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Final Technical Report
(7/1/89 - 6/30/94)

Abstract

This final report is a summary of all of the research performed on the project entitled *Termolecular Association of Ions in Gases* under AFOSR Grant no. AFOSR-89-0426 for the period 7/1/89-6/30/94. Theoretical research was completed and published on the following projects:

(A) Termolecular Recombination

$$A + B + M \rightarrow AB + M$$

(B) Laser-Assisted Electron-Excited Atom Collisions

$$e^- + A + N\hbar\omega \rightarrow e^- + A^* + M\hbar\omega$$

(C) Electron-Excited Atom Collisions

$$e^- + A \rightarrow e^- + A^*, \qquad A = H, He$$

(D) Atom-Excited Atom Collisions

$$A + B(n) \rightarrow A + B^+ + e^-$$

A total of 23 publications were obtained together with four Ph.D theses during the period of the Grant. Full reference to this work is provided. In addition, new theories of Ion-Molecule Collisions (E) and Dissociative Recombination (F) have also been developed and are provided in this report as well. Full details of the theory of ion-molecule collisions are provided in an accompanying Organization Report GIT-89-023.

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I. Introduction

This final report summarizes all of the research performed on the project entitled *Termolecular Association of Ions in Gases* during the period of July 1, 1989 through June 30, 1994. The present theoretical research was performed under the auspices of AFOSR Grant no. AFOSR-89-0426.

The objectives of the research program was to formulate, develop and implement new theoretical descriptions of various atomic and molecular processes of importance in various situations of interest to the Air Force.

II. Research Completed

Theoretical research was completed on the following projects:

(A) Termolecular Recombination

$$A + B + M \rightarrow AB + M$$

(B) Laser-Assisted Electron-Excited Atom Collisions

$$e^- + A + N\hbar\omega \rightarrow e^- + A^* + M\hbar\omega$$

(C) Atom-Excited Atom Collisions

$$A + B(n) \rightarrow A + B^+ + e^-$$

(D) Ion-Molecule Collisions

$$X^+ + AB \rightarrow (XAB^+)^* \rightarrow products$$

$$X^+ + ABC \rightarrow (XABC^+)^* \rightarrow products$$

(E) Electron-Excited Atom Collisions

$$e^- + A \rightarrow e^- + A^*, \qquad A = H, He$$

(F) Empirical and Semiempirical Representations of Ion-Atom and Atom-Atom Interaction Potentials

(G) Electron-Ion Dissociative Recombination

$$e^- + AB^+ \rightarrow A + B$$

Each of the Topics (A)-(D) were the subjects of four Ph.D thesis performed under the auspices of AFOSR during the grant period. The research was written up and published in various referred journals. Reprints and Annual Reports were sent routinely to AFOSR under report nos. GIT-89-001 through GIT-89-015. In addition to this present report (no. GIT-89-024), the reports (GIT-89-016) through (GIT-89-023), contain a copy of the most recent Ph.D thesis and the remaining reprints of published research are attachments to this basic final report.

III. Published Research

A. Publication in Reviewed Journals:

Preprints of the following research were submitted to the AFOSR under the GIT Reports specified below.

1. Mansky E. J. and Flannery M. R., *The Issue of Basis Set Size in* $e^- + H(1s \rightarrow 2s, 2p)$ *Collisions*, J. Phys. B: At. Mol. Opt. Phys. 23 501-7 (1990) (Report GIT-89-004).

2. Mansky E. J. and Flannery M. R., *Polarization Fractions for the* $2^1P, 3^1P$ *and* 3^1D *States of Helium*, J. Phys. B: At. Mol. Opt. Phys. 23 3987-92 (1990) (Report GIT-89-005).

3. Mansky E. J. and Flannery M. R., *The Multichannel Eikonal Theory of Electron-Hydrogen Collisions I. Excitation of* $H(1s)$, J. Phys. B: At. Mol. Opt. Phys. 23 4549-72 (1990) (Report GIT-89-006).

4. Mansky E. J. and Flannery M. R., *The Multichannel Eikonal Theory of Electron-Helium Collisions I. Excitation of* $He(1^1S)$, J. Phys. B: At. Mol. Opt. Phys. 23 4573-4604 (1990) (Report GIT-89-007).

5. Smith P. H. G. and Flannery M. R., *Electron-Atom Collisions in a Laser Field*, Nucl. Instr. Meth. Phys. Res. B 56/47 166-9 (1991) (Report GIT-89-011).

6. Smith P. H. G. and Flannery M. R., *Electron-Hydrogen Collisions in a Laser Field*, J. Phys. B: At. Mol. Opt. Phys. 24 L489-94 (1991) (Report GIT-89-010).

7. Mansky E. J. and Flannery M. R., *Indirect Coupling Mechanisms and Stokes Parameters for Electron-Atom Scattering*, J. Phys. B: At. Mol. Opt. Phys. 24 L551-6 (1991) (Report GIT-89-013).

8. Flannery M. R., *Transport-Collisional Master Equations for Termolecular Recombination as a Function of Gas Density*, J. Chem. Phys. 95 8205-26 (1991) (Report GIT-89-012).

9. Smith, P. H. G. and Flannery M. R., *Electron-Hydrogen Collisions with Dressed Target and Volkov Projectile States in a Laser Field*, J. Phys. B: At. Mol. Opt. Phys. 25 1021-49 (1992) (Report GIT-89-009).

10. Mansky E. J. and Flannery M. R., *Electron-Metastable Helium Differential and Integral Cross Sections*, J. Phys. B: At. Mol. Opt. Phys. 25 1591-7 (1992) (Report GIT-89-016).

11. Flannery M. R., *Termolecular Ion-Ion Recombination*, Acta Physica Universitatis Comenianal 33 119-32 (1992) (Report GIT-89-017).

12. Mansky E. J. and Flannery M. R., *Empirical and Semiempirical Interaction Potentials for Rare Gas-Rare Gas and Rare Gas-Halide Systems*, J. Chem. Phys. 99 1962-77 (1993) (Report GIT-89-018).

13. Haffad A. and Flannery M. R., *Angular-Momentum Transfer in Collisional Ionization*, Phys. Rev. A 50 429-39 (1994) (Report GIT-89-019).

B. Chapters Published in Books during Grant Period:

14. Flannery M. R., *Recombination Processes*, in *Molecular Processes in Space* T. Watanabe, I. Shimamura, M. Shimizu and Y. Itikawa (eds.), Plenum Press (1990) (Report GIT-89-002).

15. Mansky E. J., *Electron Collision Cross Sections Involving Excited States*, in *Nonequilibrium Processes in Partially Ionized Gases*, NATO ASI series B 220 349-55, M. Capitelli and J. N. Bardsley (eds.), Plenum Press (1990) (Report GIT-89-003).

16. Flannery M. R., *Microscopic and Macroscopic Theories of Termolecular Recombination between Atomic Ions*, in *Dissociative Recombination: Theory, Experiment and Applications*, NATO-ASI series B 313 205-19, B. R. Rowe and J. B. A. Mitchell (eds.), Plenum Press, NY. (1993) (Report GIT-89-020).

17. Flannery M. R., *Electron-Ion and Ion-Ion Recombination Processes*, Advances in At. Mol. Opt. Phys. 32 117-47, Academic Press (1994) (Report GIT-89-021).

18. McDaniel E. W. and Mansky E. J., *Guide to Bibliographies, Books, Reviews and Compendia of Data on Atomic Collisions, Advances in At. Mol. Opt. Phys. Special Issue: Cross Section Data* 33 389-463, Academic Press (1994) (Report GIT-89-022).

C. Book Reviews Published during Grant Period:

1. Mansky E. J., *Charge Exchange and the Theory of Ion Atom Collisions* by B. H. Bransden and M. R. C. McDowell, Oxford U. Press (1992), reviewed in Physics Today 46 124-25, October 1993.

D. Personnel Involved during the Grant Period:

- **Graduate Students awarded Ph.D degrees during Grant Period**

1. Dr. M. S. Keenan, Ph.D thesis: *Termolecular Ion-Atom Association*, awarded 3-17-90, US citizen.

2. Dr. Phillip H. G. Smith, Ph. thesis: *A Semiclassical Treatment of Laser Assisted Collisions in a Soft-photon Weak-field Regime*, awarded 6-3-91, non-US citizen.

3. Dr. A. Haffad, Ph.D thesis: *Angular Momentum Transfer in Electron-Atom and Atom-Atom Collisional Ionization*, awarded 8-16-91, non-US citizen.

4. Dr. X. Qi, Ph.D thesis: *Ion-Molecule Spiraling Collisions and Termolecular Recombination* (Report GIT-89-023), awarded 6-16-94, non-US citizen.

- **Senior Research Scientists**

1. Dr. E. J. Mansky II, Senior Research Scientist, US citizen.

IV. Research Highlights :

(A) Termolecular Recombination

$$A + B + M \rightarrow AB + M$$

Scientific Objectives

(1) Develop the first fundamental comprehensive microscopic theory of this simplest three-body *chemical* reaction.

(2) The theory to serve as a case study or proto-type for more complex three-body transport-influenced reactions.

(3) The rate of the reaction must be furnished as a function of the gas (atomic or molecular) species M and must illustrate the non-linear variation of the rate between the reaction limited regime at low gas densities and the transport limited regime in the limit of high gas densities.

Approach:

(a) Develop sets of transport-collisional master equations which govern the behavior of the microscopic distribution $n(R, E, L)$ of $(A - B)$ pairs in the gas M over their internal separation R, relative energy E and relative angular momentum L.

(b) The set of equations incorporate a blend of statistical mechanics and theories to describe the transport of A towards B through the gas M, and atomic and molecular scattering theory to describe the reactive and non-reactive collisions between the pairs $(A - B)$ with gas species M.

Accomplishments:

A major paper on the construction, development and solution of the required equations has been published in J. Chem. Phys. 95 (1991) 8205-26. Publication no. 5 of §III. Reprints sent to AFOSR as Report GIT-89-012. Additional papers on Recombination which have been published are nos. 11, 16 and 17 of §III. The latter three papers have also been sent to AFOSR as Reports GIT-89-017, -020 and -021, respectively.

Fundamental Interest:

This development has served as a textbook study of the most basic three body chemical reaction from a microscopic viewpoint. It provides quantitive and physical foundations for various macroscopic treatments. It illustrates how reaction and transort are coupled in transport-influenced reactions.

Applications:

The termolecular process is key to the basic understanding of :

- Rare gas - halide (exciplex) lasers and rare gas excimer lasers,
- combustion and rocket plumes,
- various low temperature plasmas, plasma etching and plasma decomposition processes, etc.

(B) Laser-assisted Electron-Hydrogen Collisions

$$e^- + A + nh\nu \rightarrow e^- + A^* + mh\nu$$

Scientific Objectives:

(a) To develop the first comprehensive theory of the collision in which the states of the atom A are dressed (modified) by the laser and are then closely coupled by the electron-atom interaction. The projectile electron is also affected by the field of the laser.
(b) To investigate to what extent the presence of the laser enhances and can control the degree of excitation in electron atom collisions.

Approach:

A semiclassical Floquet approach is used to find the dressed states of the atom in the laser field. Volkov states are the states of the electron in the laser field. A semiclassical multichannel eikonal treatment, previously developed for electron-atom collisions, then uses the Floquet and Volkov states in a closely coupled calculation to produce the cross sections for electron-atom collisions in a laser field.

Accomplishments:

Such a theory was developed and applied to electron-hydrogen collisions in the field of a CO_2 laser.

$$e^- + H(1s) + nh\nu \rightarrow e^- + H(2s,2p) + mh\nu$$

The three papers (nos. 5, 6 and 9 of §III) were published and reprints sent to AFOSR as Reports GIT-89-019, -010 and -011, respectively. A Ph.D. thesis entitled *A Semiclassical Treatment of Laser-assisted Collisions in a Soft-photon Weak-field Regime* was awarded to P. H. G. Smith in 1991 under the supervision of M. R. Flannery.

(C) Atom-Excited Atom Collisions

Research has been completed on computing the cross sections for angular momentum changes,

$$A + B(n\ell) \rightarrow A + B^+ + e^-(\epsilon, \ell')$$

in heavy-particle and electron-atom ($e^- - B$) collisions where the target atom is initially in highly excited states ($n \geq 10$).

The research has shown that the cross sections for $n\ell \rightarrow n\ell'$ collisional transitions increases as ℓ' is increased until a maximum ℓ'_{max} is attained after which the cross sections decrease precipitously. This effect not only can be explained by a quantum description but as shown here by classical scattering. A paper describing this research was published in Phys. Rev. A **50** 429-39 (1994) (no. 12 of §III). A Ph.D. thesis entitled *Angular Momentum Transfer in Electron-Atom and Atom-Atom Collisional Ionization* was awarded to A. Haffad in 1991 under the supervision of M. R. Flannery. The above paper and thesis have been sent to AFOSR as Report GIT-89-019.

(D) Ion-Molecule Collisions

In the course of research on recombination it was realised that cross sections were required for spiralling collisions between ions and neutral molecules with permanent dipole moments such as HCl (linear) and NH_3 (symmetric top). The ion-molecule interaction is no longer spherical but is orientation dependent eg. at long range the interaction is,

$$V(R,\theta) = -\frac{\alpha}{2R^4} + \frac{D}{R^2}\cos\theta \tag{3}$$

where α is the polarisability of the molecule with permanent dipole moment D, and θ is the angle between the R-axis joining the ion to the center-of-mass of the molecule.

The main problem in these ion-molecule collisions is how to address the rotation of the molecule during the course of the collision. During the past decade there have been several approaches advocated.

- *Semiclassical*

(a) The Lock-in Dipole Approximation
(b) The Frozen Rotor Approximation
(c) The Average Dipole Orientation Theory (ADO)
(d) The Free Energy Average Angular Motion Theory
(e) The Adiabatic Invariance Theory (ADIA)

- *Quantum Mechanical*

(a) The Perturbed Rotational State Theory
(b) The Adiabatic Capture and Centifrugal Sudden Approximation (ACCSA)

One of the results of the present research has been the modification of the adiabatic invariance theory, to account for the coupling between the internal angular momentum of the target molecule and the orbital angular momentum of the projectile about the target, in the computation of the rate k of spiralling collisions in systems as $H_3^+ - HCl$, a rate analogous to the Langevin temperature-independent rate,

$$k_L = 2.34 \cdot 10^{-9} \left(\frac{\alpha}{M}\right)^{1/2} cm^3 s^{-1} \qquad (4)$$

for spiralling collisions under the polarisation attraction alone ie. the first term of (3). In (4) α is the polarisability in units of $\AA^3$ and the ion-molecule reduced mass M is in amu. Recent experiment (D. C. Clary, D. Smith and N. G. Adams Chem. Phys. Lett. 119 (1985) 320) has shown that there is a large difference between $k(T)$ which varies with isothermal temperature T and the Langevin rate k_L which is temperature independent. Calculation of the rate k is quite complicated even for systems as $He^+ - HCl$ and $H_3^+ - HCl$ by *ab-initio* quantum mechanical theories. A Ph.D thesis, entitled *Ion-Molecule Spiraling Collisions and Termolecular Recombination*, was awarded to X. Qi in 1994, and has been sent to AFOSR as Report GIT-89-023.

(E) Electron-Excited Atom Collisions

In the development of semiclassical theories for collision processes, $e^- + A_i^* \rightarrow e^- + A_j^*$, where i and j are both excited or metastable electronic states of the atom A, the practical implementation of fully quantal theories even if desired is unfeasible with modern supercomputers. Somehow the physics essential in collisions with excited atoms is inefficiently described by modern quantal methods in the sense that in order to obtain results considered to be accurate, tour-de-force evaulation of a whole host of small terms is required. In fully quantal calculations, large amounts of computer time are spent evaluating terms which ultimately provide insignificant contribution to the cross section. In fully quantal approaches there is no *a-priori* method of isolating the region which effectively controls the cross section. Semiclassical techniques therefore have been developed and used to track the essential physics much more efficently and effectively. Case studies for the targets hydrogen and helium have been carried out.

This work has published (nos. 1-4, 7, 10 and 15 in §III) and reprints have been sent to AFOSR as Reports GIT-89-004, -005, -006, -007, -013, -016 and -003, respectively.

(F) Empirical and Semiempirical Representations of Ion-Atom and Atom-Atom Interaction Potentials

The Tang-Toennies (TT) semi-empirical model potentials for ion-atom systems is applied to the rare gas—halide negative ion exciplexes. The coefficients defining the repulsive Born-Mayer term in the TT semi-empirical potentials are determined from the equilibrium bond length, R_e, and dissociation energy, D_e, taken from *ab-initio* calculations and from transport studies of these molecular ions. The damped dispersion and induction energy terms in the TT potentials are obtained from coupled Hartree-Fock calculations for the neutral rare gas atoms and F^-, Cl^- ions. The multipole polarisabilities for the heavier halogen atomic negative ions are estimated from a knowledge of polarisability ratios across isoelectronic sequences. The resultant semi-empirical ionic potentials are compared to available *ab-initio* calculations and the results of inversion of transport theory. To facilitate the comparison of the (sparse) *ab-initio* data with the semi-empirical potentials, a simple fitting procedure is presented for determining *empirical* potentials for diatomic molecules from a set of *three* constraint equations. The fitting procedure is applied to a total of 22 rare gas excimers and rare gas–halide exciplexes (both neutral and ionic) of interest to a variety of applications in gaseous discharges and excimer lasers. A 3-term representation of the empirical potentials generated is accomplished with the use of a minimal data set which include the 'geometric' parameters $\{R_0, R_e, D_e\}$ and the additional parameters $\{\alpha_d, I.P., E.A.\}$ needed for the dispersion and induction energy terms. A novel feature of the empirical procedure is the formulation of the constraint equations at *two* nuclear displacements (1 constraint at R_0 wherein the potential passes through zero, and 2 *constraints* at R_e, the equilibrium separation) which yields an accurate fit to available *ab-initio* data and greatly extends the range of internuclear separations R for which an accurate piecewise analytical empirical potential can be generated. To test the relative importance of the different terms in the fitted 3-term empirical representations, the classical orbiting cross section $Q_{orbit}(E)$ is computed using the full empirical potential and compared against the standard Langevin orbiting cross section $Q_{pol.}(E)$ for a pure polarisation interaction.

This work has been published in J. Chem. Phys. (no. 11 of §III) and reprints have been sent to AFOSR as Report GIT-89-018.

(G) Dissociative Recombination

Although all the modern quantum (scattering and chemistry) technology has been brought to bear on dissociative recombination,

$$e^- + AB^+ \rightarrow A + B \tag{2}$$

for the simpler diatomics, there remains several inconsistencies with observational data

A new class of dissociative recombination (DR) is emerging. In contrast to normal DR, characterised by rates $\alpha_{DR}(T) \sim 2 \cdot 10^{-7}(300/T)^{1/2}$ as for $O_2^+(v_i^+ = 0)$ and NO^+ with large dissociative energies $D_0^+ \sim 7$ eV and 11 eV, a class characterised by *super* rates of $2 \cdot 10^{-6}$ are being discovered.

Therefore a need to investigate dissociative recombination *for* various *complex* systems by the development of physical theories which will furnish insight into the various mechanisms is warranted by the ongoing inconsistencies with experimental data. The *ab-initio* calculations are having a tough enough time even for the simpler species H_2^+, N_2^+, O_2^+, etc., and are totally impractical for more complicated systems of interest.

A review of electron-ion and ion-ion recombination processes has recently been published (no. 17 of §III). A reprint of this review has been sent to AFOSR as Report GIT-89-021. Among the topics covered are the new class of dissociative recombination reactions mentioned above. Progress made towards the development of a new theory is presented in §V of this report.

V. Classical Path Theory of Direct Electron-Ion Dissociative Recombination and Associative Ionisation

V.1 Background

In 1950 Bates [1] postulated that, dissociative recombination (DR) for diatomic ions can occur via a crossing at R_X between the bound and repulsive potential energy curves $V^+(R)$ and $V^{**}(R)$ for AB^+ and AB^{**}, respectively. Here, DR involves the two-stage sequence,

$$e^- + AB^+(v_i) \underset{\nu_a}{\overset{k_c}{\rightleftharpoons}} (AB^{**})_d \xrightarrow{\nu_d} A + B^* \longrightarrow A + B + h\nu \tag{1}$$

The first stage is dielectronic capture whereby the free electron of energy $\epsilon = V^{**}(R) - V^+(R)$ excites an electron of the diatomic ion AB^+ with internal separation R and is then resonantly captured by the ion at rate k_c to form a repulsive state d of the doubly excited molecule AB^{**}, which in turn can either autoionise at probability frequency ν_a, or else in the second stage predissociate into various channels at probability frequency ν_d. This competition continues until the (electronically excited) neutral fragments accelerate past the crossing at R_X. Beyond R_X the increasing energy of relative separation has reduced the total electronic energy to such an extent that autoionisation is essentially precluded and the neutralisation is then rendered permanent past the stabilisation point R_X. Bates' interpretation has remained intact and robust in the current light of *ab-initio* quantum chemistry and quantal scattering calculations for the simple diatomics (O_2^+, N_2^+, Ne_2^+, etc.). Observation of emitted radiation $h\nu$ yields information on the excited products. Mechanism (1) is termed the direct process.

In 1968 Bardsley [2] pointed out the possiblity that a three-stage sequence,

$$e^- + AB^+(v_i) \rightarrow \left[AB^+(v_f) - e^-\right]_n \rightarrow (AB^{**})_d \rightarrow A + B^* \tag{2}$$

the so-called *indirect* process, might contribute. Here the accelerating electron loses energy by vibrational excitation ($v_i \rightarrow v_f$) of the ion and is then resonantly captured into a Rydberg orbital of the bound molecule AB^* which then interacts one way (via configuration mixing) with the doubly excited repulsive molecule AB^{**}. The capture initially proceeds via a small effect - vibronic coupling (the matrix element of the nuclear kinetic energy) induced by the breakdown of the Born-Oppenheimer approximation - at certain resonance energies $\epsilon_n = E(v_f) - E(v_i^+)$ and, in the absence of the direct channel (1), would therefore be manifest by a series of characteristic very narrow Lorentz profiles in the cross section. Uncoupled from (1) the indirect process would augment the rate. Vibronic capture proceeds more easily when $v_f = v_i + 1$ so that Rydberg states with $n \approx 7 - 9$ would be involved (for $H_2^+(v = 0)$) so that the resulting longer periods of the Rydberg electron would permit changes in nuclear motion to compete with the electronic dissociation. Recombination then proceeds as in the second stage of (1) ie. by electronic coupling to the dissociative state d at the crossing point. Giusti [3] has provided a unified account of the direct and indirect processes.

O'Malley [4] later noted that the process,

$$\begin{tikzcd} e^- + AB^+(v_i) \arrow[r, shift left, "k_c"] & (AB^{**})_d \arrow[l, shift left, "\nu_a"] \arrow[r, "\nu_d"] \arrow[d, shift right, "\nu_{dn}"'] & A + B^* \\ & {[AB^+(v) - e^-]_n} \arrow[u, shift right, "\nu_{nd}"'] & \end{tikzcd} \tag{3}$$

proceeds via the first (dielectronic capture) stage of (1) followed by a two-way electronic transitions with frequency ν_{dn} and ν_{nd} between the d and n states. All (n, v) Rydberg states can be populated, particularly those in low n and high v since the electronic $d-n$ interaction varies as $n^{-1.5}$ with broad structure. Although the dissociation process proceeds here via a second order effect (ν_{dn} and ν_{nd}) the electronic coupling may dominate the indirect vibronic capture and will interupt the recombination in contrast to (2a) which as written in the one-way direction feeds the recombination. Such dip-structure has been observed. Guberman and Giusti-Suzor [5] have assessed the effect of each contribution of (1), (2a) and (2b) to the resonance shape and integral cross section.

There exist two *ab-initio* quantal treatments for dissociative recombination - one (CM) based on configuration mixing [2-4,6] , and the other (MQDT) based on multichannel quantum defect theory [3]. CM has been applied [6-9] to H_2^+ ; MQDT has been applied [10-12] to H_2^+, , to NO^+ [13], to O_2^+ [5] , to N_2^+ [14] and to CH^+ [15]. These *ab-initio* treatments [10-12,15] have shown that the indirect process interferes destructively with the direct process. The cross sections exhibit an overall preponderance of destructive interference via a series of dips falling below the $E^{-1/2}$ continuous variation for the direct process. Here the direct → indirect coupling interrupts the recombination at specified energies. The quantal theory for diatomic ions is considered to be essentially complete for cases involving favorable crossings between the ion and doubly excited neutral states. The HeH^+ case which does not involve curve crossing has been treated recently by Guberman [16] and by Sarpal *et al.* [17]. Although the crossing at ~ 8 eV for H_2^+ has been explored by Kulander and Orel [18], the large cross section behavior [19] at low energies (where there is no curve crossing) remains unresolved.

Chris Bottcher [6] in 1976 developed a rather nice semiclassical theory of dissociative recombination. The theory is semiclassical in that JWKB wavefunctions for nuclear motion were used in this stationary state quantum treatment. Miller [20] has examined associative ionnisation - the inverse of (1) - within a classical, semiclassical and quantal framework. In this paper a different semiclassical theory of dissociative recombination is developed from a time dependent theory based on a classical trajectory $R = R(t)$ for the relative motion of the dissociating neutral heavy particles.

A. Motivation: Why Another Theory ?

When the two diabatic potential energy curves $V^+(R)$ and $V_d(R)$ cross at R_X, the rate for dissociative recombination given by a first-order treatment [2,21] is,

$$\alpha_{DR}(T) = \frac{h^3}{(2\pi mkT)^{3/2}}\left(\frac{\omega^{**}}{2\omega^+}\right)\left[\frac{2\pi}{\hbar}\left|V_{de}(R(t))\right|^2 R_X\right]\left\{\frac{|\psi_v^+(R_X)|^2\, kT}{|\, dV_d/dR\,|_{R_X}}\right\} \qquad (4)$$

where $V_{de}(R)$ is the electronic energy, $\langle \phi_d(R,r) \mid H_{el}(R,r) \mid \phi_e(R,r)\rangle_r$ coupling the electronic wavefunction ϕ_d for the doubly excited repulsive $(AB)_r^{**}$ intermediate state to the electronic wavefunction ϕ_e for the scattering system $e - AB^+$. The molecular functions $\phi_{d,e}$ are diabatic in that they are *not* pure eigenstates of the full electronic fixed-nuclei Hamiltonian $H_{el}(R,r)$, and the continuum functions are energy-normalised $\langle \phi_\epsilon \mid \phi_{\epsilon'}\rangle_r = \delta(\epsilon - \epsilon')$ with consequent unit density $\rho(\epsilon)$ of states for the scattered electron of energy ϵ. The bound vibrational wavefunction for the original ion state is $\psi_v^+(R)$.

Although all the modern quantum (scattering and chemistry) technology has been brought to bear for the simpler diatomics in a way considered in general correct, simple expressions as (4) are invaluable in that they reveal tremendous insight into the essential physics, general characteristics and workings of recombination for various distinct systems. Bates [21] has demonstrated how expressions as (4) may be utilised very effectively to promote new insight for recombination involving more complex ions.

Since Bates' deductions, particularly his discovery of the new class of super dissociative recombination, characterised by rates as large as $2 \cdot 10^{-6} cm^3 s^{-1}$, in contrast to $2 \cdot 10^{-7} cm^3 s^{-1}$ for normal DR, rely on the gradient dV_d/dR of the doubly excited repulsive state, it is now of interest to see whether (a) simple expressions as (4) but more accurate can be derived without recourse to the full numerical approach of *ab-initio* treatments, and (b) if the shape of the ion potential V^+ enters as directly as does V_d in (4) over that implicitly contained in $\psi_v^+(R_X)$. Apart from the first-order treatment (4) and the full quantal treatments (CM, MQDT) above, there appears to be no intermediate simplified description. There are also no analytical results such as (4), appropriate to the case when V^+ and V_d do not cross.

The purpose of this paper is to provide such a method wherein a two state semiclassical treatment of the direct process (1) will effectively yield an expression for the rate in a form similar to but more accurate than (4).

V.2 Classical Path Theory

A. Basic Equations

In the field of the ion AB^+, the recombining electron is captured at time $t = t_i$ into an electronically doubly-excited molecular state $\phi_d(r, R)$ whose variation with R is provided by the classical trajectory $R(t)$. Competition between autoionisation to the combined state $\phi_e(r, R)$ of the emitted electron of energy ϵ and the diatomic ion $AB^+(v_i)$ continues as the nuclei move inward or outward along the trajectory $R(t)$ associated with the potential $V_d(R)$. The system wavefunction satisfies,

$$\mathcal{H}_{el}(r, R(t))\Psi(\vec{r}, t) = i\hbar\frac{\partial\Psi(\vec{r}, t)}{\partial t} \tag{5}$$

where the time dependence in the electronic Hamiltonian $\mathcal{H}_{el}(r, R(t)) = \mathcal{H} - (\hbar/2M_{AB})\nabla^2_R$ for frozen nuclei in terms of the total system Hamiltonian $\mathcal{H}$, is generated by the classical trajectory $\vec{R}(t)$ for atomic dissociation. Expand

$$\Psi(\vec{r}, t) = \sum c_j(t)\phi_e(r, R)\exp\left[-\frac{i}{\hbar}\int_{t_i}^{t} W_{jj}(\vec{R}(t))\ dt\right] \tag{6}$$

in terms of some basis set ϕ_j where W_{jj} are diagonal elements of,

$$W_{ij}(\vec{R}(t)) = \left\langle \phi_i(\vec{r}, \vec{R}) \mid \mathcal{H}_{el} \mid \phi_j(\vec{r}, \vec{R})\right\rangle_r \tag{7}$$

Insert (6) into (5), project onto the state $< \phi_i \mid$ and use $\left\langle \phi_i \mid \frac{\partial\phi_j}{\partial t}\right\rangle_r = \dot{\vec{R}} \cdot \langle \phi_i \mid \nabla_{\vec{R}}\phi_j\rangle$ so as to obtain the set of coupled equations,

$$i\,\hbar\,\dot{c}_i(t) = \sum_{i \neq j} c_j(t)\left[\frac{W_{ij}(\vec{R}(t)) - i\,\hbar\,v_i}{\dot{\vec{R}} \cdot \langle \phi_i \mid \nabla_{\vec{R}}\phi_j\rangle}\right]\exp\left(-\frac{i}{\hbar}\int_{t_i}^{t}\left[W_{jj}(\vec{R}(t)) - W_{ii}(\vec{R}(t))\right]\ dt\right) \tag{8}$$

for the transition amplitudes c_i in this classical path representation. When ϕ_j are identified with the adiabatic (molecular) functions χ_j which satisfy,

$$\mathcal{H}_{el}(\vec{r}, \vec{R})\chi_j(\vec{r}, \vec{R}) = \left[\mathcal{H}_{int}(\vec{r}) + V(\vec{r}, \vec{R})\right]\chi_j(\vec{r}, \vec{R}) = E_j(R)\chi_j(\vec{r}, \vec{R}) \tag{9}$$

then $W_{ij}(R) = E_j(R)\delta_{ij}$ in (8), curves $W_{ii}(R)$ and $W_{jj}(R)$ of the same symmetry do not cross and the $i \rightarrow j$ electronic transition occurs via the non-adiabatic dynamic coupling elements $\langle \chi_i \mid \nabla_{\vec{R}}\chi_j\rangle$. When ϕ_j are taken as (atomic) eigenfunctions of the internal electronic Hamiltonian $\mathcal{H}_{int}$ at infinite separation R, then these dynamic coupling terms vanish and the transition occurs via the potential coupling terms $W_{ij} = \langle \phi_i \mid V(\vec{r}, R) \mid \phi_j\rangle$. When ϕ_j are taken eigenfunctions of some Hamiltonian $\mathcal{H}_0$ intermediate between $\mathcal{H}_{el}$ and $\mathcal{H}_{int}$, but so chosen as to satisfy,

$$\frac{\langle \phi_i \mid \mathcal{H}_{el} \mid \phi_j\rangle_r \gg i\,\hbar\,v_i}{\dot{\vec{R}} \cdot \langle \phi_i \mid \nabla_R \mid \phi_j\rangle_r \sim 0} \tag{10}$$

where $\mathcal{H}_{el} = \mathcal{H}_0 + \mathcal{H}'$ with $\mathcal{H}' \ll \mathcal{H}_0$, then ϕ_j form a diabatic basis set since the dynamic couplings are small. A complete atomic basis set $\phi_i(r_A, r_B, R \rightarrow \infty) = \phi_A(r)\phi_B(r)$ centered on each nuclei A and B (ie. $\mathcal{H}_0 = \mathcal{H}_{int}$, $\mathcal{H}' = V$) constitutes the simplest diabatic basis, eigenfunctions of $\mathcal{H}_{int}$ of (9). Application of (8) to the electronic continuum is obtained by expanding,

$$\Psi(\bar{r},t) = c_d(t)\phi_d(r,R)\exp\left[-\frac{i}{\hbar}\int_{t_i}^{t} E_d(t)\;dt\right] + \int_0^\infty c_\epsilon(t)\phi_\epsilon(r,R)\exp\left[-\frac{i}{\hbar}\int_{t_i}^{t} E^+(\epsilon,t)\;dt\right]d\epsilon \tag{11a}$$

in terms of the diabatic orthogonal basis set $\phi_\epsilon(r,R)$ of energy normalised functions $\langle\phi_\epsilon \mid \phi_{\epsilon'}\rangle_r = \delta(\epsilon-\epsilon')$ for the continuum electron-ion system $e^- - AB^+(R)$, and of ϕ_d for the molecular system $AB^{**}(R)$ in a vibrational continuum. The energies W_{jj} are the electronic potential energy surfaces,

$$E^+(\epsilon,t) = \langle\phi_\epsilon \mid \mathcal{H}_{el} \mid \phi_{\epsilon'}\rangle = V^+(R(t)) + \epsilon \tag{11b}$$

and,

$$E_d(t) = \langle\phi_d \mid \mathcal{H}_{el} \mid \phi_d\rangle = V_d(t) \tag{11c}$$

within which nuclear motion proceeds. Assume now that all continuum states are all uncoupled ie. $\langle\phi_\epsilon \mid \mathcal{H}_{el} \mid \phi_{\epsilon'}\rangle = \delta(\epsilon-\epsilon')$. In this diabatic representation (11a-c), then (8) yields,

$$i\,\hbar\,\dot{c}_d(t) = \int_0^\infty V_{d\epsilon}(t)c_\epsilon(t)\exp i\gamma(\epsilon;t)\,d\epsilon \tag{12a}$$

and,

$$i\,\hbar\,\dot{c}_\epsilon(t) = V^*_{d\epsilon}(t)c_d(t)\exp\left[-i\gamma(\epsilon;t)\right]. \tag{12b}$$

The bound-continuum electronic coupling matrix elements are,

$$V_{d\epsilon}(t) = \langle\phi_d \mid \mathcal{H}_{el}(r,R(t)) \mid \phi_\epsilon(r,R)\rangle_{\bar{r},\hat{\epsilon}} = V^*_{\epsilon d}(t) \tag{12c}$$

where the integration is over the electronic coordinates $\bar{r}$ and the direction $\hat{\epsilon}$ of the ejected electron. The phase is,

$$\gamma(\epsilon;t) = \frac{1}{\hbar}\int_{t_i}^{t}\left[V_d(t') - \left\{V^+(t') + \epsilon\right\}\right]\;dt' \tag{12d}$$

The above classical path formulation (12) is now applied to the forward direction of,

$$A + B^* \underset{DR}{\overset{AI}{\rightleftharpoons}} AB^+ + e^- \tag{13}$$

since the relative $A - B^*$ motion can be described by the classical path $R(t)$ and the electronic motion by quantum mechanics. The strategy is therefore to solve (12a) for $c_d(t)$ subject to $c_d(t_X) = 1$ ie. the reaction does not begin to occur until the $A - B^*$ separation is R_X at t_X. Solution of (12b) then provides the probability for electron ejection within the reaction zone $R \leq R_X$ ie. for the decay probability of a discrete electronic state AB^{**} moving via the classical path $R(t)$ through an embedded electronic continuum. The cross section σ_{AI} for the forward channel (associative ionisation) of (13) can then be obtained. Detailed balance then provides the cross section σ_{DR} for the reverse channel (dissociative recombination) of (13) ie. for the transition involving molecular states initially in an electronic continuum and finally in a vibrational continuum.

B. Formal Solutions

With (12b) inserted, the formal solution of (12a), subject to the initial condition $c(\epsilon, t_X) = 0$,

$$-2\pi\hbar^2 c_d(t) = \int_{t_X}^{t} dt' \int_0^{\infty} d\epsilon \Gamma(\epsilon, t; t') c_d(t') \exp i [\gamma(\epsilon; t) - \gamma(\epsilon; t')] \tag{14}$$

at time t. This depends on the previous history of the system between t_X and t via the non-local interaction,

$$\Gamma(\epsilon, t; t') = 2\pi V_{d\epsilon}(t) V^*_{d\epsilon}(t') \tag{15}$$

and on the phase difference,

$$\gamma(\epsilon; t) - \gamma(\epsilon; t') = \frac{1}{\hbar}\int_{t'}^{t} [V_d - (V^+ + \epsilon)] \ dt \tag{16}$$

at different times. This difference can be expanded to yield,

$$\begin{aligned} \gamma(\epsilon; t) - \gamma(\epsilon; t') &\sim \left(\frac{\partial\gamma}{\partial t'}\right)_t (t - t') + \frac{1}{2}\left(\frac{\partial^2\gamma}{\partial t'^2}\right)_t (t - t')^2 + \ldots \\ &= \frac{1}{\hbar}\left\{[V_d(t) - V^+(t)] - \epsilon\right\}(t - t') + F(t - t') \\ &= \frac{1}{\hbar}[W(t) - \epsilon](t - t') + F(t - t') \end{aligned} \tag{17}$$

where F is ϵ—independent, being a function only of the difference $(t - t')$, and where,

$$W(t) = V_d(t) - V^+(t) \tag{18}$$

is the energy for vertical transitions at time t. Equation (14) with (17) therefore reduces to,

$$-2\pi\hbar^2 c_d(t) = \int_{t_X}^{t} \exp iF(t - t') \ dt' \int_0^{\infty} d\epsilon \left\{\Gamma(\epsilon, t; t') c_d(t') \exp \frac{i}{\hbar}[W(t) - \epsilon](t - t')\right\} \tag{19}$$

which is in a form suitable for further approximation. The following analysis is valid for the case $V_d(t) \geq V^+(t)$ for $R \leq R_X$ appropriate to curve-crossing between the ion and neutral states at R_X ie. for $W(t) \geq 0$. The separation R_X can however tend to infinity so that $V_d(R) > V^+(R)$ everywhere.

C. Local Approximation

The $\epsilon-$ integration in (19) involves the product of $\Gamma \cdot c_d$ which is now assumed to vary slowly with ϵ, (ie. Γ has a large width Δ in its variation with ϵ), and an exponential which oscillates over ϵ with period $\delta = 2\pi\hbar/(t-t')$. The ϵ-integral is then negligible within the $(t-t')$-range which satisfies $\delta \ll \Delta$ ie. for $t \gg t'$. The remaining range $0 \leq (t-t') \leq 2\pi\hbar/\Delta$ will therefore provide the main contribution to the ϵ-integral. Hence $c_d(t)$ of (19) has only a short memory of the previous values of c_d between t_i and t and depends only on t' immediately before t. Thus,

$$-2\pi\hbar^2 c_d(t) = c_d(t) \int_0^\infty \Gamma(\epsilon, t)\, d\epsilon \int_0^{(t-t_X)} \exp\left[\frac{i}{\hbar}(W(t)-\epsilon)\tau\right] d\tau \tag{20}$$

for all t. As $t \to \infty$, or more precisely for $t \gg 2\pi\hbar/\Delta$ when the width $\hbar/t \ll \Delta$, then

$$\int_0^{(t-t_X)} \exp\left[\frac{i}{\hbar}(\epsilon_t - \epsilon)\tau\right] d\tau = \hbar\left[\pi\delta(\epsilon_t - \epsilon) + i\mathcal{P}\frac{1}{(\epsilon_t - \epsilon)}\right]. \tag{21}$$

The $\epsilon-$ integration therefore yields,

$$\dot{c}_d(t) = -\frac{1}{\hbar} c_d(t)\left[\frac{1}{2}\Gamma(\epsilon, t) + i\delta E_d(t)\right] \tag{22}$$

where the energy width,

$$\Gamma(\epsilon, t) = 2\pi\, |V_{d\epsilon}(t)|^2, \qquad \epsilon = W(t) \tag{23}$$

is due to coupling between ϕ_d and one continuum state ϕ_ϵ with energy $W(t)$ and where,

$$\delta E_d(t) = \mathcal{P}\int_0^\infty \frac{|V_{d\epsilon}(R(t))|^2\, R(t)\, d\epsilon}{\epsilon_t - \epsilon} \tag{24}$$

is the second-order energy shift in state ϕ_d due to the coupling with all other continuum states $\phi_\epsilon(r, R)$ with energy $\epsilon \neq W(t)$; since the principal value part $\mathcal{P}$ involves the contribution from states just below $W(t)$ to be balanced by states just above $W(t)$. The solution of (22) is,

$$c_d(t) = \exp\left[-\frac{1}{2\hbar}\int_{t_X}^{t} \Gamma(t')\, dt'\right] \exp\left[-\frac{i}{\hbar}\int_{t_X}^{t} \delta E_d(t')\, dt'\right] \tag{25}$$

The probability $|c_d|^2$ for remaining on the V_d curve at time t is,

$$P_d(t) = \exp\left[-\frac{1}{\hbar}\int_{t_X}^{t} \Gamma(t')\, dt'\right] \equiv \exp\left[-\frac{2\pi}{\hbar}\int_{t_X}^{t} |V_{d\epsilon}(R(t))|^2\, R(t) dt\right] \equiv \exp\left[-\int_{t_X}^{t} \nu_a(t) dt\right] \tag{26}$$

which is the probabilitiy for survival at time t against accumulated autoionisation at frequency ν_a between t_X and t. The effect of the continuum state $\phi_\epsilon(r, R)$ on the dissociating system is therefore realised by assigning the complex energy $E_d(R) = V_d(R) + \delta E_d(R) - \frac{i}{2}\Gamma(R)$ to state ϕ_d whose occupation probability then decays with time as $P_d(t)$. The solution of (12b) is therefore,

$$i\hbar c(\epsilon, t) = \int_{t_X}^{t} c_d(t')V^*_{d\epsilon}(t')\exp[-i\gamma(\epsilon;t')]\; dt' \tag{27a}$$

with the phase,

$$\gamma(\epsilon;t) = \frac{1}{\hbar}\int_{t_X}^{t} [W(t') - \epsilon]\, dt' \tag{27b}$$

expressed in terms of the positive energy

$$W(t) = V_d(t) - V^+(t) \tag{27c}$$

When the local solution (25) for $c_d(t)$ is inserted into (27a), the amplitude $c_\epsilon(t)$ can therefore be determined by direct numerical integration. Initially at time t_X, the nuclei $A - B^*$ enter the (autoionisation) reaction zone at R_X. They continue their relative motion inward until they reverse their motion at R_c, the distance of closest approach, at time t_c, move outward and then leave the reaction zone with a diminished amplitude at time $t_X + \tau_X$ with separation R_X. On taking $t_X = 0$ and $t = \tau_X$ in (27a), the amplitude $c_\epsilon(t)$ for electron emission after the time interval τ_X following some rearrangement is given by,

$$i\,\hbar\, c(\epsilon) = \int_0^{t_c} c_d(t)V^*_{d\epsilon}(t)\exp[-i\gamma(\epsilon;t)]\;\; dt + [\exp -i\gamma(\tau_X)]\int_0^{t_c} s_d(t)V^*_{d\epsilon}(t)\exp[+i\gamma(\epsilon;t)]\;\; dt \tag{28a}$$

where,

$$c_d(t) = \exp\left(-\frac{1}{2\hbar}\int_0^t \Gamma(t)\; dt\right) \tag{28b}$$

is the amplitude for survival of travel from R_X to $R(t)$ on the inward leg ($t < t_c$), and,

$$s_d(t) = c_d(\tau_X - t) = \exp\left[-\frac{1}{2\hbar}\int_0^{\tau_X} \Gamma(t)\; dt\right]\exp\left(+\frac{1}{2\hbar}\int_0^t \Gamma(t)\; dt\right) \tag{28c}$$

is the amplitude for survival during the sequence $R_X \xrightarrow{in} R_c \xrightarrow{out} R(\tau_X - t) = R(t)$ on the outward leg and,

$$\gamma(\tau_X) = \frac{1}{\hbar}\int_0^{\tau_X} [W(t) - \epsilon]\;\; dt = 2\gamma(t_c) \tag{28d}$$

is the total phase accumulated within the full reaction zone. Note that $c_d(t)s_d(t) = c_d(\tau_X) = c_d^2(t_c)$ is the survival amplitude for the round trip $R_X \xrightarrow{in} R_c \xrightarrow{out} R_X$. The above form (28a) is useful in that it tracks the increasing accumulation of phase $\gamma(t)$ which in (27b) is measured from the time t_X of entry to the reaction zone. An equivalent but symmetrical form of (28a) follows by taking $t = 0$ at R_c such that $t_X = -t_c$ and $t = \tau_X = +t_c$ in (27a). The result is,

$$i\,\hbar\, c(\epsilon) = \exp[-i\Delta(t_\epsilon)] \int_0^{t_\epsilon} V_{d\epsilon}^*(t)\,[c_d(t)\exp\{+i\Delta(t)\} + s_d(t)\exp\{-i\Delta(t)\}]\; dt \tag{29a}$$

where the new phase,

$$\Delta(t) = \frac{1}{\hbar}\int_0^t [W(t) - \epsilon]\; dt \tag{29b}$$

is zero at $R_\epsilon = R(t = 0)$. Since $W(t)$ is even, the old and new phases are then related by,

$$\gamma(t) = \begin{cases} \Delta(t_\epsilon) - \Delta(t), & t < t_\epsilon \\ \Delta(t_\epsilon) + \Delta(t), & t > t_\epsilon \end{cases} \tag{29c}$$

The first and second terms in each of (28a) and (29a) are the respective contributions to the amplitude $c(\epsilon)$ from the inward and outward legs of the classical trajectory $R(t)$. Each form is useful for correspondence with the stationary-state quantal transition amplitudes when JWKB bound vibrational wavefunctions are taken relative to the left-hand or right-hand turning points, respectively (cf. §VI).

The basic classical path theory is represented by either the amplitudes (28a) or (29a) with any known solution of (12a) for $c_d(t)$, and $s_d(t) = c_d(\tau_X - t)$. Analytical expressions for $c(\epsilon)$ can be obtained using the local analytical solutions (28b,c) in (28a) or (29a) which can then be determined by the method of stationary phase.

V.3 Cross Sections from Classical Theory

A classical theory —in the sense of summation over probabilities rather than of amplitudes so that interference effects are ignored— is readily deduced from the local approximation (26) without direct evaluation of $c(\epsilon)$ from (28a). The theory follows from (26) with conservation of probability imposed ie. from the requirement that,

$$P_d(t) + \int_0^t P(t)\; dt = 1 \tag{30}$$

where P_d is the probability $|c_d|^2$ of survival on V_d from $t_X = 0$ to t and where $P(t)dt$ is the probability for autoionization within the time interval $[t, t + dt]$. Thus,

$$P(t) = -\frac{dP_d(t)}{dt} = \frac{\Gamma(t)}{\hbar} P_d(t) \tag{31}$$

Within this time interval $[t, t+dt]$ or range $[R, R+dR]$ of internuclear separations, an electron is emitted with energy in the range $[\epsilon, \epsilon + d\epsilon]$ about $\epsilon(t) = W(t) = V_d - V^+$ with probability,

$$P(t)\; dt = P(R)\, dR = P(\epsilon)\, d\epsilon = |c(\epsilon)|^2\; d\epsilon \tag{32}$$

The probability densities per unit interval dR or $d\epsilon$ are then,

$$P(R) = \frac{P(t)}{v(R)} = \frac{\Gamma(R)}{\hbar v(R)} exp\left(-\frac{1}{\hbar}\int_R^{R_X} \frac{\Gamma(R)}{v(R)}\, dR\right) = \frac{dP_d}{dR} \tag{33a}$$

or,

$$P(\epsilon) = |c(\epsilon)|^2 = P(t)\left|\frac{d\epsilon}{dt}\right|^{-1} \equiv P(R)\,|W'(R)|^{-1} = -\frac{dP_d}{d\epsilon} \tag{33b}$$

respectively, where the radial speed $v(R) = \dot{R}, \dot{W} = d\epsilon/dt$ and $W'(R) = dW/dR$. The cross section for disposal of all possible energies ϵ in $A - B^*$ collisions at energy E is then,

$$\sigma_I(E) = 2\pi \int_0^{b_X} b\, db \int_0^{\tau_X} P(t)\, dt \tag{34a}$$

$$= 2\pi \int_0^{b_X} b\, db \oint_{R_o(b)}^{R_X} P(R)\, dR \tag{34b}$$

where the maximum impact parameter b_X which just penetrates the reaction zone is given by,

$$b_X^2(E) = R_X^2\left[1 - \frac{V_d(R_X)}{E}\right] \tag{34c}$$

This cross section is for the full reaction involving all ϵ and all ion states, ie. for both Associative and Penning Ionisation processes. Upon R-integration (34b) with (33a) reduces to,

$$\sigma_I(E) = 2\pi \int_0^{b_X} b db\left[1 - exp\left(-\frac{1}{\hbar}\oint_{R_o}^{R_X} \frac{\Gamma(R)}{v(R)}\, dR\right)\right] \tag{34d}$$

which is the standard classical result for any absorptive reaction. For small autoionisation widths Γ which are only weakly dependent on b (or L) then,

$$\sigma_I(E) = 2\pi \int_0^{b_X} b db \oint_{R_o}^{R_X} \left[\frac{\Gamma(R)}{u(R)}\right] ds_i \tag{34e}$$

where ds_i is an element of the trajectory $s_i = s(E, b)$ traced in time $dt = ds_i/u(R) = dR/v(R)$ in terms of the radial and local speeds, $v(R) = \dot{R}$ and $u(R) = (2/M)^{1/2}[E - V_d(R)]^{1/2}$, respectively. Since,

$$2\pi \int_0^{b_X} b db \oint_{R_o}^{R_X} f(R) ds_i = 4\pi \int_0^{R_X} R^2\left[1 - \frac{V_d(R)}{E}\right] f(R)\, dR \tag{34f}$$

the cross section (34e) reduces to,

$$\sigma_I(E) = \frac{2\pi}{\hbar}\left(\frac{2M}{E}\right)^{1/2} \int_0^{R_X} \Gamma(R) R^2 \left[1 - \frac{V_d(R)}{E}\right]^{1/2} dR \tag{34g}$$

in agreement with the results of Miller. When the path length $\lambda_a = \hbar v(R)/\Gamma(R)$ towards autoionisation is independent of R then (34d) reduces to,

$$\sigma_A(E) = \frac{4\pi}{\lambda_e}\int_0^{R_X} R^2\left(1-\frac{V_d}{E}\right)dR \xrightarrow{E \geq V_d} \frac{4}{3}\frac{\pi R_X^3}{\lambda} \tag{34h}$$

a result reminiscent of Thomson's for termolecular ion-ion recombination.

Electrons of a given energy ϵ can be emitted at different times t_1 and t_2 on the incoming leg and again at $\tau_X - t_1$ and $\tau_X - t_2$ on the outgoing leg. Thus, $W(t) = \epsilon$ has four roots (see Figure 1) for t in the range $(0, \tau_X)$. The total probability density from (33b) for electron emission is then the sum of the individual probabilities,

$$P(\epsilon) = \sum_i P(\epsilon(t_i)) = \frac{2\pi}{\hbar}\sum_{i=1}^{2}|V_{d\epsilon}(R(t))|^2 R_i \left|\dot{W}(R_i)\right|^{-1} P_S(R_i) = \sum_{i=1}^{2}\frac{\Gamma(R_i)}{\hbar v(R_i)}|W'(R_i)|^{-1} P_S(R_i) \tag{35a}$$

where the total probability of survival on the incoming and outgoing legs at R is,

$$P_S(R) = P_d(t) + P_d(\tau_X - t) = |c_d(R)|^2 + |s_d(R)|^2 \tag{35b}$$

$$= exp\left[-\frac{1}{\hbar}\int_R^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right] + exp\left[-\frac{1}{\hbar}\oint_{R_c}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right] exp\left[+\frac{1}{\hbar}\int_R^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right] \tag{35c}$$

$$\equiv 2\,exp\left[-\frac{1}{\hbar}\int_{R_c}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right] cosh\left[\frac{1}{\hbar}\int_{R_c}^{R}\frac{\Gamma(R)}{v(R)}\,dR\right] \tag{35d}$$

The cross section for $(A - B^*)$ collisions for disposal (via autoionisation and vibrational excitation of AB^+) of energy ϵ in the range $\epsilon, \epsilon + d\epsilon$ is $\sigma(E,\epsilon)\,d\epsilon$ where the differential cross section is,

$$\frac{d\sigma_I}{d\epsilon} = \sigma_I(E,\epsilon) = 2\pi\int_0^{b_X} P(\epsilon, b)b\,db \tag{36}$$

and $P(\epsilon, b)$ is given by (35) which implicitly depends on the impact parameter b via the classical orbit $R = R(E, L)$ where the relative angular momentum $L^2 = (2ME)b^2$. Not only is ϵ the vertical energy separating $V_d(R)$ and $V^+(R)$ at R, but it is also (cf. §V) the vertical separation between E and the energy of the vibrational level v of AB^+ (cf. Figure 2). The probability that AB^+ is left in a vibrational level v, assumed to form a quasi-continuum is therefore,

$$P(v, b) = P(\epsilon, b)\left|\frac{d\epsilon}{dv}\right| \tag{37}$$

Since the radial action,

$$J = \oint p_+(R)\,dR = \left(v + \frac{1}{2}\right)h \tag{38}$$

is quantised for bound vibrational motion with local momenta $p_+(R)$ between the classical turning points,

$$\frac{d\epsilon}{dv} = \frac{d\epsilon}{dJ}\frac{dJ}{dv} = h\nu \tag{39}$$

where ν is the frequency for vibrational motion in level v within the potential $V^+(R)$. The probability for autoionisation with AB^+ left in level v is then,

$$P(v,b) = 4\pi^2 \sum_{i=1}^{2} |V_{da}(R(t))|^2 R_i \left\{ |W'(R_i)|^{-1} \left(\frac{\nu}{v(R_i)} \right) P_S(R_i) \right\} \tag{40}$$

which is dimensionless. The corresponding cross section for associative ionisation into $AB^+(v)$ is then,

$$\sigma_{AI}(E,v) = 2\pi \int_0^{b_X} P(v,b) b \, db \tag{41}$$

The angular momenta $L^2 = (2ME)b^2 = (\ell + 1/2)^2\hbar^2$ and $(J+1/2)^2\hbar^2$ of relative nuclear motion before and after autoionisation are so large in comparison with the angular momenta of the ejected electron that $\ell \sim J$. The cross section for associative ionisation with AB^+ left in vibrational-rotational level (v, J) is simply,

$$\sigma_{AI}(E; v, J) = \frac{\pi}{k_{AB}^2}(2J+1)P(v, b(J)) \tag{42}$$

The transition (T)-matrix element is therefore given by $P^{1/2}(v,b)$ of (40) in this classical theory. The term in braces in (40) is a classical representation (ie. excluding phases) of the Franck-Condon Factor for bound-free vibrational transitions (cf. Appendix).

From detailed balance,

$$\omega_{AB}^{*} k_{AB}^2 \sigma_{AI}(E; v, J) = (2\omega^+)(2J+1)k_e^2 \sigma_{DR}(\epsilon; v, J) \tag{43}$$

where ω_{AB}^{*} and ω^+ are the electronic statistical weights of AB^* and AB^+ and 2 is the spin-statistical weight of the incident electron, the cross section for $e^- - AB^+(v,J)$ dissociative recombination (ie. for the reverse reaction in (13)) is then,

$$\sigma_{DR}(\epsilon_e; v, J) = \left(\frac{\omega_{AB}^{*}}{2\omega^+} \right) \frac{4\pi^3}{k_e^2} \sum_i |V_{da}(R(t))|^2 R_i \left\{ \left[|W'(R)|^{-1} \left(\frac{\nu}{v(R)} \right) P_S(R) \right] \right\}_{R_i} \tag{44a}$$

$$= \left(\frac{\omega_{AB}^{*}}{2\omega^+} \right) \frac{h^3}{8\pi m \epsilon_e} \sum_i \left[\frac{\Gamma(R_i)}{\hbar} \left\{ |W'(R)|^{-1} \left(\frac{\nu}{v(R)} \right) P_S(R) \right\}_{R_i} \right] \tag{44b}$$

where the total survival probability $P_s(R)$ on the incoming and outgoing legs at R is given by (35b). It will be shown (cf. §VI) that the summation in (44b) is a representation of the quantal matrix element for the molecular autoionisation frequency, evaluated by the method of stationary phase and summed over the probabilities (rather than the amplitudes) of the contributions from the various regions of stationary phase at R_i. The term in braces in (44b) is the contribution at R_i to the Franck-Condon overlap between the bound and continuum vibrational wavefunctions.

Moreover, evaluation of $c_s(t)$ of (29a) by the method of stationary phase yields the classical path T-matrix, $a_{CP}(\epsilon) = (h\nu)c_s(t)$. Neglect of interference effects between the various contributions c_i to the amplitude c from each region i of stationary phase yields the classical probability,

$$P(v;b) = (h\nu)\sum_i |c_i|^2 . \tag{45}$$

given by (40). Further physical insight into the associative ionisation/dissociative recombination process (13) and simplified expressions for the respective cross sections with interference effects included are now obtained by evaluating the integral (29a) directly by the stationary phase approximation.

V.4 Stationary Phase Amplitudes

The main contributions to the integral (29a) arise from those time intervals surrounding points t_i of stationary phase given by $\dot{\gamma} = d\gamma(\epsilon;t)/dt = 0$. The phase variation outside these regions of stationary phase is then sufficiently rapid to justify extension of both integration limits in (29a) to infinity. For one region around t_1 (say) the upper and lower limits, on the change of variable to $s = (t-t_1)$ become $s_u = (t-t_1) \rightarrow \infty$ and $s_\ell = -(t_1 - t_T) \rightarrow -\infty$, respectively. The integrals in (29a) for the amplitudes are of the form,

$$A^{\pm}(\epsilon) = \int_{-\infty}^{\infty} g(\epsilon;t)\, exp\left[\pm i\gamma(\epsilon;t)\right]\; dt \tag{46}$$

For cases involving at most two stationary points t_1 and t_2 which correspond to phase minima (with $\ddot{\gamma}(\epsilon;t_1) > 0$) and phase maxima (with $\ddot{\gamma}(\epsilon;t_2) < 0$), respectively, insert in (46) the expansions,

$$\gamma(t) = \gamma(t_i) + \dot{\gamma}(t_i)(t-t_i) + \frac{1}{2}\ddot{\gamma}(t_i)(t-t_i)^2 \tag{47a}$$

and,

$$g(t) = g(t_i) + \dot{g}(t_i)(t-t_i) \tag{47b}$$

about each isolated stationary point t_i given by $\dot{\gamma} = d\gamma(\epsilon;t)/dt = 0$. The integral,

$$\int_{-\infty}^{\infty} exp\left(\pm\frac{1}{2}i\,|a|\,x^2\right) dx = \left[\frac{2\pi}{|a|}\right]^{1/2} exp\left(\pm i\frac{\pi}{4}\right) \tag{47c}$$

then provides the Stationary Phase Evaluation of the integrals (46) as the linear expansions,

$$A^{\pm}(\epsilon) = a_1(\epsilon)\, exp\left[\pm i(\gamma_1 + \frac{\pi}{4})\right] + a_2(\epsilon)\, exp\left[\pm i(\gamma_2 - \frac{\pi}{4})\right] \tag{48a}$$

or equivalently,

$$A^{\pm}(\epsilon) = \left[a_1(\epsilon) \mp i a_2(\epsilon)\, exp(\pm i\gamma_{21})\right] exp\left[\pm i(\gamma_1 + \frac{\pi}{4})\right] \tag{48b}$$

of the individual amplitudes with magnitudes,

$$a_i(\epsilon) = \left[2\pi/|\ddot{\gamma}_i|^{1/2}\right] g_i(\epsilon), \qquad i = 1,2 \tag{48c}$$

and phase differences,

$$\gamma_{21} = \gamma_2 - \gamma_1 \equiv \gamma(t_2) - \gamma(t_1) \tag{48d}$$

at each phase point t_i treated in isolation.

Note that the relative phase γ_{21} of the amplitude a_2 to a_1 in the term A^+ is reduced by $\pi/2$ to give the factor of $-\imath$ in (48b). The phase change from 1 → 2 in general, is given by $\frac{1}{4}[sign\,\ddot{\gamma}_2 - sign\,\ddot{\gamma}_1]\pi$. These expressions are valid for well-separated regions of Stationary Phase ie. *for* $\gamma_{21} \gg 1$. In the present application $\gamma(\epsilon, t)$ is given by (27b) such that $\dot{\gamma}(\epsilon, t) = [W(t) - \epsilon]/\hbar$ is the only derivative of γ that depends on ϵ. Expressions (48) are therefore appropriate only for that energy which satisfies $\dot{\gamma} = 0$. When $\ddot{\gamma}_i = \dot{W}/\hbar$ vanishes, as *for* an extremum value ϵ^* in $W(t)$ at time t^* when the two points t_{12} of stationary phase coalesce at t (as for a caustic or rainbow), then expression (48c) diverges. On extending the expansion (47a) for γ to include the next non-vanishing term, $\ddot{W}(t^*) < 0$, since $\ddot{\gamma}(t^*) = 0$, and on recognising that $\dot{\gamma}(\epsilon, t^*) = (\epsilon^* - \epsilon)/\hbar$ in the neighborhood of the caustic at ϵ^* evaluation of (46) then yields the finite amplitudes,

$$A^{\pm}(\epsilon) = 2\pi \left[\frac{2\hbar}{|\ddot{W}(t^*)|}\right]^{2/3} g(\epsilon, t^*) Ai(-z)\, exp \pm \imath\gamma(\epsilon; t^*) \tag{49a}$$

in terms of the Airy function Ai of argument,

$$z = \left[2\hbar/|\ddot{W}(t^*)|\right]^{1/3} \left(\frac{\epsilon^* - \epsilon}{\hbar}\right) \tag{49b}$$

Expressions (49a) are in theory valid only in the ϵ−range surrounding the caustic at ϵ^* but, in practice, only at ϵ^*.

The analysis above is formally identical to the well established analysis of classical rainbow scattering; where $\gamma(t), W(t), t$ and ϵ above are analogous to the phase shift $\eta(\ell)$, deflection function $\chi(\ell) = d\eta/d\ell$, angular momentum ℓ and scattering angle θ, respectively, in elastic scattering. The "transitional" Airy approximation (49) does not uniformly connect with the "primitive" result (48). By mapping the phase $\gamma(\epsilon; t)$ onto the integrand of the Airy function, a Uniform Airy Approximation which uniformly connects (48) and (49) at ϵ^* is well known from previous work. The result is written here in compact form as the linear combination,

$$A^+(\epsilon) = a_1(\epsilon)\, exp\left[\imath(\gamma_1 + \frac{\pi}{4})\right] F^*(\gamma_{21}) + a_2(\epsilon)\, exp\left[\imath(\gamma_2 - \frac{\pi}{4})\right] F(\gamma_{21}) \tag{50a}$$

$$\equiv [a_1(\epsilon) F^*(\gamma_{21}) - \imath a_2(\epsilon)\, exp(\imath\gamma_{21}) F(\gamma_{21})]\, exp\left[\imath(\gamma_1 + \frac{\pi}{4})\right] \tag{50b}$$

and,

$$A^-(\epsilon) = a_1(\epsilon)\, exp\left[-i(\gamma_1 + \frac{\pi}{4})\right] F(\gamma_{21}) + a_2(\epsilon)\, exp\left[-i(\gamma_2 - \frac{\pi}{4})\right] F^*(\gamma_{21}) \tag{50c}$$

$$\equiv \left[a_1(\epsilon)F(\gamma_{21}) + ia_2(\epsilon)\, exp(-i\gamma_{21})F^*(\gamma_{21})\right] exp\left[-i(\gamma_1 + \frac{\pi}{4})\right] \tag{50d}$$

where the complex function F is defined in terms of the Airy function $Ai(z)$ and its z–derivative $Ai'(z)$ by,

$$F[\gamma_{21}(\epsilon)] = \left[\pi^{1/2}z^{1/4}Ai(-z) + i\pi^{1/2}z^{-1/4}Ai'(-z)\right] exp - i\left(\frac{\gamma_{21}}{2} - \frac{\pi}{4}\right); \quad \frac{4}{3}|z|^{3/2} = \gamma_{21} > 0 \tag{51}$$

for $\gamma_{21} = \gamma_2 - \gamma_1 \leq 0$. Since γ_{21} is the area enclosed by the $W(t)$ curve and the straight line $W = \epsilon$ (cf. Figure 1) it is always positive, except when it is zero at $\epsilon = \epsilon^* = W(t^*)$. It is shown below (§V) that the divergence in the constructive interference term $(a_1 + a_2)$ at the caustic $(\bar{\gamma}_t = 0)$ is exactly balanced by the vanishing of the coefficient $z^{1/4}$ of Ai ; also the divergence in the coefficient $z^{-1/4}$ of $Ai'(-z)$ at the caustic is offset by the destructive interference term $(a_1 - a_2)$ which vanishes more rapidly. In the limit of high $z \gg 1$, or for well separated regions $\gamma_{21} \gg 1$, $F(\gamma_{21}) \rightarrow 1$, with unit amplitude and zero phase such that (50) tends to the primitive form (48). The Uniform Airy result (50) is general in that it continuously connects the Caustic $(\gamma_{12} = 0, \bar{\gamma}_t = 0)$ result (49) at ϵ^* with the result (48) for well separated regions.

Autoionisation Amplitude and Interference Patterns

Application of the above Stationary Phase Prescription (50) to the integrals (28a) for the autoionisation amplitude $c(\epsilon)$ yields after some rearrangment,

$$ic(\epsilon) = \left[\mathcal{P}_1^{1/2}(\epsilon)F_{21} + i\mathcal{P}_2^{1/2}(\epsilon)F_{21}^* exp(-i\gamma_{21}) + \mathcal{P}_3^{1/2}(\epsilon)F_{21}\, exp(-i\gamma_{31}) + i\mathcal{P}_4^{1/2}(\epsilon)F_{21}^*\, exp(-i\gamma_{41})\right] exp\left[-i(\gamma_1 + \frac{\pi}{4})\right] \tag{52a}$$

which form illustrates how the progressive contributions are added as time evoules. An equivalent form is,

$$ic(\epsilon) = \left[P_1^{1/2}(\epsilon)\left\{c_1F_{21} + ic_1F_{21}^* exp(-i\gamma_{41})\right\} + iP_2^{1/2}(\epsilon)\, exp(-i\gamma_{21})\left\{c_2F_{21}^* - ic_2F_{21}\, exp(-i\gamma_{32})\right\}\right] exp\left[-i(\gamma_1 + \frac{\pi}{4})\right] \tag{52b}$$

which illustrates the addition of the inward-outward contributions at each R. The probability densities in (52b) for autoionisation at the isolated points R_i are,

$$P_i(\epsilon) = \frac{2\pi}{\hbar}|V_{d\epsilon}(R(t))|^2 R_i \left|\frac{W'(R_i)}{v(R_i)}\right|^{-1} \equiv \frac{\Gamma(R_i)}{v(R_i)\hbar}|W'(R_i)|^{-1}, \quad (i = 1, 2) \tag{52c}$$

In (52a), the probabilities,

$$\mathcal{P}_1 = P_1 c_d^2(R_{1,2}); \qquad \mathcal{P}_2 = P_2 c_d^2(R_2)$$

$$\mathcal{P}_3 = P_2 s_d^2(R_2); \qquad \mathcal{P}_4 = P_1 s_d^2(R_1) \tag{52d}$$

already incorporates the amplitudes,

$$c_d(R) = exp\left(-\frac{\pi}{\hbar}\int_R^{R_X} \frac{|V_{d\epsilon}(R(t))|^2\, RdR}{v(R)}\right) = exp\left(-\frac{1}{2\hbar}\int_R^{R_X} \frac{\Gamma(R)dR}{v(R)}\right) \tag{52e}$$

and,

$$s_d(R) = exp\left[-\frac{1}{2\hbar}\oint_{R_c}^{R_X} \frac{\Gamma(R)}{v(R)}\,dR\right] exp\left[+\frac{1}{2\hbar}\int_R^{R_X} \frac{\Gamma(R)}{v(R)}\,dR\right] \tag{52f}$$

for survival from R_X to R on the incoming leg or from $R_X \xrightarrow{in} R_c \xrightarrow{out} R$ on the outgoing leg, respectively. The indices $i = 1 - 4$ in $\mathcal{P}_i$ are associated with quantities calculated at times $t_1, t_2, t_3 = \tau_X - t_2$ and $t_4 = \tau_X - t_1$ which correspond to $R_1 \xrightarrow{in} R_2 \xrightarrow{out} R_2 \xrightarrow{out} R_1$ on the incoming and outgoing legs of the classical path as t progresses. The phase differences in (52a) for times on the same leg are,

$$\gamma_{ji} = \frac{1}{\hbar}\int_{t_i}^{t_j} [W(t) - \epsilon]\ dt \tag{52g}$$

and for times $t_j > t_i$ on different legs are,

$$\gamma_{ji} = \frac{1}{\hbar}\int_{t_i}^{t_c} [W(t) - \epsilon]\ dt + \frac{1}{\hbar}\int_{t_c}^{t_j} [W(t) - \epsilon]\ dt \tag{52h}$$

where t_c is the time of closest approach. Thus (52) is the classical result (35) fully generalised by this classical path theory to incorporate relative phases. The autoionisation probability density $P(\epsilon) = |c_\epsilon(t)|^2$ will therefore exhibit various interference effects arising from the phase differences between the amplitudes contributing at the same R_i on the incoming-outgoing legs and at the different R_1 and R_2 on either the incoming and/or outgoing legs. For well separated regions $\gamma_{12} \gg 1$ and (52a) tends to,

$$c(\epsilon) = \mathcal{P}_1^{1/2}(\epsilon) + i\mathcal{P}_2^{1/2}(\epsilon)\, exp(-i\gamma_{21}) + \mathcal{P}_3^{1/2}(\epsilon)\, exp(-i\gamma_{31}) + i\mathcal{P}_4^{1/2}(\epsilon)\, exp(-i\gamma_{41}) \tag{53a}$$

where the (redundant) multiplicative phase factor $\left[-i\, exp -i(\gamma_1 + \frac{\pi}{4})\right]$ of (52a) has been neglected on the RHS. The full interference pattern exhibited by the probability density is then,

$$\begin{aligned} P(\epsilon) = |c(\epsilon)|^2 &= \mathcal{P}_1 + \mathcal{P}_2 + \mathcal{P}_3 + \mathcal{P}_4 + 2(\mathcal{P}_1\mathcal{P}_2)^{1/2} \sin\gamma_{21} - 2(\mathcal{P}_2\mathcal{P}_3)^{1/2} \sin\gamma_{32} \\ &+2(\mathcal{P}_1\mathcal{P}_4)^{1/2} \sin\gamma_{41} + 2(\mathcal{P}_3\mathcal{P}_4)^{1/2} \sin\gamma_{43} + 2(\mathcal{P}_1\mathcal{P}_3)^{1/2} \cos\gamma_{31} + 2(\mathcal{P}_2\mathcal{P}_4)^{1/2} \cos\gamma_{42} \\ &= \left|P_1^{1/2}(\epsilon)\left\{c_1 + is_1\, exp(-i\gamma_{41})\right\} + iP_2^{1/2}(\epsilon)\left\{c_2\, exp(-i\gamma_{21}) - is_2\, exp(-i\gamma_{31})\right\}\right|^2 \end{aligned} \tag{54}$$

This illustrates various interference effects arising (a) from different R_1 and R_2 on the same leg,

$$P_{12} = \mathcal{P}_1 + \mathcal{P}_2 + 2(\mathcal{P}_1\mathcal{P}_2)^{1/2} \sin \gamma_{21} \tag{55a}$$

$$P_{34} = \mathcal{P}_3 + \mathcal{P}_4 + 2(\mathcal{P}_3\mathcal{P}_4)^{1/2} \sin \gamma_{43} \tag{55b}$$

(b) from the in-out contributions at a given R_i,

$$P_{14} = \mathcal{P}_1 + \mathcal{P}_4 + 2(\mathcal{P}_1\mathcal{P}_4)^{1/2} \sin \gamma_{41} \tag{56a}$$

$$P_{24} = \mathcal{P}_2 + \mathcal{P}_3 - 2(\mathcal{P}_2\mathcal{P}_3)^{1/2} \sin \gamma_{32} \tag{56b}$$

and (c) from different R_1 and R_2 on different legs,

$$P_{13} = \mathcal{P}_1 + \mathcal{P}_3 + 2(\mathcal{P}_1\mathcal{P}_3)^{1/2} \cos \gamma_{31} \tag{57a}$$

$$P_{24} = \mathcal{P}_2 + \mathcal{P}_4 + 2(\mathcal{P}_2\mathcal{P}_4)^{1/2} \cos \gamma_{42} \tag{57b}$$

All of the above interference patterns $P_{ij}(\epsilon)$ oscillate with ϵ about the classical mean $[\mathcal{P}_i(\epsilon) + \mathcal{P}_j(\epsilon)]$ between the envelopes $[P_1^{1/2}(\epsilon) \pm P_2^{1/2}(\epsilon)]^2$ with frequency $2\pi/\gamma_{ji}(\epsilon)$. Since $\gamma_{ji}(\epsilon; b)$ is also a function of the impact parameter b or angular momentum $L \equiv J$, the interference patterns will be effectively washed out in the b–integration for cross sections such as Penning Ionisation in (34). For cross sections as associative ionisation or dissociative recombination involving AB^+ with specified rotational state J (ie. at a selected impact parameter b) the above interference patterns will persist. The Uniform expansion for the autoionisation probability density, provided by the present theory (52a) is,

$$\begin{aligned} P(\epsilon) &= \left|\left[\mathcal{P}_1^{1/2}(\epsilon)F_{21} + i\mathcal{P}_2^{1/2}(\epsilon)F_{21}^* \exp(-i\gamma_{21}) + \mathcal{P}_3^{1/2}(\epsilon)F_{21} \exp(-i\gamma_{31}) + i\mathcal{P}_4^{1/2}(\epsilon)F_{21} \exp(-i\gamma_{41})\right]\right|^2 && (58a) \\ &= \left|\left[P_1^{1/2}(\epsilon)\left\{c_1F_{21} + is_1F_{21}^* \exp(-i\gamma_{41})\right\} + iP_2^{1/2}(\epsilon)\left\{c_2F_{21}^* \exp(-i\gamma_{21}) - is_2F_{21} \exp(-i\gamma_{31})\right\}\right]\right|^2 && (58b) \end{aligned}$$

Here in addition to the (rapid) γ_{ji}–oscillations which vary with ϵ and b, broader oscillations due to the Airy functions within F_{21} will appear in the vicinity of the caustic at $\epsilon = \epsilon^*$. These oscillations are independent of b.

V.5 Classical Path Cross Sections for Ionisation/Recombination

In the reaction,

$$A^* + B \leftrightarrow AB^+ + e^- \tag{59}$$

the energy $\epsilon = V_d - V^+$ of disposal is distributed between the energy ϵ_e of the ejected electron and the energy $\epsilon_{n\ell}$ absorbed by the molecular ion AB^+ in vibrational-rotational level (n,ℓ). The square of the angular momentum of the $A^* - B$ orbital motion, with impact parameter b is $L^2 = (2M_{AB}E)b^2 = \ell(\ell+1)\hbar^2$, and is conserved throughout. The integral cross section for associative ionisation for disposal of all ϵ is therefore,

$$\sigma_I(E) = 2\pi \int_0^{b_X} b\, db \int_0^{\epsilon_m} P(\epsilon; E, b)\, d\epsilon \tag{60}$$

where $P = |a(\epsilon)|^2$ is given by (58), and where b_X, the maximum impact parameter which results in the distance R_X of orbital closest approach is given by,

$$b_X^2 = R_X^2 \left[1 - \frac{V_d(R_X)}{E}\right] \tag{61}$$

The ϵ–integration is over all (single valued) energies ϵ between 0 and the maximum possible ϵ_m for a specified separation $R_m = R(\epsilon_m)$ (cf. Fig. 1). The cross section (60) for population of all accessible (n,ℓ) states of AB^+ including the vibrational continuum ie. for both Penning and Associative Ionisation is then,

$$\sigma_I(E) = \frac{\pi}{(2M_{AB}E)} \int_0^{L^2_{max}} dL^2 \int_0^{\epsilon_m} P(\epsilon; E, L)\, d\epsilon \tag{62a}$$

$$\equiv \frac{\pi}{k^2_{AB}} \int_{\ell=0}^{\ell_{max}} (2\ell+1)\, d\ell \int_0^{n_{max}} P(E; n, \ell)\, dn \tag{62b}$$

$$\equiv \frac{\pi}{k^2_{AB}} \sum_{\ell=0}^{\ell_{max}} (2\ell+1) \sum\!\!\!\!\!\!\!\int_n P(E; n, \ell) \tag{62c}$$

The probability for ejection of an electron with energy $\epsilon_e = E - \epsilon_{n\ell}$ and with the ion AB^+ left in vibrational-rotational level (n,ℓ) is,

$$P(E; n, \ell) = P(\epsilon; E, L)\frac{d\epsilon}{dn} \tag{63}$$

where the vibrational energy spacing (39) is,

$$\frac{d\epsilon}{dn} = \frac{d\epsilon}{dJ}\frac{dJ}{dn} = h\nu \tag{64}$$

in terms of the quantised action $J = \oint p_R dR = (n + 1/2)h$. Hence,

$$P(E; n, \ell) = |c(\epsilon_e, t)|^2 \, (h\nu_{n\ell}) = |a(n, \ell; \epsilon_e)|^2 \tag{65}$$

with $\epsilon_e = E - \epsilon_{n\ell}$. The amplitude or the classical path transition matrix $|T_{CP}|^2$ obtained from (58) is therefore,

$$\begin{aligned} P(n) &= |T_{CP}|^2 \\ &= |a(n)|^2 = \left| \mathcal{P}_1^{1/2}(n) F_{21} + i\mathcal{P}_2^{1/2}(n) F_{21}^* \, exp(-\nu\gamma_{21}) + \mathcal{P}_3^{1/2}(n) F_{31} \, exp(-\nu\gamma_{31}) + i\mathcal{P}_4^{1/2}(n) F_{21}^* \, exp(-\nu\gamma_{41}) \right|^2 \end{aligned} \tag{66a}$$

$$= \left| P_1^{1/2}(n) \left[c_1 F_{21} + iw_1 F_{21}^* \, exp(-\nu\gamma_{41}) \right] + iP_2^{1/2}(n) \, exp(-\nu\gamma_{21}) \left[c_2 F_{21}^* - iw_2 F_{21} \, exp(-\nu\gamma_{32}) \right] \right|^2 \tag{66b}$$

The probabilities $\mathcal{P}_i$ and P_i are related by (52d) and,

$$P_i(n) = (h\nu) P_i(\epsilon_e) = 4\pi^2 \, |V_{de}(R(t))|^2 \, R_i \left\{ |W'(R_i)|^{-1} \left(\frac{\nu_{n\ell}}{v(R_i)} \right) \right\}. \tag{67}$$

is dimensionless. The cross section for autoionisation and population of AB^+ in level (n, ℓ) is therefore,

$$\sigma_{AI}(E; n, \ell) = \frac{\pi}{k_{AB}^2} (2\ell + 1) \, |a(n, \ell; \epsilon_e)|^2 = \frac{\pi}{k_{AB}} (2\ell + 1) \, |T_{CP}|^2 \tag{68}$$

where $a(n, \ell; \epsilon_e)$ defines the classical path T-matrix T_{CP}. From the detailed balance relation (43) the cross section for dissociative recombination, the inverse of (59) is,

$$\sigma_{DR}(\epsilon_e) = \left(\frac{\omega_{AB}^*}{2\omega^+} \right) \frac{\pi}{k_e^2} \, |a(n, \ell; \epsilon_e)|^2 \tag{69}$$

Since,

$$\frac{\pi}{k_e^2} 4\pi^2 \, |V_{de}(R(t))|^2 \, R = \frac{h^3}{8\pi m \epsilon_e} \left[\frac{\Gamma(R)}{\hbar} \right] \tag{70}$$

then on defining the R_X−independent partial cross section,

$$\sigma(R) = \frac{h^3}{8\pi m \epsilon_e} \left(\frac{\omega_{AB}^*}{2\omega^+} \right) \left[\frac{\Gamma(R)}{\hbar} \right] \left\{ |W'(R)|^{-1} \left(\frac{\nu_{n\ell}}{v(R)} \right) \right\} \tag{71a}$$

for capture at the stationary-phase point R, the cross section can now be expressed as,

$$\sigma_{DR}(\epsilon; n) = \left| \sigma_1^{1/2} \left[c_1 F_{21} + iw_1 F_{21}^* \, exp(-\nu\gamma_{41}) \right] + i\sigma_2^{1/2} \, exp(-\nu\gamma_{21}) \left[c_2 F_{21}^* - iw_2 F_{21} \, exp(-\nu\gamma_{32}) \right] \right|^2 \tag{71b}$$

where $\sigma_i = \sigma(R_i)$, $c_i = c(R_i)$ and $s_i = s_d(R_i)$ of (52e,f). This is the basic expression for the cross section for dissociative recombination in the present classical path theory. For one point of stationary phase then $F_{31} = 1$ and $\sigma_3 = 0$ in (71b) which reduces to,

$$\sigma_{DR}(\epsilon; n) = \sigma(R)\left[c_d^2(R) + s_d^2(R) - 2c_d(R)s_d(R)\, sin\, \gamma_{41}\right] \tag{71c}$$

and which exhibits the expected in-out interference at R. In (71b) and in the key results (52b), (58b) and (66b) above the phase-differences given formally by,

$$\gamma_{ji} = \frac{1}{\hbar}\int_{t_i}^{t_j} \left\{V_d(t) - \left[V^+(t) + \epsilon\right]\right\}\, dt \tag{71d}$$

where $R_1 = R(t_1, t_4)$ and $R_2 = R(t_2, t_3)$ are determined in practice as follows. Since,

$$\frac{1}{2}Mv_+^2(R) = \frac{\hbar^2 k_+^2(R)}{2M} = E - \left[V^+(R) + \epsilon\right] - \frac{J^2}{2MR^2} \tag{72}$$

and

$$\frac{1}{2}Mv_d^2(R) = \frac{\hbar^2 k_d^2(R)}{2M} = E - V_d(R) - \frac{L^2}{2MR^2} \tag{73}$$

where the nuclear angular momentum $J \sim L$ remains conserved, then,

$$W(R) - \epsilon = V_d(R) - \left[V^+(R) + \epsilon\right] \tag{74a}$$

$$= \frac{\hbar^2}{2M}\left[k_+^2(R) - k_d^2(R)\right] \tag{74b}$$

$$\equiv \hbar\left[k_+(R) - k_d(R)\right]\bar{v} \tag{74c}$$

where an averaged (common trajectory) radial speed is,

$$\bar{v} = \frac{\hbar(k_d + k_+)}{2M} = \frac{dR}{dt} \tag{74d}$$

The stationary phase condition, $\epsilon = W(R_i)$, therefore demands the conservation of kinetic energy of the nuclei (ie. $k_d(R_i) = k_+(R_i)$). Both the angular momentum (L,J) and kinetic energy of nuclear relative motion are therefore conserved in the CP-theory. In terms of the phase,

$$\Delta(R) = \int_{R_c}^{R}\left[k_+(R) - k_d(R)\right] dR \tag{75}$$

measured relative to that at R_c, the distance of closest approach, the phase γ,

$$\gamma(t) = \frac{1}{\hbar}\int_0^t \left[W(R) - \epsilon\right]\, dt \tag{76}$$

is expressed as,

$$\gamma(t) = \begin{cases} \Delta(R_X) - \Delta(R) & t < t_c \\ \Delta(R_X) + \Delta(R) & t > t_c \end{cases} \tag{76b}$$

The phase differences in all the previous expressions (52b), (58b) and (66b) are calculated in practice by,

$$\gamma_{21} = \Delta_1 - \Delta_2 \equiv \Delta_{12} \tag{77a}$$

$$\gamma_{31} = \Delta_1 + \Delta_2 \tag{77b}$$

$$\gamma_{32} = 2\Delta_2 \tag{77c}$$

$$\gamma_{41} = 2\Delta_1 \tag{77d}$$

where $\Delta_i = \Delta(R_i)$. The classical path amplitude,

$$a_{CP}(n) = i(h\nu)^{1/2} c(\epsilon) \tag{78a}$$

where $c(\epsilon)$ is given by (52a) is therefore,

$$\begin{aligned} a_{CP}(n) = \Big\{ & P_1^{1/2}(n) \left[c_1 F_{21} + i s_1 F_{21}^* \exp(-2i\Delta_1)\right] + i P_2^{1/2}(n) \exp(-i\Delta_{12}) \\ & \left[c_2 F_{21}^* - i s_2 F_{21} \exp(-2i\Delta_2)\right]\Big\} \exp\left[i\left(\Delta_1 - \frac{\pi}{4}\right)\right] \exp(-i\Delta(R_X)) \end{aligned} \tag{78b}$$

where $P_i(n)$ are given by (67). This expression (78b) is also confirmed by a stationary-phase evaluation of (29a), since the phases (29b) and (75) are identical.

For one region of stationary phase (78b) reduces to,

$$a_{CP}(n) = 2\pi V_{di}^*(R) \left\{ |W'(R)| \left(\frac{\nu_{nl}}{v(R)} \right) \right\}^{1/2} \left[c_d(R) + i s_d(R) \exp(-2i\Delta(R))\right] \tag{79}$$

which is in agreement with the semiclassical result of Miller.

The present classical path theory (71b) and (78b) therefore furnishes quite naturally the uniform generalisation to two regions of stationary phase including the caustic region.

Special Cases: Turning Point and Caustic

Two cases of special interest arise. One is when $R_1 = R(t_1)$ and $R_4 = R(t_4)$ coalesce at the turning point R_t where the radial speed $v(R)$ vanishes and the cross section (71a) diverges. The other case is when R_1 and R_2 coalesce at the caustic wherein $\epsilon^* = W(R)$ is maximum (cf. Figure 1) so that $W'(R_{1,2})$ vanishes and (71a) again diverges.

Turning Point Divergence: The divergence at R_c can be avoided by adopting in (71a) the speed,

$$\tilde{v}_R = \left[v_R^4 + \frac{\Gamma^2(R)}{M^2}\right]^{1/2} \xrightarrow{R \to R_c} \left[\frac{\Gamma(R_c)}{M}\right]^{1/2} \tag{80}$$

in the presence of autoionisation, rather than $v_R \to 0$ as with Miller []. A present proposal for dealing with the divergence at the turning point is based on the recognition that an average over the quantal distribution,

$$|\psi_v^+(R)|^2 \, dR = \frac{2dt}{T_{n\ell}} = 2\nu_{n\ell}dt \tag{81}$$

can be replaced by the corresponding classical average over the period $T_{n\ell}$ for vibrational motion in level $n = v$ so that $2\nu_{n\ell}/v_R$ in (71a,c) is simply $|\psi_v^+(R)|^2$. Then (71c) with $c_d(R_c) = a_d(R_c)$ and $\gamma_{41} = 0$, yields the finite result,

$$\sigma_{DR}(\epsilon_c) = \left[\frac{h^3}{8\pi m\epsilon}\frac{\Gamma(R_c)}{\hbar}\left(\frac{\omega^*_{AR}}{2\omega^+}\right)\right]\left\{|W'(R_c)|^{-1}\,|\psi_v^+(R_c)|^2 \, exp\left[-\frac{1}{\hbar}\int_{R_c}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right]\right\} \tag{82a}$$

$$= \sigma_c(R_c)P_d(R_c, R_X) \tag{82b}$$

This naturally decomposes into a cross section σ_c for capture at R_c and the probability P_d for survival to the point R_X of stabilisation. This simple result then represents a first improvement over that of Bardsley (cf. equation (4)) in that it includes $W'(R) = \frac{d}{dR}[V_d - V^+]$ rather that V_d' alone. The original result (4) is therefore valid (a) when one region of stationary phase at R_c is assumed, (b) when V^+ is so shallow that $k_+(R_c) = 0$ and (c) when V_d is so steep that the Winans-Stueckelberg wavefunction $|V_d'(R_c)|^{-1/2}\delta(R - R_c)$ can be used (see Appendix) for the continuum vibrational state.

The divergence at R_c in general originates from the normalisation of the JWKB wavefunctions implicit in the vibrational overlap S in the absence of autoionisation. The term in braces in (71a) is a JWKB approximation to this overlap. This divergence is eliminated when Airy functions rather than JWKB functions are used – even when the effect of autoionisation on the normalisation is ignored. See the Appendix for further discussion.

Caustic: The divergence in (71a) or in (67a) due to the zero in $W'(R)$ at the caustic $R(t_1) = R(t_2)$ is exactly balanced by the behavior of the function $F(\gamma_{21})$ in (66a) as $\gamma_{21} \to 0$. This becomes apparent by rewriting the contribution,

$$a(\epsilon) = P_1^{1/2}(n)F(\gamma_{21}) + iP_2^{1/2}(n)F^*(\gamma_{21})\,exp(-i\gamma_{21}) \tag{83}$$

to the amplitude (66a) from the incoming leg in the alternate form,

$$a(\epsilon) = \left[P_1^{1/2}(n) + P_2^{1/2}(n)\right]A(\gamma_{21}) + i\left[P_1^{1/2}(n) - P_2^{1/2}(n)\right]A'(\gamma_{21}) \tag{84}$$

where,

$$A(\gamma_{21}) = \pi^{1/2} z^{1/4} Ai(-z); \qquad z = [3\gamma_{21}/4]^{2/3} \tag{85}$$

$$A'(\gamma_{21}) = \pi^{1/2} z^{-1/4} Ai'(-z) \tag{86}$$

The equivalent forms (83) and (84) for a are useful for probing the separate limits $\gamma_{21} \gg 1$ and $\gamma_{21} \to 0$, respectively. In the neighborhood of the caustic at t^*, where $\epsilon^* = W(t^*)$ is maximum and $\dot{W}(t^*) = 0$ then,

$$W(t) = \epsilon^* - \frac{1}{2}\left|\ddot{W}(t^*)\right|(t-t^*)^2 \tag{87}$$

so that $\epsilon = W(t)$ at the two times,

$$t_{2,1} = t^* \pm \left[2(\epsilon^* - \epsilon)/\left|\ddot{W}(t^*)\right|\right]^{1/2} \tag{88}$$

The derivative $\dot{W}(t)$ therefore tends to zero at $t_{1,2}$ as,

$$\dot{W}(t_{1,2}) = \left[2(\epsilon^* - \epsilon)\left|\ddot{W}(t^*)\right|\right]^{1/2} \tag{89}$$

The phase is expanded consistent with (87) as,

$$\gamma(t) = \gamma(t^*) + \dot{\gamma}(t^*)(t-t^*) + \frac{1}{6}\left(\frac{d^3\gamma}{dt^3}\right)_{t^*}(t-t^*)^3 \tag{90a}$$

$$= \gamma(t^*) + \frac{1}{\hbar}(\epsilon^* - \epsilon)(t-t^*) - \frac{1}{6\hbar}\left|\ddot{W}(t^*)\right|(t-t^*)^3 \tag{90b}$$

since $\dot{\gamma}(t) = [W(t) - \epsilon]/\hbar$ and since $\ddot{\gamma}(t^*)$ vanishes. The phase difference at $t_{2,1}$ is therefore,

$$\gamma_{21}(\epsilon) = \gamma(t_2) - \gamma(t_1) = \frac{2^{5/2}}{3\hbar}\frac{(\epsilon^* - \epsilon)^{3/2}}{\left|\ddot{W}(t^*)\right|} \tag{91}$$

The argument of the Airy functions in (84) is,

$$z(\epsilon) = \left|\frac{2\hbar}{\ddot{W}(t^*)}\right|^{1/3}\frac{(\epsilon^* - \epsilon)}{\hbar} \tag{92}$$

The $(\epsilon^* - \epsilon)^{1/4}$–dependence of $z^{1/4}$ in (85) is exactly balanced in (84) by the $(\epsilon^* - \epsilon)^{-1/4}$–dependence of $\left|\dot{W}\right|^{1/2}$ in (67) of $P_i^{1/2}(\epsilon)$. Also $\left[P_1^{1/2}(\epsilon) - P_2^{1/2}(\epsilon)\right]$ tends to zero faster with ϵ than $z^{-1/4}$. The classical path cross section (71b) for dissociative recombination then reduces to,

$$\sigma_{DR}(\epsilon) = \sigma(R)\left[c_d^2(R) + s_d^2(R) - 2c_d(R)s_d(R)\sin 2\Delta(R)\right] \tag{93a}$$

where,

$$\sigma(R) = \frac{k^3}{8\pi m c_e}\left(\frac{\omega^*_{AB}}{2\omega^+}\right)\left[\frac{\Gamma(R)}{\hbar}\right]\left\{\frac{2\pi}{\hbar}\left|\frac{2\hbar}{\dot{W}(\epsilon^*)}\right|^{2/3}\nu Ai^2(-z)\right\} \tag{93b}$$

which is finite at the caustic. The term in braces represents the dominant contribution from the caustic to the Franck-Condon Factor $|S|^2$ –in effect replacing the corresponding (divergent) term in (71a).

V.6 Correspondance between Classical Path, Semiclassical and Quantal Theories of Dissociative Recombination

In order to probe with the quantal result, correspondance the symmetrical form (29a) of the basic classical path result is useful. On making the substitution (74), the classical path amplitude $a_{CP}(n) = i(h\nu)^{1/2}c(\epsilon)$ where c is given by (29a) is therefore,

$$a_{CP}(n) = 2\pi\, exp\left[-i\Delta(R_X)\right]\int V^*_{d\epsilon}(R)\left\{(\nu/h)^{1/2}g^{-1}\left[c_d(R)\, exp + i\Delta(R) + s_d(R)\, exp - i\Delta(R)\right]\right\} dR \tag{94}$$

The term in braces in (94) is essentially the product of the bound and continuum vibrational wavefunctions (see below). Stationary-Phase Evaluation of (94) yields (78b), as it should.

Quantal: The quantal expression for the autoionisation frequency, with electron energy ϵ in the range $\epsilon, \epsilon + d\epsilon$ and with the ion left in state (v, J) is,

$$\frac{d\nu_a}{d\epsilon}d\epsilon = \frac{2\pi}{\hbar}\sum_{M=-J}^{J}\left|\left\langle \phi_\epsilon(r,R)\phi^+_v(\hat{R})\mid \mathcal{H}_{el}(r,R)\mid \Psi(\vec{r},\hat{R})\right\rangle\right|^2 \rho(\epsilon)\, d\epsilon \tag{95}$$

where the system wavefunction for $A - B^*$ collisions at energy E is,

$$\Psi(\vec{r},\hat{R}) = \frac{1}{R}\psi_d(E,R)Y_{JM}(\hat{R})\phi_d(\vec{r},R) \tag{96}$$

the product of the Born-Oppenheimer electronic wavefunction ϕ_d the actual continuum (radial) vibrational wavefunction ψ_d in the presence of autoionisation and the rotational wavefunction $Y_{JM}(\hat{R})$. The rovibrational wavefunction for $AB^+(v, J)$ is,

$$\phi^+_v(\hat{R}) = \frac{1}{R}\psi^+_v(R)Y_{JM}(\hat{R}) \tag{97}$$

Both $\psi_d(E, R)$ and the continuum electronic function ϕ^+_ϵ for the $(e^- - AB^+)$ system are energy normalised with unit densities $\rho(E)$, $\rho(\epsilon)$ of states, respectively. The incident current $(dj/dE)dE$ integrated for all directions of $\vec{k}$ is therefore $(8\pi ME/h^3)dE = (k^2_{AB}/2\pi^2\hbar)dE$. The associative ionisation cross section $(d\nu_a/dj)$ is then,

$$\sigma_{AI}(E) = \frac{\pi}{k^2_{AB}}(2J+1)P_Q(E,\epsilon;J,v) \tag{98}$$

where the quantal autoionisation amplitude or transition matrix element is,

$$a_Q(v) = 2\pi \int_0^\infty V_{d\epsilon}^*(R)\left[\psi_v^{+*}(R)\psi_d(R)\right]\, dR \tag{99}$$

By detailed balance, the dissociative recombination cross section is,

$$\sigma_{DR}(\epsilon) = \frac{\pi}{k_e^2}\left(\frac{\omega_{AR}^*}{2\omega^+}\right)|a_Q|^2 = \left(\frac{h^3}{8\pi m\epsilon}\right)\left(\frac{\omega_{AR}^*}{2\omega^+}\right)\frac{d\nu_v}{d\epsilon}|a_Q|^2 \tag{100}$$

which is dimensionless.

Reduction of Quantal to Semiclassical: The product of the semiclassical JWKB vibrational wavefunctions,

$$\psi_v^+(R) = 2\left[\frac{\nu_{nl}}{v_+}\right]^{1/2} sin\left[\int_{R_0}^R k_+(R)\, dR + \frac{\pi}{4}\right] \tag{101}$$

for the discrete levels with inner (left-hand) turning point R_0 and,

$$\psi_d(R) \equiv \frac{\imath}{[hv_d(R)]^{1/2}}\left[c_d(R)\, exp -\imath\left(\int_{R_0}^R k_d\, dR + \frac{\pi}{4}\right) - s_d(R)\, exp +\imath\left(\int_{R_0}^R k_d\, dR + \frac{\pi}{4}\right)\right] \tag{102}$$

for the continuum levels subject to autoionisation is,

$$\psi_v^{+*}(R)\psi_d(R) = (\nu_{nl}/h)^{1/2}(v_+v_d)^{-1/2}\left[c_d(R)\, exp +\imath\Delta(R) + s_d(R)\, exp -\imath\Delta(R)\right] \tag{103}$$

where the phase difference is,

$$\Delta(R) = \int_{R_0}^R k_+(R)\, dR - \int_{R_0}^R k_d(R)\, dR \tag{104}$$

The highly oscillatory exponentials of the phase sums have been neglected since they provide little relative contribution to (99). The quantal amplitude (99) with the semiclassical (103) is then,

$$a_Q(\epsilon) = 2\pi(\nu/h)^{1/2}\int_0^\infty (v_+v_d)^{-1/2}V_{d\epsilon}^*(R)\left[c_d(R)\, exp +\imath\Delta(R) + s_d(R)\, exp -\imath\Delta(R)\right]\, dR \tag{105}$$

The stationary phase condition yields $k_+(R) = k_d(R)$ so that the arithmetic mean $\bar{v}(R)$ and geometric mean $[v_+(R)v_d(R)]^{1/2}$ are identical at the points of stationary phase and (105) is identical to the classical path amplitude. Stationary phase evaluation of but (105) and (94) confirms that,

$$a_Q(n) = a_{CP}(n)\, exp +\imath\Delta(R_X) \tag{106}$$

where a_{CP} is given by (78b). The classical path amplitude (94) is therefore the quantal amplitude (99) with the JWKB vibrational product (103), thereby establishing the equivalence between the matrix element (105) and its Fourier Component Representation (28a) or (29a). This equivalence for vibrational transitions is somewhat akin to the Heisenberg Correspondance Principle for electronic transitions.

When the bound vibrational JWKB wavefunction ψ_v^+ is taken with respect to its right-hand turning point R_0' then the analysis is as above but with Δ replaced by,

$$\tilde{\Delta}(R) = \int_R^{R_0'} k_+(R)\,dR - \int_{R_s}^{R} k_d(R)\,dR \tag{107}$$

which reduces with the aid of,

$$\hbar \oint_{R_0}^{R_0'} k_+(R)\,dR = \left(v + \frac{1}{2}\right) h$$

to

$$\tilde{\Delta}(R) = (v + \frac{1}{2})\pi - \left[\int_{R_0}^{R} k_+(R)\,dR + \int_{R_s}^{R} k_d(R)\,dR\right] \tag{108}$$

The smaller of Δ and $\tilde{\Delta}$ in practice would be adopted in the general result (78b).

V.7 Rate of Direct Dissociative Recombination

For a Maxwellian distribution of electron energies $\epsilon = \epsilon'(kT)$ at temperature T, the DR-rate is,

$$\alpha(T) = \bar{v} \int_{\epsilon_0}^{\infty} \sigma_{DR}(\epsilon)\epsilon' \, exp(-\epsilon' \, d\epsilon' \equiv \langle \sigma_{DR}(T) \rangle \tag{109}$$

where $\bar{v}$ is the mean electron speed $(8kT/\pi M_{AB})^{1/2}$ and $\sigma_{\bar{D}R}$ is a mean cross section at temperature T. An energy threshold $\epsilon_0 = V_d(R_0') - V_+(R_0') \geq 0$ pertains for the case when the energy $V_d(R_X)$ at the crossing exceeds the original vibrational energy of $AB^+(v)$. In terms of the probability (66) for dissociative recombination,

$$\alpha(T) = \left(\frac{\omega^*_{AB}}{2\omega^+}\right) \int_{\epsilon_0}^{\infty} |a(n;\epsilon)|^2 \, exp(-\epsilon/kT)\, d\epsilon \tag{110}$$

is the basic expression for the rate which includes all the phase information in (66). In order to obtain a simplified analytical rate, assume that there is only one region of stationary phase at R_s so that $\epsilon = V_d(R_s) - V_+(R_s)$ and that the in-out interference effect can be ignored. The probability is then,

$$|a(n;\epsilon)|^2 = \left[\frac{\Gamma(R)}{\hbar v(R)} |W'(R)|^{-1}\right]_{R_s} h\nu_{n\ell} \left[c_d^2(R_s) + s_d^2(R_s)\right] \tag{111a}$$

which with (35) is,

$$|a(n;\epsilon)|^2 = \left[\frac{\Gamma(R)}{\hbar v(R)} |W'(R)|^{-1}\right]_{R_s} 2h\nu_{n\ell} \left\{ exp\left[-\frac{1}{\hbar}\int_{R_s}^{R_X} \frac{\Gamma(R)}{v(R)}\,dR\right] cosh\left[\frac{1}{\hbar}\int_{R_s}^{R_s} \frac{\Gamma(R)}{v(R)}\,dR\right]\right\} \tag{111b}$$

where the term in braces is the average probability for survival from $R_c \overset{out}{\rightleftarrows} R_X$ and $R_c \overset{in}{\rightarrow} R_e \overset{out}{\rightleftarrows} R_X$ on $V_d(R)$. Adoption of (111) in (110) therefore demands the location R_e which depends in turn on the energy,

$$E = \frac{\hbar^2 k_d^2(R)}{2M} + V_d(R) + \frac{L^2}{2MR^2} \tag{112}$$

of relative motion under V_d. From $\epsilon = V_d(R_c) - V_+(R_c)$ and the vibrational- rotational level (v, L) of AB^+, $k_+(R_c) \sim k_d(R_c)$ and E can then be determined to provide R_c as a function of ϵ. Further reduction of (110) with (111b) is therefore not possible without additional assumptions.

(a) In the low energy limit $\epsilon \rightarrow 0$, $(R_c, R_e) \rightarrow R_X$ and,

$$|a(n;\epsilon \rightarrow 0)|^2 = 2\pi\Gamma(R_X)\,|W'(R_X)|^{-1}\left\{\left[\frac{2\nu_{nl}}{v(R_X)}\right] \equiv |\psi_v^+(R_X)|^2\right\} \tag{113}$$

such that (110) reduces at low T to,

$$\alpha(T) = \frac{h^3}{(2\pi mkT)^{3/2}}\left(\frac{\omega_{AB}^*}{2\omega^+}\right)\frac{\Gamma(R_X)}{\hbar}\left\{|\psi_v^+(R_X)|^2\, kT\, |W'(R_X)|^{-1}\right\} \tag{114}$$

The term in braces is an effective Franck-Condon factor for bound-free transitions. This analytical result is a generalised version of the original result of Bates in that it include $W'(R) = \frac{d}{dR}(V_d - V_+)$ rather than V_d' alone. It therefore allows for a distinction to be made between crossings on either side of the potential minimum. For crossings at the potential minimum the results are identical.

(b) Assume either that V^+ is so shallow that $k_+(R_e) \sim 0$ or that V_d is so steep. Then $R_c = R_e$ which is given universally by $\epsilon = V_d(R_c) - V_+(R_c)$. The recombination of electrons of energy ϵ originates at the distance of closest approach so that the cross section (82a) can be used directly in (109) to give,

$$\alpha(T) = \frac{h^3}{(2\pi mkT)^{3/2}}\left(\frac{\omega_{AB}^*}{2\omega^+}\right)(2\nu_{nl}kT)\int_0^\infty P(\epsilon)\exp(-\epsilon')\,d\epsilon' \tag{115}$$

where $P(\epsilon)$ is the probability density (33b) given by,

$$P(\epsilon) = \frac{dP_d}{d\epsilon} = \frac{\Gamma(R)}{\hbar v(R)}\,|W'(R)|^{-1}\exp\left(-\frac{1}{\hbar}\int_R^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right) \tag{116}$$

where $\epsilon = W(R)$. For constant drainage $dP_d/d\epsilon$ is constant R_c and R_X and (114) is recovered.

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Appendix: Franck-Condon Overlap for Bound-Free Vibrational Transitions with and without Autoionisation

1. JWKB Franck-Condon Overlap without Autoionisation

The JWKB normalised semiclassical wavefunctions for the bound vibrational level (n, ℓ) of AB^+ with vibrational frequency ν is,

$$\psi_+(R) = 2\left[\frac{\nu_{n\ell}}{v_+(R)}\right]^{1/2} \sin\left[\int_{R_0}^{R} k_+(R)\,dR + \frac{\pi}{4}\right], \qquad R \gg R_0 \tag{A1}$$

where $h\nu = d\epsilon_{vJ}/dv$ is the level spacing, and R_0 is the classical turning point given by the innermost zero of

$$\frac{1}{2}Mv_+^2(R) = \frac{\hbar^2 k_+^2(R)}{2M} = E - \left(V^+(R) + \epsilon\right) - \frac{J^2}{2MR^2} \tag{A2}$$

the radial speed $v_+(R)$ of relative motion of energy $(E - \epsilon)$ in potential $V^+(R)$. The JWKB wavefunction energy normalised to $\delta(E - E')$ for the vibrational continuum of AB^* without autoionisation is,

$$\psi_d(R) = \frac{2}{[hv_d(R)]^{1/2}} \sin\left[\int_{R_e}^{R} k_d(R)\,dR + \frac{\pi}{4}\right], \qquad R \gg R_e \tag{A3}$$

where R_e is determined by the innermost zero of,

$$\frac{1}{2}Mv_d^2(R) = \frac{\hbar^2 k_d^2(R)}{2M} = E - V_d(R) - \frac{L^2}{2MR^2} \tag{A4}$$

for the radial speed $v_d(R)$ of relative motion in the dissociative potential $V_d(R)$. Angular momentum of relative nuclear motion is conserved $(J = L)$. The Franck-Condon amplitude,

$$S = \int_0^\infty \psi_+^*(R)\psi_d(R)\,dR \tag{A5}$$

is then written with (A1) and (A3) as,

$$S = \left(\frac{\nu_{n\ell}}{h}\right)^{1/2} \int_0^\infty \{v_+(R)v_d(R)\}^{1/2}\left[exp + i\Delta(R) + exp - i\Delta(R)\right] dR \tag{A6}$$

where the phase,

$$\Delta(R) = \int_{R_0}^{R} k_+(R)\,dR - \int_{R_e}^{R} k_d(R)\,dR \tag{A7}$$

has a stationary point where $\Delta'(R) = d\Delta/dR = 0$ ie. where $k_+(R_s) = k_d(R_s)$. The previous condition (equation (38)),

$$V_d(R_s) = V^+(R_s) + \epsilon \tag{A8}$$

for a vertical transition at root $R = R_s$ is then recovered. The $(\pm)$ terms $exp(\pm i\Delta)$ in (A6) provide the contributions to S from the incoming $(-)$ and outgoing $(+)$ components of ψ_d. On expanding,

$$\Delta(R) = \Delta(R_s) + \Delta'(R_s)(R - R_s) + \frac{1}{2}\Delta''(R_s)(R - R_s)^2 \qquad (A9)$$

and on changing the integration variable to $s = R - R_s$ with limits $(\pm\infty)$ then (A6) can be evaluated with the aid of,

$$\int_{-\infty}^{\infty} exp\left(\pm i |\alpha| s^2\right) d\alpha = \left[\frac{\pi}{|\alpha|}\right]^{1/2} exp\left(\pm i\frac{\pi}{4}\right). \qquad (A10)$$

The Stationary-Phase Vibrational Overlap is therefore,

$$S = \left(\frac{\nu_{v\ell}}{h}\right)^{1/2} \frac{1}{v(R_s)} \left[\frac{2\pi}{|\Delta''(R_s)|}\right]^{1/2} \left\{exp +i\left[\Delta(R_s) \pm \frac{\pi}{4}\right] + exp -i\left[\Delta(R_s) \pm \frac{\pi}{4}\right]\right\} \qquad (A11)$$

where the constant phases $(\pm\pi/4)$ pertain to positive or negative values of $\Delta''(R_s) = k'_+(R_s) - k'_d(R_s)$, respectively ie. to either minima or maxima in Δ at R_s. From (A2) and (A4),

$$\Delta''(R_s) = \frac{1}{\hbar v(R_s)} \frac{d}{dR} \left(V_d - V^+\right)_{R_s} \equiv \frac{1}{\hbar v(R_s)} W'(R_s) \qquad (A12)$$

where $W = V_d(R) - V^+(R)$. The Franck-Condon Factor is then,

$$|S|^2 = \left[\frac{4\nu}{v(R_s)}\right] |W'(R_s)|^{-1} sin^2 \left[\Delta(R_s) \mp \frac{\pi}{4}\right] \qquad (A13)$$

which oscillates (rapidly for Δ large) about its average value,

$$|\bar{S}|^2 = \left[\frac{2\nu}{v(R_s)}\right] |W'(R_s)|^{-1} \qquad (A14)$$

For one root R_s of (A8) when $W' = dW/dR < 0$, the (+) sign in (A13) is appropriate. Several variations of (A13) can be constructed.

(a) In classical mechanics the quantal probability,

$$\left|\psi^+_{vJ}(R)\right|^2 dR = \frac{2dt}{T} = 2\nu dt \qquad (A15)$$

is replaced by the corresponding classical average over the period T for vibrational motion, the factor of 2 arising from inward and outward radial motion ie. $\left|\psi^+_v(R)\right|^2 = 2\nu/v(R)$. This also follows from the JWKB function (A1). Use of this correspondence in (A14) therefore yields the Franck-Condon Factor,

$$|S|_c^2 = 2\left|\psi^+_v(R_s)\right|^2 \left|\frac{d}{dR}(V_d - V^+)\right|_{R_s}^{-1} sin^2 \left[\Delta(R_s) \mp \frac{\pi}{4}\right] \qquad (A16)$$

which is advantageous in that it circumvents the divergence in the overlap (A13) at the classical turning point R_s common to all JWKB-based approximations. Then

$$|S|_c^2 = |\psi_v^+(R_c)|^2 \left|\frac{d}{dR}(V_d - V^+)\right|_{R_c}^{-1}$$

which is finite.

(b) The simplest energy normalised continuum wavefunction is the Winans-Stueckelberg function,

$$\psi_d(R) = \left|\frac{dV_d}{dR}\right|^{-1/2} \delta(R - R_c) \qquad (A17)$$

where R_c is the classical turning point. The Franck-Condon overlap is then,

$$|S|^2 = |\psi_v^+(R_c)|^2 \left|\frac{dV_d}{dR}\right|_{R_c}^{-1} \qquad (A18)$$

to be compared with the more accurate expression (A16) or (A14). It is therefore valid when, $\left|\frac{dV_d}{dR}\right| \gg \left|\frac{dV^+}{dR}\right|$ ie. the potential V_d is so steep and strongly repulsive relative to $V^+(R)$. The Franck-Condon overlap (A18) is that used by Bardsley to provide the cross section (4) for dissociative recombination.

(c) Airy Function Remedy

In order to remedy the well-known breakdown of the JWKB functions (A1) and (A3) close to the classical turning points, the JWKB functions can be replaced by their Airy function counterparts,

$$\sin\left(\int_{R_c}^{R} k\,dR + \frac{\pi}{4}\right) \Rightarrow \pi^{1/2} z^{1/4} Ai(-z), \qquad \frac{2}{3}z^{3/2} = \int_{R_c}^{R} k\,dR \qquad (A19)$$

in (A1) and (A3). The stationary phase result (A13) is then replaced by,

$$|\bar{S}|^2 = \left[\frac{4\nu}{v(R_t)}\right] |W'(R_t)|^{-1} \left[\pi^{1/2}\eta^{1/4} Ai(-\eta)\right]^2 \qquad (A20)$$

for the resulting overlap, where the argument of the Airy function Ai in terms of the phase difference (A7) is,

$$\eta(R_t) = \left[\frac{3}{2}\Delta(R_t)\right]^{2/3}. \qquad (A21)$$

For large arguments η, ie. for R_t well removed from the classical turning points R_c and R_0, then,

$$\pi^{1/2}\eta^{1/4} Ai(-\eta) \xrightarrow{\eta \gg 1} \sin\left(\Delta + \frac{\pi}{4}\right) \qquad R_t \gg R_c \qquad (A22)$$

so that (A13) is recovered (for the case $W'(R_t) < 0$). The overlap (A20) uniformly connects the classical assessible and inaccessible regions and does not diverge when R_t is located at the classical turning point R_c.

2. Franck-Condon Overlap with Autoionisation

As noted in §IIC, the effect of autoionisation on the dissociating $A - B^*$ system is realised by assigning the complex potential energy E,

$$E_d(R) = V_d(R) - \frac{i}{2}\Gamma(R) \qquad (A23)$$

to the decaying dissociative state. The JWKB solution of,

$$\frac{d^2\psi_d(R)}{dR^2} = -\frac{2M}{\hbar^2}\left[E - V_d(R) + \frac{i}{2}\Gamma(R)\right] \equiv \widetilde{k}_d^2(R)\psi_d(R) \qquad (A24)$$

which satisfies the appropriate conditions for the incoming and outgoing waves at the boundary R_X is,

$$\psi_d(R) = \frac{2}{[\hbar v_d(R)]^{1/2}}\, exp\left\{-\frac{1}{2\hbar}\int_{R_c}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right\} sin\left\{\int_{R_c}^{R}\left[k_d(R) + \frac{i}{2\hbar}\frac{\Gamma(R)}{v(R)}\,dR\right] + \frac{\pi}{4}\right\} \qquad (A25)$$

where,

$$\widetilde{k}_d^2(R) = k_d^2(R) + i\frac{M}{\hbar^2}\Gamma(R) \qquad (A26a)$$

$$\sim k_d(R) + \frac{i}{2\hbar}\frac{\Gamma(R)}{v(R)} \qquad \Gamma(R) \ll E - V_d(R) \qquad (A26b)$$

The autoionization is in effect within the reaction zone between the crossing point R_X, where $V_d = V^+$, and the distance R_c of closest approach at energy E. The physics within ψ_d above becomes apparent by rewriting (A25) as,

$$\begin{aligned}\psi_d(R) = \frac{i}{[\hbar v_d(R)]^{1/2}}&\left[\left[exp\left(-\frac{1}{2\hbar}\int_{R}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right) exp\left[-i\left(\int_{R_c}^{R}k_d\,dR + \frac{\pi}{4}\right)\right]\right.\right.\\ &\left.\left. -\,exp\left[-\frac{1}{2\hbar}\left(\int_{R_c}^{R_X} + \int_{R_c}^{R}\right)\frac{\Gamma(R)}{v(R)}\,dR\right] exp\, i\left(\int_{R_c}^{R}k_d\,dR + \frac{\pi}{4}\right)\right]\right] \qquad (A27a)\\ \equiv \frac{i}{[\hbar v_d(R)]^{1/2}}&\left[c_d(R)\, exp - i\left(\int_{R_c}^{R}k_d\,dR + \frac{\pi}{4}\right) - s_d(R)\, exp\, i\left(\int_{R_c}^{R}k_d\,dR + \frac{\pi}{4}\right)\right] \qquad (A27b)\end{aligned}$$

where,

$$c_d(R) = exp\left[-\frac{1}{2\hbar}\int_{R}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right] \qquad (A28)$$

is the survival amplitude from R_X to R on the incoming leg and,

$$s_d(R) = exp\left[-\frac{1}{2\hbar}\oint_{R_c}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right] exp\left[+\frac{1}{2\hbar}\int_{R}^{R_X}\frac{\Gamma(R)}{v(R)}\,dR\right] \qquad (A29)$$

is the amplitude for in-out survival for the sequence $R_X \xrightarrow{in} R_c \xrightarrow{out} R_i$. The stationary-phase determination of,

$$S = \int \psi_v^{+*}(R)\psi_d(R)\,dR \tag{A30}$$

with two points of well separated stationary phase where $k_+(R_i) = k_d(R_i)$ at $R_{1,2}$ yields,

$$S = [S_1\{c_1 + i s_1 \exp(-2i\Delta_1)\} + iS_2 \exp(-i\Delta_{12})\{c_2 - i s_2 \exp(-2i\Delta_2)\}] \exp i(\Delta_1 - \frac{\pi}{4}) \tag{A31a}$$

where,

$$S_i = \left[\frac{\nu}{v(R_i)}|W'(R_i)|^{-1}\right]^{1/2} \tag{A31b}$$

where $c_i = c_d(R_i), s_i = s_d(R_i)$ and,

$$\Delta_{ij} \equiv \Delta(R_i) - \Delta(R_j) \equiv \Delta_i - \Delta_j \tag{A31c}$$

in terms of Δ given by (A7). The notation is such that $R_1 > R_2$ where $W'(R_1) < 0$ and $W'(R_2) > 0$, respectively. When autoionisation is neglected, $c_d = 1 = s_d$, then (A31) reduces to (A13).

For two general regions of stationary phase then the Stationary-Phase Uniform Prescription (50) yields,

$$S = [S_1\{c_1F_{21} + i s_1 F_{21}^* \exp(-2i\Delta_1)\} + iS_2 \exp(-i\Delta_{12})\{c_2F_{21}^* - i s_2 F_{21} \exp(-2i\Delta_2)\}] \exp i(\Delta_1 - \frac{\pi}{4}) \tag{A32}$$

for the Franck-Condon overlap, and where,

$$F[\Delta_{12}] = \left[\pi^{1/2}z^{1/4}Ai(-z) + i\pi^{1/2}z^{-1/4}Ai'(-z)\right] \exp -i\left(\frac{\Delta_{12}}{2} - \frac{\pi}{4}\right); \quad \frac{4}{3}|z|^{3/2} = \Delta_{12} > 0 \tag{A33}$$

is the function introduced previously in (51). The above results (A31) and (A32) for the vibrational overlap, with and without ($c_d = 1 = s_d$) autoionisation for two general regions of stationary phase appear new to the literature, and help establish the correspondence between the present classical path theory and the quantal result.

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VI. THE MODIFIED ADIABATIC INVARIANCE METHOD FOR THERMAL ION-DIPOLE MOLECULE REACTIONS

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Abstract

The semiclassical adiabatic invariance method (AIM) is used to compute thermal energy rate coefficients for capture of various atomic and molecular ions by diatomic and triatomic molecules with permanent dipole moments. Particular ion-molecule systems studied in this paper include He^+, C^+, and $H_3{}^+$ ions reacting with polar HCl molecules; and H^+, C^+, O^+, HCO^+, and $H_3{}^+$ ions with HCN molecules. In addition, a new modification of the adiabatic invariance method is presented in this paper, which accounts for the coupling of the internal rotational angular momentum (j) of the target molecule to the orbital angular momentum (ℓ) of the projectile ion about the center of mass of the target molecule. Comparison of the AIM results with the present modifications to the adiabatic invariance method, and with available experimental data and extent theory, for the above ion-molecule reactions, indicate that the inclusion of $j - \ell$ coupling within the AIM is most important in the limit of light ion mass or weak ion-molecule interactions.

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VI.1 Introduction

The semiclassical adiabatic invariance method (AIM) was first proposed[1] for ion-molecule collisions where the interaction potential energy is an adiabatic invariant about the rotational angle of the target molecule, and has been applied to ion-molecule collisions with linear[2] and symmetric top[3] molecules with permanent dipole moments and ion-quadrupole molecule[4] collisions. However, at present no account has been made in the above AIM calculations for the coupling between the internal orbital angular momentum, j of the target molecule, and the relative angular momentum ℓ of the projectile about the center-of-mass of the projectile ion-target molecule system. In this paper a modification of the adiabatic invariance method is proposed which takes into account the coupling between j and ℓ in ion-molecule collisions.

An outline of the remainder of the paper is as follows. In §II.A.1 the modifications to the AIM are presented (hereafter denoted AIM(j,ℓ)), while in II.A.2 an overview of the original AIM is given in the notation of this paper. The details of the computation of the capture cross sections and rate coefficients into specific and quantal states of the target molecule are given in §II.B. A discussion of the present results with available theory and experimental data is provided in §III, while a summary of the paper is given in §IV. Unless otherwise noted, all quantities are in atomic units.

VI.2 Theory

2.A.1 Modified Adiabatic Invariance Method

The Hamiltonian,$\mathcal{H}$, describing the reactions

$$X^+ + AB \rightarrow (XAB^+)^* \rightarrow products \tag{1a}$$

$$X^+ + ABC \rightarrow (XABC^+)^* \rightarrow products \tag{1b}$$

of an ion X^+ with diatomic (AB) or triatomic (ABC) target molecules with permanent dipole moment D, in the body-fixed CM frame, is

$$\mathcal{H} = Bj^2 + \frac{(\vec{J}-\vec{j})^2}{2\mu r^2} - \frac{\alpha_d}{2r^4} + \frac{D\cos\theta}{r^2} \tag{2}$$

where B and α_d are the rotational constant and dipole polarisability of the molecule respectively, and with r, θ representing the intermolecular distance and angle between the dipole moment D and the intermolecular axis of AB, respectively. The interaction potential for the ion-molecule reactions (1) is,

$$V(r,\theta) = -\frac{\alpha_d}{2r^4} + \frac{D\cos\theta}{r^2} \tag{3}$$

Since J is a conserved quantity in the collision (1), we can write $(\vec{J}-\vec{j})^2$ in terms of the projection[5] (Ω) of J onto the intermolecular axis,

$$(\vec{J}-\vec{j})^2 = (J+\frac{1}{2})^2 + \vec{j}^2 - 2\Omega^2 \tag{4}$$

The Hamiltonian $\mathcal{H}$ can then be written,

$$\mathcal{H} = B\vec{j}^2 + \frac{1}{2\mu r^2}\left[(J+\frac{1}{2})^2 + \vec{j}^2 - 2\Omega^2\right] - \frac{\alpha_d}{2r^4} + \frac{D\cos\theta}{r^2}. \tag{5}$$

The adiabatic potential is defined for fixed r by

$$\epsilon(r) = (B + \frac{1}{2\mu r^2})\vec{j}^2 + \frac{D\cos\theta}{r^2}, \tag{6}$$

where $\vec{j}^2 = p_\theta{}^2 + p_\varphi{}^2/\sin^2\theta$. Since φ is cyclic, $p_\varphi = m$, the integration of p_θ over a complete cycle (range) of angle θ is an adiabatic invariant,

$$2\pi(n+\frac{1}{2}) = \oint p_\theta d\theta. \tag{7}$$

To determine the adiabatic potential $\epsilon(r)$ from the quantisation condition (7) on p_θ, an expression relating p_θ to ϵ is needed. Such an expression is obtained from the definition of j^2 (given above) in terms of p_θ and p_φ and making use of the fact that φ is a cyclic variable and results in,

$$p_\theta = \left(B + \frac{1}{2\mu r^2}\right)^{-\frac{1}{2}}\left[\epsilon(r) - \frac{D\cos\theta}{r^2} - \left(B + \frac{1}{2\mu r^2}\right)\frac{m^2}{\sin^2\theta}\right]^{\frac{1}{2}}. \tag{8}$$

Substituting (8) into (7), and defining the dimensionless variables, $\rho = \cos\theta$ and $x = r\sqrt{B/D}$, and with $u(x) = \epsilon/B$, equation (7) can be rewritten as,

$$\pi(j - |m| + \frac{1}{2}) = \frac{(2\mu D)^{\frac{1}{2}}}{(2\mu D x^2 + 1)^{\frac{1}{2}}}\int_c^b \sqrt{f(\rho)}\,\frac{d\rho}{1-\rho^2} \tag{9}$$

where we have replaced n on the left-hand side of (7) with $j - \mid m \mid$ due to the invariance of the integral of p_θ. Note that when the limit $r \to \infty$ is taken, the integral in (9) can be done analytically with the result, $n + 1/2 = \sqrt{u(\infty)} - \mid m \mid = (j + 1/2) - \mid m \mid$. The function f in the integrand of equation (9) is given by,

$$\begin{aligned} f(x) &= \rho^3 - x^2 u\rho^2 - \rho + \left((u - m^2)x^2 - \frac{m^2}{2\mu D}\right) \\ &= (\rho - a)(\rho - b)(\rho - c) \end{aligned} \tag{10}$$

where the roots $\{a, b, c\}$ of the cubic polynomial are ordered such that $a \geq b \geq c$. After some algebra, the integral equation (9) can be rewritten as a transcendental equation for the dimensionless adiabatic potential $u_{jm}(x)$,

$$
\begin{aligned}
(j-|m|+\tfrac{1}{2})\pi\left[s^2+\frac{1}{2\mu D}\right]^{\frac{1}{2}}(a-c)^{\frac{1}{2}} &= 2(u_{jm}(s)s^2-a)K(q)+2(a-c)E(q) \\
&\quad -m^2(s^2+\frac{1}{2\mu D})\left[\frac{\Pi(p_1,q)}{1-c}+\frac{\Pi(p_2,q)}{1+c}\right]
\end{aligned}
\tag{11}
$$

where K, E, and Π represent the complete elliptic integral of first, second, and third kinds[6], respectively, with moduli defined as, $q=(b-c)/(a-c)$, $p_1=(b-c)/(1-c)$ and $p_2=(c-b)/(1+c)$.

The adiabatic potential $u_{jm}(s)$ is then obtained from (11) once the roots of the cubic polynomial (10) are determined. In addition, to determine the capture cross section in §II.B, an expression is required for the first derivative of $u_{jm}(s)$ with respect to s. By applying Leibnitz's rule to (9), the required expression for the first derivative is obtained,

$$
\frac{du_{jm}(s)}{ds}=2s^{-3}\left[(a-c)\left(\frac{s^2}{s^2+(1/2\mu D)}\right)\frac{E(q)}{K(q)}-\left(a-(b+c)\frac{(1/2\mu D)}{s^2+(1/2\mu D)}\right)\right]
\tag{12}
$$

2.A.2 Adiabatic Invariance Method

In this section we provide a short overview of the original adiabatic invariance method[1-3] using the present notation for completeness. In collisions of ions with molecules with permanent dipole moments, the adiabatic potential is defined for fixed r by,

$$
\epsilon(r)=B\bar{j}^2+\frac{D\cos\theta}{r^2}.
\tag{13}
$$

The problem is again to determine the adiabatic potential using the quantisation condition (7). Neglecting the coupling between j and ℓ, the analog of (9) is,

$$
\pi s(j-|m|+\frac{1}{2})=\int_c^b\sqrt{f(\rho)}\;\frac{d\rho}{1-\rho^2}
\tag{14}
$$

with the function f in the integrand of (14) given by,

$$
\begin{aligned}
f(s) &= \rho^3-s^2u\rho^2-\rho+(u-m^2)s^2 \\
&= (\rho-a)(\rho-b)(\rho-c)
\end{aligned}
\tag{15}
$$

where the roots are ordered $a>b\geq c$, and the remaining terms in (14) and (15) are the same as in (9) and (10). Equation (14) can be converted from an integral equation to a transcendental equation in u with the result,

$$
(j-|m|+\frac{1}{2})\pi s(a-c)^{\frac{1}{2}}=2(u_{jm}(s)s^2-a)K(q)+2(a-c)E(q)-m^2s^2\left[\frac{\Pi(p_1,q)}{1-c}+\frac{\Pi(p_2,q)}{1+c}\right]
\tag{16}
$$

where K, E, Π, q, p_1, and p_2 all have the same meaning as in §II.A.1. The derivative of $u_{jm}(s)$ is obtained via Leibnits's rule in exactly the same manner as equation (12) was obtained above, with the result,

$$\frac{du_{jm}(s)}{ds} = 2s^{-3}\left[(s-c)\frac{E(q)}{K(q)} - s\right] \tag{17}$$

In comparing the AIM(j,ℓ) and AIM, it is found that the $1/2\mu D$ term has the effect of coupling the rotational angular momentum ℓ with the orbital angular momentum j. In the limit as $(1/2\mu D) \rightarrow 0$, equations (9), (11-12) reduce to (14), (16-17), respectively. Clearly, the inclusion of the coupling between j and ℓ is most important in the limit of light ionic mass or weak ion-molecule interaction (as measured by the magnitude of D, the dipole moment).

2.B Computation of the Capture Cross Sections and Rate Coefficients:

The effective potential is given by,

$$U_{eff} = \frac{L^2}{2\mu r^2} - \frac{\alpha}{2r^4} + \epsilon_{jm}(r) - B(j+\frac{1}{2})^2 \tag{18}$$

where $L^2 = 2E\mu b^2$, and with b and E the classical impact parameter and ion energy in the CM frame, respectively. In the modified AIM the angular momentum is expressed,

$$L^2 = (J+\frac{1}{2})^2 - (j+\frac{1}{2})^2 - 2\Omega^2 = 2E\mu b^2. \tag{19}$$

The capture cross section is determined by the conditions,

$$U_{eff}(r_0) = E, \tag{20a}$$

$$\left[\frac{d}{dr}U_{eff}\right]_{r=r_0} = 0. \tag{20b}$$

In order to solve the above equations, the derivative of $u_{jm}(s)$ with respect to s is needed. The required expression for $du_{jm}(s)/ds$ is given in equation (12) above. Once the above equations have been solved for r_0, the cross section for capture into a specific state of the target molecule is,

$$\sigma_{jm}(E) = \pi b_0^2 \tag{21}$$

The total cross section for capture into a given state of the target molecule summed over all possible $2j+1$ magnetic substates is,

$$\sigma_j(E) = \begin{cases} \frac{1}{(2j+1)} \sum_{m=-j}^{j} \sigma_{jm}(E) & \text{if } E > B \quad (22a) \\ \frac{1}{(2j+1)} \sum_{m=-j}^{j} \sigma_{jm}^{(Stark)}(E) & \text{if } E \leq B \quad (22b) \end{cases}$$

where, in the case when $E \leq B$ the capture cross section σ_{jm} is replaced with the second-order Stark cross section[3],

$$\sigma_{jm}^{(Stark)} = \pi \left(\frac{B}{D}\right) \left(\frac{2\alpha_d A_{jm}}{E}\right)^{1/2} \tag{23}$$

where the terms A_{jm} are equal to $\kappa - C_{jm}$ if $\kappa > C_{jm}$ and zero otherwise. The constants C_{jm} above are equal to $-1/3$ if $j = 0$ and / if $j > 0$, while $\kappa = \alpha_d B/D^2$.

The rate coefficient for capture into the state of the molecule is then given by,

$$k_j(T) = \frac{8\pi}{\mu^2}\left(\frac{\mu}{2\pi kT}\right)^{\frac{1}{2}} \int_0^\infty E\, exp^{-E/kT}\, \sigma_j(E) dE \tag{24}$$

Upon averaging over an assumed Maxwell-Boltzmann thermal distribution, an averaged rate coefficient for capture at temperature T is,

$$\langle k(T)\rangle = \frac{\sum_{j=0}^{j_{max}} (2j+1) k_j(T)\, exp^{-B(j+1/2)^2/kT}}{\sum_{j=0}^{j_{max}} (2j+1)\, exp^{-B(j+1/2)^2/kT}} \tag{25}$$

where the sums over j range from zero to j_{max} which is the maximum orbital angular momentum of the target molecule which still supports an angular momentum barrier in the effective potential.

VI.3 Results and Discussion

The molecular parameters of HCl for α_d, D and B used in the present calculations ,were 2.63 ($\AA^3$), 1.08 ($Debye$),and 10.59 (cm^{-1}), respectively, while for HCN the corresponding values used were 2.59 ($\AA^3$), 2.98 ($Debye$), and 1.48 (cm^{-1}). The adiabatic potential energy for the present modified AIM results were determined from equation (11), while the original AIM results shown were obtained from equation (16). The complete elliptic integrals of the first and second kind were computed from standard codes, while the complete elliptic integral of the third kind was computed by the method given by Carlson [7]. The capture cross sections $\sigma_j(E)$ were calculated from (22) over an energy range E from 0 to $3000B$. The averaged rate coefficients for capture were calculated from equation (25) with j_{max} equal to 20 for HCl and 40 for HCN. The weighted error in the rate coefficient for HCl for $j_{max} = 20$ at 1000 °K is less than 0.2 percent, while the error for HCN for $j_{max} = 40$ at 1000 °K is less than 3%.

Table 1 gives the comparison of the rate coefficients of the AIM(j,ℓ) and the AIM to experimental data and other theories for capture for H^+, C^+, O^+, and HCO^+ ions reacting with HCN molecule at temperature 205, 300, 440, and 540 °K. Table 2 and 3 present the rate coefficients for H_3^+ ion reacting with HCN and HCl molecule at temperature of 205, 300, 440, and 540 °K. The experimental data shown in tables 1-3 were taken from reference [8]. Table 4 shows the rate coefficients of He^+ and C^+ ions reacting with HCl molecules at 27, 68, and 300 °K with the experimental data taken from reference [9].

For the reaction $H^+ + HCN$, the rate coefficients computed from the AIM(j,ℓ) and AIM are significantly different (see figure 1). It indicates that the rotational and orbital angular momentum coupling ($j-\ell$ coupling) has significant effect during the recombination process. The AIM(j,ℓ) results are close to the results of the adiabatic capture and centrifugal sudden approximation (ACCSA).[10] The results of both AIM(j,ℓ) and the ACCSA agree well with experimental data except at 205 °K. The cause of the overestimatation by the theories is still not clear.

The rate coefficients of reaction of H_2^+ ion with HCN and HCl molecules are well predicted by the AIM(j,ℓ) and AIM as shown in figures 2 and 3, respectively. The small difference between the results of the AIM(j,ℓ) and AIM indicates that the $j-\ell$ coupling does not play an important role during the collision. In Tables 3 and 4 excellent agreement of the AIM(j,ℓ) and AIM results can be seen with the classical trajectory method (CT) [11-13], statistical method - probability weighted effective potential method (PWEPM), flux weighted effective potential method (FWEPM) [11,14,15], quantum mechanical method - statistical adiabatic channel model (SACM) [16,17] and ACCSA at temperatures above 20 °K.

For the reaction $He^+ + HCl$, table 4 and figure 4 show that there is virtually no difference between the rate coefficients computed by the AIM(j,ℓ) and the AIM. The $j-\ell$ coupling in this case is entirely negligible - thereby confirming that the $j-\ell$ coupling is important only for very light ion or weak ion-molecule interactions. The results of both the AIM(j,ℓ) and the AIM show excellent agreement with the ACCSA and the SACM results. All theories agree with the measured data to within the experimental error.

For the reaction of C^+ with HCN and HCl molecules, the AIM results, along with other theories, over estimate the rate coefficients when compared with experimental data. Studies by Clary *et al.*, [18] indicate that the overestimation is due to the open shell nature of the carbon ion C^+ in the collision. With *ab-initio* calculations, they suggested that for C^+ the final results should be multiplied by a factor of 2/3. Hence, in this paper, the present modified AIM results for the case of C^+ have been multiplied by the factor of 2/3.

A similiar situation exists in the case of the reaction $O^+ + HCN$. The overestimation of extant theories in the case of reactions of oxygen ions O^+ may again be due to the open shell nature of O^+ as was indicated by *ab-initio* calculations for the case of C^+ ions. At present, no comparable *ab-initio* calculations have been done for the case of oxygen ions reacting with HCN.

The rate coefficients for the reaction $HCO^+ + HCN$ computed by the present AIM calculations agree with the experimental data and the ACCSA. At 205 and 300 °K the present AIM results are about 25 percent above the experimental data, which is within the experimental error bars of the SIFT technique.

VI.4 Summary

A new modification to the adiabatic invariance method (AIM(j,ℓ)) has been presented and shown to be important for thermal ion-molecule reactions. The principal feature of the modification to the AIM theory is the inclusion of the coupling between the internal rotation angular momentum of the target molecule with the orbital angular momentum of the projectile ion about the CM of the target molecule.

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Tables

Table 1. Comparison of rate coefficients for capture for the reaction $X^+ + HCN$ ($X = H, C, O, HCO$)

		Temperature (°K)			
		205	300	440	540
reaction	method^a	k ($\times 10^{-9} cm^3 s^{-1}$)			
$H^+ + HCN$	AIM (j,l) (present work)	16.	13.	10.	9.2
	AIM (present work)	17.	15.	12.	11.
	ACCSA	16.	13.	11.	11.
	experiment	11.	11.	10.	9.7
$C^+ + HCN^\dagger$	AIM (present work)	3.9	3.3	2.8	2.6
	ACCSA	3.7	3.1	2.7	2.5
	experiment	3.4	3.1	3.0	2.9
$O^+ + HCN$	AIM (present work)	5.4	4.5	3.8	3.5
	ACCSA	5.0	4.2	3.6	3.4
	experiment	3.7	3.5	3.3	3.1
$HCO^+ + HCN$	AIM (present work)	4.6	3.8	3.2	3.0
	ACCSA	4.2	3.5	3.1	2.9
	experiment	3.7	3.1	2.9	2.8

(a) for definitions of the symbols see table 2. The experiment and ACCSA data were from [8].

(†) the AIM and ACCSA results have all been multiplied by 2/3. [18]

Table 2. Comparison of rate coefficients for capture for the $H_3^+ + HCN$ reaction

	Temperature (°K)														
	15	50	100	150	205	220	260	280	300	320	380	440	500	540	600
method	k ($10^{-9} cm^3 s^{-1}$)														
AIM(j,l)[a]	35.5	19.7	14.0	11.5	9.9	9.6	8.8	8.5	8.2	8.0	7.4	6.9	6.5	6.2	5.9
AIM[b]	36.8	20.2	14.4	11.9	10.3	10.0	9.3	9.0	8.7	8.4	7.8	7.3	7.0	6.7	6.5
CT[c] (A)	31.6	20.5							8.3					6.7	
(B)		22.0		13.0					9.2				7.3		
PTRAT[d]	32.8	18.6	13.5	11.3	9.9	9.6	8.9	8.7	8.4	8.2	7.6	7.2		6.6	
CVTST[e]	53.5	29.4	20.9	17.2	14.8	14.3	13.2	12.8	12.4	12.0	11.1	10.4		9.4	
ADO[f]				8.5					6.6				5.4		
PWEPM[g]	26.1	14.4	10.2	8.5	7.5	7.2	6.8	6.6	6.4	6.2	5.8	5.5		5.1	
FWEPM[h]	31.0	17.0	11.9	9.9	8.6	8.4	7.8	7.6	7.4	7.2	6.7	6.3		5.8	
ACCSA[i]	54.0	24.0		12.0	9.6				8.3			7.3		6.9	
SACM[j]		18.0		11.0					8.7				7.2		6.8
expt.[k]					9.5				8.1			7.1		6.7	

Present Work:

(a) AIM(j,ℓ): Modified Adiabatic Invariance Method

(b) AIM: Adiabatic Invariance Method

Classical Theories:

(c) CT: Classical Trajectory (A) [11] and (B) [13]

(d) PTRAT: Parametrised Trajectory [12], [13]

(e) CVTST: Canonical Variational Transition State Theory [11]

Statistical Theories:

(f) ADO: Average Dipole Orientation [8], [16], [17]

(g) PWEPM: Probability Weighted Effective Potential Method [11], [14], [15]

(h) FWEPM: Flux Weighted Effective Potential Method [11], [14], [15]

Quantum Theories:

(i) ACCSA: Adiabatic Capture and Centrifugal Sudden Approximation [8]

(j) SACM: Statistical Adiabatic Channel Model [16], [17]

(k) expt: Experiment [8]

Table 3. Comparison of rate coefficients for capture for the $H_2^+ + HCl$ reaction

	Temperature (°K)														
	15	50	100	150	205	220	260	280	300	320	380	440	500	540	600
method†	k ($10^{-9} cm^3 s^{-1}$)														
AIM(j,l)	13.2	7.4	5.6	4.8	4.3	4.2	4.0	3.9	3.8	3.7	3.5	3.4	3.3	3.2	3.1
AIM	13.5	7.6	5.7	4.9	4.4	4.3	4.0	4.0	3.9	3.8	3.6	3.5	3.4	3.3	3.2
CT‡	12.6	6.8	5.4	4.4	3.9	4.0	3.9	4.0	4.0	3.8	3.4	3.5		3.2	
PTRAT	12.6	7.6	5.8	5.0	4.4	4.3	4.1	4.0	3.9	3.8	3.6	3.5		3.3	
CVTST	19.4	10.9	8.0	6.8	6.0	5.9	5.5	5.4	5.3	5.2	4.9	4.7		4.4	
ADO									3.4						
PWEPM	9.9	5.9	4.5	4.0	3.6	3.5	3.4	3.3	3.3	3.2	3.1	3.0		2.9	
FWEPM	11.7	6.8	5.1	4.4	4.0	3.9	3.7	3.7	3.6	3.5	3.4	3.3		3.1	
ACCSA	16.0	7.6		4.5	4.1				3.6			3.3		3.2	
SACM	12.8	7.6	5.7												
expt.					4.2				3.8			3.5		3.4	

(†) for definitions and references of the symbols see table 2.

(‡) CT: Classical Trajectory [11]

Table 4. Comparison of rate coefficients for capture for the reaction $X^+ + HCl$ ($X = He, C$)

		Temperature (°K)		
		27	68	300
reaction	method[a]	k ($10^{-9} cm^3 s^{-1}$)		
$He^+ + HCl$	AIM (j,l) (present work)	8.7	5.7	3.4
	AIM (present work)	8.9	5.8	3.4
	ACCSA	8.4	5.5	3.2
	SACM	8.6	5.6	3.0
	experiment	11. ± 3.0	4.6 ± 1.4	3.3 ± 0.5
$C^+ + HCl^\dagger$	AIM (present work)	3.7	2.5	1.5
	ACCSA	3.5	2.3	1.6
	SACM	3.6	2.3	1.3
	experiment	3.8 ± 1.1	1.9 ± 0.6	1.0 ± 0.2

(a) for definitions of the symbols see table 2. The experiment, ACCSA, and SACM data were from [9].

(†) the AIM, ACCSA, and SACM results have all been multiplied by 2/3. [18]