

Campagne 2020 Contrats Doctoraux Instituts/Initiatives

Proposition de Projet de Recherche Doctoral (PRD)

Appel à projet ISCD-Institut des Sciences du calcul & des Données

Intitulé du Projet de Recherche Doctoral : Quo vadis, hydrogenium?

Directeur de Thèse porteur du projet (titulaire d'une HDR) :

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Unité de Recherche :

Intitulé : Institut des NanoSciences de Paris (INSP)
Code (ex. UMR xxxx) : UMR 7588

ED397-Physique & Chimie des
Matériaux

Ecole Doctorale de rattachement de l'équipe & d'inscription du doctorant :

Doctorants actuellement encadrés par le directeur de thèse (préciser le nombre de doctorants, leur année de 1ère inscription et la quotité d'encadrement) : 2 : T. Plé, 2017 à 50% avec S. Huppert (soutenance 2020); E. Fallacara, 2019, à 50% avec M. Ceotto, Univ. Milan (Italie)

Co-encadrant :

NOM : **Spezia** Prénom : **Riccardo**
Titre : Directeur de Recherche ou HDR
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Unité de Recherche :

Intitulé : Laboratoire de Chimie Théorique (LCT)
Code (ex. UMR xxxx) : 7616

ED388-ChimiePhysique&ChimieAnalytique

Ecole Doctorale de rattachement :

ParisCentre

Ou si ED non Alliance SU :

Doctorants actuellement encadrés par le co-directeur de thèse (préciser le nombre de doctorants, leur année de 1ère inscription et la quotité d'encadrement) : Hugo Bessone, co-encadrant (50%), directeur de thèse Prof. R.Vuilleumier, ED 388, financement d'agrégé préparateur de l'ENS. Début le 01/10/2017, soutenance prévue pour septembre 2021.

Cotutelle internationale : Non Oui, précisez Pays et Université :

Description du projet de recherche doctoral (en français ou en anglais)

3 pages maximum – interligne simple – Ce texte sera diffusé en ligne

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut. Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Indiquer les publications/productions des

encadrants en lien avec le projet. Préciser le profil d'étudiant(e) recherché.

PhD PROJECT SUMMARY. This project takes place within a joint doctoral program in condensed matter physics and theoretical chemistry that aims at simulating the quantum dynamics of nuclei in materials and molecular systems. Determining the time evolution of quantum systems is a steep conceptual and computational challenge for applied mathematics, but recent progresses let consider various applications in nano-materials (proton diffusion, spectroscopy, reactivity, isotope effects, etc.) and to emerging non-thermal processes, such as reactions controlled by ultra-strong photon-matter coupling. Specifically, this PhD project aims at developing a mathematical and simulation framework to address: (1) quantum reaction rate calculations; (2) quantum-driven diffusion of light nuclei, such as hydrogen. We envisage distinct applications in chemistry and physics, facing similar issues for both fields, and a close collaboration with researchers in mathematics.

CONTEXT. Light nuclei, protons in particular, show an intrinsic quantum delocalization which can be of the order of chemical bond lengths, so that nuclear quantum effects (NQE) can have a strong impact in chemistry and physics. The effect of quantum delocalization becomes even more significant at low temperatures or high pressures, making a theoretical description of the wave-like nature of nuclei necessary. Such effects are documented both experimentally (e.g. isotope effects) and through theory [1]. Light H atoms can "tunnel" through barriers on a potential energy surface (PES), so to explore regions of space that would be classically forbidden. Tunneling can have a significant impact on chemical reaction rates and/or product distributions. Moreover, it can also affect hydrogen diffusion and conduction so that the accurate modeling of nano-materials in fuel cells, hydrogenation catalysts or chemical sensors must include NQEs.

Accounting for NQEs in atomistic simulations is an active and fertile domain in mathematical physics and theoretical chemistry. Feynman path integrals (PI) are widely employed when studying NQEs [2]. The application of this theory to computational material physics and chemistry (path integral molecular dynamics - PIMD) relies in practice on a transformation to imaginary time for sampling the partition function. Nowadays, PIMD is the reference approach to calculate static properties at thermal equilibrium but it does not allow a direct access to dynamical properties, which demand further approximations such as centroid molecular dynamics (CMD) or ring-polymer molecular dynamics (RPMD) [3]. Despite many applications, CMD and RPMD are not formally equivalent to the real-time quantum dynamics: their drawbacks in calculating vibrational frequencies are well-documented [4,5] and extracting time-correlation functions should be verified case-by-case [5]. Among the various alternative approaches developed for NQEs, two are particularly relevant to this project: the quantum thermal bath (QTB) in which quantum delocalization is approximated via a generalized Langevin equation with colored noise [6], and the quantum mechanics formulation first suggested by Madelung and later implemented by Bohm [7]. Though the Bohmian formulation is attractive and intuitive because it keeps the concept of trajectories, the dynamics can be rather unstable and difficult to integrate through stable algorithms with error handling. Until recently, this has prevented Bohmian dynamics from becoming a widely used tool but several breakthroughs have recently shown routes to viable simulations [8].

The issues of hydrogen diffusion and reactivity calculation present an additional difficulty, as they are rare events. Consequently, they are often inaccessible to brute force simulations and call for efficient phase-space sampling methods. A variety of

such methods exist for classical nuclei, such as forward flux sampling, umbrella sampling or metadynamics [9]. The combination of these acceleration techniques with PIMD or other quantum dynamics methods poses some technical and conceptual difficulties, some of which are still open problems.

TEAM DESCRIPTION. The **INSP** group (**F. Finocchi, S. Huppert and Ph. Depondt**) is expert in computational material physics. Since 2016 they have been using PI-based techniques to investigate the behavior of several hydrogen-bonded systems (I, II). In parallel, they have been implementing a new class of approximate methods that are based on the Quantum Thermal Bath, QTB (III, IV). The group proposed a cure to zero-point energy leakage problem by adapting the system-bath coupling to enforce the quantum fluctuation-dissipation theorem (V). The expertise of the team in studying materials and developing methods to include NQEs in molecular simulations (VI) is well-recognized and the starting point for the project.

References relevant to the project: **(I)** S. Schaack, U. Ranieri, P. Depondt, R. Gaal, W. F. Kuhs, P. Gillet, F. Finocchi, L. E. Bove, PNAS 116 (2019) **(II)** S. Schaack, P. Depondt, S. Huppert, F. Finocchi. Sci. Rep. In press (2020) **(III)** Y. Bronstein, P. Depondt, F. Finocchi, A. M. Saitta, Phys. Rev. B 89, 214101 (2014) **(IV)** Y. Bronstein, P. Depondt, L. E. Bove, R. Gaal, A. M. Saitta, F. Finocchi, Phys. Rev. B 93, 024104 (2016) **(V)** E. Mangaud, S. Huppert, T. Plé, P. Depondt, S. Bonella, F. Finocchi, *J. Chem. Th. Comput.* 15, 2863 (2019) **(VI)** T. Plé, S. Huppert, P. Depondt, F. Finocchi, S. Bonella, *J. Chem. Phys.* 151, 114114 (2019)

R. Spezia (LCT) is an expert in reaction dynamics, in particular to describe uni- and bi-molecular reaction via chemical dynamics simulations. He applied these methods to gas-phase fragmentation of biomolecules to obtain reaction rate constants and to low-temperature reactions relevant to astrochemistry (VII, VIII). Recently he implemented QTB to study uni-molecular dissociations (IX). His expertise in chemical reactions makes it possible to build a fertile and interdisciplinary collaboration, aiming at computing reaction rates and diffusion coefficients accounting for nuclear quantum effects. References more relevant to the project: **(VII)** R. Spezia, Y. Jeanvoine, W. L. Hase, K. Song, and A. Largo. *Astrophys. J.* 826, 107 (2016). **(VIII)** A. Martin-Somer, V. Macaluso, G. L. Barnes, L. Yang, S. Pratihari, K. Song, W. L. Hase and R. Spezia. *J. Am. Soc. Mass Spectrom.* 32, 2 (2020). **(IX)** R. Spezia and H. Dammak. *J. Phys. Chem. A* 123, 8542 (2019).

WORKING PLAN. This PhD project aims at employing trajectory-based methods that incorporate NQEs, in combination with efficient sampling techniques for rare events that are well-established for classical nuclei, while carefully comparing different methods. Indeed, the existing approaches to NQEs offer different degrees of accuracy and computational complexity. None of them can (as of now) be considered as a universal simulation tool for theoretical Chemistry and Physics, but rather each should be evaluated on a case-by-case basis. Although many methods have been extensively tested in the past two decades, NQEs in rare events are much less known. After a careful comparison among distinct approaches, we envisage several applications in nanoscience, as detailed in this working plan: **1.** During the first PhD year, we will implement and compare different quantum dynamical methods (associated with appropriate accelerated sampling schemes) to simulate proton diffusion and reactive processes in model systems with few degrees of freedom. More precisely, we plan to explore in-depth the three approaches that we mentioned above: (1) The QTB (in its adaptive version), to provide a numerically inexpensive approximation of zero-point energy effects (but without an accurate description of tunneling); (2) The RPMD-transition state theory, as it has been shown to account for tunneling in a satisfactory way, even in the so-called deep tunneling regime [10]; (3) The Bohmian dynamics, as a more challenging (but potentially very rewarding) way to access the exact real-time dynamics of the nuclei. In this preparatory study, our objective will be to assess the

advantages and disadvantages of each technique, in particular when combined with accelerated sampling schemes, and imagine routes for possible improvements. The collaboration with **U. Boscain** and his group at **LJLL** will be very helpful, in particular to deal with fundamental questions inherent to Bohmian dynamics.

2. Based on the results on model systems, the second PhD half will be devoted to the full-scale implementation of a preferred method for computing reaction rates including NQEs within a production code, like Quantum Espresso or VENUS, which are currently developed at INSP and LCT groups. This will allow for realistic simulations of materials and molecules, and applications to relevant reactivity and hydrogen diffusion problems. Besides the specific systems that we plan to study (like e.g. metal hydrides or perovskites), we stress that the assessment of the different techniques is an unavoidable issue, as their validity will likely depend on the specific conditions (barrier height and width, thermal vs quantum effects, etc.). Method limitations in real conditions are at present largely unknown, so that an important part of the thesis work will consist in modeling complex systems in terms of problems with fewer degrees of freedom, on which the knowledge that we will have obtained during the first half of the PhD would be essential. This interplay between real and model systems will be a distinctive feature of the present PhD project, which therefore involves the implementations of methods and algorithms as well as first applications.

RELEVANCE TO ISCD SCIENTIFIC OBJECTIVES. The PhD project is part of an interdisciplinary endeavor including chemists with expertise in reactive processes (R. Spezia, LCT) and physicists who investigated nuclear quantum effects in many materials (F. Finocchi, S. Huppert, P. Depondt, INSP). Furthermore, this project will strengthen the collaboration with U. Boscain (LJLL) who is expert in quantum control. Periodic seminars at the edge between physics, chemistry and mathematics are planned. This interdisciplinary collaboration will be fostered at ISCD and it is part of its core activities. A general theoretical framework should arise, which can be applied to the specific issues of both groups and likely beyond. We also plan to call some of the leading scientists in quantum dynamics for short-term invited professorships.

PHD CANDIDATE PROFILE. The ideal candidate will have a Master degree (or equivalent) in Physics or Theoretical Chemistry with experience and interest in computational methods and simulations. Programming skills are required. Basic knowledge of material science, applied maths or astrochemistry is appreciated.

References (*JCP* = *J. Chem. Phys.* *PRL* = *Phys. Rev. Lett.*)

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- [3] J. Cao and G.A. Voth. *JCP* **101** 6168 (1994); I.R. Craig and D.E. Manolopoulos. *JCP* **121** 3368 (2004).
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- [9] C. Abrams and G. Bussi, *Entropy* **16** 163 (2013); D. Perez et al *Ann. Rep. Comput. Chem.* **5**, 79 (2009).
- [10] T.J.H. Hele and S.C. Althorpe, *JCP* **138**, 084108 (2013); *JCP* **139**, 084115 (2013).

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cd_instituts_et_initiatives@listes.upmc.fr avant le 17 avril 2020.