Phonon-assisted luminescence in hBN monolayer from first principles

Pierre Lechifflart[1], Fulvio Paleari[2], Davide Sangalli[3], Claudio Attaccalite[1,4]

1 CNRS/CINaM, Aix-Marseille Univ, Marseille, France **2** CNR-NANO, Modena, Italy **3** ISM-CNR, FLASHit, Monterotondo Scalo, Italy **4** European Theoretical Spectroscopy Facilities (ETSF)

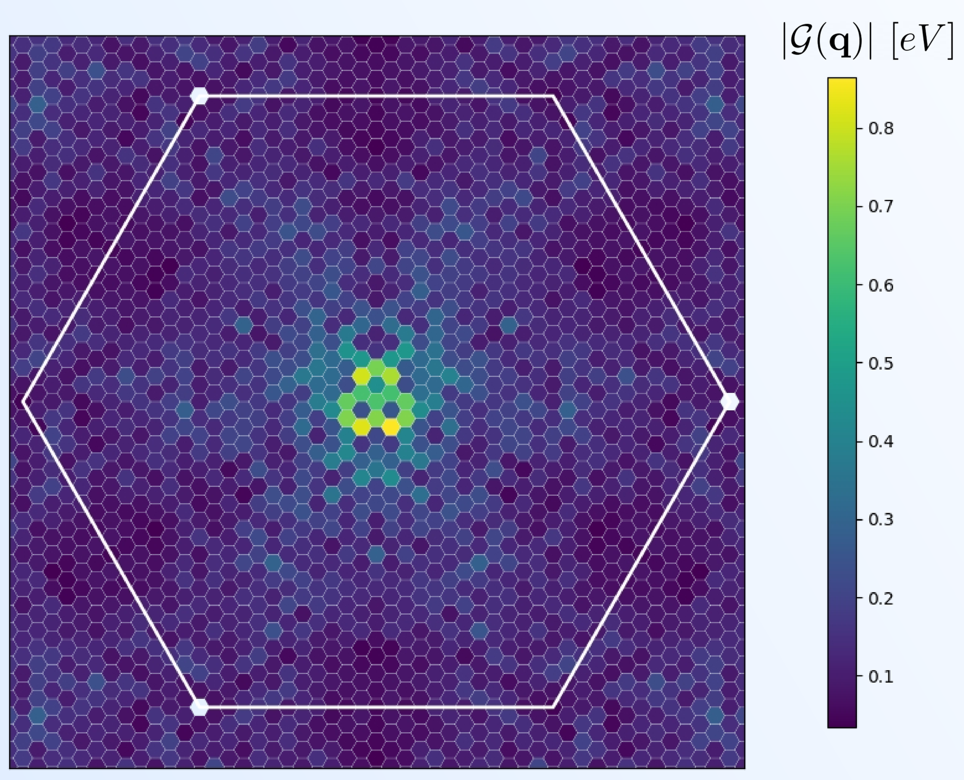
Introduction

We compute the photoluminescence of a monolayer of hexagonal Boron Nitride from first principles. Our new approach allows to have both direct peaks and satellites coming from phonon-assisted transitions in the same spectra. We combine Density Functional Theory (DFT), Density Functional Perturbation Theory (DFPT) and Many-Body Perturbation Theory (MBPT) to obtain the **exciton-phonon coupling** matrix elements *ab initio*. Then we make use of the van Roosbroeck – Shockley relation, which is a steady-state approximation, to compute the photoluminescence from the dielectric function. Finally we compare our result with three experimental measurements [1-3] and rule out the possibility of phonon satellites being visible in the spectrum of monolayer hBN.

Exciton-phonon coupling

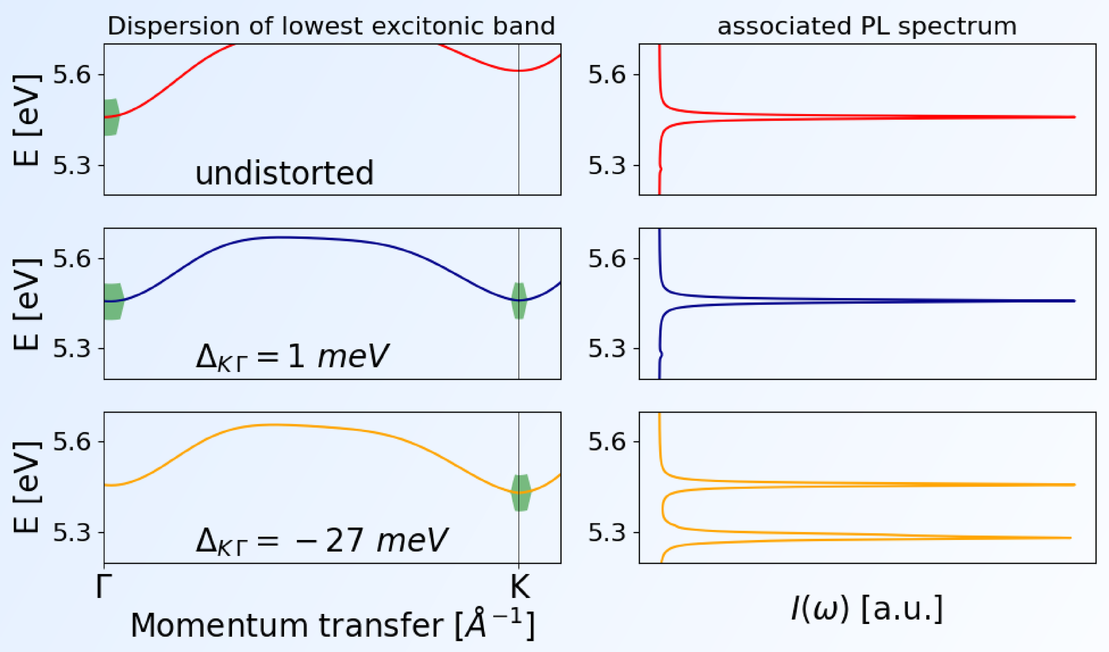
After computing the electron-phonon matrix elements in DFPT, we rotate the matrix elements for chosen bands to obtain the hole-phonon and electron-phonon matrix elements in the excitonic basis. Their difference defines the **exciton-phonon coupling** matrix elements :

$$\mathcal{G}_{\beta\alpha,\mu}(\mathbf{Q},\mathbf{q}) = \sum_{\substack{v,v'\\c,c',\mathbf{k}}} A^{v,c,\mathbf{k}}_{\alpha,\mathbf{Q}}\,[g_{vv',\mu}(\mathbf{k}-\mathbf{Q},\mathbf{q})\delta_{c,c'}]\,A^{v',c',\mathbf{k}*}_{\beta,\mathbf{Q}+\mathbf{q}} - \sum_{\substack{v,v'\\c,c',\mathbf{k}}} A^{v,c,\mathbf{k}}_{\alpha,\mathbf{Q}}\,[g^{*}_{c'c,\mu}(\mathbf{k}+\mathbf{q},\mathbf{q})\delta_{v,v'}]\,A^{v',c',\mathbf{k}+\mathbf{q}*}_{\beta,\mathbf{Q}+\mathbf{q}}$$



Magnitude of the coupling (in eV) between the lowest-lying exciton at Γ and all phonon modes over the Brillouin Zone

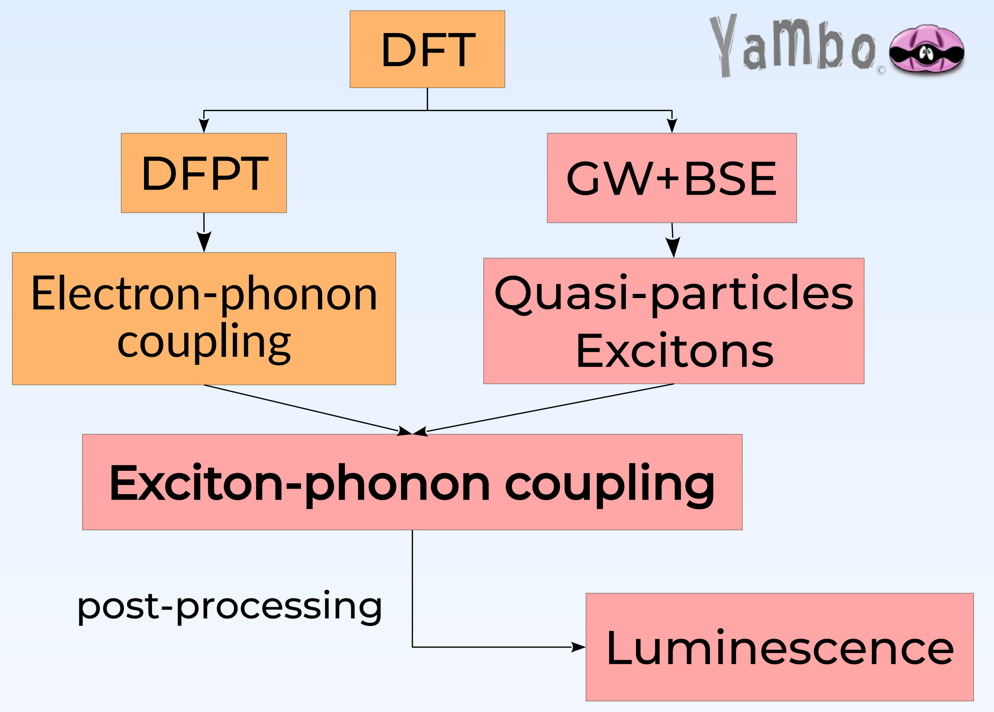
Direct/indirect energy difference



Effect of the energy difference between direct exciton and indirect exciton at K. Boltzmann occupation is displayed in green.

- The equilibrium exciton dispersion gives only the direct peak
- In the case when the substrate brings them to the same energy, only the direct peak is visible
- Only when K is lower, both direct and satellite peaks are visible

Workflow

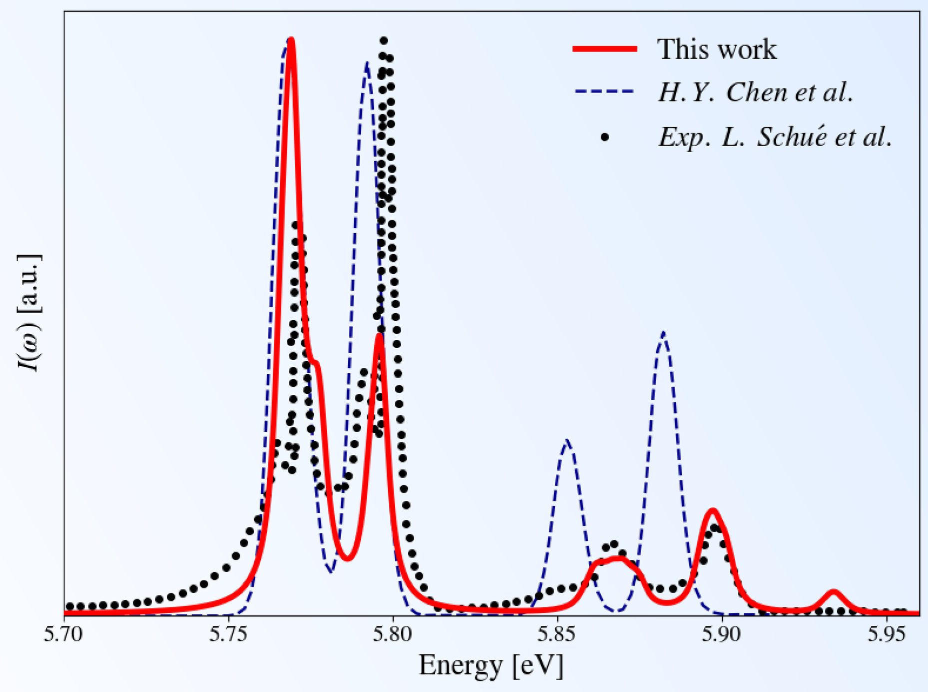


Direct peak

$$I(\omega) \propto \sum_{\alpha} \omega^3\, \mathcal{N}(E_\alpha, T_{exc})\,(1-R_\alpha)\,|T_\alpha|^2\,\delta(\omega - E_\alpha) + \sum_{\alpha\beta\mu,\mathbf{q}} \omega(\omega-\Omega_{\mathbf{q}})^2\, \mathcal{N}(E_{\mathbf{q}\beta}, T_{exc})\, R_\alpha\, |T_\alpha|^2\, \delta(\omega - (E_{\mathbf{q}\beta} - \Omega_{\mathbf{q}\mu}))$$

Phonon-assisted peaks

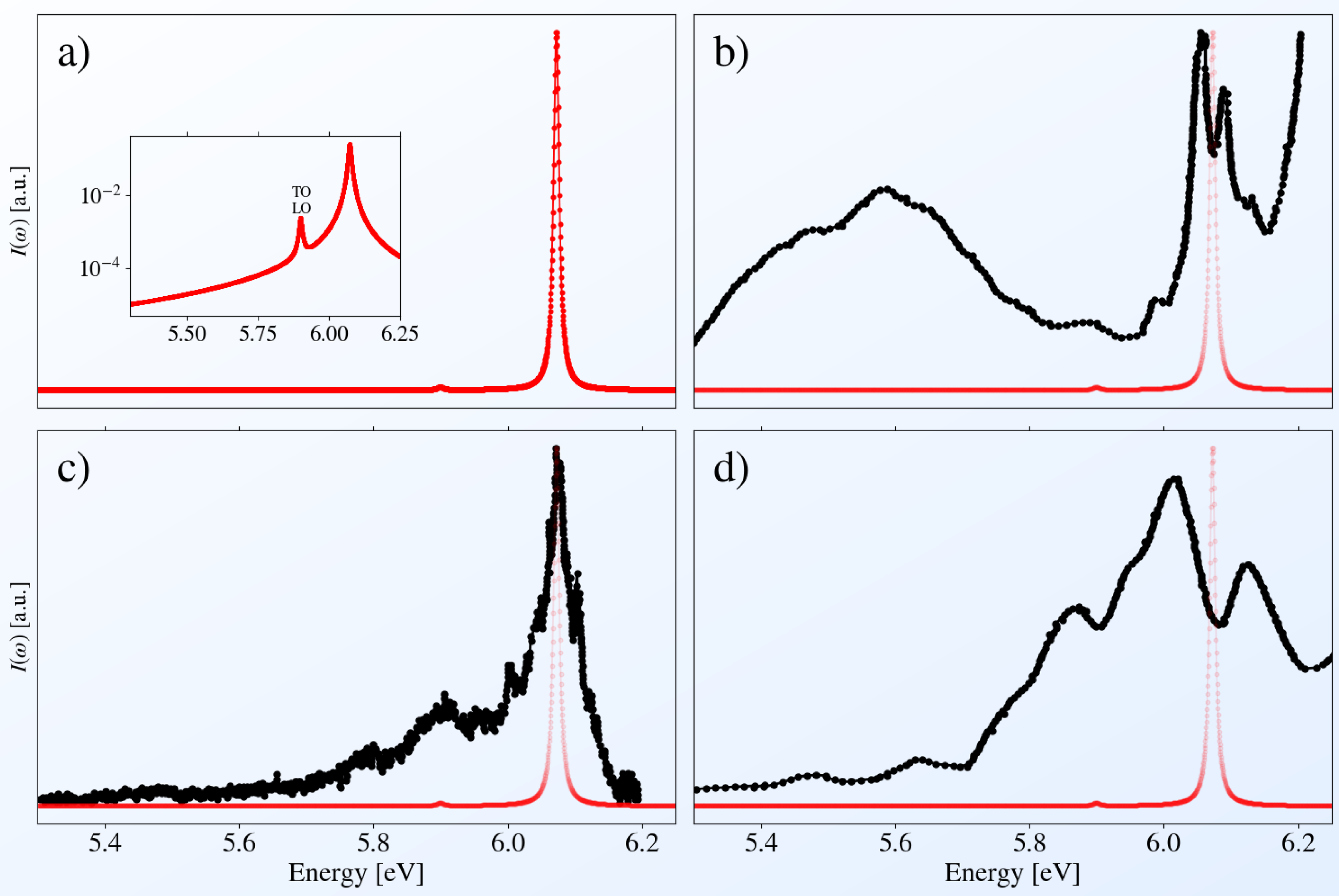
Benchmark



*Photoluminescence of **bulk AA'-hBN***
Red: this work
Black dots : experiment of Ref [4]
Blue : calculation of Ref [5]

- Correct position of all phonon-assisted satellites
- Shape is not in perfect match : probably multi-phonon processes not treated in our theory
- Intensities are in the correct order of magnitude
- Presence of a ZA replica due to numerical issues

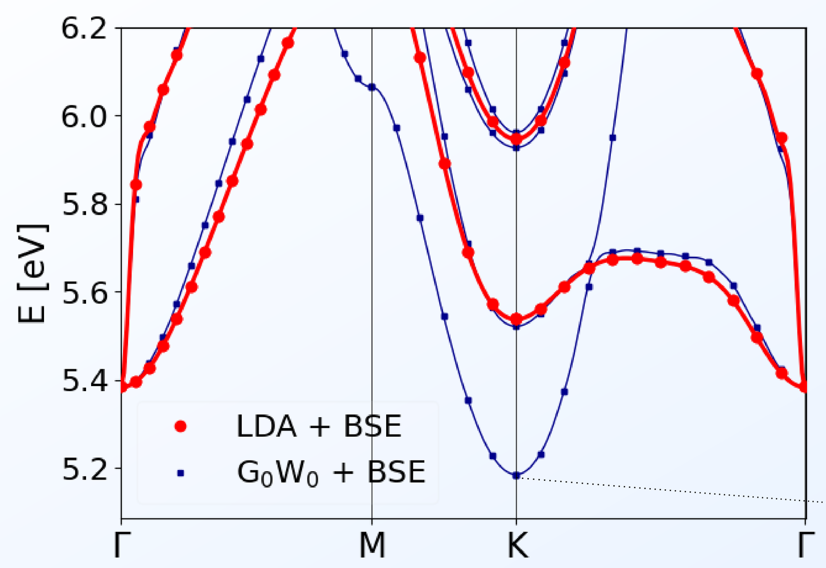
Luminescence compared to experiments



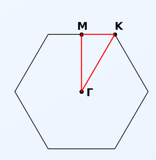
- Very intense direct peak
- Almost invisible LO/TO replica
- Indirect exciton not visible due to high energy separation

*Photoluminescence of **monolayer hBN***
a) This work (shifted to match experiments)
b) Ref [1] on Graphite c) Ref [2] on SiO_2 d) Ref [3] on Graphite

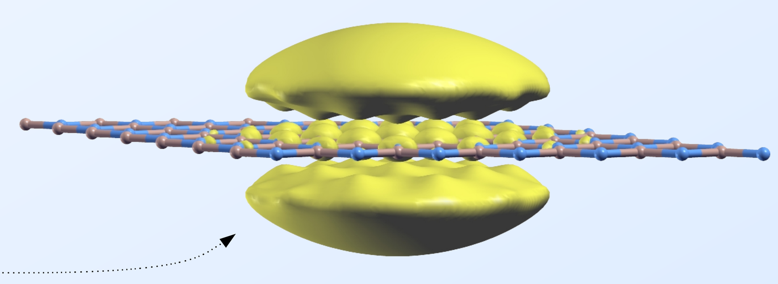
Exciton dispersion



Exciton dispersion of monolayer hBN. Depending on the level of theory, the minimum exciton can be at K or at Γ.



The lowest exciton at K comes from the nearly-free electronic states at Γ. It is not contributing to luminescence and is lifted in energy when a substrate is present.



Conclusion and perspectives

- *Ab initio* exciton-phonon coupling and phonon-assisted luminescence with quantitative comparison of direct peaks and replicas intensities
- In monolayer hBN, spectrum is dominated by direct peak and phonon-assisted satellites are not visible
- Would need the indirect exciton to be the lowest to produce a peak in the spectrum

Study of a system with direct and indirect excitons very close in energy (Bernal BN)
Work out numerical issues and release the implementation

[1] Elias, Christine, et al. "Direct band-gap crossover in epitaxial monolayer boron nitride." Nature communications 10.1 (2019)
[2] Rousseau, Adrien, et al. "Monolayer Boron Nitride: Hyperspectral Imaging in the Deep Ultraviolet." Nano Letters 21.23 (2021)
[3] Wang, Ping, et al. "Scalable Synthesis of Monolayer Hexagonal Boron Nitride on Graphene with Giant Bandgap Renormalization." Advanced Materials 34.21 (2022).
[4] Schué, Léonard, et al. "Bright luminescence from indirect and strongly bound excitons in h-BN." Physical review letters 122.6 (2019)
[5] Chen, Hsiao-Yi, D. Sangalli, M. Bernardi. "Exciton-phonon interaction and relaxation times from first principles." Physical Review Letters 125.10 (2020)