

A STUDY OF ATOMIC AND MOLECULAR  
COLLISION THEORY

by

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To Lucie

If I am inclined to suppose that a mouse has come into being by spontaneous generation out of grey rags and dust, I shall do well to examine those rags very closely to see how a mouse may have hidden in them, how it may have got there and so on. But if I am convinced that a mouse cannot come into being from these things, then this investigation will perhaps be superfluous.

L. W.

## Preface

The work reported in this thesis is to be viewed as a preliminary investigation, in collaboration with R. Wallace, B. Kuppers, and W. Corrigall, designed to establish methods of practical ( as opposed to formal ) importance in the treatment of collision theoretical models. Within a distinction among classical, semiclassical, and quantum mechanical elements of these models, this report focuses on the first. This concentration was considered to be essential but is recognized as having little value in itself. The incorporation of techniques developed for the classical elements into a semiclassical scheme has been the subject of further effort and appears to be of considerable value.

### Abstract

*This document describes how the dynamics of some chemical and physical processes are embodied in sets of coupled integral and differential equations. The general ( formal ) features of these equations are discussed and a review of current methods of approximate solution is presented. It is argued that numerical techniques adapted to high-speed digital computations provide the most penetrating attack on such problems. This is presented within the context of a study designed to establish a method for calculating multi-particle trajectories.*

## Table of Contents

	Page
<u>Section I : Introduction</u>	1
<u>Section II : Review</u>	3
A) Formal Quantum Mechanical Collision Theory	3
Direct ( Elastic and Inelastic ) Collisions	3
Born Series	6
Cross Sections	7
Distorted Wave Approximation	8
Perturbed Stationary States Method	9
General Rearrangement Collisions	10
Numerical Integration	14
A Few Applications	15
B) Semiclassical Collision Theory	18
Impact Parameter Method	18
Trajectories	20
Eikonal Method	20
A Few Applications	21
C) Classical Collision Theory	24
Equations of Motion	24
Numerical Integration	25
Molecular Models	27
A Few Applications	29

Section III : Classical Model Calculations 32

A) Coulomb (proton-hydrogen atom) Trajectories

Planar Orbits 32

Three Dimensional Orbits 33

B) Molecular Trajectories 36

Collisions of O<sub>2</sub> Molecules in Highly  
Excited Vibrational States 37

C) Numerical Integration Scheme 41

Section IV : Discussion 42

Classical, Semiclassical, and Quantum  
Mechanical Considerations 42

The Problem of Potentials 43

Appendix :

I Coupled Differential Equations ----- 45  
Conversion from Integral Form

II Coordinate Representation of the 47  
Transition Amplitude

III Impact Parameter Limit of the 48  
Eikonal Method

IV Equations of Motion for Classical 49  
Molecular Models

Bibliography 52

### List of Figures

Figure	Object	Page
1	Initial State of a Generalized Molecular Collision	3
2	Diagrammatic Representation of Transition Amplitudes	7
3	Differential Cross Section for Electron Capture in $H-H^+$ Collisions	23
4	Geometry of Classical Model for $H-H^+$ Collisions	32
5	Electron Trajectory in Planar Model (Classical) of $H-H^+$ Collisions	34
6	Electron Trajectory in Planar Model (Classical) of $H-e^-$ Collisions	35
7	Geometry of Classical Model for Collinear Collisions of Diatomic Molecules	37
8	Vibrational Energy Transfer vs. Range Parameter (Morse) for $O_2-O_2$ Collisions	39



## SECTION I: INTRODUCTION

A purely quantum mechanical theory of molecular collisions has as its distinguishing features:

- 1) the electronic, vibrational, and rotational wave functions representing the internal states of the molecules;
- 2) a wave-like description of the relative motion of the molecules; and
- 3) the Schrodinger or Lippmann-Schwinger equation to trace the dynamics of the collision from an initial to a final state. At present, computations within this scheme are prohibitively complex except for very simple models.

The inability to do practical calculations within such a framework has provided the impetus for a semiclassical approach which employs:

- 1) the internal state wave functions;
- 2) classical trajectories to represent the relative motion; and
- 3) standard perturbation theory to calculate transition probabilities.

This has proven to be a very useful scheme which, however, obviously suffers from the limitations imposed by 2) and 3), the most serious of which is the assumption of small transition probabilities implied by the use of ( usually first order ) perturbation theory.

A third frame of reference can be built around a purely classical model, provided caution is exercised in establishing its legitimacy. This method consists of:

- 1) the description of the system by a classical Hamiltonian;
- 2) integration of the classical ( Hamilton ) equations of motion from an initial to a final configuration; and
- 3) analysis of the resulting phase-space multi-particle trajectories.

These descriptions all suffer from the lack of detailed information concerning the intermolecular forces responsible for the relevant transitions. The excessive complications in *ab initio* calculations of intermolecular potentials necessitates the application of heuristically rationalized model potentials.

Ultimately, one would like to develop collision theoretical techniques to the point of rendering feasible the calculation of quantities, such as rate constants and yields, by way of investigations of the microdynamics of phenomena such as energy transfer, bond fission, and internal rotation. However, typical chemically reactive collisions involve myriads of particles, channels, and related coupled equations. In view of the complicated nature of these equations, the difficulties in determining molecular wave functions, and the inability to make a quantitative specification of the relevant intermolecular interactions, even moderate success would appear to be reserved for the fairly distant future. In the meantime, piecemeal approaches are necessary.

## SECTION II: REVIEW

### A) Formal Quantum Mechanical Collision Theory

There are several excellent books which deal with the formal basis of collision theory (1,2,3,4,5). In the following, definitions and questions of rigour are referred to the comprehensive discussions to be found therein.

#### Direct ( Elastic and Inelastic ) Collisions

Consider a generalized nonrearrangement collision as follows:

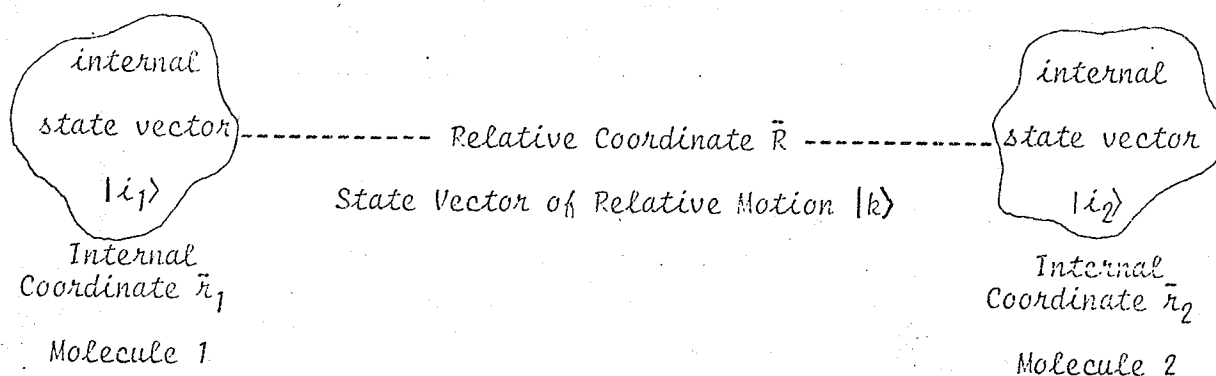


Figure 1

Define

- $h_1$  = Hamiltonian of free molecule 1
- $h_2$  = Hamiltonian of free molecule 2
- $K$  = operator of relative kinetic energy
- $H_0 = h_1 + h_2 + K = h + K$
- $H$  = full Hamiltonian of the system
- $V$  = interaction potential =  $H - H_0$
- $E$  = total energy of the system

The initial state vector  $|\bar{k}; i\rangle = |\bar{k}; i_1, i_2\rangle$  evolves into a vector with outgoing stationary wave boundary conditions  $|\bar{k}; i^+\rangle$  according to the Lippmann-Schwinger equation ( 5, Part 2 ):

$$\begin{aligned}
 |\bar{k}; i^+\rangle &= |\bar{k}; i\rangle + \lim_{\epsilon \rightarrow 0^+} (E + i\epsilon - H)^{-1} V |\bar{k}; i\rangle \\
 &= |\bar{k}; i\rangle + \lim_{\epsilon \rightarrow 0^+} (E + i\epsilon - H_0)^{-1} V |\bar{k}; i^+\rangle .
 \end{aligned}
 \tag{A(1)}$$

The  $\lim_{\epsilon \rightarrow 0^+}$  is taken after the relevant integrations have been performed and will be omitted from the subsequent notation. Also,  $E^+$  is defined by  $E^+ = E + i\epsilon$  and the Lippmann-Schwinger equation becomes

$$|\bar{k}; i^+\rangle = |\bar{k}; i\rangle + (E^+ - H_0)^{-1} V |\bar{k}; i^+\rangle . \tag{A(2)}$$

An arbitrary final state  $|\bar{R}; f\rangle$  will occur in the outgoing solution with amplitude

$$F_f(\bar{R}) = \langle f; \bar{R} | \bar{k}; i^+ \rangle . \tag{A(3)}$$

That is, in the coordinate representation the outgoing wave function

$$\Psi^+(\bar{\kappa}, \bar{R}) = \langle \bar{\kappa}, \bar{R} | \bar{k}; i^+ \rangle$$

can be expanded in the complete set of internal wave functions according to the equation

$$\Psi^+(\bar{\kappa}, \bar{R}) = \sum_j F_j(\bar{R}) \phi_j(\bar{\kappa}) \tag{A(4)}$$

where

$$\begin{aligned}
 \phi_j(\bar{\kappa}) &= \langle \bar{\kappa} | j \rangle \\
 &= \langle \bar{\kappa}_1, \bar{\kappa}_2 | j_1, j_2 \rangle \\
 &= \langle \bar{\kappa}_1 | j_1 \rangle \langle \bar{\kappa}_2 | j_2 \rangle = \phi_{j_1}(\bar{\kappa}_1) \phi_{j_2}(\bar{\kappa}_2)
 \end{aligned}$$

and

$$\begin{aligned}
 h_1 \phi_{j_1}(\bar{\kappa}_1) &= E_{j_1} \phi_{j_1}(\bar{\kappa}_1) \\
 h_2 \phi_{j_2}(\bar{\kappa}_2) &= E_{j_2} \phi_{j_2}(\bar{\kappa}_2) .
 \end{aligned}$$

The scalar product of both sides of the Lippmann-Schwinger equation A(2) with an arbitrary final state vector  $\langle f; \bar{R} |$  gives

$$\begin{aligned}\langle f; \bar{R} | \bar{k}; i^+ \rangle &= \langle f; \bar{R} | \bar{k}; i \rangle + \langle f; \bar{R} | (E^+ - H_0)^{-1} V(\bar{\kappa}', \bar{R}') | \bar{k}; i^+ \rangle \\ &= \langle \bar{R} | \bar{k} \rangle \langle f | i \rangle + \langle f | \langle \bar{R} | (E^+ - H_0)^{-1} V(\bar{\kappa}', \bar{R}') | \bar{k}; i^+ \rangle.\end{aligned}$$

Now  $\langle \bar{R} | \bar{k} \rangle = e^{i\bar{k} \cdot \bar{R}}$ ,  $\langle f | i \rangle = \delta_{fi}$ , and the spectral resolution of  $(E^+ - H_0)^{-1}$

$$(E^+ - H_0)^{-1} = \sum_j |j\rangle (E^+ - E_j - K)^{-1} \langle j|$$

are inserted into this equation.

$$\langle f; \bar{R} | \bar{k}; i^+ \rangle = e^{i\bar{k} \cdot \bar{R}} \delta_{fi} + \sum_j \langle \bar{R} | (E^+ - E_j - K)^{-1} \langle f | V(\bar{\kappa}', \bar{R}') | j \rangle \langle j | \bar{k}; i^+ \rangle$$

Define  $V_{fj}(\bar{R}') = \langle f | V(\bar{\kappa}', \bar{R}') | j \rangle$

$$= \int \phi_f^*(\bar{\kappa}') V(\bar{\kappa}', \bar{R}') \phi_j(\bar{\kappa}') d\bar{R}' \quad A(5)$$

and the Green's function  $G_0^+(\bar{R}, \bar{R}')$  according to \*

$$G_0^+(\bar{R}, \bar{R}') = \langle \bar{R} | (E^+ - E_f - K)^{-1} | \bar{R}' \rangle. \quad A(6)$$

Thus

$$\begin{aligned}\langle f; \bar{R} | \bar{k}; i^+ \rangle &= e^{i\bar{k} \cdot \bar{R}} \delta_{fi} + \int \sum_j \langle \bar{R} | (E^+ - E_j - K)^{-1} | \bar{R}' \rangle V_{fj}(\bar{R}') \langle \bar{R}' | \bar{k}; i^+ \rangle d\bar{R}' \\ &= e^{i\bar{k} \cdot \bar{R}} \delta_{fi} + \int \sum_j \langle \bar{R} | (E^+ - E_j - K)^{-1} | \bar{R}' \rangle V_{fj}(\bar{R}') \langle j; \bar{R}' | \bar{k}; i^+ \rangle d\bar{R}'\end{aligned}$$

and finally,

$$F_f(\bar{R}) = e^{i\bar{k} \cdot \bar{R}} \delta_{fi} + \int \sum_j G_0^+(\bar{R}, \bar{R}') V_{fj}(\bar{R}') F_j(\bar{R}') d\bar{R}'. \quad A(7)$$

This equation represents a set of coupled equations for the amplitudes of the internal states included in the expansion of the outgoing solution to the Lippmann-Schwinger equation in the coordinate representation. It

\* See Note at the end of Appendix I.

is perhaps more often encountered as the equivalent differential equation ( Appendix I ).

$$(E - E_f - K) F_f(\vec{R}) = \sum_j V_{fj}(\vec{R}) F_j(\vec{R}) \quad A(7')$$

### Born Series

The Neumann series ( 6, page 288 ), the simplest iterative solution to equation A(7), is commonly referred to as the Born Approximation. The elements of this approximation are outlined in the following:

Zero order;

$$F_f(\vec{R}) = e^{i\vec{k} \cdot \vec{R}} \delta_{fi} \quad A(8)$$

First order;

$$\begin{aligned} F_f(\vec{R}) &= e^{i\vec{k} \cdot \vec{R}} \delta_{fi} + \int_j \Sigma G_0^+(\vec{R}, \vec{R}') V_{fj}(\vec{R}') e^{i\vec{k} \cdot \vec{R}'} \delta_{ji} d\vec{R}' \\ &= e^{i\vec{k} \cdot \vec{R}} \delta_{fi} + \int_j \Sigma G_0^+(\vec{R}, \vec{R}') V_{fi}(\vec{R}') e^{i\vec{k} \cdot \vec{R}'} d\vec{R}' \end{aligned} \quad A(9)$$

Second order;

$$\begin{aligned} F_f(\vec{R}) &= e^{i\vec{k} \cdot \vec{R}} \delta_{fi} + \int_j \Sigma G_0^+(\vec{R}, \vec{R}') V_{fj}(\vec{R}') \{ e^{i\vec{k} \cdot \vec{R}'} \delta_{ji} + \\ &\quad \int_j \Sigma G_0^+(\vec{R}', \vec{R}'') V_{ji}(\vec{R}'') e^{i\vec{k} \cdot \vec{R}''} d\vec{R}'' \} d\vec{R}' \\ &= e^{i\vec{k} \cdot \vec{R}} \delta_{fi} + \int_j \Sigma G_0^+(\vec{R}, \vec{R}') V_{fi}(\vec{R}') e^{i\vec{k} \cdot \vec{R}'} d\vec{R}' + \\ &\quad \int_j \Sigma \Sigma G_0^+(\vec{R}, \vec{R}') V_{fj}(\vec{R}') G_0^+(\vec{R}', \vec{R}'') V_{ji}(\vec{R}'') e^{i\vec{k} \cdot \vec{R}''} d\vec{R}'' \end{aligned} \quad A(10)$$

Higher order terms can be derived by an obvious extension of this iterative procedure. However, in practical terms, A(9) represents the usual limit of such calculations. Specific Born series should be examined in terms of their convergence properties (7).

# Cross Sections

The differential scattering cross section  $\frac{d\sigma_{i \rightarrow f}}{d\Omega}$  is given by

$$\frac{d\sigma_{i \rightarrow f}}{d\Omega} = (\mu^2 / 2\pi\hbar^2)^2 |T_{fi}|^2 \quad A(11)$$

where  $d\sigma_{i \rightarrow f}$  is the number of events  $i \rightarrow f$  scattered into the element of solid angle  $d\Omega$  per unit time and per unit incident flux,  $\mu$  is the reduced mass of the system, and the elements of the transition matrix are

$$T_{fi} = \langle f; \vec{R} | V | \vec{k}; i^+ \rangle \quad A(12)$$

In the coordinate representation this expression is (Appendix II)

$$T_{fi}(\vec{R}) = \sum_j V_{fj}(\vec{R}) F_j(\vec{R}) \quad A(13)$$

Successive approximations to the  $T_{fi}$  are obtained by insertion of the Born expansion for the  $F_j(\vec{R})$  into A(13).

$$\begin{aligned} T_{fi}(\vec{R}) = & V_{fi}(\vec{R}) e^{i\vec{k} \cdot \vec{R}} + \int \sum_j V_{fj}(\vec{R}) G_0^+(\vec{R}, \vec{R}') V_{ji}(\vec{R}') e^{i\vec{k} \cdot \vec{R}'} d\vec{R}' + \\ & \int \int \sum_{j,j'} V_{fj}(\vec{R}) G_0^+(\vec{R}, \vec{R}') V_{jj'}(\vec{R}') G_0^+(\vec{R}', \vec{R}'') V_{j'i}(\vec{R}'') e^{i\vec{k} \cdot \vec{R}''} d\vec{R}'' d\vec{R}' + \\ & + \text{higher order terms} \end{aligned} \quad A(14)$$

The significance of the terms in this equation can be vividly demonstrated diagrammatically as shown in the accompanying figure.

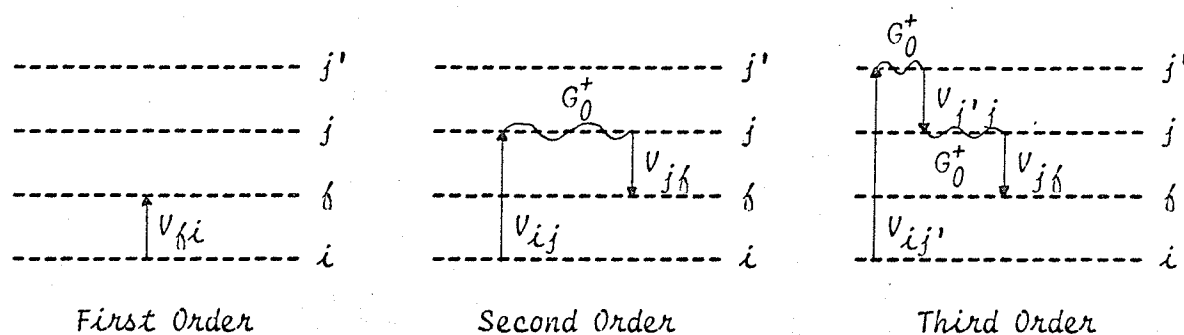


Figure 2

These diagrams also serve to point out the main inadequacy of this description. Unless the relative kinetic energy of the collision partners is very much larger than the energy transferred during the collision, the intermediate states cannot be expected to propagate as the plane wave initial state. The Born series is thus intrinsically a high energy approximation.

### Distorted Wave Approximation

Considerable improvement can be achieved in cases where the interaction potential  $V(\bar{r}, \bar{R})$  can be partitioned as

$$V(\bar{r}, \bar{R}) = U(\bar{R}) + W(\bar{r}, \bar{R}) , \quad A(15)$$

where  $W(\bar{r}, \bar{R})$  represents a small addition to  $U(\bar{R})$ , the main contribution to  $V(\bar{r}, \bar{R})$ . Since it depends on the internal coordinates,  $W(\bar{r}, \bar{R})$  is responsible for inelastic events; whereas  $U(\bar{R})$  results in elastic collisions only.

Recall the coupled equations for the amplitudes A(7)

$$F_{\delta}(\bar{R}) = e^{i\bar{k} \cdot \bar{R}} \delta_{\delta i} + \int_j \Sigma G_0^+(\bar{R}, \bar{R}') V_{\delta j}(\bar{R}') F_j(\bar{R}') d\bar{R}'$$

where

$$\begin{aligned} V_{\delta j}(\bar{R}) &= \int \phi_{\delta}^*(\bar{r}) V(\bar{r}, \bar{R}) \phi_j(\bar{r}) d\bar{r} \\ &= U(\bar{R}) \delta_{\delta j} + W_{\delta j}(\bar{R}) . \end{aligned}$$

Thus

$$\begin{aligned} F_{\delta}(\bar{R}) &= e^{i\bar{k} \cdot \bar{R}} \delta_{\delta i} + \int_j \Sigma G_0^+(\bar{R}, \bar{R}') U(\bar{R}') F_{\delta}(\bar{R}') d\bar{R}' + \\ &\quad \int_j \Sigma G_0^+(\bar{R}, \bar{R}') W_{\delta j}(\bar{R}') F_j(\bar{R}') d\bar{R}' . \end{aligned} \quad A(16)$$

The Distorted Wave Approximation proceeds on the assumption that the coupling terms  $W_{\delta j}(\bar{R})$  are small enough such that the solutions to the uncoupled equations ( pure elastic scattering ),

$$F'_{\delta}(\bar{R}) = e^{i\bar{k} \cdot \bar{R}} \delta_{\delta i} + \int_j \Sigma G_0^+(\bar{R}, \bar{R}') U(\bar{R}') F'_{\delta}(\bar{R}') d\bar{R}' , \quad A(17)$$



the so-called "distorted waves", are good candidates for substitution into the right hand side of the coupled equations A(16). Clearly, this is appropriate only for collisions in which the internal states of the molecules are not appreciably perturbed.

### Perturbed Stationary States Method

When  $V(\bar{r}, \bar{R})$  is strong enough to severely perturb the internal states, the expansion of  $\Psi^+(\bar{r}, \bar{R})$  is best effected in terms of the adiabatic eigenstates  $\chi_j(\bar{r}, \bar{R})$  of the quasi-molecule formed by the colliding systems\*.

$$\Psi^+(\bar{r}, \bar{R}) = \sum_j A_j(\bar{R}) \chi_j(\bar{r}, \bar{R}) \quad A(18)$$

Considered in this way  $V(\bar{r}, \bar{R})$  is an intramolecular potential since it is contained in the Hamiltonian  $H_a = h + V(\bar{r}, \bar{R})$  which generates the states  $\chi_j(\bar{r}, \bar{R})$ . The relevant Lippmann-Schwinger equation is

$$|\bar{R}; i^+\rangle = |\bar{R}; i\rangle + (E^+ - H_a)^{-1} K |\bar{R}; i^+\rangle, \quad A(19)$$

where it is to be recalled that  $K$  is the operator of relative kinetic energy and

$$H = H_0 + V(\bar{r}, \bar{R}) = H_a + K.$$

Analysis exactly analogous to the derivation of equation A(7) leads to

$$A_i(\bar{R}) = e^{i\bar{K} \cdot \bar{R}} \delta_{fi} + \sum_j \int G_a^+(\bar{R}, \bar{R}') K_{ij}(\bar{R}') A_j(\bar{R}') d\bar{R}', \quad A(20)$$

where

$$G_a^+(\bar{R}, \bar{R}') = \langle \bar{R} | (E^+ - H_a)^{-1} | \bar{R}' \rangle \quad A(21)$$

\* If the  $\chi_j(\bar{r}, \bar{R})$  represent electronic states of identical nuclei,  $\Psi^+(\bar{r}, \bar{R})$  must contain symmetric and antisymmetric components ( 1 chpt.15 ).

and

$$K_{fi}(\bar{R}) = \int \chi_f^*(\bar{r}, \bar{R}) K \chi_i(\bar{r}, \bar{R}) d\bar{r} \quad A(22)$$

Transitions are thus the result of perturbation of the molecular eigenstates by the relative motion of the collision partners.

The  $\chi_j(\bar{r}, \bar{R})$  are frequently expanded in terms of the eigenstates of the isolated systems;

$$\chi_j(\bar{r}, \bar{R}) = \sum_{j'} B_{jj'}(\bar{R}) \phi_{j'}(\bar{r}) \quad A(23)$$

in which case

$$\begin{aligned} K_{fi}(\bar{R}) &= \int \sum \sum B_{fi}^*(\bar{R}) \phi_{f'}^*(\bar{r}) K B_{ij''}(\bar{R}) \phi_{j''}(\bar{r}) d\bar{r} \\ &= \sum_{j'} B_{fi}^*(\bar{R}) K B_{ij'}(\bar{R}) \end{aligned} \quad A(24)$$

The usual approach ( 1 chpt. 15 , and (8) ) to the solution of A(20) is to assume that all non-diagonal terms other than direct couplings  $K_{fi}(\bar{R})$  can be ignored, leaving

$$A'_f(\bar{R}) = e^{i\bar{k} \cdot \bar{R}} \delta_{fi} + \int G_a^+(\bar{R}, \bar{R}') K_{fi}(\bar{R}') A'_i(\bar{R}') d\bar{R}' \quad A(25)$$

The evaluation of the coupling terms is not an easy task and must be approached with caution ( 5, page 175 ). However, the method of perturbed stationary states is particularly suitable for slow collisions (9); takes account of the considerable distortion of the relative motion ( 5, page 177 ); and allows for the description of electron-exchange rearrangement collisions ( 1, chpt. 15 ).

#### General Rearrangement Collisions

A general rearrangement collision is an encounter during which the collision partners exchange one or more particles ( 10 page 333 ). Chemical reactions are molecular rearrangement collisions for which the exchanged particles are constituent atoms. Formally, the

possibility of rearrangement collisions arises from the non-uniqueness of the resolution of the full Hamiltonian  $H = H_0 + V(\bar{r}, \bar{R})$ . That is,  $V(\bar{r}, \bar{R})$  is chosen according to the behavior of the molecules for  $|\bar{R}| \rightarrow \infty$ . For elastic and even inelastic collisions,  $\bar{R}$  can be taken as the separation of the centres of mass of the molecules and  $V(\bar{r}, \bar{R})$  is effectively unique. A rearrangement collision results from the fact that the final state relative coordinate can differ from that of the initial state. The various courses the collision can take are called channels (2). In this sense, a collision is elastic, inelastic, or rearrangement according to whether the collision partners remain in the same internal state of the same channel, change internal states of the same channel, or enter a different channel.

$$\text{Let the resolutions } H = H_0^\alpha + V^\alpha(\bar{r}, \bar{R}) ,$$

$$H = H_0^\beta + V^\beta(\bar{r}, \bar{R}) ,$$

$$\text{and } H = H_0^\gamma + V^\gamma(\bar{r}, \bar{R})$$

denote the initial, a final, and an arbitrary channel respectively.

The internal states are written as  $|j_\gamma\rangle$  and will have continuous as well as discrete behavior. The Lippmann-Schwinger equation analogous to equation A(2)

$$|\bar{k}; i_\alpha^+\rangle = |\bar{k}; i_\alpha\rangle + (E^+ - H_0)^{-1} V^\alpha |\bar{k}; i_\alpha^+\rangle \quad A(26)$$

represents a complete dynamical description of the collision. The following manipulations convert A(26) into a form which indicates the presence of rearranged terms.

$$(E^+ - H_0^\alpha) |\bar{k}; i_\alpha^+\rangle = (E^+ - H_0^\alpha) |\bar{k}; i_\alpha\rangle + V^\alpha |\bar{k}; i_\alpha^+\rangle$$

$$(E^+ - H_0^\alpha - V^\alpha) |\bar{k}; i_\alpha^+\rangle = (E^+ - H_0^\alpha) |\bar{k}; i_\alpha\rangle$$

$$(E^+ - H) |\bar{k}; i_\alpha^+\rangle = (E^+ - H_0^\alpha) |\bar{k}; i_\alpha\rangle$$

since  $H_0^\alpha |\bar{k}; i_\alpha\rangle = E |\bar{k}; i_\alpha\rangle$ ,

$$(E^+ - H) |\bar{k}; i_\alpha^+\rangle = i\epsilon |\bar{k}; i_\alpha\rangle^*$$

$$(E^+ - H_0^\beta - V^\beta) |\bar{k}; i_\alpha^+\rangle = i\epsilon |\bar{k}; i_\alpha\rangle$$

$$|\bar{k}; i_\alpha^+\rangle = (E^+ - H_0^\beta)^{-1} i\epsilon |\bar{k}; i_\alpha\rangle + (E^+ - H_0^\beta)^{-1} V^\beta |\bar{k}; i_\alpha^+\rangle \quad A(27)$$

The amplitude of the internal state  $|i_\beta\rangle$  at relative separation  $\bar{R}$  can thus be written as

$$\langle i_\beta; \bar{R} | \bar{k}; i_\alpha^+ \rangle = \langle i_\beta; \bar{R} | (E^+ - H_0^\beta)^{-1} i\epsilon |\bar{k}; i_\alpha\rangle + \langle i_\beta; \bar{R} | (E^+ - H_0^\beta)^{-1} V^\beta |\bar{k}; i_\alpha^+ \rangle.$$

The completeness\*\* of the  $\langle i_\beta; \bar{R} |$  and the spectral decomposition of  $(E^+ - H_0)^{-1}$  allow this to be written as

$$\begin{aligned} \langle i_\beta; \bar{R} | \bar{k}; i_\alpha^+ \rangle &= \int \langle \bar{R} | i\epsilon (E^+ - E_f - K)^{-1} | \bar{R}' \rangle \langle i_\beta; \bar{R}' | \bar{k}; i_\alpha^+ \rangle d\bar{R}' + \\ &\quad \sum_j \int \langle \bar{R} | (E^+ - E_f - K)^{-1} | \bar{R}' \rangle \langle i_\beta | V^\beta(\bar{r}', \bar{R}') | j_\beta \rangle \langle j_\beta; \bar{R}' | \bar{k}; i_\alpha^+ \rangle d\bar{R}'. \end{aligned}$$

The definitions

$$\begin{aligned} F_f^\beta(\bar{R}) &= \langle i_\beta; \bar{R} | \bar{k}; i_\alpha^+ \rangle, \\ L_0^{\beta+}(\bar{R}, \bar{R}') &= \langle \bar{R} | \frac{i\epsilon}{(E^+ - E_f - K)} | \bar{R}' \rangle, \\ G_0^{\beta+}(\bar{R}, \bar{R}') &= \langle \bar{R} | \frac{1}{(E^+ - E_f - K)} | \bar{R}' \rangle, \\ V_{fj}^\beta(\bar{R}) &= \langle i_\beta | V^\beta(\bar{r}, \bar{R}) | j_\beta \rangle, \end{aligned}$$

$$\text{and} \quad S_{fi}^\beta(\bar{R}) e^{i\bar{k} \cdot \bar{R}} = \langle i_\beta | i_\alpha \rangle e^{i\bar{k} \cdot \bar{R}}$$

result in the following equations for the amplitudes.

$$\begin{aligned} F_f^\beta(\bar{R}) &= \int L_0^{\beta+}(\bar{R}, \bar{R}') S_{fi}^\beta(\bar{R}') e^{i\bar{k} \cdot \bar{R}'} d\bar{R}' + \\ &\quad \int \sum_j G_0^{\beta+}(\bar{R}, \bar{R}') V_{fj}^\beta(\bar{R}') F_j^\beta(\bar{R}') d\bar{R}' \quad A(28) \end{aligned}$$

\* This is perhaps a less recondite statement of the L.-S. equation (11).

\*\* The summation includes integration over the continuous part.

Clearly there exists such a set of equations for an arbitrary channel  $\gamma$ .

As in equation A(13), the amplitudes relate to a  $T$  - operator according to the equation

$$\begin{aligned} T_{fi}^B(\bar{R}) &= \langle \phi_B; \bar{R} | V^B | k; i_\alpha^+ \rangle \\ &= \sum_j V_{fi}^B(\bar{R}) F_j^B(\bar{R}) \end{aligned} \quad A(29)$$

However, it is not necessary to introduce the state amplitudes if the transition amplitudes are all that is desired\*, since A(27) and A(29) are sufficient to determine an integral equation for the  $T_{fi}^B(\bar{R})$ .

$$\begin{aligned} T_{fi}^B(\bar{R}) &= \langle \phi_B; \bar{R} | V^B | \bar{k}; i_\alpha^+ \rangle \\ &= \langle \phi_B; \bar{R} | V^B (E^+ - H_0)^{-1} i_\epsilon | \bar{k}; i_\alpha^+ \rangle + \langle \phi_B; \bar{R} | V^B (E^+ - H_0)^{-1} V^B | \bar{k}; i_\alpha^+ \rangle \\ &= \sum_j \langle \bar{R} | \langle \phi_B | V^B | j_B \rangle (E^+ - E_j - K)^{-1} i_\epsilon | \bar{R}' \rangle \langle j_B; \bar{R}' | \bar{k}; i_\alpha^+ \rangle d\bar{R}' + \\ &\quad \sum_j \langle \bar{R} | \langle \phi_B | V^B | j_B \rangle (E^+ - E_j - K)^{-1} | \bar{R}' \rangle \langle j_B; \bar{R}' | V^B | \bar{k}; i_\alpha^+ \rangle d\bar{R}' \\ T_{fi}^B(\bar{R}) &= \sum_j V_{fi}^B(\bar{R}') L_0^{B+}(\bar{R}, \bar{R}') S_{ji}^B(\bar{R}') e^{i\bar{k} \cdot \bar{R}'} d\bar{R}' + \\ &\quad \sum_j V_{fi}^B(\bar{R}') G_0^{B+}(\bar{R}, \bar{R}') T_{ji}^B(\bar{R}') d\bar{R}' \end{aligned} \quad A(30)$$

Equations A(28) and A(30) contain the dynamics of the state and transition amplitudes during a collision. They are rather abstruse and not readily applied without considerable simplification. The nonorthogonality of the states of different channels, giving rise to the  $S_{ji}^B(\bar{R})$  terms, is one complicating feature. A thorough discussion of this point and rearrangement collisions in general can be found in reference 4, chapters 4 & 5.

\* The transition amplitudes alone determine the differential cross-section ( see for example, 13 page 142 and 14 page 235 ).

As these equations suggest, it is possible to construct Born series, distorted wave approximations, and perturbed stationary states calculations for rearrangement problems ( 10 and 12 ). However, success has been limited. The Born approximation is unsatisfactory even at high energies ( 13 page 149 ). The P.S.S. method has been successful with electron-exchange between simple atoms because molecular eigenstates delocalize the electron over both centres.

### Numerical Integration

Johnson and Secrest (15) have developed a numerical method for the solution of the coupled equations A(7) for elastic and inelastic processes based on the introduction of what they called " amplitude density functions", which are simply expressed by equation A(12).

$$T_{fi}(\bar{R}) = \langle f; \bar{R} | V(\bar{r}, \bar{R}') | i; i^+ \rangle \quad A(12)$$

$$= \sum_j V_{fi}(\bar{R}) F_j(\bar{R}) \quad A(13)$$

Equation A(7) for the  $F_j(\bar{R})$  results in

$$\begin{aligned} T_{fi}(\bar{R}) &= \sum_j V_{fi}(\bar{R}) \{ e^{i\bar{k} \cdot \bar{R}} \delta_{ji} + \int_{j'} G_0^+(\bar{R}, \bar{R}') V_{jj'}(\bar{R}') F_{j'}(\bar{R}') d\bar{R}' \} \\ &= V_{fi}(\bar{R}) e^{i\bar{k} \cdot \bar{R}} + \int_{j'} \sum_j V_{fi}(\bar{R}) G_0^+(\bar{R}, \bar{R}') T_{ji}(\bar{R}') d\bar{R}' \quad A(31) \end{aligned}$$

( This equation can be derived immediately from the operator equation

$$T = V + VG_0^+T . )$$

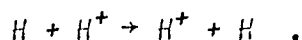
Briefly, the method consists of treating the complete problem as the sum of weaker interaction potentials and replacing the integral in A(31) with a quadrature sum ( trapezoid or Simpson's rule ).

Deistler and McKoy ( 16 and 17 ) have developed a scheme using the finite difference method which is applicable to exchange reactions as well as elastic and inelastic processes.

Gordon (18) has recently presented a method for constructing piecewise analytic solutions to  $A(7')$ .

### A Few Applications

The Born approximation provided the first means of examining the elementary collision process ( 19 and 20 )



Although all cross section calculations tend toward the Born approximation results, this convergence occurs at energies typically of the order of 100 keV ( 14 page 169 ). This method is not adequate in the intermediate to low energy range\*. Discussions of the Born approximation can be found in the articles by Bransden ( 12 and 13 ) and Holt and Moisewitsch (7).

The distorted wave approximation, on the other hand, has been extensively applied in the intermediate and low energy ranges; particularly in studies of rotation and/or vibrational inelastic collisions between simple molecules ( 21, 22, and 23 ). Jackson and Mott (24) presented the first complete calculation of translational-vibrational energy exchange between a harmonic diatomic molecule and a collinear atom exponentially repelled by the nearer atom of the molecule. Their formulae have been used repeatedly in discussions on molecular energy transfer ( 25 and 26 ). The Jackson and Mott approach is equivalent to a first order iter-

\* The following classification has been adopted in this document.

{ Chemical Energy < 10eV }

Low Energy < 100eV

Intermediate Energy 100eV to 100keV

High Energy 100keV to 1MeV

{ Relativistic Energy > 1MeV }

ation of equation A(16). Higher order terms have been considered by Thiele and Weare (27). Such considerations are necessary in order to discuss multiple-quantum transitions and the convergence of the iteration. Recently, Roberts and Ross (28) have investigated the iterative solution for the case of rotational inelastic scattering.

The distorted wave method was employed by Mies (29) in an important study of translational-vibrational energy transfer in He-H<sub>2</sub> collisions, a case for which the exact interaction potential has been calculated (30). The results of that study are rather unsettling. It would appear that the decomposition of the intermolecular potential into the sum of pairwise interactions ( the so-called dumb-bell model ) is not satisfactory and that the importance of the collinear configuration has been overemphasized.

The perturbed stationary states method has met with little application outside of its semiclassical impact parameter version ( see Section II B and (8) ). A discussion of the differential equation equivalent to equation A(20) can be found in (31).

Johnson and Secrest have applied their method of amplitude density functions ( see page 14 ) to the collinear collision of a particle and a harmonic oscillator (32) and rotational inelastic He-H<sub>2</sub> collisions (33). Perturbation approaches such as those of Thiele and Weare (27) and Roberts and Ross (28) are compared to those of Johnson and Secrest, which are considered to be exact. Evidently, the immediate numerical integration of the coupled equations is superior to conventional perturbation expansions, at least in the cases discussed.\*

\* This numerical approach to the theory of transition amplitudes can be generalized (34).



The preceding examples typify the current level of sophistication of quantitative accounts of "real" collisions. That is, model calculations are rarely presented for anything more complicated than diatomic molecules. However, the formal approach of multichannel collision theory offers qualitative insight into some general phenomena, such as radiative and collisional recombination and unimolecular decomposition. Notable in this regard are the works of Levine ( 5 and references therein ), Hall and Levine (35), Coulson and Levine (36), and Mies ( 37 and 38 ).

## Section II B) Semiclassical Collision Theory

Atoms, and even protons, are sufficiently massive such that the motion of their centres of mass can be accurately described by classical trajectories at energies above the low chemical range. This simplification invokes a picture of scattering processes in which transitions are induced among the energy levels of the collision partners by a time-dependent potential following the classical trajectory of their relative motion.

### Impact Parameter Method

The initial unperturbed system of figure 1 Section II A) is here described by the equations

$$H_0 |i\rangle = E_i |i\rangle \quad \text{and} \quad |i, t\rangle = e^{-\frac{i}{\hbar} E_i t} |i\rangle \quad \text{B(1)}$$

and the collision evolves according to the time-dependent Schrodinger equation

$$\{ H_0 + V(\vec{r}, \vec{R}) \} |\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle \quad \text{B(2)}$$

where  $|\Psi\rangle$  is expanded in the eigenstates of the free molecules

$$|\Psi\rangle = \sum_j a_j(t) |j, t\rangle = \sum_j a_j(t) e^{-\frac{i}{\hbar} E_j t} |j\rangle \quad \text{B(3)}$$

Substitution of B(3) into B(2) and use of B(1); and the scalar product with an arbitrary state vector  $\langle f, t |$  lead to the equation

$$\dot{a}_f(t) = (i\hbar)^{-1} \sum_j a_j(t) \exp\left\{\frac{i}{\hbar} (E_f - E_j) t\right\} V_{fj}(\vec{R}) \quad \text{B(4)}$$

where the  $V_{fj}(\vec{R})$  are as in equation A(5). The classical equations for the relative motion must be solved to determine the trajectory  $\vec{R}(t)$ .

The integration of the resulting set of coupled first order differential equations

$$\dot{a}_f(t) = (i\hbar)^{-1} \sum_j a_j(t) \exp\left\{\frac{i}{\hbar} (E_f - E_j) t\right\} V_{fj}(\vec{R}(t)) \quad \text{B(4')}$$

plus the classical equations ( see Section II C ), subject to the initial conditions  $a_j(t_0) = \delta_{ji}$  and a suitable relative configuration, is the fundamental problem of the semiclassical procedure, since the probability of the state  $f$  after the collision is  $P_f = |a_f(t \rightarrow \infty)|^2$ . Equation B(4') is general in the sense that the internal wave functions can represent electronic, vibrational, or rotational states.

An analogous set of equations can be derived within the method of perturbed stationary states.  $\bar{R}(t)$  is considered to be a slowly varying function, so that one can use the zero order W.K.B. solutions for the electronic molecular wave functions ( 8 page 453 ).

i.e.

$$x_j(\bar{r}, \bar{R}(t); t) = x_j(\bar{r}, \bar{R}(t)) \exp\left\{-\frac{i}{\hbar} \int E_j(\bar{R}(t')) dt'\right\} \quad B(5)$$

where  $H_a x_j(\bar{r}, \bar{R}) = E_j(\bar{R}) x_j(\bar{r}, \bar{R}) \quad B(6)$

generates the familiar states for fixed relative separation. The complete wave function is then expanded as in B(3).

$$\Psi(\bar{r}, \bar{R}(t); t) = \sum_j b_j(t) x_j(\bar{r}, \bar{R}(t)) \exp\left\{-\frac{i}{\hbar} \int E_j(\bar{R}(t')) dt'\right\} \quad B(7)$$

$$H_a \Psi(\bar{r}, \bar{R}(t); t) = i\hbar \frac{\partial}{\partial t} \Psi(\bar{r}, \bar{R}(t); t) \quad B(8)$$

Proceeding as in the derivation of equation B(4'), one obtains the following set of equations;

$$\dot{b}_f(t) = -\sum_j b_j(t) \int x_f(\bar{r}, \bar{R}(t)) \dot{x}_j(\bar{r}, \bar{R}(t)) d\bar{r} \exp\left\{-\frac{i}{\hbar} \int \{E_j(\bar{R}(t')) - E_f(\bar{R}(t'))\} dt'\right\} \quad B(9)$$

subject to the initial conditions  $b_j(t_0) = \delta_{ji}$ .

Equations B(4') and B(9) are difficult to solve and consequently they are commonly decoupled via a first order perturbation approximation in which only direct coupling between the initial and final states

is considered ( see 8 and 39 ). However, as suggested by the discussions in Section II A), numerical computer integration techniques can be adapted to these problems. The results of Rapp and Sharp (40) indicate that the inclusion of more states in equation B(4') and thus the possibility of multiquantum transitions can have a considerable effect on the transition probabilities.

### Trajectories

An important aspect of the semiclassical analysis is the approximation employed for the function  $\bar{R}(t)$ . Until recently, the "straight line approximation" has been almost universally adopted. It consists of assuming that the projectile passes the target with constant velocity and at a fixed impact parameter. This approximation appears to be valid for relative kinetic energies of the order of a few hundred electron volts in the case of proton - hydrogen atom scattering (41). Another approach consists of solving the classical equations for the relative motion resulting from a specified intermolecular potential. However, this is inadequate to the extent that the intermolecular potential depends on the internal states of the collision partners and consequently changes with the occurrence of inelastic events. A procedure that takes account of this difficulty is being developed by W. Corrigall and R. Wallace.\*

### Eikonal Method

The simplest eikonal model results from assuming the form

$$F_j(\bar{R}) = \exp(ik_j z) F'_j(\bar{R}) = \exp\left(\frac{i\mu v_j z}{\hbar}\right) F'_j(\bar{R}) \quad B(10)$$

for the amplitudes in equation A(7'), where  $\mu$  is the reduced mass of the

\* For another approach to this problem see ( 42 and 43 ).

system, the  $z$  axis is specified by the initial relative velocity, and

$$\frac{\hbar^2 k_j^2}{2\mu_j} = \frac{1}{2} \mu v_j^2 = E - E_j \quad . \quad B(11)$$

Equation A(7') here becomes

$$\begin{aligned} \left\{ \frac{1}{2} \mu v_\delta^2 - K - V_{\delta\delta}(\bar{R}) \right\} \exp\left(\frac{i\mu v_\delta z}{\hbar}\right) F'_\delta(\bar{R}) &= \sum_{j \neq \delta} V_{\delta j}(\bar{R}) F'_j(\bar{R}) \exp\left(\frac{i\mu v_j z}{\hbar}\right) \\ \left\{ i\hbar v_\delta \frac{\partial}{\partial z} - K - V_{\delta\delta}(\bar{R}) \right\} F'_\delta(\bar{R}) &= \sum_{j \neq \delta} V_{\delta j}(\bar{R}) \exp\left\{ \frac{i\mu (v_j - v_\delta) z}{\hbar} \right\} F'_j(\bar{R}) \quad . \end{aligned} \quad B(12)$$

The problem can also be formulated from the viewpoint of the perturbed stationary states method (44).

Within the eikonal approximation, equation B(12) is simplified by omitting  $K = -\frac{\hbar^2}{2\mu} \Delta_R$ , the assumption being that  $\mu \rightarrow \infty$  (45). Equation B(12) then becomes

$$i\hbar v_\delta \frac{\partial F'_\delta(\bar{R})}{\partial z} = \sum_j V_{\delta j}(\bar{R}) \exp\left\{ \frac{i\mu (v_j - v_\delta) z}{\hbar} \right\} F'_j(\bar{R}) \quad B(13)$$

The similarity of this equation with equation B(4) is obvious. Indeed, they can be made identical if certain assumptions are adopted ( Appendix III ).

An elaborate discussion of more exact eikonal techniques that makes extensive use of P.S.S.-type expansions can be found in the recent work of K.M. Watson and coworkers ( 46, 47, and 48 ).

### A Few Applications

Lichten (49) has given an illuminating discussion of resonant charge exchange in which he employed the impact parameter version of the perturbed stationary states method to obtain qualitative agreement with the results of Lockwood and Everhart (50) on electron capture probability in proton - hydrogen atom collisions at intermediate energies. An essentially similar but more detailed calculation has been reported by Bates and Williams (51).

Helbig and Everhart (52) reported accurate differential measurements of the electron capture probability in proton - hydrogen atom collisions. These data have provided a valuable gauge for comparing the various theoretical attempts to deal with this problem. At present, the most accurate calculations are those of Wilets and Gallaher ( 53 and 54 ), who applied a numerical integration scheme to the coupled equations B(4'). Their calculations (54) assume the straight line approximation and employ a basis set of travelling Sturmian functions, a feature which exposes the importance of the hydrogenic continuum. The results of (52) and (54) are compared in figure (3).

Similarly, direct numerical attacks on the coupled equations of the semiclassical approach to the theory of collisions of small molecules are becoming common in the literature. Representative of these are the publications of Locker and Endres (55) and Locker and Wilson (56)\*. They employed the method of Hamming and Hollingsworth (57) to integrate a set of equations consisting of seven coupled amplitudes ( equation B(4') ) and the classical equations of motion for the atom - diatomic molecule collision model described previously ( page 15 ). Locker and Endres accounted for the anharmonicity of the molecular vibration by using a Morse function, whereas Locker and Wilson used a harmonic model. The difference is significant even for states of low quantum number.\*\* These studies also indicate the importance of multiple quantum transitions and the effect of the phase of the classical diatomic vibration on the transition probabilities.

\* (56) contains a fairly complete list of references to previous semiclassical work in this area.

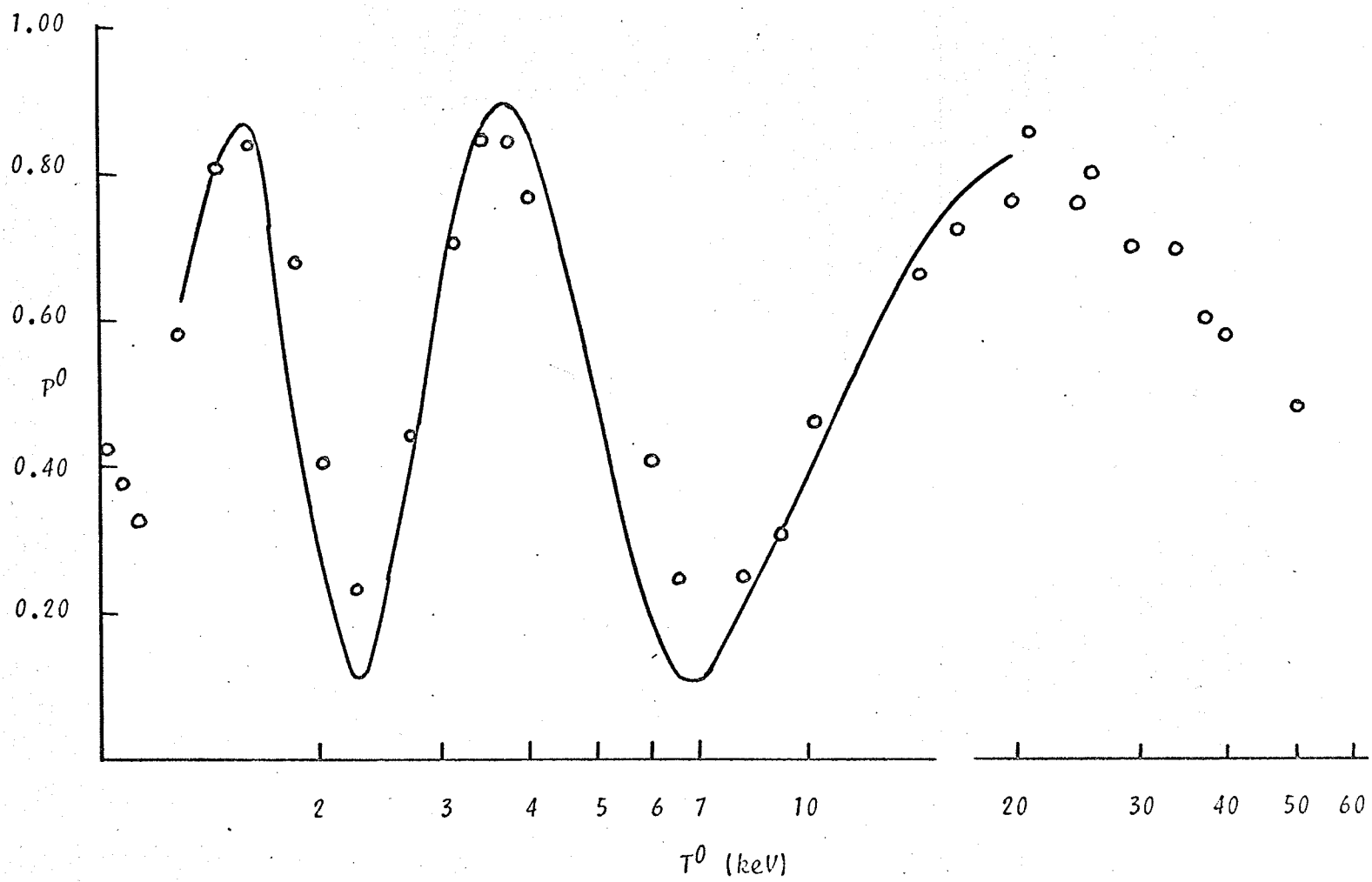
\*\* See also ( 58,59,60,61, and page 31 of this document ).

Figure 3

A comparison of theoretical and experimental determinations of electron capture probability  $P^0$  as a function of relative kinetic energy  $T^0$  ( in keV ) for proton - hydrogen atom collisions.

Circles ----- Data of Helbig and Everhart (52)  
for  $3^0$  scattering

Line ----- Theory of Gallaher and Wilets (54)





## Section II C) Classical Collision Theory

The final simplification to be made results from the treatment of the dynamical problem of collisions completely by the methods of classical mechanics. This has been attempted for cases in which classical conditions are expected to be a good approximation to the true state of affairs, in which classical energy transfer can be related to quantum mechanical transition probability, and even in which classical mechanics is customarily considered to be inadequate.

The method consists of numerical integration of the classical equations of motion a given model ( that is, a chosen potential function ) and subsequent analysis of the multi-particle trajectories to determine the behavior of dynamical properties such as the partitioning of energy among the various degrees of freedom. One of the main features of this approach is its contingency upon computer technology. That is, the calculations are exact within the context of the model but limitations enter through considerations such as storage space and processing time.

### Equations of Motion

A general potential function for a system of  $N$  particles is here given the form ( where the notation is meant to leave understood that no two indices are ever equal )

$$V(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N) \equiv V(\{\bar{r}_i\}) = \sum_i^N V_i(\bar{r}_i) + \frac{1}{2!} \sum_{i \neq j}^N \sum_{j \neq i}^N V_{ij}(\bar{r}_i, \bar{r}_j) + \frac{1}{3!} \sum_{i \neq j \neq k}^N \sum_{j \neq i \neq k}^N \sum_{k \neq i \neq j}^N V_{ijk}(\bar{r}_i, \bar{r}_j, \bar{r}_k) + \dots \quad C(1)$$

The "self-energy" terms  $V_i(\bar{r}_i)$  are omitted, leaving the interaction potential.

$$V(\{\bar{r}_i\}) = \frac{1}{2!} \sum_i \sum_{j \neq i} V_{ij}(r_i, r_j) + \frac{1}{3!} \sum_i \sum_{j \neq i} \sum_{k \neq i, j} V_{ijk}(r_i, r_j, r_k) + \dots \quad C(2)$$

The classical Hamiltonian can then be written as

$$H(\{\bar{p}_i\}; \{\bar{r}_i\}) = \sum_i \frac{1}{2m_i} \bar{p}_i \cdot \bar{p}_i + V(\{\bar{r}_i\}) \quad C(3)$$

or

$$H = \sum_i \frac{1}{2m_i} \{p_x^2(i) + p_y^2(i) + p_z^2(i)\} + V(\{x_i, y_i, z_i\}) \quad C(3')$$

The particles move according to Hamilton's equations (62), which are here written with respect to an arbitrary Cartesian coordinate system.

$$\dot{x}_i = \frac{\partial H}{\partial p_x(i)} \quad \dot{y}_i = \frac{\partial H}{\partial p_y(i)} \quad \dot{z}_i = \frac{\partial H}{\partial p_z(i)} \quad C(4)$$

$$\dot{p}_x(i) = -\frac{\partial H}{\partial x_i} \quad \dot{p}_y(i) = -\frac{\partial H}{\partial y_i} \quad \dot{p}_z(i) = -\frac{\partial H}{\partial z_i}$$

The forward integration of the 6N coupled equations from an initial configuration traces the multi-particle trajectories.

### Numerical Integration

For  $N > 2$ , the integration of equations C(4) must be carried out numerically. The Runge-Kutta numerical integration procedure has been adapted by Gill (63) to use on a digital computer (see 64 for details).

The object is to solve a system of first order ordinary differential equations of the the general form

$$\dot{s}_i = f_i(t; s_1(t), s_2(t), \dots, s_n(t)) = f_i(t; \{s_i(t)\}) \quad C(5)$$

subject to a given set of initial conditions  $(t^0; \{s_i(t^0)\})$ . The Runge-Kutta-Gill procedure consists of the following iterative prescription.

$$k_j^1 = \Delta t \delta_j(t^0; \{s_i^0\})$$

$$s_j^1 = s_j^0 + \frac{1}{2}(k_j^1 - 2q_j^0)$$

$$k_j^2 = \Delta t \delta_j(t^0 + \frac{\Delta t}{2}; \{s_i^1\})$$

$$s_j^2 = s_j^1 + (1 - \sqrt{2})(k_j^2 - q_j^1)$$

$$k_j^3 = \Delta t \delta_j(t^0 + \frac{\Delta t}{2}; \{s_i^2\})$$

$$s_j^3 = s_j^2 + (1 + \sqrt{2})(k_j^3 - q_j^2)$$

$$k_j^4 = \Delta t \delta_j(t^0 + \Delta t; \{s_i^3\})$$

$$s_j^4 = s_j^3 + \frac{1}{6}(k_j^4 - 2q_j^3)$$

$$q_j^1 = q_j^0 + \frac{3}{2}(k_j^1 - 2q_j^0) - \frac{1}{2}k_j^1$$

$$q_j^2 = q_j^1 + 3(1 - \sqrt{2})(k_j^2 - q_j^1) - (1 - \sqrt{2})k_j^2$$

C(6)

$$q_j^3 = q_j^2 + 3(1 + \sqrt{2})(k_j^3 - q_j^2) - (1 + \sqrt{2})k_j^3$$

$$q_j^4 = q_j^3 + \frac{3}{6}(k_j^4 - 2q_j^3) - \frac{1}{2}k_j^4$$

$\Delta t$  is the increment in  $t$ ,  $k_j$  is a device for keeping track of the changes in the variable  $s_j$ , and the  $q_j$ 's are introduced to control the growth of round-off error. The superscripts denote the order of the iteration. This scheme is designed to be equivalent to the truncated Taylor expansion

$$s_j(t^0 + \Delta t) = s_j(t^0) + \left\{ \frac{d}{dt} s_j(t) \right\}_{t^0} \{\Delta t\} + \frac{1}{2!} \left\{ \frac{d^2}{dt^2} s_j(t) \right\}_{t^0} \{\Delta t\}^2 +$$

$$\frac{1}{3!} \left\{ \frac{d^3}{dt^3} s_j(t) \right\}_{t^0} \{\Delta t\}^3 + \frac{1}{4!} \left\{ \frac{d^4}{dt^4} s_j(t) \right\}_{t^0} \{\Delta t\}^4. \quad C(7)$$

However, the method does not involve the evaluation of derivatives higher than the first.

Analysis of the error inherent in the truncation of the Taylor series is very difficult. A common method of error control in trajec-

tory calculations consists of monitoring constants of the motion, such as total energy and linear and angular momenta, and adjusting  $\Delta t$  so as to keep them within a given tolerance of their initial values.

The outstanding advantage of the Runge-Kutta-Gill routine is its feature of self-starting. It can proceed directly from the specification of the initial conditions. A discussion of other methods of numerical integration can be found in (65).

### Molecular Models

A classical model is distinguished by its characteristic interaction potential  $V(\{\bar{r}_i\})$ . For example, a system of charged particles results in a sum of Coulombic terms,

$$V(\{\bar{r}_i\}) = \frac{1}{2!} \sum_i \sum_{j \neq i}^N Q_i Q_j |\bar{r}_i - \bar{r}_j|^{-1}, \quad C(8)$$

where  $Q_i$  is the charge of particle  $i$ .

A useful model for molecular motion ( and hence molecular collisions ) can be constructed by extending this approach via the expansion C(2) for  $V(\{\bar{r}_i\})$ . In this case, the particles are atoms in the colliding molecules.  $V(\{\bar{r}_i\})$  is written by selectively retaining terms in C(2) which will account for known effects. The geometry is most easily visualized in terms of bond distances, bond angles ( the "valence coordinates" (66) ), and intermolecular separations.

Bonded-pair interactions are assumed to be adequately represented by the empirical Morse function (67).

$$V_{ij}^m(\bar{r}_i, \bar{r}_j) = D_{ij} \{1 - K_{ij} \exp(-B_{ij} |\bar{r}_i - \bar{r}_j|)\}^2 \quad C(9)$$

$$K_{ij} = \exp(B_{ij} |\bar{r}_i^0 - \bar{r}_j^0|)$$

$$|\bar{r}_i^0 - \bar{r}_j^0| = \text{equilibrium bond distance}$$

$$\beta_{ij} = \text{range parameter}$$

$$D_{ij} = \text{bond dissociation energy}$$

Non-bonded intermolecular pairwise interactions are assumed to be Morse or Lennard-Jones (6,12) potentials (68).

$$V_{ij}^L(\bar{r}_i, \bar{r}_j) = 4\epsilon_{ij} \{ (\sigma_{ij}/|\bar{r}_i - \bar{r}_j|)^{12} - (\sigma_{ij}/|\bar{r}_i - \bar{r}_j|)^6 \} \quad C(10)$$

where  $\epsilon_{ij}$  = depth of attractive well

$$\sigma_{ij} = 2^{1/6} |\bar{r}_i^0 - \bar{r}_j^0|$$

$$|\bar{r}_i^0 - \bar{r}_j^0| = \text{position of the minimum in the attractive well}$$

If atoms  $i$  and  $k$  are bonded to atom  $j$ , a potential crudely representing a bending mode of the molecule can be written as follows:

$$V_{ijk}^a(\theta_{ijk}) = \frac{1}{2} \delta_{ijk} (\theta_{ijk} - \theta_{ijk}^0)^2 \quad C(11)$$

where  $\delta_{ijk}$  = bending force constant

$$\theta_{ijk} = \text{bond angle}$$

$$\theta_{ijk}^0 = \text{equilibrium bond angle}$$

That this is a three-particle interaction as defined by equation C(2) can be made evident by the following transformation.

$$V_{ijk}^a(\theta_{ijk}) \rightarrow V_{ijk}(\bar{r}_i, \bar{r}_j, \bar{r}_k) = \frac{1}{2} \delta_{ijk} \left\{ \arccos \frac{(\bar{r}_{ji} \cdot \bar{r}_{jk})}{|\bar{r}_{ji}| |\bar{r}_{jk}|} - \theta_{ijk}^0 \right\}^2 \quad C(12)$$

where  $\bar{r}_{ji} = \bar{r}_i - \bar{r}_j$  and  $\bar{r}_{jk} = \bar{r}_k - \bar{r}_j$ .

It is further assumed that there are no intermolecular three-atom interactions, but that all intermolecular forces arise as a result of pairwise interactions ( see page 16 ).

In species such as  $\text{NO}_3^-$  there is a hindrance to out-of-plane bending due to the  $\pi$ -electron structure. This can be represented in terms of a four-atom interaction by an extension of the scheme presented for the bending modes. However, the resulting equations of motion are very cumbersome.

In summary, the model emerges as a classical dynamical picture of molecular translations, vibrations, and rotations based on model potentials. Ostensibly, it was designed to provide a means by which energy transfer processes could be studied.

The equations of motion corresponding to the various interactions are documented in Appendix IV.

#### A Few Applications

The success of quantum mechanics in dealing with a wide range of phenomena resulted in the submergence of classical theory. The application of classical mechanics in atomic collision work was resurrected by Gryzinski (69), who drew attention to its agreement with experiments on proton and electron impact excitation and ionization. Trajectory calculations in the Coulomb model of classical atomic collisions have received emphasis in a review by Burgess and Percival (70). They stressed the good agreement with experiment of calculations in which electrons in states of low principal quantum number are represented by orbiting classical particles. The case of large  $n$  can be rationalized in terms of the correspondence principle ( 71\* and 72 ), but the assumptions of the

\* This paper illustrates the utility of the classical model.

low  $n$  calculations are contrary to elementary notions of orthodox quantum mechanics. Burgess and Percival (70) and Watson (10 page 338) have commented on the need for investigations which will delineate the classical theory and provide a firm basis for computations.

Wall, Hiller, and Mazur (73 and 73') initiated the use of trajectory analysis in the theory of collisions of small molecules in their study of the system  $H + H_2$  interacting according to the semiempirical London-Eyring-Polanyi potential surface. The method has since received extensive application to the study of the detailed microdynamical features of molecular energy transfer, particularly in nonreactive collisions.

Benson and coworkers (74,75,76,77, and 78)\* have carried out a series of simulated experiments involving atom-diatom molecule and diatomic molecule-diatom molecule collisions in collinear and two-dimensional configurations.\*\* Their work illustrates the influence of the phases of the classical oscillations on vibrational energy transfer and the method of calculating transition probabilities from classical quantities. The probability of the transition  $n \rightarrow n + 1$  is

$$P_{n \rightarrow n+1} = \frac{\Delta E_v}{|E_{n+1} - E_n|},$$

where  $\Delta E_v$  is the phase-averaged classical energy transfer, provided

\* Errors in the work of Benson et al. were noted in the review by Rapp and Kassal (23)

\*\* The traditional method of acknowledging the limitations of using less than three dimensions is to multiply resulting cross sections by a "steric factor" (usually  $\frac{1}{3}$ ).

multiple-quantum transitions are not important.

A similar study was conducted by Kelley and Wolfsberg (79). Their calculations indicate that the common assumption\* that the internal vibrational coordinates may be replaced by their equilibrium values in the intermolecular potential is violated, even when the energy transfer is small. Their work also substantiates the claim\*\* that anharmonic oscillations should be used in energy transfer calculations, since " If, in a given collision, a Morse oscillator is substituted for a harmonic oscillator, neither with initial vibrational energy, the amount of translational energy transferred to vibration often decreases, sometimes by a factor of 10 or even more."

In vibrational energy transfer theory, rotational energy is generally neglected since collisions are thought to be completed well within one rotational period. This point has been challenged by Razner (80) who concluded that vibrational-rotational coupling can become quite large, and consequently theories of molecular relaxation and dissociation cannot be conceived in terms of unmixed vibrational and rotational modes.

Reactive collisions have also been the subject of treatment from the point of view of trajectory analysis, most notably by Karplus and coworkers ( 81, 82, and 83 ). Such calculations are usually designed to supplement molecular beam work.

\* See for example ( 25 page 124 )

\*\* See page 22 of this document.



### Section III CLASSICAL MODEL CALCULATIONS

#### A) Coulomb ( proton - hydrogen atom ) Trajectories

The Coulombic model was taken as the point of entry in this study. The proton - hydrogen atom scattering system was chosen for its *prima facie* simplicity in order to establish a foothold on trajectory calculations. Figure 4 shows the geometry of the system.

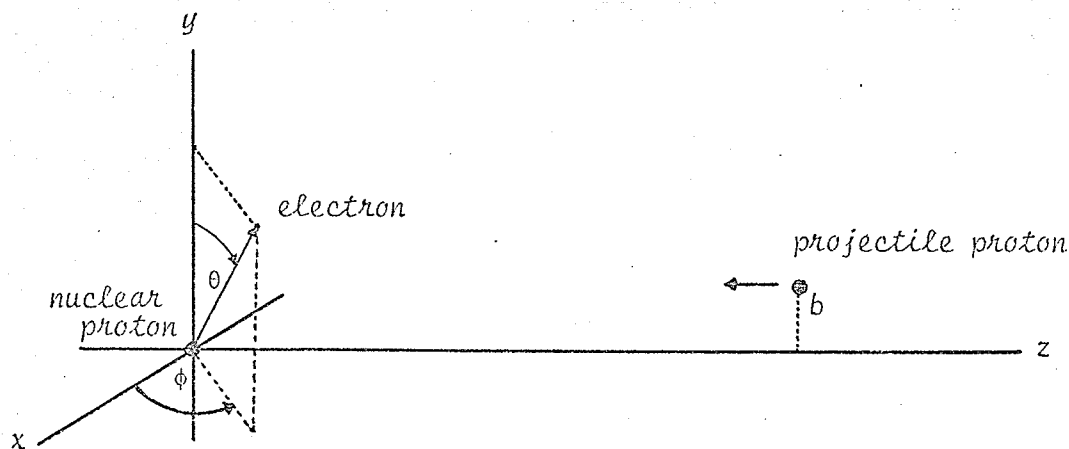


Figure 4

There is an ambiguity in the initial conditions since the classical electron cannot represent the spherical symmetry of the  $H(1s)$  state. There is clearly an infinite number of initial conditions for the hydrogen atom alone. Of them, only cases in which  $\phi^0 = 0$  or  $\pi/2$  will be considered here.\* In addition,  $b = 0$  in the examples discussed.

#### Planar Orbits

When  $\phi^0 = \pi/2$  the three-particle trajectories are two-dimensional. For low energy protons, this case exhibits an anomalous feature which presses it beyond the limits of nonrelativistic classical mechanics.

\* Abrines and Percival (84) employed a Monte Carlo procedure to secure an average over equivalent configurations.

Typical results illustrating this feature are shown in figures 5 and 6. These figures show how the projectile perturbs the trajectory of the orbital electron from its initial circular shape to an ellipse. The major axis of the ellipse remains of constant length ( the diameter of the circle ), appears initially at right angles to the internuclear line, and slowly rotates toward this line. The eccentricity decreases as the projectile approaches. Before the system has evolved to the point of maximum interaction, the electron passes so near the nuclear proton that it attains speeds of relativistic order. This effect disappears at intermediate and high energies, when the speed of the projectile proton is such that the orbital electron moves very little in the time of the collision.\* For example, if the projectile in figure 5 has  $T^0 = 17.8$  keV the final state consists of the three particles moving independently, representing ionization.

### Three Dimensional Orbits

When  $\phi^0 = 0$  the internuclear line is normal to the plane of the electron's initial rotation. In this case, the attractive singularity of the proton-electron interaction did not result in the complicating feature encountered in the case of planar orbits. It was thus possible to simulate collisions originating from this geometry.

In general, three possible final states can be distinguished.

- 1) The electron continues to be bound to the target proton ( direct scattering ).
- 2) The electron has become bound to the projectile proton ( exchange scattering ).

\* A 10 keV proton has a speed approximately  $\frac{1}{2}$  that of the classical electron in the H(1s) system.

Figure 5

An electron bound to a proton at the origin is being struck by a proton approaching from positive  $z$  with kinetic energy  $(T^0) = 13.25$  eV.

The orbit of the electron was initially a circle of radius 1 au. On the revolution following the one shown, the electron passes so near to the nuclear proton that relativistic factors cause the calculation to fail.

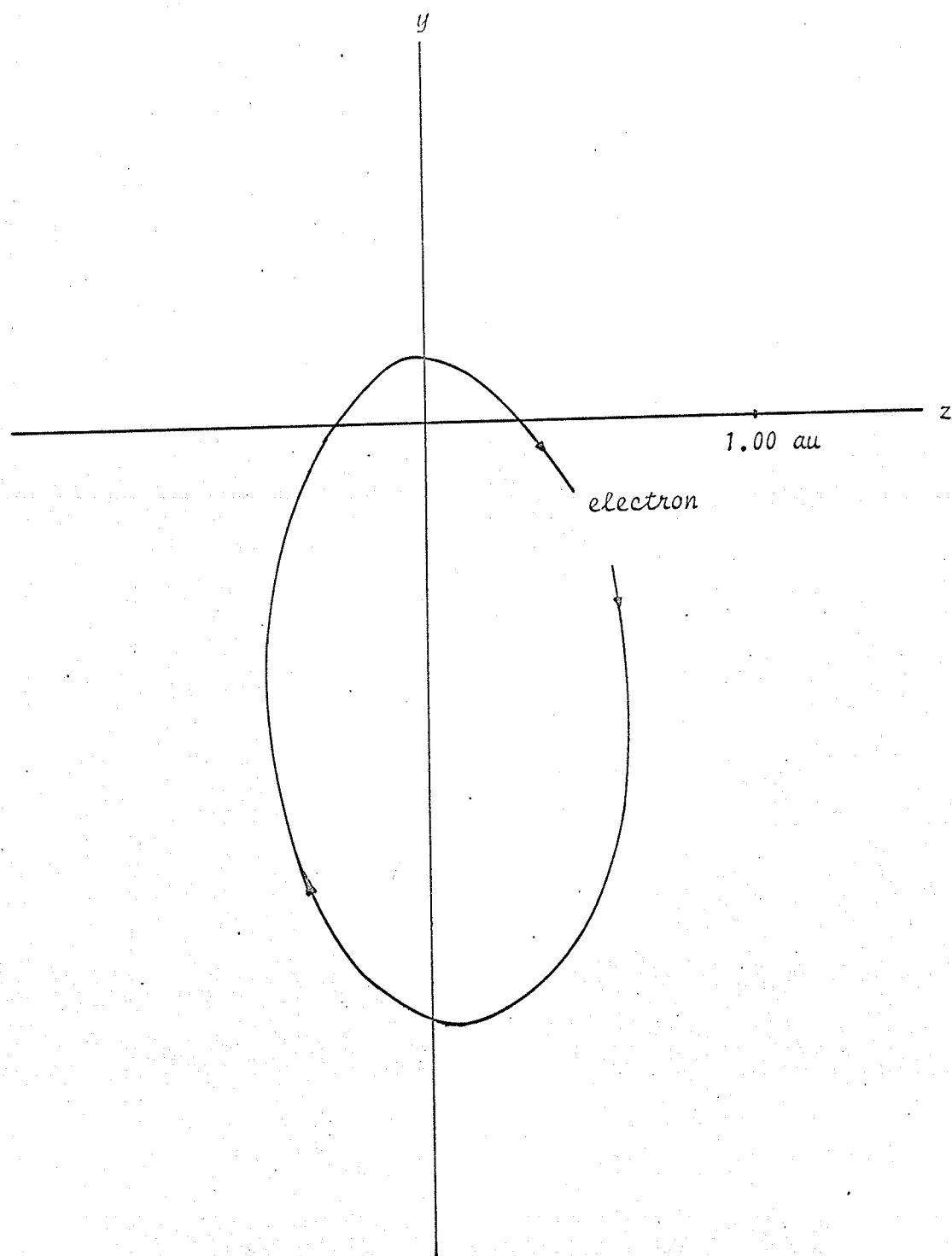
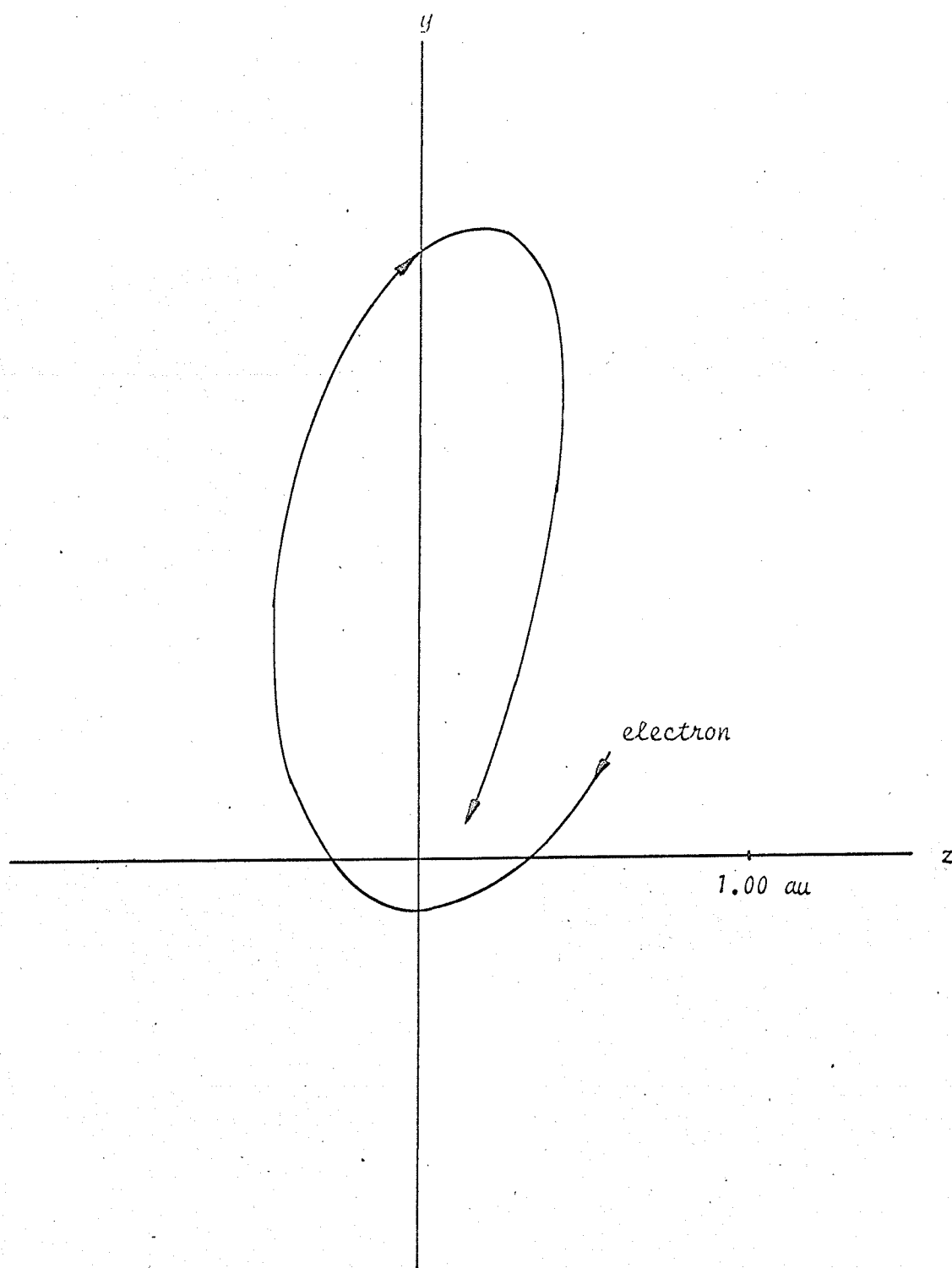


Figure 6

This is as in figure 5; the projectile here being an electron with  $T^0 = 0.80$  eV. The figure shows the last cycle before the calculation fails.



3) The electron moves unbounded ( ionization ).

The results for  $T^0$  between 1 and 10 keV are as follows:

<u>Relative Energy ( <math>T^0</math> keV )</u>	<u>Type of Collision</u>
1	direct
2	direct
3	exchange
4	exchange
5	direct
6	direct
7	direct
8	direct
9	exchange
10	exchange

Although no substantial conclusions can be drawn from it, comparison of these results with figure 3 is interesting. The exchange scattering at 3 and 4 keV occurs at points for which the quantum mechanical and experimental exchange probabilities are high; and the direct scattering occurs at points for which those quantities are low. However, the 9 and 10 keV points are not in agreement with this trend. A proper comparison must include an average over  $\phi$  for each value of  $T^0$ . This was not performed because the required computer time was prohibitive.

#### B) Molecular Trajectories

The method developed for charged particles was extended to include the two- and three-particle potentials of Section II C) in order to simulate collisions of small molecules.

Experiments, such as those of ultrasonic dispersion and shock

tube studies, reflect averages over the following quantities:

- 1) impact parameters
- 2) relative angular orientations
- 3) relative phases of internal motion
- 4) distributions of internal state populations and relative velocities.

In principle, such averages are easily obtained in simulated experiments. However, as in the case of the Coulomb model, the computer time involved has here proved to be excessive.

### Collisions of $O_2$ Molecules in Highly Excited Vibrational States

Selection of the collinear configuration ( figure 7 ) fixes the impact parameter and the relative angular orientation of the two colliding diatomic molecules. A further specification of the relative and internal energies leaves only the phases of the vibrations to determine the initial state. They are clearly somewhat arbitrary.

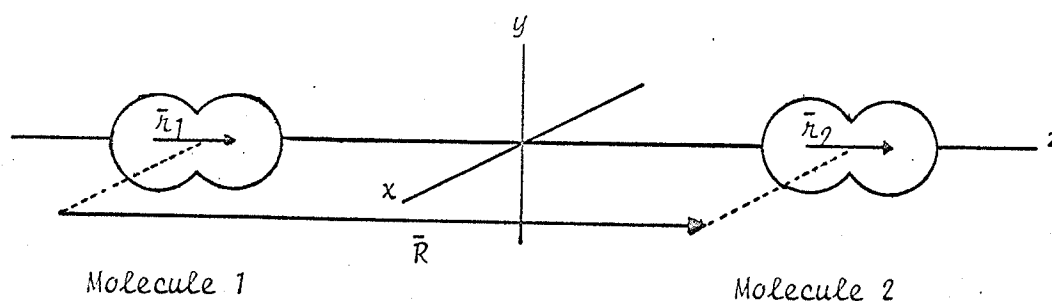


Figure 7

Define  $E_V^i(1 \text{ or } 2) = \text{initial vibrational energy of 1 or 2}$

$E_V^f(1 \text{ or } 2) = \text{final vibrational energy of 1 or 2}$

$E_R^i = \text{initial relative kinetic energy}$

$$\Delta E_V = E_V^f - E_V^i$$



The potential function was constructed from two intramolecular and four intermolecular Morse terms. The intermolecular terms were chosen to be of Morse type because they account for long-range attraction. In spite of the fact that short-range repulsion has the dominant effect in energy transfer ( 25 page 581 ), long-range attraction should not be ignored since 1) it will affect the slope in the repulsive region, upon which the energy transfer depends critically ( 29 and 1 page 689 ), and 2) it will have an increasing effect on the relative motion as the relative kinetic energy is lowered. The depth of the attractive well is known to be of minor significance compared to the range parameter ( 23 ) and can be obtained from transport property data (68). The relevant data are listed below.

Morse Parameters for  $O_2$  :

equilibrium bond distance -- 2.282 au (85)

range parameter ----- 1.404 au (86)

dissociation energy --- 0.1917 au (87)

Morse Parameters for Non-bonded O - O Interactions :

position of minimum ----- 7.28 au (88)

range parameter ----- see following

well depth -----  $0.356 \cdot 10^{-3}$  au (88)

In view of the fact that the shape of the potential exercises sensitive control over the collision dynamics, a quantitative statement of the effect of the intermolecular range parameter was sought. Figure (8) illustrates the effect of varying  $\beta$  on  $\Delta E_v$  for three initial phases and

$$E_v^i(1) = E_v^i(2) = 0.990$$

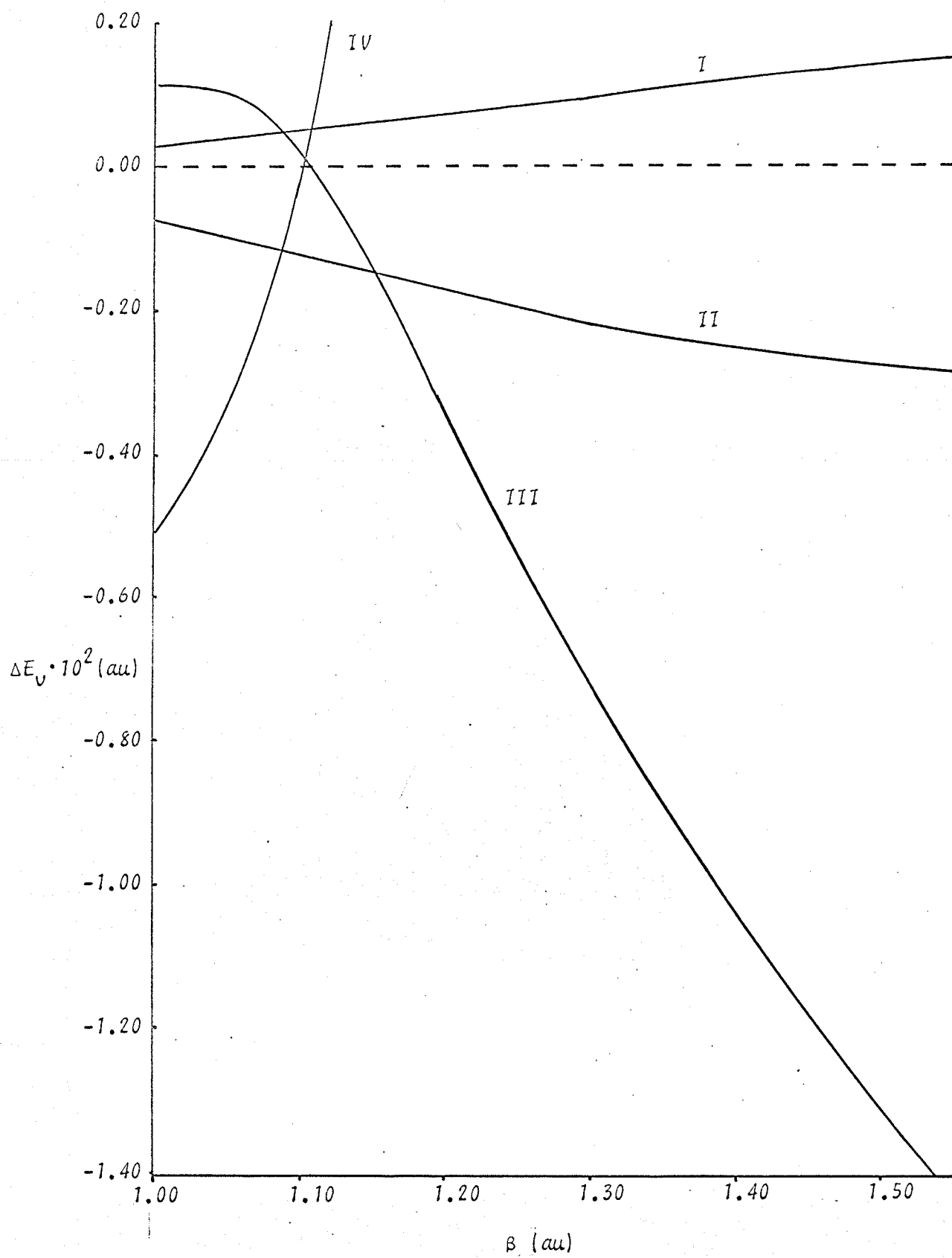
Figure 8

This graph shows the dependence of vibrational energy changes in  $O_2 - O_2$  collisions upon the range parameter in the Morse terms of the intermolecular potential for three phases.

Curve I: The phases are determined by the initial condition  $|\bar{r}_1| = |\bar{r}_2| =$  minimum classical turning point for  $E_v^i(1 \text{ and } 2) = 0.99D$ .

Curve II: In this case, both molecules begin at their maximum classical turning points.

Curves III and IV correspond to molecules 1 and 2 in a collision in which molecule 1 began at its maximum classical turning point and molecule 2 at its minimum.



$$E_R^i = 4 \cdot 10^{-3} \text{ au} = 0.11 \text{ eV}$$

$$R = 50 \text{ au}$$

The most significant energy transfer occurs when the diatomic molecular vibrations are distinctly out of phase; in which case a small change in  $\beta$  can have an enormous effect on the collision dynamics. The  $\beta$  dependence is put into perspective when it is noted that

$$\beta = 1.02 \quad (89)$$

$$1.03 \quad (76)$$

$$1.06 \quad (90)$$

$$1.20 \quad (88)$$

$$1.24 \quad (91)$$

have been applied to this model.

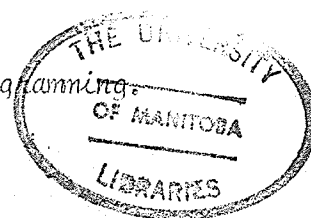
It would be foolhardy to make any far-reaching claims based on these data. Previous work in this area has concentrated on the lower vibrational states; studies which are legitimized by the equivalence of quantum mechanical and phase-averaged classical energy transfer. The dynamics of these states is quantum mechanical and the ability to invoke classical mechanics at all can only be considered fortuitous. Classical mechanics is presented here as giving an accurate picture of the evolution of a single event involving diatomic molecules at the dissociation limit. This claim is based on the fact that the vibrational level spacing of most diatomics in this region ( $H_2$  is an exception) is small compared to typical thermal energies.

### C) Numerical Integration Scheme

The calculation scheme contained a Runge-Kutta-Gill integration routine programmed in Fortran IV for use on an I.B.M. system 360/65.\* This scheme included the equations of motion of  $N$  particles subject to Morse, Lennard-Jones, and general  $1/R^n$ , and quadratic angular distortion potentials in all conceivable combinations. An attempt was made to decrease the computation time by incorporating a Hanning Predictor-Corrector routine into the program, but this failed as a result of unstable error growth. A separate program using the Runge-Kutta-Gill routine was written for the Coulomb potential.

An important consideration concerns the analysis of data. The raw information consisted of position and momentum coordinates for each particle at each iteration. Energies and geometries were extracted from these and the relevant algebraic expressions. When the evolution of a single collision was investigated, print-outs were obtained at appropriate intervals. For final state configurations, only a few print-outs at the end of each calculation were necessary. The point is that much programming effort went into determining how to obtain particular dynamical variables at particular stages of the collision.

\* The author is indebted to Mr. Bruce Koppers for all programming.



The numerical approach underlying the material of the preceding sections is offered as an alternative to the well-known approximate analytical methods discussed. As outlined in the subsections "A Few Applications", practical calculations based on numerical solutions to the equations of coupled-state amplitudes are becoming common in the literature. The value of such an approach has been generally recognized ( see for example 45 page 125 ) and will doubtless stimulate the field of atomic and molecular collision theory. The model calculations presented are a few examples from an attempt to develop an expertise in this field, beginning from a classical point of view.

Classical, Semiclassical, and Quantum Mechanical Considerations

The classical N-body problem is a straightforward but tedious exercise in standard numerical integration techniques. However, the relative ease of the classical method is countered by the lack of cases in which its validity is sufficiently sound. Its value here is considered to be heuristic.

The ability to employ rotating classical electrons in the representation of low quantum atomic states is startling. Abrines and Percival (71) suggested that this may be due to the special properties of the Coulomb interaction ( the Rutherford Scattering Identity )\*, but no proof has been given. Similarly, the accuracy of classical models of low quantum vibrational states is quite remarkable ( see 23, 76, and 78 ). It is to be emphasized that comparisons between the results of classical calculations and quantum mechanical or experimental data must be accom-

\* See also the review by Burgess and Percival (70).

panied by a process of averaging over arbitrary geometrical parameters in the classical model.

The semiclassical formulation, which results from the inclusion of quantum internal states and the retention of classical relative motion, is an accurate description of most molecular collisions. One of the main features of this method is its ability to reveal the importance of the number of internal states required for the effectively complete description of a collision. This number can be determined by finding the point at which the addition of more states becomes superfluous. Multi-quantum transitions and collisional selection rules are consequently automatically taken into account.

The rigorous formulation of atomic and molecular collision theory is the full quantum mechanical treatment, in which the relative motion as well as the internal dynamics is ascribed a wave-like behavior. The formal complexity of this approach has hindered its application to practical problems. It is anticipated that progress in this regard is forthcoming.

#### The Problem of Potentials

An accurate but workable representation of molecular interactions is the principle requirement of a practical theory of molecular collisions. The complexity of the general problem is, of course, due to its multi-electron character. To those who consider this complexity to be overwhelming, empirical potentials have provided an expedient means of avoiding an explicit account of the electrons. However, empirical parameterizations of molecular dynamics are of only terminal value since they "tend to explain everything and predict nothing" ( 23 page 62 ).

Similarly, optical potentials provide a useful phenomenological means of

analysis of scattering data. Both phenomenological and empirical methods must be supplanted by more exact techniques.

To obtain an accurate representation of molecular interactions, one must deal directly with the electronic structure and related features such as transitions, exchange, and intra- and intermolecular correlation effects. Thus, it is necessary to incorporate into multichannel collision theory the techniques of molecular orbital theory. Exact (ab initio) calculations would clearly be the most satisfactory, but approximate (HF-SCF) and perhaps even simple (Huckel) methods would be more penetrating than classical empirical rationalizations.



# Appendix

## I Coupled Differential Equations --- Conversion from Integral Form

$$F_{\delta}(\vec{R}) = e^{i\vec{k} \cdot \vec{R}} \delta_{\delta i} + \sum_j \int G_0^+(\vec{R}, \vec{R}') V_{\delta j}(\vec{R}') F_j(\vec{R}') d\vec{R}' \quad A(7)$$

multiply both sides by  $(E^+ - E_{\delta} - K)$

$$(E^+ - E_{\delta} - K) \{F_{\delta}(\vec{R}) - e^{i\vec{k} \cdot \vec{R}} \delta_{\delta i}\} = \sum_j \int (E^+ - E_{\delta} - K) G_0^+(\vec{R}, \vec{R}') V_{\delta j}(\vec{R}') F_j(\vec{R}') d\vec{R}'$$

$$(E^+ - E_{\delta} - K) G_0^+(\vec{R}, \vec{R}') = (E^+ - E_{\delta} - K) \langle \vec{R} | (E^+ - E_{\delta} - K)^{-1} | \vec{R}' \rangle \quad \text{from A(6)}$$

$$= \int (E^+ - E_{\delta} - K) \langle \vec{R} | \vec{k} \rangle (E^+ - E_{\delta} - \frac{\hbar^2 k^2}{2\mu})^{-1} \langle \vec{k} | \vec{R}' \rangle d\vec{k}$$

$$= \int (E^+ - E_{\delta} - \frac{\hbar^2 k^2}{2\mu}) (E^+ - E_{\delta} - \frac{\hbar^2 k^2}{2\mu})^{-1} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} d\vec{k}$$

$$= \int e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} d\vec{k}$$

$$= \delta(\vec{R} - \vec{R}')$$

Thus

$$(E^+ - E_{\delta} - K) \{F_{\delta}(\vec{R}) - e^{i\vec{k} \cdot \vec{R}} \delta_{\delta i}\} = \sum_j \int V_{\delta j}(\vec{R}') F_j(\vec{R}') \delta(\vec{R} - \vec{R}') d\vec{R}'$$

$$(E - E_{\delta} - K) \{F_{\delta}(\vec{R}) - e^{i\vec{k} \cdot \vec{R}} \delta_{\delta i}\} = \sum_j V_{\delta j}(\vec{R}) F_j(\vec{R})$$

And, since

$$K e^{i\vec{k} \cdot \vec{R}} \delta_{\delta i} = \frac{\hbar^2 k^2}{2\mu} e^{i\vec{k} \cdot \vec{R}} \delta_{\delta i} = (E - E_{\delta}) e^{i\vec{k} \cdot \vec{R}} \delta_{\delta i} ,$$

$$(E - E_{\delta} - K) F_{\delta}(\vec{R}) = \sum_j V_{\delta j}(\vec{R}) F_j(\vec{R}) \quad A(7')$$

or

$$\{E - E_{\delta} - K - V_{\delta\delta}(\vec{R})\} F_{\delta}(\vec{R}) = \sum_{j \neq \delta} V_{\delta j}(\vec{R}) F_j(\vec{R})$$

This equation can be derived directly by substituting the expansion A(4) into the Schrodinger equation.

Note:

Green's functions occupy a central position in the integral equation formulation of scattering theory. No elaboration of their mathematical properties is attempted here. A detailed account can be found in (92) and their role in scattering theory is extensively examined in (93).

The use of Green's functions makes formal manipulations concise and very elegant, but does not diminish the difficulties of finding solutions.

AppendixII Coordinate Representation of the Transition Amplitude

$$T_{fi}(\vec{R}) = \langle f; \vec{R} | V(\vec{r}', \vec{R}') | \vec{k}; i^+ \rangle \quad A(12)$$

$$= \int \sum_j \langle f; \vec{R} | V(\vec{r}', \vec{R}') | j; \vec{R}' \rangle \langle j; \vec{R}' | \vec{k}; i^+ \rangle d\vec{R}'$$

$$= \int \sum_j \langle \vec{R} | \langle f | V(\vec{r}', \vec{R}') | j \rangle | \vec{R}' \rangle \langle j; \vec{R}' | \vec{k}; i^+ \rangle d\vec{R}'$$

$$= \int \sum_j \langle f | V(\vec{r}', \vec{R}') | j \rangle \langle \vec{R} | \vec{R}' \rangle \langle j; \vec{R}' | \vec{k}; i^+ \rangle d\vec{R}'$$

$$= \int \sum_j V_{fj}(\vec{R}') \delta(\vec{R} - \vec{R}') F_j(\vec{R}') d\vec{R}'$$

$$= \sum_j V_{fj}(\vec{R}) F_j(\vec{R}) \quad A(13)$$

# Appendix

## III Impact Parameter Limit of the Eikonal Method (45)

$$i\hbar v_0 \frac{\partial}{\partial z} F'_0(\bar{R}) = \sum_j V_{0j}(\bar{R}) F'_j(\bar{R}) \exp\left\{ \frac{i\mu}{\hbar} (v_j - v_0) z \right\} \quad B(13)$$

Since

$$E - E_j = \frac{1}{2} \mu v_j^2, \quad B(11)$$

$$(v_j^2 - v_0^2) = \frac{2(E_0 - E_j)}{\mu}$$

$$(v_j - v_0)(v_j + v_0) = \frac{2(E_0 - E_j)}{\mu}$$

$$\mu(v_j - v_0) = \frac{(E_0 - E_j)}{\frac{1}{2}(v_j + v_0)}$$

It is assumed reasonable to define a mean velocity  $v$  which can replace  $v_0$  on the left hand side and  $\frac{1}{2}(v_j + v_0)$  on the right hand side of equation B(13) and which also satisfies

$$z = vt \quad *$$

Equation B(13) then becomes

$$\frac{\partial}{\partial z} F'_0(\bar{R}) = (i\hbar)^{-1} \sum_j V_{0j}(\bar{R}) F'_j(\bar{R}) \exp\left\{ \frac{i}{\hbar} (E_0 - E_j) t \right\},$$

which is identical in form to equation B(4).

\* The parameter  $t$  is not actually the real time ( see 44 ).

AppendixIV Equations of Motion for Classical Molecular Models

Since the potential is assumed to be momentum independent, the equations

$$\dot{x}_i = \frac{\partial H}{\partial p_x(i)} = \frac{1}{m_i} p_x(i)$$

$$\dot{y}_i = \frac{\partial H}{\partial p_y(i)} = \frac{1}{m_i} p_y(i)$$

$$\dot{z}_i = \frac{\partial H}{\partial p_z(i)} = \frac{1}{m_i} p_z(i)$$

are common to all systems. In the remaining  $3N$  equations,

$$\dot{p}_x(i) = -\frac{\partial H}{\partial x_i} = -\frac{\partial V(\{\bar{r}_i\})}{\partial x_i}$$

$$\dot{p}_y(i) = -\frac{\partial H}{\partial y_i} = -\frac{\partial V(\{\bar{r}_i\})}{\partial y_i}$$

$$\dot{p}_z(i) = -\frac{\partial H}{\partial z_i} = -\frac{\partial V(\{\bar{r}_i\})}{\partial z_i} ,$$

the gradients vary according to the model potential. The components relevant to the discussion of Section II C) are tabulated below.

(1) Coulomb Potential

$$V_{ij}^C(\bar{r}_i, \bar{r}_j) = Q_i Q_j |\bar{r}_i - \bar{r}_j|^{-1}$$

$$-\frac{\partial V^C(\bar{r}_i, \bar{r}_j)}{\partial x_i} = Q_i Q_j (x_i - x_j) |\bar{r}_i - \bar{r}_j|^{-3}$$

$$-\frac{\partial V^C(\bar{r}_i, \bar{r}_j)}{\partial y_i} = Q_i Q_j (y_i - y_j) |\bar{r}_i - \bar{r}_j|^{-3}$$

$$-\frac{\partial V^C(\bar{r}_i, \bar{r}_j)}{\partial z_i} = Q_i Q_j (z_i - z_j) |\bar{r}_i - \bar{r}_j|^{-3}$$

(2) Morse Potential

$$V_{ij}^m(\bar{r}_i, \bar{r}_j) = D_{ij} \{1 - K_{ij} \exp(-\beta_{ij} |\bar{r}_i - \bar{r}_j|)\}^2$$

$$-\frac{\partial V_{ij}^m(\bar{r}_i, \bar{r}_j)}{\partial x_i} = -2\beta_{ij} K_{ij} D_{ij} \exp(-\beta_{ij} |\bar{r}_i - \bar{r}_j|) \{1 - K_{ij} \exp(-\beta_{ij} |\bar{r}_i - \bar{r}_j|)\} (x_i - x_j) |\bar{r}_i - \bar{r}_j|^{-1}$$

$$-\frac{\partial V_{ij}^m(\bar{r}_i, \bar{r}_j)}{\partial y_i} = -2\beta_{ij} K_{ij} D_{ij} \exp(-\beta_{ij} |\bar{r}_i - \bar{r}_j|) \{1 - K_{ij} \exp(-\beta_{ij} |\bar{r}_i - \bar{r}_j|)\} (y_i - y_j) |\bar{r}_i - \bar{r}_j|^{-1}$$

$$-\frac{\partial V_{ij}^m(\bar{r}_i, \bar{r}_j)}{\partial z_i} = -2\beta_{ij} K_{ij} D_{ij} \exp(-\beta_{ij} |\bar{r}_i - \bar{r}_j|) \{1 - K_{ij} \exp(-\beta_{ij} |\bar{r}_i - \bar{r}_j|)\} (z_i - z_j) |\bar{r}_i - \bar{r}_j|^{-1}$$

(3) Lennard-Jones (6,12) Potential

$$V_{ij}^L(\bar{r}_i, \bar{r}_j) = 4\epsilon_{ij} \{(\sigma_{ij}/|\bar{r}_i - \bar{r}_j|)^{12} - (\sigma_{ij}/|\bar{r}_i - \bar{r}_j|)^6\}$$

$$-\frac{\partial V_{ij}^L(\bar{r}_i, \bar{r}_j)}{\partial x_i} = 24\epsilon_{ij} \{2\sigma_{ij}^{12}/|\bar{r}_i - \bar{r}_j|^{14} - \sigma_{ij}^6/|\bar{r}_i - \bar{r}_j|^8\} (x_i - x_j)$$

$$-\frac{\partial V_{ij}^L(\bar{r}_i, \bar{r}_j)}{\partial y_i} = 24\epsilon_{ij} \{2\sigma_{ij}^{12}/|\bar{r}_i - \bar{r}_j|^{14} - \sigma_{ij}^6/|\bar{r}_i - \bar{r}_j|^8\} (y_i - y_j)$$

$$-\frac{\partial V_{ij}^L(\bar{r}_i, \bar{r}_j)}{\partial z_i} = 24\epsilon_{ij} \{2\sigma_{ij}^{12}/|\bar{r}_i - \bar{r}_j|^{14} - \sigma_{ij}^6/|\bar{r}_i - \bar{r}_j|^8\} (z_i - z_j)$$

(4) General  $\frac{1}{r^n}$  Potential

$$V_{ij}^G(\bar{r}_i, \bar{r}_j) = k_{ij} |\bar{r}_i - \bar{r}_j|^{-n}$$

$$-\frac{\partial V_{ij}^G(\bar{r}_i, \bar{r}_j)}{\partial x_i} = nk_{ij} |\bar{r}_i - \bar{r}_j|^{-n-2} (x_i - x_j)$$

$$-\frac{\partial V_{ij}^G(\bar{r}_i, \bar{r}_j)}{\partial y_i} = nk_{ij} |\bar{r}_i - \bar{r}_j|^{-n-2} (y_i - y_j)$$

$$-\frac{\partial V_{ij}^G(\bar{r}_i, \bar{r}_j)}{\partial z_i} = nk_{ij} |\bar{r}_i - \bar{r}_j|^{-n-2} (z_i - z_j)$$

The Coulomb potential is the special case  $n=1$ ,  $k_{ij}=Q_i Q_j$ .

(5) Quadratic Angular Distortion Potential

$$\begin{aligned}
 V_{ijk}^a(\bar{r}_i, \bar{r}_j, \bar{r}_k) &= \frac{1}{2} \delta_{ijk} \{ \arccos(\bar{r}_{ji} \cdot \bar{r}_{jk}) / |\bar{r}_{ji}| |\bar{r}_{jk}| - \theta_{ijk}^0 \}^2 \\
 &= \frac{1}{2} \delta_{ijk} \{ \arccos f_{ijk}(\bar{r}_i, \bar{r}_j, \bar{r}_k) - \theta_{ijk}^0 \}^2
 \end{aligned}$$

$$\frac{\partial V^a}{\partial x_i} = \frac{\delta \{ \arccos f - \theta^0 \}}{(1 - f^2)^{1/2}} \{ (x_k - x_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| - (x_i - x_j) f / |\bar{r}_{ji}|^2 \}$$

$$\frac{\partial V^a}{\partial y_i} = \frac{\delta \{ \arccos f - \theta^0 \}}{(1 - f^2)^{1/2}} \{ (y_k - y_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| - (y_i - y_j) f / |\bar{r}_{ji}|^2 \}$$

$$\frac{\partial V^a}{\partial z_i} = \frac{\delta \{ \arccos f - \theta^0 \}}{(1 - f^2)^{1/2}} \{ (z_k - z_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| - (z_i - z_j) f / |\bar{r}_{ji}|^2 \}$$

The equations for atom  $k$  are obtained by interchanging the coordinates of  $i$  and  $k$  on the right hand side of the above equations.

The following are all to be multiplied by

$$\frac{\delta \{ \arccos f - \theta^0 \}}{(1 - f^2)^{1/2}} :$$

$$(x_i - x_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| \{ (\bar{r}_{ji} \cdot \bar{r}_{jk}) / |\bar{r}_{ji}|^2 - 1 \} + (x_k - x_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| \{ (\bar{r}_{ji} \cdot \bar{r}_{jk}) / |\bar{r}_{jk}|^2 - 1 \}$$

$$(y_i - y_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| \{ (\bar{r}_{ji} \cdot \bar{r}_{jk}) / |\bar{r}_{ji}|^2 - 1 \} + (y_k - y_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| \{ (\bar{r}_{ji} \cdot \bar{r}_{jk}) / |\bar{r}_{jk}|^2 - 1 \}$$

$$(z_i - z_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| \{ (\bar{r}_{ji} \cdot \bar{r}_{jk}) / |\bar{r}_{ji}|^2 - 1 \} + (z_k - z_j) / |\bar{r}_{ji}| |\bar{r}_{jk}| \{ (\bar{r}_{ji} \cdot \bar{r}_{jk}) / |\bar{r}_{jk}|^2 - 1 \}$$

to obtain

$$\frac{\partial V^a}{\partial x_j}, \quad \frac{\partial V^a}{\partial y_j}, \quad \text{and} \quad \frac{\partial V^a}{\partial z_j}$$

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Wipe your hand across your mouth , and laugh;  
The worlds revolve like ancient women  
Gathering fuel in vacant lots.

T. S. E.