PRACE Spring School 2016 and E-CAM Tutorial on Molecular & Atomic Modelling

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1 State of the art

Simulating the exact quantum dynamics of systems of interacting particles is presently a task beyond reach but for the smallest systems, as the numerical cost for solving the time-dependent Schrödinger equation scales exponentially with the number of degrees of freedom. Consequently, considerable effort is devoted to developing approximate algorithms to reduce the computational cost of quantum dynamical properties with an acceptable, and controlled, loss of accuracy. However, due to their intrinsic differences in the way the fundamental equations of motion are approximated the direct comparison of methods is often very difficult and in many cases unsatisfactory. Therefore, while the available approaches span a wide range of applications and formal frameworks, common goals and unifying theoretical grounds are somehow missing. Different levels of possible approximations involved in practical developments lead to a natural classification of methods in this field. There are techniques, such as multiconfiguration time-dependent Hartree (MCTDH), addressing the full quantum nature of a given set of degrees of freedom. Semiclassical methods, based on the path integral formulation of quantum mechanics, can instead be combined with a representation in terms of classical trajectories via a stationary-phase approximation and still account for quantum effects such as interference or tunneling. Moreover, these methods can be naturally combined with on-the-fly ab initio evaluation of the energies, forces, and couplings. There are also different flavors of mixed quantum-classical approaches, either considering the density matrix as basic variable (as in the partial Wigner representation of the Liouville-von Neumann equation or in the linearized version of the path integral representation of thermal correlation functions), or based on the wave function formalism (as in trajectory surface hopping, non-adiabatic Bohmian dynamics and the quantum-classical treatment of the factorized form of the electron-nuclear wave function). Finally, there exist also several successful heuristic approximate methods for dynamics at finite temperature, e.g., the centroid and ring polymer molecular dynamics. A few attempts have been reported, whose goal was analyzing the connections among those methods, comparing their shortcomings and advantages, understanding the restrictions of each approach and developing schemes with more general validity. However, it seems that these have been isolated examples, limited to only some of the methods listed above. An exhaustive and comprehensive analysis should instead include a broader sample of the state-of-the-art methods, with well-defined benchmarks to assess merits and limitations of the different approaches and to identify the different areas of applicability. These issues were discussed in the workshop.

2 Major outcomes

Two main strategies to address the problem of the validation and verification of the different solutions to quantum dynamics were identified. The first deals with the design of model systems that can be solved with the different approaches. The purpose of this test is not to judge the quality of the different methods, but to identify strengths and

weaknesses of the approaches to design possible improvements. Having a set of models for which the 'exact' solution is available will provide clear guidelines for the future development of the field. The second strategy is based on the design of a class of realistic model systems that constitute a valid challenge for all available solutions to quantum dynamics. In this case, the aim is to design problems that each community can try to solve. The quality of the different solutions can be assessed through crosschecking or by direct comparison with available experimental results. This challenge will provide important information about the quality of the results that can be obtained from the different approaches. We hope in this way to be able to provide guidelines for the selection of the most appropriate method for the evaluation of a desired observable (spectral function, quantum yield, nonadiabatic ratio, time scale for a given reaction). Finally, the comparison among the different solutions will allow the development of better theories and algorithms and the creation of synergies among the different approaches.

Some key problems in quantum dynamical simulations were also highlighted. First, the need for accurate potential energy surfaces. This is one of the main bottlenecks for quantum dynamics simulations. Traditional methods require global surfaces and at present it is not possible to calculate surfaces for systems with more than a few (3-4) atoms. In part this is down to the large number of computationally intensive electronic structure calculations required to cover the appropriate configuration space. A second problem is finding suitable fitting functions. Model potentials with suitable parameterisation are one way forward, but while these may be powerful in providing insight into dynamical behaviour, they are often limited in scope. For this reason the present state-of-the-art is developing "direct dynamics" methods in which the potential function is calculated on-the-fly only when required. The potential surface problem is exacerbated for non-adiabatic problems in which excited-state surfaces and non-adiabatic couplings are also required. New electronic structure methods are needed to cope with these problems in a straightforward way. Second, the field lacks user-friendly codes. Quantum dynamics is still an emerging field with much work presently on algorithmic development. Most software is still "one group" codes, not easy to use by someone outside a narrow circle of experts. For the development of the field it is important to create codes so that they can be broadly used, e.g. by experimentalists. This will move the field to a more main-stream discipline able to support a wider range of users and so gain validity. There is indeed some movement in this direction, especially surface hopping codes (CPMD, SHARC, Newton-X), and the MCTDH based Quantics package, but more developments are required.

3 Community needs

The community would benefit from a centralized web platform providing access to quantum dynamics software, potential energy surfaces, benchmark results, and description of the underlying algorithms. The first step has already been taken to achieve this goal—namely, a Wikimedia page (qdyn.cecam.org) has been set up at CECAM. The main purpose of this platform is to build a database of quantum dynamics algorithms: the contributors would either upload their software or provide a link to an external web site, from which this software is accessible. The format of the Wikimedia page allows each contributor to include a description of the algorithm, instructions for using the software, and explanation of provided examples. In addition to a software repository, the web platform will serve as a library of potential energy surfaces and benchmark results obtained for various systems by various methods. Maintaining this web platform will require a certain amount of data storage facilities, particularly for the collection of benchmark results. Yet, this effort will certainly pay off in facilitating the exchange of new ideas and accelerating progress.

4 Funding

The most common funding source so far have been COST actions. As the industrial interest towards quantum dynamics increases, however, new funding possibilities appear. For example, one of the Work-Packages of the recently established H2020 Center of Excellence for Computation E-CAM is devoted to quantum dynamics. Public private partnerships based on E-CAM should be explored further.

5 Will these developments bring societal benefits?

Quantum dynamical effects are increasingly important in many industrial sectors including hardware design (coherence and interference effects), pharmaceutics (radiation damage), and energy production (when light is used to induce quantum physical or chemical transformations for application, for example, to solar cells). Future increase in computational power and method improvements will make it possible to extend the methods discussed in this workshop towards technologically and experimentally relevant scales and contribute to drive innovation.n