Programme de recherche

Claudio Attaccalite

Centre Interdisciplinaire de Nanoscience de Marseille
Campus de Luminy Case 913
13288 Marseille Cedex 9

CNRS concours 03/01 (2020)

Je présente dans ce document mes perspectives de recherche pour les années à venir, sur la luminescence et le couplage electron-phonons.

Exciton-phonon coupling and luminescence in layered materials, a first-principle approach

1.1 A new efficient phonon assisted luminescence.

In standard solid state physics textbooks direct band gap semiconductors are considered efficient light emitters while indirect ones are regarded as inefficient. Silicon is a typical example: its indirect nature prohibits applications in optoelectronics. This fact has motivated significant research activity to engineer silicon and transform it into a direct gap semiconductor by means of defects, nanostructuring, etc. A more recent and remarkable example of indirect to direct gap transition is represented by MoS_2 nanostructuring. The luminescence signal increases by orders of magnitude passing from multi-layer to single layer MoS_2 with an associated indirect to direct band gap transition [1].

Hexagonal boron nitride (hBN) seems to defy this rule: it has a large indirect band gap of about 7 eV, but it has recently attracted much attention from the scientific community as a very efficient light emitter in the ultraviolet energy range [2]. An internal quantum yield of about 45% has been reported for hBN, much closer to the 50% one of ZnO (direct band gap) than to the 0.1% one of diamond (indirect band gap) [3].

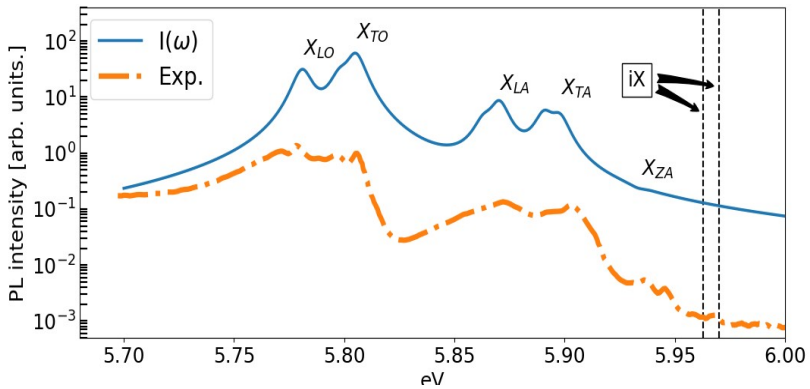

Figure 1: Theoretical luminescence spectra[6] (blue line) compared with the experiments[5] (orange dash-dotted line)

This goes against the common wisdom that indirect band gap insulators are bad light emitters. In fact the strong luminescence signal of hBN was initially attributed to direct exciton recombination [1]. Then, in order to shed some light on this phenomenon, different theories were proposed, including the presence of defects [4] or a dynamical Jahn-Teller effect. But only recently, thanks to more accurate and precise measurements and theoretical calculations, it has been possible to clarify that luminescence is due to phonon assisted transition [5,6], see Fig.1. This result was

further confirmed by measures of isotope effects in luminescence [7], and the study of excitons dispersion by means of electron-loss spectroscopy [8,9].

Motivated by these recent theoretical and experimental results, in this project I want to develop a theoretical and computational framework to study luminescence and phonon-assisted luminescence in layered materials. In a recent work [6] we derived a new approach to calculate exciton-phonon coupling by means of finite differences, and reproduced the experimental measurements on hBN. However due to the use of supercells in this kind of calculations, it is not possible to extend this approach to more complicated situations or taking in to account the temperature effects. These limitations motivate the developments of a new computational framework.

1.2 Design new light emission sources

The impact of well-managed light on everyday life is immeasurable. The light-emitting diode (LED) is one of the most prominent developments since the invention of incandescent light bulbs in the late 1800s. The latter dissipate most energy in the infrared as heat while typical white LEDs cover only the visible spectrum. Most prominent examples of white-light LEDs are based on gallium nitride. Their narrow-band ultraviolet (UV) emission is converted into visible light by applying phosphors. This cold light has tremendous advantages with respect to energy efficiency. Beyond the visible range, there are materials like hBN that is a deep UV sources that could find application in water sterilization where current sources have problem of efficiency.

This project aims to understand and develop new light emitting sources based on layered materials. Computational methods will be used to provide much insight into phonon assisted luminescence of nanostructures and to design the optimal configuration for efficient luminescence.

1.3 State of the art and scientific objectives

In this project I propose a new theoretical framework that will allow: 1) an efficient calculation of luminescence spectra mediated by phonons in bulk materials; 2) the inclusion for the first time of temperature effects and phonon replica in EELS spectra; 3) the evaluation of the exciton Auger recombinantion that is one of the most important limiting factor for the luminescence. A schematic representation of the proposed theoretical advances is presented in Fig. 2.

At the beginning all these advances will be applied to hBN where there are clear and relevant experiments. However once developed, this methodology could find application to a large spectra of materials from two-dimensional crystals to bulk semiconductors. In the next sections we will describe each of the advances proposed in this project.

2.1 Accurate description of phonon assisted luminescence

This is the core part of the project: an accurate description of exciton-phonon interaction in low dimensional materials. From the successful realization of this part different experimental results could be predicted and explained.

Optical properties of different layered materials (hBN, MoS2 etc..) are dominated by excitonic effects. In fact due to its insulating nature and layered structure the coupling between an excited electron and the hole left behind is very strong.

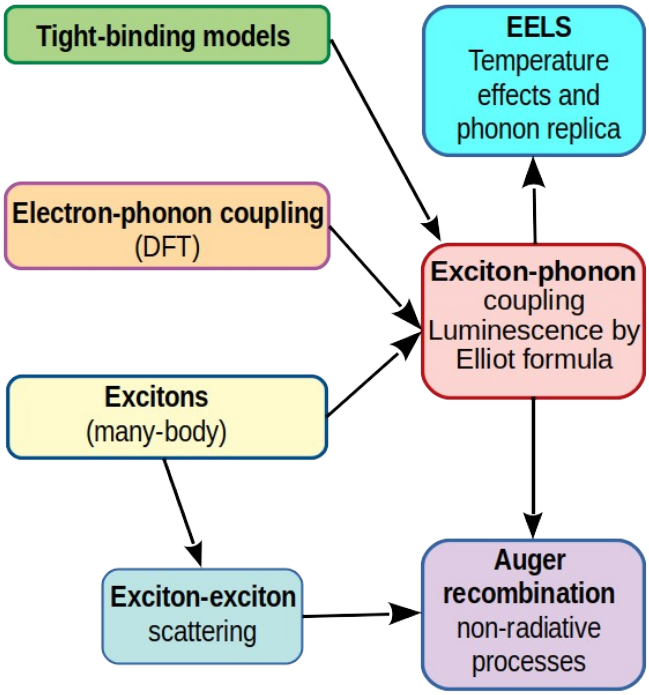

Figure 2: Schematic representation of the project workflow for the theoretical part

Therefore in order to accurately describe luminescence we need a theory that includes both electron-hole interaction and electron-phonon scattering on the same footing. In the last years we developed a new approach based on non-equilibrium Green's functions (NEGF) that is a theoretical method employed to describe the initial non equilibrium distribution of electrons that gives rise to the luminescence. Then we combined this methodology with a perturbative treatment of the electron-phonon interaction in such a way to describe phonon assisted luminescence. This approach was quite successful and allowed us to theoretically simulate the luminescence spectra in bulk hBN [6], see also Fig. 1 and confirmed its interpretation in terms of phonon-assisted emission of light from an indirect exciton.

However this method presents an important bottleneck because it requires the calculations of excitons in large supercells used to describe the phonon displacements. This fact limits the application of this approach to multiple phonon replica or to an accurate description of the role of temperature, that requires a fine sampling of exciton and phonon dispersions. In this project we propose a new strategy to go beyond these limitations by calculating both excitons and electron-phonon coupling (EPC) matrix elements in the primitive cells and then interpolating them using a basis set of localized orbitals [10]. With these ingredients we could construct the exciton-phonon interaction and calculate the luminescence spectra in the different configurations without rely on supercells. Thanks to the use of fine grids we could also describe the role of temperature on the luminescence spectra. The same methodology could then be applied to other materials as dichalcogenides or phosphorene, etc.

At the beginning the theory and the computational approach will be benchmarked on materials with an indirect band gap where excitonic effects are not so important. A typical material of this type is bulk diamond, that presents a strong electron-phonon coupling but a weaker electron-hole interaction. In this part of the project, the theory will strongly benefit from collaboration with experimental groups working on diamond properties.
Then we will include the effect of electron-hole interaction and study layered materials. Hexagonal BN will be used as a benchmark for the theory and the code before moving to more complex materials.
The final step of this development will be the inclusion of temperature effects by means of the calculation of the self-energy imaginary part and the inclusion of high order scattering processes to describe multiple-phonon replica.

All these ingredients will be essential for a realistic description of the phonon-assisted luminescence.

2.2 Limiting factors for a strong luminescence: the Auger recombination

This second part of the project is the most challenging from a theoretical point of view, and it will be developed along different years.

Although it has been shown that the luminescence in the BN is very strong [2,3], the same cannot be said for nanostrutures derived from this material. Recent experiments on exfoliated hexagonal boron nitride have shown a quenching of the luminescence in few layers flakes [13].

The explanation of this phenomenon has been attributed to the presence of a strong exciton-exciton annihilation (EEA) in bulk BN, which should be intensified in nanostructures [10], as a few layers flake.

The reported EEA rate in hBN due to the Auger recombination appears to be stronger than in other bulk semiconductors. This factor could limit the application of its nanostructure as deep UV light-sources. However, in partial contrast with these experimental results, new recent measurements have shown luminescence signal from monolayer hBN grown on graphite substrates[14].

All these contradictory results quest for a theoretical investigation of luminescence quenching by indirect Auger recombination, and this is what we plan to do in this research project.

In the scientific literature very few theoretical studies attacked the problem of Auger recombination [15]. The reason is that this phenomenon requires an involved theoretical description, and moreover, in case of indirect materials, exciton-exciton annihilation is associated with phonon emission/absorption, that makes its description even more intricate.

This part will be the most complex and risky of all project. First of all we will start from Auger recombination of independent particles mediated by phonons. This will allow us to test the theory in materials with an indirect band gap where excitonic effects are not so important. Excitonic effects will be included in the second part of the project. First they will be introduced in simple tight-binding models and then included in the ab-initio formulation.

The internal quantum yields obtained from the theory will be compared to experimental values and then we would to identify the key material properties required for an efficient phonon-assisted luminescence.

With a complete first principle description of indirect Auger recombination we will be able to understand why and when luminescence is quenched in hBN nanostructures and also the role of the substrate.

2.3 Electron-loss spectroscopy

This third part of the project is side project, mainly independent form the previous one. The study of Electron-loss spectroscopy (EELS) is motivated by the on-going collaboration with different experimental groups, and from the fact that the same numerical and theoretical tools developed in section 2.1 can be easily adapted to the study of EELS.

An alternative approach to get insights on excitation mechanisms is electron energy loss spectroscopy (EELS) [16,17]. This technique provides complementary information that can not be acquired in optics and works in wide spectral range from the long-wavelength infrared to the far UV. An import feature of EELS is that it can be performed at non vanishing momentum transfers probing non optical transitions in the reciprocal space.

The recent improvements in spectral resolution, up to few meV, made EELS able to resolve the fine structure excitation peaks including phonon replica at different temperatures.

From a theoretical point of view the EELS spectra can be obtained from linear response theory using the same tools employed to study optical absorption or luminescence spectra.

Thanks to the advances proposed in this project we will be able to provide a fine description of exciton dispersion in layered materials. The addition of electron-phonon coupling will allow us to include also temperature effects and phonon-replica in the EELS spectra. A major step forward for the theoretical description of electron energy loss spectroscopy that has been always limited at zero temperature without the coupling with phonon modes.

3 Organization and implementation of the project

Claudio Attaccalite(CA), CR at CNRS-CINaM Laboratory, will coordinate the project. CA is one of the main developer of the Yambo code (http://www.yambo-code.org/) [7] and he has a long experience in simulation of excited states and optical response of bulk materials. He has different ongoing collaboration with experimental groups working on luminescence in layered materials at ONERA Paris, Univ. de Versailles[16,17] and Barcellona University.

This project will be carried out in strong collaboration with the experimental groups and other theoreticians present at ONERA. CA will implement luminescence equations in the Yambo code, that will be then made available to the scientific community. The continuous feedback between theory and experiments will allow us to test the different approximations employed in the theoretical calculations.

I. References:

[1] A. Splendiani et al., *NanoLetters* 10, 1271(2010).
[2] K. Watanabe, T. Taniguchi, and H. Kanda, *Nature Materials* 3, 404(2004)
[3] L. Schué, L. Sponza, et al. *Phys. Rev. Lett.* 122, 067401(2019)
[4] **C. Attaccalite, M. Bockstedte, M., Marini et al., *Phys. Rev. B*, 83, 144115(2011)**
[5] G. Cassabois, P. Valvin & B. Gil, *Nature Photonics* 10, 262(2016)
[6] **E. Cannuccia, B. Monserrat, and C. Attaccalite, *Phys. Rev. B* 99, 081109(R)(2019)**
[7] Vuong, T. Q. P., et al., *Nature materials* 17 ,152(2018)
[8] R. Schuster, et al. *Phys. Rev. B* 97,041201(R)(2018)
[9] **L. Sponza, et al., *Phys. Rev. B* 97, 075121(2018)**
[10] **D. Sangalli, A. Ferretti, H. Miranda, C. Attaccalite, et al., *J. of Phys.* 31, 325902(2019)**
[11] M. B. Nardelli, et al., *Computational Materials Science* 143, 462 (2018)
[12] L. Schué, et al. *Nanoscale* 8, 6986(2016)
[13] A. Plaud et al. *Appl. Phys. Lett.* 114, 232103 (2019)
[14] C. Elias et al, *Nature Communications* 10, 2639 (2019)
[15] M. Govoni, I. Marri, S. Ossicini, *Physical Review B*, 84(7), 075215
[16] F. Fossard, et al. *Phys. Rev. B* 96, 115304 (2017)
[17] L. Sponza, et al. *Phys. Rev. B* 97, 07512 (2017)