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Nonlinear Hamiltonian Mechanics Applied to Molecular Dynamics

Theory and Computational Methods for Understanding Molecular Spectroscopy and Chemical Reactions

Springer

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Preface

The first being so, and so the second,
The third and forth deduced we see;
And if there were no first and second,
Nor third nor fourth would ever be.
from "Faust" by Goethe

The birth of nonlinear mechanics and particularly their geometrical approach is usually attributed to Henri Poincaré[1] and they were fully developed in the second half of the twentieth century. New concepts were introduced and theorems were proved by mathematicians, thus putting the foundations for understanding *ordered* (stable) and *chaotic* (deterministic) motions of nonlinear dynamical systems. Now, a plethora of diverse complex systems are studied by nonlinear mechanics, which play the role of a unifying theory. In this success the rapid development of computers unequivocally played a catalytic role. Molecules are complex nonlinear dynamical systems and several research groups around the world rushed at the same time to investigate the implications of the theory of chaos could have in the dynamics of molecules. Since atoms and molecules are treated by quantum mechanics questions of how to interpret nonlinear classical mechanical behaviours in the quantum world, they quickly became a hot subject in the 1970s giving birth to what was named *quantum chaos*.

Nevertheless, in spite of this flourishing and productive period of nonlinear mechanics, their ideas seem to have no impact on the large community of theoretical and computational chemists. Instead, most of the efforts of computational chemists are still devoted to producing *potential energy surfaces* the stationary points of which, minima, saddles, maxima, as well as minimum energy pathways provide the theoretical background for explaining experimental spectroscopic and

[1] Henri Poincaré. Les Méthodes Nouvelles de la Mécanique Céleste, Vols 1–3. Gauthiers-Villars, Paris, 1892, 1893, 1899. (English translation edited by D. Goroff, published by the American Institute of Physics, New York, 1993.)

reaction dynamics observations. In the Born–Oppenheimer approximation,[2] the potential energy surface is used to calculate the forces among nuclei and classical rather than quantum mechanics are the main theories to study the dynamics of molecules with a relatively large number of atoms. Classical mechanics combined with statistical mechanics for extracting average quantities consist what is known today as Molecular Dynamics.

The limited interest of chemists in nonlinear mechanics is understood if one considers that even today to produce a reliable potential energy surface for a medium size polyatomic molecule (up to five atoms) requires substantial effort. There are also some basic reasons for the reluctance of chemists to introduce nonlinear mechanics to their ammunition in investigating molecular dynamics. Hamiltonian mechanics and their geometrical interpretations are essential for nonlinear mechanics, topics that still remain out of the chemists curriculum in postgraduate studies. Needless to say, the lack of an introductory book in nonlinear mechanics for chemists, significantly contributes to their limited interest in this field. The aim of the present book is to partially fill this gap. On the other hand, in the last decades there has been enormous progress in experimental techniques, which provide details at the level of single molecule quantum states. Methods for spectroscopically assigning highly excited vibrational states of reactant and product molecules in chemical reactions have been developed. Molecular beams, lasers, and ion-imaging technologies have contributed to even follow in real time how a chemical bond in a molecule breaks or is formed. For these achievements in reaction dynamics Ahmed Zewail was awarded the Nobel prize in 1999.

The book focuses on the basic definitions, theorems, and computational algorithms developed by nonlinear mechanics with examples from small polyatomic molecules. No mathematical rigor is claimed and by all means this is not another book on nonlinear mechanics. Emphasis is given to numerical methods which can be extended to many degrees of freedom systems, thus, assisting one to apply them to realistic molecular potentials. Most of molecular theories in chemistry consider molecules as *conserved Hamiltonian systems*, hence, we present the theory of nonlinear mechanics pertinent to this class of dynamical systems.

The book is organized along the following directions. After the introduction in Chap. 1, which also gives a historical overview of the field and its current status, Chap. 2 presents a brief introduction to Hamiltonian mechanics. An effort is made to present the theory from the analytical mechanics point of view, which unveils the geometrical characteristics of the theory, such as its symplectic symmetry. In Chap. 3 dynamical systems are introduced and the basic invariant structures, the main subject of nonlinear mechanics, are presented by numerically studying simple one-, two- and three-dimensional model potentials. Chapter 4 deals with quantum and semiclassical molecular mechanics. Algorithms and numerical methods for treating classical nonlinear and associated quantum mechanical equations of motion

[2] M. Born and J.R. Oppenheimer. On the Quantum Theory of Molecules. *Ann. Physik*, 84:457, 1927. Translated by S.M. Blinder, http://en.wikipedia.org/wiki/Born-Oppenheimer_approximation.

are discussed in Chap. 5 with emphasis to methods developed by us. Chapter 6 is devoted to applications, which demonstrate how the numerical codes serve to study real polyatomic molecules. Finally, in Chap. 7, some ideas of how progress in computer technology will affect the field of nonlinear molecular dynamics are put forward. An extended Appendix which describes basic mathematical concepts and theorems of modern mathematical analysis of manifolds supplements the book. The aim is not to apply mathematical rigor, but to exempt the reader from the need to look for definitions and explanations of these, admittedly, not very familiar to the chemists concepts. In the book terms referred to definitions, and when they appear for first time, are written with italic fonts, whereas those terms which are also illustrated in the Appendix are written by italic-bold letters.

The book is based on the author's years of research and the work of his Ph.D. students and collaborators around the world, in the field of nonlinear mechanics applied to molecular dynamics. Manolis Founargiotakis, Rita Prosmiti, and Stamatis Stamatiadis completed their Ph.D. theses by developing parts of the software and applying it to several molecules. The postdoctoral fellows Raul Guantes and Jaime Suarez contributed together with Stamatis Stamatiadis to the development of the variable order finite difference codes for discretizing the Schrödinger equation. George Contopoulos and the late Chronis Polymilis, astronomers from university of Athens, assisted to transfer knowledge on periodic orbits from the macroscopic world of galaxies to the microscopic world of molecules by studying two- and three-dimensional model potentials, common to both molecular and galactic dynamics. Reinhard Schinke from Max-Planck Institut für Dynamik and Selbstorganisation in Göttingen has been a collaborator for almost twenty years, steadily provided me with interesting molecules, which showed spectroscopic unidentified fingerprints implying unexpected dynamics. I believe, that most of them found an explanation by treating these molecules as nonlinear dynamical systems. Hua Guo from University of New Mexico has also been a provider of accurate potential energy surfaces and results from accurate quantum dynamics of molecules showing interesting experimental behaviours. Howard Taylor from the University of Southern California introduced me to the technology of classical autocorrelation functions, a powerful method for exploring the molecular phase space. Recently, Vladimir Tyuterev from University of Reims and then his student Frederic Mauguiére are two of the latest collaborators. Projects on investigating the isotopic mass effect in the spectroscopy of highly excited molecules, such as water, by periodic orbits were carried out. Vangelis Daskalakis and Constantine Varotsis from Cyprus University of Technology are the collaborators with whom the work on the active site of the enzyme cytochrome *c* oxidase by periodic orbits was materialized.

Last, but not least, I am grateful to Stephen Wiggins and Gregory Ezra for their encouragement and useful comments in structuring this brief book. My collaboration with them and Steve's postdoctoral fellows, Peter Collins and Frederic Mauguiére, for more than a year now, has helped me to enlighten many aspects of phase space geometry related to reaction dynamics. Our 'skype meeting', almost one every week, has become for me an exciting scientific event.

The literature in the field of nonlinear mechanics is really vast. Inevitably, the references to articles and books cited in this book are those which had the most influence to the author, or stating it better, with which the author came across. By no means papers and books not mentioned here are of limited significance for the field.

Iraklion, Crete, Greece, July 2014 Stavros C. Farantos

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