Predicting the Second-Order Nonlinear Optical Responses of Organic Materials in Complex Environments: The Role of Dynamics

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The last thirty years have witnessed an ever-growing application of computational chemistry for rationalizing the nonlinear optical (NLO) responses of organic chromophores. More specifically, quantum chemical calculations proved highly helpful in gaining fundamental insights on the factors governing the magnitude and character of molecular first hyperpolarizabilities (β), be they either intrinsic to the chromophore molecular structure and arising from symmetry, chemical substitution, or π -electron delocalization, or induced by external contributions such as the laser probe or solvation and polarization effects. Most theoretical reports assumed a rigid picture of the investigated systems, the NLO responses being computed solely at the most stable geometry of the chromophores. Yet, recent developments combining classical molecular dynamics (MD) simulations and DFT calculations have evidenced the significant role of structural fluctuations, which may induce broad distributions of NLO responses, and even generate them in some instances.

This talk focuses on recent case studies in which theoretical simulations have highlighted these effects. The selected examples include organic chromophores, photochromic systems, and ionic complexes in the liquid phase, for which the effects of explicit solvation, concentration and chromophore aggregation are emphasized, as well as large flexible systems such as peptide chains and pyrimidine-based helical polymers, in which the relative variations of the responses were shown to be several times larger than their average values. The impact of geometrical fluctuations is also illustrated for supramolecular architectures through the examples of nanoparticles formed by organic dipolar dyes in water solution, whose soft nature allows for large shape variations translating into huge fluctuations in time of their NLO response, and of self-assembled monolayers (SAMs) based on indolino-oxazolidine or azobenzene switches, in which the geometrical distortions of the photochromic molecules, as well as their orientational and positional disorder within the SAMs, again highly impact their NLO response and contrast upon switching. Finally, the effects of the rigidity and fluidity of the surrounding are evidenced for NLO dyes inserted in phospholipid bilayers.

Which is the best method to compute hyperpolarizabilities?

Pau Besalú Sala

Over the past years, my PhD thesis has focused on assessing and improving quantum mechanical methods for the accurate calculation of static nonlinear optical properties, and more specifically hyperpolarizabilities. This research is crucial for the bottom-up design of smart materials with the desired electro-optical properties, and for the rationalization of experimental data.

Currently, mainstream DFT methods do not achieve the chemical accuracy attained for properties such as reaction barriers or thermodynamics, for the computation of hyperpolarizabilities. Conversely, wave function-based methods, while accurate, are impractical for medium-sized or large molecules due to their high computational cost.

In this seminar, we will summarize and explain the main features that a DFT functional must fulfill to yield accurate hyperpolarizabilities, and we will focus on the state-of-theart strategies such as the optimal tuning of range-separated (double) hybrid functionals,^[1] which redefine their parameter(s) for each particular molecule, and newer methods such as the Random Phase Approximation (RPA) correlation functional.^[2]

Finally, we will compare these against the performance of the accelerated or enhanced wave function-based methods, such as those based on Domain-based Local Pair Natural Orbtials (DLPNO) and Resolution of Identity (RI) techniques.^[3]

- [1] P. Besalú-Sala, S. P. Sitkiewicz, P. Salvador, E. Matito, J. M. Luis, *Phys. Chem. Chem. Phys.*, **2020**, 22, 11871-11880.
 - P. Besalú-Sala, P. Salvador, E. Matito, J. M. Luis, in preparation.
- [2] P. Besalú-Sala, F. Bruneval, Á. J. Pérez-Jiménez, J. C. Sancho-García, M. Rodríguez-Mayorga, *J. Chem. Theory Comput.*, **2023**, 19, 18, 6062-6069.
- [3] C. Naim, P. Besalú-Sala, R. Zaleśny, J. M. Luis, F. Castet, E. Matito, *J. Chem. Theory Comput.*, **2023**, 19, 6, 1753-1764.