Formation of Diatomic Molecules at Surfaces

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Abstract

Molecular hydrogen, H$_2$, is the most abundant molecular species in the universe. It plays a central role in most of the chemistry in the interstellar medium. However, the mechanism of its formation is poorly understood. There is a wide consensus in the astrophysical community that H$_2$ is formed by associative desorption from cosmic dust grains. The dust grains are found in interstellar dust clouds which are at low temperature and pressure. The precise nature of the dust grains is not known but there is spectroscopic evidence for the presence of graphitic carbon.

There are, broadly speaking, two mechanisms for associative desorption from surfaces, the Eley-Ridel (ER) and Langmuir-Hinshelwood (LH) mechanisms. In this work the cosmic dust grain has been modelled as a graphite (0001) surface and the ER and certain aspects of the LH reaction have been investigated. In the study of the ER mechanism a two dimensional potential energy surface was calculated using density functional theory. Quantum reactive scattering calculations were performed on this surface to determine the probability of the formation of H$_2$ on graphite (0001) and the population of the vibrational states in the product H$_2$. An investigation of the LH mechanism focussed mainly on the diffusion step of the mechanism. To this end, a model potential which incorporates the corrugation of the graphite (0001) surface via a Fourier representation was employed within a Feynman path integral
based quantum transition state theory to determine the diffusion constants for H on graphite (0001) at a range of temperatures.
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Chapter 1

Introduction

Gas-surface interactions have long been of interest in physical science [1]. Such processes are of both fundamental and technological importance, notably in the field of heterogeneous catalysis. The majority of the effort in the study of gas-surface reactions has been devoted to dissociative adsorption. Dissociative adsorption is the generic name for a process in which a molecule adsorbs at a surface and dissociates [2]. This apparently simple process lies at the heart of much of the chemical industry. For example, the synthesis of ammonia and methanol or the reduction of noxious fumes from car exhausts require molecules to dissociate on (metal) surfaces. It is no surprise, therefore, that there have been numerous experimental [3–12] and theoretical [1, 13–19] studies of this process. The inverse process of associative desorption, on which this thesis concentrates, has received much less attention, though there have been a number of experimental [20, 21] and theoretical [22–28] studies.

Much of the theory of gas-surface reactions has its roots in high quality gas-phase reactive scattering methods. There are, however, a number of important differences from the gas phase which any theoretical treatment must take into account. The
surface of a crystal can be regarded as periodic and it is much more massive than any incident atom from the gas phase. It can enhance reaction rates in a number of ways. In particular, it can steer the reactants via a minimum energy path - a feature of gas-surface reactions which can be exploited in theoretical treatments [13]. Furthermore, since atoms may be adsorbed onto the surface for some time the probability of a collision between reactants is enhanced relative to the gas phase. Note that this collision may occur directly or by a second adsorbed atom diffusing across the surface to interact with the first. The situation is further complicated by the fact that the surface atoms are in constant motion. The effects of these surface phonons on reaction rates are not well understood. Indeed, an accurate treatment of such effects is very difficult.

The following contains a brief description of the motivation for this study of the formation of molecular hydrogen on graphite (0001). The properties of the system which are of interest and the theoretical methods which are pertinent to their study are identified. A brief review of previous experimental and theoretical work in this area is given and the chapter concludes with a summary of the work carried out in the course of the research.

1.1 Motivation

Molecular hydrogen (H$_2$) is one of the fundamental constituents of the universe and accounts for much of the non-stellar baryonic matter in the Galaxy. H$_2$ can be ionised either by UV photons in diffuse clouds or by cosmic rays in dense ones. Once ionised it initiates reaction networks that, in the interstellar medium (ISM), synthesise other molecular species [29]. H$_2$ and molecules produced from its involve-
1.1 Motivation

ment in the aforementioned reaction schemes provide an efficient means of cooling interstellar clouds. This cooling tends to reduce the timescale for their collapse and hence for the formation of stars and star clusters. This, in turn has important implications for the structure, dynamics and evolution of galaxies. Furthermore, the energetics of the H$_2$ formation process directly affects the thermal balance in the interstellar medium (ISM) which is currently poorly determined.

It is clear that H$_2$ plays an important role in many astrophysical processes. This makes it somewhat surprising that the mechanism of its formation in astrophysical environments is poorly understood. A number of possible mechanisms for the formation of H$_2$ immediately spring to mind. One might naively suggest that H$_2$ could form by direct radiative association of two H atoms

$$\text{H} + \text{H} \rightarrow \text{H}_2 + h\nu.$$  

However, this process is highly improbable [30], especially at low temperatures, largely because the emitted photon results from a forbidden transition between the two Heitler-London states of the molecule ($^1\Sigma_g \leftarrow ^3\Sigma_u$). The radiative recombination of one H atom in the ground state and another in an excited state such as 2p does not suffer from this problem but the fraction of H atoms in interstellar space which are in the 2p state is too small for this mechanism to account for the observed H$_2$ abundance [30]. A similar argument applies to three-body collisions which might result in the formation of H$_2$. The regions where H$_2$ is formed are tenuous ($n \approx 10^{-3} \text{cm}^{-3}$) so the probability of such events is vanishingly small.

A further possibility is the ion-atom reaction

$$\text{H} + \text{H}^- \rightarrow \text{H}_2 + e^-.$$
1.1 Motivation

which is called associative detachment. There is no doubt that $H^-$ is present [30] in the interstellar clouds where $H_2$ formation occurs so this mechanism contributes to the observed $H_2$ abundance but it is unlikely to be the main source of $H_2$ in interstellar space [31]. This uncertainty about the mechanism for the formation of $H_2$ in the ISM has been the subject of much debate [30–33]. However, there is now a wide consensus in the astrophysical community to accept the hypothesis that $H_2$ is formed by associative desorption on dust grains in interstellar dust clouds [30,32,34]. Empirical arguments [31] suggest that the formation process must be very efficient and this is the only mechanism proposed for which calculated $H_2$ formation rates are consistent with the observed $H_2$ abundance in the ISM.

The dust in interstellar clouds is very cold ($T \approx 10K$) and the gas is at very low temperature and pressure ($T \approx 10K$, $n = 10^3$–$10^5$ cm$^{-3}$ for a dark cloud and $T \approx 100K$, $n = 10^2$–$10^3$ cm$^{-3}$ for a diffuse cloud). There is some debate about the precise nature of the dust but all models contain some amorphous carbon [35]. The grains are not expected to be made from one material with specific properties [36,37] rather they contain a large fraction of the available refractory materials and silicates [38]. There is evidence for the existence of graphitic carbon in dust grains from the observed extinction 'hump' at 217.5nm [39,40]. Clearly, identifying the nature of the dust grains and their interaction with gas is an outstanding problem in astrophysics. Indeed, it is a poor understanding of the gas-dust interaction which limits our understanding of the physical situation and our ability to interpret observational data [41].
1.2 Mechanisms of Associative Desorption

In the preceding section we explained the motivation for this work and clearly identified associative desorption on cosmic dust grains as the most plausible mechanism for the formation of $\text{H}_2$ in the ISM. At this stage we shall consider the possible mechanisms for such reactions in some detail. Broadly speaking, associative desorption may occur via one of two mechanisms: the Eley-Rideal [42] (ER) and Langmuir-Hinshelwood (LH) mechanisms. The ER mechanism is a direct mechanism. An atom, incident from the gas phase collides with another atom already adsorbed onto the surface and thermalised. The reaction occurs in a single collision typically on a timescale of the order of $10^{-12}$s and the incident atom will not accommodate to the surface temperature. For the purposes of a theory of this reaction this is an important consideration. It suggests that, to a good approximation, we can neglect the motion of the surface atoms. This simplifies the problem considerably. By contrast, the LH mechanism is a trapping-mediated mechanism. In the case of associative desorption of a diatomic the precursor state comprises two atoms adsorbed to the surface and accommodated to the surface temperature. The atoms explore the surface by diffusion and eventually meet and recombine. The energy released at this stage may be employed to desorb the product or may be absorbed by the substrate.

We may regard the ER and LH mechanisms as limiting cases. There are mechanisms which lie somewhere between these two extremes. One such mechanism is the so-called hot atom (HA) mechanism [28,43]. In the HA mechanism one atom is adsorbed onto the surface and thermalised. The incident atom impinges upon the surface in the vicinity of the target atom and the subsequent diffusion is sufficiently rapid that it does not reach thermal equilibrium with the surface before it encoun-
ters the target atom when reaction occurs and the product desorbs.

It is clear from the above that one of the significant differences between the ER and LH mechanisms lies in the transfer of energy to the products. The ER mechanism is more exothermic than the LH mechanism. Furthermore, the shorter timescale of the ER mechanism minimises interaction of the reactants with the substrate. Consequently, one observes an angular distribution in the product with a peak at the specular angle. In contrast, the LH reaction is often thermoneutral. The strong molecular bond generally has an energy close to the sum of the weaker adsorbate-substrate bonds. The reactants are thermally equilibrated with the surface and may desorb in any direction.

1.3 Previous Work

In this section we give a brief review of work in the field of surface reactions. Whilst the associative desorption of diatomics at surfaces is our main interest we shall briefly review some of the work on dissociative adsorption for completeness. The reasons for doing so are twofold. First, the majority of studies of surface-catalysed reactions have been on dissociative adsorption so it is a more mature subject and second, there are obvious parallels between the theoretical treatment of the dissociative adsorption process and its inverse, associative desorption.

1.3.1 Dissociative Adsorption

Much of the modern theoretical work on dissociative adsorption reactions is built upon the concepts described by Lennard-Jones [44] in a paper motivated by the ex-
1.3 Previous Work

Experimental work of Taylor [45] on the dissociation of H$_2$ on metal surfaces. Lennard-Jones represented a dissociation event as a radiationless transition between two adsorption potentials; one for a diatomic molecule adsorbing at a surface and the other for two widely separated atoms. The model provided a useful qualitative picture but little progress was made on the problem for many years.

In the mid 1970s the first classical molecular dynamics (MD) studies of dissociative adsorption appeared. Experimental studies of dissociative adsorption were published in the late 1960s by van Willigen [46]. In this study the angular distributions of H$_2$ desorbed following permeation through metal surfaces (Fe, Ni and Pd) were related to the desorption/adsorption barriers via a simple one-dimensional model. MD models of this process were presented by McCreery and Wolken [47-51] who constructed potential energy surfaces using the semi-empirical London-Eyring-Polanyi-Sato (LEPS) form [52] which had been applied with some success to gas-phase problems. These studies provided clear evidence of the sensitive dependence of the results of MD simulations on the potential energy surface. In the aforementioned MD studies the approach was to find the particular parameter set for a model potential which would yield the experimental results for the system in question. Following a total energy calculation on the H$_2$/Mg(0001) system by Nørskov [53] there appeared a number of low dimensional classical studies in which the main emphasis was no longer to simply interpret or rationalise experimental data but rather to investigate how cross sections in the reactive scattering of heavy molecules were affected by changes in the topography of the potential [54,55]. Harris et al. used concepts from transition state theory to investigate the associative desorption of H$_2$ from Cu. Subsequently, a number of high dimensional classical dynamics studies
1.3 Previous Work

have appeared [56,57].

An alternative approach was adopted by Jackson [58,59] who performed reduced dimensionality quantum calculations on associative desorption. In the spirit of Holloway and Gadzuk [54,55] Jackson’s philosophy was to investigate the relationship between topographical features of the potential and the derived dynamics. Subsequently, the development of the generalised gradient approximation (GGA) [60] for the exchange-correlation functional in density functional theory (DFT) and efficient algorithms for the solution of the Kohn-Sham equations in DFT-GGA based on the plane wave pseudopotential method have made it possible to calculate potential energy surfaces for small molecules on surfaces with useful accuracy for reaction dynamics calculations. The majority of the quantum mechanical calculations on dissociative adsorption have used time-dependent quantum mechanics, in particular the time-dependent wavepacket method. There have, however, been some time-independent quantum reactive scattering studies [13,61,62]. The first six-dimensional time-independent quantum mechanical calculations on dissociative adsorption were performed by Gross et al. [14]. Later, Jónsson et al. used a Feynman path integral [63–65] formulation of transition state theory to study the dissociation of H$_2$ on Cu [66,67]. The latter approach does not yield the state-resolved dynamics of the process but rather it recasts the dynamical problem as a statistical one and provides information about the rate of the process. Studies of dissociative adsorption have paid a great deal of attention to H$_2$ on Cu. Indeed, this system may be regarded as a paradigm of surface science. Very sophisticated calculations are now possible on realistic potential energy surfaces and the current state of the art are the fully quantum mechanical six-dimensional calculations of Kroes et al. [16,17]. A
useful review of studies of reactions of this type is given by Gross [68], he describes both time-independent and time dependent methods.

1.3.2 Associative Desorption

The issues involved in the study of associative desorption are very closely related to those in the inverse process described above. In particular, the need for accurate potential energy surfaces is equally apparent in the study of such processes. For many years the ER mechanism was speculated to occur on surfaces but experimental evidence for the process only emerged recently. This evidence comes from two characteristic dynamical features of the reaction mechanism. The first is the large translational and internal energies in the desorbing products and the second their sensitivity to the initial state of the gas phase atoms. In contrast, the LH mechanism is often thermoneutral because the strong molecular bond which is formed generally has an energy close to the sum of the weaker adsorbate-substrate bonds. Moreover, since the reactants are thermally equilibrated with the surface there is no memory of the state of the incident gas-phase species in the state of the product molecule.

The first dynamical evidence for an ER mechanism came from measurements of the internal state distribution in diatomic molecules formed on a metal surface. Hall et al. [69] and Eenshustra et al. [70] studied the formation of H₂ on a hot tungsten filament in a cell and observed highly vibrationally excited product H₂. The observed vibrational excitation was sufficiently large to be consistent with the energetics of an ER reaction. In one of the experiments the observed vibrational excitation was greater than that available from this mechanism making the conclusion rather less clear. The molecular beam study by Rettner [20] of the reaction of gas phase H(D)
1.3 Previous Work

with adsorbed D(H) was performed under much better defined conditions. Analysis of the HD product translational energy and angular distributions demonstrated their sensitivity to the incident energy and the particular isotope which was incident. The translational energy of the product was found to range from zero to about the maximum available energy released in the ER mechanism for this system. These and other experiments have prompted a few workers to perform quantum mechanical and classical calculations on the dynamics of the ER reaction [22–28, 43, 71–75]. Many of the earlier fully quantum mechanical models [25–27, 72] are based upon a restricted collinear model involving two degrees of freedom. They use a simple LEPS description of the potential energy surface. These studies found that the product H$_2$ was highly vibrationally excited. This is in qualitative agreement with the results of gas-cell experiments [69, 70]. The collinear model was extended to a three dimensional model in which the corrugation of the surface is neglected, the so-called flat surface approximation (FSA) by Jackson et al. [22]. Subsequently, this model has been extended beyond the FSA to include surface corrugation in a modified LEPS form [28] which has been used to perform quasi-classical trajectory (QCT) calculations. As in studies of dissociative adsorption the results obtained from calculations of the reaction dynamics depend critically upon the potential energy surface. In most modern studies of ER reactions the potential is calculated using GGA-DFT and fit to a LEPS form [76]. In common with dissociative adsorption studies most attention has been focused on reactions of H$_2$ on metal surfaces, however, there has been some work on H$_2$ formation on Si [77] and the formation of HCl on Au [27].

Thus far we have not considered the LH mechanism in detail. We have asserted that it is considered to be the more common of the two mechanisms for associative
desorption. A simple plausibility argument shows that for a relatively clean surface the LH mechanism should be favoured over the ER mechanism. That is, the probability that an atom incident from the gas phase will collide directly with an adsorbed atom is much smaller than the probability that it will impinge at some other point on the surface. There have been a number of experimental studies of processes which follow a LH mechanism [78, 79]. Experimental investigations of associative desorption reactions of this kind have been used by Hodgson and others as a probe of dissociative adsorption reactions by employing the principle of detailed balance [80–82].

LH processes have received much less theoretical attention than reactions which follow an ER mechanism. This is largely due to the complexity of modelling such a process. In this mechanism we can no longer ignore the substrate motion so we have to model a quantum system in a dissipative environment which is a difficult problem. The situation is further complicated by the fact that we wish to extract information about the internal states of the product molecules. Furthermore, an accurate treatment of the dynamics of the LH process requires an accurate potential energy surface. Such a surface should describe the motion of substrate atoms as well as the adsorbate. In many cases this would require the use of model potentials parametrized to fit data from electronic structure calculations. Clearly, any treatment of the LH mechanism must treat the three steps: adsorption of the reactants, diffusion across the surface, and finally recombination. In this work we have treated the surface diffusion step using a method based on Feynman path integrals [64, 65]. In the concluding section we suggest an approach which may be adopted to model the recombination step. A related approach was adopted by Harris et al. [83] to
1.3 Previous Work

study the associative desorption of $H_2$ from Cu. They used classical trajectory calculations to evaluate the flux of trajectories through a dividing surface separating the reactant and product regions of the potential. The calculations assume a thermal distribution of desorbing trajectories at this dividing surface. Furthermore, these calculations are performed within a flat surface approximation. The desorption barrier is assumed to be constant across the metal surface.

1.3.3 Surface Diffusion

Surface diffusion has been identified as a crucial step in the LH mechanism. Thus, in order to understand this mechanism we need to understand the diffusion of adatoms across a solid surface. The process of diffusion is intriguing from both a conceptual and a practical point of view. A number of theoretical developments owe their discovery to the analysis of diffusion. For example, Brownian motion \[84,85\] played a central role in the development of atomic theory by providing one of the more direct links between the microscopic and macroscopic realms. Aside from being of fundamental interest, the mathematics of Brownian motion \[86,87\] and techniques aimed at solving diffusion equations led, in part, to the development of a number of modern statistical methods \[88\].

Many of the early studies of surface diffusion employed classical mechanics for the dynamics of the adsorbate. However, the assumption of classical dynamics is usually adequate unless the adsorbate has low mass (e.g. hydrogen) or the system is at very low temperature. In such cases one must treat the dynamics quantum mechanically.

For an adsorbate whose dynamics may be adequately modelled using classical me-
1.3 Previous Work

Mechanics, molecular dynamics techniques [89] offer a solution in principle. In practice, however, the activated nature of the dynamics makes the application of ordinary MD techniques troublesome. For typical temperatures the timescale between adsorbate hops can be quite large on a molecular scale so that the length of the trajectories required to study such processes is impractically large. At high temperatures this problem is no longer an issue and a number of MD studies of such systems have been reported. There have been a number of studies of adatom and vacancy diffusion on various faces of a Lennard-Jones crystal [90–92]. Classical MD studies on real systems such as self-diffusion of Si on Si (110) [93], oxygen [94] and carbon [95] on Pt(111) have also been performed.

Theories of surface diffusion have avoided the rare event problem by assuming that a particular adsorbate motion such as site-to-site hopping dominates diffusive motion. With this assumption, the calculation of the diffusion constant is reduced to the calculation of the jump frequency. The dynamical problem of computing the adsorbate jump frequency may be recast as an equilibrium problem by means of transition state theory (TST) [96–99]. Indeed, applications of classical TST to surface diffusion are numerous [100–105]. However, there are a number of intrinsic problems with TST such as the neglect of barrier recrossings (these are discussed in Section 4.2) and a better estimate of the diffusion constant may be obtained by applying dynamical corrections to the TST rate. This was first applied to condensed phase problems by Bennett [106,107].

We now turn our attention to quantum mechanical models of surface diffusion. Such a description is necessary when the adsorbate is light and/or the temperature
is low. Clearly, this is true of any model of the motion of H atoms on cosmic dust grains [108] so we must employ quantum mechanics to model this process. One approach to quantum mechanical diffusion, adopted by Whaley et al. [109], involves a band theoretic treatment of the adsorbed H atom. They used this method to model the diffusion of H on metal surfaces in an attempt to explain the results of experiments by Gomer on diffusion of H on W(110) [110, 111], in particular the coverage dependence of diffusion. Such approaches are only really applicable to perfectly periodic environments at very low temperature since at higher temperatures the coherent tunnelling is destroyed by crystal vibration [112].

Quantum mechanical effects can be included within the framework of site-hopping models by computing the site-to-site hopping frequency using quantum mechanical rather than classical methods. One example of such an approach is a quantum mechanical transition state theory in which the classical TST estimate of the adsorbate's hopping frequency is modified to include quantum mechanical effects such as tunnelling and zero-point energy effects. These modifications may be either semiclassical or fully quantal. The work of Lauderdale et al. offers a summary of efforts of this type [113–115]. Such approaches are reasonable for overbarrier diffusion. At low temperatures the quality of the approximation depends upon the validity of the neglected nonadiabatic couplings.

Miller, Schwarz and Tromp [116] used Feynman path integrals [64, 65] to formulate a general theory of rate processes. Their method has been applied to general chemical processes and there have been a number of applications to diffusion of H on metals [117–119]. Other workers have used alternative applications of Feynman
1.3 Previous Work

path integrals to investigate diffusion processes \([120,121]\). A further approach which
is adopted in this work relies on the recognition by Feynman and Hibbs \([64]\) of
the centroid of a quantum path as an effective classical variable. Gillan \([122,123]\)
recognised that the probability of finding the centroid at the barrier top could be
related to the barrier crossing rate and used this to calculate diffusion constants
for H in metals. Later Voth, Chandler and Miller \([124\] rigorously derived Gillan's
result. Sun and Voth \([125]\] used the centroid method to calculate the rate of diffu-
sion of H on Cu which they compared with semi-classical calculations due to Truong
and Truhlar \([126,127]\) and the exact quantum mechanical calculations of Whaley
et al \([109]\). Their results compared favourably with those of other authors. The
centroid method is an approximate method for calculating the rate of quantum pro-
cesses. It has been developed extensively (see Chapter 4) and has been applied with
success to a number of condensed phase problems (see \([128]\) and references therein).
Recently, Makri et al. \([129]\) used numerically exact path integral techniques \([130–132]\)
to calculate the diffusion constant for H in crystalline silicon. They compared their
results with the results of classical calculations and experiments on related systems.
They predict an inverse isotope effect which appears to be consistent with experi-
mental results but they make no quantitative comparisons with experiment. Baer et
al. \([133]\) employed their surrogate Hamiltonian method \([134]\) to perform calculations
on hydrogen transport in nickel. In this method, the exact system-bath Hamiltonian
is replaced by a finite representation. The finite surrogate Hamiltonian is designed
to generate the true short-time dynamics of a primary system coupled to a bath. A
detailed wavepacket description is employed for the primary system while the bath
is represented by an array of two-level systems. The method appears to give good
results \([133,134]\) but it is more difficult to implement and lacks the intuitive appeal
1.3 Previous Work

of path-integral based theories.

1.3.4 Surfaces of Astrophysical Interest

In section 1.1 we outlined the motivation for this study. We showed that the for­

tmation of $\text{H}_2$ on the surfaces of cosmic dust grains is of fundamental importance.

It is surprising, therefore, that such systems have not received much attention in

the chemical literature. Much of the early work in the astrophysical literature fo­

cused on demonstrating that associative desorption was a plausible mechanism for

the formation of $\text{H}_2$ in the ISM \cite{32,33,135} without detailed consideration of the

chemical system. There is evidence that cosmic dust grains contain some graphitic

carbon \cite{37}. In the light of this evidence a number of theoretical models used the

(0001) surface of graphite or alternatively (in cluster models) the coronene molecule

to represent the grain surface. Until recently, the theoretical knowledge of the H-

graphite interaction came from semi-empirical calculations based on approximate

Hartree-Fock type schemes employing minimal basis set expansions of the wave-

functions (CNDO \cite{136,137}, MNDO \cite{138}, INDO \cite{139}, MINDO/3 \cite{138,140}). Ex­

tended Hückel type calculations \cite{141,142} and a perturbation-type approach \cite{143}

have also been reported. Clearly, none of these methods represents the last word in

sophistication and the poor quantitative agreement between the results of these cal­

culations reflects this fact. More recently, Jeloaica et al. \cite{144} performed GGA-DFT

calculations of the potential curve for the adsorption of H on a coronene cluster.

Their findings were somewhat different to the results reported in this work from

plane wave GGA-DFT calculations on a graphite monolayer. However, this may

reflect differences between the systems under investigation (see Section 6.1). There

have been even fewer theoretical studies of the dynamics of the formation on $\text{H}_2$. 
1.3 Previous Work

Parneix et al. [145] performed quasi-classical trajectory (QCT) calculations on a potential energy surface which was largely based upon the MINDO/3 calculations of Fromherz et al. [140]. The only other theoretical studies of the dynamics are the time-independent quantum scattering calculations described in this work [146], time-dependent quantum dynamical calculations [147] which use a three-dimensional model to study the ER mechanism and the recent calculations of Jackson et al. [148] which use a potential parametrised to fit the DFT calculations of Jeloaica et al. The LH mechanism has received very little attention, although it is mentioned as a possible mechanism in most of the astrophysical literature. Leitch-Devlin and Williams [108] performed some quantum mechanical calculations on a simple model and found that the mobility of H on graphite was very high.

Experimentally, the H-graphite system has received relatively little attention. However, in the late 1970s Mattera et al. [149] studied the interaction of H$_2$ with graphite (0001) and Valbusa et al. [150] investigated the interaction of H with graphite (0001) at about the same time. In particular, they managed to fit the experimental vibrational energy levels of H on graphite to the potential

$$V(z) = D \left[ \left( 1 + \frac{\lambda z}{p} \right)^{-2p} - 2 \left( 1 + \frac{\lambda z}{p} \right)^{-p} \right]. \quad (1.1)$$

They found that the well depth for the H-graphite potential was small, around 39 meV, which corresponds to physisorption. However, in earlier electron spin resonance studies by Nikitina et al. [151] adsorption of H onto the surface produces an extra peak in the spectrum which indicates the presence of a chemical bond between the surface and the H atom. In addition, Beitel [152,153] found that the sticking probability for H on graphite was enhanced relative to that for H$_2$ by a factor of $10^6$ which is consistent with chemisorption of H on graphite. However, it is not clear
that these latter studies were performed on a graphite (0001) surface. More recently, the formation of H\textsubscript{2} on astrophysically relevant surfaces such as olivine and amorphous carbon has been studied [154–158]. Unfortunately, none of these experiments provide state resolved information about the product H\textsubscript{2} but an experiment is in progress [159] which should yield such information. The results of these experiments should provide an excellent test of theoretical results on the H-graphite system and other surfaces of astrophysical interest.

1.3.5 This Work

The H-graphite system was adopted as a model of the cosmic dust grains upon which H\textsubscript{2} is believed to form in the ISM. In the remaining chapters we describe a number of theoretical approaches to understanding this system. In particular, we have calculated a new GGA-DFT potential energy surface for a collinear model of the formation of H\textsubscript{2} via an ER mechanism. This potential has been smoothed using bicubic splines and, in a separate calculation, fit to a LEPS form. Both potentials were used to calculate the reaction probability and product state distributions for the collinear model. The LEPS potential has been extended to three dimensions and used in time-dependent quantum scattering calculations [147]. We also describe quantum mechanical calculations of the mobility of H atoms on the graphite (0001) surface which form part of a study of the LH mechanism. Calculations were performed for a potential parametrised for physisorption and another parametrised to represent chemisorption. The results of these calculations provide some insight into the feasibility of the LH mechanism in astrophysical environments.
Chapter 2

Potential Energy Surfaces

Potential energy surfaces are central to theoretical chemistry. Indeed, at a quantitative level, the dynamics of a chemical reaction can only be understood in terms of the motion of nuclei on a potential energy surface. Accurate potentials are, therefore, essential for any theoretical treatment of these dynamics.

The concept of a potential energy surface arises from the Born-Oppenheimer approximation [160] as follows. In atomic units, the Hamiltonian for a system of \( n \) electrons and \( N \) nuclei of charge \( Z_j \) and mass \( M_j \) is

\[
\mathcal{H}(\mathbf{R}, \mathbf{r}) = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \frac{1}{2M_i} \nabla_i^2 + \sum_{i>j} \frac{Z_i Z_j}{R_{ij}} + \sum_{i} \frac{1}{r_{ij}} - \sum_{i} \frac{Z_i}{r_{iL}} \tag{2.1}
\]

where \( R_{ij}, r_{ij} \) and \( R_{L} \) are the internuclear, interelectron and electron-nucleus separations, respectively. We can write this Hamiltonian as

\[
\mathcal{H} = T_e(\mathbf{r}) + T_n(\mathbf{R}) + V_{nn}(\mathbf{R}) + V_{ee}(\mathbf{r}) + V_{ne}(\mathbf{R}, \mathbf{r}). \tag{2.2}
\]

In this expression \( T_n \) and \( T_e \) represent the kinetic energy of the nuclei and the electrons, respectively. \( V_{nn} \) represents the nucleus-nucleus interaction, \( V_{ee} \) the electron-
2.1 Density Functional Theory

electron interaction and \( V_{ne} \) the nucleus-electron interaction. The time-independent Schrödinger equation for this system is therefore

\[
\mathcal{H}\Psi(R, r) = E\Psi(R, r).
\] (2.3)

In the Born-Oppenheimer approximation we assume that since the ratio of the mass of the nuclei to the mass of an electron is very large we can effectively separate these two motions. Essentially, the electrons instantaneously adjust to any change in the nuclear coordinates. Thus, we write the wavefunction

\[
\Psi(R, r) = \psi(r; R)\phi(R).
\] (2.4)

The electronic wavefunction \( \psi(r; R) \) is the solution to the electronic Schrödinger equation

\[
\{T_e(r) + V_{ee}(r) + V_{ne}(R, r)\}\psi(r; R) = W(R)\psi(r; R)
\] (2.5)

which describes the motion of the electrons in the field of the nuclei at \( R \). In this expression, the energy of the system depends parametrically upon the nuclear coordinates. \( \phi(R) \) is the solution to the nuclear Schrödinger equation

\[
\{T_n(R) + V_{nn}(R) + W(R)\}\phi(R) = E\phi(R).
\] (2.6)

The potential energy function is represented by \( U(R) = W(R) + V_{nn}(R) \). It describes the manner in which the potential energy of the system varies as a function of the nuclear coordinates.

2.1 Density Functional Theory

In common with many other studies of the formation of diatomic molecules at surfaces \([28, 76]\) we have used density functional theory (DFT) \([161]\) to calculate the
2.1 Density Functional Theory

potential energy surface. Unlike many other electronic structure methods DFT does not work with the wavefunction directly. Instead, it begins with the concept of an electron probability density. The many-electron wavefunction \( \Psi(r_1 \sigma_1, \ldots r_N \sigma_N) \) contains all the information about the system. However, this is usually more than is necessary. The wavefunction is a function of many variables and as such it can be difficult to calculate and store. If we wish to calculate the potential energy surface for a reaction we want nothing more than the electronic energy \( E \) as a function of the nuclear coordinates \( R \). In DFT we replace the wavefunction \( \Psi \) by the ground state electronic density \( \rho(r) \) as the basic variational object. The attraction of DFT is that it is less computationally demanding than many other electronic structure methods and can give quite accurate results in some cases. Moreover, DFT permits the inclusion of electron correlation at relatively low cost which is not true of wavefunction-based methods.

Modern DFT is based on a theorem due to Hohenberg and Kohn [162] which states that the ground state electronic energy and indeed all ground state electronic properties of molecules are uniquely determined by the electronic probability density \( \rho(r) \). The total energy is a functional of \( \rho(r) \), that is, \( E = E[\rho(r)] \). A functional is a number whose value depends on specifying a complete function. For example, the area under the curve \( y = f(x) \) is a functional of the curve \( A[f] = \int f(x)dx \).

The Hohenberg-Kohn theorem proves the uniqueness of the energy functional but it does not provide a method for finding its form so one must resort to approximations. Kohn and Sham [163] devised an approximate scheme for calculating the energy using a set of one electron orbitals from which \( \rho(r) \) can be obtained. For a
2.1 Density Functional Theory

closed shell system with \( n \) electrons and \( N \) nuclei of charge \( Z_i \), the ground state electronic energy may be written

\[
E[\rho(r)] = -\frac{1}{2} \sum_{i=1}^{n} \int \psi_i^*(r_1) \nabla_i^2 \psi_i(r_1) \, dr_1 - \sum_{i=1}^{N} \int \frac{Z_i}{r_{1i}} \rho(r_1) \, dr_1 \\
+ \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} \, dr_1 dr_2 + E_{XC}[\rho(r)],
\]

(2.7)

where the one-electron spatial orbitals \( \psi_i \) are the Kohn-Sham orbitals and

\[
\rho(r) = \sum_{i=1}^{n} |\psi_i(r)|^2.
\]

(2.8)

The first three terms in the expression for \( E[\rho] \) have a straightforward classical interpretation. The first term represents the kinetic energy of the electrons, the second the Coulomb interaction between the electrons and the nuclei and the third the Coulomb interaction between the electrons [164]. The final term, \( E_{XC}[\rho] \) is the exchange-correlation energy. It contains all of the non-classical interactions between the electrons. The exchange-correlation term is the main source of error in DFT calculations because its exact form is not known. Thus, approximate forms must be used.

The Kohn-Sham orbitals \( \psi_i \) are found by solving the Kohn-Sham equations

\[
\left\{ -\frac{1}{2} \nabla_i^2 - \sum_{l=1}^{N} \frac{Z_l}{r_{1l}} + \int \frac{\rho(r_2)}{r_{12}} \, dr_2 + V_{XC}[\rho(r)] \right\} \psi_i(r_1) = \epsilon_i \psi_i(r_1)
\]

(2.9)

where \( \epsilon_i \) are the Kohn-Sham orbital energies and

\[
V_{XC}[\rho(r)] = \frac{\delta E_{XC}[\rho]}{\delta \rho}
\]

(2.10)

is the exchange-correlation potential. The Kohn-Sham equations are usually solved in a self-consistent manner. We make an initial guess at \( \rho(r) \), then, using an approximate form for \( E_{XC}[\rho] \) we calculate \( V_{XC}(\rho) \) and use the \( \psi_i \) to calculate an improved
\( \rho(\mathbf{r}) \) and hence an improved \( E_{XC}[\rho] \). This process is repeated until the exchange-correlation energy and \( \rho \) have converged to within some specified tolerance, when the total energy \( E \) is computed.

### 2.1.1 The Local Density Approximation

There are various schemes for finding approximate forms for \( E_{XC}[\rho] \). One of the simplest is the local density approximation (LDA) \([164]\) in which

\[
E_{XC}[\rho] = \int \rho(\mathbf{r}) \epsilon_{XC}^{LDA}(\rho(\mathbf{r})) \, d\mathbf{r}
\]  

(2.11)

where \( \epsilon_{XC}^{LDA} \) is the exchange-correlation energy per electron in a homogeneous electron gas. In this approximation, the electrons are assumed to move in an infinite volume with a uniform and continuous distribution of positive charge to preserve electroneutrality. In fact, this approximation is exact for a uniform free electron gas with a uniform neutralising background. However, this situation is very different from real molecules where there will be significant charge localisation.

### 2.1.2 The Generalised Gradient Approximation

There are methods for improving upon the LDA by incorporating corrective terms in \( E_{XC} \) \([165]\). In this case, we include terms in the gradient of \( \rho \) at \( \mathbf{r} \), \( \nabla \rho(\mathbf{r}) \), in addition to the electron density at \( \mathbf{r} \), \( \rho(\mathbf{r}) \). The exchange-correlation energy becomes

\[
E_{XC}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{XC}^{GGA}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) \, d\mathbf{r}.
\]  

(2.12)

Unlike the LDA, the form of \( \epsilon_{XC}^{GGA} \) is not unique and several GGA functionals exist \([164]\).
2.2 The Projector Augmented Wave Method

The wavefunctions of real materials exhibit very different behaviour in different regions of space. For example, in the bonding region the wavefunction is smooth whereas it oscillates rapidly near the nucleus due to the strong attractive potential in that region. This difference in behaviour makes it difficult for electronic structure methods to describe the bonding to a high degree of accuracy whilst accounting for the large variations near the nucleus. The strategy of the projector augmented wave method and indeed of the augmented wave methods in general, is to divide the wavefunction into parts. A partial wave expansion within an atom–centred sphere and envelope functions outside the spheres. The envelope function is then expanded into plane waves or any convenient basis set. The envelope function and partial-wave expansions are matched at the surface of the sphere to ensure continuity of the wavefunction and its first derivative.

The projector augmented wave (PAW) method was developed by Blöchl [166]. It utilises the fictitious Lagrangian approach of Car and Parrinello [167] to solve the Kohn-Sham equations. In the PAW method we define a transformation from the Hilbert space of functions orthogonal to the core states to a new so-called pseudo Hilbert space of computationally convenient functions. These functions may be identified with the envelope functions described above. A description of the electronic wavefunctions in the core region of the atoms is retained within the frozen-core approximation. The wavefunctions are expressed as

$$|\Psi\rangle = |\tilde{\Psi}\rangle - |\tilde{\Psi}^{(1)}\rangle + |\Psi^{(1)}\rangle$$

(2.13)

where $|\tilde{\Psi}\rangle$ is expanded in plane waves and $|\Psi^{(1)}\rangle$ and $|\tilde{\Psi}^{(1)}\rangle$ are one-centre expansions of the true and pseudo wavefunctions within the core region. The plane-wave
basis for $|\tilde{\Psi}\rangle$ has the advantage that the convergence is only dependent on a single cut-off parameter, the maximum energy of the plane waves. There are no basis set superposition errors or Pulay forces [166].

The use of an augmented plane-wave basis in the PAW method restricts us to work with periodic boundary conditions in three dimensions. However, this can be overcome if a sufficiently large supercell is chosen that the interactions with image particles vanish. Hence, with a judicious choice of supercell the method is well suited to the study of molecular processes at surfaces [168]. In this work on graphite, calculations were performed for a supercell with $3 \times 3$ unit cells in the (0001) plane [146]. The supercell contains a single layer of 18 carbon atoms and two hydrogen atoms. The vertical dimension is 40 bohr which is sufficient to reduce the interaction with image particles for the configurations pertinent to the study.

2.3 Model Potentials

In reactive scattering and path integral Monte Carlo calculations the potential must be evaluated at a large number of configurations of the system. Performing a separate electronic structure at each configuration is impractical. A more efficient strategy is to interpolate between the calculated points to find the value of the potential at other configurations. Fortunately, intermolecular potentials are generally fairly smooth so such a procedure is (at least in principle) fairly straightforward. Two alternative methods have been employed in this work. The first is a straightforward application of bicubic spline interpolation [169] between the calculated points and the second is to fit the results of electronic structure calculations to an analytic functional form. The former approach is described in Section 6.1 and the latter
2.3 Model Potentials

2.3.1 The LEPS Potential

The London-Eyring-Polanyi-Sato (LEPS) form [52] has been applied successfully to gas-phase scattering problems. Its use is commonplace in gas-surface problems [1]. We use a modified form of the LEPS potential due to McCreery and Wolken [47] which is appropriate for diatoms at surfaces. This form was used by Meijer et al. [147] for 3D time-dependent scattering studies of the H$_2$-graphite system.

Let $z_1$ be the height of the adsorbed H atom above the surface, $z_i$ the height of the incident atom above the surface and $r$ the separation of the two H atoms. Then the LEPS potential is given by

$$ V(r, z_i, z_t) = U_a(z_t) + U_a(z_i) + U_m(r) $$

$$ - \sqrt{Q_m^2(r) + [Q_a(z_t) + Q_a(z_i)]^2} - Q_m(r)(Q_a(z_t) + Q_a(z_i)) $$

(2.14)

where

$$ U_a(x) = \frac{D_\lambda}{4(1 + \Delta_\lambda)} \left[ (1 + 3\Delta_\lambda)e^{-\alpha_\lambda(x-x_0^{(0)})} - (2 + 6\Delta_\lambda)e^{-\alpha_\lambda(x-x_0^{(0)}/2)} \right] $$

$$ Q_a(x) = \frac{D_\lambda}{4(1 + \Delta_\lambda)} \left[ (3 + \Delta_\lambda)e^{-\alpha_\lambda(x-x_0^{(0)})} - (6 + 2\Delta_\lambda)e^{-\alpha_\lambda(x-x_0^{(0)}/2)} \right]. $$

(2.15)

$\lambda = a$ corresponds to the atom-surface interaction and $\lambda = m$ the intermolecular potential. Note that this potential describes a three dimensional problem but if we impose the constraint $z_i = z_t + r$ then we recover the collinear model. Despite the fact that this potential describes a three dimensional problem it does not contain a description of the corrugation of the graphite (0001) surface. That is, it is only valid within the flat surface approximation (FSA). The bicubic spline data was fit to the
2.3 Model Potentials

<table>
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<th>Value</th>
<th>Unit</th>
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<td>$\Delta_a$</td>
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<tr>
<td>$x_m^{(0)}$</td>
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<td>a.u.</td>
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Table 2.1: Parameters for the LEPS potential

LEPS functional form using an eight-parameter least-squares fit. The least-squares fit was performed using the NAG routine e01unf [170] with the default parameters. The details of the fit to \textit{ab initio} data are given in Section 6.1 and the full parameter set is displayed in Table 2.3.1.

2.3.2 Model Potential for Diffusion

The calculations on the diffusion of H atoms across the graphite (0001) surface use a different functional representation of the potential. We utilise a Fourier representation due to Steele [171]. The Steele potential is parametrised to describe physisorption of the H atom to the solid surface using the carbon and hydrogen Lennard-Jones parameters. The total periodic potential of one atom at position ($x, y, z$) and a graphite block with infinite extension in the basal ($x, y$) directions and semi-infinite in the $-z$ direction is

$$V_{\text{surf}}(x, y, z) = V_0(z) + V_1(z)f_1(x, y).$$  \hspace{1cm} (2.16)
2.3 Model Potentials

The laterally averaged contribution depends only upon the height \( z \) above the plane

\[
V_0(z) = \frac{4\pi \varepsilon_{CH}\sigma_{CH}}{a_s} \left\{ \frac{2}{5} \sigma_{CH} \left[ \frac{1}{z^{10}} + \frac{1}{9d(z + 0.72d)^9} \right] \right.
\]

\[
- \left[ \frac{1}{z^4} + \frac{2z^2 + 7zd + 7d^2}{6d(z + 5)^3} - \frac{d^3}{6(z + d)^7} \right] \left\} \right. \quad (2.17)
\]

and a first-order corrugation term with amplitude

\[
V_1(z) = \frac{4\pi \varepsilon_{CH}\sigma_{CH}}{a_s} \left\{ \frac{\sigma_{CH}^6}{30} \left( \frac{g_1}{2z} \right)^5 K_5(g_1z) - 2 \left( \frac{g_1}{2z} \right)^2 K_2(g_1z) \right}\} \quad (2.18)
\]

and lateral variation for the honeycomb lattice

\[
f_1(x, 2) = 2 \left\{ \cos \left( \frac{2\pi}{a} \left( x + \frac{y}{\sqrt{3}} \right) \right) + \cos \left( \frac{2\pi}{a} \left( x - \frac{y}{\sqrt{3}} \right) \right) \right. \]

\[
+ \cos \left[ \frac{4\pi}{a} \left( \frac{y}{\sqrt{3}} \right) \right] \left\} \right. \quad (2.19)
\]

where \( g_1 = 4\pi/a\sqrt{3} \) and \( K_n(z) \) are modified Bessel functions of the second kind; \( d = 3.4 \) Å is the graphite interlayer spacing, \( a = 2.46 \) Å the lattice constant of the graphite unit cell and \( a_s = 5.24 \) Å² the area of the graphite unit cell. The complete parameter set is given in Table 2.3.2. The usual rules for combining Lennard-Jones parameters apply. That is, \( \sigma_{CH} = (\sigma_{CC} + \sigma_{HH})/2 \) and \( \varepsilon_{CH} = \sqrt{\varepsilon_{CC}\varepsilon_{HH}} \).

2.3.3 LEPS with Corrugation

The two potentials above can be combined to produce a potential for two H atoms interacting with a corrugated graphite surface. We follow the treatment of Caratzoulas et al. [28] and include the corrugation in the \( D \) parameter of the LEPS potential. This combined potential may be used to study a number of aspects of the formation of \( \text{H}_2 \) on graphite (0001). In particular, it can be used to incorporate a description of the surface corrugation into the model of the ER mechanism. Furthermore, it may be used in a simple model of the LH mechanism. In the surface diffusion step it
2.3 Model Potentials

<table>
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<th>Value</th>
<th>Unit</th>
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</thead>
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<tr>
<td>(a)</td>
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</tr>
<tr>
<td>(a_s)</td>
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<tr>
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<td>(\sigma_{HH})</td>
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</tr>
<tr>
<td>(\varepsilon_{HH})</td>
<td>3.162x10⁻³</td>
<td>eV</td>
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</tbody>
</table>

Table 2.2: Parameters for Steele's physisorption potential

enables us to treat the motion of a chemisorbed atom by reparametrisng the Steele potential whilst retaining an accurate description of the H–graphite well. It could be utilised in a study of the recombination step.

We denote the positions of the atoms by \(r_1\) and \(r_2\), the \(x\) and \(y\) components of these position vectors lie in the plane of the surface and the \(z\) component is perpendicular to the surface. The vector separating the two atoms is \(r = r_1 - r_2\). We use the LEPS form

\[
V(r_1, r_2) = U_1(r_1) + U_2(r_2) + U_m(r) \\
- \sqrt{Q^2_m(r) + [Q_1(r_1) + Q_2(r_2)]^2} - Q_m(r)[Q_1(r_1) + Q_2(r_2)]
\]  

(2.20)

where

\[
U_\lambda(r_i) = \frac{D_\lambda(x_i, y_i)}{4(1 + \Delta_\lambda)} \left[ (1 + 3\Delta_\lambda)e^{\alpha_\lambda(x_i - x_i^0)} - (2 + 6\Delta_\lambda)e^{-\alpha_\lambda(x_i - x_i^0)} \right]
\]

(2.21)

\[
Q_\lambda(r_i) = \frac{D_\lambda(x_i, y_i)}{4(1 + \Delta_\lambda)} \left[ (3 + \Delta_\lambda)e^{\alpha_\lambda(x_i - x_i^0)} - (6 + 2\Delta_\lambda)e^{-\alpha_\lambda(x_i - x_i^0)} \right].
\]
2.3 Model Potentials

For the H-H interaction $U_m$ and $Q_m$ are functions of the interatomic separation $r$ only. The corresponding well depth $D_m$, and equilibrium separation $r_0$ are constants. The standard values $D_m = 4.745 \text{ eV}$, $\alpha_m = 1.943 \text{ Å}^{-1}$, and $r_0 = 0.741 \text{ Å}$ fit to both experimental and theoretical data, are used.

For the H-surface interactions the well depths $D_j$ vary across the corrugated surface. The corrugation is incorporated in $D(x_i, y_i)$ as

$$D(x_i, y_i) = D_0(1 - \varepsilon(6 - f_1(x_i, y_i)))$$

and $f_1$ is given by equation (2.19). The parameter $\varepsilon$ is chosen to fit the diffusion barrier on graphite (0001). This barrier was calculated using the PAW method. The values of the parameter which fits this barrier is $\varepsilon = -0.183 \text{ a.u.}$ The corrugation term $f_1$ is shifted so that the minimum lies at zero. All other terms in the LEPS potential are unchanged. This means that above an atop site on the graphite (0001) surface the potential is identical to the LEPS potential used in the reactive scattering calculations. It is likely that the corrugation will affect the equilibrium position in a similar manner but this is not included in the diffusion potential above. Including such an effect is possible in principle but not straightforward within Steele’s description since it alters the shape of the potential.

2.3.4 The Choice of the Diffusion Potential

An alternative approach to the diffusion potential was attempted originally. The Brenner potential for graphite [172–174] was implemented in C++. This model potential is based upon the Tersoff potential [175–177]. Its functional form is outlined below.
2.3 Model Potentials

The total potential energy is written as a sum over pairs of atoms

$$E_b = \sum_i \sum_{j(i>j)} f_{ij}(r_{ij}) [V_R(r_{ij}) - b_{ij}V_A(r_{ij})]$$  \hspace{1cm} (2.23)

where $r_{ij}$ is the separation of atoms $i$ and $j$. The attractive, $V_A$, and repulsive, $V_R$, terms are of a simple exponential form. The repulsive term is

$$V_R(r_{ij}) = \left[ 1 + \frac{Q_{ij}}{r_{ij}} \right] A_{ij} e^{-\alpha_{ij}r_{ij}}$$  \hspace{1cm} (2.24)

where the parameters $Q_{ij}$, $A_{ij}$ and $\alpha_{ij}$ depend on the atom types $i$ and $j$. The attractive term is given by a sum of exponentials

$$V_A(r_{ij}) = -\sum_{n=1}^{3} B_{ij}^{(n)} e^{-\beta_{ij}^{(n)} r_{ij}}$$  \hspace{1cm} (2.25)

which is switched off smoothly using the cutoff function, $f_{ij}(r_{ij})$. Again, the parameters $B_{ij}^{(n)}$ and $\beta_{ij}^{(n)}$ depend on the atom types $i$ and $j$.

The cutoff function which restricts the potential to nearest neighbours is given by

$$f_{ij}(r) = \begin{cases} 
1 & \text{if } r \leq R_{ij}^{(1)} \\
\frac{1}{2} \left[ 1 + \cos \left( \frac{\pi (r-R_{ij}^{(1)})}{R_{ij}^{(2)} - R_{ij}^{(1)}} \right) \right] & \text{if } R_{ij}^{(1)} < r < R_{ij}^{(2)} \\
0 & \text{if } r \geq R_{ij}^{(2)}
\end{cases}$$  \hspace{1cm} (2.26)

The term $b_{ij}$ includes the effects of bond bending, bond order and bond conjugation. It modifies the pair potential by introducing three-body interactions and second-neighbour effects essential for the description of the covalent bonding of C. This term must also account for the weakening of bonds that occurs as atoms become more highly coordinated. The $b_{ij}$ term is defined

$$b_{ij} = \frac{1}{2} (\pi_{ij}^{e\pi} + \pi_{ij}^{e\sigma}) + \pi_{ij}^{re} + \pi_{ij}^{dh}$$  \hspace{1cm} (2.27)
where
\[ p_{ij}^e = \left[ 1 + \sum_{k \neq i,j} f_{ik}(r_{ik}) g_i(\cos \theta_{jik}) e^{\lambda_{jik}} + P_{ij} \right]^{-1/2}. \] (2.28)

Note that \( p_{ij}^e \) and \( p_{ji}^e \) are not necessarily equal. The \( p_{ij}^e \) term depends upon the bond angles \( \theta_{jik} \) between the \( \mathbf{r}_{ij} \) vector and the vectors \( \mathbf{r}_{ki} \) to any neighbouring atoms.

The function \( g_i(\cos \theta_{jik}) \) imposes a cost on bonds that are too close to one another. Its functional form is a quintic spline. When the central atom is carbon the spline also depends upon the local coordination number defined as the sum of the carbon-only and hydrogen-only coordination numbers. \( N_{ij}^{(H)} \) and \( N_{ij}^{(C)} \) are the number of H and C atoms bonded to atom \( i \) excluding atom \( j \), respectively and
\[ N_{ij}^{(t)} = N_{ij}^{(C)} + N_{ij}^{(H)}. \]
In order to make the potential continuous we use \( f_{ij}(r) \) to define the connectivity in the system and thus to find the values of \( N_{ij}^{(C)} \), \( N_{ij}^{(H)} \), and \( N_{ij}^{(t)} \)
\[ N_{ij}^{(H)} = \sum_{k \neq i,j} \delta_{Hk} f_{ik}(r_{uk}) \] (2.29)
and
\[ N_{ij}^{(C)} = \sum_{k \neq i,j} \delta_{Ck} f_{ik}(r_{uk}). \] (2.30)

Using this coordination number, the angle-bending penalty function \( g_i \) switches smoothly between a form \( g_C^{(1)} \) appropriate for covalent compounds with low coordination and another form \( g_C^{(2)} \) suitable for highly coordinated bulk materials.

The additional terms are small correction factors. The \( e^{\lambda_{jik}} \) term is added to improve the potential energy surface for abstraction of H atoms from hydrocarbons,
with

\[ \lambda_{ijk} = 4\delta_{th}\left[ (\delta_{kh}\rho_{HH} + \delta_{kc}\rho_{CH} - r_{ik}) - (\delta_{jH}\rho_{HH} + \delta_{jc}\rho_{CH} - r_{ij}) \right], \tag{2.31} \]

where \( \delta_{ij} \) is the Kronecker delta for atom types \( i \) and \( j \). Finally, \( P_{ij} \) is a two-dimensional cubic spline in \( N^{(C)}_{ij} \) and \( N^{(H)}_{ij} \).

In addition to the covalent bonding interactions the Brenner potential includes contributions to the bond order from radical and conjugation effects. These enter the potential via the \( \pi_{ij}^{\text{rad}} \) term, a three dimensional spline in the variables \( N_{ij}^{(t)} \), \( N_{ji}^{(t)} \) and \( N_{ij}^{\text{conj}} \), where

\[ N_{ij}^{\text{conj}} = 1 + \left[ \sum_{k(\neq i,j)} \delta_{kc}f_{ik}(r_{ik})F(N_{ik}^{(t)}) \right]^2 + \left[ \sum_{l(\neq i,j)} \delta_{lc}f_{jl}(r_{jl})F(N_{jl}^{(t)}) \right]^2 \tag{2.32} \]

and

\[ F(N_{ik}^{(t)}) = \begin{cases} 
 1 & N_{ik}^{(t)} \leq 2 \\
 \frac{1}{2}(1 + \cos[\pi(N_{ik}^{(t)} - 2)] & 2 < N_{ik}^{(t)} < 3 \\
 0 & N_{ik}^{(t)} \geq 3 \end{cases} \tag{2.33} \]

The remaining term, \( \pi_{ij}^{\text{dih}} \), imposes a penalty for rotation around multiple bonds.

The Brenner potential has been modified by Stuart et al [174] to include long range forces via Lennard-Jones pair interactions between atoms. The full details of the potential and its parametrisation are described by Stuart et al [174].

It is clear from the brief description above that this model potential is very complicated and that it has an unwieldy functional form. This renders it somewhat expensive to evaluate. The implementation for computational work is complicated further by the presence of three-body terms (in \( b_{ij} \)). The presence of such terms
means that the neighbour-list schemes [89] used to study systems of many particles interacting via two-body potentials (e.g. the Lennard-Jones potential) are much less efficient. The presence of many-body terms in $b_{ij}$ means that we cannot consider pairs of atoms in isolation. In the implementation written in the course of this work the electronic energy of a cluster of 18 carbon atoms interacting with a single H atom took $\approx 1\text{ms}$ to evaluate on machine with a 650MHz Intel Pentium 3 processor.

The details of the path integral calculations are described in Chapter 5. However, in all Monte Carlo calculations the potential must be evaluated many times. Thus, we can discuss the feasibility of the Brenner potential for path integral Monte Carlo (PIMC) calculations before discussing the PIMC method in detail. In the calculations in this work the potential would typically be evaluated around $10^8$ times. In calculations at low temperature this increased to $10^9$. Thus, the evaluation of the potential in such a calculation would take $10^8\text{s}$ or about 100 hours. In order to estimate the diffusion constant about 50 such calculations are necessary. Clearly, such timescales make these calculations unfeasible, even on a parallel machine. The simple potential chosen in the preceding section is very cheap to evaluate and contains much of the essential physics. Using this potential the path integral calculations were completed in a few hours. The final choice, therefore, represents a compromise between an accurate description of the physical system and the need for rapid evaluation of the potential.
Chapter 3

The Eley-Rideal Mechanism

The main objective of the study of the Eley-Rideal mechanism for the formation of H₂ in the ISM is to calculate the probability and product distributions of the reaction

\[ \text{H} + \text{H/surface} \rightarrow \text{H}_2(v, j) + \text{surface} \]

where \( v \) labels the vibrational and \( j \) the rotational state of the product \( \text{H}_2 \). The model described below only considers the case of a collinear collision so that all results are for \( j = 0 \).

3.1 Theory of the Eley-Rideal Reaction in 2D

In contrast to many of the previous studies of the formation of H₂ in the ISM [140,144,145] we model the dust grain as a monolayer representing the (0001) surface of graphite rather than as a coronene cluster. In this model, which is shown in Figure 3.1, the two H atoms are constrained to lie along a vertical line above the binding site. Naturally, the choice of binding site is important. Since the model uses a graphite monolayer all the surface atoms are equivalent and there are three
3.1 Theory of the Eley-Rideal Reaction in 2D

Figure 3.1: Coordinates for the collinear Eley-Rideal reaction

possible high symmetry binding sites: directly above a surface atom (A); above the centre of a C-C bond (B); and above the centre of one of the hexagons in the graphite structure (C). Test calculations on this system using GGA-DFT agree with other workers [144] and identify the A site as the preferred binding site. In constraining the H atoms to a line we reduce the problem from a six-dimensional calculation to one in two spatial dimensions; $R$ and $r$ (see Figure 3.1).

Throughout the course of the reaction, the substrate atoms remain fixed in the perfect lattice positions. The consequences of this constraint are twofold. First,
no energy can be transferred to the surface so the total vibrational energy of the
product is fixed and second the geometry of the bound H-graphite system does not
contain any relaxation of the substrate and is therefore incorrect. However, with
present methods there is no way of dynamically removing the substrate motion as
the reaction proceeds. Thus, this approximation represents the simplest internally
consistent potential. The restriction to a collinear model means that rotational mo­
tion of H$_2$ is neglected. We anticipate that the collinear ER model will provide an
upper bound to the reaction probability for this process.

In order to determine the reaction probabilities and the product distributions we
need to solve the Schrödinger equation. This may be done using either time-
independent or time-dependent quantum mechanics. In the latter approach we solve
the time-dependent Schrödinger equation.

\[ \mathcal{H} \psi = i \hbar \frac{\partial \psi}{\partial t}. \] (3.1)

A popular approach to the solution of this equation is the time-dependent wavepacket
(TDWP) method. It has been used widely in gas-phase [178,179] and gas-surface [1]
reactive scattering problems. Indeed, the TDWP approach was used by Meijer et al.
in both a 2D and 3D study of the formation of H$_2$ on graphite [147], an extension
of this work.

In atomic units, the Hamiltonian for the model system shown in Figure 3.1 is

\[ \mathcal{H} = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial s^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial r^2} + V(r, s) \] (3.2)

where $\mu_1$ is the mass of the hydrogen molecule ($2m_H$), $\mu_2$ is the reduced mass of the
H$_2$ molecule ($m_H/2$) and $s = R + r/2$. The coordinates of the adsorbed H atom are
3.1 Theory of the Eley-Rideal Reaction in 2D

denoted by $R$ and the separation of the two H atoms by $r$. Clearly, $s$ represents the separation of the surface and the centre of mass of the $H_2$ molecule. We transform this operator to hyperspherical coordinates $(\rho, \delta)$, where

$$s = \left(\frac{M}{\mu_1}\right)^{1/2} \rho \cos \delta$$

$$r = \left(\frac{M}{\mu_2}\right)^{1/2} \rho \sin \delta$$

and $M = (\mu_1 \mu_2)^{1/2}$, $0 < \rho < \infty$ and $0 < \delta < \pi/2$. The hyperspherical coordinate system used in this work is shown in Figure 3.2.

Hyperspherical coordinates have been widely used in gas-phase time-independent reactive scattering calculations [180–183] and have also been applied to gas-surface reactions [13, 61, 62]. They satisfy many of the criteria for a coordinate system for chemical reactions outlined by Leroy and Wallace [184]. In this 2D problem the coordinates are simply mass-weighted plane polar coordinates.

In the new coordinate system, the Hamiltonian becomes

$$\hat{H} = -\frac{1}{2M} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \delta^2} \right) + V(\rho, \delta). \quad (3.4)$$

The time-independent Schrödinger equation $\hat{H}\Psi = E\Psi$ can be expressed in a more convenient form if we make the substitution $\Psi = \rho^{-1/2}\psi$. The wavefunction $\psi$ obeys the simplified Schrödinger equation $\hat{H}'\psi = E\psi$ where

$$\hat{H}' = -\frac{1}{2M} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{4\rho^2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \delta^2} \right) + V(\rho, \delta). \quad (3.5)$$

We notice that this Hamiltonian may be written in the following form

$$\hat{H}' = \frac{\rho^2}{\rho^2} h - \frac{1}{2M} \frac{\partial^2}{\partial \rho^2} + \tilde{V}(\rho, \delta) \quad (3.6)$$
where $\rho_f$ is some fixed value of $\rho$ and $\hat{h}$ is the 1D Hamiltonian at this fixed hyperradius. That is

$$\hat{h} = -\frac{\hbar^2}{2M\rho_f^2} \left( \frac{\partial^2}{\partial \delta^2} + \frac{1}{4} \right) + V(\delta; \rho_f).$$

(3.7)

In writing the Hamiltonian in this way we have effectively separated the $\rho$ and $\delta$ dependence. This immediately suggests a strategy for the solution of the corresponding Schrödinger equation. Essentially, it should be possible to solve the 1D Schrödinger equation in $\delta$ at a particular hyperradius, $\rho_f$, integrate outwards in $\rho$ to a region of the potential where all the interactions have vanished and apply scattering boundary conditions [185,186].
We represent the wavefunction $\psi$ as a linear combination of orthonormal basis functions of $\rho$ and $\delta$ viz

$$\psi(\rho, \delta) = \sum_n \Phi_n(\rho) \xi_n(\delta), \quad (3.8)$$

where the $\xi_n(\delta)$ satisfy the 1D Schrödinger equation

$$\hat{h} \xi_n(\delta) = \varepsilon_n \xi_n(\delta). \quad (3.9)$$

Comparing $\mathcal{H}$ and $\hat{h}$ we notice that we may write the potential

$$\hat{V}(\rho, \delta) = V(\rho, \delta) - \left(\frac{\rho}{\rho_f}\right)^2 V(\delta; \rho_f). \quad (3.10)$$

Thus, $\hat{V} = 0$ at $\rho = \rho_f$ and the Hamiltonian becomes

$$\mathcal{H} = -\frac{1}{2m_H} \frac{\partial^2}{\partial \rho^2} + \hat{h}. \quad (3.11)$$

Now, if we substitute the expansion of $\psi$ in equation (3.8) into the Schrödinger equation we obtain

$$\begin{align*}
\mathcal{H} \psi(\rho, \delta) &= E \psi(\rho, \delta) \\
&= -\frac{1}{2M} \sum_n \frac{\partial^2}{\partial \rho^2} \Phi_n(\rho) \xi_n(\delta) + \sum_n \Phi_n(\rho) \hat{h} \xi_n(\delta) \\
E \psi(\rho, \delta) &= -\frac{1}{2M} \sum_n \xi_n(\delta) \frac{\partial^2}{\partial \rho^2} \Phi_n(\rho) + \sum_n \Phi_n(\rho) \varepsilon_n \xi_n(\delta). \quad (3.12)
\end{align*}$$
We can exploit the orthonormality of the basis $\xi_n(\delta)$ by left-multiplying by $\xi_n^*(\delta)$ and then integrating over $\delta$. In doing so, we obtain

$$
\langle \xi_m | H | \psi \rangle = E \sum_n \Phi_n \langle \xi_m | \xi_n \rangle = E \Phi_m
$$

$$
= \sum_n \langle \xi_m | - \frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} \Phi_n + \Phi_n \varepsilon_n | \xi_n \rangle
$$

$$
= \sum_n \langle \xi_m | \xi_n \rangle \left( - \frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} \Phi_n + \Phi_n \varepsilon_n \right)
$$

$$
E \Phi_m = \left( - \frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} + \varepsilon_m \right) \Phi_m.
$$

(3.13)

The result of these manipulations are the coupled channel equations

$$
\frac{\partial^2}{\partial \rho^2} \Phi_m = 2\mu(E - \varepsilon_m) \Phi_m
$$

(3.14)

which can be solved via the $R$-matrix propagator method [187–189] detailed below. Essentially, the scheme involves numerical solution of the 1D Schrödinger equation (3.9) at a number of fixed hyperradii $\rho_f$ followed by solution of the coupled equations between sectors. The result in the final sector is compared to the asymptotic form of the wavefunction at large $\rho$ which gives the complete $S$-matrix. This, in turn, provides a complete description of the scattering process. The elements of the $S$-matrix give the state-to-state transition probabilities as follows

$$
P_{mn} = |S_{mn}|^2
$$

(3.15)

where $m$ and $n$ label $H_2$ and H-graphite vibrational states, respectively. The probability of reaction from an H-graphite state to a $H_2$ molecule is given by

$$
P_n = \sum_v |S_{vn}|^2
$$

(3.16)

where $v$ labels the vibrational state of the product $H_2$ molecule and $n$ the vibrational state of the H-graphite complex. If $E$ is the kinetic energy of the incident H atom.
then the limits of the sum are determined by $\varepsilon_v < E < \varepsilon_i$ where $\varepsilon_v$ and $\varepsilon_i$ are the vibrational energies of the $H_2$ and H-surface states, respectively.

At the temperatures of interest in astrophysical environments we assume that only the lowest H-graphite vibrational state is relevant. Thus, the total reaction probability $P(E)$ may be written in terms of the elements of $S$ as

$$P(E) = \sum_v |S_{v0}|^2.$$  

(3.17)

Similarly, the distribution of vibrational states in the product are obtained from

$$P_v(E) = |S_{v0}|^2.$$  

(3.18)

### 3.2 The R-Matrix Method

In order to calculate the state-selected probabilities for reaction from H-graphite to $H_2$ we need to follow the wavefunction of the system from initial to final states. This is by no means trivial since connecting $\Psi$ between different parts of the potential can be difficult.

One method for doing this which has been used a great deal in surface science is to employ time-dependent quantum mechanics (wavepackets) [1]. This approach has the advantage that it is possible to observe the evolution of the wavepacket in time which can give some information about the progress of the reaction.

In this work we have used time-independent quantum mechanics and hyperspherical coordinates. We integrate outwards in a single coordinate $\rho$ which eliminates many of the numerical problems associated with the Jacobi coordinates $(r, R)$. However,
3.2 The R-Matrix Method

it is still necessary to connect solutions obtained at fixed \( p \) to generate the solution at large \( p \) and hence calculate the probability of reaction.

The method involves the numerical integration of the 1D Schrödinger equation in a series of small regions or sectors. The solutions of the 1D Schrödinger equation are used to solve the coupled equations (3.14) between sectors and construct a matrix, \( \mathcal{R} \), which represents the evolution of \( \Psi \). The \( \mathcal{R} \)-matrix in the final sector is used to calculate the \( \mathcal{S} \)-matrix from which we can obtain the reaction probabilities.

The \( \mathcal{R} \)-matrix theory used here is due to formulations by Light and Walker [187] and Stechel, Walker and Light [188]. Zvijac and Light [189] describe \( \mathcal{R} \)-matrix theory in terms of a division of space into two regions: an internal or interaction region; and, outside this, an asymptotic region where the interactions have vanished. The strategy for solution of the problem is as follows. We solve the Schrödinger equation in the internal region by diagonalising the Hamiltonian in a primitive basis which satisfies the boundary conditions and then match the solutions in the internal region to the asymptotic form of the wavefunction.

Light and Walker [187] divide the dynamically accessible region of space into sectors, each with a local \( \mathcal{R} \)-matrix and integrate outwards in \( p \). The final \( \mathcal{R} \)-matrix contains all the information from previous sectors and can be used to find the \( \mathcal{S} \)-matrix.

The \( \mathcal{R} \)-matrix method has a number of advantages from a numerical point of view. Not least, the method is numerically stable and the diagonalisation of the Hamiltonian need only be done once per sector, this information can then be used at several
energies with minimal extra cost.

### 3.2.1 Definitions

The $\mathcal{R}$-matrix can be defined in the following manner

$$\mathcal{R} = \frac{1}{\Psi} \frac{d\Psi}{d\rho} = \frac{d\ln \Psi}{d\rho}. \quad (3.19)$$

More formally, if we consider the interaction region to be bounded by a closed surface, $\mathcal{S}$, with outward normal $\hat{n}$ then the $\mathcal{R}$-matrix is defined by

$$\Psi(x) = \mathcal{R}\hat{n} \cdot \nabla \Psi(x)|_{r=\mathcal{S}}. \quad (3.20)$$

Equivalently, if $F_R$ is some function at the outer surface $\mathcal{S}$ then

$$F_R(i) = \mathcal{R}F'_R(i). \quad (3.21)$$

The $\mathcal{S}$-matrix contains all the information about the scattering process so it may be used to determine the probability that the adsorbed H atom is scattered to an H$_2$ state, that is, the reaction probability. Clearly, the $\mathcal{S}$-matrix is an important quantity in reactive scattering. At the surface, $\mathcal{S}$, of the interaction region the wavefunction is of the form

$$\Psi = C(e^{-ikR} - \mathcal{S}e^{ikR}), \quad (3.22)$$

where $k^2 = 2mE/\hbar^2$. From the definition of the $\mathcal{R}$-matrix

$$\mathcal{R} = \frac{e^{-ikR} - \mathcal{S}e^{ikR}}{-ik(e^{-ikR} + \mathcal{S}e^{ikR})}, \quad (3.23)$$

we can rearrange this to obtain an expression for the $\mathcal{S}$-matrix in terms of the $\mathcal{R}$-matrix.

$$\mathcal{S} = e^{-2ikR} \left( \frac{1 + ik\mathcal{R}}{1 - ik\mathcal{R}} \right) \quad (3.24)$$

Thus, we may obtain the $\mathcal{S}$-matrix from the $\mathcal{R}$-matrix.
3.2.2 Propagation

Consider the set of second order differential equations

\[ \frac{d^2}{d\rho^2} g_n(\rho) = \sum_m E_{nm}(\rho)g_m(\rho). \]  

(3.25)

If we diagonalise \( E \) then the equation is transformed to a decoupled basis. This is accomplished by first defining \( g_n(\rho) \) as

\[ g_n(\rho) = \sum_p T_{np} F_p(\rho) \]  

(3.26)

where \( T_{np} \) are the elements of the matrix \( T \) that diagonalises \( E \). Then divide \( \rho \) into sectors labelled \( (i) \). In each sector we have the transformation matrix \( T^{(i)} \) and its inverse \( T^{-1}^{(i)} \) then \( E \) is simplified in each sector

\[ T^{(i)} E(\rho) T^{-1}^{(i)} = -k^2. \]  

(3.27)

The elements of \( k^2 \) are the channel momenta, \( k^2_\alpha \), and each eigenvector, \( F_n \), has an associated momentum, \( k_n \). This simplifies to

\[ \frac{d^2}{d\rho^2} F_n = -k^2_n F_n \]  

(3.28)

which are equivalent to equation (3.14). In the \( i \)-th sector the \( R \)-matrix is defined by

\[ \begin{pmatrix} F_n^{(i)}(a) \\ F_n^{(i)}(b) \end{pmatrix} = \begin{pmatrix} (r_1)_{nn}^{(i)} & (r_2)_{nn}^{(i)} \\ (r_3)_{nn}^{(i)} & (r_4)_{nn}^{(i)} \end{pmatrix} \begin{pmatrix} -F_n^{(i)}(a) \\ F_n^{(i)}(b) \end{pmatrix} \]  

(3.29)

where \( a \) denotes the left hand boundary and \( b \) the right hand boundary of sector \( (i) \) and, trivially, \( a < b \). We can simplify the notation by writing \( F_L = F_n(a) \) and \( F_R = F_n(b) \).

\[ \begin{pmatrix} F_L \\ F_R \end{pmatrix} = \begin{pmatrix} (r_1)_{nn}^{(i)} & (r_2)_{nn}^{(i)} \\ (r_3)_{nn}^{(i)} & (r_4)_{nn}^{(i)} \end{pmatrix} \begin{pmatrix} -F'_L \\ F'_R \end{pmatrix}. \]  

(3.30)
The second order differential equation has two linearly independent solutions, $F_1$ and $F_2$. Any linear combination of $F_1$ and $F_2$ is also a solution so we can write, without loss of generality, that

$$F_n = \alpha F_1 + \beta F_2 \quad (3.31)$$

and similarly for the derivatives

$$F'_n = \alpha F'_1 + \beta F'_2 \quad (3.32)$$

where $\alpha$ and $\beta$ are arbitrary constants. If we substitute this into equation (3.29) then we obtain

$$
\begin{pmatrix}
F_n(a) \\
F_n(b)
\end{pmatrix}
= 
\begin{pmatrix}
-(r_1)_{nn}(\alpha F'_1(a) + \beta F'_2(a)) + (r_2)_{nn}(\alpha F'_1(b) + \beta F'_2(b)) \\
-(r_3)_{nn}(\alpha F'_1(a) + \beta F'_2(a)) + (r_4)_{nn}(\alpha F'_1(b) + \beta F'_2(b))
\end{pmatrix}. \quad (3.33)
$$

We can choose $\alpha$ and $\beta$ such that at the left and right boundaries $\rho = a$ and $\rho = b$,

$$F_n = 1 \quad \text{and} \quad F'_n = 0,$$

then equation (3.33) simplifies to

$$
\begin{pmatrix}
\alpha + \beta F_2(a) \\
\alpha F_1(b) + \beta
\end{pmatrix}
= 
\begin{pmatrix}
-(r_1)_{nn} \beta F'_2(a) + (r_2)_{nn} \alpha F'_1(b) \\
-(r_3)_{nn} \beta F'_2(a) + (r_4)_{nn} \alpha F'_1(b)
\end{pmatrix}. \quad (3.35)
$$

We can see that

$$r_1 = -F_2(a)/F_2'(a) \quad (3.36)$$
$$r_2 = 1/F_1'(b) \quad (3.37)$$
$$r_3 = -1/F_2'(a) \quad (3.38)$$
$$r_4 = F_1(b)/F_1'(b). \quad (3.39)$$
The solutions to the ordinary differential equation (3.28) are of the form

\[ F_1 = \sin k \rho, \quad F_2 = \cos k \rho \quad k^2 > 0, \]

\[ F_1 = \sinh k \rho, \quad F_2 = \cosh k \rho \quad k^2 < 0. \]  

Hence, the matrices \( r_n \) are given by

\[
\begin{align*}
(r_1^{(i)})_{lm} &= (r_4^{(i)})_{lm} = \delta_{lm} \begin{cases} 
|k_m|^{-1} \cot |hk_m| & k_m^2 > 0 \\
-|k_m|^{-1} \coth |hk_m| & k_m^2 < 0
\end{cases} \\
(r_2^{(i)})_{lm} &= (r_3^{(i)})_{lm} = \delta_{lm} \begin{cases} 
|k_m|^{-1} \cosec |hk_m| & k_m^2 > 0 \\
-|k_m|^{-1} \cosech |hk_m| & k_m^2 < 0
\end{cases}
\end{align*}
\]

In this expression, \( \rho \) has been replaced by the sector width \( h = (b - a) \) to satisfy the boundary conditions.

Stechel, Walker and Light [188] derived a formula which relates the new global \( \mathcal{R} \)-matrix, \( \mathcal{R}^{(i)} \), to the sector matrix, \( r^{(i)} \), and the global \( \mathcal{R} \)-matrix from the previous sector, \( \mathcal{R}^{(i-1)} \).

\[
\mathcal{R}^{(i)} = r_4^{(i)} - r_3^{(i)} Z^{(i)} r_2^{(i)}
\]

where

\[
Z^{(i)} = [r_1^{(i)} + \bar{Q}(i - 1, i) \mathcal{R}^{(i-1)} Q(i - 1, i)]^{-1}
\]

and \( Q \) is the matrix whose elements are the overlaps between eigenvector bases in adjacent sectors. That is

\[
Q(i - 1, i) = T^{(i-1)} T^{(i)}.
\]

Alternatively, we can write \( Q \) in terms of overlap integrals of the basis functions \( \xi_n \).

\[
Q_{jk}(i - 1, i) = \langle \xi_j(i - 1) | \xi_k(i) \rangle.
\]

This formalism preserves the symmetry of the \( \mathcal{R} \)-matrix so that if both \( r^{(i)} \) and \( \mathcal{R}^{(i-1)} \) are symmetric then \( \mathcal{R}^{(i)} \) is also symmetric. The matrix \( r^{(i)} \) is diagonal and
thus trivially symmetric. Hence, if the $\mathcal{R}$-matrix in one sector is symmetric then so too is the $\mathcal{R}$-matrix in the next sector.

We define an initial $\mathcal{R}$-matrix $\mathcal{R}^{(1)}$

$$\mathcal{R}^{(1)}_{jk} = \delta_{jk}|k_j|^{-1}. \quad (3.47)$$

A solution of this form is appropriate to a system with a large repulsive potential near the origin, a feature of most chemical potential energy surfaces including the DFT potential used in this work.

The relationship between global $\mathcal{R}$-matrices in adjacent sectors may be derived using the original definition of the $F_n$

$$F_R(i-1) = T^{(i-1)} \cdot g \quad (3.48)$$

$$F_L(i) = T^{(0)} \cdot g. \quad (3.49)$$

After some straightforward manipulation of these expressions we find that

$$F_R(i-1) = Q(i-1, i) \cdot F_L(i) \quad (3.50)$$

and similarly for the derivatives

$$F'_R(i-1) = Q(i-1, i) \cdot F'_L(i). \quad (3.51)$$

We can combine equation (3.50) with the definition of the $\mathcal{R}$-matrix $\mathcal{R}^{(i)}$ in equation (3.21) so that

$$F_R(i-1) = \mathcal{R}^{(i-1)} F_R'(i-1)$$

$$= \mathcal{R}^{(i-1)} Q(i-1, i) F_L'(i). \quad (3.52)$$
Using this result to simplify the expression for $Z$, equation (3.44), we find

$$Z^{(i)} = [r_1^{(i)} + \bar{Q}(i - 1, i)F_R(i - 1)\bar{F}_L(i)]^{-1}$$  \hspace{1cm} (3.53)

then, using (3.50)

$$Z^{(i)} = [r_1^{(i)} + F_L(i)\bar{F}_L(i)]^{-1}. \hspace{1cm} (3.54)$$

Now we know from equation (3.33) that

$$F_L(i)\bar{F}_L(i) = -r_1^{(i)} + r_2^{(i)}F_R(i)\bar{F}_L(i) \hspace{1cm} (3.55)$$

hence

$$Z^{(i)} = [r_1^{(i)} - r_2^{(i)}F_R(i)\bar{F}_L(i)]^{-1} \hspace{1cm} (3.56)$$

$$= [r_2^{(i)}F_R(i)\bar{F}_L(i)]^{-1} \hspace{1cm} (3.57)$$

$$= F_L(i)F_R(i)r_2^{(i)}. \hspace{1cm} (3.58)$$

We can substitute this result into the expression for the global $R$-matrix in sector $i$, equation (3.43), to find

$$R^{(i)} = r_4^{(i)} - r_3^{(i)}F_R(i)\bar{F}_L(i)F_R(i)\bar{F}_L(i) \hspace{1cm} (3.59)$$

$$= r_4^{(i)} - r_3^{(i)}F_R(i)\bar{F}_L(i). \hspace{1cm} (3.60)$$

Rearranging this expression we find

$$R^{(i)}F_R(i) = r_4^{(i)}F_R(i) - r_3^{(i)}F_L(i) \hspace{1cm} (3.61)$$

but we recognise from equation (3.30) that the right hand side of this expression must be equal to $F_R(i)$. Hence, we have established that

$$R^{(i)}F_R(i) = F_R^{(i)}. \hspace{1cm} (3.62)$$
To summarise, we have defined an initial global $R$-matrix, $R^{(1)}$, and devised a propagation scheme so it is possible to integrate outwards in the coordinate $\rho$ to find the global $R$-matrix in the asymptotic region of the potential.

When the $R$-matrix has been calculated well into the asymptotic region of the potential we apply the scattering boundary conditions [185,186] and hence arrive at an equation for the $S$-matrix in terms of $R$.

$$S = k^{1/2}W^{-1}W^*k^{-1/2}$$  \hspace{1cm} (3.63)

where the channel momenta

$$k^2_n = 2m(E - \varepsilon_n)$$  \hspace{1cm} (3.64)

and the elements of the vector $k$ are

$$k_n = |2m(E - \varepsilon_n)|^{1/2}$$  \hspace{1cm} (3.65)

$$W = RO' - O$$  \hspace{1cm} (3.66)

and

$$O_{nq} = \begin{cases} \delta_{nq} \exp(ik_n \rho_{\text{max}}) & \text{channel n open} \\ \delta_{nq} \exp(-ik_n \rho_{\text{max}}) & \text{channel n closed} \end{cases}$$  \hspace{1cm} (3.67)

where $\rho_{\text{max}}$ is the hyperradius at which the matrix element is evaluated. A channel is said to be open when the energy of the system $E$ is greater than the vibrational energy of the channel $\varepsilon_n$. The $S$-matrix of equation (3.63) is relatively insensitive to closed channels so we can use a small $R$-matrix with few closed channels e.g. 39 are used in this work, compared with about 299 distributed gaussian basis functions. Each gaussian basis function had an exponent of $3.79 \times 10^4$. The remaining parameters used in the scattering calculations are listed in Table 3.1.
3.2 The R-Matrix Method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
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<tbody>
<tr>
<td>$\rho_{\text{min}}$</td>
<td>0.40</td>
<td>bohr</td>
</tr>
<tr>
<td>$\rho_{\text{step}}$</td>
<td>0.02</td>
<td>bohr</td>
</tr>
<tr>
<td>$\rho_{\text{final}}$</td>
<td>6.60</td>
<td>bohr</td>
</tr>
<tr>
<td>$\rho_{\text{range}}$</td>
<td>6.50 - 7.50</td>
<td>bohr</td>
</tr>
</tbody>
</table>

Table 3.1: Parameters used in the quantum reactive scattering calculations in this work. $\rho_{\text{range}}$ refers to the range of $\rho$ over which scattering boundary conditions were applied.

When the $S$-matrix has been determined we can calculate the state-to-state transition probabilities.

$$P_{nm} = |S_{nm}|^2.$$ (3.68)

The probability of a vibrational state of H on graphite, $n$ reacting to form $H_2$ is then given by

$$P_n = \sum_v |S_{vn}|^2$$ (3.69)

where $v$ labels the vibrational state of the $H_2$ molecule. The final probability of reaction is then

$$P = \sum_n P_n.$$ (3.70)

As we observed above, in astrophysical environments we assume that only the lowest H-graphite vibrational state is relevant so that $v = 0$ in the expressions for the state-to-state reaction probabilities above.
3.2.3 Probability Averaging

The scattering boundary conditions should normally be applied in cartesian coordinates. When the $S$-matrix elements are calculated using hyperspherical coordinates they oscillate as a function of $\rho$ about a mean value. In fact, the mean value is the required result [185]. Thus, we average the results over several final $\rho$ ($\rho_{\text{range}}$ in Table 3.1) to obtain the final result. The oscillations are more rapid at higher energies so we must average over more sectors. An alternative approach is to transform from hyperspherical to cartesian coordinates before applying scattering boundary conditions [190].

3.3 Numerical Methods

This section describes the numerical techniques employed in an implementation of the reactive scattering methods described above.

In any reactive scattering problem we wish to solve the Schrödinger equation $H\psi = E\psi$. In the case of the 2D Eley-Rideal reaction the Hamiltonian is

$$H = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial s^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial \rho^2} + V(r, s). \quad (3.71)$$

If we transform to hyperspherical coordinates $(\rho, \delta)$ and scale the wavefunction in the manner described in Section 3.1 the Hamiltonian becomes

$$H = -\frac{1}{2M} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{4\rho^2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \delta^2} \right). \quad (3.72)$$

As we demonstrated in Section 3.1, solving the Schrödinger equation for this Hamiltonian reduces to solving the coupled channel equations

$$\frac{\partial^2}{\partial \rho^2} \Phi_m = 2\mu(E - \epsilon_m)\Phi_m. \quad (3.73)$$
However, in deriving these equations one assumes that the $\epsilon_n$ and hence the solutions of the 1D Schrödinger equation

$$\hat{H}\xi_n(\delta) = \left\{-\frac{1}{2\mu \rho_j^2} \frac{\partial^2}{\partial \delta^2} + \frac{1}{4} + V(\rho, \delta)\right\} \xi_n(\delta) = \epsilon_n \xi_n(\delta) \quad (3.74)$$

are known.

A common approach to this problem is to rewrite $\xi_n(\delta)$ as a linear combination of $N$ basis functions. Explicitly

$$\xi_n(\delta) = \sum_{i=1}^{N} \eta_i(\delta) c_{in}. \quad (3.75)$$

Substituting this into the 1D Schrödinger equation, left-multiplying by $\eta_j^*(\delta)$ and integrating with respect to $\delta$ we find

$$\sum_{i=1}^{N} \langle \eta_j | \hat{H} | \eta_i \rangle c_{in} = \epsilon_n \sum_{i=1}^{N} \langle \eta_j | \eta_i \rangle c_{in}. \quad (3.76)$$

In matrix notation, this expression may be written

$$H_{ji}C_{in} = \epsilon_n S_{ji}C_{in} \quad (3.77)$$

where $H$ is the 1D Hamiltonian matrix and $S$ the overlap matrix of the basis functions $\eta_i(\delta)$. $T$ is the matrix which diagonalises the symmetric matrix $H$ in the basis of the $\eta_i$.

The total wavefunction can be written

$$\psi(\rho, \delta) = \sum_{n,j} \eta_j(\delta) c_{jn} \Phi_n(\rho) \quad (3.78)$$

which can be factorised in two ways. The first is

$$\sum_j \eta_j c_{jn} = \xi_n(\delta) \quad (3.79)$$
3.3 Numerical Methods

which is our original expansion of \( \xi_n \) in terms of the basis functions. The second

\[
\sum_n C_{jn} \Phi_n(\rho) = g_n(\rho),
\]

(3.80)
closely resembles equation (3.26) used in the propagation of the \( \mathcal{R} \)-matrix.

The second of these factorisations can be used to write the coupled equations

\[
\frac{d^2}{d\rho^2} g_n(\rho) = \sum_m E_{nm} g_m(\rho),
\]

(3.81)

where

\[
E_{ij} = 2m \left\langle \eta_i | \hat{H} | \eta_j \right\rangle - 2mE.
\]

(3.82)

These equations are of a suitable form for the \( \mathcal{R} \)-matrix method to be applied. \( E \) is a symmetric matrix so we can find a unitary transformation that diagonalises it \textit{viz}

\[
T^T E(\rho) T = -k^2.
\]

(3.83)

The orthonormal functions \( \xi_n \) have been found in the basis \( \{\eta_i\} \) by diagonalising \( E \). That is, the 1D Schrödinger equation has been solved so the coupled equations (equation (3.81)) may be solved using the \( \mathcal{R} \)-matrix method.

3.3.1 Distributed Gaussian Basis

Hamilton and Light [191] developed a method for using unequally spaced gaussian basis functions to represent the wavefunctions for vibrational problems. In this work, a uniformly distributed basis was chosen. The basis functions \( \{\eta_i(\delta)\} \) are gaussians centred at \( \delta_i \)

\[
\eta_i(\delta) = \left( \frac{A_i}{\pi} \right)^{1/4} \exp \left( -\frac{1}{2} A_i(\delta - \delta_i)^2 \right)
\]

(3.84)
where the gaussian coefficients are given by

\[ A_i = \frac{4c^2}{(\delta_{i+1} - \delta_{i-1})^2} \]
\[ A_1 = \frac{c^2}{(2 - \delta_1)^2} \]  
\[ A_N = \frac{c^2}{(\delta_N - \delta_{N-1})^2} \]

and \( c \) is a parameter chosen to minimise the eigenvalues in the first sector of the calculation. For large \( A_i \) the basis becomes more linearly dependent and for small \( A_i \) we obtain low kinetic energy eigenvalues. In this work, \( A_i = A \forall i \) was chosen and \( A \) was chosen to minimise the lowest eigenvalue. Furthermore, the basis consists of a set of evenly distributed functions with separation \( h \) so

\[ A = \left( \frac{c}{h} \right)^2. \]  

(3.86)

It is well known that the overlap of two gaussians is another gaussian. Since \( A_i = A \forall i \) and \( A > 0 \) the product is

\[ \eta_i^*\eta_j = \left( \frac{A}{\pi} \right)^{1/2} \exp \left( -\frac{A}{2}(\delta - \delta_i)^2 \right) \exp \left( -\frac{A}{2}(\delta - \delta_j)^2 \right). \]  

(3.87)

If we define \( \bar{\delta} = (\delta_i + \delta_j)/2 \) then this may be written

\[ \eta_i^*\eta_j = \left( \frac{A}{\pi} \right)^{1/2} \exp \left( -\frac{A}{2}(\delta - \bar{\delta})^2 \right) \exp \left( -A(\delta - \bar{\delta})^2 \right). \]  

(3.88)

Integrating with respect to \( \delta \) the elements of the overlap matrix in the gaussian basis are

\[ S_{ij} = \langle \eta_i | \eta_j \rangle = \exp \left( -\frac{A}{4}(\delta_i - \delta_j)^2 \right). \]  

(3.89)

The basis is not orthonormal, i.e. \( S_{ij} \neq \delta_{ij} \). Furthermore, \( A \) is fixed so the \( S_{ij} \) are the same for all sectors. Thus we need only calculate the overlaps, \( S_{ij} \), once. The results can be stored and re-used in subsequent calculations with the same basis set.
3.3 Numerical Methods

This represents a considerable saving in processor time. $S_{ij}$ provides a useful guard against over-completeness of the basis. The empirical relation $S_{i,i+1} \leq 0.7$ should be satisfied to avoid such problems with the basis. In this work, a value of $3.79 \times 10^4$ was found to be adequate for a basis of 299 gaussian functions.

Consider a Hamiltonian of a form similar to the 1D Hamiltonian in the scattering problem

$$\mathcal{H} = T + V = -\frac{1}{2M} \frac{\partial^2}{\partial \delta^2} + V(\delta).$$

It is straightforward to show that the elements of the Hamiltonian matrix are

$$\mathcal{H}_{ij} = \langle \eta_i | \mathcal{H} | \eta_j \rangle = T_{ij} + V_{ij}$$

where the kinetic energy matrix elements

$$T_{ij} = -\frac{1}{2M} \langle \eta_i | \frac{\partial^2}{\partial \delta^2} | \eta_j \rangle = S_{ij} \frac{1}{2M} (1 - A(\delta_i - \delta_j)^2)$$

and the potential matrix elements

$$V_{ij} = \langle \eta_i | V(\delta; \rho_f) | \eta_j \rangle = \left( \frac{A}{\pi} \right)^{1/2} \exp \left( -\frac{A}{4}(\delta_i - \delta_j)^2 \right) \int_0^{\pi/2} \exp(-A(\delta - \bar{\delta})^2)V(\delta; \rho_f)d\delta$$

$$= S_{ij} \left( \frac{A}{\pi} \right)^{1/2} \int_0^{\pi/2} \exp(-A(\delta - \bar{\delta})^2)V(\delta; \rho_f)d\delta.$$  \hspace{1cm} (3.93)

If $M$ is constant then the $T_{ij}$ do not change from sector to sector. $\delta_i$ and $\delta_j$ are the same in all sectors.
Chapter 4

Surface Diffusion

In Chapter 1 we identified diffusion on the surface of a solid as a step in the Langmuir-Hinshelwood mechanism. In this chapter we consider a theoretical model of such a process and explain the methods used to calculate the rate of diffusion at a surface.

Diffusion is an example of a Markov process. If we consider a discretized time axis, then a stationary random sequence has the Markov property if

\[ p(x_k|x_{k-1} \ldots x_1) = p(x_k|x_{k-1}). \] (4.1)

That is, the conditional probability of the state of the system depends only upon its previous state and not, as one might expect, on its history. If we consider a simple one-dimensional model of a diffusion process (e.g. flow of heat along a lagged bar or a simple transport problem) we have the diffusion equation (Fick's second law)

\[ \frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} \] (4.2)

where \( c(x,t) \) is the concentration of the diffusing substance and \( D \) is the diffusion coefficient. In this work we are concerned with evaluating the diffusion coefficient.
for H and D atoms on a graphite (0001) surface.

There are a number of different approaches to modelling diffusion of atoms on the surface of a solid [100]. However, before we consider the theoretical model we shall review the phenomenology of surface diffusion. A basic feature of surface diffusion which has important implications for the associated theory is that surface diffusion is typically an activated process i.e. it requires energy. The reason for this is simple, the interaction potential between the adsorbate and substrate is generally corrugated. It exhibits a range of possible adsorbate binding sites which are separated by potential barriers which may be large compared to thermal energies. Therefore, residence times at the binding sites are often large compared to lattice vibrational timescales. Under such circumstances we can regard surface diffusion as a series of hops from one binding site to another. Site-to-site transitions are made possible by adsorbate-lattice interactions (e.g. with surface phonons) or, for light adsorbates, quantum mechanical tunnelling.

The view of surface diffusion as a series of uncorrelated site-to-site hops suggests a Markovian random walk picture [86] of surface diffusion. In this representation, the mean-square displacement of the $x$-component of the position of the adsorbed particle is

$$\langle (\Delta x^2(t)) \rangle = \nu \ell^2 t$$

(4.3)

where $\nu$ is the frequency of jumps, $\ell^2$ the mean-square jump length, and $t$ is time. In the limit as $t \to \infty$ the ratio of the mean square displacement to the time defines a time-independent measure of the diffusion of the adsorbate. The diffusion constant
where $\Delta R$ is the displacement of the adsorbed particle and $\sigma$ is the dimensionality of the diffusion process (e.g. $\sigma = 2$ for surface diffusion). The linear time dependence of the adsorbate's mean square displacement is the signature of diffusion.

For light adsorbates at very low temperatures an alternative diffusion mechanism is possible [109,192]. If the substrate is perfectly periodic, the adsorbate may be considered to be delocalised across the surface. This coherent tunnelling is destroyed by lattice vibrations at higher temperatures where the uncorrelated hopping approximation is valid. In astrophysical environments the temperatures are sufficiently low for this type of motion. However, we anticipate that the surfaces of dust grains will be highly irregular so the uncorrelated hopping approximation should offer a reasonable estimate of the diffusion rate appropriate to astrophysical problems.

In this study, the diffusion of hydrogen atoms on solid surfaces is regarded as a series of uncorrelated hops by individual hydrogen atoms between adjacent binding sites on the surface. At sufficiently high temperatures, hops by the atoms which traverse several binding sites become increasingly important. We expect that such hops will not contribute significantly under the conditions pertinent to this study. Within the uncorrelated hopping approximation the diffusion at low surface coverage is given by [100]

$$D = \frac{1}{4} \sum_{i=1}^{N} X_i \ell_i^2 k_i$$

(4.5)

where $i$ labels the different possible binding sites on the surface. In this expression $X_i$ is the equilibrium mole fraction of the adsorbate in sites of type $i$, $\ell_i$ is the
separation of adjacent binding sites and $k_i$ the fundamental thermal rate constant for hopping out of site $i$. The central theoretical challenge of this expression is the calculation of the rate constant $k_i$, particularly at low temperatures where quantum effects are likely to be significant. The expression for the diffusion constant in equation (4.5) has been employed in a number of quantum and classical studies of hydrogen diffusion [114,119,120,126,193,194]. However, it is important to note that this expression does not allow for the possibility of coherent quantum diffusion which arises from delocalised hydrogen surface states, as described above. In the case of hydrogen diffusion on an unreconstructed graphite (0001) surface the diffusion constant is given by

$$D = \frac{\sqrt{3}}{2} \ell^2 k_{\text{hop}}$$

(4.6)

where $\ell$ is the distance between adjacent binding sites and $k_{\text{hop}}$ is the thermal rate constant for hopping between binding sites.

We adopt a Feynman path integral [63–65] approach to calculate the fundamental rate constants $k_{\text{hop}}$ of equation (4.6) and hence the diffusion constant. The method employed is the path integral quantum transition state theory (PI-QTST) for the rate constant of a general quantum activated rate process originally proposed by Gillan [123] and further developed by Voth, Chandler and Miller [124] and others [195]. In what follows we describe the Feynman path integral formulation of quantum mechanics and how it may be used to calculate the partition functions of systems of chemical interest. This formulation of quantum mechanics is used to calculate the rates of quantum activated processes in a quantum mechanical transition state theory. The thermal rate constants calculated in this manner can be used to calculate the diffusion constant using the prescription of equation (4.6). We omit
4.1 Feynman Path Integrals

The path integral formulation of quantum mechanics was developed by Feynman [63,64] and applied to quantum electrodynamics and statistical mechanics [65]. In statistical mechanics the path integral formulation enables one to write the quantum partition function as a higher dimensional classical partition function with a modified potential. That this quantum-classical isomorphism could be used to perform Metropolis Monte Carlo calculations was first demonstrated by Morita [196] and later by Barker [197]. The ideas were developed by Chandler, Wolynes and co-workers for application to atomic systems [198,199]. In recent years, the path integral approach to quantum mechanics has been applied to compute properties of many-body systems and mixed quantum-classical systems in thermal equilibrium.

4.1.1 The Path Integral Formulation of Quantum Mechanics

The usual starting point for a description of the path integral formulation of quantum mechanics is the following classical example. If a particle is at position $x_a$ at time $t_a$ and goes to a final position $x_b$ at time $t_b$, then we can express the position of the particle as a path $x(t)$, a function of $t$ defined so that $x(t_a) = x_a$ and $x(t_b) = x_b$. In classical mechanics there is a single trajectory from $a$ to $b$, the classical trajectory $\bar{x}(t)$. An elegant method for determining the classical trajectory is Hamilton's principle of least action. In essence, there is a quantity $S$ called the classical action that can be computed for each path and the classical path $\bar{x}$ is that for which $S$ is
minimised (actually an extremum). The quantity $S$ is given by

$$S = \int_{t_a}^{t_b} \mathcal{L}(\dot{x}, x; t) dt$$

(4.7)

where $\mathcal{L}$ is the Lagrangian for the system. If we consider a particle of mass $m$ moving in a potential $V(x)$, the Lagrangian is

$$\mathcal{L} = \frac{m}{2} \dot{x}^2 - V(x).$$

(4.8)

The classical trajectory $\bar{x}(t)$ is determined from the calculus of variations. We suppose that the path is displaced from $\bar{x}$ by a small amount $\delta x(t)$. Since the endpoints are fixed we require that

$$\delta x(t_a) = \delta x(t_b) = 0$$

(4.9)

and since $\bar{x}$ is an extremum of $S$ we know that

$$\delta S = S[\bar{x} + \delta x] - S[\bar{x}] = 0.$$  

(4.10)

Using the definition of the classical action in equation (4.7) we can write

$$S[\bar{x} + \delta x] = \int_{t_a}^{t_b} \mathcal{L}(\dot{x} + \delta \dot{x}, x + \delta x; t) dt$$

$$= \int_{t_a}^{t_b} \left[ \mathcal{L}(\dot{x}, x; t) + \delta \dot{x} \frac{\partial \mathcal{L}}{\partial \dot{x}} + \delta x \frac{\partial \mathcal{L}}{\partial x} \right] dt$$

$$= S[\bar{x}] + \int_{t_a}^{t_b} \left[ \delta \dot{x} \frac{\partial \mathcal{L}}{\partial \dot{x}} + \delta x \frac{\partial \mathcal{L}}{\partial x} \right] dt.$$  

(4.11)

When we integrate by parts the variation in $S$ becomes

$$\delta S = \delta \dot{x} \left. \frac{\partial \mathcal{L}}{\partial \dot{x}} \right|_{t_a}^{t_b} - \int_{t_a}^{t_b} \delta x \left[ \frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{x}} \right) - \frac{\partial \mathcal{L}}{\partial x} \right] dt.$$  

(4.12)

We know that $\delta x = 0$ at the endpoints so the first term on the right hand side of this expression vanishes. The second term vanishes for the path along which the following condition is satisfied

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{x}} \right) - \frac{\partial \mathcal{L}}{\partial x} = 0$$  

(4.13)
because $\delta x$ can take an arbitrary value between the end points. This expression is the Euler–Lagrange equation of classical mechanics.

Now we turn our attention to the quantum mechanical case. In quantum mechanics all paths contribute equal amounts to the total amplitude but at different phases. The phase of the contribution of a particular path is the classical action $S$ for the path expressed in units of $\hbar$. That is, the probability $P(a, b)$ that a particle will go from $x_a$ at time $t_a$ to the point $x_b$ at time $t_b$ is given by the absolute square of an amplitude $K(b, a)$ to go from $a$ to $b$. The amplitude is the sum of contributions $\phi[x(t)]$ from all paths between $a$ and $b$, that is

$$K(b, a) = \sum_{\text{paths}} \phi[x(t)]. \quad (4.14)$$

The contribution of each path has a phase related to the action $S$

$$\phi[x(t)] = C \exp(iS[x(t)]/\hbar). \quad (4.15)$$

The action is that of the corresponding classical system and the constant $C$ is chosen to normalise $K$ conveniently. The kernel, $K(a, b)$ of equation (4.14) may be written

$$K(a, b) = \int_a^b \mathcal{D}x(\tau) \exp(iS[x(\tau)]/\hbar) \quad (4.16)$$

where the measure $\mathcal{D}x(\tau)$ indicates that the integration is performed over all possible paths between $a$ and $b$.

### 4.1.2 Application to Statistical Mechanics

A quantum system in thermal equilibrium can exist in one of a number of energy levels. Quantum statistical mechanics shows that the probability that the system is in a state with energy $E$ at temperature $T$ is proportional to $\exp(-\beta E)$ where
\( \beta = 1/k_B T \) and \( k_B T \) measures the temperature in energy units.

We can express the exponential law as a true probability by the inclusion of the normalising factor \( 1/Q \) so that the probability that the system is in the non-degenerate state with energy \( E_i \) is

\[
p_i = \frac{1}{Q} e^{-\beta E_i}.
\]  \hspace{1cm} (4.17)

Thus, we deduce that the partition function

\[
Q = \sum_i e^{-\beta E_i}.
\]  \hspace{1cm} (4.18)

An equivalent normalisation involves the Helmholtz free energy \( F \) so that

\[
p_i = e^{-\beta (E_i - F)}.
\]  \hspace{1cm} (4.19)

The value of \( F \) is a function of temperature and it is clear that

\[
Q = e^{-\beta F}.
\]  \hspace{1cm} (4.20)

It is possible to derive the physical properties from a system in thermal equilibrium from the partition function [65,200,201]. For example, the standard thermodynamic quantities such as internal energy, entropy and pressure can be derived from simple operations on the partition function.

In certain cases we need more information than just the partition function. For example, if we consider a system in a configuration space with coordinate \( x \) and we wish to determine the probability of finding the system at a point \( x \) within this space. If the system is in the pure state defined by the normalised wavefunction \( \psi_i(x) \) then this probability is the absolute square of the wavefunction \( \psi_i^*(x)\psi_i(x) \).
Thus, if we average over all possible states, the probability of observing the system at $x$ is

$$P(x) = \frac{1}{Q} \sum_i \psi_i^*(x)\psi_i(x)e^{-\beta E_i}. \quad (4.21)$$

If we are interested in the observable $A$ then the expectation value is

$$\hat{A} = \frac{1}{Q} \sum_i \langle A_i \rangle e^{-\beta E_i} = \frac{1}{Q} \sum_i \int \psi_i^*(x)\hat{A}\psi_i(x)e^{-\beta E_i}dx. \quad (4.22)$$

It is clear from this expression that the expectation values of all such quantities can be determined if the function

$$p(x', x) = \sum_i \psi_i(x')\psi_i^*(x)e^{-\beta E_i} \quad (4.23)$$

is known. The quantity $p(x', x)$ is the thermal density matrix. We can rewrite the expression for the expectation value of an operator $\hat{A}$ in terms of this function as

$$\hat{A} = \text{Tr}\{A\rho\}. \quad (4.24)$$

It is also clear from the definition of $p(x', x)$ that

$$P(x) = \frac{1}{Q} \rho(x, x) \quad (4.25)$$

and the fact that $P(x)$ is normalised means that the partition function can be derived from $\rho$

$$Q = \int \rho(x, x)dx = \text{Tr}\{\rho\}. \quad (4.26)$$

If we are only interested in conventional thermodynamic quantities then we need only determine the trace of the density matrix which is the partition function $Q$.

The expression for the density matrix in equation (4.23) is of a similar form to the kernel

$$K(x_2, t_2; x_1, t_1) = \sum_j \psi_j(x_2)\psi_j^*(x_1)e^{-iE_j(t_2-t_1)/\hbar}. \quad (4.27)$$
4.1 Feynman Path Integrals

This expression is valid only when the Hamiltonian is constant in time and where \( t_2 > t_1 \). This situation is implicit in statistical mechanics since a system with a time-dependent Hamiltonian will not attain thermal equilibrium. We can exploit the similarity between the kernel and the thermal density matrix to derive a path integral expression for the thermal density matrix [64,65]. If the time interval \( t_2 - t_1 \) in the kernel (Equation (4.27)) is replaced by \(-i\beta\hbar\) it is clear that the expression for the density matrix is formally identical to the kernel for an imaginary time interval.

We can develop the similarity between the two expressions from a slightly different perspective if we write the density matrix in a form more reminiscent of a kernel. That is, we can write \( k(x_2, \tau_2; x_1, \tau_1) \) for \( \rho(x_2, x_1) \), where

\[
k(x_2, \tau_2; x_1, \tau_1) = \sum_j \psi_j(x_2)\psi^*_j(x_1)e^{-E_j(\tau_2-\tau_1)/\hbar}.
\]  

If \( x_2 = x', x_1 = x, \tau_2 = \hbar\beta \) and \( \tau_1 = 0 \) this expression is identical to the expression for the density matrix in equation (4.23). After some straightforward manipulation [64], one can derive a Schrödinger equation for the density matrix. It is then a relatively simple matter to show that for the simple 1D system in equation 4.8 the thermal density matrix element is

\[
\rho(x_2, x_1) = \int_{x_1}^{x_2} \mathcal{D}x(\tau) \exp\left\{ -\frac{1}{\hbar} \int_0^{\beta\hbar} \left[ \frac{m}{2} \dot{x}^2(\tau) + V(x(\tau)) \right] d\tau \right\}. 
\]  

(4.29)

In this expression we consider a path, \( x(\tau) \), as a function which gives a coordinate in terms of the parameter \( \tau \) and let \( \dot{x} \) be the derivative \( dx/d\tau \). We can write this expression as an imaginary time path integral of the general form

\[
\rho(x_2, x_1) = \int_{x_1}^{x_2} \mathcal{D}x(\tau) \exp\left( -S_E[x(\tau)]/\hbar \right)
\]  

(4.30)

where \( S_E[x(\tau)] \) is the Euclidean action of the system. In fact, the thermal density matrix of a general quantum system can be written in this form [64,65]. Hence, we
can write the partition function of a general quantum system as an imaginary time path integral over closed paths. That is,

$$Q(\beta) = \oint \mathcal{D}x(\tau) \exp(-S_D[x(\tau)]/\hbar). \quad (4.31)$$

### 4.1.3 The Classical Isomorphism

We have seen that the partition function is the trace of the thermal density matrix. For a single particle of mass $m$ in an external potential $V(x)$ we can write the partition function $Q$ as an integral over elements of the density matrix

$$Q = \int dx\langle x| \exp(-\beta \mathcal{H})|x\rangle. \quad (4.32)$$

We can interpret $\exp(-\beta \mathcal{H})$ as the propagator in imaginary time, $\tau = i\beta \hbar$. This representation of the thermal density matrix may be discretized as follows. Writing the propagator $\exp(-\beta \mathcal{H}) = [\exp(-(\beta/P) \mathcal{H})]^P$ and inserting $P - 1$ complete sets of coordinate states $\{|x_i\}$

$$Q = \int dx_1 \ldots \int dx_P \langle x_1| \exp(-\beta \mathcal{H}/P)|x_2\rangle \langle x_2| \exp(-\beta \mathcal{H}/P)|x_3\rangle \ldots \langle x_{P-1}| \exp(-\beta \mathcal{H}/P)|x_P\rangle \quad (4.33)$$

where the path is cyclic (i.e. $x_1 = x_{P+1}$) because of the trace condition associated with the partition function. We can write the Trotter product rule [202]

$$\exp(-\beta \mathcal{H}) = \lim_{P \to \infty} [\exp(-\epsilon \hat{K}/P) \exp(-\epsilon \hat{V}/P)]^P \quad (4.34)$$

where $\hat{K}$ and $\hat{V}$ are the kinetic and potential energy operators, respectively and $\epsilon = \beta/P$. The short-time (or, equivalently, high-temperature) density matrix is then

$$\rho(x_i, x_{i+1}; \beta/P) = \langle x_i| \exp(-\beta \mathcal{H}/P)|x_{i+1}\rangle$$

$$= \langle x_i| \exp(-\beta \hat{K}/P)|x_{i+1}\rangle \exp(-\beta V(x_{i+1})/P). \quad (4.35)$$
The kinetic energy operator $\hat{K} = \hat{p}^2/2m$ where $\hat{p}$ is the momentum operator so if we insert a complete set of momentum states $\{|p\rangle\}$ we obtain

$$\rho(x_i, x_{i+1}; \beta/P) = \int dp |p\rangle \exp \left( -\frac{\beta \hat{p}^2}{2mP} \right) \langle p|x_{i+1}\rangle \exp \left( -\frac{\beta V(x_{i+1})}{P} \right)$$

$$= \int \frac{dp}{2\pi \hbar} \exp \left( -\frac{\beta \hat{p}^2}{2mP} \right) \exp \left( \frac{ip(x_i - x_{i+1})}{\hbar} \right) \exp \left( -\frac{\beta V(x_{i+1})}{P} \right)$$

$$= \left( \frac{mP}{2\pi \beta \hbar^2} \right)^{1/2} \exp \left( -\frac{mP(x_i - x_{i+1})^2}{2\beta \hbar^2} \right) \exp \left( -\frac{\beta V(x_{i+1})}{P} \right).$$

(4.36)

This is the primitive approximation to the short-time density matrix. If we substitute this expression into the canonical partition function of equation (4.33) we obtain

$$Q_P = \left( \frac{mP}{2\pi \beta \hbar^2} \right)^{P/2} \int dx_1 \ldots \int dx_P \exp \left( -\beta \sum_{i=1}^{P} \left[ \frac{mP}{2\beta \hbar^2} (x_i - x_{i+1})^2 + \frac{1}{P} V(x_i) \right] \right).$$

(4.37)

Thus, the quantum particle is represented by $P$ replicas at equidistant points in imaginary time $\tau$ between 0 and $\beta \hbar$ which are given by $\{x_i\}$ where $x_1 = x_{P+1}$. In the limit $P \to \infty$ this expression becomes the exact partition function and the exponent in equation (4.37) becomes the Euclidean action $S_E[x(\tau)]$ along an imaginary time path.

$$S_E[x(\tau)] = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} \left[ \frac{1}{2} m\dot{x}^2(\tau) + V(x(\tau)) \right] d\tau.$$

(4.38)

Thus, we recover the path integral expression for the density matrix element of equation (4.30). The exponential weighting factor ensures that paths with very high action make a much smaller contribution to the density matrix element than those with low values of the action. All path integral simulation methods are techniques for sampling the physically important paths which contribute to the partition function. We leave a discussion of the numerical techniques for evaluating path integrals until Section 5.1.
We now consider equation (4.37) more carefully. This expression may be interpreted as the partition function for a classical polymer of $P$ monomer units or beads. Adjacent beads are connected by harmonic springs with force constant $mP/\beta\hbar^2$ and all the beads in the polymer experience the external potential $V$. From a computational perspective, this isomorphism implies that to any configuration of the classical system, a Boltzmann-type weight may be applied and multidimensional integration techniques such as Metropolis Monte Carlo sampling [88] can be used. The isomorphism with a classical ring polymer also makes the evaluation of path integrals amenable to Molecular Dynamics techniques [203]. We consider the evaluation of path integrals using Monte Carlo methods in greater detail in Chapter 5. However, at this stage we note that the more quantum mechanical the system, the greater the number of beads required in the chain to describe the system accurately. Thus, the dimensionality and computational cost of a path integral simulation is generally much higher than that of the corresponding classical system.

4.2 Quantum Transition State Theory

It is instructive to briefly review the basic structure of classical activated rate theory [97,204]. The classical theory of the activated rate constant is a highly evolved and powerful theory both in its rigorous formulation and the transition state theory (TST) approximation. The purpose of this brief survey is to illustrate the difficulty of directly extending the theory to the quantum regime. The rigorous expression for the classical forward rate constant is written in terms of a correlation function as

$$k_{cl} = x_R^{-1} \langle \hat{h}_P(0) \hat{h}_P(t_{pl}) \rangle_{cl} \quad (4.39)$$
where \( x_R \) is the equilibrium mole fraction of the reactant, \( \langle \ldots \rangle_{cl} \) represents classical averaging over the canonical phase space density and \( h_P \) is the product state function, usually taken to be the Heaviside step function at the dividing surface \( q = q^* \). The classical rate constant is obtained from this expression when the correlation function reaches a plateau at time \( t = t_{pl} \) [205, 206].

One can show [205] that the classical TST approximation to the rate constant is the \( t \to 0^+ \) limit of equation (4.39), that is

\[
k_{cl}^{TST} = x_R^{-1} \lim_{t \to 0^+} \langle h_P(0) h_P(t) \rangle_{cl}.
\]  

(4.40)

Thus, we can write the exact classical rate constant as

\[
k_{cl} = \kappa_{cl} k_{cl}^{TST}
\]  

(4.41)

where \( \kappa_{cl} \) is the dynamical correction factor or transmission coefficient which is usually of order unity. A great deal of theoretical effort has been directed towards the development of a general theory for the dynamical correction factor \( \kappa_{cl} \).

The TST approximation for the classical rate constant \( k_{cl} \) is often expressed in terms of the canonical partition function of the system

\[
k_{cl}^{TST} = \frac{1}{2} \langle |v| \rangle_{cl} Q^*_d / Q_{R,cl}.
\]  

(4.42)

In this expression \( Q_{R,cl} \) is the classical partition function of the total system in the reactant state, \( \langle |v| \rangle_{cl} \) is the flux across the dividing surface in the reaction coordinate \( q \) and \( Q^*_d \) is the reduced classical phase space density at the dividing surface. This quantity can be expressed in terms of the classical canonical phase space density
4.2 Quantum Transition State Theory

\[ \rho_c(q, x) \]

as

\[ Q_c^* = \int dq \int dx \delta(q^* - q) \rho_c(q, x) \]

\[ = \frac{1}{(2\pi\hbar)^{N+1}} \int dp_q \int dp_x \int dq \int dx \delta(q^* - q) \exp(-\beta \mathcal{H}). \] (4.43)

The TST expression may also be written in terms of the excess classical free energy at the dividing surface

\[ k_{cl}^{TST} = \frac{k_B T}{h Q_{R, cl}} \exp(-\beta F_{cl}^*) \] (4.44)

where

\[ F_{cl}^* = -k_B T \ln[Q_c^*/(m/2\pi\hbar^2 \beta)^{1/2}] \] (4.45)

and \( m \) is the effective mass in the reaction coordinate motion. The most important factor in equation (4.44) is the dimensionless classical free energy factor \( \exp(-\beta F_{cl}^*) \), which, in relation to the reactant state partition function, leads to the activation factor in TST. This factor dominates the temperature dependence of the rate constant.

The structure of quantum mechanics does not allow one to formulate a quantum transition state theory (QTST) approximation to the rate constant using the same mathematical procedure as in the classical case. In particular, the exact quantum mechanical activated rate constant can be written as [207]

\[ k = \frac{1}{x_R \hbar \beta} \int_0^{\beta \hbar} d\tau \langle \hat{h}_P(-i\tau)\hat{h}_P(t_{pl}) \rangle, \] (4.46)

where \( x_R \) is the equilibrium mole fraction of the reactant, \( h_P \) is the product state operator (usually the Heaviside step function in the coordinate representation) and \( t_{pl} \) is the plateau time at which the correlation function assumes an essentially constant value. However, the \( t \to 0^+ \) limit of this expression is identically zero [207]. Thus, an
alternative approach must be adopted to formulate a QTST and a theory of dynamical corrections. The path integral QTST described here is one approach. A number of alternative quantum and classical approaches have been proposed [119, 208–210] but we do not pursue them here.

The approach to a quantum mechanical transition state theory described below relies heavily on Feynman’s formulation of quantum statistical mechanics [64, 65]. As we stated above, in that formulation, the partition function for a physical system is expressed as an imaginary time path integral

$$Q = \int \ldots \int \mathcal{D}q(\tau) \mathcal{D}x(\tau) \exp\left(-S_E[q(\tau), x(\tau)]/\hbar\right)$$

(4.47)

where, for the purposes of studying activated dynamics problems, the reaction coordinate $q(\tau)$ is defined separately from the other system coordinates $x(\tau)$. Discretized versions of the Feynman path integral have been used widely to study the equilibrium states of a number of condensed matter systems [128, 211].

The progress towards a path integral quantum TST is, in part, due to the importance of the path centroid variable $\tilde{q}_0$ in path integration [123, 124, 128]. This variable is defined in the reaction coordinate, for example, by the expression

$$\tilde{q}_0 = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} dq(\tau)$$

(4.48)

or in the discretized representation by

$$\tilde{q}_0 = \frac{1}{P} \sum_{i=1}^{P} q_i.$$  

(4.49)

The centroid variable is, therefore, the imaginary time average of the quantum path $q(\tau)$. In the discretized representation it is the centre of mass of the chain of classical
quasiparticles with coordinates $q_i$ at the imaginary timeslices $\tau_i = (i - 1)\beta \hbar / P$.

Feynman and Hibbs [64] (FH) were the first to recognise that the path centroid is a useful classical-like variable in quantum statistical mechanics. However, they did not address the problem of activated dynamics. FH formulated a centroid-based effective quasiclassical Boltzmann density which is an approximation to the exact multidimensional centroid density function $\rho_c(q_c, x_c)$. The latter function can be defined as the constrained path integral

$$\rho_c(q_c, x_c) = \int \ldots \int \mathcal{D}q(\tau) \mathcal{D}x(\tau) \delta(q_0 - q_c) \delta(x_0 - x_c) \exp(\frac{-S_{\text{eff}}[q(\tau), x(\tau)]}{\hbar}).$$

(4.50)

FH arrived at their approximate theory after a simplification of the full centroid density in equation (4.50) using a variational approach based upon the reference action functional

$$S_{\text{ref}}[q(\tau), x(\tau)] = \int_0^{\beta \hbar} \left[ \frac{m_q^2(\tau)}{2} + \sum_{t=1}^N \frac{m_{\text{eff}}(\tau)}{2} + V_{\text{eff}}(\bar{q}_0, \bar{x}_0) \right] d\tau.$$ (4.51)

The FH approximation for the centroid density is only useful near the classical limit because the variational reference action functional is a high temperature approximation to the exact action functional.

Valone, Voter and Doll [120, 212] exploited the intuitive appeal of the FH quasiclassical effective potential approach to calculate an approximate diffusion constant for a hydrogen atom on a metal surface. VVD were guided by classical TST in their approach but they replaced the classical canonical density $\rho_c(q, x)$ by the FH quasiclassical density (obtained by substituting equation (4.51) into equation (4.50)). Further evidence for the importance of the centroid variable in path integration came from Sprik et al. [213] in studies of lithium atom ionisation in liquid ammonia. However, these authors studied the average energy rather than free energy as
a function of the ionising electron centroid variable.

In a number of later papers Gillan adopted a path integral simulation procedure to study the activated dynamics of hydrogen diffusion between interstitial impurity sites in a metal [122]. In Gillan’s procedure, the free energy for moving the centroid of the Feynman paths from a stable interstitial impurity to a saddle point between two neighbouring interstitial sites is calculated. Gillan speculated that this procedure might be the quantum mechanical equivalent of the classical TST method for calculating the free energy of activation. The procedure does not yield an absolute value of the activated rate constant but it does enable the relative rates at different temperatures to be studied. In a later paper [123], Gillan analysed the quantum activated rate problem for a symmetric double well coupled to a classical harmonic bath. His analysis suggested that the centroid density occupies a central role in the high and low temperature limits of the latter problem and provided some justification for the procedure adopted in his earlier calculations [122].

In general terms, the quantum activated rate constant can be calculated with a general TST-like theory if such a theory provides a means to find both the quantum activation free energy and the prefactor. The latter factor must be the QTST equivalent of the classical velocity factor in equation (4.42) or, equivalently, the classical pre-exponential factor of equation (4.44). Such a theory has been under development for a number of years [124,128,195,214–216] beginning with a paper by Voth, Chandler and Miller [124]. These authors presented an analysis of the general quantum activated rate problem from the perspective of path integral centroid statistics. Gillan also proposed a path integral formula for the activated rate constant in the
4.2 Quantum Transition State Theory

case of a double well system [123], but his expression differs in the general case from the method used in this work [217].

Recently, Cao and Voth [195] showed that several existing quantum reaction rate theories could be unified around a single mathematical framework. The theories include the high temperature parabolic barrier approximation [218], the low temperature instanton approach [209] and the path integral quantum transition state theory. In particular, they showed that for a one dimensional system the quantum reactive flux may be written

\[ F \propto \nu \text{Im} Q_b \]  

where \( Q_b \) is the barrier partition function

\[ Q_b = \int_b \mathcal{D}q(\tau) \exp(-SE[q(\tau)]/h). \]  

The simple piecewise continuous frequency factor \( \nu \) is given by

\[ \nu = \begin{cases} \omega_b/2\pi & \hbar\omega_b < 2\pi \\ 1/\hbar\beta & \hbar\beta \omega_b \geq 2\pi \end{cases} \]  

where \( \omega_b \) is the imaginary frequency at the top of the barrier. It is understood that the barrier partition function \( Q_b \) is treated in an asymptotic fashion appropriate to the temperature.

For many-dimensional systems these equations should be modified to include the effects of coupling to a thermal bath. The basic form of the reactive flux expression (equation (4.52)) is the same but the barrier partition function is defined for the complete many-dimensional system. Invoking the linear-response approximation [219]
the expression for the frequency factor becomes
\[ \nu = \begin{cases} \frac{\lambda_0^t}{2\pi} & \hbar \beta \lambda_0^t < 2\pi \\ 1/\hbar \beta & \hbar \beta \lambda_0^t \geq 2\pi \end{cases} \tag{4.55} \]

where \( \lambda_0^t \) is the Grote-Hynes frequency \([220]\), given by
\[ \lambda_0^t = \frac{\omega_0^2}{\lambda_0^t + \hat{\eta}(\lambda_0^t)/m}. \tag{4.56} \]

Here, \( m \) is the effective mass of the reaction coordinate and \( \hat{\eta}(z) \) is the Laplace transform of the classical autocorrelation function of the force fluctuations \( \delta F(t) \) from the bath modes on the reaction coordinate at the transition state (i.e. the frequency-dependent friction). Explicitly,
\[ \hat{\eta}(z) = \beta \int_0^\infty e^{-zt} \langle \delta F(t) \delta F(0) \rangle_{q^*}. \tag{4.57} \]

where \( \langle \ldots \rangle_{q^*} \) denotes classical Boltzmann averaging over bath variables which are equilibrated with the reaction coordinate fixed at \( q^* \).

Cao and Voth used the expression for the quantum reactive flux (equation (4.52)) to rationalise the central role of the imaginary time path centroid in quantum activated dynamics. Starting with the definition of the imaginary time path centroid density
\[ \rho_c(q_c) = \int \mathcal{D}q(\tau) \delta(q_c - \bar{q}_0) \exp(-S_E[q(\tau)]/\hbar) \tag{4.58} \]
where a one-dimensional model has been used for didactic purposes, the exact quantum partition function may be formally expressed as the centroid trace
\[ Q = \int dq_c \exp(-\beta V_c(q_c)). \tag{4.59} \]

The effective centroid potential is
\[ V_c(q_c) = -kT \ln[\rho_c(q_c)]. \tag{4.60} \]
The effective centroid potential may be used to evaluate the barrier partition function within the steepest descent approximation [221]. The centroid potential is expanded about its maximum at \( q^* \) giving

\[
V_c(q_c) \approx V_c(q^*) + \frac{1}{2} V''_c(q^*)(q_c - q^*)^2.
\]  

(4.61)

The maximum of the effective centroid potential is determined by the condition

\[
\langle V'(q^*) \rangle_c = 0
\]

(4.62)

and the curvature of the centroid potential is given by

\[
V''_c(q^*) = \langle V''(q^*) \rangle_c - \beta \langle [\langle V'(q^*) \rangle_c - \langle V'(q^*) \rangle_c]^2 \rangle
\]

(4.63)

where \( \langle \ldots \rangle_c \) denotes a centroid-constrained average at the transition state, that is

\[
\langle f(q^*) \rangle_c = \frac{\int \mathcal{D}q(\tau) f[q(0)] \delta(q_c - \bar{q}_0) \exp(-S_E[q(\tau)]/\hbar) \int \mathcal{D}q(\tau) \delta(q_c - \bar{q}_0) \exp(-S_E[q(\tau)]/\hbar)}{\int \mathcal{D}q(\tau) \delta(q_c - \bar{q}_0) \exp(-S_E[q(\tau)]/\hbar)}
\]

(4.64)

and

\[
\bar{V} = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} d\tau V[q(\tau)].
\]

(4.65)

If the curvature of the centroid potential is negative then the centroid variable may be used to evaluate the barrier partition function via a steepest descent approximation to equation (4.59) along the imaginary axis \( (q_c \rightarrow iq_c) \)

\[
Q_b \approx i \rho_c(q^*) \int_{-\infty}^{\infty} dq_c \exp[-\beta |V''_c(q^*)|(q_c - q^*)^2/2]
\]

\[
= i \left( \frac{2\pi}{\beta |V''_c(q^*)|} \right)^{1/2} \rho_c(q^*)
\]

(4.66)

where \( |V''_c(q^*)| \) is the absolute value of the curvature of the effective centroid potential at its maximum. Simplifying further, the expression for the quantum rate constant is given by

\[
k \approx \nu \left( \frac{2\pi}{\beta |V''_c(q^*)|} \right)^{1/2} \frac{e^{-\beta V_c(q^*)}}{\int_{-\infty}^{q^*} dq_c e^{-\beta V_c(q_c)}}.
\]

(4.67)
This expression may be evaluated using numerical path integral techniques (described in Chapter 5) and the simple prescription for the frequency factor in equation (4.55).

For high temperatures, particularly those above the quantum-classical crossover, the frequency factor is given by [195] \( \nu = \lambda_0^2 / 2 \pi \) and \( |V_c(q^*)| \) can be approximated by \( m \omega_q^2 \). With these approximations the rate constant expression in equation (4.67) reduces to the path integral QTST (PI-QTST) formula [214] for many-dimensional systems

\[
k_{\text{PI-QTST}} = \frac{\lambda_0^2}{\omega_b \sqrt{2\pi m\beta}} \frac{1}{\int_{-\infty}^{q^*} dq e^{-\beta V_c(q)}}.
\]  

(4.68)

The steepest descent approach described above provides some insight into the importance of the centroid variable and its equilibrium density at the transition state in the determination of the quantum thermal rate constant. In this approach the centroid constraint arises naturally without being artificially introduced [124]. Indeed, the quantum reaction coordinate \( q \) is clearly defined to be the coordinate which possesses the unstable centroid mode and the quantum transition state along the coordinate is specified by the value of \( q = q^* \) which maximises the effective centroid potential in the barrier region [124] (this is not necessarily the same as the classical transition state [124, 222]).

The expressions above are readily generalised to many-dimensional systems. In the latter case the effective centroid potential of equation (4.60) is replaced by the centroid potential of mean force (CPMF) along the reaction coordinate \( q \), still denoted by \( V_c(q_c) \). The definition of the latter quantity is equivalent to the one-dimensional
4.2 Quantum Transition State Theory

The centroid density treatment of the barrier partition function may be generalised to a rotated saddle point in multidimensional space if the discussion is restricted to linear transformations of the system coordinates. In particular, we define the saddle point in terms of the rotated coordinate

\[ z = \sum_{i=1}^{N} U_i q_i \]  

(4.70)

where \(|U| = 1\) and \(z\) is the reactive barrier coordinate i.e. the local reaction path. One can write the reduced centroid density along this coordinate as [214,217]

\[ \rho_c(z_c) = \int \mathcal{D}q(\tau) \delta(q_c - \bar{q}_0) \exp(-S_E[q(\tau)]/\hbar) \]  

(4.71)

where \(\bar{q}_0\) is the centroid of the reactive coordinate. The partition function can be defined

\[ Q = \int dz_c \exp(-\beta V_c(z_c)) \]  

(4.72)

and the centroid potential of mean force along \(z\) is

\[ V_c(z_c) = -k_B T \ln[\rho_c(z_c)]. \]  

(4.73)

In a manner similar to that above, the CPMF may be used to evaluate the barrier partition function within the steepest descent approximation. We begin by expanding \(V_c\) about a maximum defined to be at \(z^1\)

\[ V_c(z_c) \approx V_c(z^1) + \frac{1}{2} V_c''(z^1)(z_c - z^1)^2. \]  

(4.74)
The derivatives are given by

\[ V_c'(z^\dagger) = \langle P V(z^\dagger) \rangle_c = 0 \]  \hspace{1cm} (4.75)

and

\[ V_c''(z^\dagger) = \langle P V(z^\dagger) \rangle_c - \beta [\langle P^2 V(z^\dagger) \rangle_c - \langle P V(z^\dagger) \rangle_c^2] \]  \hspace{1cm} (4.76)

where the operator \( P \) represents differentiation along the reaction path. That is,

\[ P = \sum_{i=1}^{N} U_i \partial_i. \]  \hspace{1cm} (4.77)

The rotated dividing surface is chosen normal to the direction which corresponds to the negative eigenvalue of the centroid-constrained force constant matrix. The transition state \( z^\dagger \) is the position on the rotated reaction coordinate at which the centroid constrained free energy maximum occurs. The general centroid-constrained averages are given by expressions analogous to the 1D case

\[ \langle f(z^\dagger) \rangle_c = \frac{\int \mathcal{D}q(\tau)f[q(0)] \delta(z^\dagger - \bar{z}_0) \exp(-S_E[q(\tau)]/\hbar)}{\int \mathcal{D}q(\tau) \delta(z^\dagger - \bar{z}_0) \exp(-S_E[q(\tau)]/\hbar)}. \]  \hspace{1cm} (4.78)

The centroid density can be approximated in terms of the rotated coordinate by the saddle point expression

\[ \rho_c(z_c) \approx \rho_c(z^\dagger) \exp[-\beta V''(z^\dagger)(z_c - z^\dagger)^2]. \]  \hspace{1cm} (4.79)

If \( V_c''(z^\dagger) < 0 \) the imaginary part of the barrier partition function can be evaluated within the steepest descent approximation as before. The reactive flux is then

\[ F \approx \nu \left( \frac{2\pi}{\beta |V''(z^\dagger)|} \right)^{1/2} \rho_c(z^\dagger). \]  \hspace{1cm} (4.80)
Chapter 5

Numerical Methods

In this chapter we briefly review the numerical methods which have been employed in the study of surface diffusion. We describe the numerical techniques for evaluating imaginary time path integrals and their application in the centroid-based path integral quantum transition state theory. The chapter includes details of the test calculations performed using the code developed in the course of this work.

5.1 Path Integral Monte Carlo

The path integral formulation of quantum mechanics [64] yields algorithms for the calculation of equilibrium properties of quantum systems at finite temperature [198,199]. In particular, the isomorphism between the discretized form of the path integral and a classical system enables one to evaluate averages over the canonical ensemble for a quantum system by means of computer simulation using methods developed for classical systems [198,199]. In the isomorphic classical system each quantum particle is represented by a set of classical particles arranged in a chain with strong nearest-neighbour coupling. The effective interaction between
the classical particles is derived from a short time approximation to the quantum propagator. In the lowest order (or primitive) approximation the effective interaction is harmonic with a force constant proportional to \( P \), the number of particles in the chain. The correspondence between the equilibrium properties of a quantum system and the isomorphic classical system is exact in the limit of infinitely large \( P \). Other, more accurate, approximations to the short time propagator have been developed [130–132,223] which give accurate results for a coarser discretisation of imaginary time than the primitive approximation. However, despite their greater efficiency these approximations are less straightforward to implement than the primitive approximation.

As we showed in Chapter 4 the Feynman path integral expression for the thermal density matrix may be represented in a discrete manner. In this representation the expression is isomorphic to the partition function for a collection of classical particles connected by harmonic springs. Within the primitive approximation, described above, the partition function may be written

\[
Q = \left( \frac{mP}{2\beta \hbar^2} \right)^{P/2} \int \left( \prod_{i=1}^{P} dx_i \right) \exp \left( -\frac{mP}{2\beta \hbar^2} \sum_{i=1}^{P} (x_i - x_{i+1})^2 - \frac{\beta}{P} \sum_{i=1}^{P} V(x_i) \right).
\]

(5.1)

There are a number of methods for evaluating this integral and simulating a quantum system at finite temperature. The methods used in this work are of the Monte Carlo type. Path integral molecular dynamics (PIMD) methods can also be used [203]. In the latter approach the system is allowed to evolve according to the classical equations of motion within the canonical ensemble and the thermodynamic quantities of interest are calculated using the methods of classical molecular dynamics [89].
5.1 Path Integral Monte Carlo

5.1.1 Metropolis Monte Carlo

Monte Carlo methods require a positive weighting function, $P(r)$, for each configuration, $r$, of the system in order to evaluate averages of observables

$$
\langle F \rangle = \frac{\int P(r)F(r)d(r)}{\int P(r)d(r)}.
$$

Metropolis Monte Carlo methods \cite{88,224} generate a Markovian random walk through configuration space. The criteria which determine the random walk are set by defining a transition matrix $T(r' \rightarrow r)$ and an acceptance probability $A(r' \rightarrow r)$. The transition matrix determines the probability with which the random walk will move from configuration $r$ to $r'$ and the acceptance probability determines whether such a move will be accepted. Provided the detailed balance condition

$$
T(r \rightarrow r')A(r \rightarrow r')P(r) = T(r' \rightarrow r)A(r' \rightarrow r)P(r')
$$

is satisfied, a sufficiently long random walk will generate a set of configurations distributed according to $P(r)$. The flexibility of Monte Carlo methods arises largely from the ability to manipulate the $T$ and $A$ matrices to ensure rapid convergence and ergodicity of the random walk. We describe the most straightforward application of the procedure to the evaluation of Feynman path integrals below.

A quantum particle subject to the external potential $V(r)$ is represented by a ring polymer consisting of $P$ beads. Let the configuration $r = \{r_1, \ldots r_P\}$ and the 'energy' of the chain

$$
E(r) = U_{\text{int}}(r) + U_{\text{ext}}(r)
$$

is satisfied, a sufficiently long random walk will generate a set of configurations distributed according to $P(r)$. The flexibility of Monte Carlo methods arises largely from the ability to manipulate the $T$ and $A$ matrices to ensure rapid convergence and ergodicity of the random walk. We describe the most straightforward application of the procedure to the evaluation of Feynman path integrals below.
5.1 Path Integral Monte Carlo

where

\[
U_{\text{int}} = \frac{mP}{2\beta^2\hbar^2} \sum_{i=1}^{P} |\mathbf{r}_i - \mathbf{r}_{i+1}|^2 \\
U_{\text{ext}} = \frac{1}{P} \sum_{i=1}^{P} U(\mathbf{r}_i).
\]  

(5.5)

1. Move each bead by an amount \(\Delta \mathbf{r}_i\), a vector whose elements are chosen from a uniform random distribution.

2. Calculate the energy of the new configuration \(E(\mathbf{r}')\) and hence the energy change \(\Delta E = E(\mathbf{r}') - E(\mathbf{r})\).

3. Metropolis step: Draw \(\xi\) from a uniform distribution in \([0,1]\);
   - if \(\Delta E < 0\) accept the move and let \(\mathbf{r} = \mathbf{r}'\);
   - if \(\Delta E \geq 0\) and \(\xi \leq \exp(-\beta \Delta E)\) accept the move and let \(\mathbf{r} = \mathbf{r}'\);
   - otherwise reject the move and leave \(\mathbf{r}\) unchanged.

4. Return to step 1.

The stiffness of the springs between adjacent beads in the chain is given by \(k = \frac{mP}{\beta^2\hbar^2}\). At low temperatures we need a large Trotter number, \(P\), to describe the system accurately so the springs become very stiff. Under these circumstances movement of the beads can be very costly in energetic terms. In a straightforward application of the Metropolis importance sampling technique the stiff springs connecting adjacent beads will only allow small amplitude displacements. It is likely, therefore, that sequential chain configurations generated by the Metropolis procedure will be highly correlated and long range fluctuations will evolve very slowly. For a given simulation time the increased correlation time will lead to greater statistical errors. This phenomenon is known as critical slowing down. It is well known from
Monte Carlo studies of the Ising model near a phase transition [224].

The statistical uncertainty in the mean value $\bar{A}$ of an observable $A$ measured using a Monte Carlo importance sampling technique is given by the error estimate

$$\Delta \bar{A} = \sqrt{\frac{\sigma_{A_i}^2}{N} \sqrt{2\tau_{\text{int}}}}$$

(5.6)

where $\sigma_{A_i}^2$ is the variance of the individual autocorrelated measurements $A_i$ at time tick $i$, $\tau_{\text{int}}$ is the integrated autocorrelation time and $N$ the total number of measurements. This expression immediately suggests three possible strategies for solving the 'slowing down' problem [225]. The simplest is to increase the number of measurements $N$. However, $1/\sqrt{N}$ is a slowly decreasing function and in the continuum limit it is possible that the variance and/or autocorrelation time will diverge as some power of the chain discretisation $P$. Another, more promising, strategy is to find an estimator for $A$ with a smaller variance [225]. The approach adopted in this work was to employ an alternative update algorithm with a smaller autocorrelation time. Janke and Sauer [226] investigated this approach by comparing the Metropolis scheme with multigrid methods and the staging algorithm for PIMC. They found that the staging algorithm can completely overcome the slowing down in the continuum limit. Multigrid methods can either reduce or eliminate the problem depending on the particular method used.

Multigrid methods have been used widely in the context of partial differential equations [227]. In these methods one performs non-local updates of the variables by working on a set of successively coarser discretisations of the time axis. This accounts for long wavelength fluctuations more efficiently. To this end one performs collective updates on different length scales by visiting various coarsened grids in
a systematic order. The auxiliary variables on the coarsened grids are then inter-
polated back to the finer grids and eventually to the original grid using a specified
interpolation scheme in a recursive manner. The multigrid approach has a number
of parameters which may be adjusted for the problem in question [226]. Despite
their obvious advantages multigrid methods can be difficult to implement. An alter-
native update scheme called the staging method is described below, it has many of
the advantages of the multigrid approach but its implementation is more straight-
forward and it requires fewer operations per cycle [226]. The staging algorithm is
described below.

5.1.2 The Staging Algorithm

The equilibrium properties of a quantum system are determined by the thermal
density matrix $\rho$. The trace of the thermal density matrix is the partition function
$Q$ which may be represented by an imaginary time Feynman path integral.

$$Q(\beta) = \int dx_1 \rho(x_1, x_1; \beta)$$

$$= \int dx_1 \cdots dx_P \rho(x_1, x_2; \beta/P) \cdots \rho(x_P, x_1; \beta/P) \quad (5.7)$$

where the thermal density matrix

$$\rho(x, x'; \tau) = \langle x | e^{-\mathcal{H} \tau} | x' \rangle \quad (5.8)$$

and $\beta = 1/kT$. A one dimensional example is chosen for economy of notation but
the expressions derived are easily extended to many dimensions. The primitive high
temperature (short time) approximation to the density matrix

$$\rho(x_i, x_{i+1}; \varepsilon) = \exp \left[ -\frac{\varepsilon V(x_i)}{2} \right] \rho_0(x_i, x_{i+1}; \varepsilon) \exp \left[ -\frac{\varepsilon V(x_{i+1})}{2} \right] \quad (5.9)$$
where
\[ \rho_0(x_i, x_{i+1}; \varepsilon) = \left( \frac{m}{2\pi\hbar^2\varepsilon} \right)^{1/2} \exp \left[ -\frac{m}{2\hbar^2}\varepsilon(x_i - x_{i+1})^2 \right] \] (5.10)
can be substituted into the expression for the partition function to yield the familiar discrete FPI representation of the partition function
\[ Q_P(\beta) = \left( \frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int dx_1 \ldots dx_P \exp \left( -\beta \sum_{i=1}^{P} \left[ \frac{mP}{2\hbar^2\beta^2}(x_i - x_{i+1})^2 + \frac{1}{P}V(x_i) \right] \right). \] (5.11)
In this expression, \( m \) is the mass of the quantum particle, \( V(x) \) is the external potential, \( x_{P+1} = x_1 \) and \( \varepsilon = \beta/P \). A distinction is made between the approximate partition function \( Q_P(\beta) \) and the exact partition function \( Q(\beta) \). The two agree formally in the limit that \( P \) tends to infinity but for large, finite \( P \) the agreement is found to be good [65, 211].

The partition function need not be written or simulated in Cartesian coordinates. Indeed, the nearest neighbour harmonic couplings suggest that it would be inefficient to do so. In their staging method, Sprik, Klein and Chandler [228] recognise this and adopt the following strategy. First, establish the gross features of the chain by constructing a primary chain with the correct thermal wavelength but composed of only a few particles. Hold the configuration of the primary chain fixed and add secondary chains between adjacent vertices of the primary chain. The primary chain is labelled with the superscript \( a \) and the secondary chains \( b \). A configuration of the chain is described by the coordinates
\[ \{x_i^a\}, \ i = 0, \ldots, P_a, \ x_0^a = x_{P_a}^a \] (5.12)
for the primary chain and

\[ \{x_{j,i}^b\}, \quad j = 0, \ldots, P_b, \quad i = 1, \ldots, P_a \]

\[ x_{P_b,i}^b = x_{0,i+1}^a = x_i^a \quad (5.13) \]

for the secondary chains.

The staging transformation may be derived as follows. Consider the expression for the free particle density matrix in the primitive approximation (equation (5.10)).

After some straightforward algebra we can show that

\[ \frac{\rho_0(x_1, x_k; (k-1)\epsilon) \rho_0(x_k, x_{k+1}; \epsilon)}{\rho_0(x_1, x_{k+1}; k\epsilon)} = \left( \frac{\beta m_k \omega_P^2}{2\pi} \right)^{1/2} \exp \left( -\frac{\beta}{2} m_k \omega_P^2 (x_k - x^*_k)^2 \right) \quad (5.14) \]

where

\[ x^*_k = \frac{(k-1)x_{k+1} + x_1}{k}, \quad (5.15) \]

\[ m_k = m \left( \frac{k}{k-1} \right) \quad (5.16) \]

and

\[ \omega_P = \frac{\sqrt{P}}{\beta \hbar}. \quad (5.17) \]

Combining several products similar to that in the identity above (equation (5.14)) we arrive at the following expression.

\[ \rho_0(x_1, x_2; \epsilon) \ldots \rho_0(x_j, x_{j+1}; \epsilon) = \prod_{k=2}^j \left( \frac{\beta m_k \omega_P^2}{2\pi} \right)^{1/2} \exp \left[ -\frac{\beta}{2} m_k \omega_P^2 (x_k - x^*_k)^2 \right] \]

\[ \times \left( \frac{m}{2\pi \hbar^2 j \epsilon} \right)^{1/2} \exp \left[ -\frac{m}{2\epsilon \hbar^2} (x_1 - x_{j+1})^2 \right]. \quad (5.18) \]

It is clear from this expression that the partition function may be written in terms of \( N \) segments of length \( j \) using \( N \) such identities. Thus, we have established the staging transformation. The \( N(j-1) \) intermediate beads (beads \( 2 \ldots j, j + 1 \ldots 2j, \ldots \))
are referred to as the staging beads and the remainder (beads 1, \(j + 1, 2j + 1, \ldots\)) are the endpoint beads. The staging beads have masses \(m_k\) which are the staging masses while the endpoint beads have mass equal to the particle mass \(m\). Let the set of staging and endpoint masses be denoted \(\{m_i\}\). The parameters \(N\) and \(j\) must be chosen so that \(Nj = P\).

Substitution of the \(N\) identities into the expression for the partition function into equation (5.7) yields

\[
Q(\beta) = \left( \frac{\beta m \omega_j^2}{2\pi} \right)^{N/2} \prod_{k=2}^j \left( \frac{\beta m_k \omega_j^2}{2\pi} \right)^{N/2} \int dx_1 \ldots dx_P 
\times \exp \left[ -\sum_{s=0}^{N-1} \frac{\beta}{2} m_s \omega_j^2 (x_{s,j+1}^* - x_{s,j+1})^2 \right] \exp \left[ -\frac{\beta}{P} \sum_{i=1}^P V(x_i) \right]
\]

where

\[
\omega_j = \frac{1}{\beta \hbar} \sqrt{\frac{P}{j}}
\]

and

\[
x_{s,j+k}^* = \frac{(k-1)x_{s,j+k+1} + x_{s,j+1}}{k}
\]

A linear transformation is defined

\[
u_{s,j+1} = x_{s,j+1}
\]

\[
u_{s,j+k} = x_{s,j+k} - x_{s,j+k}^*
\]

with inverse

\[
x_{s,j+1} = \nu_{s,j+1}
\]

\[
x_{s,j+k} = \sum_{l=k}^{j+1} \frac{k-1}{l-1} \nu_{s,j+l} + \frac{j-k+1}{j} \nu_{s,j+1}
\]
The inverse may also be expressed recursively

\[ x_{s,j+k} = u_{s,j+k} + \frac{k-1}{k} x_{s,j+k+1} + \frac{1}{k} x_{s,j+1}. \] (5.24)

A change of variables from \( x \) to \( u \) yields an expression for the partition function in terms of the staging coordinates

\[
Q(\beta) = \left( \frac{\beta m \omega^2}{2\pi} \right)^{N/2} \prod_{k=2}^{j} \left( \frac{\beta m \omega^2}{2\pi} \right)^{N/2} \int du_1 \ldots du_P
\]

\[
\times \exp \left[ -\sum_{s=0}^{N-1} \frac{\beta}{2} m \omega^2_j (u_{s,j+1} - u_{s+1,j+1})^2 - \sum_{s=0}^{N} \sum_{k=2}^{j} \frac{\beta}{2} m \omega^2_P u_{s,j+k} \right] \exp \left[ -\frac{\beta}{P} \sum_{i=1}^{P} V(x_i(u)) \right].
\] (5.25)

The Jacobian for this transformation is unity. This expression immediately suggests a strategy for the evaluation of the partition function via Monte Carlo. We can rewrite the partition function to make this transparent

\[
Q(\beta) = \int \prod_{i=1}^{P} dx_i K(x_i)V(x_i)
\] (5.26)

where \( K \) and \( V \) are probability distributions which represent the kinetic and potential terms in \( Q \) respectively. The kinetic distribution is a gaussian distribution in the variables \( u_i \). It is straightforward to sample directly from this distribution. In general, the same is not true of the potential. The integral can be evaluated by sampling from the gaussian distribution of the \( u_i \) and then applying the Metropolis importance sampling method to sample from the distribution \( V \).

5.2 Implementation of the Staging Algorithm

The implementation of the staging PIMC method used in this work incorporates the staging ansatz into MC using a method similar to that used by Coker et al. [229].
5.2 Implementation of the Staging Algorithm

We work in three dimensions and the \((j - 1)\) beads are directly sampled between fixed endpoints according to the particle action using the staging transformations described above. A new configuration for the segment of the chain is generated according to Lévy's procedure for sampling Brownian paths [230]. If we consider a segment between beads 1 and \(j + 1\) where \(j\) is the staging length then the position of the \((k + 1)\)th bead in this segment is

\[
r_{k+1} = r'_{k+1} + \sigma_{k+1} \xi
\]

where \(\xi\) is a vector whose elements are chosen from a Gaussian distribution with unit variance. The mean and variance for the beads in a path segment are given by

\[
r^*_{k+1} = \frac{t_k r_k + \tau r_{j+1}}{t_{k-1}}
\]

and

\[
\sigma^2_{k+1} = \frac{\hbar^2 \tau}{m} \frac{t_k}{t_{k-1}}
\]

where \(\tau = \beta/P\) and \(t_k = \beta - k\tau\). The move is accepted or rejected according to the usual Metropolis procedure [88,224]. This effectively eliminates the harmonic coupling between the beads (i.e. they have been directly sampled). Note: the first endpoint bead is chosen at random and the second is determined by \(j\) and the periodicity of the polymer chain. A staging pass is defined as \(P/(j - 1)\) moves of \((j - 1)\) beads. The parameter \(j\) is the single tunable parameter for the method, the optimal choice for \(j\) scales with the correlation length along the path. That is, it scales with the discretisation \(P\) [226].

For the PI-QTST calculations in this work there is an additional complication. The centroid of the Feynman path representing the quantum particle must be constrained to lie at a particular point \(q_c\) in the reaction coordinate. That is, we wish
5.2 Implementation of the Staging Algorithm

The centroid density must, therefore, be incorporated into the sampling. This is achieved in a straightforward manner. Each time a new configuration is sampled according to equation (5.29) the whole chain is translated so that the centroid lies at $q_c$.

The complete algorithm is now as follows.

1. Choose the first endpoint by selecting one of the beads from a uniform random distribution.

2. The segment represents the matrix element $\rho(r_i, r_{i+1}; \beta')$ where $\beta' = j\beta/P$. The trial configuration is generated according to the iterative procedure in equation (5.29) but $t_k = \beta' - k\tau$

3. Shift the whole chain so that the centroid is at the desired position.

4. Calculate the potential energy of the new configuration and find the change in this quantity: $\Delta V = V_{\text{new}} - V_{\text{old}}$.

5. Apply the Metropolis procedure to determine whether the configuration is accepted.

6. Repeat steps 2, 3 and 4 for all the segments in the chain.

7. Sample and return to step 1.

This algorithm samples independent chain configurations very rapidly because acceptable configurations can be produced in which large numbers of particles are
displaced simultaneously.

It is worthwhile to make a comment about random number generators before we proceed to describe the way in which the path integral code written in the course of this work was tested. In order to obtain meaningful results from a Monte Carlo calculation it is essential to use a good quality random number generator [224]. There are a number of tests for a good quality random number generator which were suggested by Knuth [231]. The generator used in this work is the Mersenne Twister [232]. It is known to pass all of Knuth’s tests and has an extremely long period $2^{19937} - 1$. Thus, it should be a reliable source of pseudo-random numbers.

### 5.2.1 Testing the Staging Code

The staging algorithm was implemented in C++ according to the prescription above. The choice of the C++ programming language is slightly unusual for a scientific code but path integral calculations are well suited [233] to object oriented programming concepts [234]. Encapsulation features such as private data, inheritance and polymorphism facilitate the development of such code and enhance its re-usability. The staging code consists of a class which encapsulates the data about the FPI chain, for example, the configuration of the beads, the energy of the configuration. These properties are stored as private data and as such may only be modified by calling methods on the class. This encapsulates an FPI chain as a single entity and when the class has been defined, one can perform calculations by manipulation of the object in an intuitive manner.

In order to test the code a 1D potential was employed. The aim of the tests was
5.2 Implementation of the Staging Algorithm
to compare the efficiency of the basic Metropolis and staging methods and to reproduce the results obtained by Janke and Sauer [225] using simple potentials. The test potential was an anharmonic convex potential (CP)
\[ V(x) = \frac{1}{2} x^2 + x^4. \] (5.31)
Note that atomic units are used throughout. Following Janke and Sauer, we calculate the internal energy of a particle subject to this potential using one of two estimators. We shall not comment on the two estimators here but a discussion is given by Janke and Sauer [225]. The so-called kinetic estimator which, for a particle of mass \( m \) represented by a discretized path integral with \( P \) beads, is written
\[ U_k = \frac{P}{2\beta} - \frac{mP}{2\beta^2} \sum_{i=1}^{P} (x_i - x_{i-1})^2 + \frac{1}{P} \sum_{i=1}^{P} V(x_i) \] (5.32)
and the virial estimator
\[ U_v = \frac{1}{2P} \sum_{i=1}^{P} x_i V'(x_i) + \frac{1}{P} \sum_{i=1}^{P} V(x_i). \] (5.33)
Table 5.1 shows the internal energy, relative error (estimated via a blocking procedure [224]) and variance for path integral calculations on the convex potential using the basic Metropolis and staging algorithms as a function of the discretisation, \( P \), of the FPI. The parameters were \( m = 1 \) and \( \beta = 10 \). Note that the staging algorithm contains an additional tunable parameter relative to the basic Metropolis algorithm, i.e. the staging length \( j \). The optimal staging lengths are shown in Table 5.2 as a function of \( P \).

The first observation from these results is that the calculated energies are in reasonable agreement with the correct continuum energy obtained by numerical integration of the Schrödinger equation. For the convex potential with the parameters chosen
### 5.2 Implementation of the Staging Algorithm

<table>
<thead>
<tr>
<th>P</th>
<th>$\langle U_k \rangle$</th>
<th>$\sigma_k^2$</th>
<th>Error(%)</th>
<th>$\langle U_v \rangle$</th>
<th>$\sigma_v^2$</th>
<th>Error(%)</th>
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Table 5.1: Internal energy of a particle subject to the convex potential calculated with basic Metropolis and the staging algorithm.
### 5.2 Implementation of the Staging Algorithm

<table>
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<tr>
<th>Discretisation ($P$)</th>
<th>Staging length ($j$)</th>
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<tr>
<td>512</td>
<td>32</td>
</tr>
<tr>
<td>1024</td>
<td>64</td>
</tr>
</tbody>
</table>

Table 5.2: Optimal staging length for the $P$ used in to simulate the convex potential.

($\beta = 10$ and $m = 1$) this is the ground state energy $E_0 = 0.80377$. Furthermore, the results obtained above are in very good agreement with those obtained by Janke and Sauer [225] and demonstrate that the code written in the course of this study is a correct implementation of the staging algorithm. For the purposes of this study, this is sufficient since the aim is to investigate the diffusion of H atoms on graphite (0001) via a path integral simulation rather than to explore the subtleties of a particular update algorithm. However, a comment on the choice of the staging length is in order. In many previous applications of the staging algorithm a general rule of thumb was employed [229]. That is, the staging length is chosen such that the acceptance probability is some fixed value (often about 40%). However, Janke and Sauer [226] demonstrated that this is an inefficient way to choose the optimal value $j$. A much better approach uses the integrated autocorrelation time.
For an observable $\mathcal{O}$, the normalised autocorrelation function $A(j)$ is defined by

$$A(j) = \frac{\langle \mathcal{O}_i \mathcal{O}_{i+j} \rangle - \langle \mathcal{O}_i \rangle^2}{\langle \mathcal{O}_i^2 \rangle - \langle \mathcal{O}_i \rangle^2}$$

(5.34)

where $\mathcal{O}_i$ is the $i$th measurement of $\mathcal{O}$. In Monte Carlo simulations the number of measurements, $N_m$, is finite. The calculation of the variance for the mean $\mathcal{O}$ is straightforward and yields an estimate of the form $\Delta \mathcal{O} = \sqrt{2 \tau_{\text{int}}(N_m)} \sqrt{\sigma^2/N_m}$. In this expression $\tau_{\text{int}}(k)$ is an integrated autocorrelation time [224]

$$\tau_{\text{int}}(k) = \frac{1}{2} + \sum_{j=1}^{k} A(j) \left[ 1 - \frac{j}{N_m} \right]$$

(5.35)

For large $j$ the autocorrelation function $A(j)$ usually decays exponentially, $a \exp(-j/\tau_{\text{exp}})$, where $\tau_{\text{exp}}$ is the exponential decay time and $a$, a constant.

The exponential decay of the autocorrelation time $A(j)$ and the large number of measurements, $N_m$, in a Monte Carlo simulation mean that the factor $(1 - j/N_m)$ in equation (5.35) may be neglected. This factor accounts for the finite size of the statistical sample. In practice, the autocorrelation time may be computed from the sum in equation (5.35) without the correction factor if it is cut off at some $k_{\text{max}}$ such that $n_{\text{cut}} \tau_{\text{int}}(k_{\text{max}}) \approx k_{\text{max}} \ll N_m$. Typically $n_{\text{cut}}$ is set to 6 or 8. If exponential and integrated autocorrelation times are similar this method gives reliable estimates for $\tau_{\text{int}}$. If the two are very different this method tends to underestimate $\tau_{\text{int}}$ and an alternative approach must be adopted [235].

Alternatively, the integrated autocorrelation time for an observable $\mathcal{O}$ may be obtained using the blocking or jacknife error estimate [224]. In the blocking method, one divides the $N_m$ measurements into $n_M$ blocks of size $N_M = N_m/n_M$ and computes the averages for each block separately. The block averages are stochastic variables
with the same mean as the sampled data but reduced autocorrelations. If the block length is sufficiently large then the block averages are almost uncorrelated and we can estimate the error in the estimate of the observable from the variance of the block averages. The number of measurements per block, $N_{bi}$, is always much smaller than the total number of measurements $N_m$. The jackknife blocking method employs the same principle but here the block averages are taken over the whole run with one block excluded. Consequently, the variance in these averages is much smaller than in the blocking case. A more complete description of these procedures may be found in Newman and Barkema [224]. The blocking or jackknife estimate of the error may be used to find the integrated autocorrelation time by inverting the standard error formula

$$\tau_{int} = \frac{(\Delta \tilde{O})^2 N_m}{2\sigma_{\tilde{O}}^2} \quad (5.36)$$

where $\Delta \tilde{O}$ is the error obtained from the blocking analysis and $\sigma_{\tilde{O}}^2$ the variance of the single unblocked measurements. Note that this method of estimating the integrated autocorrelation time is only valid if the block length, $N_{bi}$, is much larger than the true integrated autocorrelation time. If this is not the case then $\tau_{int}$ will be systematically underestimated. However, it is also important to have as many blocks as possible to reduce the statistical error in the error estimates. We know that $n_{bi}N_{bi} = N_m$ is fixed for a given simulation so these are conflicting requirements. If the measurements are not too strongly correlated a reasonable compromise is $n_{bi} \approx N_{bi} \approx \sqrt{N_m}$.

The results of the test calculations are shown in Table 5.3 for the basic Metropolis method and for the staging algorithm with the optimal staging length. Both the kinetic and virial estimators of the internal energy are considered. It is clear that
### 5.2 Implementation of the Staging Algorithm

<table>
<thead>
<tr>
<th>$P$</th>
<th>$\tau_{\text{int},k}$</th>
<th>$\tau_{\text{int},v}$</th>
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<td>3157.87</td>
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<td>1.71568</td>
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<tr>
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<td>1.11659</td>
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<tr>
<td>256</td>
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<tr>
<td>1024</td>
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<td>2.05278</td>
</tr>
</tbody>
</table>

Table 5.3: Integrated autocorrelation time as a function of the discretisation $P$ for basic Metropolis and the staging algorithm.
5.3 Implementation of Path Integral QTST

The chapter concludes with an explanation of the implementation of the PI-QTST method. A simple one dimensional example serves to illustrate the method. We consider a quantum particle moving in one dimension subject to the potential \( V(x) \).

The discretised path integral expression for the partition function is

\[
Q = \left( \frac{mP}{2\pi \beta \hbar^2} \right)^{N/2} \int \cdots \int \prod_{i=1}^{P} dx_i \exp \left\{ -\frac{1}{\hbar} \left[ \frac{mP}{2\beta \hbar} (x_i - x_{i+1})^2 + \frac{\beta \hbar}{P} V(x_i) \right] \right\}.
\]  

The discretised path integral representation is isomorphic with a chain of replicas of the system at imaginary time slices \((i-1)\beta \hbar/P\). The replicas are connected by harmonic springs with force constant \(mP/2\beta^2 \hbar\). The system is simulated using the methods described above. In particular, the Feynman path integral is evaluated using the staging algorithm with the centroid constraint. The partition function may be expressed in terms of the effective centroid potential \( V_c(x) \) (equation (4.60)).

The effective centroid potential is temperature dependent and plays a role which is analogous to a free energy

\[
Q_c = \exp(-\beta V_c).
\]  

The effective centroid potential \( V_c \) is evaluated using a line integral of the mean force acting on the Feynman paths as the centroid of the path is moved from the basic Metropolis algorithm suffers from critical slowing down. As the number of beads, \( P \), increases the integrated autocorrelation time increases rapidly. When \( P \) is small the performance of the staging and basic Metropolis algorithms is similar. However, with the optimal choice of staging length the staging algorithm eliminates this problem and there is little change in \( \tau_{\text{int}} \) even at large \( P \).
reactant well to the transition state. That is,

$$V_c(x^t) - V_c(x_R) = -\int_{x_R}^{x^t} dx \left< \frac{dV}{dx} \right>_{\bar{z}_0=x}$$  \hspace{1cm} (5.39)

where \(\langle \ldots \rangle_{\bar{z}_0=x}\) indicates an average over thermal paths with the centroid fixed at \(x\). In essence, a number of FPI calculations are performed with the centroid constrained to a point between the reactant well \(x_R\) and the barrier top \(x^t\). In each path integral calculation we evaluate the mean force on the chain. The results of these calculations are used to find the effective centroid potential.

The effective potential may be converted into a thermal rate constant and hence a diffusion constant according to

$$k = \nu \left( \frac{2\pi}{\beta |V''_c(x^t)|} \right)^{1/2} \exp(-\beta V_c(x^t))$$  \hspace{1cm} (5.40)

where the frequency factor \(\nu\) is described in Chapter 4.

5.3.1 Parallelisation of the PI-QTST Code

The PI-QTST code was, again, written in the C++ programming language [234]. It uses the classes which were defined in the staging code to perform path integral calculations with the centroid constrained to various points along the reaction path. The results of these calculations are integrated with respect to the reaction coordinate and converted to a rate constant in the manner described above. It is clear that such a method may be readily adapted to run on a parallel computer. The path-integral calculation at each point along the reaction path is independent of the calculation at any other point. It is also possible to parallelise path integral evaluation (within the PIMD approach [233]) but this was not pursued. The approach adopted in this work was to use POSIX threads [236] to parallelise the code.
5.3 Implementation of Path Integral QTST

according to a boss-worker structure [236]. In the main routine, a number of threads are created (generally equal to the number of available processors) and each thread is given a path integral calculation to perform. Upon completion the result is stored and the thread is given another calculation to perform until the mean force has been evaluated at all points along the reaction path. The results are then integrated with respect to the reaction coordinate and the reaction rate evaluated.

5.3.2 Testing the PI-QTST Code

In a similar manner to the staging code, the PI-QTST code was tested with a simple one-dimensional example. In this case, the code was used to reproduce the results of Ramirez [237] on the symmetric Eckart barrier centred at \( x = 0 \)

\[
V(x) = V_b \text{sech}^2 \left( \frac{x}{a} \right).
\]  

(5.41)

The parameters were chosen to be close to typical values encountered in, for example, the diffusion of H in crystalline silicon and were as follows. The barrier height \( V_b = 0.2485 \) eV and the width parameter \( a = 0.3491 \) Å.

Ramirez considered a flux of protons with a Maxwell-Boltzmann distribution of kinetic energies moving towards the barrier. He did not, therefore, calculate diffusion coefficients. Rather, he calculated the transmission coefficient and the normalised transmitted flux at a range of incident kinetic energies. The normalized transmitted flux, \( J \), may be identified with the hopping rate term in the diffusion coefficient. This quantity may be compared directly with results obtained using the PI-QTST code developed in this work. Furthermore, this flux is known exactly for the symmetric Eckart barrier [237] and the results of the PI-QTST calculations may be compared with the exact results. Ramirez also calculated the quantum correction
Table 5.4: Convergence parameters for the one-dimensional Eckart barrier.

<table>
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<tr>
<th>Temperature</th>
<th>$P$</th>
<th>$j$</th>
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</thead>
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<tr>
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<td>4</td>
</tr>
<tr>
<td>301.96K</td>
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<td>188.73K</td>
<td>64</td>
<td>8</td>
</tr>
<tr>
<td>150.98K</td>
<td>64</td>
<td>8</td>
</tr>
<tr>
<td>105.26K</td>
<td>128</td>
<td>16</td>
</tr>
<tr>
<td>48.78K</td>
<td>128</td>
<td>16</td>
</tr>
<tr>
<td>26.60K</td>
<td>256</td>
<td>32</td>
</tr>
</tbody>
</table>

factor, $\Gamma$, for the symmetric Eckart barrier. The quantum correction factor is the ratio of the quantum to the classical transmitted flux. That is,

$$\Gamma = \frac{J}{J_d} = J \exp(\beta V_0). \quad (5.42)$$

The PI-QTST code was used to estimate the normalized transmitted flux at a range of temperatures for the symmetric Eckart barrier. At each point along the path the PIMC calculations consisted of 50000 equilibration steps and 100000 Monte Carlo steps for which the mean force was sampled. The discretisation of the paths and the optimal staging lengths are shown in Table 5.4. Figure 5.1 shows the centroid potential of mean force at five different temperatures as a function of centroid position. Note that the temperatures in this figure have been chosen to correspond to those in the figures given by Ramirez [237]. They do not match those in Table 5.5 and its equivalent in Ramirez's article [237]. The figure shows that the height of the barrier for the effective potential diminishes with temperature and the barrier top is found at $x = 0$. At very low temperatures the effective potential is almost flat in the barrier region. This flattening of the CPMF may be understood in terms of the
5.3 Implementation of Path Integral QTST

Figure 5.1: The centroid potential of mean force for the Eckart barrier at a number of temperatures.

Discrete representation of the Feynman path integral. As the temperature is lowered so is the spring constant for the harmonic springs which connect the replicas of the system. Thus, the paths can spread out without incurring a large energetic cost. As a result, the barrier region is sampled less often and chains whose centroids lie in the barrier region will be draped across the barrier. Such chain configurations are indicative of quantum tunnelling.

Table 5.5 shows the normalized transmitted flux for a selection of the temperatures chosen by Ramirez [237]. The table shows that the agreement between the exact results for the symmetric Eckart barrier and the centroid based PI-QTST
### 5.3 Implementation of Path Integral QTST

Table 5.5: Normalised transmitted flux for the symmetric Eckart barrier, $J_{\text{Exact}}$ is the exact value, $J^* = \exp(-\beta V_c(z^*))$ and $J_{\text{Full}}^*$ includes the velocity factor.

calculations is good for the range of temperatures considered. The results are also consistent with the results of other PI-QTST calculations on the symmetric Eckart barrier [124, 195]. Note that these references report quantum correction factors $\Gamma$ but it is straightforward to compare this quantity with the values of $J$ obtained in these calculations.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$J_{\text{Exact}}$</th>
<th>$J^*$</th>
<th>$J_{\text{Full}}^*$</th>
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</tr>
</tbody>
</table>
Chapter 6

Results and Discussion

This chapter contains the results of the calculations described in the preceding chapters. Naturally, the ER and surface diffusion problems are considered separately. In each section we outline the features of the model employed and the potential energy surface appropriate to the problem. The details of the calculations are described and then the results are discussed in the context of astrophysical environments.

6.1 The Eley-Rideal Mechanism

In this section we describe the results of calculations on the Eley-Rideal reaction of H on graphite. A collinear process was considered with two degrees of freedom, the H-graphite distance $R$ and the separation of the H atoms $r$ as described in Section 3.1. The results described were obtained on two potential energy surfaces. The first was a rescaled bicubic spline fit to the results of DFT calculations and the second a LEPS fit to this surface.
6.1 The Eley-Rideal Mechanism

6.1.1 The Potential Energy Surface

The model described in Section 3.1 consists of two H atoms constrained to a line above the binding site of the graphite monolayer. All atoms within this monolayer are equivalent so there are three possible binding sites: above a surface atom (A); above the centre of a C-C bond (B); and above the centre of one of the hexagons in the graphite structure (C). Test calculations agree with other workers [144] and identify the A site as the preferred binding site.

![Potential Energy Surface](image)

Figure 6.1: The potential energy surface for the collinear Eley-Rideal reaction.

Density functional calculations were performed for various configurations of two H atoms constrained to a line above a carbon atom in an (0001) graphite surface. There are two degrees of freedom, the H-surface separation, $R$, and the H-H sepa-
The electronic structure was treated within the generalized gradient approximation (GGA) to density functional theory [162, 163]. We described the exchange-correlation energy using the Becke-Perdew 86 functional [238–240]. The potential used in our first reactive scattering calculations [146] uses a bicubic spline fit to about 250 calculated points. Subsequently we used the bicubic spline fit to parametrise a LEPS potential [147] (see Section 2.3.1 for the functional form). A potential energy surface was also calculated using the local density approximation (LDA) to density functional theory. The latter calculations were rather less successful and are briefly described below.

The Kohn–Sham equations were solved using the projector-augmented wave method [166] described in Section 2.2. The use of augmented plane waves constrains us to work with periodic boundary conditions in three dimensions. Calculations were performed for a supercell with $3 \times 3$ unit cells in the (0001) plane. Thus, the supercell contains 18 carbon atoms and two hydrogen atoms. The vertical dimension is 40 bohr. This choice represents a compromise between the need to minimise the interactions between the image particles and to optimise the efficiency of the calculations.

The plane wave cutoff for the electronic wavefunctions used in the DFT calculations was 25 rydberg and only the $\Gamma$–point of the reduced Brillouin zone was sampled. The 25 rydberg cutoff has previously been shown to be sufficient for other calculations on C and H using the same one–centre expansion [241]. In the calculation of the 2D potential the surface atoms are frozen in the perfect lattice positions. The consequences of this constraint are twofold. First, no energy can be transferred to the surface so the total vibrational energy of the product is fixed and second the
6.1 The Eley-Rideal Mechanism

geometry of the bound H–graphite system does not contain any relaxation of the substrate and is therefore incorrect. However, with present methods there is no way of dynamically removing the substrate motion as the reaction proceeds. Thus, this approximation represents the simplest internally consistent potential.

After choosing the supercell, the use of periodic boundary conditions limits the range of values that $R$ and $r$ may take before interactions with image particles become significant. In order to avoid such complications, the potential was extended from the edge of the grid to large $R$ and $r$ by assuming asymptotic behaviour of the form $AR^{-3} + B$ where $A$ and $B$ are arbitrary constants. A plot of the potential calculated with the GGA is shown in Figure 6.1. The topography is relatively simple and there is no barrier to the Eley–Rideal reaction in the surface. Thus, we anticipate that under the conditions appropriate to the interstellar medium, the formation of $H_2$ via this process will be very efficient.

It is well known that DFT, with the functionals in common use, often overestimates binding energies. It is necessary, therefore, to scale the surface in order to attain the correct dissociation energies whilst preserving the topography. This scaling may be effected in a straightforward manner by multiplying the surface by a scalar constant $\lambda$ so that $V_{sc}(R, r) = \lambda V(R, r)$. However, such a transformation will alter the derivatives of $V$ which will, in turn, affect the vibrational energies of species on the surface. Therefore, we transform to the new coordinate system $(R', r')$ where $R' = \mu R$ and $r' = \mu r$. For appropriate choices of $\mu$ and $\lambda$ we can scale both the dissociation energy and the vibrational energies to the correct values for $H_2$ whilst preserving the surface topography. This approach is similar in spirit to
6.1 The Eley-Rideal Mechanism

The morphing method of Hutson [242]. The scaling factors $\lambda$ and $\mu$ were determined by minimising the difference between calculated and experimental [243] vibrational energies of $\text{H}_2$. The resulting constants were $\lambda = 0.807$ and $\mu = 1.365$. With this choice of $\lambda$ and $\mu$ the $\text{H}_2$ well depth is 4.80 eV and the $\text{H}$–graphite well depth is 1.58 eV so that the reaction has an exothermicity of 3.22 eV.

The scaled potential was used to parametrise a LEPS potential (equation 2.14) using an eight parameter least-squares fit. The NAG routine e01unf [170] was used to perform the least-squares fit. The default parameters were used and the gradient of the least-squares function was of the order $10^{-6}$. After fitting the LEPS potential to the DFT-GGA data the molecular parameters were adjusted to get better agreement with experimental ro-vibrational energies for $\text{H}_2$. The full parameter set is given in Table 6.1. We use the notation of Section 2.3.1 where the subscript $a$ labels parameters appropriate to the $\text{H}$–graphite interaction and $m$ labels the molecular parameters. With this parameter set the dissociation energy $\text{H}_2$ is 36099.2 cm$^{-1}$ which is close to the experimental value of 36118.3 cm$^{-1}$. The exothermicity of the ER reaction on this surface is 2.75 eV and the $\text{H}$–graphite binding energy is 1.72 eV, slightly larger than for the bicubic spline fit to the data. Note that the LEPS form is a 3D potential. This potential has been used to perform time-dependent quantum scattering calculations on the formation of $\text{H}_2$ on graphite [147]. In this work we have performed 2D time-independent calculations which have been shown to give identical results to the time-dependent calculations [147].

The bicubic spline and LEPS fit to the GGA-DFT data are shown in Figure 6.2, it is clear that they are very similar. Neither potential contains a barrier to the
6.1 The Eley-Rideal Mechanism

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
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<tr>
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<td>a.u.$^{-1}$</td>
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</tr>
<tr>
<td>$x_m^{(0)}$</td>
<td>1.40547</td>
<td>a.u.</td>
</tr>
</tbody>
</table>

Table 6.1: Parameters for the LEPS potential.

collinear ER reaction. There are slight differences between the two potentials. For example, the binding energy between H and graphite is different so that the exothermicity is slightly different in each case. Furthermore, there are differences in the interaction regions of the two potentials. The LEPS potential has a slightly less abrupt transition from reactants to products. These differences lead to different predictions from the reactive scattering calculations as we see below. The feature of most interest in the potential energy surface is the interaction of the H atom with the graphite (0001) surface. There have been a number of previous studies of this interaction but many of them have used semi-empirical methods (see Section 1.3.4). For example, the MINDO/3 calculations of Fromherz et al. [140] were used by Parneix and Bréchignac (PB) [145] to construct a model potential. The PB potential is qualitatively different to those used in this work. Crucially, it contains a barrier ($\approx 0.05$ eV) to the ER reaction. The H–graphite binding energy found in the MINDO/3 calculations is about 1.3 eV which is smaller than the equivalent value
for either fit to the GGA-DFT calculations here.

The only comparable electronic structure calculations to those reported here were performed by Jeloaica and Sidis (JS) [144]. JS used a coronene molecule to represent the graphite (0001) surface and calculated potential energy curves as a function of the distance of an H atom above the three possible binding sites. They used the local spin density (LSD) approximation and Perdew-Wang 91 [60,244,245] functionals to describe the exchange correlation energy. A further difference is that the JS calculations use a gaussian basis set rather than the augmented plane waves used in the PAW calculations in this work.
There are a number of qualitative differences between the JS potential and the GGA-DFT potential used in this study. In their PW91-GGA calculations Jeloaica and Sidis found that the H–coronene curves at each binding site (A, B and C) have a common outer broad (physisorption) well of depth $D \approx 0.07$ eV at about $z=2.7$ Å and no chemisorption well. This is in stark contrast to the results reported here which show no physisorption well and a chemisorption well of depth greater than 1 eV. JS also performed calculations in which they allowed the coronene molecule to relax. In this case they find a chemisorption well of depth $D \approx 0.57$ eV but the physisorption well remains. It is not commonly believed that van der Waals minima can be accurately described by GGA functionals because dispersion interactions are not explicitly included in such functionals. However, there is experimental evidence for the physisorption well predicted by JS from experiments by Ghio et al. [150]. They studied the scattering resonances in the specular reflection of H atoms from graphite (0001) and fitted the energy levels to those calculated with a potential of the form
\[
V(z) = D \left[ \left(1 + \frac{\lambda z}{p} \right)^{-2p} - 2 \left(1 + \frac{\lambda z}{p} \right)^{-p} \right]
\]
and deduced the following parameter set: $D = 43.3$ meV; $\lambda = 1.36\text{Å}^{-1}$ and $p = 4.4$. When one adopts the hypothesis that the interaction potential is the sum over layers of an atom-monolayer potential, the well depth is found to be $D^* = 39.2$ meV. Thus, the JS calculations correctly predict a physisorption interaction but they overestimate the well depth by a factor of about 1.75. It is instructive to consider the differences between the JS results and the PAW calculations. The most obvious difference is the choice of model system. We use a graphite (0001) monolayer in plane wave DFT calculations in which all the surface atoms are equivalent and JS
6.1 The Eley-Rideal Mechanism

Figure 6.3: Reaction probability as a function of translational energy of incident H for the bicubic spline fit to GGA-DFT data.

use a coronene molecule in which the surface atoms are no longer equivalent. Indeed, there are three different environments for the C atoms in coronene and one could argue that none of them are equivalent to the environment in a graphite (0001) surface since they are all ≤ 2 bonds away from a terminal H atom. The choice of GGA functional is different in each case as is the basis set. One would not expect this to qualitatively affect the results.

6.1.2 Scattering Results

The bicubic spline fit to the GGA-DFT potential (and the LEPS fit with the collinear constraint) constructed above depends explicitly on two coordinates which describe
Figure 6.4: Reaction probability as a function of translational energy of incident H for the LEPS potential.

The bonds being broken and formed. This facilitates a reduced-dimensionality quantum scattering calculation [13] on the reaction. The Hamiltonian for the problem has just two degrees of freedom: the H$_2$ bond length, $r$, and the separation of the surface and the centre of mass of the molecule, $s$. We transform from the $(r,s)$ to hyperspherical coordinates $(\rho, \delta)$ as described in Section 3.1.

The $\mathcal{R}$-matrix propagator method was used to solve the coupled-channel equations for the Hamiltonian with total energy $E$ to determine $P(E)$, the probability of the reaction

$$H + H/\text{graphite} \rightarrow H_2(v)_{(g)}$$
6.1 The Eley-Rideal Mechanism

and the vibrational state distribution of the product H_2. In the calculations on
the bicubic spline fitted surface the $R$-matrix was propagated via equally spaced
sectors (of width 0.02 bohr) from the initial value of $\rho$ (0.40 bohr) to a large value
(6.60 bohr) where the interaction between the two reaction channels (H_2 and H +
H/graphite) is negligible. We apply scattering boundary conditions over a region
of the hyperradius ($6.50 \leq \rho \leq 7.50$). The $\delta$ degree of freedom was described
by 299 distributed Gaussian basis functions. The Gaussian exponent was equal to
$3.790 \times 10^4$ and the close-coupling equations were solved for 39 channels.

The calculated wavefunction in the final sector is compared with the form of the
wavefunction in a region where all the interactions have vanished to yield a matrix S
which describes the scattering. The state-to-state probabilities are easily extracted
from this matrix and can be used to determine a number of important properties.
Among them is $P(E)$ the overall probability of the reaction. At the low tempera­
tures of interest here we assume that only the lowest H–graphite vibrational state is
relevant. Thus the total reaction probability $P(E)$ may be written in terms of the
elements of $S$ as

$$P(E) = \sum_v |S_{\nu 0}|^2. \quad (6.2)$$

It is also straightforward to obtain the distribution of vibrational states in the prod­
uct from the $S$ matrix using

$$P_v(E) = |S_{v0}|^2. \quad (6.3)$$

Scattering calculations on the bicubic spline fit to the GGA-DFT data yield the
curve shown in Figure 6.3 for the total reaction probability. The curve has the
qualitative features one would expect of a potential which contains no barrier to re­
action. The reaction probability rises quickly to one as the collision energy increases
6.1 The Eley-Rideal Mechanism

and remains at this level for the range of collision energies considered. Therefore, at collision energies appropriate to interstellar dust clouds ($T = 10-100 K$) the reaction is likely to be efficient. The results of the same calculation on the LEPS fit to the GGA-DFT data are shown in Figure 6.4. Qualitatively there is no difference from the results obtained with the bicubic spline fit. The reaction probability rises quickly to one and remains at that level as the collision energy is increased.

Whilst the total reaction probability curves are the same for the two fits to the GGA-DFT data the distributions of vibrational states in the product $H_2(v), P_v(E)$, predicted by the two potentials are qualitatively different (see Figures 6.5 and 6.6).
The distribution obtained with the bicubic spline fit to the potential (Figure 6.5) shows that the product $\text{H}_2$ is vibrationally hot with $v = 2$ the most probable vibrational state for $\text{H}_2$ for the range of collision energies considered. There is appreciable population of states up to $v = 6$. Furthermore, the distribution is insensitive to the collision energy in this energy range. The distribution obtained from the LEPS potential also predicts that the product $\text{H}_2$ will be vibrationally hot but the most probable state is $v = 5$ for collision energies below about 0.01 eV. At higher energies $v = 3$ is most probable. The most significant difference between the LEPS and bicubic spline distributions is the redistribution of probability between vibrational states at collision energies near 0.1 eV. This is a feature which is seen in many gas phase reactive scattering studies [246,247]. Such features are observed where several
vibrational states are energetically accessible and there are strong couplings between them. Plots of the hyperspherical adiabats calculated on the two potentials give a qualitative indication of the levels for which this will occur. The presence of avoided crossings between the adiabats is observed in such cases.

The reaction probabilities are calculated by considering the $S$ matrix elements which include the lowest $\text{H}_2$-graphite vibrational state. This vibrational state corresponds to the hyperspherical adiabat labelled $v = 7$. There are avoided crossings between scattering states below this level in the LEPS case (Figure 6.8). Such features do not appear in the energetically accessible channels in the bicubic spline fit (Figure 6.7). Finally, we observe that the vibrational product distribution for the LEPS case is relatively insensitive to the collision energy for this range of collision energies and that there is appreciable population of vibrational states up to $v = 5$ and $v = 6$ at higher collision energies.

The calculations on the two fits to the potential described here clearly show that the $\text{H}_2$ formed via the collinear ER mechanism has significant vibrational excitation for the collision energies considered. The results are at variance with the predictions of Parneix and Bréchignac (PB) [145]. PB performed quasi-classical trajectory (QCT) calculations on a model potential which was based upon the MINDO/3 calculations of Fromherz et al. [140]. As stated above, the PB potential contains a barrier to the ER reaction so we expect qualitatively different results from those obtained here. Indeed, PB found that the reaction probability is zero at very low collision energy ($E < 0.005 \text{ eV}$) and it climbs to about 0.8 as the collision energy increases. Furthermore, the vibrational distribution predicted by the PB calculations is a statistical
6.1 The Eley-Rideal Mechanism

![Figure 6.7: The hyperspherical adiabats for the bicubic spline fit to the GGA-DFT data. $v = 0$ to 6 correspond to $\text{H}_2$ vibrational levels and $v = 7$ is the lowest $\text{H} - \text{graphite}$ vibrational state.]

It is important to consider these results in the context of astrophysical environments. As stated above, interstellar dust clouds are characterised by very low temperatures and pressures. Thus, if a process is to be a viable mechanism for the formation of $\text{H}_2$ in space it must be favourable under these conditions. The calculations presented...
Figure 6.8: The hyperspherical adiabats for the LEPS potential. \( v = 0 \) to 6 correspond to \( \text{H}_2 \) vibrational levels and \( v = 7 \) is the lowest \( \text{H} \)-graphite vibrational state.

above show that the Eley-Rideal reaction on graphite is such a process and that the product molecules are vibrationally excited. The lifetimes of vibrationally excited states of \( \text{H}_2 \) are of the order of several years so we anticipate that there will be a high proportion of such molecules in these regions of space. Furthermore, since the Eley-Rideal reaction is highly exothermic there will be an appreciable amount of translational energy in the product molecules. The frozen surface model will overestimate this but the \( \text{H} \) atom is weakly bound to the graphite surface so energy transfer to the surface will not be large. The presence of vibrationally and translationally excited \( \text{H}_2 \) will have important consequences for subsequent chemistry in
6.1 The Eley-Rideal Mechanism

the ISM [248]. Reactions of vibrationally excited H\textsubscript{2} can have much larger rate constants than those of H\textsubscript{2}(v = 0) [249]. Thus, the presence of vibrationally excited H\textsubscript{2} means that some reactions (e.g. C\textsuperscript{+}+H\textsubscript{2}, O\textsuperscript{(3P)}+H\textsubscript{2}) might become feasible under interstellar conditions.

Recently, Tiné et al. [250] have investigated the implications of these calculations in astrophysical environments. They used a simple model to estimate the population of rotational states in the H\textsubscript{2} formed by the ER reaction on graphite. They assume that the probability of formation of a particular ro-vibrational state is dependent solely upon its energy. Thus a state \((v_1,j_1)\) and another state \((v_2,j_2)\) with equal energy will be formed with equal probability. With this assumption in hand Tiné et al. were able to predict infra red line intensities for particular regions of interstellar space. In particular, they present spectra appropriate to high and low density regions. The predicted spectra can be compared to astronomical observations and will provide an excellent test of the ER results obtained in this work.

6.1.3 The LDA Potential

As stated above, density functional calculations were also performed using the local density approximation (LDA) to the exchange-correlation energy. Again, various configurations of two H atoms constrained to a line above an atom in a graphite (0001) surface were considered. The LDA potential energy surface was a fit, using a bicubic spline to a grid of 220 points calculated using the PAW method. The LDA is known to overestimate dissociation energies and in these calculations the dissociation energy of H\textsubscript{2} in the gas phase was found to be almost 6.0 eV. The surface was re-scaled to obtain the correct H\textsubscript{2} dissociation energy in the same manner as the GGA
surface described above. After this re-scaling the H–graphite bond was found to be slightly weaker than in the GGA case (about 1.3 eV). However, the gross features of the surface are the same as in the GGA case. The potential contains no barrier to the collinear ER reaction and the reaction is highly exothermic (approximately 3.5 eV). Quantum reactive scattering calculations were performed on the LDA potential in a similar manner to those performed on the GGA and LEPS surfaces. The total reaction probability is shown in Figure 6.9. The total reaction probability is close to unity for all the collision energies considered. However, for collision energies below 0.01 eV the total reaction probability is less than one. Furthermore, for collision energies above 0.02 eV the total reaction probability drops below one again. This
is likely to be an artefact of the bicubic spline fit. It is possible that the inclusion of additional calculated LDA points or an alternative fitting procedure might have eliminated these features but the calculation of the GGA potential was pursued in preference to such methods. Similar problems were encountered with the vibrational product distributions calculated using this potential. However, it is interesting to note that many of the broad conclusions from calculations using the GGA potential are similar to those from the calculations using the LDA potential. In particular, the total reaction probability is close to unity for all collision energies considered. Furthermore, the calculations on the LDA surface predict that the product \( \text{H}_2 \) will be vibrationally excited with \( v = 2 \) and \( v = 3 \) the most probable states.

6.2 Surface Diffusion

The diffusion of an H atom on the surface of a cosmic dust grain has been identified as a step in the Langmuir-Hinshelwood (LH) mechanism for the formation of \( \text{H}_2 \) on such grains. If the diffusion constants for H on the grain surfaces are known as a function of temperature one can predict whether the LH mechanism will contribute significantly to the observed abundance of \( \text{H}_2 \) in the ISM. In particular, whether the ER or LH mechanism will dominate. It is clear that the LH mechanism should be statistically favoured. The probability that an incident H atom will impinge upon an H atom adsorbed to a dust grain is much smaller than the probability that it will collide with another part of the surface. If the H atoms move rapidly across the surface then they will soon meet and recombine according to the LH mechanism. However, if the adsorbed atoms are immobile then it may take a long time before they encounter one another. Under such circumstances the ER mechanism should dominate.
6.2 Surface Diffusion

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
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<td>eV</td>
</tr>
<tr>
<td>B</td>
<td>0.362</td>
<td>eV</td>
</tr>
<tr>
<td>C</td>
<td>1.228</td>
<td>eV</td>
</tr>
</tbody>
</table>

Table 6.2: Relative energies of the graphite (0001) binding sites for a chemisorbed H atom.

The model for the diffusion of H on a cosmic dust grain consists of a single H atom on the (0001) surface of graphite. As in the ER case there are three possible binding sites: above a surface atom (A); above the centre of a C-C bond (B); and above the centre of one of the hexagons in the graphite structure (C). DFT calculations of the binding energy at each of the surface sites give the relative energies shown in Table 6.2. The calculations were performed using a graphite (0001) monolayer with the same supercell as the reactive scattering potential. The exchange-correlation energy was described using the Becke-Perdew GGA functional [238–240]. The plane-wave cutoff was the same as for the reactive scattering calculations, 25 rydberg. However, better $k$-point sampling was employed. In addition to the $\Gamma$-point three other $k$-points were sampled in the reduced Brillouin zone, (010), (100) and (110). The PAW method restricts the $k$-point sampling [166] to real values and the geometry of the model system means that little advantage would be gained by including (111) and (001) in the $k$-point sampling. The improved $k$-point sampling makes the calculations somewhat more expensive than those of the ER potential but the description of the electronic structure is improved. It was found that convergence is obtained after fewer iterations.
There is some uncertainty about the nature of the H–graphite interaction. All the DFT calculations performed in this work have shown that the H atom is chemisorbed to the graphite (0001) surface and provide no evidence for physisorption. However, the calculations of Jeloaica and Sidis (JS) [144] suggest that there may be a physisorption well. Furthermore, experiments by Ghio et al. [150] indicate that H atoms may be physisorbed to a graphite (0001) surface. The differences between the calculations of JS and this work were discussed above. Given this uncertainty about the nature of the H–graphite interaction it is desirable to describe the diffusion of H in both regimes. In the ER reaction the precise nature of the H–graphite interaction is unlikely to have a large effect on the dynamics. That is, the crucial feature of the potential for the ER mechanism is that the H–graphite bond is much weaker than the H–H bond. In the context of surface diffusion the nature of the H–graphite interaction is crucially important. The diffusion barrier for a physisorbed atom will be much smaller than the equivalent barrier for a chemisorbed atom. This will obviously have a large effect upon the diffusion rate.

Ideally, one would like a single potential to describe both regimes. One possible candidate is the reactive empirical bond-order (REBO) potential of Brenner [172,173]. Recently, Stuart et al. [174] developed the adapted interatomic REBO (AIREBO). The latter potential is a modified version of Brenner's REBO potential which incorporates long range forces via Lennard-Jones pair potentials into the REBO potential. The AIREBO potential should be capable of describing both physisorption and chemisorption of H atoms to the graphite (0001) surface. Furthermore, it is a function of all the atomic coordinates and should, therefore, offer some insight into
the effect of the motion of the substrate on the diffusion rate. However, the potential appears to be unsuitable for the H–graphite system. In a PIMC calculation one must evaluate the potential many times. The cost of evaluating the AIREBO potential for the H–graphite model system makes such calculations very time consuming. More importantly, the AIREBO potential appears to contain some unphysical discontinuities. For example, the H–graphite dissociation curve calculated for a frozen (0001) surface is not smooth. Thus, the diffusion constants calculated using such a potential are unlikely to be reliable. In the light of these difficulties, an alternative approach was adopted, chemisorption and physisorption were described using two separate potentials. An empirical potential due to Steele [171] was used to describe the physisorption regime. The corrugation term from this potential was incorporated into the LEPS potential to describe a chemisorbed H atom. The potentials are described in Chapter 2. This description makes the advantages of the approach clear. The simplicity of the two potentials means that they are cheap to evaluate making PIMC calculations straightforward. Furthermore, within this approach it is possible to include the corrugation of the surface in a chemisorption potential whilst retaining the description of the H–graphite interaction used in the reactive scattering calculations. The chemisorption potential is shown in Figure 6.10. The diffusion barrier is represented accurately but the barrier above the C site is too high. However, this region of the potential is rarely sampled during the path integral Monte Carlo calculation so this should not be a problem.

The situation is not wholly satisfactory. For example, neither potential describes the motion of the substrate atoms. However, at the low temperatures appropriate to the ISM it is likely that such motions will be less important than quantum effects
which are described in the path integral representation. Furthermore, in the case of physisorption the interaction of the adsorbed atom with the surface is very weak so substrate motion should not affect diffusive motion significantly.

### 6.2.1 Physisorption

For the purposes of the calculations in this work diffusion is regarded as a series of uncorrelated hops between adjacent binding sites. Naturally, an important first step in such a calculation is the identification of the binding site and of the route taken between adjacent sites. The lowest energy binding site has been identified as the A site (directly above a surface atom). The H-graphite well depth is approximately 0.048 eV which is close to that in the empirical potential of Ghio et al. [150]. The
physiosorption potential has the same topography as the chemisorption potential in Figure 6.10. It is clear from the form of the potential that the smallest barrier occurs along the C-C bond between adjacent binding sites. The barrier to diffusion in this direction is very small. In fact, it is approximately $3 \times 10^{-3}$ eV which is about 10K. We anticipate that diffusion of a physisorbed atom will be facile at the low temperatures of the interstellar medium.

Having identified the path for the diffusion hop we determine the centroid potential of mean force (CPMF) in this direction. We employ the method described in Section 4.2. We define a grid of points along the diffusion path and perform path integral Monte Carlo (PIMC) simulations at each point along the diffusion path (from the A site to the transition state at the B site). The mean force was sampled in the direction of the diffusion path at each point and the results were numerically integrated with respect to the reaction coordinate to find the CPMF, $V_c(q)$. The PIMC sampling was performed using the staging algorithm. Thus, there are two adjustable parameters, the discretisation of the Feynman paths, $P$, and the staging length $j$. The values of these parameters used in the calculations are shown in Table 6.3. The CPMF curves were calculated at a range of temperatures for both hydrogen and deuterium atoms. They are shown in Figure 6.11 and Figure 6.12. The curves show some evidence of a quantum-classical crossover and the importance of tunnelling. At very low temperatures the CPMF falls below the value of the potential in the barrier region. This indicates that the effective barrier to the diffusion hop is lower than the barrier in the potential. The effect is quite small for a physisorbed atom because the diffusion barrier is low. The quantum-classical crossover should occur at very low temperature. In fact, for this system $T_c \approx 60K$. This tem-
6.2 Surface Diffusion

<table>
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<tr>
<th>Temperature</th>
<th>$P$</th>
<th>$j$</th>
</tr>
</thead>
<tbody>
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<td>32</td>
</tr>
<tr>
<td>150K</td>
<td>64</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 6.3: Convergence parameters for the physisorption potential.

Temperature is calculated within a parabolic approximation, the crossover temperature is given by $\beta_c = 2\pi/\hbar\lambda_0^2$ where $\lambda_0$ is the Grote-Hynes frequency [220]. This approximation may overestimate the crossover temperature. An alternative approach [237] defines the crossover temperature as the temperature at which $\frac{\partial U}{\partial T}$ is maximised, where $U$ is the internal energy. The formulae employed in the centroid-based QTST are based upon a parabolic approximation for the crossover temperature. This approximate value of $T_c$ determines the appropriate form of the frequency factor $\nu$ in the PI-QTST formulae. The CPMF may be used to calculate the hopping rate in a relatively straightforward manner (equation (5.40)). The hopping rate is then used to calculate the diffusion constant using a simple formula (equation (4.6)). The diffusion rate for deuterium was calculated in a similar manner. The D atom is heavier than H and therefore behaves more classically. That is, the quantum-classical crossover occurs at a lower temperature. Comparison of the hopping rates for H and D provides some indication of the importance of quantum mechanical effects in the diffusion process. If the diffusion were purely classical one would expect the ratio of the rate constants $k^H/k^D$ to be approximately $(m_D/m_H)^{1/2}$ where $m_D$ and $m_H$ are the masses of D and H respectively. A comparison of the rate constants the tables 6.4 and 6.5 shows that this is not the case. The ratio is actually significantly
larger than this value. This kinetic isotope effect indicates that there is significant quantum tunnelling in the diffusive motion.

![Figure 6.11: Centroid Potential for a physisorbed hydrogen atom.](image)

### 6.2.2 Chemisorption

The path taken by the H atom between adjacent binding sites is the same as in the physisorption potential. However, as one would expect, the diffusion barrier is significantly larger than in the physisorption potential at about 0.362 eV. This corresponds to a temperature of about 4000K. Thus, we expect a chemisorbed H (or D) atom to be much less mobile at low temperatures than a physisorbed atom. Furthermore, in the chemisorption case any diffusion at low temperatures is likely to be due to quantum tunnelling of the adsorbed atom. There is an additional
complication in the case of a chemisorbed atom. Car-Parinello calculations were performed in the course of this work using the PAW method. In these calculations the graphite (0001) surface was allowed to relax in the presence of a chemisorbed H atom. They predict that when an H atom chemisorbs to a graphite (0001) surface there is significant reconstruction. Thus, an accurate description of diffusion of a chemisorbed atom should include the effects of surface motion. Despite the absence of this property, the calculations on this rigid-surface model should provide some qualitatively useful information about the diffusion process.

The quantum-classical crossover occurs at a higher temperature, $T_c \approx 340 K$ for H and $T_c = 240 K$ for D, than in the physisorption case. This is consistent with the
Table 6.4: Hopping rates and diffusion constants for a physisorbed hydrogen atom.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k_{\text{hop}} \text{(s}^{-1}\text{)} )</th>
<th>( D(\text{Å}^2 \text{s}^{-1}) )</th>
</tr>
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<tr>
<td>100K</td>
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Table 6.5: Hopping rates and diffusion constants for a physisorbed deuterium atom.

<table>
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<tr>
<th>Temperature</th>
<th>( k_{\text{hop}} \text{(s}^{-1}\text{)} )</th>
<th>( D(\text{Å}^2 \text{s}^{-1}) )</th>
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<tr>
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<td>1.9294x10^5</td>
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<tr>
<td>100K</td>
<td>4.2900x10^5</td>
<td>7.6399x10^5</td>
</tr>
</tbody>
</table>

centroid potential curves in Figure 6.13. At high temperature the CPMF is nearly identical to the external potential but at lower temperatures the CPMF lies below the external potential. At very low temperatures the CPMF takes a form which is reminiscent of a top hat. This indicates that quantum mechanical tunnelling will contribute significantly to the observed hopping rate at such temperatures. The observed form of the CPMF may be rationalised in terms of the configuration of the Feynman paths. At low temperatures the spring constants between beads in the discrete representation of the Feynman paths become smaller. Thus, the spring forces make a smaller contribution to the classical action of the path. Under these circumstances, the acceptance, or otherwise, of a particular chain configuration in the Monte Carlo sampling is dominated by the value of the external potential. Configurations with many of the beads in or near the reactant region will be favoured. This results in a low centroid density at the transition state. The convergence pa-
6.2 Surface Diffusion

Figure 6.13: Centroid Potential of Mean Force for a chemisorbed hydrogen atom.

rameters, the discretisation of the Feynman paths, $P$, and the staging length, $j$, are shown in Table 6.6. In a similar manner to the physisorption case the hopping rate may be calculated from the CPMF and then the diffusion constant is obtained from a simple formula. Calculations were performed at a wider range of temperatures for the chemisorption potential than the physisorption potential. This is largely because the quantum-classical crossover occurs at a higher temperature in the chemisorption case. At temperatures above the crossover the CPMF follows the external potential. That is, the flattening which is characteristic of quantum tunnelling is absent. In this regime the diffusion is largely classical so there is little point in performing numerous PIMC calculations above the crossover. Comparing the hopping rates for H and D in tables 6.7 and 6.8 we see that the kinetic isotope effect is even more
6.2 Surface Diffusion

Figure 6.14: Centroid Potential of Mean Force for a chemisorbed deuterium atom.

marked than in the physisorption case. This observation is consistent with a higher value of $T_c$. That is quantum effects appear at a much higher temperature in the chemisorption regime.

6.2.3 Discussion

The calculated diffusion rates show convincing evidence for the importance of quantum tunnelling in the diffusion of H and D on graphite (0001). Furthermore, the calculations show that the diffusion rate depends critically upon the nature of the H–graphite interaction. In particular whether the atom is chemisorbed or physisorbed to the surface. If the atom is physisorbed the diffusion is rapid but a chemisorbed atom is relatively immobile. At present, the precise nature of the H–graphite in-
### Table 6.6: Convergence parameters for the chemisorption potential.

<table>
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<tr>
<th>Temperature</th>
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<tr>
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### Table 6.7: Hopping rates and diffusion constants for a chemisorbed hydrogen atom.

<table>
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<tr>
<td>200K</td>
<td>(5.0723 \times 10^{-3})</td>
<td>(9.0330 \times 10^{-3})</td>
</tr>
</tbody>
</table>

### Table 6.8: Hopping rates and diffusion constants for a chemisorbed deuterium atom.

<table>
<thead>
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<th>Temperature</th>
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<th>( D(\text{Å}^2 \text{s}^{-1}) )</th>
</tr>
</thead>
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<tr>
<td>200K</td>
<td>(5.9726 \times 10^{-4})</td>
<td>(1.0636 \times 10^{-3})</td>
</tr>
</tbody>
</table>
teraction is not fully understood and DFT calculations give conflicting results. In particular, the PAW calculations performed in this work predict the H atom is chemisorbed to the graphite (0001) surface while the calculations of Jeloaica and Sidis [144] predict a physisorption well at about 2.5Å from the surface. Until this debate is resolved one cannot determine whether the LH mechanism will make a significant contribution to the observed abundance of H₂ in the ISM.

There have been a number of studies of surface diffusion on metals [100] but the H–graphite system has not received much attention in this context. There have been no experimental studies of the diffusion of H on graphite. There have also been very few theoretical studies of this system. Leitch-Devlin and Williams (LDW) [108] used a simple quantum mechanical model to investigate the mobility of adsorbed species on the surface of cosmic grains. LDW represented the adsorbed atom as a quantum mechanical wavepacket. They calculate the group velocity of the wavepacket and use this to determine the mean group velocity of a microcanonical ensemble of non-interacting replicas of the system. The atom-surface potential is based upon a rectangular grid rather than the honeycomb structure of graphite (0001). Clearly, their treatment of the problem is different to the approach adopted here.

The results of the LDW calculations are expressed in terms of the surface coverage time and the mobility ratio, \( U_r \), which is related to the group velocity of the wavepacket. Thus, direct comparison with the diffusion constants calculated here is difficult. However, it is possible to make some qualitative comparisons. The LDW results show that a physisorbed atom will traverse the surface of a dust grain very rapidly which is consistent with the results obtained in this work. In the case of a
6.2 Surface Diffusion

chemisorbed atom the results differ significantly. LDW predict that such an atom should be highly mobile whereas the PIQTST calculations predict the opposite. The discrepancy is likely to lie in differences between the potentials used in the two sets of calculations. The potential employed by LDW for a chemisorbed H atom on graphite contains a diffusion barrier which is much smaller than that in the potential employed here. The barrier in the LDW potential is about 600K compared with about 4000K in this work. Thus, one would expect the diffusion rates calculated from the two potentials to differ significantly. The barrier in the potential used in this work was based upon a DFT calculation but the LDW barrier doesn't appear to have any sound physical basis. Rather, it arises from a reparametrisation of their physisorption potential to fit a calculated H–graphite binding energy [141].

It is important to consider the results of these calculations in an astrophysical context. The surfaces of cosmic dust grains are known to be at a temperature $T \approx 10K$. This temperature is lower than the lowest temperature considered here but the results of the calculations for $T = 25K$ are relevant. For an H atom the diffusion constants are of the order $10^{-5}$ Å²s⁻¹ for a chemisorbed atom and $10^{8}$ Å²s⁻¹ for a physisorbed atom. Cosmic dust grains are known to be a few microns across. Thus a physisorbed atom should take around $10^3$s to cover the surface of a grain and a chemisorbed atom about $10^{13}s$. It is clear that the Langmuir-Hinshelwood mechanism will not contribute significantly to the rate of formation of H₂ in the ISM if H/D atoms are chemisorbed to the grain surface. In this case the ER mechanism should dominate and the results suggest that atoms which collide with a grain surface and adsorb to the surface will remain at the same site until they interact with another H atom incident from the gas phase via an ER mechanism.
Chapter 7

Conclusions and Future Work

The formation of $H_2$ in the interstellar medium is believed to occur via associative desorption from cosmic dust grains. In this work the cosmic dust grain has been modelled as a graphite (0001) surface. Aspects of both the Eley-Rideal (ER) and Langmuir-Hinshelwood (LH) mechanisms have been investigated for this model system. A DFT potential energy surface was calculated for a collinear ER model. Two potential energy surfaces were obtained from these data. The first was a straightforward bicubic spline fit to the data and the second a parametrisation of the LEPS potential. Time-independent quantum reactive scattering calculations were performed on both potential energy surfaces. There are some differences between the results obtained from the two potentials but both predict that the probability of the reaction

$$H + H/{\text{surface}} \rightarrow H_2(v, 0) + \text{surface}$$

is essentially unity for all the collision energies considered. Furthermore, both reactive scattering calculations predict significant vibrational excitation of the product with $v = 2$ and $v = 3$ the most probable. That is, these calculations demonstrate
that the collinear ER mechanism is a viable mechanism for the formation of H$_2$ in
the ISM. The vibrational excitation of the product has important implications for
subsequent chemistry in the ISM.

The LH mechanism has been investigated by considering the surface diffusion step.
The results of these calculations are slightly less conclusive. In the simple model
used in this work a chemisorbed atom is relatively immobile at all temperatures
considered whereas the mobility of a physisorbed atom is high. Thus, a physisorbed
atom will explore the surface of a dust grain very rapidly. This means that two
physisorbed atoms are likely to encounter one another after a short time and they
may react to form H$_2$ during such an encounter. Thus, the LH mechanism can make
a significant contribution to the formation of H$_2$ if the atoms are physisorbed to the
surface. However, if the H atoms are chemisorbed to the surface the mobility is low
so that the diffusion step of the LH mechanism will take a long time. Clearly, if the
H atoms are chemisorbed to the surface it is unlikely that the LH mechanism will
play an important role in the formation of H$_2$ in the ISM.

7.1 Future Work

The work described in this thesis may be extended in a number of directions. Some
of the suggested extensions of the present work involve slight improvements to the
existing models and others involve the study of an entirely different aspect of the
problem. One of the most important issues to address is the nature of the H–graphite
interaction. The DFT calculations performed in this work show no evidence of ph­
ysisorption yet DFT calculations by Jeloaica and Sidis (JS) [144] clearly show a
physisorption well. There are a number of important differences between the JS cal-
culations and the PAW calculations in this work. These differences were discussed in Section 6.1. A full understanding of the H–graphite interaction is most important in the context of the LH mechanism. In the diffusion step, as this work has demonstrated, the nature of the H–surface is of crucial importance. If the H atom is chemisorbed to graphite (0001) the diffusion rate is too low for the LH mechanism to contribute significantly to the observed abundance of H$_2$ in the ISM. However, the details of the H–graphite interaction are unlikely to qualitatively affect the results of the ER calculations. The JS potential and the PAW potential presented in this work both show that the ER process is highly exothermic.

The model of the ER mechanism in this work is very simple. It only treats two degrees of freedom - the H–graphite separation $R$ and the interatomic distance $r$. This model does not include rotational states of the product H$_2$, nor does it include the transfer of energy to the substrate. Clearly such a model will overestimate the amount of vibrational excitation of the product H$_2$. However, the results of calculations using such a model should provide an upper bound to the reaction probabilities and the population of vibrational states of the product H$_2$. A more realistic model would include additional degrees of freedom. The model presented in this work has been extended to three dimensions by Meijer et al. [147]. Meijer’s model treats collisions of incident and target atoms other than the collinear one. However, the model still uses the flat surface approximation i.e. the corrugation of the graphite (0001) surface is ignored. Meijer solved the scattering problem using the time-dependent wavepacket (TDWP) approach. The results obtained for the two dimensional model using the TDWP were identical to those obtained using time-independent quantum mechanics and the three-dimensional calculations pre-
dict a lower total reaction probability. Work is in progress to extend the model further to include additional degrees of freedom.

Much remains to be done in the study of the Langmuir-Hinshelwood mechanism. In the diffusion step, one would like to be able to treat the motion of the substrate atoms. In the potential used in this work the substrate atoms are frozen. One might attempt to treat these degrees of freedom using the reactive empirical bond order (REBO) potential of Brenner [172,173] or the adapted interatomic REBO (AIREBO) potential due to Stuart et al. [174]. The latter potential incorporates interatomic forces via Lennard-Jones pair potentials into the REBO potential. An investigation of this potential shows that it is unsatisfactory for the H–graphite problem. The REBO potential was formulated to describe problems such as chemical vapour deposition on diamond. That is, problems involving stronger interactions than that between H and graphite (0001). The AIREBO potential which contains long range interactions was also found to be unsatisfactory for the H–graphite problem. For example, if the graphite (0001) surface is frozen the H–graphite dissociation curve is not smooth for a $z$ slightly larger than the equilibrium separation. Clearly, this is unsatisfactory. In systems where the surface reconstructs around the adsorbate the use of a potential which treats the system as frozen will introduce systematic errors in the calculated diffusion constants. Clearly, a full treatment of these features is very difficult.

In addition to the treatment of the diffusion step in the LH mechanism the other steps could be described theoretically. If the surface diffusion of the adsorbed atom is sufficiently slow then the dominant mechanism for the formation of $\text{H}_2$ in inter-
stellar environments will be ER. However, in the wider context of surface catalysed reactions the other steps in the mechanism are of interest. Furthermore, the adsorption step is also relevant to the study of the ER mechanism. Sticking probabilities have been studied for H-metal systems [251]. It should be straightforward to extend the methods used in such studies to the H-graphite system given a suitable potential. Perhaps the most theoretically challenging step in the LH mechanism is the \( \text{H}_2 \) recombination step. Ideally, one would like to predict the probability and the product distribution from the process

\[
\text{H/surface} + \text{H/surface} \rightarrow \text{H}_2(v, j) + \text{surface}
\]

where \( v \) labels the vibrational and \( j \) the rotational state of the product \( \text{H}_2 \). However, unlike the ER case we cannot ignore the motion of the substrate. That is, an accurate description of this recombination step will involve many degrees of freedom. It is possible to calculate thermal rate constants for the recombination process within transition state theory. In modelling the recombination step we consider two atoms adsorbed to adjacent binding sites. Obviously, the product state is an \( \text{H}_2 \) molecule which is a large distance from the surface. The barrier to this reaction is asymmetric. The method used to calculate the reaction rate is similar to the QTST used to calculate the diffusion rates. However, there is an additional complication. The centroid method has been shown to perform poorly for asymmetric barriers at low temperature [67, 221, 252]. Jang et al. [253] suggested a simple modification to the potential which improves the results of centroid-based QTST for asymmetric barriers. For a 1D exoergic potential \( V_r > V_p \) where \( V_r \) and \( V_p \) are the values of the potential in the reactant and product regions. In the Monte Carlo simulation the
potential $V(x)$ is replaced by

$$V_{\text{mod}}(x) = \begin{cases} 
V(x) & V(x) < V_r \\
V_r & V(x) > V_r.
\end{cases}$$

A more intuitively appealing approach to QTST for asymmetric barriers is the RAW-QTST method of Mills et al. [67, 252]. In this method one considers the minimum action path (MAP) between the reactants and products in the space of all closed Feynman paths. Having identified the MAP using the nudged elastic band method [254] one evaluates the reversible action-space work done in moving the system from the reactant well to the transition state whilst it is confined to a hypercone [67, 252]. This method has been shown to work well for an asymmetric Eckart barrier at low temperature. Furthermore, the method has been successfully applied to the dissociative adsorption of $H_2$ on Cu(110). This illustrates that RAW-QTST is applicable to large systems with many degrees of freedom such as the $H$–graphite system which is of interest here.

The LH and ER mechanisms are rather idealised reaction mechanisms. They represent extreme cases and a mechanism in between the two exists. This mechanism is referred to as the hot-atom mechanism. In this mechanism an adsorbed atom sits at a binding site on the surface. Another atom, incident from the gas phase, collides with the surface at a nearby site. The incident atom diffuses across the surface rapidly and interacts with the adsorbed atom before it has thermalised with the surface. Thus, it is 'hot' in the sense that it has not reached thermal equilibrium with the surface. Such mechanisms have been studied by Jackson and co-workers [43] for $H$ on metal surfaces. The hot-atom mechanism is likely to be of importance in the astrophysical problem. In particular, it is likely to be statistically favoured relative
to the ER mechanism because the probability of direct collision with an adsorbed atom is smaller than the probability of collision with part of the surface near the adsorbate.

In the wider context of the astrophysical problem it is important to investigate the validity of the representation of the dust grain as an (0001) surface of graphite. The true nature of the dust in the interstellar medium is poorly understood. A perfect graphite surface is clearly highly idealised. A number of other representations of the grain could be considered, for example, silicates and amorphous carbon. It would be straightforward to calculate a potential appropriate to silicates. However, it is not entirely obvious how one might represent amorphous carbon in an electronic structure method such as PAW which uses periodic boundary conditions. Many dust grains in the ISM have mantles of H$_2$O and CO$_2$ ice [38]. These mantles could be represented in a straightforward manner. Indeed, Takahashi et al. have performed classical MD calculations on the formation of H$_2$ on H$_2$O ice [255]. It is important to realise that resolution of this issue requires interaction between theory and experiment and the comparison of the predictions of theory with astronomical observation. Experimental results should be available on the formation of H$_2$ on various carbonaceous surfaces soon [159]. The results of these experiments will stand as a test of the theoretical results described in this thesis and extensions of this work.
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