

EÖTVÖS LORÁND UNIVERSITY, BUDAPEST, HUNGARY

STUDENTS' SCIENTIFIC ASSOCIATION PAPER

Quantum mechanical calculation of reaction rate coefficients

Author:

Gábor A. Ecseri

Supervisors:

Dr. Attila G. Császár

Dr. Csaba Fábri

Laboratory of Molecular Structure and Dynamics
Institute of Chemistry

January 8, 2025



SUPPORTED BY THE EKÖP-24 UNIVERSITY EXCELLENCE SCHOLARSHIP PROGRAM
OF THE MINISTRY FOR CULTURE AND INNOVATION FROM THE SOURCE OF THE
NATIONAL RESEARCH, DEVELOPMENT AND INNOVATION FUND.

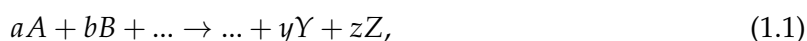
Contents

1	Introduction	1
2	Theory	3
2.1	The flux	3
2.2	Reaction rate coefficient in terms of the flux	4
2.3	Correlation functions	6
2.4	Evaluation of the trace	8
2.5	Summary of the working formulas and a related computational algorithm	9
3	Computational implementation	10
3.1	GENIUSH	10
3.1.1	On the discrete variable representation (DVR)	10
3.1.2	Podolsky form of the kinetic energy operator	11
3.2	Representation of the flux operator	13
3.3	Time propagation	13
3.4	Diagonalizing the thermal flux	15
3.5	Integration of the flux autocorrelation function	15
4	Results of model calculations	16
4.1	One-dimensional Eckart potential	16
4.1.1	Basis set size convergence	23
4.1.2	Effect of position of the dividing point	24
4.2	Collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$	25
5	The $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction	29
6	Summary, conclusions, and outlook	34
	Bibliography	36

Chapter 1

Introduction

Chemical reactions with known stoichiometry are usually described by the following chemical reaction equation:



where the capital letters refer to reaction partners (reactants and products on the left- and right-hand sides of Eq. (1.1), respectively) and $a, b, \dots$ are the so-called stoichiometric coefficients. Most important for the present study are the uni- and bimolecular elementary chemical reactions. The microscopic view of a bimolecular reaction in the gas phase is



where k is the so-called *reaction rate coefficient*. This reaction means that the reactants A and B approach each other, governed by an interaction potential, then they collide, and some of the collisions, the so-called reactive ones, will lead to rearrangement of the nuclei, yielding products Y and Z [1–5]. As in most fields of science, several models can be developed to improve our understanding of chemical reactions and determine their rates. In the present case of unimolecular and binary chemical reactions, these models help, in particular, to understand and predict the rate of chemical reactions and thus the reaction rate coefficients.

The simplest theories of macroscopic kinetics, which may still be very successful in explaining experimental observations, do not directly utilize the machinery of quantum mechanics. In other words, reaction rates and rate coefficients can be introduced phenomenologically, leading to formal reaction kinetics [3]. At the other end of the scale, the most sophisticated, microscopic models of chemical kinetics build upon the solutions of two fundamental equations of quantum chemistry, the time-independent and the time-dependent Schrödinger equations [6]. Solving the time-independent Schrödinger equations leads, in a straightforward way, to a detailed understanding of most spectroscopic phenomena. While this is the usual approach, there are also time-dependent approaches to rovibronic spectroscopy. It is usual to assume that dynamical events in chemistry, like non-reactive and reactive scattering, should be understood by solving the time-dependent Schrödinger equation. However, dynamical events, like chemical reactions, can also be related to fundamental quantities, like reaction probabilities and reactive fluxes; thus, it is perfectly feasible to start the determination of reaction rates from the solution of the time-independent Schrödinger equation, like it is done in the present study. In between these two, fully classical and fully quantum, approaches there are the many variants of semiclassical theories [7, 8].

Although classical and semiclassical theories yield sufficiently accurate reaction rate coefficients for certain reactions at sufficiently high temperatures, they break down at low temperatures or when light atoms are involved, as quantum effects become more significant under these conditions. Thus, it is important to develop efficient, fully quantum-mechanical methods for the computation of the rate coefficients, which can be used when the classical and semiclassical methods cannot provide accurate reaction rate coefficients.

The traditional approach to the quantum-mechanical computation of reaction rate coefficients involves time propagation of each quantum state of the reactants, and the calculation of the so-called scattering matrix corresponding to the reaction, and then taking the Boltzmann-weighted average of the elements of the scattering matrix, in order to determine the canonical rate coefficient. The scattering matrix contains very detailed information about the reaction; namely, the squared absolute value of its elements are the state-to-state reaction probabilities. However, if only the reaction rate coefficient is needed, not the detailed state-to-state information, the approach of calculating the scattering matrix and averaging out all the detailed information seems inefficient. In 1983, Miller, Schwartz, and Tromp [9] derived the basics of a new method, with which reaction rate coefficients can be computed directly, without the need of calculating any state-to-state data. In this method, the reaction rate coefficient is given as the time integral of the so-called flux autocorrelation function. During my work I developed a code with which the flux autocorrelation function can be evaluated, leading to temperature-dependent reaction rate constants.

The principal goal of my research was the implementation of the formulation of Miller and co-workers for the determination of reaction rate coefficients in a completely general environment, so that these coefficients could be computed for arbitrary bimolecular reactions. Following a brief introduction of the topic in this chapter, Chapter 2 presents the theoretical background of the computation of reaction rate coefficients based on flux autocorrelation functions. Chapter 3 covers the technical details of the computational implementation of the formulas derived in Chapter 2. Chapter 4 contains results of computations of reaction rate coefficients for two simple model systems, the one-dimensional Eckart potential, and the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction. Chapter 5 focuses on the $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction in full vibrational dimensionality. Finally, in Chapter 6, I summarize the main results and provide a brief outlook on my future plans.

Chapter 2

Theory

2.1 The flux

In order to understand the rate of chemical reactions within the models of quantum chemistry, we aim to derive a formula for the flux which fulfills the quantum-mechanical continuity (or transport) equation [10]

$$\nabla \cdot \mathbf{j}(\mathbf{q}, t) = -\frac{\partial \rho(\mathbf{q}, t)}{\partial t}, \quad (2.1)$$

where $\rho(\mathbf{q}, t) = |\psi(\mathbf{q}, t)|^2$ is the probability density, $\psi(\mathbf{q}, t)$ is the wave function of the system, and $\mathbf{j}(\mathbf{q}, t)$ denotes the flux density. Now, let us take the volume integral of Eq. (2.1) for a given volume B ,

$$\int_S \mathbf{j}(\mathbf{q}, t) \cdot \mathbf{n} dA = F = -\frac{d}{dt} \int_B \rho(\mathbf{q}, t) dV, \quad (2.2)$$

where the divergence theorem was used on the left-hand side of the equation, and the flux F through the surface S enclosing volume B was introduced. Furthermore, dV and dA are the infinitesimal volume and surface elements used in the integration, while $\mathbf{n}$ is a vector normal to the dA surface element, pointing outwards from the surface S . The vector $\mathbf{n}$ can be given in terms of a monotonous and continuous function, $s(\mathbf{q})$, as $\mathbf{n} = \nabla s(\mathbf{q}) / \|\nabla s(\mathbf{q})\|$, where $s(\mathbf{q})$ is negative within the surface S , positive outside, and zero at the boundary. Thus, the form of $s(\mathbf{q})$ defines the surface S . Next, let us rewrite the right-hand side of Eq. (2.2) by using the Heisenberg time derivative of operators,

$$F = -\frac{d}{dt} \int \psi^*(\mathbf{q}, t) \theta(-s(\mathbf{q})) \psi(\mathbf{q}, t) dV = -i/\hbar \int \psi^*(\mathbf{q}, t) [\hat{H}, \theta(-s(\mathbf{q}))] \psi(\mathbf{q}, t) dV \quad (2.3)$$

where i is the imaginary unit, $\hat{H}$ denotes the Hamiltonian and $\theta(x)$ is the Heaviside step function, defined as

$$\theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geq 0 \end{cases}.$$

With the help of the Heaviside function, the integration can be extended to the whole space in Eq. (2.3). After realizing that $\theta(-s(\mathbf{q})) = 1 - \theta(s(\mathbf{q}))$, we get

$$F = i/\hbar \int \psi^*(\mathbf{q}, t) [\hat{H}, \theta(s(\mathbf{q}))] \psi(\mathbf{q}, t) dV, \quad (2.4)$$

which leads to the definition of the flux operator,

$$\hat{F} = i/\hbar [\hat{H}, \theta(s(\mathbf{q}))]. \quad (2.5)$$

Since we are interested in reactive chemical systems, the $s(\mathbf{q}) = 0$ surface separates the reactant and product configurations. Then it is called the *dividing surface*. Based on the derivation of

Eqs. (2.1)–(2.4), the dividing surface, in principle, should be closed. However, in our practical applications we will use open surfaces, as these can be considered closed somewhere, at some point at infinity, where the flux is zero anyway.

In 1988, Park and Light [11] pointed out a few interesting properties of the flux operator. First, the eigenvalues of the flux operator come in $\pm$ pairs and the corresponding eigenvectors are complex conjugates of each other. Park and Light explained this observation by using the fact that the flux operator is imaginary and the relation $\hat{F}^* = -\hat{F}$ holds. Park and Light also discovered a second property, which they could not prove at the time, namely that the one-dimensional flux operator has only two nonzero eigenvalues, which diverge to infinity and minus infinity as the basis set is extended. A highly similar rule holds for the multidimensional flux operator as well: only few eigenvalue pairs are nonzero, while the rest are close enough to zero, so that they can be safely neglected. As we will see later, this property has considerable importance as it can be utilized during the calculation of the thermal reaction rate coefficient, $k(T)$. Proper proofs of these properties were given by Seideman and Miller [12], but only for the matrix representation of the 1D flux using a real basis. For the 1D flux operator the proof was given by Park in 1997 in a one-page-long paper, without the use of any basis set [13].

2.2 Reaction rate coefficient in terms of the flux

The rate coefficient of a bimolecular reaction based on quantum scattering theory can be written [5] as

$$k(T) = (2\pi\hbar Q_r(T))^{-1} \sum_J (2J+1) \sum_{n_r, n_p} \int_{E_{n_r}}^{\infty} e^{-\beta E} |S_{n_p, n_r}^J(E)|^2 dE, \quad (2.6)$$

where n_p and n_r are the indices of the rovibrational states of the products and the reactants, respectively, J is the rotational quantum number, E is the total energy of the system (containing the translational energy the relative motion of the two reacting molecules), E_{n_r} is the energy of the system without the translation between the reactants, $S_{n_p, n_r}^J(E)$ is the so-called scattering matrix [1], and Q_r is the reactant partition function per unit volume. $|S_{n_p, n_r}^J(E)|^2$ gives the probability of the reaction between the states specified in the subscript and with the energy E .

It can be shown [14] that the expectation value of the flux over the so-called stationary scattering states (originating from the reactant configuration, $\langle \phi_{n_r}^J(E) |$) gives

$$\langle \phi_{n_r}^J(E) | \hat{F} | \phi_{n_r}^J(E) \rangle = \sqrt{2\mu_{AB}(E - E_{n_r})} / (2\pi\hbar\mu_{AB}) \sum_{n_p} |S_{n_r, n_p}^J(E)|^2, \quad (2.7)$$

where $\mu_{AB} = m_A m_B / (m_A + m_B)$ is the reduced mass corresponding to the reactants. Moreover, m_A and m_B are the mass of the reactant molecules A and B , respectively. As we have seen in the previous chapter, the flux is defined through a specific dividing surface. Equation (2.7) holds for any dividing surface, which separates the reactant and product configurations of the system. This implies that the dividing surface does not have to include, for instance, the transition state of the PES. Using Eq. (2.7) the reaction rate coefficient can be expressed in terms of the flux as

$$k(T) = \frac{\mu_{AB}}{Q_r(T)} \sum_J (2J+1) \sum_{n_r} \int_{E_{n_r}}^{\infty} \frac{1}{\sqrt{2\mu_{AB}(E - E_{n_r})}} e^{-\beta E} \langle \phi_{n_r}^J(E) | \hat{F} | \phi_{n_r}^J(E) \rangle dE \quad (2.8)$$

$$= \frac{\mu_{AB}}{Q_r(T)} \sum_J (2J+1) \sum_{n_r} \int_{E_{n_r}}^{\infty} \frac{1}{\sqrt{2\mu_{AB}(E - E_{n_r})}} \langle \phi_{n_r}^J(E) | e^{-\beta \hat{H}} \hat{F} | \phi_{n_r}^J(E) \rangle dE, \quad (2.9)$$

where the relation $\hat{H}|\phi_{n_r}^I(E)\rangle = E|\phi_{n_r}^I(E)\rangle$ is used. Now, let us change the integration variable to p , *i.e.*, the initial momentum corresponding to the translation between the reactants. Then,

$$E = p^2/(2\mu_{AB}) + E_{n_r},$$

and

$$dE = p/\mu_{AB} dp.$$

As a result, Eq. (2.9) becomes much simpler,

$$k(T) = Q_r(T)^{-1} \sum_J (2J+1) \sum_{n_r} \int_0^\infty \langle \phi_{n_r}^I(p) | e^{-\beta \hat{H}} \hat{F} | \phi_{n_r}^I(p) \rangle dp. \quad (2.10)$$

One can identify the quantum mechanical trace in Eq. (2.10); however, it is not complete, as the integral goes from zero instead of $-\infty$. To correct for this, let us introduce a projector $\hat{\mathcal{P}}$, which projects onto the states where p is positive:

$$\hat{\mathcal{P}} = \sum_J (2J+1) \sum_{n_r} \int_0^\infty |\phi_{n_r}^I(p)\rangle \langle \phi_{n_r}^I(p)| dp. \quad (2.11)$$

Using $\hat{\mathcal{P}}$, we can extend the integration limits and identify the trace, arriving at

$$k(T) = Q_r(T)^{-1} \text{Tr}[e^{-\beta \hat{H}} \hat{F} \hat{\mathcal{P}}]. \quad (2.12)$$

Note that up to this point we have used the stationary scattering states as a basis; however, now the trace can be evaluated in any complete basis. Of course, in all practical applications we will use a truncated basis set.

Next, let us derive a more useful formula for the projector $\hat{\mathcal{P}}$, which does not contain the stationary scattering states. To that end, we use the so-called unperturbed scattering states $|\Psi_{n_r}^I(p)\rangle$. These states are the eigenvectors of the reactant Hamiltonian, $\hat{H}_0$, in which the interaction terms between the reactants are not included. The eigenvalue of $\hat{H}_0$ is, of course, the same total energy $E = p^2/(2\mu_{AB}) + E_{n_r}$. If we propagate the unperturbed scattering states to $t \rightarrow \infty$ by the reactant Hamiltonian, and propagate back *via* the full Hamiltonian, $\hat{H}$, we get the stationary scattering states,

$$|\phi_{n_r}^I(p)\rangle = \lim_{t \rightarrow \infty} e^{i\hat{H}t/\hbar} e^{-i\hat{H}_0t/\hbar} |\Psi_{n_r}^I(p)\rangle. \quad (2.13)$$

With this, $\hat{\mathcal{P}}$ becomes

$$\hat{\mathcal{P}} = \lim_{t \rightarrow \infty} e^{i\hat{H}t/\hbar} e^{-i\hat{H}_0t/\hbar} \underbrace{\sum_J (2J+1) \sum_{n_r} \int_0^\infty |\Psi_{n_r}^I(p)\rangle \langle \Psi_{n_r}^I(p)| dp}_{\hat{\mathcal{P}}_0} e^{i\hat{H}_0t/\hbar} e^{-i\hat{H}t/\hbar}, \quad (2.14)$$

where $\hat{\mathcal{P}}_0$ can be further simplified with some straightforward manipulations,

$$\begin{aligned} \hat{\mathcal{P}}_0 &= \sum_J (2J+1) \sum_{n_r} \int_0^\infty |\Psi_{n_r}^I(p)\rangle \langle \Psi_{n_r}^I(p)| dp \\ &= \sum_J (2J+1) \sum_{n_r} \int_{-\infty}^\infty \theta(p) |\Psi_{n_r}^I(p)\rangle \langle \Psi_{n_r}^I(p)| dp \\ &= \sum_J (2J+1) \sum_{n_r} \int_{-\infty}^\infty \theta(\hat{p}) |\Psi_{n_r}^I(p)\rangle \langle \Psi_{n_r}^I(p)| dp \\ \hat{\mathcal{P}}_0 &= \theta(\hat{p}). \end{aligned} \quad (2.15)$$

In Eq. (2.15), $\hat{p}$ is the momentum operator corresponding to the translational motion between the reactants, and we utilized the fact that $\hat{p}|\Psi_{n_r}^J(p)\rangle = p|\Psi_{n_r}^J(p)\rangle$, which follows from the observation that $\hat{p}$ commutes with $\hat{H}_0$. In the last step of the derivation, the resolution of identity was recognized.

Thanks to the fact that $\hat{p}$ commutes with $\hat{H}_0$, $\hat{\mathcal{P}}$ simplifies, as well,

$$\hat{\mathcal{P}} = \lim_{t \rightarrow \infty} e^{i\hat{H}t/\hbar} \theta(\hat{p}) e^{-i\hat{H}t/\hbar}. \quad (2.16)$$

This is the point where Miller [14] arrived in 1974, exactly half a century ago.

2.3 Correlation functions

In 1983, Miller, Schwartz, and Tromp (MST) derived different formulas for $k(T)$ in terms of different correlation functions [9]. To get these formulas, first the Boltzmann operator is split around the flux, using the facts that (a) the Boltzmann operator and the projector $\hat{\mathcal{P}}$ commute, since $\hat{\mathcal{P}}$ was originally defined in terms of the eigenvectors of $\hat{H}$, and (b) the cyclic permutation of operators within the trace is an equivalent transformation. Then,

$$k(T) = Q_r(T)^{-1} \text{Tr}[e^{-(\beta-\lambda)\hat{H}} \hat{F} e^{-\lambda\hat{H}} \hat{\mathcal{P}}] \quad (2.17)$$

where $0 \leq \lambda \leq \beta$. Note that this is only true if the infinite time limit is taken within $\hat{\mathcal{P}}$, for finite values of t it does not hold.

Next, it can be shown that the form of $\hat{\mathcal{P}}$ in Eq. (2.16) is equivalent to

$$\hat{\mathcal{P}} = \lim_{t \rightarrow \infty} e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar}. \quad (2.18)$$

The dividing surface used in Eq. (2.18), $s(\mathbf{q})$, is not necessarily exactly the same as the one used in the flux in Eq. (2.7), since the exact location of the dividing surface does not matter. However, the two dividing surfaces, the one in Eq. (2.18) and the one in Eq. (2.7), should define the same reactants and products. Nevertheless, in this work I have used the same expression for these two dividing surfaces, and I will not differentiate them in the notation either in the following.

Following the formalism of Miller, the reaction rate coefficient can be written in the form

$$\begin{aligned} k(T) &= Q_r^{-1} \lim_{t \rightarrow \infty} \text{Tr}[e^{-(\beta-\lambda)\hat{H}} \hat{F} e^{-\lambda\hat{H}} e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar}] \\ &= Q_r^{-1} \lim_{t \rightarrow \infty} C_{\text{fs}}(t). \end{aligned} \quad (2.19)$$

The term $C_{\text{fs}}(t)$ is the flux-side correlation function. If we set λ to 0,

$$C_{\text{fs}}(t) = \text{Tr}[e^{-\beta\hat{H}} \hat{F} \theta(s(\mathbf{q}), t)], \quad (2.20)$$

$\theta(s(\mathbf{q}), t) = e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar}$. In other words, $C_{\text{fs}}(t)$ is nothing else but the Boltzmann-weighted average of the expectation value of $\hat{F}(t=0) \theta(s(\mathbf{q}), t)$, that is, a correlation function defined similarly to those in statistical mechanics.

To move on, let us set $\lambda = \beta/2$ and investigate the trace in Eq. (2.19). The trace can be written in the form $\text{Tr}[\hat{A}\hat{B}]$, where $\hat{A} = e^{-\beta/2\hat{H}} \hat{F} e^{-\beta/2\hat{H}}$ and $\hat{B} = e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar}$, both are Hermitian. Then, $\text{Tr}[\hat{A}\hat{B}]^* = \text{Tr}[(\hat{A}\hat{B})^\dagger] = \text{Tr}[\hat{B}\hat{A}] = \text{Tr}[\hat{A}\hat{B}]$; thus, the trace is real valued. At the same time, the trace should be imaginary valued at $t = 0$, since the flux contains the imaginary unit explicitly, while the other operators, $e^{-\beta/2\hat{H}}$ and $\theta(s(\mathbf{q}))$ are real. These two statements can

only be true if the trace equals zero at $t = 0$. Thus, we perform the following transformations,

$$\begin{aligned}
 k(T) &= Q_r^{-1} \text{Tr}[e^{-\beta/2\hat{H}} \hat{F} e^{-\beta/2\hat{H}} e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar}] \Big|_{t=0}^{t \rightarrow \infty} \\
 &= Q_r^{-1} \int_0^\infty \frac{d}{dt} \text{Tr}[e^{-\beta/2\hat{H}} \hat{F} e^{-\beta/2\hat{H}} e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar}] dt \\
 &= Q_r^{-1} \int_0^\infty \text{Tr}[e^{-\beta/2\hat{H}} \hat{F} e^{-\beta/2\hat{H}} \underbrace{\frac{d}{dt} (e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar})}_{e^{i\hat{H}t/\hbar} \mathbf{i} / \hbar [\hat{H}, \theta(s(\mathbf{q}))] e^{-i\hat{H}t/\hbar}}] dt \\
 &= Q_r^{-1} \int_0^\infty \text{Tr}[e^{-\beta/2\hat{H}} \hat{F} e^{-\beta/2\hat{H}} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar}] dt \\
 k(T) &= Q_r^{-1} \int_0^\infty C_f(t) dt, \tag{2.21}
 \end{aligned}$$

where the flux autocorrelation function was introduced. Again, just like with $C_{fs}(t)$, $C_f(t)$ is truly a correlation function as it is the Boltzmann-weighted average of $\hat{F}(t=0)\hat{F}(t)$. One final correlation function can be derived with similar manipulations. Starting from Eq. (2.19), with a cyclic permutation of the operators, we can get

$$\begin{aligned}
 k(T) &= Q_r^{-1} \lim_{t \rightarrow \infty} \text{Tr}[e^{-\beta/2\hat{H}} \underbrace{e^{-i\hat{H}t/\hbar} \hat{F} e^{i\hat{H}t/\hbar}}_{d/dt(e^{-i\hat{H}t/\hbar} \theta(-s(\mathbf{q})) e^{i\hat{H}t/\hbar})} e^{-\beta/2\hat{H}} \theta(s(\mathbf{q}))] \\
 &= Q_r^{-1} \lim_{t \rightarrow \infty} \frac{d}{dt} \text{Tr}[e^{-\beta/2\hat{H}} \theta(-s(\mathbf{q})) e^{-\beta/2\hat{H}} e^{i\hat{H}t/\hbar} \theta(s(\mathbf{q})) e^{-i\hat{H}t/\hbar}] \\
 &= Q_r^{-1} \lim_{t \rightarrow \infty} \frac{d}{dt} C_s(t), \tag{2.22}
 \end{aligned}$$

where $C_s(t)$ is the so-called side-side correlation function. From one correlation function one can obtain the others through derivation/integration, since

$$C_f(t) = \frac{d}{dt} C_{fs}(t) = \frac{d^2}{dt^2} C_s(t). \tag{2.23}$$

These correlation functions were derived first by Miller, Schwartz, and Tromp [9]. However, Yamamoto [15] also derived a flux autocorrelation function using linear response theory,

$$C_f^{\text{Kubo}}(t) = 1/\beta \int_0^\beta \text{Tr}[e^{-(\beta-\lambda)\hat{H}} \hat{F} e^{-\lambda\hat{H}} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar}] d\lambda. \tag{2.24}$$

This Kubo-type correlation function differs from the one which is derived by Miller, Schwartz, and Tromp. However, they give the same rate coefficient [9].

Following this idea, the definition of the correlation functions can be generalized [16, 17]. In the case of the flux autocorrelation function, the generalized expression is

$$C_f(t) = \int_0^\beta \text{Tr}[e^{-(\beta-\lambda)\hat{H}} \hat{F} e^{-\lambda\hat{H}} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar}] d\nu(\lambda), \tag{2.25}$$

where $d\nu(\lambda)$ should be chosen such that $\int_0^\beta d\nu(\lambda) = 1$. With $d\nu(\lambda) = \delta(\lambda - \beta/2) d\lambda$, we can get back the MST correlation function, and if we choose $d\nu(\lambda) = 1/\beta d\lambda$, we get the Kubo-type form.

To summarize, we obtained three correlation functions, $C_f(t)$, $C_{fs}(t)$, and $C_s(t)$, with which the reaction rate coefficients can be determined *via* calculating an integral, a time limit, and a derivative along with a time limit, respectively. Each correlation function has a different form,

depending on the choice of $d\nu(\lambda)$. Thus, one has several options to calculate reaction rate coefficients. All of these forms should provide the same answer; however, their numerical behavior can be significantly different. For example, for simple systems, like a free particle or a parabolic barrier in one dimension, the flux autocorrelation function can be evaluated analytically [9, 18]. Interestingly, in the case of a free particle, the flux autocorrelation function of Yamamoto becomes singular as $t \rightarrow 0$, while the MST correlation function does not. Of course, the integral of the Yamamoto flux autocorrelation function still exists; however, during a numerical computation, the calculation of the integral of a singular function is not straightforward.

At this point the question arises which correlation function is the best to use. Generally, it can be stated that the calculation of the integral of a function ($C_f(t)$ in this particular case) is numerically more stable than the evaluation of the value of a function ($C_{fs}(t)$) at a large enough t . This is why in most applications the flux correlation function has been used, apart from a few exceptions, where the flux-side correlation function was employed [19]. Regarding the choice of $d\nu(\lambda)$, Small, Predescu, and Miller [17] showed that the MST flux correlation function is the best in terms of minimizing the so-called recrossing flux. In the present work, I utilized the MST form of the flux autocorrelation function. Now that this choice was made, the task is the evaluation of the flux autocorrelation function in the following form,

$$C_f(t) = \text{Tr}[e^{-\beta/2\hat{H}}\hat{F}e^{-\beta/2\hat{H}}e^{i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}]. \quad (2.26)$$

2.4 Evaluation of the trace

As a next step towards a numerical application, one should choose an efficient basis which can be used to evaluate the trace. In the earliest applications found in the literature [9, 20–22], eigenvectors of the Hamiltonian were used. In this case, the time integral of Eq. (2.21) can be evaluated analytically, and can be given in the form

$$k(T) = \lim_{t \rightarrow \infty} Q_r^{-1} \sum_{i,j} e^{-\beta(E_i+E_j)/2} \frac{\sin((E_i - E_j)t/\hbar)}{E_i - E_j} |\langle i|\hat{F}|j\rangle|^2, \quad (2.27)$$

where E_i and $|i\rangle$ are the eigenvalues and eigenfunctions of the Hamiltonian. The time limit is taken, of course, *via* choosing a large enough value for t ; however, it should be sufficiently small so that the time evolution is accurate in the chosen basis. Luckily, to get a converged reaction rate it is sufficient to consider only around 100 eigenpairs of the Hamiltonian [21].

A much more efficient trace evaluation method was proposed by Park and Light [11], which was further developed by Miller, Manthe, and their co-workers [23–26]. This approach introduces the so-called ‘thermal’ or ‘Boltzmannized’ flux,

$$\hat{F}(\beta) = e^{-\beta/2\hat{H}}\hat{F}e^{-\beta/2\hat{H}}. \quad (2.28)$$

If we evaluate the trace in the eigenbasis of $\hat{F}(\beta)$, we get the following form for $C_f(t)$,

$$C_f(t) = \sum_i f_i \langle \phi_i(t) | \hat{F} | \phi_i(t) \rangle, \quad (2.29)$$

where $\hat{F}(\beta)|\phi_i\rangle = f_i|\phi_i\rangle$ and $|\phi_i(t)\rangle = e^{-i\hat{H}t/\hbar}|\phi_i\rangle$. Thus, it is sufficient to include in the sum eigenpairs having the highest eigenvalues in magnitude. This is what makes this kind of evaluation of the trace so efficient as the thermal flux has only few nonzero eigenvalues, similarly to the flux. The thermal flux is also an imaginary Hermitian operator. This property implies that the eigenvalues of $\hat{F}(\beta)$ come in $\pm$ pairs, with the corresponding eigenvectors being complex conjugates of each other.

2.5 Summary of the working formulas and a related computational algorithm

In what follows, I am going to summarize the most important formulas used in the present study. Based on them, a feasible algorithm is defined for the quantum-mechanical computation of reaction rate coefficients.

First, the reaction rate coefficient is expressed as the integral of the flux autocorrelation function,

$$k(T) = Q_r^{-1} \int_0^\infty C_f(t) dt,$$

where Q_r is the reactant partition function per unit volume

Second, the flux autocorrelation function can be written in the form

$$C_f(t) = \text{Tr}[e^{-\beta/2\hat{H}} \hat{F} e^{-\beta/2\hat{H}} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar}] = \text{Tr}[\hat{F}(\beta) e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar}],$$

where the thermal flux, $\hat{F}(\beta)$, is also introduced.

Third, the trace can be evaluated in the eigenbasis of the thermal flux, $\hat{F}(\beta)|\phi_i\rangle = f_i|\phi_i\rangle$,

$$C_f(t) = \sum_i f_i \langle \phi_i(t) | \hat{F} | \phi_i(t) \rangle,$$

where $|\phi_i(t)\rangle = e^{-i\hat{H}t/\hbar} |\phi_i\rangle$.

Based on these working formulas, the steps proposed for the computation of reaction rate coefficients are as follows:

1. **Diagonalization of the thermal flux.** It is sufficient to obtain the eigenvalues highest in magnitude and the corresponding eigenvectors.
2. **Time propagation of the thermal flux eigenvectors.** Any standard time propagation technique can be used.
3. **Evaluation of the flux autocorrelation function.**
4. **Numerical integration of the flux autocorrelation function.**
5. **Division of the integral of the flux autocorrelation function by the reactant partition function.** Calculations based on simple model Hamiltonians, like the harmonic-oscillator and rigid-rotor Hamiltonians, may be sufficiently accurate for the computation of the reactant partition function.

The most time-consuming step from the above list is typically the time propagation.

Chapter 3

Computational implementation

This chapter presents an array of numerical methods used during this work and the codes based on them. One of the existing codes I utilized is called GENIUSH [27, 28], in reference to its main characteristics: general (GE) rovibrational code with numerical (N), internal-coordinate (I), user-specified (US) Hamiltonians (H). The codes I developed and interfaced to GENIUSH allow representation of the flux operator, time propagation, diagonalization of the thermal flux, and integration of the flux autocorrelation function.

3.1 GENIUSH

The set of codes GENIUSH [27, 28] is permanently under development within our research group [29–32]. GENIUSH is a general, black-box-type, completely numerical quantum-chemical code, which can accommodate any set of internal coordinates, any embedding of the molecular (body-fixed) axes, and arbitrary, reduced- or full-dimensional molecular models. Thus, it provides an ideal starting point for the development of a general code to be used for the computation of reaction rate coefficients.

The original GENIUSH code was designed to solve the time-independent nuclear Schrödinger equation in a (quasi-)variational fashion. The most time-consuming step of a GENIUSH computation is the determination of a given set of eigenstates of the rovibrational Hamiltonian set up in internal coordinates. The determination of reaction rate coefficients does not need the eigenpairs of the rovibrational Hamiltonian, but it needs the thermal flux. The same representation of the Hamiltonian can be employed for the representation of the thermal flux. In this section I summarize the most important aspects of this representation.

3.1.1 On the discrete variable representation (DVR)

Regarding the basis sets used during GENIUSH computations, they are of the so-called DVR type [33, 34] (DVR stands for ‘discrete variable representation’). In what follows, I will introduce briefly the concept of the standard DVR bases, highlighting their most important and most relevant features.

Let us consider a basis $\{\phi_i(x)\}$ applicable for a variational solution of the nuclear Schrödinger equation, with which the matrix elements of the position operator, $\hat{x}$, and of the differential operators, $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$, are known analytically. For the sake of simplicity, I will write the formulas in only one dimension:

$$Q_{ij} = \int \phi_i^*(x) x \phi_j(x) dx, \quad (3.1)$$

$$D_{ij}^{(1)} = \int \phi_i^*(x) \frac{d}{dx} \phi_j(x) dx, \quad (3.2)$$

$$D_{ij}^{(2)} = \int \phi_i^*(x) \frac{d^2}{dx^2} \phi_j(x) dx. \quad (3.3)$$

Here, the limits of integration, not shown explicitly in the equations above, are chosen according to the domain of the coordinate x . Thus, the kinetic energy matrix of the system can be constructed straightforwardly in an analytic form (if the coordinates are chosen appropriately). The elements of the potential energy matrix,

$$V_{ij}^{\text{VBR}} = \int \phi_i^*(x) V(x) \phi_j(x) dx, \quad (3.4)$$

can be calculated numerically. If the basis set is complete, this representation is called the variational basis-set representation (VBR). In practical applications, the basis set probably needs to be truncated; nevertheless, the calculated eigenvalues are still upper bounds to the exact ones, due to the variational principle. The bottleneck of the VBR approach is the calculation of the elements of the potential energy matrix. Thus, one should seek an approximation to it.

Considering the potential energy operator as a function of the position operator, $\hat{V} = V(\hat{x})$, we may propose a different matrix representation, whereby the matrix representation of the potential energy is obtained as a function of the matrix representation of the coordinate operator, $\mathbf{Q}$. Then,

$$\mathbf{V}^{\text{FBR}} = V(\mathbf{Q}). \quad (3.5)$$

This representation is exact if the basis is complete, that is $\mathbf{V}^{\text{FBR}} = \mathbf{V}^{\text{VBR}}$. However, if a truncation is applied, equivalence of the two representations will no longer be true. This is the reason why we retain the superscript FBR, meaning finite basis-set representation. Since the FBR representation introduces an additional error, the variational behavior is lost. The most straightforward way of evaluating $\mathbf{V}_{ij}^{\text{FBR}}$ is to first diagonalize the position matrix, $\mathbf{QU} = \mathbf{XU}$, where $\mathbf{X}$ is a diagonal matrix containing the eigenvalues (x_i , called grid points) and $\mathbf{U}$ is a unitary eigenvector matrix. Then the original VBR/FBR basis set can be transformed unitarily by $\mathbf{U}$,

$$\chi_i(x) = \sum_j \phi_j(x) U_{ji}. \quad (3.6)$$

This new basis is the so-called DVR basis. With a DVR basis, $V_{ij}^{\text{DVR}} = \delta_{ij} V(x_i)$, that is, the potential energy matrix is diagonal by construction. Moreover, all observables $\hat{A}$ which are functions only of the coordinates ($\hat{A} = f(\hat{x})$) can be represented by a diagonal matrix, $A_{ij} = f(x_i) \delta_{ij}$, within the DVR. It can be shown that if the coordinate matrix is tridiagonal in the VBR, then the approximation of the FBR is equivalent to a Gaussian quadrature [35]. If that is the case, the DVR is called a proper DVR, otherwise it is called improper.

Next, let us discuss how the kinetic energy can be obtained in DVR. The kinetic energy with curvilinear coordinates is some coordinate-dependent weighted sum of the differential operators. The DVR of the differential operators is a simple unitary transformation of their analytically known VBR matrices. The coordinate-dependent weights are diagonal like the potential energy. Thus it's also easy to construct the kinetic energy in the DVR.

Based on different VBR basis sets, different DVRs can be derived. For example, from the orthogonal Legendre polynomials, we can get the Legendre DVR, or from the solutions of the particle-in-a-box problem we can get the sine DVR, both of these DVRs are proper.

3.1.2 Podolsky form of the kinetic energy operator

Traditionally, the first steps toward a variational nuclear-motion computation involved the derivation of the kinetic energy operator in the internal coordinates specific for the given molecule [36–41]. GENIUSH offers a different approach: it uses a numerical representation of the general kinetic-energy operator with coordinate-dependent terms computed by the code

automatically. The user is required to provide a subroutine which calculates body-fixed Cartesian coordinates from the given set of internal coordinates. To describe the rotations, infinitesimal rotation coordinates around the three axes of the body-fixed frame are used.

Let us consider a molecular system composed of N atoms. Then, the space-fixed positions of the atoms can be given with the body-fixed Cartesian coordinates $\mathbf{x}_i$, along with three angles and a Cartesian vector describing the orientation and the position of the body-fixed frame with respect to the space-fixed frame. The origin of the body-fixed frame is chosen to be the center of mass of the N -atomic system. The three degrees of freedom describing the center of mass of the molecule are omitted, since the translational motion of the system can be decoupled exactly from the vibrations and the rotations. To describe vibrations, it is considered to be better to use internal coordinates over the body-fixed Cartesian coordinates. I denote these vibrational coordinates, along with the rotational coordinates, as q_k , where $k \leq 3N - 6$ for vibrational coordinates and $k = 3N - 5, 3N - 4$, and $3N - 3$ for rotational coordinates. In GENIUSH, the kinetic energy operator is the sum of three terms

$$\hat{T} = \hat{T}^{\text{vib}} + \hat{T}^{\text{rot}} + \hat{T}^{\text{rotvib}}, \quad (3.7)$$

where $\hat{T}^{\text{vib}}$, $\hat{T}^{\text{rot}}$ and $\hat{T}^{\text{rotvib}}$ are the vibrational, rotational, and rotational-vibrational coupling contributions to the kinetic energy. $\hat{T}^{\text{vib}}$, $\hat{T}^{\text{rot}}$, and $\hat{T}^{\text{rotvib}}$ can be given in the so-called Podolsky form [42], employing atomic units, as

$$\hat{T}^{\text{vib}} = \frac{1}{2} \sum_{k,l=1}^D \tilde{g}^{-1/4} \hat{p}_k^\dagger G_{kl} \tilde{g}^{1/2} \hat{p}_l \tilde{g}^{-1/4}, \quad (3.8a)$$

$$\hat{T}^{\text{rot}} = \frac{1}{2} \sum_{k=1}^3 G_{k+D,k+D} \hat{J}_k^2 + \frac{1}{2} \sum_{k=1}^3 \sum_{l>k}^3 G_{k+D,l+D} [\hat{J}_k, \hat{J}_l]_+ \quad (3.8b)$$

$$\hat{T}^{\text{rotvib}} = \frac{1}{2} \sum_{l=1}^3 \sum_{k=1}^D \left(\hat{p}_k^\dagger G_{k,l+D} + G_{k,l+D} \hat{p}_k \right) \hat{J}_l, \quad (3.8c)$$

where $\tilde{g} = \det \mathbf{g}$, $\mathbf{G} = \mathbf{g}^{-1}$, $\hat{p}_i = -i \frac{\partial}{\partial q_i}$ is the momentum conjugate to the coordinate q_i , $D = 3N - 6$, $\hat{J}_k$ is the component of the total angular momentum vector along the k th body-fixed axis, $[\cdot, \cdot]_+$ denotes the anticommutator, and

$$g_{kl} = \begin{cases} \sum_{i=1}^N m_i \frac{\partial \mathbf{x}_i^T}{\partial q_k} \frac{\partial \mathbf{x}_i}{\partial q_l}, & \text{if } k, l \leq 3N - 6 \\ \sum_{i=1}^N m_i \frac{\partial \mathbf{x}_i^T}{\partial q_k} (\mathbf{e}_l \times \mathbf{x}_i), & \text{if } k \leq 3N - 6 \text{ and } l = 3N - 5, 3N - 4, 3N - 3 \\ \sum_{i=1}^N m_i (\mathbf{e}_k \times \mathbf{x}_i)^T (\mathbf{e}_l \times \mathbf{x}_i), & \text{if } k, l = 3N - 5, 3N - 4, 3N - 3 \end{cases} \quad (3.9)$$

where m_i is the mass of atom i , and $\mathbf{e}_k$ is the unit vector parallel to the rotation axis associated with the k th rotational coordinate. It is important to emphasize that the Podolsky form of the kinetic energy operator is exact, there is no approximation introduced during its derivation (a usual approximation could be the decoupling of the rotations and the vibrations).

For all of the vibrational coordinates, DVR basis sets are used; consequently, the coordinate-dependent $\mathbf{g}$ matrix is diagonal. To evaluate $\mathbf{g}$ at the grid points, the proper derivatives, $\frac{\partial \mathbf{x}_i}{\partial q_l}$, are calculated numerically (or even analytically) in GENIUSH. For the three rotational coordinates, the so-called Wang functions [43] are used as basis functions, which are symmetrized versions

of the $|JKM\rangle$ symmetric-top rigid-rotor eigenfunctions.

3.2 Representation of the flux operator

Representation of the commutator form of the flux, see Eq. (2.4), in a DVR basis is straightforward,

$$\begin{aligned}
 F_{ij} &= \langle \chi_i | \hat{F} | \chi_j \rangle = i/\hbar \langle \chi_i | (\hat{H}\theta(s(\mathbf{q})) - \theta(s(\mathbf{q}))\hat{H}) | \chi_j \rangle \\
 &= i/\hbar \sum_k (\langle \chi_i | \hat{H} | \chi_k \rangle \langle \chi_k | \theta(s(\mathbf{q})) | \chi_j \rangle - \langle \chi_i | \theta(s(\mathbf{q})) | \chi_k \rangle \langle \chi_k | \hat{H} | \chi_j \rangle) \\
 &= i/\hbar \sum_k (H_{ik}\theta(s(q_j))\delta_{jk} - \theta(s(q_i))\delta_{ik}H_{kj}) \\
 &= i/\hbar H_{ij}(\theta(s(q_j)) - \theta(s(q_i))).
 \end{aligned}$$

Note that the matrix representation of $\theta(s(\mathbf{q}))$ is diagonal in DVR and a resolution of identity is applied in the second line of the previous equation. However, due to the size of the problem, in GENIUSH the matrix elements are not stored, the true engine of the code is an efficient matrix-vector multiplication subroutine. Thus, the elements of the flux matrix cannot be stored either; instead, another matrix-vector multiplication subroutine must be used,

$$\mathbf{F}\mathbf{v} = i/\hbar(\mathbf{H}\boldsymbol{\theta}\mathbf{v} - \boldsymbol{\theta}\mathbf{H}\mathbf{v}), \quad (3.10)$$

where $\boldsymbol{\theta}$ is the diagonal matrix of the dividing surface. Thus, one multiplication by the flux needs two multiplications by the Hamiltonian.

3.3 Time propagation

The multiplication by the Boltzmannized flux needs a representation of the Boltzmann operator, which can be regarded as time propagation in imaginary time,

$$e^{-\beta/2\hat{H}} = e^{-i\hat{H}t/\hbar},$$

with $t = -\hbar i\beta/2$. The evaluation of $k(T)$ also needs the real time propagation of the eigenstates of the Boltzmannized flux.

The real and imaginary time propagations can be represented by the same method. In this work I used the so-called Chebyshev expansion of the propagator to that end [44–46]. In principle, other propagation methods could be also used, like the split-operator technique. However, I employed the Chebyshev propagation as it can be implemented in GENIUSH quite easily. Since the Chebyshev propagation requires only the evaluation of matrix-vector products, it is not necessary to explicitly construct and store the Hamiltonian matrix.

The main idea of the Chebyshev method is to expand the exponential of the propagator in the basis of the complex Chebyshev polynomials, $\Phi_i(x)$. However, since the domain of the complex Chebyshev polynomials is $x \in [-i, i]$, the Hamiltonian should be normalized,

$$\hat{H}_{\text{norm}} = (\hat{H} - \hat{I}E_{\text{avr}})/\Delta E, \quad (3.11)$$

where $\Delta E = (E_{\text{max}} - E_{\text{min}})/2$, $E_{\text{avr}} = (E_{\text{max}} + E_{\text{min}})/2$, E_{max} , E_{min} are the highest and lowest eigenvalues of the Hamiltonian, respectively, and $\hat{I}$ is the identity operator. With this, the time

propagation can be expressed as

$$\psi(t) = e^{-i\hat{H}t/\hbar}\psi(0) \simeq e^{-itE_{\text{avr}}/\hbar} \sum_{i=0}^N a_i(t\Delta E/\hbar) \Phi_i(-i\hat{H}_{\text{norm}})\psi(0). \quad (3.12)$$

The expansion coefficients are

$$a_i(\alpha) = \int_{-1}^1 \frac{e^{i\alpha x} \Phi_i(x)}{\sqrt{1-x^2}} dx = (2 - \delta_{i0}) J_i(\alpha), \quad (3.13)$$

where $J_i(\alpha)$ is the i th Bessel function, and $\alpha = t\Delta E/\hbar$. The initial wave function multiplied by the Chebyshev polynomials, $\phi_i = \Phi_i(-i\hat{H}_{\text{norm}})\psi(0)$, is obtained by the recursion relation

$$\phi_{i+1} = -2i\hat{H}_{\text{norm}}\phi_i + \phi_{i-1},$$

with $\phi_0 = \psi(0)$ and $\phi_1 = -i\hat{H}_{\text{norm}}\psi(0)$. As the sum is calculated in Eq. (3.12), in every step only the last two ϕ_i functions have to be stored.

The propagation in imaginary time can be performed in a single step. However, the real time propagation is done in smaller steps, since the value of the flux autocorrelation function is needed at several times in order to calculate the integral of $C_f(t)$. In each propagation step, the calculation of the product of the Hamiltonian with a vector is needed N times, that is, the number of terms in the Chebyshev expansion. Thus, to maximize the efficiency of the Chebyshev time propagation, N should be chosen as small as possible. The number of the terms necessary in the Chebyshev expansion is ruled by the coefficients, *i.e.* the Bessel functions, $J_v(\alpha)$. Thus, to investigate the convergence of the Chebyshev expansion, it is necessary to consider how quickly $J_v(\alpha)$ converges to zero as v increases for a given α . If α is real, the case of the real time propagation, the value of the Bessel functions, $J_v(\alpha)$, at a given α decreases exponentially with increasing v , if $v \gtrsim \alpha$. If α is imaginary (in the case of imaginary time evolution, *i.e.*, evaluation of the Boltzmann operator) the turning point is about $\sqrt{\alpha}$. According to my experience regarding the convergence of the Chebyshev expansion, I found it to be more practical to determine the number of terms in the Chebyshev expansion *via* a simple threshold, C , instead of using the above-mentioned relations. Then, the smallest N is used for which the relation $J_N(\alpha)/J_0(\alpha) \leq C$ holds.

In a GENIUSH calculation, first the E_{max} and E_{min} are determined by an iterative, Lanczos-type diagonalization of the Hamiltonian. Since in each case only one eigenvalue is needed, the iteration is quite fast; it takes no more time than a few seconds for the calculations of this work.

After the highest and lowest eigenvalues of the Hamiltonian are obtained, two sets of Bessel functions are calculated and stored in the memory, separately for imaginary and real time propagations. Thus, during time propagation, the Bessel functions are not needed to be calculated again and again. Since the argument of the Bessel functions, α , depends on the time step, a constant time step is necessary in the case of the real time propagation. Otherwise, separate set Bessel functions should be calculated for each step size. In the current implementation the Bessel functions are calculated by the AMOS package [47].

The product of $\mathbf{F}(\beta)$ with a vector is carried out in three steps:

$$\mathbf{F}(\beta)\mathbf{v} = e^{-\beta/2\mathbf{H}} \left(\mathbf{F} \left(e^{-\beta/2\mathbf{H}}\mathbf{v} \right) \right) \quad (3.14)$$

where the $e^{-\beta/2\mathbf{H}}\mathbf{v}$ is calculated using Eq. (3.12). Thus, one action of the thermal flux needs $2N + 2$ actions of the Hamiltonian.

3.4 Diagonalizing the thermal flux

I utilized the ARPACK package to perform the diagonalization of the thermal flux [48]. ARPACK is a Fortran library that uses the Arnoldi method to iteratively diagonalize complex matrices.

In the Arnoldi method, diagonalization is carried out using matrix-vector products, without the need to store the entire matrix in memory. Thus, ARPACK can be integrated straightforwardly into the GENIUSH code. The current algorithm in ARPACK does not take advantage of the Hermitian nature of the thermal flux. In the future, a more efficient algorithm could be employed to utilize this property.

3.5 Integration of the flux autocorrelation function

In the present version of my code, integration of the flux autocorrelation function is performed using the simple trapezoidal rule. In the future, more accurate integration methods, such as Simpson's rule or beyond, could be employed. However, since the flux autocorrelation function is sampled at equidistant time steps, only certain integration rules can be applied.

Chapter 4

Results of model calculations

During my TDK research, I tested the code I developed for the calculation of reaction rate coefficients on several model problems. Here I will provide a brief summary of the results, with emphasis on algorithmic and implementation details.

4.1 One-dimensional Eckart potential

The one-dimensional (1D) Eckart potential [49] provides a suitable model for chemical reactions. Furthermore, it is an example from the short list of analytically solvable quantum mechanical problems. This was the first model system I used to test and validate the code I have developed.

I employed the symmetric form of the potential (see Fig. 4.1),

$$V(x) = V_0 \cosh^{-2}(x/a),$$

where I used $a = 0.734$ bohr and $V_0 = 0.425$ eV. The potential is symmetric, $V(x) = V(-x)$, implying that the potential energy of the reactant and the product is the same, *i.e.*, the reaction

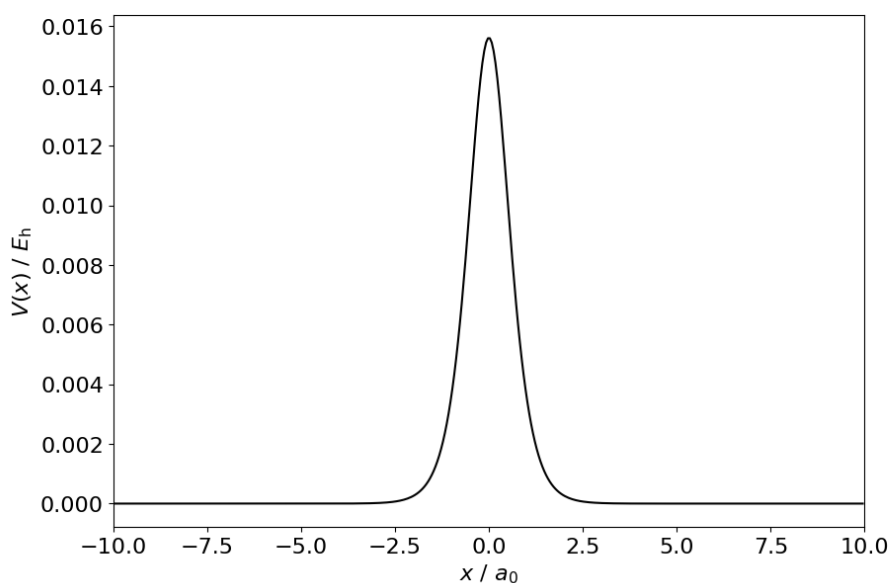


FIGURE 4.1: The one-dimensional Eckart potential, $V(x) = V_0 \cosh^{-2}(x/a)$, with $a = 0.734$ bohr and $V_0 = 0.425$ eV. The parameters of the Eckart potential are chosen to represent the collinear $\text{H} + \text{H}_2 \longrightarrow \text{H}_2 + \text{H}$ identity reaction.

Index	Original	D2	AP
1	-1.741×10^{-4}	-2.436×10^{-8}	-2.436×10^{-8}
2	1.741×10^{-4}	2.436×10^{-8}	2.436×10^{-8}
3	-2.654×10^{-8}	-1.722×10^{-14}	-1.735×10^{-14}
4	2.654×10^{-8}	1.722×10^{-14}	1.735×10^{-14}
5	-9.741×10^{-10}	2.414×10^{-20}	-3.395×10^{-16}
6	9.741×10^{-10}	-2.414×10^{-20}	3.394×10^{-16}

TABLE 4.1: The first six eigenvalues of the thermal flux (1D Eckart model) resulting from the original GENIUSH calculation ('Original'), from a calculation when T^{D2} , see Eq. (4.2), was used ('D2'), or from the GENIUSH calculation when an additional potential ('AP') was used (see the text for further explanation and for the definition of 'D2' and 'AP').

is neither exothermic nor endothermic. With this specific choice of the parameters the potential provides a one-dimensional (1D) model for the collinear $H + H_2 \longrightarrow H_2 + H$ reaction, assuming that the mass of the particle is $m = 0.582$ u. In addition, the kinetic energy operator for the 1D Eckart model can be expressed as $\hat{T} = -\frac{1}{2m} \frac{d^2}{dx^2}$ in atomic units.

For these computations I used a sine-DVR basis. Since this is a one-dimensional problem, working with a quite large basis is still inexpensive. For the results presented here a basis set containing 400 grid points was used. The dividing surface simplifies to dividing point in 1D. For the Eckart potential it is a natural choice to define the dividing point as the top of the barrier, that is, $s(x) = x = 0$.

For the propagation, the threshold of the convergence of the Bessel functions was set to $C = 10^{-10}$, and a step size of the real time propagation was $10 \hbar E_h^{-1}$. With these choices, 89 terms during the imaginary time propagation and 18 terms during the real time propagation were needed in the Chebyshev expansion. The final result of the calculations was converged with respect to both the threshold and the step size.

Since the eigenpairs of thermal flux are important intermediate results of the calculation of the reaction rate, it is worth checking both the eigenvalues and the eigenvectors. The first six eigenvalues can be found in Table 4.1, while the corresponding eigenvectors can be seen in Fig. 4.2. The eigenvalues obtained do not show any unexpected behavior. They come in $\pm$ pairs, due to the fact that the thermal flux is imaginary and Hermitian. The absolute value of the eigenvalues decreases quite quickly, ensuring that only the few largest, in magnitude, will need to be considered later on. One could argue that there should be only two nonzero eigenvalues, since it is a one-dimensional problem (see Chapter 2). However, this is not the case, due to (a) the approximate nature of the DVR matrix elements, and (b) to the shape of the flux [19].

On the other hand, the eigenvectors obtained are clearly problematic. The eigenvectors of the thermal flux should be localized in the vicinity of the dividing surface (dividing point in this case). In clear contrast, the first two eigenvectors, which form a $\pm$ pair in terms of their eigenvalues, are localized at the two edges of the grid. The same is true for the third pair, with the addition that it is also nonzero in the vicinity of the dividing point. Both the first and the third pair of eigenvectors have a strange sawtooth pattern. Nevertheless, the second pair of eigenvectors appears exactly as expected.

In principle, the eigenvector pairs should be the complex conjugate of each other. This is true for the plotted eigenvectors too, but it is not evident since the eigenvectors are undetermined up to a complex phase factor. Of course, the phase factor could be corrected, so that the eigenvector pairs were truly complex conjugates of each other. However, such a correction is unnecessary, as the phase factor drops out during the calculation of the expectation value of

the flux, see Eq. (2.29).

The next step is the propagation of the thermal flux eigenvectors, and the calculation of the

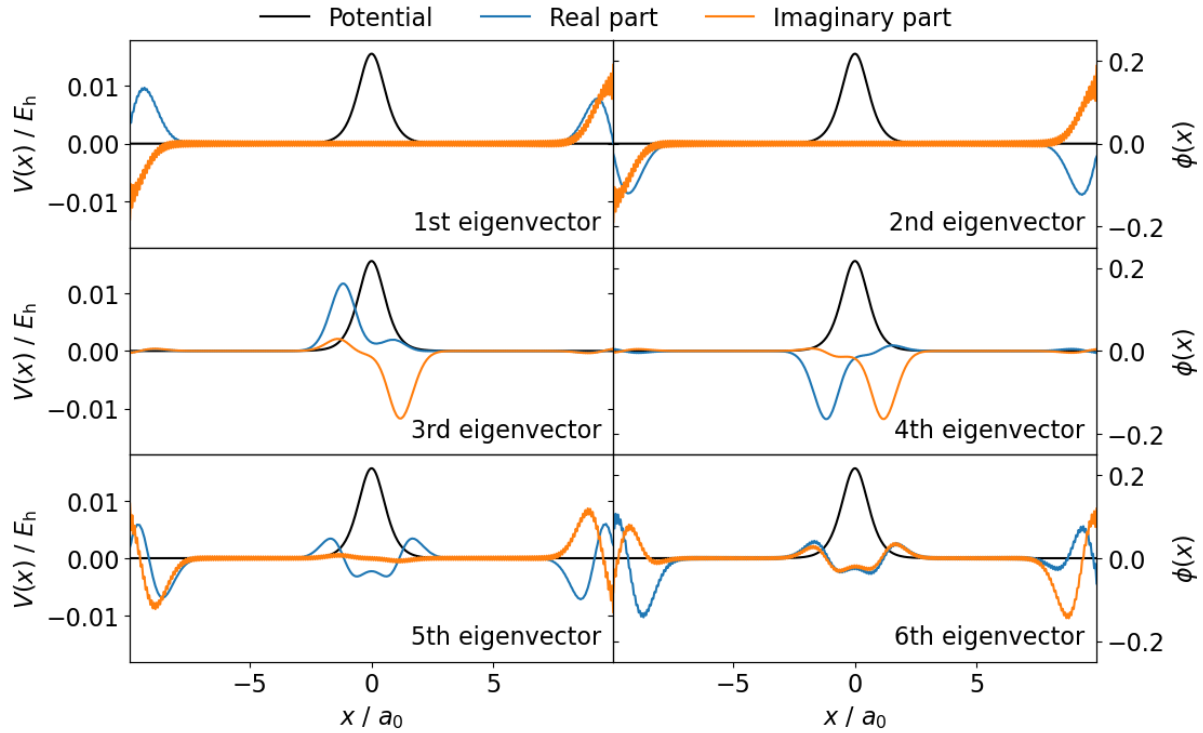


FIGURE 4.2: The first six eigenvectors of the thermal flux for the 1D Eckart model. The potential, and real and imaginary parts of the eigenvectors are depicted using different colors as indicated above the figure.

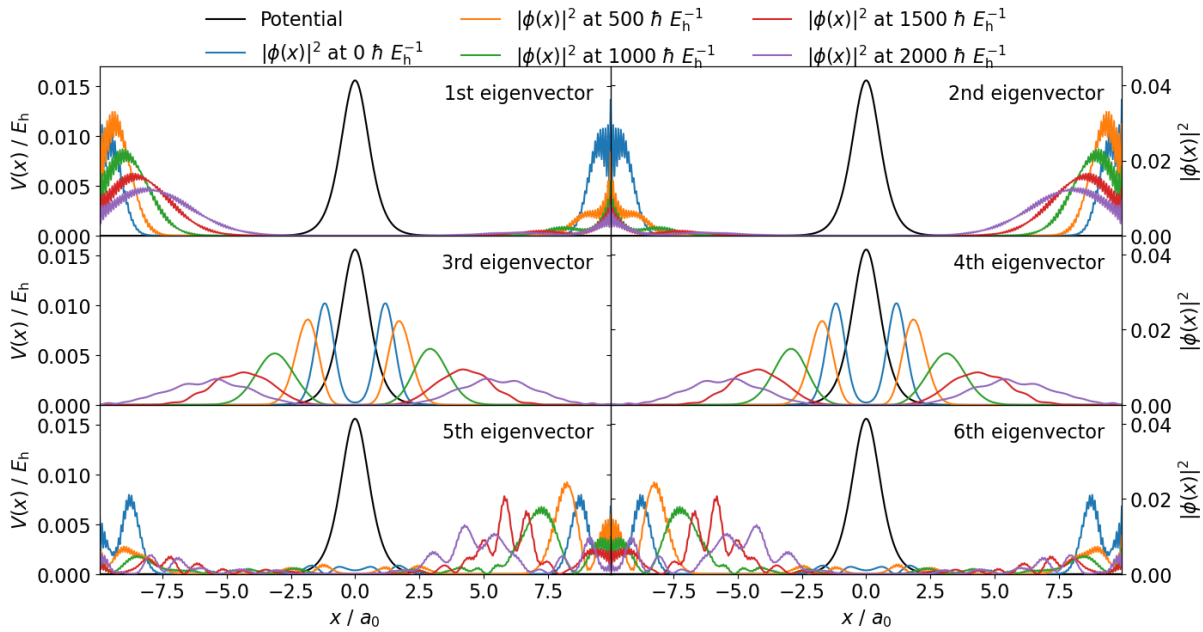


FIGURE 4.3: The first six eigenvectors (absolute square is shown) of the thermal flux at different times (atomic units are used throughout) for the 1D Eckart model. The potential, and absolute squares of the eigenvectors at different times are depicted using different colors as indicated above the figure.

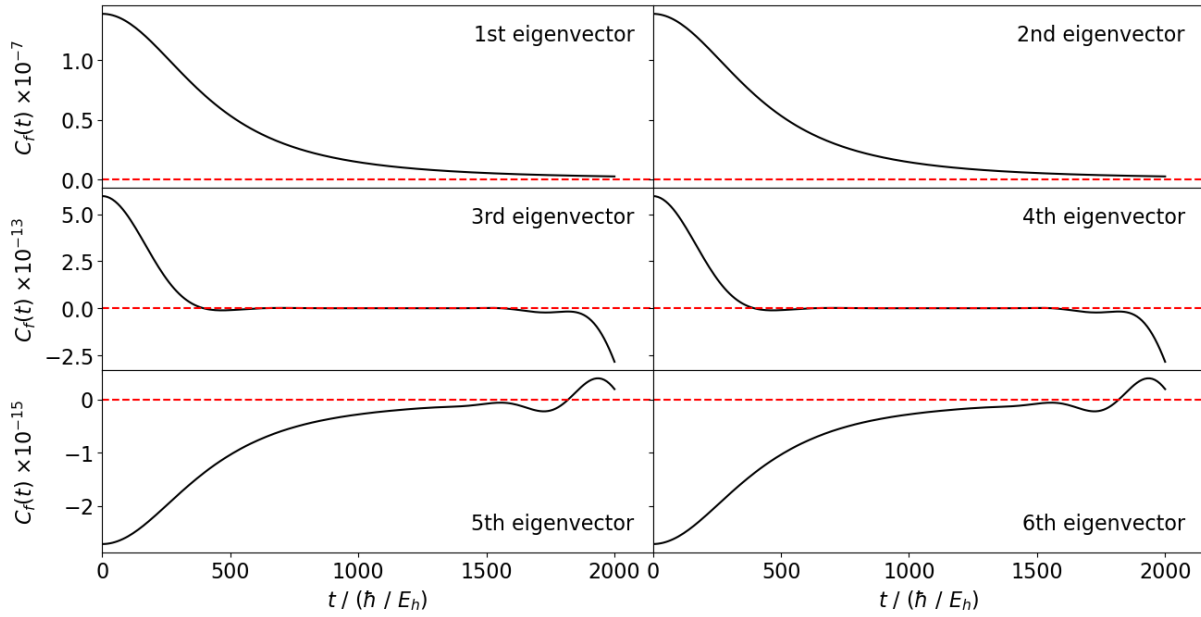


FIGURE 4.4: The contributions in the flux auto correlation function of the different eigenvectors (1D Eckart model).

flux autocorrelation function. The squared absolute value of the propagated eigenvectors can be seen in Fig. 4.3 for $t = 0, 500, 1000, 1500$ and $2000 \hbar E_h^{-1}$. As it can be seen, the squared absolute values of the third and fourth eigenvectors are the same as expected as the eigenvectors are complex conjugates. Small humps can also be observed for these two eigenvectors at longer propagation times. The eigenvectors are reflected from the end of the grid during the propagation. The still outgoing parts and the reflected parts of the eigenvector interfere with each other. The resulting interference pattern can be seen as humps on Fig. 4.3.

The flux autocorrelation function is a sum of the contributions from the eigenpairs of the thermal flux. These contributions are plotted as a function of time in Fig. 4.4. The eigenpairs whose eigenvalues form a $\pm$ pair have the exact same contribution to the full $C_f(t)$. By looking at the order of magnitude of these contributions, it becomes clear that only the first eigenpair is relevant. The contribution of the second pair of eigenvectors, which looked like the physically correct ones, converges to zero; however, after around $t = 1500 \hbar E_h^{-1}$, it becomes negative and start to diverge. This is caused by the nonphysical reflection of the eigenvectors from the edges of the grid. The third eigenvector pair gives a negative contribution even at $t = 0$, which also shows the nonphysical nature of these two eigenvectors. As mentioned above, the full autocorrelation function is the sum of all of these contributions ($C_f^{\text{full}}(t)$); however, I also investigated separately the correlation function arising from the contributions of the third and fourth eigenpairs, $C_f^{3,4}$, as well.

The time integration was carried out for the $[0 \hbar E_h^{-1}, 2000 \hbar E_h^{-1}]$ interval for $C_f^{\text{full}}(t)$. However, for $C_f^{3,4}(t)$ the upper bound was chosen to be $1000 \hbar E_h^{-1}$, as it is important to not include the parts of the autocorrelation functions which are affected by the reflections. Finally, to get the reaction rate coefficient, the reactant partition function is also needed. Since in this case the system has only one (unbounded) degree of freedom, the partition function is simply the translational partition function of a free particle, that is, in one-dimension

$$Q_r = \sqrt{\frac{m}{2\pi\hbar^2\beta}}.$$

Result	$k(T) / \text{s}^{-1}$
full	1.47647×10^{13}
3, 4	2.29984×10^7
D2	2.29978×10^7
AP	2.29959×10^7
exact	2.29982×10^7

TABLE 4.2: Reaction rate coefficients for the 1D Eckart model calculated at $T = 300$ K. The result labeled as 'full' was calculated with using six thermal flux eigenpairs, while '3, 4' calculated using only the third and fourth eigenpairs. The 'D2' rate coefficient is obtained by using the T^{D2} kinetic energy and 'AP' was calculated with the use of an additional potential (see the text for further explanation). The exact rate coefficient is also given.

As mentioned earlier, the rate coefficient for the 1D Eckart potential can be obtained analytically. The cumulative reaction probability is

$$N(E)^{\text{exact}} = \left(1 + \left(\frac{\cosh \left(\pi/2 \sqrt{8V_0 m a^2 / \hbar^2 - 1} \right)}{\sinh(a\pi \sqrt{2mE / \hbar^2})} \right)^2 \right)^{-1},$$

where E is the initial kinetic energy of the particle. Then, the reaction rate coefficient can be calculated as

$$k(T)^{\text{exact}} = \frac{1}{2\pi\hbar Q_r} \int e^{-\beta E} N(E)^{\text{exact}} dE.$$

The reaction rate coefficients calculated from $C_f^{\text{full}}(t)$, $C_f^{3,4}$, and the exact one, are given in Table 4.2. Interestingly, the 'full' rate coefficient exceeds the exact one by several orders of magnitude, while if only the third and fourth eigenvalues are considered, the rate coefficient agrees well with the exact one. Thus, the calculation is correct in the sense that accurate rate coefficients can be obtained. However, the correct result can be acquired only after some filtering of the thermal flux eigenvectors, based on visual inspection and intuition. It means that alongside the good eigenpairs, other, nonphysical eigenpairs are also obtained for some reason during the diagonalization. That is the main issue which I tried to understand and solve during my work. Unfortunately, I have not found any reference to this problem in the literature.

There are basically two reasons which can cause the appearance of nonphysical eigenpairs. First, this problem could be attributed to the Arnoldi diagonalization process, that is, the nonphysical eigenpairs do not satisfy the eigenvalue equation of the thermal flux. The second possible cause is that the representation of the thermal flux is somehow not correct. I implemented the one-dimensional Eckart model using Wolfram Mathematica in order to check the possible causes listed above. When diagonalizing the matrix of the thermal flux obtained with GENIUSH in Mathematica, I got the nonphysical states, moreover, they were truly eigenvectors and eigenvalues of the thermal flux matrix. Thus, the cause of the appearance of the nonphysical thermal flux eigenstates is not due to the Arnoldi algorithm. Further investigation has revealed that the real cause is the representation of the kinetic energy. When I used the DVR representation of the second derivative matrix for the kinetic energy, I did not get the nonphysical eigenpairs, see Fig. 4.5 and Table 4.1. For the calculation of the thermal rate coefficient, the first six eigenpairs of the thermal flux were used, the corresponding rate coefficient is listed in Table 4.2.

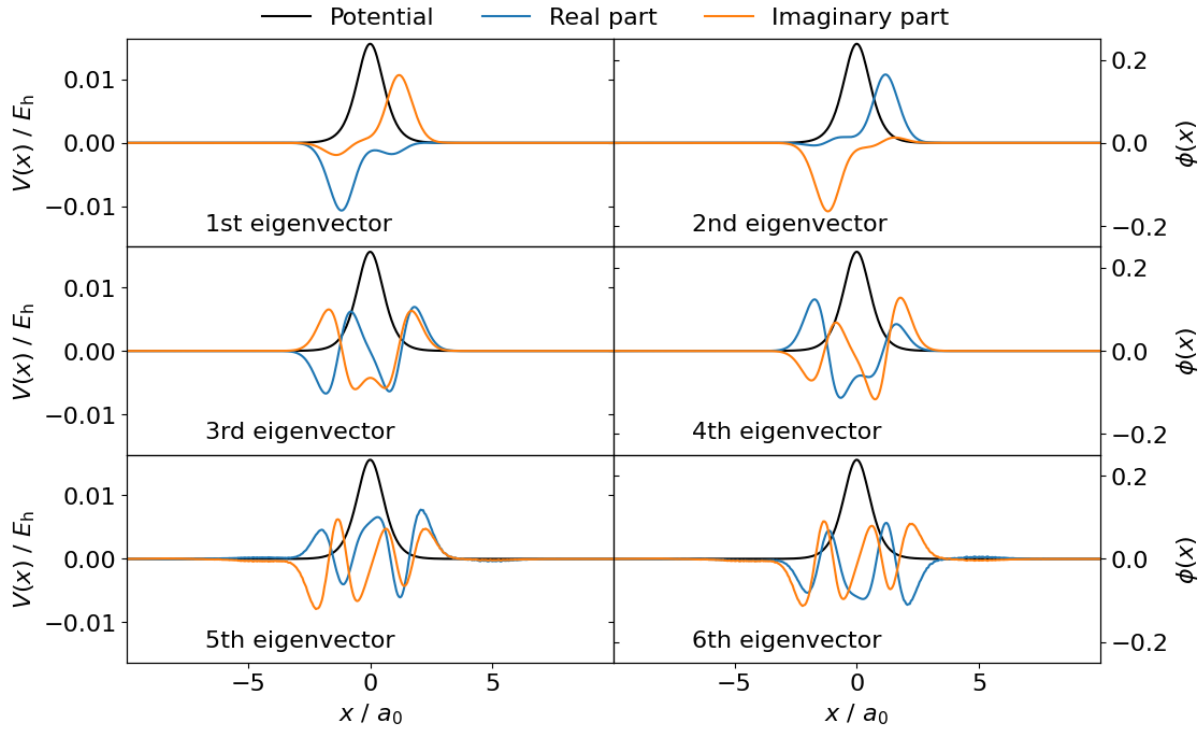


FIGURE 4.5: Thermal flux eigenvectors (1D Eckart model) when the kinetic energy $\mathbf{T}^{\text{D}2}$ of Eq. (4.2) is used. The potential, and real and imaginary parts of the eigenvectors are depicted using different colors as indicated above the figure.

In GENIUSH, the Podolsky form of the kinetic energy is used, see Eq. (3.8). In the case of this one-dimensional system, the kinetic energy matrix has the form

$$\mathbf{T}^{\text{GENIUSH}} = \frac{1}{2m} \mathbf{D}^{(1)} \mathbf{D}^{(1)} \quad (4.1)$$

in GENIUSH, where $\mathbf{D}^{(1)}$ is the DVR of the first-derivative operator. This form is numerically not equivalent to the case when the DVR of the second derivative operator, $\mathbf{D}^{(2)}$, is used instead,

$$\mathbf{T}^{\text{D}2} = \frac{1}{2m} \mathbf{D}^{(2)}. \quad (4.2)$$

Later on, I will denote all the quantities calculated using this kinetic energy with the superscript D2. $\mathbf{T}^{\text{GENIUSH}}$ differs from $\mathbf{T}^{\text{D}2}$ in an extra resolution of identity between the two $\mathbf{D}^{(1)}$ s. This would suggest that the nonphysical states are eliminated as the basis set size is increased. However, this does not hold, although the nonphysical states converge slower than the physical ones. This probably implies that the real cause is somewhat deeper and connected to the DVR itself, which requires further investigation. Nevertheless, the observation that the use of the $\mathbf{T}^{\text{D}2}$ form of the kinetic energy does not give rise to nonphysical states also holds for higher-dimensional models. This way, the fact that analytic forms of the kinetic energy operator, specific to the system and the coordinates, were used in the literature instead of the numerically-constructed general kinetic energy operator employed by GENIUSH might explain why there is no reference to this problem in the literature.

Of course, our primary goal is to use the general kinetic energy operator implemented in GENIUSH instead of analytic kinetic energy operators specific to a given set of internal coordinates. However, the nonphysical states should somehow be avoided. To that end, currently

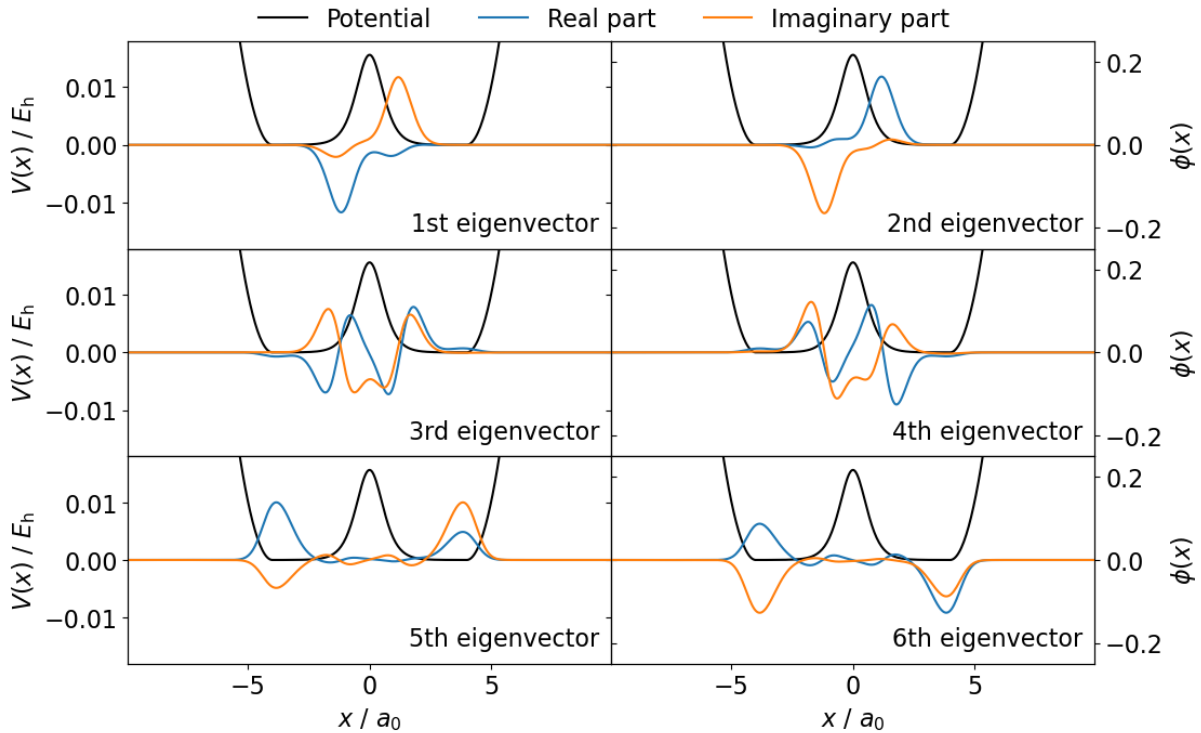


FIGURE 4.6: Eigenvectors of the thermal flux (1D Eckart model) when the additional potential, see Eq. (4.3), was used. The potential, and real and imaginary parts of the eigenvectors are depicted using different colors as indicated above the figure.

the best method I use is to introduce an additional potential (AP), added to the potential energy of the system near the boundaries of the DVR grid. The idea is that this way nonphysical eigenstates of the thermal flux, localized far away from the dividing surface, can be eliminated. Thus, they cause no problem during the evaluation of the trace.

In the present case, I used a simple quadratic form for this additional potential

$$V^{\text{AP}}(x) = \begin{cases} a(\text{abs}(x) - b)^2 & \text{abs}(x) > b \\ 0 & \text{abs}(x) \leq b \end{cases} \quad (4.3)$$

where $a = 0.01 \text{ hartree bohr}^{-2}$ and $b = 4 \text{ bohr}$. I added this extra potential to the potential energy during the diagonalization of the thermal flux, but not during the propagation.

As it can be seen in Fig. 4.6, the first two pairs of thermal flux eigenvectors are localized in the vicinity of the dividing surface, only the third pair seems to be nonphysical. However, these eigenvalues are small enough in absolute value to not cause any problems during the calculation of the flux autocorrelation function, see Table 4.1. The final result, that is, the reaction rate coefficient, can be found in Table 4.2, which is still accurate.

To summarize, the use of the GENIUSH-type general kinetic energy form causes the appearance of nonphysical eigenvalues in the spectrum of the thermal flux. These states can ruin the calculation; however, they can be avoided by a cleverly chosen additional potential. I performed the calculations at various temperatures, and the rate coefficient consistently showed excellent agreement with the exact value. In the remaining parts of this section I will elaborate on a few more general and important aspects of the calculation of the rate coefficients based on the calculations of the 1D Eckart model.

basis set size	$k(T) / \text{s}^{-1}$	$(k(T) - k^{400}(T)) / \text{s}^{-1}$
50	2.27162×10^7	-2.797×10^5
80	2.29955×10^7	-3.525×10^2
100	2.29959×10^7	6.569×10^1
200	2.29959×10^7	3.613×10^1
300	2.29959×10^7	1.055×10^1
400	2.29959×10^7	0

TABLE 4.3: Rate coefficients (1D Eckart model) for different basis set sizes and the difference of the rate coefficients from the rate coefficients with the largest basis set consisting of 400 basis functions.

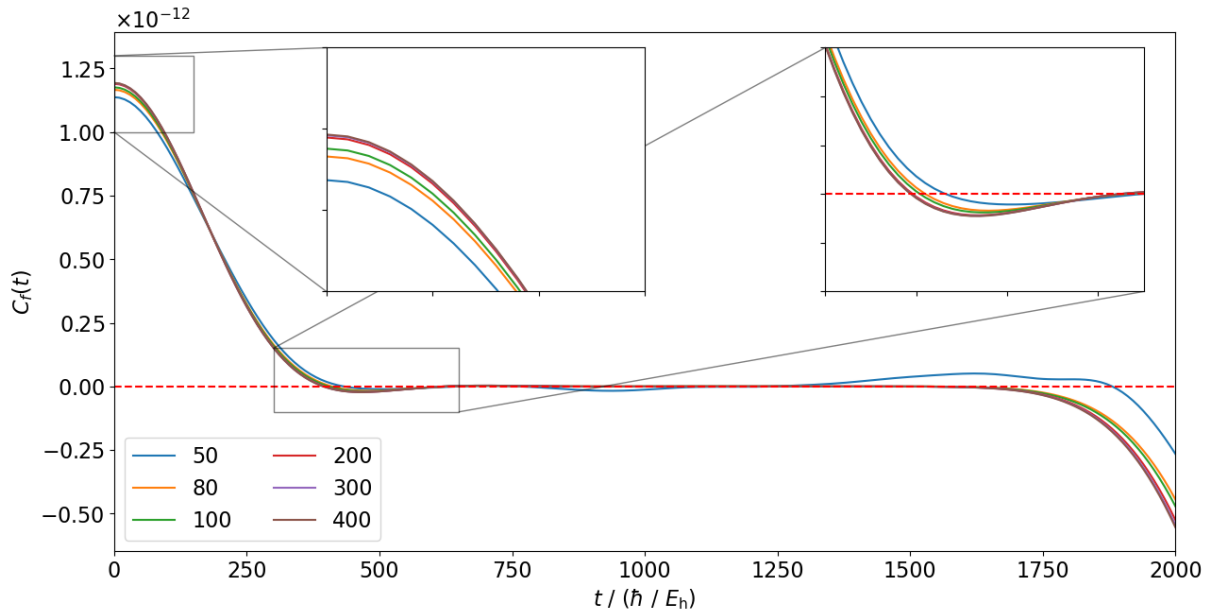


FIGURE 4.7: The flux autocorrelation function (1D Eckart model) using six different basis set sizes, detailed in the lower left corner of the figure.

4.1.1 Basis set size convergence

All of the calculations presented above were performed using 400 sine-DVR grid points. This basis set size is more than large enough to get accurate results, even when the nonphysical states are also considered, which converge much slower. In the following I will show how the flux autocorrelation function and the rate coefficient converge as the basis set size is increased if the additional potential is used to avoid nonphysical states.

The flux autocorrelation functions of different calculations for six different basis set sizes are plotted in Fig. 4.7. For the higher basis set sizes, higher or equal to 200, it is almost impossible to distinguish the different $C_f(t)$ curves. The curves corresponding to smaller basis set sizes are larger at some points, while at other points they are smaller than the correlation functions obtained using larger basis sets. This indicates that the integral of the flux autocorrelation function converges with smaller basis set sizes compared to the flux autocorrelation function itself. The reaction rate coefficients calculated with these basis sets are listed in Table 4.3. The rate coefficients are practically equal for basis sets larger than 50.

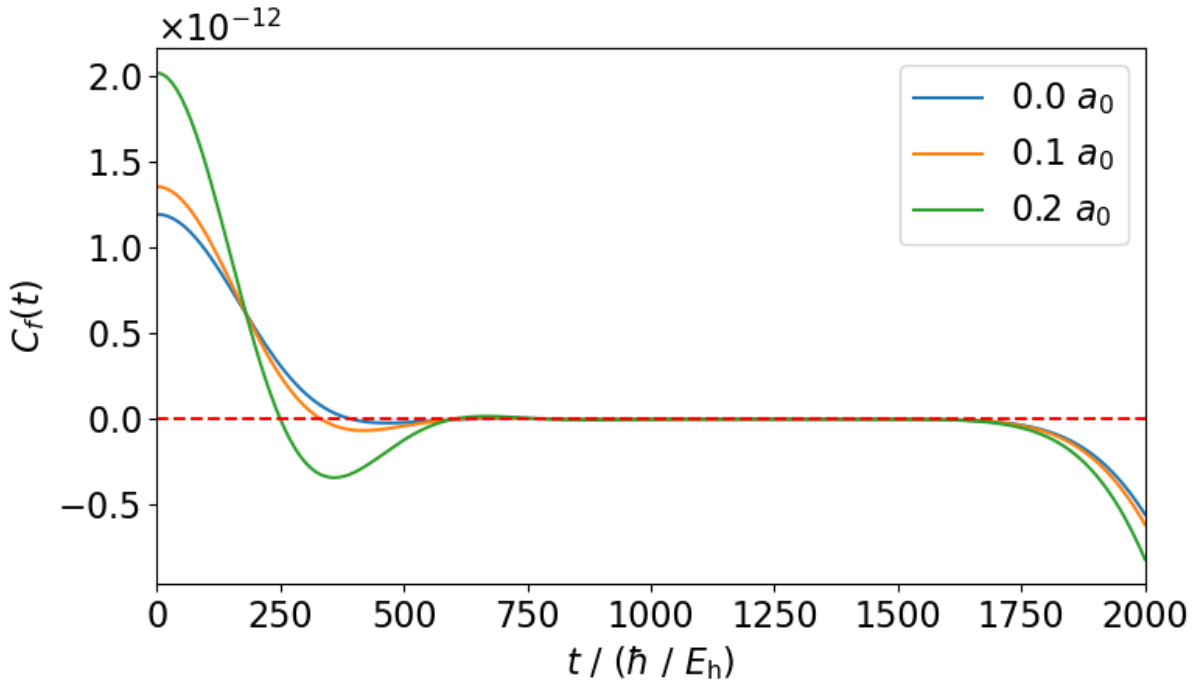


FIGURE 4.8: The flux autocorrelation function (1D Eckart model) if the location of the dividing surface is shifted away from the top of the Eckart potential by different amounts see color coding of results in the upper right corner of the figure).

x / a_0	$k(T) / \text{s}^{-1}$
0.0	2.29959×10^7
0.1	2.29958×10^7
0.2	2.29933×10^7

TABLE 4.4: Rate coefficients (1D Eckart model) if the dividing point is located at different places. $x = 0$ corresponds to the original dividing point at the top of the Eckart barrier.

4.1.2 Effect of position of the dividing point

All of the above calculations were obtained with a dividing surface (DS) placed at the top of the Eckart barrier, *i.e.*, at $x = 0$. However, in principle the reaction rate coefficient does not depend on the exact location of the dividing surface; thus, if the DS is shifted, one should still be able to compute accurate reaction rate coefficients. During my work, I examined how the location of the dividing surface affects the results. To that end, I performed two further calculations, where the DS was shifted in the positive direction by $0.1 a_0$ and $0.2 a_0$. The resulting flux correlation functions are plotted in Fig. 4.8, while the reaction rate coefficients obtained after the integration of the correlation function are tabulated in Table 4.4.

The autocorrelation functions corresponding to a shifted DS differ significantly from the autocorrelation function corresponding to the original DS. At $t = 0$, the farther the dividing surface is located from the top of the barrier the greater the value of the flux autocorrelation function is. However, the flux autocorrelation functions of the shifted DSs decrease faster, they become negative earlier, and have more pronounced negative values than the original flux autocorrelation function. Finally, all flux autocorrelation functions converge to zero, but it takes more time for the flux autocorrelation functions with shifted DSs to vanish. These results suggest that the time propagation needed in a calculation can be reduced by a careful choice of

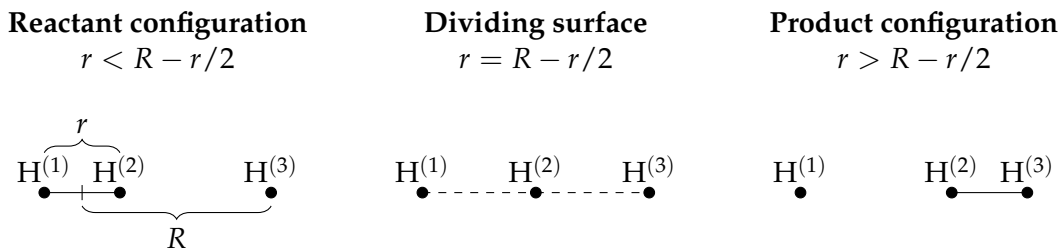


FIGURE 4.9: The schematic representation of the reactant, dividing surface and product configurations for the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction. The definition of the r and R Jacobi coordinates is also plotted.

the DS. Although in the current calculations the DS was shifted by a small amount, either $0.1 a_0$ or $0.2 a_0$, the flux autocorrelation function is affected visibly, while the rate coefficients are still accurate.

4.2 Collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$

The calculations concerning the 1D Eckart potential presented above were sufficient to study some of the most important properties of the computation of reaction rate coefficients, based on the thermal flux. However, to move forward to practically useful applications, it is important to validate the code on higher dimensional model systems.

To that end, I first studied the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction, which is a two-dimensional (2D) problem. Collinearity means that the three hydrogen atoms, $\text{H}^{(1)}$, $\text{H}^{(2)}$, and $\text{H}^{(3)}$, are located on a line in a fixed order; thus, their configuration can be described by two coordinates. Since the order of the hydrogen atoms is fixed, that is, the swapping of the hydrogen atoms is prohibited, there is no need to consider the equivalence of identical nuclei, as the hydrogen atoms are distinguishable by their spatial order.

During the computations I used the so-called Jacobi (scattering) coordinates, r and R . In fact, r is the distance between H_1 and H_2 , the two atoms of the diatom, while R is the distance between H_3 and the center-of-mass of H_1 and H_2 , which is, of course, the mid-point between H_1 and H_2 . In the case of the reactants, H_1 and H_2 are close to each other, forming a hydrogen molecule, and H_3 is far away. In the case of the products, H_2 and H_3 form the hydrogen molecule, and H_1 is the atom far away. For this reactant/product definition, it is natural to locate the dividing surface such that H_2 is half-way between H_1 and H_3 . Thus, at the dividing surface, $r = R - r/2$. The $s(r, R)$ function used in the definition of the flux, Eq. (2.4), has the following form,

$$s(r, R) = \frac{3}{2}r - R. \quad (4.4)$$

In Eq. (4.4), $s(r, R)$ is negative/positive for the reactant/product configurations, and zero at the dividing surface. The schematic representation of the reaction and the definition of the Jacobi coordinates used can be seen in Fig. 4.9.

During the computations, I used a London–Eyring–Polanyi–Sato-type (LEPS) potential energy surface (PES), developed by Varandas [50]. The collinear PES as a function of the Jacobi coordinates, r and R , is plotted in Fig. 4.10. The use of a potential cutoff, *i.e.*, setting the potential to constant above a high enough threshold, decreases the largest eigenvalue of the Hamiltonian. Thus, the Chebyshev expansion requires a smaller number of terms to converge. In the present computations, the potential energy is set to $20\,000 \text{ cm}^{-1}$ wherever it would otherwise exceed this value.

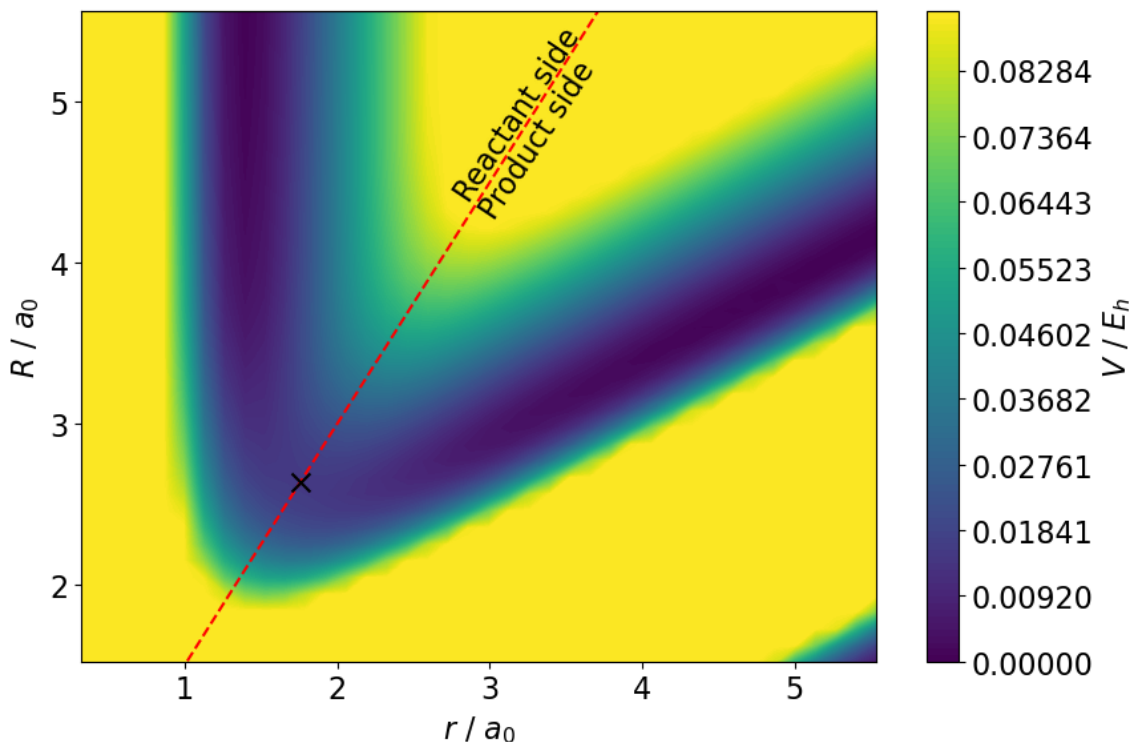


FIGURE 4.10: The potential energy surface of the collinear H_3 system plotted against the two Jacobi coordinates r and R (see text). A cut-off was employed, so for $V \geq 20000 \text{ cm}^{-1}$ the potential was set to $V = 20000 \text{ cm}^{-1}$. The red dashed line represents the employed dividing surface, and the black cross denotes the collinear saddle point.

Regarding the basis set, I used 30 sine DVR functions along both coordinates, distributed between $0.1 - 3 \text{ \AA}$ and $0.75 - 3 \text{ \AA}$ for r and R , respectively. To avoid nonphysical thermal flux eigenstates, I employed an additional potential (AP),

$$V^{\text{AP}}(r, R) = V^{\text{1D}}(r) + V^{\text{1D}}(R), \quad (4.5)$$

where $V^{\text{1D}}(x)$ has the same form as the AP used during the 1D computations, see Eq. (4.3), with the coefficients $a = 0.07 E_{\text{h}} a_0^{-2}$ and $b = 1.5 a_0$. The AP was added to the PES during the diagonalization of the thermal flux, but not during the real time propagation of the thermal flux eigenstates.

I performed the computations at several temperatures between 300 K and 1000 K; however, I will present the intermediate results (such as the flux autocorrelation function) only for $T = 300 \text{ K}$. In addition, reaction rate coefficients are given in Table 4.6 for all the temperatures at which they were computed.

The first eight eigenvalues of the thermal flux, those largest in magnitude, were computed during the iterative diagonalization of the thermal flux. The eigenvalues can be seen in Table 4.5 at $T = 300 \text{ K}$. The eigenvalues come in $\pm$ pairs and decrease quickly in magnitude. As the squared absolute value of the eigenvectors are the same for the complex conjugated pairs, only one of each pair is plotted in Fig. 4.11 for $T = 300 \text{ K}$.

The first two pairs of eigenvectors are localized in the vicinity of the dividing surface; thus, they can be regarded as physical states. However, based on visual inspection, it might be challenging to decide whether the third and fourth pairs are physical or not. Nevertheless, thanks to the quick decrease of the magnitude of the eigenvalues, the contributions from the last

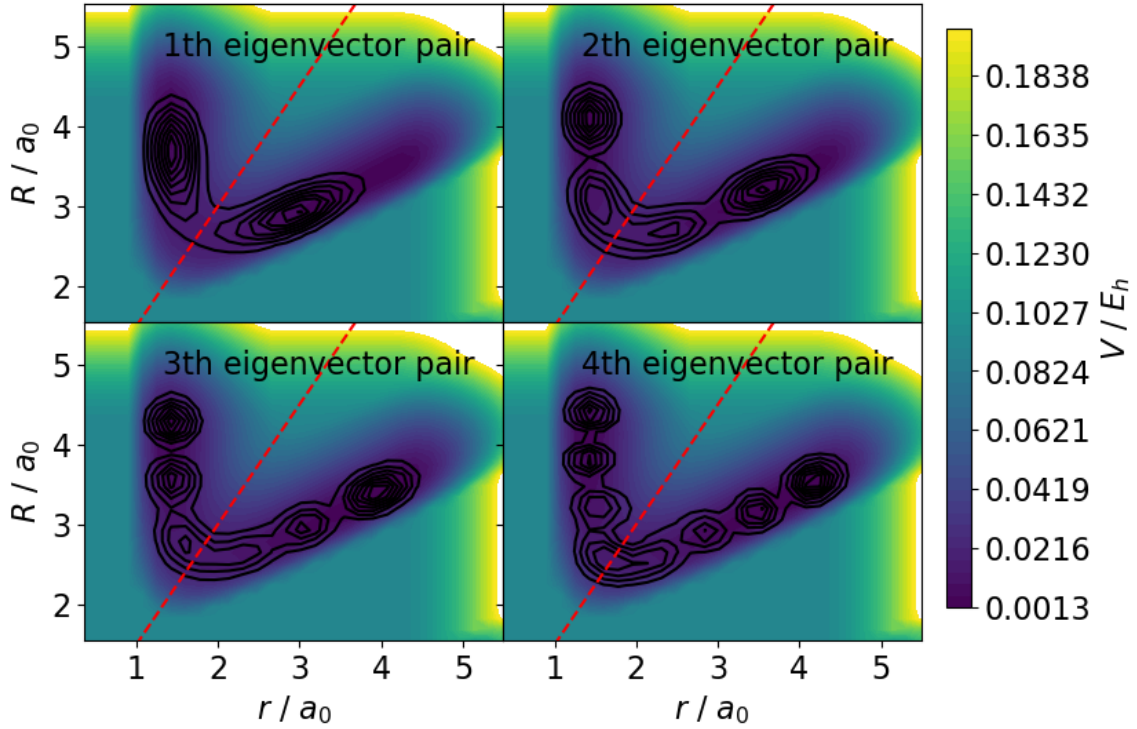


FIGURE 4.11: The absolute squared value of the thermal flux eigenvectors (collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction), one from each complex conjugated pair, is plotted with the black contour lines for $T = 300$ K. The red dashed line represents the dividing surface. In the background the sum of the potential energy surface and the additional potential is plotted.

two pairs of eigenvectors are negligible. During the computations presented here, I considered the contribution from all the eigenvectors.

The flux autocorrelation function is plotted in Fig. 4.12 for $T = 300$ K. The autocorrelation function reaches zero at about $900 \hbar/E_h$, after that the value of $C_f(t)$ is affected by reflection from the edges of the grid. I chose $900 \hbar/E_h$ as the upper bound of the integration of the flux autocorrelation function.

The reactant partition function for the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction is given by

$$Q_r(T) = \sqrt{\frac{\mu}{2\pi\hbar^2\beta}} \sum_n e^{-\beta E_n} \quad (4.6)$$

where E_n are the vibrational energy levels of the hydrogen molecule, and μ is the reduced mass associated with the relative translational motion of the hydrogen atom and the hydrogen

Index	Eigenvalues
1,2	$\pm 1.847 \times 10^{-12}$
3,4	$\pm 3.218 \times 10^{-14}$
5,6	$\pm 2.630 \times 10^{-16}$
7,8	$\pm 1.241 \times 10^{-18}$

TABLE 4.5: The first eight eigenvalues of the thermal flux for the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction at 300 K.

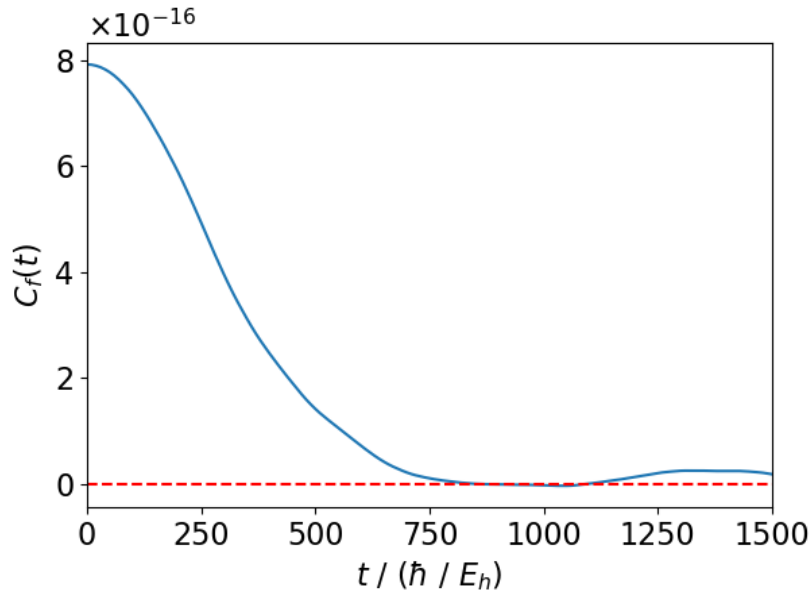


FIGURE 4.12: The flux autocorrelation function, at 300 K, for the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction. Contributions from the first eight thermal flux eigenpairs are considered. The parts after about $1000 \hbar / E_h$ should be disregarded, they are due to reflections from the edges of the grid.

T/K	$k(T)/(\text{cm molecule}^{-1} \text{s}^{-1})$	$k^{\text{ref}}(T)/(\text{cm molecule}^{-1} \text{s}^{-1})$
300	4.835	4.82
400	54.01	54.3
500	249.8	254
600	718.7	724
700	1559.2	1576
800	2823.8	2853
900	4523.8	4573
1000	6642.4	6703

TABLE 4.6: The calculated reaction rate coefficients for the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction at different temperatures. The reference values, $k^{\text{ref}}(T)$, were calculated by Thompson and Miller [19].

molecule, that is,

$$\mu = \frac{1}{(m_{\text{H}} + m_{\text{H}})^{-1} + m_{\text{H}}^{-1}} = \frac{2}{3}m_{\text{H}},$$

where m_{H} is the mass of the hydrogen atom. I calculated the vibrational energy levels of the hydrogen molecule numerically, using the LEPS potential energy surface.

The calculated reaction rate coefficients can be seen in Table 4.6, alongside the reference data from the literature, for several temperatures between 300 K and 1000 K. The calculated rate coefficients agree nicely with the literature data, regardless of the temperature.

Chapter 5

The $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction

The code I developed allowed the full-dimensional treatment of the $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction, neglecting the rotational degrees of freedom. In the $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction there are two different reaction channels, one for each of the two equivalent hydrogen atoms, $\text{H}^{(1)}$ and $\text{H}^{(2)}$. In channel 'A', $\text{H}^{(2)}\text{D}$ is formed, while in channel 'B', $\text{H}^{(1)}\text{D}$ is formed. Naturally, the two channels will have the same contribution to the full rate constant; thus, in principle it would be sufficient to compute only one of them, and multiply the result with an appropriate factor. However, since $\text{H}^{(1)}$ and $\text{H}^{(2)}$ are indistinguishable, we have to take into consideration the Pauli principle, *i.e.*, the wave function of the system should be antisymmetric to the exchange of the hydrogen atoms. In the case of the computation of the reaction rate coefficient, a basis with the proper symmetry has to be used to evaluate the trace of Eq. (2.26). Thus, we must consider the nuclear spin states of the system. There are three symmetric nuclear spin state functions under the exchange of the two hydrogen nuclei: $1/\sqrt{2}(\alpha(1)\beta(2) + \alpha(2)\beta(1))$, $\alpha(1)\alpha(2)$, and $\beta(1)\beta(2)$. Additionally, there is one antisymmetric nuclear spin state function, $1/\sqrt{2}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$. $\beta(1)$, $\alpha(1)$ denote that $\text{H}^{(1)}$ is in β , α spin state, respectively, and similarly for $\text{H}^{(2)}$. The thermal flux eigenstates, used for the evaluation of the trace, should be paired and multiplied with these nuclear spin state functions during the evaluation of the trace, so that the resulting function is antisymmetric under the exchange of the hydrogen atoms. Therefore, an antisymmetric thermal eigenfunction should be paired with a symmetric spin function, and *vice versa*. Since there are three symmetric spin functions and one antisymmetric one, consideration of the spin states will yield spin factors of 1 and 3 for the symmetric and antisymmetric thermal flux eigenfunctions, respectively. The contributions to the flux autocorrelation of each eigenfunction should be multiplied with the proper spin factor, according to the symmetry of the thermal flux eigenfunction.

The two channels of the reaction can be described with a single dividing surface, defined

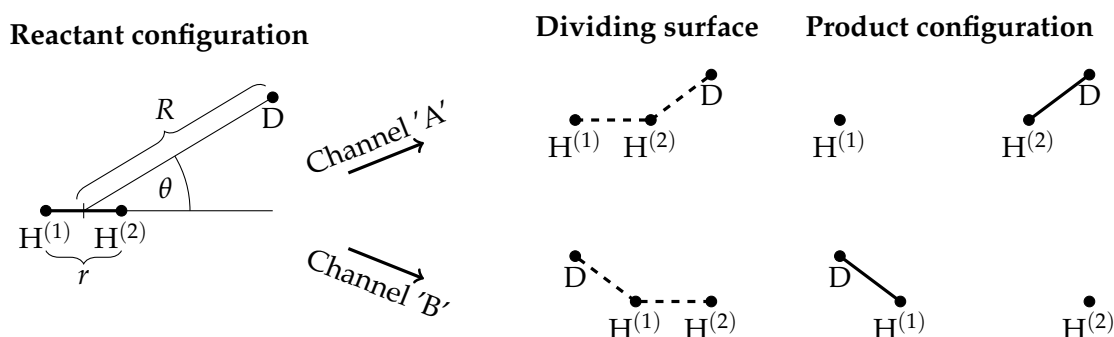


FIGURE 5.1: Schematic representation of the reactant, the dividing surface, and the product configurations of the $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction. The definition of the r , R , and θ Jacobi coordinates is also plotted. Channel 'A' describes the reaction in which HD is formed with $\text{H}^{(2)}$, while the reaction resulting in $\text{H}^{(1)}\text{D}$ corresponds to channel 'B'. The two channels are physically indistinguishable.

Coord.	DVR type	No. of basis functions	Grid boundaries	No. of primitive grid points
r	Sine	30	0.1 – 3.0 Å	300
R	Sine	30	0.75– 3.0 Å	300
θ	Legendre	30	1° – 179°	300

TABLE 5.1: The parameters of the DVR basis sets used during the 3D computations ($H_2 + D \longrightarrow H + HD$ reaction).

such that either the distance between $H^{(2)}$ and D, or $H^{(1)}$ and D, is equal to the distance between the two hydrogen atoms. All configurations, where the $H^{(2)}$ -D or the $H^{(1)}$ -D distance is smaller than the $H^{(2)}$ - $H^{(1)}$ distance, are considered as products. All the other configurations are classified as reactants.

During the present computations, I used Jacobi coordinates similar to the ones used for the collinear $H_2 + H \longrightarrow H + H_2$ reaction. Therefore, r is the distance between the two hydrogen atoms, R is the distance between the deuterium and the center of mass (COM) of $H^{(1)}$ and $H^{(2)}$, while θ is the angle formed by the three points $\mathbf{r}_2$, $\mathbf{r}_{\text{COM}(1,2)}$, and $\mathbf{r}_D$, where $\mathbf{r}_2$ and $\mathbf{r}_D$ are the positions of $H^{(2)}$ and D, respectively. Furthermore, $\mathbf{r}_{\text{COM}(1,2)}$ is the position of the center of mass of the $H^{(1)}$ and $H^{(2)}$ atoms. The definition of the Jacobi coordinates can be seen in Fig. 5.1, alongside the schematic representation of the two reaction channels.

I performed the calculations at several temperatures, similar to the 2D computations. I will present intermediate results only for the $T = 300$ K case, and give the rate coefficients for all temperatures at the end of this section.

The type and the size of the DVR basis sets used along each coordinate can be found in Table 5.1. Most of the settings are similar to the previous calculations. However, during the three-dimensional calculations I used the so-called potential optimized (PO) DVR approach [51]. In PO DVR, first one-dimensional Hamiltonians are diagonalized for each internal coordinate, using a larger number of primitive grid points. Then, the eigenfunctions of the 1D Hamiltonians are used to construct the PO DVR.

I used an additional potential (AP) during the imaginary time propagation, like in the previous calculations. The same form of AP is used in the 3D computations as in the collinear $H_2 + H \longrightarrow H + H_2$ computations, see Eq. (4.5). Thus, the AP is independent of the θ coordinate. Only the parametrization of the AP is changed, $a = 0.07 E_h a_0^{-2}$ and $b = 1.7 a_0$ are used for the 3D computations.

The eigenvalues of the thermal flux can be seen in Table 5.2 at $T = 300$ K. The eigenvalues come in pairs, as expected, and each pair appears twice with approximately the same eigenvalue. The fact that the eigenvalues pairs are doubled shows that the two reaction channels are independent, *i.e.*, there is no coupling between them, and they give the same contribution to the rate coefficient.

The eigenfunctions of the thermal flux at $T = 300$ K are plotted in Fig. 5.2. The most

Index	Eigenvalue
1,2	$\pm 2.516 \times 10^{-13}$
3,4	$\pm 2.502 \times 10^{-13}$
5,6	$\pm 7.205 \times 10^{-15}$
7,8	$\pm 7.169 \times 10^{-15}$

TABLE 5.2: The first eight eigenvalues of the thermal flux for the $H_2 + D \longrightarrow H + HD$ reaction at 300 K. Each eigenvalue pair appears twice with almost the same value.

T / K	$k(T) / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
	This study	[19]	[52]	[22]
300	8.65×10^{-18}	1.07×10^{-17}	8.17×10^{-18}	9.2×10^{-18}
400	1.13×10^{-16}			
500	5.40×10^{-16}	5.15×10^{-16}	5.22×10^{-16}	5.6×10^{-16}
600	1.51×10^{-15}			
700	3.12×10^{-15}	2.96×10^{-15}	3.00×10^{-15}	3.2×10^{-15}
800	5.29×10^{-15}			
900	7.90×10^{-15}	7.66×10^{-15}	7.59×10^{-15}	8.1×10^{-15}
1000	1.08×10^{-14}			

TABLE 5.3: The rate coefficients of the full-dimensional $H_2 + D \longrightarrow H + HD$ reaction at several temperatures. In addition to the reaction rate coefficients computed in the current work, reference values are also tabulated from three different sources.

important feature of the eigenfunctions is that they are either symmetric or antisymmetric to the $\theta \rightarrow \pi - \theta$ operation, that is, to the exchange of the hydrogen atoms. Certain $\pm$ pairs of eigenvectors of the same eigenvalue are symmetric; these are the 1,2 and 5,6 pairs, while other $\pm$ pairs are antisymmetric. As stated above, the spin factor of the antisymmetric and symmetric thermal flux eigenfunctions are 3 and 1, respectively. Since the symmetric and antisymmetric eigenfunctions come in pairs, actually, pairs of $\pm$ pairs, with equal eigenvalues, the effect of the spin factors can be treated in an averaged manner, that is, by multiplying the final result by 2 (this is the so-called symmetry number).

The flux autocorrelation function can be seen in Fig. 5.3 for $T = 300$ K. Unfortunately, there is no time range where the autocorrelation function is zero; however, it becomes small enough that the value of the integral does not depend too much on the choice of the upper integration bound. For the current computations, I integrated the correlation function in the interval $0 - 750 \hbar / E_h$.

The partition function of the reactants, *i.e.*, $H_2 + D$, can be given in the following form,

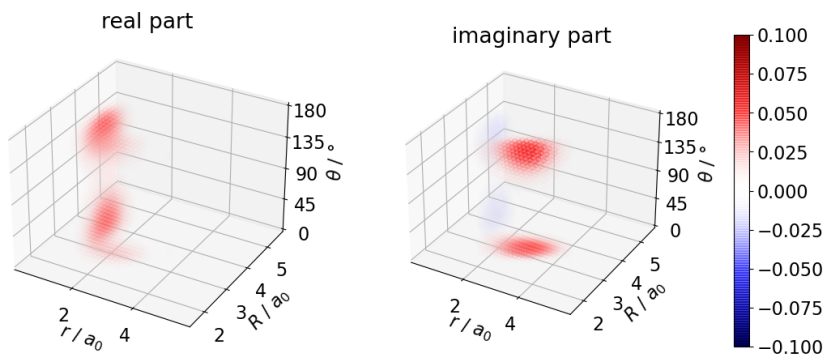
$$Q_r(T) = \left(\frac{\mu}{2\pi\hbar^2\beta} \right)^{3/2} \sum_n e^{-\beta E_n}, \quad (5.1)$$

where E_n are the rovibrational energy levels of the H_2 molecule, and μ is the reduced mass of the hydrogen molecule and the deuterium,

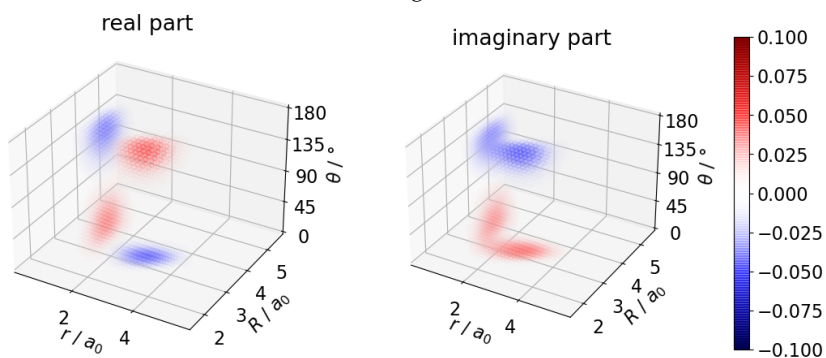
$$\mu = \frac{2m_H m_D}{2m_H + m_D} \quad (5.2)$$

where m_H and m_D are the masses of the hydrogen and the deuterium atoms, respectively. I calculated the rovibrational energy levels of the hydrogen molecule as the sum of its vibrational and rotational energy levels. I used the same numerically computed vibrational energy levels as used in the 2D computations. The rotational energy levels were calculated using the rigid-rotor approximation.

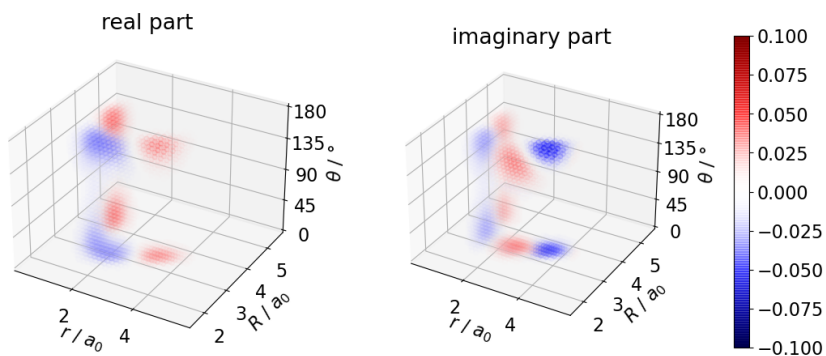
The final reaction rate coefficients for several temperatures along with literature reference values can be found in Table 5.3. We can conclude that there is a good agreement between rate coefficients computed in this work and the ones published in earlier studies (see Refs. [19, 22, 52]).



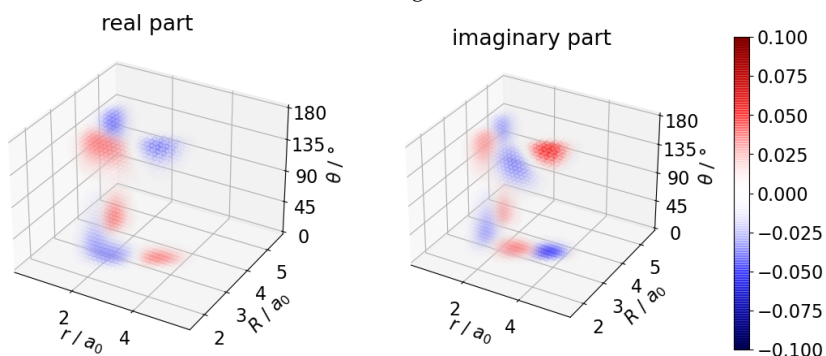
(A) First eigenvector



(B) Third eigenvector



(C) Fifth eigenvector



(D) Seventh eigenvector

FIGURE 5.2: The real and imaginary parts of the 1st, 3rd, 5th and 7th eigenvectors ($H_2 + D \longrightarrow H + HD$ reaction). One eigenvector is plotted for each complex conjugated eigenvector pair. The 1st and 5th eigenvectors are symmetric, while the 3rd and 7th eigenvectors are antisymmetric under the $\theta \rightarrow \pi - \theta$ transformation, that is, the exchange of the two hydrogen atoms.

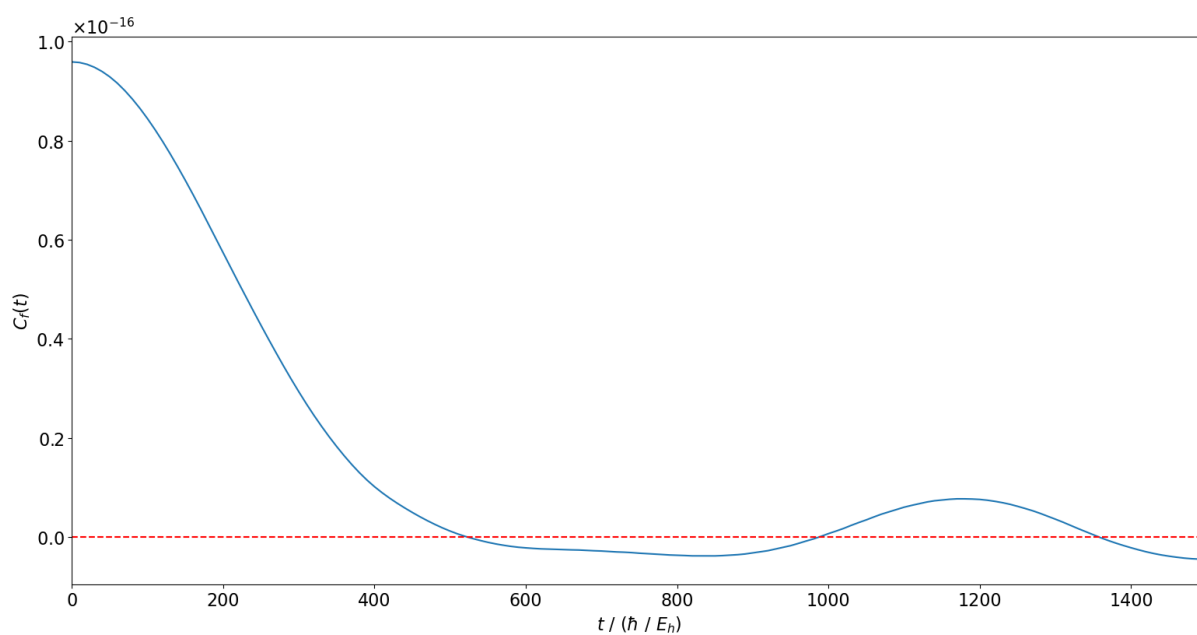


FIGURE 5.3: The flux autocorrelation function of the 3D $H_2 + D \longrightarrow H + HD$ reaction at 300 K. The values after $1000 \hbar E_h^{-1}$ are influenced by reflection from the edges of the grid. The upper integration bound should be chosen between $500 \hbar E_h^{-1}$ and $1000 \hbar E_h^{-1}$; its exact location does not significantly affect the value of the integral.

Chapter 6

Summary, conclusions, and outlook

During my TDK research I developed an efficient computer code for the quantum-mechanical calculation of bimolecular reaction rate coefficients. The determination of rate coefficients consists of five main steps, as follows: (1) Diagonalization of the so-called thermal flux. (2) Time propagation of the thermal flux eigenfunctions. (3) Evaluation of the flux autocorrelation function using thermal-flux eigenvalues and time-propagated thermal-flux eigenvectors. (4) Integration of the flux autocorrelation function. (5) Division of the integral by the reactant partition function.

My code is an extension of the GENIUSH program package, originally developed by our research group to calculate rovibrational energy levels and eigenstates of molecules variationally, solving the time-independent nuclear Schrödinger equation. The code I developed inherits the representation of the Hamiltonian by GENIUSH. In GENIUSH, a general form of the kinetic energy operator is used. Thus, the user only needs to provide the potential energy surface and the definition of the internal coordinates; there is no need to derive specific formulas for the kinetic energy.

I validated the code I developed by doing computations for two model systems, the symmetric one-dimensional (1D) Eckart barrier and the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction (a 2D model). Finally, I used my code to determine the temperature-dependent reaction rate coefficient for the $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction, employing a full-dimensional (3D) description. In the case of the 1D Eckart potential, I studied several aspects of the computation; for example, the effect of the choice of the dividing surface and basis set convergence. Unfortunately, some nonphysical eigenvalues and eigenstates of the thermal flux were also obtained, ruining the accuracy of the resulting rate coefficients. I could successfully avoid these nonphysical eigenpairs by the introduction of an extra potential (an additional potential, AP) added to the original potential energy surface. I compared the computed reaction rate coefficients to the exact values, available from analytical derivations, in the case of the 1D Eckart potential. I could also compare my results to literature data in the case of the collinear, 2D $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ and the 3D $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reactions. The correspondence between my results and the reference values is excellent at all temperatures considered.

I have developed and successfully validated my code on a few relatively simple systems. In the future, I plan to perform computations on several other systems, as well. I will study the 3D $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ reaction (including *ortho-para* conversion), which is a natural extension of the collinear $\text{H}_2 + \text{H} \longrightarrow \text{H} + \text{H}_2$ case investigated in the present work. In this case, the spin statistical weights are somewhat more difficult to derive than for the 3D $\text{H}_2 + \text{D} \longrightarrow \text{H} + \text{HD}$ reaction, also examined in the current work. The main source of complications is that the thermal flux operator does not commute with all possible permutations of the three hydrogen atoms. As a next step, I will compute the reaction rate coefficient of other chemically relevant reactions, as well. Later, I plan to use the general code I developed for systems larger than the triatomic ones considered. In this case, one can also resort to reduced-dimensional models, modeling the full-dimensional quantum-dynamical description. Reduced-dimensional models

can be readily defined in GENIUSH by fixing coordinates that are not important for the dynamical description of a given chemical reaction. While the current version of the code is already capable of performing $J > 0$ computations, where J is the rotational quantum number, I only performed $J = 0$ computations, *i.e.*, I omitted the rotational degrees of freedom in the present work. In the future, I plan to extend the current results by calculating $J > 0$ rate coefficients, as well. There are several approximate treatments of rotations for rate coefficients, such as the so-called J -shifting method, which I also plan to implement and compare its performance to the exact treatment offered by my code, an extension of the GENIUSH package.

In the future, I also plan to optimize and improve the code, as well as the applied algorithms. For example, the Arnoldi algorithm, currently employed for the iterative diagonalization of the thermal flux, does not exploit the Hermitian nature of the thermal flux operator, suggesting that there is room for significant enhancement of the numerical performance of the code. Another possible improvement is the introduction of the so-called complex absorbing potentials. Complex absorbing potentials can be used during the time evolution to absorb the thermal flux eigenstates when they reach the edges of the grid; thus, reflection from the edges can be avoided.

Bibliography

- (1) Taylor, J. R., *Scattering theory: the quantum theory of nonrelativistic collisions*; Dover, Minnerola: 1972.
- (2) Schatz, G. C. *Chemical Reviews* **1987**, 87, 81–89.
- (3) Érdi, P.; Tóth, J., *Mathematical models of chemical reactions*; Princeton University Press: 1989.
- (4) Schatz, G. C.; Ratner, M. A., *Quantum mechanics in chemistry*; Dover, New York: 2002.
- (5) Henriksen, N. E.; Hansen, F. Y., *Theories of Molecular Reaction Dynamics, The Microscopic Foundation of Chemical Kinetics*; Oxford University Press: 2008.
- (6) Tannor, D. J., *Introduction to quantum mechanics: a time-dependent perspective*; University Science, Sausalito: 2007.
- (7) Miller, W. H. *The Journal of Chemical Physics* **1975**, 62, 1899–1906.
- (8) Miller, W. H. *Science* **1986**, 233, 171–177.
- (9) Miller, W. H.; Schwartz, S. D.; Tromp, J. W. *The Journal of Chemical Physics* **1983**, 79, 4889–4898.
- (10) Kabanoff, L. P.; Baym, G., *Quantum statistical mechanics*; Benjamin, New York: 1962.
- (11) Park, T. J.; Light, J. C. *The Journal of Chemical Physics* **1988**, 88, 4897–4912.
- (12) Seideman, T.; Miller, W. H. *The Journal of Chemical Physics* **1991**, 95, 1768–1780.
- (13) Park, T. J. *The Journal of Chemical Physics* **1997**, 107, 671–671.
- (14) Miller, W. H. *The Journal of Chemical Physics* **1974**, 61, 1823–1834.
- (15) Yamamoto, T. *The Journal of Chemical Physics* **1960**, 33, 281–289.
- (16) Yamamoto, T.; Miller, W. H. *The Journal of Chemical Physics* **2003**, 118, 2135–2152.
- (17) Small, M. S.; Predescu, C.; Miller, W. H. *Chemical Physics* **2006**, 322, 151–159.
- (18) Miller, W. H. *The Journal of Physical Chemistry A* **1998**, 102, 793–806.
- (19) Thompson, W. H.; Miller, W. H. *The Journal of Chemical Physics* **1995**, 102, 7409–7417.
- (20) Tromp, J. W.; Miller, W. H. *Faraday Discussions of the Chemical Society* **1987**, 84, 441.
- (21) Park, T. J.; Light, J. C. *The Journal of Chemical Physics* **1989**, 91, 974–988.
- (22) Park, T. J.; Light, J. C. *The Journal of Chemical Physics* **1991**, 94, 2946–2955.
- (23) Thompson, W. H.; Miller, W. H. *The Journal of Chemical Physics* **1997**, 106, 142–150.
- (24) Wang, H.; Thompson, W. H.; Miller, W. H. *The Journal of Chemical Physics* **1997**, 107, 7194–7201.
- (25) Manthe, U.; Matzkies, F. *Chemical Physics Letters* **1998**, 282, 442–449.
- (26) Welsch, R.; Huarte-Larrañaga, F.; Manthe, U. *The Journal of Chemical Physics* **2012**, 136, 064117.
- (27) Mátyus, E.; Czakó, G.; Császár, A. G. *The Journal of Chemical Physics* **2009**, 130, 134112.
- (28) Fábri, C.; Mátyus, E.; Császár, A. G. *The Journal of Chemical Physics* **2011**, 134, 074105.

- (29) Fábri, C.; Quack, M.; Császár, A. G. *The Journal of Chemical Physics* **2017**, *147*, 134101.
- (30) Papp, D.; Szidarovszky, T.; Császár, A. G. *The Journal of Chemical Physics* **2017**, *147*, 094106.
- (31) Simkó, I.; Szidarovszky, T.; Császár, A. G. *Journal of Chemical Theory and Computation* **2019**, *15*, 4156–4169.
- (32) Simkó, I.; Schran, C.; Briec, F.; Fábri, C.; Asvany, O.; Schlemmer, S.; Marx, D.; Császár, A. G. *Angewandte Chemie International Edition* **2023**, *62*, e202306744.
- (33) Lill, J. V.; Parker, G. A.; Light, J. C. *Chemical Physics Letters* **1982**, *89*, 483–489.
- (34) Light, J. C.; Hamilton, I. P.; Lill, J. V. *The Journal of Chemical Physics* **1985**, *82*, 1400–1409.
- (35) Dickinson, A.; Certain, P. *The Journal of Chemical Physics* **1968**, *49*, 4209–4211.
- (36) Bucknell, M. G.; Handy, N. C. *Molecular Physics* **1974**, *28*, 777–792.
- (37) Whitehead, R. J.; Handy, N. C. *Journal of Molecular Spectroscopy* **1975**, *55*, 356–373.
- (38) Sutcliffe, B. T.; Tennyson, J. *Molecular Physics* **1986**, *58*, 1053–1066.
- (39) Carter, S.; Handy, N. C. *Computer Physics Reports* **1986**, *5*, 117–171.
- (40) Handy, N. C. *Molecular Physics* **1987**, *61*, 207–223.
- (41) Császár, A. G.; Handy, N. C. *The Journal of Chemical Physics* **1995**, *102*, 3962–3967.
- (42) Podolsky, B. *Physical Review* **1928**, *32*, 812–816.
- (43) Zare, R. N., *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics*; Wiley, New York: 1988.
- (44) Tal-Ezer, H.; Kosloff, R. *The Journal of Chemical Physics* **1984**, *81*, 3967–3971.
- (45) Leforestier, C.; Bisseling, R.; Cerjan, C.; Feit, M.; Friesner, R.; Guldberg, A.; Hammerich, A.; Jolicard, G.; Karrlein, W.; Meyer, H.-D.; Lipkin, N.; Roncero, O.; Kosloff, R. *Journal of Computational Physics* **1991**, *94*, 59–80.
- (46) Kosloff, R. *Annual Review of Physical Chemistry* **1994**, *45*, 145–178.
- (47) Amos, D. E. AMOS, A Portable Package for Bessel Functions of a Complex Argument and Nonnegative Order, <http://netlib.org/amos/>.
- (48) Lehoucq, R. B.; Sorensen, D. C.; Yang, C. ARPACK: Solution of Large Scale Eigenvalue Problems by Implicitly Restarted Arnoldi Methods, Available from netlib@ornl.gov, 1997.
- (49) Eckart, C. *Physical Review* **1930**, *35*, 1303–1309.
- (50) Varandas, A. J. C. *The Journal of Chemical Physics* **1979**, *70*, 3786–3795.
- (51) Echave, J.; Clary, D. C. *Chemical Physics Letters* **1992**, *190*, 225–230.
- (52) Mielke, S. L.; Lynch, G. C.; Truhlar, D. G.; Schwenke, D. W. *The Journal of Physical Chemistry* **1994**, *98*, 8000–8008.