Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Computer Science 18 (2013) 835 – 844

Procedia
Computer Science

International Conference on Computational Science, ICCS 2013

# Performance Analysis of Two Quantum Reaction Dynamics Codes: Time-Dependent and Time-Independent Strategies

Pablo Gamallo[a], Miguel González, and Fermín Huarte-Larrañaga[b]

*Departament de Química Física and IQTCUB, Universitat de Barcelona, Martí i Franqués 1, Barcelona 08028, Spain*

## Abstract

The computer simulation of reaction dynamics has nowadays reached a remarkable degree of accuracy. Triatomic elementary reactions are rigorously studied with great detail on a straightforward basis using a considerable variety of Quantum Dynamics computational tools available to the scientific community. In our contribution we compare the performance of two quantum scattering codes in the computation of reaction cross sections of a triatomic benchmark reaction such as the gas phase reaction Ne + $H_2^+ \rightarrow NeH^+ + H$. The computational codes are selected as representative of time-dependent (Real Wave Packet [1]) and time-independent (ABC [2]) methodologies. The main conclusion to be drawn from our study is that both strategies are, to a great extent, not competing but rather complementary. While time-dependent calculations advantages with respect to the energy range that can be covered in a single simulation, time-independent approaches offer much more detailed information from each single energy calculation. Further details such as the calculation of reactivity at very low collision energies or the computational effort related to account for the Coriolis couplings are analyzed in this paper.

Keywords: Reaction Dynamics, Time-Dependent Dynamics, Time-Independent Dynamics, Quantum Scattering, Wave packets

## 1. Introduction

Chemical reaction dynamics is the microscopic basis of chemical reaction kinetics and quantum mechanics determines their evolution at the fundamental level. According to this, the development of theoretical methods as well as the implementation of the corresponding computational tools is a key element for obtaining detailed dynamical information (i.e., cross sections, product state distributions, differential cross sections, rate constants, characterization of the microscopic mechanism, …) that enable the understanding of elementary chemical reactions from the microscopic point of view [3].

Reaction Dynamics has contributed significantly to the progress of physical chemistry and chemical physics during last decades, especially after 1980s, thanks to the development of many new experimental and theoretical techniques that have provided important support for atmospheric, astrophysical as well as combustion chemistry [4]. At the same time, advances in computer technology and quantum dynamics methods have allowed new possibilities

---

[a] gamallo@ub.edu
[b] fermin.huarte@ub.edu

Selection and peer review under responsibility of the organizers of the 2013 International Conference on Computational Science
doi:10.1016/j.procs.2013.05.248

for theoretical studies. The arrival of competitive *ab initio* quantum chemistry packages became an important tool for obtaining accurate energies as well as structural information. Thus, accurate *ab initio* based global potential energy surfaces (PESs) may now be constructed for elementary reactions and used in reaction dynamics studies. The Schrödinger equation characterizing the rearrangement evolution of the atomic nuclei over PES can be solved using time-dependent (TD) or time-independent (TI) methods. In either case, solving the Schrödinger equation is a formidable task, and many interesting chemical systems challenge the present capabilities of exact quantum dynamics techniques.

In this context, our contribution presents the comparison of two computational codes based on TD and TI quantum scattering methods in the study of a gas-phase atom + diatom reaction. In particular, we have studied the collision dynamics of the benchmark reaction,

$$\mathrm{Ne} + \mathrm{H_2^+}\,(v_0, j_0) \rightarrow \mathrm{NeH^+} + \mathrm{H}$$

for a set of selected rovibrational initial states of the diatomic $H_2^+$ ($v_0$=0-2, $j_0$=1) molecule on the recent accurate LZHH PES [5]. The dynamics of this reaction has been investigated in the past by some of us [6, 7, 8] either using the LZHH or an older PES [9]. The reactivity of this system exhibits a strong oscillatory behavior as a function of the collision energy ($E_{col}$) independently of the PES used.

Our contribution focuses on the computational aspects of both quantum dynamics studies, analyzing the computer time consumed to obtain initial-state resolved reaction probabilities and cross sections. In order to compare TD and TI strategies we have chosen two representative programs. In particular, we employ a parallel version of the time-dependent real wave packet (TDRWP) method of Gray and Balint-Kurti [1] and the time-independent ABC quantum scattering code developed by Skouteris, Castillo, and Manolopoulos [2]. In Section 2 we briefly present both approaches, paying more attention to practical implementation aspects rather than formal derivations. The results obtained in the quantum dynamics studies are commented in Section 3 together with the associated computer resources employed. Our main conclusions are listed in Section 4.

## 2. Methodology

Both quantum methods solve exactly the same equations although some differences appear depending on the set of coordinates that is chosen to solve the problem. The body fixed (BF) Hamiltonian for a triatomic system is widely developed in Ref. [10] in Jacobi coordinates and in Ref. [11] in hyperspherical coordinates. It is composed by the radial and the angular kinetic energy term, the potential energy surface term, the centrifugal energy term (associated with the value of the total angular momentum J) and the Coriolis term (associated with the value of K, the projection of J). Since the Coriolis term is considered accurately (i.e., using coupled channel (CC) equations), the dynamics of the system couples the different K values.

### *2.1. Time-Independent ABC method*

The ABC time-independent quantum scattering program[a] [2] integrates the Schrödinger equation for an atom-diatom elementary reaction using the CC method [11]. The program makes use of a TI method to integrate the nuclear Schrödinger equation on a single potential energy surface (PES), within the framework of the Born-Oppenheimer approach. The nuclear wave function, $\psi$, is expanded in terms of the hyperspherical arrangement

---

[a] Available at http://www.ccp6.ac.uk