International Conference on Quantum Energy 2025 hosted by Dipartimento di Fisica e Astronomia Galileo Galilei an event by ICQE

Contribution ID: **11** Type: **Oral presentation**

Simulation of 2DES from ab initio quantum chemistry

Friday 6 June 2025 12:00 (20 minutes)

Bidimensional electronic spectroscopy (2DES)[1] is a nonlinear optical technique that involves the interaction of a sample with a sequence of three ultrafast pulses, each separated by a precisely controlled delay. The resulting third-order signal is collected in a phase-matching direction. 2DES has proven to be an exceptional tool for probing quantum coherence in light-harvesting systems central to photosynthetic processes.[2] Over time, its applications have expanded to encompass a wide range of systems, including organic multichromophore complexes and fully inorganic materials, with many potential applications still to be explored.
The wealth of information embedded in a 2D spectrum often necessitates the use of advanced theoretical tools for accurate interpretation. Many of these approaches rely on density matrix dynamics, typically modeled through master equations and operating under the impulsive limit.[3] An alternative strategy involves wave-function propagation methods, which not only achieve results comparable to density matrix dynamics but also offer a more intuitive understanding.[4] In this case one of the possible approach which enables the extraction of the third order signal along a phase-matching direction is the phase cycling scheme.[5] Additionally, environmental effects, such as dephasing and relaxation, which lead to population and coherence decay, can be accounted for using stochastic methods like the Stochastic Schrödinger Equation.[6]
I will present a theoretical approach to compute the third order signal using a real-time approach based on wave-function dynamics and starting from ab initio calculation of the system. Our aim is to present simulations not only able to represent the final 2D spectrum, but that also closely aligns with experimental setups. This strategy will be applied to benchmark molecules and extended to systems of practical relevance in order to investigate quantum effects not still clear.

[1] Hybl, J. D., Albrecht, A. W., Faeder, S. M. G., & Jonas, D. M. (1998). Two-dimensional electronic spectroscopy. Chemical physics letters, 297(3-4), 307-313.
[2] Schlau-Cohen, G. S., Ishizaki, A., & Fleming, G. R. (2011). Two-dimensional electronic spectroscopy and photosynthesis: Fundamentals and applications to photosynthetic light-harvesting. Chemical Physics, 386(1-3), 1-22.
[3] Mukamel S. (1995) Principles of nonlinear optical spectroscopy. O.U.P, New York
[4] Albert, J., Falge, M., Keß, M., Wehner, J. G., Zhang, P. P., Eisfeld, A., & Engel, V. (2015). Extended quantum jump description of vibronic two-dimensional spectroscopy. The Journal of Chemical Physics, 142(21).
[5] Seibt, J., Renziehausen, K., Voronine, D. V., & Engel, V. (2009). Probing the geometry dependence of molecular dimers with two-dimensional-vibronic spectroscopy. The Journal of chemical physics, 130(13).
[6] Coccia, E., Troiani, F., & Corni, S. (2018). Probing quantum coherence in ultrafast molecular processes: An ab initio approach to open quantum systems. The Journal of Chemical Physics, 148(20).

Theme

Theme 3. Theoretical and experimental methods for quantum effects in energy processes

Primary author: DALL'OSTO, Giulia (University of Trieste)

Co-author: Prof. COCCIA, Emanuele (University of Trieste)

Presenter: DALL'OSTO, Giulia (University of Trieste)

Track Classification: Theme 3. Theoretical and experimental methods for quantum effects in energy processes