Recent developments in quantum dynamics, an E-CAM state-of-the-art workshop

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1 State of the art

Quantum dynamics is an active and rapidly developing area at the forefront of simulation and modelling. The intrinsic difficulty of the problem lies in the exponential cost with the number of degrees of freedom of exact numerical solutions of the basic quantum evolution equation. Consequently, several approximate methods, stemming from different formulations of the quantum dynamical problem (e.g. wavefunction vs path integral based) have been proposed. Assessing similarities and differerences, together with the relative merits in terms of accuracy and numerical efficiency of the different approaches is currently one of the key challenges. In parallel, interesting applications are pursued both coupling the approximate quantum dynamical algorithms with first principles calculation of the interactions in the ground state Born-Oppenheimmer approximation, and going beyond this approximation in the so-called non-adiabatic regime typically via advanced empirical models for excited electronic states and their couplings.

Although some recent developments in this direction have appeared, including those originating from the efforts fostered by E-CAM, very few scalable and trusted community codes exist. This originates (1) the need for frequent assessment of the state-of-the-art in the field to monitor progress and avoid duplication of efforts; (2) the coordination of software development packages with high-performance potential and the frequent update of existing packages to incorporate emerging algorithms; (3) training of junior researchers in methods and algorithms to facilitate not only new methodological developments but also the transition towards development of well-recognized community packages in the spirit of other communities (e.g. electronic structure, classical molecular dynamics).

2 Major outcomes

Continuing in the spirit of the previous E-CAM state of the art (SOA) workshop that was held in 2016 in Lausanne, a broad overview of the field of quantum dynamics was presented. Current and emerging quantum dynamics methodologies were introduced and critically

discussed from their basic assumptions to their most recent extensions, including their pitfalls and possible improvements, in the hope that the ideas exchanged will promote exciting new developments. The key aspects of the research reported in the different sessions of the workshop are detailed below. A dedicated session (see below) was devoted to high-end software development and input for the E-CAM project.

I. Theoretical Foundations of Quantum Molecular Dynamics

Hardy **Gross** presented the exact factorization of the (electron-nuclear) wave-function; its history and development, ongoing work on nonadiabatic reaction dynamics in molecules, and extensions to solids using it as a starting point to extend the original idea of time-dependent density functional theory. Stuart **Althorpe** discussed real time quantum dynamics on the ground electronic Born-Oppenheimer potential energy surface, from the perspective of imaginary time path integrals. The Matusbara dynamics allows insight into other imaginary time methods such as CMD, RPMD, and TRPMD. Nancy **Makri**, discussed her recent work on developing numerically efficient real-time path integral techniques for simulating the dynamics of complex quantum systems without approximations. A modular path-integral appproach for quantum systems embedded in harmonic environments, and a quantum-classical path-integral (QCPI) approach for general systems, were introduced and discussed.

II. Nuclear Quantum Effects and Vibrational Spectroscopy

The development of numerically efficient semiclassical dynamics methods, and ring-polymer path integral techniques, allow for the inclusion of nuclear quantum effects (zero-point energy or tunneling effects) in the computation of molecular reactions and condensed phase simulations. In this area, Michele **Ceotto** presented the latest developments in SC-IVR based methods for simulating IR spectra in complex molecular systems, like DNA nucleobases. A number of comparisons with experiment were detailed, indicating encouraging performance with increasing molecular complexity. Ari **Seitsonen** presented work on the PaPIM E-CAM software package, which has implemented the necessary infrastructure to perform for linearized semiclassical simulations of IR spectra for molecular systems. Recently, PIMD approaches are being more commonly used in combination with ab initio electronic structure methods, and in some cases machine-learned potential energy surface fits from ab initio data as well. Mariana **Rossi** discussed how nuclear quantum effects play a role in determining structure and dynamics in weakly bonded systems, using a combination of thermostatting techniques, imaginary-time path integrals, density functional theory, and machine learning methods. Reaction rates, IR spectra, and temperature dependence of transport properties for a selection of systems were presented. Michele **Ceriotti** presented work on how quantum and thermal fluctuations can be decisive to the form and function of molecules and materials, using techniques largely based on performing GLE-thermostatted path-integral molecular dynamics on machine-learned potential energy surfaces. Simon **Huppert** also presented work on using GLE thermostats, based on the fluctuation-dissipation relation, to cure the zero-point energy leakage problem within the quantum thermal bath approach.

III. Quantum Molecular Dynamics: Recent Method Development and Applications

Basile **Curchod** discussed the efficacy of a variety of approximations and approximate approaches like surface hopping, in studying the photoexcitation dynamics of LiH, mainly focusing on the ab initio multiple spawning based family of methods. Arend **Dijkstra** presented his recent work on modeling nonlinear optical spectra using exact dynamics approached like HEOM for model molecular systems, to elucidate the photochemical dynamics of adenine in solution. Federica **Agostini** presented her work on nonadiabatic dynamics via the coupled - trajectory mixed quantum-classical approach, which is based on the exact

factorization, and has been integrated with ab initio packages to perform on-the-fly simulations of photochemical relaxation in small gas phase molecules as well. In a similar spirit to the exact factorization approach. Guillermo **Albareda** discussed his work on nonadiabatic dynamics on a single potential energy surface via the conditional wavefunction approach. At the top-level this technique is equivalent to the exact factorization, but the slight change in representation leads to different possible approximate approaches. Emphasis was also placed on the discussion and analysis of the quasi-classical mapping representation. Jian **Liu** presented a perspective on developing path integral methods in the mapping representation, detailing the prescriptions for the quantum statistics and dynamics of nonadiabatic systems. In addition, Eitan **Geva** discussed quasi-classical mapping-based methods for nonadiabatic dynamics, and Jeremy **Richardson** presented two improved nonadiabatic mapping approaches.

IV. Numerically Exact Wave-function-based Methods

Tucker **Carrington** presented his work on the utility of collocation-based methods in quantum mechanics, as one can largely avoid variational theory and the calculation of integrals, at the expense of having to calculate the values of functions at points. Connections and combinations were made with MCTDH and Smolyak grids to maximize the performance of the collocation based approach. Continuing on the topic of MCTDH, Uwe **Manthe** discussed how to approach an MCTDH calculation for systems of distinguishable and indistinguishable particles using the optimized second quantization representation method for MCTDH. One goal would be to use such an approach to simulate the superfluid phase of Helium. Dmitry **Shalshilin** detailed the development of a variety of generalized coherent state methods for quantum dynamics, and reported on a selection of historical benchmark calculations using these methods, as well as recent high-level applications in photoactive materials.

V Round table - Towards the systematic development of scalable community codes in quantum dynamics

The participants engaged in a round-table discussion about the E-CAM project, and the broader issue of availability and community development of codes for quantum molecular dynamics simulations. In the quantum molecular dynamics community, one is traditionally either interested in method development, or is focused on use for applications. The ability to develop links between developers and users is hampered by the lack of a solid base of accessible software, and the tradition of writing in house codes for (almost) everything. The following main input was identified as useful future developments within E-CAM and beyond:

1. Engage with electronic structure and classical molecular dynamics to ensure that
    a. Best practices for high performance software established in these communities, more experienced in the development of high-end software, are transferred to quantum dynamics;
    b. Facilitate integration or interfacing of quantum dynamic software modules with community packages in these communities to promote, after appropriate validation, uptake by a broader community and to open the possibility of new multiscale approaches;
2. Establish recurrent schools in the area of quantum dynamics focusing not only on methodological developments, but also on uptake of HPC best practices by new generations of practitioners;
3. Disseminate existing large scale and HPC oriented packages (e.g. E-CAM flagship codes PaPIM and Quantics, the i-Pi suite) and promote modular development of scalable implementations of new functionalities;

4. Encourage the transition, already happened in ab initio and classical MD communities, towards highly performant and transferrable codes;
5. Explore interactions with groups beyond Europe (those represented at this workshops, but not only) to enhance dissemination of current coordinated software development efforts within E-CAM and to promote collaboration with similar initiatives, in particular in the USA;
6. Explore uptake of new hardware - in particular the use of GPUs - to boost performance.

From a political viewpoint, a clear problem is that the part of the community focused on development of new techniques and algorithms is rather small, and furthermore tends to reduce over time due to the decreased amount of funding dedicated to fundamental research. This tends to limit the lifetime of many (all) new codes that are built, due to the work required to maintain large codes or packages. The ability to link the needs of the various sub-communities could lie in educational materials and workshops on good coding practices, and aspects of high-performance computing. E-CAM provides an ideal environment to sustain, within CECAM, long-term initiatives to mitigate these criticalities.

3 Community needs

Timely exchange of information is critical in this constantly evolving area. The dissemination of existing software tool and the enhancement of coordinated development efforts is also a priority. The development of portable, well-documented software specifically targeted at training in the existing recurrent community schools and beyond is identified as a clear need to facilitate quicker uptake of complex methods from new practitioners. The creation of a shared set of community benchmark is recommended. Integration of methods in existing HPC oriented codes for electronic structure and classical molecular dynamics is highly desirable in view of applications beyond model systems. Finally, dissemination of reliable methods and user friendly codes to new communities should be pursued.

4 Funding

Funding opportunities for advanced meetings and for schools are ensured by CECAM and Psi-k. Importantly, these funding bodies, in particular CECAM, enables recurrent workshops and schools to take place. This has strengthened the sense of community in the teams in this area and it is critical both to enable timely information transfer and to maintain high-level training activities that have aquired a very strong reputation.
Research funding still occurs predominantly at a fundamental level, with several ERC, NSF, SNSF grants awarded in this area. Collaboration opportunities with industry are increasing, in particular due to potential interactions with developers of quantum computers where quantum dynamical methods are of interest both for technological aspects (e.g. assessment on the effect of the environment on qubits, simulation of new qubit systems) and, in the longer run, as an application domain.

5 Will these developments bring societal benefits?

In addition to the area of quantum computing, approximate methods for simulating time-dependent quantum properties are increasingly interesting in different application domains of societal interest. A clear reason for this is the ubiquitous presence in solvents and compounds of biological interest and beyond of hydrogen, an element that shows quantum behaviour also at ambient or physiological conditions. Furthermore, non-adiabatic phenomena play a role in the development of environmentally relevant devices (e.g. solar cells) or in medicine (e.g. light induced DNA mutations at the origin of some cancers). The adoption of simulation protocols to complement experimental or clinical information is of clear interest in these areas.
In spite of these interesting and challenging opportunities, care should be taken in ambitious applications. The field is rapidly aquiring maturity, but calculations are complex and typically do not permit reliable turn-key solutions. That said, progress has been continuous in the past five to ten years and perspectives are very encouraging.

6 Participant list

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