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Theory and computation of non-RRKM lifetime distributions and rates in chemical systems with three or more degrees of freedom

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Abstract

The computation, starting from basic principles, of chemical reaction rates in realistic systems (with three or more degrees of freedom) has been a longstanding goal of the chemistry community. Our current work, which merges tube dynamics with Monte Carlo methods provides some key theoretical and computational tools for achieving this goal. We use basic tools of dynamical systems theory, merging the ideas of Koon et al. [W.S. Koon, M.W. Lo, J.E. Marsden, S.D. Ross, Heteroclinic connections between periodic orbits and resonance transitions in celestial mechanics, Chaos 10 (2000) 427–469.] and De Leon et al. [N. De Leon, M.A. Mehta, R.Q. Topper, Cylindrical manifolds in phase space as mediators of chemical reaction dynamics and kinetics. I. Theory, J. Chem. Phys. 94 (1991) 8310–8328.], particularly the use of invariant manifold tubes that mediate the reaction, into a tool for the computation of lifetime distributions and rates of chemical reactions and scattering phenomena, even in systems that exhibit non-statistical behavior. Previously, the main problem with the application of tube dynamics has been with the computation of volumes in phase spaces of high dimension. The present work provides a starting point for overcoming this hurdle with some new ideas and implements them numerically. Specifically, an algorithm that uses tube dynamics to provide the initial bounding box for a Monte Carlo volume determination is used. The combination of a fine scale method for determining the phase space structure (invariant manifold theory) with statistical methods for volume computations (Monte Carlo) is the main contribution of this paper. The methodology is applied here to a three degree of freedom model problem and may be useful for higher degree of freedom systems as well.

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1. Introduction

Chemical reaction rates are usually computed using standard statistical methods, such as Rice-Ramsperger-Kassel-Marcus (RRKM) [12] theory, also known as *transition state theory* (TST) [43]. TST is based on the identification of a transition state (TS) between large *regions* of phase space that correspond to either "reactants" or "products." TST yields rates based on a local study of the TS as well as the assumption that the phase space in each region is structureless [31]. These values can be several orders of magnitude off of experimental values [4]. Despite its shortcomings, RRKM/TST has been a workhorse of the chemistry community for decades. However, it is now well known that while the structureless assumption is useful in many situations, in general these regions (often defined by potential wells) are not structureless [20].

De Leon et al. [5,6] attempted to extend the local picture near the TS in two degree of freedom (d.f.) systems to a more global one and developed reaction island theory using cylindrical manifolds [36] (now known as *tubes* [39]). Berry and collaborators (see for instance [17]) studied the local regular behavior near the saddle regions by means of Kolmogorov entropies. Marcus [29] suggested that these regularities were due to the existence of some invariants near the TS. Komatsuzaki and Berry [23–25] made further progress by using dynamical perturbative methods to study the transition near the saddle region. Uzer et al. [44], by using a general dynamical systems framework, studied the local geometric structures of rank-one saddles that regulate reactions in systems with three or more d.f. Recently, in Waalkens et al. [45], homoclinic and heteroclinic orbits in a tri-atomic molecule have been computed. But a comprehensive theory of chemical reactions and efficient computational tools for reaction rate calculations in three or more d.f. systems which takes into consideration phase space structures still needs to be developed, even for elementary reactions.

The current work, which merges tube dynamics with Monte Carlo methods, provides some enabling theoretical and computational tools needed for accurate rate calculations. In this paper, we present a methodology that uses basic tools of dynamical systems theory, merging the ideas of [26,15] and De Leon et al. (see, e.g., [5,6]). In particular, we use invariant manifold tubes mediating the dynamical process of reaction as the starting point for the computation of lifetime distributions and rates of chemical reactions and scattering phenomena. The standard RRKM assumption of an unstructured phase space fails to account for the dynamics of systems exhibiting significant non-statistical behavior. We overcome this difficulty by taking into consideration the homoclinic and heteroclinic intersection structure of tubes in the phase space. Furthermore, by working in the phase space as opposed to configuration space, we overcome the recrossing problem, i.e., the recrossing of the transition state as projected onto configuration space, which if uncorrected leads to inaccurate rate computations.

Previously, the main problem with the application of tube dynamics has been with the computation of volumes in phase spaces of high dimension [6,44]. The present work provides a starting point for overcoming this hurdle by using an algorithm that uses tube dynamics to provide the initial bounding box for a Monte Carlo volume determination. The main contribution of the paper is the combination of an accurate method for computing and understanding invariant manifolds in the problem and hence the phase space structure together with statistical Monte Carlo methods for volume computations.

We show the practical applicability of the methodology in a model three d.f. problem in which the hypotheses of TST do not hold: namely, the full-scattering of electrons in Rydberg atoms in the presence of external crossed electric and magnetic fields. We use a variety of methods and software that have been developed in the last several years for *tube dynamics* [21,26,15,39] to better understand the transport between different regions (or *realms*) of phase space. The numerical results obtained are a demonstration of accurate lifetime distribution and rate calculations which overcome the difficulties that have plagued the standard statistical methods.

The paper is organized as follows: in Section 2, we describe the global geometric structure of the phase space for reactions between two regions connected via a rank-one saddle point. We also introduce the methodology for the computation of scattering rates and lifetime distributions. The computational tool employed to produce these detailed structures is based on normal form techniques [14,13,21,22,9,10,15]. In Section 3, we apply the methodology of Section 2 to the scattering problem of Rydberg-type atoms in crossed electric