PhD Proposal 2024

School - Location: CentraleSupélec, Gif-sur-Yvette (10 miles from Paris)	
Laboratory: LGPM	Web site: https://lgpm.centralesupelec.fr/
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Title: Theoretical investigation of quantum collisions involving electron, atom and molecules: Applications ranging from nitrogen molecules to pharmaceutical ingredients

Scientific field (one among the list- remove other choices):
Engineering & Technology: Chemical engineering

Free Key words: atom-molecule collisions, quasi-classical trajectory method, atmospheric chemistry, excitation, de-excitation of molecules
Salary: "Allocation de recherche" within the framework of European project DigiQ (DIGITAL-2021-SKILLS-O1-SPECIALISED) and QuanTEdu-France (ANR: "Compétences et Métiers d'Avenir" de France 2030)
Remarks: Possible joint PhD (cotutelle) with the University of Central Florida with a planned long term exchange in Marquette University
Period: from now (for 3 years)

Details for the subject:

General context: atom-molecule and molecule-molecule collisions are of fundamental importance and have many useful applications for the modeling of discharges in low-temperature gases, laser physics, atmospheric and interstellar media, isotope separation, radiation physics, and magneto-hydro dynamics power generation. Contrary to electron-impact collisions, atom or molecules collisions with counterparts are much less known and data calculations remains a computational challenge.

In our preceding studies, we developed different models to compute the cross section and rate constants for rovibronic (de)-excitations of various molecules (HeH^+, CF^+, $CH_2NH_2^+$, NH_2CHOH^+, BF_2^+, NO_2, N_2O, H_2O, etc.) by electron-impact. See Refs. (Ayouz and Kokoouline 2016; Yuen, et al. 2019; Ayouz, et al. 2020; Ayouz, et al. 2021; Liu, et al. 2021; Forer, et al 2023) and references therein.

For this PhD, we will develop skills on the mixed quantum/classical theory (MQCT) for studying collisions between atoms and molecules. This method is not entirely new and their foundations were outlined by Gert Billing and applied to He + H_2, at two (relatively high) values of scattering energies, E = 0.1 and 0.9 eV (Billing 1976; Billing 1977). Review paper and book are also available (Billing 1984; Billing 2002). For example, Babikov's group at Marquette University (WI, USA) applied this approach with success at the Na + N system. They provide accurate calculations of rotationally inelastic scattering cross sections (Semenov and Babikov 2014).

Description of the work:
The aim of this project is to pursue the preceding studies on collisions by electron impact and enrich the models by including the atom or molecule impacts in collision. We would allow developing the methodology for computing the cross sections database for atom-molecule impact. As benchmark system, we will apply the model to the nitrogen molecule formation in their electrically excited states. The theory and the conclusions suggested in this work would serve as a route towards studying other molecules such as NO or pharmaceutical large molecule as caffeine.

In collaboration with Babikov's group, we will make use of the MQCT for describing rovibrationally inelastic scattering of molecules. In this method, translational motion is treated classically, while quantum mechanics is used for rovibrational degrees of freedom. In fact, a full-quantum scattering calculations are physically indispensable and computationally doable at low temperatures but become challenging at higher temperatures and/or for heavier (polyatomic) molecules and quenchers. Treating the intermolecular degrees classically appears here as a good compromise (Semenov and Babikov 2014). The PhD work consists of three main tasks:

Task 1 – As first step of the PhD plan, we will perform *ab intio* calculations of the potential energy surface (PES) of the studied system. For this purpose, we will use MOLPRO (Werner, et al. 2008) software to compute PES of N_2+N. The scattering of the quencher atom, here N, will be described classically using spherical polar coordinates and their evolution will be determined by conjugate momenta. We will carry on PES calculations for several N-N_2 configurations and parameters of the computational model in order to assess the uncertainty of the final results. Different basis sets and complete active space (CAS) will be tested to order to reproduce the experimental dissociation limit of N_2.

Task 2- As second step, an extension in terms of Legendre polynomials is accomplished on the potential energy (PES) similar to Ref. (Loreau, et al. 2021). The wave function of N_2 is expanded over the basis set of rovibrational eigenstates with time-dependent coefficients. Consequently, substitution of the wave function into the Schrodinger equation leads to a coupled equations system that can be solved using standard methods, here the Runge–Kutta method of fourth order. Thus, the transition matrix is obtained and the cross section can be derived.

Task 3- The above-obtained cross sections will be incorporated to a collisional-radiative (CR) model, developed by Laux's group at CentraleSupelec. This CR model is employed to predict the nonequilibrium internal distribution of N and N_2 measured in recent recombination experiments of the EM2C laboratory. Predicting the energy transfer between a recombining nitrogen plasma and its environment is a major challenge for applications such as atmospheric reentry, plasma-assisted combustion, magnetic confinement fusion, and materials processing. These transfers depend in part on the population density of the excited states of N and N_2. The accuracy of this model depends on the uncertainty in the rate coefficients especially those of electronically excited states of the nitrogen atom and diatomics for which theoretical data may differ by up to 20 orders of magnitude (Mariotto's PhD 2023).

This work will be carried out in close collaboration with a US theoretical group of Prof. Babikov at Marquette University and experimental/theoretical groups at CentraleSupélec. An exchange and long term stay in the US institution is planned during the PhD.

References:

- Ayouz Mehdi and Kokoouline Viatscheslav 2016, Atoms, 4,30.

- C H Yuen, M A Ayouz, N Balucani, C Ceccarelli, I F Schneider, V Kokoouline, Monthly Notices of the Royal Astronomical Society 2019, Volume 484, Issue 1, Pages 659–664.
- M A Ayouz, C H Yuen, N Balucani, C Ceccarelli, I F Schneider, V Kokoouline, Monthly Notices of the Royal Astronomical Society 2020, Volume 490, Issue 1, Pages 1325–1331.
- Mehdi Ayouz, Alexandre Faure, Jonathan Tennyson, Maria Tudorovskaya and Viatcheslav Kokoouline 2021, *Atoms*, *9*(3), 62.
- H. Liu, X. Jiang, C.-H. Yuen, V. Kokoouline and M. Ayouz 2021, J. Phys. B: At. Mol. Opt. Phys. 54 185201.
- Joshua Forer, Dávid Hvizdoš, Xianwu Jiang, Mehdi Ayouz, Chris H. Greene, and Viatcheslav Kokoouline 2023, Phys. Rev. A 107, 042801; X. Jiang , H. Liu , Y. Zhang , W.Jiang, M. Ayouz and V. Kokoouline 2022, Plasma Sources Sci. Technol. 31, 045016.
- Billing, G. D. 1976, J. Chem. Phys. 1976, 65, 1-6.
- Billing, G. D. 1977, Chem. Phys. Lett. 1977, 50, 320-323.
- Billing, G. D. 1984, Comput. Phys. Rep., 1, 237-296.
- Billing, G. D. 2022, Oxford University Press: New York.
- Semenov and Babikov 2014, J. Chem. Phys.,
- Werner, H.J.; Knowles, P.J.; Lindh, R.; Manby, F.R.; Schütz, M.; Celani, P.; Korona, T.; Lindh, R.;Mitrushenkov, A.; Rauhut, G.; et al. MOLPRO, Version 2008.3, a Package of Ab Initio Programs.
- Loreau, J.; Zhang, P.; Dalgarno 2011, J. Chem. Phys. 2011, 135, 174301/1-174301/8.
- Pierre Mariotto 2023, , PhD of Université Paris Saclay.