

Chapter 1

Introduction

1.1 General introduction

The description of molecules reacting with surfaces is a central topic in physical chemistry, because it plays a key role in surface catalysis, chromatography, materials science, and perhaps even biochemistry of macromolecules and cell membranes [6]. Examples for these interface reactions are

- (i) the sticking of gas phase atoms or molecules at nonrigid surfaces [7],
- (ii) the inelastic scattering of atoms and molecules from surfaces, where both adsorbate and surface modes can be excited or deexcited [8],
- (iii) the dissociative sticking of molecules on thermal surfaces [9],
- (iv) the thermal or photochemical desorption of adsorbates [10], and
- (v) the activated diffusion of atoms or molecules on surfaces [11].

These latter have been extensively studied both experimentally and theoretically in the framework of the Schrödinger equation. Often in these works, the rigid surface

approximation is made, that is the surface degrees of freedom are kept “frozen” during the reaction events. Even if there are cases where this approximation is good, the presence of surface phonons and/or electron hole pairs causes vibrational and electronic relaxation and dephasing effects of adsorbate excited states in many gas surface phenomena. From this perspective these phenomena belong to the class of nuclear dynamics problems that cannot be economically (if at all) handled by ordinary Schrödinger equations.

Recently, considerable progress has been made in extending the powerful conceptual and numerical tools already available for the quantum dynamics of small, isolated molecules [12, 13, 5] to condensed phase problems. As a matter of fact in most of chemistry a proper environment is necessary for a reaction to take place, this being true not only for surfaces and matrices acting as catalysts, but especially for reactions in solutions.

In general, the use of ordinary Schrödinger dynamics becomes problematic

- (a) when mixed (*e.g.*, thermal) rather than pure states are of interest, and/or
- (b) when a system has too many degrees of freedom, as in condensed phase chemistry.

There is a number of possible solutions to model this kind of phenomena. One way is to take a limited number of degrees of freedom of the bath explicitly into account. An exact representation inclusive of bath coordinates is a numerically expensive but possible approach, for example see [14, 15, 16]. Otherwise, approximations have to be made; examples of this approach are semiclassical methods [17], the Time Dependent Self Consistent Field (TDSCF) methods [18, 19], and their multiconfigurational versions [20, 21, 22, 23, 24, 25, 26, 27] that allow to describe up to a few tens of degrees of freedom in a mean field fashion. Further approximations lead to the quantum–classical approaches [28, 29, 30, 31] with extensions to nonadiabatic dynamics [32] and to many degrees of freedom like the Classically based Separable Potential (CSP) [33, 34, 35], and classical molecular dynamics [36] which allows for the consideration of hundreds to thousands of modes.

Another way to deal with these problems is the use of density matrix theory [37, 4]. Here, one describes explicitly only a few strongly coupled degrees of freedom, whose properties are of interest, modeling all the others as distortions and environmental fluctuations. In this case the dynamics are not anymore generated by the Schrödinger equation [1], but by the Liouville–von Neumann equation [37] (see the following chapter 2 for a more detailed introduction to density matrix theory).

Except for special examples, for which elegant analytical solutions can be found, the open system Liouville–von Neumann equations must be solved numerically and this turns out to be a hard numerical task especially for multi dimensional problems. Surface reaction problems often require a multi dimensional description and are unbound (“free”) in at least one of the relevant degrees of freedom. This implies that efficient numerical methods for large calculations have to be developed and one of the principal tasks of this dissertation is to do so.

The physical problems we are focusing upon are the inelastic scattering of H₂ or D₂ at metal surfaces [38], where interesting experimental results are available [39, 40], and NO photodesorption from Pt(111) [41], with experiments reported in [42]. As a “detour”, the characteristic line broadening of the optical spectra of molecules in condensed environments [43] will be treated using a new efficient density matrix approach.

1.2 Structure of the thesis

This work is organized as follows. After this introduction (chapter 1), in chapter 2 the density matrix formalism is outlined. In chapter 3, the numerical methods developed and/or used in this work will be described. In chapter 4, we treat the photodesorption of NO from Pt(111), while chapter 5 has to do with the quantum dynamics of hydrogen molecules scattering at noble metal surfaces. The work is summarized with a final outlook in chapter 6.

In the chapter on the numerical methods, we also include illustrative results

about various systems and phenomena, like the infrared IR absorption spectrum of solid benzoic acid. In the chapter on H_2 scattering at nonreactive metals, the formalism of a new method, the Coupled Channel Density Matrix (CCDM) method, is developed to describe this system and a specific model for the dissipation is proposed.