Mini-symposium



Pisa, CNR Research Area, 14 June 2022

Non-adiabatic Quantum Dynamics Simulations: From Grids to Gaussians *Graham Worth, University College, London*

Over the last couple of decades a number of different approaches to simulate the dynamics of photo-excited systems involving non-adiabatic coupling between electronic states. These range from accurate grid-based solutions to the time-dependent Schrödinger equation (TDSE) to simple trajectory based methods simulating the time evolution of the evolving wavepacket.

In this talk I will give an overview of the multi-configurational time-dependent Hartree (MCTDH) family of methods [1]. In the grid-based form of ML-MCTDH [2], these can accurately treat systems with many (over a hundred) degrees of freedom, but require simple Hamiltonians such as the linear vibronic coupling model [3]. In the Gaussian wavepacket-based form of G-MCTDH [4], we can use more realistic, flexible potentials, and in the form of DD-vMCG can even calculate the potential surfaces on the fly [5]. Examples will be used to show the abilities of the methods.

All of these methods (and more) have been implemented in the Quantics Package [6].

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Complementing Experiments in Complex Systems

Sandra Gómez Rodriguez, Universidad de Salamanca

One of our aims as theoretical chemists is helping experimentalists understanding their measurements. In this talk I will present three brief examples where our simulations have been key in unravelling photoinduced processes that can be observed by spectroscopists and that involve complex environments. With the aid of quantum dynamics using the Quantics package and a team of synthetic organic chemists and spectroscopists, we explore different routes to include the environment in our simulations, trying to defeat the curse of dimensionality along the way.

Excited states in DNA, from single nucleobases to base pairs, double helix and beyond: computational modelling of dynamics, spectroscopy, and environmental effects.

James A. Green, Goethe University, Frankfurt

A photochemical understanding of DNA is of fundamental relevance to life, due to damage of the genetic code by UV light, and the photoprotection mechanisms inherent in DNA that attempt to prevent this. Additionally, due to the unique and complex electronic behaviour of each of the nucleobases, and their ability to form a number of different multi-chromophoric structures, DNA provides a challenging playground for the development of methods that can be applied to related fields such as photosynthesis, optoelectronics, and biomedical devices. In this seminar, I will describe how a recently developed theoretical method to parameterise model Hamiltonians, in combination with quantum and classical dynamics calculations, can help elucidate photochemical behaviour in a range of DNA structures. At the single nucleobase level, the effect that ultrafast internal conversions have on the absorption spectrum lineshape will be demonstrated [1]. Then, the competition between these intra-base internal conversions and inter-base energy/charge transfer processes for the Guanine-Cytosine (GC) [2] and Adenine-Thymine (AT) [3] Watson-Crick base pairs will be shown. For the GC pair, initial work on including solvent effect on the quantum dynamics will be presented, with a view to accurately reproducing experimental conditions in time-resolved spectroscopy measurements. Then, towards modelling the double helix, stacking effects and the competition between single-strand and inter-strand processes will be shown for model GCGC tetrads. Finally, if time allows, an excitonic modelling simulation of the electronic circular dichroism spectrum of a non-canonical DNA structure, a Guanine-Quadruplex, will be shown, demonstrating the influence of charge transfer states and thermal fluctuations of the bases on the spectral shape [4][5].

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