Project title: Electronic Coherence in Molecules. Dynamics and Control

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Current state of the art

Coherences in molecular systems have become a focus of research, starting with the pioneering work of Zewail [1] and culminating in the discovery of the potential importance for photosynthetic light harvesting [2]. Notwithstanding the controversial discussion concerning its role in room-temperature biology [3], the very fact that quantum coherence could be a design principle not only in biology but also for artificial systems has been very inspiring [4]. Electronic superposition states created by ultrafast laser excitation are subject to decoherence due to the interaction with intramolecular vibrations and/or the environment (such as a solvent or protein). For molecules it is rather the rule than an exception that the strong coupling to vibrational degrees of freedom (vibronic coupling) renders the dynamics to become a unique molecular fingerprint showing the interplay of vibrational wavepackets moving along so-called tuning modes and changing the electronic state, e.g. at conical intersections involving coupling modes [5, 6]. In particular for complex systems this makes the interpretation of nonlinear spectroscopic signals a nontrivial task. On the other hand, electron-vibrational coupling can be used as a handle to control wavepacket dynamics [7] and even lead to surprising effects. For instance, laser control of electronic ring currents in porphyrins had been suggested using circularly polarized light exciting a superposition of the doubly degenerate E states [8]. Later, including the dynamical $E \times e$ Jahn-Teller effect it was shown that the direction of circulation depends on the actual wavelength of the laser [9].

Chlorophylls, i.e. derivatized porphyrins, and related macrocycles are particularly interesting due the fact that they feature two perpendicularly polarized excited electronic states, Q_x (S_2) and Q_y (S_1), whose energetic separation and thus the extent of vibronic coupling is tuned over a wide range, e.g., by the actual chemical composition and/or the solvent [10]. The variation in vibronic coupling causes the $Q_x \rightarrow Q_y$ relaxation time to span a range from 100 fs to 4 ps in typical systems [10]. Being the building blocks of photosynthetic pigment-protein complexes, chlorophylls were characterized by state-of-the-art two-dimensional spectroscopy [13], demonstrating various vibrational modes to contribute to electronic dephasing.

The simulation of vibronic dynamics of large molecules often rests on parametrized model Hamiltonians (e.g., the vibronic coupling Hamiltonian, VCH) [5]. The standard for high-dimensional quantum dynamics is the Multiconfiguration Time-dependent Hartree (MCTDH) method [12]. When it comes to condensed phase systems, MCTDH reaches its limits as it requires a discretization of the vibrational continuum. Here a reduced density matrix description is more appropriate [5]. In terms of numerical efficiency a stochastic unraveling of the non-Markovian dynamics was shown to lead to a versatile scheme coined Hierarchy of Pure States (HOPS) [14].

Research goals and working program

The overarching goal of this project is to provide an in-depth understanding of the quantum dynamics of electronic superposition states in molecules. To this end the project is structured into a methodological and an application part.

Method Development: The development of HOPS has been focused on the description of Frenkel excitons in environments with simple Drude type spectral densities. In cases where particular vibrational modes are of importance, one faces the problem of structured spectral densities increasing the numerical effort substantially. In the context of reduced density matrix theory we have shown that in such cases it is more advisable to include these modes into the relevant system [11]. For intramolecular dynamics including nonadiabatic transitions such a treatment of selected tuning and/or coupling modes (e.g. those being involved in a conical intersection) is mandatory. Therefore this project aims to provide the mathematical formulation and numerical implementation of a modified HOPS scheme with explicit inclusion of a certain number of vibrational modes into the relevant system. Reference calculations will be performed using MCTDH. It should be stressed that the proposed method shall be designed such as to be extendable to multichromophoric systems.

Applications: The dynamics of electronic superposition states in chlorophyll-like or related macrocycles after ultrafast excitation will be studied in close collaboration with the experimental group of S. Lochbrunner. Models of the VCH type for experimentally suitable molecules will be constructed using quantum chemical calculations. Due to the orthogonality of the two electronic transitions in these systems, laser field polarization provides an additional handle not only to unravel but also to control the excited state dynamics. Using linear or circularly polarized light, possible scenarios include broad-band excitation of both transitions and excitation of only one transition using a narrower bandwidth. In addition the type of superposition state may be controlled using polarization-shaped fields. Comparison with experiment will be performed on the basis of the wavelength-resolved signal anisotropy. Thereby the wavepacket dynamics can be linked to the experimental signal using the equation of motion approach [15].

Due to vibronic coupling the resulting dynamics will be nontrivial and a thorough understanding will require to study several systems with variable energy gap. Interesting questions to be addressed include: To what extent the electronic superposition state is influenced by vibronic coupling? Is there a special role played by strongly coupled modes as compared to the bath modes? How decoherence emerges during the passage through a conical intersection? Can the superposition state be controlled by the polarization and bandwidth of the excitation laser?

The project will be connected to related theoretical [6] and experimental (photoelectron spectroscopy) efforts of the Ottawa group.

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