A QUASICLASSICAL TRAJECTORY STUDY OF $H_2 + H_2$ ENERGY TRANSFER: A SURVEY OF APPLICABILITY OF DETAILED BALANCE

by

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Abstract

State-to-state cross sections and a survey of detailed balance for transitions among the vibrational and rotational (v, j) states of H₂ $^{1}\Sigma_{g^{+}}$ below 37 mE_h as the result of collisions in the H₂ + H₂ system were determined by using the quasiclassical trajectory (QCT) method. Study of this system is necessary for an improved understanding of the kinetics in the interstellar medium to model processes occurring in the molecular clouds.

The potential energy surface of Boothroyd *et al.* (J. Chem. Phys. 116, 666, 2002) was used for trajectory calculations. The Discrete Variable Explicit Runge-Kutta (DVERK) method was used for numerical integration. State-to-state cross sections were examined for agreement with microscopic reversibility. In the majority of cases the agreement was poor. Consequently the conclusion is that QCT is not a viable method for the evaluation of state-to-state rate coefficients in the $H_2 + H_2$ system.

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Chapter 1

Introduction

1.1 The $H_2 + H_2$ system represents a useful prototype to understand interaction of two molecules

Collisions between two hydrogen molecules – H_2 being lightest molecule in nature – are among the simplest elementary chemical processes. Quantum effects are potentially important in $H_2 + H_2$ system since the vibrational – rotational energy levels within the molecule are more widely spaced than in the case of heavier molecules (Figure 1.1). By using this simple system of four nuclei and four electrons (the $H_2 + H_2$ system) a high level of precision can be attained in the theoretical work of computational chemistry which has direct applications in astrophysics. In spacecraft modelling¹ and in combustion,^{2,3} the $H_2 + H_2$ system has also been of great interest. The rotational and vibrational transitions in H_2 induced by collisions are of practical importance in models of astrophysical environments.

1.2 H_2 is an important species in interstellar medium

In the universe, hydrogen is the most abundant element. In the interstellar medium, hydrogen is present in the dominant chemical species, mostly as H and H₂. Shock fronts and photodissociation regions in giant molecular clouds have stimulated considerable interest in the role of molecular energy transfer of H₂.^{4,5} If collisional cross sections and rate coefficients of H₂ + H₂ system can be calculated accurately then these calculations can be used to build a model that can explain the cooling mechanism in the interstellar medium where star formation occurs.

A number of collisional outcomes result from $H_2 + H_2$ collisions (Table 1.1) and these outcomes can be distinguished in classical calculations and permit the detailed exploration of dynamic effects.⁶ The $H_2 + H_2$ system allows for theoretical treatments that are very transparent and can be compared directly with other theoretical and experimental results.



H2 ENERGY LEVELS

Figure 1.1: (v, j) levels of the ground state hydrogen molecule, $H_2({}^{1}\Sigma_{g}^{+})$. The dashed line is the minimum energy required for dissociation. Energy levels above this line are quasibound. The dotted line is the internal energy boundary for the states that are studied in this research work.

Table 1.1: Collisional outcomes of $H_2 + H_2$				
\rightarrow	$H_2(v'''_{ab}, j'''_{ab}) + H_2(v'''_{cd}, j'''_{cd})$			
\rightarrow	$H_2(v'''_{ac}, j'''_{ac}) + H_2(v'''_{bd}, j'''_{bd})$			
\rightarrow	$H_2(v_{ad}''', j_{ad}'') + H_2(v_{bc}'''', j_{bc}''')$			
\rightarrow	$H + H + H_2(v_{cd}''', j_{cd}''')$			
\rightarrow	$H_2(v_{ab}''', j_{ab}''') + H + H$			
\rightarrow	$\mathrm{H}_2(v_{ac}^{\prime\prime\prime}, j_{ac}^{\prime\prime\prime}) + \mathrm{H} + \mathrm{H}$			
\rightarrow	$\mathrm{H}_2(v_{ad}^{\prime\prime\prime},j_{ad}^{\prime\prime\prime}) + \mathrm{H} + \mathrm{H}$			
\rightarrow	$H_2(v_{bc}''', j_{bc}''') + H + H$			
\rightarrow	$H_2(v_{bd}''', j_{bd}''') + H + H$			
\rightarrow	$\mathrm{H} + \mathrm{H} + \mathrm{H} + \mathrm{H}$			
	$\begin{array}{c} \rightarrow \\ \rightarrow $			

^aa, b, c, and d identifies the four atoms

1.3 Computational methods in the study of molecular collisions

There are three classes of methods in the computational study of molecular collisions. These are quantum mechanical, semiclassical, and quasiclassical trajectory methods. All the methods require a potential energy surface (PES) for computational study in molecule-molecule interaction.

1.3.1 Quantum mechanical

Quantum mechanical scattering calculations on four-atom reactions have undergone significant progress from the computational perspective. All degrees of freedom are treated quantum mechanically. Like atoms are indistinguishable. Tremendous challenge has remained for the full-dimensional quantum mechanical treatment of $H_2 + H_2$ systems due to the need to treat all bonds as reactive ones.^{7–13} The size of quantum calculations rises with the number of channels required for convergence which in turn rises with increases of total energy. Therefore, quantum calculations can be possible in principle, but not practically, at higher energies for the $H_2 + H_2$ system and its isotopic analogs.

1.3.2 Semiclassical

Semiclassical methods describe some degrees of freedom of a system quantum mechanically whereas the other degrees of freedom are treated classically.^{14,15} These methods are particularly useful for the description of the large-angle elastic scattering of chemical reactive systems. Examples of semiclassical methods include WKB approximation and wave packet methods. The theory of elastic scattering of atoms has been one of the most successful applications of semiclassical techniques. Semiclassical methods are expensive for the calculation of large number of state-to-state cross sections in $H_2 + H_2$ system.¹⁶

1.3.3 Quasiclassical trajectory (QCT)

Using classical mechanics, the quasiclassical trajectory method describes the collisions of atoms and molecules. All degrees of freedom are treated classically. Like atoms are distinguishable. This method does not increase in difficulty with increasing energy. At the present this is the most practical method of obtaining large number of state-to-state cross sections and rate coefficients for a system like $H_2 + H_2$.

1.3.4 Advantages and disadvantages of the quasiclassical trajectory method

The quasiclassical trajectory method uses the classical equations of motion to describe the collision between a target molecule and a collisional partner. Since the trajectory is classical, there is a need to assign the trajectory result to a final quantum state. Results from the QCT method can be rotationally and vibrationally hot¹⁷ if the trajectory results are assigned to final rotational and vibrational states by using the bin histogram method. The cross sections of endoergic (upward) transitions calculated by using QCT method can be shifted to higher rotational or vibrational level compared to quantum and experimental results.

The QCT method limits the validity of rate coefficients at temperature between 600 and 10000 K. The reason for the lower limit is because QCT does not include tunneling. There is also a consideration of zero point energy leak in the QCT method when the potential energy barrier to exchange is traversed classically with less than the zero point energy that would be required to do this quantum mechanically. The H₄ surface extrapolates to the H₃ surface when one H atom is removed to infinite distance. There is a conical intersection between the ground state and an electronically excited state of H₃ at energy of 100 mE_h (63 kcal/mol).¹⁸ Above 10000 K, there is a possibility of electronic excitation and then the system is not described adequately by the potential energy surface for the ground electronic state.¹⁹ For H₄ PES Boothroyd *et al.*²⁰ identified the conical intersection with the first electronically excited state but did not include it in their potential.

1.4 Motivation for this study

 H_2 molecules are the dominant molecular species in interstellar medium. Quantum calculations are expensive for the determination of large numbers of state-to-state cross sections and rate coefficients. The QCT method is comparatively inexpensive.

Rate coefficients must obey microscopic reversibility. The rate coefficients calculated by using QCT obeyed microscopic reversibility in $H + H_2$ system except at low temperatures.¹⁹ The $H_2 + H_2$ system is a system of light atoms similar to $H + H_2$ including one more atom and more degrees of freedom with a different potential. Whether detailed balance is obeyed for calculation of state-to-state cross sections and rate coefficients for $H_2 + H_2$ is important to assess the feasibility of using QCT to calculate state-to-state cross sections.

1.5 Research objectives

The goal of this study is to do a survey of detailed balance of state-to-state cross sections for the transitions resulting from the $H_2 + H_2$ system by using the QCT method. The specific objectives of this study are:

 Use the QCT method to determine state-to-state cross sections for the collisions in H₂ + H₂ system for those states of H₂ with internal energy below 37 mE_h (1 eV).
 Survey how well those cross sections follow detailed balance.

3. Assess the feasibility of the QCT method for the calculation of state-to-state rate coefficients in $H_2 + H_2$ system.

1.6 Thesis outline

The objectives of this research are addressed in the following chapters of this thesis. Chapter 2 is a survey of $H_2 + H_2$ literature including a survey of experiments on the $H_2 + H_2$ system and of H_4 potential energy surfaces and calculations thereon.

Chapter 3 describes the QCT method including issues for the binning method. There is also a discussion about numerical integration and calculation of cross section and rate coefficients in Chapter 3. Microscopic reversibility and application of microscopic reversibility in the calculation of cross sections and rate coefficients are also discussed in this chapter. The assessment of detailed balance with statistical analysis are included in Chapter 3.

Chapter 4 reports on the examination of the microscopic reversibility calculations for $H_2 + H_2$ system and results with the survey of internal energy distribution. The results of internal energy distributions and their significance of differences are also included in Chapter 4. Chapter 5 concludes with the major findings of this study and provides suggestions for the future research directions.

Chapter 2

Survey of $H_2 + H_2$ literature

Collisions that occur between two H₂ molecules in interstellar molecular clouds are of great relevance in astrophysics. In the interstellar medium, H₂ may act as a coolant in giant molecular clouds of low densities where star formation occurs. Within these clouds, strong shock waves can cause rotational and vibrational excitation of the H_2 molecules which can lead to dissociation of H_2 into free H atoms²¹ or to the emission of photons. McCaffery and Marsh used a computational model of energy flow to study translation-to-internal energy conversion in a gas ensemble consisting of H₂ in a bath of H atoms.²² Their study suggested that the translation-to-internal energy conversion within H₂ could enhance the cooling mechanism in interstellar clouds. The presence of H atoms has the potential to change the kinetics of the system because H atoms are more efficient colliders with respect to energy transfer and dissociation than are H₂ molecules. Dissociative cooling arises from the collisions leading to dissociation of the molecules. When a molecule dissociates, some of the kinetic energy and internal energy are used in dissociation and this energy can never again be available because of the low probability of recombination. The cloud cools after losing some energy in dissociation.

The cooling processes can also involve the conversion of kinetic energy to radiant energy as photons which can escape from the system. This typically occurs through collisional excitation, followed by radiative decay through quadrupole emission. Cooling is necessary for star formation. Information about these phenomena is necessary to understand the cooling mechanisms in the interstellar medium.

2.1 $H_2 + H_2$ experimental

In 1975, the vibrational relaxation rate of ortho- and para-H₂ between 40 and 500 K was measured by Audibert *et al.*²³ Nearly 12 years after this experiment, the rotational relaxation in vibrationally excited H₂ and D₂ in collisions with H₂, D₂ and He at 300 K was studied by Meier *et al.*²⁴ in 1986. From their studies it was found that, in general, the pure rotational energy transfer rate coefficients are larger than the corresponding vibrational energy transition rate coefficients. For the v = 2 vibrational level, the direct measurement of energy transfer of vibration-vibration and vibration-translation rate coefficients near 300 K were reported by Kreutz *et al.*²⁵ in 1988.

Farrow and Chandler²⁶ presented experimental results in the same year for the rovibrational energy transfer rate coefficients between H₂ molecules at 295 K colliding in their ground and first excited vibrational levels. Theoretical and experimental rate coefficients for rotational excitations in p-H₂ – p-H₂ collisions between 2 and 110 K were reported by Maté *et al.*²⁷ in 2005. Quantum mechanical calculations based on the coupled channel method were used for their theoretical study. From their experimental studies, it was found that the pure rotational energy transfer rate coefficients are larger than the corresponding vibrational energy transfer rate coefficients.

Experimental rate coefficients for vibrational-vibrational transitions for v=0-5 at 300 K were reported by Ahn *et al.*²⁸ in 2007. They studied both non-resonant and resonant VV process. For non-resonant VV process they studied $H_2(v=1) +$ $H_2(v=1) \rightarrow H_2(v=2) + H_2(v=0)$ and for resonant VV process, $H_2(v=1) + H_2(v=0)$ $\rightarrow H_2(v=0) + H_2(v=1)$. For both processes, the measured rate coefficients were found to be comparable to previous experimental results of Kreutz *et al.*²⁵ and Farrow and Chandler.²⁶

Some significant differences exist between theory and experiment for both the non-resonant and resonant vibration-vibration transitions discussed above. The semiclassical results for the resonant vibration-vibration process of Ahn *et al.*²⁸ are found to be about a factor of 30 smaller than the experimental value. The non-resonant vibration-vibration process $(1,1 \rightarrow 2,0)$ is more efficient than the resonant process predicted by semiclassical calculation while experiment showed the latter rate coefficient is 2.5 times larger.²⁸

In 2009, Kelley²⁹ studied vibration-vibration and vibration-translation energy exchange in $H_2 + H_2$ collisions. He reported results of VV and VT using a semiclassical approach in which relative translational motion is treated classically and both rotation and vibration were treated quantum mechanically. The dependence of the H_4 interaction potential on the H-H separations was modeled based on a He-H₂ potential and transition probabilities were calculated by using first order perturbation theory. For the resonant vibration-vibration process described above, this approach produced improved agreement with experiments but it is less satisfactory for the other non-resonant vibration-vibration processes for the diatom-diatom system.

2.2 H₄ potential Energy Surface and Calculations

A potential energy surface is generally developed within the adiabatic and Born-Oppenheimer approximation to model chemical reactions and interactions in simple chemical and physical systems. In the test case of molecule-molecule interactions, the potential energy surface of H_4 is of great importance for quantum chemistry since it is needed for quantum calculations. Being the simplest test case, the H_4 energy surface is necessary for the basic understanding of intermolecular energy transfer and chemical reactions between molecules. It is also important for the comparison of theoretical predictions against experimental results.

For a detailed study of the calculation of recombination rate coefficients for hydrogen containing compounds in the gas phase, Schwenke² constructed a new potential hypersurface for H_4 in 1988. This new potential was a faithful representation for *ab initio* electronic structure calculations at that time. They used high accuracy level *ab initio* energies at 92 geometries with C_{2v} symmetry. This potential is unchanged under the exchange of H atoms and reproduces the H₃ potential when one H atom is removed. They used resonance complex theory and an energy transfer mechanism over the temperature range 100-5000 K to estimate the rate coefficients of three-body recombination by using quasiclassical trajectory calculations. Over a broad temperature range, the predicted rate coefficients were approximately a factor of two smaller than experimental results.

In 1991 Boothroyd *et al.*³⁰ reported an extensive study of the H₄ PES presenting *ab initio* energies at 6101 geometries. They used the multiple reference configuration interaction (MRD-CI) program with a large basis set. In 1992, Wind and Roeggen calculated the potential energy surface of H₄ within the rigid rotor approximation by using an extended geminal model.³¹ The total electronic energies for 16 different internuclear distances from 3 to 12 au, and 7 relative orientations for each distance were calculated by using a [8s, 4p, 2d] subcontracted Gaussian type basis set and the numerical model EXRHF3. The semiclassical calculations of Billing and co-workers³²¹⁶³³³⁴ were the most widely cited results of that time. They used an angle-averaged potential based on the functional form of the potential energy surface suggested by Schwenke.²

Using an extension of Schwenke's² approach to fitting the H_4 potential this was carried out both by Keogh³⁵ and by Aguado³⁶ *et al.*. The initial 6101 points of Boothroyd *et al.*³⁰ were fitted to a six-dimensional many-body expansion form by Aguado, Suarez, and Paniagua (ASP)³⁶ in 1994. They performed a four-body generalization of the global fitting procedure proposed by Aguado *et al.*³⁷ for triatomic systems. With respect to the permutations of the H atoms this global H_4 potential energy surface is totally symmetric and satisfied the strategies that are used in quantum scattering calculations.

A slightly-improved version of the PES of Keogh³⁵ using an extension of Schwenke's approach to fitting H_4 was developed by Martin *et al.*³⁸ and used by

Mandy et al.⁶ for quasiclassical trajectory calculations of $H_2 + H_2$ collisions.

Another potential energy surface has been calculated by Diep and Johnson for the rigid monomer model of $(H_2)_2^{39}$ in 2000. They have employed the complete basis set limit using coupled-cluster theory with single, double and perturbational triple excitations [CCSD(T)]. A four-term spherical harmonics expansion model was selected to fit the surface. This potential energy surface generated the quadrupole moment to within 0.58% and the experimental Van der Waals well depth to within 1%. From the fitted potential energy surface the second virial coefficient has been computed. In the temperature range of 100-500 K, the semiclassical treatment of quantum mechanical effect on the second virial coefficient was utilized. By combining Feynman's path integral formulation and Monte Carlo integration, they have constructed a new technique for computing the quantum second virial coefficient and compared it with published experimental measurements. Diep and Johnson calculated the second virial coefficient from this PES and it showed good agreement with the experimental results from 15-500 K.

In 2002, a chemically accurate potential energy surface was calculated by Boothroyd *et al.*²⁰ which demonstrated significant inaccuracies in other analytic H_4 surfaces available at that time. They had computed 42079 new *ab initio* H_4 energies and the original 6101 *ab initio* energies to improve the coverage of the H_4 conformation space. A large portion of conical intersection of the ground state with the first excited state and both the ground state energy and first few electronically excited state energies were calculated. The 6101 *ab initio* H_4 energies from Boothroyd *et al.*³⁰ provided information to fit an H_4 PES that could approach chemical accuracy.

Boothroyd, Martin, Keogh, and Peterson $(BMKP2)^{20}$ reported a more elaborate fit of the 48180 *ab initio* points which is of chemical accuracy over a large configuration space. The PES of Boothroyd *et al.*³⁰ provided for the first time full coverage of the entire six-dimensional conformation space of H₄ that can be reached by a pair of H₂ molecules colliding with sufficient energy to dissociate one or both of the molecules. They demonstrated that the PES of Schwenke² had errors of more than an order of magnitude in the repulsive wall of H_4 interaction region.

A six-dimensional potential energy surface for the $(H_2)_2$ dimer was constructed by Hinde⁴⁰ based on coupled cluster electronic structure calculations in 2008. Large atom-centered Gaussian basis sets and a small set of midbond functions were employed at the center of mass of the dimer. The bound and quasibound states of the dimer are described by this surface. A close-coupled approach was used to compute the energies of these bound and quasibound dimer states. They have compared the computed energies for infrared and Raman transitions involving rovibrational levels (v, j) = (0,0), (0,2), (1,0) and (1,2) with experimentally measured transition energies. They have used four of the experimentally measured dimer transition energies to make two empirical adjustments to the *ab initio* potential energy surface.

Among these potential energy surfaces, only those of Aguado *et al.*, Boothroyd *et al.*, and Hinde⁴⁰ are global potential surfaces. Aguado *et al.* calculated a global potential energy surface of 6101 *ab initio* energies with root mean square error (rms) value of 2 mE_h. An accurate global potential energy surface was also calculated by Boothroyd *et al.* with an rms error of 1.43 mE_h. Based on coupled-cluster electronic structure calculations a six-dimensional potential energy surface for the H₄ was constructed by Robert J. Hinde with the objective of achieving spectroscopic accuracy.

For quantum calculations, the ASP PES is more efficient because integration over the angular coordinates can be done analytically. In QCT calculations, derivatives of the potential are needed to obtain the forces and to do numerical integration of the equations of motion. Analytical derivatives are not available for the Hinde or ASP PES. For the BMKP2 PES analytical derivatives are available. Calculating a trajectory that involves numerical evaluations of the derivatives requires about 10 times as much computer time as does a trajectory where analytical derivatives are available.

In this work, transitions of the states below 37 mE_{h} (1 eV) energy of two hydro-

gen molecules are studied by using BMKP2 PES (Table 2.1). The state-to-state cross sections for transitions among the vibrational and rotational (v, j) states of (0,0), (0,1), (0,2), (0,3), (0,4), (0,5), (0,6), (0,7), (0, 8), (0, 9), (1,0), (1,1), (1,2), (1,3), (1,4), (1,5) of each H₂ molecule as the result of collisions in H₂ + H₂ system were determined by using quasiclassical trajectory method.

State	V	j	$E_{int} (mE_h)$	E_{int} (eV)
	0	0	9.892770	0.267929187
Deve	0	2	11.50692	0.311645695
	0	4	15.21663	0.412116981
	0	6	20.89275	0.565845312
rala	0	8	28.34991	0.767810062
	1	0	28.85506	0.781491207
	1	2	30.38861	0.823024961
	1	4	33.91218	0.918454793
	0	1	10.43247	0.282546005
	0	3	13.10638	0.354964485
Ortho	0	5	17.81936	0.482607774
	0	7	24.41199	0.661158062
	0	9	32.67760	0.885018332
	1	1	29.36784	0.79537891
	1	3	31.90798	0.864174376
	1	5	36.38355	0.985387811

Table 2.1: States below 37 $\mathrm{mE_{h}}\ \mathrm{(1eV)}$

Chapter 3

Methods of calculation

3.1 An overview of the quasiclassical trajectory method

3.1.1 Quasiclassical trajectory method

Using classical mechanics, it is possible to simulate collisions of chemical species if the interaction energies are described by a well-behaved potential energy surface. The atoms are moving under the influence of an interaction potential and are assumed to be point masses moving according to Newton's equations of motion. The first derivatives of the potential are used to determine the forces involved. By integrating the equations of motion, a trajectory of a collision can be determined.

By using the BMKP2²⁰ potential energy surface, fully six-dimensional quasiclassical trajectories have been run. For each hydrogen molecule, the initial rotational and vibrational energy were assigned precisely to the corresponding quantum states while the initial translational energy was fixed at the desired value. For the collisions of $H_2 + H_2$, the maximum value of total energy is 480 mE_h (13 eV). Above this energy the electronic ground state potential energy surface is no longer an adequate description of the system. From this total energy, the translational energy is decreased in intervals of 8 mE_h (0.220 eV) until 30 mE_h (0.866 eV) above that required for dissociation of both H₂ molecules is reached. Translational energies were then decreased by 2 mE_h (0.0433 eV) from that total energy down to ensure adequate characterization of the threshold for dissociation and energy transfer. Translational energy was decreased until all trajectories were observed to be elastic. For the impact parameter, stratified sampling is used.

3.1.2 Numerical integration

After initialization, the coordinate system has been transformed from that used for selection of initial conditions to one more appropriate for integration. The forces are determined by the derivatives of the interaction potential and the motion of the atoms was treated as completely classical. Using a variable step Runge-Kutta method the equations of motion are integrated. Throughout the integration, conservation of energy and of momentum is monitored.

3.1.2.1 Runge-Kutta Method

The Runge-Kutta technique of any order is one of the general methods for constructing stable and efficient reaction integrators. For solving ordinary differential equations (ODEs), Runge-Kutta (RK) methods are among of the most efficient classes of methods. Some of these Runge-Kutta methods have excellent stability properties and they are used widely to solve stiff ODEs.⁴¹

3.1.2.2 Predictor-Corrector Method

In numerical analysis, a predictor-corrector method is an algorithm that proceeds in two steps. First, the prediction step calculates a rough approximation of the desired quantity. Second, the corrector step refines the initial approximation using another means. Predictor-corrector (PC) methods have been used as one of the major classes of methods on parallel computers for solving non-stiff ODEs. A desirable feature of a multistep method is that the local truncation error can be determined and a correction term can be included, which improves the accuracy of the answer at each step.

Predictor-corrector methods need a well-behaved function for integration. The potential for the $H_2 + H_2$ system was shown not to be sufficiently well-behaved for integration by this method.³⁵ Therefore, the DVERK program is used in this present research.

3.1.2.3 Discrete Variable Explicit Runge-Kutta (DVERK) Program

The DVERK Program is a double precision subroutine for solving systems of first-order ordinary differential equations with initial conditions based on Runge-Kutta formulas of order 5 and 6. This program attempts to keep the global error within a tolerance specified by the user. The magnitude of the relative error depends on three factors. These are: the kind of error control that is used, the function being integrated, and the range of integration i.e. step size.

There are also various options in this program including different kinds of error control, restrictions on step sizes, and interrupts that permit the examination of the state of the calculation as automatic modifications are possible during intermediate stages. The equations of motion are integrated using a variable step Runge-Kutta integrator. In this program, any options can be either initiated or altered from a previous selection prior to re-entry to the subroutine. It does not need user intervention to successfully complete a trajectory.

3.1.3 Analysis of the quasiclassical trajectory results

The behaviour of a quasiclassical trajectory is completely described by classical mechanics. Therefore some conventions need to be used in assigning the trajectory result to the final quantum states. The atoms are paired for analysis of final momenta and energy on the basis of the shortest interatomic distance. Angular momentum is determined for each pair and then within the pair, motion along the line of centers is considered and examined to determine whether the pair is bound. If the pair is bound, then quasiclassical quantum numbers are calculated. This produces continuously valued (v'', j'') quantum numbers, which are then assigned to the discrete (v''', j''') and (v'''', j''') states by using a binning method (Figure 3.1). In this study, four dimensional bins are used, based on the final vibrational and rotational quantum numbers of both H₂ molecules.

3.1.3.1 Binning Method

The cross sections can be calculated by using the bin histogram method.⁴² In this method, the continuously-valued (v'', j'') state values are assigned to a product (v''', j''') quantum state in accordance with the following criteria:

$$\begin{aligned} (v''' - 1/2) &\leq v'' < (v''' + 1/2) \\ (j''' - 1) &\leq j'' < (j''' + 1) \text{ (when } j''' \neq 0) \\ 0 &< j'' < 1 \text{ (when } j''' = 0) \end{aligned}$$

where j''' is odd for ortho and j''' is even for para. The v''' value was taken as the nearest integer to v''.

In non-reactive collisions, ortho-para interconversion is forbidden and when the initial values of j are even, then only the even j''' values are permitted. Similarly, when the initial j values are odd, then only the odd j''' values are permitted in non-reactive collisions. Thus from a para-para initial state, non-reactive trajectories lead only to para-para final states. Similarly non-reactive trajectories from an ortho-ortho initial state lead only ortho-ortho products and from an ortho-para state to ortho-para products.

The exchange reaction produces both para and ortho products, so the results of exchange trajectories must be assigned appropriately to the para and ortho states. The classical calculation does not include spin but the 3:1 ratio for nuclear spin is considered in the calculation of cross sections. The reactive trajectories are binned four times. When the final state is ortho-ortho, a weighting of $\frac{1}{16}$ is used to calculate the cross sections. When the final state is para-para, a weighting of $\frac{9}{16}$ is used. When the final state is ortho-para, a weighting of $\frac{3}{16}$ is used to calculate the cross sections. When the final state is para-ortho, a weighting of $\frac{3}{16}$ is used.



Figure 3.1: Schematic of binning method. The axes delineate (v', j') space. The \times indicates the trajectory result (v'', j''). The dotted lines represent the boundaries of the bins common to all methods.

3.1.3.2 Calculation of Cross Sections

When a batch of trajectories has been converged with respect to impact parameter the integral cross sections, σ , can be determined by using following formula:¹⁹

$$\sigma \pm d\sigma = \sum_{i} P_{i}A_{i} \pm \sqrt{\frac{\sum_{i} A_{i}^{2} \left[\frac{P_{i}(1-P_{i})}{N_{i}} + \frac{1}{N_{i}^{2}} + \frac{1}{N_{i}^{3}}\right]}{\left[\left(1 + \frac{3}{N_{i}}\right)\left(1 + \frac{2}{N_{i}}\right)^{2}\right]}}$$

By summing over the annuli of area A_i , the cross sections and their errors are obtained. The number of trajectories run in annulus *i* is N_i . Here n_i represents the number of trajectory events that lead to the outcome of interest. The probability is $P_i = \frac{n_i}{N_i}$. For non-negligible probabilities, $P_i >> \frac{1}{N_i}$ and the formula for the error reduces to that of a binomial distribution.

3.1.3.3 Calculation of Rate Coefficients

For a gas at equilibrium, the distribution of thermal energy is described by the Maxwell-Boltzmann distribution. To determine rate coefficients, the Maxwell-Boltzmann distribution is convolved with the excitation function, $\sigma(E)$. The thermal rate coefficient, $\gamma(T)$, is:¹⁹

$$\gamma(T) = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \int_{E_{\circ}}^{+\infty} \frac{E}{kT} \sigma(E) exp\left(\frac{-E}{kT}\right) d\left(\frac{E}{kT}\right)$$

The value of $\gamma(T)$ is sensitive to E_{\circ} which must be determined. For endoergic processes E_{\circ} is the energy difference between the final and initial states and, for exoergic processes, E_{\circ} is zero. At lower temperatures, the most significant contributions to $\gamma(T)$ come from the cross sections near threshold. Cross sections need to be determined at finely-spaced translational energies near threshold.

3.2 An overview of microscopic reversibility

3.2.1 Microscopic reversibility

Microscopic reversibility or detailed balance relates the cross section for a transition from state 1 to state 2 to that for the transition from state 2 to state 1. The equation is:

$$\sigma(1 \to 2; E_{1,rel})g_1E_{1,rel} = \sigma(2 \to 1; E_{2,rel})g_2E_{2,rel}$$

where $E_{2,rel} = E_{1,rel} - \Delta E$, ΔE is $E_{2,int} - E_{1,int}$, that is the difference of internal energies in the states, g is the statistical weight for each state, and $E_{1,rel}$ and $E_{2,rel}$ represent translational energies for respective states. Therefore, for each transition connecting states 1 and 2, two independent estimates of the cross section can be obtained.

The cross sections which are obtained from trajectories originating in state 1 are defined as direct cross sections and those obtained from the trajectories originating in state 2 are defined as indirect cross sections. In QCT calculations, microscopic reversibility is not expected to be obeyed rigorously because of the way of the quantization is imposed. Direct trajectories start precisely at the initial (v, j) and (v', j')bin and they end anywhere of the final (v''', j''') and (v'''', j'''') bin. Indirect trajectories are the reverse and may be thought of as starting precisely at the (v''', j''') and (v'''', j''') bin and ending somewhere in (v, j) and (v', j') bin.

3.2.2 Microscopic reversibility and rate coefficients

Microscopic reversibility can be applied with a thermal distribution of translational energy. The rate coefficients obey:

$$\gamma(1 \to 2)g_1 = \gamma(2 \to 1)g_2 \exp\left(-\frac{\Delta E}{KT}\right)$$

It is then possible to obtain two estimates of rate coefficients for a particular transition. The first is directly from state 1 to state 2. The second one is to apply microscopic reversibility or detailed balance to the rate coefficient from state 2 to state 1 to obtain a rate coefficient from state 1 to state 2. These two estimates may be combined to give improved rate coefficients that obey detailed balance. Microscopic reversibility must be obeyed if equilibrium is to be attained. If it is not obeyed, the rate coefficients will not be able to be used in a meaningful way.

3.2.3 Microscopic reversibility in $H + H_2$ system

It has been shown that for $H + H_2$ system, the rate coefficients may differ when microscopic reversibility is applied.¹⁷ At high temperature, microscopic reversibility was obeyed well for rate coefficients but at low temperature it showed discrepancies. Hence, after applying microscopic reversibility the rate coefficients determined are not precisely equal to those generated directly from cross sections with a piecewise linear excitation function convolved with the Maxwell-Boltzmann distribution. At high temperature, the forward and reverse rate coefficients may be combined to produce rate coefficients that rigorously obey microscopic reversibility. This fact suggests that the application of microscopic reversibility can be used to seek to improve the evaluation of cross sections and rate coefficients in the $H_2 + H_2$ system.

The quasiclassical cross sections for a transition in the upward or endoergic direction are susceptible to a systematic error in cross sections near threshold leading to an over-estimation of their value. This is due to trajectory results being assigned to a particular (v, j) box when the center of the box is not energetically accessible (See figure 3.1). This is known as the barely-in-the-box phenomenon. This leads "hotness" in calculating cross sections by using QCT.

3.2.4 Microscopic reversibility in $H_2 + H_2$ system

The $H_2 + H_2$ system is more complicated system than the $H + H_2$ system. For $H_2 + H_2$ system, four quantum numbers are required to describe each of the initial and final states. This means that a four-dimensional bin is used instead of a two-dimensional bin to assign the trajectory outcome to a state. In this system, the transition of one molecule may be downward in energy and other one is upward in energy. Therefore, the applicability of microscopic reversibility may be a challenge for this system with more degrees of freedom. The rate coefficients of a system must obey microscopic reversibility. The applicability of detailed balance to cross sections for the $H_2 + H_2$ system is assessed in this study.

3.3 Enumeration of transitions considered

There were 16 states considered for each hydrogen molecule below 37 mE_h (1 eV) energy (Table 2.1). Among these 16 states, there are 136 possible combinations of quantum numbers for two hydrogen molecules. There are 36 para-para, 36 orthoortho, and 64 ortho-para or para-ortho combinations for two hydrogen molecules to be considered.

For inelastic non-reactive collisions, transitions are restricted to para-para, orthoortho, and ortho-para or para-ortho states. There are total of 666 [S=36(36+1)/2=666] transitions for the 36 para-para states. There are total of 666 [S=36(36+1)/2=666] transitions for the 36 ortho-ortho states. There are total of 2080 [S=64(64+1)/2=2080] transitions for the 64 ortho-para or para-ortho states. In one direction, the total transitions are 3276 (3412-136=3276) with exclusion of 136 elastic transitions. For both directions (endoergic and exoergic), with the exclusion of elastic transitions, a total of 6552 ($3276 \times 2=6552$) transitions are considered.

3.4 Assessment of detailed balance

3.4.1 Statistical analysis

Since a total of 6552 transitions is considered, there is a need for a robust method to classify whether the cross sections for a transition are following detailed balance. The translational energy grids of endoergic and exoergic cross sections do not match each other exactly. In order for detailed balance to be applicable at the cross section level, the total energy must match.

$$E_{tot} = E_{1,int} + E_{1,rel} = E_{2,int} + E_{2,rel}$$

$$E_{2,rel} = E_{1,rel} + E_{1,int} - E_{2,int}$$

The translational energy grid $E_{1,rel}$ of one set of cross sections is taken as the reference set and the other set of cross sections is interpolated to obtain cross sections and errors at the corresponding $E_{2,rel}$.

3.4.2 Interpolation of cross sections and errors

The following mathematical calculations were used to evaluate the indirect cross section at the desired energy to assess the applicability of detailed balance to the cross sections. The cross section, σ , is assumed to be related to translational energy, E, by the following piecewise linear relationship where $E_1 < E_{2,rel} < E_2$:

$$\sigma = \text{slope} \times \text{E} + \text{intercept}$$

$$\text{Slope} = \left(\frac{\sigma_2 - \sigma_1}{E_2 - E_1}\right)$$

$$\text{Intercept} = \sigma_1 - E_1 \times \text{Slope}$$

$$= \sigma_1 - E_1 \times \left(\frac{\sigma_2 - \sigma_1}{E_2 - E_1}\right)$$

$$= \left(\frac{E_2 \times \sigma_1 - E_1 \times \sigma_1}{E_2 - E_1}\right) - \left(\frac{E_1 \times \sigma_2 - E_1 \times \sigma_1}{E_2 - E_1}\right)$$

$$= \left(\frac{E_2 \sigma_1 - E_1 \sigma_2}{E_2 - E_1}\right)$$
Therefore, σ^* will be:

$$\sigma^* = \left(\frac{\sigma_2 - \sigma_1}{E_2 - E_1}\right) \times E^* + \left(\frac{E_2 \sigma_1 - E_1 \sigma_2}{E_2 - E_1}\right)$$
$$= F(\sigma_1, \sigma_2)$$

Therefore to get $d\sigma^*$, σ^* as a function of σ_1 and σ_2 is taken into account.

$$F(\sigma_1, \sigma_2) = \sigma^*$$

$$\left(\frac{\partial F}{\partial \sigma_1}\right) = \left(\frac{-E^*}{E_2 - E_1}\right) + \left(\frac{E_2}{E_2 - E_1}\right)$$

$$= \left(\frac{E_2 - E^*}{E_2 - E_1}\right)$$

$$\left(\frac{\partial F}{\partial \sigma_2}\right) = \left(\frac{E^*}{E_2 - E_1}\right) - \left(\frac{E_1}{E_2 - E_1}\right)$$

$$= \left(\frac{E^* - E_1}{E_2 - E_1}\right)$$

Therefore
$$(d\sigma^*)^2 = \left(\frac{E_2 - E^*}{E_2 - E_1}\right)^2 (d\sigma_1)^2 + \left(\frac{E^* - E_1}{E_2 - E_1}\right)^2 (d\sigma_2)^2$$

After obtaining cross sections and errors for corresponding energies, the Z-test is used. The Z-test statistic is:

$$Z = \left(\frac{\sigma - \sigma^*}{\sqrt{(d\sigma)^2 + (d\sigma^*)^2}}\right)$$

If σ and $\sigma *$ are two independent measurements of cross sections for the same transition at the same total energy and they agree then 68% of the time Z will be between +1 and -1 and 95% of the time between +2 and -2. For large batches of trajectories N_i is large and the binomial distribution approaches the normal distribution when $P_i >> \frac{1}{N_i}$ (Section 3.1.3.2). A typical data set consists of between 180 and 300 points. Results for each data set are classified as follows:

-Direct and indirect cross sections for a transition that agree with detailed balance within one standard deviation 68% of the time and within the two standard deviations 95% of the time are classified as Strongly Agree (STA).
-Direct and indirect cross sections for a transition that agree with detailed balance within one standard deviation 68% of the time or within the two

standard deviations 95% of the time are classified as Somewhat Agree (SWA). -Direct and indirect cross sections for a transition that **neither** agree with detailed balance within one standard deviation 68% of the time **nor** within the two standard deviations 95% of the time are classified as Disagree (DIA).

3.4.3 Histograms of internal energy distribution

Three classes of agreement with detailed balance were categorized from the assessment of agreement of direct and indirect cross sections. There may be a possibility for similar internal energy distributions within each class. If there are any distinct energy distributions among the three classes of agreement then that could explain why some of the cross sections followed detailed balance and others did not. To investigate the distributions of internal energy among these three classes of agreement with detailed balance, the distribution of final internal energy is examined for selected transitions (Figure 3.2).

In this test, there are 20 bins of internal energy that used to generate histograms of energy distributions. The total energy range used is 66.63 mE_{h} to cover the internal energy span of the four-dimensional bin associated with the four quantum numbers of two hydrogen molecules. Four translational energies (approximately 100, 200, 300, and 400 mE_h) were examined.



Figure 3.2: Selected cases for three classes of agreement of direct and indirect cross sections. The vertical axis is the cross section in a_0^2 and the horizontal axis is the translational energy in E_h . The square indicates direct cross section and the circle is for indirect cross section. First three cases from Strongly Agree Class for the transitions $H_2(0,1) + H_2(1,4) \rightarrow H_2(1,1) + H_2(0,6), H_2(0,3) + H_2(0,6) \rightarrow H_2(0,7) + H_2(0,2), and H_2(0,4) + H_2(0,9) \rightarrow H_2(0,8) + H_2(0,5)$ (Top row $a_1 - a_3$). Second three from Somewhat Agree Class for the transitions $H_2(0,2) + H_2(1,5) \rightarrow H_2(0,8) + H_2(0,3), and H_2(0,4) + H_2(0,6) + H_2(0,5), H_2(0,2) + H_2(1,5) \rightarrow H_2(0,8) + H_2(0,3), and H_2(0,4) + H_2(0,1) \rightarrow H_2(1,2) + H_2(1,3)$ (Middle row $b_1 - b_3$). Last three from Disagree Class for the transitions $H_2(0,1) + H_2(0,2) \rightarrow H_2(0,7) + H_2(0,4), H_2(0,3) + H_2(1,5) \rightarrow H_2(0,7) + H_2(0,9), and H_2(0,3) + H_2(0,7) \rightarrow H_2(0,3) + H_2(1,3)$ (Bottom row $c_1 - c_3$).

3.4.4 χ^2 -test for the histograms of energy distribution

To investigate the significance of differences in distributions of internal energy distributions among the three classes of agreement of direct and indirect cross sections, the χ^2 -test is used. The *a priori* distribution is taken as the Gaussian distribution centered on exact quantum energy of the final state. χ^2 values were found from the differences of observed and expected values of the histogram bins. Selected cases from the three classes of agreement of direct and indirect cross sections were examined to assess the significance of differences in energy distributions.

Chapter 4

Insights from examination of microscopic reversibility calculation

4.1 Comparison of direct and indirect cross sections by using Z-test

4.1.1 Z-test results

A total of 6552 transitions were examined of which 472 (242 in the endoergic and 230 in the exoergic direction) were classified as in the STA Class, 590 (301 in the endoergic and 289 in the exoergic direction) as in the SWA Class, and 5490 (2733 in the endoergic and 2757 in the exoergic direction) as in the DIA Class (Table 4.1). The number of points of the translational energy grids for the transition in one direction are not equal to the number of points of the translational energy grid in the other direction for the transition. The justification for this energy grid lies in how the rate coefficients are calculated (Section 3.2.1). As a result of this algorithm the translational energy grids do not match precisely for endoergic and exoergic direction. This means that a transition in one direction may be classified differently than the same transition in the other direction.

Table 4.1: Detailed balance results for transitions of direct and indirect cross sections with respect to Z-test

Exoergic Endoergic	strongly agree	somewhat agree	disagree	total
strongly agree	170	50	10	230
somewhat agree	61	166	62	289
disagree	11	85 2661		2757
total	242	301	2733	6552

4.2 Survey of histograms of energy distribution results

4.2.1 Analysis of internal energy distribution

From each of the three classes of agreement three cases (for a total of nine cases) were selected based on the similar relative errors of the direct and indirect cross sections for the examination of histograms of internal energy distribution (Section 3.4.3). The final internal energy distribution for the transition $H_2(0,1) + H_2(1,4) \rightarrow$ $H_2(1,1) + H_2(0,6)$ was examined from the STA Class (Figure 4.1) and was found to be normally distributed according to the χ^2 -test. Additional cases for the transitions $H_2(0,6) + H_2(1,1) \rightarrow H_2(1,4) + H_2(0,1)$ (Figure 4.2), $H_2(0,3) + H_2(0,6) \rightarrow H_2(0,7)$ $+ H_2(0,2)$ (Figure 4.3), $H_2(0,2) + H_2(0,7) \rightarrow H_2(0,6) + H_2(0,3)$ (Figure 4.4), $H_2(0,4)$ $+ H_2(0,9) \rightarrow H_2(0,8) + H_2(0,5)$ (Figure 4.5), and $H_2(0,5) + H_2(0,8) \rightarrow H_2(0,9) +$ $H_2(0,4)$ (Figure 4.6) from the STA Class were examined and were also found to be normally distributed.

Similarly, the final internal energy distribution for the transition $H_2(0,2) + H_2(0,9) \rightarrow H_2(0,6) + H_2(0,5)$ (Figure 4.7) was examined from SWA Class. The histograms for the internal energy distribution were found to be normally distributed for this case. The internal energy distribution of the additional cases for the transitions $H_2(0,5) + H_2(0,6) \rightarrow H_2(0,9) + H_2(0,2)$ (Figure 4.8), $H_2(0,2) + H_2(1,5) \rightarrow H_2(0,8) + H_2(0,3)$ (Figure 4.9), $H_2(0,3) + H_2(0,8) \rightarrow H_2(1,5) + H_2(0,2)$ (Figure 4.10), $H_2(0,4) + H_2(0,1) \rightarrow H_2(1,2) + H_2(1,3)$ (Figure 4.11), $H_2(1,2) + H_2(1,3) \rightarrow H_2(0,4) + H_2(0,1)$ (Figure 4.12) from the SWA class were examined. Significant deviations from the normal distribution were found at 200 mE_h for the transition $H_2(0,2) + H_2(1,5) \rightarrow H_2(0,8) + H_2(0,3)$ (Figure 4.9). Examination of figure 4.9 (a_1) showed that at lower energy, the observed values for number of events was lower than was expected from the normal distribution. At higher energy, the number of events was greater than

was expected from the normal distribution. There were no statistically significant differences from the normal distribution among the other cases in internal energy distribution in the SWA class.

From the DIA Class, the final internal energy distribution for the transition $H_2(0,1) + H_2(0,2) \rightarrow H_2(0,7) + H_2(0,4)$ (Figure 4.13) was examined. Significant differences in internal energy distributions at 100, 200, 300, and 402 mE_h were found for this case. Additional cases for the analysis of internal energy distribution in DIA Class for the transitions $H_2(0,4) + H_2(0,7) \rightarrow H_2(0,2) + H_2(0,1)$ (Figure 4.14), $H_2(0,3)$ $+ H_2(1,5) \rightarrow H_2(0,7) + H_2(0,9)$ (Figure 4.15), $H_2(0,7) + H_2(0,9) \rightarrow H_2(0,3) + H_2(1,5)$ (Figure 4.16), $H_2(0,3) + H_2(0,7) \rightarrow H_2(0,3) + H_2(1,3)$ (Figure 4.17), and $H_2(0,3) + H_2(1,3) \rightarrow H_2(0,3) + H_2(0,7)$ (Figure 4.18) were examined. There were no statistically significant differences from normal distribution among these cases.

The results for the histograms of internal energy distributions were found to be similar for all three classes of agreement with detailed balance. There were no statistically significant differences in internal energy distributions among the three classes of agreement except for the following cases:

$$\begin{split} H_2(0,2) + H_2(1,5) &\to H_2(0,8) + H_2(0,3) \text{ (From SWA Class, Figure 4.9)} \\ H_2(0,1) + H_2(0,2) &\to H_2(0,7) + H_2(0,4) \text{ (From DIA Class, Figure 4.13)} \end{split}$$



Figure 4.1: Distribution of final internal energy for the transition: $H_2(0,1) + H_2(1,4) \rightarrow H_2(1,1) + H_2(0,6)$ (From Strongly Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures b_1 and b_2 are for translational energy 0.300 E_h and figures c_1 and c_2 are for translational energy 0.396 E_h .



Figure 4.2: Distribution of final internal energy for the transition: $H_2(0,6) + H_2(1,1) \rightarrow H_2(1,4) + H_2(0,1)$ (From Strongly Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.194 E_h respectively. Similarly figures b_1 and b_2 are for translational energy 0.294 E_h and figures c_1 and c_2 are for translational energy 0.390 E_h .



Figure 4.3: Distribution of final internal energy for the transition: $H_2(0,3) + H_2(0,6) \rightarrow H_2(0,7) + H_2(0,2)$ (From Strongly Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.100 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.300 E_h and figures d_1 to d_3 are for translational energy 0.398 E_h .



Figure 4.4: Distribution of final internal energy for the transition: $H_2(0,2) + H_2(0,7) \rightarrow H_2(0,6) + H_2(0,3)$ (From Strongly Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.098 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.198 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.298 E_h and figures d_1 to d_3 are for translational energy 0.396 E_h .



Figure 4.5: Distribution of final internal energy for the transition: $H_2(0,4) + H_2(0,9) \rightarrow H_2(0,8) + H_2(0,5)$ (From Strongly Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.100 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.300 E_h and figures d_1 to d_3 are for translational energy 0.400 E_h .



Figure 4.6: Distribution of final internal energy for the transition: $H_2(0,5) + H_2(0,8) \rightarrow H_2(0,9) + H_2(0,4)$ (From Strongly Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 to a_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.102 E_h respectively. Similarly figures b_1 to b_3 are for translational energy 0.202 E_h , figures c_1 to c_3 are for translational energy 0.302 E_h , and figures d_1 to d_3 are for translational energy 0.402 E_h .



Figure 4.7: Distribution of final internal energy for the transition: $H_2(0,2) + H_2(0,9) \rightarrow H_2(0,6) + H_2(0,5)$ (From Somewhat Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.100 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.300 E_h and figures d_1 to d_3 are for translational energy 0.396 E_h .



Figure 4.8: Distribution of final internal energy for the transition: $H_2(0,5) + H_2(0,6) \rightarrow H_2(0,9) + H_2(0,2)$ (From Somewhat Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 to a_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.105 E_h respectively. Similarly figures b_1 to b_3 are for translational energy 0.206 E_h , figures c_1 to c_3 are for translational energy 0.305 E_h , and figures d_1 to d_3 are for translational energy 0.401 E_h .



Figure 4.9: Distribution of final internal energy for the transition: $H_2(0,2) + H_2(1,5) \rightarrow H_2(0,8) + H_2(0,3)$ (From Somewhat Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 to a_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures b_1 to b_3 are for translational energy 0.300 E_h and figures c_1 to c_3 are for translational energy 0.400 E_h .



Figure 4.10: Distribution of final internal energy for the transition: $H_2(0,3) + H_2(0,8) \rightarrow H_2(1,5) + H_2(0,2)$ (From Somewhat Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.206 E_h respectively. Similarly figures b_1 and b_2 are for translational energy 0.306 E_h . Figures c_1 to c_2 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.407 E_h respectively.



Figure 4.11: Distribution of final internal energy for the transition: $H_2(0,1) + H_2(0,4) \rightarrow H_2(1, 3) + H_2(1, 2)$ (From Somewhat Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures b_1 and b_2 are for translational energy 0.300 E_h and figures c_1 and c_2 are for translational energy 0.398 E_h .



Figure 4.12: Distribution of final internal energy for the transition: $H_2(1,2) + H_2(1,3) \rightarrow H_2(0,4) + H_2(0,1)$ (From Somewhat Agree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.162 E_h respectively. Similarly figures b_1 and b_2 are for translational energy 0.264 E_h and figures c_1 and c_2 are for translational energy 0.362 E_h .



Figure 4.13: Distribution of final internal energy for the transition: $H_2(0,1) + H_2(0,2) \rightarrow H_2(0,7) + H_2(0,4)$ (From Disagree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.100 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.300 E_h and figures d_1 to d_3 are for translational energy 0.402 E_h .



Figure 4.14: Distribution of final internal energy for the transition: $H_2(0,4) + H_2(0,7) \rightarrow H_2(0,2) + H_2(0,1)$ (From Disagree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.082 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.182 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.282 E_h and figures d_1 to d_3 are for translational energy 0.384 E_h .



Figure 4.15: Distribution of final internal energy for the transition: $H_2(0,3) + H_2(1,5) \rightarrow H_2(0,7) + H_2(0,9)$ (From Disagree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 and a_2 are for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.099 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.300 E_h and figures d_1 to d_3 are for translational energy 0.399 E_h .



Figure 4.16: Distribution of final internal energy for the transition: $H_2(0,7) + H_2(0,9) \rightarrow H_2(0,3) + H_2(1,5)$ (From Disagree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 to a_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.192 E_h respectively. Similarly figures b_1 to b_3 are for translational energy 0.292 E_h and figures c_1 to c_3 are for translational energy 0.391 E_h .



Figure 4.17: Distribution of final internal energy for the transition: $H_2(0,3) + H_2(0,7) \rightarrow H_2(0,3) + H_2(1,3)$ (From Disagree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figures a_1 to a_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.200 E_h respectively. Similarly figures b_1 to b_3 are for translational energy 0.300 E_h and figures c_1 to c_3 are for translational energy 0.402 E_h .



Figure 4.18: Distribution of final internal energy for the transition: $H_2(0,3) + H_2(1,3) \rightarrow H_2(0,3) + H_2(0,7)$ (From Disagree Class). The vertical axis is the probability and the horizontal axis is the final internal energy in E_h . Figure a_1 is for impact parameter range 0.0 - 1.0 and 1.0 - 2.0 a_0 at translational energy 0.093 E_h respectively. Figures b_1 to b_3 are for impact parameter range 0.0 - 1.0, 1.0 - 2.0, and 2.0 - 3.0 a_0 at translational energy 0.192 E_h respectively. Similarly figures c_1 to c_3 are for translational energy 0.292 E_h and figures d_1 to d_3 are for translational energy 0.395 E_h .

4.2.2 Application of χ^2 -test to histograms of energy distribution

From the χ^2 -test, it is found that there were no significant differences in energy distributions for almost all the cases. The cross sections for the transition of H₂(0,6) + H₂(1,1) \rightarrow H₂(1,4) + H₂(0,1) showed significant differences at 95% confidence level (Table 4.2).

The cross sections for the transition of $H_2(0,2) + H_2(1,5) \rightarrow H_2(0,8) + H_2(0,3)$ exhibited significant differences at 99.95% and 95% confidence levels (Table 4.3). The cross sections for the transition of $H_2(0,1) + H_2(0,2) \rightarrow H_2(0,7) + H_2(0,4)$ showed significant differences at 99.95% confidence level (Table 4.4).

		Energy,	Cross section	Number of	
Initial state ^{a}	Final state ^{b}	mE_{h}	with error, a_0^2	$Trajectories^{c}$	χ^2 value ^d
0114	1106	100	$(0 \pm 2.24) \times 10^{-4}$	0	-
-	-	200	$(5.520 \pm 0.481) \times 10^{-3}$	148	6.50
-	-	300	$(9.794 \pm 1.50) \times 10^{-3}$	208	5.84
-	-	396	$(7.629 \pm 1.76) \times 10^{-3}$	237	4.71
1106	0114	94	$(0 \pm 2.24) \times 10^{-4}$	0	-
-	-	194	$(3.343 \pm 0.384) \times 10^{-3}$	102	40.77
-	-	294	$(7.391 \pm 1.13) \times 10^{-3}$	160	31.97
-	-	390	$(5.834 \pm 0.164) \times 10^{-3}$	177	32.31
0306	0702	100	$(1.061 \pm 0.007) \times 10^{-1}$	195	16.20
-	-	200	$(1.354 \pm 0.002) \times 10^{-1}$	1872	10.81
-	-	300	$(1.091 \pm 0.006) \times 10^{-1}$	208	8.50
-	-	398	$(1.061 \pm 0.008) \times 10^{-1}$	70	10.00
0702	0306	98	$(1.263 \pm 0.008) \times 10^{-1}$	207	18.81
-	-	198	$(1.656 \pm 0.001) \times 10^{-1}$	11203	29.10
-	-	298	$(1.416 \pm 0.007) \times 10^{-1}$	224	6.65
-	-	396	$(1.281 \pm 0.009) \times 10^{-1}$	93	3.93
0409	0805	100	$(9.649 \pm 0.072) \times 10^{-2}$	153	26.40
-	-	200	$(1.286 \pm 0.002) \times 10^{-1}$	1923	5.32
-	-	300	$(1.267 \pm 0.007) \times 10^{-1}$	198	5.54
-	-	400	$(1.023 \pm 0.008) \times 10^{-1}$	81	7.63
0805	0409	102	$(8.347 \pm 0.068) \times 10^{-2}$	128	15.01
-	-	202	$(1.091 \pm 0.003) \times 10^{-1}$	754	13.23
-	-	302	$(1.083 \pm 0.006) \times 10^{-1}$	157	10.14
-	-	402	$(1.027 \pm 0.008) \times 10^{-1}$	69	12.33

Table 4.2: Results for the cases of the Strongly Agree Class with respect to χ^2 -test

^{*a*}Initial states for two hydrogen molecules vjv'j'^{*b*}Final states for two hydrogen molecules v'''j'''v''''j''''^{*c*}Number of Trajectories in impact parameter range 0 - 1 a_0 that contribute to the cross section for a transition

 $[^]d$ Italic type indicates differences are statistically significant at 95% confidence level

		Energy	Cross soction	Name la su	
Initial state ^{a}	Final state ^{b}	mE _h	with error a_0^2	of Trajectories ^{c}	γ^2 value ^{de}
0209	0605	100	$(1.182 \pm 0.007) \times 10^{-1}$	206	21.55
-	-	200	$(1.659 \pm 0.003) \times 10^{-1}$	2461	8.24
-	-	300	$(1.547 \pm 0.006) \times 10^{-1}$	2819	7.27
-	-	396	$(1.341 \pm 0.009) \times 10^{-1}$	2915	7.34
0605	0209	105	$(8.347 \pm 0.699) \times 10^{-2}$	132	8.45
-	-	206	$(1.126 \pm 0.003) \times 10^{-1}$	750	11.76
-	-	305	$(1.005 \pm 0.008) \times 10^{-1}$	839	12.35
-	-	401	$(9.177 \pm 0.809) \times 10^{-2}$	903	19.06
0215	0803	100	$(1.795 \pm 1.22) \times 10^{-3}$	2	4.82
-	-	200	$(2.088 \pm 0.009) \times 10^{-2}$	466	81.61
-	-	300	$(2.701 \pm 0.339) \times 10^{-2}$	535	37.80
-	-	400	$(2.580 \pm 0.421) \times 10^{-2}$	571	23.66
0803	0215	107	$(2.243 \pm 3.17) \times 10^{-4}$	1	-
-	-	206	$(1.052 \pm 0.110) \times 10^{-2}$	102	5.37
-	-	306	$(1.272 \pm 0.207) \times 10^{-2}$	144	8.78
-	-	407	$(1.144 \pm 0.295) \times 10^{-2}$	167	9.44
0104	1312	100	$(0 \pm 2.24) \times 10^{-4}$	0	-
-	-	200	$(1.165 \pm 0.112) \times 10^{-3}$	149	13.90
-	-	300	$(8.168 \pm 1.97) \times 10^{-3}$	182	22.57
-	-	398	$(8.527 \pm 2.54) \times 10^{-3}$	202	25.72
1312	0104	64	$(0 \pm 2.24) \times 10^{-4}$	0	-
-	-	162	$(1.366 \pm 0.273) \times 10^{-3}$	45	24.63
-	-	264	$(4.241 \pm 1.02) \times 10^{-3}$	70	34.94
-	-	362	$(7.629 \pm 2.58) \times 10^{-3}$	83	35.95

Table 4.3: Results for the cases of the Somewhat Agree Class with respect to χ^2 -test

^{*a*}Initial states for two hydrogen molecules vjv'j'^{*b*}Final states for two hydrogen molecules v'''j'''v''''j''''^{*c*}Number of Trajectories in impact parameter range 0 - 1 a_0 that contribute to the cross section for a transition

 $[^]d$ Italic type indicates differences are statistically significant at 95% confidence level

 $[^]e\mathrm{Bold}$ type indicates differences are statistically significant at 99.95% confidence level

10010 101		Enorgy	Cross section	N 1	
Initial state ^{a}	Final state ^{b}	mE _b	with error a_0^2	of Trajectories ^{c}	χ^2 value ^{de}
0102	0704	100	$(7.584 \pm 0.618) \times 10^{-2}$	147	95.11
-	-	200	$(1.937 \pm 0.001) \times 10^{-1}$	12726	166.93
-	-	300	$(1.899 \pm 0.008) \times 10^{-1}$	13089	166.15
-	-	402	$(1.638 \pm 0.102) \times 10^{-1}$	13236	165.65
0704	0102	82	$(1.054 \pm 0.236) \times 10^{-2}$	20	8.40
-	-	182	$(2.625 \pm 0.120) \times 10^{-2}$	433	10.47
-	-	282	$(2.261 \pm 0.311) \times 10^{-2}$	486	15.63
-	-	384	$(1.638 \pm 0.341) \times 10^{-2}$	509	19.57
0315	0709	99	$(1.346 \pm 0.249) \times 10^{-2}$	33	2.48
-	-	200	$(6.137 \pm 0.182) \times 10^{-2}$	1089	21.69
-	-	300	$(6.518 \pm 0.517) \times 10^{-2}$	1235	17.28
-	-	399	$(5.767 \pm 0.626) \times 10^{-2}$	1308	21.64
0709	0315	91	$(1.795 \pm 1.22) \times 10^{-3}$	2	9.33
-	-	192	$(1.640 \pm 0.093) \times 10^{-2}$	321	11.85
-	-	292	$(2.356 \pm 0.317) \times 10^{-2}$	379	12.08
-	-	391	$(2.513 \pm 0.444) \times 10^{-2}$	404	13.51
0307	0313	100	$(8.975 \pm 5.01) \times 10^{-4}$	4	5.18
-	-	200	$(2.737 \pm 0.116) \times 10^{-2}$	606	26.65
-	-	300	$(3.298 \pm 0.360) \times 10^{-2}$	703	29.02
-	-	402	$(3.635 \pm 0.515) \times 10^{-2}$	741	34.42
0313	0307	93	$(3.814 \pm 1.78) \times 10^{-3}$	12	6.01
-	-	192	$(7.324 \pm 0.198) \times 10^{-2}$	1429	10.64
-	-	292	$(1.116 \pm 0.007) \times 10^{-1}$	1627	12.14
-	-	395	$(1.124 \pm 0.009) \times 10^{-1}$	1722	27.77

Table 4.4: Results for cases of the Disagree Class with respect to χ^2 -test

 d Italic type indicates differences are statistically significant at 95% confidence level

 $^e\mathrm{Bold}$ type indicates differences are statistically significant at 99.95% confidence level

^{*a*}Initial states for two hydrogen molecules vjv'j'^{*b*}Final states for two hydrogen molecules v'''j'''v''''j''''^{*c*}Number of Trajectories in impact parameter range 0 - 1 a_0 that contribute to the cross section for a transition

Chapter 5

Conclusions and Future Directions

5.1 Microscopic reversibility results in $H_2 + H_2$ system

The results of the examination of detailed balance for the collisions between two hydrogen molecules below 37 mE_h (1 eV) energy were categorized into three classes. A total of 472 transitions of direct and indirect cross sections were found to follow detailed balance very strongly, 590 to somewhat follow detailed balance, and 5490 not to follow detailed balance. The internal energy distributions among the three classes of agreement show similar normal distributions of energy except in two cases where the differences from the normal distributions were found to be statistically significant but were not correlated with the classification.

The agreement of detailed balance of state-to-state cross sections in $H_2 + H_2$ system appeared to be random and was not found to be predictable. In QCT calculations, microscopic reversibility is not expected to be obeyed rigorously because of the way of the quantization is imposed. Direct trajectories start precisely at the initial (v, j) states and they end anywhere of the final (v', j') bin. Indirect trajectories are the reverse and may be thought of as starting somewhere in the (v', j') bin and precisely ending at (v, j). The objective of this work was to survey detailed balance for the state-to-state cross sections in $H_2 + H_2$ system by using QCT method. The survey of detailed balance was hoped to provide an important foundation for the calculation of cross sections and rate coefficients in $H_2 + H_2$ system. By using these calculations a model system of $H_2 + H_2$ can be built which can further used to understand the cooling mechanism in interstellar medium where H_2 molecules are dominant chemical species. Appraisal of the results of this work demonstrated that the QCT method was not to be a feasible method for the calculation of the state-to-state cross sections in the $H_2 + H_2$ system. Since this work began there has been further development in quantum methods.

In 2014, the state-to-state rate coefficients for selected transitions involving the (v=0, j \le 10), (v=1, j \le 8), and (v=2, j \le 6) states were calculated by Bohr *et al.*⁷ quantum mechanically. They have used the coupled-states approximation and set the maximum energy at 23 mE_h (5000 cm⁻¹) above the internal energy for the initial states of two H₂ molecules. They have reduced the number of coupled channels required by using the coupled-states approximation for the initial states of two H₂ molecules. They have compared their method with the close-coupling formulation for 54 *p*-H₂ - *p*-H₂ transitions and have found good agreement.

To build a model system of $H_2 + H_2$ in the astrophysical environment, the stateto-state rate coefficients of $H_2 + H_2$ among all (v, j) states need to be calculated. A complete model would need to consider over 60,000 combinations of initial states and over 35 billion possible transitions. Total energy in excess of 170 mE_h would be needed. Quantum mechanical methods could be used to achieve this if computational power increases and improved techniques are developed.

5.2 Future directions

Additional cases with varying relative errors of direct and indirect cross sections can be investigated to assess the significance of differences in energy distributions. Marsh and McCaffery proposed a statistical mechanical model for the collisions in diatom-diatom systems based on the assumption of angular momentum conservation in rotational energy transfer.⁴³ They applied it to the N₂ + H₂ system and have found good agreement with experiments. They have examined the final rotational distributions associated with vibrational energy transfer for several systems.⁴⁴ Angular momentum constraints on the formation of products were studied by McCaffery *et al.*⁴⁵ They have suggested strategies for the examination of exit routes from the transition state subject to angular momentum constraints. This examination suggested that the reduction of angular momentum constraints in the exit channels from the transition state may act as a form of catalysis. In the collisions of different diatomic molecules, there is an asymmetry in the rotational energy levels that could promote relaxation over excitation. The quadratic dependence of the rotational energy on quantum number could be the source of this effect. They examined competitive partitioning of rotational and vibrational energy in equilibration of a gas ensemble consisting of diatomic molecules in a bath gas of different diatomic molecules.⁴⁶ They have found that the rotational distributions of two different types of molecules were distinct.

Angular momentum conservation effects on inelastic transitions in $H_2 + H_2$ system were examined by dos Santos *et al.*⁴⁷ quantum mechanically. They have found that both energy and angular momentum performed fundamental roles in the rovibrational transitions. For inelastic processes, the transitions that conserved the internal rotational angular momentum and involved small changes of internal energy of the two molecules were found to be favored.

This suggests that the angular momentum distributions for the three classes of agreement with detailed balance could be explored further. This could be investigated by rerunning selected batches of trajectories and retaining additional information about angular momentum. This is beyond the scope of the current study.

5.3 Concluding statement

Detailed balance is not obeyed well for cross sections determined by QCT for the $H_2 + H_2$ system. Therefore, it can be concluded that the QCT is not a robust method for the evaluation of energy transfer cross sections and rate coefficients in $H_2 + H_2$ system.

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Appendix

TERMINOLOGY AND ABBREVIATIONS USED IN THESIS

QCT-Quasiclassical Trajectory

PES-Potential Energy Surface

ASP-Aguado, Suarez, and Paniagua (J. Chem. Phys. **101**, 4004, 1994)

BMKP2-Boothroyd, Martin, Keogh, and Peterson Potential Energy Surface in 2002

(J. Chem. Phys. **116**, 666, 2002)

 \mathbf{VV} - Vibration-vibration

VT- Vibration-transition

DVERK- Discrete Variable Explicit Runge-Kutta

Bin Histogram Method- The continuously-valued quantum numbers is assigned to a product state by using following criteria-

$$\begin{aligned} (v''' - 1/2) &\leq v'' < (v''' + 1/2) \\ (j''' - 1) &\leq j'' < (j''' + 1) \text{ (When } j''' \neq 0) \\ 0 &< j'' < 1 \text{ (When } j''' = 0) \end{aligned}$$

 $j^{\prime\prime\prime}$ is odd for ortho state and $j^{\prime\prime\prime}$ is even for para state

Endoergic Transition- A Transition for which the initial state is of lower energy than the final state

Excergic Transition- A Transition for which the initial state is of higher energy than the final state

Direct Cross Sections- Cross sections for a transition from an initial state to final state generated from trajectories originating in the initial state

Indirect Cross Sections- Cross sections for a transition from an initial state to final state calculated from trajectories originating in the final state

DB-Detailed Balance

First Impact Parameter Stratum- Impact parameter range is $0 - 1a_0$.

STA Class- Strongly Agree with Detailed Balance Class (Direct and indirect cross
sections for a transitions that agree within the standard deviation 68% of the time AND within the standard deviation 95% of the time are classified as strongly agree.) SWA Class- Somewhat Agree with Detailed Balance Class (Direct and indirect cross sections for the transitions that agree within the standard deviation 68% of the time OR within the standard deviation 95% of the time are classified as somewhat agree.) DIA Class- Disagree with Detailed Balance Class (Direct and indirect cross sections for the transitions that NEITHER agree within the standard deviation 68% of the time NOR within the standard deviation 95% of the time are classified as disagree.)