

Coherence and decoherence in ultrafast molecular processes: non-Markovian approaches based upon a hierarchical effective-mode decomposition

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Photoinduced processes in molecular systems are often ultrafast (i.e., femtosecond to picosecond scale) and typically evolve in a non-Markovian regime where the environment --e.g., the solvent-- is neither static nor rapidly fluctuating. Quantum coherence plays an important role and can be surprisingly long-lived, in contrast to the conventional assumption that decoherence necessarily sets in within tens of femtoseconds. Against this background, the present talk summarizes our recent developments of reduced-dimensional representations of non-Markovian environments, based upon the construction of a set of effective environmental modes [1]. These effective modes, which are generated by suitable coordinate transformations from spin-boson type models, absorb the cumulative effects of the system-bath coupling and can be shown to reproduce the short-time dynamics exactly. Furthermore, inclusion of residual modes bilinearly coupled in a Mori chain type description successively accounts for the dynamics on longer times scales [2]. Termination of the chain by coupling the final chain member to a Markovian bath yields a representation of non-Markovian system-bath dynamics that converges to the exact dynamics as the chain is extended to higher orders. We have further shown that truncation of the chain at successive orders generates a family of approximate spectral densities which approach the true spectral density with increasing accuracy [3]. The approach has been applied, in particular, to non-adiabatic dynamics at avoided crossings and conical intersections [1-3]; recent applications include the study of exciton dissociation at interfaces of semiconducting polymers [2,4]. In these systems, decoherence is typically found to set in with a delay, beyond the shortest time scale which is determined by few effective modes.

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