Boosting the Efficiency of Nonadiabatic Dynamics Simulations

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Introduction

- Simulation of **ultrafast photodynamical processes** using nonadiabatic dynamics
- Computational **cost too high** for many interesting cases
- *Idea*: Application of **model potentials** to speed up the dynamics [1, 2]

Linear vibronic coupling model

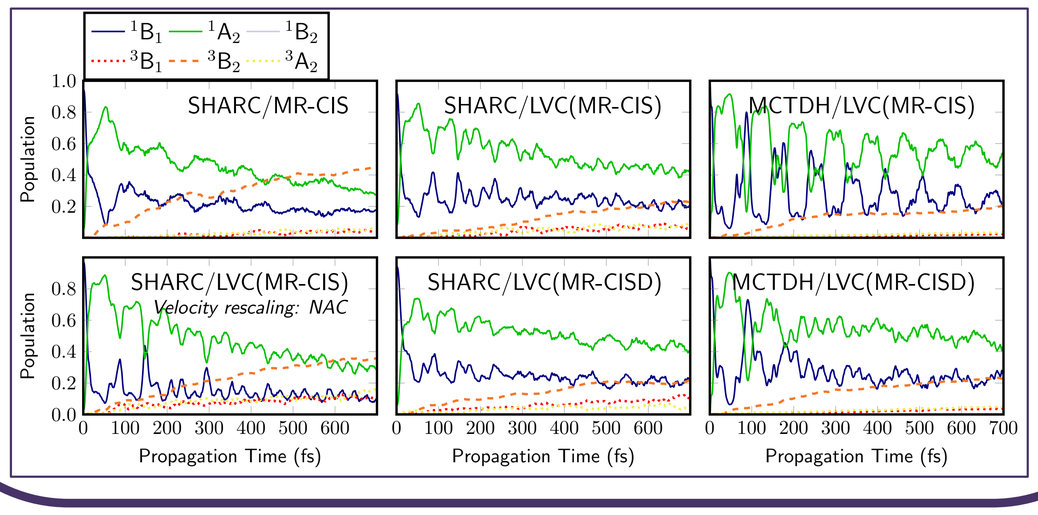
- Linear vibronic coupling (LVC) model: *Taylor expansion of the diabatic Hamiltonian matrix* [3]
- **Parameterisation:** Ground state frequencies and one single-point excited-state computation
- Overall computational **cost** of dynamics can be **reduced** by a factor **~1000** [1]

Intersystem crossing in SO_2

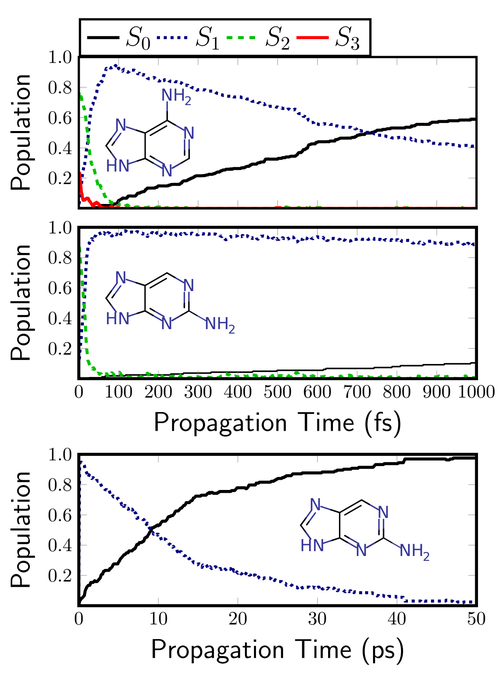
Compare dynamics at various levels of theory [1].

- Energy surfaces: *On-the-fly vs LVC model*
- Electronic structure: *MR-CIS vs MR-CISD*
- Dynamics method: *SHARC vs MCTDH*

Main physics reproduced by all methods.

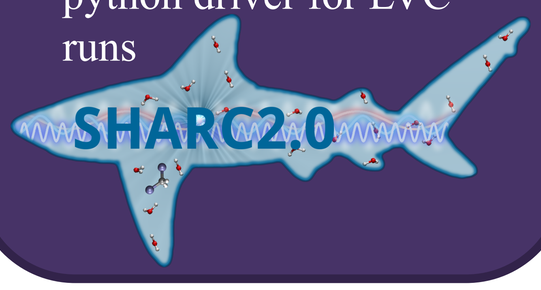


Photodynamics of adenine and 2-aminopurine



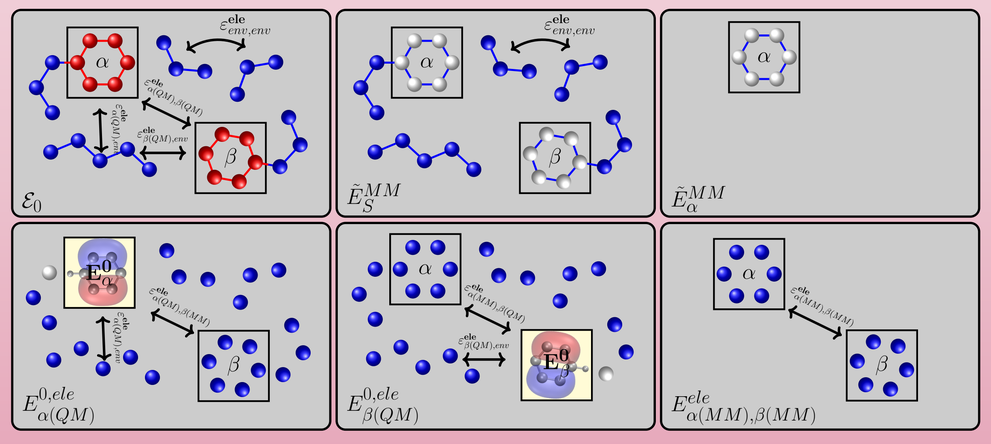
Implementation

- SHARC 2.0 molecular dynamics package https://sharc-md.org
- Exciton dynamics via Gaussian interface
- Many different electronic structure codes for LVC model parameterisation
- **PySHARC**: modular python driver for LVC runs



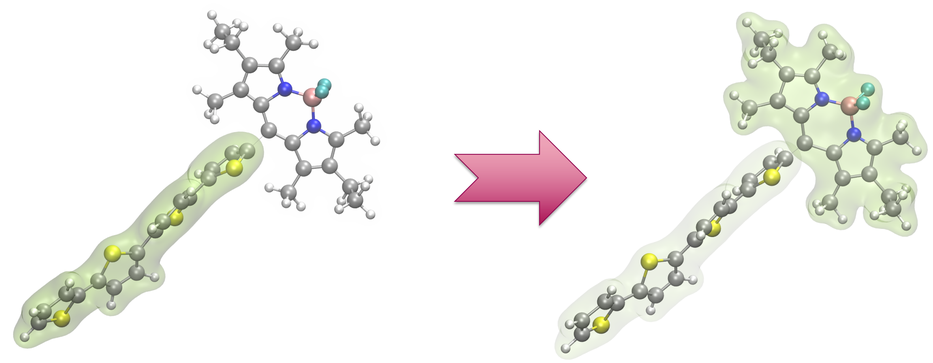
Frenkel exciton model

- Interaction of chromophores described using a Frenkel exciton model
- QM/MM electrostatic embedding
- Development of a consistent formalism including all types of interactions [2]

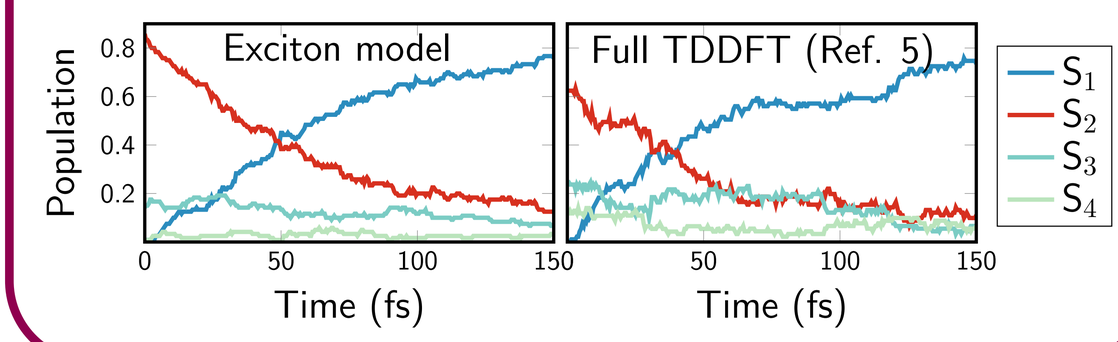


Energy transfer in a molecular dyad

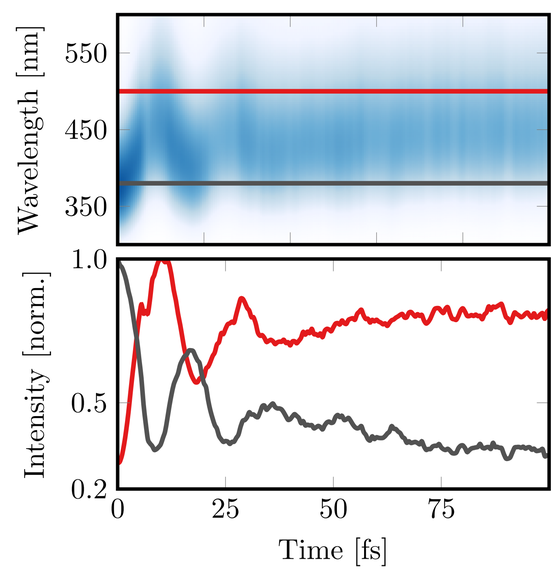
- **Sub 100 fs energy transfer** observed experimentally [4]
- Microscopic insight through computation [5]
- Compare to exciton model [2]



Reproduction of full TDDFT dynamics



New spectroscopic signature



- Early dynamics determined by **quantum beats**
- Prediction of **ultrafast oscillations** in time-resolved luminescence [2]

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