ECAM State of the Art Workshop 3: Different Routes to Quantum Molecular Dynamics
Date: June 6 – June 10, 2016, EPFL, Lausanne, Switzerland

Organisers: Basile Curchod (University of Bristol, United Kingdom), Michele Ceotto (University of Milano, Italy), Guillermo Albareda (University of Barcelona, Spain), Ali Abedi (University of Basque Country, Spain), Philipp Marquetand (University of Vienna, Austria*)*

1. Overview

Quantum molecular dynamics is a rich and rapidly growing field, involving different communities in physics, chemistry, and applied mathematics. Applications range from controlling photochemistry, to predicting the effect of hydrogen diffusion in materials, to quantum computing. The key challenge is that simulating the exact quantum dynamics of multi-component systems of electrons and nuclei is a task currently out of reach, except for the simplest molecules with a few degrees of freedom. Approximations must then be developed to surpass the exponential scaling of computational (mainly memory) power needed to solve the time-dependent Schrödinger equation, describe more realistic molecular systems, and take simulations closer to experiments by improving the accuracy of available methods and developing new ones.

Current approaches can be roughly divided in the following sets: exact quantum calculations (applicable to low dimensional systems), wave-function based methods (where the wave-functions are expanded in convenient truncated basis, variationally optimized during the evolution), trajectory-based and trajectory–guided methods (in which the properties of the quantum system are mimicked via averages over ensembles of generalized, interfering, classical trajectories), semi-classical dynamics (based on second order approximations of the path integral representation of the quantum propagator), and path integral methods (employing exact methods to sample the quantum thermal density to tackle the time-domain). The main challenge for all these schemes is to maintain the balance between efficiency and accuracy, i.e. to keep the computational costs manageable while preserving the ability to predict and interpret experiments.

The available approaches span a wide range of formal frameworks and involve different communities. However, opportunities to establish common goals, unifying theoretical grounds, and solid and shared benchmarks are missing. Comparing shortcomings and advantages, understanding the restrictions of each approach, and defining benchmarks to assess merits and limitations of the different approaches to identify the different areas of applicability were then the main goals of this workshop. In addition, the issue of transferability of the methods to the industrial community was specifically addressed.

2. Programme of the workshop

Day 1 - June, 6th 2016 Quantum dynamics
(Chaired by Ali Abedi and Guillermo Albareda)
09:00 - 10:00 - Tucker Carrington
Computing (ro-)vibrational spectra with the Lanczos algorithm

10:00 to 11:00 - Uwe Manthe
Wavepacket dynamics and the multi-configurational time-dependent Hartree approach
11:00 to 11:30 - Coffee Break
11:30 to 12:30 - Discussion
12:30 to 14:00 - Lunch
14:00 to 15:00 - Review of critical issues & identification of work groups
15:00 to 15:25 - Guillermo Albareda
Towards ab-initio Molecular Dynamics without Born-Oppenheimer Potential-Energy Surfaces
15:25 to 15:50 - Neepa Maitra
Non-Adiabatic Dynamics in Strong Fields: Enhanced Ionization
15:50 to 16:15 - Edit Matyus
Pre-Born--Oppenheimer Molecular Structure Theory
16:15 to 16:40 - Aurelien Patoz
Geometric integrators of arbitrary order of accuracy for molecular quantum dynamics in electromagnetic fields
16:40 to 17:05 - Martin Mosquera
Non-standard Approach to Linear-response TDDFT and the Calculation of Excited-state Spectra
17:05 to 17:20 - Coffee Break
17:20 to 18:00 - Round Table Discussion: Future Directions

Day 2 - June, 7th 2016 Trajectory-based and trajectory-guided methods (Chaired by Philipp Marquetand, Basile Curchod, and Ivano Tavernelli)
09:00 to 10:00 - Joe Subotnik
Surface hopping in solution and at metal surfaces: Nonadiabatic processes all around us
10:00 to 11:00 - Dmitry Shalashilin
Coherent States and their use for Multidimensional Quantum Dynamics
11:00 to 11:30 - Coffee Break
11:30 to 12:30 - Discussion
12:30 to 14:00 - Lunch
14:00 to 15:00 - Review of critical issues & identification of work groups
15:00 to 15:25 - Antoine Carof
Electron Transfer in Organic and Biological Materials
15:25 to 15:50 - Benoit Mignolet
In Silico Photochemistry of the Thioformaldehyde S-oxide Sulfine. Beyond the Initial Ultrafast Decay
15:50 to 16:15 - Clemens Rauer
GAIMS-Generalized Ab Initio Multiple Spawning for both internal conversion and intersystem crossing processes
16:15 to 16:40 - James Snyder
GPU-accelerated multireference electronic structure calculations enabling large-scale nonadiabatic dynamics simulations
16:40 to 17:05 - Seung Kyu Min
Coupled-Trajectory Approach of Mixed Quantum-Classical Dynamics Based on Exact Factorization
17:05 to 17:20 - Coffee Break

17:20 to 18:00 - Round Table Discussion: Future Directions

Day 3 - June, 8th 2016 Semiclassical methods
(Chaired by Michelle Ceotto and Jiri Vanicek)
09:00 to 10:00 - Kenneth Kay
Semiclassical Initial Value Representation Methods: Some Future Directions
10:00 to 11:00 - Eli Pollak
Ab-initio semiclassical dynamics
11:00 to 11:30 - Coffee Break
11:30 to 12:30 - Discussion
12:30 to 14:00 - Lunch
14:00 to 15:00 - Review of critical issues & identification of work groups
15:00 to 15:25 - Riccardo Conte
Simulating Vibrational Spectra of Variously-sized Molecules via Multiple Coherent Time Averaging Semiclassical Initial Value Representation
15:25 to 15:50 - Giovanni Di Liberto
Accurate and Efficient Pre-exponential Factor Approximations for the Semiclassical Initial Value Representation Ppropagator
15:50 to 16:15 - Chiara Donatella Aieta
A quantum approximate method for the calculation of thermal reaction rate constants
16:15 to 16:40 - Fabio Gabas
An Efficient Computational Approach for the Calculation of the Vibrational Density of States
16:40 to 17:00 - Coffee Break
17:00 to 17:40 - Round Table Discussion: Future Directions
19:30 to 22:00 - Dinner
Day 4 - June, 9th 2016 Path integral molecular dynamics
(Chaired by Giovanni Ciccotti)
09:00 to 10:00 - David Manolopoulos
Ring polymer molecular dynamics
10:00 to 11:00 - Stuart Althorpe
Quantum statistics + classical dynamics: what is it?
11:00 to 11:30 - Coffee Break
11:30 to 12:30 - Discussion
12:30 to 14:00 - Lunch
14:00 to 15:00 - Review of critical issues & identification of work groups
15:00 to 15:25 - Timothy Hele
Derivation of the exact non-adiabatic quantum propagator in the classical-like mapping variable representation
15:25 to 15:50 - Michael Willatt
Approximate Quantum Time-correlation Functions from Matsubara Dynamics
15:50 to 16:15 - Romain Dupuis
Path Integral Methods for Isotopic Fractionation of Li and Proton Diffusion in Hydroxides
16:15 to 16:40 - Aaron Kelly

Accurate Nonadiabatic Dynamics on the Cheap: Harnessing Quantum-Classical Theory with Generalized Quantum Master Equations

16:40 to 17:00 - Coffee Break

17:00 to 17:40 - Round Table Discussion: Future Directions

Day 5 - June, 10th 2016 Discussions on standardized outputs, benchmarks and industrial engagement

(Chaired by Dominic Tildesley)

09:00 to 11:00 - Discussion

11:00 to 11:30 - Coffee Break

3. List of participants

Last Name	First Name	Affiliation
Gomez Rodriguez	Sandra	University of Vienna, AT
Rauer	Clemens	University of Vienna, AT
Mignolet	Benoit	University of Liege, BE
Carrington	Tucker	Queen's University, Kingston, CA
Seitsonen	Ari Paavo	Ecole Normale Superieure, FR
Carof	Antoine	Phenix, UMR 8234, FR
Agostini	Federica	MPI fur Mikrostructurphysik, DE
Kelly	Aaron	MPI fur Mikrostructurphysik, DE
Manthe	Uwe	University of Bielefeld, DE
Schild	Axel	MPI fur Mikrostructurphysik, DE
Matyus	Edit	Eotvos Lorand University, HU
Kay	Kenneth	Bar-Ilan University, IL
Petersen	Jakob	Weizmann Institute of Science, IL
Pollak	Eli	Weizmann Institute of Science, IL
Aieta	Chiara Donatella	University of Milan, IT
Ciccotti	Giovanni	University of Rome, La Sapienza, IT
Conte	Riccardo	University of Milan, IT
Di Liberto	Riccardo	University of Milan, IT
Gabas	Fabio	University of Milan, IT
Min	Seung Kyu	Ulsan NIST, KR
Dupuis	Romain	Donostia IPC, ES
Bonella	Sara	EPFL, CH
Karandashev	Konstantin	EPFL, CH
Patoz	Aurelien	EPFL, CH
Tavernelli	Ivano	IBM-Zurich Research, CH
Vanicek	Jiri	EPFL, CH
Althorpe	Stuart	University of Cambridge, UK

Lu	Haichang	University of Cambridge, UK
	David	University of Oxford, UK
Shalashilin	Dimitri	University of Leeds, UK
Willatt	Michael	University of Cambridge, UK
Hele	Timothy	Cornell University, US
Maitra	Neepa	Hunter College, US
Mosquera	Martin	Northwestern University, US
Parrish	Robert	Stanford University, US
Sanchez	David	Stanford University, US
Seress	Laszlo	Stanford University, US
Snyder	James	Stanford University, US
Subotnik	Joe	University of Pennsylvania, US
Varga	Kalman	Vanderbilt University, US

4. Major outcomes

Given the spirit of the workshop, focused on a survey of the state of the art, the main outcomes of the discussions aim at setting the stage for promoting further development and creating the best research environment for them. In fact, it was recognized that quantum dynamics is transitioning from the pioneering to a more established phase of development. The consensus was that the next five years will lead to a consolidation of the different methods developed over the years, eventually producing new physical and chemical insights in the reaction dynamics of polyatomic molecules and condensed phase systems.

The following points were singled out of the discussion:

1. Given the cost of approximate quantum dynamics, its application to realistic systems usually requires accurate potentials at lower cost than full first-principles electronic structure calculations. In this context, the workshop highlighted a clear recent development extending the range of exact quantum dynamics simulation: the availability of high-dimensional high-quality potential energy surfaces (mainly for ground state reactions). Key to this achievement is the development of new fitting and interpolating techniques, in particular those based on neural networks. With these potential energy surfaces, gas-phase quantum dynamics simulations of relatively complex reactions were carried out ($CH_4 + H^+$, for example), highlighting new physics and chemistry for the reaction of polyatomic molecules. Furthermore, alternative approaches were discussed, where electronic structure calculations are avoided by defining a fully time-dependent framework for electrons and nuclei
2. The importance of communication with the electronic structure community was highlighted. In fact, while until recently the development of electronic structure techniques was focused on the simulation of large systems, it is expected that in the next years a lot of effort will be devoted to accelerate the existing algorithms, with speed-ups of several orders of magnitude. Ab initio quantum dynamics and its applications to molecular

systems will benefit greatly from this tremendous acceleration.

3. The recent development of fast Ring Polymer Path Integral techniques allows for the inclusion of nuclear quantum effects (zero-point energy or tunneling effects) in the computation of molecular reactions and condensed phase simulations, and, in some cases, at the cost of standard ab initio molecular dynamics. Semi-classical molecular dynamics is also now available on-the-fly and it has been mainly employed for spectroscopic calculations of gas phase molecules, up to hundred degrees of freedom.
4. The recent inclusion of spin-orbit coupling in more approximate methods makes it now possible to simulate complete photochemical relaxation pathways with techniques such as surface hopping or ab initio multiple spawning.
5. New areas of application for quantum dynamics were identified. In particular, Ring-polymer molecular dynamics (RPMD) at the cost of classical molecular dynamics, presented in this workshop, paves the way for the inclusion of quantum effects in condensed phase reactions and in biological processes. Other significant applications include: reaction mechanisms of polyatomic molecules, tunneling in proteins, electrochemical processes with surface hopping, photochemistry with both surface hopping and ab initio multiple spawning, hydrogen diffusion on surfaces and in the bulk in connection to battery technology and materials design via linearized approximations of the dynamics.

To fully exploit the recent progress in quantum dynamics, the discussion stressed the need to continue practical testing and theoretical analysis of the methods. This is particularly important since it was anticipated that in the near future the quantum molecular dynamics community will split into two groups: one interested in method development, and another more focusing on applications. This change is similar to the splitting that occurred in the electronic structure theory community. It will lead to the formation of a community of "computational chemistry for quantum dynamics" and it is crucial that methods are sufficiently reliable to be used as a "black box" by academic community oriented towards applications. This is also key when discussing transfer of methods and software in the field to industrial partners.

During the discussions, the community highlighted different challenges for the field. Four main questions were identified:

1. How can we reach statistical limits with the current quantum dynamics methods?
2. How can we treat electrochemical problems in the context of non-adiabatic quantum dynamics?
3. How can we deal with gas-surface reactions?

5. Community needs

The community did not express any particular need in terms of computational infrastructure. This is mostly due to the "exponential scaling" law of quantum

dynamics, which requires more brainwork than brute-force computational power to be circumvented. In this relatively young area of research then, the development of new methods and refinement of existing ones is still the major driving force. It was hence a common impression among the participants of the workshop that the major need in the community is man power.

Procuring sufficient human resources is all the more important given that the part of the community focused on development of new techniques and algorithms is rather small, and tends to reduce over time due to the decreasing funding for fundamental research.

However, the discussion also recognized that the transition from the early development stage of the different available methods to a stable production activity will drive the evolution of the software, currently mostly in house codes, towards the creation of packages, again in analogy to the history in electronic structure. In this sense, the youth of the field and the existence of the new E-INFRA5 CoEs, and in particular of E-CAM, offers a unique opportunity to create a more organic environment for software development, documentation, and maintenance. Identifying the optimal hardware architecture (GPU vs CPU, for example) for quantum dynamics is also an interesting, and at the moment largely unexplored question that will benefit from interactions with E-CAM.

The community is eager to promote opportunities for interaction and exchange that bring together a wide spectrum of researchers active in quantum dynamics. These opportunities are at the moment extremely rare but are clearly key for the development of the field. It was suggested to continue and consolidate the series of workshops hosted by CECAM in the last five years to stabilize this opportunity to exchange on recent developments. CECAM workshops are particularly suitable for this need, as the community is not yet large enough for considering the organization of a big conference, most likely scientifically sterile due to the lack of intensive discussions.

6. Funding and Resources

In terms of funding, discussions during the workshop indicated that the field of quantum dynamics would tend to be more and more application-oriented, as fundamental research tends to be harder to get funded. Horizon 2020 is clearly a potential funding channel, and recent developments, which pave the way to biological and energy-related applications, might lead to successful ERC projects. EPSRC, in the UK, is a clear source of funding for the development of new quantum dynamics methods.

7. Developments for society and industry

As technology reaches smaller time and length scales, the quantum properties of matter gains relevance for society and industry. Furthermore, the ubiquitous presence of hydrogen in materials (e.g. impurities in steal) and devices for clean energy (proton based batteries) makes these simulations relevant also in macroscopic devices and at ambient conditions. Finally, the recent interest in the potential revolution of quantum computing – both in terms of simulating devices that could be used as q-bits, and developing quantum algorithms for application

in areas ranging from chemistry to cryptography – has opened a whole new set of opportunities for interactions with hardware developers

Quantum dynamical simulations are then increasingly important in many industrial sectors, including hardware design (e.g. coherence and interference effects for quantum control or design of q-bits), pharmaceutics (tunneling in enzymatic reactions), energy production or storage (when light is used to induce quantum physical or chemical transformations).

Collaborations in these fields are already active. In the context of E-CAM, new simulation methods and algorithms for quantum computing are being developed in collaboration with IBM. Similar collaborations involve some of the participants to the workshop. Surface hopping and multiple spawning are methods of choice to simulate the excited-state dynamics of molecular systems. Applications of these techniques to dyes and emitters have been reported, and brought new insights for the design of molecules in domains such as dye-sensitized solar cells (collaborative projects, for example with, Dyesol, Greatcell) or organic light emitting diodes (collaborative projects, for example with, BASF, Novaled). Excited state, and in particular non-adiabatic, dynamics is potentially interesting also for pharmaceutical companies, for example in connection to preventing photo-damage (leading to skin cancer).

Applications of quantum dynamics techniques are also central to reveal reaction mechanisms of atmospheric molecules. Models for these reactions currently employ experimental data, but usually require to complement insufficient data with very simplified models, often not accurate enough. Using quantum dynamics to circumvent the problem of missing experimental data would lead to more accurate atmospheric composition models, with a direct societal impact related to the study of chemical reactions involving small molecules on current climate changes.

It was stressed that, while it is extremely important to evaluate each potential collaboration individually to avoid creating expectations that cannot be met, the field of quantum dynamics is now approaching sufficient maturity to pursue more actively industrial engagement. To promote this, it will be important to create communication channels between academia and industry to disseminate the potential applications of the field. It was also pointed out, however, that the technical difficulties and the earlier stage of development of quantum molecular dynamics compared to classical molecular dynamics or electronic structure calculations, currently prevent “blind” knowledge transfer to industry and that the best strategy at the moment seems to encourage one-to-one collaborations with experts.