Quantum mechanical calculations of cumulative reaction probabilities using an efficient Smolyak scheme

Lucien Dupuy[1*], Yohann Scribano[1] and David Lauvergnat[2]

[1]*Laboratoire Univers et Particules de Montpellier, UMR-CNRS 5299, Université de Montpellier, 34095 Montpellier Cedex, France.*

[2]*Institut de Chimie Physique, UMR-CNRS 8000, Université Paris-Saclay, Orsay 91405, France.*

*Presenting Author Email : lucien.dupuy@umontpellier.fr

Cumulative reaction probability plays a central role in the calculation of reaction rate constant of any bimolecular chemical reaction of interest. In order to give meaningful results, these calculations should be performed for chemical systems with a large number of degrees of freedom leading to expensive and often infeasible simulations. In this work, a new computational scheme is proposed to allow high dimensional quantum reactive simulations. This scheme is based on the Green's function operator technics combined to absorbing boundary conditions, a powerful approach introduced by W.H. Miller, T. Seideman and U. Manthe many years ago [1,2]. The new implementation takes benefit that the initial quantum reactive scattering problem can be cast into an eigenvalue problem [2] and uses the high efficiency and accuracy of Smolyak algorithm [3] to build very compact basis for eigenvalue problems [4]. Using this new computational framework, it is now possible to perform quantum dynamics simulations for multidimensional systems pushing away the curse of dimensionality problem. Some preliminary results will be presented [5] using this new powerful scheme.

References

[1] T. Seideman and W. H. Miller, J. Chem. Phys. 96, 4412 (1992).
[2] U. Manthe and W. H. Miller, J. Chem. Phys. 99, 3411 (1993).
[3] S. A. Smolyak, Dokl. Akad. Nauk SSSR. 148 (5), 1042 (1963).
[4] D. Lauvergnat et al. J. Chem. Phys. 150, 154303 (2019).
[5] L. Dupuy, Y. Scribano, D. Lauvergnat, to be submitted.