

18. (p.26, Para. 2) Note that a different interpretation is introduced for w_i to aid understanding of the derivation of Eqs. (2.27a) and (2.27b), however, w_i remains a normalised weight function.
19. (p.27) Replace *the lowest energy of all such configurations is added to the data set* with *the geometry, energy and derivatives of the configuration with the lowest such energy are added to the data set*.
20. (p.30) The confidence radius $crad(i)$ is defined in Para. 1. Note that this parameter refines the concept expressed in Eq. (2.28) using $rad(i)$.
21. (p.35, Para. 2) Append [8] and found suitable for the systems where it is used in this thesis after determined empirically.
22. (p.37) Note to the reader: The numerical trick where the **B** matrix is “augmented by zeroes” is used to deal with non-square matrices using SVD because values less than a tolerance (determined by machine accuracy) are set to zero by the procedure (because the reciprocal is too large). Usually, at least one non-zero element on each row would be required to obtain an inverse, however, the SVD procedure is used here to avoid taking the inverse of **B** or even **B'** directly.
23. (p. 39) Note in Section 2.1 that the distortion required to ensure that **B'** is invertible is used whenever necessary. As a further note, internal coordinates ensure rotational and translational invariance of the PES.
24. (pp. 41–42) Displacement has been denoted by the vector **r** in the remaining sections of this chapter, to remove confusion for readers more familiar with conventions used in the references in these sections. Also, note that the subsections in Section 2.4 define the symbols in order of use, so referring back to an earlier subsection may be necessary.
25. (pp.43–44) Specific references to the Verlet, velocity-Verlet, and SHAKE algorithms are needed: Use [28], [39] and references therein to review these techniques. Verlet: See L. Verlet, *Phys Rev.* **159**, 98 (1967) and L. Verlet, *Phys Rev.* **165**, 201 (1967). Velocity-Verlet: W. C. Swope, H. C. Andersen, P. H. Berens and K. R. Wilson, *J. Chem. Phys.* **76**, 637 (1982). SHAKE: W. F. Gunsteren and H. J. C. Berendsen, *Mol. Phys.* **34**, 1311 (1977); and, J. -P. Ryckaert, G. Ciccotti and H. J. C. Berendsen, *J. Comput. Phys.* **23**, 327 (1977).
26. (pp.45–46) SHAKE should be typeset in small caps: SHAKE.
27. (p.46, Para. 4) Replace *whihc* with *which*.
28. (p.46, Para. 4) Append: *The prime notation in Eq. (2.74) (and later in Eq. (2.76)) is used to indicate that the summation only includes the constrained bondlengths.*

Chapter 3

29. (p.55) Replace *reason why* with *reason that*.
30. (p.67) Figure 3.10 has the Intermolecular Separation in Å.
31. (p.67) Note that the use of J for angular momentum is introduced with the notion of binning trajectories.
32. (p.68) A description of action variables may be found in Ref. 34 (Goldstein, 1980) at the end of Chapter 2.
33. (p.68) Note: “halving the intervals” refers to defining the edges of the bins.

34. (p.69) Figure 3.11 is shown only as an example of binning, but represents actual results for the vdAWJ PES using 5000 trajectories. The actual number of trajectories is only important for calculating the statistical error using the statistics of proportions defined in any elementary statistical text [20]. The equation for the standard error is represented by $(N_e - (N_t - N_e) / N_t^3)^{1/2}$ where N_t is the total number of trajectories and N_e is the number of events. An estimate of the number of trajectories could therefore be deduced from the lengths of the error bars, which is a clearer method of representing the results.
35. (p.71) Sampling of initial conditions is described in Chapter 1, and applies to all subsequent chapters. Note that relevant parameters are presented in Table 3.1, and that similar tables are used in subsequent chapters.
36. (p.72, Para. 2) It was *sensible* to re-use initial conditions (positions and velocities of the atoms) generated using the analytic PES to run trajectories on the interpolated PES because the interpolated PES would approximate the analytic PES when converged.
37. (p.73) Parameters used in Table 3.1 are described in the text — the *Dynamics* parameters apply to both the interpolated and the analytic PES.
38. (p.74) Figure 3.15: Note that undulations are due to undulations in the total number of counts.
39. (p.74) The generated MEP is for association of the two monomers. Note that the number of points chosen for the MEP is arbitrary. It is sensible to choose at least a point on the repulsive wall, a point at the minimum and a point at long range. It is also sensible to add further points that were derived while running the minimisation algorithm (in this case steepest descents). Because it is difficult to know, *a priori*, how the choice of MEP points will affect the number of points required to reach convergence, it makes sense to choose a number that can be feasibly be calculated, including second derivatives, without wasting time that could be spent calculating points constructing the PES. If the MEP point is important to the PES, the methodology should add the point, otherwise it is a waste of computational effort. This PES was deliberately inexpensive to calculate to test the methodology, however, to be a realistic test case, a number that would be sensibly chosen for a modest level of *ab initio* theory was used: 33. Similar logic is applied to this choice in later chapters.
40. (p.74) The methodology for running the dynamics in Cartesian coordinates using RATTLE has been provided in Chapter 2.
41. (p.75, Para. 1) Trajectories were inexpensive to run on this system. Thus, only one point is added per iteration. The sampling method was alternated in order to study the effect of each individual point. For this system, a PES was constructed using only RMS sampling and using *h*-weight sampling, however, better results were obtained using the alternating method. Until the Bayesian sampling methodology was developed, prior papers for the iterative construction scheme by Collins and co-workers (see references in Chapters 1 and 2) indicated that a mixed sampling method produced better results, probably because the advantages of each method would offset the disadvantages of the other. The reason why the Bayesian methodology was based on the RMS sampling method is that RMS sampling actually attempts to estimate the error in the PES, whereas the *h*-weight sampling method reflects geometric criteria that space the data points in a way that we “believe” would improve the error in the PES. It is still sensible to experiment with sampling

methods and combinations of sampling methods when embarking on a new system. This was done for systems in this work. Results were not presented for initial experimentation because it was not the purpose of this work is not to examine the differences between the sampling methods. As a final recommendation, if such initial experimentation cannot be afforded, the Bayesian methodology appears to be the state-of-the-art sampling mechanism available at the conclusion of this work.

42. (p.75) Note that points sampled from trajectories for the purpose of estimating errors in the interpolated surface at different times during construction are obtained by performing calculations at configurations printed every fixed number of time steps. The number of time steps between printing configurations is irrelevant because “enough” trajectories are run. Enough trajectories are run for sampling purposes when the number of samples appears to lead to convergence in the average error. The odd number of geometries, 3481, is simply due to not knowing how many geometries will be sampled for each trajectory (which has a unique set of initial conditions). The number of geometries used to estimate the error is in excess of the number required for the average error to converge. However, since the points had been calculated anyway, there was no harm in using all of them since the remaining calculations are inexpensive because the number of interpolation calculations was only equivalent to a trajectory run for 3481 timesteps or 0.6962 ps for this system.
43. (p.77) Table 3.2: The numbers of points in the interpolated PES chosen to determine cross-sections were simply arbitrary places to stop. Only enough results are shown to demonstrate convergence (for example, results between 255 and 565 added points are clearly not required). A regular spacing was avoided in order to attach any significance to the spacing. It is also obvious that more convergence testing is advisable early in the construction to better estimate the rate of convergence and therefore how often it will be necessary to check convergence afterwards. Note that the rate of convergence, particularly for reactive systems later in this work, should not be assumed to be a monotonically decreasing function of the number of data points until enough convergence testing has been performed for this conclusion to be likely.
44. (p.77, Para. 2) The error limits for the smaller cross-sections may be “quoted as too small” because the statistics are determined from such a small number of trajectories.
45. (p.78) The *accuracy demanded of the interpolated PES* should be interpreted as the error in the PES in dynamically important regions demanded for particular applications. This point is used to raise questions in the following two sentences and is intended to be expanded further in the following chapter where these questions are answered.

Chapter 4

46. (p.82) To clarify: *may be classical forbidden*, it is possible that to obtain a measurable cross-section would be impossible without a large number of trajectories, whereas quantum scattering may provide significant cross-

- sections that result from exploration of classically forbidden regions of the PES.
47. (p.84, Para. 1) Replace *datapoints* with *data points*.
 48. (p.85) Note that the spacing of MEP points is shown in Figure 4.3. Again, the number of MEP points was arbitrary. However, a smaller number was chosen than for the previous system because the PES was less anisotropic. Apparently, this was a good choice because the results in Table 4.1 demonstrate more rapid convergence than was observed in the previous chapter. It may have been interesting to choose a much more aggressive MEP, such as one containing only three points. Unfortunately, an examination of the behaviour of the methodology under such conditions was not within the scope of this thesis.
 49. (p.86) Replace *ofspherical* with *of spherical*.
 50. (p.86) m_1 and m_2 in Eq. (4.2) should read m_A and m_B respectively.
 51. (p.88) RATTLE should be typeset in small caps: RATTLE.
 52. (p.88) The RMS sampling method was thought to be more useful in the repulsive wall region of the PES where many closely spaced points would be required to reduce the error in the PES because the energy varies greatly with small changes in configuration. It was also known that anisotropy in the PES in this region at translational energies significantly greater than the depth of the minimum (below infinite separation) would be important to the dynamics [2].
 53. (p.89) HYBRIDON should be typeset in small caps: HYBRIDON.
 54. (p.89, Para. 4) Green's work was referenced in the previous paragraph. It is assumed that the reader should again see Ref. 3.
 55. (p.90) Replace *cases(a) and (b)* with *cases (a) and (b)* (i.e., add space).
 56. (p.90) Energies were chosen for comparison with previous work, although the results of previous work are recalculated here with tighter quantum scattering convergence criteria.
 57. (p.92) Note that coordinates used in Fig. 4.4 are defined in Fig. 4.2. All coordinates are defined in the introductory section of each chapter.
 58. (p.93) Insert space into *case(c)*.
 59. (p.95) See (31) for why an odd number (2433) of configurations were sampled. Instead of using classical trajectories, partial wave analysis was used, but the principle behind regular sampling is the same.
 60. (p.98) Table 4.4: Replace E_C with E_{rel} for consistency with other chapters.
 61. (p.99) A detailed comparison with methods that involved placement of a 40 points on a grid is not provided because the results are quantitatively the same. However, the strengths of the Shepard interpolation that were addressed in Chapter 2 apply here. In addition, it is clear that calculations at grid points will not scale well to larger systems, as described in Chapter 2.
 62. (p. 100) Full close-coupled calculations were performed since this work was published. These were not performed originally because it was unclear how many calculations would be required to test convergence. It was necessary to include the original calculations in order to explain these results in more detail than was previously published, however, nothing would be added to the thesis by inclusion of the close-coupled results. As it stands, data has been omitted that supports the same rate of convergence, although all cross-sections for the analytic PES can be found in the work of Zarur and Rabitz, including close-coupled cross-sections.

Chapter 5

63. (p.111, Para. 3) Replace *an potential energy* with *a potential energy*.

Chapter 6

64. (p.117, Para. 1, last sentence) For clarity, append *than HF/3-21+G(d)*.
65. (p.118, Para. 1) Reference for *Hase and co-workers*: L. Sun, K. Song and W.L. Hase, *Science*, **296**, 875 (2002).
66. (p.119) Reference for Igarashi and Tachikawa: See Ref. [5] and [6].
67. (p.120) Replace *As in previous chapters* with *in this and subsequent chapters*.
68. (p.121) ZPVE: Zero Point Vibrational Energy.
69. (p.122) The same parameters were used for unconstrained trajectories as for constrained trajectories because these were still found to be suitable through experimentation.
70. (p.123,124) More points were selected per iteration for the “unconstrained PES” because it was anticipated that the unconstrained system would be slower to converge. It was also possible to apply additional intuition after the constrained PES was partially constructed.
71. (p.123,124) ???Alternating sampling was used again to compare the effect of each type of sampling as the PES construction progressed (no significant conclusions could be drawn so such comparisons have not been presented). Note that a discussion of the theory, including the discussion of the generation of initial conditions is discussed in Chapter 2.
72. (p.125) For clarity, the data on Fig. 6.2 is shown as a continuous function because there were a large number of points (120 along the MEP). A larger number of points were used than for previous systems because more points were required at long range and it was anticipated that a larger system than previously attempted may require more points in the converged surface. Note that software versions are only listed in the references for brevity.
73. (p.126) Table 6.3 caption: Replace *is shown* with *are shown*.
74. (p.129, Para. 1) Replace *Cl-* with *Cl⁻*.
75. (p.130) Figure 6.3 was generated using interpolated energies everywhere on the displayed grid.
76. (p.137, Para. 1) Ensure that *for this system* is surrounded by commas.
77. (p.140, p.141) Figures 6.10 and 6.11: All dynamical parameters, including the number of trajectories (1200) are shown in Tables 6.1 and 6.2. Explicit mention in the text is provided as a reminder, but note that the number of trajectories can be simply derived from the size of the cross-section and the length of the corresponding error bar.
78. (p.144) Note in the text that the only conclusion drawn from Figure 6.13 is that the number of product complexes was not sufficient to determine reliable fits which produce non-negative coefficients in Eq. (6.5) that are clearly non-physical. A fit that forces these coefficients to be non-negative was also too poor. The exponential tail clearly does not fit well for the triple exponential (physically the curve should be monotonically decreasing): more sample points would help in this area of the plot. Note that results for the product complex lifetimes are subsequently disregarded for these reasons.

79. (p.146) Figure 6.15 caption: Replace *Langevin cross-section* with *Langevin rate constant* (which does not depend on relative translational energy).
80. (p.146) Figure 6.15 caption: Add, after the first sentence, *The “Total Reaction” rate constant represents results from this work (with error bars).*
81. (p.147) Note that running backward trajectories was not required for the unconstrained system because early trajectories sampled the reactive channel very well.
82. (p.149) Note that for all figures in this chapter (including Fig. 6.17) it has been noted that errors bars are displayed and errors are quoted for two standard deviations.
83. (p.150) Leaving out ZPVE in the initial conditions for the unconstrained trajectories would not provide a meaningful comparison in this work, because previous studies have investigated the effect of ZPVE for S_N2 reactions.
84. (p.152) Space is required to separate terms as in *CH₃Cl + Cl⁻*.
85. (p.152) Add after sentence about energy disposal: *From the current understanding of IVR (See Nesbitt and Field, J. Phys. Chem., **100**, 12735 (1996)), lowest frequency modes are the best sinks (higher density of states), however, any energy that should be transferred into the C-H stretching motions is obviously ignored when constraints are used.*
86. (p. 153) For clarity: Add, *The validity of the “constrained” PES refers to the fact that the “constrained” PES is always valid for performing simulations that apply the same constraints.*

Chapter 7

87. (p.161) Software versions (e.g. Gaussian) are provided in the references.
88. (p.162) Figure 7.3: Note that the direct channel between HOC⁺ and HCO⁺ should be removed.
89. (p.163) Note that all necessary theory to understand Table 7.1, including the method of sampling initial conditions, is provided in Chapter 2. Trajectory end tests check whether or not the fragments are moving apart and if any of the internuclear distances exceed *d_{ab}*.
90. (p.164) ZPVE was defined in (49).
91. (p.166, 167) Figures 7.4 and 7.5: Note that the number of MEP points has been included in the legend of each figure and is therefore not included in each caption. Note that there is a long-range charge-dipole interaction for this system. However, the scales are chosen in these figures to better display the distribution of points in the interaction region.
92. (p.168) Figure 7.8: Replace R_{CF} for the x-axis label with R_{CO}. Add: *for the final PES (1389 points)* to the sentence in the caption. The x-axis of Figure 7.9 was truncated so that the distribution of points could be more clearly seen (note that it will be shown, later in the chapter, that the PES is already converged before the maximum extent of the x-axis).
93. (p.172) Note that the number of trajectories used to check convergence has not been included in the figures because this can easily be determined from Table 7.1, and is reflected by the size of the error bars.
94. (p.172, Para. 1) Replace *less after* with *more after*.
95. (p.173, Para. 1) Add *For example, an average of the values observed at 1000, 1200 and 1400 points could be taken.*

96. (p.175) Captions for Figures 7.15 and 7.16: Add *Results are for the final PES.*
97. (p.181) Figure 7.26 caption: Add *Error bars refer to two standard deviations.*
98. (p.185) Add *Inspection of the distributions of energy and angular momentum unfortunately yields few clues as to which degrees of freedom are more important to the dynamics.*
99. (p.186, Para. 2) Replace *H-H bonds* with *H-H distances*.

Chapter 8

100. (p.192) Note that ab initio results for higher levels of theory were performed in initial investigations for each system (where functional forms were not used) to determine the suitability of the chosen level of theory. The results of these preliminary calculations are not reported because relevant results at stationary points for very high levels of theory are contained in references for each system and it is clear that now that we know how many points are required for convergence for lower levels of theory we could attempt much higher levels with current computational resources.

Corrigenda

Chapter 1

Chapter 2

1. (p.13) Replace “abinitio” with “*ab initio*” (note use of italics).
2. (p.13) The reader is encouraged to review Ref. 3 at the end of Chapter 1 for a thorough account of the *ab initio* methods used in this thesis.
3. (p.14) Symbols in Eqs (2.6), (2.6) and (2.7) not fully described:
 - $\hbar$ = Planck’s Constant (h) divided by 2π
 - t = time
 - ψ, ϕ are wavefunctions; lower case has been used to distinguish these wavefunctions from the total wavefunctions that are additionally a function of the electronic coordinates in Eqs (2.3) and (2.4).
 - ε_n = energy eigenvalue associated with the lower case wavefunctions whereas E was used for the eigenfunctions that were written as a function of electronic coordinates.

Other variables are described earlier in Section 2.1 or in the succeeding paragraph.

4. (p.16, Para. 3) Remove the comma after *When*.
5. (p.16) R_i in Eq. (2.14) is a component of the internal coordinate vector R .
6. (p.18, Para. 1) Replace *the figure* with *Fig. 2.1*.
7. (p.18) A space is required after the first full stop in *Fig.2.1*.
8. (p.19, Para. 1) Remove full stop after *previously* in *previously*. [2].
9. (p.19) Replace E with E_{rel} for consistency.
10. (p.20, Section 2.2.1) Italicise *ab initio* (latin).
11. (p.21) Replace italicised $Z(i)$ with boldface $\mathbf{Z}(i)$.
12. (p.21) Replace *in internal coordinates* with *in internal coordinates*, R_{ij} . Other symbols can be deduced by where the defining equations occur in the corresponding sentences.
13. (p.21) The reader is referred Ref. 18 of Chapter 1 for a description of the relevance of using reciprocal distances for their asymptotic properties. In the same paper, the authors discuss a description of the redundant coordinate problem that is not fundamentally relevant to this thesis, yet is relevant to a description of the PES construction methodology.
14. (p.22) Para. 1. Replace equation reference in *normalised weight function in Eq. (2.21)* with (2.22).
15. (p.23) Para. 2. Note that i and o are used to distinguish between parameters corresponding to *inner* and *outer* neighbour lists, respectively. This convention has also been used in later chapters.
16. (p.25) For clarity, replace *The number of trajectories can be small, but large enough* with *The batch of trajectories must be large enough*.
17. (p.26) Note that the use of v_i , for any unnormalised weight-function is consistent with Eqs. (2.24) and (2.25) in the previous Section 2.2.

Scalable Iterative Potential Energy Surface
Construction using Constraints

*A thesis submitted for the
degree of Doctor of Philosophy of
The Australian National University*

by

ALEXANDER HAMISH DUNCAN

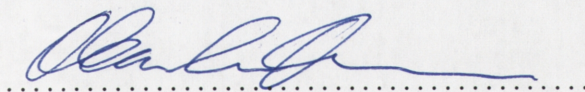
May, 2004

declaration

I declare that the research, calculations and results that appear in this thesis are solely my own work. Related publications are cited. The chapter on rotational inelastic scattering in hydrogen is based on work published in:

- A. H. Duncan and M. A. Collins, *J. Chem. Phys.* **111**, 1346 (1999).

Work in the ion-molecule reaction chapters is to be submitted for publication in collaboration with my supervisor, Dr M. A. Collins.

A handwritten signature in blue ink, appearing to read 'Alex Duncan', is written over a horizontal dotted line.

Alexander H. Duncan

May 9, 2004

acknowledgments

A good friend takes a long time to *grow*. (John Leonard)

This work is about *growing* potential energy surfaces. To grow good potential energy surfaces takes time. More about this later. For now I will discuss growing friends.

Many people could be acknowledged in the years that have passed culminating in this thesis. I have had the opportunity to work in a thriving research group with learned colleagues that I have enjoyed associating with not only in the parlance of reaction dynamics but life in general. Ryan and Fiona Bettens, Ron Pace, Damien Kuzek and of course Mick Collins would all remember fondly the lunchtime discussions about history and politics. Keiran Thompson, Ramzi Kutteh and Michael Smith deserve special mention for their contribution to the general camaraderie in the group during my time there. Others include visiting scholars such as Simon Petrie.

I thank the staff at the Research School of Chemistry and the Australian National University. I thank the Australian Partnership for Advanced Computing for generous allocations of supercomputer time, and the University for funding my ANU PhD Scholarship. My supervisor, Dr Michael (Mick) Collins, and remaining members of my advisory panel, Dr Ryan Bettens, Prof. Denis Evans and Prof. Leo Radom, have always been available for wisdom and guidance.

During my candidature as a PhD student I met the love of my life on a volleyball court and married her. Cara has been a continuing source of support. Cara also brought with her the most supportive parents-in-law I could have imagined. I also thank my parents for their unending understanding and support. Without the support of family and friends, I could not have grown so much personally.

I also thank my canine companion, Tipyn, a lovable mongrel and constant reminder that ignorance, and a chewable toy, are bliss.

abstract

Understanding reaction dynamics is central to a deeper understanding of chemistry. The dynamics of molecules as they approach and collide, as bond-breaking and bond-forming takes place, is determined by the molecular potential energy surface (PES).

The PES is simply the total electronic energy of the whole molecule, which depends on the positions of the atomic nuclei. This energy can be calculated accurately using *ab initio* (first principles) quantum chemistry. However, to study the dynamics of a chemical reaction, we need to know this energy at every relevant configuration of the atomic nuclei.

During a reaction, the molecular geometry changes a great deal as bonds are broken and formed. So the PES is a complicated function of many coordinates which span a large range of values, and cannot feasibly be calculated everywhere using *ab initio* methods.

This thesis addresses the problem of how to construct such energy surfaces so that a deeper understanding of chemical reaction dynamics can be obtained. The work builds on the methods that Collins and co-workers have developed for constructing a PES as an interpolation of *ab initio* quantum chemistry data. In particular, this thesis addresses the task of how to overcome the “dimensionality problem” associated with the large number of atomic coordinates which define the surface. The approach taken here is to constrain some of the molecular degrees of freedom, so that the PES only uses *ab initio* quantum chemistry data in a restricted range of molecular coordinates. The PES is still defined for all relevant molecular shapes, and we give examples of unrestricted reaction dynamics based on the constrained methodology.

The thesis first presents the relevant background theory on which it is based, dwelling in particular on the interpolation approach to the construction of a PES and on how constraints are applied to the dynamics of molecules undergoing reaction. The bulk of the work describes four applications of the approach to inelastic and reactive molecular collisions. These applications demonstrate, in different ways, the validity and utility of this approach to the construction of molecular potential energy surfaces for chemical dynamics.

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Part I

Potential Energy Surface Construction

Chapter 1

Towards Scalable Potential Energy Surface Construction

1.1 Role of the Potential Energy Surface in Chemistry

Understanding reaction dynamics is central to a deeper understanding of chemistry. It encompasses the processes or “physics” that occur in a chemical reaction. The dynamics of molecules as they approach and “collide” is obviously important, as bond-breaking and bond-forming are intimately related to spatial proximity of the reactants. The way the reactants are brought together will depend on the interaction between them: the course of the collision, reactive or non-reactive, is sensitive to the *potential energy surface* (PES) [1, 2]. The PES describes this interaction as a function of the displacements of all of the interacting particles.

The use of the Born-Oppenheimer approximation allows us to refer to separate potential energy surfaces for different *adiabatic* electronic states, where each surface is a function only of the relative positions of the nuclei. Application of the Born-Oppenheimer approximation is discussed further in Chapter 2. Briefly,

the Born-Oppenheimer approximation implies that the potential energy at any point on one surface can be calculated by fixing the positions of the nuclei, and determining the electronic energy at that configuration.

The electronic energy can be calculated accurately using *ab initio* theory [3]. Such calculations are a powerful tool for determination of stationary points in the PES, and are useful in characterising chemical reactions and in the calculation of many molecular properties, including electrostatic and spectroscopic properties, for example.

However, to study the dynamics of a chemical reaction, we need to know the potential energy at every relevant fixed position (configuration) of the atomic nuclei. During a reaction, the molecular geometry changes a great deal as bonds are broken and formed. In a classical (molecular dynamics) simulation of a reaction, the energy (and its gradient with respect to nuclear positions) must be calculated at every time step while this large range of configurations is explored.

Quantum simulations might require an even broader range of molecular geometries to account for *tunnelling* in classically forbidden regions. If the chemical reaction dynamics is very sensitive to the shape of the PES, including, for example, the height of some barrier, then very high levels of *ab initio* theory might be necessary. The computational expense of performing a vast number of high level *ab initio* quantum chemistry calculations is prohibitive.

In recent years, several authors have explored a direct “on-the-fly” *ab initio* calculation of the PES at each step in a classical simulation of chemical reactions. However, thus far, the simulations have used only very low levels of *ab initio* theory and/or very poor statistical exploration of the dynamics.

1.2 Feasible PES Construction for Dynamics

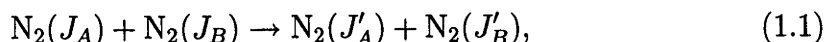
Given that direct use of *ab initio* calculations is not feasible, dynamicists have taken different approaches to the determination of accurate PES for dynamical simulations. Usually, a global functional form for the PES is fitted using not only *ab initio* data but also experimental data. Earlier fitting procedures, such as the diatomics in molecules (DIM) method, LEPS (London, Eyring, Polanyi and Sato) and many-body expansions are reviewed in Ref. 2. Fitting procedures, and the resulting PES, are system-specific and dependent on the type and accuracy of available data. Successful “fits” are therefore performed by experts exercising extensive chemical intuition. Examples are given later in this thesis of different functional forms, as these will be useful in testing new methodology.

Collins and co-workers have developed [4] a scalable iterative method for constructing an interpolated PES using only calculations of the potential energy (and first and second derivatives). The methodology has been applied to many systems [5–15], and in each case, only standard quantum chemistry techniques were required. The approach has been successively improved [5–9, 16–18]. Reference 19 provides a recent review of the methodology.

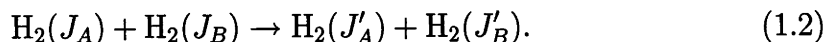
The goal of this approach is scalability. One problem with multidimensional interpolation is the number of data points required to obtain sufficient density of data in higher dimensions. In general, the PES is a function of $3N - 6$ degrees of freedom for N atoms ($3N - 5$ in a collinear system). Each additional atom adds three degrees of freedom. One only has to consider the example of equidistant grid points in multiple dimensions to see a scalability problem. To overcome this problem, a “uniform grid” of data is replaced with scattered data. The location of the data is restricted to the “dynamically important” region of molecular configurations.

The methodology of Collins and co-workers has been extended further through the work in this thesis. Constraints have been used to tackle the dimensionality problem and achieve greater scalability. The theory underlying the methodology of Collins and co-workers will be presented in Chapter 2. The iterative scheme is presented in detail, along with modifications to facilitate the use of constraints in PES construction.

We begin testing the new methodology for systems of four atoms in Chapters 3 and 4. These are small test cases for which reduced-dimensionality functional forms for the PES are available. To test the methodology, we will use the iterative scheme to approximate the functional form PES using interpolation between “data points” determined from the functional forms. Convergence of the interpolated PES can be directly observed by comparing the dynamics described by the interpolant with those described by the functional form. In the first system, we take the opportunity to examine a non-reactive energy transfer process (not previously examined by Collins and co-workers):



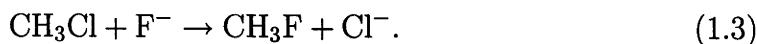
which is presented in Chapter 3. In the second system, presented in Chapter 4, the methodology has been applied to another rotational inelastic scattering example:



Here, we apply the methodology to quantum scattering. It was important to examine the application of this type of PES in quantum dynamics, because only classical dynamics is used in the construction of the PES [20]. PES were later constructed for reactive quantum scattering by Collins, Zhang, and co-workers [21–23].

In Chapters 6 and 7 we turn our attention to reactive systems. In these chapters, we construct interpolated *ab initio* PES.

Chapter 6 deals with a simple nucleophilic substitution reaction:



Reaction (1.3) is an $\text{S}_{\text{N}}2$ reaction familiar from organic chemistry. For the collision energies studied in Chapter 6, long-lived complexes of the reactants and products in reaction (1.3) can be formed. Hence, the methodology was also tested for dynamical observables other than cross-sections — the complex lifetimes.

The accuracy of the interpolation is demonstrated by the convergence of reaction cross sections and complex lifetimes to constant values as the size of the interpolation data set increases. The interpolation method must become exact at infinite data density. The feasibility of the method is demonstrated by convergence at a feasible number of data points. In this chapter, we compare the rate of convergence of the PES, with size of the data set, for surfaces constructed with and without constraints. This indicates the utility of employing constraints in the PES construction.

Chapter 7 presents the only results for an eight-atom system using a methodology based on the iterative scheme of Collins and co-workers:



This was then the largest system attempted using the iterative scheme. The many degrees of freedom provided an excellent opportunity to explore the use of different sets of constraints.

Finally, in Chapter 8 we present a summary of this work, and a discussion of the experience that was gained through its application.

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Chapter 2

Theory

Knowledge of intermolecular potentials is fundamental to understanding microscopic properties, which is in turn useful in relating these to macroscopic or bulk properties. It is impossible to determine the potential in detail using experimental data alone, although some characterisation of specific regions may be possible. The potential of interacting molecules depends not only on intermolecular displacement, but also relative orientation. When chemical reaction occurs, the potential energy of the colliding molecules is a very complicated function of the geometry.

The purpose of this thesis is to advance the methodology for constructing this complicated function. In this chapter, the concept of a molecular potential energy surface (PES) is introduced, and we will very briefly discuss the context in which a PES is used to calculate important microscopic observables such as reaction cross-sections and rate coefficients. Over the last several years, a new method for constructing a PES as an interpolation has been reported [1–9] and shown to be a very efficient approach for small molecules [1–19]. The new work [20] presented in this thesis aims to enable the application of this basic approach to reactions involving much larger molecules. It is useful, therefore, in this introduction, to also review the established interpolation method.

2.1 Reaction Dynamics

The motion of a molecule, electrons and atomic nuclei, is determined by the Hamiltonian, H :

$$H = T_{\text{nuc}} + T_{\text{elec}} + V(\mathbf{r}, \mathbf{R}), \quad (2.1)$$

$$= T_{\text{nuc}} + H_{\text{elec}} \quad (2.2)$$

where T_{nuc} represents the kinetic energy of the nuclei, T_{elec} represents the kinetic energy of the electrons and V represents the Coulomb interactions of the electrons (with coordinates $\mathbf{r}$) and the nuclei (with coordinates $\mathbf{R}$). In quantum mechanics, a stationary state Ψ of the molecule is given by a solution of the Schrödinger Equation:

$$H\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}). \quad (2.3)$$

The Schrodinger Equation is a differential equation involving all the electronic and nuclear degrees of freedom. Fortunately, the task of solving this equation can be simplified by the Born-Oppenheimer approximation. Since the mass of an electron is at least three orders of magnitude smaller than that of a nucleus, it is reasonable to assume that the electrons move very much faster than the nuclei. Hence, the nuclei can be considered as stationary on the time scale of the electronic motion. In practice, this means that T_{nuc} in Eq. (2.3) is temporarily set to zero, and we can solve the so-called electronic Schrödinger Equation:

$$H_{\text{elec}}\Phi(\mathbf{r}; \mathbf{R}) = E(\mathbf{R})\Phi(\mathbf{r}; \mathbf{R}). \quad (2.4)$$

Since the nuclei have a Coulomb interaction with the electrons, H_{elec} depends on the (fixed) positions of the nuclei, so that the electronic wavefunction, $\Phi(\mathbf{r}; \mathbf{R})$, depends parametrically on the nuclear positions. Therefore, the eigenvalue, $E(\mathbf{R})$, in Eq. (2.4) also depends on the nuclear positions. Having determined the stationary state of the electrons, the motion of the nuclei is determined by the Hamiltonian for this electronic state:

$$H_{\text{nuc}} = T_{\text{nuc}} + E(\mathbf{R}). \quad (2.5)$$

Equation (2.5) is the starting point for this thesis. It is a valid description of the motion of the atomic nuclei when the state of the electrons is well described by a single solution of Eq. (2.4). This can be the case when the total electronic energy, $E(\mathbf{R})$, for the state we are interested in, is well separated from the energy of other states. This total electronic energy, $E(\mathbf{R})$, is a function of the nuclear positions. It is the molecular potential energy surface (PES), sometimes called the Born-Oppenheimer potential energy surface.

The PES is a function of the nuclear positions which define the nuclear configuration space. The dimension of the configuration space is the number of coordinates that we need to uniquely define the configuration of the system. In Cartesian coordinates, there are three spatial coordinates for each atom, so for N atoms there are $3N$ coordinates. However, the potential does not depend on the position or orientation of the entire system. A natural way to account for this is to use interatomic distances as coordinates, since these are invariant under rotations and translations of the entire system. The number of internal coordinates required is then reduced by six for a general three-dimensional structure, or five for a linear configuration, to $3N - 6$, or $3N - 5$ for a linear system.

In the Born-Oppenheimer approach, solving the complete electronic and nuclear dynamics has been broken down into two tasks, evaluating the total electronic energy by solving the eigenvalues problem in Eq. (2.4), and then evaluating the motion of the atomic nuclei as determined by the Hamiltonian of Eq. (2.5). As these two tasks play an important role in the work presented here, it is useful to present at least some very brief remarks about each one.

***Ab Initio* Calculation of the Potential Energy**

The solution of the electronic Schrodinger Equation of Eq. (2.4) is a major computational task. Much of theoretical chemistry has been devoted to this task over the last fifty years. This effort has lead to the development of a hierarchy of methods ranging in both accuracy and computational cost, which are known collectively as *ab initio* quantum chemistry.

The simplest Hartree-Fock approach to Eq. (2.4) treats the interaction of the electrons via a self-consistent or mean field theory where each electron interacts with an average field due to the other electrons. This type of approach is rarely sufficiently accurate to describe the energy of a molecule undergoing a chemical reaction. A true many-electron solution of Eq. (2.4) accounts for the correlation between the distribution of individual electrons. For some chemical reactions, sufficient accuracy in Eq. (2.4) can be obtained with the Møller-Plesset perturbation approaches. For other molecules, high order treatments of electron correlation are necessary.

In this thesis, we are primarily concerned with the methodology for constructing the global PES from the *ab initio* calculation of the electronic energy at particular molecular geometries. The difficulty of this “global construction problem” does not depend on the chemical accuracy of the particular “abinitio” quantum chemistry method employed, so for convenience we have used simpler treatments such as the second order Møller-Plesset perturbation method (MP2). However,

it is a guiding principle in our approach that the computational cost of solving Eq. (2.4) is high, even for a single arrangement of the nuclei. An over-riding consideration will therefore be to construct the global PES with as few *ab initio* quantum chemistry calculations as possible.

The Nuclear Motion

Using the Hamiltonian of Eq. (2.5), the motion of the atomic nuclei is given by the time-dependent Schrödinger Equation:

$$i\hbar \frac{\partial \psi(\mathbf{R}, t)}{\partial t} = H_{\text{nuc}} \psi(\mathbf{R}, t). \quad (2.6)$$

Equivalently, one can deal with the time-dependent Schrödinger Equation by writing:

$$\psi(\mathbf{R}, t) = \sum_{n=1}^{\infty} c_n \phi_n(\mathbf{R}) e^{-i\epsilon_n t/\hbar}. \quad (2.7)$$

The nuclear wavefunctions $\phi_n(\mathbf{R})$ obey the time-independent Schrödinger Equation:

$$H_{\text{nuc}} \phi_n(\mathbf{R}) = \epsilon_n \phi_n(\mathbf{R}). \quad (2.8)$$

This means that if we can find all the solutions of the time-independent equation, Eq. (2.8), then the motion of the nuclei is given by Eq. (2.7) with suitable coefficients, c_n . In a later chapter, we consider the quantum inelastic scattering of two hydrogen molecules, and we employ a standard computer program to obtain all the relevant solutions to Eq. (2.8). However, in general the computational

task of solving Eqs (2.6) or (2.8) is impossibly large for most molecules undergoing chemical reactions. Thus far, only a few reactions for molecules containing as many as four atoms have been studied with exact quantum dynamics. Fortunately, the mass of most atomic nuclei is sufficiently large that classical mechanics often provides a qualitatively and quantitatively correct description of the nuclear dynamics.

In this thesis, we will use mainly classical dynamics to study chemical reactions. Since these classical simulations of the molecular motion will play such a large part in this work, it is useful to introduce some of the routine aspects of classical dynamics.

Before we start, a trivial change of notation is introduced. In electronic structure calculations, it is usual to give the total electronic energy the symbol, $E(\mathbf{R})$. However, although this quantity is exactly the potential energy surface for the nuclear motion, it is more traditional to denote the PES as $V(\mathbf{R})$, to avoid confusion with the relative translation energy which we will write as E_{rel} in this thesis.

There are a number of equivalent forms of the classical equations of motion. Since we have introduced the nuclear Hamiltonian, let us begin with Hamilton's equations. From Eq. (2.5) and the discussion of the dependence of the PES on the internal coordinates of a molecule, we write

$$H_{\text{nuc}} = \sum_{k=1}^{3N} \frac{P_k^2}{2m_k} + V[\mathbf{R}(\mathbf{X})]. \quad (2.9)$$

Here we have explicitly written the PES as a function of a vector $\mathbf{R}$ of internal coordinates, which are functions of the $3N$ -tuple of Cartesian coordinates, $\mathbf{X}$. Each Cartesian coordinate, X_k , has a corresponding momentum, P_k :

$$P_k = m_k \frac{dX_k}{dt}, \quad (2.10)$$

where m_k is the mass associated with coordinate k .

Using the Cartesian coordinates as generalised coordinates in Hamilton's equations of motion yields

$$\dot{X}_k = \frac{\partial H_{\text{nuc}}}{\partial P_k}, \quad \text{and} \quad (2.11)$$

$$\dot{P}_k = -\frac{\partial H_{\text{nuc}}}{\partial X_k}. \quad (2.12)$$

When, we discuss imposing constraints on this classical motion, it will be convenient to use the equivalent Newtonian form of these equations:

$$m_k \ddot{X}_k = -\frac{\partial V[\mathbf{R}(X)]}{\partial X_k} \quad (2.13)$$

$$= -\sum_{i=1}^{3N-6} \frac{\partial V}{\partial R_i} \frac{\partial R_i}{\partial X_k}, \quad k = 1, \dots, 3N. \quad (2.14)$$

Given the position of each atom at some time, say $t = 0$, and the velocity or momentum of each atom at that time, then standard computer algorithms can be used to integrate Eq. (2.13) over time to calculate the position and velocity of each atom at any subsequent time. The path in position and momentum space that the molecule follows in time is called a "classical trajectory." That is, if we have a PES, we can evaluate the gradient of the PES in Eq. (2.13) and hence we can know where every atom in a molecule is at any later time and how it is moving.

This knowledge provides a complete (classical) description of a chemical reaction (or any other dynamics of a molecule).

Classical trajectories conserve the total energy of the molecule. That is, the value of the total energy, the right-hand side of Eq. (2.9), is constant with time.

Here, we will be mainly interested in the chemical reactions and other dynamics which take place in bimolecular collisions. The application of classical mechanics to the simulation of bimolecular collisions is well known [21], and only the minimum of relevant details will be reprised here. The initial positions and velocities of the atoms in the colliding molecules are partially determined. We will assume that the reactant molecules are far apart before the collision (say at $t = 0$) and are moving towards each other. This basic scenario is illustrated in Fig. 2.1.

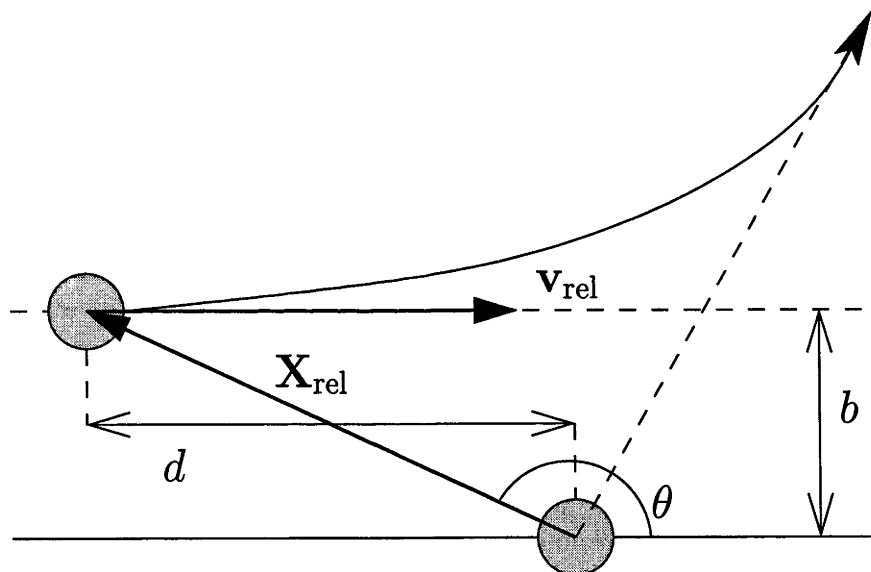


Figure 2.1: Parameters used to compute cross-sections.

The relative motion of the reactants can be viewed as initially taking place in a plane formed by the relative position vector, $\mathbf{X}_{\text{rel}}$, that connects their centers of mass, and the relative velocity vector, $\mathbf{v}_{\text{rel}}$, as shown in the figure. The impact parameter, b , measures the separation of the reactant centers of mass, perpendicular to the relative velocity vector. If the reactants did not interact with one another, then b would be the closest distance between the molecules (realised as they pass one another). The initial relative translational energy for the collision is E_{rel} :

$$E_{\text{rel}} = \frac{1}{2} \mu |\mathbf{v}_{\text{rel}}|^2, \quad (2.15)$$

where μ is the reduced mass of the pair. The angular momentum for the collision in Fig.2.1 is L (the *orbital angular momentum*):

$$L = \mu |\mathbf{v}_{\text{rel}}| b. \quad (2.16)$$

In the gas phase, each reactant molecule experiences collisions with other molecules in three dimensional space (not a single plane) so that the number of collisions that have an impact parameter of value b is proportional to the circumference of an annulus of radius b , that is $2\pi b$. After the collision has taken place, the molecules fly apart and at infinite separation, the angle, θ , reaches a constant value called the scattering angle.

In order to simulate a molecular collision in the gas phase, we must take account of the fact that there are many different collisions, because there are many different values of the initial positions and velocities of the atoms which are consistent with Fig. 2.1. Clearly, the orientation of the molecules at $t = 0$ is arbitrary. The molecules may be rotating, so the rotational motion must be specified. In this work, for convenience, we generally assume that the reactants are not rotating. The reactant molecules are vibrating before the collision, so the energies of the vibrational motions and the phases of the vibrational motions must be specified.

The selection of these initial conditions, vibrational phases, orientation angles, impact parameters, etc is achieved by a random sampling process that is called Monte Carlo sampling [21]. The details are not important here, we simply use standard techniques to simulate bimolecular collisions, as described and implemented previously. [2]. A *classical simulation* of a chemical reaction is therefore a set of hundreds or thousands of *classical trajectories* each of which has initial atomic positions and momenta, chosen by Monte Carlo sampling, consistent with a bimolecular collision. The outcome of such a simulation is a random (Monte Carlo) sample of the bimolecular event. The measures we obtain of this process are statistical measures of averages. For example, by simply counting how many trajectories have molecular fragments of different composition than obtained at $t = 0$, we can calculate the probability of reaction. To be more quantitative, we calculate the reaction cross-section, σ :

$$\sigma = 2\pi \int_0^\infty P(b)bdb, \quad (2.17)$$

where $P(b)db$ is the probability that collisions which had an impact parameter between b and $b + db$ will lead to reaction. Since our classical trajectories conserve the energy of the molecule, the reaction cross-section describes reaction at a specific energy, $\sigma(E)$. This cross-section is related to the thermal rate coefficient for the reaction by a thermal average [22]:

$$k(T) = \frac{1}{k_B T} \sqrt{\frac{8}{\pi \mu k_B T}} \int_0^\infty E \sigma(E) e^{-E/k_B T} dE. \quad (2.18)$$

Thus, one outcome of a classical simulation of a chemical reaction is the prediction of a thermal rate coefficient. However, in order to calculate important quantities like rate coefficients, we must have a PES, that is, a knowledge of how the total electronic energy depends on the shape of the molecule at every molecular configuration required in Eq. (2.13). The basic approach used to achieve this is via interpolation of *ab initio* quantum chemistry calculations of $V(\mathbf{R})$.

2.2 Interpolation of Potential Energy Surfaces

Since the computational cost of evaluating $V(\mathbf{R})$ by *ab initio* methods is very high, the number of molecular configurations at which $V(\mathbf{R})$ is calculated will be small. In order to approximate $V(\mathbf{R})$ elsewhere, we will use an interpolation method.

For reactions involving only three atoms, a number of interpolation methods have been reported [23–25]. However, in this work, we are concerned with the development of methods which can be applied to large molecules. The only systematic and efficient interpolation method yet reported for reacting molecules of more than three atoms is the Shepard interpolation approach introduced by Collins and coworkers [1–13].

2.2.1 Shepard Interpolation

The *ab initio* quantum chemistry programs which evaluate the total electronic energy can also provide the derivatives of that energy with respect to the nuclear coordinates. For some levels of *ab initio* theory, first and second and even higher order derivatives can be obtained efficiently from so-called analytic gradient methods. Of course, derivatives can also be evaluated by finite differences of the energy (or analytic derivatives, if available). We will assume that the Cartesian first and second derivatives of the energy are available at some geometry (at a cost). It is

possible then to approximate the PES in the vicinity of that geometry by a second order Taylor series. To ensure that this approximation to the PES is invariant to translation and rotation of the molecule, the Taylor series must be expressed in internal coordinates. As suggested earlier, the atom-atom distances provide a convenient basis for internal coordinates. Actually, it is more appropriate on physical grounds to use the reciprocal distances,

$$Z_\alpha = \frac{1}{R_{ij}}, \quad i, j = 1, \dots, N; \alpha = 1, \dots, N(N-1)/2. \quad (2.19)$$

Thompson, Jordan and Collins [7] showed how to construct $3N-6$ independent internal coordinates as linear combinations of the Z_α :

$$\rho_k = \sum_{\alpha=1}^{N(N-1)/2} U_{k\alpha} Z_\alpha, \quad k = 1, \dots, 3N-6. \quad (2.20)$$

The energy derivatives with respect to Cartesian coordinates can then be transformed into derivatives with respect to these internal coordinates to write a Taylor expansion about some “data point”, $Z(i)$:

$$\begin{aligned} T_i(\mathbf{Z}) = V[\mathbf{Z}(i)] &+ \sum_{k=1}^{3N-6} [\rho_k - \rho_k(i)] \left. \frac{\partial V}{\partial \rho_k} \right|_{\rho=\rho(i)} \\ &+ \frac{1}{2!} \sum_{k=1}^{3N-6} \sum_{l=1}^{3N-6} [\rho_k - \rho_k(i)] [\rho_l - \rho_l(i)] \left. \frac{\partial^2 V}{\partial \rho_k \partial \rho_l} \right|_{\rho=\rho(i)} + \dots \end{aligned} \quad (2.21)$$

If we have such Taylor expansions for $i = 1, \dots, N_d$ data points, then we can write the PES as a weighted average or Shepard interpolation [26, 27]:

$$V(\mathbf{Z}) = \sum_{g \in G} \sum_{i=1}^{N_d} w_{goi}(\mathbf{Z}) T_{goi}(\mathbf{Z}). \quad (2.22)$$

The rather compact notation in Eq. 2.22 requires some explanation. First, the symbol G stands for the symmetry group of the molecule; the Complete Nuclear Permutation Inversion (CNPI) group. Permutation of the coordinates of indistinguishable nuclei in the molecule does not change the energy and simply permutes the atomic labels on the energy derivatives. Hence, if we evaluate the coefficients in the Taylor series of Eq. (2.21) at some $Z(i)$, we can easily form a Taylor series expansion about any permuted point, $g \circ Z(i)$. Thus, the sum over g in Eq. (2.21) implies that all symmetry equivalent versions of one data point are included in the data set. This ensures that the PES has the correct symmetry (and provides data points “for free”). The normalised weight function in Eq. (2.21) is given by

$$w_i(\mathbf{Z}) = \frac{v_i(\mathbf{Z})}{\sum_{g \in G} \sum_{k=1}^{N_d} v_{g \circ k}(\mathbf{Z})} \quad (2.23)$$

where the unnormalised weight function v is

$$v_i(\mathbf{Z}) = \frac{1}{\|\mathbf{Z} - \mathbf{Z}(i)\|^{2p}}, \quad (2.24)$$

using the greater value of $p > 3N-6$ or $p > n_{Taylor}$ where n_{Taylor} is the degree of the Taylor polynomial¹. Second order Taylor expansions are typically favoured, since higher order derivatives are expensive to calculate and are not such a significant boon as to make the effort worthwhile [4].

For appropriate weight functions, including that in Eq. (2.24), the interpolation formula of Eq. (2.22) becomes *exact* in the limit of high data density. Hence, *convergence* of the PES to the exact value should be observed as the size of the data set increases.

In actual fact there is usually only a small fraction of the data set which significantly influences the potential in any particular region of the PES. To reduce the

¹The Taylor series is truncated to include only terms of n_{Taylor} or lower order derivatives.

number of computations to a necessary minimum, the concept of a *neighbour list* may be invoked, a concept from molecular dynamics [2, 28]. The requisite assumption is that normalised weights below a given tolerance, w_{tol} are not included in the neighbour list and are therefore not used to calculate the interpolated potential in Eq. (2.22).

In a trajectory calculation, every fixed number of timesteps the neighbour list is updated to ensure that the correct neighbours in the new region of configuration space are used. This update is performed only often enough to keep the introduced discontinuities small but still reduce the computation time. Hence, the aim should be to keep the tolerance, w_{tol} , small enough that the identity of the neighbours changes slowly. An extension of this idea is to use *inner* and *outer* neighbour lists, where one list is updated less frequently but contains a larger list of points. The outer neighbour list is larger because it includes data points whose weight exceeds $w_{\text{tol},o}$, where $w_{\text{tol},o} \ll 1$.

Other functional forms have been tried for the unnormalised weight function [7]. A *two-part* unnormalised weight function has been suggested for larger systems such as $\text{CH}_4 + \text{H}$ [7]:

$$v_i(\mathbf{Z}) = \left\{ \left\| \frac{\mathbf{Z} - \mathbf{Z}(i)}{\text{rad}(i)} \right\|^{2p} + \left\| \frac{\mathbf{Z} - \mathbf{Z}(i)}{\text{rad}(i)} \right\|^{2q} \right\}^{-1}, \quad (2.25)$$

which is consistent with the asymptotic limits of the former, *one-part* formula, where p and q are adjustable parameters. A form of the two-part weight function has recently been introduced using information about the accuracy of the Taylor expansions to modify the function [8, 9], which will be discussed later in this chapter as it has become the method of choice, and has been used towards the end of this work.

2.3 Sampling Important Regions of the PES

The interpolation formula Eq. (2.22) should converge to the exact result as the size of the data set increases. However, we cannot just calculate a series of *ab initio* data points to produce a reasonably continuous data set that can be accurately interpolated because of computational feasibility. If some number of data points, M , was required for a dense set (or grid) of data in one dimension, then a dense set in $3N-6$ dimensions would require M^{3N-6} data points. This is an impossibly large number of *ab initio* computations for $N > 3$. Also, one must be aware that as the number of atoms in a system is increased (worse if these have many electrons, or are so-called “heavy atoms”), the complexity of these calculations increases rapidly with this increased dimensionality. Hence, we would prefer to obtain an accurate surface by interpolation using as few *ab initio* points as possible, particularly in systems larger than triatomics.

The essential idea for solving this “dimensionality problem” is to produce a PES from data points that have been sampled only from the most dynamically important regions of the PES. If the region of configuration space where dynamics takes place is much smaller than the whole space, and data points are only placed there, then Eq. (2.22) might be accurate in the most dynamically important regions for a relatively small number of data points. To identify the “most dynamically important regions” and only place data there, an iterative scheme using classical trajectories has been developed [1].

2.3.1 Iterative Scheme

1. Choose a small set of data point geometries on intuitive, physical, grounds. For example, configurations that lie on the minimum energy path (MEP) for some reaction of interest. There are standard methods in *ab initio* quantum chemistry programs for finding such paths. The PES from Eq. (2.22) is now defined with this data set.
2. Evaluate classical trajectories to simulate the bimolecular collision using the interpolated PES with the current data set.
3. Molecular configurations are sampled from this batch of trajectories. The number of trajectories can be small, but large enough to represent the relative importance of different regions of configuration space for different reaction channels.
4. Choose a trajectory configuration from this sample to be a new data point. The choice is made using criteria described below. The basic idea is to choose configurations that are most likely to improve the accuracy of the interpolated PES.
5. Perform the necessary *ab initio* calculations and add this point to the data set.
6. Repeat this process from step (2) until the PES is “converged.”

2.3.2 Selection Criteria

In step (4), we have to choose which (of thousands) of molecular configurations will be a new data point.

To decide on regions that are important, it is profitable to observe which regions classical trajectories visit the most (based upon the current PES). A new point can be calculated and placed in this region. This is the basis for *h-weight sampling* devised by Ischtwan and Collins [1] in 1994. In this method, the sample of trajectory configurations from step (3) are weighted using the weight function

$$h[\mathbf{R}(j)] = \frac{1}{N_t - 1} \sum_{n=1, n \neq j}^{N_t} \left\{ \frac{v_i[\mathbf{R}(n)]}{\sum_{g \in G} \sum_{k=1}^{N_d} v_{g \circ k}[\mathbf{R}(j)]} \right\}, \quad (2.26)$$

which has a large value when the j^{th} point is near some of the N_t trajectory points and far from the current calculated data points. New data points are chosen with the largest values of h . This criterion is entirely geometric in nature.

An alternative, introduced by Thompson and Collins [5], is to interpret the interpolation formula as an average of Taylor expansions in some probability distribution $w(\mathbf{R})$. An estimate of the error in the potential, and in the derivatives, at some configuration, is made by analogy with statistical variance

$$\sigma_V^2[\mathbf{R}] = \sum_{i=1}^{N_d} w_i(\mathbf{R}) [T_i(\mathbf{R}) - V(\mathbf{R})]^2, \quad \text{and} \quad (2.27a)$$

$$\sigma_{\nabla V}^2[\mathbf{R}] = \sum_{i=1}^{N_d} w_i(\mathbf{R}) \sum_{k=1}^{3N-6} \left[\left. \frac{\partial T_i}{\partial R_k} \right|_{\mathbf{R}} - \left. \frac{\partial V}{\partial R_k} \right|_{\mathbf{R}} \right]^2. \quad (2.27b)$$

For example, the variance in the energy, from Eq. (2.27a), is evaluated for each configuration in the sample from step (3). A large value of the variance at some geometry implies that different Taylor series (with large weights) give very different values of the energy. The energy at such a configuration is highly uncertain. The average, from Eq. (2.22), is likely to be inaccurate. Therefore, under the *variance sampling* criterion, we choose the configuration of highest variance to be the new data point.

Early experience with this iterative procedure showed that, especially when the data set is small, the interpolated PES can display large “holes”; regions where the energy is unphysically low. This problem was overcome by adding an additional selection criterion. If a trajectory encounters a configuration where the interpolated energy is below the lowest value in the current data set, then the trajectory is terminated, and the lowest energy of all such configurations is added to the data set [2].

In this work, we have used the “low energy”, h -weight and energy variance criteria to choose new data points.

This completes an outline of the basic interpolation and iterative construction scheme which was developed by Ischtwan, Jordan, Thompson and Collins in a number of papers [1–7]. However, important improvements in the methodology were subsequently implemented by Bettens and Collins [8, 9], which we describe below.

2.3.3 Bayesian Analysis

An improvement to the interpolation formula uses a Bayesian approach [29] to estimate the accuracy of each Taylor series and modify the form of the weight function accordingly. This approach is in the spirit of the iterative *learning* algorithm used to construct the surface.

The fundamental concept is of a *Bayesian confidence volume*. First, a generalised expression of the two-part weight function in Eq. (2.25) was examined:

$$v_i(\mathbf{Z}) = \left\{ \left[\frac{\|\mathbf{Z} - \mathbf{Z}(i)\|}{\text{rad}(i)} \right]^{2q} + \left[\frac{\|\mathbf{Z} - \mathbf{Z}(i)\|}{\text{rad}(i)} \right]^{2p} \right\}^{-1} \quad (2.28)$$

where $q \ll p$ and $\text{rad}(i)$ is the *confidence radius*. For convenience and accuracy [7], $q = 2$ and $2p \gg 3N - 3$. If $\|\mathbf{Z} - \mathbf{Z}(i)\| < \text{rad}(i)$ then the first term dominates,

however, if $\|\mathbf{Z} - \mathbf{Z}(i)\| > \text{rad}(i)$ the second term is the dominant term. Thus, if the distance between the data point and the configuration where the interpolation is to be performed is larger than the confidence radius, the unnormalised weight vanishes rapidly as $\|\mathbf{Z} - \mathbf{Z}(i)\|$ increases. However, the unnormalised weight falls relatively slowly as $\|\mathbf{Z} - \mathbf{Z}(i)\|$ increases if $\mathbf{Z}$ is within the confidence radius of $\mathbf{Z}(i)$. An advantage of using these two terms is that the weights for two or more data points near $\mathbf{Z}$ vary only slowly with varying $\mathbf{Z}$, reducing the observed errors in the gradient of the PES.

If possible, $\text{rad}(i)$ should represent the distance $\|\mathbf{Z} - \mathbf{Z}(i)\|$ within which the Taylor polynomial $T_i(\mathbf{Z})$ is accurate within some small tolerance. The accuracy of the Taylor polynomial is determined by the magnitude of neglected higher-order terms in the series expansion, which in turn depends on the magnitude of the higher order derivatives.

By first considering the derivation of a hyperspherical confidence radius as used in Eq. (2.28), a generalised confidence volume will then be derived [8, 9].

For a data set of N_d data points, the error in each $T_i(\mathbf{R})$ is actually known at another $|G| \times (N_d - 1)$ points. Some of these errors are then used in a Bayesian analysis to yield the confidence radius at each data point.

Suppose that $P(X, Y | I)$ represents the probability that propositions X and Y are both true, given that proposition I is true. The product rule yields

$$P(X, Y | I) = P(Y | X, I)P(X | I), \text{ and} \quad (2.29)$$

$$P(X, Y | I) = P(X | Y, I)P(Y | I). \quad (2.30)$$

By substitution, *Bayes' Theorem* [29] can be derived:

$$P(X | Y, I) = \frac{P(Y | X, I)P(X | I)}{P(Y | I)}. \quad (2.31)$$

Bayes' Theorem can be used to estimate the optimum value of parameters in data analysis and is used here to estimate the average confidence radius of a truncated Taylor expansion. To begin with, a system of no more than four atoms will be assumed.

The error in a Taylor series truncated to second order may be written as

$$\begin{aligned}
 V(\mathbf{Z}) - T_i[\mathbf{Z}] = & \frac{1}{3!} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} \sum_{l=1}^{3N-6} [Z_j - Z_j(i)] \\
 & \times [Z_k - Z_k(i)] [Z_l - Z_l(i)] \frac{\partial^3 V}{\partial Z_j \partial Z_k \partial Z_l} \bigg|_{\mathbf{Z}(i)} \\
 & + \text{fourth and higher order terms.}
 \end{aligned} \tag{2.32}$$

Third and higher order derivatives are generally not known. However, consider the distribution of these errors over an ensemble of points $\{\mathbf{Z}\}$ which lie at some small distance, $\|\mathbf{Z} - \mathbf{Z}(i)\|$ from $\mathbf{Z}(i)$. Since a small distance is specified, fourth- and higher-order contributions to the error may be neglected. If this ensemble of points is randomly distributed, for a given value of the distance, the ensemble average error must vanish as the sign of each displacement, $Z_j - Z_j(i)$, is random. The average may therefore be stated as

$$\langle V(\mathbf{Z}) - T_i[\mathbf{Z}] \rangle = 0. \tag{2.33}$$

The distribution of errors must have a non-zero second moment. Thus,

$$\langle [V(\mathbf{Z}) - T_i[\mathbf{Z}]]^2 \rangle \propto \|\mathbf{Z} - \mathbf{Z}(i)\|^6 \tag{2.34}$$

A confidence radius, $\text{crad}(i)$ for the data point $\mathbf{Z}(i)$, can now be defined as the distance, $\|\mathbf{Z} - \mathbf{Z}(i)\|$ within which $\langle [V(\mathbf{Z}) - T_i[\mathbf{Z}]]^2 \rangle$ does not exceed some given tolerance, E_{tol}^2 . That is, $\text{crad}(i)$ is defined by

$$\langle [V(\mathbf{Z}) - T_i[\mathbf{Z}]]^2 \rangle \equiv E_{\text{tol}}^2 \left[\frac{\|\mathbf{Z} - \mathbf{Z}(i)\|}{\text{crad}(i)} \right]^6. \quad (2.35)$$

If Eqs (2.33) and (2.35) represent all the information available with regard to the distribution of errors in the truncated Taylor expansion in the vicinity of $\mathbf{Z}(i)$, the principle of maximum entropy implies that the probability distribution of those errors is given by the normal distribution with the variance of Eq. (2.35). Hence, given the confidence radius $\text{crad}(i)$:

$$P[V(\mathbf{Z}) - T_i(\mathbf{Z}) \mid \text{crad}(i)] = \frac{\text{crad}(i)^3}{\sqrt{2\pi} \|\mathbf{Z} - \mathbf{Z}(i)\|^3} \times \exp \left\{ -\frac{[V(\mathbf{Z}) - T_i(\mathbf{Z})]^2 \text{crad}(i)^6}{2E_{\text{tol}}^2 \|\mathbf{Z} - \mathbf{Z}(i)\|^6} \right\} \quad (2.36)$$

where $P[V(\mathbf{Z}) - T_i(\mathbf{Z})] dE$ is the probability that the error in the Taylor expansion at some point $\mathbf{Z}$ takes a value between $V(\mathbf{Z}) - T_i(\mathbf{Z})$ and $V(\mathbf{Z}) - T_i(\mathbf{Z}) + dE$. For a set of M points $\{\mathbf{Z}^{(k)}\}$ in the vicinity of $\mathbf{Z}(i)$, the total probability distribution for the set of corresponding errors in the Taylor expansion is the product of the individual probability distributions:

$$P[\{V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)})\} \mid \text{crad}(i)] = \prod_{k=1}^M P[V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)}) \mid \text{crad}(i)]. \quad (2.37)$$

In Eq. (2.37), the probability distribution of a set of M errors is described, given the proposition that the confidence radius takes the value $\text{crad}(i)$.

After application of Bayes' Theorem, Eq. (2.31),

$$P [\text{crad}(i) \mid \{V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)})\}] \propto P [\{V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)})\} \mid \text{crad}(i)] \quad (2.38)$$

$$\times P [\text{crad}(i)]. \quad (2.39)$$

The denominator of Eq. (2.31) has been neglected as it is a constant of proportionality which does not depend on the confidence radius, $\text{crad}(i)$. That is, the probability that the confidence radius associated with the data point $\mathbf{Z}(i)$ takes the actual value $\text{crad}(i)$, within some small range, is proportional to the total probability that the set of M errors take the values shown, given that the confidence radius is $\text{crad}(i)$ times the probability that the confidence radius is $\text{crad}(i)$.

In Bayesian analysis, $P [\text{crad}(i)]$ is known as a *prior* probability distribution function, because it does not depend on the observations, $\{V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)})\}$. Nothing is known, *a priori*, about the higher-order derivatives of the Taylor expansions, so any (positive) value of $\text{crad}(i)$ is as likely as any other. Therefore, a uniform probability distribution for $P [\text{crad}(i)]$ is assumed where $P [\text{crad}(i)]$ is assumed to be independent of $\text{crad}(i)$.

An actual value of $\text{crad}(i)$ can be estimated as that value for which $P [\text{crad}(i) \mid \{V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)})\}]$ is a maximum: the *maximum likelihood* value. Given the exponential form of the normal distribution in Eq. (2.36), it is more convenient to look at

$$\ln P [\text{crad}(i) \mid \{V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)})\}] = \sum_{k=1}^M 3 \ln \text{crad}(i) \quad (2.40)$$

$$- \frac{[V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z}^{(k)})]^2 \text{crad}(i)^6}{2E_{\text{tol}}^2 \|\mathbf{Z}^{(k)} - \mathbf{Z}(i)\|^6} + \text{terms independent of crad}(i). \quad (2.41)$$

Setting

$$\frac{\partial \ln P [\text{crad}(i) \mid \{V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z})^{(k)}\}]}{\partial \text{crad}(i)} = 0 \quad (2.42)$$

yields

$$\text{crad}(i)^{-6} = \frac{1}{M} \sum_{k=1}^M \frac{[V(\mathbf{Z}^{(k)}) - T_i(\mathbf{Z})^{(k)}]^2}{2E_{\text{tol}}^2 \|\mathbf{Z}^{(k)} - \mathbf{Z}(i)\|^6} \quad (2.43)$$

It is sensible that this stationary value of $\text{crad}(i)$ must be the most, rather than the least, probable value. The error in the Taylor expansion for the energy about data point $\mathbf{Z}(i)$ is known at each of the other $N_d - 1$ configurations in the data set. The nearest M neighbouring data points are then taken from the remaining $|G| \times (N_d - 1)$ independent points in the data set. The errors at these data points are all that is required to estimate a confidence radius. Since the set of $|G| \times (N_d - 1)$ points is totally symmetric with respect to the CNPI symmetry group, each permuted data point, $g \circ \mathbf{Z}(i)$, has the same confidence radius as $\mathbf{Z}(i)$.

To use the result of Eq. (2.43) in the unnormalised weight function of Eq. (2.28) requires the final assumption that $\text{crad}(i)$ is a suitable confidence radius to be used instead of $\text{rad}(i)$ so that Eq. (2.28) becomes

$$v_i(\mathbf{Z}) = \left\{ \left[\frac{\|\mathbf{Z} - \mathbf{Z}_i\|}{\text{crad}(i)} \right]^{2q} + \left[\frac{\|\mathbf{Z} - \mathbf{Z}_i\|}{\text{crad}(i)} \right]^{2p} \right\}^{-1} \quad (2.44)$$

As the number of data points in the data set increases during the PES construction algorithm, the confidence radius for every data point is re-evaluated. At each iteration, the addition of a new data point adds extra information which is used to refine the confidence radii of pre-existing data points.

So far, the weight function of Eq. (2.44) treats equivalently all locations, $\mathbf{Z}$, on the surface of a hypersphere of radius $\|\mathbf{Z} - \mathbf{Z}(i)\|$, centred on $\mathbf{Z}(i)$. The averaging over the variation of the error in $T_i(\mathbf{Z})$ with varying direction in the hyperspace, $\mathbf{Z} - \mathbf{Z}(i)$, was performed considering only the distance, $\|\mathbf{Z} - \mathbf{Z}(i)\|$, dependence of the error. Clearly, however, simple consideration of molecular vibrations shows that the gradient and curvature of a PES are strongly dependent on the direction of the displacement considered. The third derivatives will also generally vary substantially in magnitude. Thus, the error in the Taylor expansion can be expected to be dependent on the direction of $\mathbf{Z} - \mathbf{Z}(i)$.

In practice, a generalised confidence volume is used where at least partial account of the anisotropy in the error of the Taylor expansions is made. Consider the error in the gradient of the PES at $\mathbf{Z}$, associated with $T_i(\mathbf{Z})$:

$$\begin{aligned} \frac{\partial V(\mathbf{Z})}{\partial Z_n} - \frac{\partial T_i(\mathbf{Z})}{\partial Z_n} = & \frac{1}{2} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} [Z_j - Z_j(i)] [Z_k - Z_k(i)] \left. \frac{\partial^3 V}{\partial Z_j \partial Z_k \partial Z_n} \right|_{\mathbf{Z}(i)} \\ & + \text{third- and higher-order terms.} \end{aligned} \quad (2.45)$$

The error in the gradient with respect to Z_n will almost certainly vary in a systematic way since an ensemble average of terms like $[Z_j - Z_j(i)]^2$ cannot vanish. Instead, it is useful to consider a related quantity:

$$\begin{aligned} \delta V_n \equiv & \left[\frac{\partial V(\mathbf{Z})}{\partial Z_n} - \frac{\partial T_i(\mathbf{Z})}{\partial Z_n} \right] [Z_n - Z_n(i)] \\ = & \frac{1}{2} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} [Z_j - Z_j(i)] [Z_k - Z_k(i)] \\ & \times [Z_n - Z_n(i)] \left. \frac{\partial^3 V}{\partial Z_j \partial Z_k \partial Z_n} \right|_{\mathbf{Z}(i)} \\ & + \text{fourth- and higher-order terms.} \end{aligned} \quad (2.46)$$

The ensemble average of δV_n should vanish for points of given small $\|\mathbf{Z} - \mathbf{Z}(i)\|$ using the same reasoning applied to Eq. (2.32). However, the second moment, $\langle \delta V_n^2 \rangle$, will not vanish. The magnitudes of the second moments can be quantified by defining quantities by analogy with Eq. (2.35) using

$$\langle \delta V_n^2 \rangle \equiv E_{\text{tol}}^2 \left[\frac{\|\mathbf{Z} - \mathbf{Z}(i)\|}{d_n(i)} \right]^6. \quad (2.47)$$

It follows that each error, δV_n , has a different normal distribution over an ensemble of points near $\mathbf{Z}(i)$ characterised by the variances, $\langle \delta V_n^2 \rangle$. As shown in Eq. (2.46), the third derivatives which determine δV_n all involve derivatives with respect to Z_n . If such third derivatives are larger in magnitude in some directions than in others, the quantity in Eq. (2.47) will be larger in these directions and the corresponding confidence lengths, $d_n(i)$, will be smaller in those directions than in others.

By analogy with the specific case in Eq. (2.43),

$$d_n(i)^{-6} = \frac{1}{M} \sum_{k=1}^M \frac{\left\{ \left[\frac{\partial V(\mathbf{Z}^{(k)})}{\partial Z_n} - \frac{\partial T_i(\mathbf{Z}^{(k)})}{\partial Z_n} \right] [Z_n^{(k)} - Z_n(i)] \right\}^2}{E_{\text{tol}}^2 \|\mathbf{Z}^{(k)} - \mathbf{Z}(i)\|^6} \quad (2.48)$$

where the nearest M data points are used, as before. Again, each confidence length $d_n(i)$ has the same value as that associated with the internuclear distance $g \circ n$ at the data point $g \circ \mathbf{Z}(i)$. Thus, the confidence lengths are only calculated at one symmetry version of each data point. In subsequent chapters, the number of neighbouring data points, M , is given the more descriptive symbol, n_{neigh} .

The confidence lengths, $\{d_n(i), n = 1, \dots, N(N-1)/2\}$, are then used to define a confidence volume. Thus, the unnormalised weight function of Eq. (2.44) is generalised to

$$v_i(\mathbf{Z}) = \left\{ \left[\sum_{k=1}^{N(N-1)/2} \left(\frac{Z_k - Z_k(i)}{d_k(i)} \right)^2 \right]^q + \left[\sum_{k=1}^{N(N-1)/2} \left(\frac{Z_k - Z_k(i)}{d_k(i)} \right)^2 \right]^p \right\}^{-1} \quad (2.49)$$

where the first term dominates if the components $Z_k - Z_k(i)$ lie within their respective confidence lengths. Specifically, if $\sum_{k=1}^{N(N-1)/2} \left(\frac{Z_k - Z_k(i)}{d_k(i)} \right)^2 < 1$, then $\mathbf{Z}$ is regarded as lying within the confidence volume of $\mathbf{Z}(i)$.

The M data points closest to some $\mathbf{Z}(i)$ may not provide a distribution of coordinate variations, $Z_k - Z_k(i)$, in every direction that satisfies the assumptions made in the derivations above. In particular, if all $M [Z_k - Z_k(i)]$ are small, Eq. (2.48) assumes the character of an extrapolation for $d_k(i)$, resulting in a large overestimate of the magnitude of $d_k(i)$. This problem is particularly prominent for data points in asymptotic regions of the surfaces which were included in the initial data set, where abnormally large estimates of some $d_k(i)$ are obtained. If $\text{crad}(i)$ or some $d_k(i)$ is substantially underestimated, then the data point $\mathbf{Z}(i)$ will rarely have significant weight in the PES of Eq. (2.49). This “waste” of data point $\mathbf{Z}(i)$ is inefficient, but produces no excessive error in the PES. In contrast, if $\text{crad}(i)$ or some $d_k(i)$ is substantially overestimated, then this data point will be allocated a substantial weight in Eq. (2.49), even when the Taylor expansion about $\mathbf{Z}(i)$ is inaccurate. Hence, no $d_k(i)$ is allowed to exceed 2.5 times the median for the data set of all $d_k(i)$. The factor of 2.5 was determined empirically.

Finally, the problem of redundant coordinates arises for molecules of more than four atoms. However, we can still write

$$V(\mathbf{Z}) - T_i(\mathbf{Z}) = \frac{1}{3!} \sum_{j=1}^{N(N-1)/2} \sum_{k=1}^{N(N-1)/2} \sum_{n=1}^{N(N-1)/2} C_{jkn}(i) \quad (2.50)$$

$$\times [Z_j - Z_j(i)] [Z_k - Z_k(i)] [Z_n - Z_n(i)]. \quad (2.51)$$

Here the $C_{jkn}(i)$ cannot be interpreted as third order partial derivatives, since the $\{Z_n\}$ are not all independent variables. Nevertheless, the $[Z_n - Z_n(i)]$ can be regarded as random variables, with the caveats discussed above, and the derivation of Eq. (2.50) holds for than four atoms. The weight function of Eq. (2.50) can then also be employed for the case of more than four atoms.

2.3.4 Planar and Linear Geometries

In Sec. 2.2.1, we baldly stated that a set of internal coordinates, $\{\rho_k\}$, could be written as in Eq. (2.20) for use in the Taylor expansion of Eq. (2.21). The latter equation contains derivatives of the PES with respect to these internal coordinates. The definition of the internal coordinates, and the transformation of the *ab initio* Cartesian derivatives of the PES into derivatives with respect to internals, is achieved with the aid of a singular value decomposition of the Wilson B-matrix (as discussed below) [7]. However, this coordinate transformation is not valid if the molecular geometry for a data point is flat (all the atoms lie in a plane) or linear. The Wilson B-matrix is singular for planar geometries, and cannot be inverted to achieve the necessary transformations. This coordinate problem is removed by distorting any “flat” molecular geometry to a nonplanar one before accepting it as a new data point.

How the geometry is distorted is determined using a *singular value decomposition* (SVD) [30] to determine which of the Cartesian coordinates require incremen-

tal changes. This is an iterative procedure which stops when the coordinates are deemed unlikely to cause the B-matrix to be singular and therefore ensure that it is invertible. The B-matrix, with elements defined by $B_{ij} = \frac{\partial R_i}{\partial X_j}$, is a $3N - 6 \times 3N$ matrix. It represents a means of associating changes in $3N - 6$ internal coordinates (which are linear combinations of reciprocal internuclear distances) with changes in the Cartesian coordinates $\mathbf{X}$ of the system as shown by (the changes are represented by column vectors)

$$\delta \mathbf{R} = \mathbf{B} \delta \mathbf{X}. \quad (2.52)$$

The B-matrix can be augmented with rows of zeroes so that it is a square matrix. The justification for this is that six ways of changing the Cartesian coordinates will correspond to rotations or translations of the entire system and do not correspond to changes in any internal degrees of freedom. Call the new matrix $\mathbf{B}'$. A published SVD algorithm [31] will yield the right hand matrices in $\mathbf{B} = \mathbf{U} \mathbf{W} \mathbf{V}^T$ where $\mathbf{U}$ and $\mathbf{V}^T$ are orthogonal matrices and $\mathbf{W}$ is a diagonal matrix. When the B-matrix is padded with zeroes, $\mathbf{U}$ and $\mathbf{W}$ are also padded as a consequence by the SVD, this padding being denoted by primes as follows:

$$\mathbf{B}' = \mathbf{U}' \mathbf{W}' \mathbf{V}'^T. \quad (2.53)$$

Each matrix is then square, and it is then possible to denote an inverse of $\mathbf{B}'$, which is the main aim, since a method is then available which facilitates the reverse transformation from internal coordinates to Cartesian coordinates as

$$\delta \mathbf{X} = \mathbf{B}'^{-1} \delta \mathbf{R} \quad (2.54)$$

$$= \mathbf{V} \mathbf{W}'^{-1} \mathbf{U}'^T \delta \mathbf{R}. \quad (2.55)$$

It makes more sense to think of $\mathbf{U}$ and $\mathbf{V}$ as unitary transformations (which they are) into different spaces which are connected by another transformation $\mathbf{W}$ as follows

$$\begin{array}{ccc} \mathbf{R} & \xrightarrow{\mathbf{B}} & \mathbf{X} \\ \mathbf{U} \downarrow & & \downarrow \mathbf{V} \\ \mathbf{\mathcal{R}} & \xrightarrow{\mathbf{W}} & \mathbf{\mathcal{X}} \end{array}$$

The diagonal elements of $\mathbf{W}$ are known as *singular values*. If the ratio of the largest to smallest non-zero singular values is large, then $\mathbf{B}'$ is near enough to be singular to be non-invertible numerically. Thus, the Cartesian coordinate corresponding to the smallest non-zero singular value is changed to distort the molecule and raise the value of that singular value. What this means is that the internal coordinate least sensitive to changes in the Cartesian coordinates is the one that is chosen to be changed. This, in effect, minimises the distortion that needs to be applied to the molecule to ensure that $\mathbf{B}'$ is invertible. This is actually an iterative process, which stops when the ratio previously described is not unacceptably large. The actual direction to change a coordinate is determined using derivatives, but this introduces detail not warranted in a brief discussion.

There is a further complication in the general, unconstrained case: “interfragment” and “intrafragment” internuclear distances need to be considered separately because they can otherwise cause severe distortions in each other. This is performed for each type (as determined by a cutoff distance criterion) of internuclear coordinate simply by subtracting away the relevant elements of $\mathbf{B}$ so that they are zero, leading to zero singular values corresponding to a type of internuclear coordinate so that those coordinates are not chosen for distortion.

Of course, the constrained internuclear distances may change in this procedure. This complicates matters very little, since these distances may be reset to their

starting values, and the distortion process restarted if the “reverse-distortion” leads back to an unsatisfactory geometry.

A relevant question might be: Why do everything in internuclear distances? The answer lies in the fact that our interpolation scheme relies on internal coordinates, yet it needs to retain its “black-box” appeal, that is, to remain system non-specific.

2.4 Constrained Dynamics

As the number of atoms, N , in a molecule increases, the number of internal degrees of freedom increases as $3N - 6$. The total volume of the internal configuration space could therefore increase exponentially as l^{3N-6} , for some length, l . As we have pointed out earlier, simple interpolation of the PES over a uniform grid of data points in this volume is not feasible. Thus far, the iterative PES construction procedure has attempted to minimise the number of necessary *ab initio* data points in two ways: By placing data only in the dynamically significant regions, and by choosing new data points that are most likely to improve the accuracy of the PES.

It is important to realise that the “dynamically significant region” will not increase in volume as l^{3N-6} . To see this, suppose that the reaction of interest has reactants with n_1 and n_2 atoms ($n_1 + n_2 = N$). The total number of internal degrees of freedom in the reactants is $3n_1 - 6 + 3n_2 - 6 = 3N - 12$. The number of internal degrees of freedom of the whole molecule is $3N - 12 + 6$. The latter six describe the relative separation and orientation of the two reactants. These six coordinates have large ranges of values in a bimolecular collision. The $3N - 12$ intra-reactant coordinates may only have small ranges of values. We could make the same argument about the product molecules with n_3 and n_4 atoms ($n_3 + n_4 = N$).

So, in large regions of the configuration space, the dynamically significant region must have a volume that is proportional to $l^6 d^{3N-12}$, where $d \ll L$. The idea is that in many reactive or inelastic bimolecular collisions involving large molecules, many degrees of freedom are effectively *spectator modes*; modes that undergo only very small amplitude motion throughout the collision. We might hope that the number of data points needed to interpolate the PES is then proportional to a number like $m^6 k^{3N-12}$, where $k \ll m$.

If the motion in all $3N - 12$ *spectator* degrees of freedom is small enough, then the variation of the PES in these directions might be described by a single Taylor expansion. If this were true, the number of data points needed to interpolate the PES might be proportional to $m^6 \cdot 1^{3N-12} = m^6$. That is, the number of data points would be independent of the size of the molecule, and the problem of dimensionality disappears.

Of course, the situation is complicated by the fact that the six large amplitude degrees of freedom are not the same degrees of freedom in the reactant and product regions. In the *interaction region* where bonds are broken and formed, more than six coordinates may be greatly perturbed. Moreover, for very large molecules, spectator torsion modes may involve relatively large amplitude motions. However, the principle remains that the number of data points required by the Shepard interpolation may increase relatively slowly with N .

In this thesis, we examine the possibility that we can reduce the number of data points in some dimensions to just one, by constraining or fixing the value of those coordinates. For example, suppose a molecule contains a methyl group which is not directly involved in a reaction. Then why not “freeze” the methyl group, so that no internal motion of the CH_3 structure occurs during the classical simulations used to sample the molecular configuration space. The resulting interpolation data set will then effectively have only one data point distributed in those “frozen” degrees of freedom.

Will the resultant PES be sufficiently accurate? That remains to be seen. However, this approach ought, in principle, to make it feasible to construct a PES by Shepard interpolation in high dimensions. The Taylor expansions are still valid in $3N-6$ dimensions, so the interpolated PES is well defined in the full dimensional space. The question is only whether the PES is sufficiently accurate to describe the chemistry.

In order to implement this idea in the PES construction process, we will need to deal with some practical aspects of constrained classical dynamics. In the following (final) sections of this theory chapter, we will describe the way constraints on the atom-atom distances are programmed into the procedure.

2.4.1 Revision of Unconstrained Dynamics

The classical, Newtonian equation of motion for the force $\mathbf{F}_i$ on an atom i is:

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i, \quad (2.56)$$

with mass m_i and acceleration $\ddot{\mathbf{r}}_i$ which is the second time derivative of the position vector $\mathbf{r}_i$.

The force $\mathbf{F}_i$ due to intermolecular interactions is given by the gradient of the potential V :

$$\mathbf{F}_i = -\nabla V, \quad (2.57)$$

and is a *gradient vector field*.

2.4.2 Application of Distance Constraints

For two atoms i and j , we define

$$\sigma_{ij}(\{\mathbf{r}(t)\}) \equiv \|\mathbf{r}_i(t) - \mathbf{r}_j(t)\|^2 - d_{ij}^2 \quad (2.58)$$

where d_{ij} is the distance to be fixed between the two atoms, by imposing the pairwise distance constraint

$$\sigma_{ij}(\{\mathbf{r}(t)\}) = 0. \quad (2.59)$$

The time derivatives of the constraint equations given by Eq. (2.58) give constraints on the velocities, i. e.,

$$[\dot{\mathbf{r}}_i(t) - \dot{\mathbf{r}}_j(t)] \cdot [\mathbf{r}_i(t) - \mathbf{r}_j(t)] = 0. \quad (2.60)$$

The equation of motion for atom i , implements these constraints via a constraint force $\mathbf{G}_i$:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i + \mathbf{G}_i. \quad (2.61)$$

Using Eq. (2.57), the constraint force $\mathbf{G}_i$ is written in terms of time-dependent, unknown, Lagrange multipliers $\lambda_{ij}(t)$ associated with intramolecular forces of the constraints, where a summation over all particles j to which i is constrained (denoted by a prime):

$$\mathbf{G}_i = - \sum_j' \lambda_{ij}(t) \nabla_i \sigma_{ij}. \quad (2.62)$$

2.5 Numerical Methods for Constrained Dynamics

There are several approaches involving particular choices of coordinates [32–34]. We will avoid these approaches because we wish to use Cartesian coordinates to describe the relative positions of our particles. Ideally, the method should also conform to our preferred integrator for the classical equations of motion, velocity-Verlet, which has been tested thoroughly in our interpolation scheme.

Analytical methods Analytical techniques include direct matrix methods to solve for the Lagrange multipliers [35, 36]. These techniques are prone to numerical drift, since the Lagrange multipliers are in fact time-dependent and are only updated at the end of a trajectory time-step (aside from other usual causes of drift). Methods have been designed to circumvent this with a drift correction [37, 38], but it may be more desirable to avoid this entirely, if possible. Another unappealing aspect of such methods is that they must deal with the quadratic character of the constraints, whereas iterative methods are able to make linear approximations, as will be discussed. There has been work on reducing some of the constraints to be linear, by means of constraining coordinates of “secondary” atoms to a “primary” structure (carefully chosen from the system of atoms) [36–38]. The problem remains that there are still *some* quadratic constraints, in particular those associated with the primary structure.

Iterative methods These iterative methods include SHAKE, RATTLE, and others. These share the common theme of solving the equations of motion using a numerical integrator, moving the particles, and then using some iterative system of adjustment to restore the constrained variables to within a specified tolerance. The name of the algorithm in general refers to the integrator

chosen, for example SHAKE incorporates the Verlet algorithm, and RATTLE, although based on a similar concept, uses velocity-Verlet, and as such is self-starting and shares other advantages with SHAKE. The manner in which these methods are presented follows loosely the pattern followed by H.C. Andersen when he published details of RATTLE for the first time in 1983 [39].

2.5.1 RATTLE

For the *Verlet* algorithm, first consider (in mass-scaled coordinates)

$$\ddot{r}(t) = f(r). \quad (2.63)$$

To integrate this equation of motion forward for one time step, h , we write

$$r(t+h) = 2r(t) - r(t-h) + h^2 f(r(t)). \quad (2.64)$$

This is correct except for a local error of order h^4 .

We can start the integrator if we know $r(0)$ and $r(-h)$. The velocities need to be evaluated using (some elementary finite difference calculus):

$$\dot{r}(t) = \frac{[r(t+h) - r(t-h)]}{2h} \quad (2.65)$$

which has an error of order h^2 . Clearly, the velocity can only be calculated after r at time $t+h$ has been obtained. The algorithm is therefore not self-starting.

In the *velocity-Verlet* algorithm, on the other hand, positions at time t are advanced using velocities at time t also, hence

$$r(t+h) = r(t) + h\dot{r}(t) + \frac{h^2}{2}f(r(t)), \text{ and} \quad (2.66)$$

$$\dot{r}(t+h) = \dot{r}(t) + \frac{h}{2}[f(r(t)) + f(r(t+h))]. \quad (2.67)$$

Local error in each of these expressions is of order h^3 . The global error (after sufficient time) is h^2 .

Suppose there are constraints. Then Eq.(2.63) becomes

$$\ddot{r}(t) = f(r(t)) + g(r(t), \dot{r}(t)). \quad (2.68)$$

To solve this using the Verlet algorithm,

$$r(t+h) = 2r(t) - r(t-h) + h^2[f(r(t)) + g(r(t), \dot{r}(t))]. \quad (2.69)$$

Even if the exact g were known and used, the constraints will be eventually violated since the algorithm itself is not exact. Therefore we can approximate g , only requiring $r(t+h)$ such that $r(t+h)$ satisfies the constraints within a desired accuracy. Such an approximation makes errors of the same order as the local order of the Verlet algorithm. This approximation forms the basis for SHAKE. What we need now, is a proper choice of time-dependent Lagrange multipliers in expressing the constraint forces. This will be dealt with in discussing RATTLE.

We cannot have a velocity version of SHAKE because such a formulation as in Eq.(2.69) would lead to the following expressions:

$$r(t+h) = r(t) + h\dot{r}(t) + \frac{h^2}{2} [f(r(t)) + g(r(t), \dot{r}(t))], \text{ and} \quad (2.70)$$

$$\dot{r}(t+h) = \dot{r}(t) + \frac{h}{2} [f(r(t)) + f(r(t+h)) + g(r(t), \dot{r}(t)) + g(r(t+h), \dot{r}(t+h))]. \quad (2.71)$$

In the first equation we need to know $\dot{r}(t)$ in order to calculate $g(t)$. In the second equation we need $g(t+h)$ so that we can calculate $\dot{r}(t+h)$. This clearly inconsistent with a simple iterative scheme.

The basis for RATTLE is that we do not need to approximate g in the velocity equation with the same approximation for g in the position equation. In fact, it is sufficient that the g which appears only in the velocity equation (as a function of $t+h$) satisfies the *time derivatives* of the constraints within a specified tolerance. Hence two approximations are made.

The following definitions (and notation) are made by Andersen:

$$g_{ij} = h\lambda_{RRij}(t), \quad (2.72)$$

$$k_{ij} = h\lambda_{RVij}(t+h), \text{ and} \quad (2.73)$$

$$\mathbf{q}_i = \dot{\mathbf{r}}_i(t) + \left(\frac{h}{2m_i}\right) \mathbf{F}_i(t) - \left(\frac{1}{m_i}\right) \sum_j g_{ij} \mathbf{r}_{ij}(t). \quad (2.74)$$

where: $\lambda_{RRij}(t)$ is the value of the Lagrange multiplier (see Eq. (2.62)) which appears in the velocity-Verlet equation for the *coordinates* at $t+h$; and $\lambda_{RVij}(t)$ is the value of the Lagrange multiplier which appears in the velocity-Verlet equation for the velocity at time $t+h$. The $\lambda_{RRij}(t)$ are determined by the condition that the bondlengths are constrained. The λ_{RVij} are determined by the condition that the constrained bondlengths have zero time-derivative.

We can then write:

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{q}_i, \text{ and} \quad (2.75)$$

$$\dot{\mathbf{r}}(t+h) = \mathbf{q}_i + \frac{h}{2m_i}\mathbf{F}_i(t+h) - \frac{1}{m_i} \sum_j' k_{ij}\mathbf{r}_{ij}(t+h). \quad (2.76)$$

A good starting point is to solve for $\mathbf{q}_i$ by iteration. We begin the iterative loop with

$$\mathbf{q}_i(t) = \dot{\mathbf{r}}(t) + \left(\frac{h}{2m_i}\right)\mathbf{F}_i(t), \quad i = 1, \dots, N. \quad (2.77)$$

The position equation is then as it would be for an unconstrained system. Next, one of the constraints is chosen, say between particle i and particle j . Then the current approximation, at some stage of the iteration, of the vector displacement of the two particles is

$$\mathbf{s} = \mathbf{r}_i(t+h) - \mathbf{r}_j(t+h) \quad (2.78)$$

$$= \mathbf{r}_i(t) + h\mathbf{q}_i(t) - \mathbf{r}_j(t) - h\mathbf{q}_j(t). \quad (2.79)$$

If $|\mathbf{s}|^2 - d_{ij}^2$ is zero, or at least is less than the specified tolerance, a new constraint is chosen and we return to the beginning of the iterative loop. Otherwise, $\mathbf{q}_i$ and $\mathbf{q}_j$ need to be corrected to satisfy this condition. The positions at $t+h$ are then corrected by adding terms proportional to g on to $\mathbf{q}_i$ and $\mathbf{q}_j$:

$$\mathbf{r}_i^C = \mathbf{r}_i(t) + h \left[\mathbf{q}_i - \frac{g\mathbf{r}_{ij}(t)}{m_i} \right], \text{ and} \quad (2.80)$$

$$\mathbf{r}_j^C = \mathbf{r}_j(t) + h \left[\mathbf{q}_j + \frac{g\mathbf{r}_{ij}(t)}{m_j} \right]. \quad (2.81)$$

After corrections proportional to g are made using Eqs. (2.80) and (2.81) we obtain new positions at time $t + h$: $\mathbf{r}_i(t + h) = \mathbf{r}_i^C$, and; $\mathbf{r}_j(t + h) = \mathbf{r}_j^C$.

The criterion is the same as before if we use the vector displacement between the positions of the particles, this time after they have been corrected: $|\mathbf{r}_i^C - \mathbf{r}_j^C|^2 = d_{ij}^2$. Substitution and consequent rearrangement in terms of g yields (ignoring quantities of order g^2):

$$g = \frac{s^2 - d_{ij}^2}{2h [\mathbf{s} \cdot \mathbf{r}_{ij}(t)] (1/m_i + 1/m_j)}. \quad (2.82)$$

Then q_i and q_j are replaced by these corrected values, we return to the beginning of the iterative loop, and choose a new constraint. The iterative loop is forced to continue unless all of the constraints are satisfied to within the desired tolerance. For the next part, the positions $\mathbf{r}_i(t + h)$ and $\mathbf{q}_i$ (which are velocities) are stored as positions and velocities at time t . Now we want to solve for $\dot{\mathbf{r}}_i(t + h)$ by iteration, starting with

$$\dot{\mathbf{r}}_i(t + h) = \mathbf{q}_i + \left(\frac{h}{2m_i} \right) \mathbf{F}_i(t + h), \quad i = 1, \dots, N. \quad (2.83)$$

Again choose any constraint. Compare the dot product of $\mathbf{r}_{ij}(t+h)$ and $\dot{\mathbf{r}}_{ij}(t+h)$ to zero (so that they are perpendicular, and the only velocities allowed cannot alter the interatomic distance of the constraint). If the agreement is within a sensible tolerance, then we return to the beginning of the iterative loop to choose another constraint. Otherwise the velocities $\dot{\mathbf{r}}_i$ and $\dot{\mathbf{r}}_j$ need to be corrected. Using a similar idea (and arguments) as before:

$$\dot{\mathbf{r}}_i^C = \dot{\mathbf{r}}_i(t + h) - \left(\frac{k}{m_i} \right) \mathbf{r}_{ij}(t + h), \text{ and} \quad (2.84a)$$

$$\dot{\mathbf{r}}_j^C = \dot{\mathbf{r}}_j(t + h) + \left(\frac{k}{m_j} \right) \mathbf{r}_{ij}(t + h). \quad (2.84b)$$

These are newly corrected velocities at time $t+h$, with corrections proportional to some constant k . To satisfy the condition that the displacement vector and the vector difference of the velocities of particles i and j are perpendicular, i. e., that their dot product is zero, then choose

$$k = \mathbf{r}_{ij}(t+h) \cdot \frac{[\dot{\mathbf{r}}_i(t+h) - \dot{\mathbf{r}}_j(t+h)]}{d_{ij}^2 (1/m_i + 1/m_j)}. \quad (2.85)$$

Then, the velocities at $t+h$ are replaced by their corrected values from Eq. (2.84a), we return to the beginning of the iterative loop, choose another constraint until we have looped over all constraints, and iterate until all the constraints are satisfied within the desired tolerance. Clearly RATTLE is an algorithm that is carried out in two steps, with two independent successive iterative loops, the first for positions, and the second for the velocities.

This completes our description of the technical background which is applied in this work. In the following chapters we examine several applications of the theory and answer the following questions: Is a PES constructed using constraints sufficiently accurate, and does such a PES converge faster than a PES constructed without constraints?

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Part II

Rotational Inelastic Scattering

Chapter 3

Growing a PES for a Constrained System: $\text{N}_2 + \text{N}_2$

3.1 Introduction

This chapter considers the classical rotationally inelastic scattering of two nitrogen molecules as the first test case for the validity of constructing PES using constrained trajectories. We have chosen to study this system for a number of reasons.

Firstly, the relatively large mass of this system, where no hydrogen atoms are present, implies that classical mechanics should provide a qualitative, and reasonably quantitative, picture of the actual dynamics. It is reasonable, therefore, to restrict our attention to the classical dynamics. Secondly, the $\text{N}_2 + \text{N}_2$ system has been extensively studied both experimentally [1–4] and theoretically [5–14]. The rotational inelastic scattering of N_2 molecules determines the lineshapes of the transitions observed in coherent anti-Stokes Raman spectroscopy (CARS) of gas phase N_2 [2]. The Q-branch of N_2 is spectroscopically convenient, and since N_2 is the most abundant gaseous component in air, CARS studies of N_2 have provided a convenient probe in temporally and spatially inhomogeneous environments such

as flames. Modelling lineshapes in the CARS spectra requires a knowledge of the rotational inelastic scattering cross-sections. The experimental importance of this system has led to the development of an analytic functional form for the $N_2 + N_2$ PES, the third reason why this system is a convenient test case here.

The analytic PES used herein is that developed by van der Avoird, Wormer and Jansen, referred to hereafter as the vdAWJ PES [5]. The PES has been used successfully in classical calculations of transport properties by Heck and Dickinson [6]. This surface was constructed for rigid N_2 molecules, so we can directly compare the classical dynamics on the vdAWJ PES with the corresponding dynamics on a constrained interpolated approximation to it. In this chapter we show that the dynamics on a constrained interpolated PES converge to the correct results as the size of the data set increases.

The chapter begins with a description of the analytic PES to present a qualitative idea of the nature of this type of diatom-diatom surface. Some relevant details of the scattering calculations are contained in a section that deals with scattering on the analytic surface. The construction of the constrained interpolated PES is described and scattering cross-sections are presented and compared with exact (i.e. direct use of the functional form) results. A brief statement of conclusions completes the chapter.

3.2 An Analytic Test Potential

A good test of the surface-growing method is to use it to try and reproduce a realistic test PES. A recent (1986) and demonstrably accurate [6–10, 10] functional form for rigid body bimolecular collisions in nitrogen, is the PES of van der Avoird, Wormer and Jansen [5] (vdAWJ). The vdAWJ PES is a modification of a surface published earlier (1980) by Berns and van der Avoird [11] (BvdA), which was

based upon *ab initio* calculations [15]. These modifications included fitting the entire surface to second virial coefficients and solid state properties.

Both surfaces are reviewed by Brocks and van der Avoird in Ref. 10. An interesting difference is that the surfaces have different absolute minima. The minimum of the BvdA PES is a crossed (D_{2d}) structure, whereas the equilibrium structure of the vdAWJ PES is predicted to be a configuration where the two monomers have parallel internuclear axes yet slightly off-centred. The review explains that this system is the epitome of van der Waals systems, in that it is difficult to determine potential energy surfaces which are accurate enough to extract equilibrium structures and barriers to internal rotation, by *ab initio* calculations alone. This, by itself, presents an interesting challenge for our method, given that the authors also point out that dynamical calculations and comparisons to rovibrational spectra of van der Waals molecules are the best way to discriminate between different surfaces. This last point is central to our interpolation scheme, where dynamical calculations are included in the convergence testing step as the PES is iteratively improved.

A graph of the vdAWJ potential for different sets of coordinates required to prescribe the orientation of the monomers is presented as a function of the distance between the centres of mass of each of the monomers in Fig. 3.1.

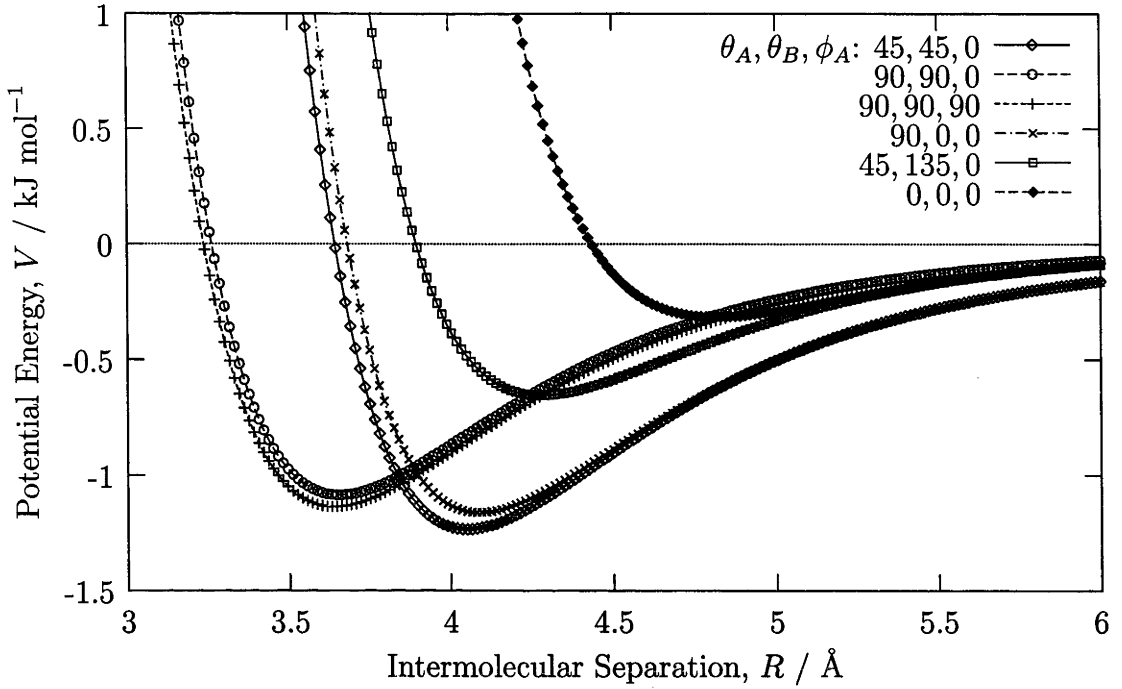


Figure 3.1: The potential energy of different orientations (see Fig. 3.2) of the monomers in the nitrogen dimer as a function of the distance R between the centres of masses of the two monomers. Markers show interpolated energies for selected geometries on the final interpolated PES. Lines are generated for the vdAWJ PES.

3.2.1 Functional Forms by Expansion in Terms of Scalar Functions

Stone [16] has shown that the energy of interaction between molecules of arbitrary shape can be expanded in terms of scalar functions which depend on the orientations of the molecules:

$$S_{l_1, l_2, j}^{k_1, k_2} = i^{l_1 - l_2 - j} \sum_{m_1, m_2, m} \mathcal{D}_{m_1 k_1}^{l_1}(\Omega_1)^* \mathcal{D}_{m_2 k_2}^{l_2}(\Omega_2)^* \mathcal{D}_{m 0}^j(\Omega_{12})^* \begin{pmatrix} l_1 & l_2 & j \\ m_1 & m_2 & m \end{pmatrix}, \quad (3.1)$$

which the author refers to as “ S functions”, where the $\mathcal{D}$ functions are Wigner rotation matrices, which are functions of the orientations in solid angles Ω in space-fixed axis systems for molecules 1 (Ω_1) and 2 (Ω_2), and of the direction (Ω_{12}) of the vector from the origin of molecule 1 to the origin of molecule 2.

The phase factor $i^{l_1-l_2-j}$ has the effect of making the definition symmetrical with respect to exchange of labelling of the two molecules, and is also always real for $k_1 = k_2 = 0$. The term in parentheses is a Wigner $3j$ symbol which is a more symmetric way of expressing the Clebsch-Gordan coefficients [17] using the following definition:

$$\begin{pmatrix} l_1 & l_2 & j \\ m_1 & m_2 & m \end{pmatrix} \equiv (-1)^{l_1-l_2-m_3} (2j+1)^{-\frac{1}{2}} \langle l_1 m_1, l_2 m_2 | j - m \rangle, \text{ and} \quad (3.2)$$

$$\langle l_1 m_1, l_2 m_2 | j m \rangle \equiv (-1)^{l_1-l_2+m} (2j+1)^{\frac{1}{2}} \begin{pmatrix} l_1 & l_2 & j \\ m_1 & m_2 & m \end{pmatrix}. \quad (3.3)$$

Clebsch-Gordan coefficients are elements of the unitary transformation from the uncoupled representation of the angular momenta $|l_1 m_1, l_2 m_2\rangle$ to the coupled representation $|j m\rangle$ and vice versa. An excellent treatment of angular momentum is provided by Zare [17].

For linear molecules, the rotation operators are just spherical harmonics Y_{l_1, m_1} , Y_{l_2, m_2} and $Y_{j, m}$, because each molecule can be described by a vector in spherical polar coordinates. Also, the only S functions which will arise are those with $k_1 = k_2 = 0$. A slight notation change in labelling the quantum numbers is used in the following treatment to be consistent with that used by Berns and van der Avoird [11], although the former notation is more common. Thus, when expanding the intermolecular potential at sufficiently long range, one can write

$$V(\mathbf{R}, \hat{r}_A, \hat{r}_B) = (4\pi)^{3/2} \sum_{L_A, L_B, L} v^{L_A, L_B, L}(R) A_{L_A, L_B, L}(\hat{R}, \hat{r}_A, \hat{r}_B), \quad (3.4)$$

where the S functions have been replaced by a complete orthogonal set of angular functions, $A_{L_A, L_B, L}$. The internuclear axis of each molecule defines a vector so that the unit vectors $\hat{r}_A = (\theta_A, \phi_A)$ and $\hat{r}_B = (\theta_B, \phi_B)$ describe their orientations; the vector $\mathbf{R} = (R, \hat{R}) = (R, \Theta, \Phi)$ points from the centre of mass of molecule A to the centre of mass of molecule B. The coordinates are illustrated in Fig. 3.2 below.

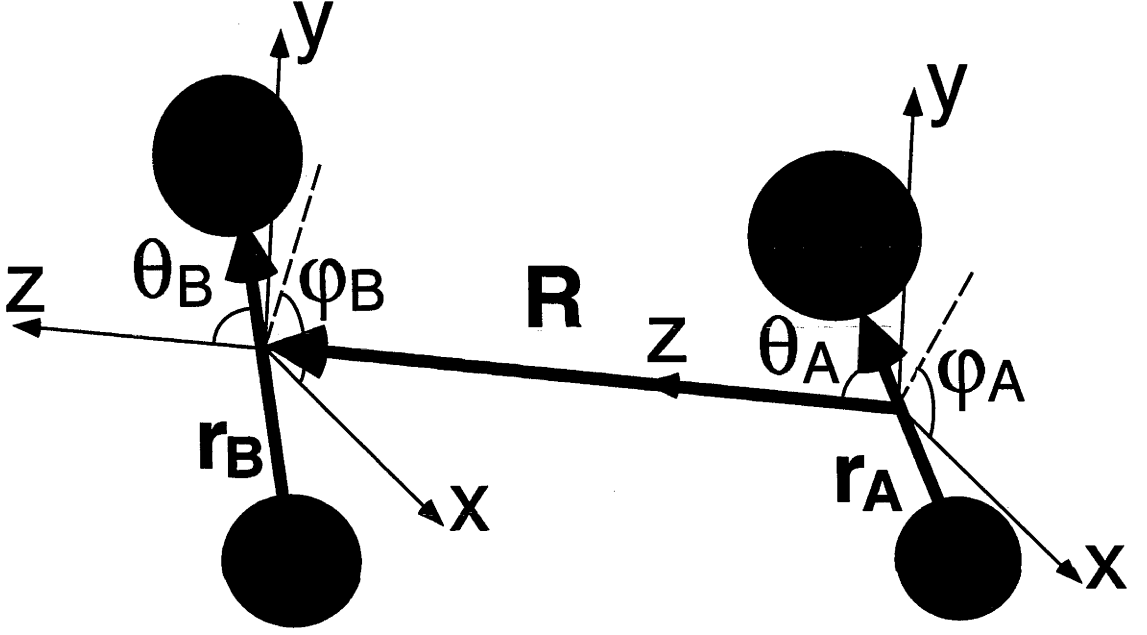


Figure 3.2: A schematic representation of the internal coordinates used in Eq. (3.4).

Eq. (3.4) and Fig. 3.2 employ the notation of Berns and van der Avoird rather than that of Stone, as in Eq. (3.1). The angular functions in Eq. (3.4) are given by

$$A_{L_A, L_B, L}(\hat{R}, \hat{r}_A, \hat{r}_B) = \sum_{M_A, M_B, M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} \quad (3.5)$$

$$\times Y_{L_A, M_A}(\hat{r}_A) Y_{L_B, M_B}(\hat{r}_B) Y_{L, M}(\hat{R}) \quad (3.6)$$

and the coefficients $v^{L_A, L_B, L}(R)$ are functions only of the distance R between the origins of the two molecules. Berns and van der Avoird expressed these coefficients as a linear sum of contributions due to electrostatic, induction and dispersion interactions,

$$v^{L_A, L_B, L}(R) = v_{\text{elec}}^{L_A, L_B, L}(R) + v_{\text{overlap}}^{L_A, L_B, L}(R) + v_{\text{disp}}^{L_A, L_B, L}(R), \quad (3.7)$$

where the most important short range interactions are the effects of charge penetration and exchange on the first order multipole-multipole interactions and on the second order dispersion interactions. Hence, the first order interaction contains the long range electrostatic multipole-multipole interactions, given for linear molecules in a Σ electronic state using the molecular quadrupole moments Q_{L_A} and Q_{L_B} by [14]

$$v_{\text{elec}}^{L_A, L_B, L}(R) = \delta_{L_A+L_B, L} C^{L_A, L_B} R^{-L_A-L_B-1}, \quad (3.8)$$

where

$$C^{L_A, L_B} = (-1)^{L_A} \left[\frac{(2L_A + 2L_B)!}{(2L_A + 1)!(2L_B + 1)!} \right]^{\frac{1}{2}} Q_{L_A} Q_{L_B}. \quad (3.9)$$

Electrostatic interactions not accountable by this expansion and exchange effects, owing to overlap between the molecular charge clouds, are represented by

$$v_{\text{overlap}}^{L_A, L_B, L}(R) = F^{L_A, L_B, L} \exp(-\alpha^{L_A, L_B, L} R - \beta^{L_A, L_B, L} R^2). \quad (3.10)$$

Charge penetration and exchange have effects on second order dispersion and induction interactions, but these are far smaller and more difficult to calculate (by *ab initio* methods) than the first order overlap contributions. In their paper, van der Avoird, Wormer and Jansen list references concerned with the use of damping functions to include these effects. They chose damping functions that were proportional to the first order overlap effects, which are due to penetration and exchange, that have the advantage of not introducing more fitting parameters. Such damping functions were used to damp the long range London dispersion interactions

$$v_{disp}^{L_A, L_B, L}(R) = - \sum_{n=6,8,\dots} f_n^{L_A, L_B, L}(R) C_n^{L_A, L_B, L} R^{-n}, \quad (3.11)$$

using

$$f_n^{L_A, L_B, L}(R) = 1 - \left[\sum_{k=0}^n a_k^{L_A, L_B, L} R^k \right] \quad (3.12)$$

$$\times \exp(-\alpha^{L_A, L_B, L} R - \beta^{L_A, L_B, L} R^2), \quad (3.13)$$

with

$$a_k = \sum_{i=k/2}^k \frac{\alpha^{2i-k} \beta^{k-i}}{(2i-k)!(k-i)!}. \quad (3.14)$$

A graph of the damping functions used in the expansion when $L_A = L_B = L = 0$ and $\theta_A = 45^\circ$, $\theta_B = 45^\circ$ and $\phi_A = 0$ is shown in Fig. 3.3.

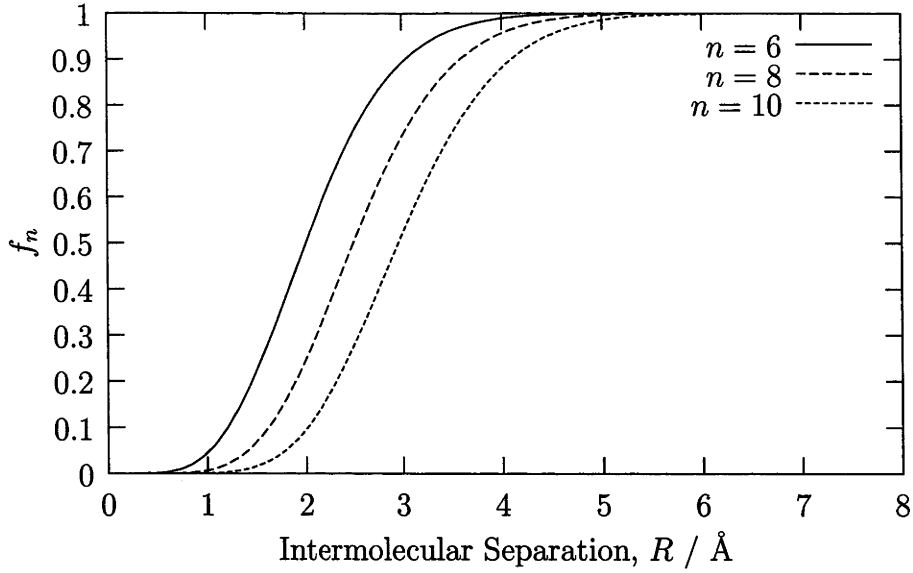


Figure 3.3: Damping functions used in the nitrogen potential where $\theta_A = 45^\circ$, $\theta_B^\circ = 45^\circ$, $\phi_A = 0^\circ$, $L_A = 0$, $L_B = 0$ and $L = 0$.

The damping functions were modified by van der Avoird, Wormer and Jansen [5], because the form of this repulsion is quadratic and the series pre-exponential factor is actually a Taylor expansion of the exponential of *positive* power. Thus, the modified damping functions satisfy the following conditions, as originally imposed by Tang and Toennies [18],

$$\begin{aligned} f_n^{L_A, L_B, L}(R) &\rightarrow 1 && \text{if } R \rightarrow \infty, \text{ and} \\ f_n^{L_A, L_B, L}(R) &\rightarrow 0 + O(R^{n+1}) && \text{if } R \rightarrow 0. \end{aligned} \quad (3.15)$$

The coefficients in these expansions, are tabulated in the original paper of van der Avoird, Wormer and Jansen [5]. Details of their calculations and of their justifications are omitted from this review. The effects of the individual radial contributions are illustrated in Figs 3.4, 3.5 and 3.6.

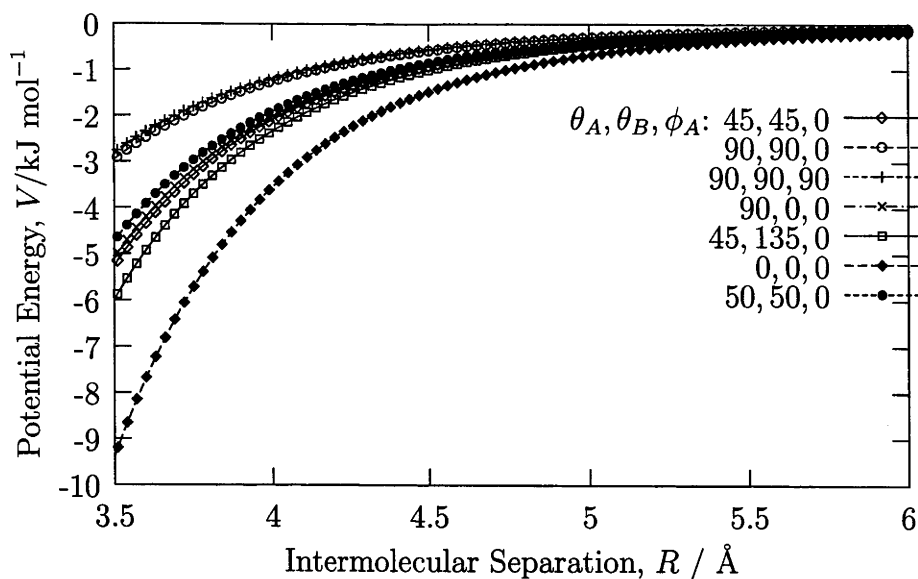


Figure 3.4: Nitrogen potential using only the dispersion part of the radial contribution.

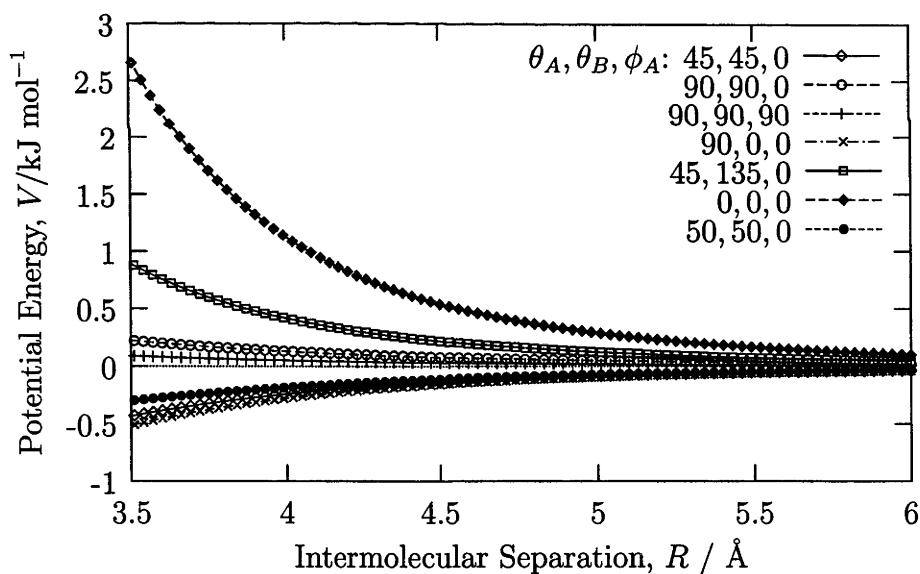


Figure 3.5: Nitrogen potential using only the electrostatic part of the radial contribution.

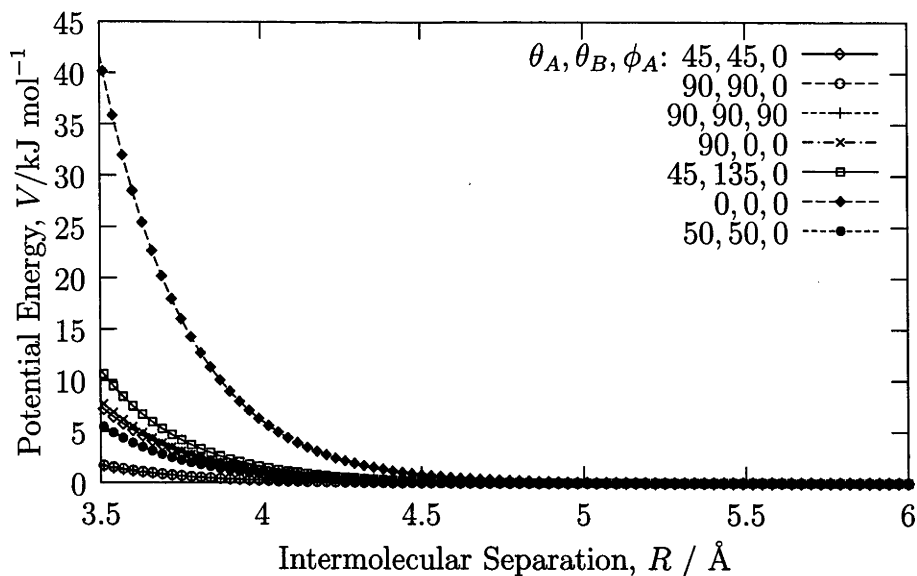


Figure 3.6: Nitrogen potential using only the overlap part of the radial contribution.

Note that the series expansion of the potential diverges at short range, but in our case the repulsive wall of the potential will be physically reasonable to sufficiently short range for the translational energies we will be using. The possibility of tunneling does not arise in our classical treatment.

The potential is also presented as a function of one or the other azimuthal angle, in Figs 3.7, 3.8, 3.9 and 3.10. The π -periodicity is evident in the figures. Similarly, although not shown, there is a 2π -periodicity with respect to the polar angles.

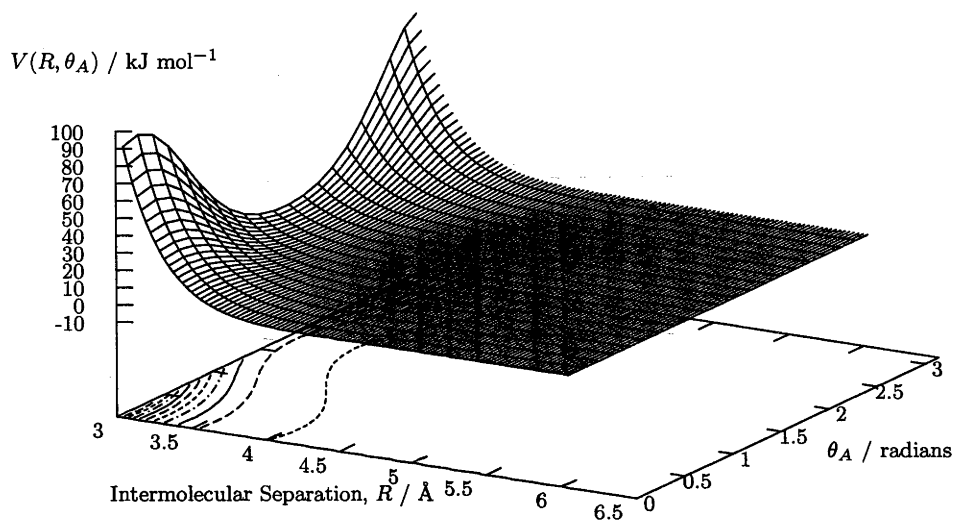


Figure 3.7: Nitrogen potential as a function of one azimuthal coordinate θ_A and R for fixed $\theta_B = 135^\circ$ and $\phi_A = 0^\circ$.

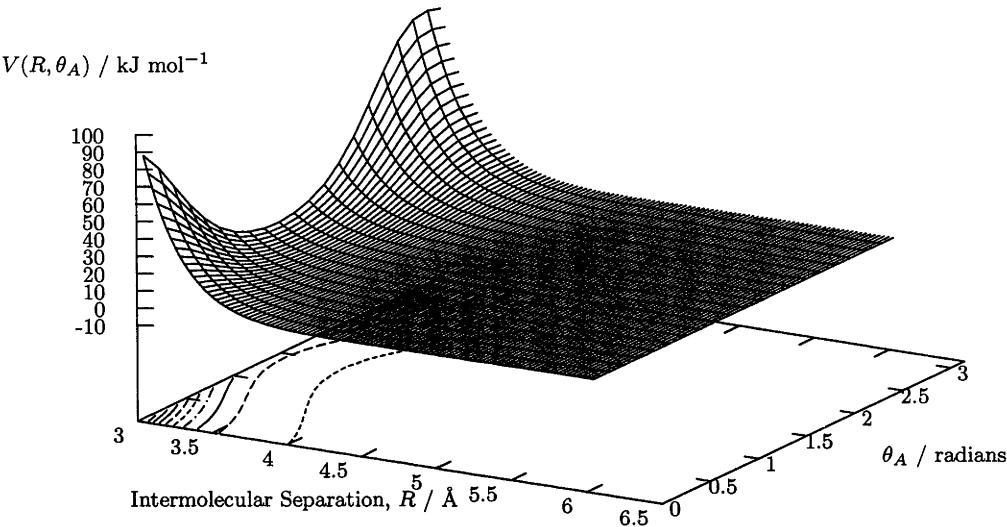


Figure 3.8: Nitrogen potential as a function of one azimuthal coordinate θ_A and R for fixed $\theta_B = 45^\circ$ and $\phi_A = 0^\circ$.

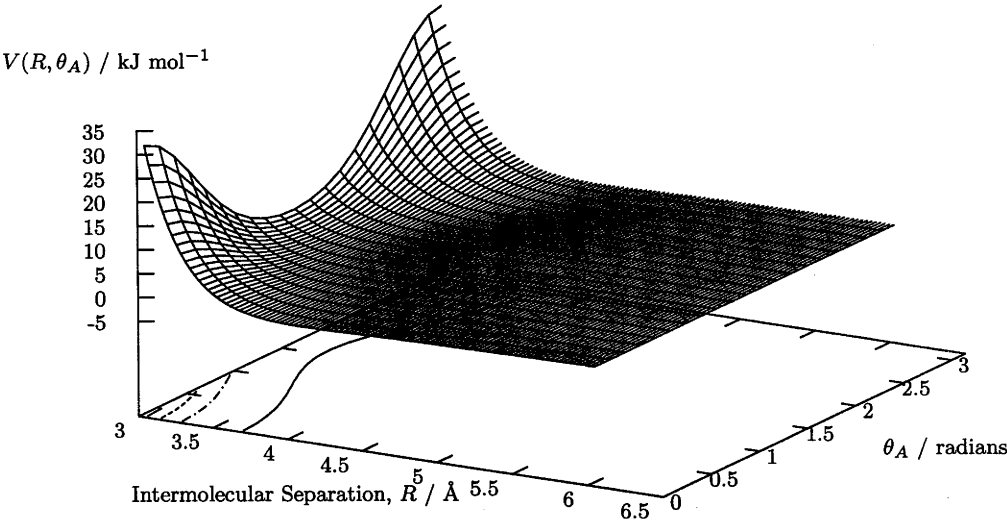


Figure 3.9: Nitrogen potential as a function of one azimuthal coordinate θ_A and R for fixed $\theta_B = 90^\circ$ and $\phi_A = 0^\circ$.

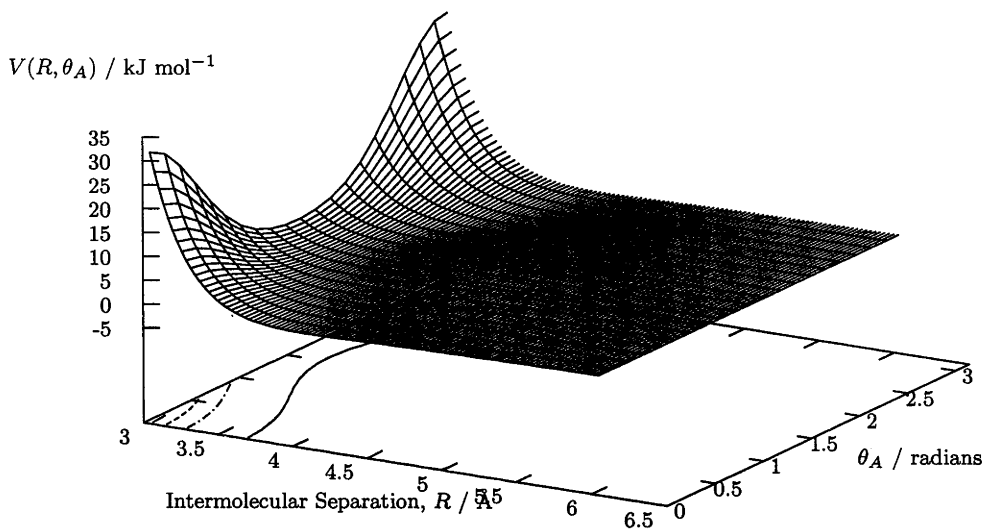


Figure 3.10: Nitrogen potential as a function of one azimuthal coordinate θ_A and R for fixed $\theta_B = 90^\circ$ and $\phi_A = 90^\circ$.

3.3 Classical Dynamics on the Analytic Surface

3.3.1 Classical Dynamics of Rotational Energy Transfer

Classically [19], the state-to-state integral cross-section for a diatomic-diatomic molecule collision, which has been averaged using a sufficiently large set of initial conditions including velocities and orientations, is given by

$$\sigma(J_A, J_B \rightarrow J'_A, J'_B) = 2\pi \int_0^\infty b P(b | J_A, J_B \rightarrow J'_A, J'_B) db \quad (3.16)$$

where $P(b | J_A, J_B \rightarrow J'_A, J'_B)$ is the conditional probability that a collision between two molecules initially prepared with angular momenta J_A and J_B which have

angular momenta J'_A and J'_B after the collision collide with impact parameter b . The classical rotational angular momentum $\mathbf{L}_i$ of a diatomic molecule i is

$$\mathbf{L}_i = \mu_i \mathbf{x}_i \times \dot{\mathbf{x}}_i, \quad (3.17)$$

where the cross product has been taken of the internuclear displacement vector $\mathbf{x}_i$ and the velocity $\dot{\mathbf{x}}_i$, where μ_i is the reduced mass of the diatomic. This angular momentum vector is a constant of the motion if there is no interaction with another molecule. The rotational energy, however, depends upon internuclear distance. To separate out the rotational energy, conserved quantities known as action variables are introduced for vibration v_i and rotation J_i , defined as

$$v_i = -\frac{1}{2} + \frac{2\mu_i}{h} \int_{x_{i<}}^{x_{i>}} \dot{x}_i dx_i \quad (3.18)$$

$$J_i = -\frac{1}{2} + \frac{1}{2} \sqrt{1 + \frac{4L_i^2}{\hbar^2}} \quad (3.19)$$

where v_i depends on a phase integral between the inner and outer turning points of the vibrational motion. The values of v_i can be “binned” into vibrational quantum numbers, and J_i may be binned into rotational quantum numbers. The binning, for purposes of counting, is achieved by halving the intervals between allowed quantum numbers. In this study of rotational energy transfer between two constrained linear rotors, only J_i will be of interest. An example of this binning of J_i is shown in Fig. 3.11, for the final angular momenta of the two molecules.

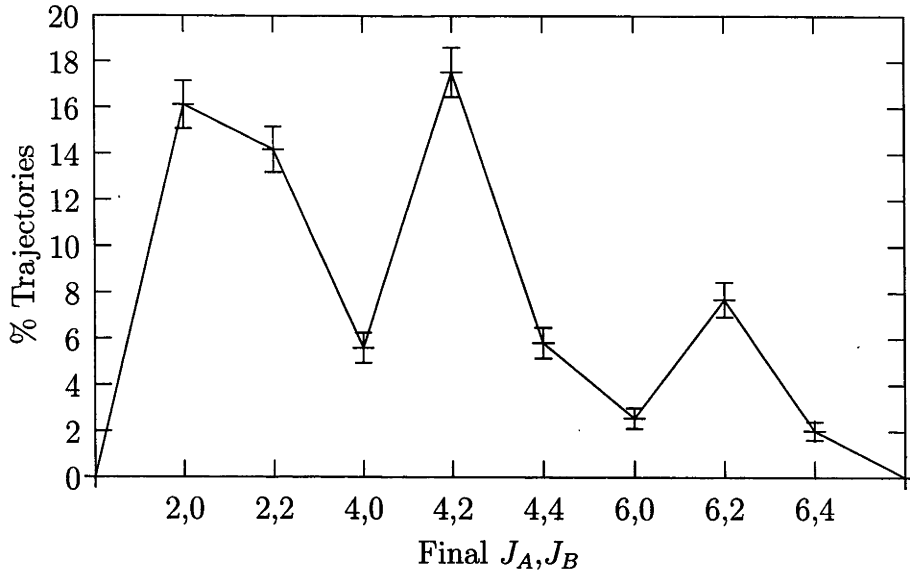


Figure 3.11: Fraction of trajectories initially in $J_A = 0, J_B = 0$ finishing with J'_A, J'_B for the analytic PES. Error bars represent two standard deviations (from the statistics of proportions).

In Fig. 3.11 and generally in this chapter, $(J_A, J_B) = (n, m)$ means $J_A = n, J_B = m$ or $J_A = m, J_B = n$ as the monomers are treated as indistinguishable.

The conditional probability in Eq. (3.16) is evaluated with an additional “binning” procedure as illustrated by the following example. Figure 3.12 shows the percentage of all (5000) trajectories in a simulation, which begin with an impact parameter in a particular “bin”. Figure 3.13 shows the percentage of trajectories which finish with $(J_A, J_B) = (4, 0)$ (actually $3.5 \leq J_A < 4.5$ and $0 \leq J_B < 0.5$ or vice versa), as a function of their initial impact parameter “bin”. The conditional probability, $P(b \mid J_A, J_B \rightarrow J'_A, J'_B)$ in Eq. (3.16) is simply the ratio of the corresponding bin counts (not percentages) in Figs 3.12 and 3.13.

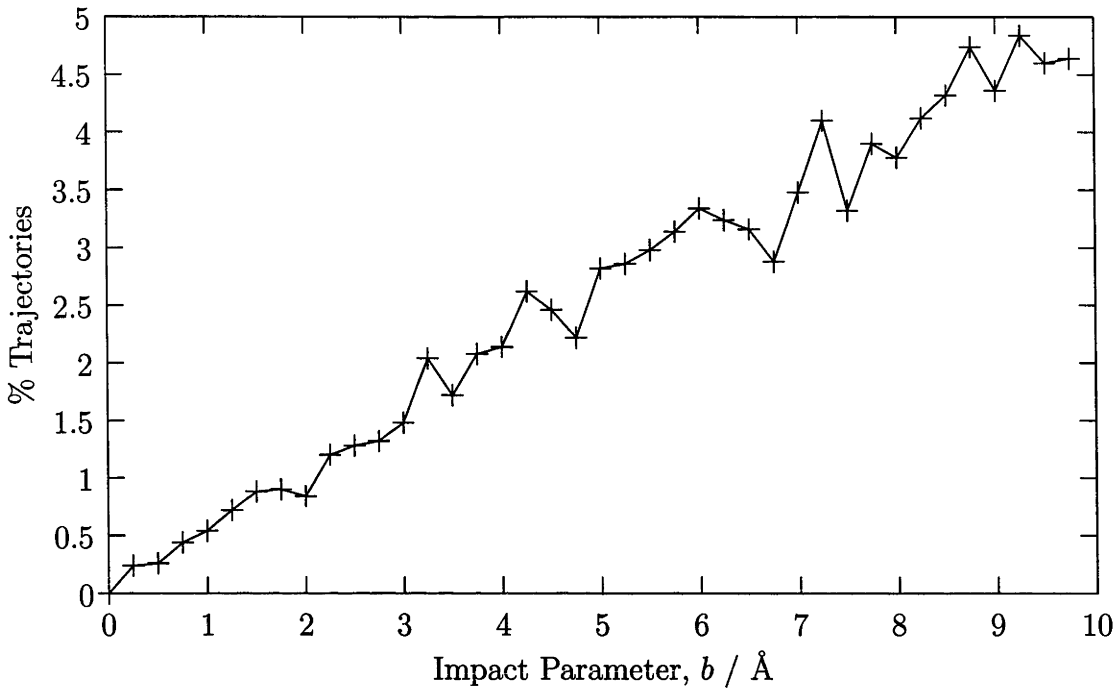


Figure 3.12: Fraction of all trajectories as a function of impact parameter for the analytic PES. Error bars not shown for pictorial convenience.

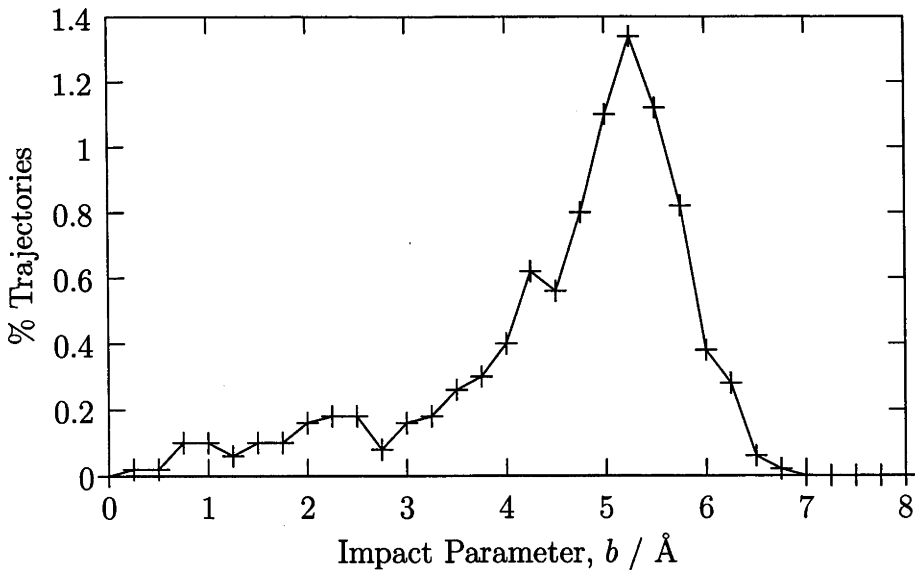


Figure 3.13: Fraction of trajectories initially in $J_A = 0, J_B = 0$ finishing with $(J'_A, J'_B) = (4, 0)$ for the analytic PES as a function of impact parameter.

The maximum impact parameter was 10 Å in this example. The corresponding cross-section, from Eq. (3.16) and Figs. 3.13 and 3.12 is $9.2 \pm 1.5 \text{ Å}^2$. The stated error is two standard deviations, based on a normal distribution of outcomes for the finite number of trajectories evaluated.

The cross-sections for a number of rotational transitions have been calculated from samples of 5000 trajectories and are shown in Table 3.2.

3.4 Interpolation of the Analytic Surface

Before we begin to construct an interpolated PES we must enforce the correct symmetry on the data set.

The permutation-inversion (PI) molecular symmetry group is $S_4 \otimes I$, less permutations which would involve breaking the constrained bonds, that is the subgroup $S'_4 \otimes C_i$ of “feasible” PI symmetry operations. This symmetry is naturally inherent in the analytic vdAWJ potential in the sense that only even values of L_A , L_B and L are used in the spherical expansion, and because the radial coefficients satisfy $v_{L_A, L_B, L}(R) = v_{L_B, L_A, L}(R)$ [12]. The elements of the group are: the identity E , body-fixed inversions of the monomers (1 2) and (3 4), the reflections (1 2)(3 4) and (1 3)(2 4), the rotations (1 4)(2 3) and the inversions (1 3 2 4) and (1 4 2 3). The way these elements, which relate to permutation of the labelled yet indistinguishable nuclei, affect permutation of the actual labelled internuclear distances are currently “hard-coded” into the programs used in the surface-growing scheme. This is only performed once per system, but in future this may be automated to make the scheme more transparent.

3.4.1 Computational Details

A schematic representation of the internuclear distance coordinates used in the interpolation is shown in Fig. 3.14 below, where the constrained distances are also shown.

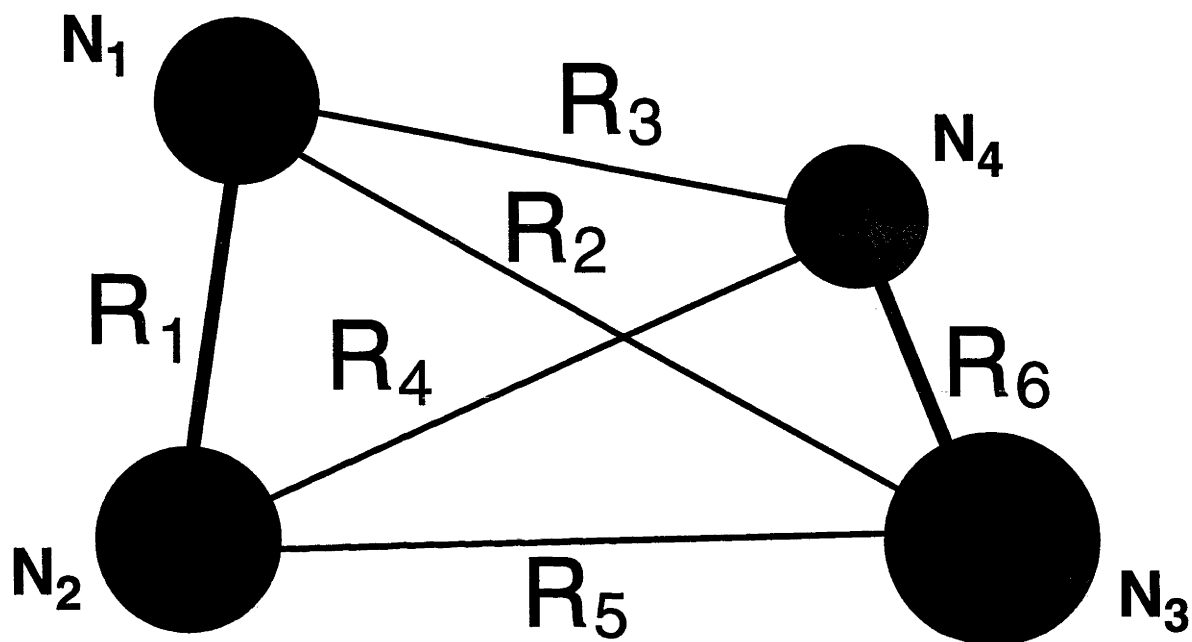


Figure 3.14: A schematic representation of the six internuclear distances, defining the N_2/N_2 system. R_1 and R_6 are constrained.

The purpose of running trajectories on the analytic surface is for comparison with the results obtained through interpolation. The fact that the true surface is the analytic surface means that it is possible to determine sensible initial conditions for all trajectories. A functional form that is relatively less expensive than the interpolated PES is useful to determine parameters such as the size of the timestep. The relevant parameters are summarised in Table 3.1.

The parameters in Table 3.1 have been introduced in Chapter 2, however “Neighbour list updates” requires further explanation. Neighbour lists are not updated every timestep, Δt . Instead the neighbour lists are updated using the frequencies listed in Table 3.1 (the reciprocal of the period between updates), where the first expression is for the outer neighbour list, which is updated less frequently than inner neighbour list (given by the second expression expressed in terms of Δt).

Table 3.1: Parameters used in PES construction and in trajectory calculations.

Parameter	Symbol	Construction	Dynamics
<i>Constraints</i>			
N-N bondlength		1.0977 Å	
<i>Dynamics</i>			
Maximum Impact Parameter	$b_{\max}$	7 Å	7 Å
Initial Fragment Separation	d_{ab}	12 Å	12 Å
Timestep	Δt	0.2 fs	0.2 fs
Number of trajectories	n_{traj}	10	5000
Relative Translational Energy	E_{rel}	240 cm ⁻¹	240 cm ⁻¹
<i>Sampling</i>			
Trajectory Sampling Frequency	f_{print}	1/1000 Δt	
Points selected/iteration		1	
<i>Interpolation</i>			
Weight function terms		1	1
Weight function powers		9	9
Weight function cutoffs	$w_{\text{tol},i}, w_{\text{tol},o}$	10 ⁻⁸ , 10 ⁻⁵	10 ⁻⁸ , 10 ⁻⁵
Neighbour list updates		1/10 Δt , 1/5 Δt	1/30 Δt , 1/5 Δt
Neighbours in confidence radius	n_{neigh}	10	10

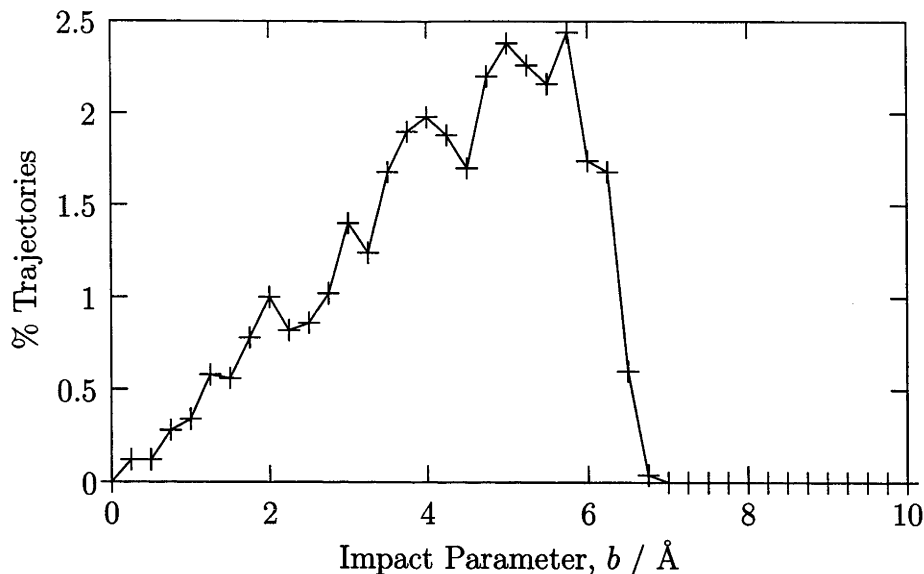


Figure 3.15: Fraction of all trajectories which result in inelastic scattering, as a function of impact parameter for the analytic PES.

For the trajectories used in Fig. 3.12, a conservative maximum impact parameter of 10 Å was used. From Fig. 3.15 it was clear that a maximum impact parameter of 7 Å was sufficient to describe inelastic collisions. Therefore, to reduce the statistical error in the state-to-state inelastic scattering probabilities, a maximum impact parameter of 7 Å was used.

As this is a system of four atoms, with less degrees of freedom, after imposing two bond-length constraints than other four atom systems which have been studied using the interpolation scheme, the one-part unnormalised weight function of Eq. (2.24) was employed. Neighbour list parameters were adjusted so that the number of neighbours in each list is moderate.

A data set consisting of 33 points from the minimum energy path (MEP) was generated for the analytic surface using first derivatives in a steepest descent algorithm. The MEP is simply a logical starting point for the surface-growing scheme.

The iterative construction of the PES was initiated from this MEP data set. The h -weight sampling and variance sampling criteria for selecting new points were used in alternate iterations until the data set reached 565 points.

3.4.2 Discussion of Computational Results

A qualitative idea of how well the interpolated PES, with 565 points in the interpolation data set, reproduces the analytic functional form can actually be seen in Fig. 3.1. In the figure, the symbols represent points that have been calculated by interpolation using a data set of 565 points. Different symbols are associated with different orientations of the monomers. Any vertical difference between a symbol and the corresponding line for that orientation and intermolecular distance represents an error. The lines themselves are generated using only the functional form.

Attempting to characterise the PES during construction is useful in order to avoid too many expensive dynamics calculations. A better way than examining Fig. 3.1 to investigate the accuracy of the surface, is to quantify the interpolation error in regions relevant to the dynamics. To this end, 3481 geometries were sampled from actual trajectories on the *analytic* surface. The energies and first derivatives are recorded with these geometries. The average absolute error will be defined as the mean of all the absolute values of the differences between the recorded energies for each geometry and the interpolated energy using the same geometry. The average relative gradient (∇V) error is given by the average of g :

$$g = \frac{\|\nabla V_{\text{interpolated}} - \nabla V_{\text{exact}}\|}{\frac{1}{2} (\|\nabla V_{\text{interpolated}}\| + \|\nabla V_{\text{exact}}\|)}. \quad (3.20)$$

The trends in these two measures of the accuracy of the interpolated PES are shown in Fig. 3.16.

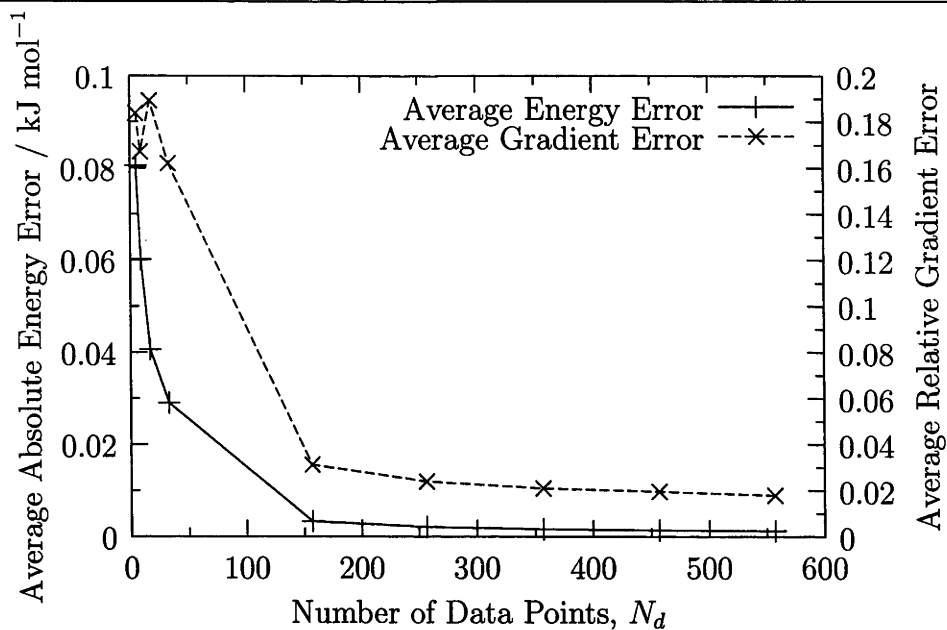


Figure 3.16: Average absolute errors in energies and gradients are shown.

Convergence of errors in both the energies and gradients is apparent after ≈ 150 points. The agreement in Fig. 3.1 and the convergence in Fig. 3.16 is pleasing. However, better agreement may be necessary in some regions than in others. To determine whether or not the PES is sufficiently accurate requires one to run dynamics.

Inelastic cross-sections calculated on an interpolated PES with various numbers of data points are compared with results for the analytic PES in Table 3.2. Initial conditions were selected for the nitrogen molecules in their rotational ground states.

Table 3.2: Results from classical trajectories for $N_2(J=0) + N_2(J=0)$ where ($E_{\text{rel}} = 240 \text{ cm}^{-1}$)

Rotational levels $J_1, J_2 \rightarrow J'_1, J'_2$	Selected total cross-sections / $\text{\AA}^2$				
	Functional Form	Initial Data: 33 Points	154 Points	255 Points	565 Points
0,0 $\rightarrow$ 2,0	24.8 ± 1.6	27.8 ± 2.4	22.7 ± 1.6	24.5 ± 1.7	24.0 ± 2.2
0,0 $\rightarrow$ 2,2	21.8 ± 1.5	23.2 ± 2.2	21.0 ± 1.5	18.6 ± 1.5	20.9 ± 2.1
0,0 $\rightarrow$ 4,0	8.6 ± 1.0	8.7 ± 1.4	10.4 ± 1.1	10.2 ± 1.1	9.2 ± 1.5
0,0 $\rightarrow$ 4,2	27.0 ± 1.7	24.6 ± 2.3	24.9 ± 1.7	25.9 ± 1.7	27.5 ± 2.4
0,0 $\rightarrow$ 4,4	8.9 ± 1.0	6.8 ± 1.3	8.3 ± 1.0	8.0 ± 1.0	7.9 ± 1.4
0,0 $\rightarrow$ 6,0	3.9 ± 0.7	3.7 ± 0.9	5.1 ± 0.8	5.2 ± 0.8	5.1 ± 1.1
0,0 $\rightarrow$ 6,2	11.9 ± 1.2	7.6 ± 1.3	12.2 ± 1.2	11.3 ± 1.1	9.6 ± 1.5
0,0 $\rightarrow$ 6,4	3.1 ± 0.6	3.1 ± 0.9	4.0 ± 0.7	3.5 ± 0.7	3.6 ± 0.9

The most striking feature of the results in Table 3.2 is that the initial data set performs moderately well and that convergence is rapid, if not immediate. Cross-sections for 154 points agree better with results for the functional form than those for the initial data set. Error limits, which represent two standard deviations from the simple statistical analysis of proportions [20] could be reduced by averaging consecutive converged values. Note, however, that error limits are perhaps quoted as too small for the smaller, e.g. (0,0) $\rightarrow$ (6,4), cross-sections where the number of sampled trajectories is low.

3.5 Conclusions

The rapid convergence of the inelastic cross-sections implies that the methodology could have been used to construct a PES using high-level *ab initio* data. This would avoid the use of intuition about the dynamics or knowledge of damping functions as described by Tang and Toennies [18] and employed in the vdAWJ PES, for example.

There may be applications of this methodology for which the accuracy demanded of the interpolated PES implies slower convergence of the relevant dynamical properties. An application that may exhibit such demands might be a highly isotropic potential where the small anisotropy that exists is highly influential on the dynamics. It is also possible that quantum scattering calculations will require broader knowledge of the PES, particularly in classically forbidden regions. Such an application is examined in the next chapter.

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Chapter 4

Quantum Dynamics for the PES of a Constrained System: $\text{H}_2 + \text{H}_2$

An established method for constructing molecular potential energy surfaces by interpolation of *ab initio* data has been coupled with a new approach to sampling molecular configurations which uses constrained classical dynamics. In this chapter, the first application of the interpolation methodology to quantum dynamics is presented.

4.1 Introduction

So far we have considered classical inelastic scattering for a system of heavy atoms. Armed with the knowledge that the methodology can reproduce the classical dynamics for a simple non-reactive system we also wish to know whether or not a PES constructed using classical dynamics can be used for quantum scattering calculations. Quantum rotational inelastic scattering of H_2 with H_2 provides an excellent test case. Diatomic hydrogen is simply the lightest molecule and therefore has the longest de Broglie wavelength of any molecule moving at the same velocity.

Diatomic bonds are again constrained in the colliders. Rigid rotors have traditionally been used to model the rotational inelastic quantum scattering of two diatomic molecules [1–5]. Rather than using *ab initio* calculations as the source of interpolation data, we have employed a simple model PES for H_2/H_2 scattering developed by Zarur and Rabitz (ZR) [2]. The aim is simply to examine the efficiency of this approach, not to derive a new *ab initio* PES [6]. The interpolation method can thus be tested by its ability to produce an interpolated PES which reproduces the dynamics of the model PES.

This choice of model system allows us to examine the utility of interpolated PES in areas not previously considered. Weak interactions have not been closely examined using the interpolation method. This work tests the suitability of the method for producing surfaces which are sufficiently accurate for rotational inelastic scattering, particularly when inelastic collisions are infrequent, owing to the near isotropy of the potential. Hydrogen molecules have no permanent dipole moment and only a very weak quadrupole moment [5, 7]. The interaction in the binary collision of the diatoms therefore resembles that of relatively hard bodies with a very shallow attractive well, and weak anisotropy [5]. This work also reports the first attempt to use this type of interpolated PES in quantum dynamics, in this case rotational energy transfer [8].

Rotational inelastic scattering in hydrogen has been a well-studied prototype application for coupled-channel or close-coupled (CC) calculations [2–4]. This is due primarily to the comparatively large rotational constant of 60.8 cm^{-1} , which restricts the number of open channels at any particular scattering energy. Quantum scattering, as opposed to classical scattering, is necessary for this system as the hydrogen dimer is a light system and indistinguishable particle symmetry results in important quantum exchange effects [2]. Further, inelastic scattering events in the relatively isotropic potential for H_2/H_2 collisions are improbable at low energy and hence may be classically forbidden [2].

4.2 Theory

The interpolation formula for the PES and the iterative construction scheme have been described in Chapter 2. In previous studies the convergence of the PES has only been tested using classical trajectory methods. Here, some details of the interface of the interpolated PES with quantum scattering calculations are presented.

The potential is expressed using the modified Shepard interpolation of Eq. (2.22) where the potential is expressed in terms of local distance-weighted Taylor expansions. In general, the Taylor expansions incorporate first and second order derivatives that may be obtained by finite difference methods or analytically from *ab initio* calculations. These derivatives are determined analytically for the ZR surface. Rotational and translational invariance of the PES is assured by the use of internal coordinates, specifically internuclear distances, $\mathbf{R} = \{R_1, R_2, \dots, R_6\}$. The six internuclear distances required to describe every possible configuration of the H_2/H_2 system have been labeled in Fig. 4.1. In practice, we use inverse internuclear distances, $\mathbf{Z}$ (where $Z_k = 1/R_k$), discussed in Chapter 2, as they provide more physically reasonable asymptotic properties.

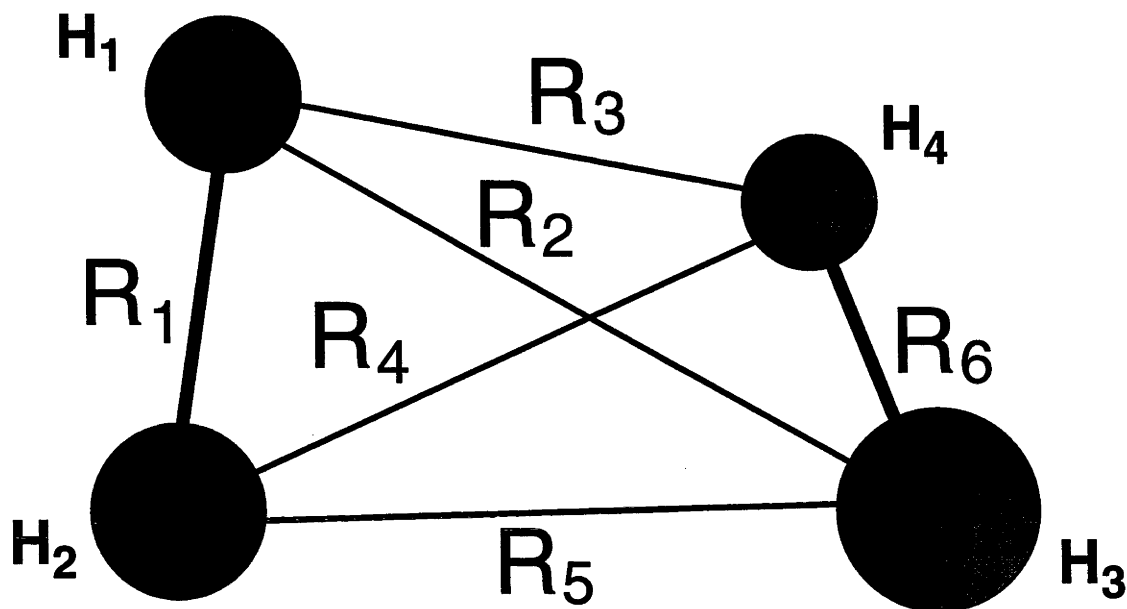


Figure 4.1: A schematic representation of the six internuclear distances, defining the H_2/H_2 system. R_1 and R_6 are constrained.

In Eq. (2.22), a summation is performed over the appropriate symmetry group, G . Here, G is S'_4 , a subgroup of the permutations of the four hydrogen nuclei, in which the intramolecular degrees of freedom are constrained [9, 10]. Here, $g \circ i$ denotes that the i th data point, $\mathbf{Z}(i)$, is replaced by a data point transformed by the group element g . The summation in Eq. (2.22) implies that all permutationally equivalent datapoints are included in the data set. This augmentation of the data set does not require further calculations of energies or derivatives. The data set is “symmetrized”, so the PES of Eq. (2.22) exhibits the full molecular symmetry [11].

Equation (2.24) is a “one-term” weight function. The more complicated “two-term” weightfunction of Ref. [12] was also used to construct the PES. The two-term weight function was found to be more accurate for interpolating first derivatives of the PES at the expense of a small increase in the error in interpolating the energy. However, the one-term weight function was found to give more accurate cross-sections, and all results reported below have employed Eq. (2.24).

4.2.1 Placement of Data Points in Configuration Space

The iterative PES interpolation construction scheme consists of the algorithm described in Chapter 2: (1) start with an initial set of data; (2) run classical trajectories on the crude interpolated surface and sample the molecular configurations encountered; (3) add some sampled points to the interpolation data set, where the choice is based on certain selection criteria and weighting of trajectory configurations; (4) check convergence after adding a certain number of points by running a dynamical simulation if the desired properties are not yet converged, return to step (2), or else stop.

The first step in this procedure is to choose an initial data set. The minimum energy configuration on the ZR surface was chosen as one initial data point. Fixing the relative orientation of the diatoms at the minimum energy configuration, 11 additional initial data points were selected at different intermolecular separations.

In the second step, classical trajectories are used to determine dynamically important regions of the PES [13]. The underlying assumption is that although quantum dynamics are required to calculate the actual cross-sections and determine convergence, the dynamically important part of configuration space can be searched using classical trajectories [13]. The validity of this assumption will be revealed by the success of the method in reproducing the quantum dynamics given by the ZR surface. Internuclear distance constraints were used to limit the trajectories to a reduced-dimensional manifold. Rigidity of the diatoms was ensured by using the molecular dynamics algorithm, RATTLE [14], to integrate the classical equations of motion.

In the third step, new data point configurations were chosen using the variance (see Eq. (2.27a)) method. Preliminary testing showed that variance sampling more rapidly improved the accuracy of the surface at the repulsive wall, which was found to be extremely important to the dynamics for the energies considered.

The final step in the construction algorithm is to test for convergence of the dynamical observables.

4.2.2 Convergence of the PES

After adding a number of points to the dataset, the accuracy of the surface was tested using a quantum scattering calculation.

The theory of quantum rotational scattering in bimolecular collisions of identical homonuclear diatomic molecules has been treated in detail elsewhere [3, 5]. The method used to solve the close-coupled equations was a conventional partial wave analysis [15] as implemented in MOLSCAT [16]. For such treatments it is convenient to expand the potential in the form [17]:

$$V(\hat{\mathbf{R}}_A, \hat{\mathbf{R}}_B, \mathbf{R}) = \sum_{l_A l_B l} v_{l_A l_B l}(R) A_{l_A l_B l}(\hat{\mathbf{R}}_A, \hat{\mathbf{R}}_B, \hat{\mathbf{R}}), \quad (4.1)$$

where the angles corresponding to the unit vectors $\hat{\mathbf{R}}_A = (\theta_A, \phi_A)$, $\hat{\mathbf{R}}_B = (\theta_B, \phi_B)$ and $\hat{\mathbf{R}} = (\Theta, \Phi)$ are shown in Fig. 4.2. The angular terms are given by

$$A_{l_A, l_B, l}(\hat{\mathbf{R}}_A, \hat{\mathbf{R}}_B, \hat{\mathbf{R}}) = \sum_{m_1 m_2 m} \langle l_A m_A l_B m_B | l_A l_B l m \rangle Y_{l_A m_A}(\hat{\mathbf{R}}_A) Y_{l_B m_B}(\hat{\mathbf{R}}_B) Y_{lm}(\hat{\mathbf{R}})^*, \quad (4.2)$$

which is a sum of products of spherical harmonics and Clebsch–Gordan coefficients [18]. The radial coefficients in Eq. (4.1) were determined by numerical quadrature of the interpolated PES.

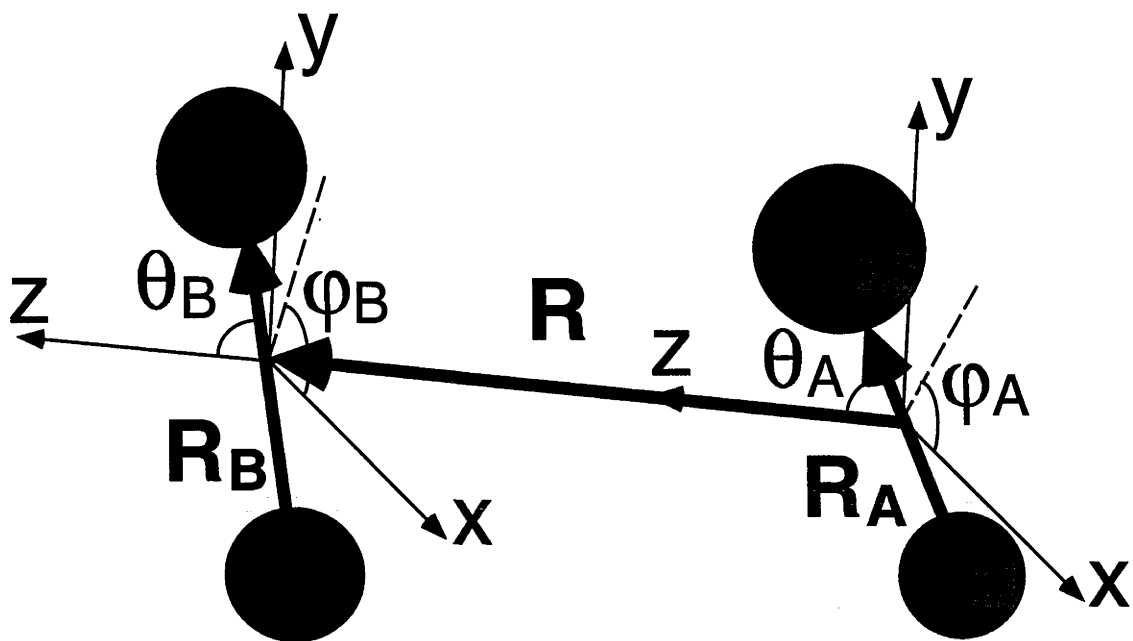


Figure 4.2: A schematic representation of the internal coordinates used in Eq. (4.1).

4.3 Calculations

4.3.1 Computational Details

New data points for the interpolation of the PES are chosen from configurations encountered during classical simulations of the H_2/H_2 collision. The starting separation of the centres of mass of the collision partners was 12 Å. The impact parameter, b , for each trajectory was selected at random from a distribution of values limited by a maximum value of 0.7 Å, and in which the probability of a trajectory having an impact parameter between b and $b + db$ was proportional to b . The colliders were randomly oriented prior to the collision.

In previous work with the interpolation scheme, the velocity-Verlet [19] algorithm was used to integrate the classical equations of motion in the $3N$ Cartesian coordinates. The constrained dynamics algorithm, RATTLE, was used to ensure rigidity. RATTLE consists of the velocity-Verlet integrator coupled with an iterative method of imposing the constraints [19].

Classical trajectories were run using a timestep of 20 fs. This was chosen to be small enough to ensure that the trajectories conserve energy within a tolerance of 0.2%. The constrained bondlength for each monomer was 0.74166 Å [3]. For each iteration of the interpolation scheme, configurations were sampled every 100 timesteps along 10 trajectories assuring that at least 1000 points were recorded. At the end of an iteration, the trajectory point with the highest variance, using Eq. (2.27a), was selected to generate a new data point.

In addition, if a trajectory configuration was found for which the interpolated energy was lower than the minimum energy of all points in the data set, this point was also chosen to be added to the interpolation data set. This prevents the problem of “spurious wells” described in earlier work using the interpolation method [6].

The energy and its first and second derivatives were calculated using the ZR potential at the chosen configuration. The new point was then added to the data set. The effect of adding different numbers of data points at each iteration has been explored elsewhere [6].

The weight function in Eq. (2.24) was used with $p = 9$. Higher values of p were tested but led to increased error in the interpolation, as the resulting surfaces were less smooth. Interpolation was carried out using a neighbor list as described previously [6]. Only data points with weights greater than 10^{-5} were included in the sum in Eq. (2.22).

MOLSCAT [16] was used to solve the close-coupled equations for the rotational scattering cross-sections. The interpolated potential was expressed, using a simple

coordinate transformation, as a function of spherical polar angles of each rotor and the vector connecting the centres of mass of the diatoms as shown in Fig. 4.2. A subroutine with the PES in this form was appended to MOLSCAT. Expansion of the potential in the form of Eq. (4.1) is performed internally by MOLSCAT where the radial coefficients in Eq. (4.1) are projected out using a Gauss-Legendre quadrature in the angular coordinates, using ample points to obtain cross-sections within 1%.

The truncation of the series expansion in Eq. (4.1), by limiting the values of l_A , l_B and l , was the same as that used in the ZR potential. For the converged interpolated PES it was found that increasing the size of the expansion to include terms up to an orbital angular momentum quantum number of four had no noticeable effect on the cross-sections. This result confirms that the expansion for the interpolated PES yields only the angular terms present in the ZR potential function.

Green [3, 20] showed that the results of CC calculations for the ZR potential were approximately reproduced using the effective potential (EP) method [21] with a larger basis set. Mainly EP calculations were used in this work to compare the ZR and interpolated PES as they are less computationally expensive. The basis sets used for EP calculations on *para-para*, *ortho-ortho*, and *ortho-para* collisions were the largest sets used by Green [3]. Convergence of the reported cross-sections with increasing basis set size has already been demonstrated [3]. Note that the interpolated surfaces are constructed using classical trajectories, in which the particles are necessarily treated as distinguishable.

In a slight departure from Green's approach to the scattering calculation, we used the hybrid log derivative-Airy integrator, HYBRIDON [22], instead of the older Gordon integrator [23]. Integration parameters were adjusted in order to efficiently obtain cross-sections converged within 1%. The rotational constant used to compute rigid rotor energy levels was $B_0 = 60.8 \text{ cm}^{-1}$, and the reduced mass of the collision was 1.0 amu in accordance with values used by Green.

4.3.2 Data Location in Configuration Space

Figure 4.3 depicts the locations of the data points for three PES constructed at total energies of: (a) 2621 cm^{-1} ; (b) 403.3 cm^{-1} ; and (c) 41.8 cm^{-1} . The definitions of the internuclear distances are shown in Fig. 4.1. In Fig. 4.3, each point in the interpolation data set has been plotted using each of the following ordered pairs: (R_2, R_3) ; (R_3, R_2) ; (R_4, R_5) ; and (R_5, R_4) . This procedure gives some indication of the symmetry of the data set. The open circles indicate points in the initial data set. Five of the twelve initial data points are beyond the range of the axes. There are 50 unique interpolation data points (including the initial data set) represented in each plot.

Figure 4.3 shows clearly that there is no data at very short internuclear distances. The short-range region of the surface is classically forbidden. Data points are confined within the dashed lines; regions outside the dashed lines are forbidden by triangle inequalities imposed by the constraints. Note that the intersection of the dashed lines with the appropriate axes coincide with the constrained values of R_1 and R_6 . In cases(a) and (b), a lot of data lies near the classical turning points. There are two apparent reasons for this: since the diatoms are moving more slowly near a classical turning point, more configurations are sampled there; and secondly, the variance may be large where the potential is changing rapidly, as it is at the repulsive wall. Notable also in Fig. 4.3 is the relatively large number of points added near the potential minimum, between R_2 (or R_4) = 3 and 4 Å (see also Fig. 4.4). This may be caused by the fact that the potential is relatively anisotropic near the minimum.

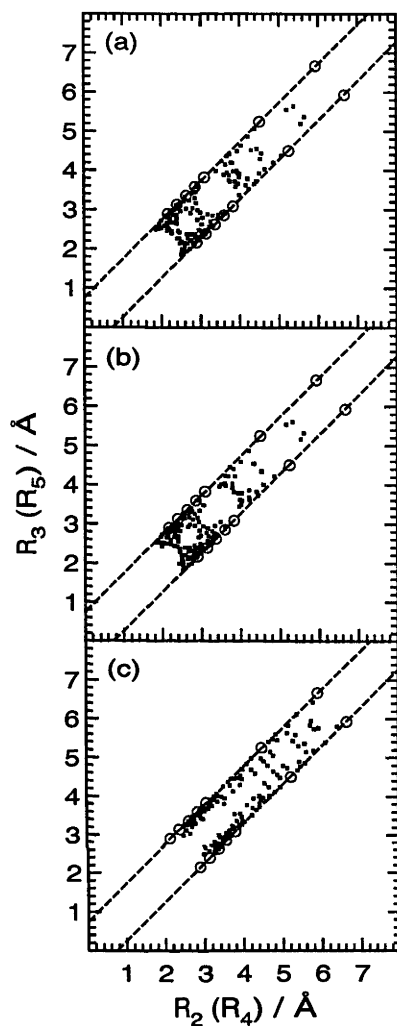


Figure 4.3: Two dimensional projections of data point configurations for the H_2/H_2 system. Each point represents one of the (R_2, R_3) , (R_3, R_2) , (R_4, R_5) , or (R_5, R_4) coordinates of a point in a PES data set. The data sets were constructed using variance sampling from trajectory simulations at (a) 2621 cm^{-1} , (b) 403.3 cm^{-1} , and (c) 41.8 cm^{-1} . The open circles are points in the initial data set.

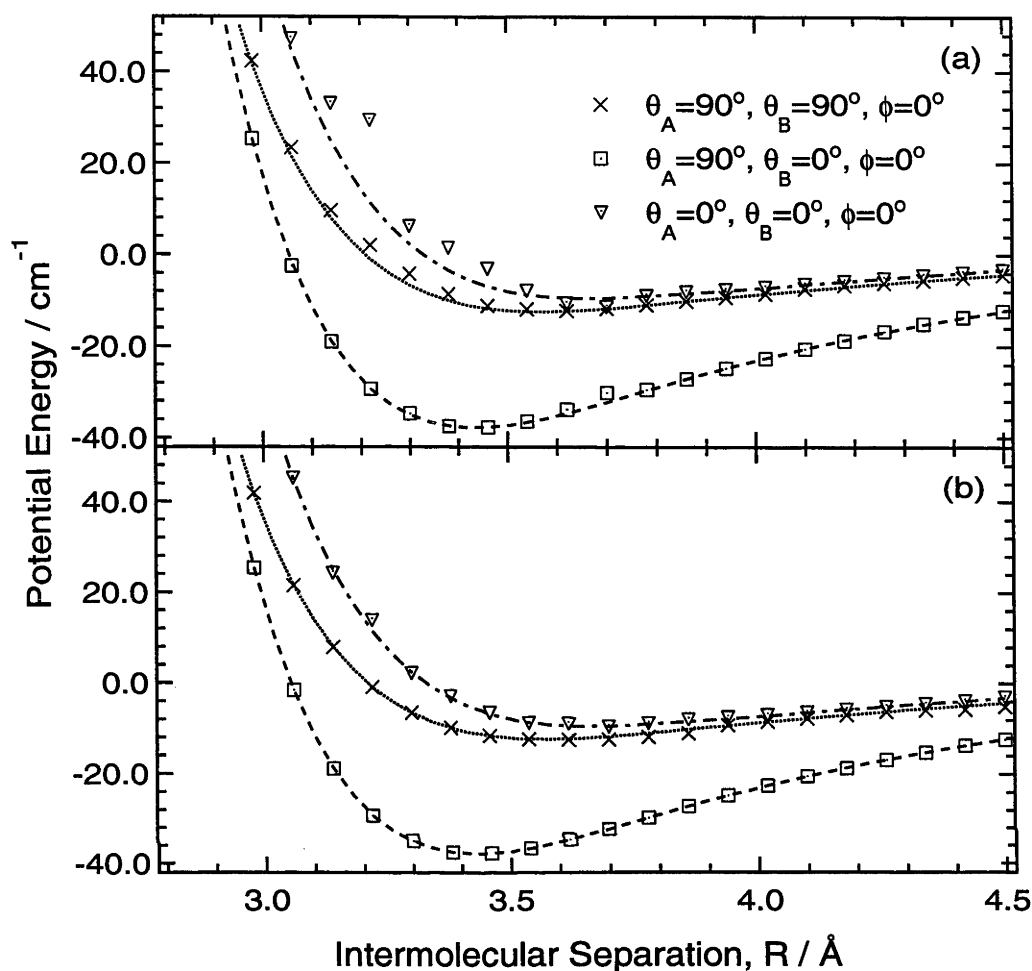


Figure 4.4: Symbols at discrete points represent interpolated surfaces (containing 50 data points) constructed at (a) 2621 cm⁻¹ and (b) 41.8 cm⁻¹ for particular relative orientations of the diatoms, as indicated. For comparison, the lines represent the ZR surface for the particular angular orientations shown, as the intermolecular separation is varied.

Comparison of Figs 4.3(a) and 4.3(c) reveals that the position of the repulsive wall is more clearly delineated at high energy. The energy used in (b) is still large in comparison with the depth of the potential energy minimum and consequently the distribution of points does not appear to be markedly different from that shown

in (a). However, case(c) demonstrates that the placement of data depends on the energy used to construct the surface.

4.3.3 Convergence of the Rotational Cross-sections

The convergence of rotational cross-sections (calculated using the EP approximation) as a function of the size of the data set is demonstrated in Tables 4.1, 4.2, and 4.3 for PES constructed using the highest and lowest energies considered by Green for *para-para*, *ortho-ortho*, and *ortho-para* collisions. Note that the interpolated PES used in each scattering calculation was constructed using classical trajectories with the same relative translational energy. The quantitative trends in the magnitudes of the cross-sections appear to have been reproduced in each table.

Table 4.1: EP cross sections, for excitation from initial rotational levels J_A and J_B to final levels J'_A and J'_B of the diatoms, are given for PES containing 12, 20, and 50 data points and compared to results from the ZR surface for *para-para* collisions, for two values of the relative translational energy of the diatoms.

Energy/ cm^{-1}	$J_A, J_B \rightarrow J'_A, J'_B$	Cross section/ $\text{\AA}^2$			
		$N_d = 12$	20	50	ZR surface
403.3	0,0 $\rightarrow$ 0,0	109.4	111.3	110.5	111.4
	0,0 $\rightarrow$ 2,0	0.039	0.025	0.018	0.022
	2,0 $\rightarrow$ 2,0	118.5	122.1	118.7	118.6
2419.7	0,0 $\rightarrow$ 0,0	93.7	94.3	94.1	93.9
	0,0 $\rightarrow$ 2,0	1.69	1.42	1.35	1.39
	0,0 $\rightarrow$ 2,2	0.152	0.112	0.140	0.129
	0,0 $\rightarrow$ 4,0	0.0045	0.0030	0.0026	0.0029
	0,0 $\rightarrow$ 4,2	0.00078	0.00047	0.00045	0.00037
	2,0 $\rightarrow$ 2,0	47.8	48.2	48.1	48.1
	2,0 $\rightarrow$ 2,2	1.43	1.15	1.21	1.23
	2,0 $\rightarrow$ 4,0	0.112	0.085	0.077	0.085
	2,0 $\rightarrow$ 4,2	0.0053	0.0032	0.0035	0.0036
	2,2 $\rightarrow$ 2,2	97.5	98.2	97.9	97.6
	2,2 $\rightarrow$ 4,0	0.0076	0.0042	0.0062	0.0050
	2,2 $\rightarrow$ 4,2	0.149	0.109	0.112	0.114
	4,0 $\rightarrow$ 4,0	50.0	50.4	50.3	50.4
	4,0 $\rightarrow$ 4,2	0.407	0.300	0.327	0.323
	4,2 $\rightarrow$ 4,2	50.8	51.0	51.0	51.0

Table 4.2: EP cross sections, as in Table 4.1, for *ortho-ortho* collisions.

Energy/ cm^{-1}	$J_A, J_B \rightarrow J'_A, J'_B$	Cross section/ $\text{\AA}^2$			
		$N_d = 12$	20	50	ZR surface
1008.0	1,1 $\rightarrow$ 1,1	103.3	103.7	103.7	103.5
	1,1 $\rightarrow$ 3,1	0.052	0.038	0.042	0.033
	3,1 $\rightarrow$ 3,1	61.3	62.3	62.0	61.6
2621.0	1,1 $\rightarrow$ 1,1	92.4	92.7	92.7	92.7
	1,1 $\rightarrow$ 3,1	0.818	0.718	0.712	0.731
	1,1 $\rightarrow$ 3,3	0.016	0.012	0.011	0.013
	3,1 $\rightarrow$ 3,1	47.4	47.7	47.7	47.7
	3,1 $\rightarrow$ 3,3	0.520	0.384	0.418	0.420
	3,3 $\rightarrow$ 3,3	99.4	100.2	100.0	100.1

Table 4.3: EP cross sections, as in Table 4.1, for *ortho-para* collisions.

Energy/ cm^{-1}	$J_A, J_B \rightarrow J'_A, J'_B$	Cross section/ $\text{\AA}^2$			
		$N_d = 12$	20	50	ZR surface
500.0	0,1 $\rightarrow$ 0,1	55.9	56.7	56.5	56.3
	0,1 $\rightarrow$ 2,1	0.015	0.011	0.0079	0.010
	2,1 $\rightarrow$ 2,1	162.5	167.3	164.9	162.8
1350.0	0,1 $\rightarrow$ 0,1	49.4	49.8	49.8	49.7
	0,1 $\rightarrow$ 2,1	0.442	0.310	0.301	0.340
	0,1 $\rightarrow$ 0,3	0.095	0.062	0.059	0.072
	0,1 $\rightarrow$ 2,3	0.0018	0.00087	0.0012	0.0011
	0,1 $\rightarrow$ 4,1	0.000004	0.000005	0.000004	0.000005
	2,1 $\rightarrow$ 2,1	50.4	50.7	50.6	50.6
	2,1 $\rightarrow$ 0,3	0.0029	0.0036	0.0022	0.0022
	2,1 $\rightarrow$ 2,3	0.042	0.029	0.025	0.028
	2,1 $\rightarrow$ 4,1	0.00025	0.00053	0.00054	0.00046
	0,3 $\rightarrow$ 0,3	53.3	53.6	53.3	53.3
	0,3 $\rightarrow$ 2,3	0.123	0.102	0.086	0.101
	0,3 $\rightarrow$ 4,1	0.000008	0.00001	0.000005	0.000005
	2,3 $\rightarrow$ 2,3	56.6	57.5	57.3	57.2
	2,3 $\rightarrow$ 4,1	0.00018	0.00037	0.00004	0.000002
	4,1 $\rightarrow$ 4,1	174.3	178.7	178.3	174.7

In each case, convergence of each of the elastic cross-sections within 1% of the corresponding exact ZR cross-sections has been achieved within 50 data points. Generally, the larger inelastic cross-sections are converged within 10%. All cross-sections are converged within 20% with the exception of the smallest ZR inelastic cross-section reported, that of $2,3 \rightarrow 4,1$ in Table 4.3. Additional data points ensure that this cross-section converges.

Another measure of the improvement in accuracy of the surface with increasing data set size is given by the average absolute error in the energy for a sample of molecular configurations. A sample of 2433 configurations were obtained by randomly selecting configurations from those at which MOLSCAT evaluates the PES in the course of a scattering calculation. The absolute interpolation error in the energy was determined for each configuration. Configurations with energies larger than 3000 cm^{-1} and with absolute values less than 0.5 cm^{-1} were not used as these bias the average towards configurations high on the repulsive wall and at long intermolecular separations. The average of the absolute errors, for several data sets, is plotted as a function of the number of points in the data set in Fig. 4.5. Convergence within 3 cm^{-1} is apparent after 50 points. For illustrative purposes, the interpolated and ZR surfaces are compared in Figs 4.4 and 4.6, for a selection of relative orientations of the diatoms.

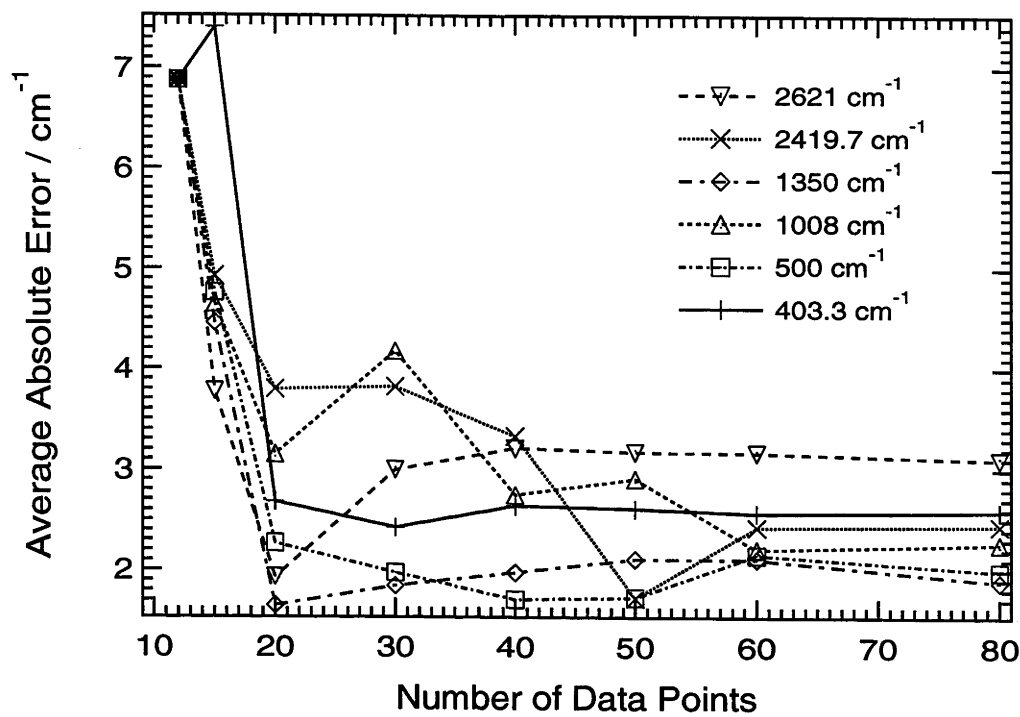


Figure 4.5: The average absolute interpolation error in the energy for a sample of molecular configurations (see text) is shown as a function of the size of the data set. Results are shown for six surfaces constructed using classical simulations at the energies indicated.

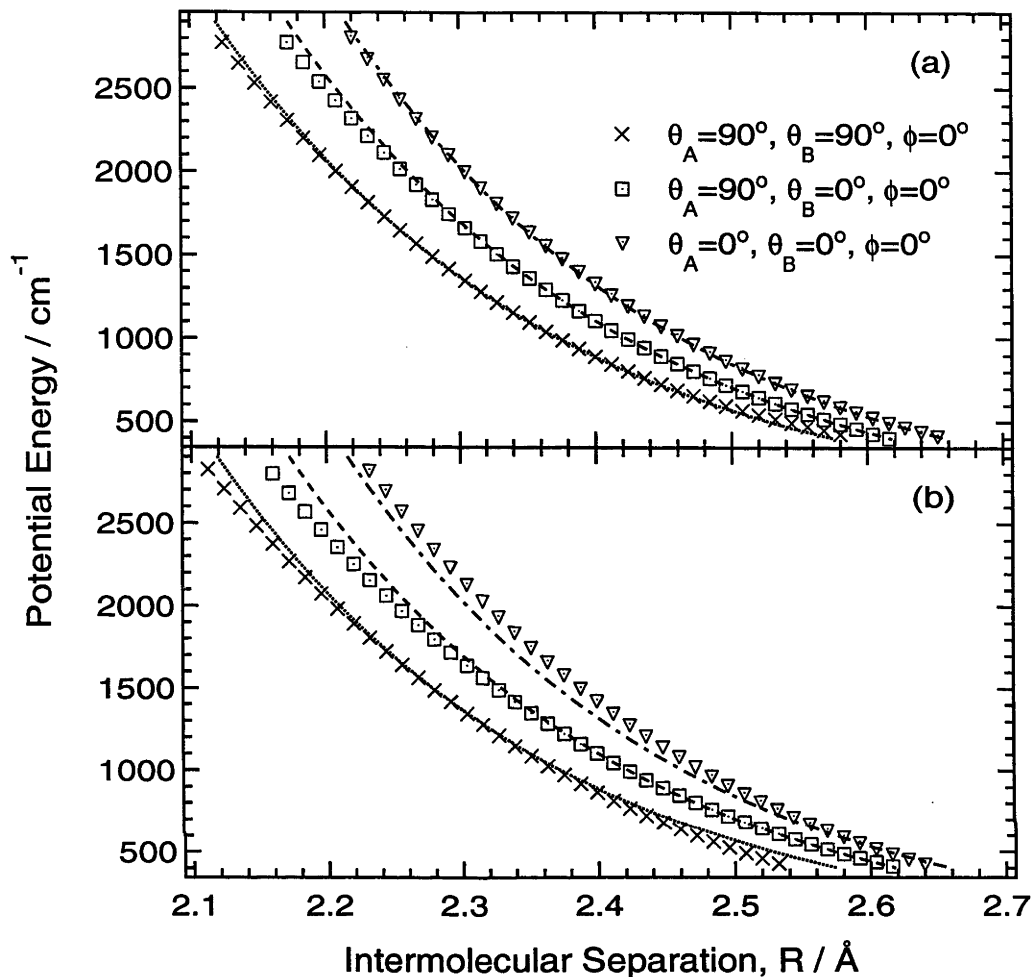


Figure 4.6: Similar to Fig. 4.4, except that the energy range has been altered to show the repulsive wall over the range of scattering energies considered.

4.3.4 Energy Dependence of the Interpolated PES

Tables 4.1, 4.2, and 4.3 demonstrate the accuracy of each interpolated PES at the energy at which it is constructed. How wide is the energy range in which equally accurate scattering may be performed for an interpolated PES constructed at a particular energy?

Inspection of Fig. 4.3 indicates that if the energy is large relative to the depth of the potential well, the distribution of data points does not vary significantly with the energy used in construction. Further, in Fig. 4.5, the average interpolation error is not obviously dependent on the energy at which the PES is constructed. However, Figs 4.4 and 4.6 indicate that a PES constructed at high energy is less accurate at low energy than a PES constructed at low energy and *vice versa*. To clarify the effect of this variation in accuracy on the rotational cross-sections, results for *para-para* scattering at a range of energies are shown in Table 4.4 for interpolated PES constructed at the largest and smallest energies considered.

The results in Table 4.4 show that, at this level of convergence, there is little or no energy dependence observed in the errors in the cross-sections over the range of scattering energies considered. Results for *ortho-ortho* and *ortho-para* scattering have been omitted as these data support the same conclusion.

Table 4.4: EP cross-sections, for *para-para* collisions, at two translational energies are shown for PES constructed at translational energy E_C/cm^{-1} and compared with corresponding values for the ZR potential.

Scattering energy/ cm^{-1}	$J_A, J_B \rightarrow J'_A, J'_B$	Cross section/ $\text{\AA}^2$		
		$E_C = 403.3$	2419.6	ZR surface
403.3	0,0 $\rightarrow$ 0,0	110.5	110.7	111.4
	0,0 $\rightarrow$ 2,0	0.018	0.019	0.022
	2,0 $\rightarrow$ 2,0	118.7	118.6	118.6
2419.7	0,0 $\rightarrow$ 0,0	94.2	94.1	93.9
	0,0 $\rightarrow$ 2,0	1.31	1.35	1.39
	0,0 $\rightarrow$ 2,2	0.137	0.140	0.129
	0,0 $\rightarrow$ 4,0	0.0025	0.0026	0.0029
	0,0 $\rightarrow$ 4,2	0.00045	0.00045	0.00037
	2,0 $\rightarrow$ 2,0	48.1	48.1	48.1
	2,0 $\rightarrow$ 2,2	1.19	1.21	1.23
	2,0 $\rightarrow$ 4,0	0.075	0.077	0.085
	2,0 $\rightarrow$ 4,2	0.0033	0.0035	0.0036
	2,2 $\rightarrow$ 2,2	98.0	97.9	97.6
	2,2 $\rightarrow$ 4,0	0.0065	0.0062	0.0050
	2,2 $\rightarrow$ 4,2	0.108	0.112	0.114
	4,0 $\rightarrow$ 4,0	50.4	50.3	50.4
	4,0 $\rightarrow$ 4,2	0.311	0.327	0.323
	4,2 $\rightarrow$ 4,2	51.0	51.0	51.0

4.3.5 Comparisons with Other Methods

A very different interpolation method has been applied to the H_2/H_2 system in previous work. Ramaswamy, Rabitz, and Green [4] performed quantum scattering studies on H_2/H_2 using an interpolation of *ab initio* energies [24, 25]. These authors used a fifth-order Lagrange (local polynomial) interpolation [26] of the radial coefficients in Eq. (4.1). The radial coefficients were determined at each intermolecular separation by fitting to *ab initio* energies calculated on a grid of intermolecular orientations. Various surfaces were constructed using different sets of *ab initio* calculations of the energy. Ramaswamy, Rabitz, and Green also extrapolated the radial coefficients at short-range and at long-range in the intermolecular separation.

We constructed an interpolated-extrapolated approximation to the ZR surface using the method of Ramaswamy, Rabitz, and Green. This employed calculations of the ZR energy at 40 configurations. Cross-sections calculated from this potential were compared with those obtained using the modified Shepard interpolation formula with the same data locations. The two sets of results were not significantly different. Hence, a similar number of data points intuitively located on a grid are sufficient to describe this particular potential using either method.

4.4 Summary and Conclusions

An iterative interpolation construction scheme for molecular potential energy surfaces has been modified to allow partial constraint of the molecular configurations represented in the data set. This approach has been demonstrated by application to the rotational inelastic scattering of two hydrogen molecules on a model surface.

Limiting the dimension of the configuration space in which data points are scattered allowed an accurate description of the model PES with only about 50

data points. A quantitative description of the very small inelastic cross-sections was obtained. By comparison, interpolation of reactive systems of four atoms in full dimensionality has required from 200 to 1000 data points [6, 27–32].

Convergence of the rotational inelastic cross-sections has been demonstrated for calculations using the effective potential approximation. Full close-coupled calculations have been found to show similar convergence.

We have found that data located on a grid, as in earlier studies on H_2/H_2 , results in an adequate interpolation in this four-dimensional case. However, it is likely that a prohibitively large number of grid points would be required for higher dimensional problems. Moreover, the iterative PES construction scheme is generic and has the advantage that it does not require intuition in spacing and locating the data.

In the general application of this approach, each data point is the center of a Taylor expansion for the PES in the full $3N-6$ dimensional configuration space, even though the data locations are confined to a lower dimensional subspace. This means that the potential is defined over the full configuration space. If only small amplitude motion takes place in the degrees of freedom which were constrained during the construction of the PES, the resultant surface may be sufficiently accurate in the whole relevant region of configuration space. The constrained degrees of freedom may well correspond to simple bond displacements, as in the case considered here. It has been demonstrated previously that a single second order Taylor expansion in reciprocal bondlengths is remarkably accurate for such small amplitude bond displacement motions. Nevertheless, it remains to be shown that this type of interpolated PES is sufficiently accurate to describe the dynamics in the degrees of freedom which were constrained during the construction of the PES, in addition to describing the motion in the unconstrained degrees of freedom.

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Part III

Ion-Molecule Reactions

Chapter 5

Ion-Molecule Reaction Dynamics

5.1 The Systems Studied

Reactions of ions with neutral molecules are important in many areas of chemistry. Ions are important in solution, and a study of the effects of solvation would be amenable to a methodology that employs constrained dynamics for the solvent molecules. However, solvated systems will remain a long-term goal while more modest systems still contain more atoms than previously attempted and provide more insight into the scalability of the methodology. The dynamics of ion molecule reactions are reviewed by Farrar [1].

Two ion-molecule systems have been studied: an anionic system and a cationic system. Anion species are typically excellent nucleophiles, and the chosen reaction is a classic example of nucleophilic substitution of an alkyl halide. To keep the system small, a primary alkyl halide has been chosen so the reaction is S_N2 , where the bulk kinetics are observed to be bimolecular. Solvation will be ignored here and a potential that considers only the interaction between the two reactants and ignores many-body terms involving neighbouring molecules limits the present study to the gas-phase. In the gas-phase, a double-well PES with stable complexes for geometries either side of the barrier are possible.

The cationic system examined in this thesis involves two cations that have featured in studies of interstellar chemistry [2]: the formyl cation, HCO^+ , and its structural isomer, the isoformyl cation, HOC^+ . Here, we consider the collision between HOC^+ and an alkyl halide. The alkyl halide is either protonated during the collision, or it can catalyse rearrangement of the HOC^+ cation to form HCO^+ . In the rearrangement, the halide atom is briefly protonated as it transfers the proton before exiting the reaction region. As for the $\text{S}_{\text{N}}2$ reaction, a complex on either side of the barrier is present.

5.2 Ion-Molecule Reaction Dynamics

A brief introduction to the terminology and simple collision models used in the treatment of the dynamics of ion-molecule reactions is presented. A comparison with the rates determined by these simple collision theories will be useful when analysing the results.

Collisions between ions and neutral molecules are typically more attractive than between neutral species [3, 4]. Collision theories were therefore developed for intermolecular potentials that account for the additional electrostatic forces. Different low energy collision models [5] are discussed below.

5.2.1 The Langevin Model

The Langevin-Gioumoussis-Stevenson model [6, 7] is derived from an ion-induced dipole theory for non-polar molecules and some elementary collision theory using point charges.

At large radial separation, r , between a point charge and a polarisable, non-polar, structureless molecule, the charge-induced dipole interaction energy, $V(r)$, is

$$V(r) = -\frac{\alpha q^2}{2r^4}, \quad (5.1)$$

where α is the static electric polarisability, and q is the charge. For the systems under study, $q = e$, the electronic charge. By convention, the units are assumed to e.s.u. so that the SI $(4\pi\epsilon_0)^{1/2}$ proportionality constant does not appear in subsequent expressions. The interaction potential for each system is shown in Fig. 5.1.

Considering only the relative motion of the structureless ion and polarisable neutral molecule, the Hamiltonian, H_L , is given by

$$H_L = \frac{p^2}{2\mu} + \frac{L^2}{2\mu r^2} - \frac{\alpha q^2}{2r^4} \quad (5.2)$$

$$= \frac{p^2}{2\mu} + V_{\text{eff}}(r), \quad (5.3)$$

where p is the radial linear momentum, μ is the reduced mass of the collision pair, and L is the orbital angular momentum of the pair which gives rise to a “centrifugal barrier” or maximum in the effective potential, V_{eff} at intermediate separations, as shown in Fig. 5.1

If the total energy of the collision is E , and the impact parameter is b , then $L = b\sqrt{2\mu E}$. The local maximum in V_{eff} occurs at a critical separation, $r_c(b, E)$, which is a function of b and E . The Langevin model assumes that reaction will always occur if the classical turning point, r_t , in the radial motion is smaller than r_c . This will be the case when the impact parameter is below a critical value, b_c :

$$b_c = \left(\frac{2q^2\alpha}{E} \right)^{\frac{1}{4}}, \quad (5.4)$$

which can be derived using elementary calculus because $\partial V_{\text{eff}}(r)/\partial r = 0$ and $V_{\text{eff}}(r) = E$ when $b = b_c$. Rearrangement in terms of b_c is afforded by the substitution of the rotational energy $L^2/2\mu r_c^2$ with Eb^2/r_c^2 .

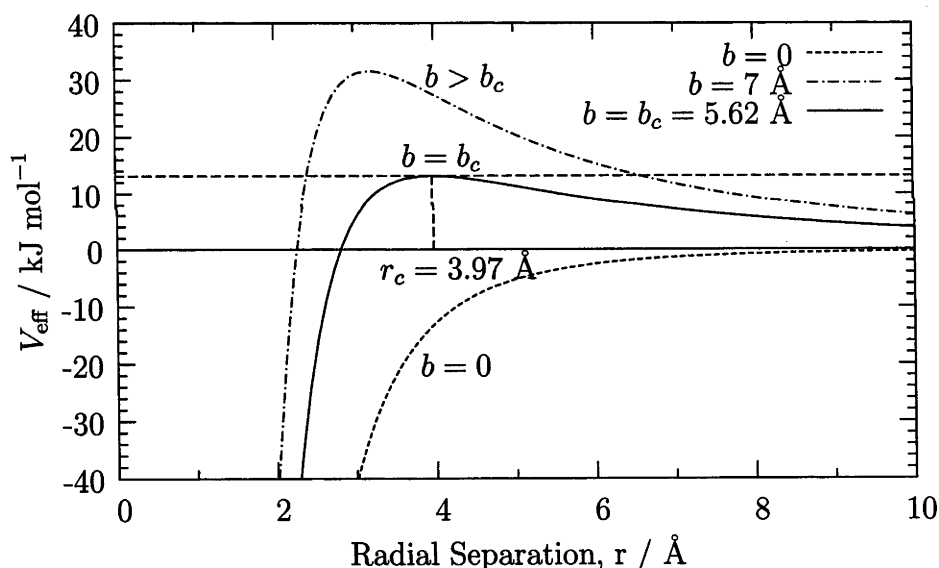


Figure 5.1: $V_{\text{eff}}(r)$ shown for three different impact parameters for $\text{CH}_3\text{Cl} + \text{F}^-$ where the volume polarisability of CH_3Cl is $4.72 \text{ \AA}^3$ [8]. The critical radial separation r_c is related to the critical impact parameter b_c by $r_c = b_c/\sqrt{2}$.

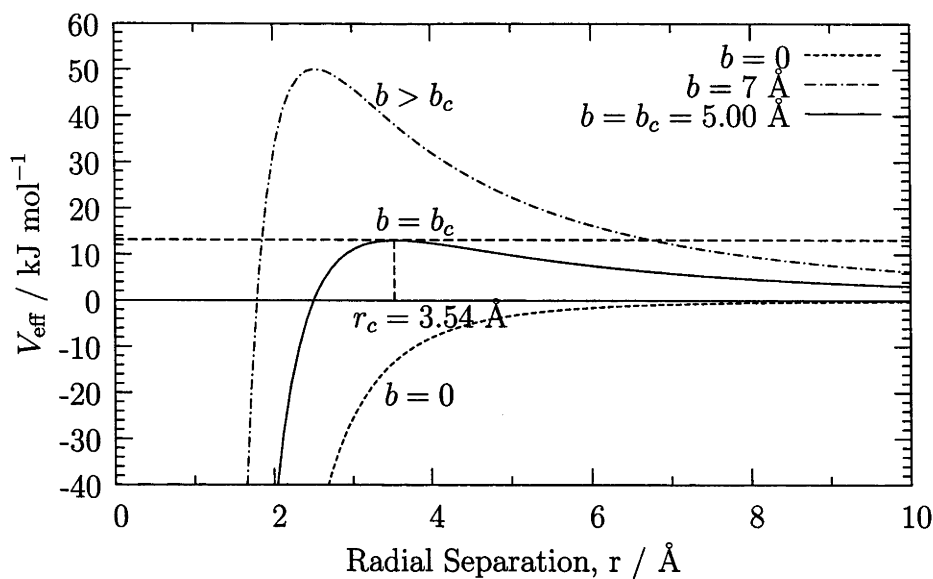


Figure 5.2: $V_{\text{eff}}(r)$ shown for three different impact parameters for $\text{CH}_3\text{F} + \text{HOC}^+$ where the volume polarisability of CH_3F is $2.97 \text{ \AA}^3$ [8]. The critical radial separation r_c is related to the critical impact parameter b_c by $r_c = b_c/\sqrt{2}$.

The relationship between the impact parameter and the probability of collision, assumed to be the probability of reaction, is shown in Fig. 5.3 for the Langevin model.

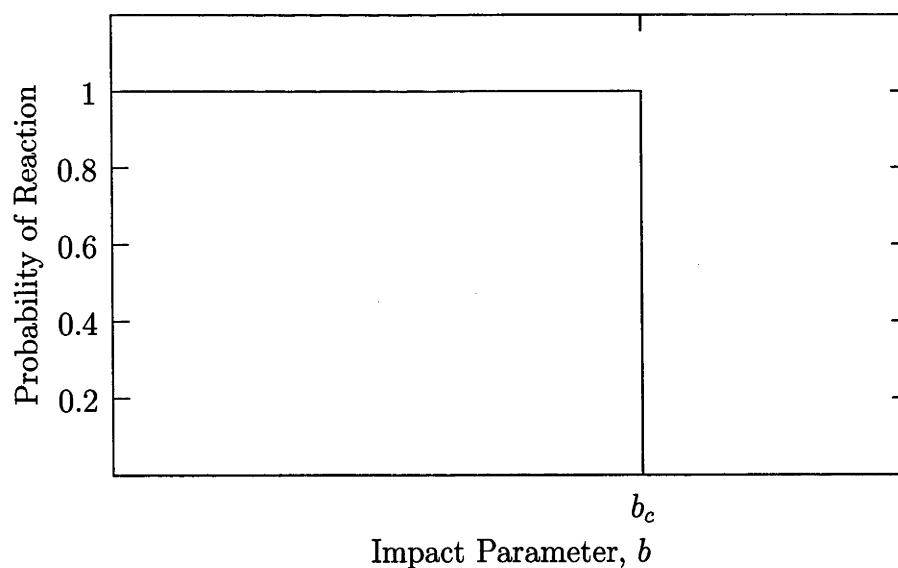


Figure 5.3: Langevin probability of reaction as a function of impact parameter.

With these assumptions, it is a simple matter to derive the consequent expression for the thermal rate constant:

$$k_L = 2\pi q \sqrt{\frac{\alpha}{\mu}}, \quad (5.5)$$

and reaction cross-section:

$$\sigma_L(v) = \frac{2\pi q}{v} \sqrt{\frac{\alpha}{\mu}} \quad (5.6)$$

at a given velocity easily derived from the relative translational energy using $v = \sqrt{2E/\mu}$.

The Langevin rate constant tends to underestimate the rate constants of ion-polar molecule collisions by not accounting for the affect of the dipole moment μ_D of the neutral molecule on the interaction potential:

$$V(r, \theta) = -\frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2} \cos \theta \quad (5.7)$$

where θ is the angle formed by the dipole and the line of centres.

Theories such as the Average Dipole Orientation (ADO) and Angular (momentum conservation) Average Dipole Orientation (AADO) theories can be invoked to derive temperature dependent rate-constants that account for the effect of a permanent dipole moment [5]. Further theories, such as the Average Quadrupole Orientation (AQO) theory, deal with quadrupole moments or induced dipole-induced dipole forces. However these effects are typically small [5]. Su and Chesnavich [9–11] have determined a parametrised capture rate theory based on classical trajectory calculations that is useful between 50 K and 1000 K in the low

energy regime, using the interaction potential in Eq. (5.7). In this thesis, we compare rate constants and cross-sections with values determined from the Langevin theory because of its inherent simplicity, only noting where previous authors have compared with values derived from other theories for the system under study.

5.2.2 The Double-Well Model for Ion-Molecule Reactions

Due to the ion-dipole and ion-induced dipole attractions between ions and molecules, the collision rate constants are larger than if the partners in the bimolecular collision are both uncharged. A bimolecular reaction is considered “fast” [12] if the rate constant is greater than $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature. Ion-molecule reactions usually fit this definition [13].

Originally, the potential along the reaction coordinate for an ion-molecule reaction was believed to be epitomised by a deep single well. After experimental work was completed which measured slow rates of proton transfer to delocalised anions it was suggested that the potential along the reaction coordinate was a double well, as depicted in Fig. 5.4, where a transition state, although possessing an potential energy below the energy of the reactants, does exist [13, 14]. The existence of such a central barrier slows the reaction, and indicates the presence of two intermediates, I_R and I_P .

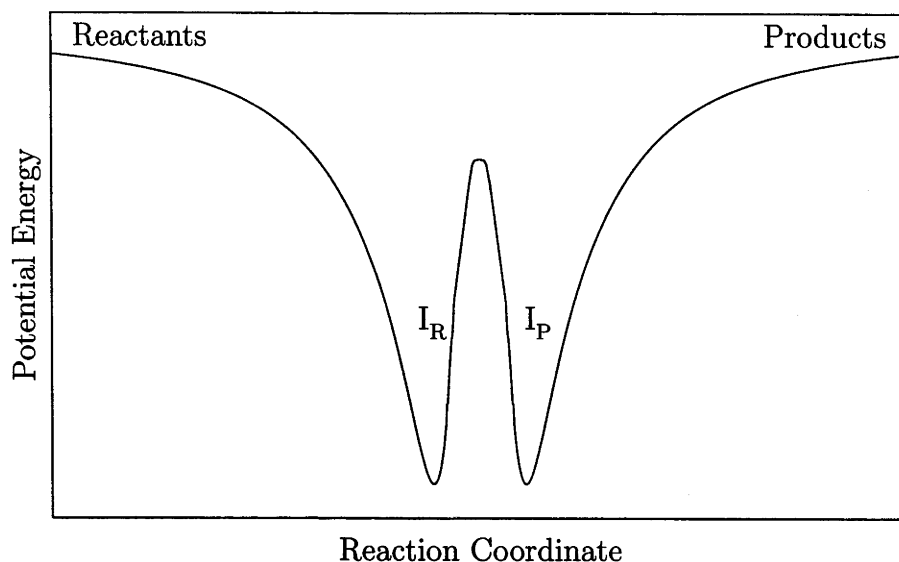


Figure 5.4: Schematic energy profile for ion-molecule reactions that follow the double well model.

The observation [15] of slow rates for nucleophilic substitutions of closed-shell anions provided additional evidence that the existence of central barriers could be generalised to all ion-molecule reactions. The rates for these substitutions were compared with those calculated by Rice-Ramsperger-Kassel-Marcus (RRKM) theory to determine the height of the central barrier. Early calculations indicated small central barriers for reactions such as $F^- + CH_3F$ [16–18], and experimental and theoretical studies of S_N2 ion-molecule reactions that support this feature of the PES continue to be reported [19].

A consequence of the existence of a tight transition state between the two separate intermediates I_R and I_P is that the kinetics are controlled by competitive unimolecular reactions involving the intermediates [20]. Fragmentation may occur to reactants or products through an “orbiting” transition state, or rearrangement via the tight transition state between the intermediates.

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Chapter 6

An S_N2 Reaction: CH₃Cl + F⁻

Energy transfer processes are important in many reaction mechanisms, but so far only non-reactive systems have been discussed. Here we discuss the application of the construction of PES for reactions using constrained dynamics for the first time.

6.1 Introduction

Larger systems are usually studied using classical trajectories, where quantum and even semi-classical methods become unfeasible. A full-dimensional quantum treatment is so far out of the question for more than four atoms [1–4]. With the choice of how to study the dynamics of large systems having been decided, it remains to choose a suitable method of calculating the potential which will yield accurate dynamical results.

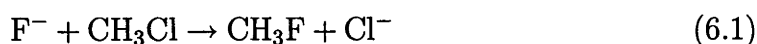
Several possibilities for calculating the potential sufficiently cheaply have been proposed and discussed in earlier chapters. One possibility is the “brute-force” approach. On-the-fly calculation of the *ab initio* energy and gradients at every timestep of a dynamical simulation is known as “direct *ab initio* dynamics” or

simply as *direct dynamics*. This approach wins favour through its simplicity. However, the computational expense involved necessarily limits the level of *ab initio* theory that can be used and therefore the accuracy of the PES is compromised further than if an accurate approximation is chosen. The problem is exacerbated by scalability: Computation time of *ab initio* methods is typically greatly increased when even a modest increase in accuracy is desired — resulting from increases in basis set size and level of theory.

Consider that a trajectory might run for 2 ps in 0.1 fs timesteps, and that 500 of these trajectories may be required in order to obtain a statistically precise result — 10^7 gradient evaluations will be required. To make matters worse, higher levels of theory which afford the electron correlation that is almost always essential for reactive systems increase the time for computation by orders of magnitude. Trajectories are amenable to parallelisation, but if 30 minutes are required to calculate the forces at each timestep then the process is still horrendously expensive using current technology. Finally, there will always be systems larger than those possible to study accurately with direct dynamics, and other techniques will be used.

It is assumed that the algorithm discussed in this work can be verified as equivalent to the *ab initio* surface used in direct dynamics, because the dynamics must be seen to *converge*.

As a recent example of this difficulty, theoretical gas-phase studies of the reaction



by direct dynamics have been published for collinear [5] and near-collinear classical trajectories [6], by Tachikawa and co-workers. Due to the large computational cost of the trajectories, only the results from one trajectory are reported. The authors

chose a level of theory which appeared to be adequate to the task at stationary points and separated equilibrium structures, and was fortunately inexpensive to calculate. However, this level of theory did not include electron correlation which may be important at geometries that are encountered during a trajectory. The basis set is also much smaller than would be expected to be required for a system with three heavy, polarisable, atoms (3-21+G(d)). In our work, it was decided that electron correlation must be included and that the PES construction method must be tested with a higher level of the theory.

Tachikawa and co-workers later (2002) studied [7] the effect of solvation by one water molecule on the fluoride ion reactant, because it is known [8, 9] that the reaction rate with $F^-(H_2O)$ is significantly smaller than the rate for the F^- reaction. The authors note that the large number of degrees of freedom make fitting the potential difficult. However, in using direct dynamics they have once more been limited to a lesser level of theory, not accounting for electron correlation and using the STO-3G basis set for the water molecule. A small number (100) trajectories were run. However, these were sufficient to determine branching ratios (there are three channels for the solvated system), at three different collision (initial translational) energies. Random orientations were chosen in the initial conditions in contrast to previous studies of the non-solvated system. The authors conclude that the level of theory used was adequate to discuss the dynamics qualitatively and comment that the development of faster processors will allow a more detailed study. Nevertheless, it is clear that such a direct dynamics calculation cannot yet employ a reliable level of *ab initio* theory.

In the same year (2002), Hase and co-workers reported classical direct dynamics results for $\text{OH}^- + \text{CH}_3\text{F}$ using an MP2/6-31+G(d) PES. Again only a small number (64) of trajectories were performed, this time only from the central barrier. The investigators demonstrate a relationship between inability of the trajectories to explore the deep potential minimum for the system and inefficient intramolecular vibrational energy redistribution (IVR). Again, it is stressed that these were qualitative results that required serious computational resources.

More recently (2003), Mugnai, Cardini and Schettino [10] performed *Car-Parrinello* [11–13] molecular dynamics on $\text{CH}_3\text{Cl} + \text{F}^-$. The authors performed “impact trajectories” using only a small number of non-collinear starting geometries at a separation of only 4 Å. The resulting excitation of the C–F stretching mode was in agreement with work by Tachikawa and Igarashi [6]. However, Mugnai, Cardini and Schettino also found that energy is particularly transferred to the umbrella motion, after overcoming the barrier.

An excellent review of experimental and theoretical investigations into $\text{S}_{\text{N}}2$ reactions, prior to 2002, can be found in Ref. 14.

The energy profile (presented later in Fig. 6.2) for reaction (6.1) corresponds to the double well profile introduced in Chapter 5 (compare with Fig. 5.4). Formation of complexes with significant lifetimes is therefore possible.

When considering complex formation in the $\text{CH}_3\text{Cl} + \text{F}^-$ reaction, it is useful to review similar $\text{S}_{\text{N}}2$ reactions. The symmetric reaction, $\text{CH}_3\text{Cl} + \text{Cl}^-$, has been studied by Hase and co-workers [15] using classical trajectories with a fitted potential. The energy profile for the symmetric reaction does possess a barrier above the energy of the reactants (and products) with possible complex formation in both the reactant and product channels. Trajectories were performed with a collision energy less than the height of the barrier above the energy of the reactants in order to study the lifetimes of the formed complexes. Trajectories with energy sufficient

to overcome the barrier (approximately 13 kJ mol^{-1}) were also examined and also displayed significant complex formation.

Igarashi and Tachikawa performed classical trajectories for the $\text{CH}_3\text{Cl} + \text{F}^-$ reaction. However, the initial conditions were chosen to examine specific mechanisms. There, the impact parameter and relative translational energy were both set to zero. In addition, the maximum initial C–Cl distance was $6.38 \text{ \AA}$; a distance where the orientation dependence of the potential is still significant. The authors discovered that a near-collinear collision ($\angle\text{F–C–Cl} = 179.8^\circ$) led to substitution through a direct mechanism; and that side-attack (150.3°) initially rebounded the F^- anion but was followed by a second collision that led to substitution. Complex formation is not reported in their work with single trajectories, yet it is possible that a different angle of attack or different impact parameter could lead to formation of a complex with a significant lifetime.

An $\text{S}_{\text{N}}2$ reaction with a similar energy profile to $\text{CH}_3\text{Cl} + \text{F}^-$ is the reaction of $\text{CH}_3\text{Br} + \text{Cl}^-$. This reaction has been studied by Wang, Peslherbe and Hase [16] using classical trajectories. Association was found to be significant in comparison with the small cross-sections (at different collision energies) determined for substitution. In terms of the energy profile, the barrier is not as far below the energy of the reactants as it is for $\text{CH}_3\text{Cl} + \text{F}^-$, so that complex formation may be relatively less important for the latter system.

For $\text{CH}_3\text{Cl} + \text{Cl}^-$, Vande Linde and Hase [15] defined direct substitution as a single barrier crossing before reaching an inner turning point for the intermolecular R_{CCl^-} distance and formation of products without passing through an inner turning point in the product channel. Otherwise association is assumed to have taken place. Trajectories running for 25 ps were considered captured, if these were not found to satisfy the non-reactive end-test.

Trajectory calculations for $\text{CH}_3\text{Cl} + \text{F}^-$, with measurements of average complex

lifetimes between¹ approximately 0.2 ps and 2 ps were reported by Su, Wang and Hase [17] at collision energies between 4.8 kJ mol⁻¹ and 67 kJ mol⁻¹ (0.05–0.70 eV) respectively. The results of the these authors are compared with the present calculations below.

6.2 Computational Details

6.2.1 Constraints

The degrees of freedom to be constrained are the C–H internuclear distances. In accord with studies of the non-reactive scattering systems the distances are constrained during trajectories using RATTLE. A pictorial representation of the set of 15 internuclear distances used in the interpolation is shown in Fig. 6.1. As in previous chapters, the internuclear distance between atoms A and B is represented as R_{AB} in the text.

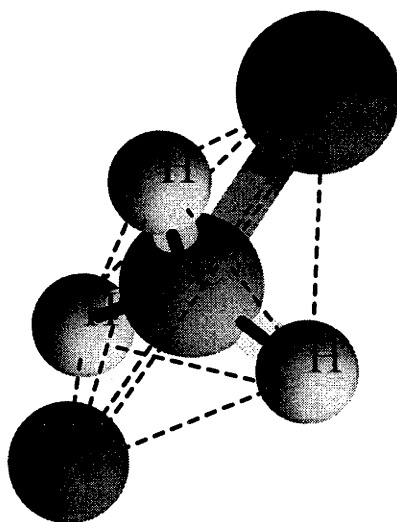


Figure 6.1: Internuclear distances used in the interpolation where the constraints are marked by solid lines.

¹A small temperature-dependence between 50 and 488 K was observed. Average lifetimes for reactant and product complexes differed by a maximum of 0.5 ps.

Validity of Constrained Dynamics

For a reactive system, the colliders can undergo structural changes. The validity of constraining the C–H bonds will be investigated. ZPVE in the C–H stretching modes has been removed from the internal energy used in the trajectory simulations. Owing to the frequencies of these modes, a large proportion of the internal energy of the unconstrained molecule is in these modes. In effect, freezing these modes does not allow this part of the ground state vibrational energy to leak into the rest of the molecule. Leakage of ZPVE, an age-old problem of classical trajectories for larger polyatomic systems, is actually reduced through the use of constraints. A technique that is often employed is the removal of all ZPVE from the system. In previous studies of S_N2 reactions [15, 16] the effect of ZPVE has been examined by running trajectories with and without ZPVE.

Vande Linde and Hase [15] reported in classical trajectory studies of $\text{CH}_3\text{Cl} + \text{Cl}^-$ that vibrational mode-specific reaction rate enhancement leads to measurable deviations from statistical theories such as RRKM [18] theory. Experimental evidence of non-statistical behaviour was provided by Graul and Bowers by the observation of vibrational excitation in the dissociation products of $\text{Cl}^-(\text{CH}_3\text{Br})$. A range of evidence of non-statistical behaviour in other S_N2 reactions has been reviewed by Ryaboy [19]. Importantly, Vande Linde and Hase suggested that only the $\text{Cl}^- \cdots \text{CH}_3\text{Cl}$ stretch and the two $\text{Cl}^- \cdots \text{CH}_3\text{Cl}$ bending modes are active degrees of freedom. Therefore, normal modes where the R_{CH} internuclear distances are most involved are likely to be spectator modes.

Whether the substitution is direct or indirect, the C–H stretching modes are not required for the Walden inversion to take place. For a direct substitution, which occurs on the timescale of a vibrational period for the C–F and C–Cl stretching modes, we postulate that the C–H stretches will not be significant because the vibrational period for these higher frequency modes will be short in comparison.

6.2.2 Parameters

Parameters used in the construction of PES and subsequent dynamics are shown in Tables 6.1 and 6.2 below. The meaning of these parameters has been explained in detail in Chapter 2 and for a specific application in Chapter 3. Parameters used in the dynamics were different to the construction parameters only to allow more efficient sampling in the interaction region but without restricting the volume of configuration space explored. Unconstrained trajectories were also performed on the final surface constructed *with* constraints, however, the parameters used for constrained dynamics (apart from the constraints themselves) on the same surface were appropriate. The same timestep was found to be sufficient for the unconstrained dynamics as for the constrained dynamics, despite the presence of high frequency C–H stretching motions. The surfaces were constructed using alternating h -weight and variance sampling.

Table 6.1: Parameters used in PES construction and in trajectory calculations where all trajectories have been performed with constrained degrees of freedom.

Parameter	Symbol	Construction ^a	Dynamics ^a
<i>Constraints</i>			
C–H bondlengths	R_{CH}	1.069 Å(saddle point)	1.069 Å
<i>Dynamics</i>			
Maximum Impact Parameter	b_{max}	5 Bohr	22 Bohr
Initial Fragment Separation	d_{ab}	50 Bohr	50 Bohr
Timestep	Δt	0.02 fs	0.02 fs
Number of trajectories	n_{traj}	10	1200
CH ₃ Cl Internal Energy	ZPVE, $T_{\text{rot}} = 0$ K	17 mHartree	17 mHartree
Relative Translational Energy	E_{rel}	5 mHartree	5 mHartree
<i>Configuration Sampling</i>			
Trajectory Sampling Frequency	f_{print}	1/200 Δt	
Points selected/iteration		1	
<i>Interpolation</i>			
Weight function terms		2	2
Weight function powers		2,12	2,12
Weight function cutoffs	$w_{\text{tol},i}, w_{\text{tol},o}$	$10^{-6}, 10^{-9}$	$10^{-6}, 10^{-10}$
Neighbour list updates	n_i, n_o	1/5 Δt , 1/10 Δt	1/5 Δt , 1/15 Δt
Neighbours in confidence radius	n_{neigh}	64	64

^a Atomic units (Hartree and Bohr) were used in the calculations and are not converted here to avoid rounding off. Units are converted to S.I. recommended units in the text as appropriate.

Table 6.2: Parameters used in construction of the PES without constraints and in unconstrained trajectory calculations on the full-dimensional surface.

Parameter	Symbol	Construction	Dynamics
<i>Dynamics</i>			
Maximum Impact Parameter	$b_{\max}$	5 Bohr	22 Bohr
Initial Fragment Separation	d_{ab}	50 Bohr	50 Bohr
CH ₃ Cl Internal Energy	ZPVE, $T_{\text{rot}} = 0$ K	39 mHartree	39 mHartree
Relative Translational Energy	E_{rel}	5 mHartree	5 mHartree
Timestep	Δt	0.01 fs	0.02 fs
Number of trajectories	n_{tra}	10	1200
<i>Configuration Sampling</i>			
Trajectory Sampling Frequency	f_{print}	$1/500\Delta t$	
Points selected/iteration		4	
<i>Interpolation</i>			
Weight function terms		2	2
Weight function powers		2,12	2,12
Weight function cutoffs	$w_{\text{tol},i}, w_{\text{tol},o}$	$10^{-5}, 10^{-8}$	$10^{-6}, 10^{-10}$
Neighbour list updates	n_i, n_o	$1/5\Delta t, 1/15\Delta t$	$1/5\Delta t, 1/15\Delta t$
Neighbours in confidence radius	n_{neigh}	64	64

The total ZPVE in the unconstrained CH₃Cl was estimated using one half of the sum over the frequencies for CH₃Cl. A normal mode analysis of unconstrained CH₃Cl indicated the presence of modes where C–H stretching motions were predominant. Thus, these modes were simply removed from the summation when the R_{CH} distances were constrained. The ZPVE in the constrained molecule was still calculated using frequencies for the unconstrained molecule.

6.2.3 *Ab Initio* Calculations

The reaction profile for reaction (6.1) is shown in Fig. 6.2.

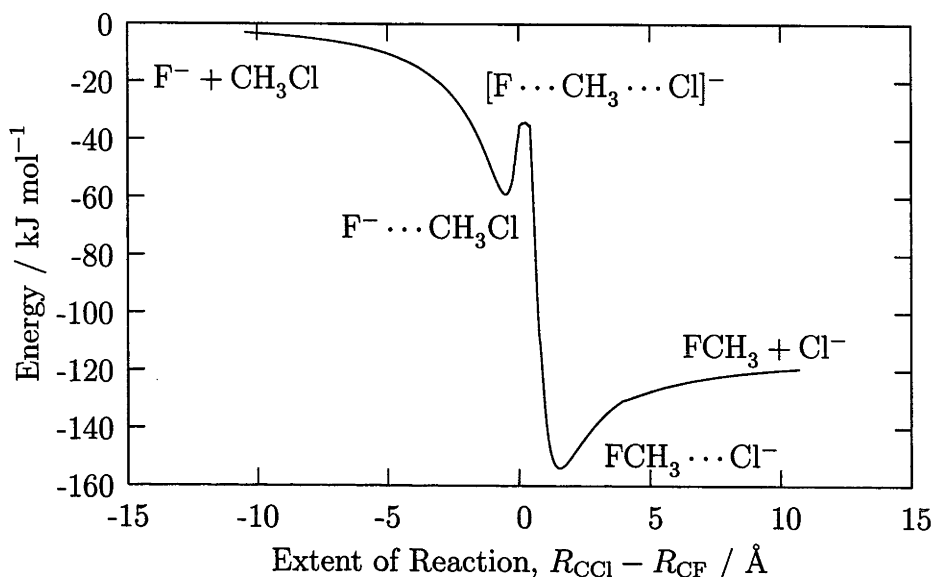


Figure 6.2: Potential energy as a function of extent of reaction ($R_{\text{CCl}}-R_{\text{CF}}$) for the $\text{CH}_3\text{Cl} + \text{F}^-$ reaction where each point was optimised and calculated using MP2/6-31+G(d). Constraints have been applied. Note that the graph does not extend to a sufficient distance to judge the energies of either separated reactants or products.

Preliminary energetics calculations for reaction (6.1) are summarised in Table 6.3, and a comparison of calculated frequencies with experiment are shown in Table 6.4. All *ab initio* calculations were performed using the GAUSSIAN package [20].

Calculations in Tables 6.3 and 6.4 are representative: It is important to investigate a wide range of basis sets and levels of theory to ensure that an accurate surface can be constructed in time that is practical. As this study was the first application of the methodology to a system this size, the *ab initio* calculations should use the least costly method required because the number of calculations needed to obtain a converged surface was not known *a priori*. Further experience with

larger systems with different potential energy ranges and features will be useful in the estimation of time requirements in future.

Table 6.3: Comparison of energies (relative to the energies of the reactants) and geometries from *ab initio* calculations. Relative energies optimised with the R_{CH} distance constrained to the value at the saddle point is shown in parentheses.

Level of Theory/ Basis Set	Bond Length/Å			Angle/°		$V_{\text{rel}}/$ kJ mol ⁻¹
	R_{CF}	R_{CCl}	R_{CH}	$\angle$ Cl-C-H	$\angle$ H-C-H	
F ⁻ + CH ₃ Cl reactants						
HF/3-21+G(d) ^a	∞	1.806	1.076	108.2	110.7	0.0
MP2/6-31+G(d)	∞	1.781	1.089	108.9	110.1	0.0
MP2 ^b	∞	1.778	1.083	108.6	110.3	0.0
CCSD(T) ^c	∞	1.787	1.086	18.4	110.5	0.0
F ⁻ ... CH ₃ Cl complex						
HF/3-21+G(d) ^a	2.481	1.904	1.068	106.4	112.3	-66.1
MP2/6-31+G(d)	2.617	1.833	1.083	108.5	110.4	-58.4(58.0)
MP2 ^b	2.511	1.837	1.077	108.1	110.8	-66.1
CCSD(T) ^c	2.502	1.853	1.080	107.6	111.2	-66.1
[F ... CH ₃ ... Cl] ⁻ saddle point						
HF/3-21+G(d) ^a	2.170	2.139	1.061	98.0	118.1	-59.0
MP2/6-31+G(d)	2.016	2.142	1.074	84.4	119.1	-33.2
MP2 ^b	1.997	2.106	1.069	95.9	119.0	-48.5
CCSD(T) ^c	2.030	2.121	1.072	96.3	118.8	-53.3
FCH ₃ ... Cl ⁻ complex						
HF/3-21+G(d) ^a	1.464	3.273	1.073	72.8	111.6	-190
MP2/6-31+G(d)	1.438	3.255	1.086	72.0	110.9	-153.5(-153.0)
MP2 ^b	1.413	3.178	1.082	70.9	109.9	-172
CCSD(T) ^c	1.417	3.188	1.086	71.1	110.1	-178
FCH ₃ + Cl ⁻ products						
HF/3-21+G(d) ^a	1.434	∞	1.077	72.6	111.4	-144
MP2/6-31+G(d)	1.407	∞	1.090	71.9	110.9	-113.8(-113.5)
MP2 ^b	1.383	∞	1.083	71.4	110.3	-131
CCSD(T) ^c	1.387	∞	1.090	71.3	110.2	-138

^aReference 5.

^bReference 21. Basis set: 6-311++G(2df,2pd).

^cReference 22. Basis set: 289 contracted Gaussian-type orbitals (cGTOs). Geometries optimised with 244 cGTOs.

Table 6.4: Comparison of frequencies from *ab initio* calculations and experiment.

Mode	HF / 3-21+G(d)	MP2 / 6-31+G(d)	MP2 ^a / 6-311++G(2df,2pd) Frequency/cm ⁻¹	CEPA-1 ^b	Experiment ^c
F + CH ₃ Cl Reactants					
A ₁ , C-Cl stretch	717	779	769	741	751
E, CH ₃ rock	1143	1079	1042	1043	1037
A ₁ CH ₃ deform.	1542	1464	1397	1397	1396
E CH ₃ deform.	1653	1529	1502	1503	1496
A ₁ , C-H stretch	3255	3141	3120	3088	3088
E, C-H stretch	3350	3251	3232	3184	3183
F ⁻ ... CH ₃ Cl Complex					
E, F ⁻ bend	131	73	78	107	
A ₁ , F-C stretch	171	157	174	181	
A ₁ , C-Cl stretch	470	639	612	560	
E, CH ₃ rock	1087	1014	966	962	
A ₁ CH ₃ deform.	1433	1358	1277	1280	
E CH ₃ deform.	1605	1491	1463	1483	
A ₁ , C-H stretch	3339	3210	3186	3157	
E, C-H stretch	3470	3340	3317	3273	
[F ... CH ₃ ... Cl] ⁻ Saddle Point					
E, F-C-Cl bend	231	254	257	230	
A ₁ , F-C-Cl stretch	277	289	305	289	
E, CH ₃ rock	1079	1039	1007	1043	
A ₁ , out-of-plane bend	1328	1199	1151	1159	
E CH ₃ deform.	1555	1450	1427	1426	
A ₁ , C-H stretch	3386	3258	3224	3202	
E, C-H stretch	3573	3460	3422	3374	
reaction coordinate	373i	520i	501i	401i	
FCH ₃ ... Cl ⁻ Complex					
E, Cl ⁻ bend	108	90	94	96	
A ₁ , C-Cl stretch	103	101	113	109	
A ₁ , F-C stretch	972	955	989	982	
E, CH ₃ rock	1239	1169	1165	1162	
A ₁ CH ₃ deform.	1571	1473	1446	1449	
E CH ₃ deform.	1638	1534	1504	1507	
A ₁ , C-H stretch	3296	3172	3138	3095	
E, C-H stretch	3407	3298	3255	3191	
FCH ₃ + Cl ⁻ Products					
A ₁ , F-C stretch	1075	1051	1086	1078	1078
E, CH ₃ rock	1263	1211	1211	1212	1204
A ₁ CH ₃ deform.	1611	1525	1505	1502	1496
E CH ₃ deform.	1653	1550	1521	1511	1515
A ₁ , C-H stretch	3247	3126	3097	3057	3075
E, C-H stretch	3339	3237	3199	3134	3147

^aReference 21.^bReference 23.^cExperimental harmonic frequencies for CH₃Cl and CH₃F from Refs 24 and 25, respectively.

The Taylor expansion in Eq. (2.21) will be truncated to second order. Frequency calculations will therefore be performed for all points added to the interpolation data set. As points are added to a particular region of configuration space, the contribution derivatives make to the interpolated energy decreases. However, a comparison of the frequencies with experimental values is useful to determine whether or not the shape of the PES at stationary points is realistic.

The method chosen from this investigation was MP2/6-31+G(d) due to reasonable agreement with larger basis sets and levels of theory. The agreement with Hartree-Fock was considered to be accidental — neglecting the electron correlation at geometries different to the stationary points listed in these tables was judged unwise.

6.2.4 Trajectory End-Tests

Previous applications of the interpolation methodology [26] have been concerned with the determination of cross-sections, rate constants and branching ratios. In this work, the methodology has been applied to a system with significant complex formation for the first time. Studies of S_N2 reactions by Hase and coworkers [15–17] have investigated lifetimes of complexes formed during classical trajectories. It is interesting to consider lifetime measurement as another dynamical observable for testing the interpolated PES.

Basic end-tests for reactive and non-reactive trajectories involve determining that the separation between the fragments is large enough and testing the velocities to ensure that the separation is increasing.

It is important to distinguish between indirect and direct reactive collisions. This is because indirect collisions should also be considered association reactions. Association was defined to occur if multiple turning points in the interfragment motion were reached during a trajectory. The complex lifetime was defined as the

time interval between the first turning point and the last turning point encountered before a barrier crossing or successful end-test for products or non-reaction. Barrier crossing was determined by comparing the difference between the distance from the centre-of-mass of the CH_3Cl to the F^- ion, $R(\text{CH}_3\text{Cl}_{\text{c.o.m}} \cdots \text{F}^-)$, and the distance from the centre-of-mass of the CH_3F to the Cl^- ion, $R(\text{CH}_3\text{F}_{\text{c.o.m}} \cdots \text{Cl}^-)$. A correction, δ , is applied to the difference to set the difference to zero at the transition state. If $R(\text{CH}_3\text{Cl}_{\text{c.o.m}} \cdots \text{F}^-) - R(\text{CH}_3\text{F}_{\text{c.o.m}} \cdots \text{Cl}^-) - \delta$ changes sign during the course of a trajectory, the barrier has been crossed. The number of times barrier recrossing occurred during each trajectory was recorded. The sign is used to determine whether the trajectory is on the “reactant-side” or the “product-side” of the reaction. The appropriate distance $R(\text{M}_{\text{c.o.m}} \cdots \text{X}^-)$ is monitored every time-step.

6.3 Analysis of Results

6.3.1 Distribution of *Ab Initio* Points

Initial data points were chosen along the MEP using standard optimisation techniques to find minimal energy configurations for local minima and configurations for saddle points.

Data was successfully added to the PES following the iterative scheme, and convergence of cross-sections, and distribution of angular momentum and relative kinetic energy were achieved. Unfortunately, in the early stages of PES construction, the dynamics tend to be inaccurate and many trajectories fail to conserve energy even when allowed relatively small timesteps. Such behaviour is normal, and desirable, because such trajectories spend proportionately more time in wildly inaccurate parts of the surface, where there very few data points and where there will commonly be spurious wells [27]. This allows plenty of timesteps to sample these regions.

The fully constructed interpolated PES is illustrated in Fig. 6.3.

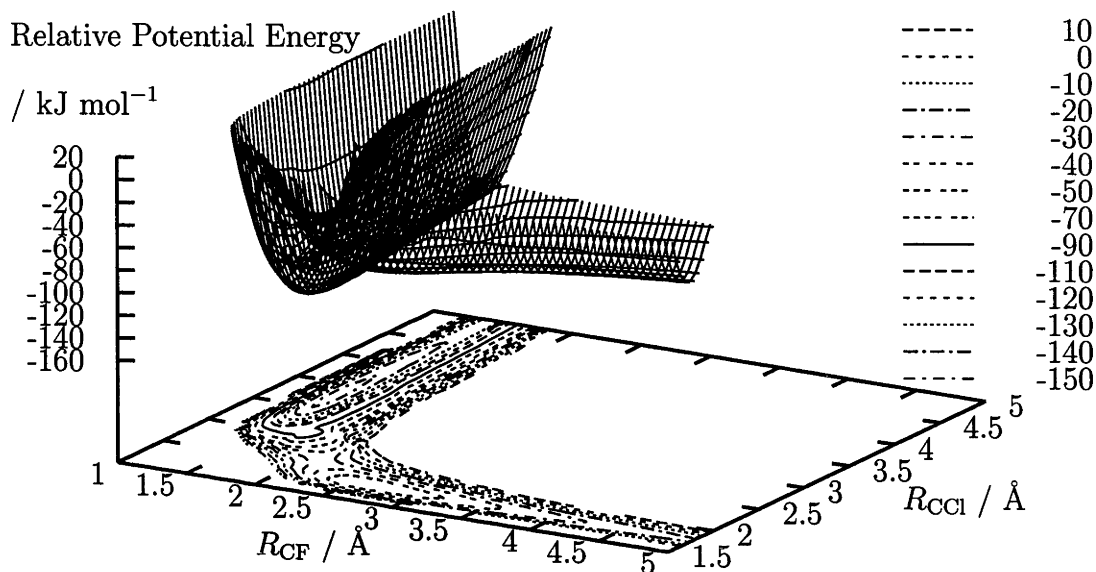


Figure 6.3: Interpolated PES for the reaction of $\text{CH}_3\text{Cl} + \text{F}^-$ generated using configurations where all other degrees of freedom have been optimised to minimise the energy at each point on the grid.

Figures 6.4, 6.5 and 6.6 illustrate snapshots of the PES so that the placement of configurations may be analysed from a purely geometric viewpoint without analysis of the corresponding energies and first and second derivatives.

From Fig. 6.4 it is clear that the first 200 data points are placed mostly where strong interaction between the reactants occurs. From Fig. 6.5, the next 300 data points span more of the entrance valley and begin to sample the products. Fig. 6.6 shows that eventually the product valley is heavily populated with data points.

Interpreting these graphs with some knowledge of the dynamics helps to understand the process. As expected, clustering of points along one horizontal and on vertical line correspond to configurations near equilibrium geometries of stable reactants and products. Note the favouring of configurations along the vertical

line formed by the equilibrium bondlength of the C–Cl bond. Because CH_3Cl is a reactant, many more trajectories are sampled for this species because reactions *do not occur for every trajectory*! This simple but important fact is the reason that the MEP should contain points for the products — without hinting the existence of this pathway in advance it could certainly take many iterations for a trajectory to discover this region of the surface.

After approximately 1450 total data points, the PES was constructed with trajectories which simulate the reverse reaction, $\text{Cl}^- + \text{CH}_3\text{F}$. Fifty data points were added in this fashion. The PES construction was then recommenced for the forward reaction. The purpose behind performing trajectories for the reverse reaction will be explained in Section 6.3.3.

As for the studies of inelastic scattering of diatomic molecules, triangle inequalities affect the distributions of configurations in these figures.

Particularly striking in Fig. 6.6 is the presence of a high density region on the product side to match a similar high density region present for the reactants much earlier. Points in this region for the products were already present in the MEP. However, it is clear that the minimum on the product side is important to the reaction and, because it is a deep minimum, trajectories may spend proportionately more time there. The space between the “clumps” of data in Fig. 6.6 is quite distinct. The double-well character of the PES is clearly reflected in the data distribution despite the fact that regions of the PES where the potential varies rapidly are favoured for placement of points by the variance sampling scheme (used to choose every second point).

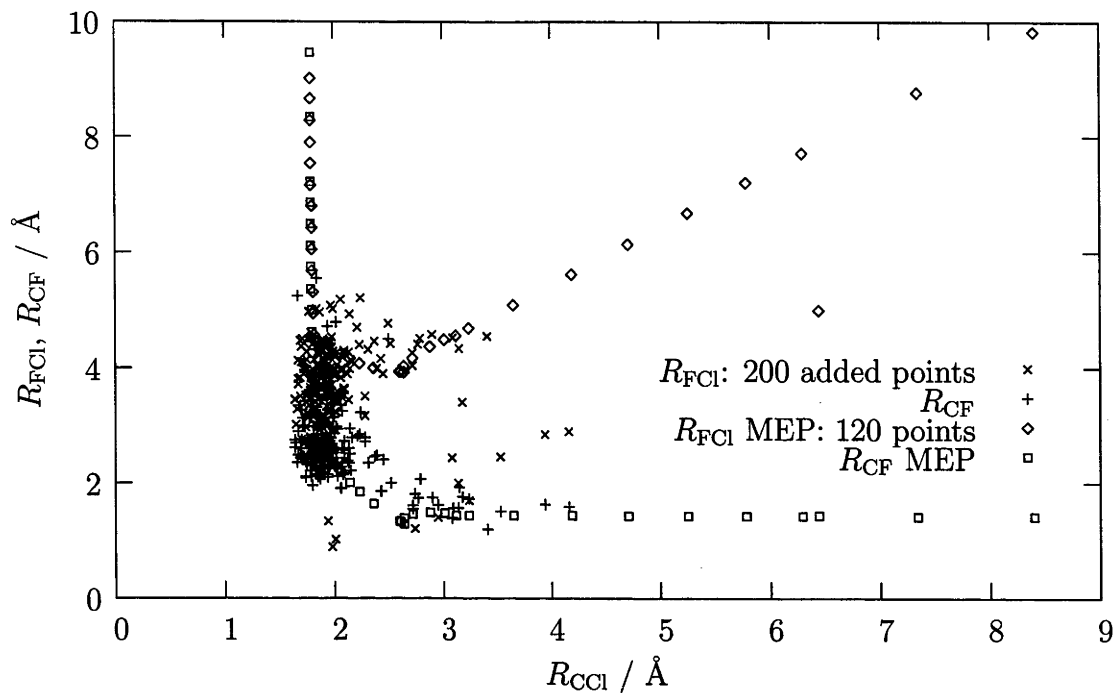


Figure 6.4: Distribution of 200 additional points (to 120 MEP points) in the PES data set. The same points are indicated using two different ordered pair choices for internuclear distances: $(R_{\text{CCl}}, R_{\text{FCl}})$ and $(R_{\text{CCl}}, R_{\text{CF}})$. The representation of the resulting sets of plotted points differ in location most for configurations on the product side of the reaction and occurs because of triangle inequality constraints.

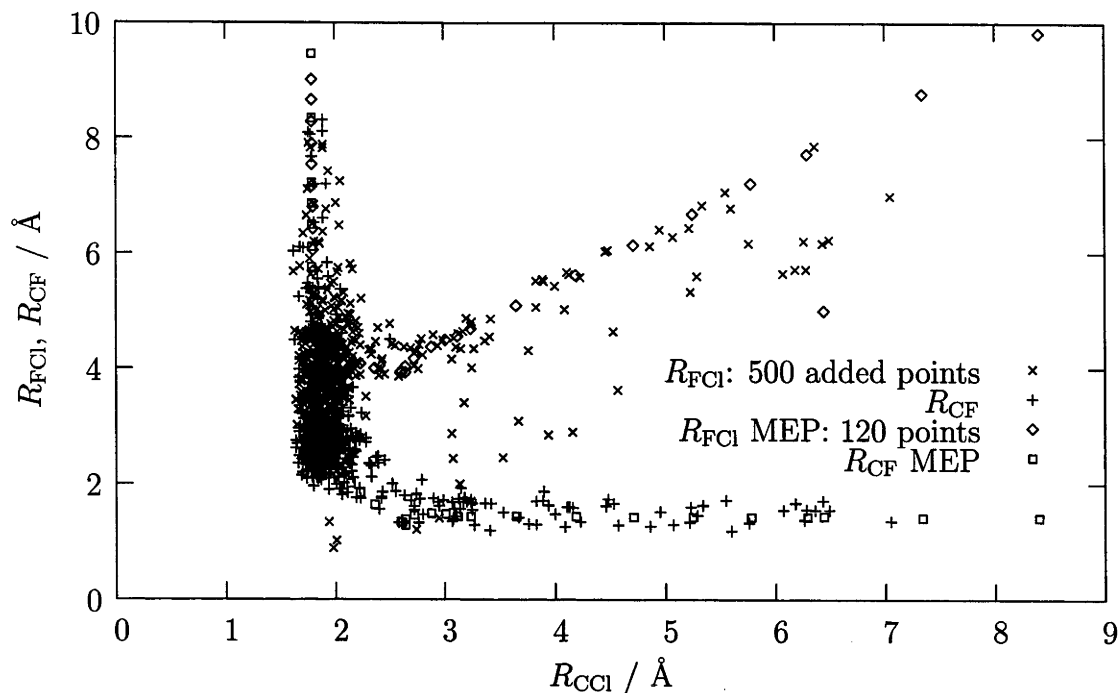


Figure 6.5: Distribution of 500 additional points, totalling 620 points in the PES data set. Variables displayed on the axes are the same as in Fig. 6.4.

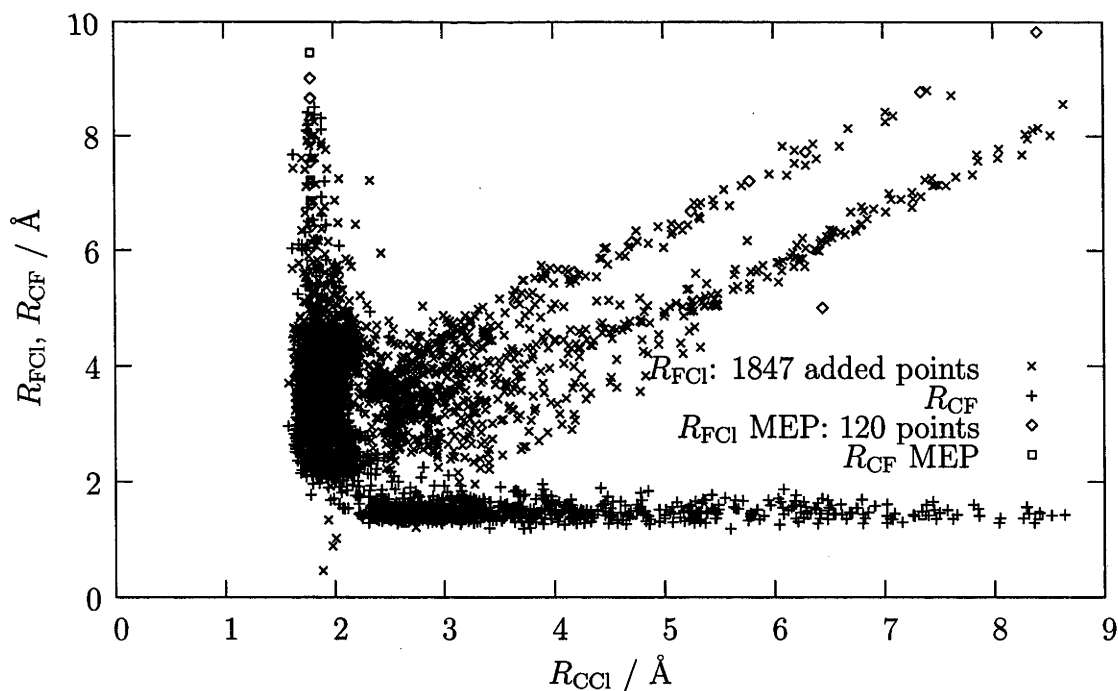


Figure 6.6: Distribution of 1847 additional points. Variables displayed on the axes are the same as in Fig. 6.4.

6.3.2 Complex Formation

Placement of PES data points in the potential wells can be observed most distinctly in the less cluttered graph of Fig. 6.4. Placement of points in these regions does not necessarily imply complex formation, simply that these regions are important to the dynamics. It is useful to inspect the trajectories used to construct the PES. Few trajectories are used in each iteration, however, major changes in the dynamics can sometimes be observed. The behaviour of individual but characteristic trajectories for the full surface are depicted in Figs 6.7 and 6.8.

Categories of individual trajectories can be identified based on events that occur as the simulations progress. Obviously, trajectories react or not. There are no competing reactions. Observation of the reactive trajectories does indicate that a *direct* mechanism is possible, as shown in Fig. 6.7(a). The trajectory in Fig. 6.7(a) ran for 2.53 ps.

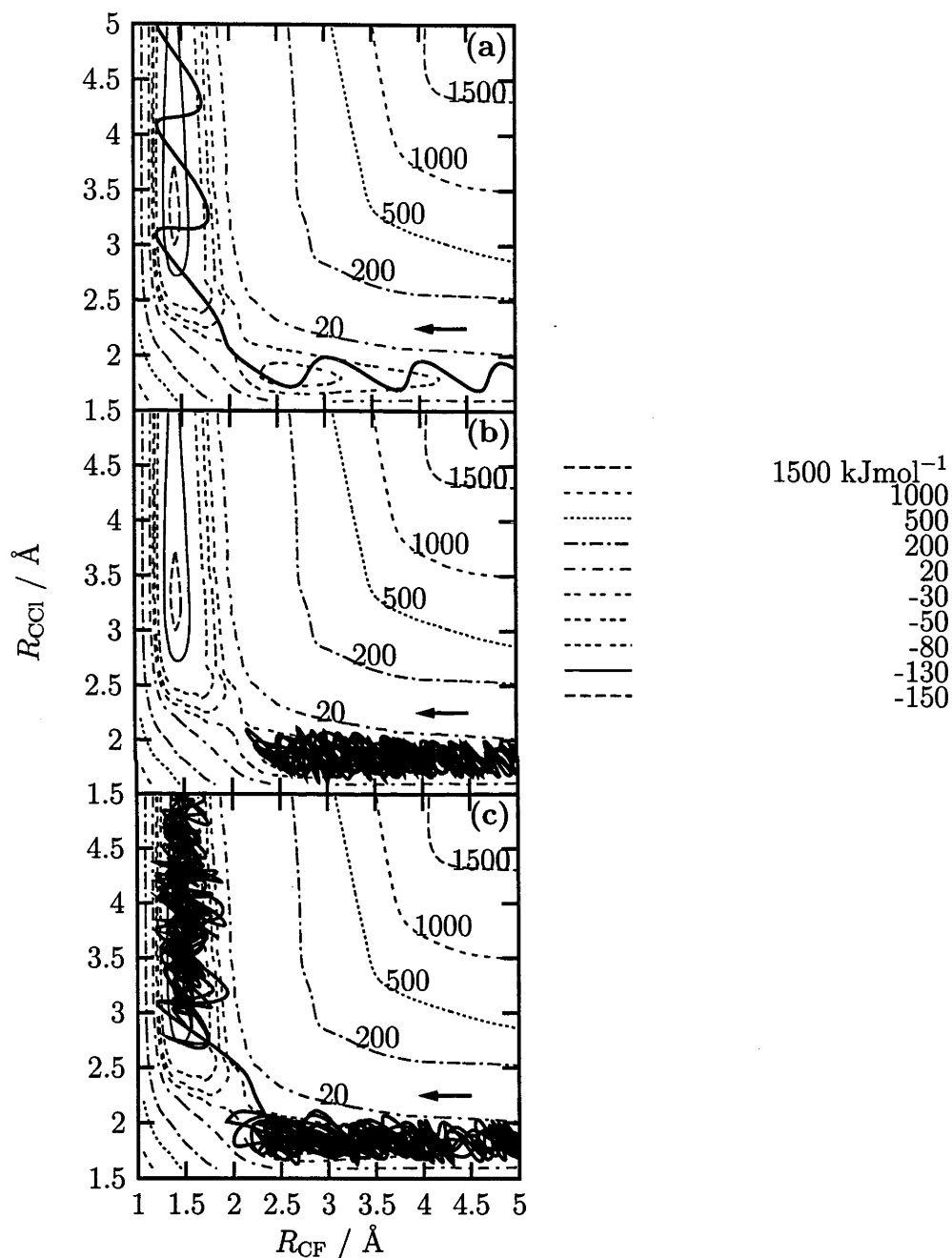


Figure 6.7: Individual trajectories that proceed via: (a) a direct substitution mechanism, (b) an association reaction that produces a complex on the reactant side of the barrier and (c) an indirect substitution reaction that forms complexes on both sides of the barrier.

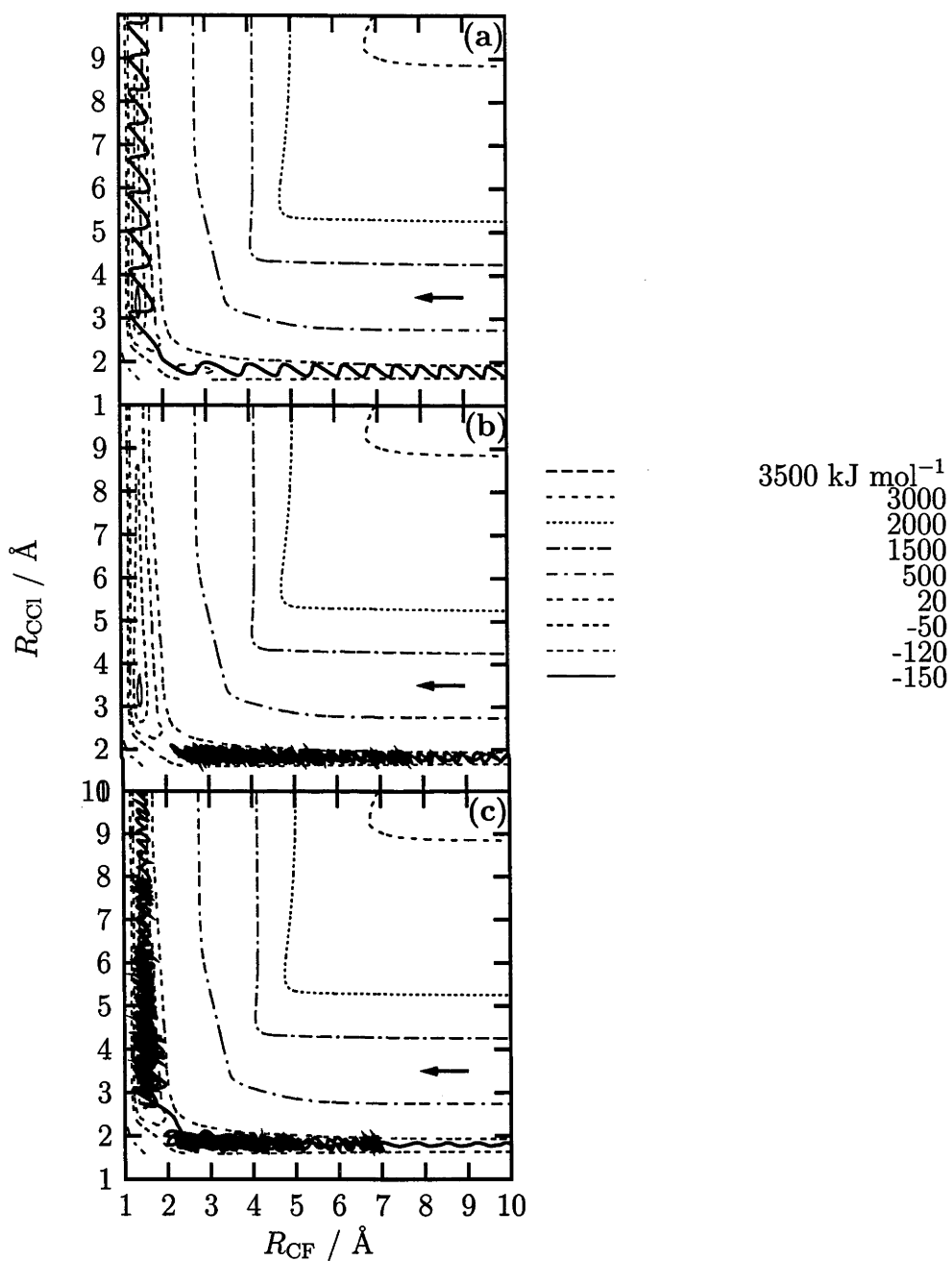
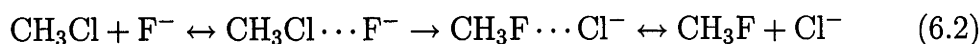


Figure 6.8: Trajectories are shown as per Fig. 6.7 only extended to long range so that distances where association and dissociation of complexes occur can be displayed.

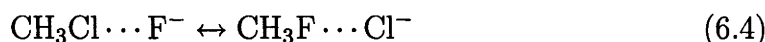
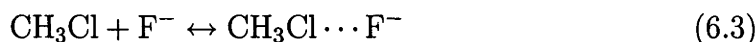
Complex formation is apparent in Fig. 6.7(b) and 6.7(c) where a trajectory no longer proceeds only from right to left and then upwards as in Fig. 6.7(a). In Fig. 6.7(b), the reactive (in terms of substitution) trajectory reaches at least two turning points in the R_{CF} distance on the way to the barrier. For this trajectory, there appears to be a short-range complex and a long-range complex, consistent with findings by Hase and co-workers [15] for the symmetric $\text{CH}_3\text{Cl} + \text{Cl}^-$ reaction, although those workers note that such a bimodal distribution may not exist for other ion-molecule reactions. Later, Su, Wang and Hase studied [17] $\text{CH}_3\text{Cl} + \text{F}^-$ and did not note this behaviour, though short and long-range complexes may have been observed for a small number of trajectories. However, a graph of average residence times for trajectories by those authors, for this system reveals that this effect is not insignificant, at least when averaging has been performed. Examination here of positions of recorded turning points for a large number of trajectories for this system, and a similar analysis of residence times for a small number of trajectories, did not indicate distinct short-range and long-range complexes, in accord with the results for residence times of Su, Wang and Hase.

The indirect substitution in Fig. 6.7(c) undergoes the following reaction:



The barrier crossing only occurred once in Fig. 6.7(c). However, indirect substitution trajectories have been observed that cross the barrier an odd number of times, although multiple crossings were rare for the conditions selected.

Trajectories that do not lead to substitution but lead to complex formation that eventually dissociates back to reactants can be considered reactive in either of the following association reactions:



An example of reaction 6.3 is illustrated in Fig. 6.7(b). The trajectory appears to leave with approximately the original vibrational energy. If vibrational energy had been transferred to translation or rotation, the molecule would have been left with less than ZPVE, an unphysical result.

Formation of a complex in the product channel does not guarantee successful substitution taking place. Trajectories that form product-side complexes but are unreactive are uncommon, yet do occur and involve recrossing the barrier.

6.3.3 Is the PES Accurate?

Inspection of the geometric distribution of the data points reveals information related to the dynamics of the trajectories used in its construction. Before looking at the convergence of dynamical properties, however, it is useful to analyse the average absolute error calculated from the difference between interpolated and *ab initio* energies of a sample of trajectory configurations. The error has been plotted as a function of the number of data points for two different samples in Fig. 6.9. The “product” sample was generated using 1200 trajectories performed on the PES with 1450 data points, simulating the reverse collision $\text{CH}_3\text{F} + \text{Cl}^-$. The “reactant” sample was generated from trajectories initiated at $\text{CH}_3\text{Cl} + \text{F}^-$.

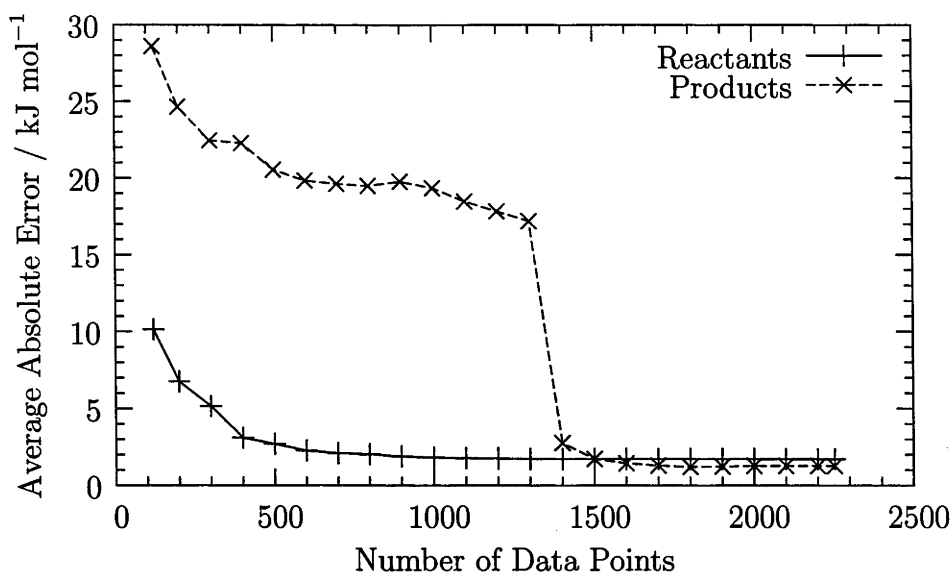


Figure 6.9: Average absolute errors using 750 “reactant” and 250 “product” configurations.

At 1450 data points, it was clear that the PES did not describe the product channel as well as the reactant-side of the barrier.

Addition of 50 geometries sampled from trajectories performed for the reverse reaction was important for improving the accuracy in the product channel of the PES, evident in the sharp drop in the average error for the sample of product configurations in Fig. 6.9.

Although we know that the interpolation error for points sampled from actual trajectories is reduced by the addition of points and that the addition of more points leads to a less rapidly diminishing error, the observed convergence of the interpolation error to within 1 % of the maximum energy range of the MEP does not prove that the PES is sufficiently accurate to determine dynamical properties accurately. To establish whether or not the PES is ready for calculation of such properties, we must observe the properties themselves.

6.3.4 Convergence of Cross-Sections

There is no simple relationship between the average interpolation error and the effect of such errors on the dynamics. Even a knowledge of the distribution of errors in magnitude and across the relevant configuration space would not provide an estimate of the effect of errors on the dynamics. We must rely on the convergence of dynamical observables as a direct measure of convergence of the PES to the required accuracy.

Convergence of the association cross-section as points are added to the PES data set is shown in Fig. 6.10. Convergence of the substitution cross-section is shown in Fig. 6.11.

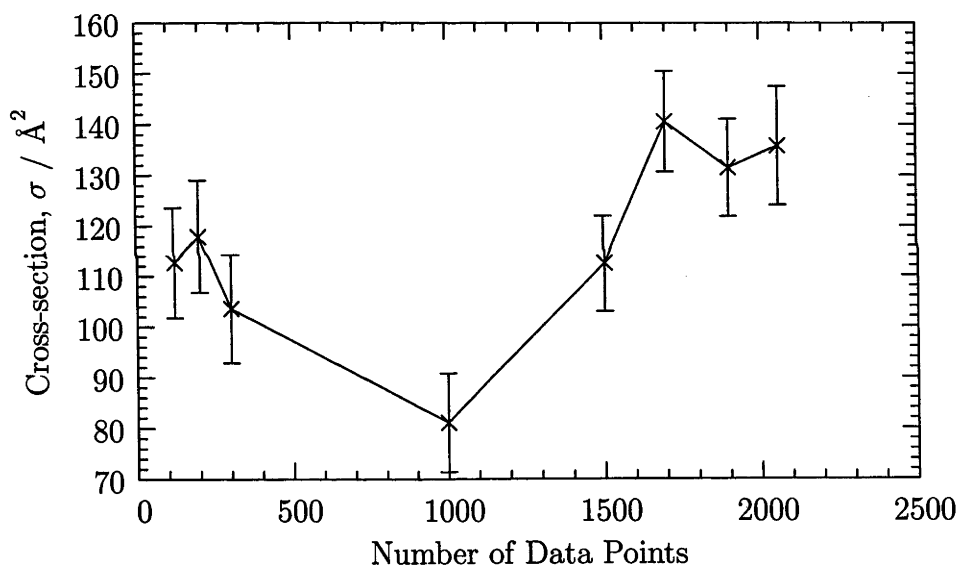


Figure 6.10: Association cross-sections as a function of the number of data points in the PES data set. The first graph point corresponds to a data set of 120 MEP points. The error bars represent two standard deviations.

The association cross-section changes dramatically during addition of about 1500 points to the MEP data set, but appears to have converged when the set contains at least 1700 points.

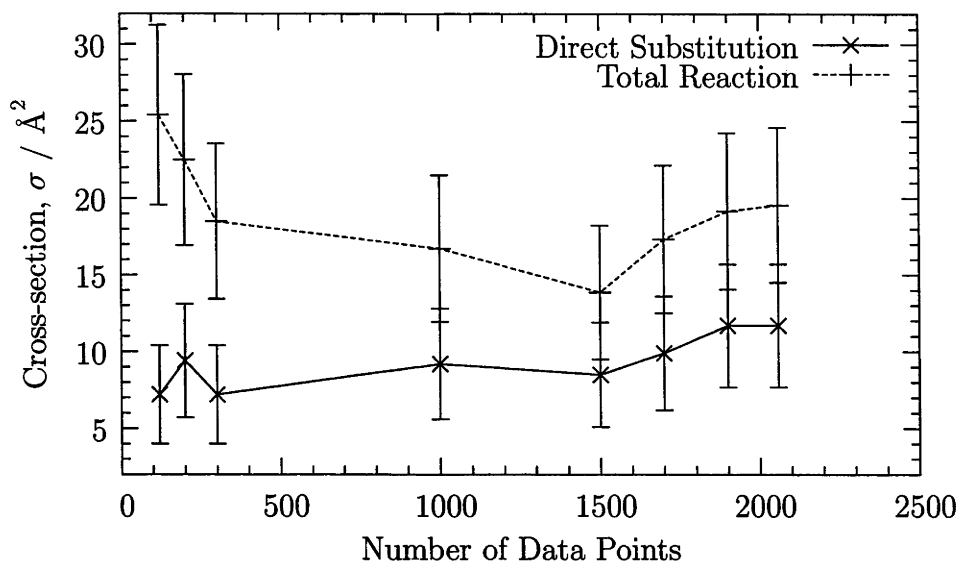


Figure 6.11: S_N2 cross-sections as a function of the number of data points used in the interpolated PES. Direct cross-sections correspond to collisions that lead to substitution via a direct mechanism. Total reaction cross-sections are determined from the total probability of substitution, also including reactions that occur via an indirect mechanism. The error bars represent two standard deviations.

Convergence is demonstrated in Fig. 6.11 for the total reaction cross-section and the cross-section for reaction via the direct mechanism alone. The purpose behind reporting the direct reaction cross-section is simply to emphasise the existence of the two qualitatively different mechanisms for this reaction. The variation in the total reaction cross-section with the size of the data set is similar to the trend seen for the association cross-section.

6.3.5 Convergence of Complex Lifetimes

The formation of a transient collision complex is an important characteristic of ion-molecule reactions, and represents another property of the PES that ought to be faithfully described by an accurate surface.

To quantify the dynamics of the collision complex, we consider how the population of complexes decays with time. Complex lifetimes have been fitted using the relative population of complexes, $N(t)/N(0)$, that exists at any moment in time. Trajectory endtests were discussed in Sec. 6.2: the lifetime of a “reactant complex” is defined as the time interval between the first classical turning point reached while not “in” a reactant complex and the last turning point reached while “in” a reactant complex before crossing the barrier or reaching an internuclear separation that triggers a non-reaction end-test. The requirements for determination of the lifetime of a “product complex” are similar: if in the exit valley consecutive turning points are encountered then a complex must have formed and the lifetime is the difference between the time at the first turning point and the last turning point before either recrossing the barrier or the intermolecular separation is large enough to indicate that products have been formed. Note that multiple complexes may be formed during a trajectory.

For the symmetric reaction of $\text{CH}_3\text{Cl} + \text{Cl}^-$, Vande Linde and Hase [15] reported that the relative population of complexes did not decay exponentially with time. Rather, multiple exponentials were necessary:

$$\frac{N(t)}{N(0)} = \sum_i a_i e^{-k_i t}, \quad (6.5)$$

where $\sum_i a_i = 1$, because the relative population is unity when the time $t = 0$. Vande Linde and Hase reported that biexponential and triexponential fits to the lifetime data ($i = 2$ and $i = 3$ in Eq. (6.5)) were necessary for the symmetric reaction.

An example of fitting lifetimes for the $\text{CH}_3\text{Cl} \cdots \text{F}^-$ reactant complexes is shown in Fig. 6.12. The single exponential function is clearly not a good fit. The biexponential function was found to produce an adequate fit and was used to fit all decay curves for reactant complexes.

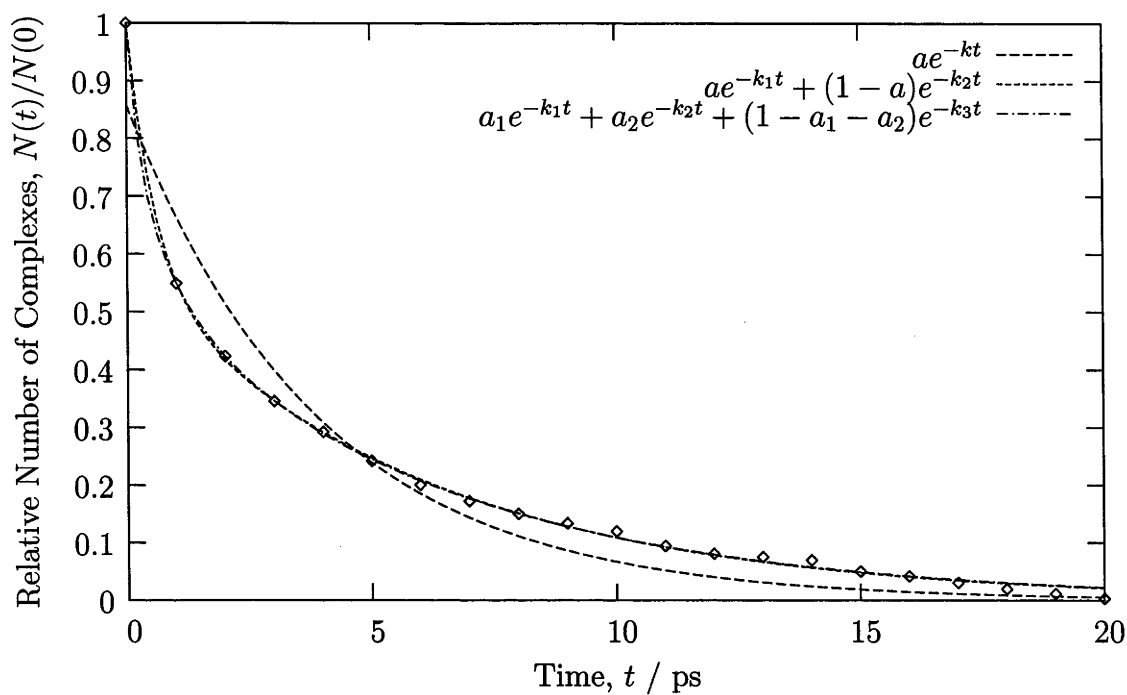


Figure 6.12: Fits for reactant complex lifetimes using Eq. (6.5) and 1200 trajectories performed on the final PES.

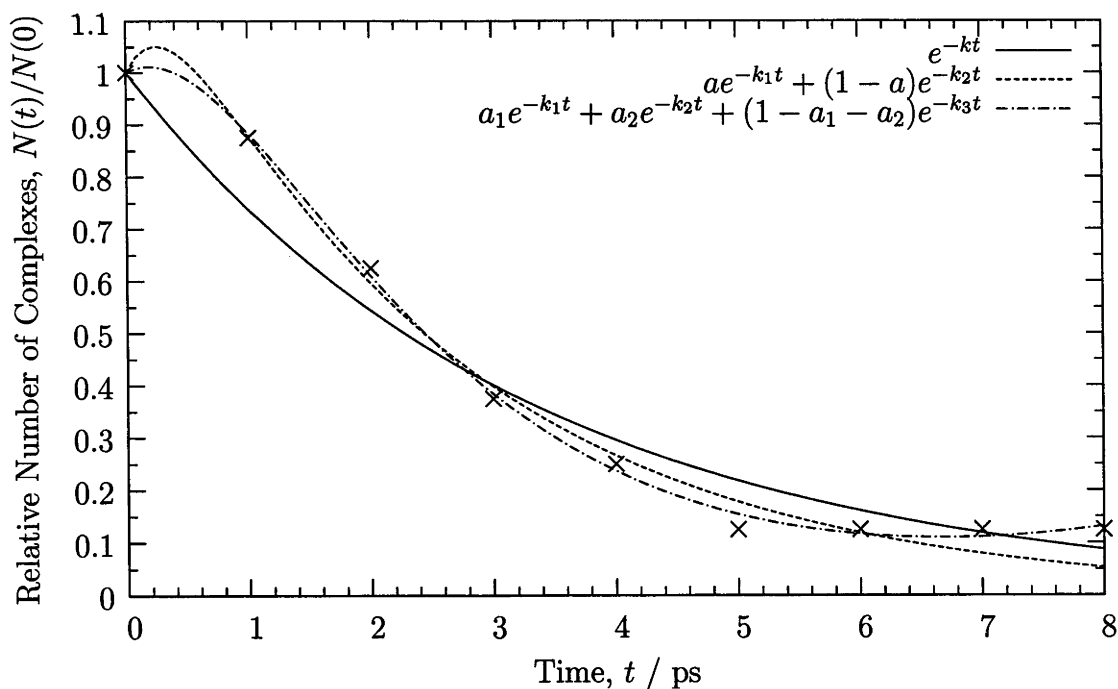


Figure 6.13: Fits for product complex lifetimes using Eq. (6.5) and 1200 trajectories performed on the final PES.

A similar procedure was followed for the product complexes, resulting in the fits shown in Fig. 6.13.

Unfortunately the number of product complexes formed for 1200 trajectories was not sufficient to determine reliable fits. Error bars have been omitted from these plots for clarity, but are much larger for the product complexes. At least an order of magnitude more trajectories would be necessary to determine parameters from Eq. (6.5) assuming such forms are adequate for the product complexes.

Restricting our attention to reactant complexes, an assessment of whether reactant complex lifetimes can be determined from the PES requires analysis of the behaviour of the biexponential fitting parameters as the number of data points is increased, shown in Fig. 6.14.

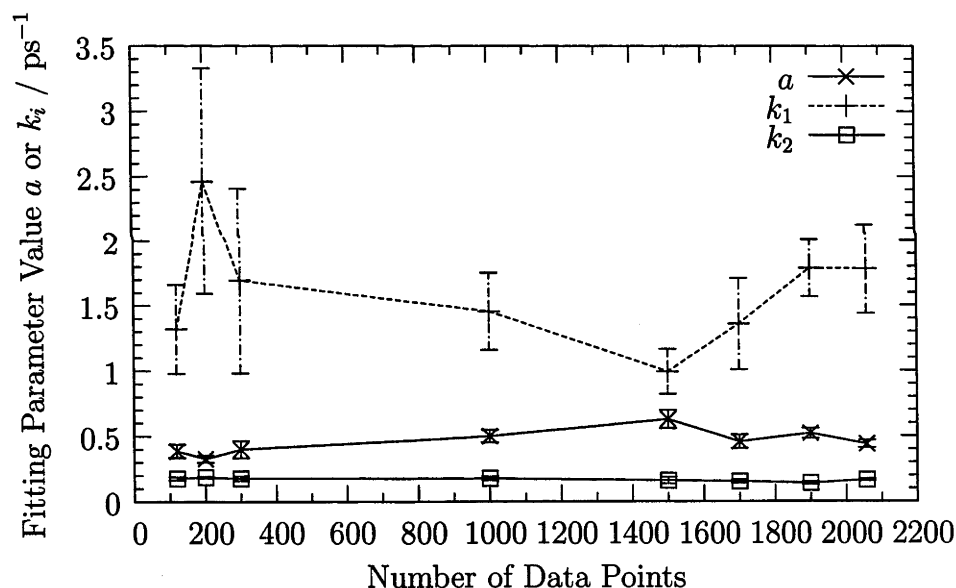


Figure 6.14: Fits for reactant complex lifetimes as a function of the number of data points used in the interpolated PES.

Surprisingly, the convergence in the lifetimes of the reactant complexes in Fig. 6.14 improves most after 1500 points in the same manner as the cross-sections. The result is surprising because most of the data before 1500 points was placed on the reactant-side of the barrier. Perhaps a general improvement in the interaction region close to the barrier only became possible as an overall pathway to products became more accessible.

6.3.6 Energy-Dependence of the Reaction Dynamics

We have constructed a PES for $\text{CH}_3\text{Cl} + \text{F}^-$ at a very modest level of *ab initio* theory because the purpose of the study was to examine the use of constraints, not to pursue a quantitative investigation of the chemistry. However, it is useful to compare the results we have obtained for the reactivity of this reaction with other studies, if only to demonstrate that we have considered the role of constraints for a PES which is chemically relevant.

In order to compare with recent classical simulations of this reaction by Su, Wang and Hase [17], we have calculated cross-sections at three different relative translational energies, $E_{\text{rel}} = 7.88, 13.14$ and $18.39 \text{ kJ mol}^{-1}$ using the PES constructed with constraints and construction trajectories at an energy of $13.14 \text{ kJ mol}^{-1}$. The substitution cross-sections $\sigma(E_{\text{rel}})$ were converted to energy-dependent rate coefficients $k(E_{\text{rel}})$ for comparison with previous theoretical [17] and experimental [28] studies using

$$k(E_{\text{rel}}) = \sqrt{\frac{2E_{\text{rel}}}{\mu}} \sigma(E_{\text{rel}}), \quad (6.6)$$

where μ is the reduced mass of the reactants. The results are compared in Fig. 6.15 below.

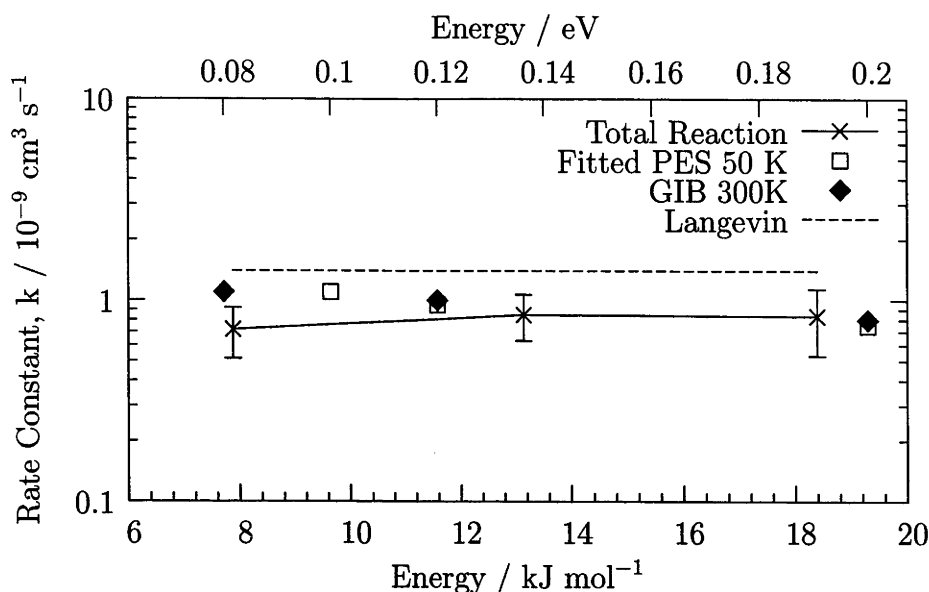


Figure 6.15: Substitution rate constants are shown for three energies. The most recent experimental [28] (using guided ion beam (GIB) tandem mass spectrometry) and theoretical [17] results are shown. The Langevin cross-section (using the average electric dipole polarisability from Ref. 29) is also shown as a line that is independent of the relative translational energy.

The energy range was necessarily narrow because the interpolated PES is expected to be less accurate at energies significantly higher than the energy used to construct the PES. Previous theoretical results [17] indicate that the energy range studied here corresponds to the “low-energy regime” where the energy dependence was found in that study to be $E_{\text{rel}}^{-0.3}$ at 296 K.

The Langevin rate constant is too high in this case because the probability of reaction at small impact parameters is very much less than unity.

Differences between the rate coefficients calculated here and the earlier classical trajectory [17] and experimental results [28] may easily be due to the low level of *ab initio* theory employed here. It is pleasing (and possibly fortuitous) that the differences are so small. It is reasonable to infer that the PES constructed here is at the very least qualitatively correct. Hence, the effect of constraints on the dynamics that we observe can be taken to represent the effect of constraints on a realistic PES for this reaction.

6.3.7 Unconstrained Dynamics

We have attempted to construct a PES for this system without constraints, using the standard methods developed by Collins and co-workers [26]. The initial conditions for trajectories used in this procedure are generated in the same manner as those used for the constrained PES, except that the internal energy of the CH_3Cl reactant was increased to account for the zero point vibrational energy (ZPVE) of the three C–H stretching modes. The initial (MEP) data set was taken to be the same as that used for the constrained PES, and the iterative construction procedure was carried out until a data set of 2534 points was accumulated.

At least partial convergence of this PES has been achieved by 2534 data points. This is indicated in Fig. 6.16 which shows how the average interpolation error varies with data set size, for the same set of (constrained) configurations used in Fig. 6.9. It is likely that the average error for a sample of unconstrained configurations would exceed that shown in Fig. 6.16. However, the figure does indicate that the average error is reduced as the data set increases in size. The errors are somewhat larger than those shown in Fig. 6.9 for the constrained PES.

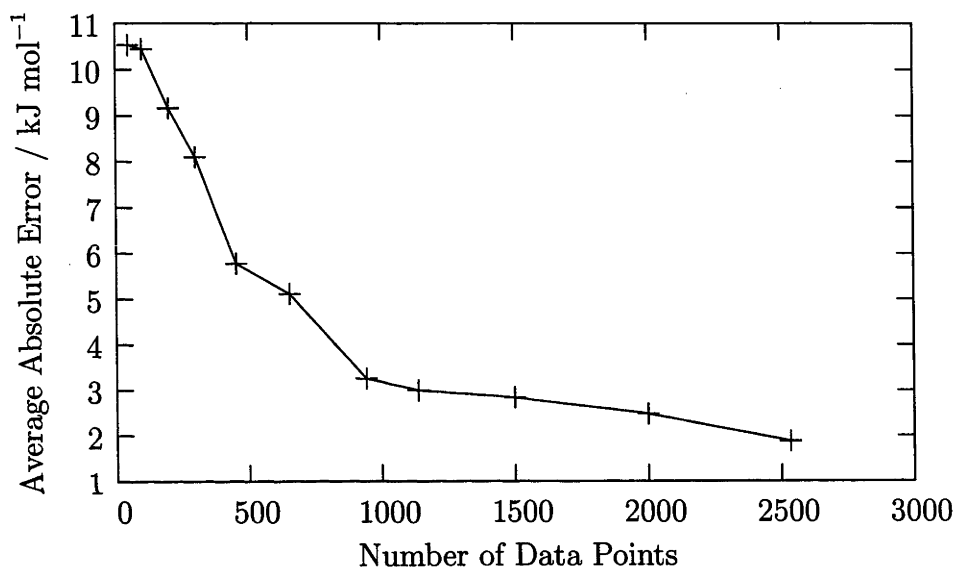


Figure 6.16: The average absolute error for 1000 “constrained” configurations are shown as a function of the number of data points in an PES constructed without constraints.

Figure 6.17 presents the variation of the cross-section for substitution with the number of data points in the PES constructed without constraints. The trajectories used to test convergence were also unconstrained. This graph also suggests that the PES is converging.

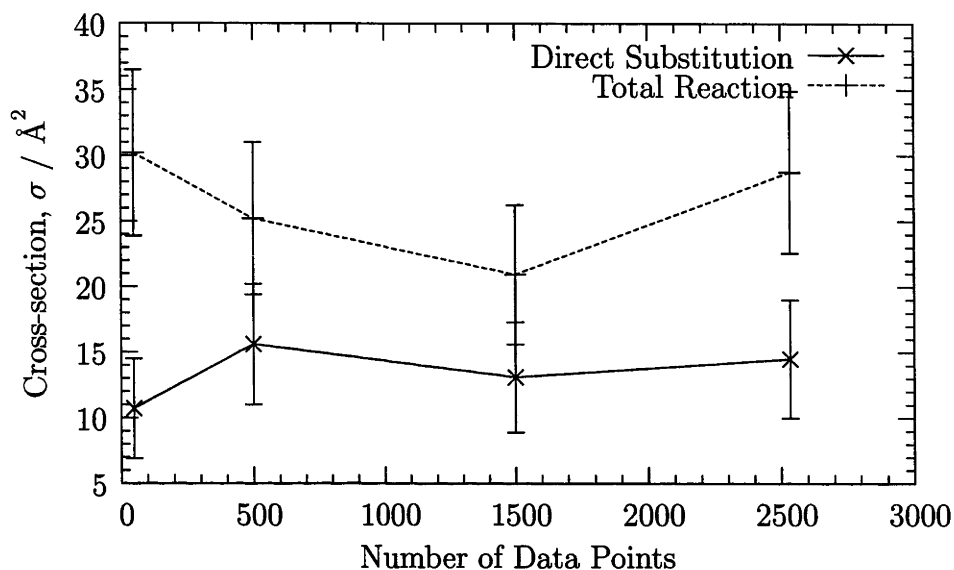


Figure 6.17: Substitution cross-sections for a PES constructed without constraints. Trajectories used for testing convergence were also performed without constraints.

However, Fig. 6.18 presents the variation of the cross-section for association on this PES as a function of the number of data points. Here, there is no clear evidence of convergence, as the cross-section increases by a factor of three from 1500 to 2534 data points.

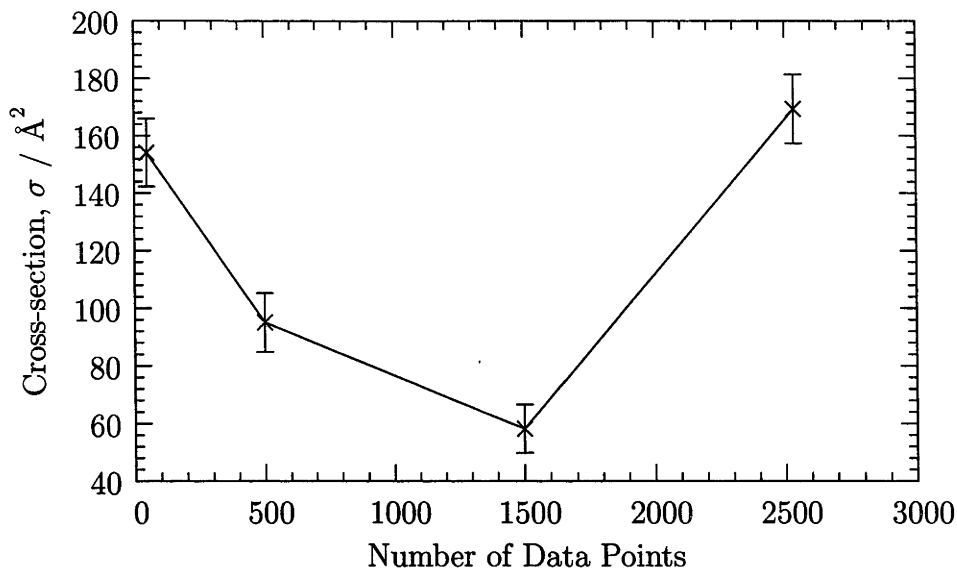


Figure 6.18: Association cross-sections for a PES constructed without constraints. Trajectories used for testing convergence were also performed without constraints.

It appears then that the unconstrained PES may be somewhat slower to converge than the constrained PES as the number of data points increases. A possible reason for this is that the collision complexes survive long enough so that a large volume of configuration space can be explored. If the C–H bonds are unconstrained, then energy may flow into and out of the C–H stretches in either the “reactant” or “product” complexes, allowing more complex motion. The large amount of ZPVE associated with the high frequency C–H stretching modes is not “conserved” in a classical simulation. This energy may flow out of C–H stretching motion into other modes. A collision complex might provide the time for such intra-molecular vibrational redistribution (IVR) to take place. It is an interesting aspect of the use of constraints that possibly unphysical (non-quantum) aspects of classical mechanics, associated with the non-conservation of ZPVE, may be avoided.

Although convergence of the cross-section for substitution is not perfectly established, it is interesting that this cross-section is systematically larger ($29 \pm 6 \text{ \AA}^2$) for the unconstrained PES than for the constrained dynamics on the constrained PES ($20 \pm 5 \text{ \AA}^2$). This begs the question: Is this difference in substitution cross-section due to differences in the PES or differences in the dynamics?

6.3.8 Unconstrained Dynamics on the Constrained PES

An important question raised in this study is whether or not unconstrained dynamics can be performed on a PES constructed using constrained dynamics. The Taylor expansions are performed using the full set of degrees of freedom. The first and second derivatives in the Taylor expansion around each data point are probably sufficient to provide an accurate PES within some local region near the previously constrained geometry. Far from the constrained value in the internuclear distance coordinate, the dynamics might still be well-behaved because the Taylor expansion will keep motion in that coordinate reasonably contained, as demonstrated in Fig. 6.19.

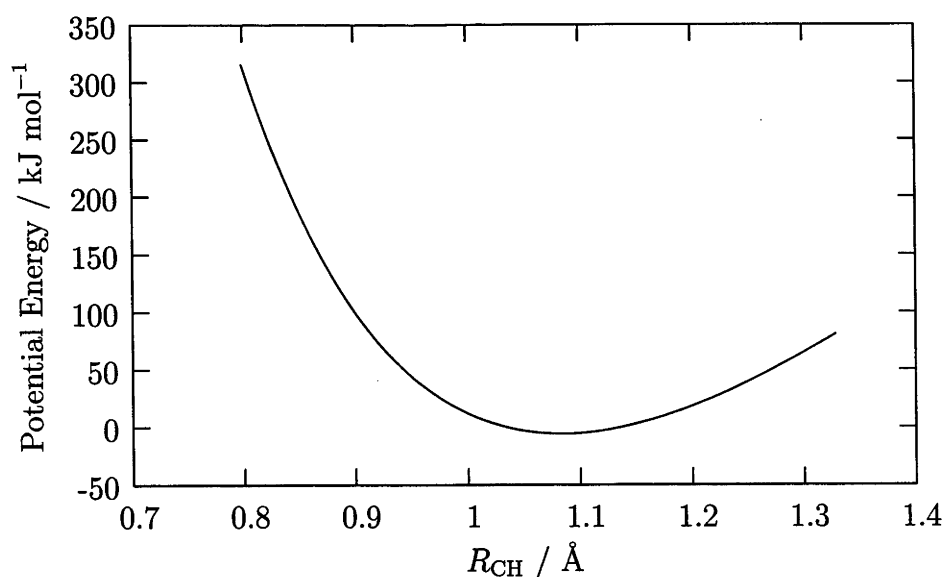


Figure 6.19: Evaluation of the interpolated potential about one constrained CH bond for a sample geometry.

We have carried out an unconstrained classical simulation of $\text{CH}_3\text{Cl} + \text{F}^-$ on the PES constructed using constraints. The total substitution cross-section for these unconstrained dynamics does not vary widely with the number of data points (within the error limits). The total substitution cross-section from 1200 unconstrained trajectories, using all 2059 constrained data points, is $31 \pm 6 \text{ \AA}^2$. This is clearly close to the value obtained for the unconstrained data set ($29 \pm 6 \text{ \AA}^2$). It is more relevant to note that this value is larger than the total cross-section ($20 \pm 5 \text{ \AA}^2$) determined using constrained trajectories on the same surface. Hence, we could reasonably infer that the relaxation of the constraints has a direct effect on the dynamics in that it raises the calculated reaction cross-section. The fact that the unconstrained dynamics yield about the same cross-section on surfaces constructed with and without constraints suggests that the “constrained” PES is valid for unconstrained motion.

6.4 Remarks

It is not possible to be completely certain why the calculated cross-sections are different for constrained and unconstrained dynamics. The additional ZPVE in the unconstrained trajectories is available to assist in substitution. Such an effect was suggested by Vande Linde and Hase [15] from mode-selective classical trajectories for $\text{CH}_3\text{Cl} + \text{Cl}^-$. It is also the case that the C–H stretching motions can serve as sinks for energy disposal. Moreover, the stretching molecule is a larger target (leading to a larger maximum impact parameter for reaction and therefore larger cross-section). These C–H motions could also at any point in time have an effect on the cone of acceptance (steric effect). It is also not clear whether unconstrained trajectories provide a more accurate simulation of the “true” dynamics, because of the flow of ZPVE.

There is a clear indication that the PES constructed with constraints is useful for the description of both constrained and unconstrained dynamics. The validity of the “constrained” PES relies on the assumption that the amplitude of motion of the constrained modes is small in the absence of constraints. The validity of the “constrained” PES is independent of whether or not such small amplitude motions have a quantitative effect on the reaction dynamics.

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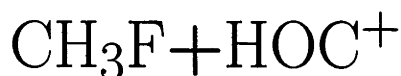
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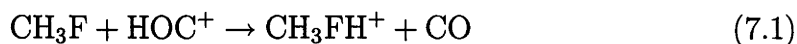
Chapter 7

An Eight-Atom System:



7.1 Introduction

The ultimate goal of using constrained dynamics is to construct potential energy surfaces efficiently for large systems. This chapter presents investigations of the following reactions:



The system was chosen in order to apply similar constraints to those in the $\text{S}_{\text{N}}2$ problem explored in the previous chapter by freezing the methyl group in a simple alkyl halide. As before, the C–H stretching motions have been constrained, however, because the important reaction channels do not involve substitution of the halogen atom, the bends have also been constrained by constraining the distances between the hydrogen atoms. The effect is to completely constrain the methyl

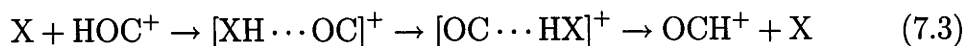
group in C_{3v} symmetry. In addition, the fluorine atom has been constrained to give a rigid CH_3F reactant.

In contrast to the S_N2 reaction, there are two competitive reactions. The first is an abstraction reaction that protonates the alkyl halide at the electronegative fluorine atom. The chosen system is particularly interesting because of the catalysed rearrangement of the HOC^+ to form HCO^+ .

It is well established that the isoformyl cation (HOC^+) is much less stable than its isomer, the formyl cation (HCO^+). The energy difference is approximately 160 kJ mol^{-1} [1–12]. However, there is a substantial barrier of about 150 kJ mol^{-1} separating the two forms [1–8, 12]. Therefore, both isomers can be separately observed as stable species in the gas phase [9–11, 13–15]. In proof, microwave spectra of both HOC^+ and HCO^+ have been recorded [13, 14]. Both HOC^+ and HCO^+ are established interstellar species [16–20].

The barrier for the rearrangement of HOC^+ to HCO^+ has been found to be substantially reduced, or in some cases eliminated, as the result of interaction with an appropriate neutral molecule (X) [1, 11, 12, 15, 21]. This is an example of what Bohme has described as catalysed proton transport [22], or is referred to broadly as ion-transport catalysis [23].

There is a straightforward reason for the reduced barrier. Complexation of X with HOC^+ weakens the H–O bond, thus facilitating the rearrangement:



Equivalently, the proton is more weakly bound in the transition structure for rearrangement than in the reactant or product ions. The proton can therefore interact more effectively with X. A recent systematic theoretical study of the $[XCHO]^+$ system [21], found that when X has a proton affinity less than that of CO at either O or C (e.g. X = He, Ne and Ar), the barrier to rearrangement is

reduced but not eliminated. If X has a proton affinity lying between that of CO at O and C (e.g. X = HF and N₂), the barrier disappears. Finally, for molecules X with a proton affinity greater than that of CO at O or C (e.g. X = H₂O and NH₃), the barrier for rearrangement again disappears, but in such cases an alternative reaction, hydrogen abstraction (or protonation), is energetically preferred:



Although the calculations of the energies of reactions (7.3) and (7.4) provide valuable information, it is of interest to go further and investigate the dynamics of these reactions. Collins et al [24] studied the reactions of HOC⁺ with the rare gas atoms X = Ne, Ar and Kr, demonstrating that it is possible to produce complete potential energy surfaces for such systems. Collins and Radom subsequently developed PES for reactions of HOC⁺ with HF and H₂O [25].

For Ne + HOC⁺, the barrier to rearrangement was very high and rearrangement was thus proved impractical [24]. However, for Ar + HOC⁺, and particularly for Kr + HOC⁺, the barrier was sufficiently low that cross sections for the rearrangement reaction could be evaluated. Interestingly, it was found that once the collision energy was sufficiently high for the abstraction reaction (7.4) to be feasible, this process dominated over the energetically-preferred rearrangement reaction (7.3).

7.2 Computational Details

7.2.1 Constraints

During the construction of the PES, all 10 internuclear distances in the CH_3F reactant are constrained, as shown in Fig. 7.1.

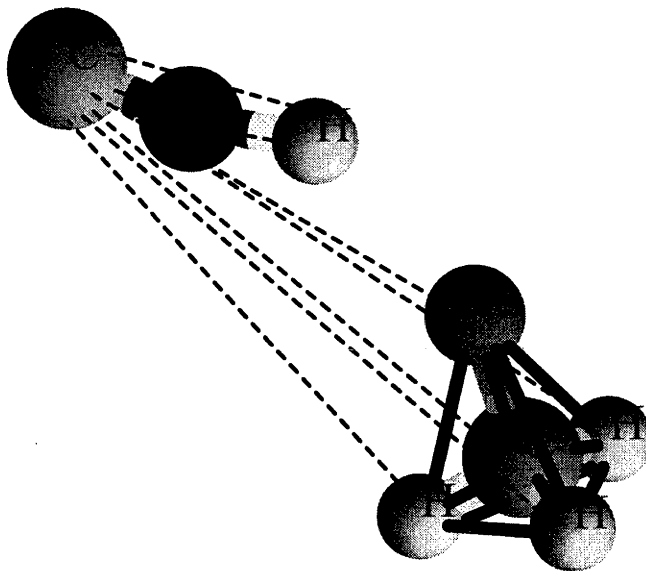


Figure 7.1: The internuclear distances used in the interpolation are shown, where the constraints are marked by solid lines. Only intermolecular internuclear distances between the C in the HOC^+ and atoms in CH_3F are shown. Other intermolecular distances have been omitted for clarity, because the same number of internuclear distance coordinates will extend from each of the O and H atoms in HOC^+ to the CH_3F molecule.

In our discussion, we will describe the dynamics for different combinations of constraints. Combinations that are used to perform trajectories, using a PES constructed with all ten constraints depicted in Fig. 7.1, are shown in Fig. 7.2 below. More combinations are possible. However, it was decided that the constrained bond most likely to participate in the competing reactions would be the stretching motion in the C–F bond, so this was relaxed first. Experience with the

S_N2 reaction in the last chapter indicated that construction of surfaces without constraints for larger systems would take many points to converge, and therefore was not performed for this system.

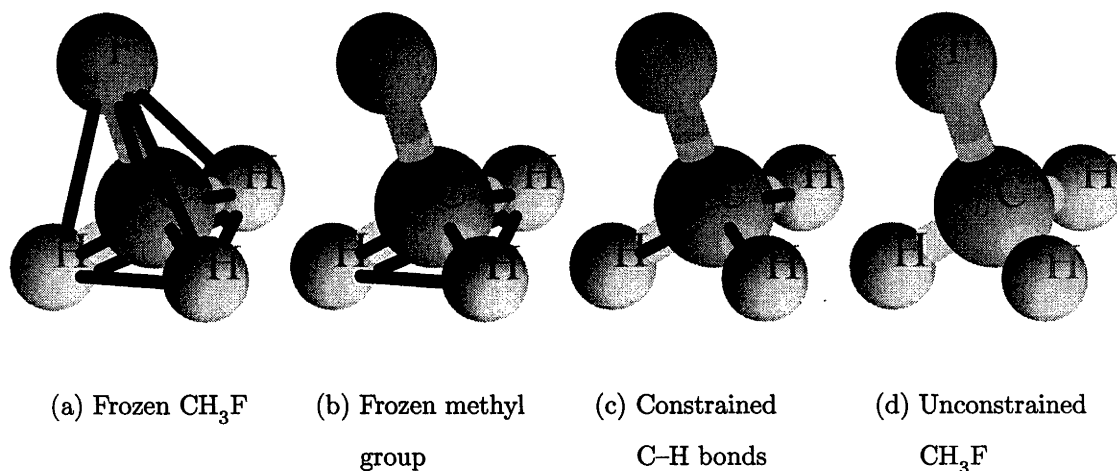


Figure 7.2: Combinations of constraints. More combinations are possible that were not used for physical reasons explained in the text.

7.2.2 *Ab Initio* Calculations

Preliminary *ab initio* investigations were performed for $\text{CH}_3\text{F} + \text{HOC}^+$ to obtain the optimal level of theory and basis set size so that accurate dynamics can be achieved on the interpolated PES without undue computational cost during construction of the surface. For this system, with a more ambitious number of atoms, only a modest level of accuracy was deemed necessary, since the primary purpose is to investigate the PES construction methodology. Electron correlation has been included by using the MP2 method, however, only a small basis set, 3-21G, was employed. All *ab initio* calculations were performed using the GAUSSIAN package [26].

A schematic energy profile of the reaction at MP2/3-21G is shown in Fig. 7.3 with constraints.

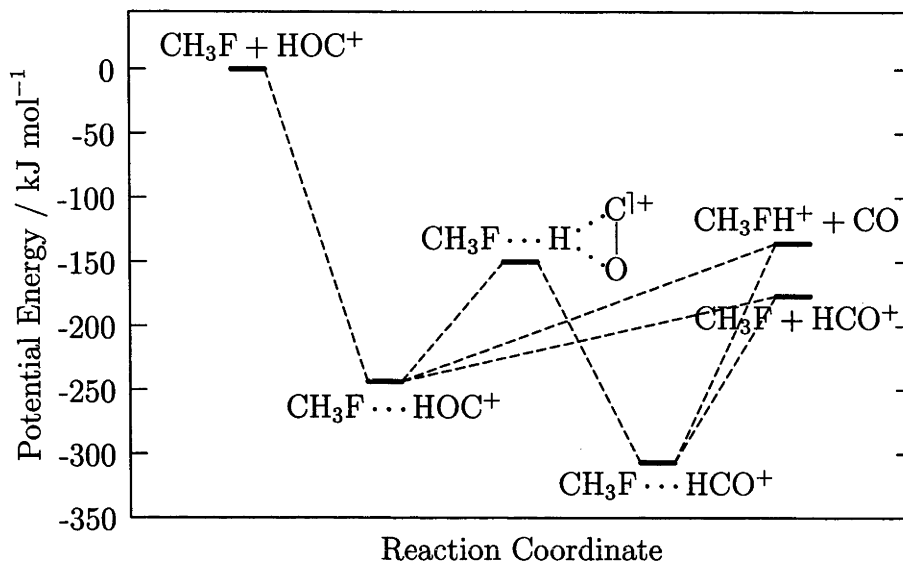


Figure 7.3: Schematic energy profile for the $\text{CH}_3\text{F} + \text{HOC}^+$ reaction where stationary points were optimised at MP2/3-21G with C-H and H-H bond lengths constrained to their CH_3F equilibrium values.

7.2.3 Construction of the PES

Standard methods were used to evaluate the MEP connecting the stationary points on the PES which are indicated in Fig. 7.3. The initial set comprised 143 configurations chosen from these paths. The PES was then iteratively constructed using trajectories initiated from the $\text{CH}_3\text{F} + \text{HOC}^+$ reactants, with the parameters shown in Table 7.1.

The data point selection criterion was again alternated between the *h*-weight and variance sampling methods. The convergence of the reaction cross-sections was examined at several stages in the growth of the data set, and the construction process was terminated when 1389 total data points had been accumulated.

Table 7.1: Parameters used in PES construction and in trajectory calculations.

Parameter	Symbol	Construction ^a	Dynamics ^a
<i>Constraints (CH₃F)</i>			
C-H bondlengths	$3 \times R_{\text{CH}}$	1.0859 Å	See note. ^b
C-F bondlength	R_{CF}	1.3900 Å	See note. ^b
H-H distances	$3 \times R_{\text{HH}}$	1.7793 Å	See note. ^b
H-F distances	$3 \times R_{\text{HF}}$	2.0277 Å	See note. ^b
<i>Dynamics</i>			
Maximum Impact Parameter	b_{max}	5 Bohr	20 Bohr
Initial Fragment Separation	d_{ab}	21 Bohr	21 Bohr
Timestep	Δt	0.02 fs	0.015 fs
Number of trajectories	n_{traj}	10	1000
CH ₃ F Internal Energy	ZPVE ($T_{\text{rot}} = 0$ K)	0	0 mHartree ^c 8 mHartree 18 mHartree 40 mHartree
HOC ⁺ Internal Energy	13 mHartree		
Relative Translational Energy	E_{rel}	5 mHartree	5 mHartree
<i>Sampling</i>			
Trajectory Sampling Frequency	f_{print}	1/200Δt	
Points selected/iteration		1	
<i>Interpolation</i>			
Weight function terms		2	2
Weight function powers		2,12	2,12
Weight function cutoffs	$w_{\text{tol},i}, w_{\text{tol},o}$	$10^{-5}, 10^{-10}$	$2 \times 10^{-5}, 2 \times 10^{-9}$
Neighbour list updates	n_i, n_o	1/5Δt, 1/20Δt	1/5Δt, 1/15Δt
Neighbours in confidence radius	n_{neigh}	125	125

^aAtomic units have been used in the table as they have been used in calculations. These values are converted to S.I. when used in the text.

^bPES construction was performed with all constraints. Convergence testing was also performed using all constraints. In addition, trajectories using different combinations of constraints were examined for the converged PES.

^cInitial internal energy in CH₃F while examining convergence was identical (i.e. 0) to that used in PES construction.

After the PES had been constructed, reactions (7.1) and (7.2) were simulated using this PES with fewer constraints on the motion. The trajectory initial conditions for these simulations differ from those on the constrained surface only in that Monte Carlo sampling of the now unconstrained vibrations was carried out, with a corresponding adjustment to the initial vibrational energy. In all cases the

initial vibrational energy was chosen to approximate the total zero point energy of the unconstrained motion. An estimate of the internal energy in the HOC^+ reactant was determined using a frequency calculation for the isolated molecule. The parameters governing these trajectory simulations are the same as those for the maximum number of constraints except for the initial internal energies listed for CH_3F in Table 7.1 which increases as the number of constraints is relaxed.

The total ZPVE in the unconstrained CH_3F was estimated using one half of the sum over the frequencies for CH_3F . A normal mode analysis of unconstrained CH_3F indicates that the lowest frequency mode is predominantly C–F stretching motion. Thus, this mode was simply removed from the summation whenever R_{CF} was constrained. When only the methyl group was constrained, the ZPVE was estimated to include only the C–F stretch and a doubly degenerate CH_3F rocking mode. Constraining only the C–H stretching motions led to inclusion of frequencies for the CH_3 deformation modes, neglecting only the modes that were mainly characterised by C–H stretching motion. The ZPVE was calculated using frequencies for the unconstrained molecule in each case. This simplistic estimation of the ZPVE is suitable because we are deliberately using a low level of *ab initio* theory.

7.3 Analysis of Results

The spread of data in configuration space is demonstrated in Figs. 7.4, 7.5, 7.6 and 7.7 below. Triangle inequalities are apparent in the graphs, as discussed in previous chapters.

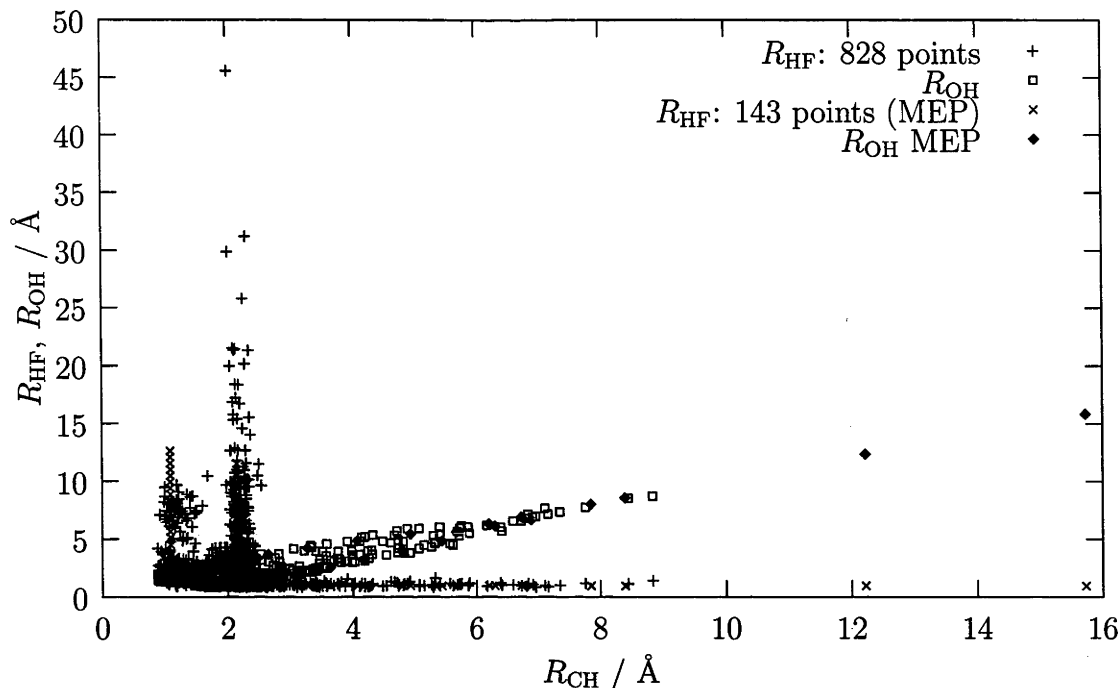


Figure 7.4: Distribution of points after 828 points have been added so that the PES comprises a total of 971 points. The hydrogen atom chosen for this graph is the hydrogen atom transferred in each reaction.

In all of these plots, The clustering at the intersection of “lines” of data points and at “corners” in the plots at short range is associated with areas where bonds are broken and formed. The energy varies rapidly with small changes in configuration where clustering occurs at short range which may lead, via variance sampling, to a concentration of data points.

Points lying along the diagonal in each plot are always representative of the O–H distance along the y-axis. If R_{OH} and R_{CH} increase, then protonation has occurred. The result of the protonation can also be observed in the nearly constant H–F bondlength as R_{CH} increases.

Two parallel lines extend vertically on each graph when R_{CH} is short ($< 3 \text{\AA}$) and the distribution of points along these lines are largely independent on the R_{HF} distance. Each line corresponds to a different isomer of HOC^+ (or HCO^+).

The shortest R_{CH} distance denotes the HCO^+ formyl cation where the hydrogen is directly bonded to the carbon. The rearrangement channel is therefore represented by the leftmost vertical line. After only 150 points have been added, very few points have been distributed into this channel in Fig. 7.5.

Figures 7.6 and 7.7 indicate that as the PES data set grows, this rearrangement channel is explored by the classical trajectories and data is accumulated there.

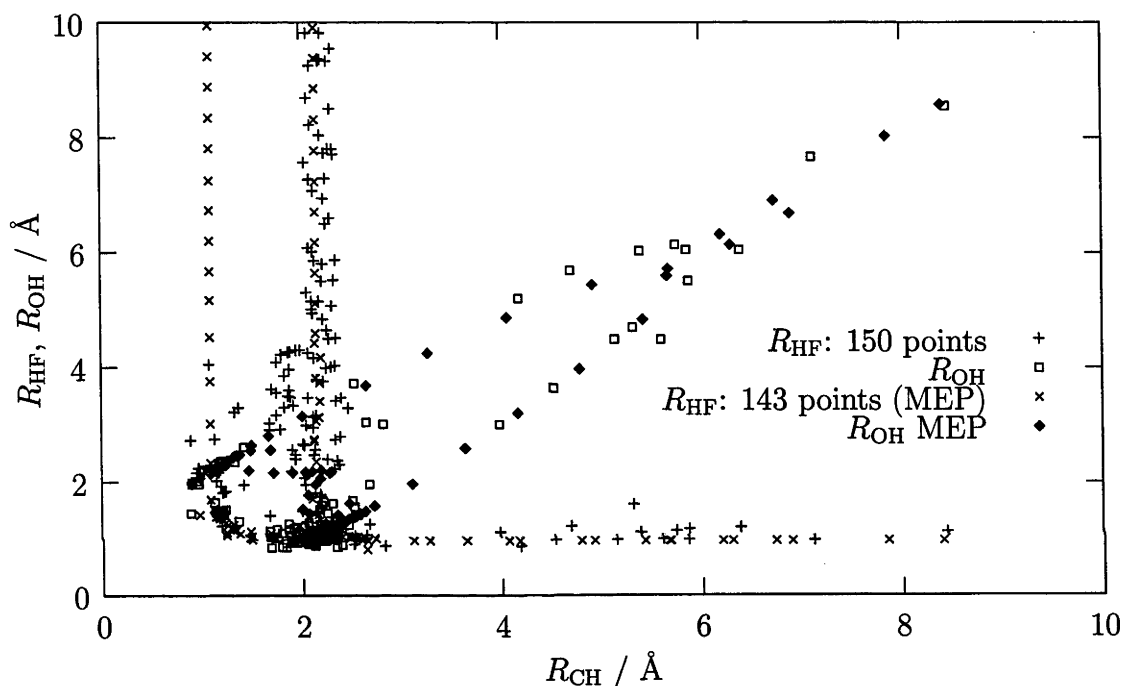


Figure 7.5: The distribution of points is shown after only 150 points have been added to the MEP data set. The scales have been shortened to emphasise the clustering of points in the reaction region.

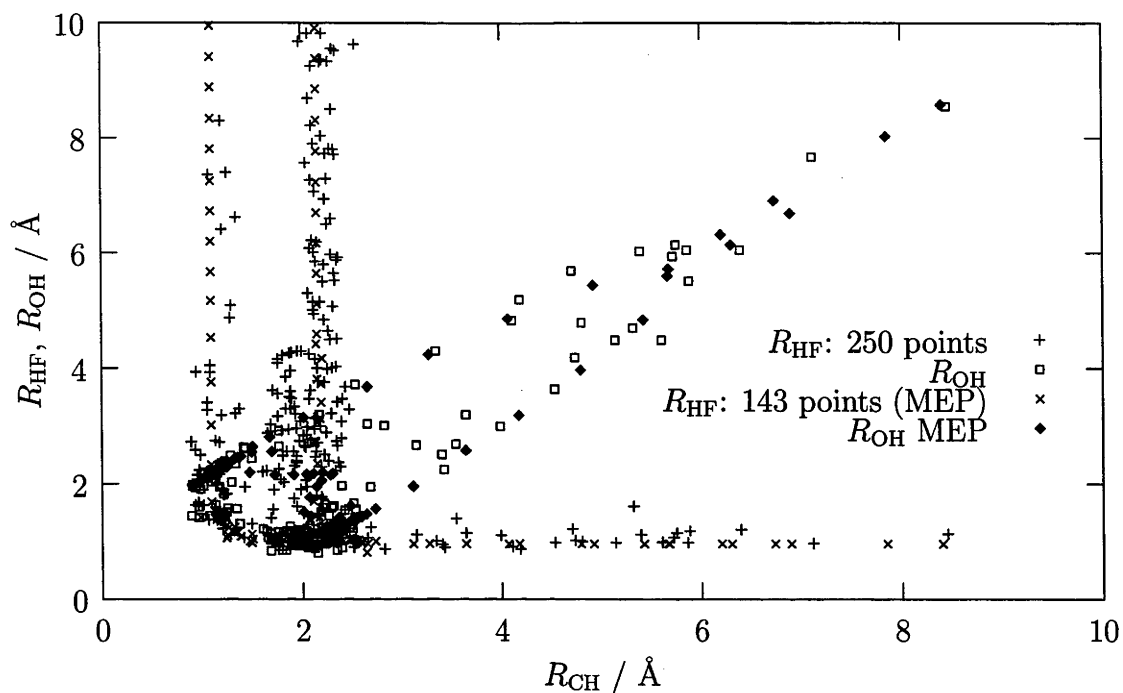


Figure 7.6: The distribution of points is shown after only 250 points have been added to the MEP data set.

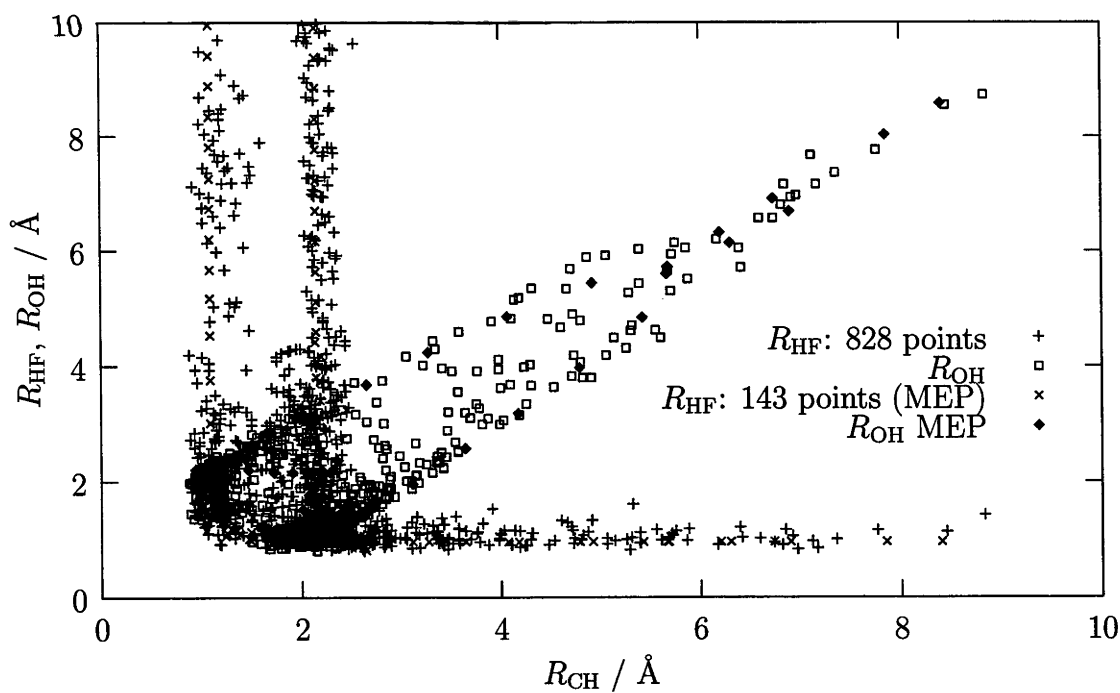


Figure 7.7: An enlargement of Fig. 7.4 for shorter scales on the axes.

Note that existence of the CO moiety can be inferred from these plots when protonation is observed to occur (where R_{CH} is large). Throughout either rearrangement or alkyl halide protonation, the C–O bond will change significantly in character but on the scale of these plots the change would not be obvious. Distribution of data in the R_{CO} bondlength is shown in Fig. 7.8. Additional data has clearly been added to describe vibrational motion and changes in the character of the bonding.

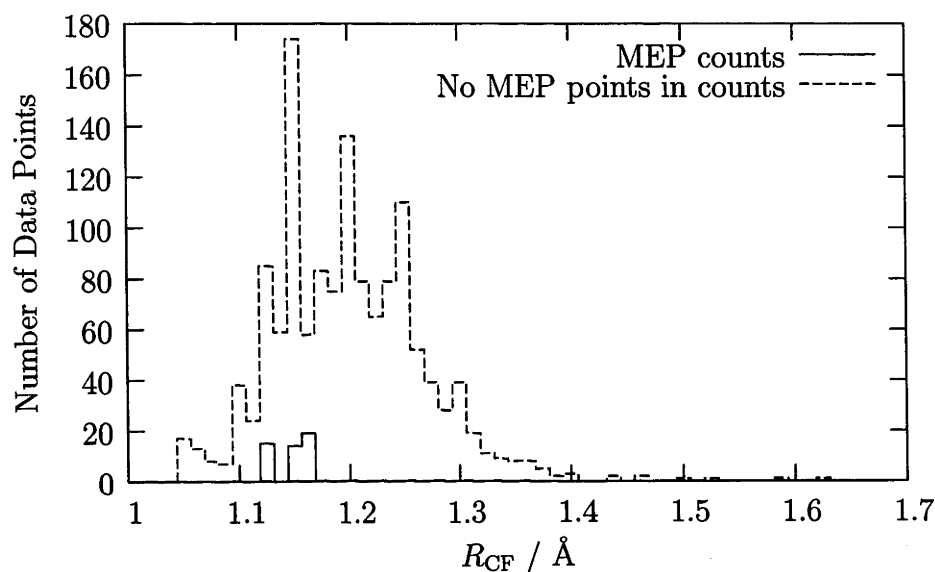


Figure 7.8: Histogram showing placement of points for R_{CO} internuclear distance in 0.0125 Å bins.

The R_{CH} distance has been plotted for 971 interpolation data points in Fig. 7.9 so that configurations can be identified as a function of point addition. Initially, a modest number of points (certainly not the majority) were added for large R_{CH} distances, corresponding to protonation. Two rough horizontal lines for short R_{CH} distances once again correspond to the formyl and isoformyl cationic isomers. Between 200 and 500 points the two horizontal lines have become indistinct where perhaps rearrangement has become more likely.

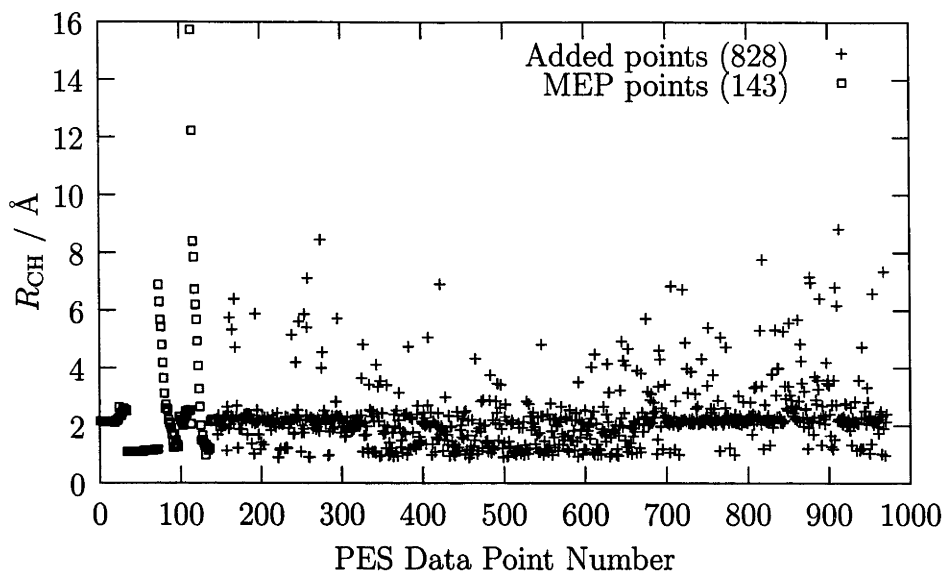


Figure 7.9: Internuclear C–H distance represented for each data point.

The geometric features of these plots of intermolecular distances alone are useful for qualitative predictions of where the PES may be accurate. The accuracy of the PES is quantified using a sample of configurations with known *ab initio* energies and gradients, as presented in Figs 7.10 and 7.11. As for studies of other systems in this work, a sample of trajectories on the full (all data points) surface was taken and the interpolated energies and gradients were compared with *ab initio* values. The sample used in the following graphs contained 500 points sampled from 1200 trajectories.

Absolute errors are shown for the full sample in Fig. 7.10. Different symbols identify various numbers of data points used in the interpolation. It is apparent that many of the large errors decrease as the number of data points is increased.

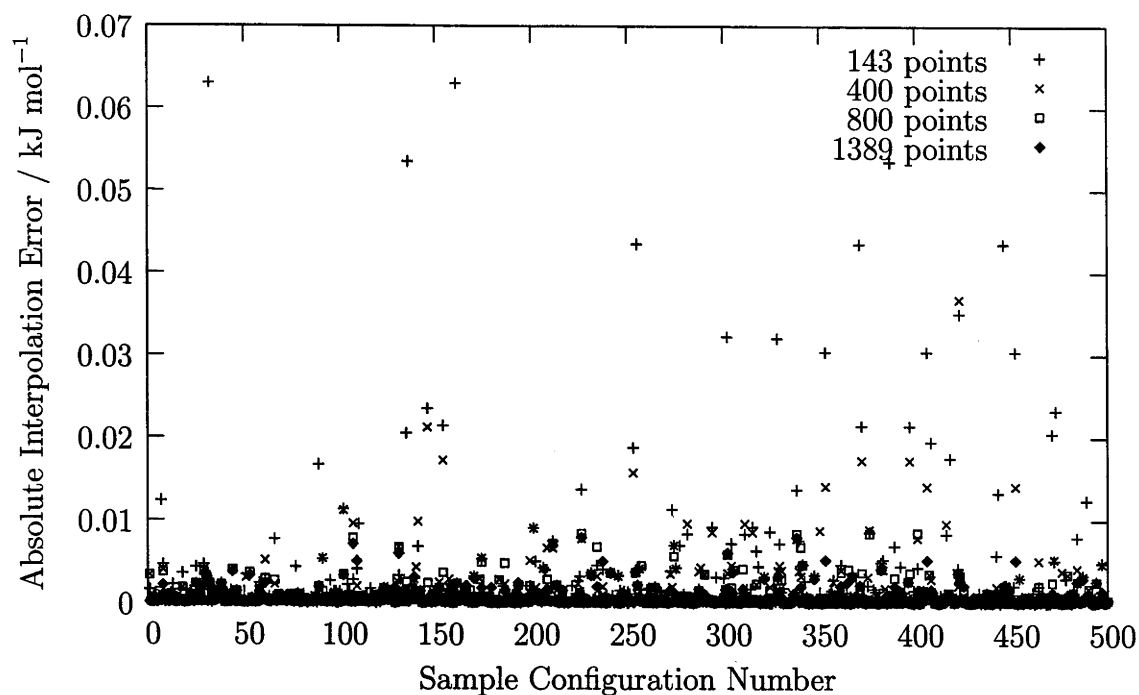


Figure 7.10: Absolute errors using 500 configurations sampled from a set of 1200 trajectories, evaluated for a PES with different numbers of data points.

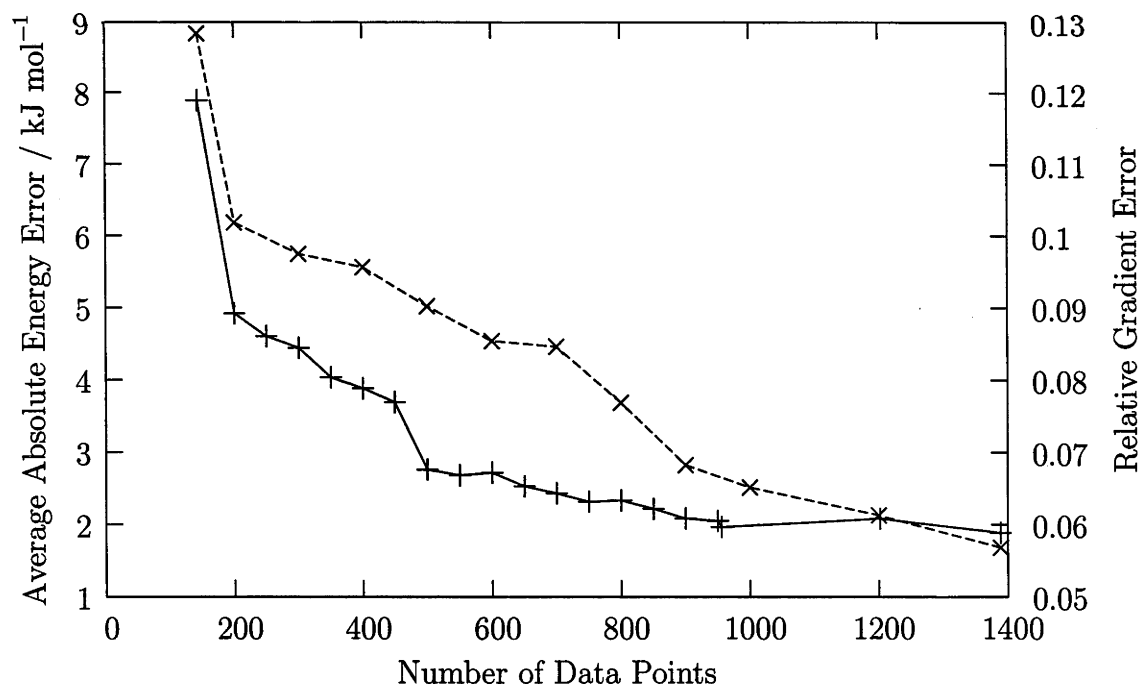


Figure 7.11: Average absolute energy errors and relative gradient errors using configurations sampled from a set of trajectories.

An average of all the absolute errors shown for the 500 configurations is presented in Fig. 7.11 as a function of the numbers of data points.

The relative error in the derivatives (see Eq. (3.20)) as a function of the number of interpolation data points is also shown in Fig. 7.11. The decrease in the relative error in the gradients reveals a similar trend to the decrease in absolute error in the energies. There is a subtle difference. Early in the process of adding points, the errors in the energies and gradients drop quickly and the vertical distance between the curves is relatively constant. Between 200 and 400 points the curves are divergent as the errors in the energies follow a form normally associated with convergence, that of diminishing returns, and the gradients decrease more slowly. Between 400 and 500 points there was a sharp decrease in average error for the energies that did not correspond to a similarly rapid decrease for the gradients. Further it can be noted for other intervals that the addition of important points to correct the energies were not necessarily sufficient to bear an equivalent improvement for the gradients.

To reiterate comments made for other systems, only convergence in the dynamical properties of interest is physically significant. For $\text{CH}_3\text{F} + \text{HOC}^+$, cross-sections for the competing reactions and branching ratio are significant dynamical properties for this study.

Convergence in both cross-sections in Fig. 7.12 is apparent after 400 points. The protonation cross-section actually converged at 200 points. The rearrangement channel is converged within the error bars (± 2 standard deviations) at 400 points, however, the cross-sections deviate less after 1000 points than between 400 and 1000 points.

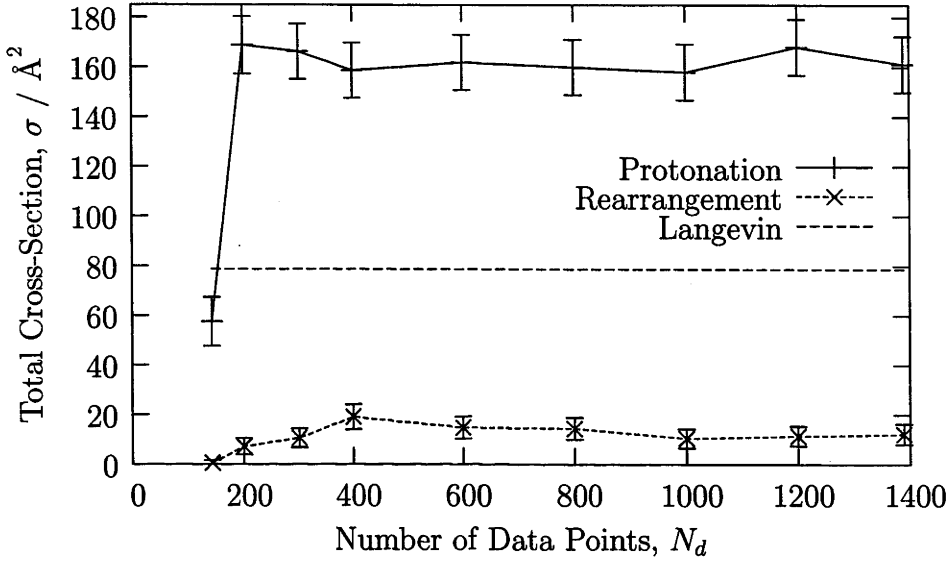


Figure 7.12: Convergence of reaction cross-sections with the number of data points in the PES. Error bars represent two standard deviations calculated using the number of events.

The branching ratio between the two product channels is shown as a function of the number of data points in Fig. 7.13. The error bars are large. However, convergence within a range less than half the error range is suggested. Error bars in graphs that show an observable as a function of the number of data points are for a single observation; however, neighbouring observations can be used in a statistical average if convergence is apparent.

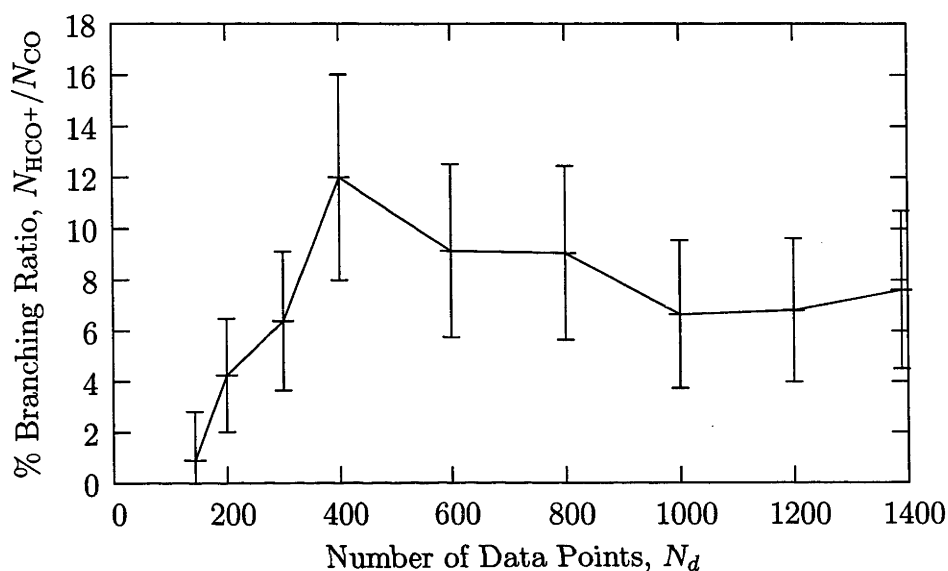


Figure 7.13: Convergence of the branching ratio in the reactive trajectories with the number of data points in the PES. Error bars represent two standard deviations calculated using the number of events and summing the relative errors for the proportions (which were derived from the simple binomial distribution).

A comparison of the distribution of product relative translational kinetic energy between the reactive channels is shown in Fig. 7.14. Protonation leads to greater energy disposal into translation in the products.

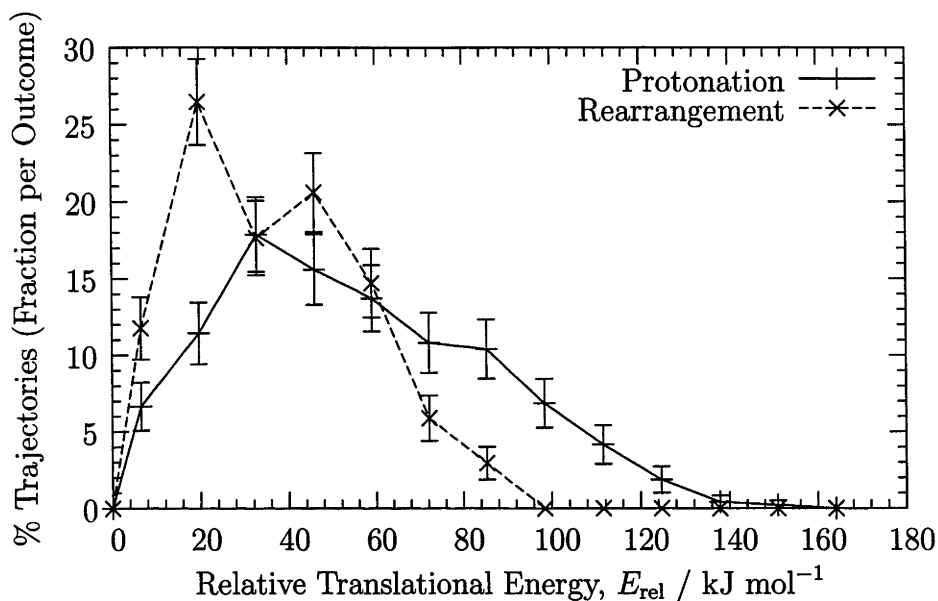


Figure 7.14: Distribution of translational kinetic energy of the products in trajectories by reaction pathway. The proportion of trajectories in each 13.1 kJ mol^{-1} bin, expressed as a percentage, is the proportion of the total number of trajectories for a specific product. Error bars represent two standard deviations calculated using the number of events. Results are for the final PES (1389 data points).

The angular momentum distributions for the CO and HCO^+ products are compared in Fig. 7.15. The corresponding angular momentum distributions for CH_3FH^+ and CH_3F are shown in Fig. 7.16.

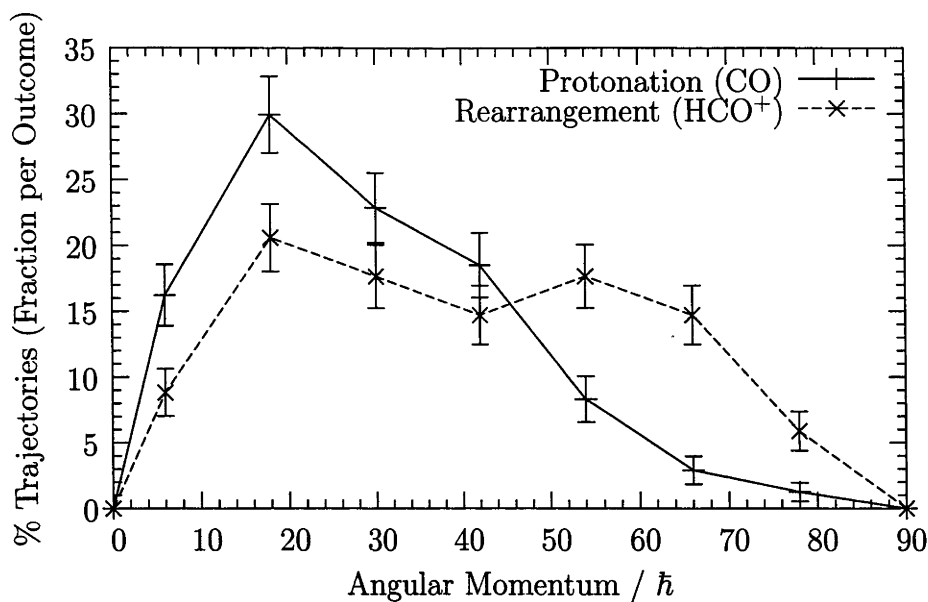


Figure 7.15: Distribution of angular momentum in the smaller products of trajectories by reaction pathway. The proportion of trajectories in each $12 \hbar$ bin, expressed as a percentage, is the proportion of the total number of trajectories for a specific outcome. Error bars represent two standard deviations calculated using the number of events.

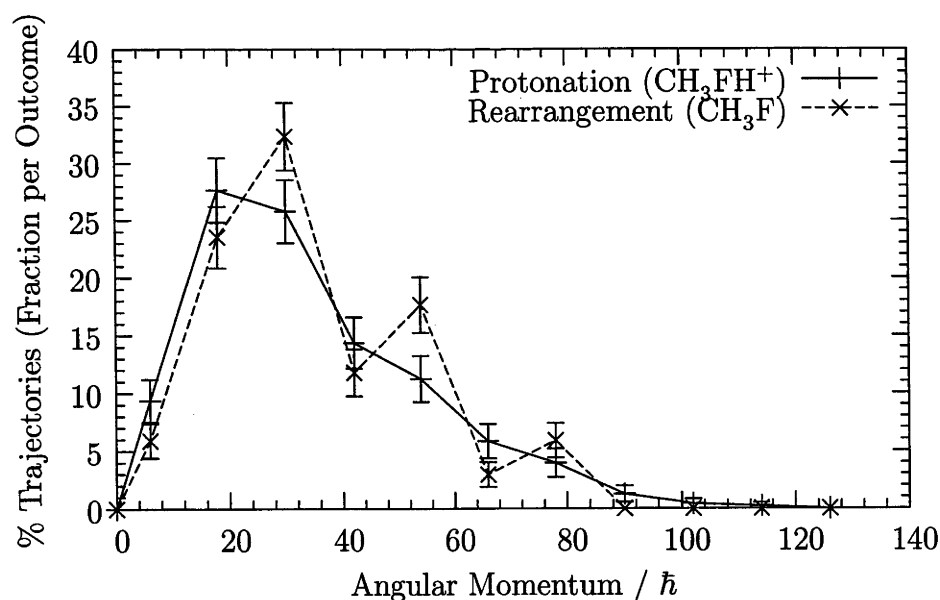


Figure 7.16: Distribution of angular momentum in the larger products of trajectories by reaction pathway. Error bars determined as in Fig.7.15.

The angular momentum and translational energy in the products has been examined for different numbers of data points in Figs 7.17 to 7.25. In some cases, the statistical errors are too large for a meaningful comparison, so we simply state this. Where possible, results from the initial data set are present on each plot, unless these statistical errors were simply too large. Instead, 200 points are used on those graphs.

Error bars in Figs 7.14, 7.15 and 7.16 are indicative of errors in the following graphs and have therefore been omitted for clarity. However, when there are less data points there were sometimes less trajectories in a specific channel, and this is manifest in the appearance of noise that would otherwise not be expected from Figs 7.14, 7.15 and 7.16.

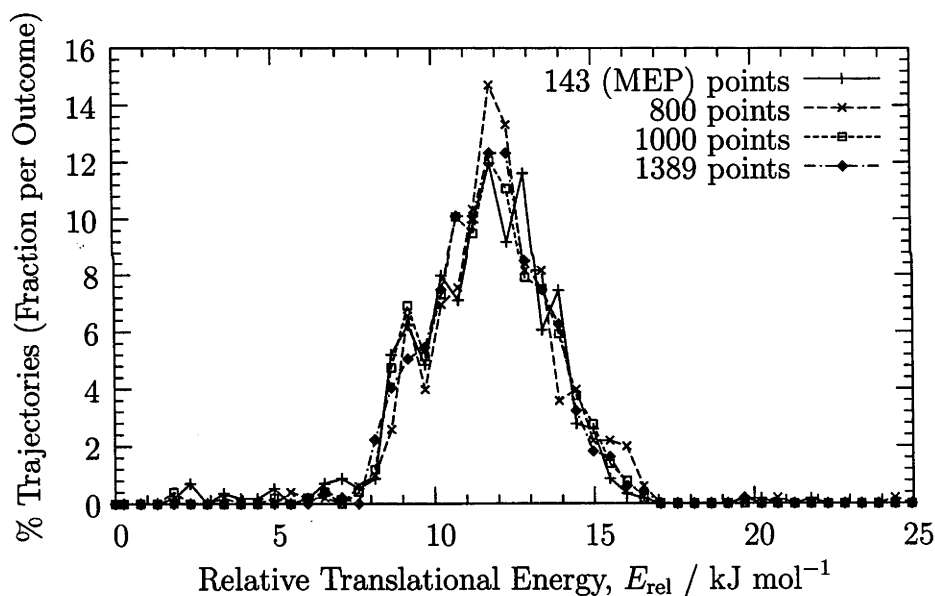


Figure 7.17: Convergence of kinetic energy distributions for the non-reactive channel with the number of data points in the PES. Error bars represent two standard deviations calculated using the number of events.

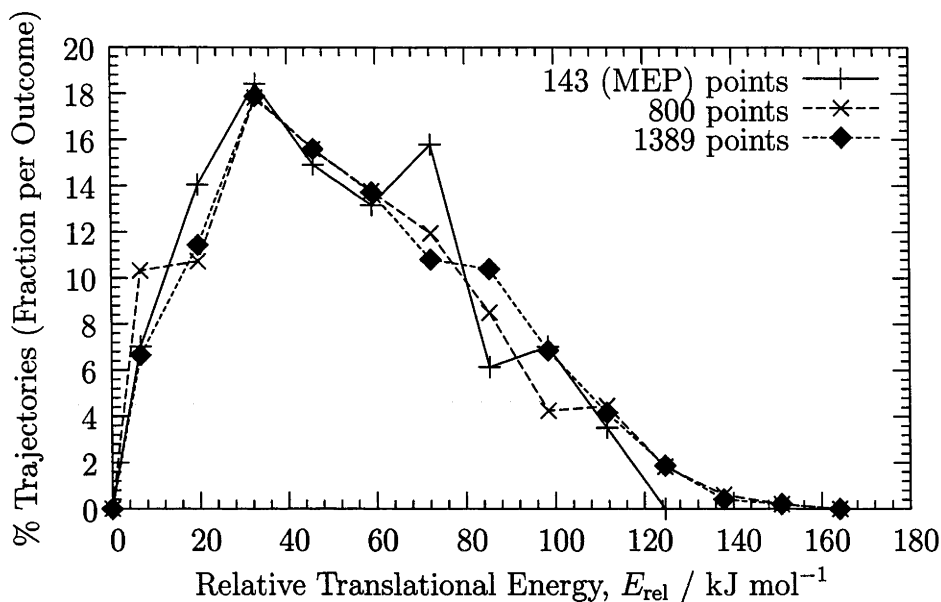


Figure 7.18: Convergence of kinetic energy distributions for the protonation channel with the number of data points in the PES.

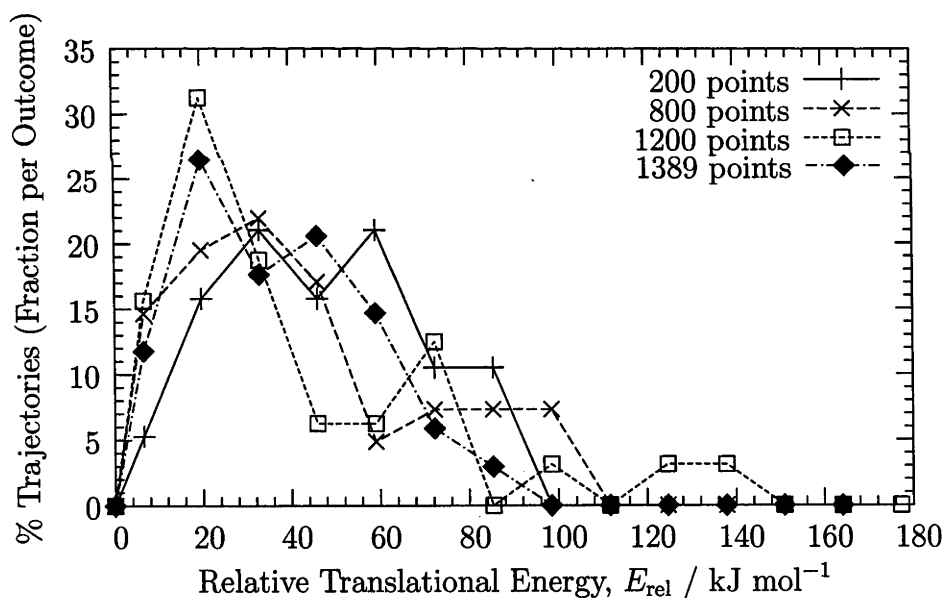


Figure 7.19: Convergence of kinetic energy distributions for the rearrangement channel with the number of data points in the PES.

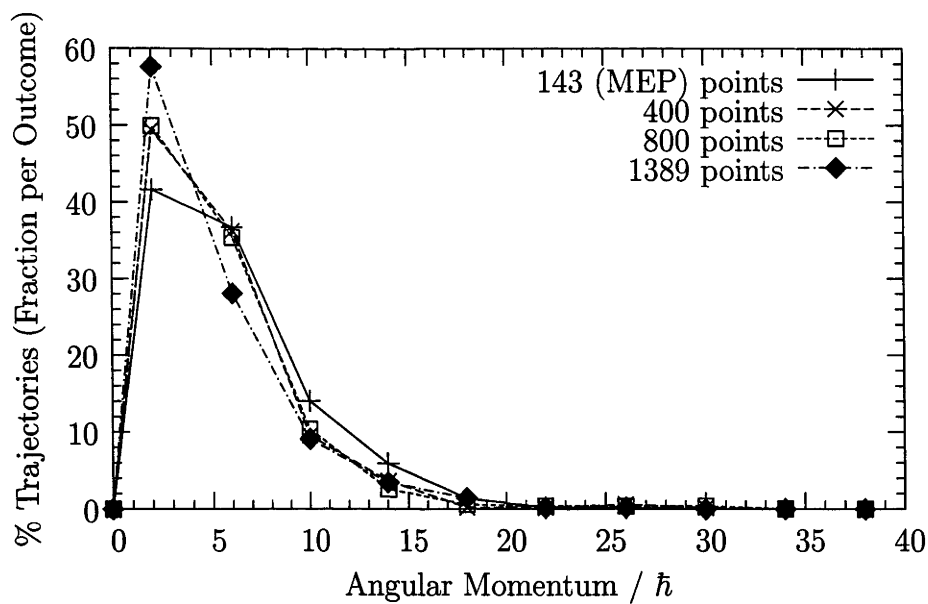


Figure 7.20: Convergence of angular momentum in HOC^+ in the non-reactive channel.

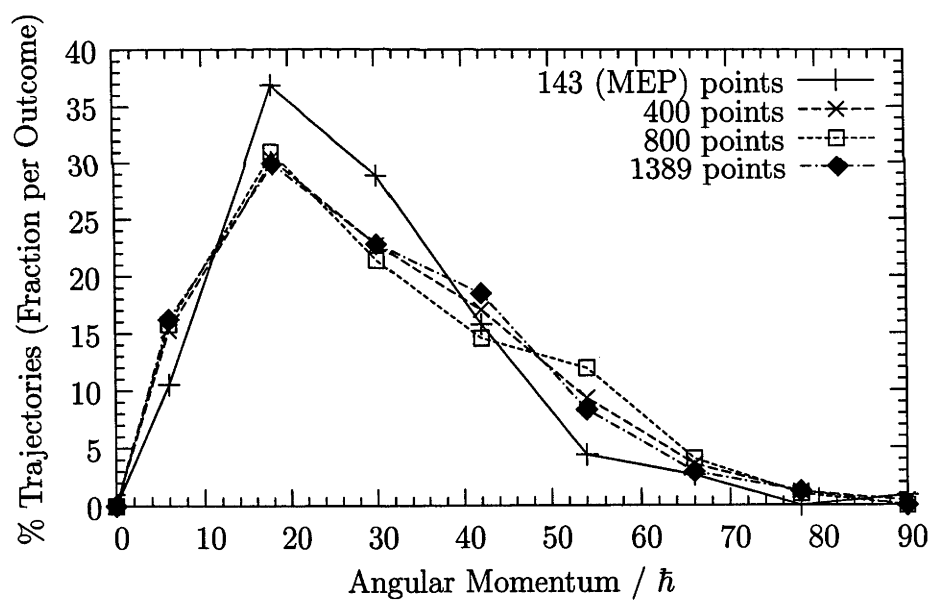


Figure 7.21: Convergence of angular momentum in the CO product.

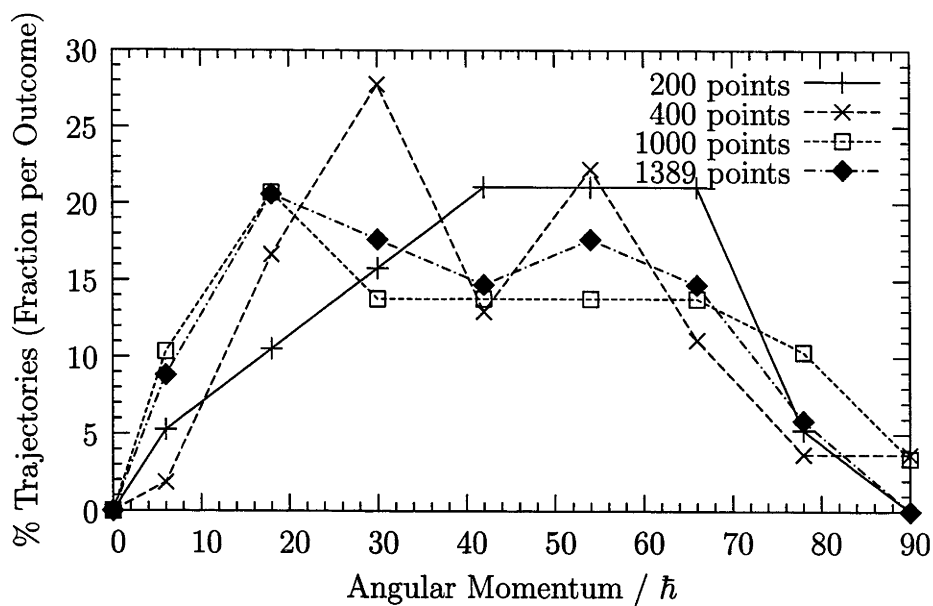


Figure 7.22: Convergence of angular momentum in the HCO^+ product.

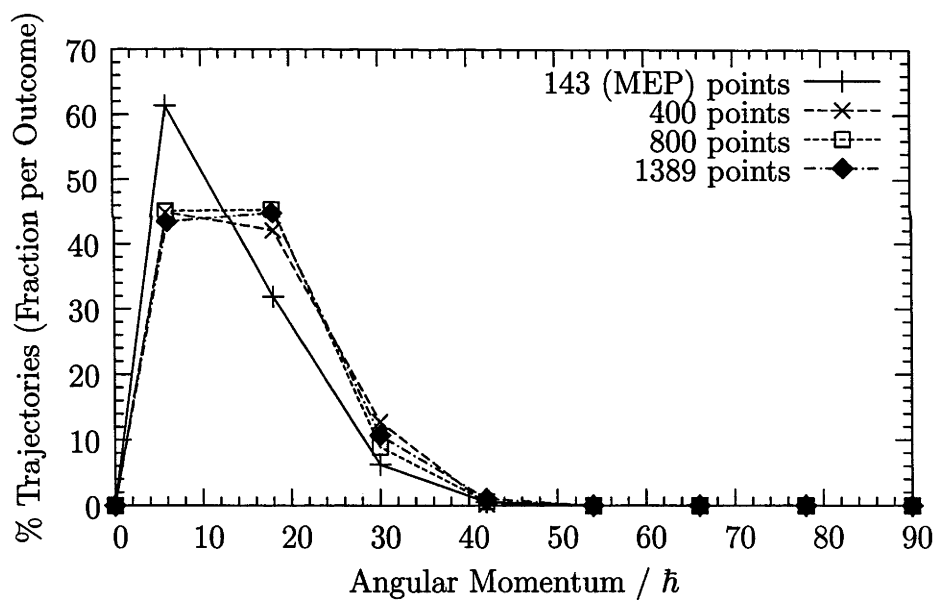


Figure 7.23: Convergence of angular momentum in CH_3F in the non-reactive channel.

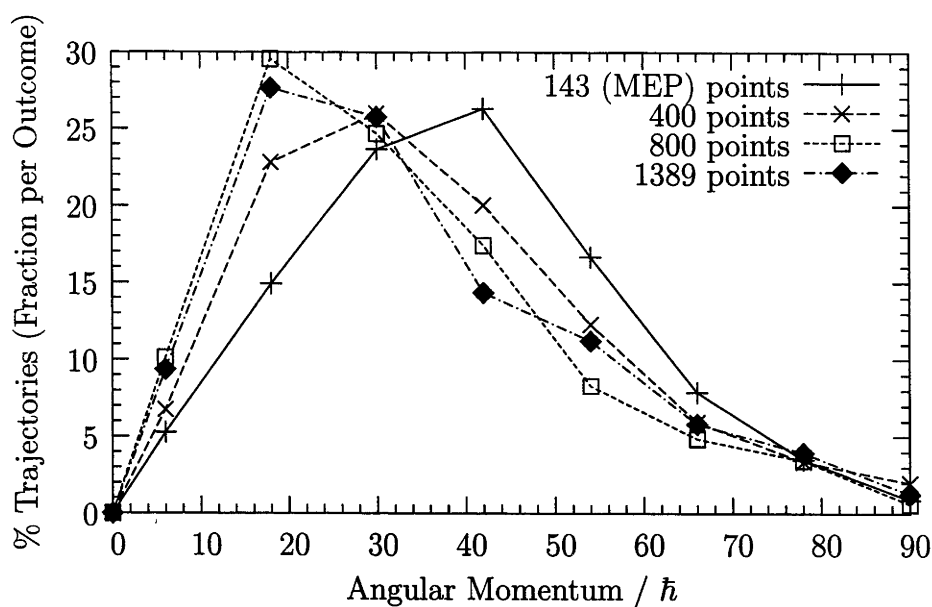


Figure 7.24: Convergence of angular momentum in the CH_3FH^+ product.

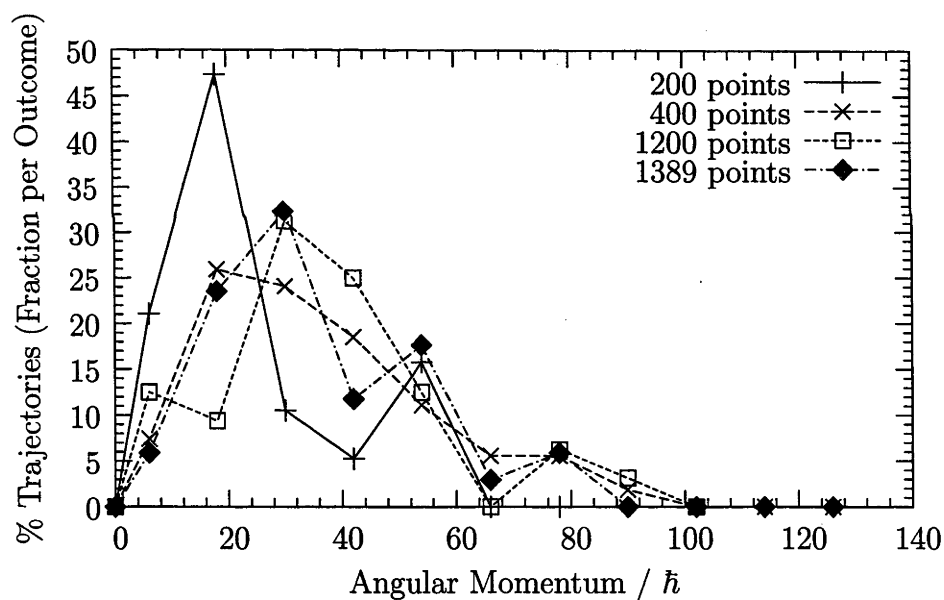


Figure 7.25: Convergence of angular momentum in the CH_3F collider after HOC^+ rearrangement to HCO^+ product.

In general, there is very good agreement in all these distributions for 400 or more data points and the distribution in each figure appears to converge to a stable distribution.

7.3.1 Unconstrained Dynamics on the Constrained PES

1000 trajectories were performed using the final PES (1389 data points) for each set of constraints depicted in Fig. 7.2. Figure 7.26 compares the cross-sections as a function of the number of constraints, where the varying numbers of constraints correspond to those defined in Fig. 7.2.

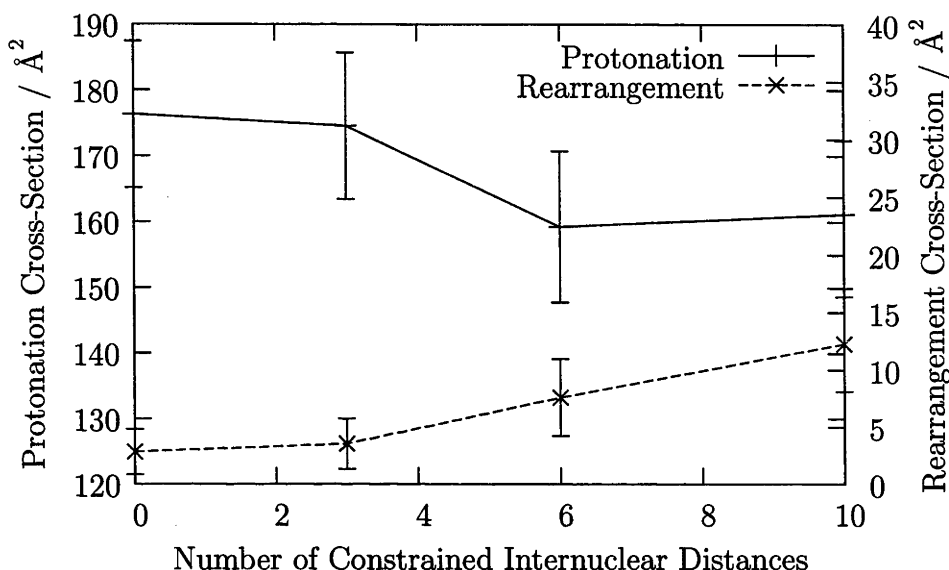


Figure 7.26: Cross-sections for each channel are shown for an increasing number of constraints. The number of constraints is discrete, and corresponds to the following sets of constraints: $\{\{R_{\text{CH}}\}, \{R_{\text{HH}}\}, \{R_{\text{FH}}\}, R_{\text{CF}}\} \equiv 10$, $\{\{R_{\text{CH}}\}, \{R_{\text{HH}}\}\} \equiv 6$, $\{\{R_{\text{CH}}\}\} \equiv 3$, and $\emptyset \equiv 0$.

The cross-section for hydrogen abstraction decreases as the number of constraints in the the CH_3F collider is increased in Fig. 7.26. A corresponding increase in the rearrangement cross-section is observed for larger sets of constraints. Agreement between the cross-section for unconstrained dynamics and the cross-section for only constrained R_{CH} distances in CH_3F indicate that the C–H stretching motions are less important to the dynamics.

It is interesting to study the effect of constraints on the distribution of relative translational energy and of angular momentum. If the constraints lead to similar

energy disposal to that observed for unconstrained dynamics, then it is possible that the constraints have had a negligible impact on the dynamics. Distributions of relative translational energy for each channel are shown in Figs 7.27 and 7.28 below. Again, error bars have been omitted for clarity.

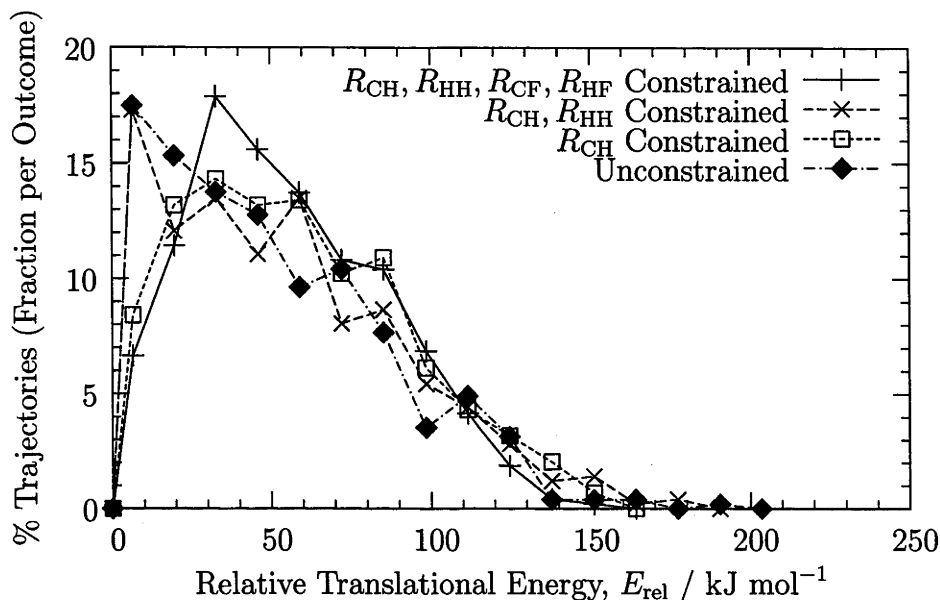


Figure 7.27: Kinetic energy distributions for the protonation channel with different constraints.

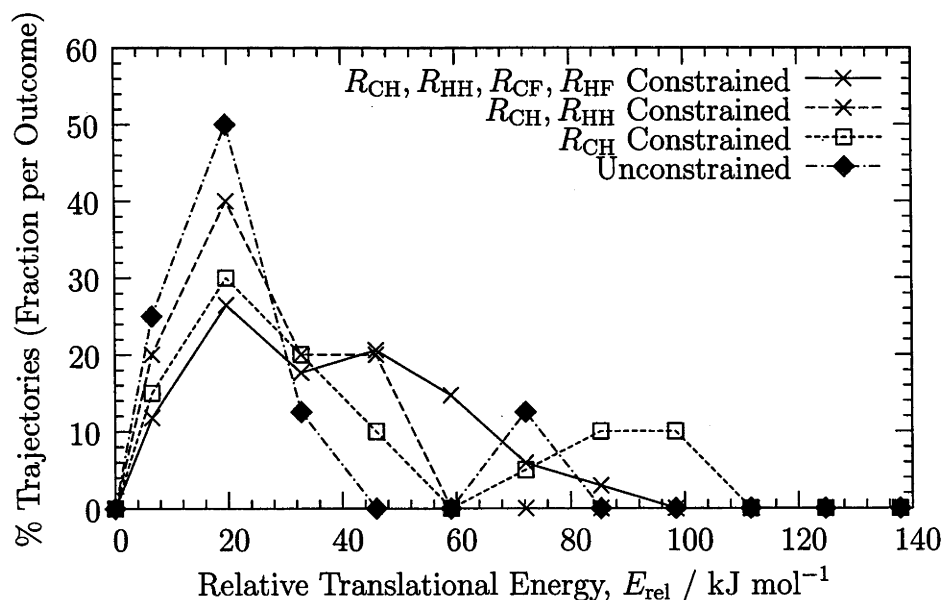


Figure 7.28: Kinetic energy distributions for the rearrangement reaction with different constraints.

Different distributions can be clearly recognised in Figs 7.27 and 7.28. For each reaction, unconstrained trajectories tend to scatter with less relative translational energy. The excess energy may be present in additional rotation or vibration in the products. The question of what is happening to the excess energy is answered by observing angular momentum distributions in the products for the different sets of constraints, in Figs 7.29, 7.30, 7.31 and 7.32.

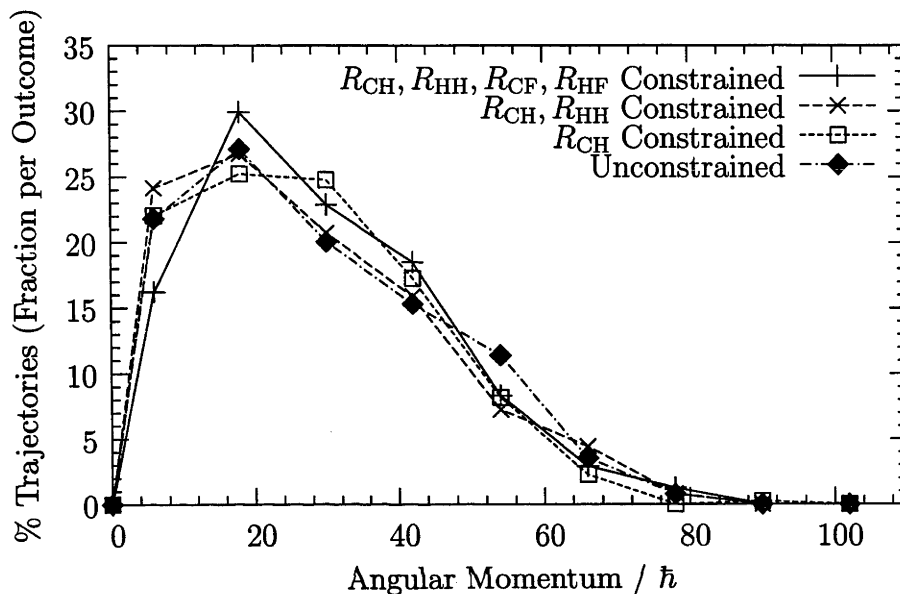


Figure 7.29: Angular momentum in the CO product for different sets of constraints.

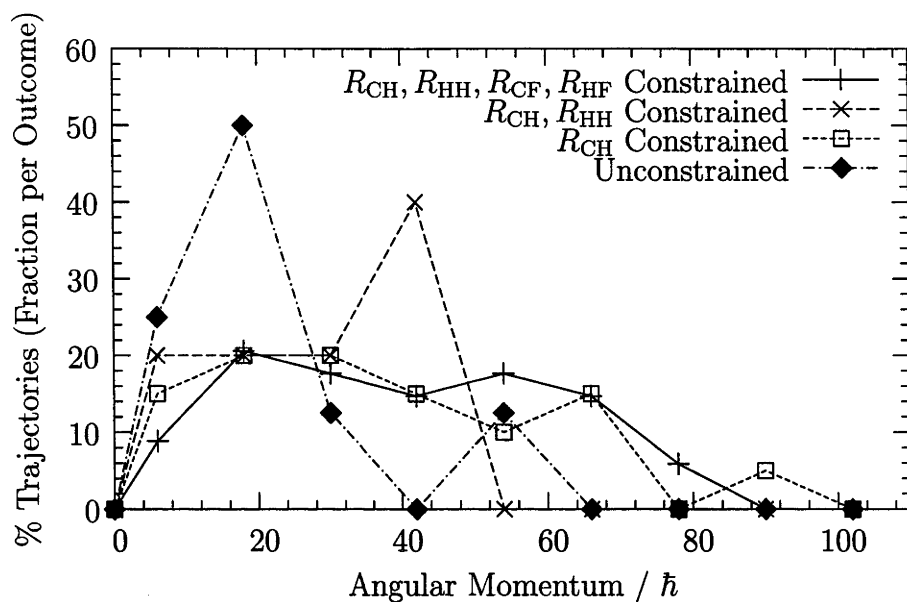


Figure 7.30: Angular momentum in the HCO^+ product for different sets of constraints.

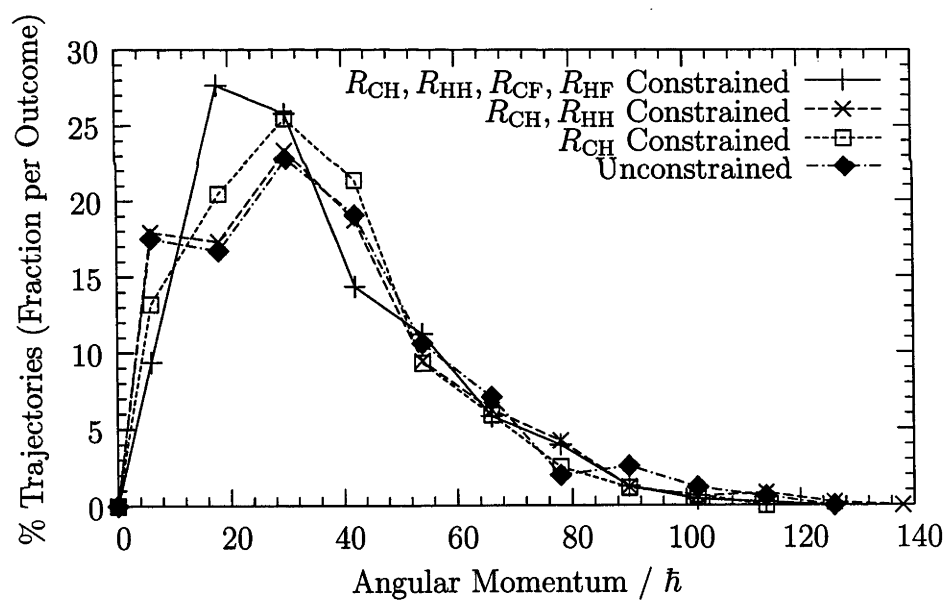


Figure 7.31: Angular momentum in the CH_3FH^+ product for different sets of constraints.

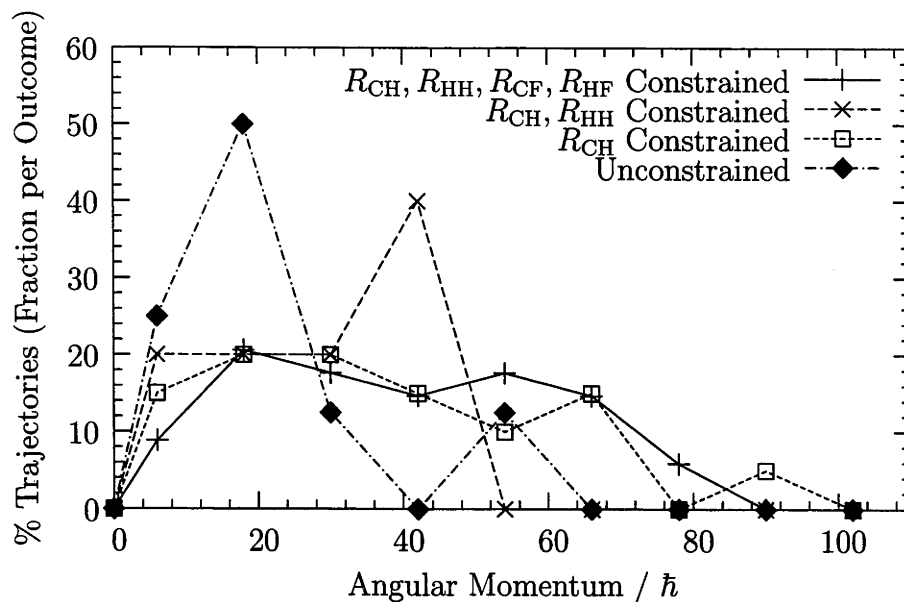


Figure 7.32: Angular momentum in the CH_3F collider after HOC^+ rearrangement, for different sets of constraints.

On average, less angular momentum is present in the products in the results from unconstrained trajectories than for constrained trajectories shown in Figs 7.29, 7.30, 7.31 and 7.32. There is clearly additional vibrational energy distributed in the unconstrained CH_3F molecule where additional degrees of freedom are available. There appears to be one exception in both the translational energy and angular momentum distributions and that is the set of constraints that constrains the entire methyl group that more closely resembles the unconstrained results than when only the R_{CH} distances are constrained. This exception may arise because the constrained R_{CF} distance was not set to its corresponding value in the optimised transition state geometry.

7.4 Conclusions

Here we have constructed a PES for an eight-atom system using 10 constrained atom-atom distances to maintain a rigid CH_3F reactant. Since, one of these bondlengths is redundant, nine of the 18 internal degrees of freedom of $\text{CH}_3\text{F} + \text{HOC}^+$ have been constrained. It is apparent from Fig. 7.11 that the interpolation errors in both the value and gradient of the PES reduces as the data set increases in size. The series of figures from Fig. 7.12 to Fig. 7.30 demonstrate that a range of important observable properties of this PES converge as the data set increases. Clearly, then this test case shows that convergent PES can be obtained under constraints in this system.

Interestingly, Fig. 7.26 shows that classical simulations on this PES with relaxation of some constraints do not give the same values of the reaction cross section as the constrained case. These observations reflect a similar observation for the $\text{CH}_3\text{Cl} + \text{F}^-$ PES. It may be reasonable to assume that the “constrained” PES is valid for unconstrained motion, since the amplitude of these motions is small when unconstrained. If this assumption is valid, then the variation in Fig. 7.26 is a true reflection of the effect on the motion of relaxing the constraints. We note that the cross-section when the three C–H bondlengths are constrained is very similar to that for no constraints. We might tentatively infer that the stretching of the C–H bonds does not play much of a role in these reactions. Constraining the three H–H bonds to form a rigid CH_3 group significantly affects both cross sections. The rearrangement channel is further affected by constraining the R_{CF} distance. A detailed examination of the affect of these various motions on the overall reaction dynamics is beyond the scope of this thesis.

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Part IV

Summary

Chapter 8

Concluding Remarks

In Chapters 1, 2 and later Chapter 5 we introduced the context and theoretical background for this thesis. The remaining chapters dealt with application of the theory to a variety of systems. The systems fall into two classes.

The first class includes two non-reactive inelastic scattering systems, N_2+N_2 in Chapter 3, and H_2+H_2 in Chapter 4. In each case, we examined the methodology for PES constructed using evaluations of a fitted functional form. The PES were tested by comparing constrained dynamics on the interpolated PES with the dynamics of the functional form. Reduction of the degrees of freedom meant that the PES converged appreciably faster than previous four-atom reactive systems. In the case of N_2+N_2 , it was found that the initial data set with only 33 data points was sufficiently accurate to obtain meaningful results within reasonable error limits. The interpolation did improve with additional data points, but it was clear that the Shepard interpolation performed very well for the relatively anisotropic potential in this case.

The success of the methodology for N_2+N_2 prompted study into another test case with more challenging characteristics. A suitable test case was the inelastic scattering of H_2+H_2 , where a functional form could also be used, and where the PES was known to be nearly isotropic. The small anisotropy means that dynamical

observables are likely to be sensitive to even subtle changes in the topology of the PES. Such a light system implied that only quantum dynamics would be sensible to test the convergence of the PES. As a consequence, the first quantum studies using a PES constructed using classical dynamics were attempted. Successful convergence for this system was therefore a significant benchmark. Later, Collins and co-workers applied quantum scattering techniques to reactive systems [1, 2].

In the second class of systems, we studied two reactions involving molecules larger than those previously attempted using the iterative scheme: six atoms in Chapter 6 and eight atoms in Chapter 7. The eight-atom system was the largest system attempted using the iterative scheme. We chose two ion-molecule reactions for this study.

In Chapter 7 we demonstrated that a PES constructed using constrained trajectories converged more rapidly than a PES constructed without constraints. Both reaction cross-sections and complex lifetimes were found to converge for the PES constructed using constraints. It was concluded that constraints do affect the dynamics. However, it is not clear that the use of constraints to partially inhibit the flow of ZPVE did not in fact produce more physical results. Comparisons with experiments and previous theoretical treatments were only in semi-quantitative agreement, a result possibly expected from the inexpensive model chemistry used in the *ab initio* calculations. The important inference drawn in this chapter is that a PES constructed with constraints can still be valid for unconstrained motion.

To complement earlier studies [3–5] of reactions of the HOC^+ ion, which involve proton-transport catalysis in competition with proton abstraction, the reaction of $\text{CH}_3\text{F} + \text{HOC}^+$ was studied in Chapter 7. The dimensionality of the eight-atom system implied that the *ab initio* calculations should be low cost. Qualitative agreement in the energetics with larger basis sets was obtained using 3-21G, so MP2/3-21G was chosen as the model chemistry. The convergence of the PES was very clear and was demonstrated for the branching ratio as well as the cross-

sections. By studying a larger system, it was possible to consider different sets of reasonable constraints for dynamics on the converged PES. Different numbers of constraints did affect the dynamics, with additional constraints lowering the protonation cross-section yet increasing the rearrangement cross-section. Due to concerns regarding ZPVE in classical trajectories, the unconstrained trajectories do not necessarily provide a more correct answer. What is most important is that all of these trajectories were run on a PES constructed using the highest number of constraints and that relevant results were obtained in each case.

In summary, Chapters 3 and 4 tested the new methodology for four atoms. Chapter 6 compared the construction of PES with and without constraints, and Chapter 7 explored the utility of a PES constructed using constraints for dynamics with a decreased number of constraints.

Along the way, the first quantum scattering results using the iterative scheme were presented. The first application of the iterative scheme to a popular organic reaction, nucleophilic substitution, was also presented. Further, a system larger than those previously studied using the iterative scheme was also presented here, pushing the tested limit to eight atoms, paving the way for future dynamical studies of a wider range of reactions using the constrained methodology.

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