Real time dynamics of Luminescence using *Ab-initio* Non-Equilibrium Green's Function (NEGF): Theory and Simulation

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January 6, 2009

Abstract

Photoluminescence and non-linear optics are important technological fields under intense experimental development. Despite their importance, there is a lack of theoretical studies on these fields, mostly reduced to simple phenomenological models. *Ab-initio* calculations for realistic systems and nanostructure are completely absent. In this project, we propose to develop a theoretical framework, based on *Ab-Initio* Non-Equilibrium Green's Function (NEGF) to address photoluminescence and non-linear optics. With a step-by-step strategy we will shed light on the different aspects of the photo-excitation, internal conversion, and final de-excitation. This will make possible, for the first time, to simulate the real time evolution of the photo excited carriers revealing the microscopic mechanisms responsible for photoluminescence process. The project will be embedded in the Neel environment where there is an intense and remarkable research activity on non-linear optics and luminescence, and a tight collaboration will be established with the experimental groups.

Photoluminescence: Context and Background

The Nobel price assigned this year for the discovery and development of the green fluorescent protein (GFP) [1] have shown the importance of luminescence processes in biology. In fact proteins normally are not visible in a microscope, but GFP absorbs ultraviolet or blue light and then glows green. Using GFP and similar proteins nowadays researchers are able to label proteins inside the cell and see how they move and interact with a simple microscope.
But luminescence and in general light emission processes are relevant not only for biological systems, in physics and in particular in semiconductor physics they play fundamental role in basic and applied research. The wide range of potential applications of light-emitting devices span optoelectronic, lasers, ultra-fast optical switches, gates based on absorption changes etc. Therefore it is clear that the possibility to engineering materials to increase their efficiency or to tune their emission spectra play a crucial role in technological applications. Experimentally different strategies are currently employed to tune luminescence properties as the introduction of impurities or the use of nanostructure. For example in recent year it has been possible to tune silicon, the most important material for electronics, whose poor optical properties are well known, in a controllable light emitting material, with the introduction of impurities[2] (see fig. 1). Another possibility under intense investigation is the use of nanostructure as polymers, nanotubes, nanowires and nanocrystals as emitting devices[3]. In this case the quantum confinement allows to tune the optical properties as for instance in the case of nanocrystals which can fluoresce brilliantly at specific, sharply defined colors[4] (see fig. 2), according to their size and shape.

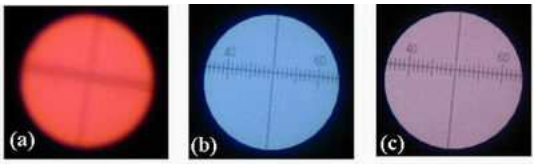

Figure 1: Electroluminescence based on a Si metal-oxide-semiconductor structure doped with Eu

Motivations for this Project

The most strategic application of photoluminescence (PL) is the search of new optoelectronic devices with technological interest (e.g. optical communication, DVD heads, hybrid computation,etc.), and phosphors for fluorescence lighting. In this context it is crucial to design nanoscale molecular devices with tunable electronic and optical properties. This will permit to have materials with high quantum efficiency (the dimensionless ratio of photons emitted to the number of photons absorbed), high emission brightness, long-lasting fluorescence, easy to use and manufacture. From a theoretical point of view interaction of light with the matter and subsequently light emission are very complicated processes[5] [6] be-

Figure 2: Brightly glowing water soluble CdSe/ZnS nanocrystals

[1] http://nobelprize.org/nobel_prizes/chemistry/laureates/2008/
[2] S. Prucnal, W. Skorupa, J. M. Sun, M. Helm, Applied Physics Letters **90**, 181121 (2007)
[3] S. Godefroo et al. Nature Nanotechnology **3**, 174 - 178 (2008)
[4] M. D. Roy, A. A. Herzing, S. H. De Paoli Lacerda and M. L. Becker Chem. Commun., 2106 - 2108 (2008)
[5] H. Haug and S. Schmitt-Rink, Prog. Quant. Electr. **9**,3 (1984)
[6] F. Rossi and Tilmann Kuhn, Rev. Mod. Phys. **74** 895 (2002)

cause they involve electronic relaxation processes, electron-electron interaction, electron-phonon interaction, structure changes, emission by defects levels and so on. Despite of their importance, there are entire journals dedicated only to luminescence experiments[7], there is a lack of theoretical studies on this field. Simple models have been applied to bulk semiconductors but *ab-initio* calculations for realistic systems and nanostructure are mainly absent.

Introduction to the Photo-Luminescence

Several investigators reported luminescence phenomena, but it was the British scientist Sir George G. Stokes who first described fluorescence in 1852.

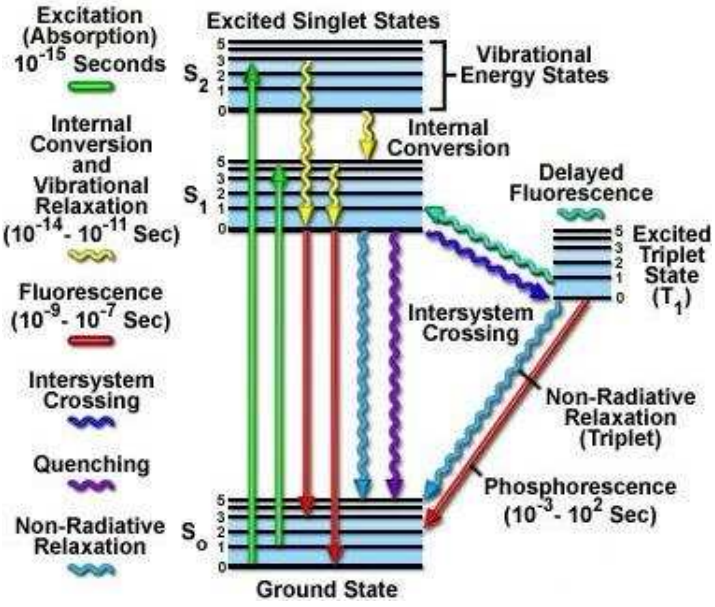

Figure 3: PL energy diagram

In general, when light of sufficient energy is incident on a material, photons are absorbed and the whole system is promoted to an excited state. Eventually, the system can relax back to its ground state. If this relaxation is radiative, the process is called photoluminescence(PL) which is formally divided into two categories, fluorescence and phosphorescence, depending upon the emission pathway. PL is simple, versatile, and non destructive. The instrumentation that is required for ordinary PL work is modest: an optical source and an optical power meter or spectrometer. If the PL spectra is measured under the action of an external steady optical source we have steady-state PL. In time-resolved PL (TRPL), instead, a series of short laser pulses, with a rate of excitation much shorter than the average recombination time, is used. In TRPL the system is constantly out of equilibrium and the electrons (more precisely the electron-hole pairs) recombination rate and intrinsic recombination path are measured in real-time. Because of the sensitive emission profiles, spatial resolution, and high specificity PL and TRPL are commonly used techniques to perform qualitative investigations like material composition, defects, impurities, surface adsorbates. It is clear, at this point, that to improve the PL properties of nanoscale materials and to strengthen their technological application there is a clear need of accurate theoretical and numerical tools to quantitatively interpret and predict the physical mechanisms involved in the PL light emission.

[7] Journal of Luminescence(Elsevier) http://www.sciencedirect.com/science/journal/00222313, see also http://www.opticsinfobase.org/

State of the art of Photo-Luminescence theory

In the theory to describe PL should one has to take into account three important events governing a PL process, all of which occur on time scales that are separated by several orders of magnitude. First the excitation by the incoming of a pulse lasers happens in femtoseconds (10-15 fs), followed by a fast relaxation due to electron-electron scattering. Then the electrons transfer part of their energy to the crystal lattice emitting phonons, typically on a time scale of picoseconds (1-3 ps). The final process, emission of a longer wavelength photon and return of the system to the ground state, occurs on the relatively long time scale of nanoseconds ($> 100ps$). To understand the PL process in nanoscale materials, we must keep in mind that the optically excited electron-hole states cannot be described using simple interband transitions, e.g. assuming that the light is absorbed by independent electron-hole pairs, but interaction between electrons has to be taken in to account. Although much progress has been done in the *ab-initio* community to study the absorption spectrum, there is hardly any work using first-principles approaches to study the competing relaxation processes from the excited state (phonon or photon emission, auger mechanisms, etc.) what mainly motivate this project.

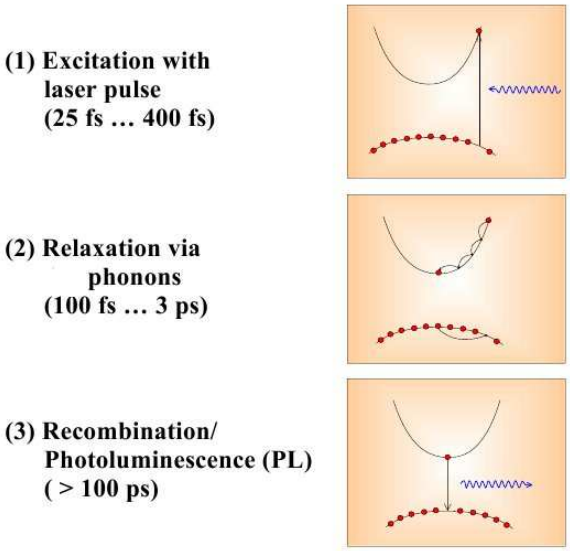

Figure 4: Schematic diagram of the processes in a two-band model

In the past empirical models, mainly two-bands models[8] have been frequently employed to explain luminescence experiments. In particular, using these models, it was possible to clarify different relevant aspects of light emission as: 1) optical Stark effect in coherently driven exciton systems[9]; 2) gap shrinkage due to the enhanced electronic screening[10]; 3) excitonic effects [11]; 4) Paoling blocking [12]; 5) optical gain[13].

Although simple models allowed, even if with adjustable parameters, to explain luminescence for simple bulk semiconductors and quantum wells they cannot handle nanostructure, organic molecules or defect mediated luminescence. For these reasons we propose to extend the theory, partially developed in model systems to realist one, in such way to create an *ab-initio* parameter-free numerical and theoretical tool to simulate and predict luminescence properties.

State of the art of Linear Optics and Absorption

In contrast to the light-emission case, nowadays there are highly developed techniques to describe linear optics and in particular absorption. At present the combination of density-functional theory

[8] T. J. Inagaki and M. Aihara Phys. Rev. B **65** 205204
[9] Schmitt-Rink, D. S. Chemla and H. Haug, Phys. Rev. B **37**, 941 (1988)
[10] G. Ropke, T.Seifert, H. Stolz and R. Zimmermann, Phys. Stat. Sol. (B) **100**, 215 (1980)
[11] K. Hannewald, S. Glutsch and F. Bechstedt, Phys. Rev. B **62** 4519 (2000)
[12] Kilimann, K. Kremp, D. Röpke, G., Theor. and Math. Phys.,**55** 611 (1983)
[13] W. W. Chow, P. M. Smowton, P. Blood, A. Girndt, F. Jahnke, and S. W. Koch, Appl. Phys. Lett. **71**, 157 (1997)

(DFT) with many-body perturbation theory (MBPT) allows to study optical absorption of non-trivial systems, like bulk, molecules, nanowires or nanotubes[14] at different levels of approximations. One can start from the simple Random Phase Approximation (RPA) that takes in to account the band structure and the inhomogeneity of the materials through the so called non local field effects. Subsequently it is possible to include the quasi-particle band structure, usually in the GW (dressed Greens function G and dynamically screened Coulomb interaction W) approximation[15] [16] and also the electron-hole attraction or excitonic effects, through the Bethe-Salpeter equation[17]. Today there are different available codes, free or commercial, that implement these techniques[18], and optical properties of hundreds of materials ranging from bulk semiconductors[19], nanotubes[20], nanowires[21], biological molecules and oxides that are currently studied and/or predicted.

My Project and Planned Developments

Despite the success of *ab-initio* MBPT theory to study optical absorption spectra, relatively few attempts have been done to use it for light emission. The reason stems from its fundamental inadequacy in systems driven out of equilibrium. Indeed in *ab-initio* MBPT, the physical picture of an exciton is based on some restrictive approximations that, while being well motivated to describe the features observed in the absorption spectra, are not adequate at all to explain excitonic PL and TRPL:

1. The external field is assumed steady and weak;
2. The exciton formation is instantaneous and its lifetimes is assumed infinite;
3. The exciton is not coupled to the atomic oscillations (phonons) and the effect of thermal disorder is neglected.

Approximations (1) and (2) clearly contradict the basic TRPL experimental setup where the external field is changing on a time scale comparable with the exciton formation time. Approximations (2) and (3) imply that the excitons are steady states. No internal conversions are possible, an exciton cannot change its electronic state, for example by emitting phonons (Stokes shifts). Moreover in most of the experimental setups the PL spectra is measured at room temperature. However, neglecting the exciton-phonon interaction, the fine sensitivity of PL to the temperature cannot be explained. In conclusion, this approach is inadequate to yield a consistent approach to the theoretical interpretation of the excitonic PL and TRPL.

In this project, we plan to extend the MBPT developments for linear optics toward a full **ab-initio Non-Equilibrium Green's Function (NEGF) theory** [22] which is an **adequate framework to describe Photo-Luminescence**. Indeed, the ordinary 0-temperature or finite temperature Green's function MBPT formalism cannot account for the out-of-equilibrium situation of systems under intense excitation, such as in Photo-Luminescence or Non-linear Optics.

[14] G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).
[15] L. Hedin, Phys. Rev. **139**, A796 (1965).
[16] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
[17] G. Strinati, Rivista del nuovo cimento **11**,1 (1988).
[18] YAMBO, DP, EXC, ABINIT, VASP.
[19] S. Albrecht, L. Reining, R. Del Sole and G. Onida, Phys. Rev. Lett. **80**, 4510 (1998).
[20] C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie Phys. Rev. Lett. **92**, 077402 (2004).
[21] M. Bruno, M. Palummo, A. Marini, R. Del Sole, and S. Ossicini Phys. Rev. Lett. **98**, 036807 (2007).
[22] Quantum Statistics of Nonideal Plasmas D. Kremp, M. Schlanged and W. D. Kraeft, Springer (2005).

Very recently there have been sporadic and isolated attempts along the direction of *ab-initio* NEGF theory that we propose to develop. Among them we want to mention: 1) an attempt[23] to generalize the GW approximation to NEGF in order to describe Quasi-particle band structures of semiconductors under intense (laser) excitation, showing the importance of the out-of-equilibrium effect to enhance the screening and reduce the band gap; 2) the calculation[24] of optical properties of a semiconductor with a finite population of excited electrons and holes. However in these studies the electrons and holes distributions have not been calculated *ab-initio* but introduced as adjustable external parameters. There have been also several developments of non-equilibrium many-body theory in quantum transport, but most of them are done in a non-well founded hybrid framework of DFT[25] or do not explore a far-from-equilibrium situation [26] [27].

We point out that there has been no attempt to develop NEGF theory for Photo-Luminescence purposes. We think that today there is a strong experimental motivation to the development of an *ab-initio* theory of luminescence and we feel that NEGF is the more promising candidate for such a theoretical framework. In fact the key feature of the NEGF approach is that it is a parameter-free theory. The single particle electronic states are first evaluated using density functional theory (DFT) starting from the material atomic configuration and this makes NEGF predictive and more accurate than any semi-empirical approach.

Working Plan: developments of ab-initio NEGF for luminescence

The final goal of this proposal is to go beyond the linear response exciton theory, by deriving an *ab-initio* theory of the excitonic PL and TRPL using NEGF, and implementing a set of numerical tools to simulate and predict the PL properties in nanoscale materials. The project will be divided in three parts:

- *Short term objectives: NEGF and e-e interaction for PL*
  We will implement the NEGF in order to treat time-dependent perturbations. In particular the Dyson equations for the retarded green function G^R that describes the quasi particle levels and the equation of motion for the $G^>$ and $G^<$ that are related to the electrons and holes distributions. All these equations will be implemented using an e-e self-energy and scattering function in the GW approximation. The same will be done for the Bethe-Salpeter equation, that describes excitonic effects. At the beginning these equation will be used to simulate the steady-state of simple semiconductors under a monochromatic laser field. This will allow us to calculate optical properties of semiconductors subjected to monochromatic beam. In the case of a weak field the results will be compared with the ones coming from the linear response theory. Our implementation of NEGF will be checked against the PL of simple semiconductors as Si or GaAs, where there are clear experiments on high quality samples will allow us to verify the approximations employed in the theory and to evaluate the importance of different effects due to pumping laser as Pauli blocking, enhanced screening, decreased electron-hole attraction, optical Stark effect. Just after these test cases we plain as first application the study of luminescence and non-linear optical properties in $YAlO$ and $YCOB$ crystals that in

[23] C. D. Spataru, L. X. Benedict, and S. G. Louie, Phys. Rev. B **69** 205204 (2004).
[24] L. X. Benedict, Phys. Rev. B, **63**, 075202 (2001).
[25] TranSiesta.
[26] T. Frederiksen, M. Brandbyge, N. Lorente, and A. P. Jauho, Phys. Rev. Lett., **93**, 256601 (2004).
[27] P. Darancet, A. Ferretti, D. Mayou, and V. Olevano, Phys. Rev. B **75**, 075102 (2007)

this period are under intense study in the NEEL laboratory[28] for their promising characteristics. Another system that we will study is YAl$(BO_3)_4$, which preliminary experiments at the Neel and LETI have found it an interesting material for white light PL with quantum yield of 12% in the visible range. This luminescence is associated with defects levels in the band gap. The open experimental questions that the theory will answer are: 1) which type of defects causes the luminescence such as oxygen vacancies or non bridging oxygens 2) the improvements achievable by replacements of Y with Ca or Al with Si to favor the formation of defects; 3)the role of rare earth doping (Er, Nd, Yb...) in order to achieve a higher yield without modify the emission spectra.

At the end of this part of the project we will be able to describe:

(a) optical absorption and emission in weak and intense fields (non-linear optics)

(b) optical gain

(c) steady-state luminescence

- *Medium term objectives: NEGF and e-ph interaction*

  Later we will introduce thermal disorder and spin-flip transitions in the excitonic dynamics in order to allow vibrational relaxation through emission of phonons and transition to triplet trap states. Electron-phonon coupling will be calculated from density-functional theory and introduced in the electron dynamics through a electron-phonon self-energy in the SCBA (Self-Consistent Born Approximation), in a way much similar to what was done recently for the optical absorption[29]. This will allow us to calculate phonon replica of the emission peaks, see for instance[30], and also phonon assisted transition in indirect band gap semiconductors. At the end of this part will be able to give a quantitative description of

  (d)the different peak positions and intensities observed in the optical absorption and in the PL spectra as a function of the temperature;

  (e)the phonon and no-phonon assisted excitonic transitions;

  (f)the dependence of the PL quantum efficiency on the temperature and on the different nanoscale parameters (size, degree of electronic confinement, defects, etc.).

  (g) thermoluminescence spectra

- *Long term objectives: Atomic relaxations and toward Photovoltaics*

  Forces in the excited state will be introduced[31]. This will allow atomic structure relaxation once a quasi-equilibrium electronic configuration is reached.This is extremely important for the application of the previous theory to low dimension systems as cluster, wires, polymers. In fact in these systems excitations are often couple with lattice deformations and/or change in the bonding alternation[32]. Once all these advanced will be introduced in the theory and in the code it will be possible to simulate excitation in organic system. In one of our final goal we will be able to simulate the full process of light-excitation, lattice deformation, charge transfer and subsequently lattice relation, that is at the base of modern solar cells[33].

[28] L. J. Q. Maia, C. R. Ferrari, V. R. Mastelaro, A.C. Hernandes, A. Ibanez. Solid State Sciences. DOI: 10.1016, In press, (2008)

[29] A. Marini, Phys. Rev. Lett. **101**, 106405 (2008)

[30] M. G. Silly et al. Phys. Rev. B **75**, 085205 (2007)

[31] S. Ismail-Beigiand S. G. Louie, Phys. Rev. Lett. **95**, 156401 (2005)

[32] C.J. Brabec, N.S. Sariciftci: in Semiconducting Polymers, ed. by G. Hadziioanou and P.F. van Hutten(1999)

[33] Organic Photovoltaics, C.J. Brabec, V. Dyakonov, J. Parisi and N.S. Sariciftci, Springer(2003)

Collaborations and International context

Experimental Collaborations
From the experimental point of view in the NEEL laboratory there is already an intense experimental activity in photo-Luminescence performed by the group of A. Ibanez[34] [35]. They are studing new luminescent materials such as organic nanocrystals[36], glasses[37], in collaboration with the LETI-MINATEC and the Instituto de Física de São Carlos Universidade de São Paul (Brazil). There is at the moment a strong need for a theoretical support in order to understand the mechanisms at the base of the PL processes and to do a theoretical engineering of materials. Non-linear optics [38] is another important research topic at the Neel, and a tight collaboration will be also established with the experimental group of B. Boulanger on materials, such as YCOB, showing a dual PL and non-linear behaviour. At the Institut Neel there is longstanding tradition of fruitful collaboration between theory and experiment which is of great values in the context of this project and that we plan to continue.

Moreover, the Neel experimental activity on Optics is very well surrounded in a more general Grenoble environment with many technological actors . Beyond the LETI-MINATEC we want also to mention. : 1) CEA-Liten (Laboratory of Innovation for New Energy Technologies and Nanomaterials)[39]. 2) *Grenoble-Isre* that just started at the end of 2007 a new research line on photovoltaic materials[40]; 3) *Photowatt Technologies*[41] one of the worlds leading manufacturers of photovoltaic cells that is located in the neighbor of Grenoble; 4) *INES (Institute for Solar Energy)*[42] a center of excellence in solar energy technologies that will be realized in Chambery.

Theoretical Collaborations
On the local level, this project will take place within the theoretical physics group of NEEL (in particular in collaboration with X. Blase, V. Olevano, and D. Mayou). It will benefit, complement and also enforce the group's activities on electron-phonon, optical properties, especially in nanostructures. The development of an *ab-initio* theory for the study luminescence and non-linear optics will bring an essential tool to the group. Since NEGF is an adequate theory also for Quantum Transport, the developments of this project will be transferred on the long term also to applications in this field which is one of the main lines of the theory at the Neel.

International context
On the international level, the project will be in connection with the network of the European Theoretical Spectroscopy Facility (ETSF)[43], under the NMP3 priority of the European Commissionś 7th Framework Programme.

[34] N. Sanz et al., Solid State Sciences **3**, 867 (2001)
[35] E. Botzung-Appert et al. Chemistry of materials, 1609 **16** (2004)
[36] http://neel.cnrs.fr/spip.php?article1191
[37] E.M. Yoshimuraa, C.N. Santosb, A. Ibanezc and A.C. Hernandesb, in press on Journal of Optical Materials (http://dx.doi.org/10.1016/j.optmat.2008.08.004)
[38] Comptes Rendus Physique **8**, 206 (2007)
[39] http://www.cea.fr
[40] Grenoble Isere Report - Dcember 2007 (http://english.grenoble-isere.com/381-grenoble-isere-report.htm)
[41] http://www.photowatt.com/
[42] http://www.ines-solaire.fr
[43] http://etsf.eu/