PhD 2021-2024

MODELING FLUORESCENCE WITH BSE/*GW*

DESCRIPTION: PhD position in theoretical chemistry: 3 years from Sept/Oct. 2021.
Financed by the ANR – Project BSE-Forces.

LOCATION: Team **ModES**: *Modélisation Et Spectroscopie*
Lab: CEISAM, UMR CNRS 6230 Université de Nantes
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CONTEXT AND OBJECTIVE

The **importance of processes related to electronic excited states (EES) in chemistry, physics, and applied technology will continue to rapidly increase during the next decades as they are central in many fields such as photovoltaics, photosynthesis, photocatalysis, etc.** The related phenomena originate in the interactions between matter and time-dependent external fields, typically light. In sharp contrast to their ground-state (GS) counterparts, EES are short-lived and far from equilibrium which makes their experimental characterizations difficult. For instance, if one can find X-Ray diffraction data for numerous molecular GS structures of any size and nature, accurate EES geometries have been experimentally determined for a very limited number of (tiny) molecules only. This is why theories able to predict EES properties (structures and vibrations, dipoles, etc.) at a reasonable cost are often necessary to completely understand experimental outcomes. One can state that the palette of theories able to model absorption properties is now rather large. **However, fluorescence constitutes a much greater challenge for theoreticians** notably because the emission wavelength depends on the unknown EES geometry. **The present PhD thesis is proposed in the framework of the BSE-Forces project supported by the ANR and aiming to develop an alternative to mainstream TD-DFT and wavefunction techniques for the study, with increased reliability, of large emissive molecules. To this end, we will use the so-called *GW* and Bethe-Salpeter equation formalisms for modelling emission properties.**

RESEARCH PROGRAM

A first objective of the thesis will be to **assess the accuracy of the EES geometries obtained with BSE/*GW***. To this end, the candidate will develop reliable benchmarks, that is, geometries and potential energy surfaces that are very accurate. It has been shown that both CC2 and CCSD are not sufficiently precise to deliver EES geometrical parameters reliable enough for benchmarking “lower-order” methods, especially for the polar C=O and C=N bonds, that play a key role in many fluorophore. Consequently, the use of CC approaches including triples and/or multi-reference methods will be mandatory to reach sufficiently accurate results.

A second objective will be to **model "real-life" fluorophores treated in aprotic solution**, so as to be able to apply a continuum solvation model without significant loss of accuracy. It is noteworthy that the BSE/*GW* approach is able to include simultaneously the so-called linear-response and state-specific solvation effects, and has thus the edge for the modeling of (dielectric) environmental effects as compared to TD-DFT. Indeed BSE/*GW* can more accurately treat EES with a mixed local/CT character. As direct comparisons between theoretical vertical transition energies and experimental fluorescence wavelengths are physically ill-defined, a first target will be to reproduce the auxochromic shifts measured on two series of homologous fluorescent molecules, namely coumarins and 1,8-naphthalimides, before going to other classes of fluorophores.

Eventually, the candidate will turn towards **fluorescent dyes in water**, as this is one of the most interesting media for practical applications, and will strive to **design new structures with more red-shifted transition energies.** Various chemical strategies will be used to attain that goal, i.e., dyes showing with very large or in contrast small Stokes shift will be considered. The modelling of the water environment likely requires the application of advanced hybrid BSE/*GW*:MM approaches.

In addition, the successful candidate will be required to have direct interactions with the theoretical team developing and implementing the BSE/*GW* formalism (X. Blase and I. Duchemin in Grenoble) as well as with experimental teams developing new dyes collaborating with the team of the supervisor.

PROFILE OF THE CANDIDATE

The candidate should have a Master degree in chemistry, chemistry-physics, chemistry-theoretical, physics or equivalent obtained in 2020 or in 2021 and must have a solid training in physical and theoretical chemistry. Experience in *ab initio* molecular calculations as well as programming skills (Fortran, Python...) will be highly appreciated. Applicants must send a CV and a cover letter to denis.jacquemin@univ-nantes.fr