Editorial

Quantum dynamics in molecular systems

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This special issue brings together 12 original research contributions under the title "Quantum dynamics in molecular systems." It is related to the Groupement de Recherche (GDR) THEMS, a research network encompassing many groups throughout France that develop theoretical methods in atomic, molecular, and chemical physics, and employ them in a wide variety of domains. These methods require mastering the structure and dynamics of quantum systems involving a finite number of bodies. The studied systems can be isolated in gas phase or submitted to electromagnetic fields or embedded in some environment.

The GDR THEMS, which stands for *"Dynamique quantique dans les systèmes moléculaires: théorie, modélisation, simulation"* ["Quantum dynamics in molecular systems: theory, modeling, and simulation"], was created in January 2013 and renewed in January 2017. This network evolved under the auspices and sponsorship of the Institut de Physique (INP) of the CNRS, the French national center for scientific research. The GDR has been very successful: it allowed the initiation of new collaborations, the training of young researchers through schools, while the 2-day annual meetings held in various cities in France provided opportunities for enriching oral and poster presentations by its members or by external invited speakers. Formally and administratively, the GDR THEMS ceased to exist at the end of 2021.

In 2022, the GDR community believed it would be useful to have a written record of its current scientific activities. The idea beyond this special volume is thus to provide a picture of the GDR THEMS topics, by proposing a variety of contributions on theory, modeling, and simulations of quantum dynamics in molecular systems. While this volume intends to present this global theme, the content will show the diversity of applied systems and the richness of methods (theoretical or numerical) used or developed. The covered topics aim, in general, to present how the GDR THEMS research groups characterize the response of atomic and molecular systems to various stimuli, for instance interactions with an external field or through a scattering process. Specifically, we have collected contributions describing efforts toward (i) controlling the behavior of molecules under the effect of external fields, (ii) developing simulation techniques to address collision reactions or vibrational predissociation, (iii) tackling the problem of scattering and absorption of atoms and molecules at surfaces, and (iv) understanding photochemical reactions involving excited-state dynamics.

Below, we provide a brief overview of the 12 articles contained in this special issue. They have the common characteristic of dealing with theoretical and/or numerical methods. Some are more dedicated to development, while others are more focused toward applications. In spite of the diversity of methods and systems, one may group the contributions as follows:

1 Development of methods

The paper by Mangaud et al. [1] is dedicated to Osman Atabek's memory. It provides a pedagogical survey of the hierarchical equations of motion combined with tensor-train implementation, a well-established method to study open quantum systems. In addition to the method description, the authors give some examples such as a qubit interacting with a bath described by a Lorentzian spectral density.

Dupuy and Scribano [2] propose to tackle, using a quantum trajectory method, the node problem in deep resonant tunneling, which is due to one or several

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metastable states along the reaction coordinates, and more difficult to capture than quantum tunneling. The quantum trajectory method represents a very promising tool for the study of complex chemical reactions characterized by important quantum effects, which are missed, by construction, by classical trajectory methods.

Bindech and Marquardt [3] study the mean square displacement of the position of a free particle. They evaluate it quantum mechanically, using thermal Gaussian wave packets. The approach allows one to address the evaluation of the mean square displacement in the continuum as well as under periodic boundary conditions.

Panadés-Barrueta et al. [4] analyze and compare different possible strategies for the transformations among low-rank tensor approximations. The motivation behind this study is to achieve compact yet accurate representations of potential-like operators (scalar fields) in symbolic or analytical form.

2 Excited states

The article by Kechoindi et al. [5] employs several ab initio methodologies to characterize the electronic structure of isolated XCO_2 (X = F, NH_2, CH_3) molecules produced by the degradation of volatile organic compounds in the atmosphere. Computations are carried out using both standard and explicitly correlated versions of coupled cluster methods, and multi-configurational approaches.

Pereira et al. [6] apply and compare different simulation methods to describe the photochemical *cis–trans* isomerization reaction in a model for the retinal of rhodopsin with the inclusion of environment effects via secondary modes. The authors focus on purely quantum vibronic wavepacket techniques and on various trajectory-based schemes, discussing their capability to accurately capture the isomerization process.

Giri et al. [7] investigate charge migration induced by an attosecond laser pulse in five-membered ring molecules and study the effect of electronegativity and molecular symmetry. The numerical simulations are carried out using the hybrid time-dependent density functional theory/configuration interaction methodology, and the ensuing field-free charge migration is investigated by means of transient electronic flux density maps.

3 Molecular processes

The contribution of Freixas-Lemus [8] presents a simulation of the F + HCl collision in a wide range of energies. Employing quasiclassical trajectory with hyperspherical coordinates, the authors compute the reaction probability of various processes. At low energies, the H exchange reaction (F + HCl → Cl + HF) is dominant;

then as the energy increases, the Cl exchange reaction (F + HCl → FCl + H) and dissociation (F + HCl → H + Cl + F) successively take over.

Lara-Moreno and Stoecklin [9] study the radiative association reactions H_2 + Cl^- → H_2Cl^- + $h\nu$ and D_2 + Cl^- → D_2Cl^- + $h\nu$, using a time-independent quantum-mechanical formalism on a 3D potential-energy surface. Interestingly, the rate of the second reaction is found to be three orders of magnitude larger than the first one.

In their article, Mezei et al. [10] explore the dissociative recombination of N_2H^+ in the framework of multi-channel quantum defect theory (MQDT). In a simplified model where only the N_2–H^+ motion is included, the results demonstrate the importance of the indirect mechanism where at low collision energies the electron is captured into bound Rydberg states that then predissociate. A more elaborate 3D approach based on the normal mode approximation combined with R-matrix theory and MQDT yields results in satisfactory agreement with storage-ring measurements.

4 Atom–surface scattering

Michoulier et al. [11] study the collision of a hydrogen atom on a silver surface. To do so the authors use the density functional based tight-binding approach where the idea of electronic friction has been adapted to account for the energy transfer related to electron–hole pair excitation in the metal.

The contribution of Barrios et al. [12] investigates the scattering of a hydrogen atom off a tungsten surface that is clean or covered with hydrogen atoms. With quasi-classical trajectory simulations, the authors confirm that the coverage tends to increase the energy loss of the scattered hydrogen atom. On the other hand, the scattering probability decreases with coverage.

This volume leaves a written trace of a successful research network. In the 2021 annual meeting, a special focus was put on the role that machine learning and quantum computing tools already play, and may play in the future, for studying quantum dynamics. We believe that this fast-evolving area opens up new and exciting perspectives for our community. Obviously, investigations in the current scientific topics continue, at both national and international levels, so this volume is just a snapshot. We hope that it will contribute to discussions on advances in the field of quantum dynamics of molecular systems and stimulate further studies.

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