

Networked computing for ab initio modeling the chemical storage of alternative energy: first term report (September-November 2015)

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Abstract

In this ESR04 first paper report I describe the research environment, the objectives, the work plan and the progress made in the first term of my doctoral studies. Problems arisen and solutions adopted during such period of activity in Perugia are briefly illustrated.

Report

Since my first arrival at the Computational Dynamics and Kinetics (CDK) group of the Department of Chemistry, Biology and Biotechnology of the University of Perugia, the target of my research studies became quite clear. The CDK group is part of a mixed experimental, theoretical and computational laboratory dealing, on the experimental side, with gas phase (beam-beam, beam-bulk and electron-molecule) measurements of scattering elementary processes while on the theoretical side the scattering theory of the mentioned processes, including reactions, are investigated and related computational procedures are developed and implemented on distributed computing infrastructures (DCI) for massive runs.

Accordingly, among the first duties there was that of deepening my competences in the theoretical treatment of collision processes. To this end I had several tutorials with Dr. Leonardo Pacifici and Prof. Antonio Laganà and frequent discussions with the other members of the group (including the experimentalists). Part of this preliminary training was also the participation to the core course started in Madrid at the end of September and aimed at allowing us to improve our “soft skills” background. During the Core course the following activities were undertaken:

School on Sustainable Entrepreneurship. Training has been received on how to start a spin-off or a start-up, how to use some of the specifically designed modern tools for enabling potential young entrepreneurs to better achieve their goals and how to learn from the experience of entrepreneurs who have succeeded in starting new companies. We also paid a visit to the facilities of the Madrid Scientific Park in order to better know the suitable

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environment for incubating new small companies.

Supercomputing: Projects and networks. This seminar consisted in the illustration of how a supercomputer centre is organized and how to apply for computer time allocation. In particular the presentation was concerned about the High Performance Computing (HPC) PRACE centres and their calls to have compute time allocated on their supercomputers. The seminar was concluded by a visit to the supercomputing facilities of the Universidad Autónoma de Madrid (UAM).

Tutorial on scientific Publication and Scopus. In this part, Rob van Daelen from Elsevier and Manuel Yáñez from UAM illustrated the procedure for paper submission and acceptance by scientific journals. They also illustrated some tips and tricks useful to facilitate the publication of a paper. The main features of Scopus aimed at facilitating the search for papers were also illustrated.

4th Workshop on Theoretical Chemistry and Computational Modelling. For two days we had also 20 minute presentations by several European PhD students carrying out research work on Theoretical Chemistry and Computational Modelling. The presented projects were as different as Protein-Drug modelling, electron density dynamics, energetic applications of materials or the kinetics and dynamics of chemical reactions.

Writing successful proposals. The main goal of the presentation was to illustrate the main change in European trends in research. The key target is at present to focus on knowledge transfer from university to companies. It has been also described how to apply for European calls to funding.

Workshop on Communication in Science. The need for a better way to explain science to a large audience was the main topic of this workshop. Some strategies to better arrive at the heart of people were discussed and how this could be important for the role that science wishes to play in the society.

After returning to Perugia my activities continued both by studying the notes of Prof. Laganà when checking the content of the draft of the book “Reactivity: Basic Theory and Computing” he is writing jointly with G.A. Parker for Springer and by attending, as well, a course on the Italian

language at the linguistic centre of the university (level B2).

Under the supervision of Dr. L. Pacifici I started also practising the use of distributed computing to the end of carrying out *ab initio* simulations of chemical processes. This type of studies rely on the adoption of the so called Grid Empowered Molecular Simulator (GEMS) [1] that is articulated into four modules:

INTERACTION (devoted to the distribution of the calculations and/or to the collection of the necessary high level *ab initio* information on the electronic structure of the system available from the literature),

FITTING (devoted to the carrying out of a combined theory versus experiment optimization of the parameters of an analytical formulation of the Potential Energy Surface (PES)),

DYNAMICS (devoted to the performing of the appropriate dynamical calculations aimed at feeding the last module

OBSERVABLES (devoted to the running of the statistical elaborations necessary to build the related cross sections and rate coefficients in order to quantify the efficiency of the investigated processes).

GEMS leverages on a proper combination of HPC and HTC (High Throughput Computing) to the end of meeting the different requests of concurrency and scalability of the programs used [2].

The key use of GEMS during my PhD work will be focused on the study of the processes related to the storage of alternative energies as chemical energy thanks to the reduction of carbon dioxide to methane [3]. To this end the Perugia group is already providing me with the necessary competences and access to the grid infrastructure as well as with the basic expertise necessary to make an appropriate usage of the resources. Efforts are also being spent to introduce me to the various groups of the Virtual Organization COMPCHEM [4] and to help me in trying to restructure some of the relevant codes to run efficiently on heterogeneous platforms.

As a specific example, I am considering the porting of the quantum-classical method for a collision of two diatoms of G. Billing [5]. In the mentioned quantum-classical method, molecular vibrations of molecule "a" and molecule "b" are treated quantum-mechanically (by integrating the related

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time (t) dependent Schrödinger equations) while the translational and rotational degrees of freedom are treated classically (by integrating the related classical Hamilton equations). The two subsystems, and the corresponding equations of motion, are dynamically coupled through the definition and calculation of a time-dependent "effective" Hamiltonian, H_{eff} , (of the Ehrenfest type) defined as the expectation value of the intermolecular interaction potential over the wavefunction $\Psi_{ra,rb,t}$ of the system

$$H_{eff} = \langle \Psi_{ra,rb,t} | V_{inter} R(t) | \Psi_{ra,rb,t} \rangle$$

where $V_{inter} R(t)$ is the interaction potential evaluated at each time step of the classical "mean" trajectory $R(t)$.

The time evolution of the total wavefunction is obtained by expanding $|\Psi_{ra,rb,t}\rangle$ over the manifold of the product, rotationally-distorted, Morse wavefunctions of the two isolated molecules $\Phi_{v'a}(ra,t)$ and $\Phi_{v'b}(rb,t)$ as follows:

$$\Psi_{ra,rb,t} = \sum_{v'a, v'b} A_{v'av'b} \Phi_{v'a}(ra,t) \Phi_{v'b}(rb,t) \exp[-i(E_{v'a}(ra) + E_{v'b}(rb))t/\hbar]$$

in which $A_{v'av'b}$ is the amplitude of the vibrational transition from va and vb to $v'a$ and $v'b$, $E_{v'i}(t)$ is the eigenvalue of the $v'i$ Morse wavefunction $\Phi_{v'i}(ri,t)$ corrected by the Coriolis coupling element $H_{v''_a v'_b}$ as follows:

$$\Phi_{v'i}(ri,t) = \Phi_{0v'i}(ri) + v''_i \neq v'_i \Phi_{0v''_i}(ri) H_{v''_a v'_b} / (E_{0v'i}(ri) - E_{0v''_i}(ri))$$

In which the second term represents the first-order centrifugal stretching contribution coupling diatomic rotations and vibrations of diatom with $\Phi_{0v'i}(ri)$ and $E_{0v'i}(ri)$ being the eigenfunction and the eigenvalue, respectively, of the same Morse oscillator.

The Hamilton equations for the roto-translational motions are integrated self-consistently together with the Schrödinger equations of the vibrational amplitudes.

To this end the Toulouse contribution to the ESR04 project concerns the theoretical study of the electronic structure of the involved molecular systems with particular reference to the necessity of developing standard formats for data produced by different *ab initio* packages and its extension to

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dynamical calculations [6] whereas the role of the non-academic partner (PLC System srl in Acerra) for the secondment is to provide the access to a prototype apparatus on which testing experimental and theoretical features of the project.

The chemical reaction occurring inside the experimental prototype apparatus (named PROGEO) has been assembled at the industrial premise of the PLC System, at which I shall have my secondment. From theoretical calculations in fact I shall derive (either exact or approximate) estimates of the probabilities, cross sections and rate coefficients of the Paul Sabatier one whose stoichiometrically balanced form reads:



From PROGEO we shall obtain measurements for the reaction of carbon dioxide provided by a bottle with the hydrogen produced by a water electrolyser. The reaction is catalyzed by Nickel at high temperature (300-400 °C) and high pressure to produce methane and water (a more efficient catalyser is ruthenium on alumina). The figure below shows typical yields obtained from preliminary runs of PROGEO.

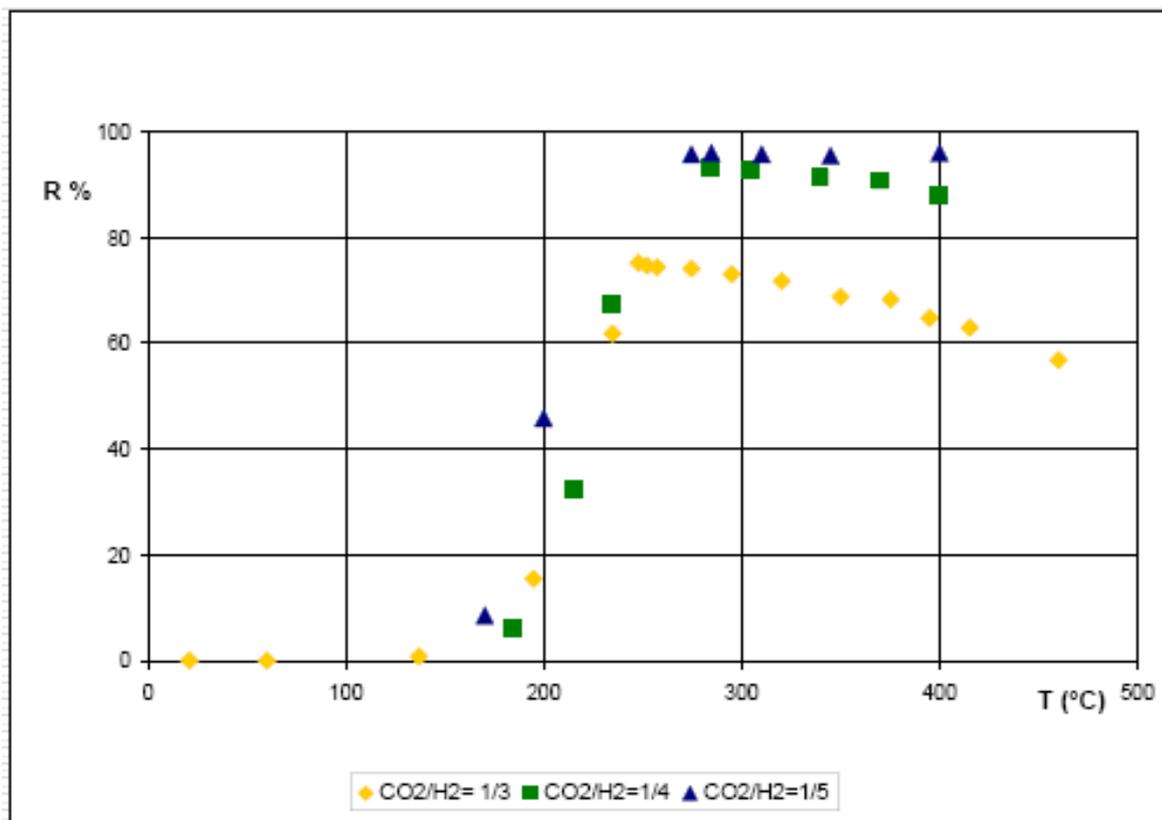


FIG. 1 – CH₄ per cent yield plotted as a function of T at different CO₂/H₂ ratios

In order to facilitate my future secondment I have already paid a visit to the PLC System. In this

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occasion talks have been started between Prof. A. Laganà and Francesco Esposito (the PLC System CEO) to the end of planning the transfer of PROGEO in a location closer to the Department of chemistry so as to make the secondment more effective.

To go into more detail of my PhD research work concerning the theoretical study of chemical reactions and the computation of their efficiency parameters (probabilities, cross sections and rate coefficients) to be compared with measured efficiency data, I shall:

- 1 decompose the pure gas phase $H_2 + CO_2$ reaction into elementary components
- 2 design the procedure for carrying out the *ab initio* calculations of the related potential energy values in collaboration with Toulouse in anticipation for the work to be carried out during my stay there after month 20
- 3 try to build in the meantime in Perugia a model PES by fitting existing experimental and theoretical data and carry out on such PES a systematic preliminary dynamical study
- 4 after trying to understand the main features of the pure gas phase reaction, concentrate on the study of the effect of adding a catalyst to the process by performing specific high level *ab initio* studies in Toulouse (after month 20) and then carrying out dynamical calculations on the PES fitted to those data.
- 5 draw final conclusions of my research and write the thesis.

THE ESR04 ROADMAP

The resulting roadmap of my PhD studies will therefore result to be as follows:

Months 1-6. Literature overview of the problem and definition of the gas phase elementary processes

Months 7-9 Assemblage of a PES fitted to existing data and preliminary dynamical calculations

Months 10-12 Experimental measurements for comparison to theoretical results

Months 13-20 High level calculations and fitting of a more accurate PES for gas phase processes and fitting of the calculated data

Months 21-26 Further High level calculation of the PES for the gas-catalyst complex and fitting of the calculated data

Months 27-33 Massive dynamical calculations and platform optimization

Month 34-36. Analysis of the results and writing and discussion of the doctoral Thesis

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