Intitulé du Sujet de Thèse : Controlling, Shaping, and Imaging Conical Intersections in Molecules

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Descriptif du projet

Conical intersections are points of degeneracy between electronic potential energy surfaces that act as ultrafast funnels for photochemical reactions. They are ubiquitous in photochemistry and photobiology, governing processes as fundamental as DNA photoprotection, vision, and photosynthesis, and represent one of the most striking manifestations of the breakdown of the Born–Oppenheimer approximation[1]. At a conical intersection, nuclear and electronic degrees of freedom become strongly coupled, giving rise to geometric phase effects, non-adiabatic population transfer, and the generation of electronic and vibrational coherences on femto- to attosecond timescales [2,3]. Understanding, and ultimately controlling, the passage of a molecular wavepacket through a conical intersection is therefore one of the central challenges of modern chemical physics.

This PhD project aims to develop and exploit a set of complementary theoretical and computational tools to control, shape, and image molecular wavepacket dynamics at conical intersections. The project is structured around three interconnected objectives.

The first objective is to actively control **non-adiabatic dynamics near conical intersections** using tailored laser fields. A series of timed laser pulses will be designed and applied to steer the nuclear wavepacket as it traverses the intersection, modifying the branching ratio between adiabatic and non-adiabatic pathways, and sculpting the resulting coherences. These simulations will be carried out using in-house quantum dynamics codes that allow a fully quantum-mechanical treatment of both nuclear and electronic degrees of freedom in model systems [4].

The second objective is to extend this framework to **full-dimensional, chemically realistic molecules** by implementing four-wave mixing pulse sequences in the PySpawn code [5-7], a trajectory-guided quantum dynamics platform suited for high-dimensional molecular systems. This implementation will enable the direct simulation of nonlinear spectroscopic experiments on molecules of genuine chemical interest, bridging the gap between model-system insight and experimental reality.

The third objective is the **development of new nonlinear spectroscopic methods**, based on four-wave mixing, capable of imaging the wavepacket as it passes through the conical intersection [8]. Particular emphasis will be placed on observables that are sensitive to the electronic and vibrational coherences generated during non-adiabatic passage, quantities that carry direct signatures of the geometric phase and the entanglement of nuclear and electronic motion.

Throughout, the project is embedded in a close, ongoing collaboration with Dr. Patrick Rupprecht (UC Berkeley), who performs FWM and attosecond spectroscopy in tabletop setups.

This synergy between theory and experiment will allow theoretical predictions to be directly tested. It will guide the design of new experimental observables, ensuring that the developed methods are not only computationally rigorous but also experimentally actionable.

Références Bibliographiques

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