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A general theory of electron detachment in negative ion collisions

Tzuu-Shin Wang
College of William & Mary - Arts & Sciences

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A GENERAL THEORY OF ELECTRON DETACHMENT IN NEGATIVE ION COLLISIONS

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A GENERAL THEORY OF ELECTRON DETACHMENT
IN NEGATIVE ION COLLISIONS

A Dissertation

Presented to

The Faculty of the Department of Physics

The College of William and Mary in Virginia

In Partial Fulfillment

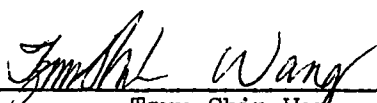Of the Requirements for the Degree of

Doctor of Philosophy

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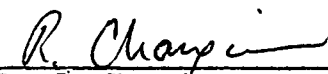

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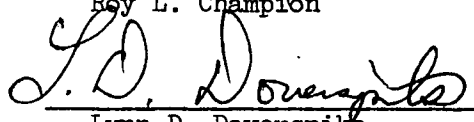
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ABSTRACT

In this thesis a general theory of electron detachment in slow collisions of negative ions with atoms is presented. The theory is based upon a semiclassical close-coupling framework, following the work of Taylor and Delos. The Schrodinger equation is reduced, under certain assumptions, to a non-denumerably infinite set of coupled equations. We develop a new method for solving these equations that is more general than the methods used by Taylor and Delos. A zero-order approximation of our solution is applied to the case of $H^-(D^-)$ on Ne collisions, the results are compared with the experimental data, and we find good agreement between theory and experiment, particularly with regard to the isotope effect. A first-order approximation of the solution is proved to be very close to the exact solution, and it is applied to the case of $H^-(D^-)$ on He collisions. We use quadratic and quartic approximations for the energy gap $\Delta(t)$ to calculate, among other things, the survival probability and electron energy spectrum. There are some interesting results for the electron energy spectrum which have not yet been observed in experiments.

A GENERAL THEORY OF ELECTRON DETACHMENT

IN NEGATIVE ION COLLISIONS

Chapter I

INTRODUCTION

1.1 OBJECTIVES

There are many processes that involve strong coupling between a discrete state and a continuum. Among them are electron detachment in collisions of negative ions with atoms,[1,2]

$$A^- + B \rightarrow A + B + e^- \qquad (1.1-1)$$

Penning ionization,[3,4]

$$A^* + B \rightarrow A + B^+ + e^- \qquad (1.1-2)$$
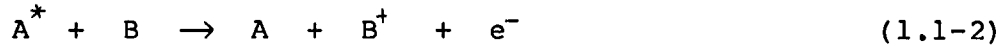
dissociative recombination[5,6] and dissociative attachment[7,8]

$$e^- + AB^+ \rightarrow A + B \qquad (1.1-3)$$

$$e^- + AB \rightarrow A^- + B \qquad (1.1-4)$$

and positron production in heavy ion collisions[9,10]

$$U^{n+} + U^{m+} \rightarrow (UU)^{(n+m)+} \rightarrow (UX)^{(n+m+1)+} + e^+$$

$$\rightarrow U^{n+} + X^{(m-1)+} + e^+$$

$$(1.1-5)$$
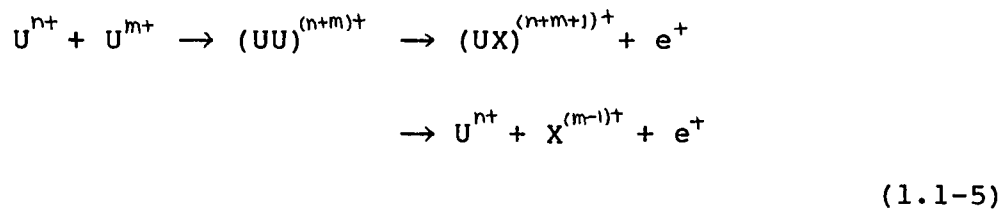
In this thesis a new theoretical method for calculating cross sections and associated rates for such processes is given. The theoretical methods developed in this thesis can be used to study any of the processes listed above (and others as well) but in our discussion we will especially consider electron detachment (1.1-1) for which there is a wealth of recent experimental data.[1,2,11~20]

In the next section we give a simple description of the background for this work. The complex-potential model and the zero-range-potential model, both of which have been applied successfully to some cases, are described briefly.

In chapter II we give a short history of the close-coupling model which we use as a foundation of our theory. Also we present the basic assumptions used in this work and the derivation of the new formulation.

In chapter III we apply a zero-order approximate solution to the case of $H^-(D^-)$ on Ne. Special examination has been made of the isotope effect, which, in the case of H^- (D^-) on Ne, has been found to be opposite to that of $H^-(D^-)$ on He collisions.

Chapter IV gives in detail the properties of a function we call the "propagator". This function plays an important role in the formulation of our solution.

In chapter V, we show that our new formulas can be converted to the complex potential formulas under a slow

collision approximation. Chapter VI describes the method for numerical solution. Then in chapters VII and VIII, we apply our new formulas to the case of $H^-(D^-)$ in collisions with He. We discuss there, among other things, the survival probabilities and the electron energy spectra.

Finally, in chapter IX we give a summary of the present work and we discuss prospects for future developments.

1.2 BACKGROUND

Early experiments on electron detachment in collisions of negative ions with atoms showed evidence that detachment could be described by a local-complex-potential model, in which it is assumed that the energy of the discrete bound state of the negative ion crosses into that of the continuum of states of a free electron (Fig.I-1), and that the discrete state becomes a resonance. This resonance or quasi-bound state is assigned a complex energy

$$\epsilon(R) = V(R) - 1/2\ i\ \Gamma(R) \tag{1.2-1}$$

and the state decays with a half-life inversely proportional to $\Gamma(R)$. Then the probability that the electron does not detach (the survival probability) is given by

$$P_S = \exp\{-2\int_{R_o}^{\infty} dR\ \Gamma(R)/v_R\} \tag{1.2-2}$$

Fig. I-1 Curve Crossing with a Continuum
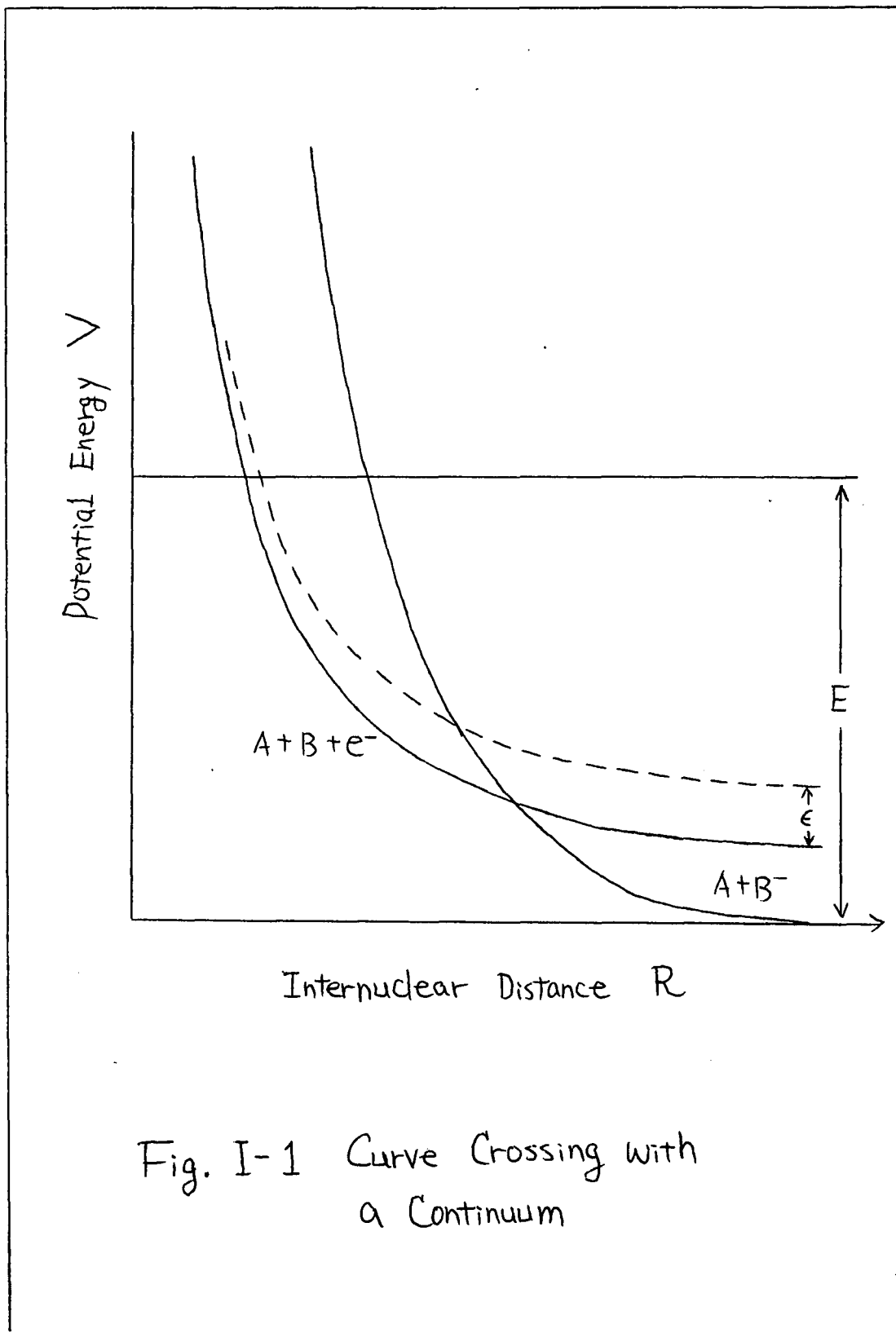
This model predicts that if we compare collisions involing H$^-$ with those involing D$^-$ at the same relative collision energy, the heavier, slower isotope will have a larger cross section for electron detachment because it spends more time in the unstable region. This "normal" isotope effect is seen in collisions of H$^-$ or D$^-$ with He, and in that case the model is in quantitative agreement with low-energy experiments.[1]

On the other hand, the opposite isotope effect was found in collisions of H$^-$ or D$^-$ with Ne or Ar.[4] No simple modification of the theory has been found to explain this isotope effect. Also, at higher energy, further discrepancies between this complex-potential model and experiments appear. These results showed that a different model of electron detachment is required.

Using a zero-range-potential (ZRP) model, Gauyacq[21] was able to explain the inverse isotope effect observed in the case of H$^-$(D$^-$) on Ne for collision energies up to 30 eV. In the ZRP model it is assumed that the active electron is bound to the atom by a potential well of very short range; as the atoms approch each other, the potential binding the active electron changes, and it might for some time interval become too weak to hold a bound state. The ZRP model involves solving the free Schroedinger equation

$$(-\hbar^2/2m)\nabla^2\psi = i\hbar\partial\psi/\partial t \qquad (1.2\text{-}3)$$

outside the range of the potential (i.e. $r > 0$), subject to a time-dependent boundary condition

$$(\psi'/\psi)_{r=0} = f(t) \qquad\qquad (1.2\text{-}4)$$

In the present thesis, we use a different approach to study electron detachment. Basically we treat these processes in a semiclassical, close-coupling framework. In its purpose, and in its basic assumptions, the theory developed here is similar to one developed by Taylor and Delos;[22] we improve on their work by using assumptions that are both more general and more suited to the specific cases we study.

Chapter II

DERIVATION OF THE NEW FORMULAS

2.1   INTRODUCTION

In this chapter, a general theory describing elec-
tron detachment processes in slow negtive ion-atom colli-
sions is derived.

Our theory is based on a close-coupling model
first developed by Demkov.[23-25] The essence of this approach
is to treat the continuum states of the free electron as an
infinite set of parallel curves and to find the solution of
the resulting coupled equations.

In close-coupling theories of electronic excita-
tion and electron detachment, two quantities are of primary
importance: the energy gap $\triangle(t)$ between the initial and fi-
nal states, and the coupling between the states, referred to
here as $V_{l,\epsilon}(t)$. In all earlier work on electron detachment,
the time-dependence of the coupling has been neglected, and
various assumptions have been made about the time-dependence
of the energy gap $\triangle(t)$. These are presented in Fig.II-1.
In (a) a stationary energy level is embedded in a continuum
This time-independent configuration interaction problem was
solved by Fano.[26] Then Demkov and his collaborators[23-25] solved

CONTINUUM

(a)   (b)   (c)   (d)
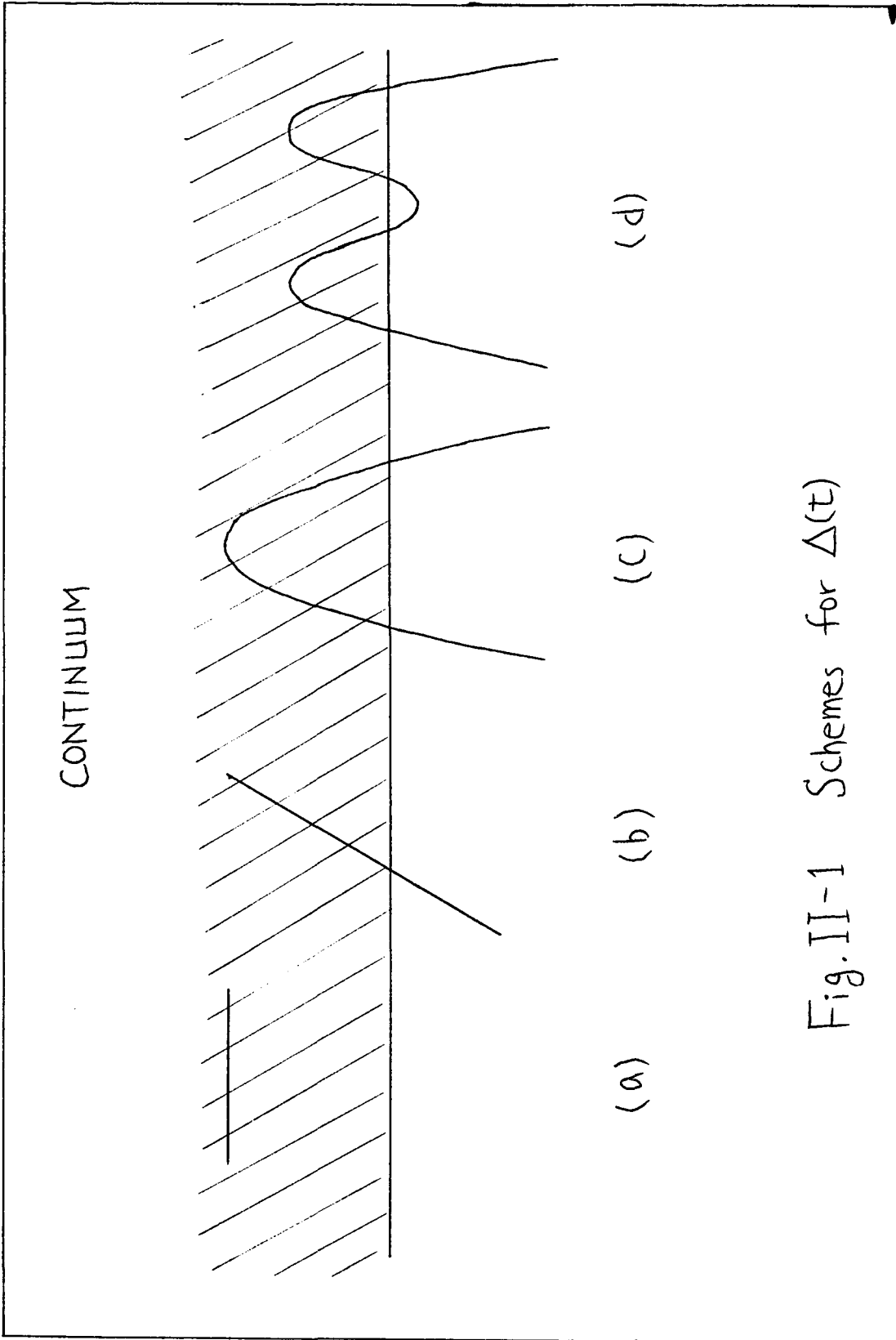
Fig.II-1 Schemes for $\Delta(t)$

the case where the energy level moves through a continuum as a linear function of time as seen in (b). In the case of a crossing between two discrete states, their formulation leads to the well-known Landau-Zener formula; for a crossing between a discrete state and a continuum, their formulas become those of the local-complex-potential model.

Recently, Taylor and Delos[22] have gone one step further by assuming a quadratic time-dependence of the potential difference, as seen in (c). Such a model can be used for describing threshold and turning-point phenomena. They applied their new formulas obtained under the quadratic approximation to calculate differential and total cross sections for $H^-(D^-)$ on He collisions. The agreement between the theoretical calculation and the experiment is good.

In this work, we take another step to make the close-coupling model more general, to handle more complicated potential differences like the case shown in (d). The present formulation allows both the energy gap and the coupling strength to be arbitrary functions of time.

Most of the assumptions defining the limits of the present approach are similar to those given by Taylor and Delos,[22] but their special assumptions about $\Delta(t)$ and $V_{-1,\varepsilon}(t)$ are eliminated. The new formulation can be used more generally to describe physical systems.

In the next section, we give the fundamental assumptions used in this work. In section 2.3, the coupled

equations are solved and the solutions are given. Section 2.4 gives the boundary conditions and the general properties of the solutions.

2.2   HYPOTHESES

We are given a molecular collision system described by a Schroedinger equaion for electrons (with coordinates collectively denoted $\vec{r}$) and nuclei (with coordinates collectively denoted $\vec{R}$)

$$H(\vec{R},\vec{r}) \; \psi(\vec{R},\vec{r}) \; = \; E \cdot \psi(\vec{R},\vec{r}) \tag{2.2-1}$$

and we are given an approprite set of boundary conditions. Assuming (i) that semiclassical approximations are applicable, this full stationary Schroedinger equation can be reduced to a "time"-dependent electronic Schroedinger equation

$$h(\vec{r},\vec{R}(t)) \; \Upsilon(\vec{r},t) \; = \; i\hbar \partial \Upsilon(\vec{r},t)/\partial t \tag{2.2-2}$$

where h is the electronic Hamiltonian, Υ is an electronic wave-function and $\vec{R}(t)$ is a trajectory for the nuclei.

The electronic wave-function $\Upsilon(\vec{r}$ t) is expanded in a carefully chosen basis containing both discrete (bound) and continuum (free) states.

$$\Upsilon(\vec{r},t) \; = \; \sum_n b_n(t) \cdot \phi_n(r;t) \; + \; \int_0^\infty b_\epsilon(t) \cdot \phi_\epsilon(\vec{r};t) \cdot \rho_\epsilon(t) d\epsilon$$

$$\tag{2.2-3}$$

where $\rho_{\epsilon}(t)$ is the density of states in the continuum ($\rho_{\epsilon}(t) > 0$ for all ϵ, t). Assuming (ii) that the basis states are orthogonal, we obtain coupled equations for the vector of coefficients b(t)

$$i\hbar d\underline{b}/dt = \{ \underline{h} + \vec{v} \cdot \vec{\underline{P}} \} \underline{b} \qquad (2.2-4)$$

where $\vec{v}$ is the nuclear velocity and

$$h_{kn} = \int \phi_{k}^{*}(\vec{r};\vec{R}) h(\vec{r},\vec{R}) \phi_{n}(\vec{r},\vec{R}) d\vec{r} \qquad (2.2-5)$$

$$\vec{P}_{kn} = \int \phi_{k}^{*}(\vec{r},\vec{R}) * (-i\hbar\nabla_{\vec{R}}) \phi_{n}(\vec{r},\vec{R}) d\vec{r} \qquad (2.2-6)$$

Electron translation factors have not been explicitly written in the expansion (2.2-3) because they are believed to be unimportant for most (but not all) of the processes of interest.

Writing spherical components of the vector $\vec{v}$, $\vec{P}$ as

$$\vec{v} = (v, v^{\theta}, v^{\Phi}) \qquad (2.2-7)$$

$$\vec{\underline{P}} = (\underline{P}, \underline{P}^{\theta}, \underline{P}^{\Phi}) \qquad (2.2-8)$$

so that v and $\underline{P}$ are the radial components of $\vec{v}$ and $\vec{\underline{P}}$, we have

$$i\hbar d\underline{b}/dt = \{ \underline{v} + v \cdot \underline{P} \} \underline{b} \qquad (2.2-9)$$

with

$$\underline{\mathcal{V}} = \underline{h} + v^\theta \cdot \underline{P}^\theta + v^\Phi \cdot \underline{P}^\Phi \qquad (2.2\text{-}10)$$

The most important assumptions are that the basis functions $\{ \phi_n(\vec{r};\vec{R}) , \phi_\epsilon(\vec{r};\vec{R}) \}$ form a partially diabatic and partially adiabatic representation having the following properties. (iii) There is one bound state ϕ_{-1} and one continuum $\{\phi_\epsilon\}$. (iv) Coupling between ϕ_{-1} and $\{\phi_\epsilon\}$ is represented diabatically, with vanishing $P_{-1,\epsilon}$ and non-vanishing $\mathcal{V}_{-1,\epsilon}$. (v) Coupling within the continuum itself is negligible,

$$\mathcal{V}_{\epsilon\epsilon'} \approx 0 , \qquad P_{\epsilon\epsilon'} \approx 0 \qquad \epsilon' \neq \epsilon \qquad (2.2\text{-}11)$$

Thus, transtions are possible from the bound state to the free states and vice versa, but direct transitions from one free state to another are neglected.

Under these conditions, the coupled equations (2.2-9) take a simple form: defining

$$C_{-1}(t) = b_{-1}(t) \cdot \exp\{i/\hbar \int_{t_o}^{t} \mathcal{V}_{neutral}(t') dt'\} \qquad (2.2\text{-}12a)$$

$$C_\epsilon(t) = b_\epsilon(t) \cdot \exp\{i/\hbar \int_{t_o}^{t} \mathcal{V}_{neutral}(t') dt'\} \qquad (2.2\text{-}12b)$$

we have

$$i\hbar dC_{-1}(t)/dt = \Delta(t) C_{-1}(t) + \int_{0}^{\infty} V_{-1,\epsilon}(t) C_\epsilon(t) \cdot \rho_\epsilon(t) d\epsilon \qquad (2.2\text{-}13a)$$

$$i\hbar dC_\epsilon(t)/dt = V_{\epsilon\epsilon}(t)C_\epsilon(t) + V_{\epsilon,-1}(t)C_{-1}(t) \qquad (2.2\text{-}13b)$$

where

$$\triangle(t) = U_{-1,-1}(t) - U_{neutral}(t) \qquad (2.2\text{-}14a)$$

$$V_{\epsilon\epsilon}(t) = U_{\epsilon\epsilon}(t) - U_{neutral}(t) \qquad (2.2\text{-}14b)$$

$$V_{\epsilon,-1}(t) = U_{\epsilon,-1}(t) \qquad (2.2\text{-}14c)$$

Eqs (2.2-13) are a non-denumerably infinite set of coupled equations. The purpose of this paper is to develop a general method for solving such equations.

The assumptions (i)-(v) listed above are regared as defining "generic" properties of a broad class of systems. Specific forms of the matrix element -- i.e. the time-dependence and ϵ -dependence of $\triangle(t)$, $V_{\epsilon\epsilon}(t)$ and $V_{\epsilon,-1}(t)$ -- are regared as "constitutive" properties, which depend upon the particular system being considered. Of course it is assumed that all of the matrix elements are bounded, continuous, differentiable functions of ϵ and t; also, a sufficient condition for validity of our manipulations is that

$$\int_0^\infty d\epsilon \int_{t_0}^t dt' |V_{-1,\epsilon}(t')V_{\epsilon,-1}(t')| \, \rho_\epsilon(t') \qquad (2.2\text{-}15)$$

converges for all finite t_o, t, and in the limits $t_o \rightarrow -\infty$, $t \rightarrow +\infty$.

In the work of Taylor and Delos[22] several additional assumptions were made. (vi) Diagonal continuum matrix elements form parallel curves, so $V_{\epsilon\epsilon}(R) - V_{\epsilon'\epsilon'}(R)$ has a negligible dependence on R, and

$$V_{\epsilon\epsilon}(R) = V_{neutral}(R) + \epsilon \qquad \emptyset < \epsilon < \infty \qquad (2.2\text{-}16)$$

with ϵ independent of R. Also the density of states ρ_ϵ is independent of R. (vii) The R-dependence (or t-dependence) of the coupling matrix element $V_{\epsilon,-1}$ between the bound and free states can be neglected. (viii) The energy gap $\Delta(t)$ is approximately a quadratic function of time.

The main contribution of the present work is the demonstration that, by using different mathematical and computational techniques, eqs (2.2-13) can be solved without these additional assumptions.

Later in our calculations, we will again use assumptions (vi), not because it is essential, but because we believe it is valid for the systems of interest to us. Later also, instead of (vii) we will use the approximation that all bound-free coupling matrix elements have the same time-dependence

$$V_{-1,\epsilon}(t) \approx V_{-1,\epsilon} \cdot g(t) \qquad (2.2\text{-}17)$$

This approximation should be reasonably accurate for most molecular collision processes and it is very convenient. It greatly simplifies the formulas and the calculations, but we emphasize that it is not essential to the present theory. Assumption (viii) is abandoned, and we allow in principle a general time-dependence of $\triangle(t)$. In a calculation we use a quartic approximation to $\triangle(t)$.

2.3 UNCOUPLING THE EQUATIONS

The infinite set of coupled equations (2.2-13) is easily reduced to a single equation because it is possible to solve Eq.(2.2-13b) for $C_\epsilon(t)$ in terms of $C_{-1}(t)$:

$$C_\epsilon(t) = \exp\{-i\,\Phi_\epsilon(t,t_o)/\hbar\}*\{\ C_\epsilon(t_o)$$

$$+ (1/i\hbar)\int_{t_o}^{t} dt'\cdot V_{\epsilon,-1}(t)\cdot \exp\{i\,\Phi_\epsilon(t',t_o)/\hbar\}C_{-1}(t')\ \}$$

$$(2.3-1)$$

where

$$\Phi_\epsilon(t_2,t_1) = \int_{t_1}^{t_2} V_{\epsilon\epsilon}(t)\,dt \qquad (2.3-2)$$

Substituting (2.3-1) into (2.2-13a) we obtain

$$i\hbar dC_{-1}(t)/dt = \triangle(t)C_{-1}(t)$$

$$+ \{\ (i\hbar)^{-1}\cdot\int_{0}^{\infty} d\epsilon\cdot\rho_\epsilon(t)\cdot V_{-1,\epsilon}(t)\cdot \exp\{-i\Phi_\epsilon(t,t_o)/\hbar\}$$

$$* \int_{t_o}^{t} dt' \cdot V_{\epsilon,-1}(t') \cdot \exp\{i\Phi_\epsilon(t',t_o)/\hbar\} C_{-1}(t') \; \}$$

$$+ \int_0^\infty d\epsilon \cdot \rho_\epsilon(t) \cdot V_{-1,\epsilon}(t) \cdot \exp\{-i\Phi_\epsilon(t,t_o)/\hbar\} C_\epsilon(t_o) \qquad (2.3\text{-}3)$$

and, reversing the order of integration (valid if (2.2-15) converges)

$$\{i\hbar d/dt - \Delta(t)\} C_{-1}(t) - \int_{t_o}^{t} \mathcal{B}(t,t') C_{-1}(t') dt' = \mho(t) \qquad (2.3\text{-}4)$$

where

$$\mathcal{B}(t,t') = (i\hbar)^{-1} \int_0^\infty d\epsilon \cdot \rho_\epsilon(t) V_{-1,\epsilon}(t) \exp\{-i\Phi_\epsilon(t,t')/\hbar\} V_{\epsilon,-1}(t') \qquad (2.3\text{-}5)$$

$$\mho(t) = \int_0^\infty d\epsilon \cdot \rho_\epsilon(t) V_{-1,\epsilon}(t) \exp\{-i\Phi_\epsilon(t,t_o)/\hbar\} C_\epsilon(t_o) \qquad (2.3\text{-}6)$$

2.4   BOUNDARY CONDITIONS AND FORMAL PROPERTIES

There are two sets of boundary conditions that apply to normal collisions. If the system begins in the bound state,

$$C_{-1}(t_o) = 1 \qquad ; \qquad C_\epsilon(t_o) = 0 \qquad (2.4\text{-}1)$$

from which it follows that

$$\mho(t) = 0 \qquad (2.4\text{-}2)$$

If the system begins in one of the free states.

$$C_{-1}(t_0) = 0 \quad ; \quad C_{\epsilon}(t) = \delta(\epsilon - \epsilon_0)/\rho_{\epsilon_0}(t) \qquad (2.4\text{-}3)$$

then

$$\mathbb{Q}(t) = \rho_{\epsilon}(t) \cdot \rho_{\epsilon_0}^{-1}(t) \cdot \underline{V}_{-1,\epsilon_0}(t) \exp\{-i\Phi_{\epsilon_0}(t,t_0)/\hbar\} \qquad (2.4\text{-}4)$$

In the present paper, we will only consider the boundary conditions (2.4-1), so $C_{-1}(t)$ satisfies the homogenous conterpart to (2.3-4).

$$\{i\hbar d/dt - \Delta(t)\}C_{-1}(t) - \int_{t_0}^{t} \mathcal{S}(t,t')C_{-1}(t')dt' = 0 \qquad (2.4\text{-}5)$$

The matrices $\underline{h}$, $\underline{P}$, $\mathcal{V}$, and V are all Hermitian, so the total probability for finding the system in bound and free states is conserved,

$$|C_{-1}(t)|^2 + \int_0^{\infty} |C_{\epsilon}(t)|^2 \rho_{\epsilon}(t)d\epsilon = 1 \qquad (2.4\text{-}6)$$

The quantities $\mathcal{S}(t,t')$, $\partial\mathcal{S}(t,t')/\partial t$, $\mathbb{Q}(t)$, $d\mathbb{Q}/dt$, $C(t)$, $dC(t)/dt$ and $d^2C(t)/dt^2$ all are continuous functions of t, provided that certain integrals converge. For those who are interested we give proofs of continuity in Appendix A.

In the limit as $t \rightarrow \infty$, $C_{-1}(t)$ is oscillatory but $|C_{-1}(t)|$ and $|C_{\epsilon}(t)|$ must approach definite limits -- after

all, $|C_{-1}(\infty)|^2$ is supposed to be the survival probability for
the negative ion, and $|C_\epsilon(\infty)|^2|\rho_\epsilon$ is the probability that an
electron will be detached with energy near ϵ. We show in
Appendix B that if $\int_{t_0}^{t}\mathcal{D}(t,t')dt'$ goes to zero sufficiently
rapidly as $t \to \infty$, then

$$\hat{C}_{-1}(t) \equiv C_{-1}(t)\exp\{-i\int_{t_0}^{t}\Delta(t')dt'/\hbar\} \qquad (2.4\text{-}7)$$

approaches a finite limit as $t \to \infty$.

2.5 DISCUSSION

The complete solution to the coupled equations
(2.2-13) under the boundary condition (2.4-1) is now accom-
plished in three steps. (1) Evaluate the propagator $\mathcal{D}(t,t')$
defined in Eq.(2.3-5); (2) Solve the fundamental integro-
differential equation (2.4-5) for $C_{-1}(t)$; (3) Use $C_{-1}(t)$ in
Eq.(2.3-1) to obtain $C_\epsilon(t)$.

We will explain in detail the properties of
$\mathcal{D}(t,t')$ in chapter IV, and in subsequent chapters we will
solve Eq.(2.4-5) by various approximate methods. Before do-
ing this, however, it is worthwhile to examine a very simple
"zero-order" approximation in which $\mathcal{D}(t,t')$ is entirely neg-
lected. In the following chapter we show that this leads to
the standard "first-order" formulas of time-dependent per-
turbation theory. This approximation is then used to calcu-
late cross sections for $H^-(D^-)$ on Ne.

Chapter III

ZERO-ORDER APPROXIMATION AND H⁻(D⁻) ON NEON COLLISIONS

3.1   INTRODUCTION

As was discussed in the first chapter, there have been measurements of electron detachment in collisions of H⁻ (D⁻) on He, Ne, Ar etc. done recently to elucidate the mechanism of the processes involving coupling between a discrete state and a continuum. The complex potential model was successfully applied to the case of H⁻(D⁻) + He by Lam et el.[1] But that model failed to explain the reverse isotope effect in the case of H⁻(D⁻) on Ne. Gauyacg[21] suggested that in the case of weak coupling the detachment comes from direct dynamical transtions from the bound state to continuum. In so doing he was able to explain the reverse isotope effect observed in the case of H⁻(D⁻) + Ne for collision energies from threshold up to 30 eV.

In this chapter we use a zero order approximation in the formulation given in the preceding chapter to calculate the total cross section for electron detachment, σ_d, for collisions of H⁻ or D⁻ with Ne. The results of this calculation are very interesting: at low energy the "anomalous" isotope effect occurs, i.e. the faster isotope gives

more detachment; however, at higher energies the system shows the "normal" isotope effect, with the slower isotope giving more detachment. Identical phenomena were found in new measurements by Huq et al.[28]

3.2 ZERO-ORDER APPROXIMATION

A "zero-order" solution to Eq.(2.4-5) is obtained by making the approximation

$$\mathcal{S}(t,t') \simeq 0 \tag{3.2-1}$$

in Eq.(2.4-5). Using $\Phi_\epsilon(t,t') = \epsilon \cdot (t-t')$ (this will be explained in section 4.2), we immediately obtain

$$C_{-1}(t) = \exp\{-i\int_0^t \Delta(t')dt'/\hbar\} \tag{3.2-2}$$

and

$$C_\epsilon(t) = \int_{-\infty}^t dt' \cdot V_{-1,\epsilon}(t') \cdot \exp\{-i/\hbar \int_0^{t'} (\Delta(t'')-\epsilon)dt''\} \tag{3.2-3}$$

These formulas are immediately recognized as being equivalent to the result of forst-order time-dependent perturbation theory.

The cross section for detachment is obtained by three numerical integrations: changing variable from t to R, we have

$$C_\epsilon(\infty) = 2\int_{R_{TP}}^\infty dR \cdot (V_{-1,\epsilon}(R)/v(R)) \cdot \exp\{-i/\hbar \int_{R_{TP}}^R dR' \cdot (\Delta(R')-\epsilon)/v(R')\}$$

$$(3.2-4)$$

where $v(R) = dR/dt$. The probability that the electron does not detach (the survival probability) is given by

$$P_S = 1 - \int_0^\infty |C_\epsilon(\infty)|^2 \rho_\epsilon \cdot d\epsilon \qquad (3.2-5)$$

The total detachment cross section is

$$\sigma_d = 2\pi \int_0^\infty \{1-P_S(b)\} b\, db \qquad (3.2-6)$$

3.3   CALCULATIONS FOR $H^-(D^-)$ ON NEON

Three quantities are needed for the calculation: the trajectory $R(t)$, which is calculated from an average potential energy, the difference between ionic and neutral potential curves $\Delta(R(t))$, and the coupling function $V_{-1\epsilon}(R(t))$.

Calculations of $h_{ion}(R)$ and $h_{neutral}(R)$ have been made by Gauyacq[21] and by Olson and Liu;[29] the results are quite close together, but $\Delta(R(t))$ that we obtained from Gauyacq's calculation is slightly lower than that obtained by Olson and Liu. Here we use the one derived from Gauyacq (Figs III-1,2). We see that in the case of $H^-(D^-)$ on Ne the negative-ion potential curve grazes the continuum as shown in Fig.III-1. This dtffers from the case of $H^-(D^-)$ on He, where the negotive-ion potential curve crosses into the continuum.

The coupling function is assumed to be of the form

Fig. III-1 Curve Crossing for
H⁻ on Ne

Fig. III-2 $\Delta(R)$ for $H^-(D^-)$ on Ne
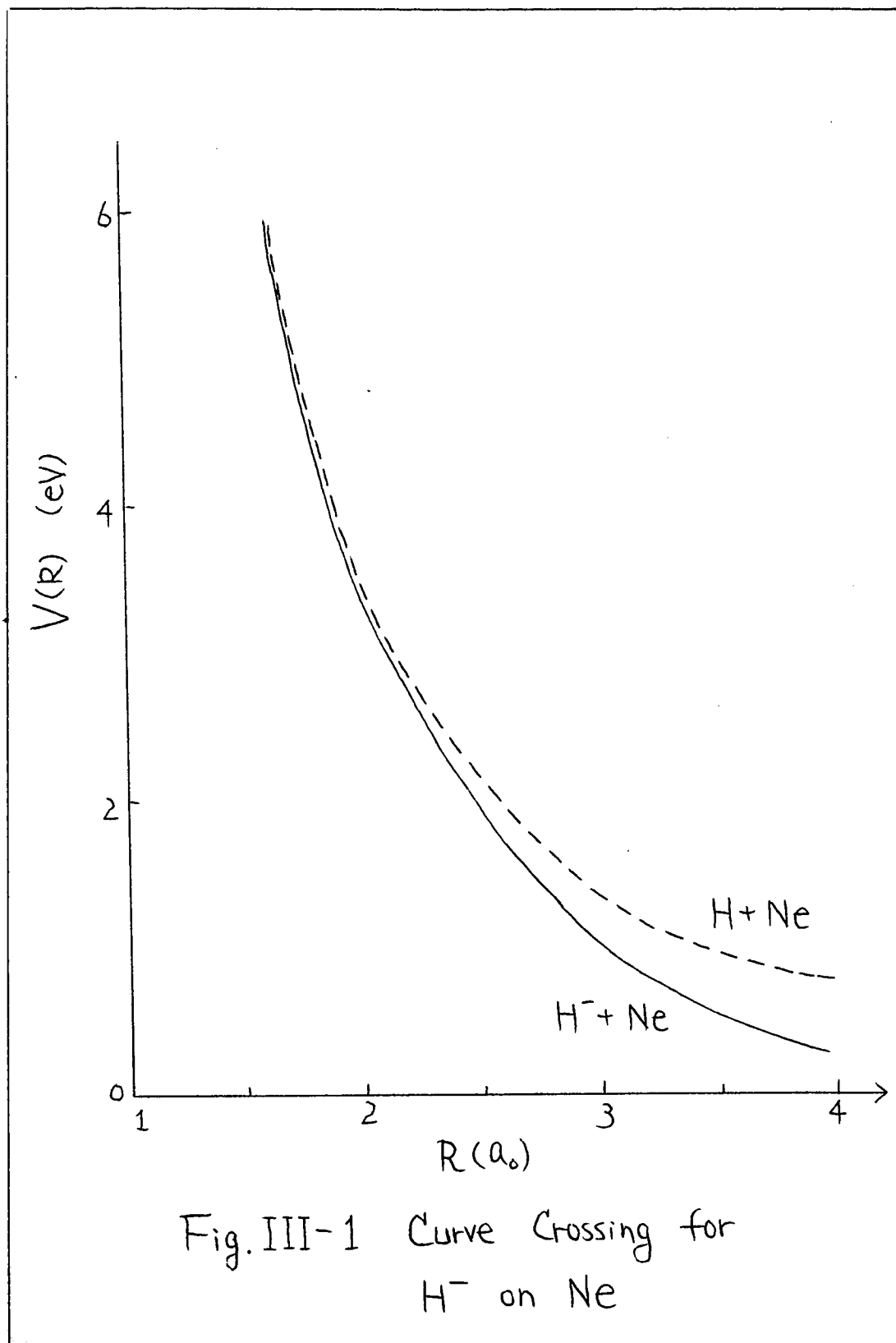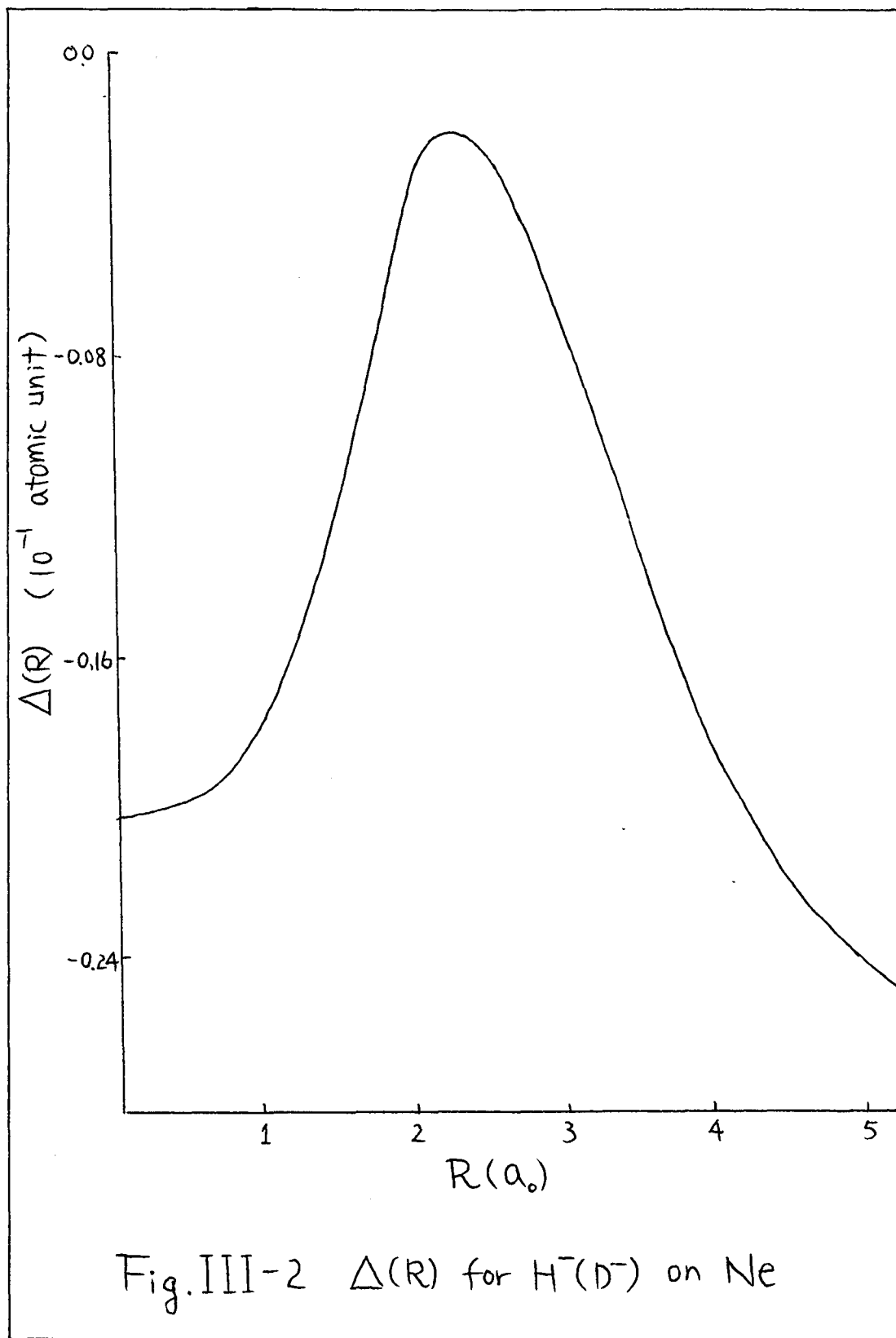
$$V_{e,1}(R) = \alpha \sqrt{2m\epsilon} \cdot \exp(-\beta R) \qquad (3\ 3\text{-}1)$$

where $\alpha = 2.58$ and $\beta = 0.66$ are chosen to fit the experimental data. This form can be justified in a number of ways, for example by taking the target Ne to be a hard repulsive core and by assuming that the bound and free wave functions for the active electron are s-waves with radial functions $e^{-\beta r}$ and $\sin(kr)$.

The calculation is now straightforward. We compute $C_\epsilon(\infty)$ in zero order using equation (3.2-2); then equation (3.2-3) gives the survival probability and (3.2-4) gives the total detachment cross section.

The experimental results for $H^-(D^-)$ + Ne have been reported by Lam et al.[1] for collision energies up to 100 eV. Recently the experiment has been reported by Huq et al.[28] in this institution for energies up to 200 eV. The comparison between the calculation and the new experiment is shown in Fig.III-3.

3.4   DISCUSSION

We see that the agreement between the calculation and the experiment is good. We not only find the "anomalous" isotope effect (H^- above D^-) at low energies, but we also find at high energies the "normal" isotope effect (D^- above H^-) in both the calculation and the experiment.
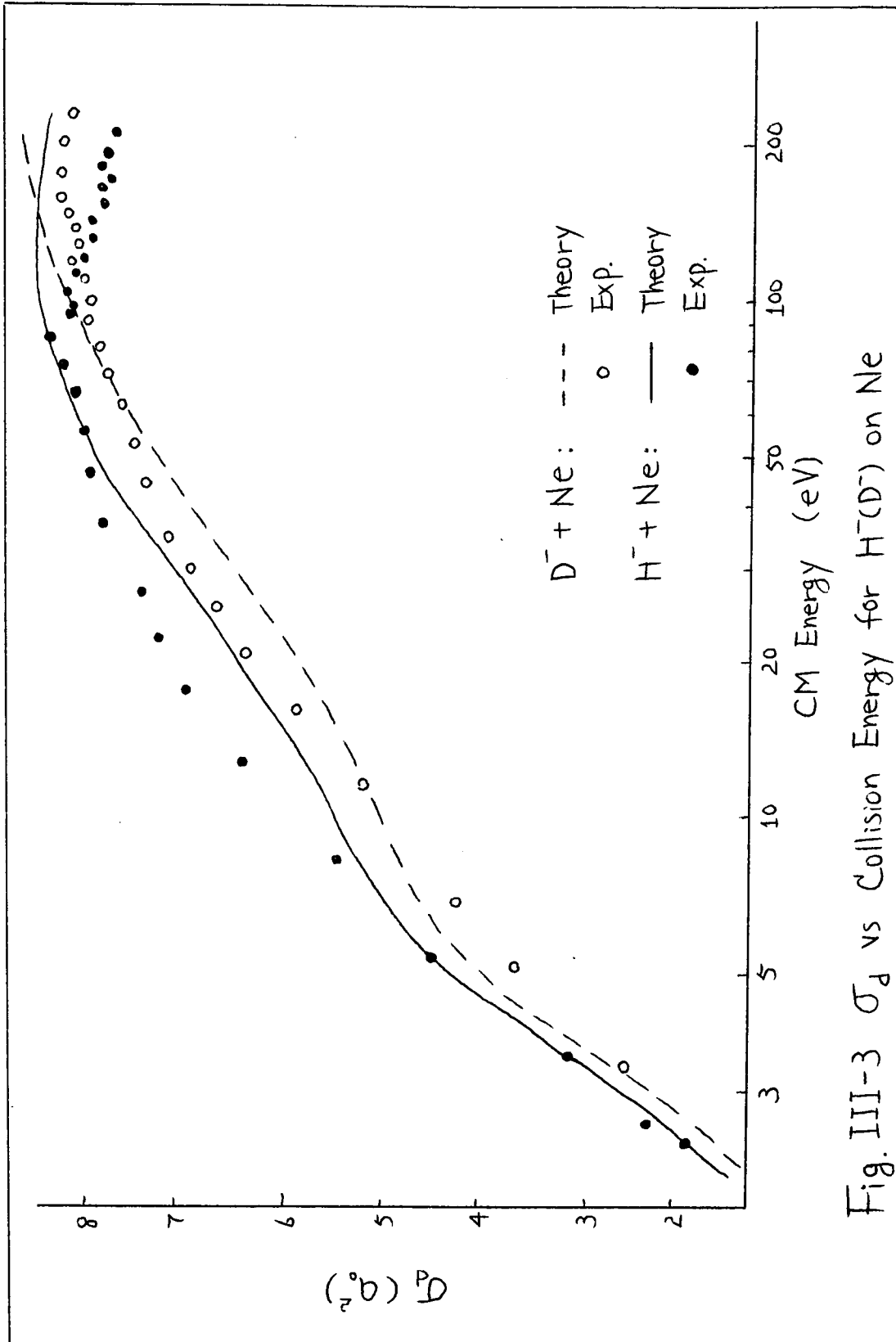
Fig. III-3 σ_d vs Collision Energy for $H^-(D^-)$ on Ne

Legend within figure:

$D^- + Ne$: Theory ---- Exp. o

$H^- + Ne$: Theory —— Exp. ●

Axis labels: $\sigma_d\ (a_o^2)$ (vertical), CM Energy (eV) (horizontal)

The "anomalous" isotope effect arises because the energy of the discrete state does not cross the continuum but just grazes it. Electrons undergo detachment only by making a jump across a small energy gap, and such jumps are more probable at higher nuclear velocity. Hence the lighter faster isotope gives more detachment. In faster collisions, we show in Fig.III-4 that the detachment cross section depends only on the relative velocity of the colliding pair, and not on their relative energy. Because the cross section gradually decreases with increasing velocity, the curves in Fig.III-3 cross over each other, and at high velocity the heavier isotope gives more detachment when cross sections are compared at the same center-of-mass energy.

It is also interesting to notice that at identical center-of-mass energies, the lighter isotope undergos detachment at somewhat larger impact parameters than does the heavier isotope (Fig.III-5).

We see, therefore, that in the case of H^- (D^-) on Ne, where there is a weak coupling between the discrete state and the continuum, the zero order approximation gives reasonable agreement between the calculation and the experiment.

In the case of strong coupling, however, the propagator $\mathcal{D}(t,t')$ can no longer be ignored. In the next chapter we shall discuss in detail the properties of the
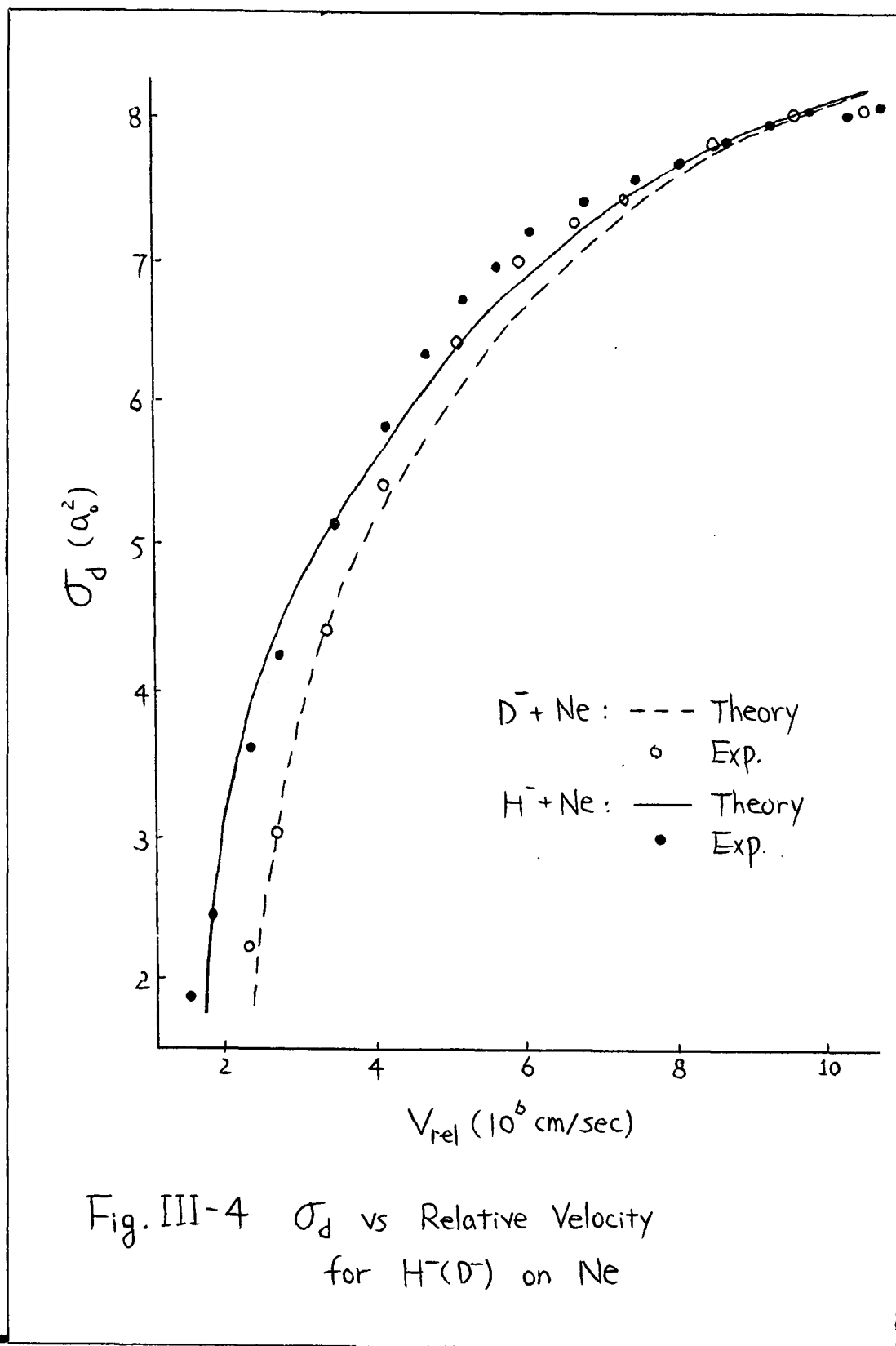
Fig. III-4 σ_d vs Relative Velocity
for $H^-(D^-)$ on Ne
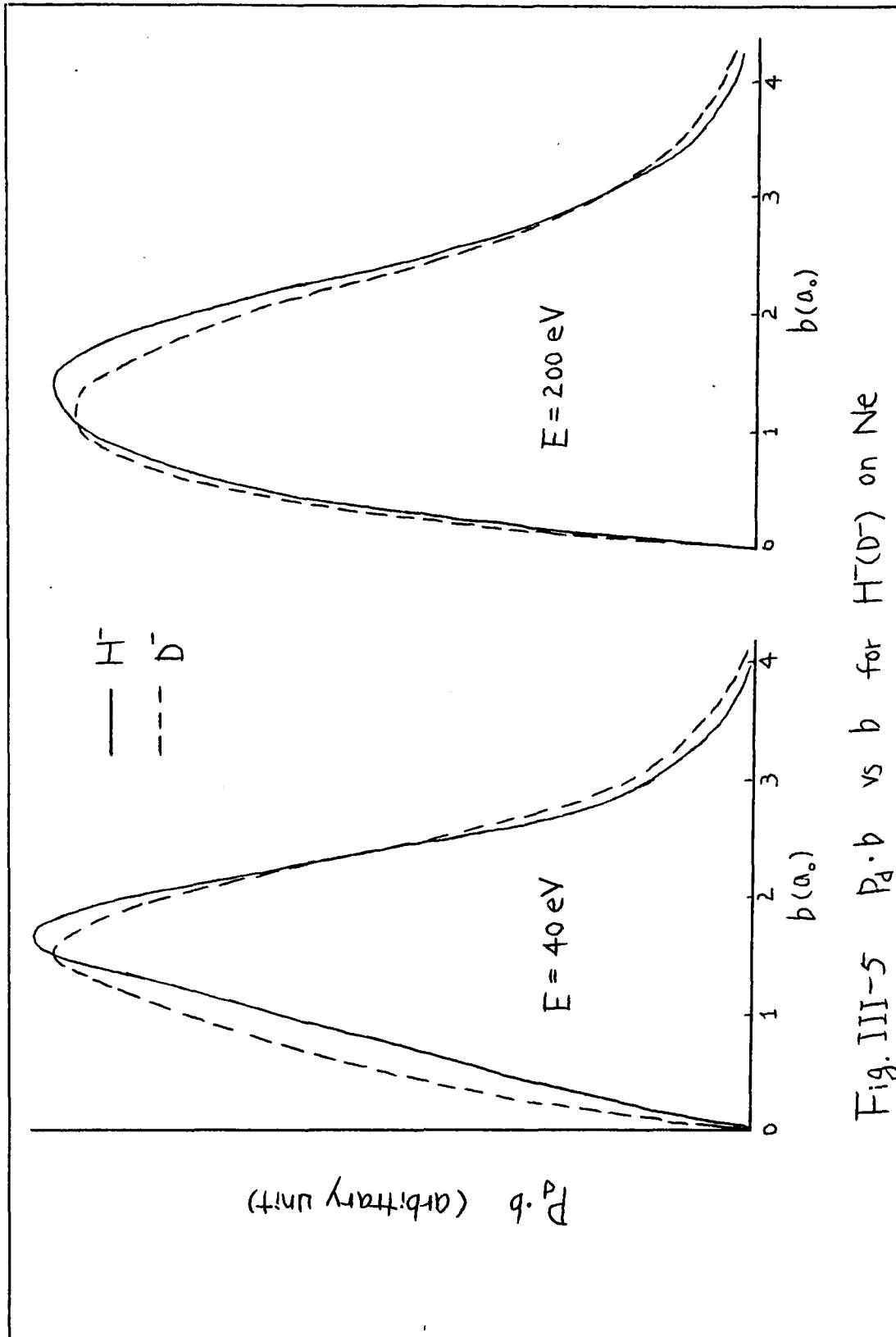
Fig. III-5 $P_d \cdot b$ vs b for $H^-(D^-)$ on Ne

propagator $\mathcal{D}(t,t')$ before applying our theory to other cases of interest.

Chapter IV

THE PROPAGATOR

4.1 INTRODUCTION

According to Eqs (2.3-4) and (2.4-2), collisions in which the electron is originally bound are governed by two functions, $\Delta(t)$ and $\mathcal{D}(t,t')$. In principle, both of these functions can be obtained from ab initio calculations. $\Delta(t)$ is the gap between the negative-ion and neutral-molecule energy curves, and this has been calculated for a number of systems. However a more elaborate calculation would be required to obtain $\mathcal{D}(t,t')$.

The properties of $\mathcal{D}(t,t')$ follow from those of the phase function $\Phi_\epsilon(t,t')$, the density of states $\rho_\epsilon(t)$, and the coupling matrix element $V_{1,\epsilon}(t)$. In the next section we shall examine each of these constituents of $\mathcal{D}(t,t')$. In Section 4.3, we give general properties of $\mathcal{D}(t,t')$ and we present an important simplifying approximation, which we call a "short-memory" approximation. In section 4.4 a reduced propagator $\hat{\mathcal{D}}(\tau)$ is given under a "separable" approximation. In section 4.5 we show some calculations related to $\hat{\mathcal{D}}(\tau)$ and its Fourier transform.

To help the reader avoid getting lost in detail, let us state the main result: under conditions discussed in this chapter, $\mathcal{S}(t,t')$ can be written approximately as

$$\mathcal{S}(t,t') \simeq |g(t)|^2 \cdot \hat{\mathcal{S}}(t-t') \qquad (4.1\text{-}1)$$

where $\mathcal{S}(t-t') \equiv \hat{\mathcal{S}}(\tau)$ has a shape like that shown in Fig.IV-1, and $g(t)$ has a shape like that shown in Fig.IV-2. Also the Fourier transform of $\hat{\mathcal{S}}(\tau)$ is called $\hat{G}(\epsilon)$, and it has a shape like that shown in Figs.IV-3,4. This is all we need to know in order to understand the calculations given in later chapters.

4.2 CONSTITUENTS

A. PHASE FUNCTION

If assumption (vi) of section 2.2 holds, i.e. if the basis function $\phi_\epsilon(\vec{r},\vec{R})$ are chosen such that their energies $U_{\epsilon\epsilon}(R)$ form a set of parallel curves then we can take ϵ to be that energy relative to the lowest state in the continuum

$$\epsilon = U_{\epsilon\epsilon}(R) - U_{neutral}(R), \qquad 0 < \epsilon < \infty \qquad (4.2\text{-}1)$$

and ϵ will be independent of R. Hence from Eqs.(2.3-2) and (2.2-14b) we have

Fig. IV-1 $\hat{\mathcal{B}}(\tau)$
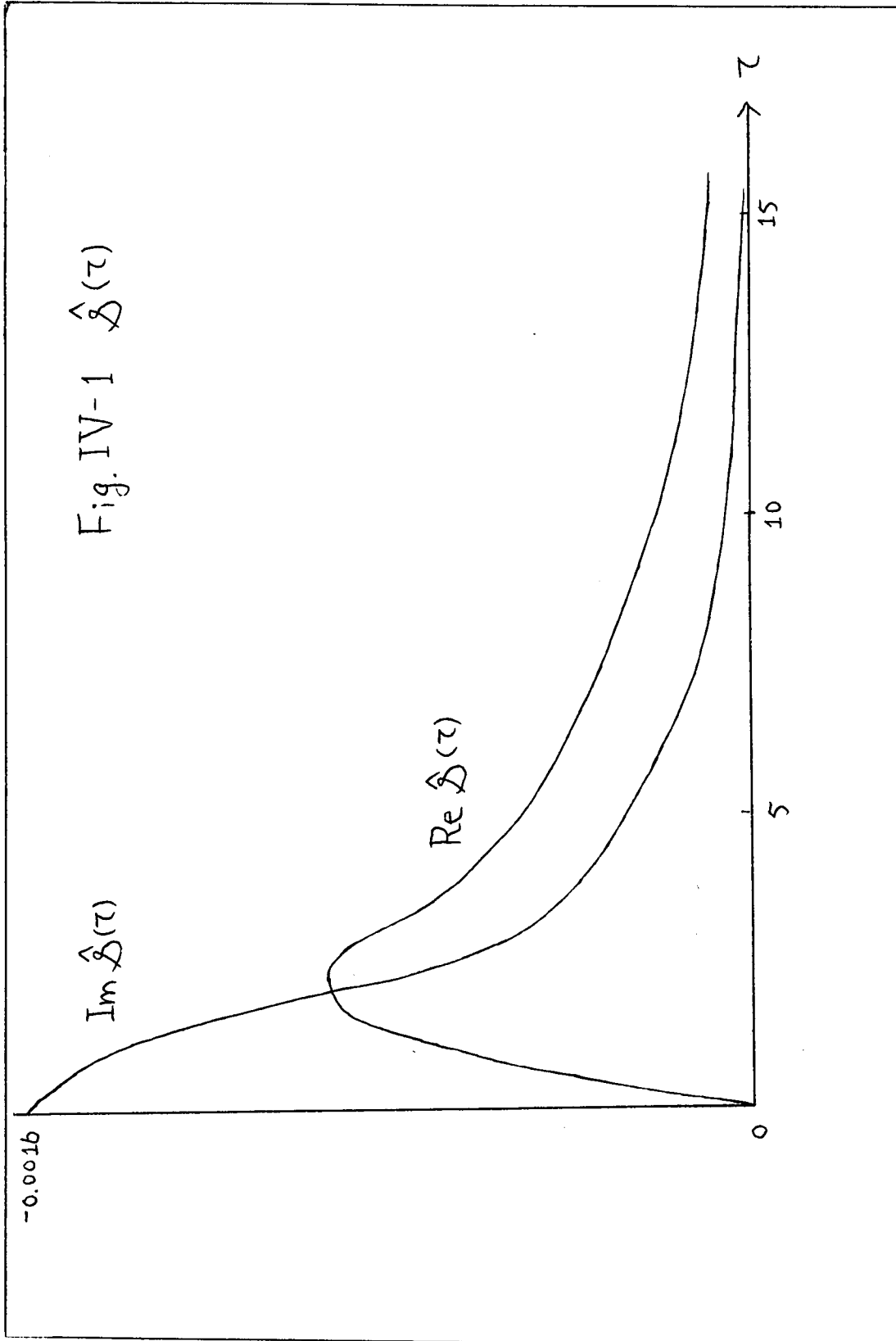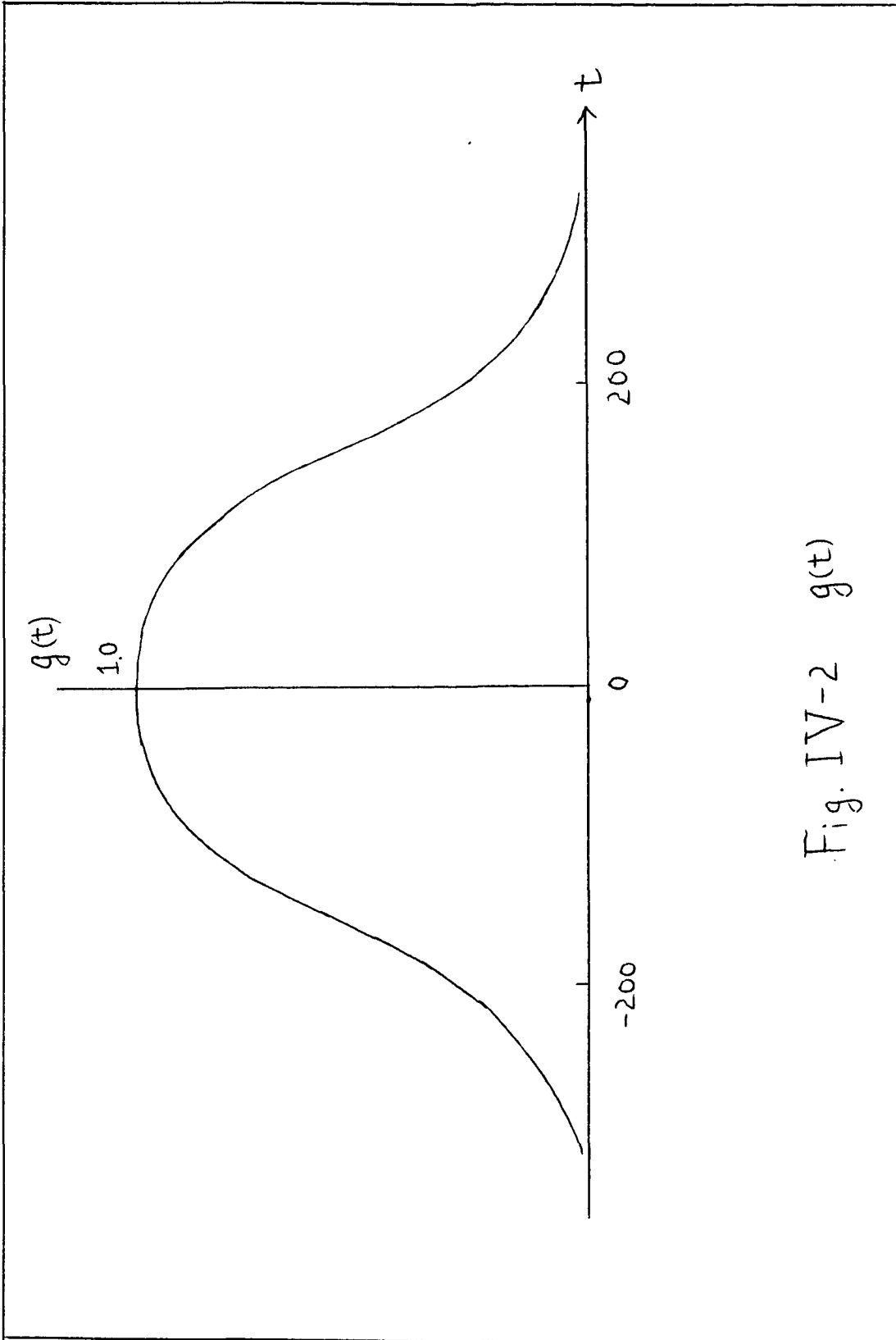
Fig. IV-2 g(t)
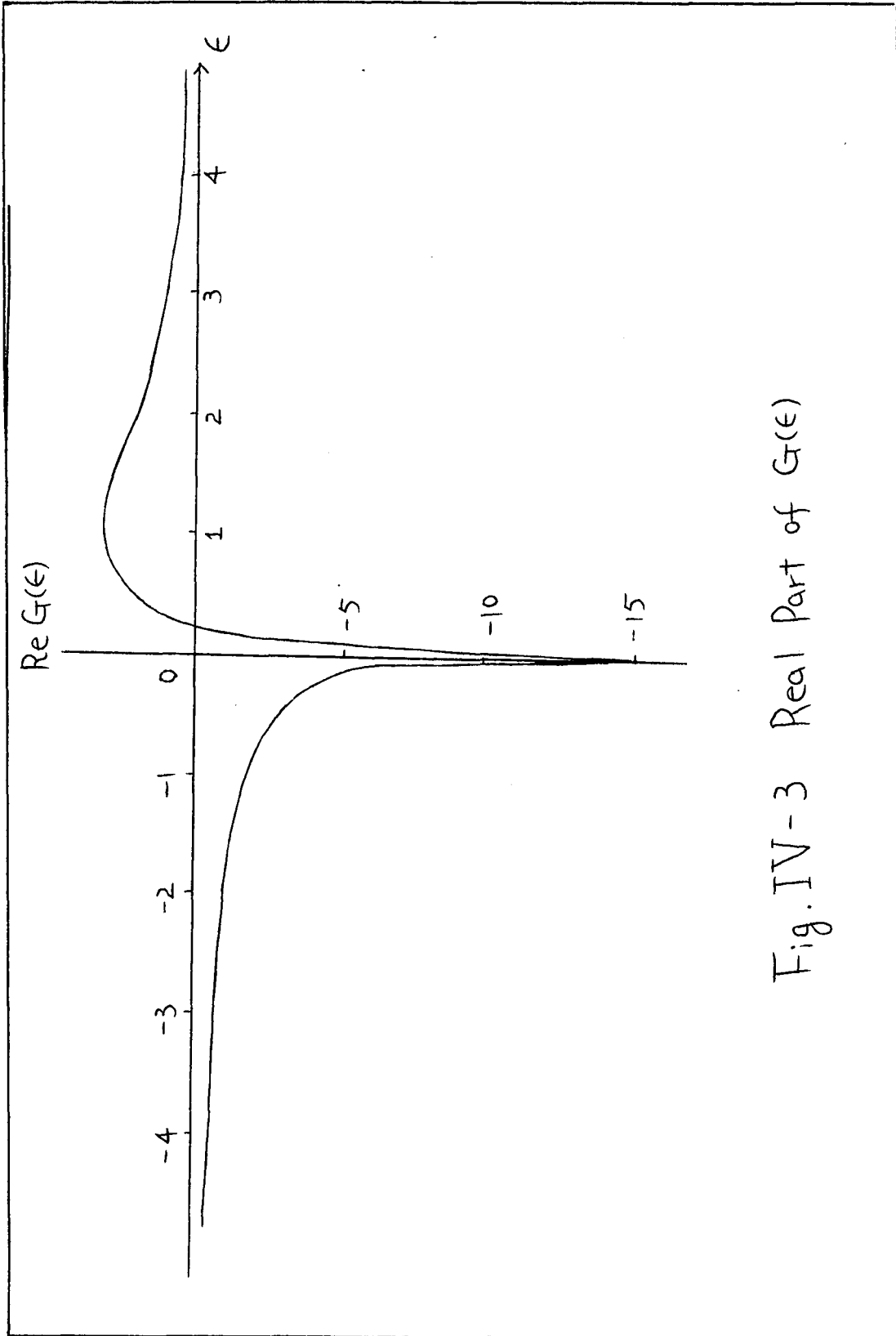
Fig. IV-3 Real Part of $G(\epsilon)$
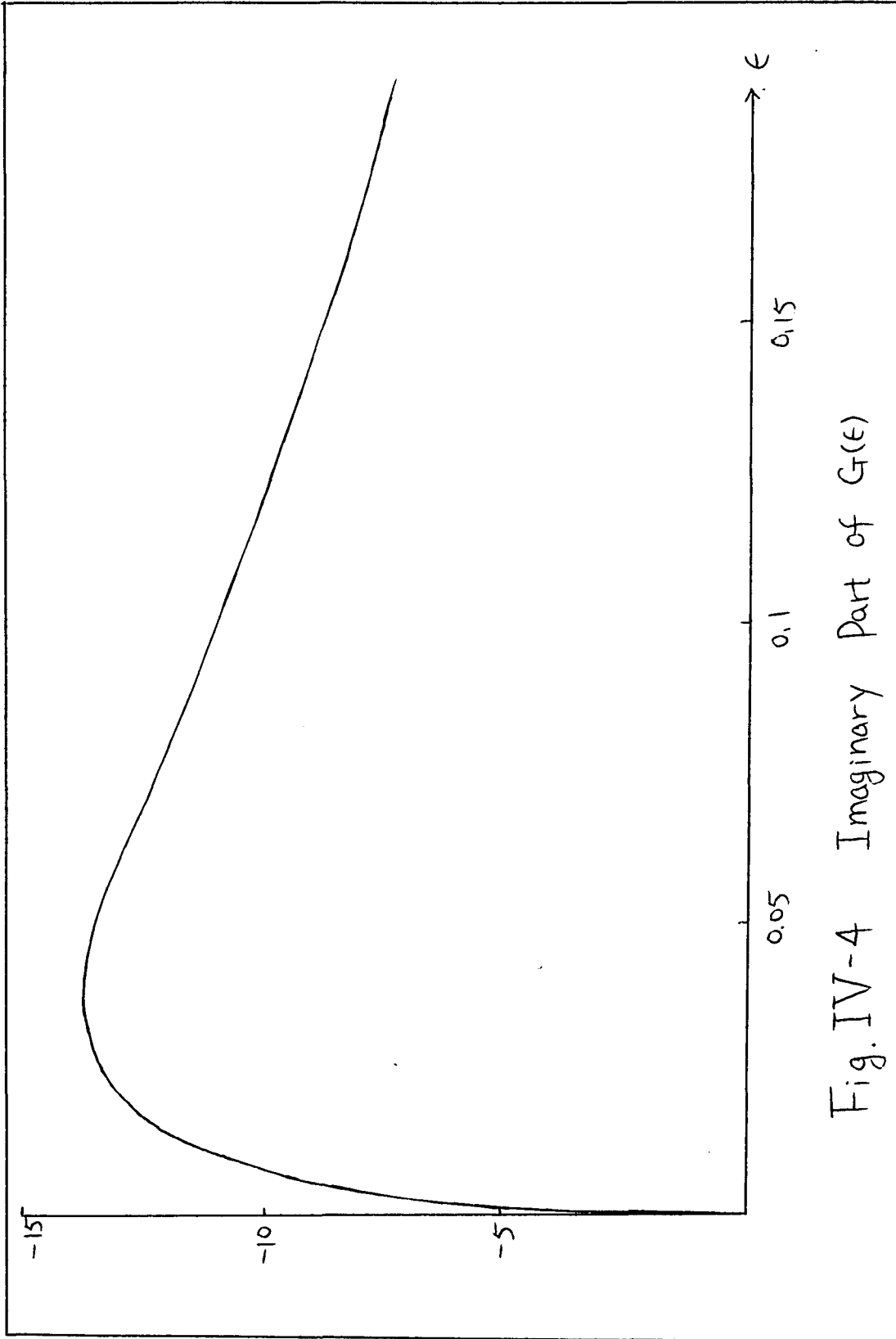
Fig. IV-4 Imaginary Part of $G(\epsilon)$

$$\Phi_\epsilon(t,t') = \epsilon \cdot (t-t') \qquad\qquad (4.2\text{-}2)$$

It is difficult to imagine a representation for a negtive-ion system in which Eq.(4.2-2) would not hold.

B. DENSITY OF STATES

For a typical collision between a negative ion and an atom, $\rho_\epsilon(t)$ will be independent of time, and it will be the same as the density of states for a free electron. A semiclassical formula states that the number $N(\epsilon)$ of quantum states having energy less than ϵ is proportional to the volume $\Omega(\epsilon)$ of phase space contained inside the energy surface $h(r.R) < \epsilon$:

$$N(\epsilon) = \Omega(\epsilon)/(2\pi\hbar)^d \qquad\qquad (4.2\text{-}3)$$

where $2d$ is the dimension of the phase space. To ensure that $\Omega(\epsilon)$ is finite, let us enclose the whole system in a box of volume $(4/3)\pi L^3$. Assuming that only one electron can be detached, we divide $\Omega(\epsilon)$ into two parts: $\Omega_1(\epsilon)$ is that part of $\Omega(\epsilon)$ in which the electron is within a few a_0 of either atom A or B, and $\Omega_2(\epsilon)$ is all the rest of $\Omega(\epsilon)$. If the electron is free to move in three dimensions, then $\Omega_2(\epsilon)$ is practically equal to

$$\Omega_2(\epsilon) = (4/3)\,\pi\,(2\mu\epsilon)^{\frac{3}{2}} \cdot (4/3)\pi L^3 \qquad\qquad (4.2\text{-}4)$$

$\Omega_1(\epsilon)$ depends on the details of the electron Hamiltonian $h(r;R)$, and it will in general depend on R (or t). However it will normally be finite, and it will have a finite limit as L $\rightarrow \infty$. Hence $\Omega(\epsilon) \simeq \Omega_2(\epsilon)$ and the density of states for three-dimensions is

$$\rho(\epsilon) = dN(\epsilon)/d\epsilon$$

$$= (2\mu)^{\frac{3}{2}} \cdot \epsilon^{\frac{1}{2}} \cdot L^3/(3\pi\hbar^3) \tag{4.2-5}$$

For slow collisions involving negative ions, the electronic wave-function will frequently be dominated by its s-wave component. Then the configuration space is effectively one-dimensional, and the phase-space volume is

$$\Omega(\epsilon) \simeq \Omega_2(\epsilon) \simeq 2(2\mu\epsilon)^{\frac{1}{2}} \cdot L \tag{4.2-6}$$

and the density of states for one-dimensional motion is

$$\rho(\epsilon) = (2\mu)^{\frac{1}{2}} \cdot \epsilon^{-\frac{1}{2}} \cdot L/(2\pi\hbar) \tag{4.2-7}$$

Obviously if the ground state of the neutral atom is degenerate, these results would be multiplied by an appropriate factor. Note also that the above argument does not apply to an electron moving away from a positive ion, nor does it apply to an electron interacting with a very singular attractive potential, such as $-r^{-2}$.

C COUPLING MATRIX ELEMENT

The coupling matrix element depends upon the system the type of coupling (electrostatic, rotational, ...) and the representation that is chosen. As $t \to \infty$, $V_{1,\epsilon}(t)$ goes to zero faster than $1/t$, but not faster than $e^{-t/\hat{t}}$ where $\hat{t}$ is some constant. We have seen in section 3.2, for example, that after changing variable from t to R, $V_{1,\epsilon}(R)$ can take the form $f(\epsilon) \cdot e^{-\beta R}$.

4.3 GENERAL PROPERTIES OF $\mathcal{D}(t,t')$ AND SHORT-MEMORY APPROXIMATION

Based on the above properties, we can write

$$\mathcal{D}(t,t') = (i\hbar)^{-1} \int_{0}^{\infty} V_{-1,\epsilon}(t) \cdot \exp\{-i\epsilon(t-t')/\hbar\} \cdot V_{\epsilon,-1}(t') \, \rho_{\epsilon} \, d\epsilon$$

(4.3-1)

from which follows the symmetry

$$\mathcal{D}(t',t) = - \mathcal{D}^{*}(t,t')$$

(4.3-2)

Also, for any fixed t

$$\lim_{t' \to \pm\infty} \mathcal{D}(t,t') = 0$$

(4.3-3a)

and for any fixed t'

$$\lim_{t \to \pm\infty} \mathcal{D}(t,t') = 0$$

(4.3-3b)

Since the range of the coupling matrix element is normally a few Bohr radii, it follows that the time scale on which $\mathcal{S}(t,t')$ is significant is no more than a few atomic length units divided by the collision velocity. For example, consider a slow collision, with the nuclear velocity .01 atomic units. In this case $\mathcal{S}(t,t')$ is negligible unless both $|t|$ and $|t'|$ are less than a few hundred atomic time units.

Eq. (4.3-1) also contains $(t-t')$ in the exponent. To see its effects, let us momentarily ignore the time dependence of $V_{i,\epsilon}(t)$. Then as $|t-t'| \to \infty$, $\mathcal{S}(t,t') \to 0$ again. However this happens on a much shorter time scale: with $\tau = t-t'$, the span of time intervals $\Delta\tau$ over which $\mathcal{S}(t,t')$ is significant is inversely related to the range of energy $\Delta\epsilon$ in which $V_{i,\epsilon}$ is significant:

$$\Delta\tau \cdot \Delta\epsilon \approx \hbar \tag{4.3-4}$$

Since the order of magnitude of $\Delta\epsilon$ would be one atomic unit of energy (27.2 eV), the order of magnitude of $\Delta\tau$ would be one atomic unit of time ($2.42 * 10^{-17}$ sec). Thus $\mathcal{S}(t,t')$ would be negligible for any t, t' such that $|t-t'| >$ a few atomic time units.

This important fact provides a useful simplifying approximation for $\mathcal{S}(t,t')$. The fundamental integrodifferential equation, (2.3-4), may be said to be a differential equation with " memory ": the time-derivative of $C_{i}(t)$ de-

pends not only upon the present value of $C_{-1}(t)$, but also upon its value at all times in the past. The argument above indicates that the equation's memory is short.

To make use of this, let us rewrite Eq.(4.3-1) in terms of variables t and $\tau = t-t'$:

$$\mathcal{D}(t,t') = \mathcal{D}(\tau;t) \tag{4.3-5a}$$

$$= \int_0^\infty V_{-1,\epsilon}(t) \cdot \exp(-i\epsilon\tau/\hbar) \cdot V_{\epsilon,-1}(t-\tau)\, \rho_\epsilon\, d\epsilon \tag{4.3-5b}$$

Eq.(4.3-5) is exact. Suppose now $\Delta\tau$ is small compared to the time over which $V_{\epsilon,-1}(t)$ changes significantly:

$$(dV_{\epsilon,-1}/dt) \cdot (\Delta\tau/V_{\epsilon,-1}) \ll 1 \tag{4.3-6}$$

or, using $V_{\epsilon,-1}^{-1} \cdot dV_{\epsilon,-1}/dt = v/a_0$ and Eq.(4.3-4),

$$\hbar v/(a_0 \Delta\tau) \ll 1 \tag{4.3-7}$$

If this condition is satisfied we may substitute $V_{\epsilon,-1}(t-\tau) \simeq V_{\epsilon,-1}(t)$ in Eq.(4.3-5b) to obtain

$$\mathcal{D}(\tau;t) \simeq \mathcal{D}_s(\tau;t)$$

$$= \int_0^\infty |V_{-1,\epsilon}(t)|^2 \cdot \exp(-i\epsilon\tau/\hbar)\, \rho_\epsilon\, d\epsilon \tag{4.3-8}$$

$\mathcal{D}_s(\tau;t)$ will be referred to as the short-memory approximation to $\mathcal{D}(\tau;t)$.

For later reference, let us introduce a Fourier transform of $\mathcal{D}(\tau;t)$:

$$G(\epsilon;t) \equiv \int_0^\infty \exp(i\epsilon\tau/\hbar) \cdot \mathcal{D}(\tau;t)\, d\tau \qquad (4.3-9)$$

Using the short-memory approximation, we have

$$G(\epsilon;t) \simeq G_s(\epsilon;t)$$

$$\equiv \int_0^\infty \exp(i\epsilon\tau/\hbar) \cdot \mathcal{D}_s(\tau;t)\, d\tau \qquad (4.3-10)$$

If ϵ is given a small positive imaginary part, using Eq.(4.3-8) we may reverse the order of integrations over τ and ϵ to obtain

$$G_s(\epsilon,t) = \int_0^\infty |V_{-1,\epsilon'}(t)|^2 \cdot (\epsilon-\epsilon')^{-1} \cdot \rho_{\epsilon'}\, d\epsilon' \qquad (4.3-11)$$

4.4 A SEPARABLE APPROXIMATION AND A REDUCED PROPAGATOR

A further approximation provides physical insight and an additional simplification. Even if the coupling matrix elements are significant over a broad range of the continuum, transtions might only occur into a rather narrow

range. For example, if the collision is very slow, usually only very low-energy electrons are produced. Within that narrow range of continuum energies, it may be reasonable to assume that all of the coupling matrix elements have the same time-dependence

$$V_{-1,\epsilon}(t) = g(t) \cdot V_{-1,\epsilon} \qquad (4.4\text{-}1)$$

where $V_{-1,\epsilon}$ is independent of t and g(t) has a shape as shown in Fig.IV-2. This gives

$$\mathcal{D}(t \ t') \simeq \mathcal{D}^{sep}(t,t') = g(t) \cdot g(t') \cdot \hat{\mathcal{D}}(t-t') \qquad (4.4\text{-}2)$$

where

$$\hat{\mathcal{D}}(\tau) = \hat{\mathcal{D}}(t-t') = (i\hbar)^{-1} \int_{o}^{\infty} d\epsilon \, \rho_{\epsilon} \, |V_{1,\epsilon}|^{2} \cdot \exp(-i\epsilon\tau/\hbar) \qquad (4.4\text{-}3)$$

is a reduced propagator. The corresponding short-memory approximation is

$$\mathcal{D}^{sep}(\tau;t) \simeq \mathcal{D}^{sep}_{s}(\tau;t) = g^{2}(t) \cdot \hat{\mathcal{D}}(\tau) \qquad (4.4\text{-}4)$$

The following properties of $\hat{\mathcal{D}}(\tau)$ are easily proved. Separating real and imaginary parts,

$$\hat{\mathcal{D}}(\tau) = \hat{\mathcal{D}}_{R}(\tau) + i \hat{\mathcal{D}}_{I}(\tau) \qquad (4.4\text{-}5a)$$

$$\hat{\mathcal{D}}_{R}(\tau) = -\hbar^{-1} \int_{o}^{\infty} d\epsilon \, \rho_{\epsilon} \, |V_{1,\epsilon}|^{2} \cdot \sin(\epsilon\tau/\hbar) \qquad (4.4\text{-}5b)$$

$$\hat{\mathcal{S}}_I(\tau) = -\hbar^{-1} \int_0^\infty d\epsilon \, \rho_\epsilon |V_{-1,\epsilon}|^2 \cdot \cos(\epsilon\tau/\hbar) \qquad (4.4\text{-}5c)$$

$\hat{\mathcal{S}}_R(\tau)$ is an odd function of τ, so $\hat{\mathcal{S}}(0) = 0$. Also

$$|d\hat{\mathcal{S}}_R/d\tau|_{\tau=0} = -\hbar^{-2} \int_0^\infty d\epsilon \cdot \epsilon \cdot \rho_\epsilon |V_{-1,\epsilon}|^2 < 0 \qquad (4.4\text{-}6)$$

if the integral converges. $\hat{\mathcal{S}}_I(\tau)$ is an even function of τ and $\hat{\mathcal{S}}_I(0) < 0$, $|d\hat{\mathcal{S}}_I/d\tau|_{\tau=0} = 0$. For all τ,

$$|\hat{\mathcal{S}}(\tau)| < \hat{\mathcal{S}}(0) \qquad (4.4\text{-}7)$$

and

$$\lim_{\tau \to \infty} \hat{\mathcal{S}}(\tau) = 0 \qquad (4.4\text{-}8)$$

By the same argument as before, the period of time over which $\hat{\mathcal{S}}(\tau)$ is significant may typically be only a few atomic units.

The Fourier transform of $\hat{\mathcal{S}}(\tau)$ is

$$\hat{G}(\epsilon) \equiv \int_0^\infty d\tau \cdot \exp(i\epsilon\tau/\hbar) \cdot \hat{\mathcal{S}}(\tau) \qquad (4.4\text{-}9a)$$

If ϵ is given a small positive imaginary part, then we may use (4.4-3) in (4.4-9a) and reverse the order of integration to obtain

$$\hat{G}(\epsilon) = \int_0^\infty d\epsilon' \, \rho_{\epsilon'} |V_{-1,\epsilon'}|^2 / (\epsilon - \epsilon') \qquad \text{Im}\,\epsilon > 0 \qquad (4.4\text{-}9b)$$

4.5 A MODEL FOR $\hat{\mathfrak{H}}(\tau)$ AND $\hat{G}(\epsilon)$

In the last section we obtained $\hat{G}(\epsilon)$ (4.4-9a), the Fourier transform of $\hat{\mathfrak{H}}(\tau)$. Eq.(4.4-9b) shows that for $\text{Im}\,\epsilon$ > 0, this $\hat{G}(\epsilon)$ is the same quantity that Taylor and Delos obtained in Eq.(2.20) of Ref.22, denoted there $G(\epsilon)$. Therefore we can take over many of their results. For $\epsilon < 0$, $G(\epsilon)$ is real, negative, and it goes to zero when $\epsilon \to -\infty$ as $|\epsilon|^{-1}$. For $\epsilon > 0$, $G(\epsilon)$ is complex, and its imaginary part is negative:

$$\text{Im } G(\epsilon) = -\pi |\underline{V}_{1,\epsilon}|^2 \, \rho_\epsilon \qquad (4.5\text{-}1)$$

At $\epsilon = 0$, the derivative of $G(\epsilon)$ is discontinuous. Further details are given in Ref.22.

For $\underline{V}_{1,\epsilon}$, which is needed in the calculation of $\hat{G}(\epsilon)$ and $\hat{\mathfrak{H}}(\tau)$, we use a form derived from a square-well model by Taylor and Delos.[22] We give in Appendix C a simple description of it. Figs.IV-3,4 show the real and imaginary parts of $G(\epsilon)$ from Taylor and Delos.[22]

For this model, numerical integration of Eq.(4.4-3) leads to results for $\hat{\mathfrak{H}}(\tau)$ that are shown in Fig.IV-1.

4.6 SUMMARY

In this chapter we have discussed in detail the constituents and the general properties of the "propagator" $\mathcal{J}(t,t')$. The characteristic "short memory" of $\mathcal{J}(t,t')$ enables us to simplify it as in Eq. (4.3-8). In the next chapter we show that this slow collision approximation leads, under proper additional assumptions, to the well-known local-complex-potential formulas.

We have also shown in this chapter that an additional "separable" approximation leads to a reduced propagator $\hat{\mathcal{J}}(\tau)$ and a Green function $\hat{G}(\epsilon)$ which has been presented before by Taylor and Delos. The relationship between $\hat{\mathcal{J}}(\tau)$ and $\hat{G}(\epsilon)$ has been illustrated through numerical calculations.

Chapter V

SLOW COLLISION APPROXIMATION AND COMPLEX POTENTIAL FORMULAS

5.1 INTRODUCTION

We have shown in chapter II that the coupled equations (2.2-4) can be reduced to a single integrodifferential equation and that, for the boundary conditions (2.4-1), that equation is homogeneous

$$\{i\hbar d/dt - \Delta(t)\}\, C_{-i}(t) - \int_{t_0}^{t} \mathcal{D}(t,t') \cdot C_{-i}(t')\,dt' = 0 \qquad (5.1\text{-}1)$$

We have also given in chapter IV some information about the propagator $\mathcal{D}(t,t')$. Now we have to find ways of solving this fundamental equation.

In the present chapter we give an approximate analytic solution, which is suitable for slow collisions, and which, under appropriate conditions, can be reduced to the local-complex-potential formulas. In section 5.2 the fundamental equation (5.1-1) is written in a different way, then in section 5.3 we make a slow collision approximation. The results are shown to be identical to those of the local-complex-potential model.

5.2 THE DYNAMICAL COMLEX POTENTIAL

The analytic solution is based upon the short-memory approximation for $\mathcal{D}(t,t')$ that was given in chapter IV. Let us define $\mathcal{E}(t)$ such that

$$C_{-1}(t) = \exp\{-i\int_{t_o}^{t} \mathcal{E}(t')dt'/\hbar\} \qquad (5.2\text{-}1a)$$

i.e.

$$\mathcal{E}(t) = i\hbar\cdot\{dC_{-1}(t)/dt\}/C_{-1}(t) \qquad (5.2\text{-}1b)$$

These equations have the same form as equations obtained in the local-complex-potential model, but they have a different meaning. Local-complex-potential formulas may be regarded as results of a model, or as results of an approximation method. However, (5.2-1a) is supposed to represent the exact solution to the fundamental equation (5.1-1). $\mathcal{E}(t)$ may therefore be regarded as an "exact" or "dynamical" complex potential, which might or might not have some relationship to the local-complex-potential. In this chapter we give conditions under which $\mathcal{E}(t)$ will be close to the local-complex potential, and in the following chapter we will calculate $\mathcal{E}(t)$ numerically.

For all t such that $C_{-1}(t) \neq 0$, $\mathcal{E}(t)$ is finite, continuous and differentiable. Substituting (5.2-1) into (2.4-5), we obtain an integral equation for $\mathcal{E}(t)$:

$$\mathcal{E}(t) = \Delta(t) + \int_{t_o}^{t} \mathcal{D}(t,t')\exp\{i\int_{t'}^{t} \mathcal{E}(t'')dt''/\hbar\}dt' \qquad (5.2\text{-}2)$$

with the boundary condition

$$\xi(t_o) = \Delta(t_o) \qquad (5.2-3)$$

We take t_o to be a time long before the collision, when $\mathcal{D}(t,t')$ is insignificant. Then $\xi(t)$ remains equal to $\Delta(t)$ until $\mathcal{D}(t,t')$ becomes substantial, at which time $t-t'$ is large. Changing to variables t, $\tau = t-t'$, Eq.(5.2-2) becomes

$$\xi(t) = \Delta(t) + \int_o^{t-t_o} \mathcal{D}(\tau;t) \exp\{i \int_{t-\tau}^{t} \xi(t'') dt''/\hbar\} d\tau \qquad (5.2-4)$$

So far, everything is exact, and (5.2-4) is just another form of the fundamental homogenous equation (2.4-5).

5.3   SLOW COLLISION APPROXIMATION

Let us now assume that the time scale on which $\xi(t)$ changes is comparable to that on which $\Delta(t)$ and $V_{\cdot,\xi}(t)$ change, and that this time scale is long compared to the time Δ on which $\mathcal{D}(\tau;t)$ is significant. Then in (5.4-4) we can replace $\xi(t'')$ by $\xi(t)$, to obtain

$$\xi(t) = \Delta(t) + \int_o^{t-t_o} \mathcal{D}(\tau;t) \exp\{-i\xi(t)\tau/\hbar\} d\tau \qquad (5.2-5)$$

Since $\Delta\tau$ is also small compared to $t-t'$, we can replace the upper limit by infinity, and, using (4.3-9) and (4.3-10), Eq.(5.2-5) becomes approximately

$$\mathcal{E}(t) = \triangle(t) + G_S(\mathcal{E}(t);t) \qquad (5.2-6)$$

Let us define $\mathcal{E}_S(t)$ as the exact solution to this approximate equation (5.2-6). Once $G_S(\varepsilon;t)$ is known, $\mathcal{E}_S(t)$ can be obtained by an iterative algebraic process: the zero-order approximation is

$$\mathcal{E}_S^{(0)}(t) = \triangle(t) \qquad (5.2-7a)$$

and, substituting this back into (5.2-6), the first-order approximation is

$$\mathcal{E}_S^{(1)}(t) = \triangle(t) + G_S(\triangle(t);t) \qquad (5.2-7b)$$

and so on. For a slow collision, the exact $\mathcal{E}(t)$ defined in Eq.(5.2-1), will be close to $\mathcal{E}_S(t)$.

The result of this slow-collision approximation is

$$C_{-1}(t) = \exp\{-i\int^{t}\mathcal{E}_S(t')dt'/\hbar\} \qquad (5.2-8)$$

5.4 LOCAL-COMPLEX-POTENTIAL FORMULAS

From Eq.(5.2-8), using Eq.(5.2-7b) we obtain the survival probability for the negative ion

$$P_S = |C_{-1}(\infty)|^2 = \exp\{2\int_{-\infty}^{\infty} \text{Im } G_S(\triangle(t);t)dt/\hbar\} \qquad (5.3-1a)$$

$$= \exp\{-\int_{-\infty}^{\infty} \Gamma(t)\,dt/\hbar\} \qquad (5.3\text{-}1b)$$

where

$$\Gamma(t) = -2 \text{ Im } G_s (\Delta(t);t) \qquad (5.3\text{-}2a)$$

$$= 2\pi |V_{-l,\Delta(t)}(t)|^2 \rho_{\Delta(t)} \qquad (5.3\text{-}2b)$$

Eqs (5.3-1) and (5.3-2) constitute the classical formulas of the local-complex-potential model.

5.5   DISCUSSION

It is very pleasing to arrive at the local-complex-potential formulas because they are familiar results, known to be applicable to a variety of systems. The above is one of the most general derivations of these formulas that has yet been given. Other treatments have relied upon the hypothesized existence of a long-lived quasibound resonance, and Taylor and Delos's treatment (following Demkov) made use of special assumptions about $\Delta(t)$ and $V_{-l,\epsilon}(t)$. The present derivation uses only the general assumptions listed in chapter II and the approximations leading from (5.2-5) to (5.2-7b).

On the other hand, it is well known that the classical local-complex-potential formulas have some problems: not that they are slightly inaccurate, but rather that they

give hopelessly wrong answers for some systems -- for $H^-(D^-)$ on Ne, Ar, Kr, or Xe, they predict an isotope effect that is opposite to what is observed. This is because they do not properly describe phenomena that arise when the discrete curve just grazes the continuum. A related but rather subtle inconsistency of the above equations also appears when calculations are made. We showed that $\hat{G}(\epsilon)$ has a discontinuous derivative at $\epsilon = 0$; $G_s(\epsilon;t)$ must have the same behavior. As a consequence, $\xi(t)$, the solution to Eq.(5.2-6), will have a discontinuous derivative with respect to time when $\dot{G}_s = 0$. However, in Appendix A, we took some care to prove that $C_{-1}(t)$, dC_{-1}/dt and d^2C_1/dt^2 all are continuous functions of time, and this implies that the exact $\xi(t)$ has a continuous derivative. The exact solution $C_{-1}(t)$ glides smoothly through the region where the slow-collision approximation would give bumps.

Chapter VI

ITERATIVE CALCULATION OF $\mathcal{E}(t)$ AND FIRST-ORDER APPROXIMATION

6.1 INTRODUCTION

In chapter V we converted the fundamental equation for $C_{-1}(t)$

$$\{i\hbar d/dt - \Delta(t)\}C_{-1}(t) - \int_{t_0}^{t} \mathcal{D}(t,t')C_{-1}(t')dt' = \emptyset \qquad (6.1\text{-}1)$$

into a new equation

$$\mathcal{E}(t) = \Delta(t) + \int_{0}^{t-t_0} \mathcal{D}(\tau;t)\cdot\exp\{i\int_{t-\tau}^{t}\mathcal{E}(t')dt'/\hbar\}d\tau \qquad (6.1\text{-}2a)$$

with the relationship

$$C_{-1}(t) = \exp\{-\int_{t_0}^{t}\mathcal{E}(t')dt'/\hbar\} \qquad (6.1\text{-}2b)$$

Equations (6.1-1) and (6.1-2) are exactly equivalent (a solution to one implies a solution to the other) and $\mathcal{E}(t)$ is finite, continuous, and has a continuous derivative for all t such that $C_{-1}(t) \neq \emptyset$

In the preceding chapter, we showed that the fundamental integrodifferential equation (6.1-2a) could be

solved using a slow collisoon approximation, and that the result is the familiar locai-complex-potential formula.

In the present chapter we give an iterative method for solving this equation, and we show the results of a "first-order" calculation. We find that $\xi^{(1)}(t)$, obtained from this first-order calculation, is comparable to that obtained in the local-complex-potential approximation, but this first-order approximation also describes tunneling and interference effects.

6.2   ITERATIVE METHOD AND FIRST-ORDER APPROXIMATION

The zero order approximation of $\xi(t)$, of course is

$$\xi^{(0)}(t) = \Delta(t) \tag{6 2-1}$$

AS we discussed in chapter III, this "zero-order" approximation is equivalent to first-order time-dependent perturbation theory. This approximation was used therein to describe electron detachment in collisions with $H^-(D^-)$ with Ne.

Starting from Eq.(6.2-1), an iterative scheme for solving it is obvious: given an "n^{th} - order" approximation $\xi^{(n)}(t)$, the "$(n+1)^{th}$ - order" approximation is

$$\xi^{(n+1)}(t) = \Delta(t) + \int_0^{t-t_0} \phi(\tau;t) \cdot \exp\{i\int_{t-\tau}^{t} \xi^{(n)}(t')\,dt'/\hbar\} \cdot d\tau \tag{6.2-2}$$

In the present work, we shall consider only the first-order approximation. Furthermore, we shall use the separable approximation and slow collision approximation defined in Eq.(4.4-4). Also, in the case of interest, the time dependence of g(t) is less important than that of $\Delta(t)$, so we will use the additional approximation $g(t) \simeq 1$. Then taking $t_o = -\infty$, we have

$$\mathcal{E}^{(1)}(t) = \Delta(t) + \int_o^\infty d\tau \cdot \hat{\mathcal{D}}(\tau) \cdot \exp\{i \int_{t-\tau}^t \Delta(t') dt'/\hbar\} \qquad (6.2-3)$$

This formula is the basis of most of our subsequent calculations. Henceforth we drop the superscript on $\mathcal{E}^{(1)}$, and just call it $\mathcal{E}$.

Although our zero-order approximation is equivalent to first-order time-dependent perturbation theory, there is in general no direct correspondence between our n^{th} order approximation and some level of the standard perturbation theory. Even the first-order approximation (6.2-3) contains parts of all orders of perturbation theory.

6.3 AN ILLUSTRATIVE CALCULATION

Let us now examine consequences of the above first-order approximation in a special case. Suppose $\Delta(t) = E_o - \beta t^2$; then we have

$$\mathcal{E}(t) - \Delta(t) = \int_o^\infty d\tau \cdot \hat{\mathcal{D}}(\tau) \cdot \exp\{i [(E_o - \beta t^2)\tau + \beta t\tau^2 - \frac{\beta}{3}\tau^3]\}$$

$$(6.3-1)$$

We have seen in Fig. IV-3 that $\hat{\mathcal{D}}(\tau)$ gets small as τ gets larger. So, temporarily neglecting the terms involving τ^2 and τ^3 in the exponent, we have

$$\mathcal{E}(t) - \Delta(t) \simeq \int_0^\infty d\tau \cdot \hat{\mathcal{D}}(\tau) \cdot \exp\{i(E_o - \beta t^2)\tau\} \qquad (6.3\text{-}2a)$$

$$= \hat{G}(E_o - \beta t^2) \qquad (6.3\text{-}2b)$$

This is a special case of the slow collision approximation that was discussed in chapter V, and we have again arrived at the local-complex-potential formula.

The neglected terms in the exponent of Eq (6.3-1) have surprising effects: they give oscillations in $\mathcal{E}(t)$. To see this, let us define

$$f_1(\tau;t) = (E_o - \beta t^2)\tau \qquad (6.3\text{-}3a)$$

$$f_2(\tau;t) = f_1(\tau;t) + \beta t \tau^2 \qquad (6.3\text{-}3b)$$

$$f_3(\tau;t) = f_2(\tau;t) - (\beta/3)\tau^3 \qquad (6.3\text{-}3c)$$

i.e. $f_k(\tau;t)$ is a kth degree approximation to the exponent in Eq. (6.3-1). Also, define

$$F_k(t) \equiv \int_0^\infty \hat{\mathcal{D}}(\tau) \cdot \exp\{if_k(\tau;t)\} \cdot d\tau \qquad (6.3\text{-}4)$$

In fig.VI-1 we give the comparison between $F_1(t)$ and $F_2(t)$. The calculations are the numerical evaluation of Eq.(6.3-4) with $E_0 = 0.2$ and $\beta = 5*10^{-6}$. Fig.VI-2 shows the comparison between $F_2(t)$ and $F_3(t)$.

6.4 SIMPLIFYING APPROXIMATIONS

In the last section we showed the calculations of $\xi(t) - \triangle(t)$ using first order approximation. We have seen that $\xi(t) - \triangle(t)$ is, except for the oscillatory structures, similar in shape to $\hat{G}(\triangle(t))$. We can better understand these results by considering some simplifying approximations.

Contributions to the integral appearing in Eqs.(6.2-3) and (6.3-1) mainly come from certain small ranges of τ. For general values of τ, $\hat{\delta}(\tau)$ is small and the exponent is rapidly varying, so the contribution to the integral is negligible. Significant contributions come from the region near $\tau = 0$, where $\hat{\delta}(\tau)$ is large, and from stationary phase points, where the exponent is slowly varying.

The contribution from the region near $\tau = 0$ may be estimated by using the "slow-collision approximation" defined in chapter V:

$$\int_0^{\text{``}\infty\text{''}} d\tau \cdot \hat{\delta}(\tau) \cdot \exp\{i\int_{t-\tau}^{t} \triangle(t')dt'/\hbar\} \simeq \int_0^{\text{``}\infty\text{''}} \hat{\delta}(\tau) \cdot \exp\{i\tau \triangle(t)/\hbar\}d\tau$$

$$= \hat{G}(\triangle(t)) \qquad (6.4-1)$$

Re

Im

--- $F_1(t)$

—— $F_2(t)$
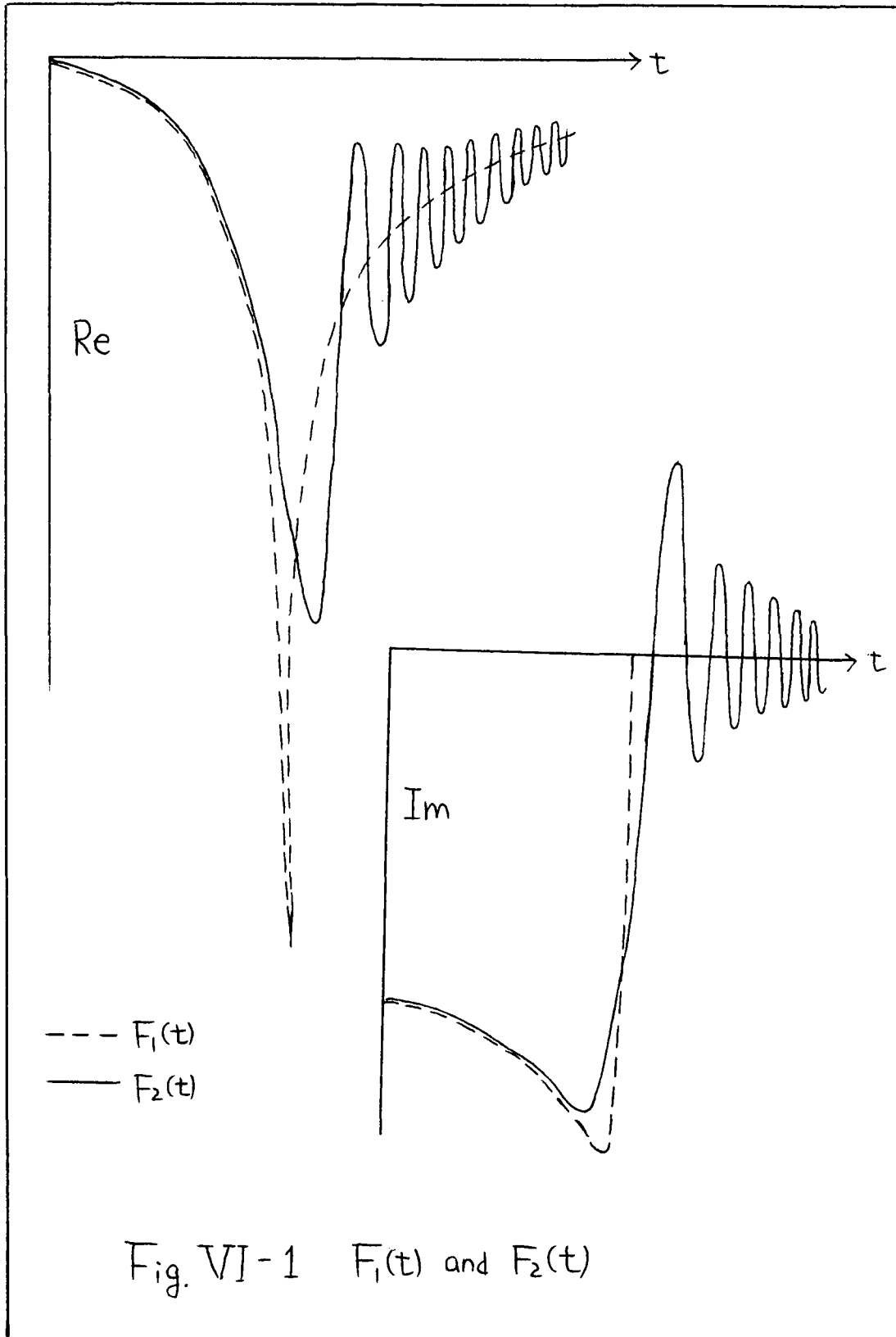
Fig. VI-1 $F_1(t)$ and $F_2(t)$
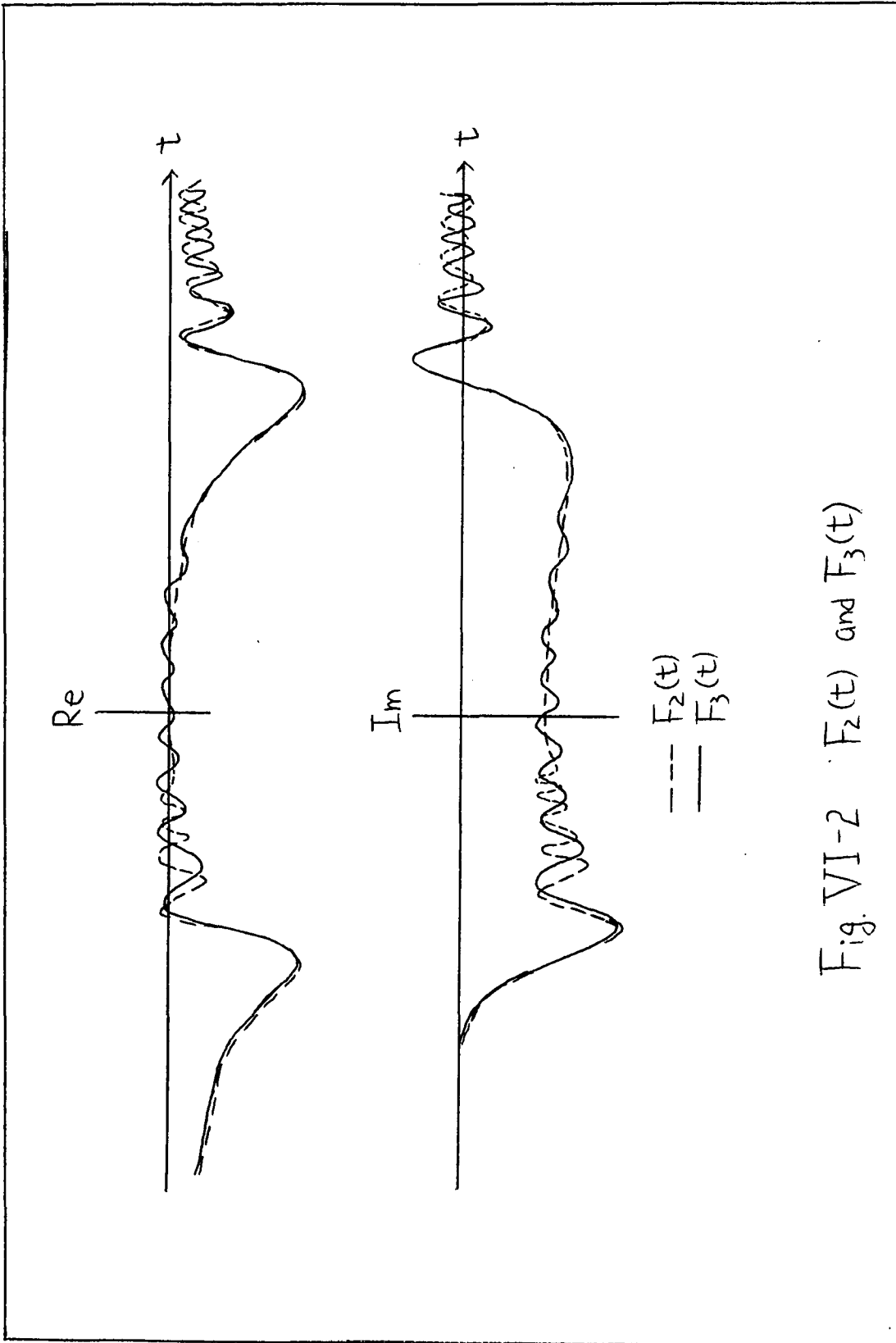
Fig. VI-2 · $F_2(t)$ and $F_3(t)$

--- $F_2(t)$
——— $F_3(t)$

Here "∞" is a value of τ that is sufficiently large that $\hat{\Delta}($"∞"$)$ is small, but sufficiently small that $\Delta(t)$ does not change significantly in the range from $t-\tau$ to t.

Stationary phase contribution to the integral (6.2-3) arise from regions near the points τ_{sp} at which

$$\frac{d}{d\tau}\int_{t-\tau}^{t}\Delta(t')dt'\Big|_{\tau_{sp}} = \Delta(t-\tau_{sp}) = 0 \qquad (6.4\text{-}2a)$$

i.e.

$$\tau_{sp} = t - t^{x} \qquad (6.4\text{-}2b)$$

where t^{x} is a time at which $\Delta(t) = 0$. In the quadratic approximation there are two such points, t^{x}_{in} and t^{x}_{out}, where the discrete curve crosses into the continuum and where it crosses back out. However, the integral in Eq (6.2-3) involves only positive values of τ, so the stationary phase contributions should only be considered for $t^{x}_{in} < t$. Hence we have the following:

$t < t^{x}_{in}$ no stationary phase contribution

$t^{x}_{in} < t < t^{x}_{out}$ one stationary phase contribution near t^{x}_{in}

$t^{x}_{out} < t$ two stationary phase contributions, near t^{x}_{in} and t^{x}_{out}

In each case, the contribution to the integral from the region of stationary phase is

$$|\frac{2\pi}{\Delta'(t^x_{in})}|^{\frac{1}{2}}\cdot\exp\{i\frac{\pi}{4}\text{sign}\cdot\Delta(t^x_n)\}\cdot\hat{\delta}(t-t^x_n)\cdot\exp\{i\int_{t-t^x_n}^{t}\Delta(t')dt'/\hbar\} \tag{6.4-3}$$

The integral in Eq.(6.2-3) is then estimated by combining (6.4-1) with zero, one or two terms of the form (6.4-3). From the quadratic approximation, $\Delta(t) = E_o - \beta t^2$, with $E_o = 0.2$ and $\beta = 5*10^{-6}$, the result is shown in Fig.VI-3; it is very close to the result obtained by numerical evaluation of Eq.(6.3-1).

Why do oscillations appear in $\mathcal{E}(t)$ and what do they mean? In discrete curve-crossing problems, Stueckelberg[32] showed in 1932 that the transition probability would be oscillatory because of interference between transitions that occur on incoming and outgoing parts of a trajectory. Similar oscillations are also known to occur in Penning ionization, which involves transitions between a discrete state and a continuum. Such oscillations are also possible in systems undergoing electron detachment (though they have not yet been seen in experiments). Oscillations in the transition probability must manifest themselves in $C_{-1}(t)$, and, therefore, also in the dynamical complex potential $\mathcal{E}(t)$. Like Stueckelberg oscillations, the phase of the oscillatary part of Eq.(6.4-3)

$$\int_{t-t^x}^{t}\Delta(t')dt' \tag{6.4-4}$$

Re

Im

— $F_3(t)$

• • • $F(t) = F_1(t) + F_3(t)$

Fig. VI-3 $F_3(t)$ and $F(t)$
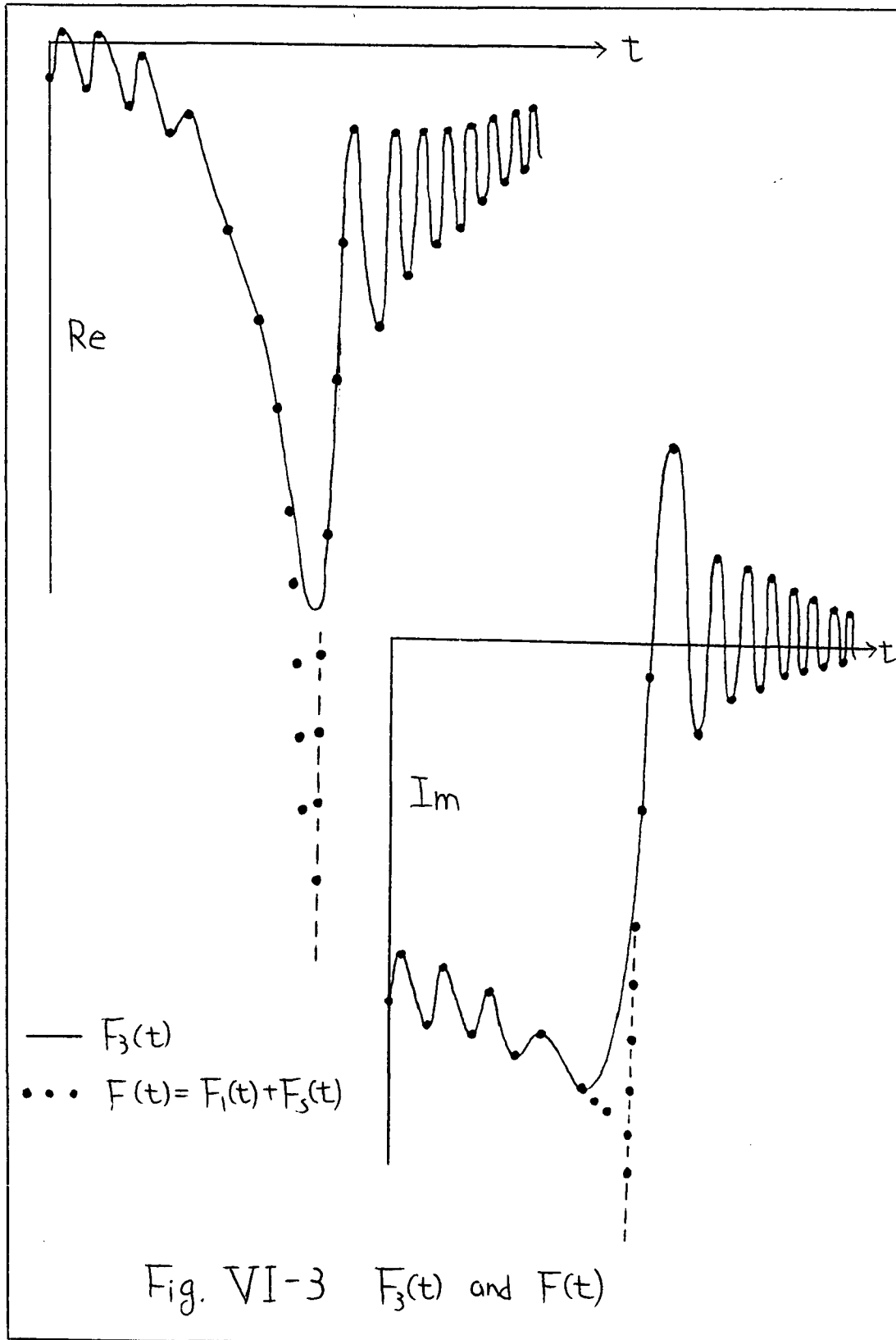
is related to the integral of the energy gap $\Delta(t)$ from the time of crossing to t.

Since $C_{-1}(t)$ is obtained by integrating $\xi(t)$ over t, these oscillations will usually have relatively little effect on $C_{-1}(t)$ and the survival probability. However, in certain cases, oscillations may be important in the electron energy spectrum. This will be shown in the next chapters.

Chapter VII

ELECTRON DETACHMENT FOR H⁻(D⁻) IN COLLISIONS WITH HELIUM

PART I: QUADRATIC APPROXIMATION

7.1 INTRODUCTION

Before going further, let us summarize what has been accomplished so far. Referring back to Figure II-1, we recall that in earlier developments of close-coupling theory, solutions were obtained for models in which $\Delta(t)$ is either constant (Fano), a linear function of time (Demkov), or a quadratic function of time (Taylor and Delos). The purpose of the present work is to obtain solutions to the close-coupled equations under more general assumptions.

In the preceeding chapters we developed a framework for doing this. The probability of survival of the negative ion is

$$P_S = |C_{-1}(\infty)|^2 \qquad (7.1-1)$$

and the probability that an electron with energy near will be detached is

$$P_d(\epsilon) = |C_\epsilon(\infty)|^2 \rho_\epsilon \qquad (7.1-2)$$

Under the assumptions given in chapter II, if $C_{-|}(t)$ is known, and if $V_{\epsilon\epsilon}(t) \simeq \epsilon$, then $C_\epsilon(t)$ can be calculated from

$$C_\epsilon(t) = (i\hbar)^{-1} \int_{-\infty}^{t} \underline{V}_{|,\epsilon} \cdot \exp\{-i\epsilon(t-t')/\hbar\} \cdot C_{-|}(t') \cdot dt' \qquad (7.1-3)$$

Hence if we can obtain $C_{-|}(t)$, the problem is solved. Under assumptions stated earlier, we obtained an integrodifferential equation for $C_{-|}(t)$ (Eq.(2.3-4)) and we transformed this into an equation for $\mathcal{E}(t)$, defined by

$$C_{-|}(t) = \exp\{-i\int_{-\infty}^{t} \mathcal{E}(t')dt'/\hbar\} \qquad (7.1-4)$$

$\mathcal{E}(t)$ was interpreted as a "dynamical complex potential" and we considered some approximate methods for solving Eq.(6.1-2a) to determine it. In our subsequent calculations, we will use what we called the "first-order" approximation to $\mathcal{E}(t)$

$$\mathcal{E}(t) = \Delta(t) + \int_{0}^{\infty} \hat{\mathcal{S}}(\tau) \cdot \exp\{i\int_{t-\tau}^{t} \Delta(t')dt'/\hbar\} \cdot d\tau \qquad (7.1-5)$$

From this we obtain $C_{-|}(t)$, $C_\epsilon(t)$, and the desired probabilities and the cross sections. As we have seen in section 6.2 this first order approximation is much better than the first order pertubation theory, which corresponds to the zero-order approximation in our picture.

In the present chapter we consider a quadratic approximation of $\Delta(t)$ as was done by Taylor and Delos.[22] The reasons that we repeat the calculations using the same approximation are: (i) to illustrate the "dynamical complex potential". (ii) to see if our results of calculation agree with those of Taylor and Delos. (iii) to extend the calculation to the electron energy spectrum which was not obtained by Taylor and Delos. (iv) to lay the ground for quartic approximation of $\Delta(t)$ which will be discussed in the next chapter.

7.2   THE DYNAMICAL COMPLEX POTENTIAL

Suppose now we have $\Delta(t) = E_o - \beta t^2$. This quadratic approximation to $\Delta(t)$ corresponds to situations where, as R goes smaller, the discrete state crosses into the continuum and does not cross back out as shown in Fig.I-1. Calculations have been performed for several combinations of E_o and β; the values chosen are listed in Table VII-1, and we denote them cases A1 to A4.

Table VII-1 E_o and β for $\Delta(t)$

Case	A1	A2	A3	A4
E_o	0 2	0.016	-0.01	-0.01
$\beta(*10^{-6})$	5.0	3.7	3.7	0 87

In Figs.VII-1,2 we show respectively for case Al the calculations of the real and imaginary parts of (i) $\Delta(t)$, (ii) $\hat{G}(\Delta(t))$, (iii) $\xi(t)-\Delta(t)$ calculated from Eq.(7.1-5).

We see several things from these figures. First, the real part of $\xi(t)-\Delta(t)$ is very small compared with $\Delta(t)$ (except of course where $\Delta(t)$ goes through zero). The imaginary part is comparable in magnitude to the real part. This justifies the approximation we used in Eq (7.1-5) where we substituted $\Delta(t)$ in the right-hand side for $\xi(t)$. Second both the real and imaginary parts of $\xi(t)-\Delta(t)$ are, except for the oscillations, similar in shape to those of $\hat{G}(\Delta(t))$. The oscillations can be explained by the stationary phase approximation, which we have discussed in section 6.3. In that approximation we find that the wavelength of the oscillations is proportional to $2\pi/\Delta(t)$, so rapid oscillations correspond to regions where $\Delta(t)$ is large. This is consistent with the results shown in Figs.VII-3,4.

7.3 THE SURVIVAL PROBABILITY

In Fig.VII-5 we show the survival probability for $\beta=10^{-6}$ calculated from Eqs.(7.1-1) and (7.1-4). Also included in the figure are the results calculated from the classical local-complex-potential (CLCP) model[1] and the Taylor-Delos formulas.[27] Our result lies between that of Taylor and Delos and that of the CLCP model. Both the present calcula-
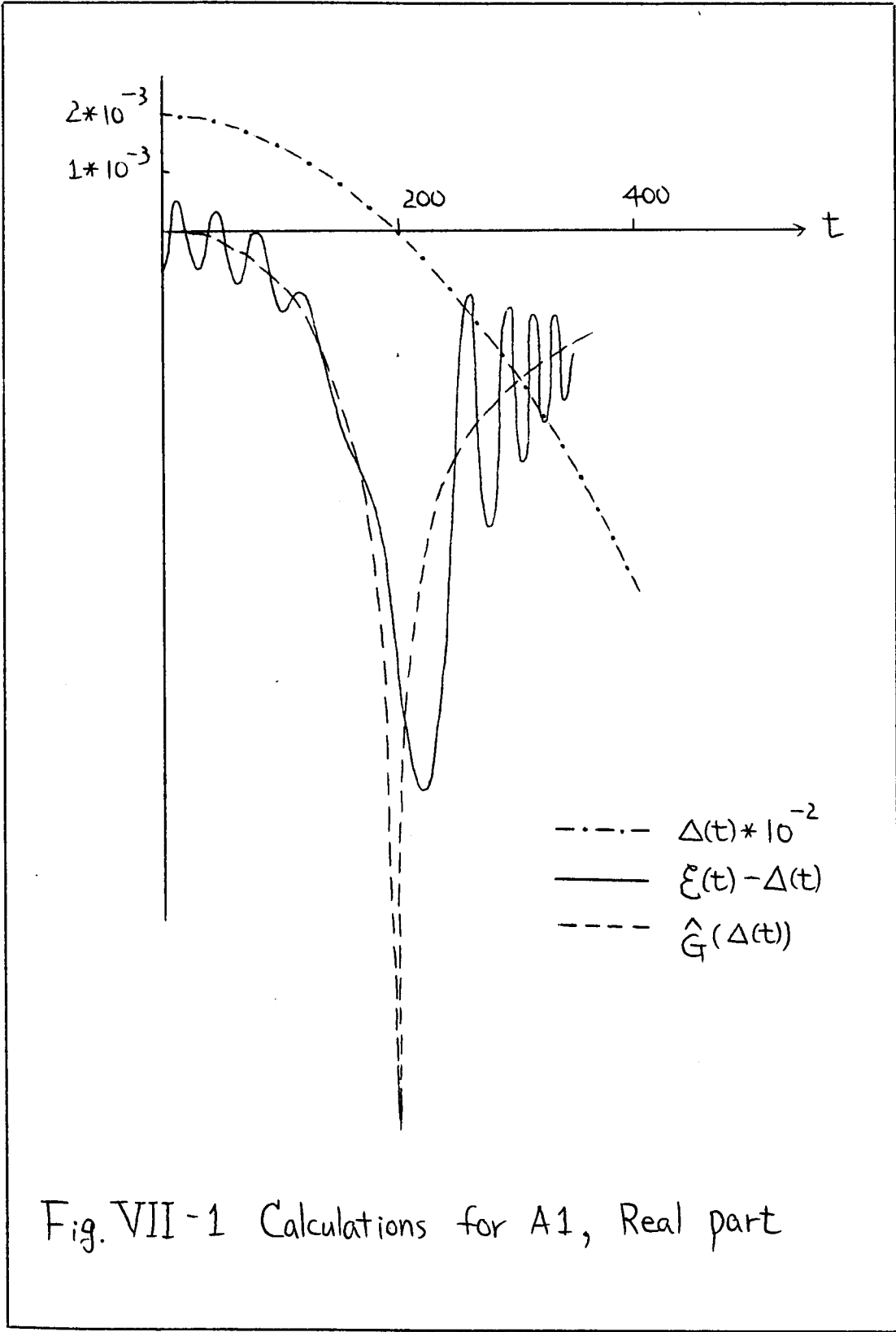
Fig. VII-1 Calculations for A1, Real part

Legend:
- $-\cdot-\cdot-$ $\Delta(t) * 10^{-2}$
- ——— $\mathcal{E}(t) - \Delta(t)$
- – – – $\hat{G}(\Delta(t))$

Axis labels: $2*10^{-3}$, $1*10^{-3}$, 200, 400, t

Fig. VII-2

Calculations for A1,
Imaginary Part

$\xi(t) - \Delta(t)$ —

$\hat{G}(\Delta(t))$ - - -

Fig. VII-3 $\mathcal{E}(t) - \Delta(t)$ for A2 and A3

Fig. VII-4 $\xi(t) - \Delta(t)$ for A3 and A4

Fig. VII-5 Survival Probability for $\beta = 10^{-6}$

--- Complex Potential Model
-·-·- Taylor - Delos Formula
——— Present Calculation

P_s

1.0

E_o (a.u)

-0.03   -0.02   -0.01   0   0.01   0.02   0.03   0.04   0.05   0.06   0.07
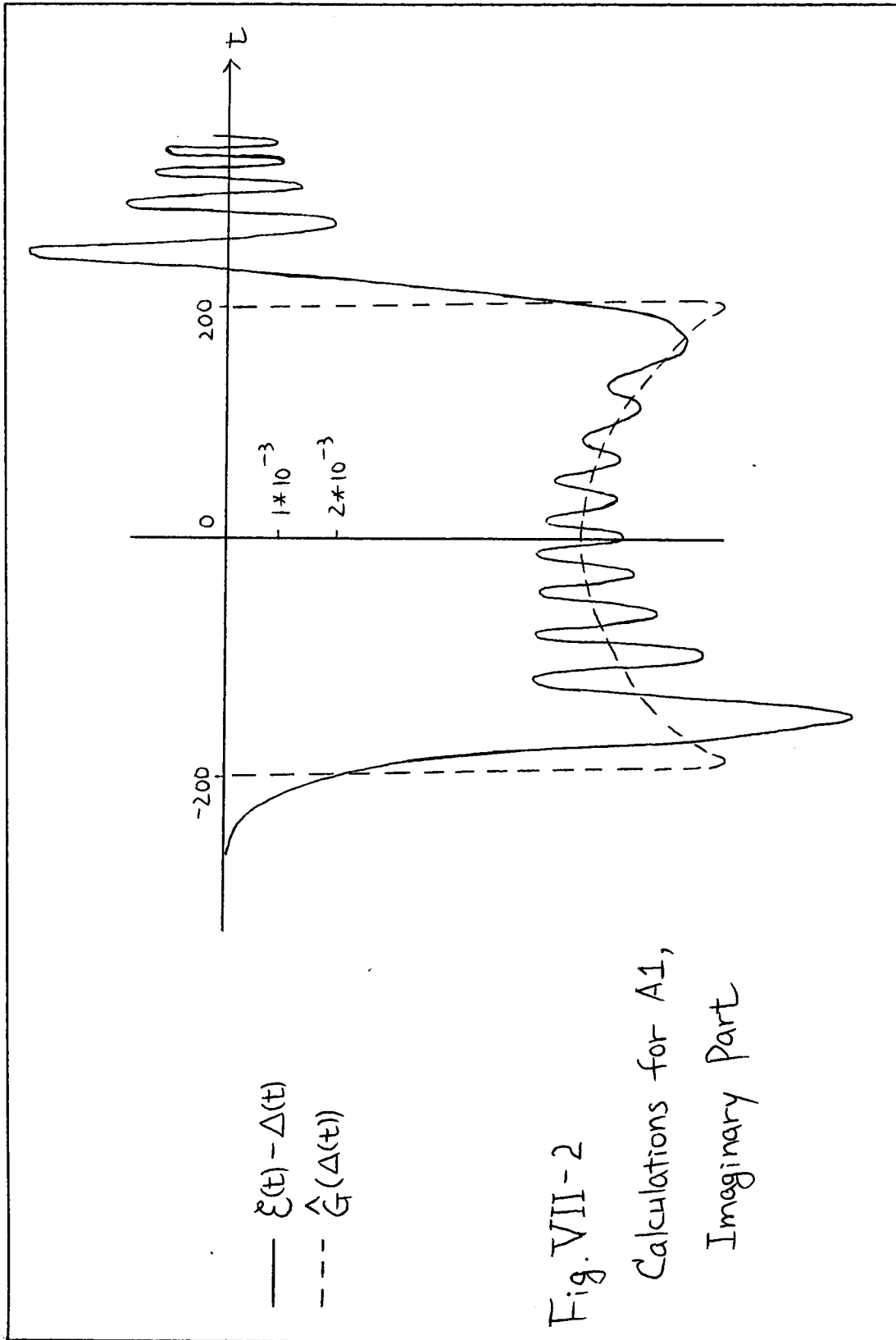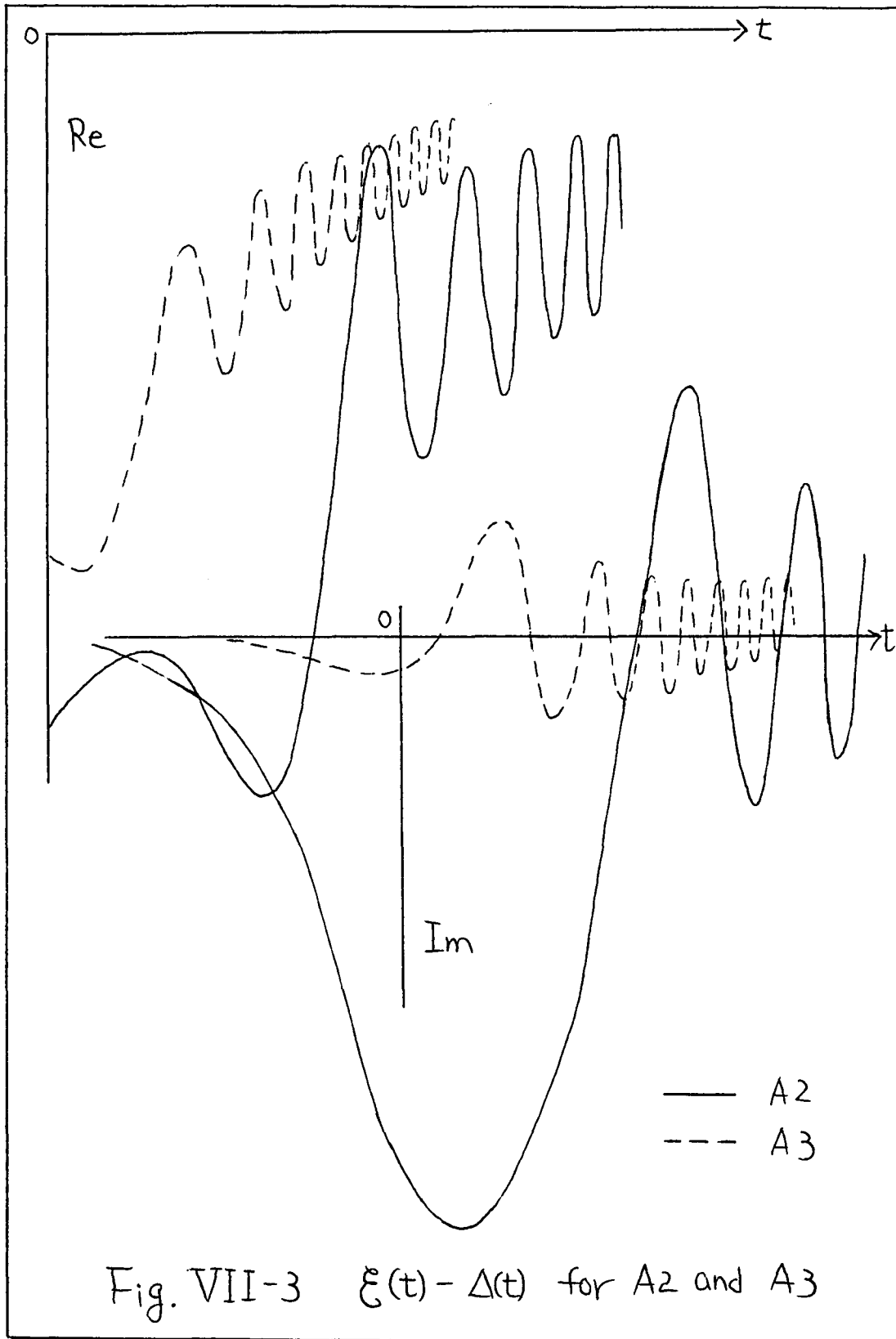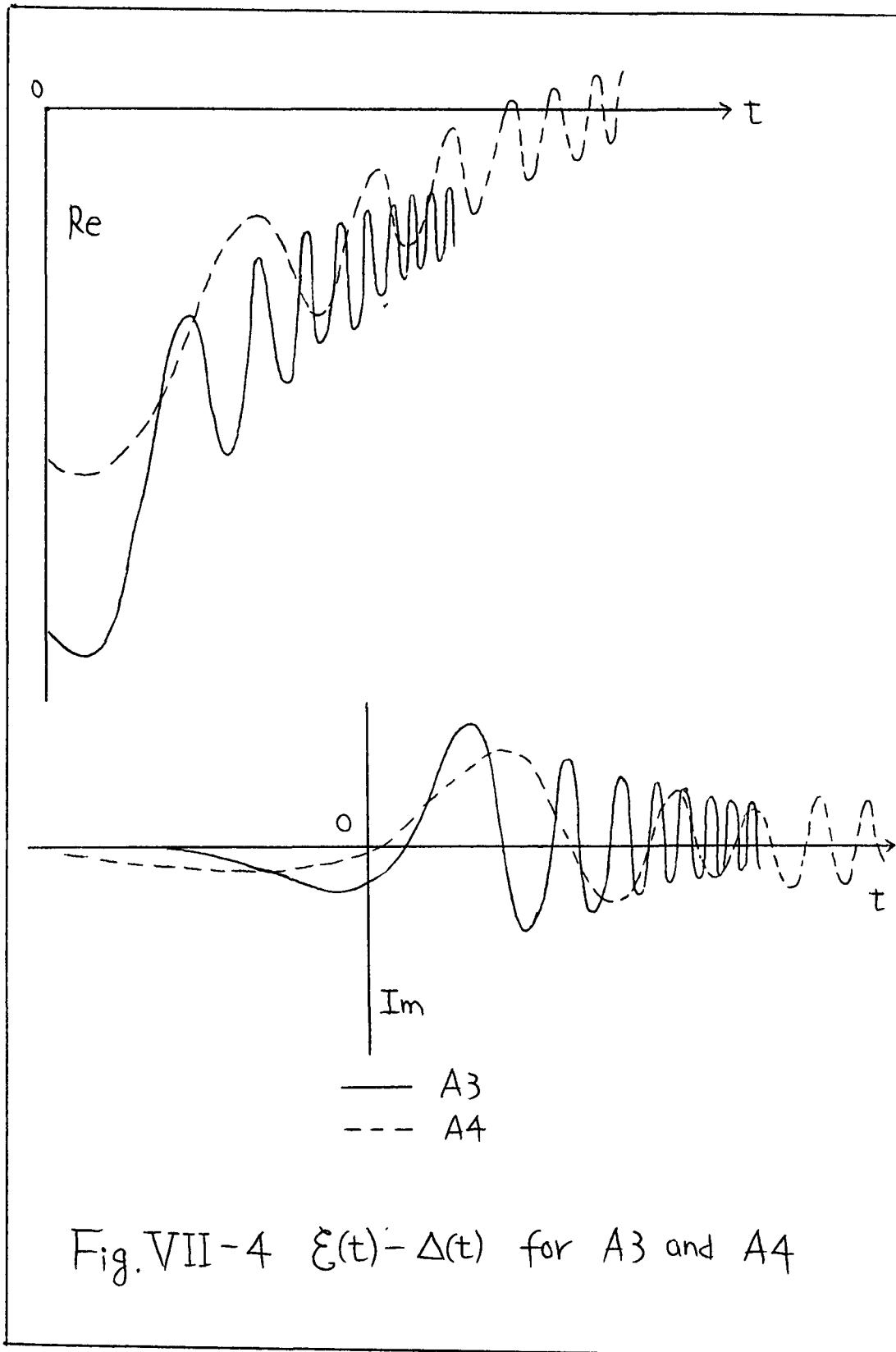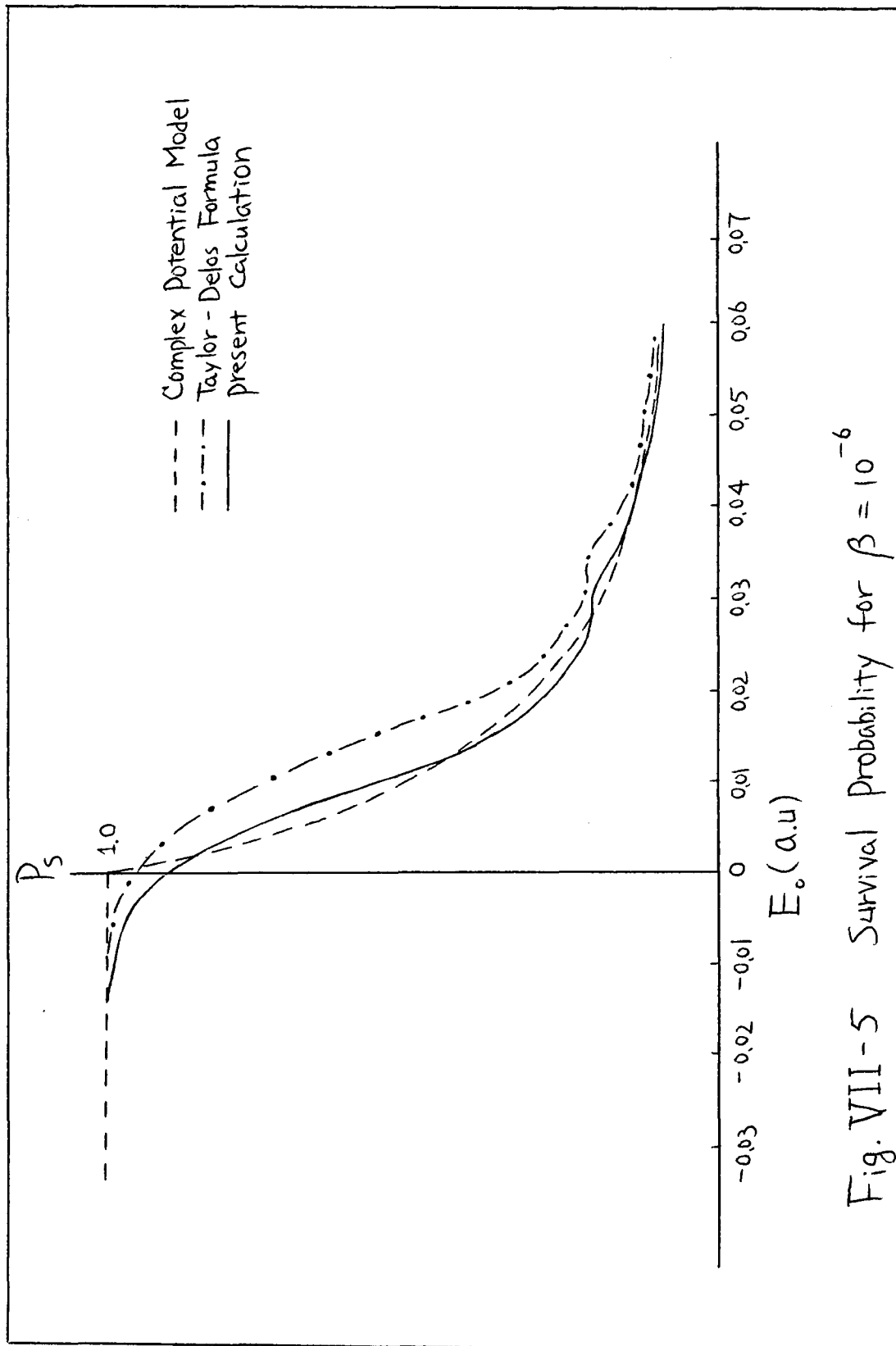
tion and the Taylor-Delos calculation improve upon the CLCP model in that they take into account "tunneling" transitions (which occur for $E_o < 0$) and interference effects (small oscillations when $E_o > 0$). However it is not possible to say with certainty whether the present result or the Taylor-Delos result is the more accurate. Both are reasonable, and they do not differ by much.

From Fig.VII-5 we would expect, that for the $H^-(D^-$) on He system at low energies, the total detachment cross section calculated by the present method would be slightly higher than that calculated by Taylor and Delos. The present result would therefore be closer to the experimentally measured results for that system. But since the calculations of the total detachment cross section by the complex potential model and Taylor-Delos formulas are close to each other, we see no need to carry out the calculation once again.

7.4   ELECTRON ENERGY SPECTRUM

We now proceed to calculate the electron energy spectrum. The direct numerical computation of Eq.(7.1-3) would be very time-consuming, so we are going to use two different approximate methods to calculate $C_\epsilon(\infty)$. One is a stationary phase approximation. This gives a very simple result which turns out to be accurate for most of the spectrum. It fails, however, near $\epsilon = E_o$. To get a result that

is accurate in that region we use a uniform approximation developed by Connor et al.,[30,31] which is described in Appendix D.

a. STATIONARY PHASE APPROXIMATION

Here we use a stationary phase approximation to the integral in Eq.(7.1-3). (In chapter VI we used a stationary phase approximation to a different integral.)

The stationary phase points are two roots of $\triangle(t) - \epsilon = 0$, i.e.

$$t_1 = -\sqrt{(E_o - \epsilon)/\beta} \qquad (7.4\text{-}1a)$$

$$t_2 = -t_1 \qquad (7.4\text{-}1b)$$

We get two different results depending upon whether t_1 and t_2 are real or not.

(1) $\epsilon < E_o$

For this classically accessible region, t_1 and t_2 are both real, and the stationary phase approximation gives

$$|C_\epsilon(\infty)|^2 = (\pi \, V_{1,\epsilon}^2/\beta t_2)(s_1^2 + s_2^2 + 2s_1 \cdot s_2 \cdot \sin\gamma) \qquad (7.4\text{-}2)$$

where

$$s(t) = \exp\{-\int_{-\infty}^{t} \text{Im} \, \mathcal{E}(t') \, dt'/\hbar\} \qquad (7.4\text{-}3a)$$

$$s_1 = s(t_1) \qquad (7.4\text{-}3b)$$

$$s_2 = s(t_2) \qquad\qquad (7.4\text{-}3c)$$

$$\gamma = (4/3)\beta^{-\frac{1}{2}} \cdot (E_o - \epsilon)^{\frac{3}{2}} \qquad\qquad (7.4\text{-}3d)$$

From Eq.(7.4-3a) we have $|s(t)|^2$ equal to the survival probability at time t. We also know that $\pi V_{-1,\epsilon}^2$ is the detachment rate and that $4\beta t_2$ is the rate of change of ϵ_{sp} which we get from $\Delta(t) - \epsilon_{sp} = 0$. Hence we see from Eq.(7.4-2) that the first two terms of the right-hand side correspond to two probabilities of detachment at time t_1 and t_2 respectively and that the third term corresponds to the interference between these two processes. This is illustrated in Fig VII-6 where we see two different paths leading to detachment: (i) the electron makes a transition, at t_1 on the incoming part of the trajectory, to the continuum state of energy ϵ, and (ii) the electron remains in the bound state and makes a transition to the continuum state at t_2 on the outgoing part of the trajectory.

(2) $\epsilon > E_o$

In this classically inaccessible region we have two stationary phase points t_1 and t_2 which are both purely imaginary. From the condition that the integral must be convergent we know that the contour of integration goes through the point t whose imaginary part is positive. Taking only the real part of t when calculating s(t), we have $s(t_2) \simeq s(0)$ and

$$\Delta(t) = E_0 - \beta t^2$$
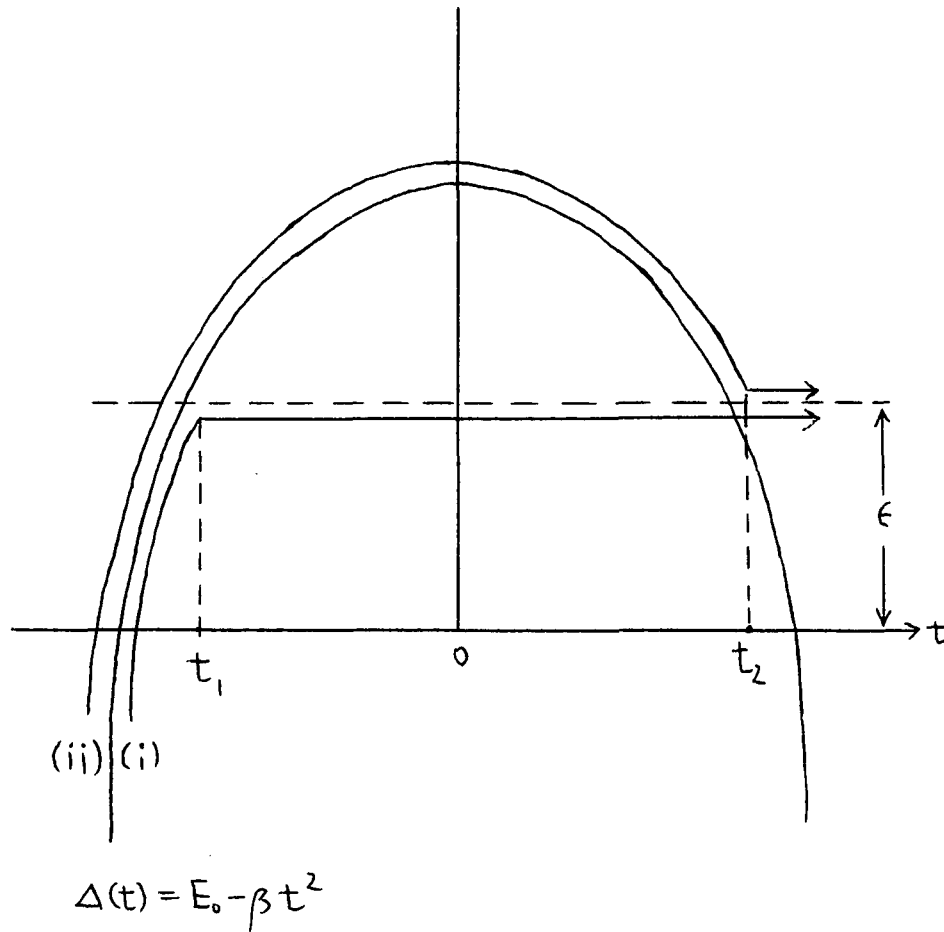
Fig. VII-6 Two Different Paths to the
Same Continuum State for
Quadratic Approximation

$$|C_{\epsilon}(\infty)|^2 = (\pi V_{1,\epsilon}^2/\beta|t_2|) \cdot s(\emptyset) \cdot \exp(-\gamma/2) \qquad (7.4-4)$$

We see that $|C_{\epsilon}(\infty)|^2$ decreases exponentially in the forbidden region. The stationary phase approximation breaks down at regions where $E_o - \epsilon$ is close to zero.

b UNIFORM APPROXIMATION

A derivation of the uniform approximation is given in Appendix D. Here we just state the result. Let us define

$$y = (E_o - \epsilon)\beta^{-\frac{1}{3}} \qquad (7.4-5a)$$

$$s^2 = s_1 \cdot s_2 \qquad (7.4-5b)$$

$$f_1 = 2\beta t_1 \qquad (7.4-5c)$$

$$f_2 = 2\beta t_2 \qquad (7.4-5d)$$

where t_1, t_2, s_1 and s_2 are the same as in Eqs. (7.4-1) and (7.4-3).

We can express $|C_{\epsilon}(\infty)|^2$ as follows depending on whether ϵ is smaller than E_o or not.

(1) $\epsilon \leqslant E_o$

In this classically accessible case, where t_1 and t_2 are real, we have

$$|C_\epsilon(\infty)|^2 = \frac{\pi^2 V_{-1,\epsilon}^2}{\beta t_2 \hbar^2} \{ \ (s_1+s_2)^2 \cdot y^{\frac{1}{2}} \cdot Ai^2(-y)$$

$$+ (s_1-s_2)^2 \cdot y^{-\frac{1}{2}} \cdot Ai'^2(-y) \ \} \qquad (7.4-6)$$

where Ai is the Airy function.

(2) $\epsilon > E_0$

In this classically inaccessible region we have

$$t_1 = - i\sqrt{(\epsilon - E_0)/\beta} \qquad (7.4-7a)$$

$$t_2 = -t_1 \qquad (7.4-7b)$$

and

$$|C_\epsilon(\infty)|^2 = \frac{4\pi^2 s^2 V_{-1,\epsilon}^2}{f_0 \hbar^2} \{ \ [1-\sin(\alpha-\pi/2)] \cdot |y|^{\frac{1}{2}} \cdot Ai^2(|y|)$$

$$+ [1+\sin(\alpha-\pi/2)] \cdot |y|^{-\frac{1}{2}} \cdot Ai'^2(|y|) \ \} \qquad (7.4-8)$$

where

$$\alpha = i \ \{ \int_{t_1}^{t_2} Im \ \mathcal{E}(t) dt/\hbar \} \qquad (7.4-9a)$$

$$f_o = \sqrt{4\beta(\epsilon - E_o)} \qquad\qquad (7.4-9b)$$

There is a problem in applying Eq.(7.4-8). The quantity α in (7.4-9a) involves an integral over $\xi(t)$ for purely imaginary t, but we have only calculated $\xi(t)$ for real t. There are several ways of estimating α, of which the simplest is the approximation $\alpha = 0$. This can be justified in the following way. The classically inaccessible region starts where $\epsilon - E_o$ is zero, and both t_1 and t_2 are zero. As ϵ increases, t_1 and t_2 move out the imaginary axis and the magnitude of α increases. However when ϵ is large enough that α is significant, the Airy functions and $|C_\epsilon(\infty)|^2$ have become very small. In the range of ϵ in which $|C_\epsilon(\infty)|^2$ is significant, α is close to zero, and Eq.(7.4-8) can be simplified as

$$|C_\epsilon(\infty)|^2 = \frac{8\pi^2 s^2 V_{i,\epsilon}^2}{f_o \hbar^2} |y|^{\frac{1}{2}} \cdot Ai^2(|y|) \qquad (7.4-10)$$

c. RESULT

In Fig.VII-7 we show the calculations of $|C_\epsilon(\infty)|^2 f_\epsilon$ as functions of ϵ using both the uniform approximation and stationary phase method for $\beta = 10^{-6}$ and $E_o = 0.02$. In Fig.VII-8 we show the same calculations for $E_o = 0.05$.

In Fig.VII-7 we see only one peak but in Fig.VII-8 there are three peaks in the electron energy spectrum. The number of peaks is determined by the value of $E_o - \epsilon$ as can
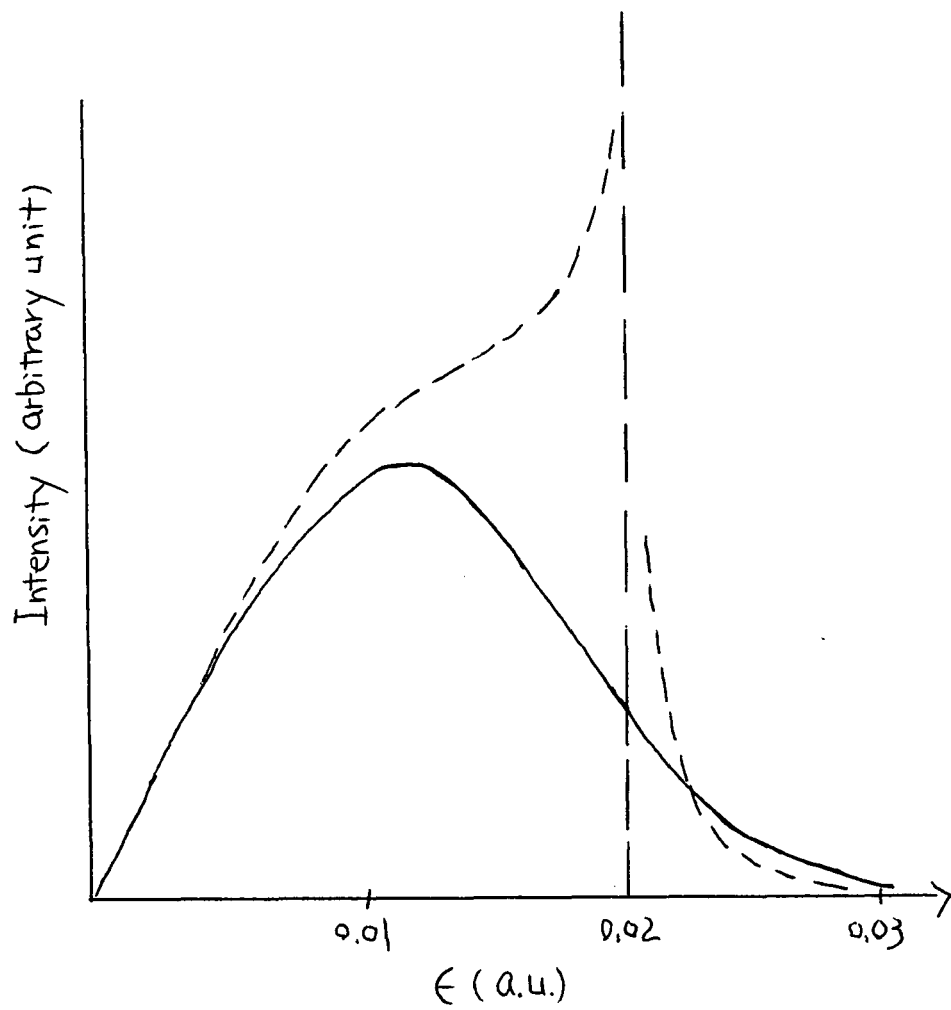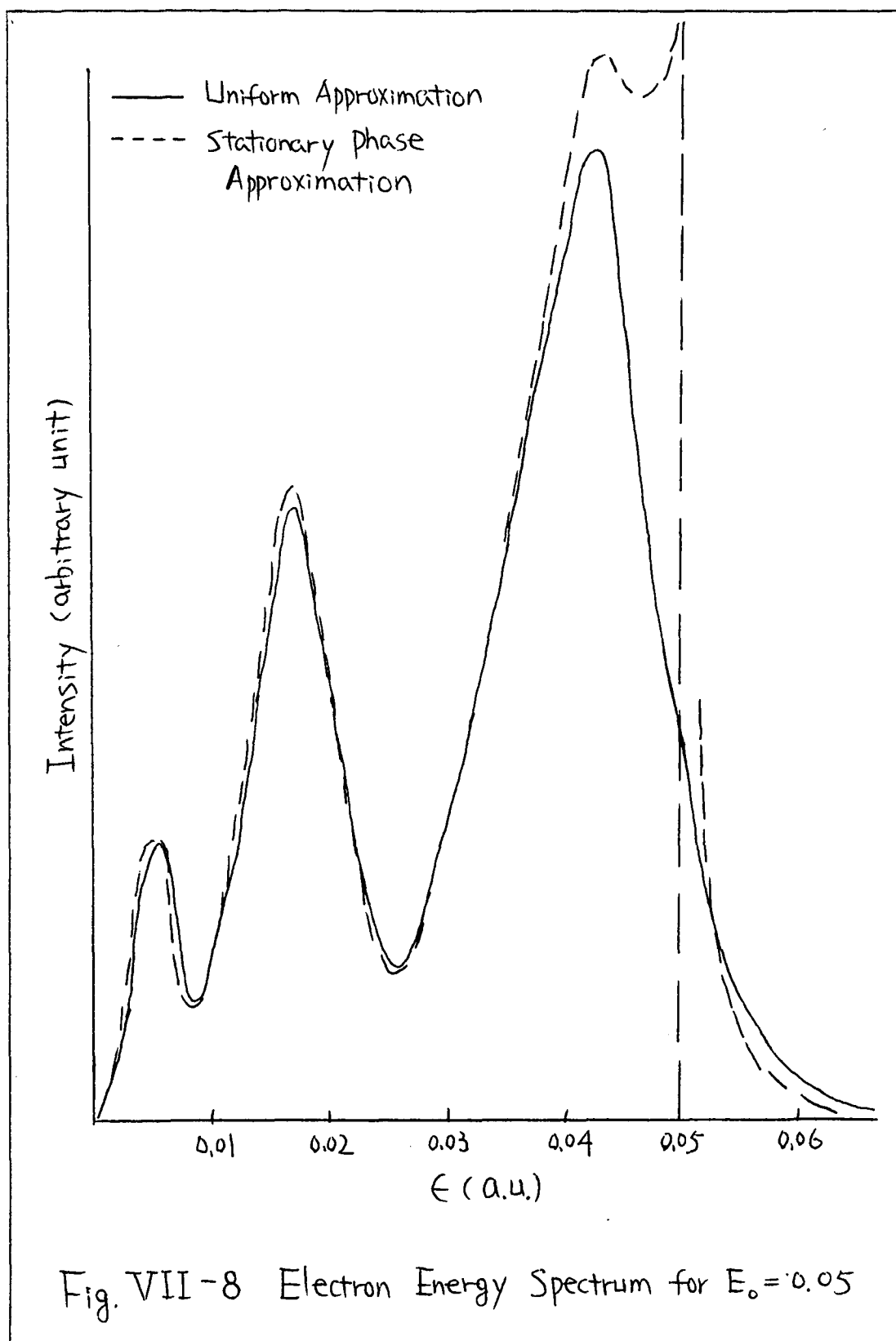
Fig. VII-7 Electron Energy Spectrum for $E_o = 0.02$

Fig. VII-8 Electron Energy Spectrum for $E_o = 0.05$

be seen from $\sin\gamma$ in Eq.(7.4-2) or Ai(-y) in Eq.(7.4-6). The kind of oscillatory electron energy spectrum shown in Fig.VII-8 has not yet been seen in measurements involving electron detachment, but it does appear in measurements on Penning ionization.

From Figs.VII-5 and VII-7 a simple calculation gives, for $E_o = 0.02$ and $\beta = 10^{-6}$

$$P_S + \int_o^\infty P_d(\epsilon)d\epsilon = 1.0 \pm 10^{-2} \tag{7.4-11}$$

Because we used a first-order approximation, we could not be sure that these probabilities would add to unity; the fact that they nearly do so suggests that our calculations are accurate and the approximations used are justified.

7.5 SUMMARY AND DISCUSSION

In this chapter we have applied our formulas to the case of $H^-(D^-)$ in collisions with He using a quadratic approximation for $\triangle(t)$. We have calculated the dynamical complex potential and shown how it differs from the local complex potential. We have calculated the survival probability, and compared it with that obtained from the local complex potential model and that obtained by Taylor and Delos. In this case it is found that the results are quite close to each other. This is not surprising: in chapter V, we showed that our formulas reduce to those of the local-

complex-potential model under appropriate conditions. In Appendix E we give an analytic proof that under appropriate conditions our results must agree with those of Taylor and Delos.

We have also calculated the electron energy spectrum which is found to have oscillatory structures that have not previously been calculated or observed for electron detachment. We have shown analytically why those oscillations arise. Finally, by checking conservation of probability we have shown that the approximations used and the calculations presented in this formulation should be accurate.

Chapter VIII

ELECTRON DETACHMENT FOR $H^-(D^-)$ IN COLLISIONS WITH HELIUM

PART II: QUARTIC APPROXIMATION

8.1 INTRODUCTION

In this chapter we apply our formulas (Eqs.(7.1-1,2,3,4,5)) to the case of electron detachment for $H^-(D^-)$ in collisions with He using a quartic approximation for $\triangle(t)$. This approximation can be related to the situations where, as R decreases, the discrete state crosses into the continuum and comes out again as shown in Fig.VIII-1. Such behavior was found by Olson and Liu for the $H^-(D^-)$ — He system.[28]

In the last chapter we have applied our formulas to the same case using a quadratic approximation for $\triangle(t)$. We are going to see in this chapter what differences arise from the more accurate quartic approximation. The calculations we make in this chapter parallel those made in sections 7.2, 7.3, and 7.4.

To see why a quartic approximation is needed, let us examine the H — He energy curves shown in Fig.VIII-1. For impact parameter $b = \emptyset$, at energies near $E = E_a$, a graph
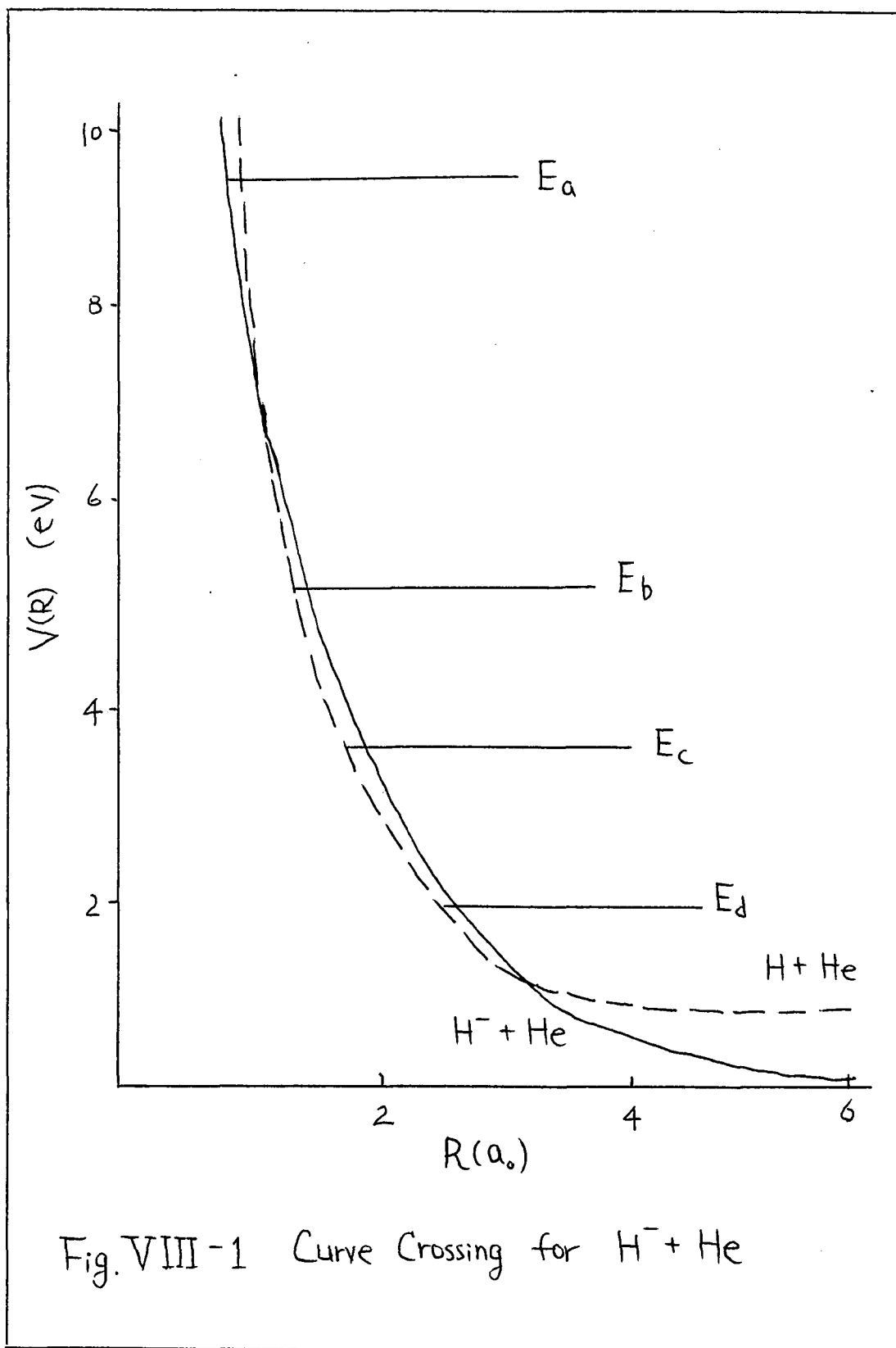
Fig. VIII-1 Curve Crossing for H⁻ + He

of $\triangle(t)$ vs t has the behavior indicated in Fig.VIII-2a, because the discrete state goes into the continuum then comes back out at smaller R (smaller $|t|$). At lower energies, near E_b, $\triangle(t)$ has two maxima and a minimum but the minimum is still within the continuum. For $E = E_c$, if the turning point coincides with the point at which $\triangle(R)$ is a maximum, then $\triangle(t)$ has the form shown in Fig.VIII-2c, and for still lower energies, we revert to the case of Fig.VIII-2d, for which the simpler quadratic approximation should usually be adequate.

The same types of behavior are found if we hold the energy fixed (near or above E_α) and increase the impact parameter. Since the electron energy spectrum directly reflects the behavior of $\triangle(t)$, we see that this quartic approximation can lead to much more complicated and interesting behavior than can the quadratic approximation.

8.2 THE DYNAMICAL COMPLEX POTENTIAL AND SURVIVAL PROBABILITY

We suppose $\triangle(t) = E_o + \alpha t^2 - \beta t^4$. In Table VIII-1 we we give values for different combinations of E_o, α, and β and we denote them cases B1 to B5. In Figs.VIII-3,4 we show respectively for case B1 the calculations of the real and imaginary parts of (i) $\triangle(t)$, (ii) $\hat{G}(\triangle(t))$, and (iii) $\xi(t) - \triangle(t)$. In Figs.VIII-5,6 we show the calculations of Im $\xi(t)$ for cases B2, B3 and B4, B5 respectively. The case B2
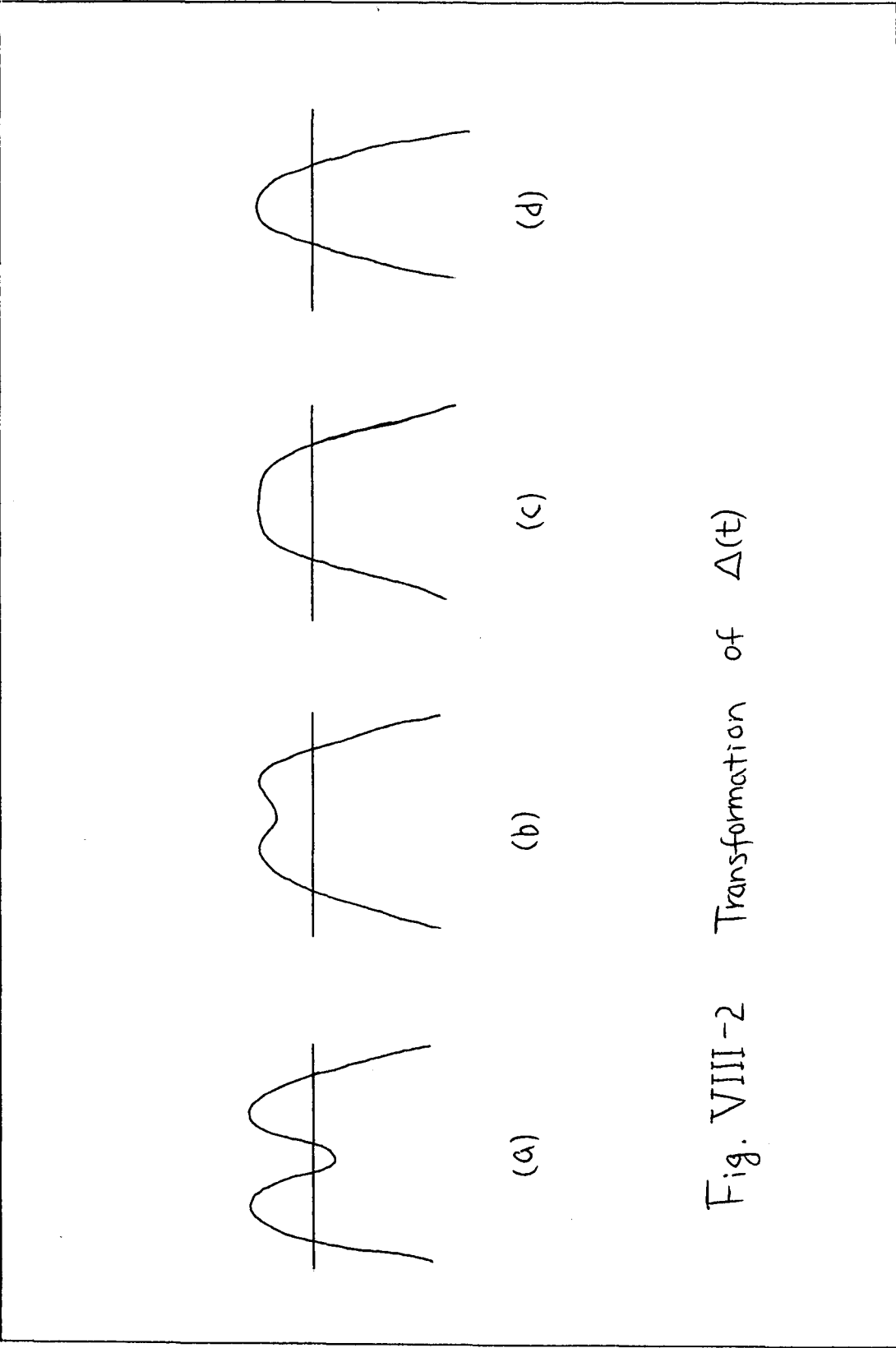
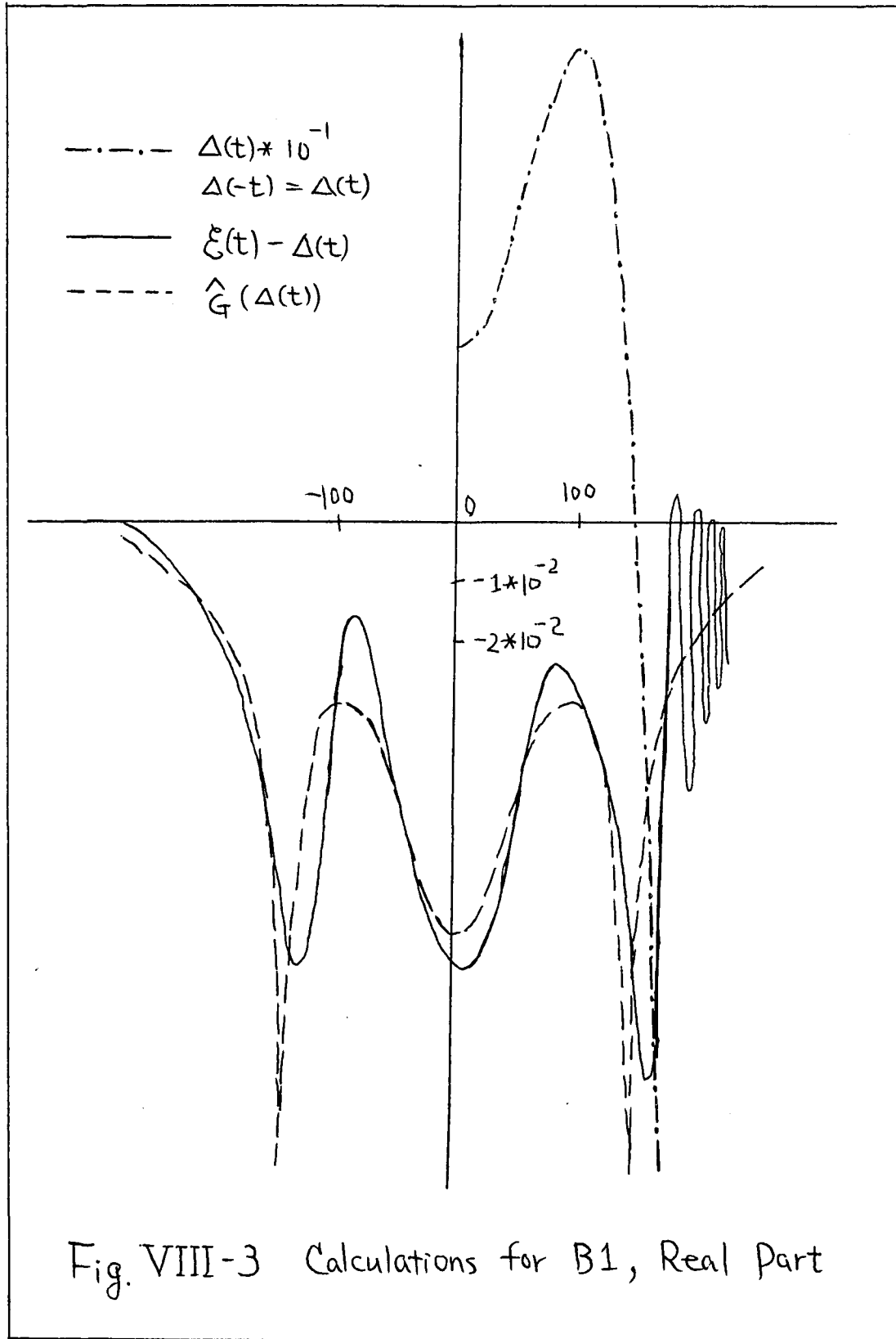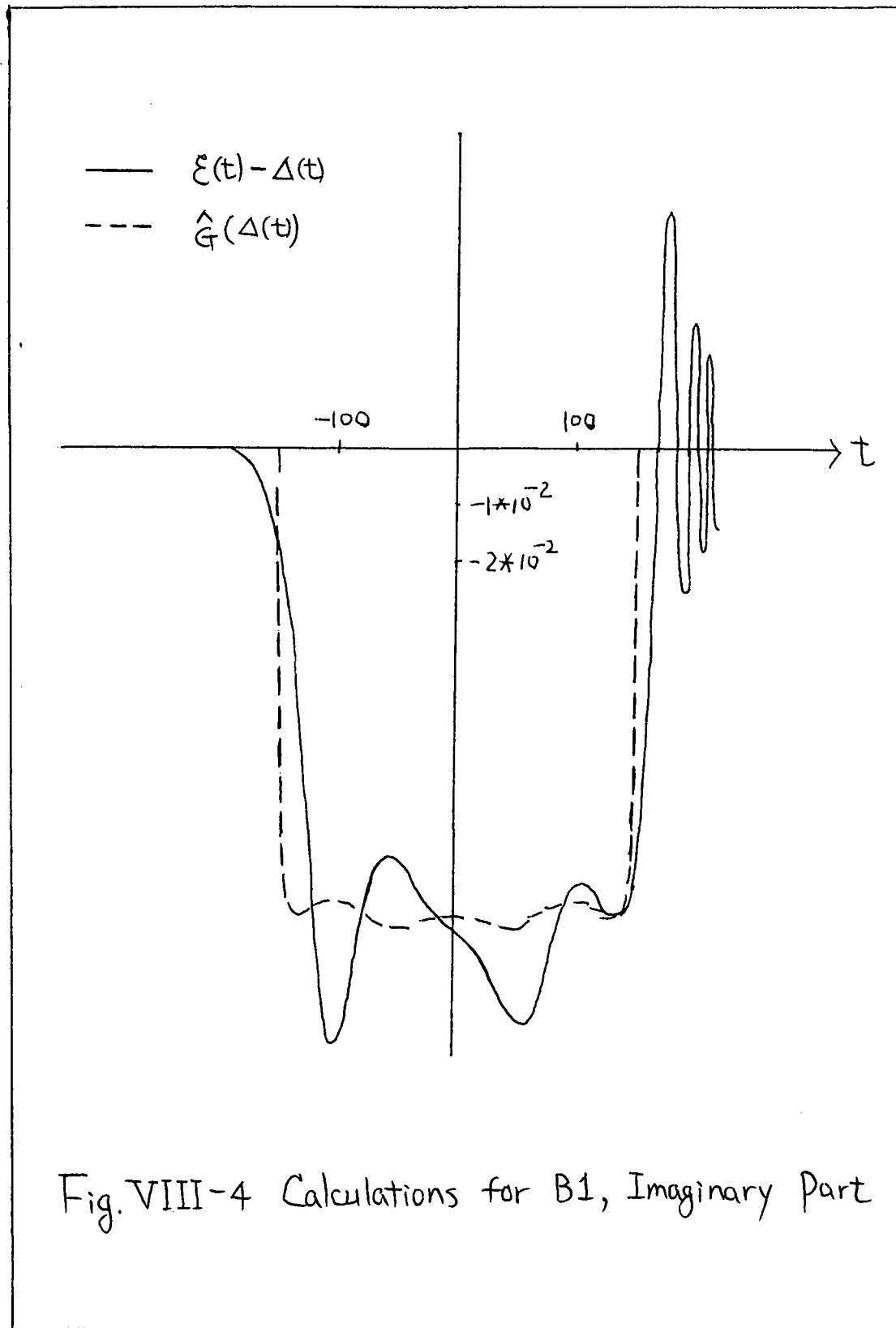(a)   (b)   (c)   (d)

Fig. VIII-2 Transformation of $\Delta(t)$

Fig. VIII-3 Calculations for B1, Real Part

Fig. VIII-4 Calculations for B1, Imaginary Part
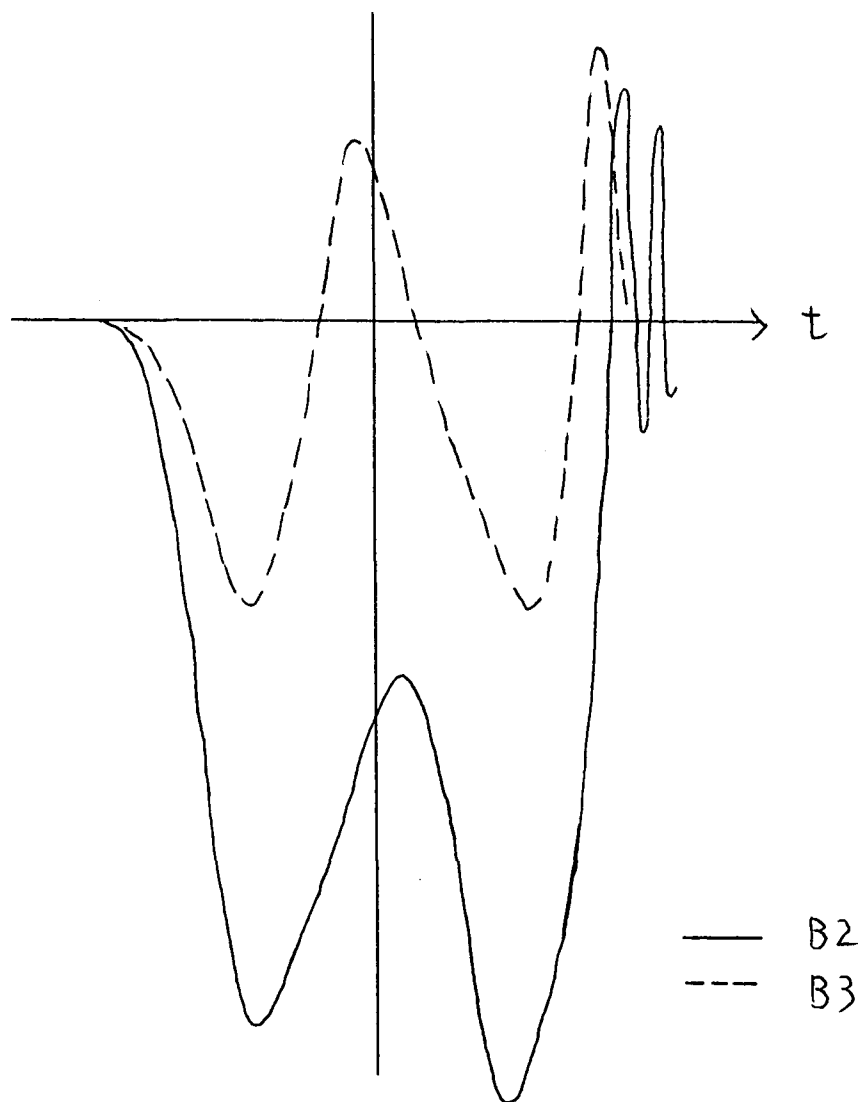
Fig. VIII-5   Im $\xi(t)$ for B2 and B3

Fig. VIII-6   Im $\mathcal{E}$(t) for B4 and B5
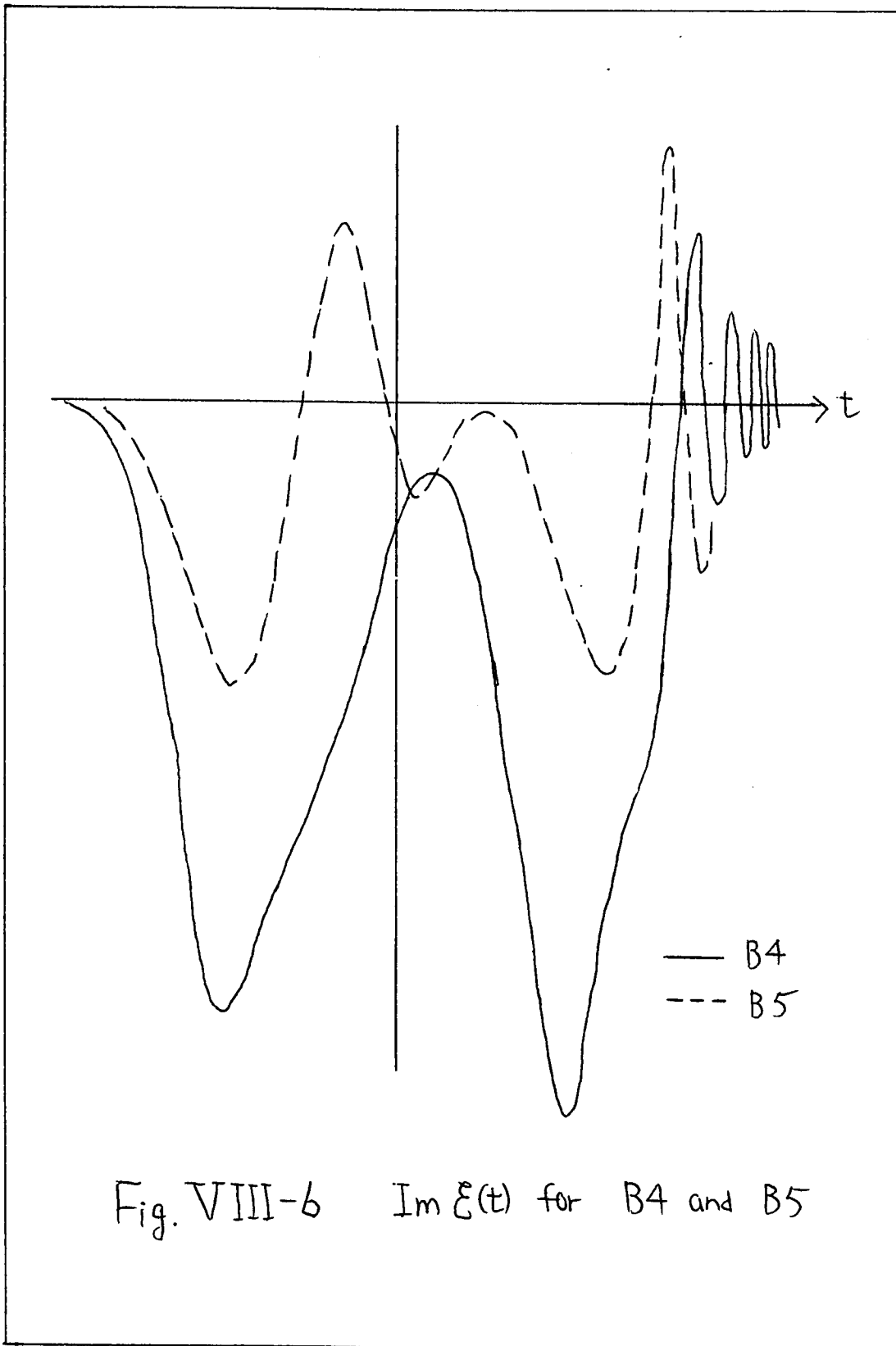
and B4 are easiest to interpret. In case B4, $\bigwedge(t)$ has the form shown in Fig.VIII-2a. When $\bigwedge(t)$ increases toward its first maximum $\hat{G}(\bigwedge(t))$ also increases, and $|Im\, \xi(t)|$ has a corresponding maximum. Then as $\triangle(t)$ decreases, so does $\hat{G}(\triangle(t))$, and $|Im\, \xi(t)|$ moves back toward zero. Hence $|Im\, \xi(t)|$ has a sharp peak for negative t, and a second sharp peak for positive t. Besides these, interference structures are visible, especially at large t.

Cases B3 and B5 are similar to B2 and B4, except that $\triangle(t)$ is displaced negatively, so $|Im\, \xi(t)|$ does not become so large.

In Fig.VIII-7 we give the survival probabilities for different combinations of α and β. The survival probability for $\beta = 10^{-6}$ in the quadratic case is also included in the figure. The main effect of the quartic approximation is to "lower the threshold" for electron detachment. In the quadratic approximation, if $E_o \leqslant 0$ the discrete curve does not penetrate into the continuum, and the survival probability is close to unity. In the quartic approximation, this threshold is shifted to $E_o = -\alpha^2/4\beta$.

Table VIII-1 E_o, α, and β for $\bigwedge(t)$

Case	B1	B2	B3	B4	B5
E_o	0 03	0	-0 04	-0.01	-0.05
α (*10^{-6})	10	10	10	5	5
β (*10^{-16})	5	5	5	1	1

P_S

1.0

E_o (a.u.)

0.04

0.02

0

-0.02

-0.04

-0.06

—— $\Delta(t) = E_o - 10^{-6} * t^2$

---- $\Delta(t) = E_o + 5*10^{-6} * t^2 - 10^{-10} * t^4$

—·—· $\Delta(t) = E_o + 10^{-5} * t^2 - 5*10^{-10} * t^4$
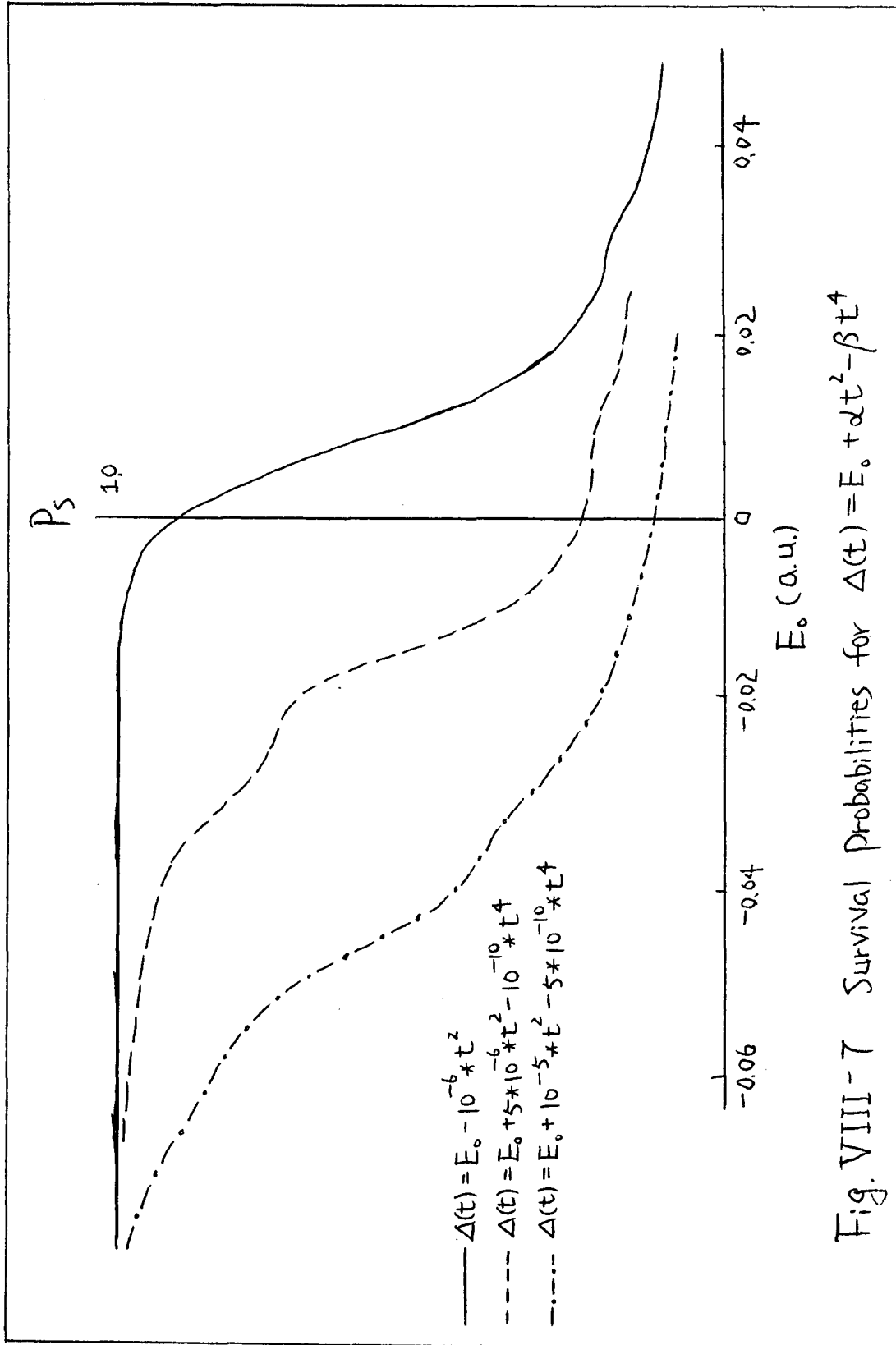
Fig. VIII-7 Survival Probabilities for $\Delta(t) = E_o + \alpha t^2 - \beta t^4$

8.3 ELECTRON ENERGY SPECTRUM

As in the last chapter we use both the stationary phase approximation and uniform approximation to calculate the electron energy spectrum for $\alpha = 10^{-5}$ and $\beta = 5*10^{-10}$.

a STATIONARY PHASE APPROXIMATION

Defining

$$f(t) = \frac{1}{5}\beta t^5 - \frac{1}{3}\alpha t^3 - (E_o - \epsilon)t \qquad (8.3-1)$$

the stationary phase points are the roots of $df(t)/dt = 0$; from which we have

$$t_1 = \sqrt{(\alpha + \sqrt{\alpha^2 + 4\beta(E_o - \epsilon)})/2} \qquad (8.3-2a)$$

$$t_2 = -t_1 \qquad (8.3-2b)$$

$$t_3 = \sqrt{(\alpha - \sqrt{\alpha^2 + 4\beta(E_o - \epsilon)})/2} \qquad (8.3-2c)$$

$$t_4 = -t_3 \qquad (8.3-2d)$$

We must calculate $C_\epsilon(\infty)$ differently according to whether $\alpha^2 + 4\beta(E_o - \epsilon)$ is real or not. For classically accessible region we have $\alpha^2 + 4\beta(E_o - \epsilon) > 0$, i.e., $E_o - \epsilon > -(\alpha^2/4\beta)$, so we

(i)

(ii)

(iii)
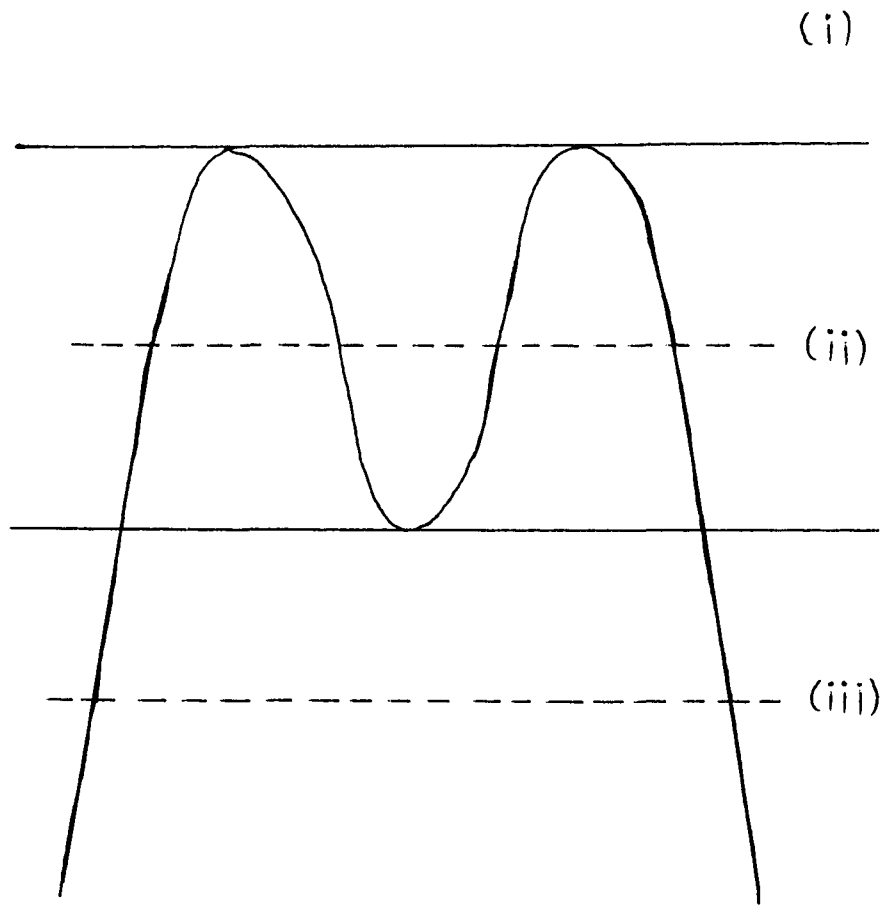
Fig. VIII-8 Stationary Phase Points

can express $C_{\epsilon}(\infty)$ as follows depending upon whether ϵ is smaller than $E_o + \alpha^2/4\beta$ or not. From Fig.VIII-8 we see that in region (i), i.e. for $\epsilon > E_o + \alpha^2/4\beta$, there are four complex stationary phase points; in region (ii) we have $E_o < \epsilon < E_o + \alpha^2/4\beta$ and there are four real stationary phase points and in region (iii) ϵ is less than E_o and there are two real and two complex stationary phase points.

(1) $\epsilon < E_o + \alpha^2/4\beta$

We have for this classically accessible region

$$C_{\epsilon}(\infty) = \sum_{k=1}^{4} \left(\frac{2\pi}{|\Delta'(t_k)|}\right)^{\frac{1}{2}} \cdot V_{-l,\epsilon} \cdot s(t_k) \cdot \exp\{i[\frac{\pi}{4}\mathrm{sign}\Delta'(t_k) + \int_{-\infty}^{t_k}(\Delta(t)-\epsilon)dt]\}$$

(8.3-3a)

where

$$s(t_k) = \exp\{-\int_{-\infty}^{t_k} \mathrm{Im}\,\xi(t)dt/\hbar\}$$

(8.3-3b)

In case of $\epsilon < E_o$, t_3 and t_4 are complex. Their absolute values are very small as can be seen from Eqs.(8.3-2c) and (8.3-2d), so we make the approximation that $t_3 = t_4 = 0$.

(2) $\epsilon > E_o + \alpha^2/4\beta$

For this classically inaccessible region we have

$$t_1 = a_o + ib_o$$

(8.3-4a)

$$t_2 = -t_1$$

(8.3-4b)

$$t_3 = a_o - ib_o \qquad (8.3\text{-}4c)$$

$$t_4 = -t_3 \qquad (8.3\text{-}4d)$$

where

$$a_o = \sqrt{(\sqrt{4\beta\,(\epsilon - E_o)/\alpha^2} + 1)/2} \qquad (8.3\text{-}5a)$$

$$b_o = \sqrt{(\sqrt{4\beta\,(\epsilon - E_o)/\alpha^2} - 1)/2} \qquad (8.3\text{-}5b)$$

Since t_1, t_2, t_3, t_4 are all complex numbers we see from Fig.VIII-9, which is the contour of integration of $C_\epsilon(\infty)$, that the path of integration goes through only two stationary points. From the condition that as $\epsilon \to \infty$ the imaginary part of f(t) must be positive, we know the stationary points we need are t_1 and t_4. The stationary phase method then gives

$$C_\epsilon(\infty) = \sum_{k=1,4} (\frac{2\pi i}{|\Delta'(t_k)|})^{\frac{1}{2}} \cdot V_{1,\epsilon} s(t_k) \cdot \exp\{i \int_{-\infty}^{t_k} (\Delta(t') - \epsilon)dt'\} \qquad (8.3\text{-}6)$$

Once again we use the approximation $s(t_k) = s(\mathrm{Re}\,t_k)$. We also notice that the stationary phase approximation breaks down in regions where ϵ is close to E or to $E_o + \alpha^2/4\beta$, where $d\Delta(t)/dt = 0$.

b. UNIFORM APPROXIMATION

Defining

$$U = \int_{-\infty}^{\infty} dx \cdot \exp\{if(x)\} \qquad (8.3\text{-}7)$$
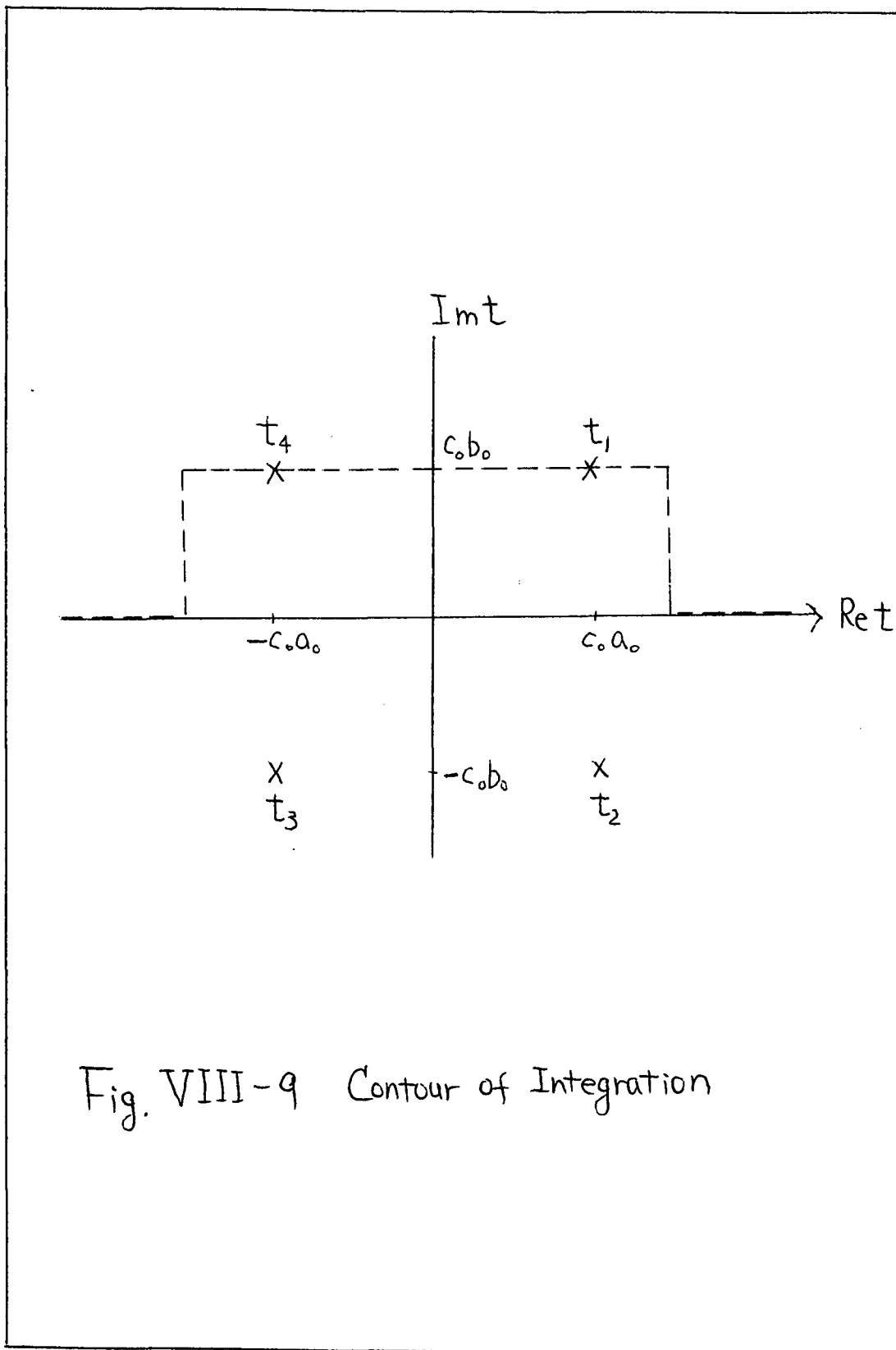
Fig. VIII-9   Contour of Integration

where

$$f(x) = z_1 x + z_3 x^3 + x^5 \qquad (8.3\text{-}8a)$$

$$z_1 = -(E_o - \epsilon)(\beta/5)^{-\frac{1}{5}} \qquad (8.3\text{-}8b)$$

$$z_3 = -(\alpha/3)(\beta/5)^{-\frac{3}{5}} \qquad (8.3\text{-}8c)$$

the uniform approximation gives

$$C_\epsilon(\infty) = V_{-1,\epsilon}\{q_o \cdot U - q_2 \cdot \frac{\partial^2 U}{\partial z_1^2} - i(q_1 \cdot \frac{\partial U}{\partial z_1} + q_3 \cdot \frac{\partial U}{\partial z_3})\} \qquad (8.3\text{-}9)$$

We have to calculate q_o, q_1, q_2 and q_3 differently according to whether ϵ is in classically accessible or inaccessible regions. This accessibility depends upon whether the saddle points of U, i.e. the roots of $df(x)/dx = 0$, are real or not.

From $df(x)/dx = 0$ we have

$$x^2 = \bar{c}_o^2 \cdot (\alpha \pm \sqrt{\alpha^2 + 4\beta(E_o - \epsilon)})/2\beta \qquad (8.3\text{-}10)$$

where

$$c_o = (\beta/5)^{-\frac{1}{5}} \qquad (8.3\text{-}11)$$

As in the case of stationary phase approximation we can express $C_\epsilon(\infty)$ as follows depending upon whether ϵ is smaller than $E_o + \alpha^2/4\beta$ or not.

(1) $\epsilon < E_o + \alpha^2/4\beta$

In this classically accessible region we have

$$q_o = (c_o/2)\{x_3^2 \cdot (s_1+s_2) - x_1^2 \cdot (s_3+s_4)\}/(x_3^2-x_1^2) \qquad (8.3-12a)$$

$$q_1 = (c_o/2)\{x_3^3 \cdot (s_1-s_2) - x_1^3 \cdot (s_3-s_4)\}/(x_1 x_3^3 - x_3 x_1^3) \qquad (8.3-12b)$$

$$q_2 = (c_o/2)(s_1+s_2-s_3-s_4)/(x_1^2-x_3^2) \qquad (8.3-12c)$$

$$q_3 = (c_o/2)\{x_3(s_1-s_2) - x_1(s_3-s_4)\}/(x_3 x_1^3 - x_1 x_3^3) \qquad (8.3-12d)$$

where

$$x_1 = \sqrt{(\alpha + \sqrt{\alpha^2+4\beta(E_o-\epsilon)})/2\beta}/c_o \qquad (8.3-13a)$$

$$x_2 = -x_1 \qquad (8.3-13b)$$

$$x_3 = \sqrt{(\alpha - \sqrt{\alpha^2+4\beta(E_o-\epsilon)})/2\beta}/c_o \qquad (8.3-13c)$$

$$x_4 = -x_3 \qquad (8.3-13d)$$

$$s_k = \exp\{-c_o/\hbar \int_{-\infty}^{x_k} \text{Im}\,\xi(c_ox)dx\} \qquad (8.3-13e)$$

The function U and its derivatives can be expressed in terms of gamma functions:

$$U = 2\sum_{\ell_1=0}^{\infty}\sum_{\ell_3=0}^{\infty} (z_1^{\ell_1}/\ell_1!)(z_3^{\ell_3}/\ell_3!)\cdot F(\ell_1,\ell_3) \qquad (8.3-14a)$$

$$\partial U/\partial z_1 = 2\sum_{\ell_1=1}^{\infty}\sum_{\ell_3=0}^{\infty} \{z_1^{\ell_1-1}/(\ell_1-1)!\}(z_3^{\ell_3}/\ell_3!)\cdot F(\ell_1,\ell_3) \qquad (8.3-14b)$$

$$\partial^2 U/\partial z_1^2 = 2 \sum_{l_1=2}^{\infty} \sum_{l_3=0}^{\infty} \{ z_1^{l_1-2}/(l_1-2)! \} (z_3^{l_3}/l_3!) \cdot F(l_1, l_3) \qquad (8.3\text{-}14c)$$

$$\partial U/\partial z_3 = 2 \sum_{l_1=0}^{\infty} \sum_{l_3=1}^{\infty} (z_1^{l_1}/l_1!) \{ z_3^{l_3-1}/(l_3-1)! \} \cdot F(l_1, l_3) \qquad (8.3\text{-}14d)$$

where

$$F(l_1, l_3) = \Gamma\{(1+l_1+3l_3)/5\} \cdot \cos\{\pi(1+6l_1+8l_3)/10\} \qquad (8.3\text{-}15)$$

In case of $\in < E_o$, we make the approximation that $x_3 = x_4 = 0$ for the same reason stated in the case of the stationary phase approximation.

(2) $\in > E_o + \alpha^2/4\beta$

In this classically inaccessible region we have the same difficulty as is encountered in the quadratic case, i.e. we do not know what $\mathcal{E}(x)$ is if x is not real. In this case x is a complex number. We have

$$x_1 = c_o(a_o + ib_o) \qquad (8.3\text{-}16a)$$

$$x_2 = -x_1 \qquad (8.3\text{-}16b)$$

$$x_3 = c_o(a_o - ib_o) \qquad (8.3\text{-}16c)$$

$$x_4 = -x_3 \qquad (8.3\text{-}16d)$$

where a_o and b_o are defined in Eqs. (8.2-5a,b).

Since the classically inaccessible region starts when $4\beta(\in-E_o)/\alpha^2 = 1$ we see that $a_o = 1$ and $b_o = 0$. So

we assume the imaginary part of x_k can be neglected when we calculate $s = \exp\{-c_c/\hbar \int_{-\infty}^{x_k} \text{Im}\, \mathcal{E}(c_o x)dx\}$ where $k = 1,2,3,4$. Then we have

$$q_o = c_o (s_1 + s_2)/2 \qquad\qquad (8.3\text{-}17a)$$

$$q_1 = c_o (s_1 - s_2)(3a_o^2 - b_o^2)/\{4a_c^2(a_o + b_o)\} \qquad (8\ 3\text{-}17b)$$

$$q_2 = 0 \qquad\qquad (8.3\text{-}17c)$$

$$q_3 = -c_o (s_1 - s_2)/\{4a_c \cdot (a_c^2 + b_o^2)\} \qquad (8.3\text{-}17d)$$

but we do not think it is right to have $q_2 = 0$ so we take q_2 equal to the limit in the classically accessible region.

c. RESULT

In Fig.VIII-10 we show the calculations of $|C_\epsilon(\infty)|^2 \rho_\epsilon$ as functions of ϵ using both the stationary phase and uniform approximations for $\alpha = 10^{-5}$, $\beta = 5*10^{-10}$ and $E_o = 0.03$. Figs.VIII-11 12 show the same calculations for $E_o = 0$ and -0.03 respectively.

Interesting structure is found in these spectra. At points corresponding to $d\Delta(t)/dt = 0$, the stationary phase approximation blows up; usually the uniform approximation will also show a peak in this region. Also there are valleys corresponding to interference minima as explained earlier.

Fig. VIII-10 Electron Energy Spectrum
for $E_0 = 0.03$, $\alpha = 10^{-5}$
and $\beta = 5 * 10^{-10}$
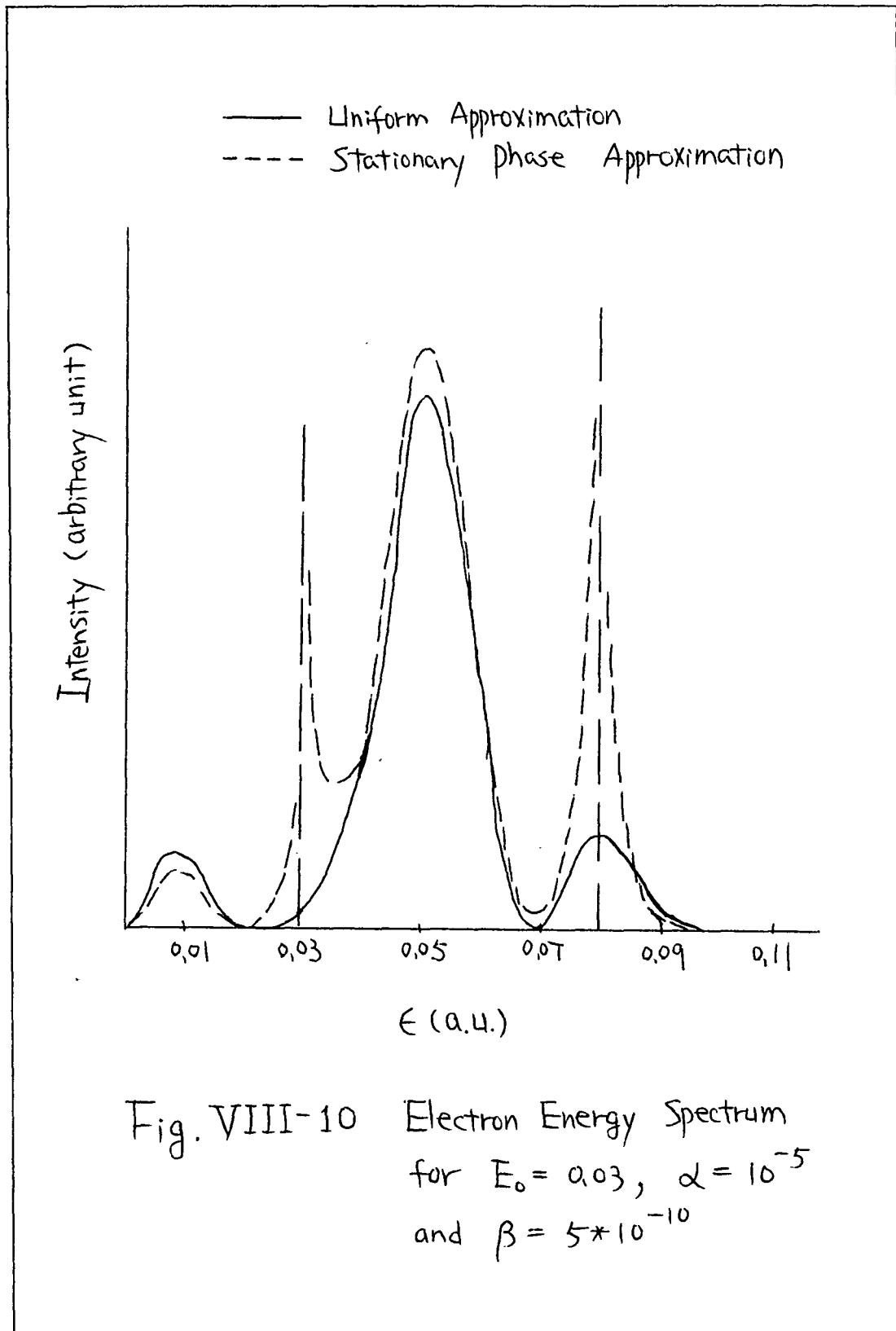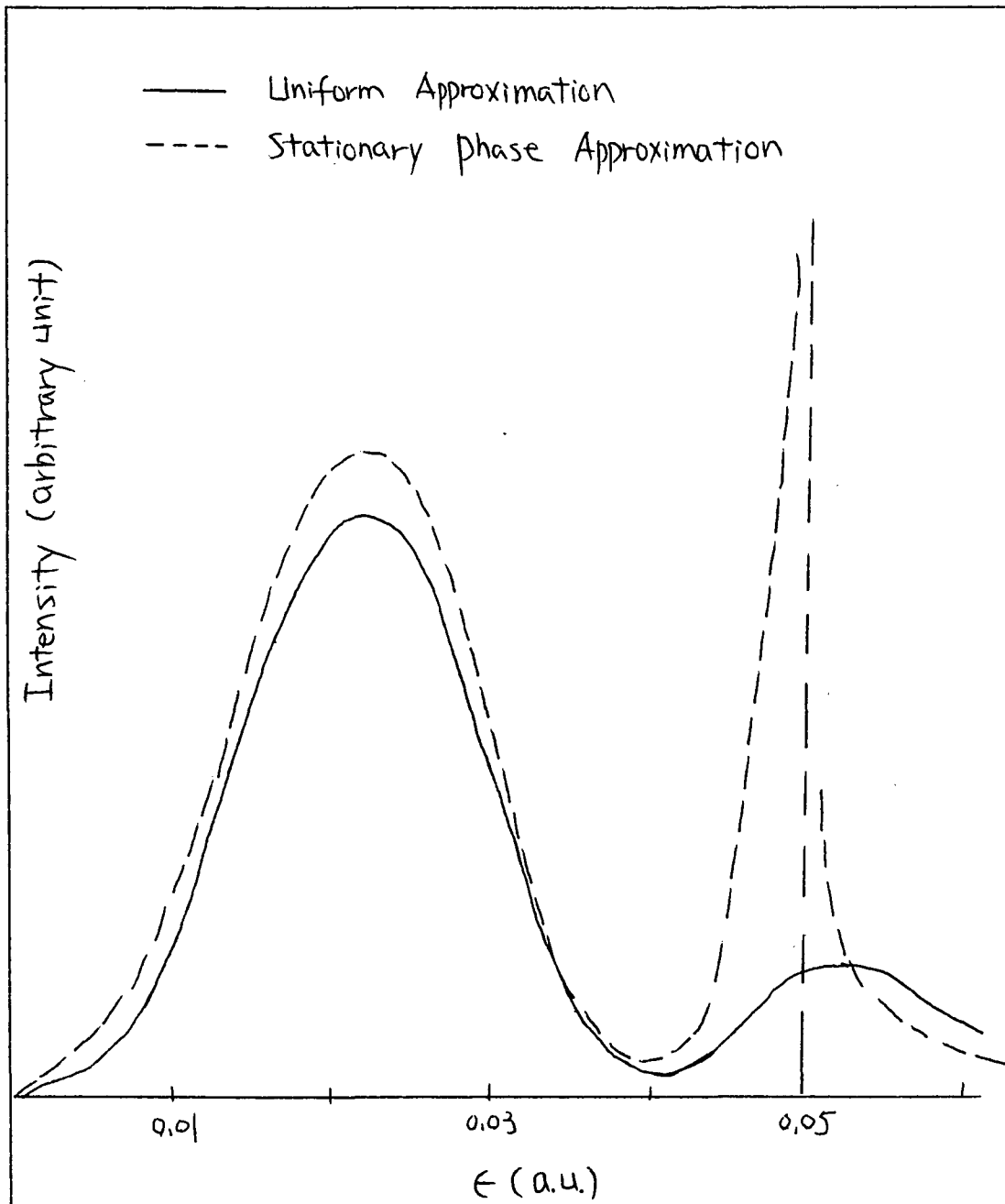
Fig. VIII-11 Electron Energy Spectrum
for $E_0 = 0$, $\alpha = 10^{-5}$
and $\beta = 5 * 10^{-10}$

Fig. VIII-12 Electron Energy Spectrum for $E_0 = -0.03$, $\alpha = 10^{-5}$ and $\beta = 5 * 10^{-10}$
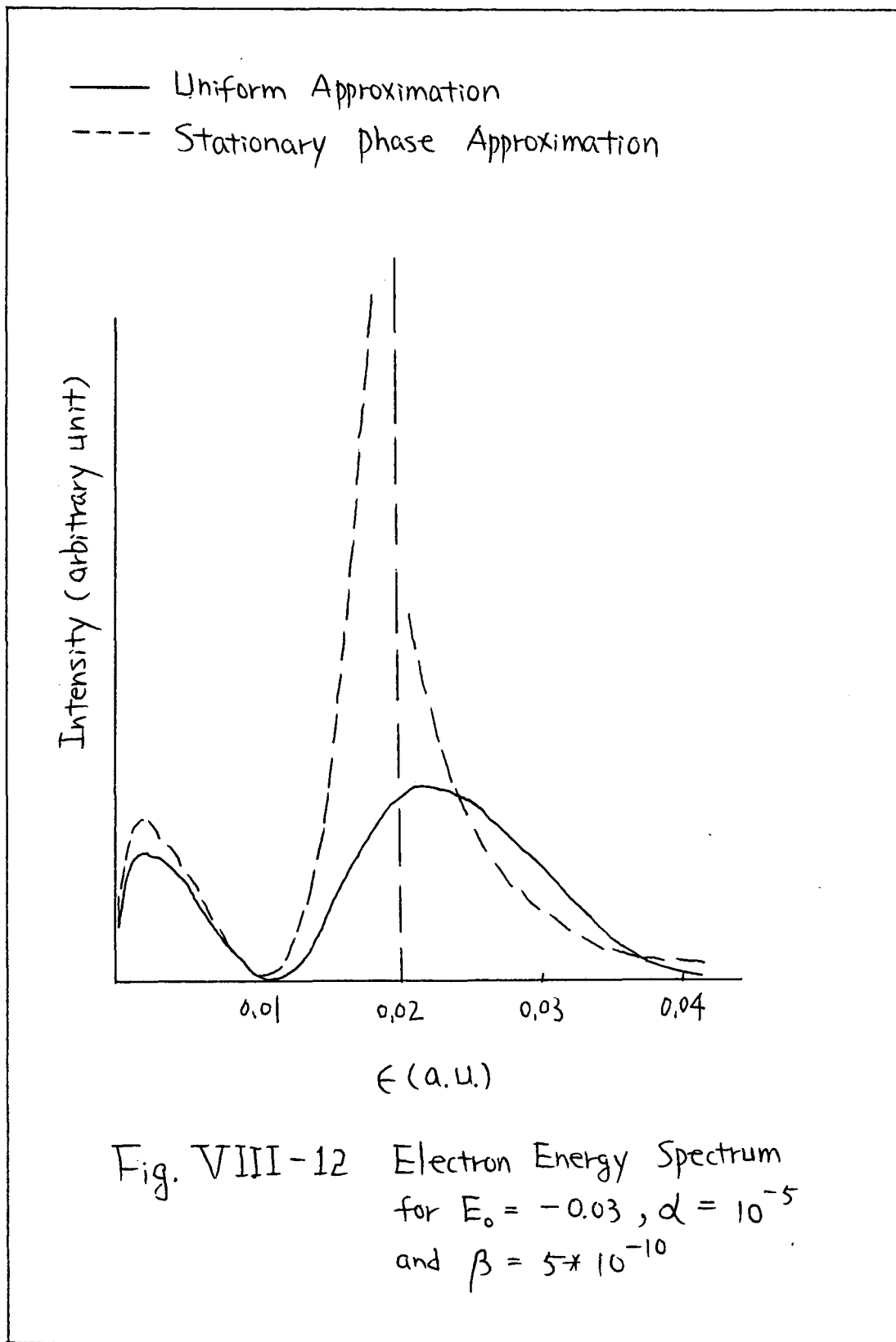
8.4   DISCUSSION

In this chapter we have applied our formulas to the case of $H^-(D^-)$ in collisions with He using a quartic approximation for $\triangle(t)$. Although the Taylor-Delos formulas (based on the simpler quadratic approximation) had been used to account for the survival probability and differential and total cross sections for this system, we find that the more accurate quartic approximation ought to be used to calculate the electron energy spectrum.

The electron energy spectrum shows in some cases interesting structure, with peaks corresponding to points where $d(t)/dt = 0$, and an interference pattern which arises because several paths lead to the same final state.

Chapter IX

CONCLUSION

9.1   SUMMARY

We have presented here a general theory of elec-
tron detachment for negative ions in collisions with atoms.
The thoery is based upon the close-coupling model developed
by Taylor and Delos, but we have found a new way to solve
the coupled differential equations.   Our new methods are
more general than those developed earlier, and they permit a
more accurate representation of the behavior of the systems
that we study.

We showed in chapter II the derivation of our new
formulas and applied in chapter III a zero order approximate
solution to the case of $H^-(D^-)$ in collisions with Ne.   The
theoretical calculation of the total detachment cross sec-
tion were found to be in good agreement with experiments.
Then in chapter IV we discussed in detail the properties of
a propagator $\hat{\delta}(\tau)$ which was neglected in the zero-order
approximation.

In chapter V we showed that our formulas can be
reduced, under appropriate conditions, to the local-complex-
potential formulas, which are well-known and which have been

applied successfully to some cases. However, we noted some defects in this approximation: in theory we found that $C_{-1}(t)$ and all its derivatives are continuous, but the complex-potential formula leads to some discontinuous derivatives; more significantly, it has been found in experiments that the local-complex-potential formulas predict an isotope effect that is opposite to what is found in experiments. Therefore, in chapter VI, we found an improved (first-order) approximation to the solution. The solution is described in terms of a "dynamical complex potential", which goes in the slow-collision limit to the local-complex-potential, but which shows interesting oscillatory structure.

In chapters VII and VIII we applied our formulas to the case of $H^-(D^-)$ colliding with He. The new formulas have been shown to be comparable and consistent to those developed by Taylor and Delos in the case of a quadratic approximation for $\Delta(t)$. Using a quartic approximation to $\Delta(t)$, some interesting results are given for the electron energy spectra. These results have not yet been found in experiments.

9.2 PROSPECTS

There are many further developments that can be made in connection with the new formulation we have presented in this thesis.

First, since there have been several calculations for $\Lambda(t)$ (or $\Lambda(R(t))$), for example: H^- on Ar, Cl^- on Ar[33] and Br^- on He,[34] we can apply our formulas to calculate cross sections for electron detachment for these cases. Probably for these processes, $\Lambda(t)$ can be well fitted to either the qradratic or quartic approximation of time, and such approximations provide simplicity and physical insight. However, as we have emphasized before, in the present formulation we can take any form for $\Lambda(t)$, so many systems can be described regardless of whether or not these additional approximations are valid.

Second, we hope that direct numerical computation of Eq.(7.1-3) can be made in the near future so that the various approximations we used for calculations in chapters VI, VII and VIII can be tested for their applicability and accuracy.

Finally, the framework developed here can also be applied to other processes, such as Penning ionization, associative detachment, dissociative recombination and dissociative attachment, and positron production in heavy ion collisions. The results may provide helpful comparisons to the various theories used at present to study those processes.

Appendix A

CONTINUITY PROOF

In this appendix, we sketch proofs which give suf-
ficient (but not necessary) conditions that $C_{-1}(t)$ and its
first two derivatives, $\mathcal{D}(t,t')$ and its derivative, and $d\mathcal{V}$
/dt are all continuous.

As stated earlier, it is assumed that $\Delta(t)$, $P_\epsilon(t)$,
$V_{\epsilon\epsilon}(t)$ and $V_{\epsilon,-1}(t)$ are differentiable functions of t. If in
addition, for all t, t'

$$| P_\epsilon(t) \cdot V_{-1,\epsilon}(t) \cdot V_{\epsilon,-1}(t') | \leqslant M_1(\epsilon) \qquad \text{(A-1a)}$$

and

$$\int_0^\infty M_1(\epsilon) d\epsilon \qquad \text{converges} \qquad \text{(A-1b)}$$

then $\mathcal{D}(t,t')$ is a continuous function of t (Weierstrass M-
test), and so is $\mathcal{D}(t',t)$. If

$$| P_\epsilon(t) \cdot V_{-1,\epsilon}(t) | \leqslant M_2(\epsilon) \qquad \text{(A-2a)}$$

and

$$\int_0^\infty M_2(\epsilon) d\epsilon \qquad \text{converges} \qquad \text{(A-2b)}$$

then $\mathcal{V}(t)$ is a continuous function of t. It then follows that Eq.(2.3-4) has solution $C_{-1}(t)$ which are continuous and differentiable; futhermore $dC_{-1}(t)/dt$ is also continuous. If

$$\left| \frac{\partial}{\partial t}\{ \, \rho_{\epsilon}(t) \cdot V_{-1,\epsilon}(t) \cdot \exp\{-i\,\Phi_{\epsilon}(t,t')/\hbar\} \cdot V_{\epsilon,-1}(t)\,\} \right| \leqslant M_3(\epsilon) \qquad \text{(A-3a)}$$

and

$$\int_0^{\infty} M_3(\epsilon)\,d\epsilon \qquad \text{converges} \qquad \text{(A-3b)}$$

then $\partial\mathcal{S}(t,t')/\partial t$ exists and it is continuous. Likewise if

$$\left| \frac{\partial}{\partial t}\{ \, \rho_{\epsilon}(t) \cdot V_{-1,\epsilon}(t) \cdot \exp\{-i\,\Phi_{\epsilon}(t,t')/\hbar\}\,\} \right| \leqslant M_4(\epsilon) \qquad \text{(A-4a)}$$

and

$$\int_0^{\infty} M_4(\epsilon)\,d\epsilon \qquad \text{converges} \qquad \text{(A-4b)}$$

then $d\mathcal{V}/dt$ exists and is continuous.

Differentiating Eq.(2.3-4) we have

$$i\hbar d^2 C_{-1}(t)/dt^2 = \frac{d}{dt}\Delta(t)\,C_{-1}(t) + \mathcal{S}(t,t')C_{-1}(t)$$

$$+ \int_{t_o}^{t} dt'\{\partial\mathcal{S}(t,t')/\partial t\}C_{-1}(t') + d\mathcal{V}/dt \qquad \text{(A-5)}$$

and since the right-hand-side is continuous, so is the left-hand-side.

Derivatives of $\mathcal{S}$ and $\mathcal{V}$ are given by

$$\partial \mathcal{S} / \partial t = (i\hbar)^{-1} \int_0^\infty d\epsilon \cdot \frac{\partial}{\partial t} \{ \, \rho_\epsilon(t) \cdot \underline{V}_{-1,\epsilon}(t) \cdot \exp\{-i \, \Phi_\epsilon(t, t')/\hbar\} \} V_{\epsilon,-1}(t')$$

$$\text{(A-6)}$$

$$d\mathcal{Q} / dt = \int_0^\infty d\epsilon \, \frac{\partial}{\partial t} \{ \, \rho_\epsilon(t) \cdot \underline{V}_{-1,\epsilon}(t) \cdot \exp\{-i \, \Phi_\epsilon(t, t')/h\} \} C_\epsilon(t_0) \quad \text{(A-7)}$$

provided that the integrals converge.

Appendix B

CONVERGENCE PROOF

We give here a proof that the quantity $\hat{C}_{-1}(t)$, defined in Eq.(2.4-7) approaches a finite limit as $t \to \infty$. A sufficient (but by no means necessary) condition for this result is that

$$\lim_{T \to \infty} \int_{-T}^{T} dt \int_{t_o}^{t} dt' |\mathcal{D}(t,t')| < \infty \tag{B-1}$$

Under this condition, the proof is simple. The statement that $\hat{C}_{-1}(t)$ approaches a finite limit as $t \to \infty$ is equivalent to the statement that

$$\lim_{T \to \infty} \int_{T}^{T+a} |d\hat{C}_{-1}(t)/dt| \, dt = 0 \tag{B-2}$$

for any finite a. Now

$$d\hat{C}_{-1}(t)/dt = \exp\{i \int_{t_o}^{t} \Delta(t'') dt''/\hbar\} \int_{t_o}^{t} \mathcal{D}(t,t') C_{-1}(t') dt' \tag{B-3}$$

and

$$|d\hat{C}_{-1}(t)/dt| \leq \int_{t_o}^{t} |\mathcal{D}(t,t')| dt' \tag{B-4}$$

so

$$|\lim_{T \to \infty} \int_{T}^{T+a} \frac{d\hat{C}_{-1}(t)}{dt} \, dt| \leq \lim_{T \to \infty} \int_{T}^{T+a} |\frac{d\hat{C}_{-1}(t)}{dt}| \, dt$$

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$$\leqslant \lim_{T \to \infty} \int_T^{T+a} \int_{t_o}^t |\mathcal{D}(t,t')| \, dt' \cdot dt$$

$$= \emptyset \tag{B-5}$$

if the limit (B-1) exists.

Appendix C

$V_{1,\epsilon}$ FROM SQUARE WELL MODEL

In this appendix $V_{1,\epsilon}$ is calculated from a square well model derived by Taylor and Delos. For details see Ref. 22.

The simplest single electron wave functions (ϕ_{-1}, ϕ_ϵ) can be approximated by solving the Schreodinger equation for a particle in a square well capable of supporting a single bound state (Fig. C-1).[22] The normalized bound state wave function is

$$
\phi_{-1} =
\begin{cases}
(\frac{2}{N})^{\frac{1}{2}} \cdot \sin(k_{o1} r) & 0 \leqslant r \leqslant r_o \quad \text{(C-1a)} \\[2ex]
(\frac{2}{N})^{\frac{1}{2}} \cdot \sin(k_{o1} r) \cdot \exp\{-k_{o2}(r-r_o)\} & r > r_o \quad \text{(C-1b)}
\end{cases}
$$

where

$$
k_{o1} = \{\frac{2m}{\hbar^2}(E_o' + V_o)\}^{\frac{1}{2}} \tag{C-2a}
$$

$$
k_{o2} = (- \frac{2m}{\hbar^2} E_o')^{\frac{1}{2}} \tag{C-2b}
$$

$$
N = r_o + (v_o/(E_o' + V_o)) \cdot (\sin^2(k_{o1} r_o)/k_{o2}) \tag{C-2c}
$$

Under the following boundary conditions

$$
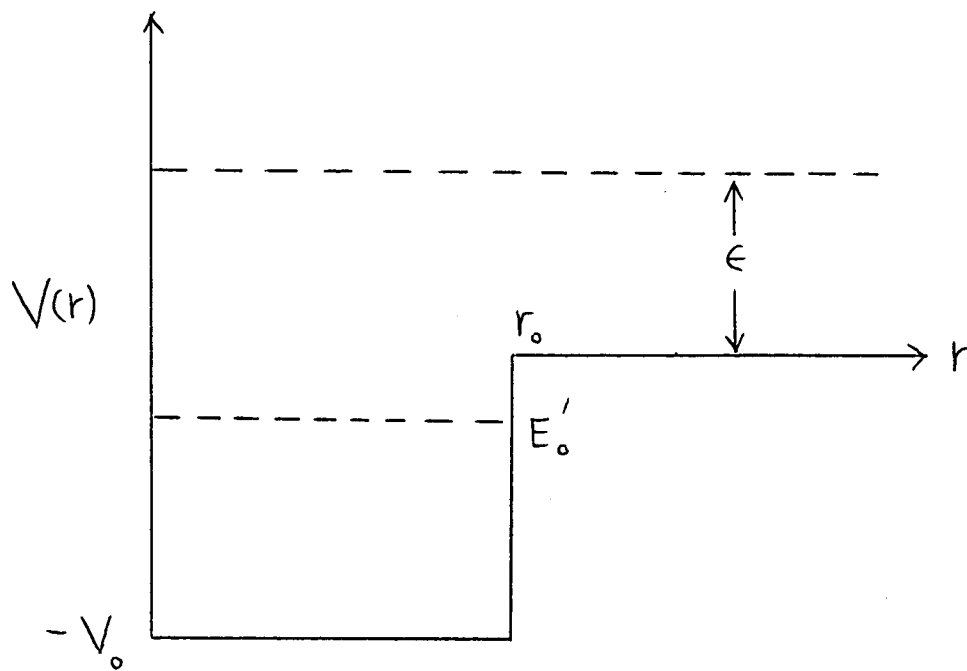\phi_\epsilon(r=0) = 0 \tag{C-3a}
$$

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Fig. C-1   Square Well Model

$$\phi_\epsilon(r=L) = 0 \qquad\qquad\qquad (C\text{-}3b)$$

the normalized continuum wave function are

$$\phi_\epsilon = \begin{cases} (\dfrac{2}{LM})^{\frac{1}{2}} \cdot \sin k_1 r & (C\text{-}4a) \\[2ex] \dfrac{-i}{(2LM)^{\frac{1}{2}}} \cdot \{\ \exp\{ik_2(r-r_o)\}(\dfrac{k_1}{k_2}\cos(k_1 r_o)+i\cdot\sin(k_1 r_o)) \\[2ex] \quad + \exp\{-ik_2(r-r_o)\}(-\dfrac{k_1}{k_2}\cos(k_1 r_o)+i\cdot\sin(k_1 r_o))\ \} & (C\text{-}4b) \end{cases}$$

where

$$k_1 = \{2m(\epsilon + V_o)/\hbar^2\}^{\frac{1}{2}} \qquad\qquad (C\text{-}5a)$$

$$k_2 = (2m\,\epsilon\,/\hbar^2)^{\frac{1}{2}} \qquad\qquad (C\text{-}5b)$$

$$M = \dfrac{k_1^2}{k_2^2}\cos^2(k_1 r_o) + \sin^2(k_1 r_o) \qquad\qquad (C\text{-}5c)$$

Then we have

$$V_{\epsilon,1} = V_{1,\epsilon} = \int_0^{r_o}\phi_1 V_1\phi_\epsilon\,dr$$

$$= \int_c^{r_o}(\dfrac{2}{N})^{\frac{1}{2}}\cdot\sin(k_{o1}r)\cdot V_1\cdot(\dfrac{2}{LM})^{\frac{1}{2}}\cdot\sin(k_1 r)\cdot dr$$

$$= \dfrac{2\,V_1}{(LMN)^{\frac{1}{2}}}\cdot\{k_1\sin(k_{o1}r_o)\cdot\cos(k_1 r_o)$$

$$\qquad\qquad -k_{o1}\cos(k_{o1}r_o)\cdot\sin(k_1 r_o)\}/(k_{o1}^2-k_1^2) \qquad (C\text{-}6c)$$

where V_1 is a constant coupling potential.

Appendix D

UNIFORM APPROXIMATION

This appendix is mainly an abstract from Ref.31.

The uniform approximation is used to calculate the following integral

$$I(\alpha) = \int g(x) \cdot \exp\{if(\alpha;x)\}dx \qquad \text{(D-1)}$$

Asymptotically, the main contribution to the integral (D-1) arises from the saddle-points of f, i.e. the roots $x = x_1, x_2, \ldots x_n$ which satisfy

$$\partial f(\alpha;x)/\partial x = 0 \qquad \text{(D-2)}$$

The first step in the calculation is to introduce a new variable u into the integral (D-1) by mapping $f(\alpha;x)$ onto a polynomial:

$$f(\alpha;x) = h^{(n)}(\alpha;u) \qquad \text{(D-3)}$$

where $h^{(n)}(\alpha;u)$ is a polynomial in u of degree $n+1$

$$h^{(n)}(\alpha;u) = \zeta_0(\alpha) + \sum_{j=1}^{n-1} \zeta_j(\alpha) u^j + u^{n+1} \qquad \text{(D-4)}$$

Notice that the term in u^n is absent and the the coefficient of the term in u^{n+1} has been nomalized to unity.

The mapping (D-3) is one-to-one and uniformly analytic if the saddle-points on either side of Eq.(D-3) correspond

$$x = x_i(\alpha) \quad \longleftrightarrow \quad u = u_i(\alpha) \qquad i=1,2,\ldots n \qquad (D-5)$$

The saddle-points $x_i(\alpha)$ are found from Eq (D-2) and the $u_i(\alpha)$ satisfy the equation

$$\partial h^{(n)}(\alpha;u)/\partial u = 0 \qquad (D-6)$$

Substituting the saddle-points (D-5) into Eqs.(D-3) and (D-4) leads to

$$f(\alpha;x_i) = \zeta_o(\alpha) + \sum_{j=1}^{n-1} \zeta_j(\alpha) u^j + u^{n+1} \qquad i=1,2,\ldots n \qquad (D-7)$$

After changing variables from x to u, the integral (D-1) becomes

$$I(\alpha) = \int G(u) \cdot \exp\{ih^{(n)}(\alpha;u)\} du \qquad (D-8)$$

where

$$G(u) = g(x) \cdot \frac{dx}{du} \qquad (D-9)$$

The second step in the calculation is to expand G(u) in a power series in u. Retaining the first n terms of this series, we have

$$G(u(\alpha)) = \sum_{k=0}^{n-1} q_k(\alpha) \cdot u^k(\alpha) \tag{D-10}$$

From Eqs.(D-5), (D-9), and (D-10) we have

$$g(x_i) \cdot \left(\frac{dx}{du}\right)_{x_i} = \sum_{k=0}^{n-1} q_k \cdot u_i^k \qquad i=1,2,\ldots n \tag{D-11}$$

where

$$\left(\frac{dx}{du}\right)_{x_i} = \{h^{(n)''}(\alpha;u_i)/f''(\alpha;x_i)\}^{\frac{1}{2}} \qquad i=1,2,\ldots n \tag{D-12}$$

Inserting Eq.(D-10) into Eq.(D-8) and extending its limit to $(-\infty,+\infty)$ gives

$$I(\alpha) = \sum_{k=0}^{n-1} q_k \int_{-\infty}^{\infty} u^k \exp\{i(\sum_{j=1}^{n-1} z_j u^j + u^{n+1})\} du \cdot \exp(iz_0) \tag{D-13}$$

Eq.(D-13) can be written in terms of the cannonical integral

$$U^{(n)}(z_1, z_2, \ldots z_{n-1}) = \int_{-\infty}^{\infty} \exp\{i(z_1 u + z_2 u^2 + \ldots + z_{n-1} u^{n-1} + u^n)\} du \tag{D-14}$$

and its derivatives. The result is

$$I(\alpha) = (q_0 U - i \sum_{k=1}^{n-1} q_k \frac{\partial U^{(n)}}{\partial z_k}) \cdot \exp(iz_0) \tag{D-15}$$

In Ref.31 three limiting cases of the above result are dis-
cussed: (i) all saddle-points are close together, (ii) all
saddle-points are well separated from one another, and
(iii) a group s of saddle-points out of the total number n
are close together but are separated from the remaining n-s.
Also in Ref.31 is presented, the series representation of the
canonical integral (D-14) using complex variable techniques.
Notice though in Ref.31, Eq.(4.10) is wrong as we consider
the case n=4 in which P_2 should be equal to P_1.

In the case n=2 we see in Ref.30 that the result
(D-15) can be reduced to the Airy expansion.

Appendix E

EQUIVALENCE PROOF

In this appendix we show that our formulas are equivalent to those of Taylor and Delos at least for some simple form of $G(\epsilon)$.

We have from Ref.22

$$C_{-1}(t \to \infty) = \lim_{t \to \infty} \exp\{-i\triangle(t)t/\hbar\} \cdot \exp(\tfrac{2}{3}y_{\triangle(t)}^{\frac{3}{2}}) \tag{E-1a}$$

$$C_{\epsilon}(t \to \infty) = \lim_{t \to \infty} (\pi V_{1\epsilon}/\beta^{\frac{1}{3}}) \exp(-i\epsilon t/\hbar) \cdot \exp(-\tfrac{2}{3}y_{\epsilon}^{\frac{3}{2}}) \tag{E-1b}$$

where

$$y_x = \{\tfrac{3}{2}\int_{x_{TP}}^{X}\{(x'-E_o-G(x'))/\beta\}^{\frac{1}{2}}dx'\}^{\frac{2}{3}} \tag{E-1c}$$

So we have

$$y_{\epsilon}^{\frac{3}{2}} = \tfrac{3}{2}\int_{x_{TP}}^{\epsilon}\{(x-E_o-G(x))/\beta\}^{\frac{1}{2}}dx \tag{E-2a}$$

$$y_{\triangle(t)}^{\frac{3}{2}} = \tfrac{3}{2}\int_{x_{TP}}^{\triangle(t)}\{(x-E_o-G(x))/\beta\}^{\frac{1}{2}}dx \tag{E-2b}$$

with

$$x_{TP} - E_o - G(x_{TP}) = \emptyset \tag{E-2c}$$

Suppose $G(x) = ax+b$ and $\Delta(t) = E_0 - \beta t^2/\hbar^2$; then we have

$$y_{\Delta(t)}^{\frac{3}{2}} = \left(\frac{1-a}{\beta}\right)^{\frac{1}{2}} \cdot \left(E_0 - \beta t^2/\hbar^2 - \frac{E_0+b}{1-a}\right)^{\frac{3}{2}} \tag{E-3a}$$

$$y_\epsilon^{\frac{3}{2}} = \left(\frac{1-a}{\beta}\right)^{\frac{1}{2}} \cdot \left(\epsilon - \frac{E_0+b}{1-a}\right)^{\frac{3}{2}} \tag{E-3b}$$

and

$$\lim_{t\to\infty} y_{\Delta(t)}^{\frac{3}{2}} = -i \cdot \left(\frac{1-a}{\beta}\right)^{\frac{1}{2}} \cdot t^3/\hbar^3 \tag{E-3c}$$

From Eq.(E-1) we then have

$$C_{-1}(\infty) = \lim_{t\to\infty} \exp\{i\Delta(t)t/\hbar\} \cdot \exp\{-i\left(\frac{1-a}{\beta}\right)^{\frac{1}{2}} t^3/\hbar^3\} \tag{E-4a}$$

and

$$C_\epsilon(\infty) = \lim_{t\to\infty} \frac{1}{i\beta^{1/3}} \cdot V_{-1/\epsilon} \cdot \exp(-i\epsilon t/\hbar) \cdot \int_0^\infty \exp\{i(\frac{x^3}{3}+y_\epsilon x)\}dx \tag{E-4b}$$

From Eq.(6.2-2a) we have

$$\partial(\tau) = i\hbar \cdot a \cdot \delta'(\tau) + b \cdot \delta(\tau) \tag{E-5}$$

then

$$\xi^e(t) = \Delta(t) + a \cdot \xi(t) + b \tag{E-6}$$

This gives

$$\mathcal{E}(t) = \frac{\Delta(t) + b}{1 - a} = \frac{E_o - \beta t^2/\hbar^2 + b}{1 - a} \qquad (E\text{-}7)$$

So from Eq.(7.1-2) we have

$$C_{-1}(t) = \exp\left\{-\frac{i}{\hbar} \cdot \left[\Delta(t) \cdot t + \frac{aE_o t}{1 - a} + \frac{(\frac{2}{3} - a)\beta t^3/\hbar^2}{1 - a} \right] \right\} \qquad (E\text{-}8a)$$

$$= \exp\{-i\Delta(t)t/\hbar\} \exp\left\{-\frac{i}{\hbar} \cdot \frac{(\frac{2}{3} - a)\beta t^3/\hbar^2 + aE_o t}{1 - a} \right\} \qquad (E\text{-}8b)$$

as $t \rightarrow \infty$ we have

$$C_{-1}(\infty) = \lim_{t \rightarrow \infty} \exp\{-i\Delta(t)t/\hbar\} \cdot \exp\left\{-\frac{i}{\hbar}\frac{2}{3}\beta\left(\frac{1 - \frac{3}{2}a}{1 - a}\right) t^3/\hbar^2 \right\} \qquad (E\text{-}9)$$

Compare Eqs.(E-4a) and (E-9) we see they are very close. For small a we have

$$(1 - a) = 1 - a/2 - a^2/8 + \ldots\ldots \qquad (E\text{-}10a)$$

$$(1 - a)/(1 - a) = 1 - a/2 - a^2/2 + \ldots\ldots \qquad (E\text{-}10b)$$

So Eqs.(E-4a) and (E-9) are equal to the first order of a. From Eq.(7.1-3) we have

$$C_{\epsilon}(t) = \frac{V_{-1,\epsilon}}{i\hbar} \exp(-i\epsilon t/\hbar) \cdot \int_{-\infty}^{t} \exp\left\{\frac{i}{\hbar}\left[\epsilon t' - \int_{o}^{t'}\frac{\Delta(t'') + b}{1 - a}dt'' \right] \right\} dt' \qquad (E\text{-}11)$$

Since

$$\epsilon t' - \int_0^{t'} \frac{\Delta(t'') + b}{1-a} dt = (\epsilon - \frac{E_0 + b}{1-a}) t' + \frac{1}{3} \cdot \frac{\beta t^3}{(1-a)\hbar^3} \qquad \text{(E-12a)}$$

$$= y_\epsilon \cdot (\frac{\beta}{1-a})^{\frac{1}{3}} \frac{t'}{\hbar} + \frac{1}{3} \{ (\frac{\beta}{1-a})^{\frac{1}{3}} \cdot \frac{t'}{\hbar} \} \qquad \text{(E-12b)}$$

we have

$$C_\epsilon(\infty) = \lim_{t \to \infty} \frac{1}{i\beta^{1/3}} \cdot V_{-\frac{1}{\epsilon}} \cdot \exp(-i\epsilon t/\hbar) \cdot \int_0^\infty \exp\{i(\frac{x^3}{3} + y_\epsilon \cdot x)\} dx \qquad \text{(E-13a)}$$

where

$$X = (\frac{\beta}{1-a})^{\frac{1}{3}} \cdot \frac{t}{\hbar} \qquad \text{(E-13b)}$$

Eqs. (E-4b) and (E-13a) are exactly the same. So we have shown that our formulas are almost equivalent to those of Taylor and Delos in the quadratic case at least for some simple form of $G(\epsilon)$.

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