Activity report

2016-2021

Theoretical chemistry @ IN2P3

CONSEIL SCIENTIFIQUE

Foreword

This report is intended for the members of the IN2P3 scientific council (Theory) in support of the plenary meeting - June 29 and 30, 2021. It was written by Yves Pipon (IP2I) with the participation of Rémi Maurice (Subatech), Jérôme Roques (IJCLAB) and A.G. Kalinichev (Subatech).

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1. Introduction

First, it is important to note that **"theoretical chemistry"** is often associated with **"computational chemistry"**. The association of both terms describes the use of computer **modelling and simulation** to study **chemical objects** (molecules, macromolecules, solids, ...) based on the laws of physics. Theoretical approaches used in computational chemistry can be divided into four main methods[1]: *ab initio*, DFT (Density Functional Theory), semi-empirical and molecular mechanics. Some characteristics of each method are indicated in Table 1.

Table 1: *Characteristics of main Theoretical methods used in computational chemistry*

	Theoretical formalism	**Objects**	**Performance criterion**
Ab initio	Quantic	Small molecules, solids with a maximum of 100 atoms	In direct link with quantum mechanics
DFT	Quantic (with global parametrization[2])	Bigger molecules, solids with a maximum of 1000 atoms	Electronic prediction
Semi-empirical	Classical + additional terms	Bigger and numerous molecules, solids with 10^3-10^5 atoms	Themodynamic prediction
Molecular mechanics	Classical (parametrization by atom type)	Macromolecules, solids with more than 1 million atoms	Conformational prediction

The use of these methods allows one to predict atomic/molecular structure, bonding, reactivity, physical properties, spectroscopic response ... The choice of a specific method is always a compromise between the will to be physically meaningful and the pragmatic constraints relating to the accuracy, speed, computing cost, and even -in some cases- implementation (some combinations of methods, in theory possible, main not be implemented in the used codes). These « static » approaches do not deal explicitly with the time variable (stationary states). In order to take it into account, the selected method is usually coupled with the methods of molecular dynamics (MD). In MD methods, the atom positions or the wave functions of the nuclei are propagated in time from a classical or quantum master equation, respectively. It is also possible to couple several methods which is called a **multiscale approach**. Research projects are now directed more and more towards multiscale approaches stimulated by considerable interest from industrial applications in particular for "virtual testing" of materials. For instance, we can indicate:

- The QM / MM (Quantum mechanics / molecular mechanics) hybrid modeling methods which allow simulations for much larger systems than accessible by QM methods alone and,
- The use of a bottom-up approach which combines DFT calculations with kMC (kinetic Monte Carlo) simulations in order to access much larger physical time scales.

It should be noted that the use of the multiscale approaches was the subject of a recommendation by GT11 in its report for the “2020-2030 French Strategic Plan for Nuclear Physics, Particle Physics, Astroparticle Physics, associated technologies & applications”. This highlights the importance of this approach in the future years in particular in order to be closer to realistic conditions. This also implies that the research in “theoretical chemistry” is most often done in connection with experimental activities carried out elsewhere to identify the key parameters to be simulated, to validate (semi-) empirical potentials of interatomic interactions or to guide experimental researchers on the conditions to be applied or the properties to be measured.

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[1] From: B. Bensaude-Vincent & R.-E. Eastes(Eds.), Philosophie de la Chimie, Paris: De Boeck Supérieur

[2] Although there may be “ab initio” approaches in DFT, the use of these remains marginal compared to the use of so-called “parameterized” methods.

2. Presentation of the researcher activities in "theoretical chemistry" held in IN2P3 laboratories

The activities presented in this document are in the field of nuclear energy and environment. It concerns materials irradiated in the past, present or foreseen (fusion or fission) nuclear reactors with an important part dedicated to the **back end of the present nuclear fuel cycle**, whether for nuclear waste or for the reprocessing of the spent nuclear fuel (steps 7 and 9 in Figure 1).

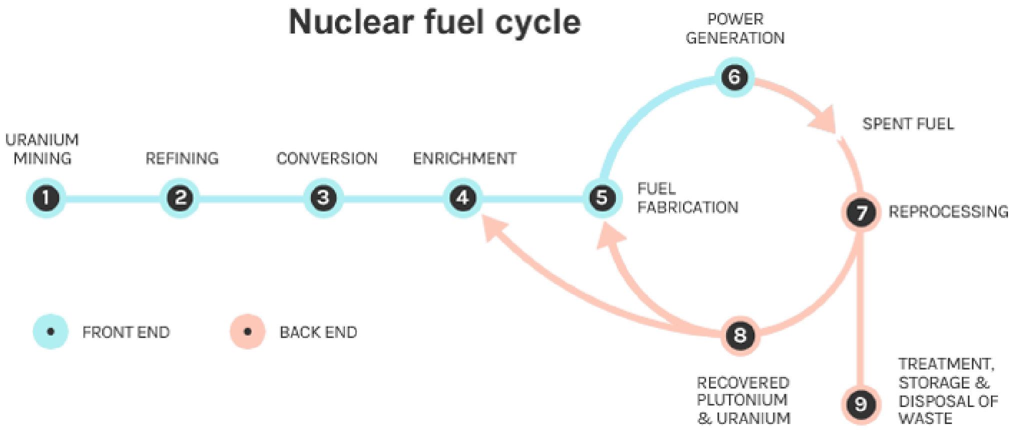

Figure 1: *Nuclear fuel cycle scheme*

These latter activities are traditionally at the heart of what is called **"radiochemistry"** embedding several experimental research groups tagged "IN2P3" and researchers in theoretical chemistry located in three IN2P3 laboratories:

- IJCLAB (J. Roques, MCF),
- IP2I (Y. Pipon[3], MCF) and,
- SUBATECH (R. Maurice[4], CR and A.G. Kalinichev, PR).

Each researcher is specialized in one or two computational methods with his own research topics called afterwards "activities" which are detailed in the remainder of the document. Table 2 summarizes the number of researchers (permanent or not) associated with the main funded projects carried out since 2016 in the framework of each activity.

Table 2: *Human potential in relation to main funded projects carried out since 2016*

Activity	Permanent staff	Temporary staff	Funded projects
2.1	1 PR (Subatech)	4 PhD students 5 Postdoctoral fellows	H2020-SXT H2020-S4CE ANDRA, Orano, EDF (industrial funding)
2.2	1 CR (Subatech)	2 PhD students 1 Postdoctoral fellow	Region contract « étoile montante » CNRS MITI programme
2.3	0.33 MCF (IP2I)	1 Postdoctoral fellow	Europe contract with JRC
2.4	1 MCF (IJCLAB) 0.66 MCF (IP2I)	2 PhD students 2 Postdoctoral fellows 3 PhD students	Region contract « DIM OxyMORE » EDF (industrial funding) ANR RECA // ANR Pluton CNRS NEEDS programme IRSN (industrial funding)

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[3] Y. Pipon research activities are divided into two parts: experimental one based on ion irradiation experiments and ion beam analysis (~50%) and, theoretical one.

[4] R. Maurice will leave IN2P3 to join INC through his transfer to ISCR Rennes on September 1, 2021

2.1 Study of clay / cement system interfaces with fluids

These researches are carried out by A.G. Kalinichev at Subatech in the context of the **radioactive waste disposal**, which is a theme of major interest for ANDRA (National Agency for Radioactive Waste). A research and teaching industrial chair "Storage and Disposal of Radioactive Waste" was created in 2009 in partnership with ANDRA, EDF, Orano, and IMT Atlantique to study on the fundamental molecular scale the materials and processes relevant to the safe and sustainable disposal and storage of radioactive wastes. This chair was renewed in 2015 and 2019.

A.G. Kalinichev primarily uses classical atomistic simulations of materials for the quantitative understanding of the properties and processes of clay and cement systems and their interfaces with fluids at the fundamental atomistic scale. Indeed, **cement matrices**[5] are being considered in particular to coat MA-LL (Long lived - Medium Activity) waste before being stored in a deep geological layer. The "host" rocks selected have a predominantly **clay**-based composition and, more precisely, Callovo-Oxfordian clay "COx" is often studied in the geological waste disposal reference scenario in France (see Figure 2).

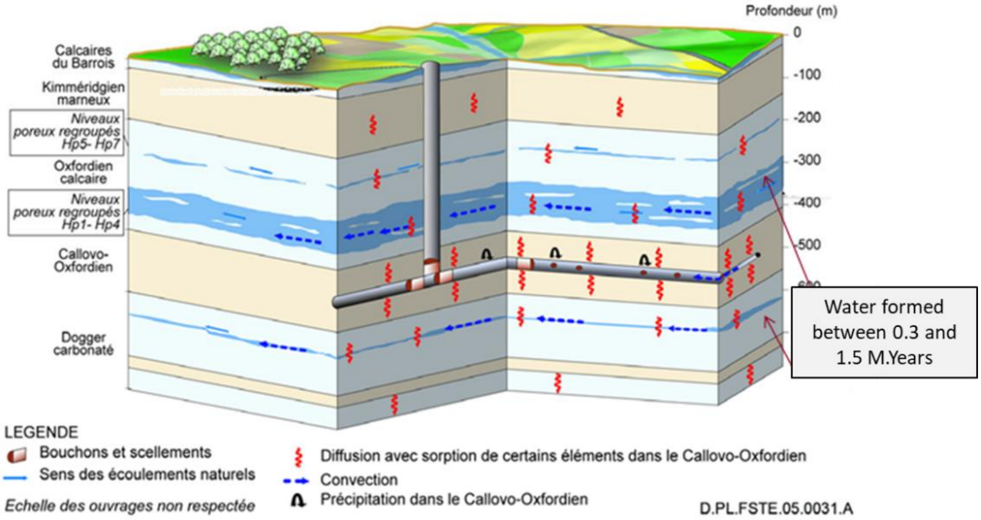

Figure 2: *Scenario to evaluate the containment of various radionuclides in biosphere for long periods (> 100,000 years)*

Therefore, researches relate first to the development of **realistic models**:

- illite, smectite, and interstratified illite/smectite (I/S) clays as models of COx clay rock and its mineral constituents (Figure 3),
- the C-S-H phase modeling of the cement with a variable C / S ratio reflecting the different stages of cement degradation,
- role of nanoparticle edges in clay and cement modeling.

From these models (and other similar disordered materials), further research is being conducted on:

- the effects of organic matter on the complexation of ions in systems linked to cement and clay,
- the quantification of the effects of specific surface sites on the adsorption and transport of ions in clays and other disordered materials

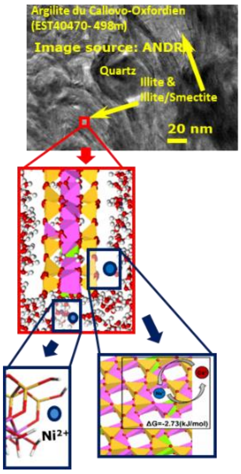

Figure 3: *Cox clay model*

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[5] Portland cement (the most common) is made up of 95% "clinker" which is a mixture of several phases: C (for CaO), S (for SiO_2), H (for H_2O), A (for Al_2O_3), … There is a wide variety of cements by reducing the proportion of clinker and adding other elements (ashes, etc.)

The funding provided by the industrial chair, other ANDRA projects, European consortia H2020-SXT (ShaleXenvironmenT) andH2020-S4CE (Science 4 Clean Energy) supported in 2016-2021:

- **4 PhD theses:** M. Pouvreau (defended on 12/2016), I. Androniuk (defended on 02/2017), D. Banerjee (to be defended on 10/2021) and P. Citli (to be defended on 03/2023)
- **5 postdoctoral research fellow positions:** M. Pouvreau (6 months in 2017); I. Androniuk (2 years in 2017-2019); S. Kraevskiy (2 years in 2016-2018); B F. Ngouana-Wakou (2 years in 2017-2019) and S. Mutisya (2 years in 2018-2020)

2.2 Theoretical Molecular Chemistry

This part is devoted to the research carried out by R. Maurice in the Radiochemistry team (2017-2018) then Theory (2019-2021) of Subatech. The majority of research focuses on the **chemical (radiochemical) or physical (magnetism) properties** dependent on the energy and / or wave functions of a system determined using *ab initio* or DFT methods. For the part concerning molecular radiochemistry, structural and reactivity properties are correlated, and chemical bonds are studied using innovative tools developed "in-house" as it was done in the PhD thesis of Cecilia Gomez Pech (defended in 2021). An important highlight concerning the 2016−2021 is the proof-of-concept that calculations can be used to strongly guide heavy element chemistry experiments, in particular for selecting the experimental domain to be targeted (published in *Angewandte Chemie*). Two important and representative projects are currently being carried out:

2.2.1 Behavior of protactinium in solution

Protactinium is part of the actinide family, located between thorium and uranium. In the context of the reprocessing of nuclear fuel (based on uranium or thorium), this element will therefore be difficult to separate from valuable isotopes such as Uranium-238 (PUREX process) or Thorium-232 (THOREX process). Rémi Maurice received funding via a region young researcher project (AAP “Etoile Montante” project in the Pays de la Loire region) entitled: “Theoretical radiochemistry: Protactinium and the first actinides”. He seeks to show that one can predict this particular chemistry by calculations, in particular by **predicting the thermodynamic equilibrium constants** as well as the absorption spectra upstream of the experiments, which are very complex to implement due to the capricious nature of this element in solution (adsorption on the surface of the container, precipitation, etc.) The first step, a methodological exploration, is currently in progress. This is also the research topic of Hanna Oher (2021) in her postdoctoral internship.

2.2.2 Multiscale modeling of polonium chemistry in solution

Polonium is one of the rarest elements on Earth and one of the most radiotoxic. As a result, there are relatively few experiments on this element and the physicochemical properties of this element, especially in solution, are still poorly understood. Preliminary work having shown the crucial role of solvation on the structural and spectroscopic properties of polonium (IV) complexes, R. Maurice proposed to carry out a rigorous and systematic study of these properties using innovative methods coupling the approaches quantum and classical, in particular via the generation of a polarizable force field that best reproduces “ab initio” calculations. This is a collaborative project, funded by the CNRS via MITI (80 | Prime) with INP (PhLAM, Lille) and INC (CEISAM, Nantes). This tedious work began with a first methodological study aimed at determining which static reference approach can be used for the generation of the force field.

2.3 Modeling of the irradiation of Mo nanoparticles suspended in water

This part presents a new topic of research developed at IP2I by Y. Pipon in connection with nuclear medicine seen through the "material" prism.

^{99m}Tc is one of the most widely used radiotracers in medical imaging. It is obtained by the beta-decay of ^{99}Mo. In the majority of cases, the latter is obtained by intense neutron irradiation of a highly enriched uranium target. Two reactors around the world provide more than two-thirds of production. Alternative ways of producing ^{99}Mo are therefore being studied to avoid the shortage in the event of one of the reactors being shut down. JRC[6] Petten has proposed a new synthetic route from the irradiation of nanoparticles (NP) of Mo-100 in water. Two nuclear reactions are being studied: ^{100}Mo (γ, n) ^{99}Mo and ^{100}Mo (n, 2n) ^{99}Mo.

This research has been initiated through a European contract with JRC Petten which has paid the postdoctoral internship of C. Panetier (1 year in 2020). EAM[7] interatomic potential for Mo-Mo interaction and TIP4P rigid model for water molecules are used (see figure 4) in MD simulations in order to evaluate the NP sputtering depending on each reaction and on the NP size.

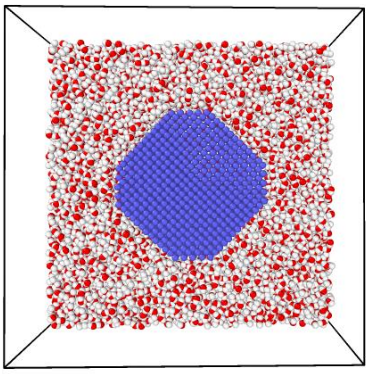

Figure 4: *Mo NP of ~5 nm (~5 000 atoms) placed in a water cube of 10x10x10 nm^3 (~30 000 H_2O molecules) at 300 K*

MD simulation is particularly suitable for systems of this size and for the characteristic times associated to elastic collision cascades occurring within the NP. First results have permit to help the experimental setup prior to irradiation.

2.4 Diffusion of (radio) elements in irradiated nuclear materials

Several research projects arise from this theme and are performed at IJCLAB (J. Roques) and a little at IP2I (Y. Pipon). This theme is linked to the **diffusion of atoms in solids** which may have a certain degree of disorder (defects) linked to irradiation. The diffusion coefficient is a macroscopic quantity related to a flow of matter (according to Fick's theory) which can also be determined at the atomic scale by statistical considerations analogous to the Brownian displacement of a particle in a fluid. It is therefore tempting to try to unify the two worlds. However, atomic diffusion can be a "slow" process (sometimes several ms to have several events called atomic jumps) which generally requires the use of multiscale models. Depending on the system, to obtain data on the diffusive properties of elements of interest, different approaches are used, among which:

- **Classic MD with (semi) potentials.** They are used to simulate self-diffusion in a matrix or the diffusion of mobile heteroatoms,
- **DFT & kMC coupling**. DFT allows the determination of migration energies from one atomic site to another pre-selected atomic site based on considerations of system energy minimization. These data, along with the calculation of the probability of atomic jumps from neighboring site to neighboring site, constitute input data for kMC methods which make it possible to determine a diffusion coefficient at different temperatures.

The research projects grouped under this theme are related to:

- the aging of materials during their nuclear reactor operations,

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[6] The Joint Research Centre (JRC) is the European Commission's science and knowledge service.

[7] The embedded atom model (EAM), related to the tight binding theory second moment approximation, is a semi-empirical potential.

- the aging of materials considered as nuclear wastes and,
- the evaluation of "innovative" materials that can be used in reactors of different technology (fission) or future generation of fission reactors (generation IV).

2.4.1 Apatite thermochronology (2016-2021)

This project is the result of a multidisciplinary collaboration between the Orsay geology laboratory (GEOPS) and the IJCLAB (formerly IPNO). The objective was to gain a detailed understanding of the diffusion processes of helium in apatites in order to better parameterize the theoretical dating models of geologists. This activity was funded by the "DIM OxyMORE" region contract (18-month postdoctoral internship of H. Balout) as well as by the ANR RECA, "RElation entre Changement climatique et formation des lAtérites" (18 months postdoctoral internship of F. Bassal).

Thermochronology (U-Th) / He on apatite is a technique in development to determine the age of relief creation as well as the exhumation rates of mountain ranges. The decay of ^{238}U, ^{235}U and ^{232}Th produces alpha (He) particles which will accumulate in apatite crystals as a function of temperature. Measuring the level of helium contained in samples of apatite crystals, as a function of temperature, allows rock dating. However, the understanding of Helium diffusion phenomena for this mineral is still poorly understood and the interpretation of the ages (U-Th) / He can be tricky or even erroneous.

Apatite models were developed (see figure 5) and diffusion coefficients were determined using a theoretical approach combining periodic DFT and kMC calculations on different apatite chemical compositions.

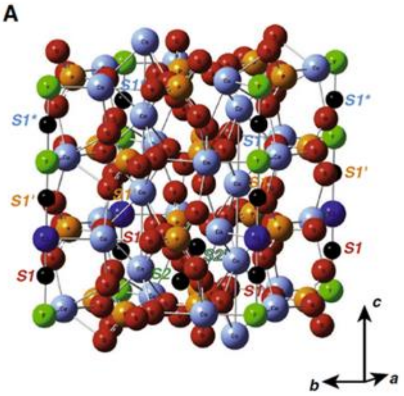

Figure 5: *Apatite structure and helium incorporation sites (in black)*

The simulations made it possible to calculate the He diffusion coefficients very precisely. These data have significantly improved the dating models.

2.4.2 Diffusion of carbon-14 in spent fuel cladding (2016-2019)

The research associated with this theme took place, for the modeling aspect, at the IJCLAB in connection with experiments carried out at Subatech and IP2I within the framework of NEEDS (waste) projects.

The cladding of spent fuel rods from pressurized water nuclear reactors (PWRs) are made of a zirconium alloy which contains numerous activation products, including ^{14}C. After treatment of the spent fuel assemblies, the cladding sections are compacted and then placed in a Standard Compacted Waste Package before being stored and then dispose in deep geological sites. The behavior of radionuclides contained in zirconium is poorly characterized so far. In the absence of data, ANDRA considers that all of the ^{14}C contained in the waste is released in organic form into the geosphere.

The diffusion coefficient of ^{14}C in Zr cladding was calculated using a multiscale {DFT + kMC} approach. Figure 6 presents the identified paths for the migration of one carbon atom in a zirconium crystal.

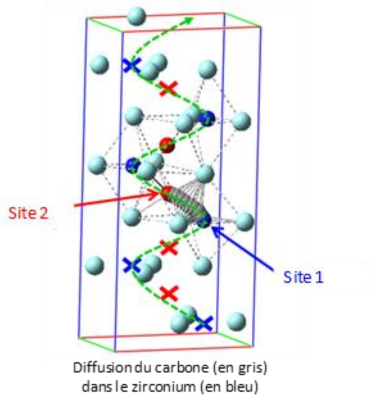

Figure 6: *Diffusion paths of carbon (in grey) incorporated in Zr crystal*

This approach was then used to study the behavior of carbon in zirconium dioxide which forms on the internal and external faces of cladding by oxidation in contact respectively with the oxidized fuel and with the water of the primary circuit.

2.4.3 Helium behavior in new ODS materials (2019-).

This study is the result of a collaboration between J. Roques (IJCLAB) and the experimenters of IJCLAB (ex CSNSM Orsay) and those of CENBG. ODS (for Oxide Dispersion Strengthened) steels are structural materials considered for both fusion reactors and fourth generation fission reactors. To overcome the shortcomings of conventional steels for applications in fusion environments, it has been suggested to employ nano-structured ferritic alloys (NFAs), in particular, ODS steels. They are characterized by a fine distribution of nanometer-sized oxide particles in steel that act as obstacles for dislocation motion and are metastable up to very high temperatures. Fusion environments are characterized by an abundance of energetic helium ions that are produced in the fusion reaction as well as via nuclear transmutation reactions in the plasma facing components. The project is focused on the mechanisms that govern the interactions of the oxide-matrix interface with helium. For that, a combination of experimental and numerical simulations must be employed to predict the material performance.

In the experimental part, the objective is to introduce different concentrations of helium in ODS materials (iron with yttrium oxide inclusions) and then to measure the diffusion coefficients by thermal desorption spectroscopy. Multi-scale modeling here consists in determining, by DFT, the helium insertion sites in the different phases (pure Fe, pure Y_2O_3 and interface) then the migration paths with their associated energies (see figure 7).

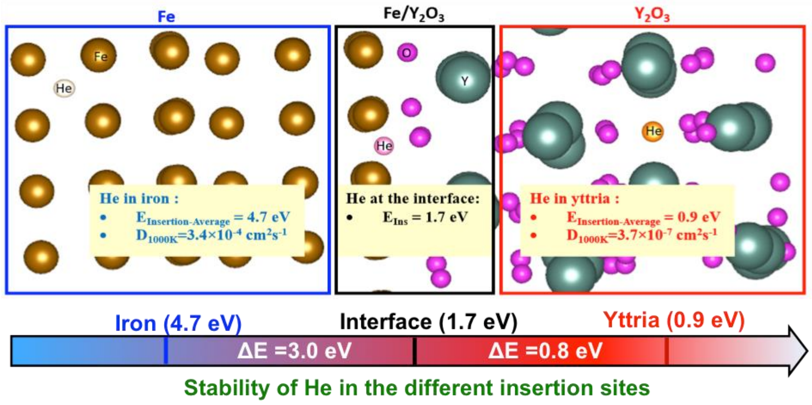

Figure 7: *Helium stability in different incorporation sites for different systems (Fe ; Y_2O_3 and their interface)*

In a next step, He diffusion coefficients in the oxide, in iron, and at the interface will be determined by kMC.

2.4.4 Behavior of Mo and Cs fission products (PFs) in UO_2 nuclear fuel (2016-)

This study is being carried out at IP2I through collaboration with IRSN and JRC Karlsruhe. Uranium dioxide (UO_2) is the most common fuel for the PWRs and research is still active to improve the data knowledge on the behavior of fission products (FPs) during reactor operations and during accidents. Each industrial involved in the nuclear industry (Orano, CEA, IRSN[8], …) owns its multiscale performance code which requires some input data which can be extracted from experiments or atomic scale simulations. In this context, two PhD theses funded by IRSN (L. Sarrasin, defended in 12/2017 and C.

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[8] IRSN – *Institute for Radiological Protection and Nuclear Safety* – is the French national public expert in nuclear and radiological risks

Panetier, defended in 11/2019) were done at IP2I including a theoretical research part (~25%) and an experimental one. They aimed at determining the diffusion coefficients of two particular FPs (Mo and Cs) in UO_2 in accidental conditions (oxidizing atmosphere and high temperature).

One objective was to obtain data on the preferential sites of Mo incorporation, by DFT, in UO_2 and UO_{2+x} (oxidized nuclear fuel). Through an analysis of Bader charges in particular, the results showed a preferential configuration of Mo in UO_{2+x} (see figure 8) which evolved towards an MoO_3 oxide structure in agreement with the results obtained by X-ray absorption spectroscopy.

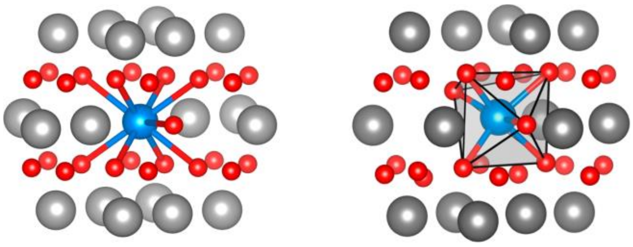

Figure 8: *Configuration before (left) and after relaxation (right) of the supercell containing one Mo atom in UO_{2+x}. U atoms in gray, oxygen atoms in red, and molybdenum atom in blue*

The mobility of cesium being clearly greater than that of molybdenum in UO_2, a methodological approach by DFT and by classic MD with semi-empirical potentials was carried out. If the atomic jumps of Cs could be observed in MD between two uranium vacancies (V_U); no diffusion could be observed in a perfect crystal (without defect). These data, in agreement with the migration energies determined in DFT, clearly highlight the limiting factor: the diffusion of the uranium vacancies.

A specific problem with these materials is the charge of each atom which should evolve with the movement of the different atoms in particular with the presence of defects (vacancies, interstitials, …) and heteroatoms (Mo or Cs). As the potentials deal with fixed charges, the problem was not addressed. Therefore, a new thesis (starting in September 2021) will focus on the development of SMTB-Q (Secondary Moment Tight Binding with variable charge) potentials developed at ICMMO (INC) by Robert Tétot and which have already demonstrated their interest in oxide systems.

3. Collaborations

Collaborations are an important and mandatory part for the theoretical chemistry activities. It concerns different partnerships or punctual collaborations with researchers in the theoretical chemistry field and with experiment researchers. This part contributes to show the visibility of the different activities and the international/national influence of the IN2P3 researchers. It is divided into three sections: (i) the first one presents the collaborations outside IN2P3 with theorists; (ii) the second one presents the collaborations with colleagues dealing with experimental activities (inside and outside IN2P3); and (iii) a last section is dedicated to french structures which contribute to favor national collaborations. It should be noted that several collaborations between theorists have occurred or are still active between IJCLab and Subatech (inside IN2P3).

3.1 Collaboration with partners studying theoretical chemistry in non-IN2P3 laboratories

Table 3 summarizes the different levels of collaboration in relation with the projects presented in this report. The collaborations concern here "theoretical chemistry" researchers in non IN2P3 laboratories highlighting the visibility of each activity.

Table 3: *Summary of the various collaborations specific to the activities presented in the present report and in connection with non-IN2P3 "theoretical chemistry" laboratories*

Activity	Local	National	International
2.1	-	ANDRA (Paris) BRGM (Orleans)	USA: Michigan State Univ. USA: Sandia National Lab. Poland: Polish Academy of Sciences China: Nanjing Univ. Turkey: Hacettepe Univ. Russia: HSE Univ.[9]
2.2	CEISAM (INC, Nantes)	PhLAM (INP, Lille) LCT (INC, Paris) LCPQ (INC, Toulouse)	Netherlands: Groningen Univ.
2.3	INSA MATEIS (Lyon)	-	-
2.4	INSA MATEIS (Lyon)	ICMUB (Dijon) CEA, IRSN (Cadarache)	-

3.2 Collaboration with partners devoted to experimental research

Bridging computational simulations and experimental data in material field is now a pretty common thing. However, that does not mean that this is an easy task. Time is often required before successing to build the bridge. Table 4 indicates the close collaborations with experimental research colleagues. It should be noted that the four theorists involved in this report always collaborate at a local level with colleagues in the same laboratory and dealing with experimental activities. This shows a good relationship between IN2P3 theoretical and experimental activities and allows to build pluridisciplinary projects quite comfortably.

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[9] A.G. Kalinichev contributes to the international laboratory for supercomputer atomistic modelling and multiscale analysis as chief research fellow

Table 4: *Summary of the various collaborations with researchers.*

Activity	Local	National	International
2.1	G.Montavon, C.Landesman, B.Grambow, D.Grekov (Subatech, Nantes)	C. Tournassat, S. Grangeon (BRGM, Orleans) P.Henocq (ANDRA)	USA : R.J. Kirkpatrick, G. Bowers (Michigan State Univ.) Poland : M. Szczerba (Polish Acad. Sci.) Turkey: A.N. Ay, B. Zumreoglu-Karan (Hacettepe Univ.)
2.2	G. Montavon & J. Champion (Subatech, Nantes)	C. Le Naour & M. Maloubier (IJCLab, Paris)	USA: J. Gibson, Berkeley
2.3	-	-	Netherlands: A. Moreno, JRC Petten
2.4	C. Gautheron (GEOPS, Orsay) A. Gentils, C. Le Naour, M. Maloubier, V. Sladkov (IJCLAb Orsay) C. Gaillard & N. Moncoffre (IP2I, Lyon)	J. Vanderborre & T. Suzuki (Subatech, Nantes) D. Horlait & E. Gilabert (CENBG, Bordeaux) D. Mangin (IJL, Nancy)	Russia: V. Borodin & O. Emelianova, NRNU MEPhI & NRC Kurchatov Institute Germany: T. Wiss, JRC Karlsruhe

3.3 National structures favoring collaborations

Several french structures exist and permit to favor collaboration at a national level to build interdisciplanary projects with modelers and experimenters especially in the framework of the activites indicated in this report.

3.3.1 GDR SCINEE (IN2P3 & INC)

The nuclear physics and radiochemistry research teams concerned with nuclear energy and the environment at IN2P3 and INC, joined forces in 2017 to create the « Groupement de Recherche » (GDR) untitled SciNEE ("Nuclear Sciences for Energy and the Environment").

No project is financially supported but the GDR objective is to favor the exchanges and to ultimately build some strong consortiums able to answer to Europe or ANR calls for proposals.
For instance, in June 2019 (SciNEE workshop on the irradiation damage in nuclear reactors: modeling and experiments at all scales for aging studies), Y. Pipon gave a talk on the modeling, at the atomic scale, of the damage under irradiation of nuclear ceramics and the diffusion in these solids. The objective was to discuss about potential projects bridging experimental and theoretical research. More recently, in March 2021 a workshop (nuclear materials and transfer: experimental and theoretical approaches) was held in Lille. The theme was designed to promote exchanges between experimenters and modelers around issues related to the fuel cycle chemistry, the behavior of materials during nuclear reactor operation, the storage or disposal of nuclear waste, and migration of radionuclides in the geosphere.

3.3.2 Master Project RCT (IN2P3)

It consists of a first phase (2019–2021) plus a potential renewal for a second period (2022–2024).

Phase 1: 2019-2021

This project was initiated by R. Maurice in order to strengthen the theory-experiment link in molecular radiochemistry. Phase 1 was a success as it has indeed enabled the establishment of a strong

interaction between theorists from IN2P3 and outside IN2P3 (INC, INP, CEA) and experimentalists from IN2P3 and outside IN2P3 (CEA). This project was essential in initiating the two main projects (protactinium and polonium) mentioned above.
However, following the announcement of R. Maurice's willingness to quit Nantes for Rennes, the management of the Subatech laboratory decided not to allocate a budget to this project in 2021. Therefore, the money dedicated to this project was never dispatched to others partners (in Subatech and IJCLab).

Phase 2: 2022-2024 (potential renewal mentioned during EAP 2020)
The objective of this second phase would be to strengthen the links between IN2P3 theorists and in particular concerning the molecular-periodic link, multi-scale approaches, and the solid. Although this project was announced before R. Maurice's transfer request, its relevance is in fact reinforced by his departure. It will therefore be a question of creating a synergy around the solid, with 3 main partners: IP2I (Yves Pipon), IJCLab (Jérôme Roques), and Subatech (Andrey Kalinichev). We therefore propose to transfer the national responsibility of this MP, if it turns out to be renewed, to one of these three partners. R. Maurice would remain one of the external collaborators of the project.

3.3.3 NEEDS interdisciplinary programme (CNRS & industrial partners)

NEEDS aims to mobilize academic research on the major scientific questions related to nuclear power. It provides multi-partner scientific facilitation, and helps build structuring research projects that address fundamental science questions of interest to nuclear energy and environment.

Unlike the GDR SCINEE, NEEDS funds different size projects which is an efficient way to initiate collaborations. For instance, two different projects funded in 2020: IVAN (Y. Pipon, promoter) and CarboLitHy (G. Roma, CEA Saclay) have been unified in one only project in 2021: CIAN (Y. Pipon). Both projects aimed at studying boron carbide (B_4C) as a neutron absorber for GEN IV reactors. G. Roma and Y. Pipon now collaborate in order to study Li behavior in B_4C by DFT.
Another example stems from a NEEDS project which associates IP2I (C. Gaillard) and IJCLab (F. Garrido) in order to improve our knowledge on UO_2 single crystal oxidation from an experimental point of view. From this point, a consortium between IJCLab, IP2I, CEA, IRSN and Framatome was formed and lead to propose the BENEFICIA project for the ANR 2021 (project currently accepted for phase 2). If the project is accepted, Y. Pipon (IP2I), M. Freyss (CEA Cadarache) and R. Ducher (IRSN) will collaborate for studying, by DFT and MD with SMTB-Q potentials, the diffusion of Mo, Cs and I in Cr_2O_3-doped UO_2 as a new near-term accident tolerant fuel (designed by Framatome).

3.3.4 Thémosia Research Federation (INC)

This RF will be created on January 1, 2022 by the INC (leading institute). We contributed to its construction (R. Maurice, co-promoter of the project, A.G. Kalinichev speaker of the « Rencontres Prospectives 2019 » during which the outlines of the project were discussed, and Y. Pipon, co-writer of the research project). It is important to note that the IN2P3 did not wish to be a secondary institute because of the too small number of IN2P3 researchers in theoretical chemistry. However, IJCLab and IP2I, which have previously expressed some interest, will soon be invited to position themselves as bearer (signatory of the agreement) or as an associate (simple letter of association, with less commitment). Note that the position of Subatech is not yet clear.
In any case, we must underline the importance, for IN2P3 theorists, to participate in this type of initiative, so as not to be isolated from potential national partners. Indeed, the Federation aims to put computational tools at the center of discussion, to bring together developers and users, and researchers from different communities from the point of view of applications. This is a unique chance to step up the efforts on the multiscale problematic.

4. SWOT and conclusion

As a summary guide, this part presents the strengths, weaknesses, opportunities and threats of the activities in theoretical chemistry.

Strengths	Weaknesses
- The richness of collaborations with theoretical AND experimental teams. - The visibility of the activities at the national and international levels. - The diversity of computational methods (and multiscale). - The essential nature of theoretical studies in the IN2P3 interdisciplinary activities.	- Activities 2.1, 2.3 and 2.4 are only held by professors or assistant professors. - The importance of this somewhat marginal theoretical work at IN2P3 is not sufficiently recognized. - The subcritical size at IN2P3.
Opportunities	**Threats**
- Collaboration with other french experimental research teams. - Recommendation of the Energy Working Group (CS CNRS) to support modeling actions. - Potential renewal of the MP RCT with a new "coloration" (focused on solid studies).	- The departure of R. Maurice and associated molecular activities. - Potential disappearance of the MP RCT despite a project adapted to the present forces.

Theoretical chemistry in IN2P3 laboratories concerns a lot of different topics which mainly deal with problematics of radioactivity in environment and irradiated materials in nuclear reactors of different technology. This is clearly the expertise field of IN2P3 researchers with theoretical chemistry activities. All the results can have a huge impact on the nuclear industry and a large part of projects, presented in this report, are funded by French industrial partners (ANDRA, Orano, Framatome, EDF, IRSN…). This highlights the excellent visibility of these activities especially if we add the international collaborations.

These issues are very broadly multidisciplinary and interdisciplinary, involving the study of chemical bonds, chemistry at interfaces, diffusion of atoms (or fluids) in solids, physical properties, physics of defects, etc. Therefore, the researches involve different theoretical methods at different timescales and space scales. More recently, a lot of efforts have been put together to combine different methods to build multiscale approaches which allow to be closer to realistic conditions. This new methodology is more and more wanted from experimenters (and industrials) because it allows bridging experimental data and theoretical simulations and helps a lot to understand the underlying mechanisms. This a strength of the IN2P3 theoretical chemistry researchers which can be seen through the different collaboration networks with experimenters and theorists inside and outside IN2P3. In particular, several "big" projects (ANR, European contracts or projects) have been build or are currently done with this objective of multiscale approach in a close connection with experimenters. Moreover, the continuation of this approach is a recommendation of the CNRS energy working group and of the "2020-2030 French Strategic Plan for Nuclear Physics, Particle Physics, Astroparticle Physics, associated technologies & applications" report.

However, it is not possible, with only a few modelers/theorists (3 after the departure of R. Maurice), to respond to all the experimental needs of IN2P3 researchers (and outside of IN2P3) in the field of materials chemistry / radiochemistry. It is especially prejudicial for the collaborations between IN2P3 experimenters and theorists because it is known that the proximity between researchers favors the elaboration of projects. It should also be noted that these topics (especially nuclear wastes) should be more and more important in the next years and the probable decommissioning of several nuclear power plants.

In order to carry out the various projects simultaneously, to maintain and develop the relationships with experimenters and to continue to be competitive, it should be therefore imperative to have quickly a recruitment, in adequacy and complementarity with the current interests at IN2P3 (multiscale modeling, solid state chemistry, nuclear waste, *etc.*).

5. Mini CVs (2016-2021 period)

This part presents the usual indicators in order to evaluate the visibility of each researcher. In total (for theoretical chemistry activities), it represents almost 80 papers in high quality journals, 33 invited talks and 45 talks at international conferences. The last paragraph indicates a few papers representative of each topic.

5.1 ***A.G. Kalinichev*** *– IMT Atlantique*

- **27 papers** in high quality journals (*J.Phys.Chem. C, PCCP, Cement and Concrete Research, Appl. Geochem., Minerals, Applied Clay Science, Clays and Clay Minerals …)*
- **26 invited talks** at international conferences (Goldschmidt, American Chemical Society, Clay Minerals Society, International Clay Conferences…)
- **33 « normal » talks and 9 posters** at international conferences
- **8 special sessions or symposiums** organized at major international conferences
- **Invited editor for special issues**: Clays and Clay Minerals (2016); Journal of Molecular Liquids (2017) and Minerals (2018)
- **President of the Clay Minerals Society** (2019-2020)

5.2 ***R. Maurice*** *– CNRS*

- **HDR defended in October 2018** (Nantes)
- **Deputy director of GDR 3333** (the French Theoretical Chemistry Network)
- **Elected member of the IN2P3 Scientific Council**
- **20 papers** in high quality journals (*Inorg. Chem., J. Comput. Chem., Nat. Chem., Chem. Eur. J., PCCP, Angew. Chem. Int. Ed. …)*
- **1 book chapter** (in *Handbook of Relativistic Quantum Chemistry*)
- **5 invited talks** at international conferences
- **3 « normal » talks** at international conferences

5.3 ***Y. Pipon*** *– Univ. Lyon*

- **HDR defended in December 2020** (Lyon)
- **PEDR obtained in October 2020**
- **Elected member of the research commission** of the UCBL Academic council (2016-2020)
- **12 papers** in high quality journals (*Inorg. Chem, JECS, JNM*)
- **1 invited talk** at international conference (Actinides)
- **5 « normal » talks and 3 posters** at international conferences

5.4 ***J. Roques*** *– Univ. Paris-Saclay*

- **20 papers** in high quality journals (*Inorg. Chem., JNM, Computational Materials Science, Dalton Transactions, Metallomics, Geochimica and Cosmochimica Acta…)*
- **1 invited talk** at international conferences
- **4 « normal » talks** at international conferences

5.5 Ten papers relative to activities described in the present report

We have selected a few papers representative of each topic. These papers can help the readers of this report to complete their understanding of the theoretical chemistry activities.

Activity 2.1: clay / cement system interfaces with fluids

- N. Loganathan, A.G. Kalinichev (2017) *J. Phys. Chem. C*, **121**, 7829–7836.
- M. Pouvreau *et al.* (2019) *J. Phys. Chem. C*, **123**, 11628–11638.
- I. Androniuk, A.G. Kalinichev (2020) *Appl. Geochem*., **113**, 104496.
- S.M. Mutisya, A.G. Kalinichev (2021) *Minerals*, **11**, 5.

Activity 2.2: molecular theoretical chemistry

- Guo *et al.* (2016) *Angew. Chem. Int. Ed.,* **55**, 15369–15372.
- A. Stoïanov *et al.* (2019) *Inorg. Chem.,* **58**, 7036–7043.

Activity 2.4: diffusion in nuclear materials

- Y. Xu *et al.* (2016) *J. Nucl. Mater.,* **473**, 61–67.
- C. Gerin *et al.* (2017) *Geochimica and Cosmochimica Acta*, **197**, 87–103.
- L. Sarrasin *et al.* (2019) *Inorg. Chem*., **58**, 4761–4773.
- Gautheron *et al.* (2020) *Geochimica and Cosmochimica Acta*, **268**, 348–367.

Note: *two internal and confidential reports for JRC were written in the framework of the activity 2.3*