A theory of associative detachment

Susan Elizabeth. Haywood

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A THEORY OF ASSOCIATIVE DETACHMENT

A Dissertation
Presented to
The Faculty of the Department of Physics
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In Partial Fulfillment
Of the Requirements for the Degree of
Doctor of Philosophy

by

Susan Elizabeth Haywood

1984
APPROVAL SHEET

This dissertation is submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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ABSTRACT

In this thesis a theory of associative detachment (A⁻ + B → AB + e⁻) is presented. The theory is based on the close-coupling theory of Wang and Delos, but is more general in that final states of the nuclei (AB) are treated quantum mechanically. This is necessary since the molecule may be in any one of several vibrational states. The Schrödinger equation is reduced to an infinite set of coupled equations using carefully chosen assumptions. The coupled equations are uncoupled and the resulting equation for the wave function of the negative ion is solved to zero and first order. The first order solution is then used to find the wave function for the final states of the molecule. Two systems were examined: H (D) + Cl⁻ and H (D) + F⁻. In both cases the survival probability of the negative ion showed a striking isotope effect, with the survival probabilities found for D + Cl⁻ and D + F⁻ much smaller than those found for H + Cl⁻ and H + F⁻. Experimental rate constants were reproduced for H + Cl⁻ and H + F⁻.
A THEORY OF
ASSOCIATIVE DETACHMENT
INTRODUCTION

A. Introduction

There has been a great deal of interest in negative ions in recent years. Negative ion reactions are important in a variety of fields: flame chemistry, studies of the upper atmosphere, and plasma physics. There is much recent experimental data on the various reactions of negative ions, and also of ionization processes. These reactions include:

\[
\begin{align*}
\hat{A}^− + B & \rightarrow AB + e^- \quad \text{associative detachment} \quad 1.1 \\
AB + e^- & \rightarrow A^- + B \quad \text{dissociative attachment} \quad 1.2 \\
A^- + B & \rightarrow A + B + e^- \quad \text{direct detachment} \quad 1.3 \\
A^+ + B & \rightarrow A + B^+ + e^- \quad \text{Penning ionization} \quad 1.4 \\
A^+ + B & \rightarrow (AB)^+ + e^- \quad \text{associative ionization} \quad 1.5 \\
(AB)^+ + e^- & \rightarrow A + B \quad \text{dissociative recombination} \quad 1.6
\end{align*}
\]

A common aspect of these reactions is the close coupling between a single state of the system in which there is no free electron and states in which the system contains a free electron. The free electron states form a continuum which interacts strongly with the discrete state.
In this thesis we will examine the case of associative detachment, studying the reactions \( \text{H(D)} + \text{Cl}^- \rightarrow \text{H(D)Cl} + e^- \) and \( \text{H(D)} + F^- \rightarrow \text{H(D)F} + e^- \). A quantum mechanical theory will be developed to study these reactions. By the use of certain approximations, the theory may be shown to lead to the close-coupling theory of Wang and Deros,\textsuperscript{28,29} and from there the local-complex-potential model may be derived.\textsuperscript{30,31} Our theory may easily be extended to apply to direct detachment or dissociative attachment. With more effort, it can be further extended to apply to ionization processes as well.

B. Overview

In this section we give a brief description of this work. The next section is devoted to a description of associative detachment with a discussion of the experimental data that is available. The following section will deal with the background of the present theory, the complex potential model and with the zero-range potential model.\textsuperscript{32,33} The latter has been used successfully to find rate constants for associative detachment in some systems.

In chapter II the assumptions used in this work are presented and a set of coupled equations for the nuclear wave functions is derived using the assumptions. The nuclear wave functions are: 1) a single discrete state for the negative ion and 2) a continuum of states in which there is a free electron. The coupled equations are uncoupled in
chapter III. This results in a single integro-differential equation for the nuclear wave function of the negative ion. A function $G_{-}(R,R')$ is introduced which describes the transitions from the negative ion state to the continuum, and from the continuum to the negative ion state.

The integro-differential equation found in chapter III is solved to zero and first order in the following two chapters. A complex momentum $\Pi^{(2)}$ is defined which contains the function $G_{-}(R,R')$. The complex momentum is used to find the survival probability of the negative ion. In chapter V the complex momentum is written in terms of a time $\tau$ and the close coupling theory of Wang and Delos is found using $\Pi^{(\tau)}$. From here the complex potential model may be derived.

In chapter VI the bound states of the molecule are discussed. The probability of associative detachment into excited vibrational states is found. In the final chapter the equations are applied to the systems $H(D) + Cl^-$ and $H(D) + F^-$. The detachment rate constant $k(T)$ is compared with experimental results in the case of $H + Cl^- .

C. Associative Detachment

Associative detachment (1.1) is likely to occur only at very low energies. If the collision energy is above the binding energy of the resulting molecule, direct detachment (1.3) may occur. For such collision energies direct detachment is more likely to take place than
associative detachment. Typically experimental studies of associative detachment are done at thermal energies. At these low energies, the reaction has a rate constant that is near the Langevin limit for most of the systems studied.

The Langevin limiting rate constant is obtained in the following way. If \( \alpha \) is the polarizability of the target, the potential may be written as

\[
V(r) = -\frac{e^2}{4\pi \varepsilon_0 r^4}
\]

so that the total energy of the system is

\[
E = \frac{1}{2} m_0 (\mathbf{v}_0^2 + r^2 \dot{\phi}^2) - \frac{e^2}{4\pi \varepsilon_0 r}
\]

The incoming atom will be in a circular orbit about the target at \( r_c \):

\[
r_c = \left( \frac{\mu \omega}{m_0 v_0^2 \alpha} \right)^{1/3} \quad v_0 = \sqrt{\frac{2E}{m_0}}
\]

The impact parameter corresponding to this radius is

\[
b_c = \left( \frac{\mu \omega}{m_0 v_0^2 \alpha} \right)^{1/2}
\]

Then in the Langevin limit, any collision with an impact parameter less than \( b_c \) will result in a reaction, while there will be no reaction if the impact parameter is greater than \( b_c \).

The systems that have been studied experimentally include \( F^- + H(D), Cl^- + H, I^- + H, I^- + H_2 \), and \( O^- \) with various diatomic targets. The molecule produced by associative detachment usually occupies the highest energetically available vibrational state. Thus one would expect the
energy of the detached electron to be small. The average energy of the detached electron has been found to be roughly half of the difference in energy between adjacent vibrational states of the molecule in several cases.

D. Theoretical Background

Some measurements of electron detachment from negative ions have been successfully described using a local complex potential model in which the potential energy of the bound state of the negative ion is assumed to cross into a continuum of free electronic states. The discrete state then becomes a resonance with a complex energy

\[ \tilde{E} = E - i \pi \gamma / \lambda \]

with the survival probability of the negative ion given by

\[ P_i = e^{- \int \sigma(R) d\sigma} \]

The time dependence of the crossing of the curves was assumed to be linear by Demkov \(^{11}\) and quadratic by Taylor and Delos \(^{12},^{13}\).

A dynamical complex potential theory developed by Wang and Delos \(^{12},^{13}\) allows one to use an arbitrary time dependence for the crossing of the negative ion potential energy and the lowest continuum state.

The zero range potential has been used by Gauyacq to calculate detachment probabilities, rate constants and detachment rates for \( F^- + H \) and \( Cl^- + H \). \(^{24,25}\) In this theory the electronic wave function is assumed to be significant only at
a large enough distance from the nuclei that their influence on the electron may be reduced to a boundary condition on the wave function at the origin:

\[ \frac{\partial}{\partial \tau} \langle \hat{R} \rangle \psi(\hat{x}, \hat{y}, \hat{z}) \bigg|_{r_0} = f(R) \]

A common feature of the complex potential models and of the zero-range potential model in its application to direct detachment is that the motion of the nuclei is described classically or semiclassically, so the wave function for the electron obeys a time dependent Schrödinger equation. For collisions leading to associative detachment, a semiclassical theory would not be adequate for describing the bound vibrational states of the molecule resulting from the reaction and therefore a fully quantum mechanical theory is needed. The theory developed here follows mainly along the lines developed by Taylor and by Wang, but differs from their approach in that the present theory treats the nuclei according to quantum mechanics.
A. Introduction

The Schrodinger equation cannot be solved exactly for negative ion collisions. It is therefore necessary to make several simplifying assumptions. The most important of these involve the wave functions which describe the outer electron. The assumptions will be discussed in this chapter; they result in a fully quantum mechanical set of equations for the nuclear wave functions. The coupled equations may be used to describe many of the reactions discussed in Chapter I. In particular, dissociative attachment and associative detachment differ only in the boundary conditions, which are discussed in this chapter. In both reactions any one of several vibrationally excited states may be occupied by the molecule AB in the final state and at collision energies above the binding energy of AB direct detachment may take place. Both possibilities are implicit in the coupled equations.

B. The Complete Schrodinger Equation

The Schrodinger equation in coordinate representation is:
As shown in Figure 1, \( \mathbf{R} \) is the internuclear distance and \( \mathbf{r} \) is the coordinate from the nucleus of the negative ion to the outer electron. The Hamiltonian is written as

\[
H(\mathbf{r}; \mathbf{R}) = T + h(\mathbf{r}; \mathbf{R})
\]

where \( T \) is the nuclear kinetic energy and \( h(\mathbf{r}; \mathbf{R}) \) is an electronic Hamiltonian.

\[
\mathcal{H}(\mathbf{r}; \mathbf{R}) = T_{\mathcal{H}} + \mathcal{U}(\mathbf{r}; \mathbf{R})
\]

\( T_{\mathcal{H}} \) is an electronic kinetic energy and \( \mathcal{U} \) is the potential energy, which includes all of the binary Coulombic interactions among the electrons and nuclei. The wave function \( \psi(\mathbf{r}; \mathbf{R}) \) is expanded as a product of electronic and nuclear basis functions, which are denoted by \( \varphi_{\mathbf{n}}(\mathbf{r}; \mathbf{R}) \) and \( u_{\mathbf{n}}(\mathbf{R}) \) respectively:

\[
\psi(\mathbf{r}; \mathbf{R}) = \varphi_{\mathbf{n}}(\mathbf{r}; \mathbf{R}) u_{\mathbf{n}}(\mathbf{R})
\]

The subscript \(-1\) refers to the state in which the electron
is bound, and $k$ refers to the free states in the continuum. $\rho_k$ is the density of states in the continuum, which is discussed in Appendix A. The electronic wave function $\Psi_n(F; \hat{R})$ is assumed to be centered on the nucleus of the colliding negative ion throughout the collision. As the atoms approach, this bound state must be deformed to some extent, but it maintains its character as a bound state. The continuum states $\Psi_{\infty}(F; \hat{R})$ describe a free electron with energy $\epsilon_n$, which is related to $k$ by

$$\epsilon_n = \frac{\hbar^2 k^2}{2m}$$

2.5

The continuum states are also centered on the nucleus of the colliding atom.

In principle it is possible to calculate the electronic functions $\Phi_n$ and $\Psi_{\infty}$, but this would be a major undertaking, which is not attempted in this work. Instead we develop a theory that is based upon certain assumptions about these functions and their matrix elements. In practice, the calculations are done using a square well model which will allow one bound state in place of the actual potential of the loosely bound outer electron. This model, which is discussed in Appendix A, has been used successfully by Taylor and Delos $^{31,32}$ and by Wang and Delos $^{33,34}$.

If the electronic basis functions are orthogonal (assumption (i)), then eq. 2.4 implicitly defines the set of nuclear wave functions:
A differential equation may now be obtained for the vector of nuclear wave functions $\psi(\vec{r})$.

\[(1 + \Delta - \hbar^2 \nabla^2 + \mathbf{P}^2) \psi(\vec{r}) = 0\]  

where the matrices $\hbar$ and $\mathbf{P}$ are

\[\hat{H}_{ij} = \int d\vec{r} \varphi_i^*(\vec{r}; \vec{k}) \hat{h}(\vec{r}; \vec{k}) \varphi_j(\vec{r}; \vec{k})\]  

\[P_{ij} = \frac{\hbar^2}{2} \int d\vec{r} \varphi_i^*(\vec{r}; \vec{k}) \nabla^2 \varphi_j(\vec{r}; \vec{k})\]  

The most important assumptions to be made concern the nature of the electronic basis functions and the resulting matrix elements of $\hbar$ and $\mathbf{P}$. The basis states are assumed to form a partially diabatic and partially adiabatic representation with the following properties:

(i) There is one bound state $\varphi_{\text{bnd}}$ and one continuum $\{ \varphi_{\text{cont}} \}$. (iii) The coupling between the bound state and continuum states is represented diabatically, with $P_{\text{bnd},\text{cont}}$ negligible and $\hbar_{\text{bnd},\text{cont}}$ non-negligible. (iv) Intra-continuum coupling is negligible, so
that

\[ \Delta_{h^4} (x) = 0 \quad ; \quad \rho_{h^4} (x) = 0 \]

According to this assumption, transitions occur from the bound state to the free states, and vice-versa, but direct transitions from one free state to another are neglected. The neglect of free-free transitions may be justified by considering the collision classically. It is known that an electron colliding with a molecule does not excite the molecule vibrationally unless the electron is captured, because the electron is too light to have an effect on the heavy nuclei. An alternative argument leads to the same conclusion. As a detached electron escapes from a molecule, the nuclei continue to move as the electron travels away, and the motion of the nuclei can affect the electron's motion, changing its energy or its direction. However, such effects should be small because the velocity of the escaping electron is normally much larger than the nuclear velocity. In the case of associative detachment a typical detached electron has an energy of 0.01 au and the nuclear kinetic energy is on the order of keV. The velocity of the detached electron is then a factor of 10 larger than that of the nuclei. In the time 500 au (10^{-10} sec), corresponding to a vibrational period or to the collision time, the electron has moved 40 a₀. Hence the electron is out of reach of the nuclear influence long before the nuclei
have moved very far.

The coupled equation 2.8 may now be written

\[ (E - A(\mathbf{r}) + \frac{p^2}{2m} \phi_\mathbf{r}) \psi(\mathbf{r}) = 0 \]  \hspace{1cm} 2.12

We also assume \((\nu)\) that the angular momentum of the nuclei is essentially constant through the collision. In a typical collision, the nuclei have some hundreds of quanta of angular momentum, while the light electron might carry off only one or two quanta, so the angular momentum quantum number does not change significantly during a collision. This approximation can be expressed mathematically by writing the nuclear wave function as a sum of products of radial factors and spherical harmonic angular factors,

\[ \psi(\mathbf{r}) = \sum \frac{\psi_{n l m}(\mathbf{r}, \mathbf{\Omega})}{R} \gamma_{l m}(\mathbf{\Theta}, \mathbf{\Phi}) \]  \hspace{1cm} 2.13

The spherical harmonics \(\gamma_{l m}(\mathbf{\Theta}, \mathbf{\Phi})\) are eigenfunctions of the angular part of the nuclear kinetic energy with eigenvalues \(l(l + 1) \hbar^2\).

\[ \mathbf{\hat{r}}^2 \gamma_{l m}(\mathbf{\Theta}, \mathbf{\Phi}) = \mathbf{l(l + 1)} \gamma_{l m}(\mathbf{\Theta}, \mathbf{\Phi}) \]  \hspace{1cm} 2.14

A new radial potential energy may be defined using eq. 2.14.
On further assumption is necessary to do the calculations: (vi) the continuum curves \( V_k \) are assumed to be parallel. Then the continuum potential energy is

\[
V_k(R) = V_0(R) + E_k
\]

where \( V_0(R) \) is the lowest continuum curve. The potential energy matrix may now be written as

\[
\begin{pmatrix}
V_0(R) & V_{-1}(R) & V_{-2}(R) & \\
V_{-1}(R) & V_{-2}(R) & V_{-3}(R) & \\
V_{-2}(R) & V_{-3}(R) & V_{-4}(R) & \\
& & & \ddots
\end{pmatrix}
\]

A set of typical potential energy curves \( V_0(R) \) and \( V_{-1}(R) \) are shown in figure 2. The assumptions listed above are believed to be quite generally applicable to a wide variety of collision systems. They lead to an infinite set of coupled differential equations for the nuclear wave functions \( u_{-1}(R) \) and \( u_k(R) \); by substituting eq. 2.17 into eq. 2.8, we obtain
**Figure 2**

**Potential Energies**

\[ E = \text{collision energy} \]
\[ e = \text{electron energy} \]
\[ E_i = \text{bound state energy} \]
\[ V_{_{m0}}(R_{op}) \leq E \]
In this thesis we develop techniques for solving such infinite sets of coupled equations and we solve them for the boundary conditions of associative detachment. Specifically, the collisions of Cl + H → HCl + e<sup>-</sup>, F<sup>-</sup> + H → HF + e<sup>-</sup> are studied.

In those calculations, specific assumptions and approximations are made about the potential energy curves and about the coupling matrix elements V<sub>k-l</sub>. In particular (viii) the approximation is made that V<sub>k-l</sub>(R) and V<sub>k,-l</sub>(R) are equal and have a separable R and ε dependence, so that
In the work of Wang and Delos\textsuperscript{22,33}, some additional assumptions were made. The most important of these is that the semiclassical approximation may be used to describe nuclear motion. In this way, the stationary Schrödinger equation was reduced to a \textquoteleft time\textquoteright-dependent electronic Schrödinger equation. Their treatment is applicable to a reaction such as direct detachment, but it cannot be applied to associative detachment since in the final state the vibrational motion of the nuclei is quantized, and a classical-trajectory description of the nuclear motion is not appropriate. The major purpose of this work is to obtain a theory similar to that of Taylor, Wang and Delos, but in which nuclear motion is described quantum mechanically. The theory is in this regard more general, so it is not limited to systems in which the nuclei are bound in the final state, but may be applied to direct detachment as well. Dissociative attachment may also be described by this theory.

C. Projection Operators and Basis States

It is sometimes more convenient to deal with abstract vectors instead of wave functions. In this section we repeat the development given in the preceding section, but using Dirac bra and ket notation instead of wave-
function notation. Later projection operators which greatly simplify the analysis will be defined, and they are much more simply expressed in terms of bras and kets than in terms of wave-functions.

The Schroedinger equation is

\[ (E - \hat{H}) \psi = 0 \]

with the state vector \( \psi \) related to the wave function \( \psi (\vec{r}; \vec{R}) \) by

\[ \psi (\vec{r}; \vec{R}) \propto \langle \psi | \psi \rangle \]

\( | \psi \rangle \) is a position eigenstate with the following properties

\[ | \psi \rangle = \frac{1}{\sqrt{\pi}} | R \rangle | \rho \rangle \]

\[ \langle \psi | \psi \rangle = \delta(\rho - \rho') \]

\[ \int d\rho | \psi \rangle \langle \psi | = 1 \]

\[ \langle \psi | \psi \rangle = \delta(\rho - \rho') \]

\[ \langle \psi | \psi \rangle \langle \psi | \psi \rangle = \delta(\rho - \rho') \]

\[ \int d\rho | \psi \rangle \langle \psi | = 1 \]

\[ \int d\rho | \psi \rangle \langle \psi | = 1 \]

The ket \( | \rho \rangle \) is an eigenket of the electronic position operator \( \hat{r} \), and \( | R \rangle \rangle \) is an eigenket of the nuclear radius operator \( \hat{R} \). \( | R \rangle \rangle \) is an eigenket of the nuclear angle
operators $\mathcal{O}$ and $\mathcal{E}$.

$|\psi\rangle$ has been expanded as a product of electronic and nuclear states, and in vector notation, the wave function of eq. 2.4 is

$$|\psi\rangle = \langle -i \Omega | \psi \rangle + \int dk \rho_n(k) |k\rangle |k\rangle$$

$$\langle -i \Omega | = \frac{1}{i} \langle -i \Omega | \Omega \rangle$$

$$|k\rangle = \frac{1}{\sqrt{2}} |k, S\rangle |k\rangle$$

The double brackets denoting nuclear states and single brackets electronic states. Since the electronic basis function $\psi_i(\mathbf{r}; \mathbf{R})$ depends parametrically upon the nuclear coordinate $\mathbf{R}$, we are required to use Dirac's notation in a slightly unconventional way. The state vectors are related to the electronic basis functions and nuclear wave functions as follows.

$$\frac{\psi_i(R)}{R} = \langle R | \psi_i \rangle$$

$$\psi_i(\mathbf{r}; \mathbf{R}) \langle R | \psi_i \rangle = \langle R | \psi_i \rangle$$

$$\gamma_{f,m}(\theta, \phi) = \langle \theta | \psi_i \rangle |m\rangle$$
Again, \( | -i \rangle \) represents the state of the negative ion, \( (K) \) is a continuum electronic state, and \(| -i_k \rangle \) and \(| k \rangle \) are nuclear states corresponding to \( u_{r_i}^{(s)}(R) \) and \( u_k^{(s)}(R) \). Throughout this derivation and those that follow, we will consider the collision to take place at a fixed value of \( l \) (by assumption \((\nu)\)), and the sum over angular momentum states will be dropped. Then \( u_{r_i}^{(s)}(R) \) and \( u_k^{(s)}(R) \) are \( u_{r_i}(R) \) and \( u_{k}(R) \) of eqs. 2.19 to 2.22. The sum over angular momentum states will return for the calculation of the rate constants and cross sections. We may then rewrite \(| \xi \rangle \) as

\[
| \xi \rangle = | -i \rangle | -i \rangle + \int d k \rho_k | k \rangle | k \rangle
\]

\[
| -i \rangle = | -i_k \rangle ; \quad | k \rangle = | k_k \rangle
\]

It follows from the orthogonality of the electronic basis functions (assumption \((i)\)) that the electronic state vectors have the following orthogonality properties.

\[
\langle -i | -i \rangle = 1
\]

\[
\langle k | k \rangle = \frac{\delta(k-k')}{\rho_k}
\]

\[
\langle -i | k \rangle = 0
\]

\[
\langle k | -i \rangle = 0
\]
The electronic basis vectors will be used to define two projection operators, $P$ and $Q$:

$$ P = \left| -1 \times -1 \right| $$  \hspace{1cm} 2.34a

$$ Q = \int d\mathbf{k} \rho_k \left| k \times \mathbf{k} \right| $$  \hspace{1cm} 2.34b

Eqs. 2.29 may be used to show that:

$$ P^2 = P $$  \hspace{1cm} 2.35a

$$ Q^2 = Q $$  \hspace{1cm} 2.35b

$$ QP = 0 $$  \hspace{1cm} 2.35b

$$ PQ = 0 $$  \hspace{1cm} 2.35b

$$ Q + P = 1 $$  \hspace{1cm} 2.35b

These projection operators provide a convenient way to derive coupled equations for the nuclear state vectors $\left| -1 \right>$ and $\left| k \right>$ since by eq. 2.27,

$$ \mathcal{P} \left| \Phi \right> = \left| -1 \right> \left| -1 \right> $$  \hspace{1cm} 2.36a
D. The Coupled Equations

Using the definitions in eq. 2.30, a few trivial manipulations may be performed on eq. 2.24

\[ (E - H)(P + Q)\phi = 0 \]  
\[ P(E - H)\phi = PH\phi \]  
\[ Q(E - H)\phi = QHP\phi \]  
\[ (E - PHP)P\phi = PHQ\phi \]  
\[ (E - QHP)Q\phi = QHP\phi \]

It is not obvious, but in coordinate notation the above equations are the infinite set of coupled differential equations that specify the nuclear wave functions \( u_+^k(R) \) and \( u_-^k(R) \). Eq 2.8, or, under the assumptions stated earlier, eqs 2.18 and 2.19 may be obtained from eqs. 2.40 by operating on the latter with \( \langle \phi \rangle \) and using the orthogonality properties of \( P \) and \( Q \).
First, let us consider the Hamiltonian matrix elements PHP, PHQ, QHP and QHQ. An operator \( O \) is related to its corresponding coordinate space operator \( O(\vec{r}; \vec{R}) \) by

\[
O(\vec{r}) = \int \text{d} \vec{r}' \langle \vec{r} | 0 | \vec{r}' \rangle X_{\vec{r}' \vec{r}} \tag{2.41a}
\]

\[
O(\vec{r}) \delta(\vec{r}) = \int \text{d} \vec{r}' \langle \vec{r} | 0 | \vec{r}' \rangle \delta(\vec{r} - \vec{r}') \tag{2.41b}
\]

\[
\langle \vec{r} | 0 | \vec{r}' \rangle = \int \text{d} \vec{r} \delta(\vec{r} - \vec{r}') O(\vec{r}) \delta(\vec{r}) \tag{2.42a}
\]

\[
\delta(\vec{r}) = \langle \vec{r} | 0 | \vec{r} \rangle \tag{2.42b}
\]

so that

\[
\langle \vec{r} | 0 | \vec{r}' \rangle = O(\vec{r}) \delta(\vec{r} - \vec{r}') \tag{2.43}
\]

Then, in order to find the coordinate space form of PHP we must first evaluate \( \langle \vec{r}_1 \vec{p}_1 \vec{r}_1' \vec{p}_1' \rangle \) using \( \{-1 \times -1\} \) for \( \vec{P} \).

\[
\langle \vec{r}_1 \vec{p}_1 \vec{r}_1' \vec{p}_1' \rangle = \langle \vec{r}_1 \vec{p}_1 \vec{r}_1' \vec{p}_1' \rangle \tag{2.44}
\]

\[
\langle \vec{r}_1 \vec{p}_1 \vec{r}_1' \vec{p}_1' \rangle = \int \text{d} \vec{r} \int \text{d} \vec{r}' \delta(\vec{r}_1 - \vec{r}_1') \delta(\vec{p}_1 - \vec{p}_1') \langle \vec{r}_1 \vec{p}_1 \vec{r}_1' \vec{p}_1' \rangle \tag{2.45}
\]

We will first evaluate \( \{-1 \times -1\} \) using eqs. 2.28 to
2.31, so that

\[ \langle -1|H|1-i \rangle = \int d\mathbf{R}^n \int d\mathbf{R}^m \left[ \langle -1| \mathbf{R}^n \rangle \right] \]

\[ \langle \mathbf{R} | H | \mathbf{R} \rangle = \int d\mathbf{R}^n \int d\mathbf{R}^m \left[ \langle \mathbf{R} | \mathbf{R}^n \rangle \langle \mathbf{R}^m | \mathbf{R}^n \rangle \right] \]

Now \( H(\mathbf{F}; \mathbf{R}) \) is the coordinate space Hamiltonian defined in eq. 2.2 as

\[ H(\mathbf{F}; \mathbf{R}) = T + h(\mathbf{R}) \]

\[ = T + L(\mathbf{R}) \]

with the nuclear kinetic operator \( T \)

\[ T = -\frac{\hbar^2}{2m} \nabla_\mathbf{R}^2 \]

Replacing the Hamiltonian \( H(\mathbf{R}) \) with \( T + h(\mathbf{R}) \) will give us

\[ \langle -1|H|1-i \rangle = \int d\mathbf{R}^n \int d\mathbf{R}^m \left[ \langle -1| \mathbf{R}^n \rangle \right] \]

\[ \langle \mathbf{R} | (T + h(\mathbf{R})) | \mathbf{R} \rangle \]

\[ \langle \mathbf{R} | \mathbf{R} \rangle \]

This will be evaluated in two parts. First consider the integral containing the electronic Hamiltonian \( h(\mathbf{R}) \).
The integral containing the nuclear kinetic energy must be found using integration by parts, since at present it contains the second derivative of a delta function. Then

\[
\int dR^o \left(-\frac{\hbar^2}{2m} \nabla^2_R \right) \delta(R^o - R^m) \phi_{-n}(R^m) \ll R^o \]

\[
= -\frac{\hbar^2}{2m} \int dR^o \left[ \delta(R^o - R^m) \left(-\frac{\hbar^2}{2m} \nabla^2_R \right) \delta(R^o - R^m) \phi_{-n}(R^m) \ll R^o \right]
\]

\[
= -\frac{\hbar^2}{2m} \left\{ (\nabla^2_R \delta(R^o - R^m)) \phi_{-n}(R^m) \ll R^o \right\}
\]

\[
- \int dR^o \left(\nabla^2_R \delta(R^o - R^m)\right) \left(\nabla^2_R \phi_{-n}(R^o) \ll R^o \right)
\]

\[
= -\frac{\hbar^2}{2m} \nabla^2_R \phi_{-n}(R^o) \ll R^o
\]

Combining eqs 2.50 and 2.54 and integrating will give us a more tractable form for \(\langle -1 | H | -1 \rangle \):

\[
\langle -1 | H | -1 \rangle = \int dR^o \left(\nabla^2_R \phi_{-n}(R^o) \right)
\]

\[
\phi_{-n}(R^o) \left(-\frac{\hbar^2}{2m} \nabla^2_R + \Delta_R(R^o) \phi_{-n}(R^o) \ll R^o \right)
\]

Now
\[ \int \sigma R = \int \sigma R \int \rho \]

and by eqs. 2.9 - 2.10, integrating over \( r \) will give us

\[ \langle \mathbf{r} \rangle = \int \rho d \mathbf{r} \mathbf{r} \left[ -\frac{\mathbf{v}_n^2}{2} + \lambda_{-n} \mathbf{r} \right] \langle \mathbf{r} \rangle \]

This may be substituted into eq. 2.44 to give us

\[ \langle \mathbf{r} | \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r}' \rangle = \]

\[ \langle \mathbf{r} | \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r}' \rangle = \int \rho d \mathbf{r} \langle \mathbf{r} | \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r}' \rangle \]

We are now ready to consider the coordinate space form of \( \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r} \rangle : \)

\[ \langle \mathbf{r} | \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r} \rangle = \int \rho d \mathbf{r} \left[ \int \rho d \mathbf{r} \mathbf{r} \left[ -\frac{\mathbf{v}_n^2}{2} + \lambda_{-n} \mathbf{r} \right] \langle \mathbf{r} | \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r} \rangle \right] \]

\[ \langle \mathbf{r} | \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r} \rangle = \int \rho d \mathbf{r} \left[ \int \rho d \mathbf{r} \mathbf{r} \left[ -\frac{\mathbf{v}_n^2}{2} + \lambda_{-n} \mathbf{r} \right] \langle \mathbf{r} | \mathbf{P} \mathbf{H} \mathbf{P} | \mathbf{r} \rangle \right] \]

We know that

\[ \Phi_n (\mathbf{r}) = \int \rho d \mathbf{r} \Phi_n (\mathbf{r}) \]
so that in coordinate space, \( \langle \Phi | \Phi \rangle \) is just

\[
\langle \Phi | \Phi \rangle = \int dR^* \Psi_+ (\mathbf{R}) \int d\mathbf{R} \left[ \langle R | \Phi \rangle \right]
\]

\[
\left( -\frac{\hbar^2}{2m} \nabla_{R^*}^2 + \lambda_{-n}(R^*) \right) \langle R^* \Phi \rangle \Psi_+ (\mathbf{R})
\]

Now recall that the potential \( V_{-1,-1}(R) \) is \( h_{-1,-1}(R) \) with an angular momentum term added. Then integrating over the nuclear angles,

\[
\langle \Phi | \Phi \rangle = \frac{1}{2} \int dR^* \Psi_+ (\mathbf{R}) \int d\mathbf{R} \left[ \lambda(R - R^*) \right]
\]

\[
\left( -\frac{\hbar^2}{2m} \nabla_{R^*}^2 + \frac{\hbar^2 \partial^2}{2m R^*} + \lambda_{-n}(R^*) \right) \Psi_+ (\mathbf{R})
\]

\[
\langle \Phi | \Phi \rangle = \Psi_+ (\mathbf{R}) \left( -\frac{\hbar^2}{2m} \nabla_{\mathbf{R}}^2 + V_{-1}(\mathbf{R}) \right) \Psi_+ (\mathbf{R})
\]

This is the Hamiltonian \( h_{-1,-1}(R) \) of eq. 2.19 operating on the nuclear wave function of the negative ion multiplied by the electronic wave function \( \Psi_+ \).

Now consider PHQ. The coordinate space operator corresponding to PHQ will be found in the same way that the coordinate space operator corresponding to PHP was found. The major difference between the two is the integral over free electronic states in PHQ. In coordinate space we have
Once again we will first consider \( \langle -1|H|k \rangle \). In coordinate space it is

\[
\langle \mathbf{R}_1<-1|H|\mathbf{R}'> \rangle = \int d\mathbf{r} \Phi^* \mathcal{J} \Phi' \mathbf{R}_1 \langle \mathbf{R}_1<-1|H|\mathbf{R} \rangle \langle \mathbf{R} | \mathbf{R}' \rangle
\]

2.66

\[
\langle \mathbf{R}_1<-1|H|\mathbf{R} \rangle \langle \mathbf{R} | \mathbf{R}' \rangle 
= \int d\mathbf{r} \Phi^* \mathcal{J} \Phi' \mathbf{R}_1 \langle \mathbf{R}_1<-1|H|\mathbf{R} \rangle \langle \mathbf{R} | \mathbf{R}' \rangle
\]

2.67

\[
\Phi^*_n(\mathbf{r}^\ast) \left[ H(\mathbf{r}^\ast) \Phi_n(\mathbf{r}^\ast) \right] \Phi^*\Phi' \mathbf{R}_1 \langle \mathbf{R}_1<-1|H|\mathbf{R} \rangle \langle \mathbf{R} | \mathbf{R}' \rangle
\]

2.68

As before, this is

\[
\langle \mathbf{R}_1<-1|H|\mathbf{R} \rangle \langle \mathbf{R} | \mathbf{R}' \rangle 
= \int d\mathbf{r} \Phi^* \mathcal{J} \Phi' \mathbf{R}_1 \langle \mathbf{R}_1<-1|H|\mathbf{R} \rangle \langle \mathbf{R} | \mathbf{R}' \rangle
\]

2.69

Once again the nuclear kinetic energy operates on a delta
function. Integrating by parts as before will give us the off-diagonal elements of the matrix \( P_{k-r} \) (eq. 2.10). Since (iii) this has been assumed to be negligible, we have

\[ \langle R|<111111111R'>\rangle = \delta(R-R') \Lambda_{-h}(R') \quad 2.70 \]

Substituting this into eq. 2.85 will give us

\[ \langle RHPQ1\Phi\rangle = \text{Sol} R' \text{Sol} k \rho_k \langle R-1 \rangle \text{Sol} R'' \langle 1R'' \rangle \]

\[ \langle R'1<111111111R'\rangle \text{Sol} R'' \langle 1R'' \rangle R' \]

\[ \langle R|1R'XR'1\Phi\rangle \]

\[ \langle RHPQ1\Phi\rangle = \text{Sol} R' \text{Sol} k \rho_k \varphi_{-n}(R') \langle R1 \rangle \text{Sol} R'' \langle 1R'' \rangle \]

\[ \text{Sol} R'' \Lambda_{-h}(R'') \delta(R''-R') \langle R''|1R'\rangle \varphi_{h}(R') \bar{\psi}(R') \quad 2.72 \]

\[ \langle RHPQ1\Phi\rangle = \text{Sol} k \rho_k \varphi_{-n}(R) \nabla_{-h}(R) \psi_{-h}(R) \quad 2.73 \]

\[ \nabla_{-h} = -\Lambda_{-h}(R) \]

Coordinate space forms of QHQ and QHP may be derived in the same way. Then we have

\[ \langle R|QHQ1\Phi\rangle = \text{Sol} k \rho_k \varphi_{h}(R) H_{kh}(R) \psi_{k}(R) \quad 2.74 \]
\[ \langle \mathbf{R} | \mathbf{H} | \mathbf{P} \rangle = \int d^3 \mathbf{r} \rho_\mathbf{R} \varphi_\mathbf{R}(\mathbf{r}) V_{\mathbf{R} \mathbf{p}}(\mathbf{r}) \mathit{u}_\mathbf{p}(\mathbf{r}) \]

The coordinate representations of eqs. 2.40 are therefore

\[ \varphi_{-i}(\mathbf{r}) \left( \mathbf{E} - H_{-i}(\mathbf{r}) \right) \mathit{u}_{-i}(\mathbf{r}) = \varphi_{-i}(\mathbf{r}) \int d^3 \mathbf{r} \rho_\mathbf{R} \mathit{V}_{-i \mathbf{R}}(\mathbf{r}) \mathit{u}_\mathbf{R}(\mathbf{r}) \]

\[ \int d^3 \mathbf{r} \rho_\mathbf{R} \varphi_\mathbf{R}(\mathbf{r}) \left( \mathbf{E} - H_{\mathbf{R}}(\mathbf{r}) \right) \mathit{u}_{\mathbf{R}}(\mathbf{r}) = \int d^3 \mathbf{r} \rho_\mathbf{R} \varphi_\mathbf{R}(\mathbf{r}) \mathit{V}_{\mathbf{R} - i}(\mathbf{r}) \mathit{u}_{-i}(\mathbf{r}) \]

Now using the orthogonality of the \( \varphi_i \)'s we have

\[ \left( \mathbf{E} - H_{-i}(\mathbf{r}) \right) \mathit{u}_{-i}(\mathbf{r}) = \int d^3 \mathbf{r} \rho_\mathbf{R} \mathit{V}_{-i \mathbf{R}}(\mathbf{r}) \mathit{u}_\mathbf{R}(\mathbf{r}) \]

\[ \left( \mathbf{E} - H_{\mathbf{R}}(\mathbf{r}) \right) \mathit{u}_{\mathbf{R}}(\mathbf{r}) = \mathit{V}_{\mathbf{R} - i}(\mathbf{r}) \mathit{u}_{-i}(\mathbf{r}) \]

which is the desired result. Then eqs. 2.40 are the vector form of the coupled integro-differential equations derived in the preceding section.

B. Boundary Conditions

Associative detachment (AD) is set apart from
direct detachment by the boundary conditions of the reaction. The energy of the collision is usually below the asymptotic limit of $V_{\infty}(\infty)$, so that the only reaction possible is AD. This results in a free electron and a bound molecule. The molecule may be vibrationally excited, but as discussed earlier, in assumption (xix), there is negligible change in the nuclear rotational angular momentum. Then when the nuclei are far apart, the only state that is accessible to the system is that in which the electron is bound. Thus the first boundary condition is:

$$\lim_{R \to \infty} \Psi(F; R) = \lim_{R \to \infty} \varphi_{-i}(F; R) \ U_{-i}(R)$$ 2.77

As the electronic coordinate $r$ becomes large, the bound electronic wave function $\varphi_{-i}(F; R)$ vanishes, so that the only contribution to $\Psi$ comes from free electron states. Then

$$\lim_{R \to \infty} \Psi(F; R) = \lim_{R \to \infty} \int d\Phi_k \varphi_k(F; R) \ U_k(R)$$ 2.78

There is one further problem to be considered. Eq. 2.40 involves an integral over all continuum energies, however the molecule has only a few quantum mechanically allowed bound states, for which the wave functions $\psi_n$ are solutions to the homogeneous continuum Hamiltonian

$$\hat{H}_{\infty}(R) \psi_n(R) = E_n \psi_n(R)$$ 2.79
where

\[ H_{oo}(R) = V_{oo}(R) - \frac{k^2}{\epsilon^2} \frac{d^2}{dR^2} \]

Now conservation of energy implies that the total initial energy \( E \) must be equal to the final energy \( E_m + \varepsilon_h \), where again \( E_m \) is the (discrete) energy of the \( n \)th bound vibrational state of the molecule, and \( \varepsilon_h \) is the energy of the escaping electron. It follows that as \( r \to \infty \), the integral over \( k \) must collapse into a discrete sum, with

\[ \varepsilon_{k_m} = E - E_m \]

The boundary conditions can then be expressed in the following way. The wave functions \( \psi_{m} (R) \) form a complete set and therefore the continuum functions \( \psi_{k} \) may be written in terms of them:

\[ \psi_{k} (R) = \sum_{m \geq 0} \alpha_{m}^{k} \psi_{m} (R) \]

where \( \alpha_{m}^{k} \) is defined by

\[ \alpha_{m}^{k} = \int dR_{1} \int dR_{2} \psi_{m}^{*} (R_{1}) \Phi_{m}^{*} (R_{1}; R_{2}) \overline{\psi} (R_{2}; R) \]

Then as \( r \to \infty \), the full wave function must be

\[ \omega_{m} \psi_{m} (R) = \frac{\xi}{\tau} \alpha_{m}^{\omega} \Phi_{m} (R; \overline{R}) \psi_{m} (R) \]
A proof of this result, that the integral (2.47) reduces to the discrete sum (2.84) is given in Appendix B. Also, boundary conditions for the reverse process, dissociative attachment, and for direct detachment are given in Appendix C.

F. Summary

An infinite set of coupled integro-differential equations has been derived for a carefully chosen electron basis set. The assumptions which were made about the electron basis set and the matrices $h$ and $P$ are similar to those which had been used by Wang and Delos. However in the present work, the nuclei are treated quantum mechanically rather than semi-classically. The boundary conditions for associative detachment have been discussed and these may easily be extended to apply to direct detachment. In the next chapter the coupled equations 2.40 will be uncoupled using a Greens function solution to the continuum equation.
CHAPTER III
AN INTEGRAL-DIFFERENTIAL EQUATION
FOR THE NEGATIVE ION WAVE FUNCTION

A. Introduction

The coupled equations 2.40 may be uncoupled using a Green's function solution to the continuum equation 2.40b. The resulting equation, when transformed into coordinate space, is an integro-differential equation which has as its solution the wave function \( u(R) \).

B. The Continuum Green's Function

The projection of \( |\Psi\rangle \) onto the continuum states, \( Q|\xi\rangle \), may be found in terms of its projection onto the bound state \( P_i|\Phi\rangle \) using a Green's function \( G_q \). \( G_q \) is the solution to

\[
(\varepsilon - q H) G_q = q
\]

so that

\[
G_q = (\varepsilon - q H)^{-1} q
\]

Normally the operator form of a Green's function is the
solution to

\[(E - H)Q = 1 \tag{3.3}\]

Here the matrix \(Q\) is a unit matrix for the continuum, which is a restricted portion of the vector space (the full vector space has \(P+Q\) as its unit operator). Since the equation which is to be solved using the Green's function is restricted to the continuum, \(Q\) may be used as a unit matrix in this derivation. Then with the continuum equation

\[(E - Q \cdot HA - W) \langle \Psi | Q \cdot R \cdot \Phi \rangle = \langle \Psi | Q \cdot R \cdot \Phi \rangle \tag{2.40b}\]

we have

\[Q \langle \Psi | = (E - Q \cdot HA)^{-1} Q \cdot A \cdot H \cdot P \cdot \Phi \rangle \tag{3.4}\]

\[Q \langle \Psi | = \langle Q \cdot A \cdot H \cdot P \cdot \Phi \rangle \tag{3.5}\]

By transforming eq. 3.3 to coordinate space, we will show that the coordinate space operator corresponding to \(Q\) is a Green's function.

\[\int dR' \langle \Phi | (E - Q \cdot HA) | R' \cdot \Phi' \rangle G_A(R') = \langle \Phi | Q \cdot \Phi' \rangle \tag{3.6}\]

\[\int dR' \{ E \langle \Phi | R' \rangle - \delta(R' - R) \int dR \int dR \int dR \int dR \int d\alpha \int d\alpha \int d\alpha \int d\alpha \} G_A(R'; \Phi') = \tag{3.7}\]

\[\int dR \int dR' \int d\alpha \int d\alpha \int d\alpha \int d\alpha \phi_A^*(R'; \Phi') \phi_A(R'; R') \delta(R - R') \]
The continuum electron states have the property that

\[ \int d^3 k \, \rho_k \, \alpha^*_k (\mathbf{r} ; \mathbf{R}) \, \alpha_k (\mathbf{r}' ; \mathbf{R}') = \delta (\mathbf{R} - \mathbf{R}') \]  

\[ \alpha_k (\mathbf{r} ; \mathbf{R}) \to \int d^3 k \, \alpha_k (\mathbf{r} ; \mathbf{R'}) \, \alpha_k (\mathbf{r}' ; \mathbf{R}') \]  

Then

\[ (E - H_{\text{kh}}(\mathbf{R})) \,(\alpha_k (\mathbf{r} ; \mathbf{R}) \, \alpha_k (\mathbf{R}, \mathbf{R'})) = \alpha_k (\mathbf{R}, \mathbf{R'}) \, \delta (\mathbf{R} - \mathbf{R'}) \]  

\[ G_\mathbf{R} (\mathbf{R}, \mathbf{R'}) \] is the Green's function for the continuum Hamiltonian \( H_{\text{kh}}(\mathbf{R}) \).

\[ G_\mathbf{R} \] may also be written as a sum of solutions to the homogeneous equation

\[ (E - \omega^2 \mathbf{Q}) \, \chi_i > = \omega \chi_i > \]  

Recalling that

\[ \omega^2 \mathbf{Q} = \int d^3 k \, \rho_k \, \chi_k \chi_k \]  

\[ \langle \chi_k \chi_k \rangle = \int d^3 R \, \int d^3 R' \, [\alpha^*_k (\mathbf{R}) \, H(\mathbf{R}) \, \alpha_k (\mathbf{R'})] \, \delta (\mathbf{R} - \mathbf{R'}) \]  

with

\[ H_{\text{kh}}(\mathbf{R}) = \int d^3 k \, \alpha^*_k (\mathbf{R}) \, H(\mathbf{R}) \, \alpha_k (\mathbf{R}) \]  

we have

\[ H_{\text{kh}} = \langle \chi_k \chi_k \rangle \]  

\[ \langle \chi_k \chi_k \rangle = \int d^3 R \, \int d^3 R' \, H_{\text{kh}}(\mathbf{R}) \, \chi_k (\mathbf{R}) \]
Then, since

$$V_{n,k}(R) = V_{oo}(R) + E_n$$  \hspace{1cm} 2.17

$$Q_{n,m} = \int dA \rho_n (E_n + V_{oo} + T) <k|$$  \hspace{1cm} 3.14

The complete set of state vectors $|\psi\rangle$ with eigenvalues $E_n$ defined in eqs. 2.79 and 2.80 are solutions to

$$(T + V_{oo}) |\psi\rangle = E \psi |\psi\rangle$$  \hspace{1cm} 3.15

These represent the eigenstates for nuclear motion in the potential energy $V_{oo}(R)$. For $n < V_{oo}(\infty)$, $|\psi\rangle$ is the $n^{th}$ vibrational state. (For higher energies, the state vector represents free nuclei and the sum over $n$ becomes an integral over free states. As described in Appendix B, the free states result from direct detachment, while the bound states are the result of associative detachment.) Then with

$$(E - Q_{n,m}) |\psi\rangle = (E - E_n - E_m) |\psi\rangle$$  \hspace{1cm} 3.16

we may write $Q_{n,m}$ as

$$Q_{n,m} = \frac{\sum k \rho_k}{\delta E_n - \delta E_m}$$  \hspace{1cm} 3.17
This is a solution to 3.1, as may be seen by bringing \((E-QHQ)\) inside the sum and integral:

\[
(E - QHQ) G_a = \sum_k \frac{\delta \theta_k \rho_k (E - QHQ) 1_k \left| 1_{\text{max}} \times m \leq k \right)}{E - E_m - E_k} \tag{3.18}
\]

\[
(E - QHQ) G_a = \sum_k \delta \theta_k \rho_k \left| 1_k \right> \left< 1_{\text{max}} \times m \leq k \right) \tag{3.19}
\]

\[
(E - QHQ) G_a = Q \tag{3.20}
\]

since the nuclear state vectors \(1_{\omega} \rangle\) form a complete set.

With this definition of \(G_Q\), we are ready to uncouple eqs. 2.40. The projection \(Q | \gamma \rangle\) may be written in terms of \(P | \gamma \rangle\) using \(G_Q\).

\[
(E-QHQ)\, Q | \gamma \rangle = QHQP | \gamma \rangle \tag{2.40b}
\]

\[
Q | \gamma \rangle = G_Q\, QHQP | \gamma \rangle \tag{3.21}
\]

\[
Q | \gamma \rangle = \sum_k \delta \theta_k \rho_k \frac{1_k \left< 1_{\text{max}} \times m \leq k \right|}{E - E_m - E_k} QHQP | \gamma \rangle \tag{3.22}
\]

Then 3.22 may be used in 2.40a to give an equation for
The orthogonality properties of the state vectors \( \{n\} \) given in eqs. 2.28 to 2.43 may be used to simplify eq. 3.23.

\[
(E - PhP) |P\rangle = PHQ \left( \sum \frac{n \times \langle m | H | k \rangle}{E - E_m - E_k} \right) \langle \phi | H | P \rangle |E\rangle
\]

Substituting \( \Gamma^\dagger \psi \) for \( P \), eq. 3.25 may be written as

\[
1 \rightarrow (E - \langle \Gamma | H | \psi \rangle) |1\rangle \langle 1| = 1 \rightarrow \left( \sum \frac{n \times \langle m | H | k \rangle}{E - E_m - E_k} \langle \phi | H | P \rangle |E\rangle \right) |1\rangle \langle 1|
\]
This may be written more compactly as

\[
(E - H_{-1})|\psi\rangle = \int dk \rho_k H_{-1k} \frac{(m \times m')}{E - E_{\omega_k} - E_{\omega'} - i\epsilon} |\psi\rangle
\]

3.27

Now defining an operator \( G_{-1} \) as

\[
G_{-1} = \int dk \rho_k H_{-1k} \frac{(m \times m')}{E - E_{\omega_k} - E_{\omega'} - i\epsilon} \]

3.28

allows us to write

\[
(E - H_{-1})|\psi\rangle = G_{-1}|\psi\rangle
\]

3.29

As will be seen in the next section, eq. 3.29 is an integro-differential equation for \( u_{-1}(R) \).

C. The Green's Function in Coordinate Space

In this section \( G_{-1} \) will be transformed to the coordinate space function \( G_{-1}(R, R') \) which will be evaluated using an approximation to the \( k \) dependence of the coupling potential energy \( V_{-1k}(R) \). Since the electronic and nuclear basis states are independent of each other, the integration
over \( k \) in eq. 3.26 may be performed without affecting the state vectors.

Defining \( G_{-1}(R,R') \) as the coordinate space version of \( G_{-1} \),

\[
G_{-1}(R,R') = \langle R | G_{-1} | R' \rangle \tag{3.30}
\]

Using 3.28, this is

\[
G_{-1}(R,R') = \langle R | \sum_k \rho_k \hat{H}_{-1,k} \sum_{\alpha} \frac{|m\alpha x c\alpha |}{E - E_{\alpha} - E_k} | H_{-1,k} | R' \rangle \]

Now we must have

\[
\langle R | H_{-1,k} | R' \rangle = V_{-1,k}(R') \delta(R - R') \tag{3.32}
\]

so that, with the Hamiltonian of II B,

\[
G_{-1}(R,R') = \sum_k \rho_k V_{-1,k}(R) \sum_{\alpha} \frac{|m\alpha x c\alpha |}{E - E_{\alpha} - E_k} \langle R | \sum_k \rho_k \hat{H}_{-1,k} | R' \rangle \tag{3.33}
\]

Now the vector states \( |m\alpha x c\alpha \rangle \) are eigenfunctions of the
then correspond to the eigenfunctions of the Hamiltonian $\hat{H}$ discussed in II 

$$\psi_{n} = \langle R | n \rangle $$

Then with 

$$\psi_{n} = \langle R | n \rangle $$

as in eq. 2.27, we have 

$$\int_{\mathcal{R}} \mathcal{R}' G_{-1}(\mathcal{R},\mathcal{R}') \psi_{-1}(\mathcal{R}') =$$

$$\int_{\mathcal{R}} \int_{\mathcal{R}'} \psi_{m}(\mathcal{R}) \frac{\psi_{-1}(\mathcal{R})}{E - E_{m} - E_{k}} \psi_{m}(\mathcal{R}') \psi_{-1}(\mathcal{R}')$$

Now defining $l_{m}(\mathcal{R},\mathcal{R}')$ as 

$$l_{m}(\mathcal{R},\mathcal{R}') = \int_{\mathcal{R}} \frac{\psi_{m}(\mathcal{R})}{E - E_{m} - E_{k}}$$

we may write $G_{-1}(\mathcal{R},\mathcal{R}')$ as 

$$G_{-1}(\mathcal{R},\mathcal{R}') = \int_{\mathcal{R}} \frac{\psi_{m}(\mathcal{R})}{E - E_{m} - E_{k}} l_{m}(\mathcal{R},\mathcal{R}') \psi_{m}(\mathcal{R}')$$
$V_{k-1}(R)$ is given in Appendix A for a square well potential energy with one bound state and a continuum of free states. The integral $I_m(R, R')$ was evaluated numerically by Taylor and Delos for the case in which $V$ has no $R$ dependence. We will take $V_{k-1}(R)$ to have a separable $R$ and $\phi_n$ dependence.

$$V_{k-1}(R) = \phi_n(R) \phi_{n-1}$$

Then

$$C_{k-1}(R, R') = \frac{\mathcal{L}}{\mathcal{M}} \mathcal{V}_n(R) \rho(R) \int \frac{d\rho}{4\pi} \frac{C_{n-1} \phi_{n-1}}{E - E_m - E_n} \phi_n(R') \mathcal{V}_m(R')$$

The following was found to be a good approximation to the numerical evaluation of the integral $I_m$.

$$I_m(R, R') = \frac{3}{\mathcal{M}} \left( \frac{a_e}{2 \mathcal{M}_e} \right)^{1/2} g(R) g(R') \frac{\alpha}{E - E_m - E_n} \quad E \leq E_m$$

$$I_m(R, R') = \frac{3}{\mathcal{M}} \left( \frac{a_e}{2 \mathcal{M}_e} \right)^{1/2} g(R) g(R') 2 \alpha \quad E \geq E_m$$

$$\phi_{n-1} = \frac{a_e + a_n (E - E_m)}{(E - E_m - a_s)^2} + \frac{a_s (E - E_m)^{1/2}}{(E - E_m + a_s)}$$
\[ a_1 = 2.017 \quad a_5 = 0.909 \]
\[ a_2 = 1.0826 \quad a_6 = -1.4356 \]
\[ a_3 = -1.5915 \quad a_7 = 0.105 \]
\[ a_4 = 28.5304 \]

Then with \( I_{\alpha}(R, R') \) of eqs. 3.42, eq. 3.39 may be written

\[
C_{\alpha}(R, R') = \frac{2}{\hbar N} \left( \frac{2 \pi}{\hbar} \right)^{3/2} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \sum_{n=0}^{N_{\text{max}}} \frac{|\alpha_n\rangle g(R) \psi_n(R) \psi_n(R') g(R')}{E_n - E_n - E_0}
\]

This sum over \( n \) is a sum over eigenstates, which have eigenvalues \( E_n \). Since \( \alpha_n \) is defined only for \( n \) such that \( E > E_n \), there may be only a finite number of terms in the first sum. \( E_{\text{max}} \) is the highest eigenvalue which is smaller than \( E \). The second sum contains all the terms for which \( E < E_n \). In physical terms, \( E_{\text{max}} \) is the energy of the highest allowed vibrational state, \( n_{\text{max}} \) being the vibrational quantum number for that state. The second sum is then a sum over forbidden states, since their energies are higher than the total kinetic energy \( E \).

Equation 3.43 may be rewritten in such a way that the second term becomes a Green's function of the Hamiltonian \( H_{\alpha\alpha}(R) \). First we will define \( \lambda_n \) as

\[
\lambda_n = \frac{2}{\hbar N} \left( \frac{2 \pi}{\hbar} \right)^{3/2} \left( \alpha_n - \frac{\alpha}{E - E_n - E_0} \right) \quad n \leq N_{\text{max}} \]
Then eq. 3.42 is

\[ G_{-1}(R, R') = \sum_{m=0}^{\text{Max}} \lambda_m g(R) v_m(R) v_m(R') g(R') \]

\[ + \frac{2}{\pi n} \left( \frac{R^2}{\alpha m} \right)^{1/2} \alpha \frac{\pi}{m=0} g(R) \frac{v_m(R) v_m(R')}{E - E_m - \alpha} g(R') \]

Let us consider the second term

\[ \frac{2}{\pi n} \left( \frac{R^2}{\alpha m} \right)^{1/2} \alpha \frac{\pi}{m=0} g(R) \frac{v_m(R) v_m(R')}{E - E_m - \alpha} g(R') \]

Now \( v_m(R) \) is an eigenfunction of the Hamiltonian \( H_{ee} (R) \), and the Green's function of this Hamiltonian may be written as

\[ \mathcal{G}_{-\alpha_e} (R, R') = \sum_{m=0}^{\text{Max}} \frac{v_m(R) v_m(R')}{E - E_m - \alpha_e} \]

with

\[ (E - \alpha_e - H_{ee} (R)) v_m \equiv (E - \alpha_e - E_m) v_m \]

Then eq. 3.45 contains a Green's function of the equation

\[ (E - \alpha_e - H_{ee}) \mathcal{G}_{-\alpha_e} (R, R') = \delta(R-R') \]

The 'energy' in eq. 3.49 has been shifted by an amount \( \alpha_e \). Then \( G_{-1} \) may be written as

\[ G_{-1}(R, R') = \sum_{m=0}^{\text{Max}} \lambda_m g(R) v_m(R) v_m(R') g(R') \]

\[ + C g(R) \mathcal{G}_{-\alpha_e} (R, R') g(R') \]
The function $\mathcal{J}$ may also be written as a product of solutions to the homogeneous equation

$$ (E - \mathcal{Q}_t - H_{so}(R)) \psi(R) = 0 \quad 3.51 $$

Since the shifted energy is unlikely to be an eigenstate of the Hamiltonian, there are no solutions which fulfill the boundary conditions. Of the two solutions, one ($\psi_<(R)$) is finite at the origin and infinite at $R \to \infty$, while the other ($\psi_>(R)$) is finite at large $R$ and infinite at the origin. With $W$ as the Wronskian of these two functions, we may write

$$ \mathcal{J}(R,R') = \frac{1}{W} \psi_<(R_4) \psi_>(R_5) \quad R_4, R_5 = R, R' \quad 3.52 $$

$$ W = \psi_<(R) \frac{d}{dR} \psi_>(R) - \left( \frac{d}{dR} \psi_<(R) \right) \psi_>(R) \quad 3.53 $$

where $R_<$ and $R_>$ are the smaller and larger of $R$ and $R'$,
respectively. A good approximation to the eigenfunctions \( \psi_m \) and \( \psi_s(R) \) may be found using the WKB approximation, with Airy functions used at the turning points. This is discussed in Appendix C.

D. An Integro-Differential Equation

We have found the representation of the operator \( G \) in coordinate space, and now must transform the rest of eq. 3.29 into coordinate space.

\[
\langle E - \mathcal{H}_{-\nu} \rangle |\psi\rangle = C_{-\nu} |\psi\rangle
\]

3.29

\[
\int dR' \langle R | (E - \mathcal{H}_{-\nu}) | R' \rangle \langle R' | \psi \rangle = \int dR' \langle R | C_{-\nu} | R' \rangle \langle R' | \psi \rangle
\]

3.55

Now by eqs. 3.30 and 2.29, the right hand side of this is

\[
\int dR' G_{-\nu}(R, R') U_{-\nu}(R')
\]

3.56

and the left side is

\[
\int dR' (E - \mathcal{H}_{-\nu}(R')) \delta(R-R') U_{-\nu}(R')
\]

3.57

which was shown in section II D. to be

\[
(E - V_{-\nu}(R) + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2}) U_{-\nu}(R)
\]

3.58
we then have an integro-differential equation for the wave function \( u_{-1}(R) \):

\[
(E - V_{-1}(R) + \frac{a^2}{R} \frac{d^2}{dR^2}) u_{-1}(R) = \\
\int_0^{\infty} dR' G_{-1}(R, R') u_{-1}(R')
\]

This is a single integro-differential equation for \( u_{-1}(R) \); it describes the effects of transitions into and out of the allowed bound states by means of the term on the right hand side containing the Green's function.

E. Summary

An integro-differential equation has been found for the wave function \( u_{-1}(R) \) using a Green's function solution to the continuum equation 2.406. The function \( G_{-1}(R, R') \) which describes transitions into and out of the continuum contains two parts: a sum over the allowed bound vibrational states, and a Green's function with a shifted energy, \( E - a_2 \). For energies below \( a_2 \), the contribution of the second term is negligible, so that the only transitions which need be considered are to and from the bound states. In the next chapter a zero order solution to eq. 3.57 will be found using the semiclassical approximation. This in turn will be used to find a first order solution to eq. 3.57.
A. Introduction

In the previous chapter we derived an integro-differential equation which has as its solution the nuclear wave function for the negative ion state $u_{-, \lambda} (R)$. In this chapter the wave function $u_{-, \lambda} (R)$ will be found to zero order and to first order. Transitions into and out of the continuum, which are neglected in the zero order approximation, are included in the first order approximation.

B. A Zero Order Wave Function

The integro-differential equation for the negative ion wave function may be solved to zero order using the semiclassical approximation. This is based upon the assumption that the momentum of the negative ion does not change significantly with $R$, so that $\xi \varphi_{-, \lambda} (R) \ll \varphi_{-, \lambda}^2 (R)$ throughout most of the collision, i.e. away from the classical turning points. The momentum $\varphi_{-, \lambda} (R)$ is defined in the usual way:

$$\varphi_{-, \lambda} (R) = \left[ 2 m (E - V_{-, \lambda} (R)) \right]^{\frac{1}{2}}$$ 4.1
In the zero-order approximation the coupling between the discrete state and the continuum is neglected. The zero order wave function \( \psi_0(x) \) is then the approximate solution to the homogeneous equation

\[
(E - H_n) \psi_0(x) = 0
\]

With eq. 4.1 and

\[
H_n(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_n(x)
\]

we have

\[
\left( \frac{\partial^2}{\partial x^2} + \frac{\hbar^2}{2m} \right) \psi_n(x) = 0
\]

so that away from the turning points where \( \Theta_n(x) = 0 \),

\[
\psi_n(x) = -i \left( \frac{\hbar}{\pi} \right)^{1/2} \left( e^{\frac{i}{\hbar} \int \Theta_n(x') dx'} + e^{-\frac{i}{\hbar} \int \Theta_n(x') dx'} \right)
\]

The phases \( \pm \pi/4 \) have been added so that the wave function has the form which an Airy function \( \text{Ai}(x) \) has as \( x \) becomes large. Near the turning points the potential may be approximated as a straight line. Then the solution to eq. 4.2 is a linear combination of Airy functions \( \text{Ai}(a(R-R_v)) \) and \( \text{Bi}(a(R-R_v)) \). To the left of the turning point (in the forbidden region) we know that the wave function must decrease exponentially. Eq. 4.5 is still valid but the momentum is imaginary in that region so that the zero order solution is

\[
\rho_n(x) = \frac{1}{\Theta_n'} \left[ \int_{R_v}^{R} \rho_{n'}(x') dx' \right]
\]

\( R < R_v \)
where the exponentially increasing part of the solution has been discarded. Now eq. 4.6 is the asymptotic form of 
\( \text{Ai}(a(R-R_{np})) \) as \( a(R-R_{np}) \to \infty \). Then, since the asymptotic form of \( \text{Bi}(a(R-R_{np})) \) is the (discarded) exponentially increasing solution, we may say

\[
\mu_{\infty, i}^0(R) = \text{Ai}(-\alpha(R-R_{np})) \quad R > R_{np}  \tag{4.7}
\]

\[
\frac{d^2}{dR^2} \mu_{\infty, i}^0(R) = \frac{2\mu_i}{a} \nu_{\infty, i}'(R_{np}) (R-R_{np}) \mu_{\infty, i}^0(R) \quad R > R_{np}  \tag{4.8}
\]

with

\[
\alpha = \left[ \frac{4\mu_i}{a} |\nu_{\infty, i}'(R_{np})| \right]^{\frac{1}{2}} \tag{4.9}
\]

Then the wave function to zero order is:

\[
\mu_{\infty, i}^0(R) = \begin{cases} 
2c \left( \frac{\mu_i}{\sigma_{\infty}} \right)^{\frac{1}{2}} \sin \left( \frac{R_{np}}{a} \nu_{\infty, i}(R) \right) R > R_{np} \\
2c' \text{Ai}(-\alpha(R-R_{np})) \quad R > R_{np} \tag{4.10} \\
\left( \frac{\mu_i}{\sigma_{\infty}} \right)^{\frac{1}{2}} e^{-\int_{R_{np}}^R \nu_{\infty, i}(R') dR'} R < R_{np} 
\end{cases}
\]

The constants \( C \) and \( C' \) are determined by the condition that \( \mu_{\infty, i}^0(R) \) be a smooth continuous function of \( R \).

\[
C = 1  \tag{4.11}
\]

\[
C' = 2c \left[ \frac{2\mu_i}{a} |\nu_{\infty, i}'(R_{np})| \right]^{\frac{1}{2}}
\]
C. A First Order Solution

1. A Semi-Classical Approximation

As stated above, the zero order solution describes an elastic collision with no possible transitions. We are now ready to find a first order solution to the integro-differential equation (14). The wave function $u_{-1}(R)$ may be written in terms of an incoming part and an outgoing part:

$$u_{-1}(R) = -i\sqrt{\hbar} \left( \exp\left(\frac{i}{\hbar} \left( \int_0^R \varphi_1 dR' + \int_0^R f_1 dR' \right) + i\beta \nu \right) \right)$$

$$- \exp\left(\frac{i}{\hbar} \left( \int_0^R \varphi_1 dR' + \int_0^R f_1 dR' \right) - i\beta \nu \right) \right) \quad 4.12$$

Again, the phases are included so that the wave function is in the form which an Airy function $Ai(x)$ takes at large negative $x$. Since there is only one equation (4.5) and there are two unknowns, we are free to choose $f_+$ and $f_-$ in such a way that

$$f_+(R) \exp\left[ \frac{i}{\hbar} \left( \int_0^R \varphi_1 dR' + \int_0^R f_1 dR' \right) + i\beta \nu \right] + f_-(R) \exp\left[ -\frac{i}{\hbar} \left( \int_0^R \varphi_1 dR' + \int_0^R f_1 dR' \right) - i\beta \nu \right] = 0 \quad 4.13$$

Then the derivatives of $u_{-1}(R)$ are

$$\frac{d u_{-1}(R)}{dR} = -i\sqrt{\hbar} \left( \frac{i}{\hbar} \int_0^R \exp\left[ \frac{i}{\hbar} \left( \int_0^R \varphi_1 dR' + \int_0^R f_1 dR' \right) + i\beta \nu \right] \right)$$

$$+ \exp\left[ -\frac{i}{\hbar} \left( \int_0^R \varphi_1 dR' + \int_0^R f_1 dR' \right) - i\beta \nu \right] \right) \quad 4.14$$
\[
\frac{d^2 u_{\pm}}{d R^2} = -\frac{\partial^2}{\partial R^2} u_{\pm}(R) + \frac{\mu^2}{4} \left\{ \left( \frac{1}{\hbar} \right)^2 - \frac{\mu^2}{4} \right\} u_{\pm}(R)
\]

\[
\exp\left[ -\frac{i}{\hbar} \left\{ \frac{\partial}{\partial R} + \frac{\mu^2}{4} \right\} + \frac{i\mu^2}{4} \right]
\]

\[
\left( \frac{1}{\hbar} \right)^2 + \frac{\mu^2}{4} \exp\left[ -\frac{i}{\hbar} \left\{ \frac{\partial}{\partial R} + \frac{\mu^2}{4} \right\} \right]
\]

By substituting this form of \( u_{\pm}(R) \) into eq. 3.57, an equation for \( f_+ \) and \( f_- \) may be found which is valid in the allowed region. Now with the momentum of eq. 4.1, we may write the integro-differential equation (3.57) as

\[
\left( \frac{\partial^2}{\partial R^2} + \frac{\mu^2}{4} \right) u_{\pm}(R) = \frac{2\pi}{\hbar} \int dR' G_{\pm}(R,R') u_{\pm}(R')
\]

and using eqs 4.2 to 4.4, we have the following equation.

\[
\frac{1}{\hbar} \left\{ \left( \frac{1}{\hbar} \right)^2 - \frac{\mu^2}{4} \right\} \exp\left[ -\frac{i}{\hbar} \left\{ \frac{\partial}{\partial R} + \frac{\mu^2}{4} \right\} + \frac{i\mu^2}{4} \right]
\]

\[
\left( \frac{1}{\hbar} \right)^2 + \frac{\mu^2}{4} \exp\left[ -\frac{i}{\hbar} \left\{ \frac{\partial}{\partial R} + \frac{\mu^2}{4} \right\} \right]
\]

\[
= \frac{2\pi}{\hbar} \int dR' G_{\pm}(R,R') u_{\pm}(R')
\]

This may be partially uncoupled using the condition given in eq. 4.13.
\[
\phi_s(R) = \frac{i k \phi_n'}{2 \sigma_s} \left( 1 + e^{\mp \frac{i}{\hbar} \left( \int_{R_s}^R \rho_n \phi_n' \phi_n'' - \int_{R_s}^R \phi_n^* \phi_n \right) \phi_n' + \frac{k}{h} \left( f_s + f_n \right) \phi_n' dR' - i \eta_R \right) \right)
\]

\[
-i \frac{i k \rho_n'}{2 \sigma_s} \left( e^{\mp \frac{i}{\hbar} \left( \int_{R_s}^R \rho_n \phi_n' \phi_n'' - \int_{R_s}^R \phi_n^* \phi_n \right) \phi_n' + \frac{k}{h} \left( f_s + f_n \right) \phi_n' dR' - i \eta_R \right) \right)
\]

The equations may be simplified further using the following approximation. To the right of the turning point, \( \Phi_s(R) \) is purely real and \( e^{\mp \frac{i}{\hbar} \left( \int_{R_s}^R r \rho_n \phi_n' \phi_n'' - \int_{R_s}^R \phi_n^* \phi_n \right) \phi_n' + \frac{k}{h} \left( f_s + f_n \right) \phi_n' dR' - i \eta_R \) is rapidly oscillatory. In addition, \( \hbar \Phi_s(R) \) is small compared to \( \Phi_s(R) \) over most of the space. Then

\[
\int_{R_s}^R \frac{\rho_n'}{2 \sigma_s} e^{\mp \frac{i}{\hbar} \left( \int_{R_s}^R r \rho_n \phi_n' \phi_n'' - \int_{R_s}^R \phi_n^* \phi_n \right) \phi_n' + \frac{k}{h} \left( f_s + f_n \right) \phi_n' dR' 
\]

so that the exponential parts of the first terms on the r.h.s of eqs. 4.18 and 4.19 may be dropped. Physically this means that the colliding nucleus is unlikely to change the direction of its motion from incoming to outgoing except through interaction with the continuum. We then have
A zero order approximation may be made to \( f_+ \) and \( f_- \) which will give the zero order wave function \( u_+^* (R) \). Then, away from the turning point

\[
\psi_+ (R) = \frac{i \hbar \partial}{\partial R} - i \frac{\imath \hbar}{\partial R} \left[ e^{\frac{i}{\hbar} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} \right)} - \imath \frac{\partial}{\partial R} \int_{r}^{R} G_+ (R', r') u_+ (r') \right]
\]

\[
f_+ (R) = \frac{i \hbar \partial}{2 \partial R} - i \frac{\imath \hbar}{2 \partial R} \left[ e^{\frac{i}{\hbar} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} \right)} + \imath \frac{\partial}{\partial R} \int_{r}^{R} G_+ (R', r') u_+ (r') \right]
\]

so that \( f_+^* \) and \( f_-^* \) are

\[
f_+^* (R) = -i \frac{\imath \hbar}{\partial R} e^{-\frac{i}{\hbar} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} \right)} - \imath \frac{\partial}{\partial R} \int_{r}^{R} G_+ (R', r') u_+ (r')
\]

\[
f_-^* (R) = i \frac{\imath \hbar}{\partial R} e^{\frac{i}{\hbar} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} \right)} + \imath \frac{\partial}{\partial R} \int_{r}^{R} G_+ (R', r') u_+ (r')
\]

We then have for \( u_{-1} (R) \),

\[
\varepsilon \times P \left( \frac{1}{2} \int_{r}^{R} G_+^* (r') \psi_+ (r') \right) = [\mathcal{G}_{-1} (R)]^{-1/2}
\]
When there are no transitions, \( f_+ \) and \( f_- \) are zero, so \( u_{-1}(R) \) is the zero order wave function found in the preceding section.

In finding \( f_+ \) and \( f_- \), an additional approximation is made: we assume that the transition term, containing \( G_{-1}(R,R') \), is small, and we will use in this term the zero order approximation to \( u_{-1}(R') \). Then using eqs. 4.22 and 4.23, we have

\[
\begin{align*}
    f_+(R) &= -i \sqrt{\theta_0} \ e^{-\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} - i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar} + \frac{i}{\hbar} \mathbf{q}_0 \cdot \mathbf{p}_0} \ \int \! dR' \ G_{-1}(R,R') \ u_{-1}(R') \ \quad 4.28 \\
    f_-(R) &= i \sqrt{\theta_0} \ e^{\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} + i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar} - \frac{i}{\hbar} \mathbf{q}_0 \cdot \mathbf{p}_0} \ \int \! dR' \ G_{-1}(R,R') \ u_{-1}(R') \ \quad 4.29
\end{align*}
\]

We may now write the first order wave function \( u_{-1}(R) \):

\[
\begin{align*}
    u_{-1}(R) &= -i \sqrt{\theta_0} \ \left\{ e^{\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} + i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} \ \exp \left[ \int \! dR' \ \frac{\mathbf{q}_0 \cdot \mathbf{p}_0}{\hbar} e^{-\frac{i}{\hbar} \mathbf{q}_0 \cdot \mathbf{p}_0 - i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} \right] \\
    &\quad \times \left[ G_{-1}(R,R') u_{-1}(R') \right] - e^{\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} - i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} \ \exp \left[ \int \! dR' \ \frac{\mathbf{q}_0 \cdot \mathbf{p}_0}{\hbar} e^{\frac{i}{\hbar} \mathbf{q}_0 \cdot \mathbf{p}_0 - i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} \right] \right\} \\
    &= -i \sqrt{\theta_0} \ \left[ e^{\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} + i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} \ \int \! dR' \ G_{-1}(R,R') u_{-1}(R') - e^{-\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} - i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} \ \int \! dR' \ G_{-1}(R,R') u_{-1}(R') \right] \\
    &= -i \sqrt{\theta_0} \ \left[ e^{\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} + i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} G_{-1}(R,R') u_{-1}(R') - e^{-\frac{i}{\hbar} \frac{\mathbf{p}_0 \cdot \mathbf{r}}{\hbar} - i \frac{\mathbf{q}_0 \cdot \mathbf{r}}{\hbar}} G_{-1}(R,R') u_{-1}(R') \right] \\
\end{align*}
\]

Eq. 4.30 is our basic formula for \( u_{-1}(R) \) in the classically
allowed region.

2. The Turning Point Region

It is clear that the solution found in the previous section is not valid near the turning point. One approach which may be taken in that region is the uniform approximation, in which the potential is assumed to be linear over a short range near the turning point so that \( u_1(R) \) may be written in terms of Airy functions may be found.

As before, the potential near \( R_{cp} \) may be approximated as a straight line using a Taylor expansion. Then the integro-differential equation is

\[
( - \frac{2m}{\hbar^2} V_{\infty}(R_{cp})(R-R_{cp}) + \frac{d^2}{dR^2} ) u_n(R) = \frac{A m}{\hbar^2} \int_{R_{cp}}^{R} G_{\infty}(R,R') u_n(R') dR'
\]

The solution to the corresponding homogeneous equation is known to be an Airy function. The Airy functions \( Ai \) and \( Bi \) and their derivatives \( Ai' \) and \( Bi' \) are related to the exponentials in eq. 4.1 by

\[
\int \frac{dR'}{\sqrt{R'}} e^{\frac{R'}{\hbar} \theta - \frac{2m}{\hbar^2} (R-R_{cp})} \rightarrow \frac{\sqrt{\pi}}{2} \left( Bi(-\alpha (R-R_{cp})) + iAi(-\alpha (R-R_{cp})) \right)
\]
Then replacing the exponentials of eq. 4.37 by their corresponding Airy functions, we have

\[ u_{-1}(R) = \frac{c'}{2 \pi} \left\{ (A_i - iB_i) e^{\frac{R}{2} \int_0^{R'} \frac{1}{R} \, dR'} - (A_i + iB_i) e^{-\frac{R}{2} \int_0^{R'} \frac{1}{R} \, dR'} \right\} \]

As before, there is one equation (4.31) and two unknowns. We will choose \( f^1_+ \) and \( f^1_- \) so that

\[ (A_i - iB_i) f^1_+ e^{\frac{R}{2} \int_0^{R'} \frac{1}{R} \, dR'} - (A_i + iB_i) v^1_- e^{-\frac{R}{2} \int_0^{R'} \frac{1}{R} \, dR'} = 0 \]

By replacing the Airy functions with their asymptotic forms for large \( R \), we may see that \( f^1_+ \) and \( f^1_- \) correspond to those defined in eq. 4.22 for the allowed region. Then the derivatives of \( u_{-1}(R) \) are

\[ \frac{du}{dR} = -c' \left\{ (A_i' - iB_i') e^{\frac{R}{2} \int_0^{R'} \frac{1}{R} \, dR'} + (A_i' + iB_i') e^{-\frac{R}{2} \int_0^{R'} \frac{1}{R} \, dR'} \right\} \]
$$\frac{d^2 u_j}{dx^2} = a^2 \left\{ (A \epsilon - iB \gamma) e^{\frac{2}{a} \int_0^x dt'} + \frac{1}{n} [ (A \epsilon + iB \gamma) f_1^\prime - (A \epsilon - iB \gamma) f_1^\prime ] \right\} \frac{e^{\frac{2}{a} \int_0^x dt'}} {\int_0^\infty d^2 R' G_{\infty}(R, R') u_\infty(R')}$$

Substituting this into eq. 4.31 gives us an equation for $f^\prime$ and $f^\prime_1$:

$$- a^2 \left\{ \frac{2}{a} \int_0^x (A \epsilon - iB \gamma) f_1^\prime e^{\frac{2}{a} \int_0^x dt'} + \frac{1}{n} [ (A \epsilon + iB \gamma) f_1^\prime e^{\frac{2}{a} \int_0^x dt'} - (A \epsilon - iB \gamma) f_1^\prime e^{\frac{2}{a} \int_0^x dt'} ] \right\} = \frac{2n}{k} \int_0^\infty d^2 R' G_{\infty}(R, R') u_\infty(R')$$

Using eq. 4.37, this may be written as

$$- \frac{ao^2}{2} \left\{ \left[ (A \epsilon - iB \gamma) - (A \epsilon + iB \gamma) \frac{B \gamma B}{A \epsilon + B \gamma} \right] f_1^\prime e^{\frac{2}{a} \int_0^x dt'} \right\} = \frac{2n}{k} \int_0^\infty d^2 R' G_{\infty}(R, R') u_\infty(R')$$

\[ f_1^\prime(R) e^{-\frac{4}{a} \int_0^R dR'} = \frac{2n}{k} \int_0^\infty d^2 R' G_{\infty}(R, R') u_\infty(R) \]

Now since
we have

\[ \omega(\alpha_i, \beta I) = \sqrt{\frac{2}{a}} \]

Now throughout this derivation, it has been assumed that \( G_{-1} \) is small. In addition, the region near the turning point where the Airy function solution is valid is very small. Therefore we will assume that

\[ \frac{\alpha}{a} (\alpha + i \beta) \]

Then

\[ \frac{\alpha}{a} \]

\[ \frac{\alpha}{a} \]

\[ \frac{\alpha}{a} \]

\[ \frac{\alpha}{a} \]
The wave function near the turning point is then

\[
\psi_{\pm}(R) = \frac{1}{\sqrt{2}} \left[ (a - i b) \exp \left( -\frac{i}{\sqrt{2}} \frac{\sqrt{R}}{\epsilon} \int dR' \left( \frac{a}{t} - t \frac{a}{A} \right) \right) + (a + i b) \exp \left( \frac{i}{\sqrt{2}} \frac{\sqrt{R}}{\epsilon} \int dR' \left( \frac{a}{t} + t \frac{a}{A} \right) \right) \right]
\]

Replacing the Airy functions in eq. 4.60 by the asymptotic forms at large negative \( R \) will give the wave function found in the previous section. Thus the two forms for \( \psi_{\pm}(R) \) are compatible.

3. The Forbidden Region

We must now find a solution to the integro-differential equation which is valid in the forbidden region. Care must be taken here since the wave function \( \psi_{\pm}(R) \) must go to zero at the origin. Therefore, \( \psi_{\pm}(R) \) must go to zero faster than \( R \) as \( R \to 0 \). In addition, our wave function in the forbidden region must match the turning point wave function in the region where both are valid. The wave function for the turning point region given in eq. 4.60 contains \( Bi(-a(R-R^p)) \), which becomes an exponentially increasing function at large \( -a(R-R^p) \), or at small \( R \). Then
it seems that replacing the Airy functions with \( \exp \left( \frac{\alpha}{\hbar} \right) \) in the forbidden region will give a wave function which does not satisfy the boundary conditions. Throughout this section, the exponentially increasing solution will be used in addition to the exponentially decreasing solution. In the end, it will be shown that the wave function obtained in this way does satisfy the boundary conditions. In addition, by keeping the exponentially increasing part of the wave function, transitions into and out of the continuum may be included. The alternative, using the zero order wave function to the left of the turning point, results in the omission of transitions between the continuum and negative ion states.

Now, we know that

\[
\lim_{R \to 0} \left| \sum_{n} \phi_{n}(R') dR' \right| = 0
\]

and we must have

\[
\lim_{R \to 0} u_{-}(R) = 0
\]

Suppose that

\[
u_{+}(R) = \frac{\sqrt{\alpha}}{\beta} \left( e^{\frac{\alpha}{\hbar} \sigma \cdot P_{F} \psi_{R} / \hbar - i e^{\frac{\alpha}{\hbar} \sigma \cdot P_{F} \psi_{R} / \hbar}} \right) e^{\frac{\alpha}{\hbar} \sigma \cdot P_{F} \psi_{R} / \hbar} 4.52
\]

Then in order that \( u_{-}(R) \) be zero at the origin, we must have
As before we have one equation and two unknowns. The condition on \( f^1 \) and \( f^2 \) is similar to that which was chosen in the allowed region (eq. 4.13):

\[
\frac{i}{\xi} \left( e^{\frac{i}{R^d} \sigma_{-r} dr'/\kappa} - i e^{\frac{i}{R^d} \sigma_{-r} dr/\kappa} \right) f^1(R) e^{\frac{i}{R^d} \sigma_{+r} dr} = 0 \quad 4.53
\]

That this condition is met by \( u_{-1}(R) \) will be shown in this section.

Now since the momentum in the forbidden region is purely imaginary, the integro-differential equation (3.59) may be written as


\[- \frac{\partial}{\partial R^2} + \frac{\partial}{\partial R^2} \] \( u_+ (R) = \frac{1}{R^2} \int dR' G_+ (R, R') u_+ (R') \) 4.57

so that with eqs. 4.52 and 4.56

\[- \frac{\partial}{\partial R^2} \left\{ \left( \frac{1}{2} \frac{\partial}{\partial R} f_+ (R) + 1 \sigma_{11} \right) \left( e^{- \frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} - e^{\frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} \right) \right\} e^{\frac{1}{2} \int dR' f_+ (R') \right\} + \left( \frac{1}{2} \frac{\partial}{\partial R} f_- (R) + 1 \sigma_{11}' \right) \left( e^{- \frac{1}{2} \frac{\partial}{\partial R} f_- (R)} - e^{\frac{1}{2} \frac{\partial}{\partial R} f_- (R)} \right) \right\} e^{\frac{1}{2} \int dR' f_- (R') \right\} + i e^{\frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} \right\} e^{- \frac{1}{2} \int dR' f_+ (R')} = \frac{\alpha}{\hbar} \int dR' G_+ (R, R') u_+ (R') \]

\(+/-\) separation may be performed using eq. 4.54. Once again we have equations for \( f_+ \) and \( f_- \) which are coupled only in the exponentials \( \exp(\pm \int dR' / \hbar) \).

\[- \frac{\partial}{\partial R^2} \left\{ \frac{1}{2} \left\{ \left( - e^{- \frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} \right) - \left( e^{- \frac{1}{2} \frac{\partial}{\partial R} f_- (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_- (R)} \right) \right\} f_+(R) e^{\frac{1}{2} \int dR' f_+ (R')} \right\} + \left( e^{- \frac{1}{2} \frac{\partial}{\partial R} f_- (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_- (R)} \right) \left( \frac{e^{\frac{1}{2} \int dR' f_+ (R')} - i e^{\frac{1}{2} \int dR' f_- (R')}}{e^{-\frac{1}{2} \int dR' f_+ (R')} + i e^{\frac{1}{2} \int dR' f_- (R')}} \right) \left( \frac{e^{\frac{1}{2} \int dR' f_+ (R')} - i e^{\frac{1}{2} \int dR' f_- (R')}}{e^{-\frac{1}{2} \int dR' f_+ (R')} + i e^{\frac{1}{2} \int dR' f_- (R')}} \right) \right\} f_-(R) e^{\frac{1}{2} \int dR' f_- (R')} \right\} + \frac{\partial}{\partial R} \left\{ \left( - e^{- \frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} \right) e^{\frac{1}{2} \int dR' f_+ (R')} + \left. \left( e^{- \frac{1}{2} \frac{\partial}{\partial R} f_- (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_- (R)} \right) e^{\frac{1}{2} \int dR' f_- (R')} \right\} - i \int dR' G_+ (R, R') u_+ (R') \]

\[- \frac{\partial}{\partial R} \left\{ \frac{1}{2} \left\{ \left( - e^{- \frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} \right) \left( \frac{e^{-\frac{1}{2} \int dR' f_+ (R')} - i e^{\frac{1}{2} \int dR' f_- (R')}}{e^{\frac{1}{2} \int dR' f_+ (R')} + i e^{\frac{1}{2} \int dR' f_- (R')}} \right) \right\} f_+(R) e^{\frac{1}{2} \int dR' f_+ (R')} \right\} - \left. \left( e^{- \frac{1}{2} \frac{\partial}{\partial R} f_- (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_- (R)} \right) \left( \frac{e^{\frac{1}{2} \int dR' f_+ (R')} - i e^{\frac{1}{2} \int dR' f_- (R')}}{e^{-\frac{1}{2} \int dR' f_+ (R')} + i e^{\frac{1}{2} \int dR' f_- (R')}} \right) \right\} f_-(R) e^{\frac{1}{2} \int dR' f_- (R')} \right\} + \frac{\partial}{\partial R} \left\{ \left( - e^{- \frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_+ (R)} \right) e^{\frac{1}{2} \int dR' f_+ (R')} + \left( e^{- \frac{1}{2} \frac{\partial}{\partial R} f_- (R)} - i e^{\frac{1}{2} \frac{\partial}{\partial R} f_- (R)} \right) e^{\frac{1}{2} \int dR' f_- (R')} \right\} e^{- \frac{1}{2} \int dR' f_+ (R')} = \frac{\alpha}{\hbar} \int dR' G_+ (R, R') u_+ (R') \]
\[ - \frac{ie^{\theta_i}}{2}\pi \int_{\mathbb{R}} \frac{(-it) e^{-it\lambda_{11}^i} + i e^{it\gamma_{1i}^i}}{e^{-it\lambda_{11}^i} + i e^{it\gamma_{1i}^i}} \psi_i(R) e^{i \int_{R'} \lambda_i} dR' = \]
\[ - \frac{ie^{\theta_i}}{2}\pi \int_{\mathbb{R}} \left[ \frac{(e^{-it\lambda_{11}^i} + i e^{it\gamma_{1i}^i}) e^{i \int_{R'} \lambda_i} dR'}{e^{-it\lambda_{11}^i} + i e^{it\gamma_{1i}^i}} \right] \]
\[ + \left( - e^{-it\lambda_{11}^i} + i e^{it\gamma_{1i}^i} \right) e^{-i \int_{R'} \lambda_i} dR' \]
Again, \( f_+ \) and \( f_- \) will be separated into zero and first order terms, with the \( f_+^0 \) being the first term of eqs. 4.63 and 4.64. Then

\[
f_+(R) = f_+^0(R) + f_+^1(R) \tag{4.65}
\]

\[
f_-(R) = f_-^0(R) + f_-^1(R) \tag{4.66}
\]

Then

\[
f_+^0(R) = \frac{\kappa (\Theta_{-1})}{410 - 1} \left[ (e^{-2i\frac{k^2}{4\kappa} dR'}/k + 2i - e^{2i\frac{k^2}{4\kappa} dR'}/k) + (e^{-2i\frac{k^2}{4\kappa} dR'}/k + e^{2i\frac{k^2}{4\kappa} dR'}/k) e^{-2i\kappa(t + \xi_-) dR'} \right] \tag{4.67}
\]

\[
f_+^0(R) = \frac{\kappa (\Theta_{-1})}{410 - 1} \left[ (e^{-2i\frac{k^2}{4\kappa} dR'}/k + 2i - e^{2i\frac{k^2}{4\kappa} dR'}/k) + (e^{-2i\frac{k^2}{4\kappa} dR'}/k + e^{2i\frac{k^2}{4\kappa} dR'}/k) e^{-2i\kappa(t + \xi_-) dR'} \right] \tag{4.68}
\]

Now in eq. 4.53, \( f_+ \) and \( - f_- \) were required to approach each other at least as fast as \(-\frac{\kappa}{R_{K+0}}\) in the limit as \( R \to 0 \). Now in order that the exponentially increasing terms of eqs. 4.67 and 4.68 cancel, we must also have

\[
\lim_{R \to 0} e^{2i\frac{k^2}{4\kappa} dR'}/k (e^{i\kappa(t + \xi_-) dR'} - 1) = 0 \tag{4.69}
\]
That this condition is met as \( R \to 0 \) will be shown later. Then dropping the exponentially small terms and cancelling the exponentially large terms of eqs. 4.67 and 4.68 we have

\[
\xi_+^0(R) = -\frac{4}{\bar{a}} \frac{1}{i \bar{a} a_{\pm}}
\]

\[
\xi_-^0(R) = \frac{4}{\bar{a}} \frac{1}{i \bar{a} a_{\pm}}
\]

Once again we find that if \( Q_{-1}(R, R') \) is zero (so that \( f_+^i \) and \( f_-^i \) are zero) we have the zero order wave function for the forbidden region found in section IV B. Following the derivation of \( u_{-1}(R) \) in the allowed region, we will use the zero order wave function in finding \( f_+^i \) and \( f_-^i \). Then

\[
f_+^i(R) e^{\frac{i}{2} \frac{\hbar^2}{\bar{a}^2}} = -\frac{\partial}{\partial a_{\pm}} \left( e^{-i\frac{\hbar^2}{\bar{a}^2} R} + i e^{i\frac{\hbar^2}{\bar{a}^2} R} \right)
\]

\[
\int_{\text{col}} R' G_{-1}(R, R') u_{-1}(R')
\]

\[
f_-^i(R) e^{-\frac{i}{2} \frac{\hbar^2}{\bar{a}^2}} = -\frac{\partial}{\partial a_{\pm}} \left( e^{-i\frac{\hbar^2}{\bar{a}^2} R} - i e^{i\frac{\hbar^2}{\bar{a}^2} R} \right)
\]

\[
\int_{\text{col}} R' G_{-1}(R, R') u_{-1}(R')
\]

Using \( f_+^0 \) in the exponents of eqs. 4.72 and 4.73 we have

\[
f_+^i(R) = -\frac{\sqrt{a_{\pm}}}{\bar{a} \cdot a_{\pm}} \left( e^{-i\frac{\hbar^2}{\bar{a}^2} R} + i e^{i\frac{\hbar^2}{\bar{a}^2} R} \right)
\]

\[
\int_{\text{col}} R' G_{-1}(R, R') u_{-1}(R')
\]
The wave function in the forbidden region is now

\[ u_-(r) = \sqrt{\frac{2}{\pi}} \int e^{-\frac{r^2}{2}} \left( e^{-i \int \Phi(r')/\hbar} - i e^{i \int \Phi(r')/\hbar} \right) e^{ir' r'} \frac{1}{(r-r')} \left| \psi_{-}(r', r'') \right| u_-(r') \, dr' \]

\[ + i e^{i \int \Phi(r')/\hbar} \int e^{i \int \Phi(r')/\hbar} \left| \psi_{-}(r', r'') \right| u_-(r') \, dr' \]

\[ + e^{-i \int \Phi(r')/\hbar} \int e^{-i \int \Phi(r')/\hbar} \left| \psi_{-}(r', r'') \right| u_-(r') \, dr' \]

\[ - i e^{i \int \Phi(r')/\hbar} \int e^{i \int \Phi(r')/\hbar} \left| \psi_{-}(r', r'') \right| u_-(r') \, dr' \]

\[ \frac{1}{(r-r')} \left| \psi_{-}(r', r'') \right| u_-(r') \, dr' \]

Earlier we found that replacing the exponentials of the allowed region with Airy functions gave the wave function which was derived in the turning point region. Now we find that replacing the Airy functions of the turning point wave function (eq. 4.50) with exponentials will give us \( u_-(r) \) of eq. 4.76.

We must now consider the behavior of the wave function as \( R \to 0 \). As was stated in the beginning of this section, the wave function must go to zero at the origin. The exponentially large terms of the wave function must therefore cancel, and the wave function goes as \( \exp(-i \int \Phi_{m}/\hbar) \). This is consistent with the requirement of eq. 4.69. Now the exponentially increasing part of \( u_-(r) \) is
and it must be on the order of \( \exp(-\frac{1}{2} \Phi_{\nu}(R)/\alpha) \), so that

\[
\exp \left[ \int_{R} \int_{R'} e^{i \Phi_{\nu}/\alpha} \left( \frac{1}{\Phi_{\nu}(R')} \right) \int_{R'} G_{\nu}(R', R) \mu_{\nu}(R') \right] \sim \exp \left( \int_{R} \int_{R'} e^{i \Phi_{\nu}/\alpha} \left( \frac{1}{\Phi_{\nu}(R')} \right) \int_{R'} G_{\nu}(R', R) \mu_{\nu}(R') \right) \quad 4.77
\]

\[
\geq e^{-2 \Phi_{\nu}(R) \mu_{\nu}(R')/\alpha}
\]

Once again using the assumption that \( \Phi_{\nu}(R, R') \) is small, and that the argument of the sine is exponentially small, we have

\[
\exp \left[ \int_{R} \int_{R'} e^{i \Phi_{\nu}/\alpha} \left( \frac{1}{\Phi_{\nu}(R')} \right) \int_{R'} G_{\nu}(R', R) \mu_{\nu}(R') \right] \sim \exp \left( \int_{R} \int_{R'} e^{i \Phi_{\nu}/\alpha} \left( \frac{1}{\Phi_{\nu}(R')} \right) \int_{R'} G_{\nu}(R', R) \mu_{\nu}(R') \right) \quad 4.78
\]

\[
\geq e^{-2 \Phi_{\nu}(R) \mu_{\nu}(R')/\alpha}
\]

Earlier we found \( G_{\nu}(R, R') \) in terms of the eigenfunctions for the Hamiltonian \( H_{\nu}(R) \). These eigenfunctions \( \psi_{\nu}(R) \) are found in Appendix D using the uniform approximation. In the forbidden region, we have

\[
G_{\nu}(R, R') = \sum_{m=0}^{\infty} \lambda_{m}(R) \psi_{m}(R) \psi_{m}(R') \psi(R')
\]

\[
\quad + C g(R) g(R') \delta_{R,R'}
\]

with
where the momentum of the $n$th vibrational state is

$$\phi_m(R) = \left[ 2 M (E_{m}(R) - \nu_m(R)) \right]^{1/2}$$  \hspace{1cm} 4.80

Eq. 4.78 is then

$$e^{\frac{1}{2} \int_{0}^{\infty} \frac{dR}{R} \int_{0}^{\infty} \frac{dR'}{R'} \left( \frac{R'}{R} \right)^{1/4} \left( \frac{R}{R'} \right)^{1/4} \phi_{n}^{(R')} \phi_{m} \phi_{n}^{(R')} \phi_{m} \right]$$

Now suppose that the momentum $\phi_{-1}(R)$ goes as $R^{-m}$ as $R \to 0$, while $\phi_{m}(R)$ goes as $R^{a-d}$ as $R \to 0$. Then

$$A_{m} = \int dR' \ A_{m} \phi^{(R')} \ \phi^{(R')}$$  \hspace{1cm} 4.82

Using these approximations to the momenta, eq. 4.81 may be written in terms of powers of $R$ as

$$e^{\frac{1}{2} \int_{0}^{\infty} \frac{dR}{R} \int_{0}^{\infty} \frac{dR'}{R'} \left( \frac{R'}{R} \right)^{1/4} \left( \frac{R}{R'} \right)^{1/4} \phi_{n}^{(R')} \phi_{m} \phi_{n}^{(R')} \phi_{m} \right]$$

There are three cases that must be considered.

First suppose that $a = 0$. Then
Therefore if \( \phi_+ \) and \( \phi_- \) have the same behavior in the forbidden region, the wave function is exponentially decreasing in that region. Now if \( a < 0 \), the \( v_m(R) \) goes to zero at the origin faster than \( \exp(-|s_2|\cdot d\tau'/\hbar) / \sqrt{s_1} \), so that the wave function is again exponentially decreasing in the forbidden region. The third case, in which \( a > 0 \) is slightly different. Here the exponential term dominates:

\[
\exp\left[ \int d^3r' \cdot \mathbf{v} \cdot \mathbf{r}' \cdot \mathbf{v}_m(\mathbf{r}' - \mathbf{r}_m) \right] \sim e^{-\frac{R}{\hbar} \cdot \mathbf{v}_m(R)}
\]

\[
\exp\left[ \int d^3r' \cdot \mathbf{v} \cdot \mathbf{r}' \cdot \mathbf{v}_m(\mathbf{r}' - \mathbf{r}_m) \right] \sim e^{-R^{-\alpha}(\pi \hbar \alpha)}
\]

Now if the momentum of the bound state \( \Phi_m(R) \) is no smaller than \( R^{3 - \alpha} \phi_+(R) \) as \( R \to 0 \), and if the product of the momenta goes to infinity no faster than \( R^{3 - 2\alpha} \) as \( R \to 0 \), the wave function will be exponentially small in the forbidden region. Therefore the wave function derived in this section has the correct behavior in the forbidden
region in most cases.

D. Summary

In this chapter we have found the wave function to zero order using the uniform approximation. The zero order solution was then used to find a first order solution in each of three regions: allowed, turning point, and forbidden. In the next chapter a complex momentum will be defined using $f_+ (R)$ and $f_- (R)$. This will be used to simplify the wave function.
CHAPTER V

A COMPLEX MOMENTUM THEORY

A. Introduction

The incoming and outgoing parts of the first order wave function derived in the previous chapter will be written here in terms of complex momenta. The complex momenta will then be related to the nonlocal complex potential of Wang and Delos. The complex momenta may be used to find the survival probability of the negative ion as a function of the ion's kinetic energy and impact parameter.

B. The Complex Momenta

In the previous chapter a first order wave function was found in three regions: near the turning point, to the right and to the left of the turning point.

\[ \psi_{in}(r) = \sqrt{\frac{2}{\pi \sigma}} \left\{ \left( e^{-i \phi_{in}/\lambda} - e^{i \phi_{in}/\lambda} \right) \exp\left[ -\frac{i}{\hbar} \int_{r}^{r'} \mathbf{k} \cdot d\mathbf{r}' \right] \right. \]

\[ + \left. \left( e^{i \phi_{in}/\lambda} + e^{-i \phi_{in}/\lambda} \right) \exp\left[ \frac{i}{\hbar} \int_{r}^{r'} \mathbf{k} \cdot d\mathbf{r}' \right] \psi_{in}(r') \right\} \tag{5.1a} \]

\[ \psi_{out}(r) = \sqrt{\frac{2}{\pi \sigma}} \left\{ \left( e^{-i \phi_{out}/\lambda} - e^{i \phi_{out}/\lambda} \right) \exp\left[ -\frac{i}{\hbar} \int_{r}^{r'} \mathbf{k} \cdot d\mathbf{r}' \right] \right. \]

\[ + \left. \left( e^{i \phi_{out}/\lambda} + e^{-i \phi_{out}/\lambda} \right) \exp\left[ \frac{i}{\hbar} \int_{r}^{r'} \mathbf{k} \cdot d\mathbf{r}' \right] \psi_{out}(r') \right\} \tag{5.1b} \]
\[
\begin{align*}
\tilde{u}_-(R) &= -\frac{i}{\beta} \int_{\Re} \left[ e^{\frac{\beta}{4} (R, R')} \exp \left\{ \frac{\beta}{4} \int_{\Re} \frac{dR''}{R''} \left\{ e^{-\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_-(R', R'') \tilde{u}''(R'') \right\} \right. \\
&\quad \left. e^{-\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_-(R', R'') \tilde{u}''(R'') \right\} \right]\exp \left\{ \frac{\beta}{4} \int_{\Re} \frac{dR''}{R''} \left\{ e^{\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_-(R', R'') \tilde{u}''(R'') \right\} \right\} \right]\exp \left\{ \frac{\beta}{4} \int_{\Re} \frac{dR''}{R''} \left\{ e^{\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_-(R', R'') \tilde{u}''(R'') \right\} \right\} \right] \end{align*}
\]

We would like to use \( R = 0 \) as the lower limit on the integrals of the transition terms (those with \( G_-(R, R') \)). This may be done by defining two functions as follows.

\[
\begin{align*}
\tilde{w}_-(R) &= \left\{ \begin{array}{ll}
-\frac{i}{\beta} \int_{\Re} \left[ e^{-\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_-(R', R'') \tilde{u}''(R'') \right] \\
&\quad \cdot \left[ e^{\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_-(R', R'') \tilde{u}''(R'') \right] \right] \end{array} \right\} \quad \Re > \Re_0 \\
\tilde{w}_+(R) &= \left\{ \begin{array}{ll}
-\frac{i}{\beta} \int_{\Re} \left[ e^{-\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_+(R', R'') \tilde{u}''(R'') \right] \\
&\quad \cdot \left[ e^{\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_+(R', R'') \tilde{u}''(R'') \right] \right] \end{array} \right\} \quad \Re > \Re_0
\end{align*}
\]

Then \( \tilde{u}_-(R) \) may be written

\[
\begin{align*}
\tilde{u}_-(R) &= -\frac{i}{\beta} \left[ \tilde{w}_+(R) e^{\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_+(R', R'') \tilde{u}''(R'') \right] \\
&\quad \cdot \left[ e^{\frac{i}{\beta} \int_{\Re} \frac{dR'}{R'} G_+(R', R'') \tilde{u}''(R'') \right] \right] \end{align*}
\]
This must be normalized so that at large $R$ the incoming term is

$$u_{-1}^{in}(R) = u_{-1}(R)$$

In this way we will have unit incoming flux when the sum over angular momentum states has been performed. Then the wave function is

$$u_{-1}(R) = -\frac{i}{\hbar} \left[ \psi_{+}(R) \exp \left( \frac{i}{\hbar} \int dR' \psi_{+}(R') + \int dR' \psi_{-}(R') \right) \int dR'' G_{-1}(R', R'') u_{-1}(R'') \right]$$

$$+ \psi_{-}(R) \exp \left( \frac{i}{\hbar} \int dR' \psi_{-}(R') \int dR'' G_{-1}(R', R'') u_{-1}(R'') \right)$$

We will now define two complex momenta $\Pi^{+}(R)$ and $\Pi^{-}(R)$ as

$$\Pi^{+}(R) = \int dR' \psi_{+}(R') + \int dR' \psi_{-}(R') \int dR'' G_{-1}(R', R'') u_{-1}(R'')$$

$$\Pi^{-}(R) = \int dR' \psi_{-}(R') \int dR'' G_{-1}(R', R'') u_{-1}(R'')$$

Then

$$u_{-1}(R) = -\frac{i}{\hbar} \left( \psi_{+}(R) e^{\frac{i}{\hbar} \Pi^{+}(R)} + \psi_{-}(R) e^{\frac{i}{\hbar} \Pi^{-}(R)} \right)$$
Figures 3-6 show calculations of the wave function and complex momenta, both incoming and outgoing. As was expected, $\Pi^+ (R)$ and $\Pi^- (R)$ are largest in the region where the bound states are largest. The incoming and outgoing momenta are related as follows. Recalling that

$$C_m (R, R') = \sum_{m=0}^{M} \alpha_m \varphi_m (R) \varphi_m (R') \varphi_m (R')$$

3.60

and that $\Pi^+ (R) = \Pi^- (R)$, as is shown in eqs. 5.2 and 5.3, a function $P_m (R)$ may be defined as

$$P_m (R) = \sum_{m=0}^{M} \alpha_m \varphi_m (R) \varphi_m (R') \varphi_m (R') \varphi_m (R')$$

5.10

then

$$\Pi^- (R) = \sum_{m=0}^{M} \lambda_m P_m (R)$$

5.11

$$\Pi^+ (R) = \sum_{m=0}^{M} \lambda_m P_m (R) + \sum_{m=0}^{M} \lambda_m (P_m (R) - P_m (R))$$

5.12

$$\Pi^+ (R) = \sum_{m=0}^{M} \lambda_m (2 \Re (P_m (R)) - P_m (R))$$

5.13
COMPLEX MOMENTUM, IMAG INCOMING PART

$L = 0$
$E_1 = 0.078$

$H + G^+ \rightarrow H + G^+ e$
COMPLEX MOMENTUM, IMAG OUTGOING PART

$L = 0$

$E_1 = 0.076$

$H + Cl^- \rightarrow HCl + e^-$

FIG 4
COMPLEX MOMENTUM, REAL INCOMING PART

$E_1 = 0.042$

$W + 2I - 4 + 2 + i$
COMPLEX MOMENTUM, REAL OUTGOING PART

$L = 0$

$E_1 = 0.056$

$\mu + e^- \rightarrow \mu + e^- + e$
Since the Green's function $G_{\omega}(R,R')$ contains a sum over the allowed vibrational states, it is clear that the structure of $T_\omega^-$ and $T_\omega^+$ are dictated by the number of bound vibrational states $v_\omega(R)$ with eigenvalues $E_\omega$ which are less than the kinetic energy of the negative ion $E$. In addition the overlap integral between the zero order wave function $u_{-i}(R)$ and the eigenfunctions of the bound states $v_\omega(R)$ determines the contribution of each term in the sum.

C. The Survival Probability

The survival probability $P_s$ is given by the magnitude of the outgoing part of the wave function squared as $R \to \infty$. Then

$$P_s = |\Psi_s(R)|^2 = \frac{1}{\omega} e^{-\frac{Q}{\omega}} \int dr' \left[ \frac{1}{E} \int dR'' G_{\omega}(R',R'') u_{-i}(R'') \right] \left| \frac{d}{dR'} G_{\omega}(R',R'') u_{-i}(R'') \right|$$

Using the complex momentum defined in the previous section, this is

$$P_s = e^{-\frac{Q}{\omega} \phi_{\text{w}}(\text{w})}$$
SURVIVAL PROBABILITY

$L = 10$

Figure 7
As is shown in Figure 7, this can have a good deal of structure when it is found as a function of the ion's kinetic energy. The survival probability has a local minimum near the energy of each bound vibrational state $E_n$. When a collision takes place slightly above this energy, detachment into the state $n$ is very likely, so the survival probability decreases there. The survival probability increases as the wave function and the highest allowed bound state eigenfunction become dissimilar. This will be discussed more fully in Chapter 5.

D. Stationary Phase Integration

The complex moments may be found by evaluating the integrals of eqs. 5.7 and 5.8 using stationary phase integration. The reader is referred to reference for a complete discussion of stationary phase integration. Each of the integrals involved has a stationary phase point at the crossing of the potential of the negative ion and a shifted continuum potential $W_m(R)$

\[ W_m(R) = E - E_n + V_{\infty}(R) \]  

If there is no crossing in the allowed region the method of steepest descents must be used.

Neglecting for the moment the possibility of
direct detachment, let us consider the following. Using the form of \( G_{-1}(T, T') \) given in eq. 3.60 in the following integral from eq. 4.32, we have

\[
\xi \frac{\partial m}{\partial n}(T) = \xi \frac{\partial m}{\partial n} \left[ \int_{T}^{T'} w_{e}(T') g(T') v_{m}(T') \right]
\]

\[
\times \int_{T}^{T'} g(T') v_{m}(T') u_{m}(T') dt
\]

Now in the allowed region, \( v_{m}(T) \) is given by

\[
v_{m}(T) = 2 \frac{r}{\partial m} \sin \left( \frac{r}{\partial m} dR_{m} + \pi/4 \right) \quad (\partial m(T_m) = 0)
\]

as was shown in Appendix C. Then in the allowed region, using eq. 5.3 for \( w_{e}(T) \) and \( u_{m}(T) \) given by eq. 4.5, the integral has the form

\[
\Phi_{m}(T) = \beta \left[ \int_{T}^{T'} \frac{dR}{\partial m} \int_{T}^{T'} g(T') dR_{m} \right] \sin \left( \frac{r}{\partial m} dR_{m} + \pi/4 \right)
\]

\[
+ \frac{1}{2} \int_{T}^{T'} g(T') dR_{m} \sin \left( \frac{r}{\partial m} + \pi/4 \right) \sin \left( \frac{r}{\partial m} + \pi/4 \right)
\]

Now this may be evaluated by the stationary phase method if the exponents are large away from the stationary phase point. A stationary phase integral is

\[
I = \int_{a}^{b} e^{iQ(x)/h} f(x) dx
\]
with the conditions that

\[ \xi \ll 1 \quad \eta \ll \gamma \ll B \]

\[ \frac{d^{(p-1)}}{d \gamma^{(p-1)}} Q(x) \bigg|_{x_0} = 0 \quad \xi(x_0) = 0 \]

\[ Q^{(p)}(x_0) = 0 \quad p > 1 \]

and \( \exp(i \varphi_0 / \xi) \) must oscillate rapidly away from the stationary phase point so that the contribution to the integral of function in the region away from the stationary phase point is negligible. Then

\[ \int \psi(x_0) e^{i \varphi(x_0)} e^{i \text{sgn}(Q^{(p)}(x_0)) \pi/2p} \left[ \frac{e^{p \pi i \xi}}{1 - e^{p \pi i \xi}} \right]^{1/p} \frac{\Gamma(p)}{p} \]

The sign of the phase \( i \pi/2p \) is that of the derivative. Then our integral is:

\[ P_m(R) = -N^2 \oint_{R} e^{i \xi \frac{\partial^2}{\partial x^2}} \left[ e^{\frac{R_0^m + k_0^m}{\xi}} + \frac{k_0^m}{\xi} \right] - \frac{1}{\xi} e^{i \xi \left( k_{00}^m - \xi \sigma_m \right)} - i \pi/2 \]

\[ - e^{i \xi \left( k_{00}^m - \xi \sigma_m \right)} - e^{i \left( k_{00}^m - \xi \sigma_m \right)} - e^{i \left( k_{00}^m - \xi \sigma_m \right)} - i \pi/4 \]

Dropping the terms without stationary phase points, we have
\[ P_m(R) = N^2 \int dR^2 \frac{g(R)}{\Omega_m} \left( + e^{i \left( \frac{\delta_R}{\hbar} - \frac{\delta_m}{\hbar} \right)} \right) \]

\[ = \int dR^2 \frac{g(R)}{\Omega_m} \left( e^{i \left( \frac{\delta_R}{\hbar} - \frac{\delta_m}{\hbar} \right)} + e^{-i \left( \frac{\delta_R}{\hbar} - \frac{\delta_m}{\hbar} \right)} \right) \]

Then integrating the inner term only,

\[ P_m(R) = N^2 \int dR^2 \frac{g(R)}{\Omega_m} e^{i \left( \frac{\delta_R}{\hbar} - \frac{\delta_m}{\hbar} \right)} \]

\[ \frac{g(R_c)}{\sqrt{\Omega_m(R_c)/\sigma_m(R_c)}} \left[ e^{i \left( \frac{\delta_{R_c}}{\hbar} - \frac{\delta_m}{\hbar} \right)} \pm i \frac{\delta_m}{\hbar} \right] \left[ \frac{\delta_m}{\hbar} \right]^{1/2} \]

\[ \sigma_m(R_c) = \sigma_m(R_c) \]

A further stationary phase integration gives a result similar to the Landau-Zener formula, shown in eq. 5.34, for the crossing of several discrete potential curves.
Similarly, if we define an integral $J$ as

$$ J = \int \mathcal{W}_N (R') \, dR' \int \mathcal{W}_N (R') \, G_{R'} (R', R'') \, u_R^2 (R'') \\ \text{where}$$

$$ \mathcal{W}_N (R) = \mathcal{W}_N (R) $$

we have

\begin{align*}
J &= \mathcal{P}_N^* (R) \\
\mathcal{P}_N^* (R) &= 2 \mathcal{A} \frac{\mathcal{A}}{a (R)} \frac{h}{2 a (R)} a \mathcal{F}_{R'} (R) e^{i \mathcal{F} (a_i - \sigma_i)} e^{i \mathcal{F} (a_i - \sigma_i)} \\
&= e^{i \mathcal{F} (a_i - \sigma_i)} e^{i \mathcal{F} (a_i - \sigma_i)}
\end{align*}

Now by eqs. 5.14 and 5.17,

$$ \Pi^2 (a) = \mathcal{P}_N (a) \, 2 \Re (\mathcal{P}_N (a)) $$

and

$$ P_N = e^{- \frac{i \mathcal{F}}{2} \mathcal{F} (a_i - \sigma_i) \Re (\mathcal{P}_N (a)) } $$

Then
\[ P_s = \exp \left[ - \frac{k}{E_{00}} \frac{\Sigma_{nm}^{\text{max}}}{\Delta E} - \frac{\Pi}{\Delta E} \right] (\frac{-2 \hbar \nu}{\Delta E}) \]

\[ \frac{\Pi}{\Delta E} \left[ \cos^2 \left( \frac{\beta}{\hbar} (\frac{\Sigma_{np}}{\Sigma_{nm}} - \left\{ k_{np} \right\} \pm \frac{\pi}{\nu}) \right) \right] \]

So that with

\[ \Theta_{\pm}(R_L) = \Phi \nu \]

\[ \Delta F = \frac{\Theta_{\pm}(R_L)}{R_L} \left[ \Theta_{\pm} - \Theta_{\pm} \right] \]

the survival probability is

\[ P_s = \exp \left[ - \frac{k}{E_{00}} \frac{\Sigma_{nm}^{\text{max}}}{\Delta E} \right] \theta_{n}^{\pm}(R_L) \]

\[ \left\{ \cos^2 \left( \frac{\beta}{\hbar} \left( \frac{\Sigma_{np}}{\Sigma_{nm}} - \left\{ k_{np} \right\} \pm \frac{\pi}{\nu} \right) \right) \right\} \]

The Landau-Zener result for the crossing of two potential energy curves with a constant coupling potential energy \( V_{\text{coupling}} \) is

\[ P_s = \exp \left[ - \frac{k}{E_{00}} \frac{\Sigma_{nm}^{\text{max}}}{\Delta E} \right] \]

\[ \theta_{n}^{\pm}(R_L) \]

where \( F_0 \) and \( F_1 \) are the forces, given by

\[ F_1 = \frac{\partial \theta_{\pm}(R_L)}{\partial R_L} \]

\[ \Delta \]

Once again, as each bound state becomes energetically accessible another term is added and the survival probability decreases.
and a numerical integration of the survival probability are compared in Figure 10 for the collision H + Cl⁻.

There are energies for which the stationary phase integration is not the major term of the integral. When the moments of the ionic and molecular states are similar throughout the allowed region the zero order wave function \( u_{-\frac{1}{2}} (R) \) may be nearly the same as the bound state eigenfunction \( v_{\infty} (R) \). At these energies, the overlap integral is roughly

\[
\int dR \, v_{\infty} (R) u_{-\frac{1}{2}} (R) g(R) \approx \bar{g}
\]

It is this that is responsible for the peaks in the survival probability, which is now

\[
P_s \approx e^{-\frac{1}{2} \int \omega_{\infty} (E) \bar{g}^4}
\]

The stationary phase term in the survival probability then applies only when there is no significant overlap between the wave function \( u_{-\frac{1}{2}} (R) \) and the eigenfunction \( v_{\infty} (R) \).

E. A Complex Potential Approximation

It has not been possible to define a time dependence for associative detachment, since a classical
trajectory for the nuclei would come to a stop with the formation of the molecule. The formulas which have been derived may, however, be written in terms of a time dependence for energies above the direct detachment threshold. Using a time dependent formulation, the non-local complex potential formulas of Wang and Delos may be derived.\textsuperscript{33,34}

Defining a time \( \tau \) as \textsuperscript{33}

\[
\frac{dR}{d\tau} = \frac{\sqrt{\sigma_{+}\sigma_{-}}}{\sigma} \quad \tau \rightarrow 0 \quad 6.39
\]

the integrals of the momentum \( \sigma_{\pm}(R) \) used in chapter IV in finding \( u_{\pm}(R) \) may be changed to integrals of the potential energy over time as follows

\[
\int_{a_{\pm}}^{b_{\pm}} \sigma_{\pm} \, dR' = \int_{a_{\pm}}^{b_{\pm}} \sigma_{\pm} \, \sqrt{\sigma_{-}\sigma_{+}} \, \frac{d\tau}{\sigma} \quad 5.40
\]

\[
\int_{a_{\pm}}^{b_{\pm}} \sigma_{\pm} \, dR' = \int_{a_{\pm}}^{b_{\pm}} \sigma_{\pm} \, \sigma_{\pm} \, \frac{d\tau}{\sigma} \quad 5.41
\]

Throughout this derivation, it will be assumed that the potential energy curves \( V_{\pm}(R) \) and \( V_{\pm}(R) \) are similar enough that we may say that

\[
\sqrt{\sigma_{-}\sigma_{+}} = \frac{\sigma_{\pm} \, \sigma_{\pm}}{\sigma} \quad 5.42
\]

Then
The wave function of eq. 5.9 is then
\[ u(\tau) = -i \sqrt{\mathcal{A}} \left( e^{i \int_{\tau_0}^{\tau} \mathcal{A} \, d\tau'} + e^{-i \int_{\tau'_0}^{\tau'} \mathcal{A} \, d\tau''} \right) \]

In the allowed region, this is
\[ u_+(\tau) = -i \sqrt{\mathcal{A}_+} \left( e^{i \int_{\tau_0}^{\tau} \mathcal{A}_+ \, d\tau'} + e^{-i \int_{\tau_0}^{\tau} \mathcal{A}_- \, d\tau'} \right) \]

In addition, the incoming part of the wave function is associated with a negative time, while the outgoing part refers to positive time. The coupling between incoming and outgoing waves must be dropped, so that with
\[ u_-(\tau) = i \sqrt{\mathcal{A}_-} \left( e^{i \int_{\tau'}^{\tau} \mathcal{A}_- \, d\tau'} + e^{-i \int_{\tau'}^{\tau} \mathcal{A}_- \, d\tau'} \right) \]
\[ u_-(\tau') = -i \sqrt{\mathcal{A}_-} \left( e^{i \int_{\tau_0}^{\tau} \mathcal{A}_- \, d\tau'} + e^{-i \int_{\tau_0}^{\tau} \mathcal{A}_- \, d\tau'} \right) \]

The integro-differential equation then has the following first order solution
\[ (\mathcal{A} - \mathcal{H}_- \mathcal{A} \tau) u_-(\tau) = \int_{-\infty}^{\tau} \frac{d\tau'}{\mathcal{A} - \mathcal{A}' \mathcal{A} \tau} \left( \mathcal{A} G_-(\tau, \tau') \right) u_-(\tau') \]
\[ u_-(\tau) = -\frac{i}{\mathcal{A}_-} \sqrt{\mathcal{A}_-} \int_{-\infty}^{\tau} e^{i \int_{\tau_0}^{\tau} \mathcal{A}_- \, d\tau'} \int_{\tau_0}^{\tau} \mathcal{A}(\mathcal{A} - \mathcal{A}_- \mathcal{A} \tau) \]
The complex moments written in time dependent form are then

\[ \bar{n}_-(\tau) = \frac{\partial^R}{\partial \tau} \int_0^\tau \frac{d\tau'}{\sqrt{\pi}} e^{-\frac{1}{2} \int_{\tau'}^{\tau} d\tau'' (2 \pi - \Delta(\tau''))} \]

\[ \bar{n}'_-(\tau) = \bar{n}_-(\tau) + \frac{\partial^R}{\partial \tau} \int_0^\tau \frac{d\tau'}{\sqrt{\pi}} e^{-\frac{1}{2} \int_{\tau'}^{\tau} d\tau'' (2 \pi - \Delta(\tau''))} \]

The limit \( R \rightarrow \infty \) of the incoming wave is changed to a limit as \( t \rightarrow -\infty \). In addition, the momentum integrals may be written as:

\[ e^{-\frac{i}{2} \int_{\tau'}^{\tau} d\tau'' (2 \pi - \Delta(\tau''))} \]

\[ e^{\frac{i}{2} \int_{\tau'}^{\tau} d\tau'' (2 \pi - \Delta(\tau''))} \]

\[ e^{\frac{i}{2} \int_{\tau'}^{\tau} d\tau'' (2 \pi - \Delta(\tau''))} \]

\[ e^{\frac{i}{2} \int_{\tau'}^{\tau} d\tau'' (2 \pi - \Delta(\tau''))} \]
\[ T_+ (\tau) = T_- (\tau) + \frac{2}{K} \int_0^\tau \frac{\partial}{\partial \tau'} \left( \frac{\partial}{\partial \tau'} + \frac{\partial}{\partial \tau'} \right) T_+ (\tau - \tau') d\tau' \]  \hspace{1cm} 5.56

where

\[ G_{\pm} (\tau, \tau') e^{\frac{\beta}{2} E (\tau - \tau')} e^{-\int_\tau^{\tau'} d\tau' \lambda (\tau')} \]

Similarly,

\[ \int_{\tau'}^{\tau} \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \tau} + \frac{\partial}{\partial \tau} \right) T_+ (\tau - \tau') d\tau' = \int_{\tau'}^{\tau} \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \tau} + \frac{\partial}{\partial \tau} \right) \mu d\tau \]

We then have

\[ u_{\mp} (\tau (r)) = -i \sqrt{\frac{\mu}{\beta}} e^{\frac{\mu}{2} \beta \lambda (\tau)} \left[ \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \tau} + \frac{\partial}{\partial \tau} \right) \right] \]

This is now valid for both \( \tau > 0 \) and \( \tau < 0 \).

The Green's function may be written as

\[ G_{\mp} (\tau, \tau') = \frac{1}{\hbar} \int_\Theta \rho_\Theta (\tau) \frac{e^{i (\tau - \tau') \left( \mu - \sqrt{\frac{\beta}{2}} \lambda (\tau') \right)}}{\sqrt{\Theta (\tau - \tau') \Theta (\tau')}} V_\Theta (\tau') \]

is now the semiclassical Green's function for the continuum function with \( \Theta > V_{\Theta} (\infty) \):

\[ (\mathcal{E}_0 - \mathcal{E} + \frac{\hbar^2}{2m} \partial^2_{\mathcal{E}}) u_0 = 0 \]

5.50
so that

\[ u_0^* = \sqrt{\frac{2\pi}{\hbar^2}} \ e^{-\frac{i}{\hbar} \int_0^R \varphi_0(R') \, dR'} \]

\[ u_n(t) = -i \sqrt{\frac{2\pi}{\hbar^2}} \ e^{\frac{i}{\hbar} \int_0^R \varphi_n(R') \, dR'} \ \exp \left\{ \frac{i}{\hbar} \int_0^{R} \varphi(R') \, dR' \right\} \]

\[ \int \! d\sigma \rho_e \ |V_n(\tau)|^2 \int_0^t \! d\tau' \ e^{\frac{i}{\hbar} \left( \Delta \left( \tau' - \tau \right) - \frac{1}{2} \int_0^{R' \rightarrow R} \Delta(x') \, dx' \right)} \]

With the approximation that the coupling potential energy \( V_{n}(R) \) is a slowly varying function, we may set \( V_n(\tau) \), equal to \( V_n(t) \) over the range in which the integral is significant. Then as \( \tau \to \infty \),

\[ u_n(\tau) \approx -i \sqrt{\frac{2\pi}{\hbar^2}} \ e^{\frac{i}{\hbar} \int_0^R \varphi_n(R') \, dR'} \ \exp \left\{ \frac{i}{\hbar} \int_0^{R} \varphi(R') \, dR' \right\} \]

When the wave function is normalized at \( t = -\infty \), we have

\[ c_n(\tau \to \infty) = e^{-\frac{i}{\hbar} \int_0^R \Delta(x) \, dx} \ \exp \left\{ -\frac{i}{\hbar} \int_0^R \int_0^\tau \ \rho_e \right\} \]

\[ |V_{n-1}(\tau)|^2 \int_0^\tau \! d\tau' \ e^{\frac{i}{\hbar} \left( \Delta \left( \tau' - \tau \right) - \frac{1}{2} \int_0^{R' \rightarrow R} \Delta(x') \, dx' \right)} \]
which is the most general formula for direct detachment collisions derived by Wang and Delos. From this, the local complex potential formula may be derived.

V. Summary

In this chapter a form of the wave function for the negative ion was derived. Using this formula, the equations of Wang and Delos and a stationary phase formula were derived. Transitions directly from incoming to outgoing parts of the wave function were dropped, but such transitions are kept with the intermediate step of a transition into the continuum. In the next chapter, the probability of detachment into each bound state will be derived and the probability of detachment into a state with an energy between bound states is discussed (and found to be very small). Two systems with widely differing potentials will be studied in the following two chapters: \( \text{H} + \text{Cl}^- \) and \( \text{H} + \text{F}^- \).
A. Introduction

The previous chapters have dealt entirely with the wave function of the negative ion state. Here, we will discuss the vibrationally bound states of the molecule AB and the probabilities of detachment into those states. In addition, the wave function $u_k(R)$ may be found by solving the original continuum equation

$$ (E - H_{kk}(R)) u_k(R) = V_{k-1}(R) u_{k-1}(R) $$ \hspace{1cm} 2.22

B. Transitions into the Bound Vibrational States

Two types of transitions must be considered: those in which energy is conserved and those in which it is not conserved. The latter may take place only in or near the collision region. The conservation of energy in the limit as the electronic coordinate becomes large results in boundary condition eq. 2.84. This boundary condition also states that the molecule must be in an eigenstate of the Hamiltonian $H_{00}(r;N)$ as $r \to \infty$, where
The projection of $|\Psi\rangle$ onto the continuum vector $Q|\Xi\rangle$

is therefore

$$\langle \Phi | Q | \Xi \rangle = \int dk \rho_k \langle \Phi | \Psi_k \rangle \langle \Psi_k | Q | \Xi \rangle$$

The probability of detachment into a state with electron energy $E$ and nuclear energy $E_n$ is then

$$1e^{-\hbar} = |\langle \Psi | Q | \Xi \rangle|^2$$

The probability of detachment into a given bound state $n$ with arbitrary electron energy we will define as $\langle m | n \rangle$:

$$|\langle m | n \rangle|^2 = \int dk \rho_k \langle k | \langle m | n \rangle k \rangle$$

To find $\langle m | n \rangle$ we must begin with the continuum equation

$$(E - Q | h | k \rangle \langle k | Q | \Xi \rangle = Q | h | P \langle \Xi |$$

Then with the Green's function defined in section III B, we
have

\[ G_m = \sum_\alpha \sum_\beta \sum_\sigma \left( \frac{1}{\sqrt{E - E_m - E_h}} \right) \]

so that

\[ \langle \psi | P | \psi \rangle = \sum_\alpha \sum_\beta \sum_\sigma \left( \frac{1}{\sqrt{E - E_m - E_h}} \right) \]

Now we wish to find two quantities: \( \alpha_m^k \) and \( \alpha_m^{k*} \). This may be done using \( G_m \) as defined in eq. 3.5, and the definitions of \( P \) and \( Q \) given in eq. 2.34

\[ \langle \psi | P | \psi \rangle = G_m Q_{\psi} \]

so that

\[ \sum_\alpha \sum_\beta \sum_\sigma \left( \frac{1}{\sqrt{E - E_m - E_h}} \right) \]

Then using the orthogonality of the electronic and nuclear basis vectors, we have
\[ \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle = 6.6 \]

\[ \text{E} \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle \frac{\text{Solv}_{\rho_{ab}} \langle \mu | k + 1 \rangle \rangle}{\text{E} - \text{E}_{\mu} - E_R} \]

which is equivalent to

\[ \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle = \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle \frac{\text{Solv}_{\rho_{ab}} \langle \mu | k + 1 \rangle \rangle}{\text{E} - \text{E}_{\mu} - E_R} \quad 6.7 \]

Now the integral over the continuum contains a first order poles at \( E_E = E - E_{\mu} \). Adding a small imaginary term to \( E - E_{\mu} \) and integrating around the contour of figure 10 results in the following.

\[ \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle = \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle \frac{\text{Solv}_{\rho_{ab}} \langle \mu | k + 1 \rangle \rangle}{\text{E} - \text{E}_{\mu} - E_R} \quad 6.8 \]

\[ \text{This is similar to the integration performed in Appendix B in the discussion of the boundary condition as } r \rightarrow \infty \text{. The contour was chosen so that in the coordinate representation the purely outgoing wave } \langle \text{R} | \text{R} \rangle \text{ would go to zero as } k \text{ approached } \infty \text{ on the complex plane.} \]

Now we know that

\[ \lim_{r \rightarrow \infty} \langle \text{R} | \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle \rangle = \langle \text{R} | \text{Solv}_{\rho_{ab}} \langle m | k \rangle \rangle \rangle \]

so that at large \( r \), \( \rho_{ab} \) should be equal to \( \langle m | k \rangle \rangle \). Then
Equation 6.11 is then the probability that the system will be in the state \( n \) when the electron is at large \( r \), or the probability of transition to state \( n \).

Eq. 6.11 may be evaluated by first transforming it to coordinate space. The reader is referred to section II D in which it was shown that the coordinate space function corresponding to \( \Psi_{n-1} \) is \( V_{n-1} \).
\[ \langle \mathbf{E} | H_{k-1} | R' \rangle = V_{k-1} s(R - R') \]

we have

\[ \langle m | H_{k-1} | -1 \rangle = \int dR' \, V_{m}^{*}(R') \, V_{k-1}(R) \, U_{-1}(R) \quad 6.13 \]

With the coupling potential energy \( V_{k-1}(R) \) having separable \( R \) and \( m \) dependence as discussed earlier, this is

\[ \langle m | H_{k-1} | -1 \rangle = \int dR' \, V_{m}^{*}(R') \, g(R) \, U_{-1}(R') \quad 6.14 \]

\[ \frac{m \cdot n}{|k|} = \int dR' \, \frac{V_{m}^{*}(R') \, g(R) \, U_{-1}(R)}{\sqrt{E - E_{\infty}}} \quad 6.15 \]

so that the transition probability \( |V_{k-1}|^2 \) depends on the overlap between the bound state nuclear wave function and the wave function of the negative ion \( u_{-1}(R) \) in addition to the dependence of the coupling potential energy on the energy of the free electron.

As before, this integral may be evaluated either numerically or with stationary phase integration. Using the first order wave function \( u_{-1}(R) \) of eq. 4.30, and the semi-classical \( v_{\infty}(R) \) for the allowed region given in Appendix D.
This is similar to the integral that was evaluated in section V B. Once again, it has a stationary phase point at the crossing between the two momenta \( \Phi_3 \) and \( \Phi_m \). If there is little similarity between the wave functions, so that the overlap integral is small, a stationary phase evaluation of eq. 6.16 gives

\[
\int_{\Omega} v_\nu(R) g(R) u_\mu(R) = H \left[ \frac{\delta^2}{2i(\Phi_3 - \Phi_m)} \right] U_L
\]

so that the transition probability is, using eq. 6.15,

\[
|\Delta_{\mu \nu}|^2 = \frac{1}{\pi} \frac{1}{\delta^2} \frac{m^2 \rho(r)}{2(\Phi_3 - \Phi_m)} \times \left| e^{\frac{i}{\hbar} (\Phi_3 - \Phi_m + \Pi_3(R))} - e^{-\frac{i}{\hbar} (\Phi_3 - \Phi_m - \Pi_3(R))} \right|^2
\]
C. Continuum States

We will now consider transitions into states with an arbitrary nuclear kinetic energy. A transition into a state for which the free electron has a kinetic energy which is not the difference between the total kinetic energy and the energy of a vibrational state:

$$E_k \neq E - E_\omega$$

is unlikely to occur, since the state is not quantum mechanically allowed. The wave functions for these states are solutions to the continuum equation

$$(E - E_k - \omega \kappa (R)) \psi_k = \psi_{-k}, \psi_{-k}(R)$$

Since the energy is not that of a bound state, the wave functions $\psi_k(R)$ are not eigenfunctions of the homogeneous continuum Hamiltonian $H_\omega$, and therefore may be found using the continuum Green's function of eq. 3.52.

$$\hat{G}_{E-E_\omega}(R,R') = \psi_e(R) \psi_e(R') / \omega$$

$$\left(E - H_{\omega} - H_0\right) \phi_e(R) = 0$$

Then

$$\psi_k(R) = \int dR' \hat{G}_{E-E_\omega}(R,R') \phi_{-k}(R') \psi_{-k}(R')$$

This integral has been performed numerically for several energies. The probability of detachment into these
states has been found to be insignificant in comparison to the probability of detachment into the bound vibrational states.

D. Rate Constants and Cross Sections

The wave function $u_-(R)$ and the detachment probabilities may be used to calculate the cross section for associative detachment and the rate constants. The detachment cross section is related to the survival probability in the usual way:

$$\sigma_{el+} = \frac{2\pi}{\hbar} \frac{Z}{\rho_0} \left(2J+1\right) \left(1 - P_{L^d}\right)$$  \hspace{1cm} 6.22

The reaction rate constant $k$ is then

$$k = \int_0^\infty \frac{3}{kT \sqrt{4\pi \hbar}} \sigma(E) \sqrt{\frac{E}{kT}} e^{-E/kT} dE$$  \hspace{1cm} 6.23

The only experimental data that is available is at thermal energies.

E. Summary

The detachment probabilities for the bound states have been found in the limit as $r \to \infty$. These may be used to find the detachment cross section and rate constants. In the next chapters, the equations which have been derived.
will be applied to collision systems. The results will where possible be compared with experimental data.
CHAPTER VII

SURVIVAL AND DETACHMENT PROBABILITIES
FOR ASSOCIATIVE DETACHMENT PROCESSES

A. Introduction

Calculations of the reaction rate constant $k$, detachment probabilities, and survival probabilities have been performed for the reactions

$$H(D) + Cl^- \rightarrow H(D)Cl + e^-$$

$$H(D) + F^- \rightarrow H(D)F + e^-$$

In the case of $H + Cl^-$, our rate constants were found to be in good agreement with experimental data. No experimental data is available for the reaction $D + Cl^- \rightarrow DCl + e^-$, but we found a significant isotope effect in the survival probability. In the case of $H(D) + F^- \rightarrow H(D)F + e^-$ there is a similar isotope effect in the survival probability. Again, no experimental rate constants are available for the case of $D + F^-$. The rate constant for $H + F^-$ is known to be $1.6 \times 10^{-9} \text{ cm}^3/\text{sec}$. Our coupling potential energy was chosen to give this rate constant.
1. The Potential Energy

In order to perform the calculations, three potential energy curves are needed: 1) the potential energy of the negative ion state, 2) the potential energy of the molecule, and 3) the coupling potential energy \( V_{\text{c}}(R) \).

The region near the minimum of \( V_{\text{c}}(R) \) (the equilibrium distance of HCl) is well understood. The crossing of the two curves \( V_{\text{c}}(R) \) and \( V_{\text{c}}(R) \) takes place in this region and the structure of the curves there determines the final vibrational state distribution of the molecule HCl. In addition, the behavior of \( V_{\text{c}}(R) \) and \( V_{\text{c}}(R) \) at large \( R \) is well known. There is some uncertainty regarding the exact behavior of the potential curve \( V_{\text{c}}(R) \) at intermediate distances (at \( R = 3, 4 \) a.u.). The structure of the curves in this region determines the probability of detachment.

We used a Morse potential fitted to the potential energy curves of Goldstein et. al. for \( V_{\text{c}}(R) \) and \( V_{\text{c}}(R) \). The coupling potential was assumed to have the form

\[
V_{\text{c}}(R) = \omega_0 \hat{V}_{\text{c}}(R) \exp(-.66R)
\]

where the coefficients \( \omega_0 \) and -.66 were chosen to fit the measured rate constants.

2. The Survival Probability
The survival probability of the negative ion has been found as a function of the ion's kinetic energy for several values of the angular momentum quantum number \( l \). In both reactions \( (H + Cl^- \) and \( D + Cl^- \)), the survival probability is oscillatory. The oscillations are related to the energies of the vibrational states of the molecule, as is shown in figures 7 and 8. The survival probability is given by

\[
P_j = e^{-\sum_n \left( \frac{\hbar}{2m} 2 \pi \alpha (\omega_n) \right)}
\]

where the sum is over the vibrational states which have energies less than the ion's kinetic energy. The dependence of the survival probability on the bound state energies is therefore not unexpected.

Associative detachment into a particular vibrational state is most likely to take place when the ion's kinetic energy is near the energy of that state, so that as each bound state becomes energetically accessible the survival probability may be expected to drop sharply. This does not always take place at \( E = E_\omega \), as may be seen in figure 11. At low energies and large angular momentum, such as \( l=30 \), the overlap integral \( \int dR u(R) g(R) v(R) \) is at a maximum close to \( E_\omega \) so the survival probability is at a minimum there.

The change in \( P_\omega \) with increasing \( l \) must also be considered. At small impact parameters and therefore small \( l \), the molecule HCl has three vibrational states below the
asymptotic limit of \( \Psi_{l-n}(R) \). As the angular momentum increases, the lower states become inaccessible. In the case of \( l=30 \), there are no accessible vibrational states below \( \Psi_{l-n}(\infty) \). This explains the large oscillations of this curve in relation to the survival probability at \( l=10 \), which has three vibrational states below the minimum ion energy.

The isotope effect may also be explained by the positions of the vibrational states. For the reaction \( D + Cl^- \rightarrow DCl + e^- \) the energies of the vibrational states are closer together than for associative detachment of \( H + Cl^- \). This reduces the effect on the survival probability of the bound states and reduces the magnitude of the oscillations.

3. The Rate Constants

The rate constant for associative detachment is related to the survival probability as follows

\[
\sigma(E) = \frac{\pi \hbar^2}{2m(\omega)} \sum_{j} (2j+1) (1 - P_j \leftrightarrow j)
\]

\[ k(T) = \left[ \frac{\sigma(E)}{m^2 h^4} \right] \int_{0}^{\Sigma} \sigma(E) \, e^{\frac{-E}{kT}} \, dE
\]

where \( \sigma(E) \) is the total cross section. The survival probabilities discussed in the previous section were used to find the rate constants \( k(T) \) for associative detachment.

The rate constant for associative detachment in
The rate constant $k(T)$ was found to be roughly constant as a function of temperature with a value of about $9 \times 10^{-9}$ cm$^2$/sec. As is shown in figure 9, our calculations are in good agreement with the experimental data above average energies of 60 meV. Also in good agreement with the experimental points are values of $k(T)$ obtained by J. P. Guayacq using the zero radius potential approximation discussed in the introduction. The experimental results are about half of the value of the Langevin rate constant. This is smaller than rate constants which have been obtained for other associative detachment processes such as $H + F^- \rightarrow HF + e$. The low rate constant may be due to a slight potential barrier in the potential $V_{\text{eff}}(R)$, or by the fact that the lifetime of $\text{HCl}^-$ is comparable to the collision time.

4. Detachment Probabilities

The probabilities for associative detachment into the vibrational states were found for several values of $l$. Detachment probabilities for the first five vibrational states are shown as a function of energy in figure 14 at $l = 30$. Each curve has a maximum at an energy $E = (E_{\text{max}} + E_{\text{max+1}})/2$, or half way between the two bound state energies. Then we would expect the energy spectrum of the detached electrons to have a maximum at $-(E_{\text{max}} - E_{\text{max+1}})/2$. The average
**Figure 11**

- Experimental results of McFarland et al.
- Howard et al.

- Theoretical results ERP model J.P. Gauyacq

- Present results
SURVIVAL PROBABILITY  DCL

$P_s$ vs $E$

$L = 30$
SURVIVAL PROBABILITY  DCL

L = 15
energy of the detached electrons has been found to be about half of the energy difference of the vibrational states.

It is noteworthy that the detachment probability for each state \( n \) becomes small as additional states become energetically accessible. No significant contribution was seen from the ground vibrational state, either experimentally or in our calculations.

C. \( \text{H(D)} + F^- \)

1. The Potential Energy

Again a Morse potential was used to fit the curves of Goldstein and Segal for HF and HF\(^-\).\(^1\)\(^2\)\(^3\)\(^4\) This system differs from the HCl in that there are five vibrational states below the negative ion's potential \( V_{n\rightarrow}(R) \) as \( R \rightarrow \infty \). The coupling potential energy was chosen to be

\[
V_{k-1}(R) = 0.93 \exp(-0.75R) \hat{V}_{n\rightarrow}
\]

Using this coupling potential our calculations give a rate constant of \( 1.6 \times 10^{-9} \text{ cm}^3/\text{sec} \) at thermal energy, which is the experimental result found by Howard et. al.\(^3\) This rate constant is close to the Langevin limit, so that we can expect the survival probabilities to be smaller than those found for HCl and DCl.

2. The Survival Probability

The survival probability for HF is small in comparison with that for HCl. This is in accordance with the larger rate constant found for HF. Survival
probabilities are shown in figures 10 and 11 as a function of energy at two values of \( \ell \) for HF and DF. The isotope effect was found to be similar to that found for the previous collision system. A striking isotope effect has been found for the distribution of detachment probabilities into the vibrational states by Zweir et. al. The detachment probabilities for HF are sharply peaked, while for DF there is very little difference in the detachment probabilities into the bound vibrational states. The isotope effect on the survival probability found in this work is in accordance with the experimental results.

D. Summary

The experimental rate constants for the system \( \text{H} + \text{Cl}^- \) have been reproduced by our calculations. A large isotope effect was found in the survival probability for both systems studied. In the case of \( \text{H(D)} + \text{F}^- \), this was not unexpected, since a large isotope effect has been seen in the distribution of final states of the molecule.
CHAPTER VIII

CONCLUSION

A. Summary

We have presented a quantum mechanical theory of associative detachment. The theory is based on the work of Taylor, Wang and Delos, in which a close-coupling theory was used. The present theory is more general in that the nuclei are treated quantum mechanically rather than semi-classically.

Chapter II dealt with the boundary conditions of the reaction and with two projection operators which greatly simplified the analysis. In the next chapter an integro-differential equation for the wave function of the negative ion was derived and a 'Green's function' describing transitions into and out of the continuum was found. The equation was solved to first order in the chapters III and IV using complex momenta. These complex momenta then were used to find the survival probability of the negative ion. Transition probabilities and the wave function \( u(R) \) came in chapter VI.

The equations were applied to the reactions

\[
H(D) + Cl^- \rightarrow HCl + e
\]
H (D) + F^- \rightarrow HF + e

In all cases, the rate constants were large at thermal energies. The isotope effect on the survival probability was found to be very large for both systems.

B. In the Future

A more thorough study of the detachment probabilities into each vibrational state would be worthwhile. The isotope effect in these detachment probabilities has been measured for H (D) + F^- . It would be interesting to study that effect using this theory.

The extension of the theory given here to direct detachment and dissociative attachment would not be difficult. The boundary conditions for doing so were given in Appendix C. It would be interesting to apply this theory to the direct detachment, for which there is a great deal of data and many calculations. In addition, many experiments have been done on dissociative attachment. The relationship between rate constants for associative detachment and dissociative attachment would be interesting to study.
APPENDIX A

THE COUPLING POTENTIAL ENERGY

In this appendix the coupling potential energy \( V \) and the density of states in the continuum are discussed. Since it has been assumed that \( V \) has separable \( H \) and dependence, we may use the model of Taylor and Delos in which the electronic potential energy was assumed to be a square well with one bound state.\(^{35}\) The potential energy was also assumed to be independent of \( H \). The density of states is that for a free electron and may also be found using the square well model.

The single electron states found by solving the Schrödinger equation for a square well model with one bound state (shown in figure 12) are

\[
q_{\alpha}(r) = \begin{cases} \frac{\sqrt{\pi}}{2} \sin(k_{\alpha} r) & r < r_0 \\ \frac{\sqrt{\pi}}{2} \sin(k_{\alpha} r_0) e^{-\frac{\hbar k_{\alpha}}{2m}(r-r_0)} & r > r_0 \end{cases} \quad A \ 1
\]

\[
q_{\sigma}(r) = \begin{cases} \sqrt{\frac{2}{\pi \hbar}} e^{-\frac{1}{2} k_{\sigma} (r-r_0)} & r < r_0 \\ \sqrt{\frac{2}{\pi \hbar}} (\frac{r}{r_0}) \left[ e^{i \frac{\hbar k_{\sigma}}{4m}(r-r_0)} \left( \frac{2}{\hbar \sqrt{m \hbar}} \cos k_{\sigma} r_0 \right) \right. \\ + i \sin k_{\sigma} r_0 \left. e^{-i \frac{\hbar k_{\sigma}}{4m}(r-r_0)} \left( \frac{2}{\hbar \sqrt{m \hbar}} \cos k_{\sigma} r_0 + i \sin k_{\sigma} r_0 \right) \right] & r > r_0 \end{cases} \quad A \ 2
\]

with
Figure 12

Electronic Potential Energy

![Graph showing an electronic potential energy diagram]
\[ k_n = \frac{\sqrt{2m(E_n - V_0)}}{\hbar} \]

\[ k_{nm} = \frac{\sqrt{2m(E + V_0)}}{\hbar} \]

\[ k_n = \frac{\sqrt{2m(E - V_0)}}{\hbar} \]

\[ k_n = \frac{\sqrt{2mE}}{\hbar} \]

\[ N = r_n + \frac{\frac{\sqrt{2mE}}{\hbar} \cos^2(k_n r_n) + \sin^2(k_n r_n)}{E_{nm}} \]

\[ n = \frac{h^2}{k_n^2} \cos^2(k_n r_n) + \sin^2(k_n r_n) \]

The wave functions are required to be zero at the origin and at \( L \), where \( L \) is the length of the box in which the wave functions are normalized. Later this will be allowed to go to infinity.

Then the coupling potential \( \hat{V}_{n-} \), is

\[ \hat{V}_{n-} = \int dr \phi_{n-}(r) V_e \phi_{n+}(r) \]

Since the states \( \phi_{n-} \) and \( \phi_{n+} \) are real, \( V_{n-} \) is equal to \( V_{n+} \).

The density of states \( \rho_n \) for a free particle is found by applying the boundary condition at \( L \) to the free wave functions. Then
so that

\[ e^{-i k x L} - e^{i (k x L + 2 \pi)} = 0 \]  

Now \( \rho_{k_n} \) is the density of states per unit wave number \( k \), so that

\[ k x L + \gamma = N \pi \quad N = 0, 1, 2, \ldots \]  

\[ \rho_{k_n} = \frac{d \rho_{k_n}}{d k_n} = \frac{k_n}{\pi} + \pi \frac{d \gamma}{d k_n} \]  

Then as \( L \to \infty \),

\[ \rho_{k_n} \to \frac{k_n}{\pi} \]  

It will be necessary to find the integral

\[ \int \frac{d V_{k_n}}{E - E_{k_n}} \]  

The reader is referred to ref. for a full discussion of this. Briefly, the integrand has two poles on the real
axis, at \( \sqrt{\frac{E}{\hbar^2}} \). On the imaginary axis there are also two:

\[ \sqrt{\frac{E}{\hbar^2}} = E_0. \]

In the complex plane the normalisation term \( N \) of the continuum wave function \( \Phi_{\epsilon n} \) contributes an infinite number of first order poles, making a numerical solution preferable to complex integration. The following functions were found by Taylor and Delos to be a good fit to the curve resulting from a numerical integration of eq. A 15

\[
f d \hbar \rho_n \frac{1}{E - \epsilon_n} = \frac{2}{3N \alpha m^2} \frac{\alpha_n}{E - \alpha_n} \quad E < 0 \quad A 16
\]

\[
f d \hbar \rho_n \frac{1}{E - \epsilon_n} = \frac{2k}{3N \sqrt{\alpha m^2}} \left( \frac{\alpha_n + \alpha_n E}{(E + \epsilon_n)^2} + i \frac{\alpha_n \sqrt{\alpha}}{((E + \epsilon_n)^2)} \right) \quad E > 0 \quad A 17
\]

These functions will be used for the integral in eq. A 15 throughout this work.
APPENDIX B

BOUNDARY CONDITIONS

A proof that the boundary condition on the free electronic states

\[ \sum_{\omega} \mathcal{E}(\mathbf{r}; \mathbf{r}') = \int d\mathbf{r} \rho_{\mathbf{r}} \phi_{\mathbf{r}}(\mathbf{r}; \mathbf{r}') \psi_{\mathbf{r}}(\mathbf{r}) \]  

reduces to a discrete sum over bound molecular state energy levels

\[ \sum_{\omega} \mathcal{E}(\mathbf{r}; \mathbf{r}') = \sum_{\omega} \psi_{\omega}(\mathbf{r}; \mathbf{r}') \psi_{\omega}(\mathbf{r}) \]

is given in this appendix. In addition, it will be shown that each electronic wave function in the final sum must be purely outgoing.

First consider the projection \( \mathcal{E} \). If a set of basis vectors \( |\omega\rangle \) are defined as the vector representation of the basis states \( \psi_{\omega}(\mathbf{r}) \), so that

\[ |\omega\rangle = \int d\mathbf{r} |\omega \mathbf{r}\rangle \psi_{\omega}(\mathbf{r}) \]

with

\[ H_{\omega \mathbf{r}} \psi_{\omega}(\mathbf{r}) = E_{\omega} \psi_{\omega}(\mathbf{r}) \]
\[ H_{00}(R) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + V_{00}(R) \]

we have

\[ \langle E_{n} \rangle = \int d\mathbf{r} \rho_{n} \phi_{n} \langle \phi_{n} | \mathbf{H} | \phi_{n} \rangle \]

\[ \langle R | \mathbf{Q} | \mathbf{E} \rangle = \int d\mathbf{r} \rho_{n} \phi_{n} \phi_{n}^* \phi_{n}^* \mathbf{Q} \phi_{n} \mathbf{\nabla}_{n} \langle \mathbf{n} | \mathbf{n} \rangle \]

with

\[ \phi_{n} = \frac{\langle \mathbf{n} | \mathbf{n} \rangle}{E - E_{n} - \hbar \omega} \]

as was shown in Chapter VI.

Now it is known that in the limit as \( r \to \infty \),

\[ \lim_{r \to \infty} \langle \mathbf{n} | \mathbf{n} \rangle = \frac{\hbar^2}{2M} \langle \mathbf{n} | \mathbf{n} \rangle / \hbar \]

Now the coordinate representation of \( \ket{\mathbf{n}} \) is a mixed outgoing and incoming state. Then

\[ \lim_{r \to \infty} \langle R | \mathbf{Q} | \mathbf{E} \rangle = \int d\mathbf{r} \rho_{n} \phi_{n} \left\{ \frac{\mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} + \mathbf{e}^{-i\mathbf{k} \cdot \mathbf{r}}}{E - E_{n} - \hbar \omega} \right\} \]

\[ \times \mathbf{\nabla}_{n} \langle \mathbf{n} | \mathbf{n} \rangle \langle \mathbf{n} | \mathbf{n} \rangle \]

\[ = \int d\mathbf{r} \rho_{n} \phi_{n} \left\{ \frac{\mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}} + \mathbf{e}^{-i\mathbf{k} \cdot \mathbf{r}}}{E - E_{n} - \hbar \omega} \mathbf{\nabla}_{n} \langle \mathbf{n} | \mathbf{n} \rangle \langle \mathbf{n} | \mathbf{n} \rangle \right\} \]

\[ \times \mathbf{\nabla}_{n} \langle \mathbf{n} | \mathbf{n} \rangle \langle \mathbf{n} | \mathbf{n} \rangle \]

Now at large \( r \), \( \exp(i\mathbf{k} \cdot \mathbf{r}) \) is a rapidly oscillating function
so that when it is multiplied by a smooth function of \( k \), the integral is zero. Then, since \( \langle k | H | -1 \rangle \) is a smooth function on the real axis,

\[
\lim_{r \to \infty} \int dk \rho_k \frac{e^{ikr}}{E - E_m - i\delta} \langle k | H | -1 \rangle = 0
\]

so that as \( r \to \infty \), the integral is equal to the value of the residue at \( E - E_m = \frac{i\delta}{2} \).

The contour, shown in figure 13, is chosen to lie on the upper half of the complex plane for the integration on the outgoing part of the wave function and on the lower half for the incoming part. In this way the integral converges as \( |k| \to \infty \). To find the integral of the outgoing part of the wave function, small positive imaginary part is added to the term \( (E - E_m) \). Then we have

\[
\lim_{r \to \infty} \langle k | \mathcal{Q} | -1 \rangle = \pi \rho_k \left( \frac{e^{ikr}}{E - E_m - i\delta + \frac{i\delta}{2}} \right)^2 \langle k | H | -1 \rangle \quad B.11
\]

\[
\lim_{r \to \infty} \langle k | \mathcal{Q} | -1 \rangle = -\pi i \rho_k \left( \frac{e^{ikr}}{E - E_m - i\delta - \frac{i\delta}{2}} \right) \langle k | H | -1 \rangle \quad B.12
\]

\[
\delta = \frac{i\delta}{2} \quad B.13
\]

so that only the pole on the positive real axis is included in the integration of the outgoing part of the wave function.
function. The pole on the negative real axis must be included in the integration of the incoming part so we again add a small imaginary term to $E-E_m$ for this integral. Then

$$\int_{\Omega} \frac{e^{-i \mathbf{K} \cdot \mathbf{r}}}{(E-E_m)^{\nu_+} + i \epsilon + \frac{\nu_m}{2 \Omega}} \frac{<m_1 | H_{m-1} | 1>}{\nu_m(r)}$$

and

$$\frac{1}{i \hbar} \int_{\mathbf{K} \cdot \mathbf{r}} \frac{e^{-i \mathbf{K} \cdot \mathbf{r}}}{(E-E_m)^{\nu_+} + i \epsilon + \frac{\nu_m}{2 \Omega}} \frac{<m_1 | H_{m-1} | 1>}{\nu_m(r)}$$

so that

$$\lim_{r \to \infty} \Xi(r; \mathbf{K}) = -\pi i \frac{\nu_m}{\sqrt{E-E_m}} \left( \frac{<m_1 | H_{m-1} | 1>}{\sqrt{E-E_m}} \right) e^{i \hbar m r} \nu_m(r)$$

For $E < E_m$ the poles lie on the imaginary axis and the integration is performed so that the exponential term goes to zero as $r \to \infty$.

Thus the limit as $r \to \infty$ of $\Xi$ is a sum over vibrational states and the electronic wave functions are purely outgoing.
APPENDIX C

MORE BOUNDARY CONDITIONS

The theory presented in this work may be easily extended to the reactions direct detachment and dissociative attachment. The boundary conditions for doing so will be discussed in this appendix.

The boundary condition on \( Q(V) \) was presented in section II B. as a sum over bound vibrational states as \( r \to \infty \). For direct detachment the energy is high enough that free nuclear states must be included, and the sum becomes

\[
\sum_{m} \left\{ \psi_{m}^{*} \phi_{m} \right\} + \int_{0}^{L} \sqrt{\psi_{m}^{*} \phi_{m}} d\sigma_{m} \]

where \( \psi_{m}(R) \) are the free nuclear states. In the sum, they are normalized over a space of length \( L \), and there is a condition that \( \psi_{m}(L) = 0 \). Now these states are similar to the electronic states discussed in Appendix A, so that the sum over free states can become an integral over a continuum, with a density of states defined as

\[
\rho_{n} = \frac{1}{\pi} \frac{d\sigma_{m}}{dE} \]

Then
The limit as $R \to \infty$ is also different from that of associative detachment. Before, the bound states went to zero exponentially at large $R$. Now the free states must be purely outgoing in the limit as $R \to \infty$. Then in exactly the same way as the electronic states $\Phi_k$ were made to be purely outgoing in Appendix B,

$$ \lim_{R \to \infty} E(\vec{r}, \vec{R}) = \Phi_k(\vec{r}, \vec{R}) u_{\infty}(R) $$

$$ + \sum_k \lambda_k \Phi_k(\vec{r}, \vec{R}) \frac{\pi i k}{\sqrt{e_k - e_{\infty}}} e^{ik\cdot R} \delta(\varepsilon - \varepsilon_{\infty}) $$

The sum over bound states has remained, so that the above conditions permit associative detachment, direct detachment, or both depending on the energy and the presence or absence of bound nuclear states $\nu_{\infty}(R)$.

Dissociative attachment has boundary conditions similar to those of associative detachment. In the limit as $R \to \infty$ there is only one possible state: $u_{\infty}(R)$. It must be purely outgoing as $R \to \infty$, which changes the normalization given in Chapter IV. Suppose that the state of the molecule corresponding to the incoming electron is $N$. Then $u_{\infty}(R)$ may be found in the same way that $u_{\infty}(R)$ was found in Chapter V: using a semiclassical Green's function. In this case, it is
\[ A_{-1}(R, R') = \frac{\epsilon}{\sqrt{\rho(R)\rho(R')}} e^{i\frac{R_1^2}{\rho(R)}} \int_{R}^{R'} \rho_{-1}(R') dR' \]  

so that

\[ (\mathcal{E} - \mu_{-1}) \psi_{-1} = \mathcal{V}_{-1,\kappa} \psi_{-1} \]

\[ (\mathcal{E} - \mu_{-1}) \psi_{-1}(R, R') = \delta(R - R') \]

\[ \psi_{-1}(R) = \int_{R}^{R'} \psi_{-1}(R, R') \mathcal{V}_{-1,\kappa}(R') \psi_{\kappa}(R') \]

The wave function is then

\[ \psi_{-1}(R) = e^{-\frac{i}{\hbar} \int_{R}^{R'} \mathcal{V}_{-1,\kappa}(R') \psi_{\kappa}(R') dR'} \]  

\[ \psi_{-1}(R) = e^{-\frac{i}{\hbar} \int_{R}^{R'} \mathcal{V}_{-1,\kappa}(R') \psi_{\kappa}(R') dR'} + \int_{R}^{R'} \psi_{-1}(R) \psi_{\kappa}(R') \psi_{-1}(R') \psi_{\kappa}(R') dR' \]  

The use of an outgoing Green's function has automatically fulfilled the requirement that \( \psi_{-1}(R) \) be purely outgoing at large \( R \).

The bound states have the condition that at large \( r \), there is one state with an incoming electronic wave function. Classically this is the state of the molecule before the collision. Provision is made for the molecule to change its vibrational state during the collision by requiring that wave functions of these states be purely outgoing at large \( r \). Then, drawing on the results for \( \psi_{-1}(R) \) and \( \psi_{\kappa}(R) \) found earlier, we have
The derivations given in this work may then be made to apply to other reactions by extending the sum over bound states into the continuum and/or changing the normalization given in eq. 6.5.
APPENDIX D

THE BOUND STATE EIGENFUNCTIONS

The nuclear eigenfunctions for the bound vibrational states \( \psi_n(R) \) are solutions to the equation

\[
H_n(R) \psi_n(R) = E_n \psi_n(R)
\]

A uniform approximation to the eigenfunctions will be presented here. There are up to 7 regions for which \( \psi_n(R) \) must be found, since the angular momentum peak may result in the potential having three turning points, as is seen in figure .

Semiclassical solutions to the regions away from turning points are

\[
\psi_m(A) = \frac{1}{\sqrt{A}} e^{i \frac{\alpha_m}{2} A} + \frac{1}{\sqrt{B}} e^{-i \frac{\alpha_m}{2} B} \quad \text{(D 2)}
\]

\[
\psi_n(B) = \frac{1}{\sqrt{B}} e^{i \frac{\alpha_n}{2} B} + \frac{1}{\sqrt{M}} e^{-i \frac{\alpha_n}{2} M} \quad \text{(D 3)}
\]

Near the turning points, combinations of \( A_1 \) and \( B_1 \) are used.
There are several conditions on the wave function. First is the bound state condition on the energy

\[ \frac{1}{R} \int_{R_{np}}^{R} \omega_{m}(R) dR = (m + \frac{1}{2}) \pi \quad m = 0, 1, \ldots \]

In this way in the absence of the third turning point the wave function goes to zero as \( R \to 0 \) and \( R \to \infty \). Then

\[ \psi_{m}(R) = \frac{C_{1}}{\sqrt{\omega_{m}}} e^{\frac{i}{\hbar} \int_{R_{np}}^{R} \omega_{m}(R') dR'} \sin \left( \frac{1}{\hbar} \int_{R_{np}}^{R} \omega_{m}(R') dR' + \frac{\pi}{2} \right) \]

Now if there is a third turning point tunnelling is possible. The wave function must be purely outgoing in the region outside of the outer turning point and must go to zero at small \( R \) as before. Then

\[ \psi_{m}(R > R_{np}) = \frac{C}{\sqrt{\omega_{m}}} e^{\frac{i}{\hbar} \int_{R_{np}}^{R} \omega_{m}(R') dR'} \]

The functions \( \psi_4 \) and \( \psi_5 \), used in the Green's function \( \mathcal{G} \), may be found in a similar way, but they have different boundary conditions. If there are only two turning points,

\[
\lim_{R \to R_p} \psi_4(R) = 0 \quad D\ 9
\]

\[
\lim_{R \to R_p} \psi_5(R) = 0
\]

If there are three, however,

\[
\lim_{R \to R_P} \psi_4(R) = \frac{2a'}{R_{R_P}^2} \sin \left( \frac{R_{R_P} \theta_P}{R_{R_P}^2} k + \eta_4 \right) \quad D\ 10
\]

Then with the basic solutions in the separate regions the same as those for \( \psi_4(R) \), we have

\[
\psi_4(R) = \psi_4^0 \ e^{i \int_{R_{R_P}}^R \theta_P \ dR'} \quad R < R_{R_P}, \quad D\ 11
\]

\[
\psi_5(R) = \frac{2c}{\theta_P} \ \sin \left( \int_{R_{R_P}}^R \theta_P \ dR' + \eta_4 \right) \quad R > R_{R_P},
\]

\[
\psi_4(R) = \sqrt{\theta_P} \ \sin \left( \int_{R_{R_P}}^R \theta_P \ dR' + \eta_4 \right) \ e^{i \int_{R_{R_P}}^R \theta_P \ dR'} + \cos \left( \int_{R_{R_P}}^R \theta_P \ dR' + \eta_4 \right) \ e^{-i \int_{R_{R_P}}^R \theta_P \ dR'}
\]
Connecting the solutions so that the $\psi$'s are continuous and have the proper boundary conditions,

$$\psi_c(R = R_{BP}) = \frac{\psi_0}{\sqrt{c_0}} \left[ \sin \left( \int_{R_{BP}}^{R_{r}} \frac{\phi_0}{c} + n_i u \right) \right]$$

For three turning points,

$$\psi_c(R > R_{BP}) = \frac{\psi_0}{\sqrt{c_0}} \left[ \sin \left( \int_{R_{BP}}^{R_{r}} \frac{\phi_0}{c} + n_i u \right) \right]$$

$$\psi_c(R = R_{BP}^*) = \frac{\psi_0}{\sqrt{c_0}} \left[ \sin \left( \int_{R_{BP}}^{R_{r}} \frac{\phi_0}{c} + n_i u \right) \right]$$
The above forms of $v_\mu (R)$ and $\Psi$ were used in the calculations to find $u_-, (R)$ and the detachment probabilities.
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