

THE APPLICATION
OF THE
GENERALIZED IMPACT PARAMETER METHOD
TO A NUMBER OF
CHEMICAL PROCESSES

by

Bruce Alan Roy Koppers

A Thesis Submitted to
The Faculty of Graduate Studies and Research
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In Partial Fulfillment of the Requirements
for the Degree
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DEDICATED

to

my parents

ACKNOWLEDGEMENTS

To say the least, my stay at the University of Manitoba has been educational. It has also included many good times and memories that will be cherished.

To give thanks individually to all those that assisted in this work, directly and indirectly, would be a task in itself. I therefore hereby acknowledge and thank these silent partners in this work.

Of course, special thanks goes to my supervisor, Dr. R. Wallace, whose patience has been tried often by my sometimes exasperating inability 'to learn'.

The other members of staff also bear mention, and, of course, the department's financial assistance in the form of Teaching Assistantships is duly appreciated.

PREFACE

The work reported in this thesis is part of a collaborative investigation, involving R. Wallace, B. Pettitt, B. Corrigall, and A. Penner among others, aiming at the development of practical methods in the theoretical treatment of collisional processes. The author was involved in the evaluation of a number of models, but his major effort was directed at the development and testing of the semi-classical Generalized Impact Parameter method. The emphasis has been in general on qualitative and semi-quantitative rather than quantitative treatments since most chemical problems become intractable if attacked in an 'ab initio' manner. The general success of the method has been its applicability to a variety of processes including among others atom-atom collisions and photo-induced molecular rearrangement. A continued investigation of the application of this method to the study of de-excitation processes could be fruitful.

ABSTRACT

A generalization of a well known method, the impact parameter method, is investigated and the feasibility of its application to reactive collision theory considered. The basis of choice of a semi-classical method is discussed.

A general form of the equations are developed and various features of the equations discussed. The use and advantages of various representations and transformations are examined.

This is followed by a discussion of the numeric and computational aspects of the problem which is concluded by the choice of the Runge-Kutta-Gill algorithm as the integration procedure to be applied to the general system of equations.

The method was applied in its classical limit form to the study of bimolecular vibrational energy exchange in highly excited oxygen molecules.

Next the proton-hydrogen system was studied using the general method. Both low and high energy collisions were analyzed. The photo-decomposition of H_2^+ was also simulated. The agreement of the high energy results with available experimental information was one of the more satisfying aspects of this study. The photo-decomposition study lead to an estimate of the lifetime of the excited species.

The next two investigations were model studies of molecular systems. The first study was of photo-induced cis-trans isomerization of simple ethylenes. The role of vibration and rotation of the methylene groups in the de-excitation process was considered. An estimate of the de-excitation time was obtained. The second study examined

the factors involved in electronic energy exchange in the bimolecular collision of pi bonded systems. The system coupling was taken to be short range and coulombic in nature.

The study is concluded by a summary and brief discussion of the results of the study and future possibilities.

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Chapter I

INTRODUCTION

I.1 General Background

The dynamics of atomic and molecular processes have for some time presented the chemist, both experimentalist and theoretician, with an area of study which is both intriguing and difficult but also of fundamental importance to the discipline. The belief that a predictive understanding of chemical dynamics can be gained through a knowledge of fundamental collisional phenomena is the main motivation for the work offered herein.

The following discussion is intended to provide a qualitative overall view of the field of collision theory within the context of its application to the study of chemical processes. The practical impossibility of providing a more quantitative treatment is made manifest by the number of texts (1-7) and reviews (8-13*) available; the more formal aspects being examined in some detail in the former. It will perhaps clarify the following discussion to mention that the work reported in this dissertation was aimed at the development of a theory capable of application to actual physical systems, an objective receiving considerable support from Levine (10).

Collision theory describes an event in three distinct stages (4). One starts with an initial system which then undergoes an interaction leading to a final system. The system may consist of two initially isolated molecules which are allowed to approach, interact, and produce a system of molecule(s) as a result of the interaction. Such collisions are termed bimolecular. Alternately, the system may be an

* These references are only indicative. For a more comprehensive list see introduction of (10).

unstable molecule prepared at some starting time which undergoes an intra-molecular interaction leading to the formulation of a stable system, often called a unimolecular process.

Physically, it is possible to observe the initial reactants and final products but not the interaction complex of a collision (4). A quantum mechanical wave function which satisfies the boundary conditions imposed by the definition of the starting and final compounds of a reaction is called an asymptotic state. Since such states have a physical interpretation it is useful to describe the collision in terms of such states (3). The interaction is then described in terms of couplings among the various asymptotic states. Unfortunately the analytic aspects of such a description can become extremely complex and it is often necessary to develop the theory so it takes into account the special features of a given process.

Collision theories take advantage of the specifics of a given system by employing classical and semi-classical treatments rather than the more complex quantum mechanical treatment. However, two central problems are common to all approaches. The first is the handling of the translational modes of the collision while the other is the difficulty of managing the strong coupling of asymptotic states. These two difficulties are related. The absence of coupling amongst the electronic asymptotic states in the interaction region reduces the problem to one electronic channel, that is only one chemical product is expected from the reaction. The presence of such couplings introduces the possibility of alternate electronic channels and associated with each channel is a translational mode. In quantum and semi-classical

nuclear treatments these translational modes tend in general to be coupled. This difficulty may be expressed in other fashions, as in the case of classical nuclear treatments which require some form of statistical averaging of initial conditions to produce physically meaningful results, but the central problem remains.

To avoid this dual difficulty, total quantum theories, that is both the nuclei and electrons are treated as quantum particles, have commonly adopted either the adiabatic or Born-Oppenheimer approximations. Kolos (14) gives an analytic definition of these two related approximations but physically these two approximations take that the electronic and nuclear behaviours are independent; each only "seeing" a static potential representing the other set of particles. As has been mentioned (15), this is a static model which attempts to describe dynamic events. This approximation will fail whenever there are degeneracies in the electronic states involved in the process (16). Kolos (14) has considered the accuracy of the adiabatic approximation and some calculations have been attempted which include non-adiabatic behaviour (17-19). The main reason for imposing such a constraint is the resulting reduction in the complexity of the equations. Also, a number of events can be adequately described by such a model.

However, besides this pair of approximations one other approximation appears rather frequently in total quantum treatments, this being the use of perturbation theory. The formal aspects of this topic will not be considered here, the reader being referred to Messiah (1), but instead some general comments will be made. The extensive use of perturbation theory (8-10) reflects the fact that this method is one of

the more powerful analytic techniques available for the analysis of Schrodinger's equation. For a variety of phenomena which satisfy conditions described in (20) this method is indeed useful.

As a result of the common adoption of these approximations, almost all work using total quantum treatments have been restricted to non-rearrangement collisions. Emphasis has been on the analysis of translational-vibrational and/or rotational energy transfer; the usual systems being atom-diatom and diatom-diatom collisions. The reviews of Takayanagi (8), Rapp and Kassel (9), and Levine (10) indicate the level of present interest in this topic. Recently, with the advent of exact quantum calculations by Johnson and Secrest (21) and Clark and Dickinson (22) a great deal of effort has been directed toward a comparison of exact and various approximate methods.

However, some work has been done on rearrangement or reactive collisions with total quantum models. For instance, the system ($H+H_2$) has received considerable attention (23-24). Though other systems have been investigated the treatments employed generally incorporate adiabatic electronic potential energy surfaces and consider the reaction to be dominated by the collinear event.

Other work that has been done which is of relevance to this thesis is the study of electronic relaxation by a full quantum treatment by Jortner et al (25-28). However, this work has been more qualitative than computational in nature.

Not wishing to incorporate the adiabatic potential surface approximation in the general method, and seeing at the present time no way to manage the quantal description of translational modes in a

computationally oriented study, the full quantum treatment was abandoned.

The difficulties associated with total quantum descriptions has led to the re-investigation of the use of total classical theories to describe atomic and molecular events. Until recently this area has been largely neglected after the advent of quantum mechanics (see introduction of 29). However, interest has expanded rapidly as may be discerned from the review articles by Burgess and Percival (11), Bates and Kingston (12) and Keck (13). It is to be noted that few classical treatments actually consider the electron as a particle. However, both Abrines and Percival (29, 30) and Pettitt (31) have analyzed the system (p, H) wherein the electron was treated as a charged classical particle. Pettitt commented that "The ability to employ rotating classical electrons in the representation of low quantum atomic states is startling", (P. 42; 31). However, this approach is severely limited by the possibility of the electrons colliding with the nuclei, an almost unavoidable difficulty for systems of many electrons.

The more common approach is to represent the electrons by a suitable potential field. The use of Monte Carlo and statistical averaging techniques are common. The advantage of the total classical treatments is that the problem is solvable if somewhat time consuming. The disadvantages are associated with interpretation and choice of the proper potential surfaces (13). These methods tend to depend heavily on empirical and semi-empirical curve fits to define the potential surfaces and it has been noted (31) that the potential parameters are rather arbitrary yet their choice has significant effect on the interactions of the system. This difficulty will be elucidated by the study

reported in Chapter IV. Having no desire to be so limited from the start in the treatment of electronic behaviour, the semi-classical theories were considered.

Semi-classical theories divide naturally in two groups; the division being based on whether a classical or semi-classical nuclear treatment is employed. The latter treatment will be considered first.

The use of this group of semi-classical collision theories has been quite limited. However, there has been a recent renewal of interest in this particular approach. For example, Pechukas (32) and more recently Miller (33) have undertaken studies of vibrational phenomena within this semi-classical framework. Others such as Eu (126), Eu and Tsien (127), and Marcus (128) have developed methods for analyzing both non-rearrangement and rearrangement processes. Cross (129) divides the available methods into two general categories, the perturbed elastic trajectory methods (130) where the inelastic scattering is treated as a time dependent perturbation, and the exact semi-classical method (32,33,128) in which quantum mechanical information is obtained by integrating a phase over the exact classical trajectory. However, these studies have been concerned more with the development of techniques than the study of actual systems and it is too early to draw conclusions on the general usefulness of this model (34). For a more complete discussion of this approach to the collisional problem the reader is referred to the work of the author's co-workers Penner and Wallace (35,36). However, considering the difficulties encountered in these developmental studies this approach was deemed inadvisable.

A variety of semi-classical theories which treat the nuclei as classical particles have been developed. Their range of application has

been rather extensive. For instance; Watson et al (37-39) have adapted the eikonal approximation to a semi-classical theory and applied it to reactive collisions. The study of classical trajectories along representative potential surfaces has received considerable attention from Polanyi et al (40-45) amongst others (46-47). A variety of processes have been studied including reactive collisions. Much effort has been directed towards an analysis of the effect of the shape of the potential surface on the reaction.

Unfortunately, these studies tend to adopt in one fashion or another the adiabatic approximation in that most studies consider only one electronic state. For this reason the study of Gallaher and Wilets (48) was of particular interest since it allowed the possibility of contribution from the electronic excited states in the evaluation of the transition possibilities. Their method, however, is not directly applicable to chemical systems since they were analyzing the collision of medium energy protons (KeV) with hydrogen atoms by a standard impact-parameter method. It is known that these methods fail when the initial and final state trajectories are significantly different (49), behaviour expected in chemical processes.

However, the more general existence of semi-classical methods (classical nuclei) which have been used to analyze reactive collisions and the ability of the impact-parameter method to investigate simultaneously the importance of various electronic states in a given process suggested the investigation of the possibility of developing a generalization of the impact-parameter method which would not be limited to relatively high energy events.

This thesis reports the development of a method and its application to a number of systems resulting from such an investigation.

I.2 Scope of Dissertation

In the next chapter the equations of motion representative of the generalized impact parameter method are developed. The general form and necessary properties of the multi-electron functions are discussed followed by the introduction of the general use of transformation theory on this set of equations.

Chapter three undertakes to find the optimum method of solving the systems of equations developed in Chapter two. Taking into consideration both numeric and computer aspects of the problem, the fourth order Runge-Kutta Gill method was chosen and program coding was done in the Fortran IV computer language.

In the first study employing the generalized impact parameter method the equations were developed to a form appropriate for the total classical limit and applied to the analysis of the collision of oxygen molecules in highly excited vibrational states. The study employed empirical potentials and the results are indicative of the difficulties associated with their use.

Chapter five undertakes the study of low and high energy collisions of the proton-hydrogen (p-H) system as well as the photo-decomposition of excited states of H_2^+ using the generalized impact parameter method. The results of the high energy collision study are perhaps most significant.

In the next chapter, the cis-trans isomerization of photo-excited ethylenes is examined. This is a unimolecular reaction involving non-radiative de-excitation processes. The relative importance of the various available modes for energy transfer is considered and the time for

the process to take place estimated.

Chapter seven contains an investigation of intermolecular electronic energy transfer in π bonded systems. This final study examines the factors which control short range electrostatically induced electronic energy transfer in the collision of ethylene like molecules where one of the colliding partners is electronically excited.

The dissertation is concluded by a general discussion of results and possible directions for development.

Chapter II

DEVELOPMENT OF GENERALIZED IMPACT PARAMETER METHOD

II.1 Introductory Comments

Standard impact parameter methods usually employ the approximations that the relative velocity is constant and that the particles follow straight line trajectories. As a result these methods are implicitly limited to the study of relatively high energy events since it is realized that non-linear motion will be important for low energy collisions (2, 49):

It was apparent, therefore, that a method applicable to low energy collisions could employ neither of these approximations. The resulting theory takes the nuclei to be classical particles moving along trajectories determined by an electronic potential which dynamically depends on the internal states of the colliding molecules and these states have an implicit dependence on the nuclear motion through their explicit dependence on the potentials defined in terms of the time dependent nuclear positions. In this way, all changes happening during the collision are coupled, and these time dependent couplings represent the interactions which result in the processes that are to be investigated. The use of numeric methods and standard approximate electronic treatments resulted in it being feasible to undertake at least model calculations of actual chemical systems.

Before proceeding it is perhaps appropriate to deal briefly with the questions raised by the employment of a classical nuclear treatment for collisions of such low energy. First, one may wonder how valid such a treatment is for low energy processes. Thorson and Delos (50) investigated the applicability of the classical equations of motion and concluded that they were valid in situations in which the classical

picture did not apply. They were able to derive sufficient conditions to guarantee the validity of the classical equations but did not show them to be necessary conditions. The other major question is the practicality of a method that inherently requires multiple trajectory calculations for statistical averaging in the calculation of physical quantities such as cross sections. This point will not present this research with much difficulty since the present interest lies more in revealing the basic mechanism of the reaction than obtaining quantitative calculations of physically unmeasurable events.

In the following chapters, two alternative reference frames are used. The first is the laboratory frame, denoted by the set $\{\tilde{q}^i\}$ while the other is the centre of mass frame specified by the set $\{\tilde{R}^i\}$. The relation between the two frames for a two body case is shown in figure one.

The derivation presented in this chapter is general in nature. The quantum mechanical equations are developed in the centre of mass frame (1) while the classical equations can be considered to lie in either frame.

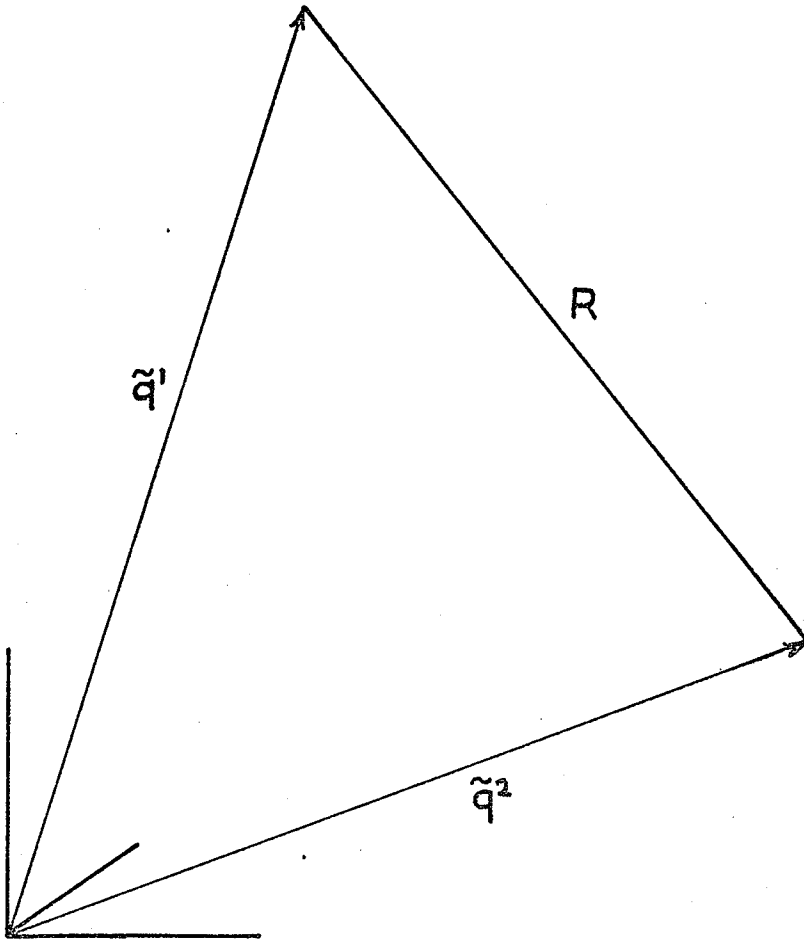
Throughout the rest of this thesis atomic units are used in which Planck's constant \hbar , the electronic mass m , and charge e are unity. For the definition of these units see Appendix A.

Figure 1

Relation between the laboratory (\tilde{q}^1, \tilde{q}^2)
and centre of mass (R) frames of reference

for a two body system where

$$\begin{aligned} R &= | \tilde{q}^1 - \tilde{q}^2 | \\ &= \sqrt{(\tilde{q}^1 - \tilde{q}^2) \cdot (\tilde{q}^1 - \tilde{q}^2)} \end{aligned}$$



II.2 Development of Equations Describing Electronic Dynamics

The time evolution of the electronic wave function $|\Psi(\tilde{\mathbf{r}}, t)\rangle$ is given by the time-dependent Schrödinger equation

$$i \left(\frac{\partial}{\partial t} \right)_{\tilde{\mathbf{r}}} |\Psi(\tilde{\mathbf{r}}, t)\rangle = H |\Psi(\tilde{\mathbf{r}}, t)\rangle \quad (\text{II.1})$$

where H is the Hamiltonian describing the motion of the electrons in the centre of mass frame, $\tilde{\mathbf{r}}$ represents all electronic co-ordinates in the centre of mass frame, t is the variable time, and $\left(\frac{\partial}{\partial t} \right)_{\tilde{\mathbf{r}}}$ is the partial differential operator with respect to time under the constraint that $\tilde{\mathbf{r}}$ remains fixed. To develop from (II.1) a manageable set of equations, it is necessary to examine the forms of H and $|\Psi(\tilde{\mathbf{r}}, t)\rangle$.

The Hamiltonian H is defined for a given system by a set of rules which are well established (1). However the present interest is not in the specific resolution of H but the general separation

$$H = H_0 + V \quad (\text{II.2})$$

which has general applicability.

The choice of an appropriate form for the multi-electron function $|\Psi(\tilde{\mathbf{r}}, t)\rangle$ is a more difficult problem, the scope of the topic being suggested by the extensive work that has been done for its time-independent counter-part (51 - 54). Certain ramifications of this topic will be discussed in the next section but it will be taken that $|\Psi(\tilde{\mathbf{r}}, t)\rangle$ has the form

$$|\Psi(\tilde{\mathbf{r}}, t)\rangle = \sum_{\mathbf{I}} b_{\mathbf{I}}(\tilde{\mathbf{R}}, t) |\chi_{\mathbf{I}}(\tilde{\mathbf{r}})\rangle \quad (\text{II.3})$$

where $\tilde{\mathbf{R}}$ represents all nuclear co-ordinates and $\{ |\chi_{\mathbf{I}}(\tilde{\mathbf{r}})\rangle \}$ is a set of time independent multi-electron functions. The coefficients $b_{\mathbf{I}}(\tilde{\mathbf{R}}, t)$ contain all the time dependence of the many electron wave function. The choice of the set $\{ |\chi_{\mathbf{I}}(\tilde{\mathbf{r}})\rangle \}$ is somewhat arbitrary but it is often