Studies of $He+HeH^+$ and $H_2+OH(CN)$ reactive scattering systems using multiconfiguration time-dependent Hartree approach

A thesis submitted by

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to

Indian Institute of Technology Guwahati

for the award of the degree of

Doctor of Philosophy

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November, 2011

SYNOPSIS

Studies of quantum reactive scattering systems using the time-dependent wave packet approach provides an opportunity to understand the underlying picture of the reaction dynamics. The objective of this work is to carry out a molecular level analysis of the reaction dynamics of three different systems: one tri-atomic ion-molecule system, the He + H^+He and two different tetra-atomic systems, the H_2 + OH and H_2 + CN. The quantum dynamics has been studied by propagating wave packets using the MCTDH algorithm. The importance of inclusion of Coriolis coupling on the reaction attributes for both the tri-atomic ion-molecule and the tetra-atomic reaction systems is investigated. This being the first quantum dynamical study for the reaction probabilities and cross sections on the He + H^+He system, standard wave packet propagation studies using the split operator methodology have also been performed for the same to estimate the accuracy of the MCTDH approach. The H_2 + OH system has been studied on three different potential energy surfaces with this being the first quantum dynamical study on the WSLFH surface. The aim of this comprehensive study is to determine the dependence of the reaction dynamics of the system on the surface characteristics and topology. The H_2 + CN system has been studied with the aim of determining the accuracy of the TSH3 potential energy surface and the exact nature of the C-N bond, which has an ambiguous spectator bond nature, unlike the O-H bond in the H_2 + OH reaction system.

Chapter 1 provides an introduction to the field of quantum reactive scattering.

Chapter 2 presents the MCTDH methodology and the derivation of the working equations. Various features of the MCTDH algorithm like mode combination and

the product representation of the Hamiltonian, which improve the performance of this method, have been discussed.

Chapter 3 discusses the Hamiltonian operator for the tri- and tetra-atomic molecules in the appropriate coordinate system. This is followed by a discussion on the preparation of initial wave packets for both tri- and tetra-atomic reaction systems and the formulation of the reaction cross sections and rate constants for the reaction systems.

Chapter 4 consists of the results derived from the study of the He + H^+He system. Both centrifugal sudden and coupled channel studies have been performed using the MCTDH methodology, while the studies performed using the split operator method have been carried out under centrifugal sudden approximation. The centrifugal sudden results obtained from both the MCTDH and the split-operator methodologies have been compared to establish the accuracy of the calculations. The coupled channel results show a distinct difference from the centrifugal sudden results. The observed differences for this system have been analyzed and explained in this study. The importance of inclusion of Coriolis coupling for the reaction in its ro-vibrational excited states have been determined. The importance of the initial orientation of the reagents and the presence of preferred pathways of approach in the reaction dynamics of this system has been discussed.

Chapter 5 presents the dynamics of the H_2 + OH reaction on three different potential energy surfaces. The MCTDH reaction probabilities and cross sections on the WDSE and YZCL2 surfaces are compared with the literature results to determine the accuracy of the MCTDH algorithm in studying the tetra-atomic reactive systems. The quantum dynamical reaction probabilities and cross sections

on the WSLFH surface are reported for the first time. The significant differences observed in the cross sections on the different surfaces have been analyzed on the basis of differences in the surface characteristics and the transition state structure on the three surfaces. Vibrationally excited cross sections on the YZCL2 surface are reported for the first time, while previous studies on the WSLFH surface have involved quasi-classical trajectory studies. The study of the reaction cross sections and rate constants for the ro-vibrational excited states of the diatoms reveals a significant dependence of the reaction attributes on the properties of the surfaces considered, along with the pathways of approach and the initial orientation of the reactants.

Chapter 6 reports the results of the application of the MCTDH algorithm to study the H_2 + CN reaction. Reaction probabilities and cross sections are obtained for the ground and vibrational excited states of H_2 and CN. The effect of using an exact form of the Hamiltonian on the reaction dynamics has been analyzed. The exact nature of the CN bond in the reactive system has been ambiguous till date. This study aims to determine the validity of labelling the CN bond as a spectator bond. The accuracy of the TSH3 potential energy surface, on which the reaction dynamics is studied, has also been investigated.

Chapter 7 presents a summary of the work done along with the conclusions derived from our studies on the different systems.