Simulation of Laser Properties in Molecular Compounds from First Principles

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The accurate and reliable prediction of absorption and emission spectra of molecular compounds by means of quantum mechanical (QM) computations is fundamental for the understanding and discovery of many photophysical, photonic, or laser processes in which an experimental determination becomes unfeasible and/or cannot provide insights into the underlying physics. A computational strategy that is attracting significant attention is the so-called Nuclear Ensemble Approach (NEA) [1], that relies on generating a representative ensemble of nuclear geometries around the equilibrium structure and computing the vertical excitation energies (ΔE) and oscillator strengths (f) and phenomenologically assigning each transition a lineshaped function with a "manually-selected" full-width δ. Recently, we developed a new approach to reconstruct NEA absorption spectra, dubbed GMM-NEA, based on the use of Gaussian Mixture Models (GMMs), a probabilistic machine learning (ML) algorithm, that circumvents the phenomenological broadening assumption and that systematically outperforms other data-driven models to automatically select δ [2]. Still, this methodology is limited to absorption spectra and thus hinders the simulation, from first principles, of emission processes in photonic or laser devices based on molecular compounds.

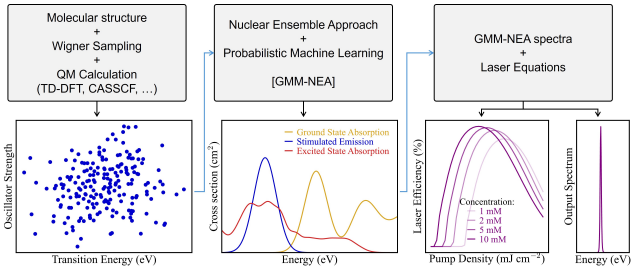

Figure 1: Sketch of the proposed theoretical framework to predict laser properties

Here, we report a theoretical framework to simulate the laser properties of molecular compounds from first principles (Fig. 1). It consists first on a QM calculation step to compute, for each of the NEA geometries sampled from a Wigner distribution, the transition energies and oscillator strengths of all relevant transitions (ground and excited state). These sets of data are processed with our probabilistic ML methodology (GMM-NEA), that we have extended to emission processes, to reconstruct the absorption and stimulated emission cross section spectra. Finally, the generated spectra, together with the fluorescence lifetime and quantum yield (obtained as well from QM calculations), are ingested into a rate equation laser model, allowing us to obtain spectro-temporal information on the laser process. We have tested this methodology on *anti*-$B_{18}H_{22}$, the first example of a boron hydride compound showing laser emission [3]. Using in the first step the multiconfigurational QM method CASSCF/MS-CASPT2 [4], and assuming for the last step the conventional laser rate equations of laser solutions, we have obtained a remarkable agreement between experiment and simulation [5]. These results, which can be extended to other QM methods and laser systems (*e.g.*, in nanophotonics), serves in helping to understand experimental results and enables the simulation, from first principles, of the laser properties and behaviour of hypothetical and/or non-yet-synthesized compounds (*i.e.*, *in-silico* screening).

References

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