Networked computing for ab initio modeling the chemical storage of alternative energy: Fifth term report (September-November 2016)

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Abstract

During the last term, the work was centered in the implementation of a long range potential, based on the Electrostatic interaction plus van der Waals (as Improved Lennard-Jones by Pirani) to the CXZ PES, the development of the finite reactor script, to enable gas species changes along kinetic Monte Carlo simulations, and the ROBO coordinates applied to the PES MF1 and MF2 which describe the long-range interaction for the $N_2 + O_2$ system.

Report

1) Implementation of the Long Range potential (Improved Lennard-Jones plus Electrostatic) into the CXZ PES for the OH + H_2 system.

Quantum-Classical calculations on the vibrational energy redistribution in the OH + H_2 collisions[1] allowed us to single out a non-physical behaviour of the Chen *et al.* (CXZ) PES[2] when predicting potential energy at intermolecular distances higher than 8 Å. This encouraged us to switch at long range from the CXZ formulation into a more appropriate one to the end of fixing the above mentioned non-physical behaviour. The functional formulation adopted for the long range potential was the sum of electrostatic interaction (up to second order in the electrostatic multipole expansion) and the Improved Lennard-Jones potential, developed by Pirani[3], to model the London dispersion forces. In order to implement

the combined intermolecular potential a subroutine in Fortran90 has been written, to be used ontop of the CXZ PES. A switching function of the logistic type was used to pass from the CXZ PES to the long range one.

The implementation of this long range potential tail allowed us to run calculations on the OH + H_2 system at starting distances larger than 8 Å, the maximum value at which the CXZ PES was fitted, which is important for an accurate description of vibrational and rotational processes.

2) Implementation of the ROBO Coordinates in the MF1 and MF2 PES for N_2 + O_2 system.

The MF1 and MF2 PES developed by Pirani *et al.* describe the intermolecular interaction between N_2 and O_2 by making use of electrostatic quadrupole-quadrupole interactions and the Improved Lennard-Jones, by Pirani [2], to describe the London dispersion forces. The Improved Lennard-Jones potential makes use of bond polarizability embodying into the intermolecular interaction the dependence on the internal excitation of the reactants. On their side, the ROBO coordinates provide away for expressing the diatomic interaction as a pure polynomial and reaction coordinates as an angle while offering representations focused on the close interaction zone. A combination of both concepts has been utilized to the end of plotting some fixed internuclear diatomic distance isoenergetic contours. Typical plots of this type are shown in Figure 1.

3) Implementation of the continuous reactor script for the kinetic Monte Carlo Method.

In former reports, the kinetic study of the Sabatier reaction has been

reported[4]. The used kinetic Monte Carlo (kMC) method is probably the best one to simulate the kinetics of chemical reactions.
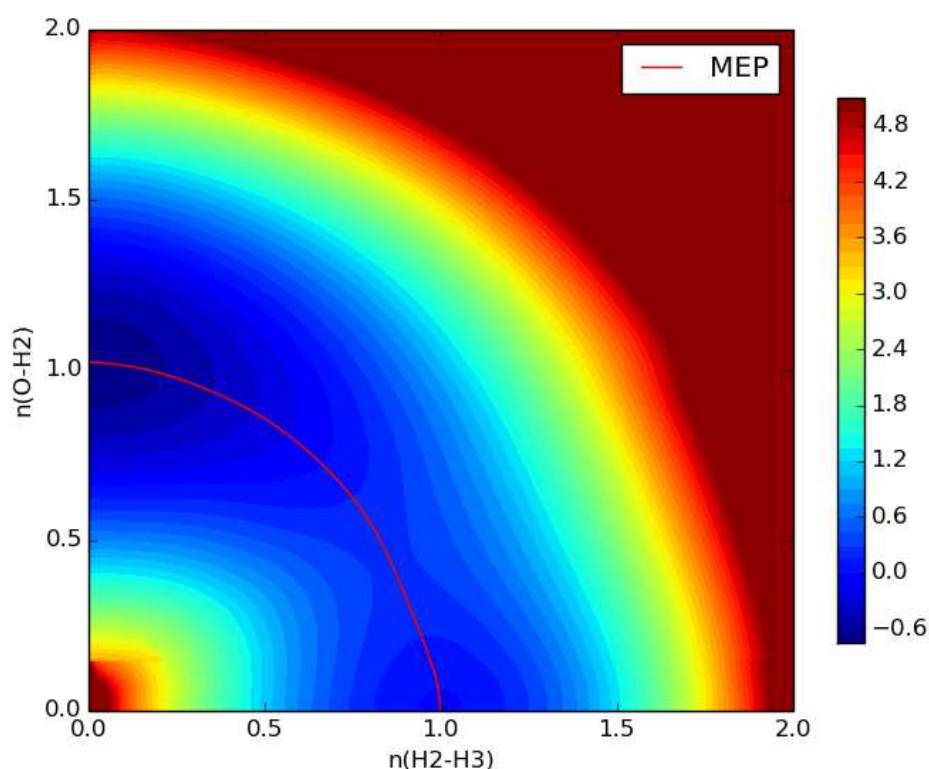

Figure 1. Contour plot of the MF1 PES in the ROBO coordinates

It makes use of reaction rate constants and a pseudo-random generator to stochastically solve the Master equations of the kinetic system. One of the main drawbacks of the methodology, however, is the impossibility to simulate processes involving gas species whose concentrations vary along the flow direction of the simulated reactor. In order to take into account this feature of the system we have modified the model by splitting the simulation in time intervals. The simulation starts at the input-given conditions, and runs a kMC simulation at these conditions. Once the first interval ends, partial and total pressures are recalculated taking into account the number of reacted species. The next simulation starts at these new conditions of total and partial pressures. This procedure is repeated until the initial ending criterion is achieved. With this finite-volume-

reactor model we can obtain more accurate results of how a reaction occurs. Gaseous intermediates can be desorbed and re-adsorbed during the simulation to give a more complete view of the kinetic process.
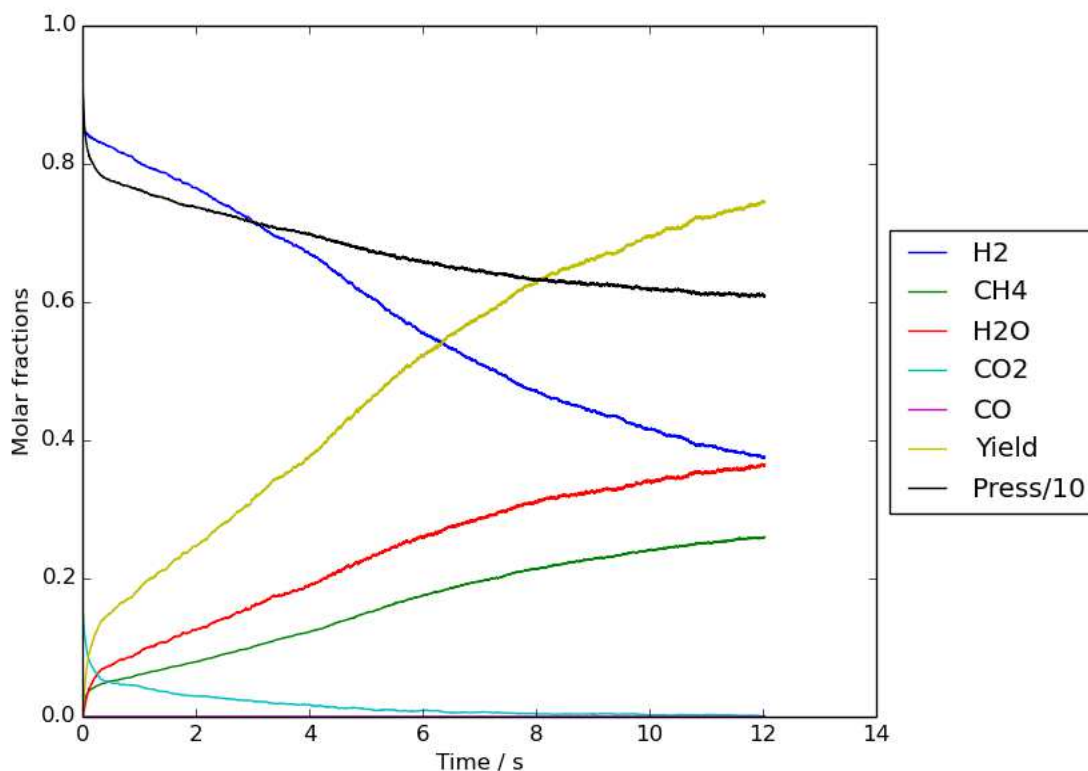

Figure 2. Change on the gas phase species molar fractionsfor the Sabatier reaction.

5) Participation on the SHARC school at Vienna.

The last workshop of the year was organized by the L. González group at the University of Vienna. The workshop focused on nuclei dynamics on electronic excited states with a specific emphasis on the use and basic principles of the molecular dynamics package SHARC (Surface Hopping including ARbitrary Couplings). In Time-Independent Schrödinger Equation (TISE) techniques the wavefunction depends only parametrically on the nuclear coordinates and the kinetic energy operator for the nuclei is not considered. In the case of photochemical reactions, the process is

triggered by photoexcitation of the system into an excited state. These time-dependent phenomena cannot be described by the TISE and Time-Dependent Schrödinger Equations (TDSE) needs to be integrated.

The main topic of the workshop was the surface hopping approach. Surface hopping is a hybrid approach, in which the nuclei are treated as particles following the classical mechanics equation of motions, while the electrons are treated full quantum mechanically. In the first sessions basic concepts of photochemistry were presented and ways to solve the time dependent Schrödinger equation were revisited. The main focus was on the accurate description of excited states.

Next a closer look was taken on the visualisation and interpretation of the output of excited state calculations, with a main focus on the interpretation of properties of the electronic wavefunction. In this context the program suite TheoDORE (Theoretical Density, Orbital Relaxation and Exciton analysis) was introduced and its many options for the analysis of excited states were illustrated. The second day was entirely devoted to explore different types of dynamics, starting from classical and semi-classical methods to end with full quantum dynamics. After this general overview the third and fourth days were devoted to illustrate the main topic of the course: the surface hopping method. In this context Tully's fewest switches method was discussed and the difference with respect to the method used in the SHARC program were evidenced. Next the different representations of the potential energy hypersurfaces were discussed. Hands on sessions were a good opportunity for gaining experience on SHARC and see how it works (from the setting of the different trajectories to the analysis of the output).

To complete the picture on excited state dynamics, different invited speakers presented their approaches on the fifth and final day. During the morning session the MCTDH method and its variants, the Gaussian-MCTDH and the variational Multi-Configurational Gaussians (vMCG) were illustrated, by Graham Worth one of its main developers. Next Basile Curchod gave a lecture on the more approximate multiple spawning method, followed by the last speaker Gerrit Groenhof, who gave an introduction to experimental methods to study excited states. Later a group discussion about the challenges in chemical dynamics and future applications followed. During the discussion a particular emphasis was given to options to enhance the interplay between experiment and theory.

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