

LEARNING OBJECTS FOR THE COURSE: CHEMICAL REACTIONS BASIC THEORY AND COMPUTING

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Abstract

Recently G.A. Parker and myself published the book *Chemical Reactions: basic theory and computing* ([Springer International Publishing 2018, ISBN 978-3-319-62355-9](#)) based on the lectures delivered to the [European Erasmus⁺ Master Theoretical Chemistry and Computational Modelling](#). Here we discuss the articulation of the Learning Objects related to that course and book with the purpose of structuring them for the [Grid Learning Objects Distributed Repository](#).

1. Introduction

The course we discuss here, *Chemical Reactions: basic theory and computing* written by Gregory .A. Parker and myself, has been designed to help the students of the European Erasmus Mundus Master in "Theoretical Chemistry and Computational Modelling" (TCCM) to familiarize with both theoretical methods and computational techniques useful to handle the treatment of chemical reactive processes at microscopic level. The general scheme of the book is illustrated by the Learning Object (LO) LO00. In it the reader is driven to disentangle elementary events out of the kinetics of complex systems in which reactive and non-reactive processes combine and compete in different ways depending on the interactions and momenta of the involved species. Then theoretical and computational techniques for dealing with two-, three-, four- and many-body collisions are discussed (by leveraging preferentially elementary gas phase processes) and out of the obtained detailed microscopic information complexity is regained in order to extend the treatment to very large systems by introducing the necessary approximations, using the appropriate experimental and computational apparatuses with specific reference to Open Science approaches.

2. Further articulation of the course

Chapter 1

The book begins by considering the modelling of the experimental outcomes (the thermal rate coefficients) using the Transition State (TS) approach within a thermodynamics formulation of the problem. From the analysis of the inconsistencies of the TS model (useful for a phenomenological systematization of experimental data yet useless for predictions) the efficiency of chemical processes is rationalized in terms of collisions of two structure-less bodies using classical mechanics (in which atoms are considered as mass points) and simple model interactions (like pure Coulomb attraction and/or repulsion, hard sphere, mixed attraction at long range plus repulsion at short range (Sutherland, Morse and Lennard-Jones)). This is discussed in LO 01a.

The classical mechanics conceptual machinery, relying on analytical procedures tackling the problem of solving related Newton and Hamilton equations for simple model interactions, is analysed in this chapter by associating an estimate of the final properties (like the angle of deflection, cross sections and rate coefficients, all quantities of experimental relevance) for different initial conditions. This is discussed in LO 01b.

Pseudo-codes designed for computational classical mechanics procedures based on basic numerical procedures devoted to the integration of the mentioned Newton or Hamilton equations, are provided in this chapter by associating a set of trajectories starting from different initial conditions to the angle of deflection, cross sections and rate coefficients. This is discussed in LO 01c.

Chapter 2

The observed failure of the classical mechanics treatment to reproduce some key features of measured data (like the elastic differential cross section in two body collisions) is traced back to the quantum nature of molecular processes and to the related uncertainty principle. This drives the reader to the use of quantum techniques for evaluating the properties of both bound and elastically scattered atom-atom systems by integrating the Schrödinger equation both in its time dependent and time dependent form. Related quantum treatments are then discussed and analytical solutions are first worked out for some prototype cases to the end of guiding the reader to use of special functions. This is discussed in LO 02a

Then some of the most popular techniques and related pseudo-codes useful for integrating numerically the already mentioned corresponding Schrödinger equation for generic atom-atom interactions are illustrated and applied in order to compare related results with corresponding classical ones. This is discussed in LO 02b.

Chapter 3

At this point the assumption that atoms are structure-less can be abandoned and theoretical treatments more properly handling the electronic structure can be adopted. To move along this direction we discuss here some techniques commonly used for evaluating *ab initio* electronic energies and discuss the adoption of both one-electron functions and variational principle. Along this line, the electronic structure of polyatomic molecules, molecular orbitals, Hartree-Fock and Self Consistent Field (SCF) Molecular Orbital (MO) treatments are discussed in some detail and post Hartree-Fock Configuration Interaction, Multi configuration self-consistent fields and Perturbation methods for the calculation of electronic energies and other molecular properties are illustrated. This is discussed in LO 03a.

To better deal with reactive processes the general nuclei + electrons systems are considered and the various components of the Hamiltonian are described in both the time dependent and the time independent schemes by decoupling electrons and nuclei dynamics and making specific reference to atom diatom systems. This is discussed in LO 03b.

Chapter 4

In this chapter concepts and techniques to be used for carrying out dynamical calculations of reactive systems starting from atom-diatom elementary collisions are considered. To this end the motion of nuclei is disentangled from the electronic one by introducing the Born-Oppenheimer approximation. Then the different sets of coordinates (Jacobi, internuclear distances, natural, etc.) for atom-diatom systems and their bias towards specific uses are discussed. The aim of this is the singling out of the coordinates better suited for formulating the different terms of the many body expansion of the interaction potential, the Bond Order (BO) variables, the Rotating BO (ROBO) models, the Many Process Expansion (MPE) of the interaction, the mobile least square fitting of the potential and other coordinates tailored to better adapt to other molecular dynamics studies needs. This is discussed in LO 04a.

Different formulations of dynamics equations are discussed for the classical and quantum treatments of molecular dynamics including time dependent and time independent approaches. The integration of these equations allows to figure out the typical features of the microscopic phenomenology of elementary atom-diatom processes such as the effect of a different allocation of energy to the various degrees of freedom in promoting reactivity, the importance of providing an accurate representation of the potential energy surface, the merits and demerits of adopting reduced dimensionality approaches or treating quantumly some degrees of freedom while handling classically the others. Then the discussion is extended also to the usefulness of singling out the periodic orbits of dynamical systems for rationalizing the key features of their reactive properties (including the categorization of transition state effects) and the design of proper statistical treatments for long living processes. Finally, relationships connecting the various angular momenta are illustrated in LO 04b.

Chapter 5

In this final chapter a detailed account of some other elementary atom-molecule and molecule-molecule processes is given and some considerations are made on the road map to adopt when investigating systems of higher complexity

The first LO (05a) illustrates the basis of modern concurrent computing paradigms and technologies (from micro level to grids and cloud) starting with the four and more atom ones processes.

The second LO (05b) illustrates the application of concurrent computing (together with the mention to some popular computing packages) to some prototype reactions and comments the results obtained in terms of features of the potential energy and of the energy allocation to different degrees of freedom. Mention to the virtual organization COMPCHEM established in order to support the computational chemistry community is also made.

The third LO (05c) illustrates some extension of the dynamical studies to large systems both in terms of adopting Force Field techniques to build related potential energy surfaces and in terms of using classical mechanics treatments of atoms (or group of atoms).

Finally in the fourth LO (05d) truly complex computational applications dealing with systems concerned with some technological innovations (e.g. particle flux through nanopores or catalytic conversion of CO₂ in methane) and the crediting of community computational services provision are considered.