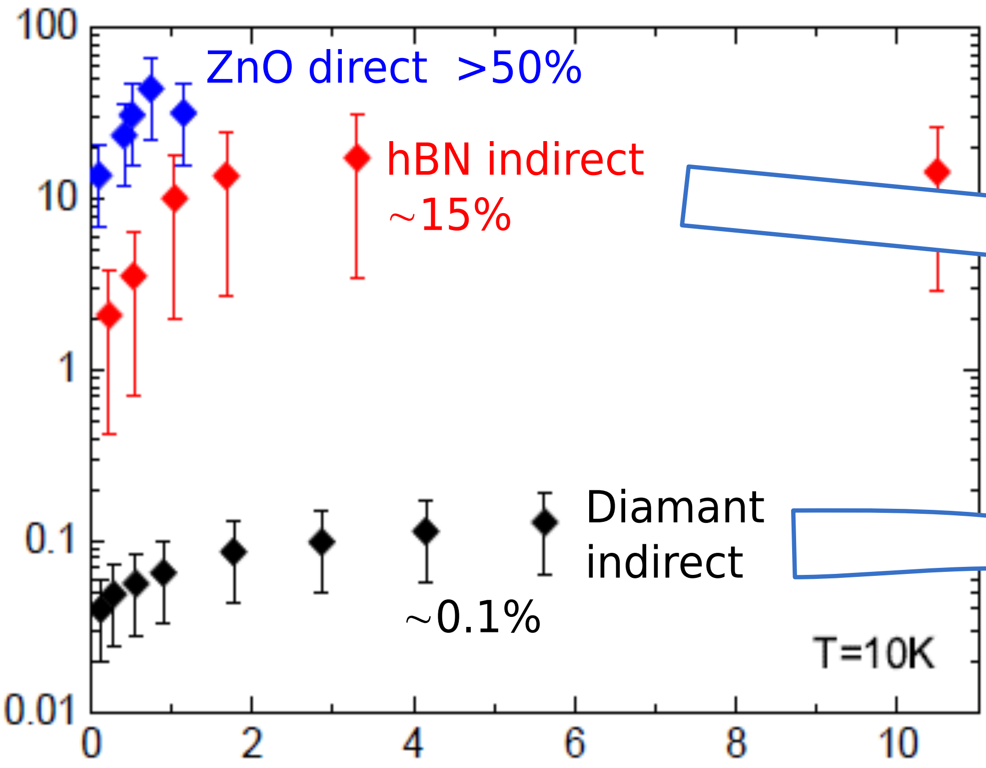
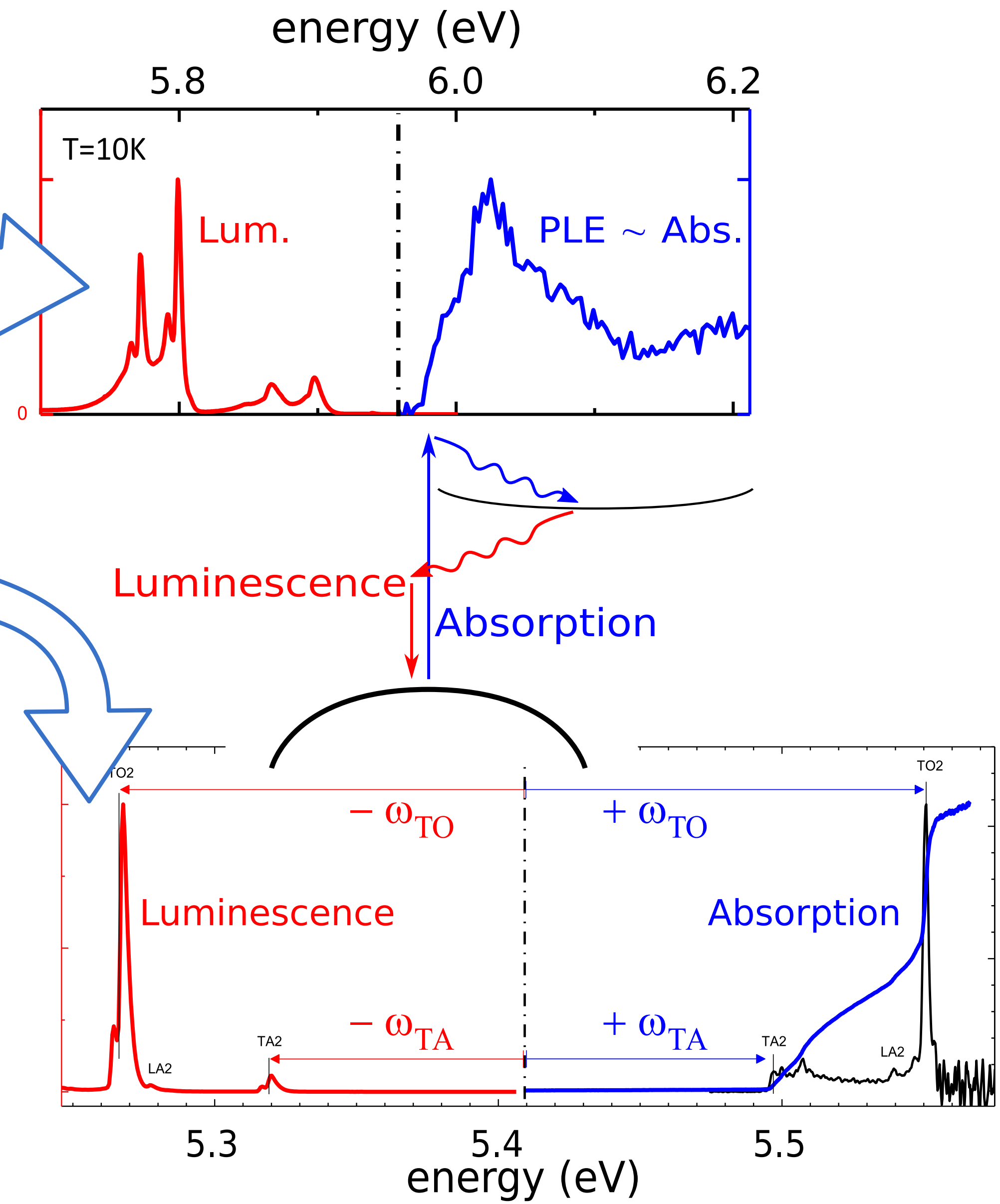
High luminescence efficiency



No abs/lum mirror symmetry



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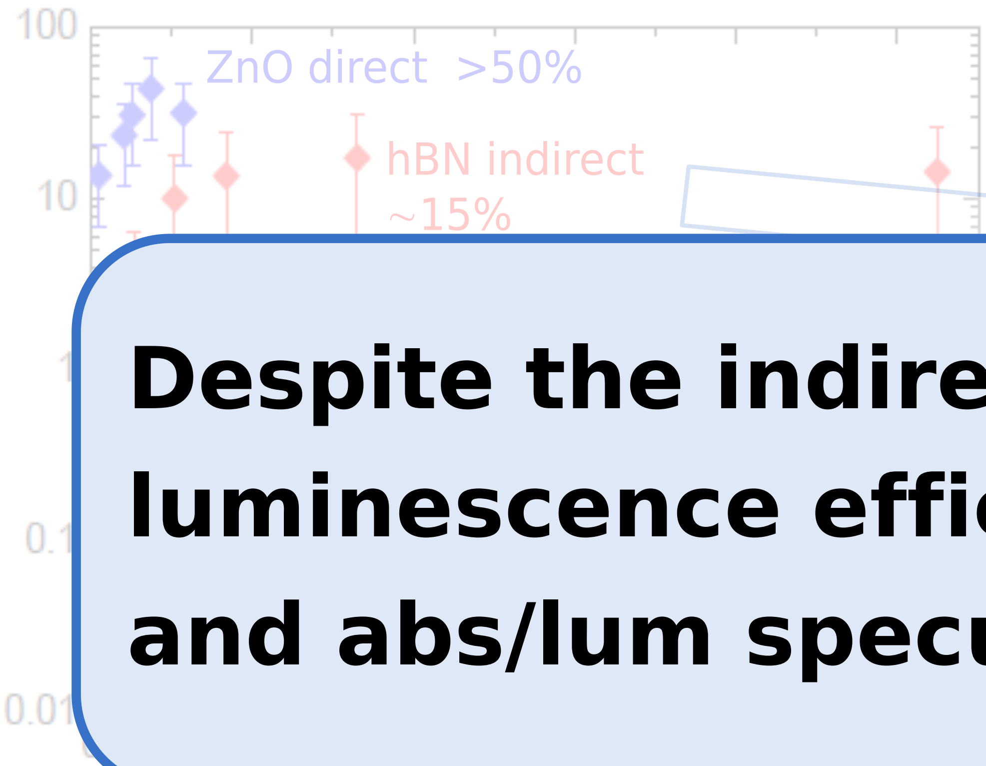
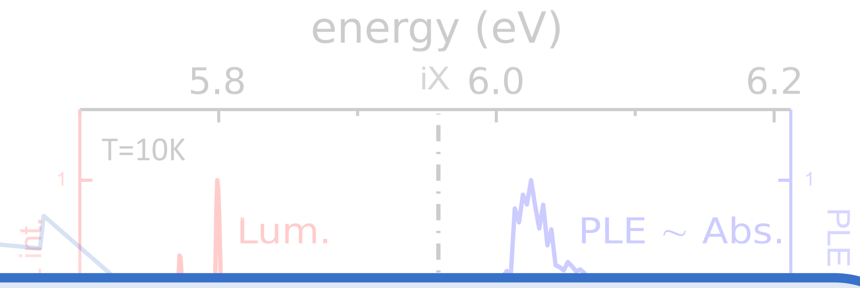
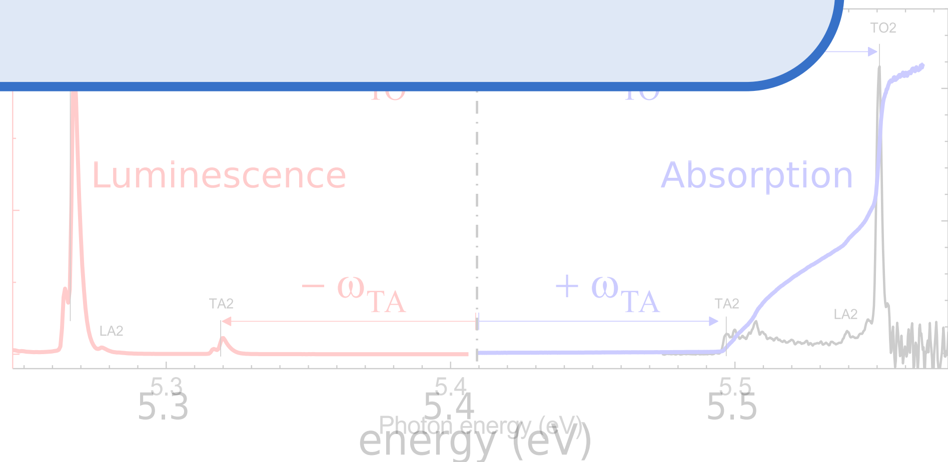




Despite the indirect gap of bulk hBN, luminescence efficiency is very high and abs/lum specularity does not hold



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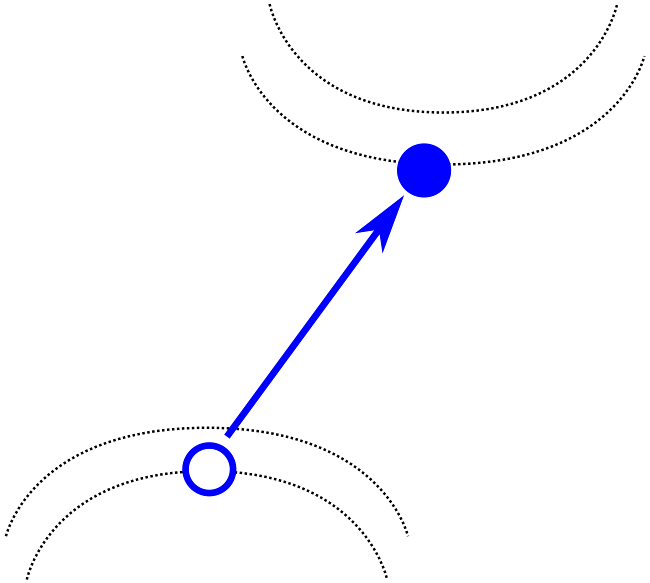
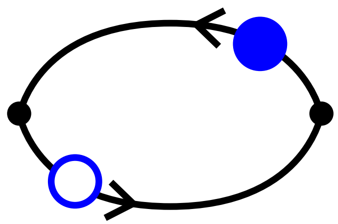
1-particle and 2-particle excitations

Free carriers: electron + hole

Quasiparticle: scissor, GW...
two 1-particle propagators

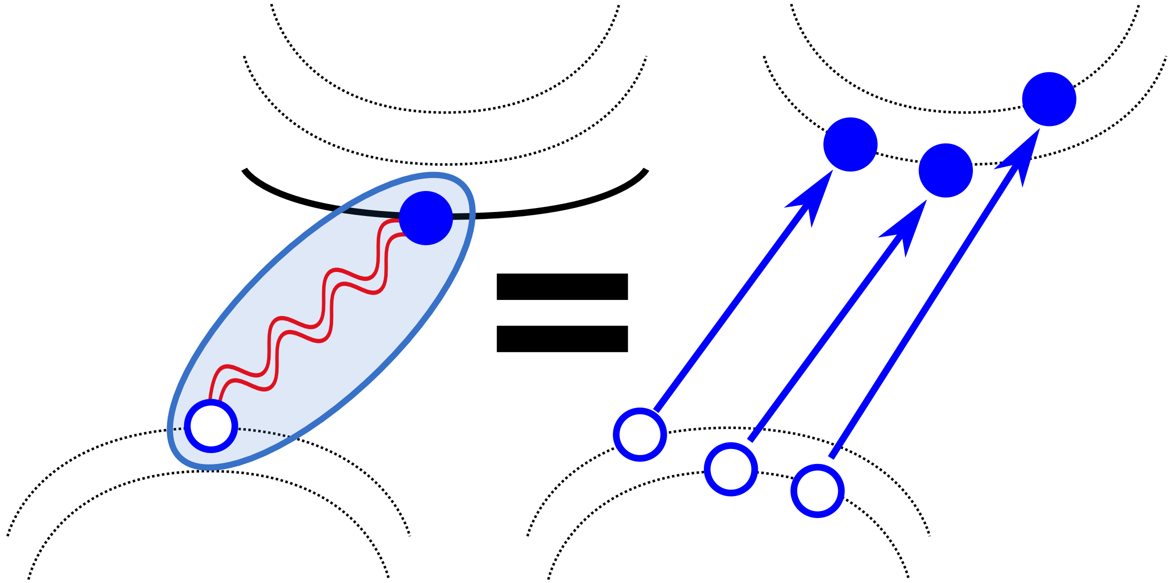


Dipole-allowed transitions between points of the **band structure**.

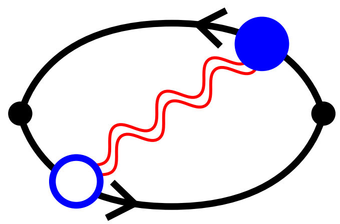


Exciton: electron-hole pair

Bethe-Salpeter equation
single 2-particle propagator

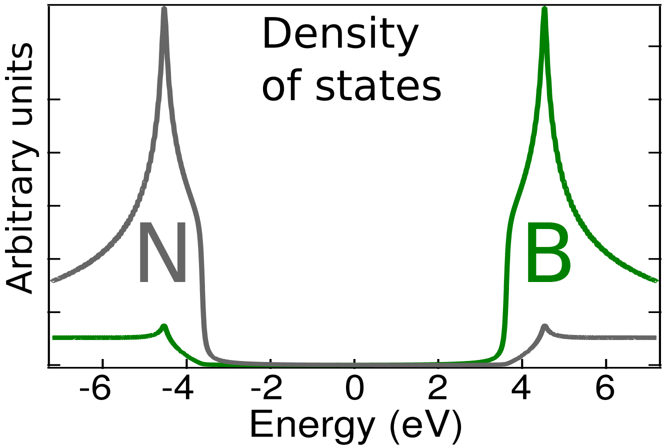


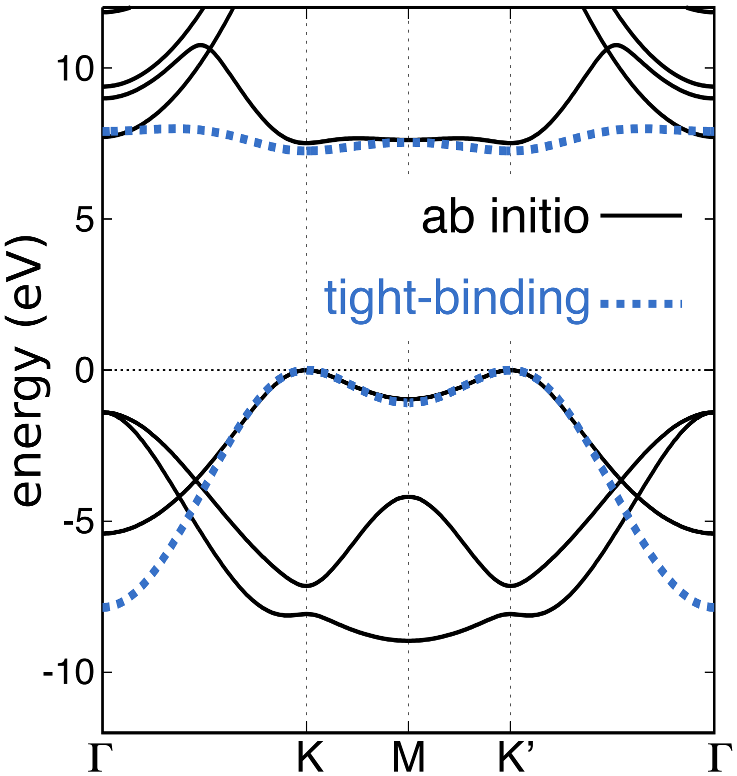
Excitonic Hamiltonian on a basis of free carriers. **Excitonic levels**.



1-particle and 2-particle excitations

1-particle model





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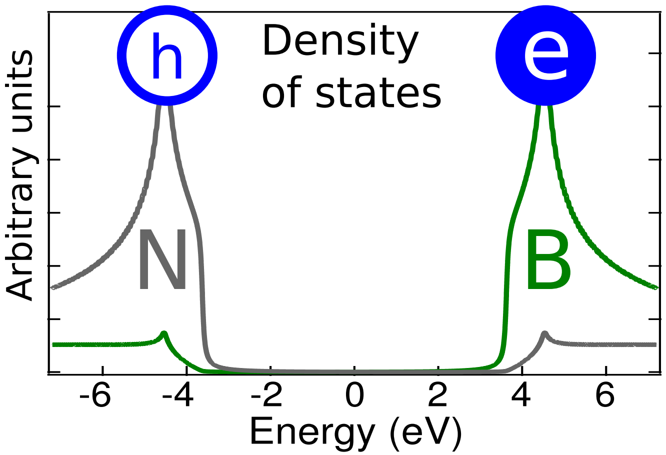
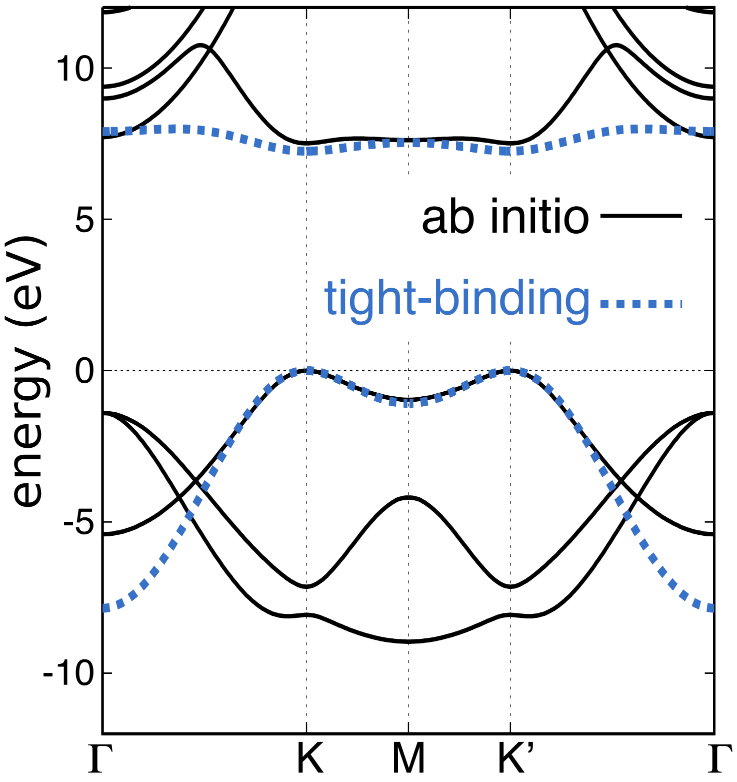
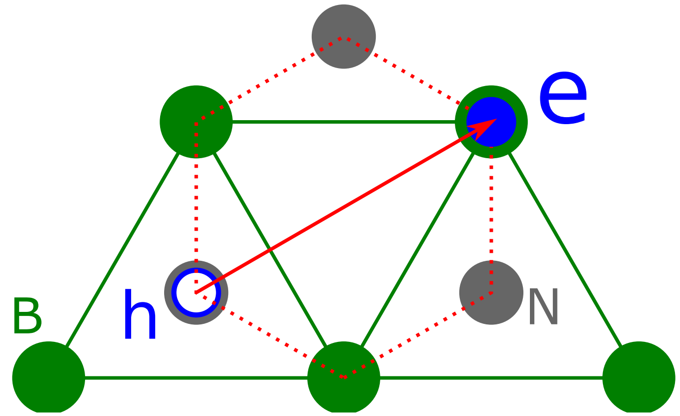




Excitonic model

T. Galvani, PRB **94** (2016)

1-particle
triangular lattice
attractive source



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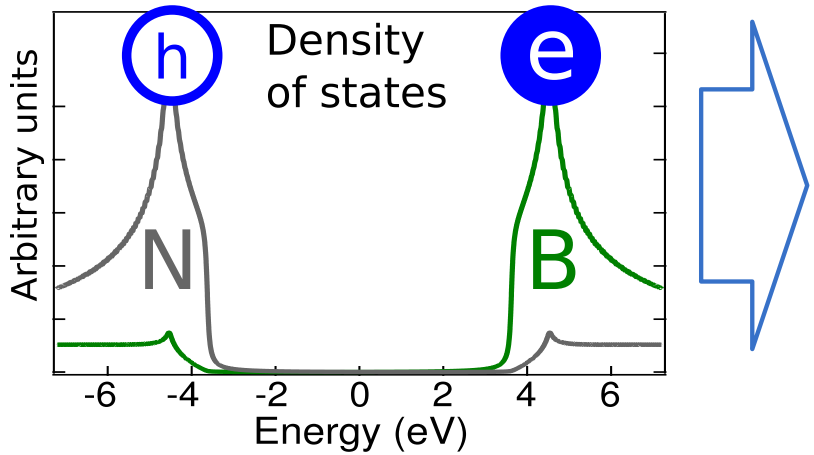

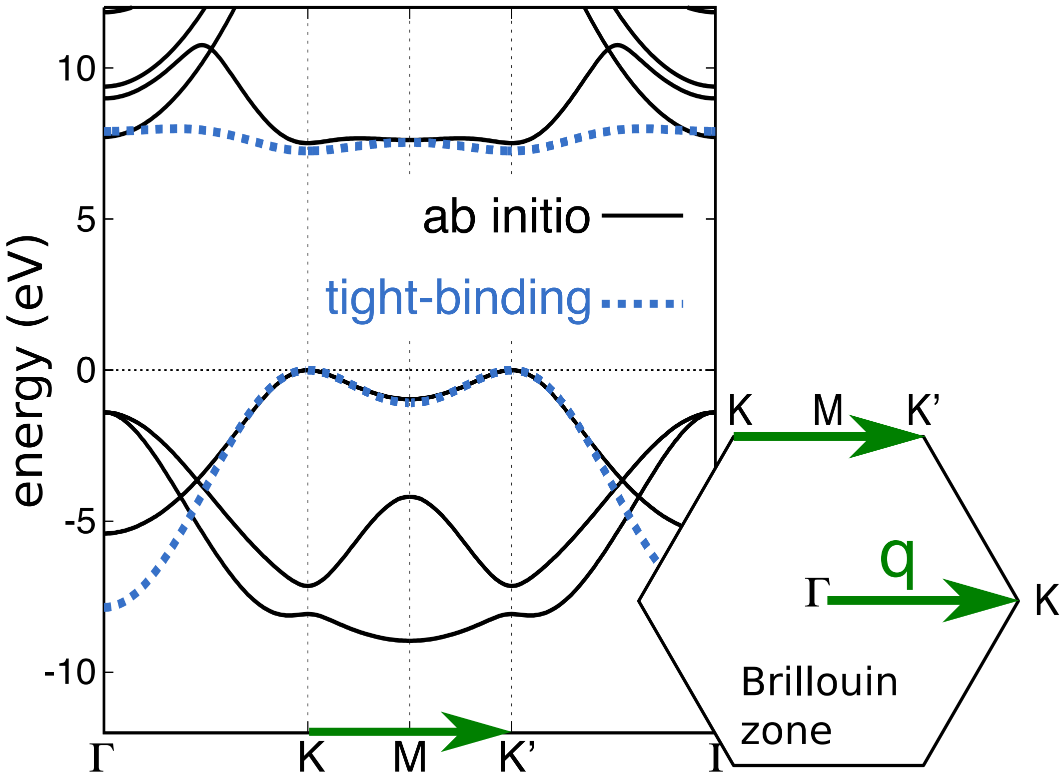

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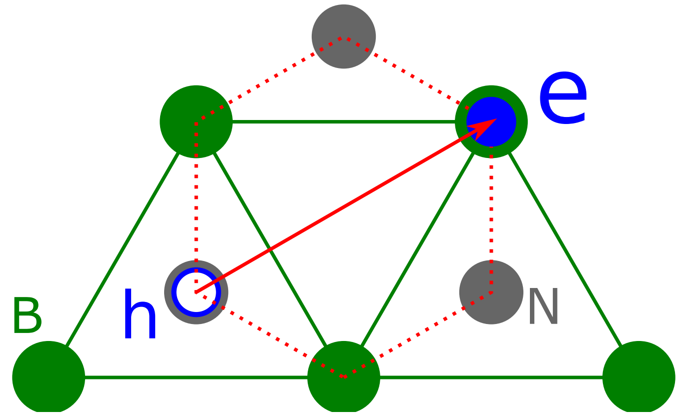

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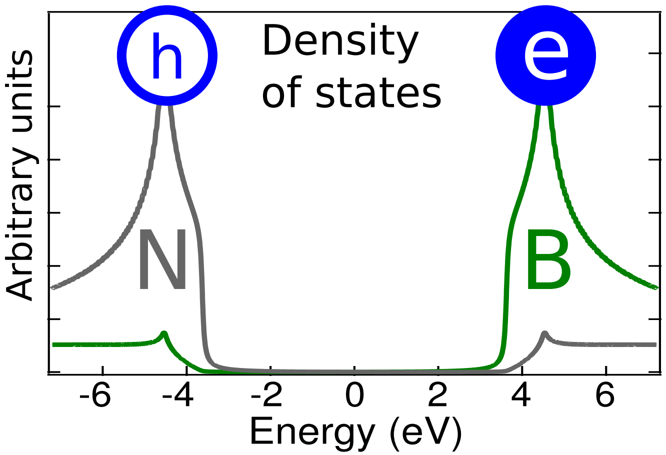

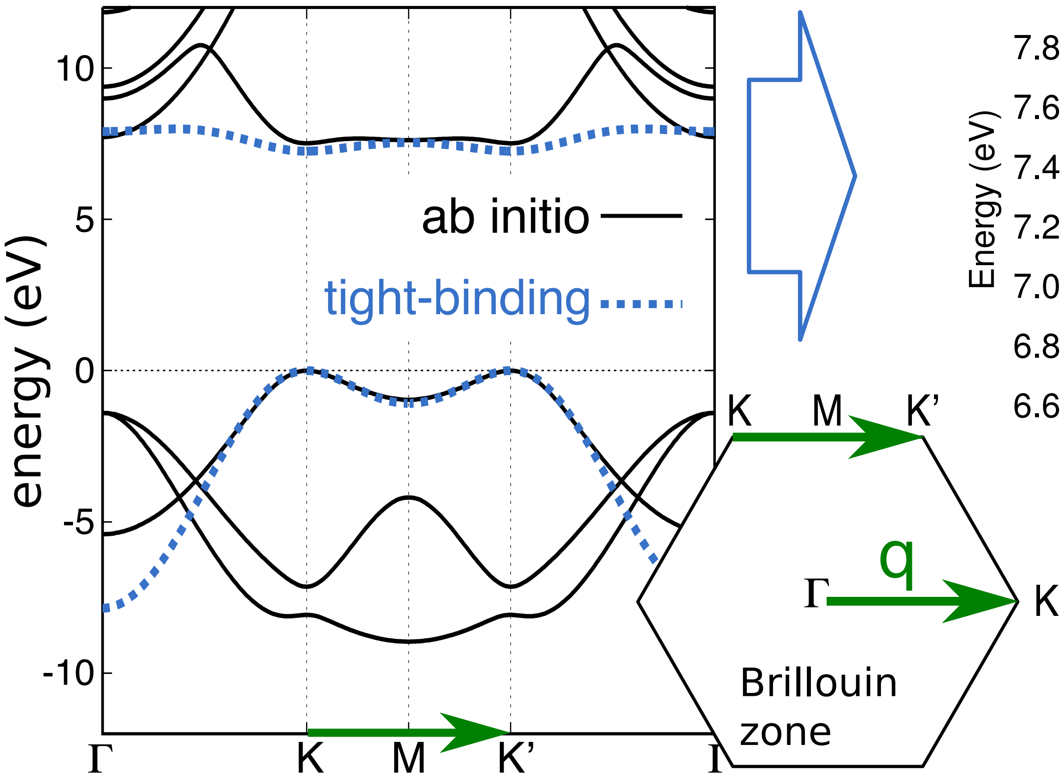

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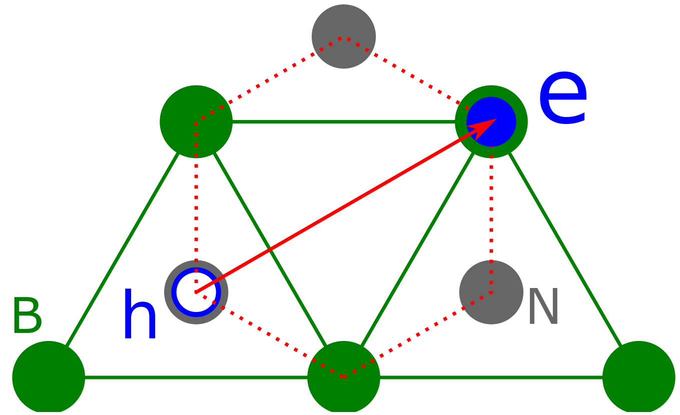

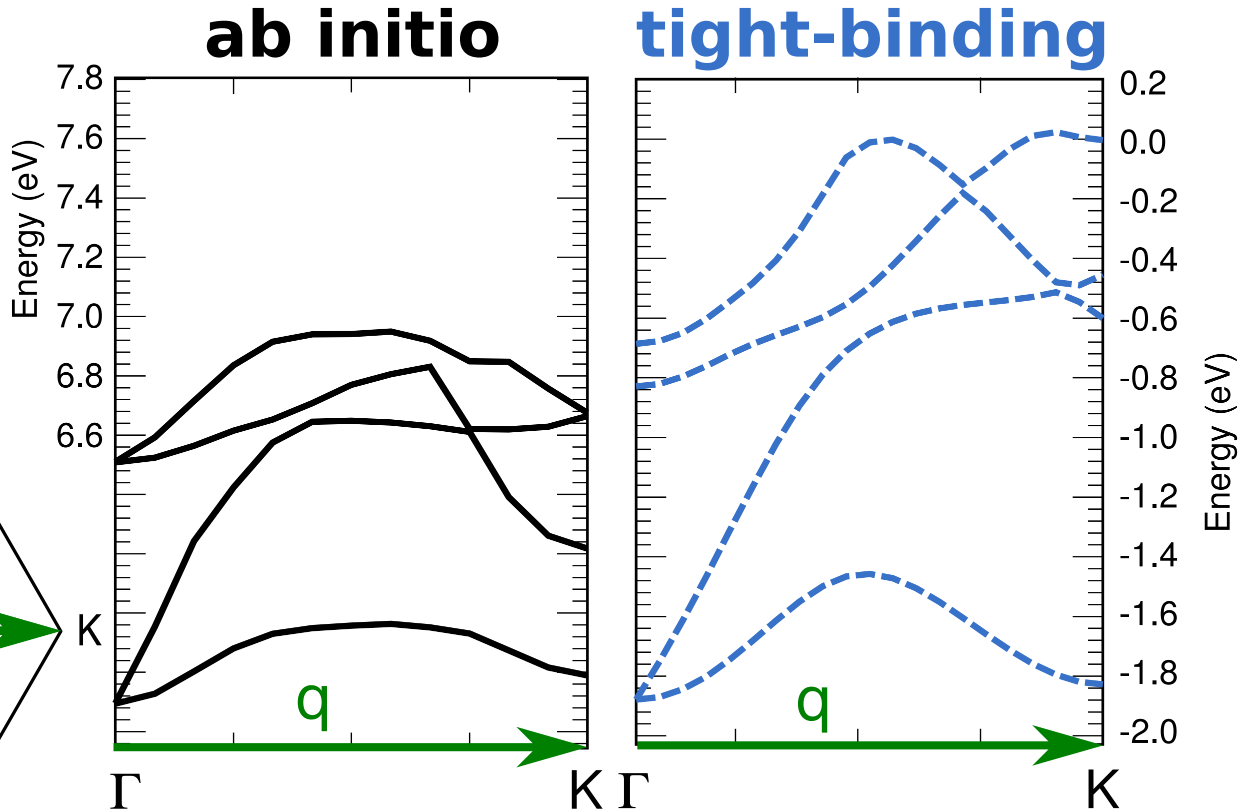

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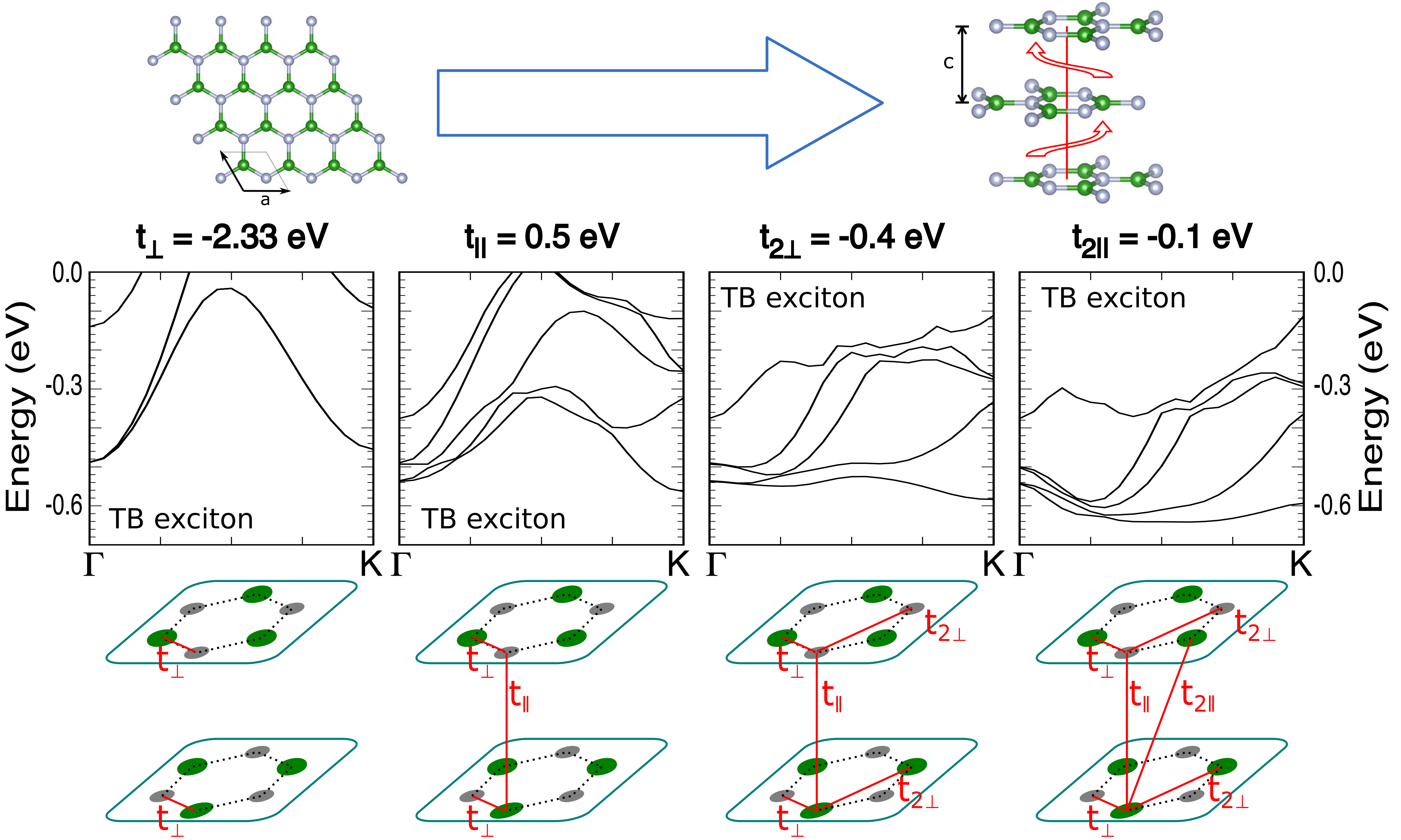
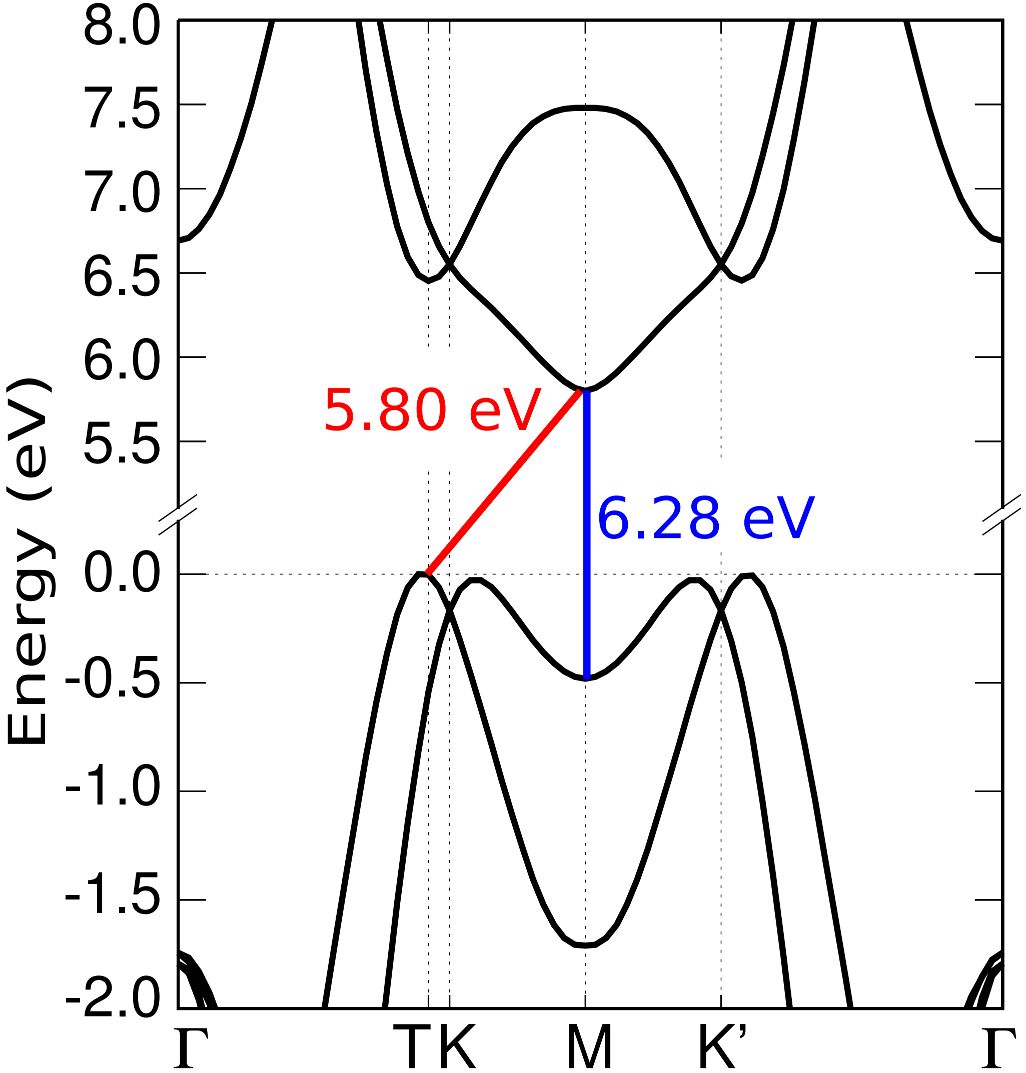
From monolayer to bulk AA'



L. Sponza et al., arXiv:1806.06201 (2018)

Exciton dispersion in bulk AA'

ab-initio band structure



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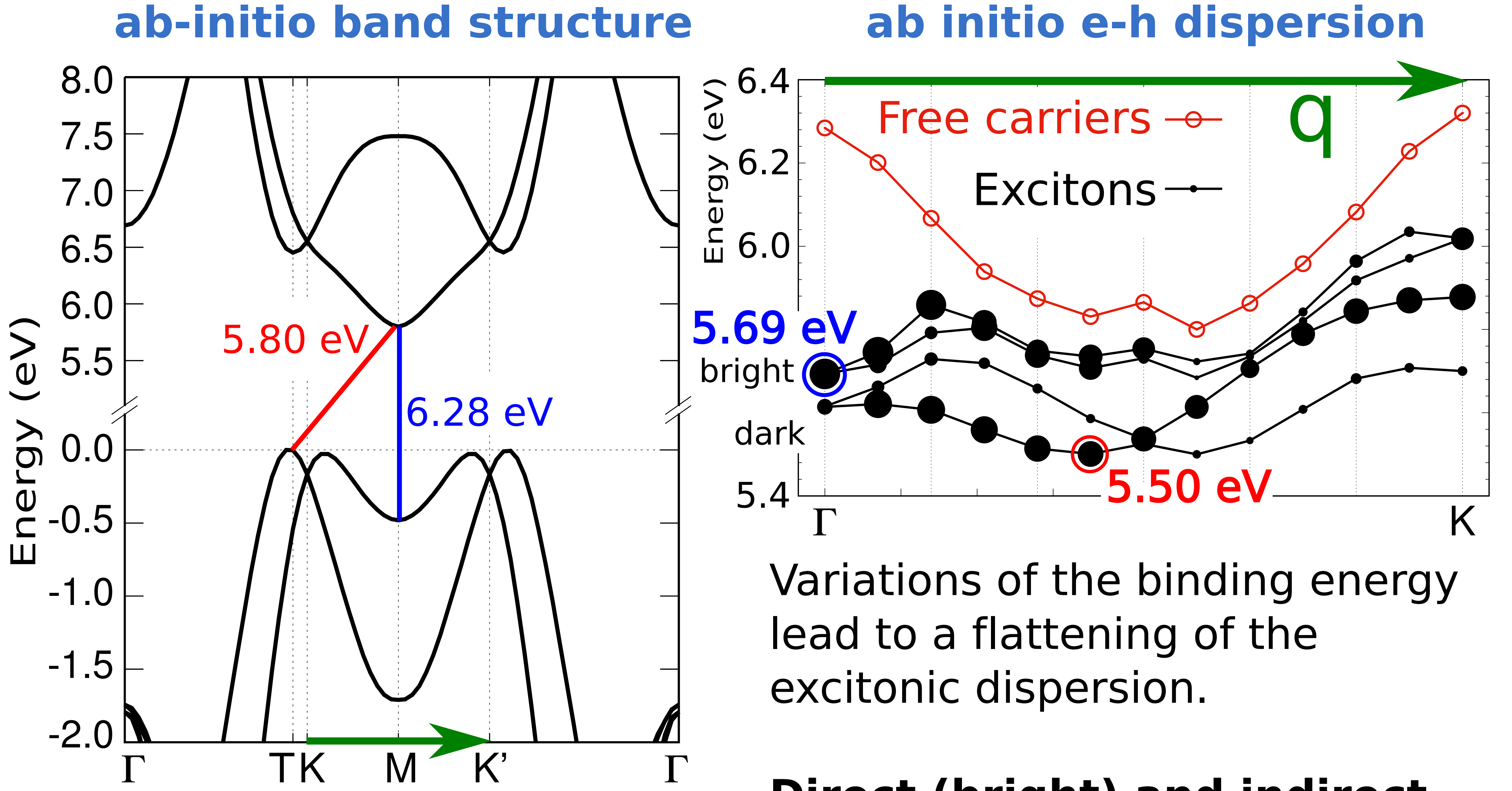


Variations of the binding energy lead to a flattening of the excitonic dispersion.

Direct (bright) and indirect excitons lie within 0.2 eV.

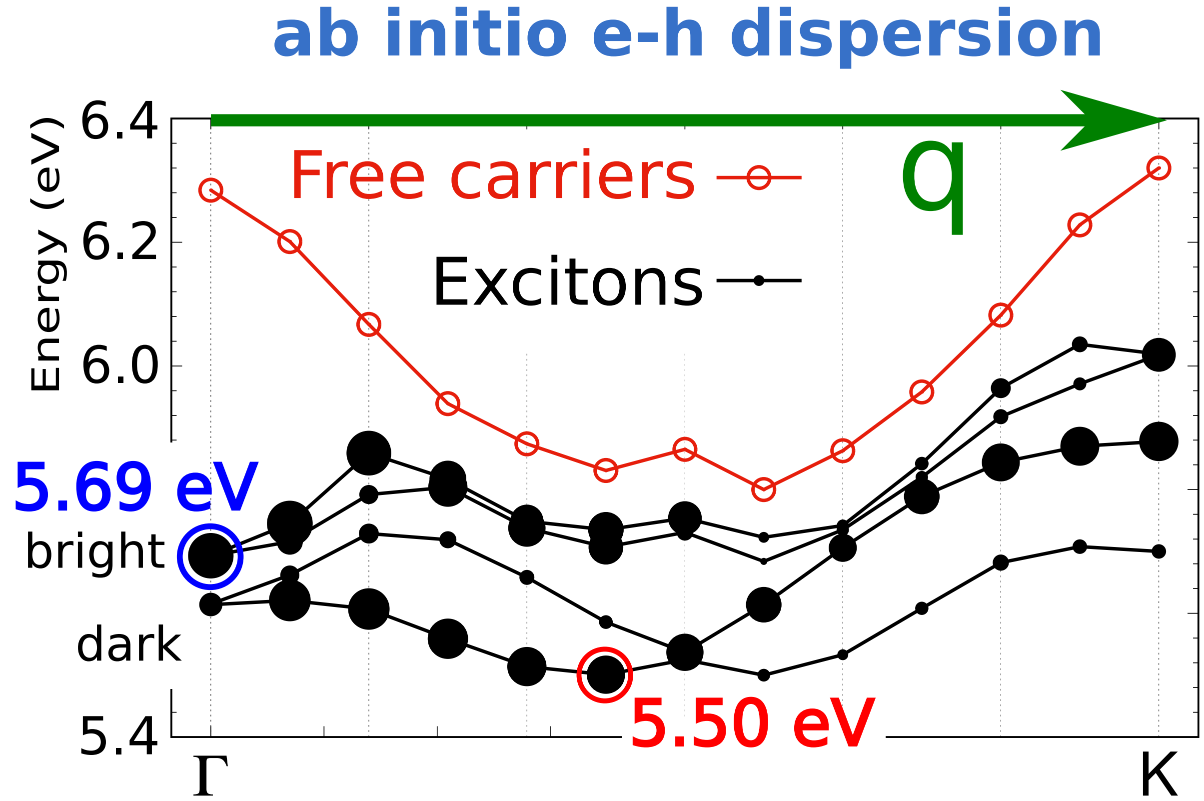
L. Sponza et al., arXiv:1806.06201 (2018)

Consistent explanation of the optical properties

Flat dispersion = localized e-h

a) Electron and hole spatially close (high overlap)

b) Strong exciton-phonon coupling.



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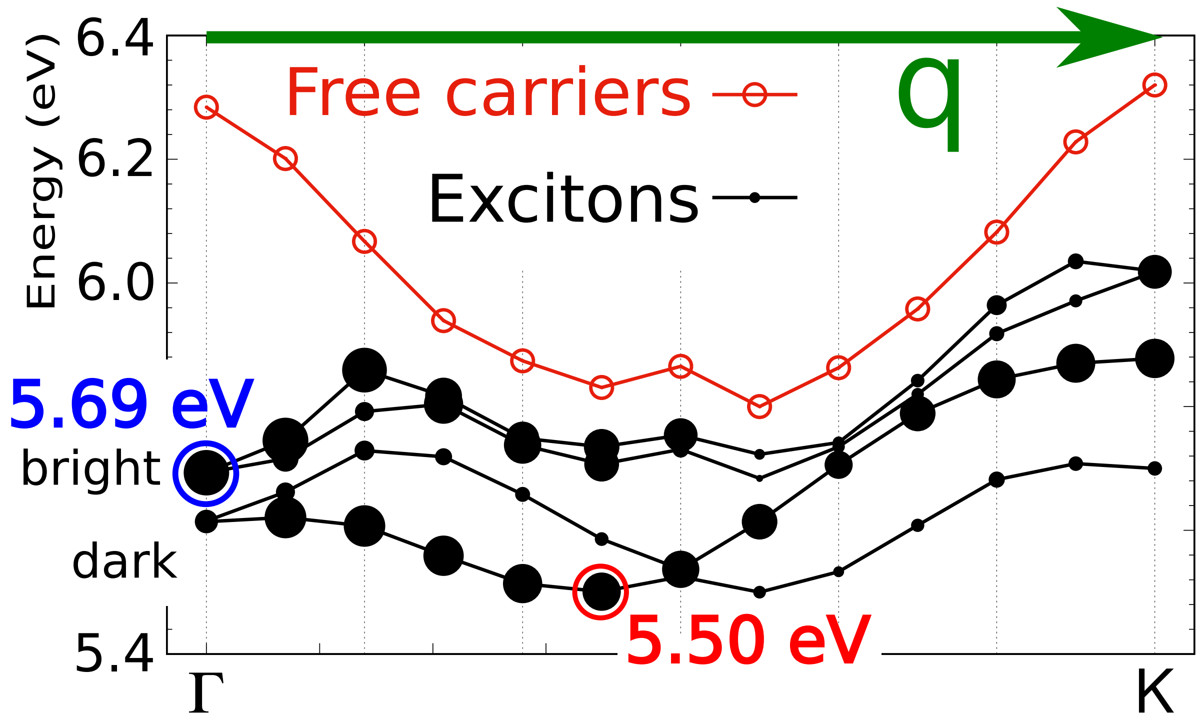

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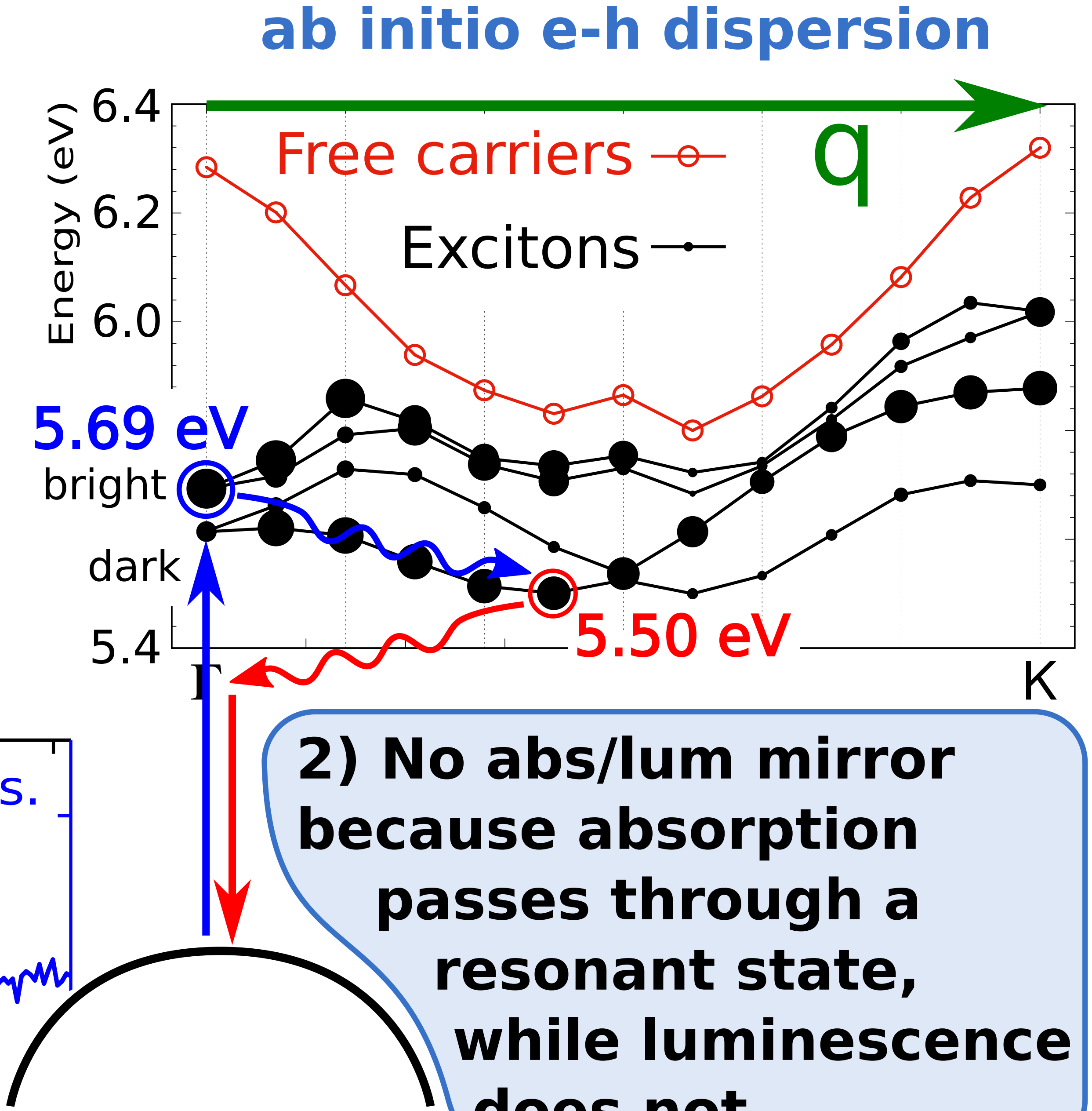
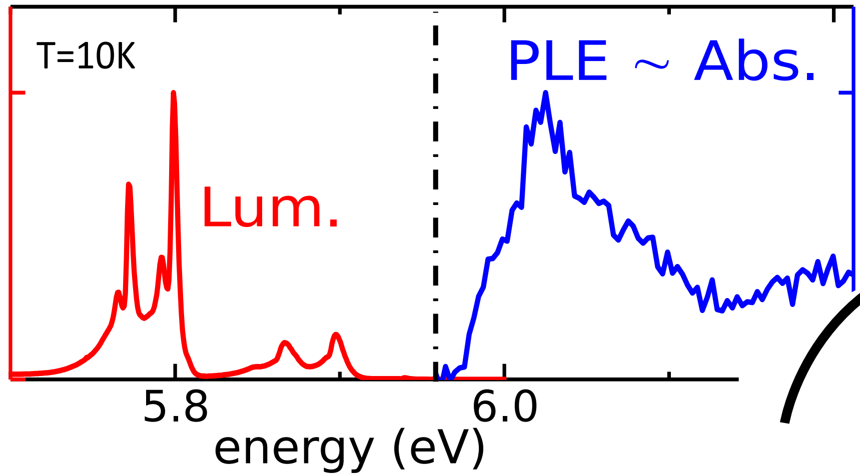


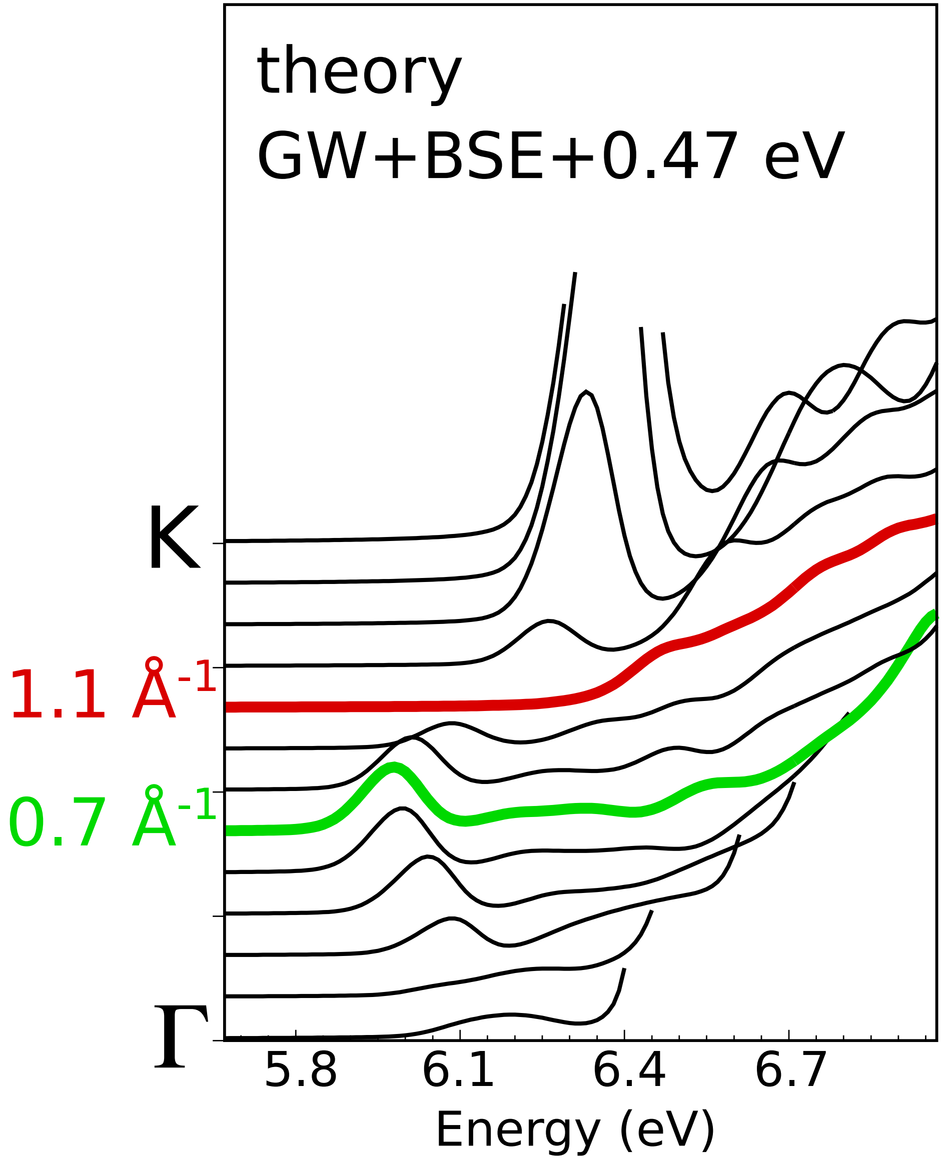


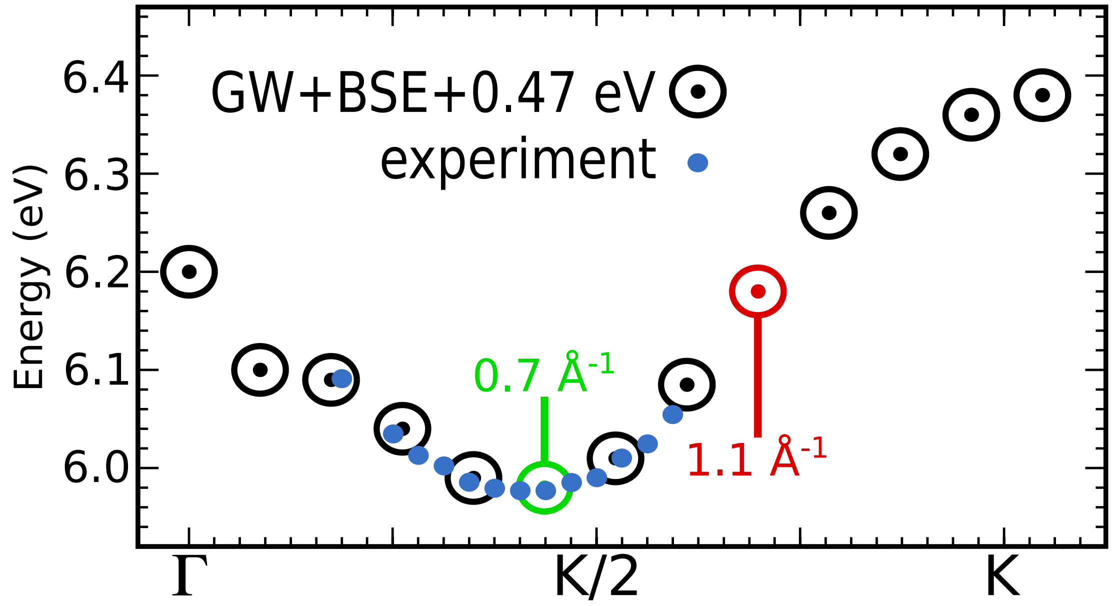
2) No abs/lum mirror because absorption passes through a resonant state, while luminescence does not.

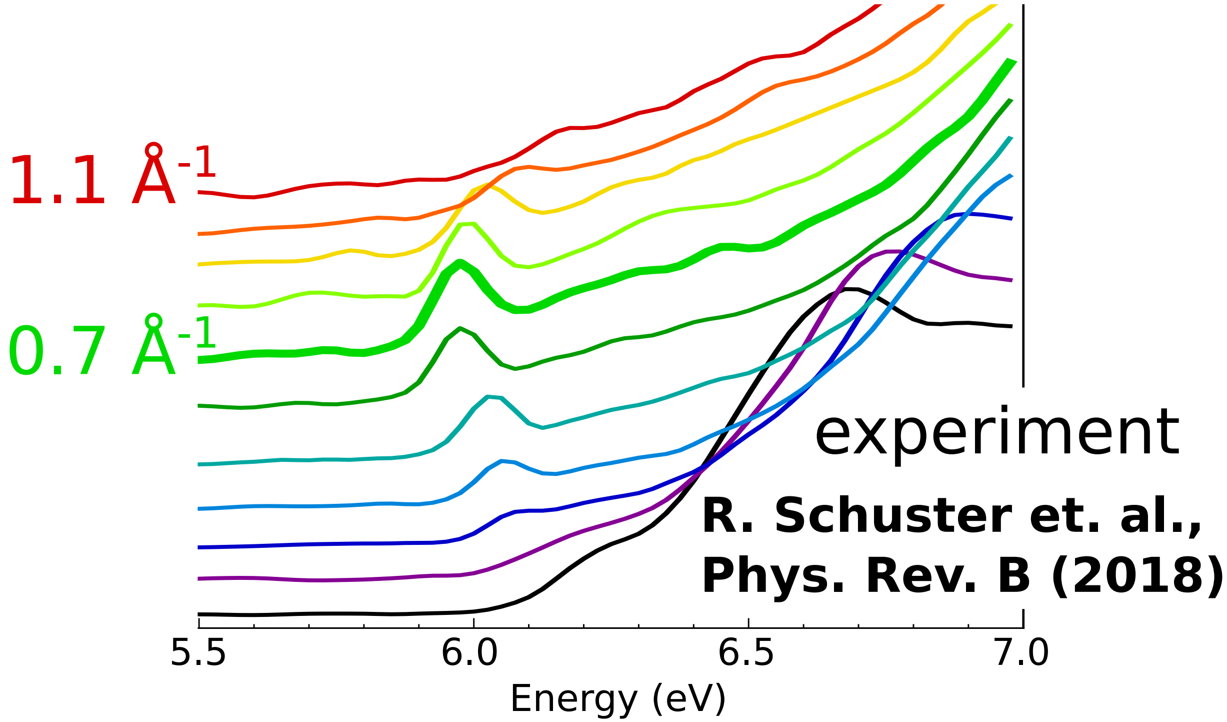
L. Sponza et al., arXiv:1806.06201 (2018)

Confirmation from experimental evidences

Loss function at finite q



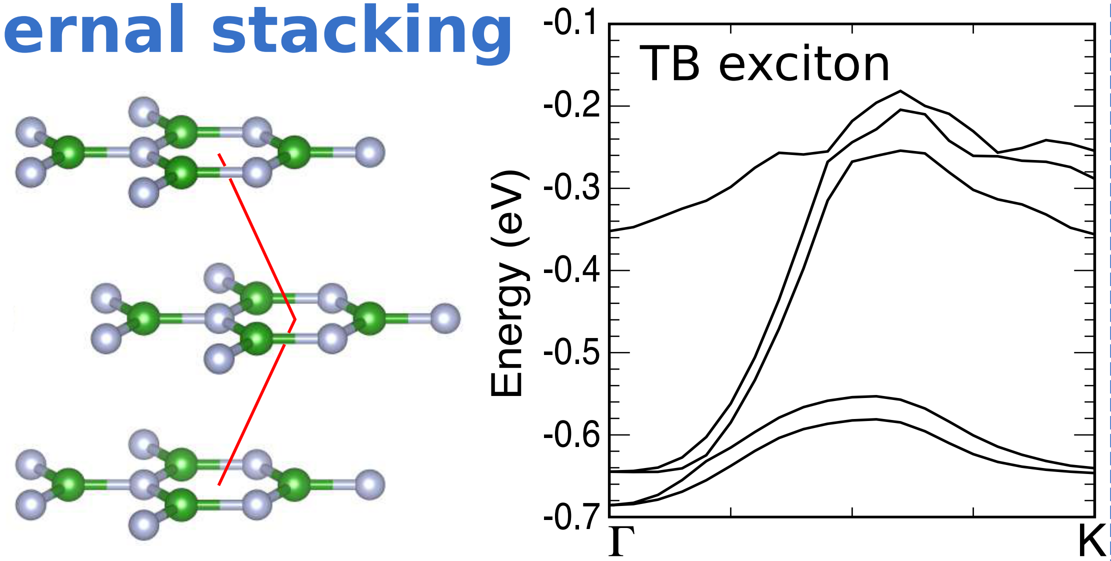




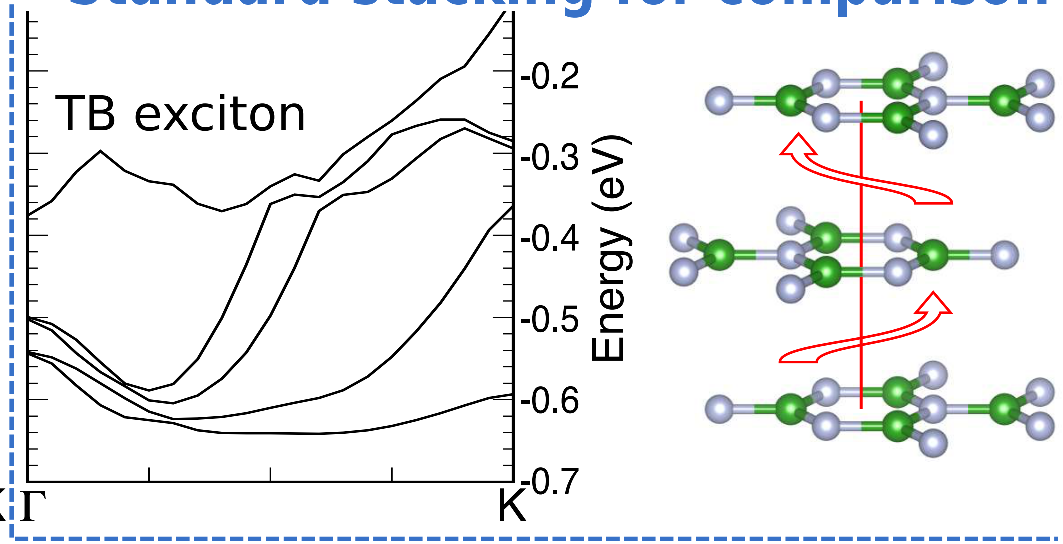
L. Sponza et al., Phys. Rev. B 97, 075121 (2018)

Intriguing prediction about Bernal stacking

Bernal stacking



Standard stacking for comparison



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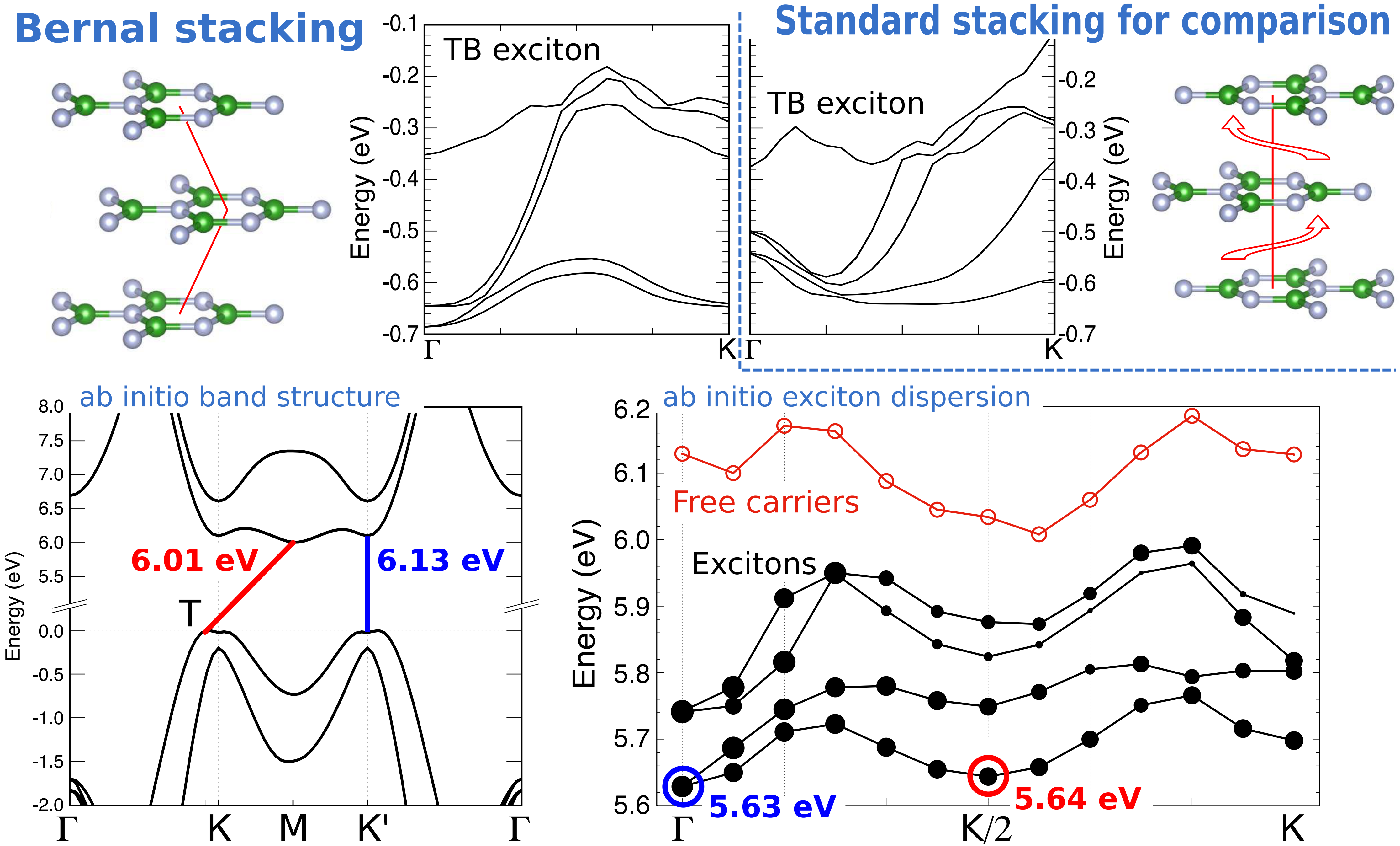

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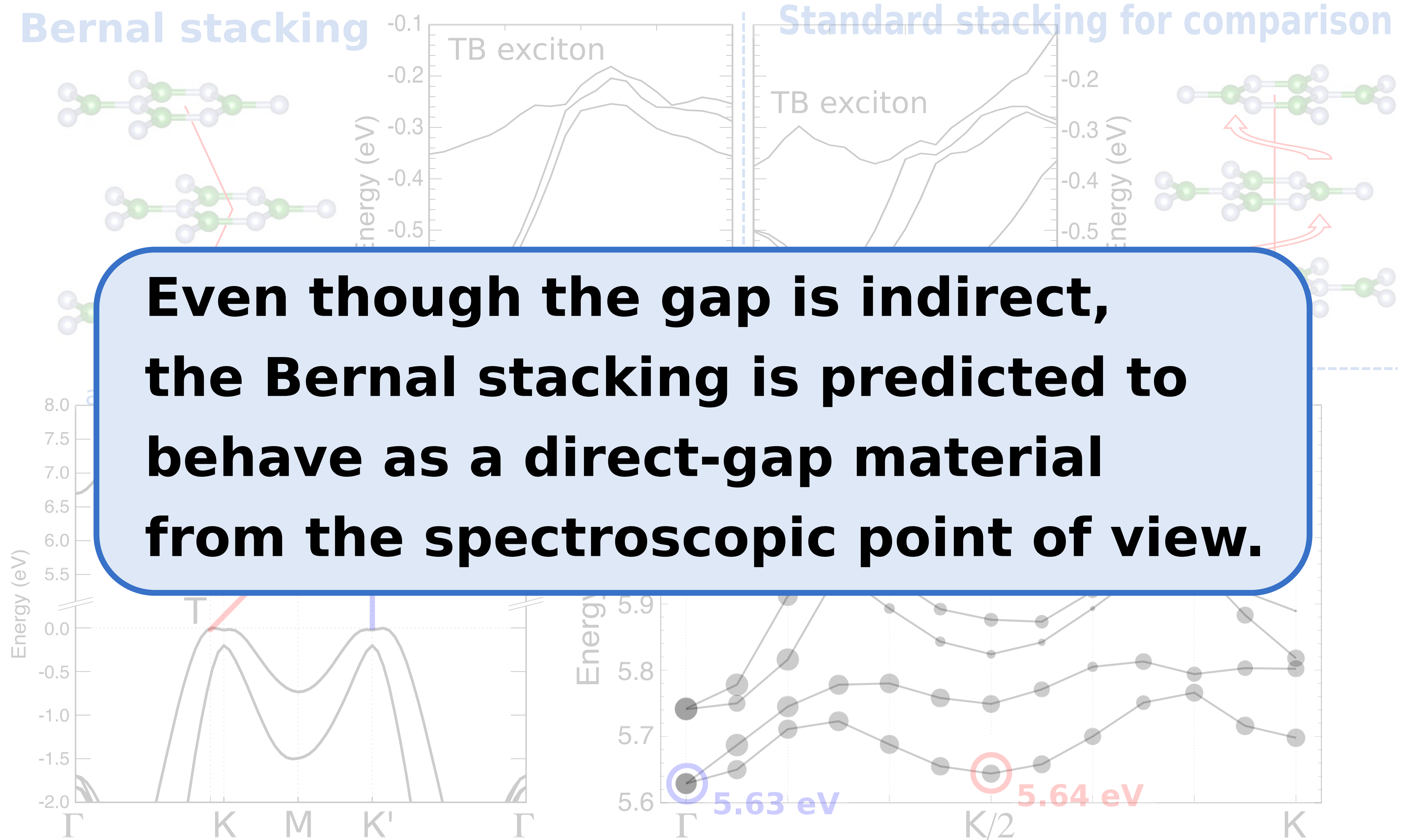

Even though the gap is indirect, the Bernal stacking is predicted to behave as a direct-gap material from the spectroscopic point of view.

L. Sponza et al., arXiv:1806.06201 (2018)

Conclusions

1) **Tight-bidning model for excitons in 2D** and layered hBN.
   Insight when applied to bulk and to different polymorphs.

2) **Flattening of the exciton dispersion** in hBN leads to a
   strong electron-phonon coupling and high emission efficiency.
   Consistent explanation of conflicting data coming from
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   Experimental evidence of the theoretical explanation.

3) **Prediction of even stronger effect in Bernal hBN.**

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2)

Thanks for your attention

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