### THE UNIVERSITY OF MANITOBA

# SOME APPLICATIONS OF SEMICLASSICAL THEORY TO ATOM-ATOM AND ATOM-DIATOM

### COLLISION PROBLEMS

by

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# SOME APPLICATIONS OF SEMICLASSICAL THEORY TO ATOM-ATOM AND ATOM-DIATOM COLLISION PROBLEMS

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A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

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- M. Polanyi

TO MY LANDLORD



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#### ABSTRACT

The application of semiclassical theories to low energy atom-atom and atom-diatom collisions is discussed. The theories are developed in such a way that translational motion is treated classically while internal degrees of freedom (electronic or vibrational) are treated quantum mechanically. The emphasis is on the development of an intuitively suggestive "picture" of the collision process, occasionally at the expense of mathematical rigor. For the cases studied here, the translational and internal degrees of freedom of the system are intimately coupled to each other during the collision, and it is shown that some care must be taken in the treatment of this coupling. Particular attention is given to the effect of a change in the internal states of the system on the translational degree of freedom.

A relatively simple version of semiclassical theory is applied to low energy collisions between H and Be<sup>++</sup> in order to obtain some qualitative information about the effect of translational motion on the electronic state of the system during a "curve-crossing" event. A more sophisticated semiclassical theory, based on Feynman's path-integral formulation of quantum mechanics, is then developed and applied to collisions between He<sup>+</sup> and Ne. In this case the effect of the electronic rearrangement on the translational motion is very important. It is found that this effect can be taken account of in a variety of ways, and some qualitative comparisons of different available methods are made. The application of this type of theory to vibrationally inelastic collisions

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between He and  ${\rm H}_2$  is also discussed.

It is concluded that semiclassical theories are a useful tool in the qualitative interpretation of experimental results, but that the precise form of the appropriate theory can often be determined only by trial and error. A purely mathematical comparison of different available theories is not always sufficient to determine which one will be most useful in practice.

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#### CHAPTER I. INTRODUCTION

The role of semiclassical theories in the study of atomic and molecular collisions is a somewhat curious one, in the sense that the practical usefulness of such theories is generally recognised while, at the same time, it is almost impossible to give a precise a priori justification of such theories, at least for the examples to be discussed in this thesis. In many cases the "justification" of the theories discussed here is one which has been developed after the fact on the basis of intuitive, instead of mathematical, arguments. A mathematical derivation of the theories used in this thesis will be given (or referred to) whenever possible, but the final arguments in favor of (or against) a particular theory will invariably be qualitative arguments which can be developed only after the fact (and only after a rather detailed comparison of numerical results obtained in the different theories). It does not seem very likely that this situation will change significantly within the foreseeable future, for reasons which will be discussed below.

The interest in semiclassical collision theory has normally arisen from two types of experimental situations:

- 1) Electronically inelastic atomic collisions (1,2).
- 2) Electronically adiabatic, but vibrationally and/or rotationally inelastic, collisions between small molecules (3).

A certain amount of interest has also been generated by information obtained from ion-molecule reactions (4), but these will not be discussed

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in any detail. No attempt will be made to discuss either collisions between large molecules or unimolecular rearrangement problems, since the theories which are likely to be useful in these cases are rather different from the theory used in this thesis. The following processes will be considered:

1)	$A + B \rightarrow A^{+} + B^{-}$	(electron transfer)
2)	$A + B \rightarrow A + B^*$	(electron excitation)
3)	$A + BC \rightarrow A + BC^*$	(vibrational excitation)

where A and B are atoms, and the asterisk indicates either electronic or vibrational excitation. These processes will be termed "inelastic", while the process

 $A + BC \rightarrow AB + C$ 

will be termed a "rearrangement". Rearrangement collisions are somewhat more difficult to study than inelastic collisions, especially if one wishes to quantize the vibrational states of the diatom before and after the collision, and will therefore be mentioned only briefly. For practical purposes, the only type of experiment to which the present discussion is relevant is the "state-selected" experiment; i.e. one in which the initial and final electronic and vibrational states are known for each individual collision.

A semiclassical collision theory will be defined as one in which some degrees of freedom of the system (such as relative translational motion) are treated classically while other degrees of freedom (such as electronic or vibrational motion) are treated quantum mechanically. It is perhaps worthwhile noting that a quantum mechanical treatment implies that

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not only the initial and final stationary states of a degree of freedom, but also the evolution of this degree of freedom in time, are treated quantum mechanically. In some theories (see Chapter IV) a distinction between these two problems is made, but these theories will not be called semiclassical. Whenever a classical degree of freedom is coupled to a quantum mechanical degree of freedom the definition of "classical" becomes a non-trivial problem. A general definition of "classical" motion will be attempted only in Chapter III. For the moment, it is sufficient to say that a classical degree of freedom behaves, at least mathematically, like a point particle. The theory is therefore of the following type: in an atomic collision the nuclei are treated as point particles while electrons are treated quantum mechanically; in an atomdiatom collision the vibrational motion is treated quantum mechanically is treated classically. If the quantum mechanical while translation state is a unique function of the classical state then the problem will be termed "single-channel", and if not, then it will be called a multichannel problem. Single-channel theory is useful at very low energies where the quantum mechanical state has time to respond uniquely (adiabatically) to changes in the classical state. For curve-crossing problems (see the discussion of Landau-Zener theory) there may also be a high energy (diabatic) limit in which single-channel theory is useful. A channel is specified in terms of initial and final quantum mechanical states; i.e. the initial state,  $\alpha$ , and the final state,  $\beta$ , collectively

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define a particular channel. It will normally be taken for granted that two different channels are experimentally distinguishable except when degeneracies occur at large separations.

The motivation for using a semiclassical theory is two-fold: to decrease computational labor, and to simplify the problem of interpreting experimental information. For some low energy atomic collision problems it is found that the experimentally observed differential cross sections display a surprisingly complex behaviour as a function of the scattering angle. This behaviour clearly reflects at least some of the details of the interaction between the different electronic states of the composite system formed during the collision, regardless of whether or not the composite system is stable. In particular, if a detailed interpretation of the differential cross section is made, it should be possible to extract information about the nature of interatomic (or intermolecular) forces at small, as well as large, separations. Semiclassical theories have long been used to perform this type of interpretation for single-channel problems, but it is only recently that extensions to multichannel situations have been attempted (5-9).

The most interesting atomic collision problem is that in which the impact energy is sufficiently high that the electrons no longer behave adiabatically, but still low enough so that the nuclei are significantly perturbed by the electronic rearrangement which occurs. (A low energy collision is defined as one in which the impact energy is of the same order of magnitude as the energy spacing between the relevant quantum

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mechanical states, whether they be electronic or vibrational.) For this type of problem a fully quantum mechanical treatment is often feasible (10,11), but will not normally yield much insight into the nature of the process. A semiclassical approach, on the other hand, can lead to a very detailed understanding of the way in which the system evolves in time. Unfortunately, it is exactly this type of process for which the semiclassical theory is very difficult to justify. In the high energy limit, in which the nuclei are not significantly affected by changes in the electronic state, it is not too difficult to justify semiclassical theories such as impact parameter, eikonal, and related approaches (1,2, 12). Similarly, in the very low energy limit in which the process may be reducible to a single-channel problem, it is again easy to justify semiclassical approaches (13,14). For intermediate energies, however, the process is neither a single-channel one, nor are the nuclear equations of motion easy to determine. Some controversy exists as to the appropriate form of semiclassical equations in this case. Two basic equations approaches suggest themselves: time-dependent and time-independent. The most sophisticated time-dependent approach seems to be that of Pechukas (15), while the time-independent theory has been brought to a comparable level of sophistication by Eu (16-18) and by Eu and Tsien (19-20). In the time-dependent approach one is concerned with the evolution of a quantum state in time, under the influence of a perturbation due to "classical" nuclear motion. This theory is the natural extension of impact parameter theory to low energy collisions. The time-independent approach is concerned with the

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evaluation of matrix elements between stationary scattering states of the system, where the nuclear contribution to the state of the entire system is determined using a generalization of single-channel WKB theory (21). Both theories use equations which can be regarded as truncated asymptotic expansions (22,23) of the corresponding quantum mechanical expressions, but the original expressions used in each case are different and the resulting semiclassical theories are apparently not equivalent. The time-dependent approach starts by defining the quantum mechanical scattering amplitude in terms of a Feynman path integral (24) and by developing a second-order asymptotic approximation to this integral expression. The time-independent approach begins with the multichannel Schroedinger equation appropriate to the problem and developes a uniformly asymptotic approximation to the solution of this equation. Although the original (quantum mechanical) definitions of the scattering amplitude in each case are compatible (i.e. the Schroedinger and Feynman formulations of quantum mechanics are equivalent), the final semiclassical approximations obtained in the two cases are not. At the present moment there does not seem to be any way of determining a priori which procedure is better. This apparent ambiguity in the definition of semiclassical theories for multichannel processes is part of the reason why it was stated earlier that the semiclassical theories used here can be justified only after the fact. In the discussion to follow, only time-dependent theories will be used, largely because of their close relationship to "impact parameter type" theories, which have

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already been studied extensively.

In the discussion of semiclassical theory it is instructive to distinguish between those theories in which one can, at least in principle, observe the classical nature of the nuclei during the collision and those in which one cannot. For example, during an atomic collision, if the nuclear trajectories for the  $\alpha \rightarrow \alpha$  and  $\alpha \rightarrow \beta$  events are identical then it is at least conceivable that one could observe the nuclei as classical particles (or possibly wave packets) during the course of the entire collision. This is not a sufficient condition for "observability" but it is at least necessary. On the other hand, if the nuclear trajectories for these two events are different, then one cannot even conceive of how the point particle nature of the nuclei can be experimentally observed during the collision. The distinction between these two types of theories has been discussed by Delos and Thorson (25,26). As far as the present discussion is concerned, the main point is that the derivation of the semiclassical equations used here will normally be developed independently of whether or not the classical particles are observable as such. It is possible to use semiclassical theory to interpret experimental information even though the classical nature of the particles cannot be observed during the collision. For example, it will be shown below that the differential cross section for a multichannel scattering process is uniquely defined by the classical trajectories which the nuclei follow during the collision, and by the electronic response to this nuclear motion. The problem of "interpreting" an experimentally observed differential cross section can therefore be broken up into two smaller problems if a semiclassical theory is used. The

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first problem is that of understanding how the nuclei behave during a collision. It can be solved either by inspecting the classical nuclear trajectories themselves, or by inspecting the potential energy surfaces which determine these trajectories. The second problem is that of understanding how the electrons are perturbed by nuclear motion during the collision. This problem can be solved by inspecting the behaviour of the coefficients which define the electronic state within a particular basis set. Once both of these individual problems are understood it is not too difficult to interpret the differential cross section as well. Although the nuclear trajectories which are used in this interpretation are not necessarily observable they are still very useful, in the sense that they help one to develop an intuitively suggestive picture of the collision process.

The theories used here will be put into two categories, depending on whether the nuclei obey initial-value or boundary-value equations of motion in time. In the initial-value theories the nuclear trajectories for the series of events  $\alpha \rightarrow \alpha$ ,  $\alpha \rightarrow \beta$ ,  $\alpha \rightarrow \gamma$  will all be the same and one can therefore, in principle, visualize the nuclei as being wavepackets which are observable under the right conditions at high impact energies (27). The inadequacy of an initial-value theory for low energy collisions will be discussed in Chapter II. In a boundary-value theory the nuclear trajectories for the  $\alpha \rightarrow \alpha$  and  $\alpha \rightarrow \beta$  events are different and this type of semiclassical theory can therefore be derived only using relatively sophisticated mathematical arguments. Two different versions of the boundary-value theory will be discussed in Chapter III, while vibrational excitation will be considered in Chapter IV.

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CHAPTER II. ELECTRONIC EXCITATION: INITIAL-VALUE THEORIES

In a time-dependent approach the theory of low energy atomic collisions can be developed in two stages, the first of which deals with the effect of the nuclear motion on the electronic state, while the second deals with the reverse effect. Because of this partial separation of the two problems it is also possible to develop an interpretation of experimental results in two stages, by first considering the effect of simple nuclear motion on the electronic state and then developing better nuclear models. The first stage will be discussed in this chapter. The form of the electronic equations of motion is independent of the way in which the nuclear motion is determined and the same electronic equations can therefore be used in conjunction with progressively more sophisticated nuclear models until acceptable results are obtained. The simplest nuclear model which will be considered is one in which the nuclei move in response to a stationary energy surface; i.e. an energy surface which is a unique function of the internuclear distance. A more sophisticated theory is obtained when an "average energy surface" is used: the energy surface is defined as an average over the existing electronic state at any particular time (28-30). The "appropriateness" of these two theories, for low energy collision problems, will be mentioned at the end of this chapter once the electronic equations of motion are known. Both of these theories are called initial-value theories because the nuclear force law at a

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particular time recognizes only the present and past electronic states. The solution of the equations of motion is therefore characterized completely by the specification of nuclear and electronic states long before the collision. (In a boundary-value theory the nuclear force law at a particular time recognizes future, as well as past and present, electronic states.)

The main emphasis in this thesis will be on problems in which the electronic (or vibrational) rearrangement during the collision exerts a significant effect on the nuclear motion. The type of problem to be considered will therefore be one in which the effect of nuclear motion on electronic (or vibrational) motion is relatively simple, so that more attention can be given to the reverse effect (which is more difficult to handle properly). All of the calculations reported in this thesis were performed either by using very simple electronic basis sets or by using "model" electronic interactions based on molecular-orbital calculations performed by other research groups. The discussion of electronic equations of motion which is given below will therefore not be utilized very fully in the actual calculations reported here, but was undertaken in order to show that it is possible to develop fairly general, internally consistent, electronic equations if the need for them should arise. (Note that atomic units (36) will be used throughout.)

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### A. Electronic Equations of Motion

Consider a system consisting of two nuclei (masses  $m_A$  and  $m_B$ ) and an arbitrary number of electrons. The relative position of nucleus B with respect to nucleus A is  $\vec{R}$ . Within the centre-of-mass coordinate system the position of the ith electron is  $\vec{r}_i$ . The distance between the ith electron and nucleus B is

$$\mathbf{r}_{1B} = \begin{vmatrix} \vec{r}_1 & - & \frac{m_A}{m_A} + \frac{\vec{r}_B}{m_B} \end{vmatrix}$$

(Note that the mass of the electrons has been ignored in the definition of the centre-of-mass.) The full hamiltonian, H  $_{\rm op}$  , can be written as

$$H_{op} = -\frac{1}{2u} \nabla_{R}^{2} + H_{op}^{el}(\vec{r},\vec{R})$$

where  $\mu = m_A m_B / (m_A + m_B)$  and  $\dot{\vec{r}}$  stands for the ensemble of electron coordinates. The operator  $H_{op}^{el}(\vec{r},\vec{R})$  contains the electronic kinetic energy operators as well as the electron-electron, electron-nuclear, and nuclearnuclear potential energies. If the nuclei are treated as classical particles then  $H_{op}^{el}(\vec{r},\vec{R})$  can be regarded as a time-dependent hamiltonian which determines the electronic response to a particular nuclear trajectory. Clearly,  $H_{op}^{el}(\vec{r},\vec{R})$  has no explicit time-dependence, but it has an implicit dependence on time through  $\vec{R}(t)$ . In what follows, it will be assumed that the function  $\vec{R}(t)$  is known in some sense, without yet specifying how it is known; i.e.  $\vec{R}(t)$  is determined by some external criterion which is of no interest at the moment. (This procedure can be best understood within a path-integral notation (24, pages 68-71).) The electronic response to the nuclear motion is given by the solution of Schroedinger's timedependent equation

$$H_{op}^{e1}(\vec{r},\vec{R}) \ \Psi(\vec{r},\vec{R},t) = i \left(\frac{\partial}{\partial t}\right)_{\vec{r}} \Psi(\vec{r},\vec{R},t)$$
(1)

where it must be remembered that  $\vec{R}$  is not an independent variable; for example:

$$\left(\frac{\partial}{\partial t}\right)_{\stackrel{\rightarrow}{r}} = \left(\frac{\partial}{\partial t}\right)_{\stackrel{\rightarrow}{r},\stackrel{\rightarrow}{R}} + \frac{d\vec{R}}{dt} \cdot \left(\nabla_{R}\right)_{\stackrel{\rightarrow}{r},t}$$
(2)

where the subscripts indicate which variables are held fixed. The electronic state is re-expressed as

$$\Psi(\vec{r},\vec{R},t) = \sum_{j} b_{j}(R,t) \Phi_{j}(\vec{r},\vec{R}) . \qquad (3)$$

The validity of Eq.(3) will be discussed in more detail below. The states  $\Phi_j(\vec{r},\vec{R})$  are chosen in such a way that they approximately represent the possible electronic behaviour for all values of R. The form of the equations of motion does not really depend on how this choice is made. It will not be assumed that the states  $\Phi_j(\vec{r},\vec{R})$  form a complete, orthonormal, basis set; in addition to this, the  $\Phi_j(\vec{r},\vec{R})$  may be atomic orbitals or molecular orbitals, and in a many-electron problem they may be single Slater determinants (31) or linear combinations of many Slater determinations.

ants. Substitution of Eq.(3) into Eq.(1) yields

$$\sum_{j}^{\tilde{b}} b_{j}(\mathbf{R},t) \stackrel{\mathrm{H}^{\mathrm{el}}(\vec{r},\vec{R})}{\mathrm{op}} \Phi_{j}(\vec{r},\vec{R}) = i \sum_{j}^{\tilde{b}} \left( \frac{\mathrm{d}b}{\mathrm{d}t^{j}}(\mathbf{R},t) \right) \Phi_{j}(\vec{r},\vec{R}) + i \sum_{j}^{\tilde{b}} b_{j}(\mathbf{R},t) \left( \nabla_{\mathrm{R}} \Phi_{j}(\vec{r},\vec{R}) \right) \cdot \frac{\mathrm{d}\vec{R}}{\mathrm{d}t}$$

$$(4)$$

After pre-multiplying by  $\Phi_{i}^{*}(\vec{r},\vec{R})$  and integrating over  $\vec{r}$  one obtains the matrix equation

$$\underline{\mathbf{H}} \underline{\mathbf{b}} = \mathbf{i} \underline{\mathbf{N}} \frac{d\underline{\mathbf{b}}}{d\underline{\mathbf{t}}} + \mathbf{i} \underline{\vec{\mathbf{P}}} \underline{\mathbf{b}} \cdot \underline{d\underline{\vec{\mathbf{R}}}}_{d\underline{\mathbf{t}}}$$
(5)

where  $\underline{H}$ ,  $\underline{N}$ , and  $\dot{\underline{P}}$  are the hamiltonian, overlap, and momentum matrices (32), respectively:

$$\frac{H}{ij} = \int \Phi_{i}^{*}(\vec{r},\vec{R}) H_{op}^{e1}(\vec{r},\vec{R}) \Phi_{j}(\vec{r},\vec{R}) d\vec{r} ,$$

$$\frac{N}{ij} = \int \Phi_{i}^{*}(\vec{r},\vec{R}) \Phi_{j}(\vec{r},\vec{R}) d\vec{r} ,$$

$$\frac{P}{ij} = \int \Phi_{i}^{*}(\vec{r},\vec{R}) \{\nabla_{R}\Phi_{j}(\vec{r},\vec{R})\} d\vec{r} .$$
(6)

(Note that <u>N</u> and <u>H</u> are hermitian (33, page 120) while  $\overrightarrow{P}$  is neither hermitian nor anti-hermitian in general.) The quantity <u>b</u> is a column vector whose elements are the coefficients b (R,t). Before proceeding further it will be convenient to discuss Eq.(3) in more detail. It is important to recognize that Eq.(3) incorporates the so-called "low-energy approximation"; i.e. the assumption that the electronic states depend only on  $\vec{r}$  and  $\vec{R}$ . As an illustration of this approximation, consider the protonhydrogen scattering problem. The electronic behaviour for this problem can be described fairly adequately (34,35) using three hydrogenic orbitals (1s, 2s, 2p) centred on each nucleus. In atomic units (36) the orbitals centred about nucleus A are given by

$$\Phi(1sA) = \pi^{-\frac{1}{2}} e^{-rA}$$

$$\Phi(2sA) = (32\pi)^{-\frac{1}{2}} (2 - r_A) e^{-rA/2}$$

$$\Phi(2pA) = (32\pi)^{-\frac{1}{2}} z_A e^{-rA/2}$$
(7)

where the z axis is parallel to the relative nuclear velocity  $\dot{\vec{R}}$  at large R and  $r_A = |\vec{r} + \vec{R}/2|$  (see page 11). These three orbitals are normalized eigenstates of the isolated hydrogen atoms; that is,

$$(-\frac{1}{2} \nabla_{r_A}^2 - 1/r_A) \Phi = E \Phi$$
.

However, they do not satisfy the time-dependent Schroedinger equation for finite nuclear velocities even at large R. This is due to the fact that the operators in the Schroedinger equation (Eq.1) are defined within a centre-of-mass coordinate system while the orbitals are defined relative to moving nuclei. For example, when the operator  $(\partial/\partial t)_{\overrightarrow{T}}$  is applied, the nuclear position  $\overrightarrow{R}$  is allowed to move (since  $\overrightarrow{R}$  is dependent on t) while  $\overrightarrow{r}$  is fixed, which has the effect of changing the electron-nuclear distance  $r_A$ . As a result of this change it is found that

$$\left(\frac{\partial}{\partial t}\right)_{\overrightarrow{T}} \Phi(\mathbf{r}_{A}) = \nabla_{\mathbf{R}} \Phi(\mathbf{r}_{A}) \cdot \frac{d\overrightarrow{\mathbf{R}}}{dt}$$
$$\neq 0$$

Because this term is not zero, the orbital  $\Phi(r_A)$  will not satisfy Eq.(1) at large R. As R approaches infinity, the left hand side of Eq. (1) will contain a term of the type  $\mathrm{E}\Phi(r_{A})$  which is easily cancelled on the right hand side by the introduction of a phase factor e in the definition of  $\Phi(r_A)$ . The term due to the dependence of  $\Phi(r_A)$  on R, however, will not cancel with any other term, even at large R. In general, therefore, if a basis set of the type represented by Eq. (3) is substituted into the time-dependent Schroedinger equation, Eq. (1), it will be found that the Schroedinger equation will not be satisfied in the limit as  $R \rightarrow \infty$ , even if the states  $\Phi_{i}(\vec{r},\vec{R})$  are eigenstates of the individual atoms. The inadequacy of this type of basis set was initially recognized by Brinkman and Kramers (37) but has occasionally led to difficulties in subsequent treatments of the problem (38). For the purposes of the present discussion, the formal inadequacy of Eq. (3) is of no particular interest except insofar as it may lead to practical difficulties when the solution of the Schroedinger equation is attempted. The most obvious way in which these difficulties may arise is through the presence of "non-physical" off-diagonal coupling terms which do not disappear as  $R \rightarrow \infty$ . If a transition probability for a particular process is to be uniquely defined, it is necessary that  $\underline{H}$ ,  $\underline{N}$ , and  $\stackrel{\rightarrow}{\underline{P}}$  become diagonal as  $R \rightarrow \infty$ . The basis set used in Eq. (3) does not always satisfy this requirement. As an example,

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consider the following matrix element of  $\overrightarrow{P}$ , as it is defined for the proton-hydrogen problem:

$$\int \Phi(2pA) \left( \frac{\partial}{\partial Z} \Phi(1sA) \right) d\vec{r}$$

where  $\overrightarrow{R} = (X, Y, Z)$  and  $\overrightarrow{R} = (0, 0, Z)$  at large R. This matrix element can be evaluated to yield (-8/2/81). The  $\overrightarrow{P}$  matrix is therefore not diagonal as  $R \rightarrow \infty$ , even though the <u>N</u> and <u>H</u> matrices are. The coefficients  $b_j(R,t)$ will therefore not approach stationary values asymptotically. It is important that this type of off-diagonal coupling be recognized as being spurious, in the sense that it is due to improper definition of the electronic basis set at large R. A formal solution to this difficulty is available and has been discussed by Bates and McCarrol (39,40) in connection with the perturbed-stationary-state theory (41). It consists of multiplying the orbitals  $\Phi_j(\vec{r},\vec{R})$  by a phase factor  $e^{ivz}$ , where v is proportional to the relative nuclear velocity and z is an electronic coordinate. (Strictly speaking, this phase factor is applied to individual atomic orbitals, not molecular orbitals. A discussion of the problem of developing a general, workable, prescription for choosing these phase factors has been given by Riley and Green (42).) The effect of the phase factor is to take account of the fact that the electrons possess translational energy (by virtue of being bound to a moving nucleus) in addition to orbital energy. The formal difficulties mentioned above are removed when these phase factors are used, but are usually replaced by practical problems. In practice, the main difficulty introduced by the

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factor  $e^{ivz}$  is that one can no longer evaluate matrix elements of <u>N</u>, <u>H</u>, and  $\vec{P}$  analytically since the term  $e^{ivz}$  introduces a Bessel function into the integrand of a two-dimensional integral over the electronic coordinate (43). From a qualitative point of view, ignoring the phase factors mentioned above is tantamount to ignoring the translational energy energy of the electron compared to its orbital energy. This approxim=t ation will always be used in the present discussion, since it is quite reasonable for the processes considered here. (For example, for the proton-hydrogen system the translational and orbital energies of the electron become comparable only at an impact energy of 12 keV in the centre-of-mass frame.)

An associated approximation, which will also be used in this discussion, is that of ignoring rotational coupling between electronic states. This coupling arises from the fact that the operators in the Schroedinger equation are originally defined in an inertial, non-rotating, reference frame, while the electronic states are most naturally defined within a non-inertial, rotating, frame. The importance of this type of coupling in proton-hydrogen scattering has been discussed previously (44,45) and some experimental evidence concerning its importance in other scattering problems is also available (46,47). A thorough treatment of rotational coupling, as it applies to impact ionization collisions, has been given by Thorson and co-workers (48, and references cited therein). If rotational coupling is ignored, the operator  $\nabla_{\mathbf{R}}$  in the definition of  $\underline{\vec{P}}$  [Eq. (6)] can be replaced by  $\partial/\partial \mathbf{R}$ . The equations of motion [Eq. (5)] therefore have the form

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$$\frac{H}{D} = i \frac{N}{dt} \frac{db}{dt} + i \frac{P}{D} \frac{b}{dt} \frac{dR}{dt}$$
(8)

where

$$\underline{P}_{ij} = \int \Phi_{i}^{*}(\vec{r},\vec{R}) \left\{ \partial \Phi_{j}(\vec{r},\vec{R}) / \partial R \right\} d\vec{r} .$$
(9)

(Provide units (36) will be used from dow on )

The procedure of ignoring the phase factors mentioned above can have two serious consequences in practice, even though the approximation may in fact be a valid one, in the sense that the translational kinetic energy of the electron is much less than its orbital kinetic energy. First of all, it can lead to spurious off-diagonal coupling between states at large R. If it is clear that the low-energy approximation is valid, then these coupling terms can simply be deleted from the <u>P</u> matrix. The second problem which may be introduced by the low-energy approximation concerns normalization conservation. Green (49) has shown that this approximation may destroy both normalization conservation and detailed balancing, particularly when it is made within a non-orthogonal basis set. A brief discussion of both of these features of the equations of motion will therefore be given, in order to show that the equations can be developed in such a way that these two properties are not destroyed.

If the basis set in Eq. (3) is regarded as a valid representation of the electronic state at arbitrary  $\vec{R}$  and t, then the equations of

motion of the electronic state are given by Eq. (8), which can be rewritten as

$$\frac{d\mathbf{b}}{d\mathbf{t}} = -\mathbf{i} \, \underline{\mathbf{N}}^{-1} \underline{\mathbf{H}} \, \underline{\mathbf{b}} - \underline{\mathbf{N}}^{-1} \underline{\mathbf{P}} \, \underline{\mathbf{b}} \, \frac{d\mathbf{R}}{d\mathbf{t}} \quad . \tag{10}$$

The following property of  $\underline{N}$  is of interest:

$$\frac{d}{dR} \underbrace{\mathbf{N}}_{\mathbf{i}\mathbf{j}} = \frac{d}{dR} \int \Phi_{\mathbf{i}}^{*}(\vec{r},\vec{R}) \Phi_{\mathbf{j}}(\vec{r},\vec{R}) d\vec{r}$$

$$= \int \{\partial \Phi_{\mathbf{i}}^{*}(\vec{r},\vec{R})/\partial R\} \Phi_{\mathbf{j}}(\vec{r},\vec{R}) d\vec{r}$$

$$+ \int \Phi_{\mathbf{i}}^{*}(\vec{r},\vec{R}) \{\partial \Phi_{\mathbf{j}}(\vec{r},\vec{R})/\partial R\} d\vec{r}$$

$$= \underbrace{\mathbf{P}}_{\mathbf{i}\mathbf{j}} + \underbrace{\mathbf{P}}_{\mathbf{j}\mathbf{i}}^{*}.$$

Therefore

$$\underline{P} + \underline{P}^{\dagger} = \underline{d}_{R} \underline{N}$$
(11)

where it must be remembered that  $\partial/\partial R$  operates with the electrons held fixed within a centre-of-mass, Cartesian, coordinate system so that  $\partial \Phi_j/\partial R$ is non-zero even though  $\Phi_j$  may be an atomic orbital of the form  $\Phi_j(r_A)$ or  $\Phi_j(r_B)$ . The radial momentum matrix, <u>P</u>, is clearly anti-hermitian if (and only if) the basis set is orthogonal. Fortunately, a proof of normalization conservation does not require that <u>P</u> be anti-hermitian, although the hermiticity of <u>N</u> and <u>H</u> is needed. The "normalization constant" is given by

$$\int \Psi^{*}(\vec{r},\vec{R},t) \Psi(\vec{r},\vec{R},t) d\vec{r} = \underline{b}^{\dagger}\underline{N} \underline{b}$$
(12)

after using Eqs. (3) and (6). (Note that  $\underline{b}^{\dagger}$ , the hermitian conjugate of  $\underline{b}$ , is a row vector whose elements are complex conjugates of the corresponding elements of  $\underline{b}$ .) Normalization will be conserved if  $d(\underline{b}^{\dagger}\underline{N} \ \underline{b})/dt = 0$ , where

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\underline{\mathbf{b}}^{\dagger}\underline{\mathbf{N}} \ \underline{\mathbf{b}}\right) = \left(\frac{\mathrm{d}\underline{\mathbf{b}}}{\mathrm{d}t}^{\dagger}\right)\underline{\mathbf{N}} \ \underline{\mathbf{b}} + \underline{\mathbf{b}}^{\dagger}\left(\frac{\mathrm{d}\underline{\mathbf{N}}}{\mathrm{d}R}\right)\underline{\mathbf{b}} \ \frac{\mathrm{d}R}{\mathrm{d}t} + \underline{\mathbf{b}}^{\dagger}\underline{\mathbf{N}} \ \frac{\mathrm{d}\underline{\mathbf{b}}}{\mathrm{d}t} \ . \tag{13}$$

The first and last terms on the right hand side of Eq. (13) are given by

$$\left(\frac{d\underline{b}}{d\underline{t}}^{\dagger}\right)\underline{N} \ \underline{b} = \underline{i} \ \underline{b}^{\dagger}\underline{H} \ \underline{b} - \underline{b}^{\dagger}\underline{P}^{\dagger}\underline{b} \ \frac{dR}{d\underline{t}} ,$$
$$\underline{b}^{\dagger}\underline{N} \ \underline{d\underline{b}} = -\underline{i} \ \underline{b}^{\dagger}\underline{H} \ \underline{b} - \underline{b}^{\dagger}\underline{P} \ \underline{b} \ \frac{dR}{d\underline{t}} .$$

Therefore, after using Eq. (11), we find

$$\frac{\mathrm{d}}{\mathrm{dt}} \left( \underline{\mathbf{b}}^{\dagger} \underline{\mathbf{N}} \ \underline{\mathbf{b}} \right) = 0 \quad . \tag{14}$$

Normalization is therefore conserved within the low-energy approximation even if the basis set is not orthogonal. The only properties of the matrices which have been used in this derivation are the hermiticity of <u>N</u> and <u>H</u>, and the fact that <u>P</u> satisfies Eq. (11). The matrices <u>N</u>, <u>H</u>, and <u>P</u> display these properties quite generally; i.e. they display them independently of the nature of the basis set, whether it be orthogonal

or non-orthogonal and whether it consist of atomic orbitals or molecular orbitals. This conclusion is somewhat more optimistic than that reached by Green (49, section 6) concerning normalization within the low-energy approximation, apparently because the equations of motion used on page 1027 of Ref. 49 do not contain any equivalent of the <u>P</u> matrix. (Note that it is not claimed that the present equations of motion constitute an unambiguous formulation of the low-energy approximation, but simply that they are internally consistent. Furthermore, the problem of evaluating P in practice may well be non-trivial in some cases.)

Before discussing detailed-balancing (49-51) we will first show that the equations of motion are invariant under a transformation of the electronic basis set and will mention a few properties of the different types of basis sets which are available. If the equations of motion are invariant under transformation then it is possible to carry out formal proofs of certain properties of the equations within special representations of the electronic state instead of continuing to use the general basis set described above. For example, it will be possible to show that detailed-balancing is satisfied within the diabatic representation (32). If an expression of detailed-balancing within a general basis set is required, it can be obtained simply by transformation of the diabatic expression of this property, assuming that the equations of motion are invariant under transformation.

Consider a situation in which the original description of the electronic wave-function  $\Psi(\vec{r},\vec{R},t)$  is given in terms of the basis set  $\{\Phi_j(\vec{r},\vec{R})\}$ as shown by Eq. (3). A new description of the same state,  $\Psi(\vec{r},\vec{R},t)$ , is

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desired, in terms of a new basis set  $\{\Phi_{j}^{i}(\vec{r},\vec{R})\}$  where the  $\Phi_{j}^{i}(\vec{r},\vec{R})$  are R-dependent linear combinations of the  $\Phi_{j}(\vec{r},\vec{R})$  states. The new description of  $\Psi(\vec{r},\vec{R},t)$  is given by

$$\Psi(\vec{r},\vec{R},t) = \sum_{j} b'_{j}(R,t) \Phi'_{j}(\vec{r},\vec{R})$$

The relationship between the new and old basis sets is given by

$$\Phi_{i}'(\vec{r},\vec{R}) = \sum_{j} \underline{W}_{ji}(R) \Phi_{j}(\vec{r},\vec{R})$$
(15)

where  $\underline{W}(R)$  is an arbitrary square matrix. The transformation procedure is to be developed in such a way that it does not change the "physical content" of the equations; i.e. the state  $\Psi(\vec{r},\vec{R},t)$  is to be unaffected by the transformation. The constraint that  $\Psi(\vec{r},\vec{R},t)$  be unaffected by the transformation defines a relationship between the  $\underline{b}(R,t)$  and  $\underline{b}'(R,t)$ vectors:

$$\underline{\mathbf{b}}' = \underline{\mathbf{W}}^{-1} \underline{\mathbf{b}} \tag{16}$$

where  $\underline{b}(\mathbf{R},t)$  contains the components of  $\Psi(\vec{r},\vec{R},t)$ , as it is projected onto the old basis set,  $\{\Phi_j(\vec{r},\vec{R})\}$ , while  $\underline{b}'(\mathbf{R},t)$  contains the components of the same state  $\Psi(\vec{r},\vec{R},t)$  in the new basis set. It is also possible to relate the matrices defined using the old basis set to those defined using the new basis set. The <u>N</u>, <u>H</u>, and <u>P</u> matrices transform according to the following equations:

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$$\underline{\mathbf{N}}^{*} = \underline{\mathbf{W}}^{\dagger} \underline{\mathbf{N}} \underline{\mathbf{W}}$$

$$\underline{\mathbf{H}}^{*} = \underline{\mathbf{W}}^{\dagger} \underline{\mathbf{H}} \underline{\mathbf{W}}$$

$$\underline{\mathbf{P}}^{*} = \underline{\mathbf{W}}^{\dagger} \underline{\mathbf{P}} \underline{\mathbf{W}} + \underline{\mathbf{W}}^{\dagger} \underline{\mathbf{N}} \underline{\mathbf{d}}_{\overline{\mathbf{R}}} \underline{\mathbf{W}}$$
(17)

where the primes indicate matrices defined using the basis set  $\{\Phi_{i}^{\dagger}(\vec{r},\vec{R})\}$ . For problems in which there are no electronic degeneracies at large R the transformation W(R) will be defined to approach the identity as  $R \rightarrow \infty$ . If Eqs. (16) and (17) are used to derive new equations of motion (for  $\underline{b}'(R,t)$  in terms of transformed matrices), then it is clear that the observable results defined by the new equations of motion will be the same as those defined by the original equations of motion in the old basis set. What is not clear, however, is the form of the new equations of motion. If the equations of motion for  $\underline{b}'(R,t)$  possess a different form than those for  $\underline{b}(R,t)$  then, for practical purposes, it will be very difficult to relate numerical results obtained using two different types of basis sets even though the basis sets may be physically equivalent in the sense implied by Eq. (15). To display invariance under transformation it is necessary to derive equations of motion for  $\underline{b}$ ', starting from Eq. (10) and using Eqs. (16) and (17). The following identities are useful:

$$\underline{\mathbf{N}}^{-1}\underline{\mathbf{H}} \underline{\mathbf{b}} = \underline{\mathbf{W}} (\underline{\mathbf{N}}')^{-1}\underline{\mathbf{H}}' \underline{\mathbf{b}}' , \qquad (18)$$

$$\underline{\mathbf{N}}^{-1}\underline{\mathbf{P}} \underline{\mathbf{b}} = \underline{\mathbf{W}} (\underline{\mathbf{N}}')^{-1}\underline{\mathbf{P}}' \underline{\mathbf{b}}' - \left(\frac{\mathrm{d}}{\mathrm{dR}} \underline{\mathbf{W}}\right)\underline{\mathbf{b}}' .$$

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Equations (10) and (18) imply

$$\frac{d}{dt} \left( \underline{W} \ \underline{b}' \right) = -i \ \underline{W} \ \left( \underline{N}' \right)^{-1} \underline{H}' \ \underline{b}' - \underline{W} \ \left( \underline{N}' \right)^{-1} \underline{P}' \ \underline{b}' \ \frac{dR}{dt} + \left( \frac{d}{dR} \ \underline{W} \right) \underline{b}' \ \frac{dR}{dt} .$$

Therefore

$$\frac{d\mathbf{b}'}{d\mathbf{t}} = -\mathbf{i}(\underline{\mathbf{N}'})^{-1}\underline{\mathbf{H}'} \underline{\mathbf{b}'} - (\underline{\mathbf{N}'})^{-1}\underline{\mathbf{P}'} \underline{\mathbf{b}'} \frac{d\mathbf{R}}{d\mathbf{t}}$$

The form of the electronic equations of motion is therefore invariant under a transformation of the electronic basis set. (Note that this invariance is not something that can be taken for granted; for example, the equations of motion used in the average-energy-surface theory (28-30) do not display it.) Because of the invariance of the form of the equations, it is possible to transform from non-orthogonal to orthogonal basis sets quite easily, at least in principle. (The practical difficulties associated with such transformations are discussed below.) For example, within an adiabatic representation (32), where  $\underline{N} = \underline{1}$  and  $\underline{H} = \underline{H}_{\underline{D}}$  (diagonal), the equations of motion can be written down by inspection:

 $\frac{d\underline{b}}{dt} = -i \underline{H}_{D} \underline{b} - \underline{P} \underline{b} \frac{dR}{dt}$ (19)

where  $\underline{P}$  is an anti-hermitian matrix [see Eq. (11)] defined using

adiabatic molecular orbitals. Similarly, in a diabatic representation (32), where  $\underline{N} = \underline{1}$  and  $\underline{P} = \underline{0}$ , the equations of motion are:

$$\frac{d\mathbf{b}}{dt} = -\mathbf{i} \underline{\mathbf{H}} \underline{\mathbf{b}} \tag{20}$$

where H is defined using diabatic states. The formal invariance of the equations is of interest for the following reason: it is often convenient to perform numerical calculations within a non-orthogonal atomic orbital basis set while, at the same time, the interpretation of the results may be simplest within an orthogonal, either diabatic or adiabatic, representation. The invariance of the equations of motion allows one to transform at will between different basis sets whenever the need arises. This procedure does not simplify the numerical problem in any way, but it does allow for more flexibility in the interpretation of results. If the original basis set consisted of non-orthogonal atomic orbitals (AO's) and if expressions for N, H, and P in this basis set are available, then there will not normally be any point in trying to transform these matrices into an orthogonal basis set before the equations of motion are solved. The best procedure will usually be to solve the equations of motion within the original basis set and then to transform the results into a different representation if desired. However, some exceptions to the rule exist. For example, in resonant charge exchange problems it may be possible to partially de-couple the equations within an adiabatic representation using symmetry arguments. In this case the advantages of de-coupling override the numerical diff-

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iculties associated with the transformation to an adiabatic basis set. Similarly, in some cases it may be found that a transformation to a new representation allows one to truncate the basis set even further than originally supposed.

The difficulties associated with the transformation from an AO to an adiabatic (or diabatic) basis set can be seen by inspecting Eq. (17). In each case the transformation is uniquely defined by  $\underline{W}(R)$ . In the transformation from an AO to an adiabatic basis set,  $\underline{W}(R)$  must satisfy [see Eq. (17)]

$$\underline{W}^{\mathsf{T}}\underline{N} \ \underline{W} = \underline{1}$$

$$\underline{W}^{\mathsf{T}}\underline{H} \ \underline{W} = \underline{H}_{\mathsf{D}}$$
 (diagonal) (21)

where  $\underline{H}_{D}$  is the adiabatic hamiltonian. This can be rewritten as an eigenvalue problem:

 $\underline{N}^{-1}\underline{H} \underline{W} = \underline{W} \underline{H}_{D} .$  (22)

The solution of this eigenvalue problem is not very much more difficult than the diagonalization of a single hermitian matrix (52, page 188); however, it would still be impractical to try to solve Eq. (22) at each particular R value encountered in a collision calculation. The only practical way to perform this transformation would be to solve Eq. (22) at a small number of discrete values of R and then obtain  $\underline{W}(R)$  (and incidentally  $\underline{H}_{D}(R)$  and  $\underline{P}(R)$ ) by interpolation or curve-fitting. The resulting

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matrices allow one to solve the electronic equations within an adiabatic representation.

The  $\underline{W}(R)$  matrix which effects the transformation from an AO to a diabatic basis set must satisfy the equations [see Eq. (17)]:

$$\underline{W}^{\dagger}\underline{N} \ \underline{W} = \underline{1}$$
(23)

$$\underline{W}^{\dagger}\underline{P} \underline{W} + \underline{W}^{\dagger}\underline{N} \underline{d}_{R} \underline{W} = \underline{0}$$
(24)

where  $\underline{P}$  and  $\underline{N}$  are known within an AO basis set. It can be shown that a simultaneous solution of Eqs. (23) and (24) is given by the solution of the following equation:

$$\frac{\mathrm{d}}{\mathrm{dR}} \frac{\mathrm{W}}{\mathrm{m}} = - \frac{\mathrm{N}^{-1} \mathrm{P}}{\mathrm{P}} \frac{\mathrm{W}}{\mathrm{W}}$$
(25)

subject to the initial conditions that  $\underline{W}(\infty)$  be unitary (i.e.  $\underline{W}^{\dagger}\underline{W} \rightarrow \underline{1}$ as  $R \rightarrow \infty$ ). If  $\underline{W}(R)$  satisfies Eq. (25) then it will clearly satisfy Eq. (24) as well. All that remains is to show that a solution of Eq. (25) is also a solution of Eq. (23). Consider

$$\frac{\mathrm{d}}{\mathrm{dR}} (\underline{W}^{\dagger} \underline{N} \underline{W}) = (\mathrm{d}\underline{W}^{\dagger} / \mathrm{dR}) \underline{N} \underline{W} + \underline{W}^{\dagger} (\mathrm{d}\underline{N} / \mathrm{dR}) \underline{W} + \underline{W}^{\dagger} \underline{N} (\mathrm{d}\underline{W} / \mathrm{dR}) .$$

If  $\underline{W}(R)$  satisfies Eq. (25), then

$$\frac{\mathrm{d}}{\mathrm{dR}} (\underline{W}^{\dagger} \underline{N} \ \underline{W}) = \underline{W}^{\dagger} \left[ -\underline{P}^{\dagger} + (\mathrm{dN}/\mathrm{dR}) - \underline{P} \right] \underline{W}$$

and Eq. (11) implies

$$\frac{\mathrm{d}}{\mathrm{dR}} \left( \underline{W}^{\dagger} \underline{N} \ \underline{W} \right) = \underline{0} \quad .$$

Therefore, if a solution of Eq. (25) satisfies Eq. (23) at a particular value of R, then it will do so for all R; furthermore, the initial conditions associated with Eq. (25) ensure that  $\underline{W}(R)$  will satisfy Eq. (23) as  $R \rightarrow \infty$ , since the basis set will invariably be defined in such a way that  $\underline{N} \rightarrow \underline{1}$  as  $R \rightarrow \infty$ . The transformation matrix  $\underline{W}(R)$  can therefore be obtained by solving Eq. (25), which should not be too difficult in principle since it is a linear, first-order, equation. It is therefore possible to rigorously transform the  $\underline{N}$ ,  $\underline{H}$ , and  $\underline{P}$  matrices from a non-orthogonal AO basis set to a diabatic basis set, so that the equations can be solved within this representation. In practice, of course, the only feasible approach would be to calculate  $\underline{W}(R)$  at discrete values of R and obtain intermediate versions of W(R) [and the diabatic hamiltonian  $\underline{H}'(R)$ ] by interpolation.

The preceding discussion shows that, although it is possible to transform rigorously from an AO basis set to a diabatic (or adiabatic) basis set, this transformation procedure will not normally be of any practical value, except in those cases where the basis set within the new representation can be drastically truncated compared to the one used in the AO representation. The main value of the transformation procedure lies in the fact that it allows one to develop a set of alternative viewpoints of the collision process, all of which are physically equivalent but look quite different mathematically.

A serious problem encountered in ab initio discussions of electronic excitation is that of deciding what kind of basis set to use.

Most molecular orbital (MO) calculations are performed using adiabatic states, which may be very convenient in discussions of molecular spectroscopy, but are not nearly as useful in collision problems. In collision theory the diabatic representation would frequently be the most convenient one to use (36,55), except for the fact that it is not easy to develop a diabatic basis set rigorously in practice. A very promising method of handling this problem has recently been discussed by Sidis and Lefebvre-Brion (56). Their approach makes full use of existing MO theory, while at the same time ensuring that the results of the MO calculation will be of interest to the collision theorist. The choice of basis set for the three physical systems considered in this thesis was not very difficult. For the H-Be system an ab initio calculation was performed (30) using an atomic orbital (non-orthogonal) basis set. The interpretationng was aided by transforming to an adiabatic basis set, but this transformation was performed only after the original equations had been solved. For the He - Ne system (Ref. (53) and Chapter III) the equations were solved within the diabatic representation. In this problem the diabatic hamiltonian was obtained semi-empirically (54); no attempt was made to perform a rigorous transformation into the diabatic representation. For the vibrational excitation problem (Chapter IV) it was possible to define a diabatic basis set quite rigorously, because of the simple form of the hamiltonian operator, and the equations were solved within this basis set.

It is perhaps worthwhile noting that the problems associated with the calculation of  $\underline{P}$  will depend a lot on the nature of the basis set.

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For example, if an AO basis set (in which the orbitals are all of the type  $\Phi(\mathbf{r}_A)$  or  $\Phi(\mathbf{r}_B)$ ) is used, then only one type of contribution to  $\underline{P}$  will arise: that due to the dependence of  $\mathbf{r}_A$  and  $\mathbf{r}_B$  on R, when  $\overrightarrow{\mathbf{r}}$  is fixed. In a molecular orbital basis set two quite different contributions to  $\underline{P}$  will arise since the molecular orbitals will be R-dependent linear combinations of atomic orbitals: the molecular orbitals will depend on R through  $\mathbf{r}_A$  and  $\mathbf{r}_B$  as mentioned above, but they will also have have an R-dependence due to the coefficients in the linear combination of atomic orbitals. There is, however, one feature of  $\underline{P}$  which slightly simplifies the problem. It can be shown that any square matrix such as  $\underline{P}$  (which is neither hermitian nor anti-hermitian) can be uniquely written

$$\underline{A} = (\underline{P} + \underline{P}^{\dagger})/2 \qquad (hermitian) ,$$
  
$$\underline{B} = (\underline{P} - \underline{P}^{\dagger})/2 \qquad (anti-hermitian)$$

Equation (11) now implies that  $\underline{A} = \frac{1}{2} \frac{dN}{dR}$ . Therefore  $\underline{P}$  can always be written in the form

 $\underline{P} = \frac{1}{2} \frac{d}{dR} \underline{N} + \underline{B}$ (26)

where <u>B</u> is anti-hermitian. The interesting feature of Eq. (26) is that it may provide a worthwhile starting point for an approximate method of evaluating <u>P</u>, for two reasons: 1) as long as <u>B</u> is anti-hermitian, normalization of the wave-function will automatically be conserved; i.e. one can evaluate <u>B</u> approximately without destroying normalization conservation. 2) In an atomic orbital

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2) In an atomic orbital basis set <u>B</u> will probably not be very important as a source of off-diagonal coupling (see proton-hydrogen example below). If the basis set is strongly non-orthogonal, then the <u>N</u>, <u>H</u>, and <u>dN</u>/dR matrices may well contain all of the interesting off-diagonal coupling terms and it may be reasonable to evaluate <u>B</u> only approximately. (Note that in the adiabatic representation the situation is quite different since, in this case, <u>B</u> is the only source of off-diagonal coupling.)

An example of a case where  $\underline{P}$  can be easily evaluated and where the transformation theory developed above can be used to good advantage is given by the proton-hydrogen system. Consider the basis set and coordinate system of Ref. (28); it will be shown here that the  $\underline{P}$  matrix for this problem possesses a fairly simple structure and that the implications of the present equations of motion [Eq. (10)] are rather different from those used in Ref. (28). The  $\underline{P}$  matrix consists of the following type of matrix elements:

$$\int \phi_{i}^{*} (\partial \phi_{j} / \partial Z) d\vec{r}$$
,

where the Z axis is parallel to  $\vec{R}$ , and where  $\Phi_i$  and  $\Phi_j$  are any members of the set of orbitals  $\{ls(A), 2s(A), 2p_z(A), ls(B), 2s(B), 2p_z(B)\}$ . An evaluation of  $\underline{P}$  shows that the major contributions are of the type represented by  $\frac{1}{2} d\underline{N}/dR$  in Eq. (26). (The matrix elements of  $\underline{N}(R)$  have been tabulated by Corrigall (57).) That is,  $\underline{P}$  is almost entirely hermitian. This is due largely to the fact that the centre-of-mass of the system lies at the midpoint of  $\vec{R}$ . If  $\underline{P}$  is expressed in the form of Eq. (26), then it can be shown that B is given by

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where the ordering of the states is as shown above,  $\alpha = 8\sqrt{2}/81$ , and the non-zero matrix elements are all of the type discussed on page 16. The matrix <u>B</u> therefore consists entirely of spurious terms, due to the neglect of the high-energy phase factor e<sup>ivz</sup>. If these terms are ignored the equations of motion for the proton-hydrogen system become [see Eqs. (10) and (26)]

$$\frac{d\mathbf{b}}{d\mathbf{t}} = -\mathbf{i} \, \underline{\mathbf{N}}^{-1} \underline{\mathbf{H}} \, \underline{\mathbf{b}} - \frac{1}{2} \, \underline{\mathbf{N}}^{-1} \left( \frac{d}{d\mathbf{R}} \, \underline{\mathbf{N}} \right) \underline{\mathbf{b}} \, \frac{d\mathbf{R}}{d\mathbf{t}} \, . \tag{27}$$

From Ref. (28) it is known that  $\underline{N}$  and  $\underline{H}$  (and therefore  $\underline{dN}/dR$ ) have the structure

$$\underline{\mathbf{M}} = \begin{pmatrix} \underline{\mathbf{C}} & \underline{\mathbf{D}} \\ \underline{\mathbf{D}} & \underline{\mathbf{C}} \end{pmatrix}$$
(28)

where <u>C</u> and <u>D</u> are  $3 \times 3$  hermitian matrices. This structure expresses the fact that the charge-exchange process in the proton-hydrogen system is resonant. Consider a change of basis set, defined by the transformation matrix

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$$\underline{W} = \begin{pmatrix} \underline{1} & -\underline{1} \\ \underline{1} & \underline{1} \end{pmatrix}$$
(29)

where  $\underline{1}$  is a 3 × 3 identity matrix. The states in the new basis set are either gerade or ungerade linear combinations of atomic orbitals. The transformed version of a matrix of the type shown in Eq. (28) is

$$\underline{\mathbf{M}}^{\prime} = 2 \begin{pmatrix} \underline{\mathbf{C}} + \underline{\mathbf{D}} & \underline{\mathbf{0}} \\ \underline{\mathbf{0}} & \underline{\mathbf{C}} - \underline{\mathbf{D}} \end{pmatrix} \qquad . \tag{30}$$

The transformed matrices ( $\underline{N}'$ ,  $\underline{H}'$ , and  $d\underline{N}'/dR$ ) are therefore block diagonal. After making use of Eqs. (16) and (17) it can be seen that the equations of motion for the coefficients in the new basis set are partially de-coupled. Instead of six coupled equations of motion for the old coefficients one has two independent sets of three coupled equations for the new coefficients. Furthermore, the three coefficients for the gerade states (which may be labelled  $1s_g$ ,  $2s_g$ ,  $2p_g$ ) obey a normalization conservation law independently of the three coefficients for the ungerade states, and vice-versa. If the expression for the average-energy-surface (28),  $\overline{E}(R,t) = \underline{b}^{\dagger}\underline{H} \underline{b}$ , is examined, it can be seen that  $\overline{E}(R,t)$  is assum of two terms (within the new basis set), one of which comes from the three gerade states while the other comes from the three ungerade states. An inspection of the individual terms shows that the gerade contribution to  $\overline{E}(R,t)$  is necessarily greater than  $\frac{1}{2}V(1\sigma_g)$  where  $V(1\sigma_g)$  is the energy of the (adiabatic) ground state, while the ungerade contribution is necessarily greater than  $\frac{1}{2}\mathbb{V}(1\sigma_{_{11}})$ , the energy of the first (adiabatic) excited state. The present prediction of the absolute minimum of the average energy surface is therefore greater than any of the dynamic energy sur-

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faces shown in Fig. (3) of Ref. (28). From a qualitative point of view this conclusion is quite important; the calculation of Ref. (28) implies that there is no low-energy "adiabatic" limit even when the impact energy is below thermal energies, while the equations discussed here [Eq. (27)] imply that a low-energy limit can be defined, in which the energy surface is simply an average of the two lowest adiabatic energy surfaces,  $V(1\sigma_g)$  and  $V(1\sigma_u)$ . (Note that symmetry arguments of this type are very useful in the general theory of resonant charge-exchange (58-60). This point will be re-examined in Chapter III.)

Given the fact that conclusions reached in one basis set can be applied to other basis sets as well, by transformation of the appropriate equations, the discussion of detailed-balancing can be carried out within the diabatic representation. It is convenient to first convert the equations into an evolution matrix notation. Consider the column vector  $\underline{b}^{i}(R,t)$ representing a state at time t which in the far past, at time t', was the i th eigenstate of an unperturbed atom. If a second column vector  $\underline{b}^{J}(R,t)$ is defined as representing a state which initially was the j th eigenstate, then it is found that  $\underline{b}^{i}(\mathbf{R},t)$  and  $\underline{b}^{j}(\mathbf{R},t)$  evolve independently in time. In general, if the basis set consists of n states, one can visualize n unique ways of preparing the column vector b(R,t) initially, each of which leads to a unique final state. Consider a square "evolution matrix" U(t,t'), defined such that the i th column of  $\underline{U}(t,t')$  represents a state  $[\underline{b}^{i}(R,t)]$ which was initially the i th eigenstate of the system. The evolution matrix contains all of the information needed to follow the evolution of any state in time, regardless of how that state was prepared. Because the

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columns of  $\underline{U}(t,t')$  evolve independently, Eq. (10) can be re-written as an equation for the evolution matrix:

$$\frac{\mathrm{d}}{\mathrm{dt}} \underline{\mathrm{U}}(\mathsf{t},\mathsf{t}') = -\mathrm{i} \, \underline{\mathrm{N}}^{-1} \underline{\mathrm{H}} \, \underline{\mathrm{U}}(\mathsf{t},\mathsf{t}') - \underline{\mathrm{N}}^{-1} \underline{\mathrm{P}} \, \underline{\mathrm{U}}(\mathsf{t},\mathsf{t}') \, \frac{\mathrm{dR}}{\mathrm{dt}} \quad . \tag{31}$$

Within the diabatic representation this becomes:

$$\frac{\mathrm{d}}{\mathrm{dt}} \underline{\mathrm{U}}(\mathrm{t},\mathrm{t}') = -\mathrm{i} \underline{\mathrm{H}}(\mathrm{R}) \underline{\mathrm{U}}(\mathrm{t},\mathrm{t}') . \tag{32}$$

It can readily be shown that  $\underline{U}(t,t')$  has the following properties within the diabatic representation:

$$\underline{\underline{U}}(t',t') = \underline{\underline{1}}$$

$$\underline{\underline{U}}(t'',t') = \underline{\underline{U}}(t'',t) \underline{\underline{U}}(t,t') \qquad (33)$$

$$\underline{\underline{U}}^{-1}(t,t') = \underline{\underline{U}}^{\dagger}(t,t') = \underline{\underline{U}}(t',t) .$$

Consider a problem in which the origin of the time axis is defined such that t = 0 at the turning point of the nuclear motion. With this restriction a scattering matrix <u>S</u> will defined such that

 $\frac{S}{\tau \to \infty} = \lim_{\tau \to \infty} \frac{U(\tau, -\tau)}{\tau}$ (34)

From Eq. (33), therefore:

 $\underline{S} = \lim_{\tau \to \infty} \underline{U}(\tau, 0) \underline{U}(0, -\tau)$ 

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By comparing the equations of motion (and initial conditions) of  $\underline{U}(\tau, 0)$ and  $U(0, -\tau)$  it can be shown that

$$\underline{U}(\tau,0) = \underline{U}^{\dagger}(0,-\tau)$$
(35)

if (and only if) the classical trajectories R(t) for the incoming and outgoing portions of the collision are mirror images of each other; i.e. if R(t) = R(-t). (See, for example, Eq. (26) of Ref. (61).) Therefore,

$$\underline{S} = \lim_{\tau \to \infty} \underline{U}(\tau, 0) \ \underline{U}^{\dagger}(\tau, 0) .$$
(36)

That is, the <u>S</u> matrix is symmetric as well as being unitary. Since <u>S</u> is symmetric the transition probability for the  $\alpha \rightarrow \beta$  event will equal that for the  $\beta \rightarrow \alpha$  event. For two-body scattering this symmetry is observed only when the potential energy surfaces for the incoming and outgoing portions of the collision are identical. Equation (36) is the desired expression of detailed-balance. It is of some interest as a check on computational precision (51) as well as being useful in formal manipulations of the equations of motion. It must be noted that this expression of detailed-balance has meaning only when the same nuclear trajectory is used for all electronic events  $i \rightarrow j$ , regardless of i and j. When a more sophisticated nuclear model is developed (Chapter III) the definition of detailed-balance must be appropriately revised.

In practice, the origin of the time axis will not be at the turning point of the nuclear motion. Instead, time will be zero at some point  $R_0$ 

long before the interaction region is reached. The effect of this change in the time axis is simply to introduce additional phase factors into  $\underline{U}(t",t')$  without changing the magnitudes of any transition probabilities.

Before an attempt is made to solve Eq. (10) or Eq. (31) in practice, it is convenient to introduce a modification in the definition of the states  $\Phi_j(\vec{r},\vec{R})$  of Eq. (3). Normally, as  $R \rightarrow \infty$ , the <u>N</u>, <u>H</u>, and <u>P</u> matrices will become the identity, diagonal, and zero, respectively. Because the <u>H</u> matrix does not approach zero as  $R \rightarrow \infty$  the phase of the coefficients  $\underline{b}_j(R,t)$  [or  $\underline{U}_{ji}(t,t')$ ] will not be stationary at large R, although their magnitudes will be constant. For example, if

$$\lim_{R \to \infty} \frac{H(R)}{E} = E$$

where  $\underline{E}$  is diagonal, then at large R

$$\underline{\mathbf{b}}_{\mathbf{j}}(\mathbf{R},\mathbf{t}) = |\underline{\mathbf{b}}_{\mathbf{j}}(\infty)| e^{-\underline{\mathbf{i}}\underline{\mathbf{E}}_{\mathbf{j}}\underline{\mathbf{j}}^{\mathbf{t}}}$$
(37)

where  $|\underline{b}_{j}(\infty)|$  is constant. The time-dependence of the phase factor of  $\underline{b}_{j}(\mathbf{R},t)$  decreases the efficiency of the calculation and can be analytically removed by a transformation  $\underline{W}(t)$  [Eq. (15)], where

$$\underline{W}_{ij}(t) = \delta_{ij} e^{-i\underline{E}jjt} .$$
(38)

The introduction of this transformation is tantamount to using states of the type  $\Phi_j(\vec{r},\vec{R})e^{-iEjjt}$  in Eq. (3). The transformed matrices and equations of motion can be quickly derived, and it is seen that the phases of the

new coefficients,  $\underline{b}'(R,t)$ , are stationary at large R, while their magnitudes are unaffected by  $\underline{W}(t)$ .

## B. Stueckelberg-Landau-Zener Theory

Since both of the electronic excitation calculations presented here involve curve-crossing (1,2) of two electronic states it is convenient to discuss a few of the ideas associated with the Stueckelberg-Landau-Zener (SLZ) theory of curve-crossing. The simplest example of this phenomenon is an atomic collision in which the electronic state can be described as a linear combination of two atomic orbitals, which may or may not be on the same atomic centre. If the energies of the two orbitals are accidentally degenerate at a particular internuclear distance  $R_x$  and if the off-diagonal coupling in a neighbourhood of  $R_x$  is a non-zero, slowly varying, function of R, then it will be said that the system displays a curve-crossing. In general, the two states which become degenerate at R, do not have to be atomic orbitals: all that is required is that they violate the "non-crossing rule" (62). For the purposes of a qualitative discussion, states which violate the non-crossing rule will be loosely termed "diabatic" (36,55), keeping in mind that it is possible to define diabatic states quite precisely (32). It will normally be taken for granted that the behaviour of the atomic orbital and diabatic hamiltonian matrices is qualitatively similar, as described above.

The curve-crossing problem is of fairly general interest as an efficient mechanism for electron transfer and/or excitation during atomic and molecular collisions. It was originally discussed by Landau (63,64) and Zener (65). Zener's treatment made use of the fact that the timedependent semiclassical equations of motion within a two-state diabatic

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representation can be reduced to the form of Weber's equation (66) if the hamiltonian matrix elements are evaluated approximately. Both theories assume that the difference between the two diagonal elements of the diabatic hamiltonian,  $\underline{H}_{11}(R) - \underline{H}_{22}(R)$ , is a linear function of R (at least within a small region around  $R_x$ ) and that the off-diagonal coupling  $\underline{H}_{12}$  is constant. There is no need to assume that these restrictions are satisfied at all R, but they must be satisfied within the neighbourhood in which the "transition" occurs (see below). The probability of a nonadiabatic transition during a single passage through the curve-crossing region is then given by

$$P = \exp(-2\pi \frac{H^2}{12} / v | d(\underline{H}_{11} - \underline{H}_{22}) / dR |)$$
(39)

where v is the radial velocity at  $R = R_x$  and the matrix elements are evaluated at  $R_x$ . During a collision the nuclei will pass through the curve-crossing region twice. The Landau and Zener theories assume that these two events are essentially independent; i.e. the probabilities for the two events can be calculated separately and multiplied together to obtain a final transition probability. (For example, the probability of an inelastic event would be 2P(1 - P).) A more sophisticated treatment of the problem was developed by Stueckelberg (67) using "connection formulae" to relate the solution valid for  $R > R_x$  to that which is valid for  $R < R_x$ . This method is reminiscent of the procedure sometimes used in singlechannel WKB theory to relate the WKB solution valid in the classically allowed region to that valid in the classically forbidden region (see the

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discussion on page 656 of Ref. (20)). Stueckelberg's procedure has been discussed in detail by Delos and Thorson (61,68). It yields the following expression for the final transition probability,  $\mathcal{P}$ , for an inelastic event:

$$\mathbf{P} = 4P(1 - P) \sin^2 \phi \tag{40}$$

where P is given by the Landau-Zener formula [Eq. (39)] and  $\phi$  introduces the possibility of rapid oscillations in  $\mathcal{P}$  as a function of impact energy or impact parameter. (These will be called Stueckelberg oscillations.) The exact definition of  $\phi$  depends to some extent on the nature of the nuclear model and will be discussed in more detail below.

As mentioned above, the original version of SLZ theory made use of the idea that the two passages of the nuclei through the curve-crossing region could be regarded as independent events. This will be true if the off-diagonal coupling (in the adiabatic representation) is sharply peaked about  $R_x$  and if the turning point of the nuclear motion,  $R_o$ , is sufficiently far away from  $R_x$  that the off-diagonal coupling at  $R_o$  is negligible. More recent treatments of SLZ theory have somewhat relaxed this restriction (69-71), but it remains an essential part of the SLZ "picture" of the curve-crossing mechanism. The assumption that the matrix elements of the diabatic hamiltonian are linear in R has also been modified to include the possibility that <u>H</u> may be an exponential function of R (72-74). In addition, the SLZ theory of electronic motion has been discussed in connection with nuclear models which are considerably more sophisticated than those used in the original development of the theory

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(18,75,76).

For the purposes of this discussion, two features of SLZ theory are of special interest: 1) the concept of a fast transition, and 2) the behaviour of the phase  $\phi$  in Eq. (40). It is clear that within the diabatic representation the electronic transition will not appear to occur quickly, because the off-diagonal coupling  $\underline{H}_{12}(\mathbf{R})$  is a non-zero (generally monotonic) function which induces "transitions" over a broad range of R (see Section C of this chapter). Within the adiabatic representation, however, the electronic transition will appear to occur within a relatively localized region around  $\mathbf{R}_{\mathbf{x}}$ . (Note that the final, observable, transition probability is the same in both cases.) This can be illustrated by considering a twostate diabatic hamiltonian  $\underline{H}(\mathbf{R})$ , defined such that  $\underline{H}_{11}(\mathbf{R}_{\mathbf{x}}) = \underline{H}_{22}(\mathbf{R}_{\mathbf{x}})$ . Within the diabatic representation the off-diagonal coupling is given by  $\underline{H}_{12}(\mathbf{R}) = \underline{H}_{21}(\mathbf{R})$ . It can be shown (32) that the off-diagonal coupling in the adiabatic basis set is peaked about  $\mathbf{R} = \mathbf{R}_{\mathbf{x}}$ . The transformation,  $\underline{\Psi}(\mathbf{R})$ , into the adiabatic basis set must satisfy [Eq. (17)]:

 $\underline{W}^{\dagger}\underline{W} = \underline{1}$ 

(41)

 $\underline{W}^{\dagger}\underline{H} \underline{W} = \underline{H}_{D}$  (diagonal)

where  $\underline{H}_{D}(R)$  is the adiabatic hamiltonian. The  $\underline{W}(R)$  matrix is therefore given by

$$\underline{W}(R) = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix}$$
(42)

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where

$$\tan(2\alpha) = 2 \underline{H}_{12} / (\underline{H}_{11} - \underline{H}_{22}) .$$
 (43)

In the adiabatic basis set the off-diagonal coupling is given by  $\underline{P}_{12}$ , where  $\underline{P}$  satisfies [Eq. (17)]:

$$\underline{P} = \underline{W}^{\dagger}(d\underline{W}/dR) \tag{44}$$

 $= \begin{pmatrix} 0 & -d\alpha/dR \\ \\ d\alpha/dR & 0 \end{pmatrix}$ 

If it is now assumed that  $\underline{H}_{12}$  and  $d(\underline{H}_{11} - \underline{H}_{22})/dR$  are constant within a neighbourhood of  $R_x$ , then it is easily shown that  $\underline{P}_{12}(R)$  has a Lorentzian line-shape, centred about  $R = R_x$ , with a full-width-at-half-maximum of  $\delta R_x$  units and a peak height of  $1/\delta R_x$ , where

$$\delta \mathbf{R}_{\mathbf{x}} = |4\underline{\mathbf{H}}_{12}(\mathbf{R}_{\mathbf{x}})/[d(\underline{\mathbf{H}}_{11} - \underline{\mathbf{H}}_{22})/d\mathbf{R}]_{\mathbf{R}=\mathbf{R}_{\mathbf{x}}}| \quad .$$
(45)

Therefore, as long as the linear approximation to the matrix elements of  $\underline{H}(R)$  is valid, the off-diagonal coupling within the adiabatic representation will be localized within the curve-crossing region, where the extent of this region is given by  $\delta R_x$ . (A more general discussion of the shape of  $\underline{P}_{12}(R)$  in an adiabatic representation has been given by Oppenheimer (77).) If one considers a collision in which the turning point of the nuclear motion,  $\rm R_{_{O}},$  is less than  $\rm R_{_x}$  -  ${}^{1}_{2} \delta \rm R_{_x},$  then within the adiabatic representation the electronic rearrangement will seem to occur in two well defined stages, one for each passage through the crossing point. The quantity  $\delta R_{\rm v}$ can be regarded as a definition of the width of the "transition zone" about  $R_{_{\mathbf{y}}}$ . (Note that at high impact energies this definition may fail (73,78,79).) The collision process, as it is viewed within the adiabatic representation, can therefore be broken up into segments. Beginning at time t' in the far past, the system will evolve adiabatically until the point  $R_x + \frac{1}{2} \delta R_x$  is reached (at time  $t_1 - \epsilon$ ), at which time it will temporarily evolve non-adiabatically until  $R = R_x - \frac{1}{2} \delta R_x$  (at time  $t_1 + \epsilon$ ). It will then evolve adiabatically (if  $R < R_x - \frac{1}{2}\delta R_x$ ) until the second curve-crossing region is reached on the outgoing portion of the collision (at time  $t_2 - \epsilon$ ) and will experience a second non-adiabatic perturbation in the time-interval (t $_2$  -  $\epsilon$ , t $_2$  +  $\epsilon$ ), after which it leaves the interaction region and concludes its journey adiabatically. The corresponding evolution matrix can be written as

$$\underline{U}(t'',t') = \underline{U}(t'',t_2+\varepsilon)\underline{U}(t_2+\varepsilon,t_2-\varepsilon)\underline{U}(t_2-\varepsilon,t_1+\varepsilon)\underline{U}(t_1+\varepsilon,t_1-\varepsilon)\underline{U}(t_1-\varepsilon,t')$$
(46)

where  $\underline{U}(t_2 + \varepsilon, t_2 - \varepsilon)$  and  $\underline{U}(t_1 + \varepsilon, t_1 - \varepsilon)$  represent the evolution during nonadiabatic portions of the motion, and are therefore non-diagonal in any basis set. The other three evolution matrices in Eq. (46) represent adiabatic evolution and are diagonal within the adiabatic representation. If the transitions at  $t_1$  and  $t_2$  occur sufficiently quickly, then Eq. (46) can written as (74):

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$$\underline{U}(t'',t') = \underline{A}(t'',t_2) \underline{T}^{t} \underline{A}(t_2,t_1) \underline{T} \underline{A}(t_1,t')$$
(47)

where the  $\underline{A}$  and  $\underline{T}$  matrices are defined within an adiabatic basis set, and a typical  $\underline{A}$  matrix is given by

$$\underline{A}_{ij}(t_2, t_1) = \delta_{ij} \exp(-i \int_{t_1}^{t_2} \underbrace{\mathbb{E}}_{t_1}(\mathbf{R}) dt)$$
(48)

where  $\underline{E}_{jj}(\mathbf{R})$  is an adiabatic energy surface. (The discrepancy between the present definition of the <u>A</u> matrices and that of Ref. (74) will be discussed in Section C of Chapter III.) The <u>T</u> matrix represents non-adiabatic evolution and is determined entirely by the diabatic matrices  $\underline{H}(\mathbf{R}_{\mathbf{X}})$  and  $(\underline{d}\underline{H}/d\mathbf{R})_{\mathbf{R}=\mathbf{R}_{\mathbf{X}}}$ , and the nuclear velocity at  $\mathbf{R} = \mathbf{R}_{\mathbf{x}}$ . Equation (47) contains the assumption that the nuclear motion at time  $t_2$  is a mirror image of the motion at time  $t_1$ ; i.e.  $\dot{\mathbf{R}}(t_2) = -\dot{\mathbf{R}}(t_1)$ . This will not always be strictly true (see Chapter III) but it is a good first approximation since the two adiabatic surfaces,  $\underline{E}_{11}(\mathbf{R})$  and  $\underline{E}_{22}(\mathbf{R})$ , will be quite close to each other at  $\mathbf{R} = \mathbf{R}_{\mathbf{x}}$  and the ambiguity in  $\dot{\mathbf{R}}(\mathbf{R}_{\mathbf{x}})$  is therefore not very great. It is interesting to note that Eq. (47) may be sensible even if SLZ theory is not valid. The only major assumption incorporated in Eq. (47) is that the transition occurs quickly, regardless of what the mechanism for the transition is. Since <u>T</u> is unitary it can be written as (74):

$$\underline{T} = \begin{pmatrix} (1-P)^{\frac{1}{2}} e^{i\alpha} & P^{\frac{1}{2}} e^{i\beta} \\ -P^{\frac{1}{2}} e^{-i\beta} & (1-P)^{\frac{1}{2}} e^{-i\alpha} \end{pmatrix}$$
(49)

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where P is the probability of a non-adiabatic transition during a single passage through the curve-crossing region. The phases  $\alpha$  and  $\beta$  will be called non-adiabatic phases. The final elastic and inelastic transition amplitudes are therefore given by

$$\underline{U}_{11}(t'',t') = \exp(-i \underbrace{\int_{t_{z}}^{t''} (R) dt}_{t_{z}} [(1-P)e^{i(2\alpha-\eta_{1})} + Pe^{-i(2\beta+\eta_{2})}] \times \underbrace{t_{t_{z}}}_{exp(-i \underbrace{\int_{t_{z}}^{E} (R) dt}_{t'} (R) dt} (50)$$

$$\underline{U}_{21}(t'',t') = P^{\frac{1}{2}}(1-P)^{\frac{1}{2}} \exp(-i\int_{t_{z}} E_{22}(R)dt) \left[e^{i(\alpha+\beta-\eta_{1})} - e^{-i(\alpha+\beta+\eta_{2})}\right] \times \exp(-i\int_{t_{1}} R)dt)$$
(51)

where  $n_i = \int_{t_i} \frac{E}{t_i}$  (R) dt, i = 1,2. Equations (50) and (51) are useful in the discussion of multi-trajectory curve-crossing theories (15,54) where the phase of  $\underline{U}_{11}(t'',t')$  and  $\underline{U}_{21}(t'',t')$  determines the nuclear trajectory.

The inelastic transition probability obtained from Eq. (51) can be written as:

$$\left|\underline{U}_{21}(t'',t')\right|^{2} = 4P(1-P)\sin^{2}[\alpha + \beta + (\eta_{2}-\eta_{1})/2]$$
(52)

which has the form of Eq. (40), with  $\phi = \alpha + \beta + (n_2 - n_1)/2$ . It is now possible to identify the source of Stueckelberg oscillations. The phase  $\phi$ , which induces the oscillations, is composed of an adiabatic contribution given by  $\frac{t_z}{t_1} (\underline{\mathbf{R}}) - \underline{\mathbf{E}}_{22}(\mathbf{R})$  dt, and a "non-adiabatic" phase shift represented by  $\alpha + \beta$ . The adiabatic contribution to the Stueckelberg oscillation allows one to relate the frequency of the oscillation to the splitting between adiabatic energy surfaces in a way which is strongly reminiscent of resonant charge-exchange theory [see Eq. (13) of Ref. (36)].

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(Note that the discussion presented here assumes that only one nuclear trajectory is found within a particular channel. If more than one nuclear trajectory is used within one channel then the interpretation of the adiabatic contribution to the Stueckelberg phase changes somewhat (see Ref. (54) and Section C of Chapter III).) The non-adiabatic phase shift has been discussed by Child (73,80) and Kotova (8) and is of interest whenever a direct comparison between SLZ theory and the exact result is attempted (81,82). For the purposes of the present discussion it can be taken to be  $\frac{1}{4\pi}$  (82).

Before concluding this section it is useful to discuss the behaviour of the Landau-Zener result at very low and very high energies. At low energies the probability P of a non-adiabatic transition during a single passage through the curve-crossing approaches zero and therefore  $|U_{01}(t'',t')|^2 \rightarrow 0$  in Eq. (52). This type of behaviour will be called the adiabatic limit. At high energies, however, we again find that  $|\underline{U}_{21}(t'',t')|^2 \rightarrow 0$  since  $P \rightarrow 1$  in this limit. The behaviour of the system during a collision in which  $P \sim 1$  will be called diabatic. In both the adiabatic and diabatic limits the collision problem may be handled using single-channel theory (keeping in mind that the behaviour at high energies may be complicated by the presence of a manifold of highly excited states). The theoretical interest in the diabatic representation (32,36,55) seems to stem from the fact that some of the most interesting experimental information produced for systems such as He-He<sup>+</sup> and Ne-He<sup>+</sup> has been obtained in the high energy limit. The behaviour of the final transition probability as a function of impact parameter is qualitatively different

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in the adiabatic and diabatic limits. At low energies the "envelope", 4P(b)(1 - P(b)), under which the final transition probabilities lie, is a monotonically decreasing function of the impact parameter b, while at high energies this envelope displays a single peak near the threshold region in which  $R_o \sim R_x$ . The H-Be<sup>++</sup> calculation of Section C of this chapter is an example of the adiabatic limit (P <  $\frac{1}{2}$ ) while the He<sup>+</sup>-Ne calculation exhibits diabatic behaviour (P >  $\frac{1}{2}$ ).

Although the numerical results presented in this thesis do not make explicit use of SLZ theory, the interpretation suggested by it is quite useful. For example, the fact that the off-diagonal coupling in the adiabatic representation is peaked about  $R = R_x$  helps one to understand the behaviour of the coefficients in this representation (see following Section). Similarly, the behaviour of the phases in Eqs. (50) and (51) allows one to qualitatively rationalize the success of multi-trajectory=curve-crossing theories (Ref. (54) and Chapter III).

The impact parameter, b, is that distance which would be the distance of closest approach of the two atoms if they did not interact with each other during the collision. It is related to the angular momentum,  $\ell$ , of the system by the equation  $\ell = bp$ , where p is the initial relative momentum.

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C. Collisions between H and Be

The H-Be<sup>++</sup> system was studied (30) in order to obtain some qualitative understanding of the behaviour of the electrons during a curvecrossing event. The process of interest is asymmetric charge-exchange between two atoms:

 $H + Be^{++} \rightarrow H^{+} + Be^{+}$ .

This process was previously investigated by Bates, Johnston, and Stewart (83) using linear-trajectory (constant velocity) impact parameter theory. The present calculation was performed using the average-energy-surface theory of Corrigall, Kuppers, and Wallace (28). The nuclear trajectories in this theory are obtained from a potential energy surface of the form  $\underline{b}^{\dagger}\underline{H}$   $\underline{b}$ , which is an average of the hamiltonian matrix over the existing electronic state at any time t. The trajectories therefore reflect at least some of the details of the electronic behaviour during the collision, although it is not yet clear whether they do so "correctly". For low-energy collisions of the type considered here this nuclear model is ultimately unsatisfactory regardless of how accurately the electronic motion is evaluated, but it represents a distinct improvement upon linear-trajectory impact-parameter theory.

The electronic equations of motion used in this calculation have the form (28):

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$$\frac{d\underline{b}}{dt} = -i \underline{N}^{-1}\underline{H} \underline{b} - \frac{1}{2}[\underline{b}^{\dagger}(d\underline{N}/dR) \underline{b}] \underline{b} \frac{dR}{dt} .$$
(53)

According to the derivation of Section A of this chapter, Eq. (53) is not the correct electronic equation of motion. The results of this calculation are therefore not quantitatively reliable; however, they can be expected to be qualitatively reasonable. For a curve-crossing problem the quantity  $\underline{N}^{-1}\underline{H}$  is the most important term in the equation of motion since it contains the matrix elements  $\underline{H}_{11}(R)$  and  $\underline{H}_{22}(R)$  which become degenerate at R =  $R_x$ . The main effect of the second term on the right hand side of Eq. (53) is to ensure conservation of normalization, in the sense that  $\underline{b}^{\dagger}\underline{N} \underline{b} = 1$ . (Note that the equations used by Bates, Johnston, and Stewart (Ref. (83), denoted BJS) are also not compatible with the discussion of Section A of this chapter, since they use the "symmetrization procedure" described by Green (49) in which the matrix  $\underline{N}^{-1}\underline{H}$  is replaced by  $\frac{1}{2}[\underline{N}^{-1}\underline{H} + (\underline{N}^{-1}\underline{H})^{\dagger}]$ . The BJS equations therefore yield a modified normalization conservation law:  $\underline{b}^{\dagger}\underline{b} = 1$ .) Because of the approximate nature of the nuclear and electronic equations used here, no attempt will be made to draw quantitative conclusions from the H-Be++ results; instead, attention will be focused on the qualitative behaviour of the coefficients which describe the electronic state in different representations.

The electronic motion is described within the one-electron approximation (84,85). It is assumed that two of the electrons are "passive" in the sense that they occupy the same atomic orbital, Be(ls), throughout the entire collision. This orbital is given by

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$$\Phi_{Be}(1s) = (z^3/\pi)^{\frac{1}{2}} e^{-zr_{Be}}$$

where z = 3.6875. The third electron is "active" in the sense that it may move from the H atom to the Be<sup>++</sup> core. The active electron is assumed to be distinguishable from the two passive electrons. The state of the active electron is represented as

$$\Psi(\vec{r},\vec{R},t) = \underline{b}_1(R,t)\Phi_H(1s) + \underline{b}_2(R,t)\Phi_{Be}(2s)$$
(54)

where  $\Phi_{\rm H}(1{\rm s})$  is a hydrogenic orbital with an ionization energy of 13.60 eV. The Be(2s) orbital is given by (84):

$$\Phi_{Be}(2s) = N(1 - cr_{Be}) e^{-\gamma r_{Be}}$$

where N is a normalization constant and c ensures orthogonality of  $\Phi_{Be}(1s)$ and  $\Phi_{Be}(2s)$ : c = ( $\gamma$  + z)/3. The parameter  $\gamma$  is chosen to minimize the energy of Be<sup>+</sup>. Using integrals tabulated by Moiseiwitsch (86) it can be shown that the optimum value of  $\gamma$  is 1.329, which yields an ionization energy of 17.90 eV for the Be(2s) orbital. The one-electron hamiltonian operator is given by

$$H = -\frac{1}{2}\nabla_{r}^{2} - \frac{4}{r_{Be}} - \frac{1}{r_{H}} + \frac{2}{r_{12}} + V(R)$$
(55)

where  $r_{Be}$  and  $r_{H}$  are electron-nuclear separations and  $r_{12}$  is an interelectron separation between passive and active electrons. V(R) represents

the classical electrostatic interaction between  $H^+$  and  $Be^{++}$ . (At large R,  $V(R) \sim 2/R$ , while at small R,  $V(R) \sim 4/R$ .) In the evaluation of the hamiltonian matrix, some two-electron (two-centre) integrals are encountered. These can all be re-expressed in terms of one-electron, two-centre, integrals using a method outlined by Schiff (87, page 258). The remaining oneelectron integrals have been tabulated by Coulson (88). Appendix I of this document contains the final expressions for the matrix elements used in the calculation. The (AO) potential energy surfaces  $H_{11}(R)$  and  $H_{22}(R)$ cross at  $R_x = 6.3$  a.u. (3.3 Å) and the separation of the two adiabatic surfaces at this point is approximately 0.025 a.u. (0.7 eV). The equations of motion were integrated using the program discussed by Corrigall (see Appendix II of Ref. (57)), with appropriate modifications in the definition of <u>N</u> and <u>H</u> (Appendix I of this document).

Numerical calculations were performed in two rather distinct energy ranges. One such set at high energy (relative kinetic energy: 56.2 eV; total kinetic energy:  $10^{2.75}$  eV), was carried out largely for purposes of comparison with the calculation of Bates, Johnston, and Stewart (83). The impact parameters for these calculations were so high that our nuclear trajectories did not deviate very much from linearity and the electronic motion was quite simple. The asymptotic transition probabilities, plotted as a function of impact parameter, are shown in Fig. 1, along with the corresponding results of Bates, Johnston, and Stewart (83). The two sets of results are sufficiently similar that there is no point in attempting to attribute any significance to the differences between them. The total cross sections obtained from these probabilities are as follows: Figure 1.

Electron exchange probability as a function of impact parameter. Total initial kinetic energy:  $10^{2.75}$  eV. Solid curve: present calculation. Dashed curve: Bates, Johnston, and Stewart (Ref. 83).



$$\sigma_{\rm Bates} \sim 16 \pi a_0^2$$
,  $\sigma_{\rm this calc.} \sim 25 \pi a_0^2$ 

where a is the Bohr radius. The main feature of interest in the present results is the history of the collision process as the system evolves towards its final state. This history allows us to interpret the final transition probability in relatively physical terms. For example, if we choose those impact parameters,  $\rho$ , for which the final exchange probability is a maximum and plot the exchange probability as a function of time from the initial to the final state, the results are as shown in Fig. 2. Considering that the initial state is H-Be<sup>++</sup>, one can see that at  $\rho = 6.25$  a.u. the active electron simply exchanges once and is captured by the Be<sup>++</sup> ion. At  $\rho$  = 5.25 a.u. the electron is first "captured" by Be<sup>++</sup>, then "re-captured" by H<sup>+</sup>, and finally exchanges once again. The other graphs, at  $\rho = 4.5$  a.u. and 4.0 a.u., can be interpreted in a similar manner. One can therefore interpret the results by identifying each exchange peak in Fig. 1 with a given number of multiple electron exchanges, as shown in Fig. 2. This interpretation is a direct result of the fact that an AO basis set has been used in the calculation, since only in an AO basis set can we uniquely identify a coefficient such as  $\left|\frac{b_1}{b_1}(R,t)\right|^2$  with a charge density around a particular nucleus. In an adiabatic basis set the history of the collision process shows itself in quite a different way, as seen below.

In order to demonstrate the flexibility of the present model (independently of its "validity") we also performed some calculations for lowenergy head-on collisions. The exchange probabilities for these collisions

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Figure 2.

Electron exchange probability as a function of time through the interaction region. Relative kinetic energy: 56.2 eV. Dashed vertical lines indicate times at which  $R = R_x$ . The interaction time is roughly equal to the time spent between the dashed lines.



are shown in Table I as a function of impact energy in the centre-ofmass frame. The main feature which can be seen in Table I is a reasonably well defined threshold energy for electron exchange at about 2 - 3 eV relative kinetic energy. The history of the exchange probability throughout the collision is shown in Fig. 3 for various impact energies. The low-energy head-on collisions in Fig. 3 display roughly the same type of multiple electron exchange as did the high energy collisions. One interesting feature of Fig. 3 is that, during the collision, the AO coefficients can undergo a significant amount of perturbation away from their original values without necessarily yielding a large final transition probability. For example, during the 1 eV collision in Fig. 3, the charge distribution experiences a major shift from the H atom to the Be atom during the incoming portion of the collision, so that one might expect a large final exchange probability; however, what actually occurs is that this shift in charge distribution reverses itself almost entirely during the outgoing portion of the collision, so that the final transition probability is only 0.001. One might say that the electronic motion during the incoming portion of the collision was reversible, in the sense that the final transition probability is very small. As the impact energy is increased to 4 eV, however, we find that the electronic motion during the outgoing portion of the collision bears less and less resemblance to the behaviour during the incoming portion. In this case the electronic behaviour during the first half of the collision is no longer completely "reversible" and we obtain a large final transition probability. One can therefore decompose the behaviour of the AO coeff-

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## Table I

Asymptotic exchange probabilities  $P(\infty)$  as a function of energy for zero-impact-parameter collisions.

**-**57**-**

Kinetic energy (eV)	Ρ(∞)
1.0	0.001
2.0	0.034
3.0	0.214
4.0	0.456
4.5	0.197
5.0	0.010
5.5	0.288
6.0	0.503
7.0	0.660
8.0	0.716
9.0	0.758

Figure 3.

Electron exchange probability in terms of atomic states as a function of internuclear distance for a variety of zero-impact-parameter collisions. The dashed curves represent the square of the Be(2s) coefficient in the upper adiabatic state.




icients into two types of motion: that which is reversible (and which leads to no net transition probability) and that which is irreversible, in the sense that it does lead to a net transition probability. We anticipate that the reversible component of the electronic motion is related to the nature of the basis set (i.e. whether it be AO or MO) while the irreversible component is independent of the nature of the basis set. To illustrate this we define the adiabatic MO's for this problem and consider the contribution of  $\Phi_{Be}^{}(2s)$  to the upper molecular orbital which leads to H + Be<sup>++</sup> as R  $\rightarrow \infty$ . We find that, as R decreases,  $\Phi_{_{\mathsf{R}_{\mathsf{P}}}}(2s)$  makes an increasingly strong contribution to this MO. Therefore, even if the system evolves adiabatically we will see a significant (reversible) transfer of electron density from H(1s) to Be(2s) during the first half of the collision. The extent of this reversible electron transfer is given by the square of the Be(2s) coefficient in the upper adiabatic state, and is shown as a dashed line in Fig. 3. The difference between the solid and dashed lines of Fig. 3 is a rough measure of the "irreversible" (in this case non-adiabatic) contribution to the electronic motion. A more precise measure is given by transforming the coefficients in the AO representation [Eq. (54)] to their counterparts in the adiabatic representation, using the equations of Section A of this chapter. The resulting transition probabilities are shown in Fig. 4. Figure 4 shows that, if the electrons experience a non-adiabatic perturbation during the first half of the collision, then it is unlikely that they will be able to find their way back to the state in which they were originally located. (Note that the final transition probabilities of Fig. 4 are identical to

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-60-

Figure 4.

Electron exchange probability in terms of adiabatic states as a function of internuclear distance for the same collisions as shown in Fig. 3.



those of Fig. 3, even though the electronic behaviour inside the interaction region (R <  $R_{v}$ ) is quite different.)

In the high energy limit the roles of the adiabatic and AO representations are, to some extent, interchanged. If the impact energy is sufficiently high, then the coefficients in the adiabatic representation will display a large amount of "reversible" motion during the collision, while the AO coefficients will not.

The main feature of interest in Fig. 4 is that the electronic transitions appear to occur within two relatively localized regions of space surrounding the point  $R = R_x$ . This is in keeping with the discussion of the previous section. Within the AO basis set (Fig. 3) the electrons undergo rearrangement throughout the entire course of the collision, not just at  $R = R_{y}$ . The two basis sets used here yield rather different pictures of the electronic behaviour during the collision. These two pictures must not be regarded as being mutually exclusive; they are, instead, complementary views of the same process. Both pictures provide us with a description of the evolution of an electronic state  $\Psi(\vec{r},\vec{R},t)$  in time, where  $\Psi(\overrightarrow{r},\overrightarrow{R},t)$  is initially the  $\Phi_{H}(1s)$  orbital. This electronic state is the same regardless of which basis set is used to describe it (in fact, the transformation procedure has explicitly been defined in such a way that the state  $\Psi(\overrightarrow{r},\overrightarrow{R},t)$  is unaffected by the transformation); however, the appearance of the state  $\Psi(\overrightarrow{r,R},t)$ , as it is projected onto a particular basis set, changes whenever the basis set is changed. Neither of the above two pictures can be regarded as a complete description of the electronic state, since a complete description would have to contain

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information about the phases of the  $b_i(R,t)$  coefficients, as well as their magnitudes. Because these two pictures describe the evolution of the same state in time, and since neither picture is complete, we may say that they enhance each other instead of conflicting with each other. It must be remembered that the electronic state  $\Psi(\vec{r},\vec{R},t)$  is not directly observable when the two atoms are interacting strongly with each other. (This is due partly to the fact that  $\Psi(\vec{r},\vec{R},t)$  is changing rapidly in time.) There are only two pieces of information which are of direct interest in the calculation of observable quantities: 1) the final value of the  $b_i(R,t)$  coefficients, and 2) the trajectory which the nuclei follow during the collision. Neither of these two pieces of information are affected by the change of basis set which is described above, and therefore the differences between the above two pictures of the collision process do not affect the quantities which are actually observed in practice.

The potential energy surfaces for the low energy collisions are shown in Fig. 5. The surfaces are given by  $\underline{b}^{\dagger}\underline{H}$   $\underline{b}$ , as previously discussed (28). Figure 5(a) refers to collisions in which there is a high exchange probability; Fig. 5(b) refers to collisions which have low exchange probability. In and of themselves, these surfaces are of no particular interest since the present nuclear model is not very good at low energies, but they show that the quantity  $\underline{b}^{\dagger}\underline{H}$   $\underline{b}$  is surprisingly well-behaved, considering the complexity of the behaviour of the AO coefficients. The well-behaved, nonoscillatory, nature of  $\underline{b}^{\dagger}\underline{H}$   $\underline{b}$  is a definite asset in the study of more

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Figure 5.

Dynamic potential energy surfaces for a variety of zero-impact-parameter collisions. Dashed curves represent upper and lower adiabatic energy levels. Figure 5(a) portrays collisions with high exchange probability. Solid curves, top to bottom: 4 eV and 9 eV, respectively. Figure 5(b) portrays collisions with small exchange probability. Solid curves, top to bottom: 2 eV, 5 eV, and 10 eV, respectively.



sophisticated nuclear models since, even when a more sophisticated forcelaw is developed (Chapter III), the quantity  $\underline{b}^{\dagger}\underline{H}$  <u>b</u> still represents an important contribution to the energy surface.

The high and low energy collisions discussed above are examples of two extreme types of nuclear motion during a collision: almost-linear motion during high-impact-parameter (glancing) collisions, and linear motion during zero-impact-parameter (head-on) collisions. The intermediate type of nuclear motion was studied by performing collisions at a relative kinetic energy of 4 eV with a wide range of impact parameters. The results are shown in Fig. 6. The area under the curve in Fig. 6(a) represents the total cross section for electron transfer at 4 eV, which works out to be  $5\pi a_0^2$ . (It is encouraging to note that the shape of the curve in Fig. 6(a) is similar to that which can be obtained from a fully quantum mechanical calculation (10).) Figure 6(b) shows the scattering angle in the centre-of-mass frame as a function of impact parameter. The nuclear trajectories for these collisions show the intermediate type of behaviour, between the "glancing" and "head-on" extremes.

The numerical results shown above make it clear that the present model is capable of producing intelligible information about electronic motion during a collision. What is not yet clear is the role of the nuclei in low-energy collisions. The question which must be answered is whether a simple classical nuclear model such as that used above is adequate for the description of low-energy inelastic processes. In singlechannel scattering problems this question is not too difficult to answer since, if the classical nuclear model is not good enough, then this inad-

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Figure 6.

(a) Electron exchange probability multiplied by the impact parameter as a function of impact parameter. Relative kinetic energy 4 eV.

(b) Scattering angle of the nuclei in the centre-of-mass frame as a function of impact parameter.



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equacy will often show itself quite dramatically as a singularity in the classical prediction of the observable (see, for example, rainbow scattering, glory scattering, and metastable states (13,89-91)). In a multichannel scattering problem, however, a classical nuclear model may be inadequate even though the observable calculated using this model is a well-behaved quantity. A few of the features of a "good" nuclear model for low-energy collisions will therefore be mentioned here, in an anticipation of the results presented in the next two chapters:

1) It should be possible to show how the semiclassical equations of motion are related to the corresponding quantum mechanical equations. In the impact-parameter, eikonal, and average-energy-surface theories it is assumed that the nuclear trajectory for the  $\alpha \rightarrow \alpha$  event is the same as that for the  $\alpha \rightarrow \beta$  event (unless these two channels can be de-coupled using symmetry arguments). The relationship between this type of semiclassical theory and the fully quantal theory has been discussed by Bates and Holt (92). They conclude that the relationship is a simple one only if the impact energy is so high that the differences between the various possible nuclear trajectories, corresponding to different electronic eigenstates, can be ignored. For the processes considered here this type of nuclear model will therefore be unintelligible in the sense that the relationship between the semiclassical and quantal equations cannot be clearly defined.

2) For the  $\alpha \rightarrow \beta$  event one would expect the nuclei to move along the  $\alpha$  th eigensurface before the collision takes place, and the  $\beta$  th eigensurface after the collision is over. That is, if the electrons lose the energy  $\underline{E}_{\beta\beta} - \underline{E}_{\alpha\alpha}$  during the collision, then the nuclei should gain the same amount. In general, the nuclei will satisfy this condition only if they obey boundary-value equations of some type, where the boundary conditions are either spatial or temporal.

3) A good nuclear model should satisfy the detailed-balancing requirement. However, since the nuclear motion for the  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \alpha$ events will not normally be the same, it will be necessary to revise the original definition [Eq. (36)] of detailed-balance. The revised definition [for example, Eq. (3.11) of Ref. (15)] must include a statement about the relationship between the nuclear trajectories (as well as the electronic transition probabilities) for the  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \alpha$  events. This statement imposes a rather stringent condition on any low-energy semiclassical theory. It also provides us with a good test of the "usefulness" of a particular theory, since there will not normally be any point in comparing the semiclassical and quantum mechanical predictions if it is not satisfied.

4) At sufficiently low energies one would expect a good semiclassical theory to recognize the existence of energetically forbidden events (which will be called closed channels). There are situations in which the presence of closed channels will affect the behaviour of the system in the open (energetically allowed) channels (93,94). If these channels are included in the basis set of a multichannel semiclassical collision theory (as they should be), and if the theory does not recognize the existence of energetically forbidden events, then it will predict non-zero transition probabilities for events which are known

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to be forbidden. More specifically, such a theory will not be able to describe the threshold behaviour in a particular channel just after it becomes energetically allowed.

The nuclear model used in this chapter does not satisfy these four "requirements". In Chapter III a more sophisticated model will therefore be developed, and applied to a problem for which the average-energysurface theory is inadequate. CHAPTER III. ELECTRONIC EXCITATION: BOUNDARY-VALUE THEORIES

A. Derivation of nuclear model

In this section a familiarity with Ref. (15) and pages 68-71 of Ref. (24) will be assumed. The nuclear model discussed here is designed to overcome some of the shortcomings of impact-parameter and eikonal theories (1,2,59), with regard to which the statement has been made (12): "There remains a general collision problem which has not yet been satisfactorily solved by either treatment: the problem of how to carry out calculations if the classical trajectories in the initial and final states differ markedly." The qualitative discussion of the present nuclear model will be postponed until later.

For the sake of simplicity, consider a one-dimensional scattering problem in which the nuclei can initially and finally be regarded as point particles, while the electrons (or the vibrational degree of freedom) are treated quantum mechanically at all times. In time-dependent quantum mechanics this problem is characterized by a reduced Feynman propagator (15,24):

$$K_{\beta\alpha}(x''t'',x't') = \int_{x't'}^{x''t''} \underbrace{U}_{\beta\alpha}(t'',t') \exp\{iS_{o}[x(t)]\} \mathcal{D}x(t) .$$
(56)

The quantity  $K_{\beta\alpha}(x"t",x't')$  is a quantum mechanical transition amplitude that the state defined at t'  $(t' \rightarrow -\infty)$  will lead to the state defined at t"  $(t" \rightarrow \infty)$ . The state at t' is given by the relative nuclear position x' and the electronic state  $\alpha$ . At t" it is defined analogously. A centre-ofmass reference frame will be used throughout. (A general discussion of

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the reduced propagator, in the context of formal scattering theory, has already been given (15).)

The path integral in Eq. (56) represents a summation over all conceivable nuclear paths  $\{x(t)\}$  which have the end-points (x',t') and (x'',t''), with the evolution matrix  $\underline{U}(t'',t')$  being evaluated exactly for every individual path, using the methods of Chapter II. The functional  $S_o[x(t)]$  is given by

$$S_{o}[x(t)] = \int_{t'}^{t''_{1}} m \dot{x}^{2} dt .$$
 (57)

Within the diabatic representation,  $\underline{U}(t,t')$  satisfies Eq. (32). (The generalization to arbitrary basis sets is carried out most simply by deriving the properties of the nuclear model in the diabatic representation, and then transforming the final results, if desired.) When evaluating the response of  $\underline{U}(t'',t')$  to a change in the nuclear trajectory it will be convenient to use the following representation of  $\underline{U}(t'',t')$ :

$$\underline{U}(t'',t') = \lim_{N \to \infty} \prod_{j=0}^{N} [\underline{1} - i\epsilon \underline{H}(x_j)]$$
(58)

where  $x_i = x(t_i)$ , N $\epsilon = t'' - t'$ , and  $t_o(t_N)$  equals t' (t''). We re-express Eq. (56) in the form

$$K_{\beta\alpha}(x''t'',x't') = \int_{\alpha}^{x''t''} |\underline{U}_{\beta\alpha}(t'',t')| \exp(i\phi) \exp\{iS_0[x(t)]\} \mathcal{J}_x(t)$$
(59)

where  $\phi = \text{Im } \ln \underline{U}_{\beta\alpha}(t'',t')$ . In a semiclassical theory we wish to make

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use of the fact that some paths {x(t)} may be more important than others. The integrand of Eq. (59) is highly oscillatory, especially if we consider the limit as  $\hbar \rightarrow 0$ , which is the usual way of approaching the classical limit of quantum mechanics (see Section 2-3 of Ref. (24)). We therefore anticipate that some nuclear paths will not be very important, in the sense that they will be surrounded by neighbourhoods of destructive interference between paths. The paths which are most important are those which are surrounded by neighbourhoods of constructive interference. If we can define a path (or a finite set of paths) whose phase,  $S_0[x(t)] + \phi$ , is stationary with respect to first-order variations in x(t), then it is clear that this path (which will be called classical), together with a small neighbourhood surrounding it, will represent an important contribution to the path integral.

The semiclassical equations of motion will therefore be derived using the method of stationary phase (22, page 27), which is a special kind of (second-order) asymptotic expansion. Two distinct problems are encountered: 1) determination of which trajectories are most important, and 2) evaluation of the contributions of the neighbourhoods surrounding each "important" trajectory. It will be assumed here that only one trajectory is important within each channel, since the generalization to many trajectories is not very difficult if they are "well separated". We therefore consider a second-order Volterra expansion (95, pages 33-34) of  $\phi$  about the "classical" path given by { $\overline{x}(t)$ }, where the classical path satisfies a stationary-phase constraint analogous to the Principle of Least Action used in single-channel problems (96). The phase of the integ-

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the reduced propagator, in the context of formal scattering theory, has already been given (15).)

The path integral in Eq. (56) represents a summation over all conceivable nuclear paths  $\{x(t)\}$  which have the end-points (x',t') and (x'',t''), with the evolution matrix  $\underline{U}(t'',t')$  being evaluated exactly for every individual path, using the methods of Chapter II. The functional  $S_o[x(t)]$  is given by

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Within the diabatic representation,  $\underline{U}(t,t')$  satisfies Eq. (32). (The generalization to arbitrary basis sets is carried out most simply by deriving the properties of the nuclear model in the diabatic representation, and then transforming the final results, if desired.) When evaluating the response of  $\underline{U}(t'',t')$  to a change in the nuclear trajectory it will be convenient to use the following representation of  $\underline{U}(t'',t')$ :

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(58)

where  $x_i = x(t_i)$ , N $\epsilon = t'' - t'$ , and  $t_o(t_N)$  equals t' (t''). We re-express Eq. (56) in the form

$$K_{\beta\alpha}(x''t'',x't') = \int_{\alpha}^{x''t''} |\underline{U}_{\beta\alpha}(t'',t')| \exp(i\phi) \exp\{iS_0[x(t)]\} \mathcal{J}_x(t)$$
(59)

where  $\phi = \text{Im } \ln \underline{U}_{\beta\alpha}(t'',t')$ . In a semiclassical theory we wish to make

-69-

rand of Eq. (59) is given by  $S_0[x(t)] + \text{Im } \ln \underline{U}_{\beta\alpha}(t'',t')$ . If this phase is extremized (96, page 32) with respect to first-order variations in the nuclear path [using Eqs. (57) and (58)], the following equation of motion is obtained after some manipulation:

$$m \vec{\overline{x}}(t) = -\operatorname{Re}\left\{ \underbrace{\left[ \underline{U}(t'',t) \frac{\partial \underline{H}(x)}{\partial \overline{x}(t)} \underline{U}(t,t') \right]}_{\underline{\partial \overline{x}(t)}} \beta_{\alpha} \right\}$$
(60)

with  $\bar{\mathbf{x}}(t') = \mathbf{x}', \ \bar{\mathbf{x}}(t'') = \mathbf{x}''$ . This result is comparable to that obtained by Pechukas [Eq. (3.3) of Ref. (15)], after allowing for differences in notation. It is a force law governing (classical) nuclear motion for a collision in which the electrons are prepared in state  $\alpha$  and observed in state  $\beta$ . (Note that the force law is non-causal in the sense that it recognizes future electronic and nuclear states before they in fact occur.) We now ignore variations in  $|\underline{U}_{\beta\alpha}(t'',t')|$  as the path varies about the classical path  $\{\bar{\mathbf{x}}(t)\}$ , and factor  $|\underline{U}_{\beta\alpha}^{c1}(t'',t')|$  out of the path integral in Eq. (59), where  $|\underline{U}_{\beta\alpha}^{c1}(t'',t')|$  is evaluated along the path  $\{\bar{\mathbf{x}}(t)\}$ . The phase  $\phi$  is approximated by:

$$\phi \sim \operatorname{Im} \ln \underline{\underline{u}}_{\beta\alpha}^{c1}(t'',t') + \phi^{(1)}[y(t)] + \phi^{(2)}[y(t)]$$
(61)

where  $\phi^{(1)}[y(t)]$  (and  $\phi^{(2)}[y(t)]$ ) are linear (and quadratic) in  $y(t) = x(t) - \overline{x}(t)$ . From the definition of  $\overline{x}(t)$  in Eq. (60) we can easily show that  $\phi^{(1)}[y(t)]$  will cancel with a term linear in y(t) which comes from  $S_o[\overline{x}(t) + y(t)]$ . The semiclassical approximation to the path integral in

Eq. (59) is now given by

$$K_{\beta\alpha}^{c1}(x"t",x't') = \underline{U}_{\beta\alpha}^{c1}(t",t') \exp\{iS_{o}[\overline{x}(t)]\} K(0t",0t')$$
(62)

where K(Ot", Ot') is the "normalizing integral":

$$K(0t'',0t') = \int_{0t'}^{0t''} \exp\{iS_{0}[y(t)] + i\phi^{(2)}[y(t)]\} \mathcal{D}y(t) .$$
(63)

Equation (62) is a semiclassical transition amplitude [as opposed to the quantum mechanical amplitude given in Eq. (56)] for an event in which the initial and final nuclear and electronic states are known. It is composed of three parts:  $\underline{U}_{\beta\alpha}^{cl}(t",t")$  is the electronic transition amplitude, evaluated using a classical nuclear trajectory;  $\exp\{iS_o[\bar{x}(t)]\}$ is the contribution due to the single classical nuclear trajectory, and has a magnitude of one; K(0t",0t') contains the contributions of nuclear paths within a small neighbourhood of the classical path. We note that the semiclassical approximation, as defined here, consists of ignoring all variations in the magnitude of the integrand of Eq. (59) (and taking account of the phases only to second order) as the path varies about the classical path. (It is perhaps worthwhile noting that K(0t",0t') is actually a functional of  $\bar{x}(t)$ , although the notation does not show this dependence (95, pages 33-34).)

The problem is now one of calculating K(0t",0t'). We assume that the path  $\{\overline{x}(t)\}$  is known and concentrate instead on the independent variable y(t).  $\phi^{(2)}[y(t)]$  is expressible as (95):

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$$\phi^{(2)}[y(t)] = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial}{\partial \overline{x}_{i}} \frac{\partial}{\partial \overline{x}_{j}} [\operatorname{Im} \ln \underline{U}_{\beta\alpha}(t'',t')] y_{i} y_{j}$$
(64)

where the time interval (t'' - t') has been broken up into N steps of length  $\varepsilon$  (with N arbitrarily large), and where  $\underline{U}(t'',t')$  is given by Eq. (58). It is convenient to distinguish three cases in Eq. (64), namely j < i, j = i, and j > i, in order to avoid confusion in the time-ordering of operators. After some manipulation we obtain

$$\phi^{(2)}[y(t)] = g(0t'', 0t')$$
(65)

where g(Ot", Ot') is a special case of the functional

$$g(yt,0t') = -\frac{1}{2} \operatorname{Re} \int_{t}^{t} ds \frac{\frac{F_{\beta\alpha}^{(2)}(s) y(s)^{2}}{\underline{U}_{\beta\alpha}^{c1}(t'',t')}}{-\frac{1}{2} \operatorname{Im} \int_{t}^{t} ds \int_{t}^{s} dr \frac{F_{\beta\alpha}(s,r) y(s) y(r)}{\underline{U}_{\beta\alpha}^{c1}(t'',t')}$$

$$(66)$$

$$-\frac{1}{2} \operatorname{Im} \int_{t}^{t} ds \int_{s}^{t} dr \frac{F_{\beta\alpha}(r,s) y(s) y(r)}{\underline{U}_{\beta\alpha}^{c1}(t'',t')}$$

$$+ \frac{1}{2} \operatorname{Im} \left\{ \left[ \int_{t}^{t} ds \frac{\underline{F}_{\beta\alpha}^{(1)}(s) \ y(s)}{\underline{U}_{\beta\alpha}^{c1}(t'',t')} \right]^{2} \right\}$$

The notation g(yt,0t') implies that the path  $\{y(s)\}$  has endpoints y(t) = y, y(t') = 0. The <u>F</u> matrices are given by:

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$$\underline{\underline{F}}^{(1)}(t) = \underline{\underline{U}}^{c1}(t'',t) \underbrace{\partial \underline{\underline{H}}(\underline{x})\underline{\underline{U}}^{c1}(t,t')}_{\partial \overline{\underline{x}}(t)}$$

$$\underline{\underline{F}}^{(2)}(t) = \underline{\underline{U}}^{c1}(t'',t) \underbrace{\partial^{2}\underline{\underline{H}}(\underline{x})\underline{\underline{U}}^{c1}(t,t')}_{\partial \overline{\underline{x}}(t)^{2}}$$
(67)

$$\underline{F}(s,t) = \underline{U}^{c1}(t'',s) \frac{\partial \underline{H}(x)}{\partial \overline{x}(s)} \underline{U}^{c1}(s,t) \frac{\partial \underline{H}(x)}{\partial \overline{x}(t)} \underline{U}^{c1}(t,t') , \quad s > t.$$

The definition of  $\phi^{(2)}[y(t)]$  in Eq. (65) is to be compared with Eq. (3.5) of Ref. (15).

There are two distinct types of contributions to  $\phi^{(2)}[y(t)]$ . The first type is contained within a single integral in Eq. (66), and has been taken account of in the previous normalization of this path integral (15). This type of term has a fairly well defined single-channel analogue (14). The second type is due to double integrals in Eq. (66), and has no singlechannel analogue. (We are not aware of any previous attempts to take exact account of these double integral terms.) It represents coupling between two first-order deviations from classical motion, occurring at different times, and is a reflection of the non-causal nature of the theory. This type of coupling is due to the fact that the potential energy which controls the nuclear motion cannot be expressed in the form  $V(\bar{x},t)$ , but must be regarded as a functional of the entire path  $\{\bar{x}(s)\}$ . The presence of such coupling terms in a closely related problem has been noted by Feynman, and the remarks made at the end of Section 3-10 of Ref. (24) apply here. In particular, we note that it is not possible to define a WKBtype wave function for the translational motion of the nuclei, and that

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we are therefore quite unable to observe the "classical nature" of the nuclei during the course of the collision. It should, however, be possible to define this type of wave function long before, or long after, the collision if the net effect of the non-causal terms is constant in these regions.

Despite the conceptual difficulties associated with the double integral contributions, it is possible to evaluate the normalizing integral exactly in practice. One possible approach would be to try to find a change of variable from y(t) to  $z(\tau)$  such that the definition of  $\phi^{(2)}[z(\tau)]$  in terms of  $z(\tau)$  would contain only single integrals. The relationship between  $z(\tau)$  and y(t) would have to be of the type:

$$z(\tau) = \int_{t}^{t''} A(\tau, t) y(t) dt$$

In this way the non-causal contributions would be temporarily hidden within the definition of  $z(\tau)$  and the treatment of them could be postponed until later in the derivation. An approach similar to this has been used by Friedrichs and Shapiro (97, page I-18), and is probably more amenable to rigor than our approach. We use a method similar to that of Pechukas (Appendix of Ref. (14)).

Consider the quantity K(0t,0t'), satisfying the constraint that  $K(0t,0t') \rightarrow K(0t'',0t')$  as  $t \rightarrow t''$ . K(0t,0t') is not uniquely specified by this constraint and we arbitrarily choose a definition which yields the simplest possible dependence on t. Define K(0t,0t') as the limit as  $y \rightarrow 0$  of

$$K(yt,0t') = \int_{0t'}^{yt} \exp\{iS_{o}(yt,0t') + ig(yt,0t')\} \mathcal{D}_{y}(t)$$
(68)

where g(yt, 0t') is defined by Eq. (66), and where

$$S_{o}(yt,0t') = \int_{t'}^{t} \frac{1}{2} m \dot{y}^{2} dt$$
 (69)

We are interested in the time-dependence of K(0t,0t'), but it is convenient to first consider the dependence of K(yt,0t') on y. To determine this dependence we consider the particular path which makes the phase of the integrand of Eq. (68) stationary with respect to first-order variations in the path. This path (denoted by  $\{\overline{y}(s)\}$ ) will move between the space-time points (0,t') and (y,t), and can be shown to satisfy the integro-differential equation

$$m \overline{y}(s) = - f[\overline{y}(s)], \quad t' < s < t, \quad (70)$$

where

$$f[z(s)] = \operatorname{Re}\left[\frac{\underline{F}_{\beta\alpha}^{(2)}(s) \ z(s)}{\underline{U}_{\beta\alpha}^{c1}(t'',t')}\right]$$

+ 
$$\operatorname{Im}_{t'} \int dr \frac{\underline{F}_{\beta\alpha}(s,r) z(r)}{\underline{U}_{\beta\alpha}^{c1}(t'',t')} dr$$

+ (continued on next page)

+ 
$$\operatorname{Im}_{s} \int_{\alpha}^{t} dr \frac{\underline{F}_{\beta\alpha}(r,s) z(r)}{\underline{U}_{\beta\alpha}^{c1}(t'',t')}$$
 (71)

$$- \operatorname{Im} \left\{ \frac{\underline{F}_{\beta\alpha}^{(1)}(s)}{\underline{\underline{U}}_{\beta\alpha}^{c1}(t'',t')} \int_{t'}^{t} dr \frac{\underline{F}_{\beta\alpha}^{(1)}(r) z(r)}{\underline{\underline{U}}_{\beta\alpha}^{c1}(t'',t')} \right\}$$

Because K(yt,0t') has an "action" which is quadratic in y(s) we can perform an exact quadratic expansion of K(yt,0t') about the path  $\{\overline{y}(s)\}$ in terms of the variable  $\eta(s) = y(s) - \overline{y}(s)$  to obtain

$$K(yt,0t') = K(0t,0t') \exp(i\theta)$$
(72)

where  $\theta = S_0(yt,0t') + g(yt,0t')$ , and  $\theta$  is evaluated using the path  $\{\overline{y}(s)\}$ in Eqs. (66) and (69). In Eq. (72), K(0t,0t') is defined using the variable n(s), but is identical to K(0t,0t') defined as the limit of Eq. (68) as  $y(t) \rightarrow 0$ . Furthermore, K(0t,0t') has no dependence on the path  $\{\overline{y}(s)\}$ . Because  $\theta$  is evaluated along a path of stationary phase, we have

$$\partial \theta / \partial y(t) = m \, \overline{y}(t)$$
 (73)

The quantity  $\partial^2 \theta / \partial y^2(t)$  is also of interest and can be re-expressed as

$$\partial^2 \theta / \partial y^2(t) = m \frac{d}{dt} \ln u(t)$$
 (74)

where  $u(t) = [\partial \overline{y}(t) / \partial \overline{y}(t')]_{\overline{y}(t')}$ , and where u(t) is a solution of the

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equation

$$m \ddot{u}(s) = - f[u(s)] \tag{75}$$

which is solved between the times t' and t, with f[u(s)] given by Eq. (71) and with u(t') = 0,  $\dot{u}(t') = 1$ . We note that u(t) does not depend on the path  $\{\overline{y}(s)\}$  and that  $\theta$  is therefore a quadratic function of the endpoint y(t). We consider a Taylor Series expansion of  $\theta$  about the point y(t) = 0and note that it can be truncated to second order without introducing any error. In order to determine the zeroth-order and first-order coefficients in the expansion it is necessary to find the path  $\{\overline{y}(s)\}$  between the points (0,t') and (0,t). A solution of the equation of motion for  $\overline{y}(s)$ , subject to these endpoint constraints, is the path  $\overline{y}(s) = 0$  for t > s > t'. The "action" developed along this path and the momentum  $m\overline{y}(t)$  are both zero. Therefore the first two terms of the expansion do not contribute, and we find

 $\theta = \frac{1}{2} m \left[ \frac{d}{dt} \ln u(t) \right] y^2 .$  (76)

The dependence of K(yt, 0t') on y is therefore known exactly.

Given this result, it is now possible to relate  $K(0,t+\epsilon;0t')$  and K(0t;0t'):

$$K(0,t+\varepsilon;0t') = \int_{-\infty}^{\infty} \frac{dz}{A} \int_{0t'}^{zt} \exp[iS_{0}(0,t+\varepsilon;0t') + ig(0,t+\varepsilon;0t')] \mathcal{D}_{y}(s)$$
(77)

where A =  $(2\pi i\epsilon/m)^{\frac{1}{2}}$  [see Ref. (24)]. From Eq. (69) we find

$$S_{o}(0,t+\varepsilon;0t') = S_{o}(zt,0t') + mz^{2}/2\varepsilon .$$
(78)

The relationship between  $g(0,t+\epsilon;0t')$  and g(zt,0t') is not as simple as Eq. (78), because the difference of these two quantities is itself a functional of the path  $\{y(s)\}$  between the points (0,t') and (z,t). However, it is possible to show that

$$g(0,t+\varepsilon;0t') = g(zt,0t') + \varepsilon zh[y(s)]$$
(79)

where h[y(s)] is a linear functional of the path  $\{y(s)\}$ . Because the second term in Eq. (79) is of order  $\varepsilon$ , one might expect it to contribute only negligibly. We substitute Eqs. (78) and (79) into Eq. (77) and make use of the definition of K(zt,Ot') in Eq. (68), to obtain

$$K(0,t+\varepsilon;0t') = \int_{-\infty}^{\infty} [K(zt,0t') + \varepsilon z \tilde{h}(z,t)] \exp(imz^2/2\varepsilon) \frac{dz}{A}$$
(80)

where  $\tilde{h}(z,t)$  is the leading term due to h[y(s)] in Eq. (79). Using Eqs. (72) and (76) to specify the z-dependence of K(zt,Ot'), and integrating over z, we obtain

$$K(0,t+\varepsilon;0t') = K(0t,0t') \left[1 + \varepsilon \frac{d}{dt} \ln u(t)\right]^{-\frac{1}{2}} + O(\varepsilon^{3/2}) .$$
(81)

In the limit as  $\varepsilon \rightarrow 0$  this becomes

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$$\frac{d K(0t,0t')}{dt} = -\frac{1}{2} K(0t,0t') \frac{d \ln u(t)}{dt}$$
(82)

and integration yields

$$K(0t, 0t') = C u^{-\frac{1}{2}}(t)$$
 (83)

where C is a constant. The expression obtained here for K(Ot,Ot') is comparable to Eq. (A4) of Ref. (14), except that in our case u(t) is determined by an integro-differential equation [Eq. (75)] instead of an initial-value differential equation.

We now consider the limit as  $t \to t''$ . In this limit we find that K(0t'',0t') is determined by  $[\partial \overline{y}(t'')/\partial \dot{\overline{y}}(t')]_{\overline{y}(t')}$ . Since this quantity is known to be independent of the path  $\{\overline{y}(t)\}$ , we anticipate that it may be uniquely determined by the path  $\{\overline{x}(t)\}$ . In particular, it can be shown that

$$\left( \frac{\partial \overline{\mathbf{x}}(\mathbf{t}^{"})}{\partial \dot{\overline{\mathbf{x}}}(\mathbf{t}^{"})} \right)_{\overline{\mathbf{x}}(\mathbf{t}^{"})} = \left( \frac{\partial \overline{\mathbf{y}}(\mathbf{t}^{"})}{\partial \dot{\overline{\mathbf{y}}}(\mathbf{t}^{"})} \right)_{\overline{\mathbf{y}}(\mathbf{t}^{"})}$$
(84)

The left hand side of Eq. (84) is obtained by differentiating Eq. (60) with respect to  $\dot{\overline{x}}(t')$  and deriving an integro-differential equation of motion for  $[\partial \overline{x}(t)/\partial \dot{\overline{x}}(t')]_{\overline{x}(t')}$ , taking account of the fact that  $\underline{U}(t'',t)$ ,  $\underline{U}(t,t')$ , and  $\underline{U}(t'',t')$  [as well as  $\partial \underline{H}(x)/\partial \overline{x}(t)$ ] are all functions of  $\dot{\overline{x}}(t')$ ; for example:

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$$\frac{\partial \underline{U}(t,t')}{\partial \dot{x}(t')} = -i \int_{t'}^{t} \underline{U}(t,s) \frac{\partial \underline{H}(x)\underline{U}(s,t')}{\partial \overline{x}(s)} \begin{pmatrix} \frac{\partial \overline{x}(s)}{\partial \dot{x}(t')} \end{pmatrix}_{\overline{x}(t')} ds .$$
(85)

A comparison of the resulting equation for  $[\partial \bar{x}(t')/\partial \dot{\bar{x}}(t')]_{\bar{x}}(t')$  with Eq. (75) will yield the equality in Eq. (84). We therefore find that

$$K(0t'',0t') = \left[ \frac{m}{2\pi i \left[ \frac{\partial \overline{x}(t'')}{\partial \overline{x}(t')} \right]_{\overline{x}(t')}}{\overline{x}(t')} \right]^{\frac{1}{2}}$$
(86)

where the proportionality constant is determined by the free-particle limit, and where the phase may undergo discontinuous changes at turning points of the nuclear motion (14). For a scattering problem this result can be rewritten as (14)

$$K(0t'',0t') = \left[ \frac{m}{2\pi i (t''-t')} \left[ \frac{\partial \overline{x}(t'')}{\partial \overline{x}(t')} \right]_{\underline{x}(t')} \right]_{\underline{x}(t')}$$
(87)

where t" is a time just after the scattering has occurred, and t' is a time in the far past. With t" and t' defined in this way it can be seen that the partial derivative in Eq. (87) is given by the ratio of the final momentum over the initial momentum.

A generalization to three dimensions is also possible (14), in which case the partial derivative in Eq. (87) becomes a Jacobian determinant of a final position with respect to an initial position. The expression for K(0t",0t') in a three dimensional problem will therefore contain the quantity  $d\Omega/d\sigma$ , which yields the classical expression for the differential cross section.

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The form of the result obtained here for the normalization constant [Eq. (87)] is identical to that obtained in Eq. (3.9) of Ref. (15) in the sense that both normalizations are determined by the response of the endpoint of a classical trajectory to a change in the initial position, but the way in which this response is calculated in practice in the two cases is quite different. To evaluate the normalization constant derived by Pechukas (15) one must perform a single trajectory calculation with a particular set of initial conditions, parameterize the resulting energy surface to have the form  $V(\bar{x},t)$ , and subsequently constrain the energy surface to retain this form as the response of the trajectory to a change in the initial conditions is evaluated. To evaluate our result for the normalization we would perform two entirely independent classical trajectory calculations, with slightly different initial conditions, and the partial derivative which is required would be evaluated numerically using these two trajectories. In this case it is clear that no constraints are being imposed on the "response" of the energy surface to a change in initial conditions. The difference between these two methods of determining the normalization is due precisely to the presence of double integrals in the expression for  $\phi^{(2)}[v(t)]$  in Eq. (65). To some extent, this result has been anticipated by Pechukas [see the paragraph following Eq. (3.9) of Ref. (15)], but we are not aware of any previous derivation of it.

It is of some interest to consider situations in which the two definitions of the normalization yield different numerical results. To do this, it is necessary to consider a three dimensional problem since

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the normalization for a one dimensional problem is determined entirely by the long-range behaviour of the energy surface and will therefore be the same regardless of which definition is used. In a three dimensional calculation we find that K(Ot",Ot') is related to  $d\Omega/d\sigma = \sin\theta \ d\theta/b$  db. The quantity  $d\theta/db$  is of particular interest, since the two procedures described above for the calculation of this type of derivative will yield different answers. The actual energy surface for the collision can be put into the form  $V_{\beta\alpha}(\bar{\mathbf{R}}, \mathbf{t}, \mathbf{E}, \mathbf{b})$ , where E and b are the total impact energy and impact parameter, respectively. If this energy surface is used to evaluate the quantity  $d\theta/db$ , then we will not obtain the same result as we would if the energy surface were constrained to have the form  $V_{\beta\alpha}(\bar{\mathbf{R}}, t)$ while  $d\theta/db$  was evaluated. The difference between these two methods of evaluating  $d\Omega/d\sigma$  will be due to the dependence of the energy surface on the impact parameter b. (For an example of a situation in which this dependence is rather pronounced, see Figure 8.)

The importance of the normalizing integral K(0t",0t') lies in the fact that it contains the expression for the differential cross section in a three dimensional scattering problem. Using the arguments of formal scattering theory, and the value of K(0t",0t') given by Eq. (87), it can be shown (15) that the differential cross section for the  $\alpha \rightarrow \beta$  event is given by

 $\frac{b \ db}{\sin\theta \ d\theta} |\underline{U}_{\beta\alpha}(t'',t')|^2$ 

where b and  $\theta$  are the impact parameter and scattering angle, respectively,

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and where it must be remembered that no constraints are imposed on the potential energy surface while  $d\theta/db$  is evaluated. The interpretation of this expression has been given by Pechukas (15): "The cross section for scattering in a given direction and with a given quantum transition is simply the classical cross section for scattering of the atoms in that direction times the probability for the quantum transition." This completes the formal aspect of the boundary-value nuclear model. Applications will be discussed below.

## B. Collisions between He<sup>+</sup> and Ne

The He<sup>+</sup>-Ne system is a good test of the usefulness of the boundaryvalue theory described above since it displays new qualitative features which are experimentally observable, and which cannot be understood in terms of an initial-value nuclear model. Experimental information about this system has been produced by Aberth and Lorents (98) and has been given an extensive theoretical analysis (5-9). The present calculation is an attempt to supplement the existing interpretation of some of this information. We present the results of elastic and inelastic scattering of He<sup>+</sup> off Ne, at an impact energy of 70.9 eV, using a two-state electronic basis set together with a classical nuclear model. The impact energy is sufficiently low so that the exact nature of the nuclear model is quite important for both elastic and inelastic processes. This therefore allows one to critically test the value of the nuclear model used here even though the comparison with experimental results is only a qualitative one.

The main experimental feature in which we are interested is a perturbation (99) in the elastic scattering differential cross section which has been observed for He<sup>+</sup>-Ne, as well as for other systems. It has been associated with the onset of inelastic processes due to a curve-crossing of diabatic energy surfaces. A number of theoretical discussions of this perturbation have already been given (54,81,100-102). They have been successful in qualitatively explaining the fact that the perturbation is localized in the threshold region where the classical turning point

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is close to the point at which the energy levels cross. However, they suffer from the fact that the interpretation is based on a Stueckelberg-Landau-Zener (SLZ) model of electronic behaviour. The present calculation is an attempt to find out whether the same interpretation is obtained when SLZ theory is not appealed to. In the course of the calculation it was found that the precise nature of the nuclear model was crucial in determining the form of this perturbation, and therefore the theory presented here concentrates only on the nuclear motion, assuming that the electronic interactions are known in some sense. The nuclear model used here was developed by Pechukas (15) and has been discussed in the previous section. The classical equations are retrieved by performing a stationary-phase approximation to a reduced Feynman propagator [Eq. (56)]. As a result, one obtains an interpretation of the electronic motion which is qualitatively quite similar to the impact-parameter interpretation, although the nuclear equations of motion are quite different. In the present theory it is found that the nuclear trajectory can only be determined through the solution of a non-linear two-point boundary-value problem (103). The reason for this is that the force law governing nuclear motion has a dependence on the future behaviour of the electrons, as well as their past behaviour. In special cases it has been shown (15,104) that this difficulty can be removed (or at least simplified) if one is willing to make analytical approximations, such as SLZ, in the electronic equations of motion. In general, however, one is left with a boundary-value problem whose numerical solution is non-trivial.

Before attempting a boundary-value calculation we might briefly

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consider two other "classical" nuclear models: stationary-energy-surfaceimpact-parameter (SESIP) theory, and the corresponding average-energysurface theory. For the reasons discussed at the end of Chapter II, neither of these theories yielded worthwhile information in the present case, but both were helpful in the qualitative interpretation of the electronic motion. The SESIP theory will also be used here as a first approximation in an iterative procedure to be described below.

Two problems which must be dealt with before a numerical calculation can be attempted are: how to interpret the force law of Eq. (60), and how to numerically solve the boundary-value problem represented by Eqs. (32) and (60). The numerical method will be discussed below. The discussion of the force law centres around this question: How many trajectories contribute to any particular event and how are they interrelated? We mention here three ways in which multiple nuclear trajectories can occur in the present model. The first way can be seen by noting that the trajectory for the  $\alpha \rightarrow \alpha$  (elastic) event is in general not the same as that for the  $\alpha \rightarrow \beta$  (inelastic) event. It is at this point that the present calculation differs from both the stationary- and the average-energy-surface theories since they do not make this distinction. An example of the second type of multiplicity is the rainbow-scattering phenomenon, where two or more trajectories with different impact parameters lead to the same scattering angle. This type of multiplicity did not occur in the present calculation, although it could have, if the matrix elements and impact energy had been different. As a result, our interpretation of the perturbation in the

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elastic cross section states that it is not a rainbow-scattering effect. in contrast to the interpretation given by other workers (54,102). In order to understand the rainbow-scattering interpretation (54), one must consider a third type of multiplicity of trajectories. This occurs when the same impact parameter leads to two different scattering angles. For a two-state curve-crossing problem, if SLZ theory is used, it occurs for the following reason: It is assumed that the electronic transition occurs instantaneously. Once this assumption is made it is natural to treat the region inside the crossing point separately from the outside region. In the inside region the nuclear motion is decomposed into two components, each following a different diabatic energy surface. (This procedure will be discussed in more detail in the following section.) These two components are regarded as representing two distinct physical situations, whose relative probability is given by SLZ theory. As a result of this decomposition one finds a single impact parameter leading to two different scattering angles. In special cases (54) this decomposition incidentally leads one to conclude that rainbow-scattering will occur. (Note that the numerical results obtained by Olson and Smith do not depend on this assumption, although their interpretation does.) An interesting formal motivation for this procedure has been given by Pechukas and Davis [see the paragraph following Eq. (2.6) of Ref. (104)]. However, we emphasize that this procedure is reasonable only if one is willing to make the assumption that the transition at the crossing point occurs essentially instantaneously. In the present calculation we have not made this assumption and therefore observe only one trajectory corresponding to any part-

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icular impact parameter.

Because of the fact that the equations of motion are non-linear the present boundary-value problem must be solved iteratively; i.e. in addition to the iterative procedure (Runge-Kutta-Gill) used to solve the initial-value electronic equations of motion, a separate iterative procedure is required before the nuclear force law can be satisfied exactly. Quadratically convergent algorithms for the solution of non-linear boundary-value problems are available (103), but were not thought to be very useful in the present case; instead, an ad hoc algorithm was developed. The rate of convergence of this algorithm is not known apriori but it has the advantage of requiring very little modification in the program used to solve the initial-value problem encountered in the averageenergy-surface theory (28,57). The algorithm proceeds by changing the original boundary-value problem into a sequence of initial-value problems which ultimately converge to a boundary-value solution. This is done by isolating all of the dependence on the future within a single constant matrix U(t'',t'). Given Eq. (33), the force law [Eq. (60)] is rewritten as

$$m \overrightarrow{R} = -Re \left( \frac{[\underline{U}(t'',t')\underline{U}^{\dagger}(t,t')\nabla_{\underline{R}\underline{H}}(\underline{R})\underline{U}(t,t')]}{\underline{U}_{\beta\alpha}(t'',t')} \right) .$$
(88)

The form of this force law suggests the following procedure: Guess an energy surface and perform a SESIP calculation, using it to obtain an approximate estimate of  $\underline{U}(t",t')$ . Given this estimate one can then calculate an improved force law using Eq. (88) and eventually an improved value of U(t",t'). In this way a sequence of initial-value problems is

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solved until two estimates of  $\underline{U}(t",t')$  agree. The specific form of the force law which was used was, therefore,

$$m \overset{::}{R} = - \operatorname{Re}\left(\frac{[\underline{U}^{n-1}(t'',t')\underline{U}^{n\dagger}(t,t')\nabla_{\underline{R}}\underline{H}(\underline{R})\underline{U}^{n}(t,t')]_{\beta\alpha}}{\underline{U}^{n-1}_{\beta\alpha}(t'',t')}\right) \quad (89)$$

Equation (32), which determines  $\underline{U}^{n}(t,t')$ , is solved simultaneously with Eq. (89). The label n refers to the n <u>th</u> initial-value collision. The force law for the n <u>th</u> collision recognizes the future electronic behaviour through the matrix  $\underline{U}^{n-1}(t",t')$ , obtained from the previous collision. The first question which must be answered is the following: Does the fact that two successive estimates of  $\underline{U}(t",t')$  agree necessarily imply that we have converged to a true solution of the boundary-value problem represented by Eqs. (32) and (60)? This can be quickly answered by setting n = n - 1 in Eq. (89). We might also ask whether this algorithm necessarily converges, or how quickly it converges, or even whether it converges to a unique solution. None of these questions have been given a general answer here, but they will be partially answered below.

It is of some interest to note the behaviour of the potential energy, both exact and approximate, before and after the collision. First of all, we note that if convergence has been obtained, then an energy conservation law can be proven, in the sense that

$$\frac{1}{2} \text{ m } \dot{\vec{R}}^2 + \text{Re}\left(\frac{[\underline{U}(t'',t)\underline{H}(R)\underline{U}(t,t')]_{\beta\alpha}}{\underline{U}_{\beta\alpha}(t'',t')}\right) = \text{constant.}$$
(90)

Second, it can be shown that even if convergence has not been obtained,

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one still has the identity

$$\frac{1}{2} \operatorname{m} \dot{\vec{R}}^{2} + \operatorname{Re} \left( \frac{\left[ \underline{U}^{n-1}(t'',t') \underline{U}^{n\dagger}(t,t') \underline{H}(R) \underline{U}^{n}(t,t') \right]_{\beta\alpha}}{\underline{U}^{n-1}_{\beta\alpha}(t'',t')} \right) = \operatorname{constant.} \quad (91)$$

This last identity is very useful in practice since it provides one with a sensible criterion with which to determine the time interval in the Runge-Kutta-Gill procedure used to solve the initial-value problem. Equation (90) is of formal interest but is of no value in the actual numerical calculation. Formally, Eq. (90) shows that at time t' the potential energy is given by  $\underline{H}_{\alpha\alpha}(\infty)$  and at time t" it is given by  $\underline{H}_{\beta\beta}(\infty)$ , as was anticipated on page 65. Equation (91), on the other hand, shows that at time t' the potential energy is given by  $\underline{H}_{\alpha\alpha}(\infty)$ , and at time t" the potential energy could be anything, depending on how close one is to convergence. When convergence is obtained Eq. (91) reduces to Eq. (90).

The program used to solve this problem is a modified version of one developed for use with the average-energy-surface theory. (One version of the boundary-value program is given in Appendix II.) The main difference is the presence of a new force law [Eq. (89)]. In addition, the original program was modified so that it automatically performed a whole series of collisions with the same initial conditions but with a revised estimate of  $\underline{U}(t",t')$ . The calculation was initiallized by choosing the diabatic energy surface  $\underline{H}_{11}(R)$  and performing one SESIP calculation. The succeeding collisions at that impact parameter were then performed using Eq. (89) to generate the force law. The most sensitive criterion for convergence was found to be the scattering angle. The iterative procedure was normally continued until two successive scattering angles differed by less than 0.001°. An additional convergence criterion was the final value of the potential energy, since this value is known for any particular electronic event.

The matrix  $\underline{H}(R)$ , which governs the electronic interaction between He<sup>+</sup> and Ne, was identical to that already used by Olson and Smith (54), and will not be repeated here. The impact energy was 70.9 eV, with an excitation energy of 16.8 eV for the inelastic collisions. The pseudo-crossing occurs at  $R_x = 2.02$  a.u., with  $\underline{H}_{11}(R_x) = \underline{H}_{22}(R_x) = 0.530$  a.u. and  $\underline{H}_{12}(R_x) = 0.00819$  a.u.

The elastic differential cross section was obtained by performing collisions at fifty different impact parameters, with a constant spacing of 0.02 a.u. between neighbouring impact parameters. At any given impact parameter b, less than five initial-value collisions were required in order to obtain convergence. (Each initial-value collision took about 60 sec. computing time on an IBM 360-65 system.) The reason for this was that the diabatic surface  $\underline{H}_{11}(R)$  provided a very good initial estimate of the true energy surface, at least for elastic scattering. However, the deviations of the true energy surface from the diabatic surface led to pronounced effects in the differential cross section.

Figure 7(b) shows the quantity  $P_{12}$  plotted as a function of angular momentum. The angular momentum  $\ell$  is obtained from the relation  $\ell = bp$  where p is the initial momentum (178.76 a.u.). It can be seen that  $P_{12}$  shows the usual oscillations associated with a curve-crossing. A rough estimate of the threshold for these oscillations is given by  $\ell_x = 322$ .

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- (a)  $_{\rm BV}^{}/_{\rm DIAB}^{}$  as a function of angular momentum & for elastic collisions.
- (b)  ${\rm P}_{12}$  as a function of  ${\rm l}$  for the same collisions as in (a).



If  $l > l_x$ , then the nuclei will not reach the crossing point at R = R<sub>x</sub>. The results in Fig. 7(b), however, do not explicitly recognize this threshold since SLZ theory is not being used. It is of some interest to compare Fig. 7(b) with the distorted-wave (DW) result [Fig. 4 of Ref. (54)]. Qualitatively, the two results are very similar, although there are quantitative differences. The present calculation displays a spacing of about 25% units between successive peaks, whereas the DW spacing is approximately 16% units. This discrepancy is presumably due to the fact that P<sub>12</sub> in Fig. 7(b) has been calculated using an elastic trajectory. If P<sub>12</sub> is obtained using an inelastic scattering trajectory the comparison is much more encouraging (see below). Another feature of Fig. 7(b) is the fact that the value of P<sub>12</sub> was essentially the same regardless of whether the diabatic surface or the final (dynamic) surface was used. That is, the electronic behaviour for elastic scattering was quite insensitive to changes in the nuclear model.

We now consider the effect of the electronic behaviour on the nuclear motion. It is this effect which is particularly dramatic in the present calculation, and in fact provides the only justification for taking the trouble to solve the full boundary-value problem in the first place. It can be seen by an inspection of the deflection function (scattering angle  $\theta$  vs. impact parameter b). For elastic scattering,  $\theta$  was invariably very close to the diabatic prediction, which excludes the possibility of rainbow-scattering. The difference between the two angles was never more than  $0.5^{\circ}$ . Instead of plotting  $\theta$  directly we have shown, in Fig. 7(a), a plot of  $\theta_{\rm BV}/\theta_{\rm DIAB}$  vs.  $\ell$ .  $\theta_{\rm BV}$  is obtained from the boundary-

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value calculation and  $\theta$  is the diabatic prediction. The most striking DIAB (and unexpected) feature of Fig. 7(a) is the fact that  $\theta_{\text{BV}}/\theta_{\text{DTAB}}$  is oscillatory and can be correlated closely with the oscillations of P<sub>12</sub>. The only exception to the correlation is the shallow minimum at l = 334. This minimum comes from a collision where the turning point is greater than the crossing point and is therefore in the "subexcitation" region. It can be qualitatively understood by noting that the nuclei display a tendency to follow the bottom adiabatic, not the diabatic, surface in this region. For collisions where  $\ell$  < 322 this initial tendency towards adiabatic behaviour is quickly replaced by a tendency to follow the diabatic prediction instead. The interpretation of the scattering angle can best be done by an inspection of the energy surfaces for these collisions. Fig. 8 shows the energy surfaces for collisions at impact parameters 1.42, 1.50, 1.60, and 1.70 a.u. The quantity  $\overline{E}(R,t) - \underline{H}_{11}(R)$  has been plotted vs. R, where  $\overline{E}(R,t)$  is the potential energy obtained in the boundary-value calculation. For comparison, the adiabatic surfaces, which display an avoided crossing, have also been shown. The impact parameters 1.50 and 1.70 correspond to the first two maxima in Fig. 7. The other two impact parameters generate minima in Fig. 7. One can see that the energy surface for any particular collision is very smooth (non-oscillatory), but that the surface as a whole displays an oscillatory dependence on b. It is this dependence on b which generates the oscillatory behaviour in the function  $\theta_{\rm BV}/\theta_{\rm DIAB}$ . The fact that this oscillation is correlated with P can be analytically understood by an inspection of Eq.(90). However, we have not been able to analytically explain why the energy surfaces at b = 1.50 and

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Figure 8.

Difference between the dynamic energy surface  $\overline{E}(R,t)$  obtained from the boundary-value calculation and the diabatic surface  $\underline{H}_{11}(R)$ , plotted as a function of internuclear separation, for elastic collisions at impact parameters 1.42, 1.50, 1.60, and 1.70 a.u. The dashed lines are the corresponding adiabatic surfaces.

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1.70 a.u. are above instead of below the other two surfaces; i.e. the existence of the correlation is reasonable, but there is a plus or minus ambiguity as to which way it should affect the energy surface. Another feature seen in Fig. 8 is the fact that the energy surfaces corresponding to a zero in  $P_{12}$  fall completely between the two adiabatic limits, whereas those corresponding to  $P_{12} \neq 0$  do not. This can be easily understood by setting  $P_{12} = 0$  in Eq. (90) and making use of the unitarity of  $\underline{U}(t,t')$ . A final feature of Fig. 8 is the fact that the energy surface is a unique function of R; i.e. the incoming and outgoing surfaces are reflections of each other. This reflection symmetry is presumably a consequence of the fact that the formal theory satisfies the detailed-balancing requirement (15). Computationally, it provides a non-trivial test of numerical accuracy, since the symmetry exists only after good convergence to a boundary-value solution has been obtained.

As has already been pointed out (15,104), it is difficult to obtain mathematical assurance that any particular solution at a given b is unique. We have numerically searched for other possible solutions by using an initial estimate different from that given above. The collisions at b = 1.16, 1.22, 1.60, 1.70, and 1.86 a.u. were re-calculated using the bottom adiabatic, instead of the diabatic, surface as an initial estimate. In every case it was found that the final solution obtained was the same as the one shown above, even for those values of b where the adiabatic and diabatic predictions of  $\theta$  differ greatly. We therefore feel justified in regarding the above solution as unique.

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Having rationalized the behaviour of  $\theta$  in terms of the energy surfaces one can now consider the effect that this behaviour of  $\theta$  will have on the cross section. The reduced (54) differential cross section is given by the quantity  $b\theta(db/d\theta)P_{11}$  . If this were calculated using SESIP theory then the quantity  $b\theta(db/d\theta)$  would be a monotonic function of  $\theta$  and the only source of oscillations would be the term P  $_{11}$ . In the boundary-value calculation, however, both terms can now contribute oscillations since Fig. 7(a) implies that  $db/d\theta$  is an oscillatory function of  $\theta$ . Figure 9 shows the results of a SESIP calculation of the cross section, as well as the boundary-value result. Both are compared to the DW result (54). The DW result shows two major features, an isolated peak at 1450 eV-deg. and a smooth series of oscillations between 3000 and 5000 eV-deg. Essentially the same features are seen experimentally [Fig. 9(c) and Refs. (5)-(7)]. The SESIP result does not display any peaks in the threshold region, although it does qualitatively reproduce the smooth oscillations at large  $\theta$ . The boundary-value calculation shows the same oscillations at large  $\theta$ , but they are strongly accentuated due to the fact that  $db/d\theta$  is also oscillatory. The main new feature of the boundaryvalue result is that the peaks in the differential cross section rise above the single-channel prediction. These peaks are predominantly due to peaks in the function  $dB/d\theta$  and can be easily understood if one considers the behaviour of  $heta_{
m BV}$  in Fig. 7(a). It can be seen that the boundaryvalue theory used here generates a perturbation in the elastic cross section which looks quite different from the perturbation that one would expect if the rainbow-scattering interpretation were used. In particular,

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Figure 9.

Comparison of three theoretical calculations of the reduced differential cross section for elastic scattering at 70.9 eV. The long dashed lines are the single-channel (diabatic) predictions. The theories used are: (a) SESIP, (b) boundary-value, and (c) distorted-wave [Ref. (54)]. The short dashed line in (c) is the experimental result at 83.5 eV, raised by 0.2 units [Refs. (5)-(7) and (54)].



the numerical results presented here are not compatible with those obtained by Kotova and Ovchinnikova (102). On the basis of the comparison with experimental results it would appear that their results (102) are superior to ours, at least for elastic processes. This is presumably due to the fact that the decomposition procedure, which leads to rainbowscattering, yields a more detailed picture of nuclear motion inside the crossing region than our approach does. The relative merits of the two interpretations for those systems where SLZ theory is not necessarily reliable (10) remain to be seen.

The above comparisons lead us to the following conclusions:

1) SESIP theory, as expected, does not even begin to provide a reasonable account of the perturbation in the elastic differential cross section, since this perturbation is due to the effect of the electronic rearrangement on the nuclear motion.

2) Boundary-value theory, in the form in which we have used it,

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takes account of the effect of the electrons on the nuclei and therefore predicts a perturbation in the elastic results, but the form of the perturbation is not correct.

3) The only three dimensional semiclassical theory which predicts the correct perturbation is that of Olson and Smith (54) and Kotova and Ovchinnikova (102). (Note that it is relatively easy to obtain the correct perturbation if a "one-dimensional" semiclassical theory is used (20,105), but that the one-dimensional theories are not as easy to "interpret". A "one-dimensional" theory is one in which angular motion is treated quantum mechanically and only radial motion is treated classically.)

The inelastic scattering calculation was performed using the same set of impact parameters and initiallization procedure as for elastic scattering. The only difference was that the force law was altered to correspond to the  $1 \rightarrow 2$  electronic event. From a qualitative point of view the results are not particularly exciting since the behaviour of the differential cross section is very similar to the DW prediction. The main difference between the boundary-value and SESIP calculations for inelastic scattering is that the angular threshold predicted by the boundary-value calculation is considerably lower than the SESIP prediction since the final energy surface is 16.8 eV higher than the initial energy surface. From a numerical point of view some interesting problems were encountered in the inelastic calculation. The main one was that of initiallizing the iterative procedure reasonably. The present calculation used the elastic diabatic surface as an initial estimate, even though this surface does not possess the correct long-range behaviour after the concurses.

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collision. For strongly inelastic collisions a more sophisticated procedure would probably be required (see page 121). Another difficulty was encountered for those collisions which display a transition probability  $P_{12}$  which is close to zero. In this case the force law [Eq. (89)] consists of a ratio of two arbitrarily small terms and the calculation is numerically ill-conditioned. The main effect of these two problems was simply to decrease the efficiency of the calculation. It was found that ten iterations were normally required to obtain convergence to a boundaryvalue solution.

We begin the discussion of the inelastic results by considering  $P_{12}$  as a function of &. As expected, the qualitative behaviour is the same as for elastic scattering, although significant quantitative differences were observed since the trajectories are different. When  $P_{12}$  for inelastic scattering was compared to the DW prediction [Fig. 4 of Ref. (54)], it was found that the agreement was so close that the differences could probably be attributed to plotting errors. This is quite encouraging since it implies that a single-trajectory calculation may be capable of providing a quantitatively, as well as qualitatively, reasonable account of inelastic processes.

The next feature of the inelastic collisions is the behaviour of the energy surface. Figure 10 presents energy surfaces for collisions at b = 1.44 and 1.90 a.u. The collision at b = 1.44 corresponds to the top of the third excitation peak ( $P_{12} = 0.115$ ). The one at b = 1.90 corresponds to a collision where the nuclei do not even reach the crossing point ( $P_{12} = 0.005$ ). The arrows indicate the direction in which the

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Figure 10.

Energy surfaces  $\overline{E}(R,t)$  obtained from the boundary-value calculation, as a function of internuclear separation, for inelastic collisions at impact parameters 1.44 and 1.90 a.u. The dashed lines are the adiabatic surfaces. The arrows indicate the direction in which the nuclei move along the surface.



nuclei move along the surface since the energy is a two-valued function of R. The adiabatic surfaces are shown for comparison. In both collisions the nuclei originally follow the bottom and finally follow the top adiabatic (or diabatic) surface. In the intermediate region they follow a surface which smoothly switches over from the bottom to the top eigensurface. It was found that the energy surfaces for the other collisions had essentially the same shape as the ones shown here. In every case the energy near the nuclear turning point was roughly the average value of the two adiabatic surfaces. As already observed for elastic collisions, the energy surface is not necessarily bounded by the two adiabatic extremes, especially near the pseudocrossing.

A test of detailed-balancing was performed at b = 1.44 a.u., mostly as a check on numerical accuracy. This was done by changing the force law to correspond to the electronic event  $2 \rightarrow 1$ , as well as changing the initial conditions on the nuclear motion to correspond to the final behaviour observed for the  $1 \rightarrow 2$  electronic event. It was found that the transition probability and scattering angle for the two runs were identical. In addition to this, the two events followed the same energy surface, but in opposite directions.

Figure 11 shows the reduced differential cross section for inelastic scattering, given by the quantity  $b\theta(db/d\theta)P_{12}$ , as well as the DW result (54). The overall shapes of the two results are quite similar. The main difference is that the present calculation is shifted to the right by about 200 eV-deg. compared to the DW result. This shift is not enough to seriously affect the comparison with the experimental results.

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Figure 11.

Comparison of the boundary-value and the distorted-wave [Ref. (54)] calculations of the reduced differential cross section for inelastic scattering at 70.9 eV. The dashed line is the experimental result [Refs. (5)-(7) and (54)].



A certain amount of ambiguity as to the exact behaviour of the differential cross section near the minima exists in the present calculation. This is because of the zero-over-zero problem mentioned earlier. It is possible that these minima may not rigorously approach zero although we know them to be quite small. This ambiguity was not felt to be of any great importance in the present calculation and was ignored.

The results obtained for inelastic scattering are much more encouraging than those obtained for elastic scattering. First of all, the function  $P_{12}(\ell)$ , which displays Stueckelberg oscillations, agrees very well with the DW prediction, and secondly, the inelastic differential cross section (Fig. 11) is quite similar to the DW result. There are two main features of the inelastic cross section which are of experimental interest: the frequency of the Stueckelberg oscillations, and the angular threshold at which the first inelastic peak (Fig. 11) appears. The present calculation implies that both of these features are adequately described by a single-trajectory theory of the type used here.

The most obvious shortcoming of the present theory is that it does not predict a localized perturbation (99) in the elastic differential cross section close to the threshold angle, while the theory of Refs. (54) and (102) does. It is therefore of interest to discuss the relationship between the present theory, which will be called a singletrajectory theory, and that of Olson and Smith (54), referred to as a multi-trajectory theory.

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C. Mu

## Multi-trajectory Curve-crossing Theory

Briefly, a multi-trajectory curve-crossing theory (54,76,102) yields the following picture of the collision process: The nuclei proceed along the initial adiabatic energy surface until they reach a curve-crossing. At this point the nuclei are faced with two alternatives since there are two diabatic surfaces which become degenerate at  $R = R_x$ . Both of these alternatives are taken into account. That is, the nuclei may follow the top or the bottom diabatic surface after going through a curve-crossing, and the probability in each case is given by SLZ theory. When the second curve-crossing is reached, on the outgoing portion of the collision, the choice is again made, and the way in which this choice is made will determine whether the event is to be elastic or inelastic. In any particular channel, whether it be elastic or inelastic, there will therefore be at least two nuclear trajectories. (For the He -Ne system there are three trajectories in the elastic channel just above the threshold for inelastic processes.) The different branches of the nuclear motion are regarded as interfering alternatives [page 14 of Ref. (24)], not mutually exclusive alternatives, since they are not experimentally distinguishable. (A good qualitative discussion of this type of theory, as it applies to threebody reactive collisions, has been given by Tully and Preston [Section IV of Ref. (106)].)

In terms of a path-integral approach, a multi-trajectory theory can be rationalized quite easily, provided that one is not concerned with rigor. The problem is characterized by the path integral [Eq. (56)]:

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$$K_{\beta\alpha}(\vec{R}''t'',\vec{R}'t') = \int_{\vec{R}'t'}^{\vec{R}''t''} \underbrace{\underline{U}}_{\beta\alpha}(t'',t') \exp\{iS_{o}[\vec{R}(t)]\} \mathcal{D}_{\vec{R}}(t) . \quad (92)$$

In a single-trajectory theory we develop a stationary-phase approximation to Eq. (92) directly, without making use of the possibility that  $\underline{U}_{\beta\alpha}(t'',t')$ may be expressible in a simpler form than that given by Eq. (58). For curve-crossing problems, however, it is clear that this procedure is not entirely satisfactory, for the following reason: the stationary-phase method incorporates the assumption that  $|\underline{U}_{\beta\alpha}(t'',t')|$  does not change very much as the path  $\{x(t)\}$  is varied. That is, we assume that the variations in the integrand of Eq. (92) due to variations in the phase are much more important than those due to variations in  $|\underline{U}_{\beta\alpha}(t'',t')|$ . If the magnitude of the integrand has a monotonic dependence on the path then this assumption may be fairly reasonable, but for a curve-crossing problem  $|\underline{U}_{\beta\alpha}(t'',t')|$  behaves in a highly oscillatory fashion as the path is varied. (See, for example, the behaviour of  $P_{12}(\ell)$  in Fig. 7(b).) The validity of the stationary-phase method is therefore questionable if it is applied directly to Eq. (92). As an alternative, we might consider reexpressing Eq. (92) as a sum of (hopefully simpler) path integrals which may be more amenable to approximation by the stationary-phase method. That is, if Eq. (92) can be re-expressed as a sum of path integrals  $(\kappa^{(1)})$ and  $K^{(2)}$ ) whose integrands have magnitudes which vary more slowly than  $|\underline{U}_{\text{R}\alpha}(\texttt{t",t'})|$  as the path is varied, then it would clearly be desirable to perform separate stationary-phase approximations to the individual path integrals,  $K^{(1)}$  and  $K^{(2)}$ , rather than performing a single stationaryphase approximation to Eq. (92). For curve-crossing problems, SLZ theory

allows us to carry out this procedure. (Note that a similar procedure can be carried out quite rigorously for resonant charge-exchange (15,58).) In Chapter II it was shown that  $\underline{U}(t",t")$  can be re-expressed as a sum of two terms if the transition occurs quickly. For example, for the  $1 \rightarrow 1$ event we have [see Eq. (50)]:

$$\underline{U}_{11}(t'',t') = (1 - P) e^{2i\alpha} e^{-i\phi_1} + P e^{-2i\beta} e^{-i\phi_2}$$
(93)

where P is the Landau-Zener transition probability given by Eq. (39) and the non-adiabatic phase shifts  $\alpha$  and  $\beta$  are essentially constant (74). The phases  $\phi_1$  and  $\phi_2$  can be obtained from Eq. (50):

$$\phi_{1} = \int_{t'}^{t_{1}} E_{11}(R) dt + \int_{t_{1}}^{t_{2}} E_{11}(R) dt + \int_{2}^{t''} E_{11}(R) dt , \qquad (94)$$

$$\phi_2 = \int_{t'}^{t_1} E_{11}(R) dt + \int_{t_1}^{t_2} E_{22}(R) dt + \int_{t_2}^{t''} E_{11}(R) dt , \qquad (95)$$

where the E (R) are the adiabatic energy levels. We re-express  $\phi_1$  and  $\phi_2$  as

$$\phi_{1} = \int_{t'}^{t''} V_{1}(R) dt ,$$

$$\phi_{2} = \int_{t'}^{t''} V_{2}(R) dt ,$$
(95)

where  $V_1(R) = E_{11}(R)$  everywhere,  $V_2(R) = E_{11}(R)$  if  $R > R_x$ , and  $V_2(R) = E_{22}(R)$ 

if  $R < R_x$ . If Eq. (93) is substituted into Eq. (92) we will have succeeded in re-expressing the original path integral in terms of two simpler path integrals,  $K^{(1)}$  and  $K^{(2)}$ . The magnitudes of the integrands of these two path integrals are given by P and (1 - P). It is clear that both P and (1 - P) will vary much more slowly than does  $|\underline{U}_{11}(t",t')|$  as the path is varied, and that the stationary-phase approximation will therefore be more reliable if it is applied separately to  $K^{(1)}$  and  $K^{(2)}$ , instead of being applied to the original path integral in Eq. (92). If we now ignore variations in P as the path varies about the classical path, we obtain

$$K_{11}(\vec{R}''t'',\vec{R}'t') = (1 - P) e^{2i\alpha} K^{(1)} + P e^{-2i\beta} K^{(2)}$$
 (96)

where P,  $\alpha$ , and  $\beta$  are evaluated using classical trajectories (which are not yet known), and

$$K^{(i)} = \int_{\vec{R}'t'}^{\vec{R}''t''} \exp\{iS_{o}[\vec{R}(t)] - i\phi_{i}\} \mathcal{D}\vec{R}(t), \quad i = 1, 2.$$
(97)

Equation (97) can be put into the form

$$\mathbf{K}^{(\mathbf{i})} = \int_{\mathbf{R}' \mathbf{t}'}^{\mathbf{R}'' \mathbf{t}''} \exp\{\mathbf{i} \int_{\mathbf{t}'}^{\mathbf{t}''} \mathbf{L}_{\mathbf{i}}(\mathbf{\vec{R}}, \mathbf{\vec{R}}, \mathbf{t}) \, d\mathbf{t}\} \, \mathcal{D} \, \mathbf{\vec{R}}(\mathbf{t})$$
(98)

where  $L_{i}(\vec{R},\vec{R},t)$  has the form of a Lagrangian:

$$L_{i}(\vec{R},\vec{R},t) = \frac{1}{2} m \vec{R}^{2} - V_{i}(R) .$$
(99)

A stationary-phase evaluation of  $K^{(i)}$  therefore yields a classical trajectory which follows the energy surface  $extsf{V}_{i}( extsf{R})$  during the collision and which, incidentally, determines the value of P,  $\alpha$ , and  $\beta$  in Eq. (96). The transition amplitude for the elastic event which is actually observed is therefore a sum of two terms. The first term has an (Landau-Zener) amplitude of (1 - P) and corresponds to a trajectory which follows  $E_{11}(R)$ everywhere. In this case the electrons have not experienced a nonadiabatic transition during either passage through R =  $R_x$ . The second term has an (Landau-Zener) amplitude of P and corresponds to a trajectory which follows the surface  $E_{11}(R)$  if  $R > R_x$  and the surface  $E_{22}(R)$  if  $R < R_x$ . In this case the electrons have experienced a non-adiabatic transition during both passages through  $R = R_x$ . This interpretation is compatible with that of Olson and Smith (54) and Kotova and Ovchinnikova (102). The final expression which is obtained for the differential cross section [see, for example, Eq. (32) of Ref. (54)] will therefore contain contributions from each individual term of Eq. (96), as well as containing an oscillatory contribution due to interference between the terms of Eq. (96).

A multi-trajectory curve-crossing theory differs from a singletrajectory theory both in its description of Stueckelberg oscillations and in the description of the localized perturbation (99) observed in the elastic scattering cross section for He<sup>+</sup>-Ne collisions. In a single-trajectory theory Stueckelberg's oscillations can be regarded as a multiple charge-exchange effect in the sense that the electrons seem to move back and forth between atomic centres (or between two states on the same atomic centre). The frequency of the Stueckelberg oscillation in this case is

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related to  $E_{11}(R) - E_{22}(R)$  [see Eq. (52)]. In a multi-trajectory theory the Stueckelberg oscillation arises as an interference pattern between two "branches" of the combined nuclear-electronic motion. The phase of the Stueckelberg oscillation in this case is closely related to the difference in the phases of  $K^{(1)}$  and  $K^{(2)}$  in Eq. (96). The phase of the semiclassical approximation to K<sup>(i)</sup> [Eq. (98)] is given by the classical action,  $\int_{\mu'}^{r} L_{i}(\vec{R},\vec{R},t) dt$ , evaluated along a classical path which follows the energy surface  $V_i(R)$ . The phase difference between  $K^{(1)}$  and  $K^{(2)}$  is therefore a difference between two classical actions, evaluated using  $V_1(R)$  and  $V_2(R)$ , respectively. Both the single-trajectory and multitrajectory theories regard the Stueckelberg oscillation as an interference pattern, but in the single-trajectory theory this interference pattern is a purely electronic effect which can be understood quite independently of the nuclear equations of motion, while in the multitrajectory theory the interference pattern contains some "nuclear" contributions (due to the kinetic energy term in  $L_i(\vec{R},\vec{R},t)$ ) and some "electronic" contributions (due to the potential energy term in  $L_i(\vec{R},\vec{R},t)$ ). From a gualitative point of view, the interpretation of the Stueckelberg oscillation is therefore quite different in the two cases even though both theories are closely related within a path-integral formalism.

Finally, the reason why the two theories differ in their description of the perturbation (99) in the elastic scattering pattern is that the multi-trajectory theory may yield three "branches" in the nuclear motion (54,102), two of which coalesce and disappear near the inelastic threshold, thus leading to a "rainbow" effect, while the single-trajectory theory does not predict any such effect, at least not for the case studied here.

In conclusion, it should be noted that multi-trajectory curvecrossing theories can be used to describe three-body rearrangement collisions without too much difficulty (76,106), where the rearrangement occurs only after an electronic transition at a curve-crossing has taken place. This type of theory has already been applied (106,107) to the reaction

 $H^+ + D_2 \rightarrow HD^+ + D$ .

A multi-trajectory curve-crossing theory has also been used to discuss the quenching of electronically excited atoms by diatoms (108,109), and would probably be useful in the interpretation of certain ion-molecule reactions, such as (110-112):

 $0^+ + N_2 \rightarrow N0^+ + N$ .

## CHAPTER IV. VIBRATIONAL EXCITATION

The boundary-value semiclassical theory of Chapter III was applied to the problem of vibrational excitation during collinear atom-diatom collisions, partly in order to show the flexibility of the model, and partly to compare our results with the predictions of other semiclassical theories. Since the three atoms of the system are constrained to lie on a straight line, and since this constraint would not be present in an actual collision, it will not be possible to compare the present theoretical results with any experimental work. The purpose of the calculation is simply to determine the value of the present theory by comparing it with other theories. If the present theory compares favorably with other available theories, then there might be some point in trying to perform calculations in the absence of the collinear constraint so that a comparison with experimental work could be made. There are currently two types of time-dependent "semiclassical" theory which have been applied to the problem of vibrational excitation during collinear atom-diatom collisions. The first type has been developed recently by Miller (113-115) and Marcus (116, and references cited therein) and will be called S Matrix theory. In this theory the "dynamics" of both the vibrational and translational motion are treated classically during the collision itself, while the initial and final stationary states are constrained to satisfy quantum mechanical boundary conditions. In addition to this, a certain amount of care is taken in the definition of the observable, especially in those cases where two classical solutions coalesce or become complex. This theory has been applied to a wide range of vibrationally inelastic

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events (114,115,117,118), and the results have been compared with exact quantum mechanical calculations (94). The second type of theory, which will be called semiclassical, treats the vibrational motion completely quantum mechanically while translation is described classically. In principle, a semiclassical description of vibrational excitation should be superior to the S Matrix theory since the dynamics of the vibrational motion during the collision is treated quantum mechanically. (Both theories satisfy essentially the same boundary conditions, before and after the collision, but the way in which they treat the motion of the system during the

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the collision is different.) Unfortunately, it is quite difficult to derive general equations of motion for the semiclassical theory, and even more difficult to solve them exactly in practice. The difficulty is due to the fact that the "dynamics" of the classical and quantum mechanical degrees of freedom are coupled to each other, and that this coupling is non-causal. As a result, only approximate semiclassical descriptions of vibrational excitation have been given so far. One such description is the ITFITS theory of Heidrich, Wilson, and Rapp (119). In that theory the vibrational motion is treated within the Landau-Teller approximation (120) and the translational motion is obtained using an energy surface which does not respond to changes in the vibrational state during the collision. The energy surface is an average of the surface which is initially appropriate and that which is finally appropriate. The success of the ITFITS theory is rather surprising, considering the approximations that are made, and leads to the conjecture that it might be possible to produce nearly perfect results if a more sophisticated semiclassical theory were used. We have therefore performed calculations using the semiclassical theory of Pechukas (15), as described in Chapter III (Section A) of this document. The theory is based upon the Feynman path-integral formulation of quantum mechanics and is quite general in the sense that, in principle, it allows one to develop semiclassical equations of motion for virtually any collision problem in which some degrees of freedom are to be treated quantum mechanically while others are treated classically. For the vibrational excitation problem, the quantity of interest is a transition amplitude for an event in which the translational coordinate moves from x' (at time t')

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to x" (at time t") while the (quantum mechanical) vibrational state changes from  $\alpha$  to  $\beta.$  If a completely quantum mechanical calculation of this quantity were desired it would be necessary to consider all possible translational trajectories between the points (x',t') and (x",t"), and to calculate the vibrational transition amplitude from state  $\alpha$  to state  $\beta$ along each trajectory. The vibrational transition amplitudes obtained from the individual trajectories would then have to be added coherently to produce the transition amplitude for the event which is actually observed. In a semiclassical theory we are interested in selecting a particular trajectory (one which extremizes the phase of the path integral) and using it to evaluate the transition amplitude for this event approximately. This trajectory is of particular interest because the paths which lie within a small neighbourhood around it will interfere constructively with each other. For low-energy collision problems it is sometimes quite important that the translational trajectory be chosen as carefully as possible and we anticipate that the trajectories used in our theory should yield better results than those used in the ITFITS theory.

Another interesting possibility regarding the present calculation is that one might expect it to yield worthwhile information on "strongly forbidden" events (117,118) without having to resort to the use of complex translational trajectories. This possibility has been discussed previously (104) and is sufficiently intriguing to warrant an application of semiclassical theory in its original form.

The physical system we are concerned with consists of an atom and a

diatom constrained to lie on a straight line. We want to calculate a transition probability from a vibrational state  $\alpha$  to a state  $\beta$  of the diatom during a collision with the atom. Within the coordinate system of Secrest and Johnson (94), the full hamiltonian is given by:

$$H_{\rm op} = -\frac{1}{2m} \partial^2 / \partial x^2 - \frac{1}{2} \partial^2 / \partial y^2 + \frac{1}{2} y^2 + A e^{-\alpha (x-y)}$$
(100)

where y is the vibrational coordinate of a harmonic oscillator and x is the translational coordinate between the atom and the diatom. The potential  $Ae^{-\alpha(x-y)}$  represents the interaction between the atom and the diatom. The parameters m and  $\alpha$  are chosen to correspond to a collision between He and H<sub>2</sub> (from Ref. (94), m = 2/3,  $\alpha$  = 0.3). The value of the parameter A is arbitrary in this calculation since A has no effect on transition probabilities (94). In our calculation we used the value A = 30. In a semiclassical theory the hamiltonian of interest is:

$$h_{op} = -\frac{1}{2}\partial^{2}/\partial y^{2} + \frac{1}{2}y^{2} + Ae^{-\alpha(x-y)}$$
(101)

where  $h_{op}$  contains all of the dependence of  $H_{op}$  on y. If the translational trajectory  $\{x(t)\}$  is known, then  $h_{op}$  can be regarded as a time-dependent hamiltonian governing quantum mechanical evolution of the vibrational state of the diatom. The vibrational state is expressed as a time-dependent linear combination of the eigenstates of the unperturbed harmonic oscillator, whose coefficients define an evolution matrix  $\underline{U}(t,t')$ . The  $\alpha$  th column of  $\underline{U}(t,t')$  represents a state, at time t, which in the far

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past, at time t', was the  $\alpha$  th eigenstate of the oscillator. The evolution matrix satisfies Eq. (32), with H(x) given by

$$\underline{H}_{ij}(x) = \int_{-\infty}^{\infty} \Psi_{i}^{*}(y) h_{op} \Psi_{j}(y) dy . \qquad (102)$$

The wave function  $\Psi_i(y)$  is the i <u>th</u> eigenstate of the unperturbed oscillator. (We note that, because of the simple form of  $h_{op}$ , the basis set for this problem is automatically a diabatic one.) The matrix elements of <u>H</u>(x) can be re-expressed as

$$\underline{H}_{mn}(\mathbf{x}) = A e^{-\alpha \mathbf{x}} e^{\alpha^2/4} \underline{V}_{mn} + \underline{E}_{mn}$$
(103)

where  $\underline{E}_{mn} = (n + \frac{1}{2}) \delta_{mn}$  and the symmetric matrix  $\underline{V}$  is given by (121)

$$\underline{\underline{V}}_{mn} = \left(\underline{\underline{m!}}_{n}\right)^{\underline{L}_{2}} \left(\underline{\alpha}_{\sqrt{2}}\right)^{n-m} \underline{L}_{m}^{n-m}(-\alpha^{2}/2) , \qquad m \leq n.$$
(104)

An important feature of the hamiltonian  $\underline{H}(x)$  is that the dependence on x enters only as a scalar factor  $e^{-\alpha x}$ . The only non-trivial calculation which must be performed before  $\underline{H}(x)$  is known is the evaluation of  $\underline{V}$ , which is expressed in terms of associated Laguerre polynomials. In practice, we evaluated  $\underline{V}$  using the recurrence relations

 $\underline{\underline{V}}_{0n} = (n!)^{-\frac{1}{2}} (\alpha/\sqrt{2})^{n} ,$  (105)  $(m+1)^{\frac{1}{2}} \underline{\underline{V}}_{m+1,n+1} = (n+1)^{\frac{1}{2}} \underline{\underline{V}}_{m,n} + (\alpha/\sqrt{2}) \underline{\underline{V}}_{m,n+1} , m \le n.$ 

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These relations eliminate the need to derive explicit analytical expressions for the Laguerre polynomials. The hamiltonian  $\underline{H}(x)$  can now be calculated readily for arbitrary x, and Eq. (32) can be solved for  $\underline{U}(t,t')$ if the translational trajectory is known.

The classical trajectory  $\{x(t)\}$  satisfies the equation of motion [Eq. (60)]:

$$m \ddot{x}(t) = -Re \left\{ \frac{\left[ \underline{U}(t'',t) \frac{\partial \underline{H}(x)}{\partial x(t)} \underline{U}(t,t') \right]}{\underline{U}_{\beta\alpha}(t'',t')} \beta_{\alpha} \right\}, \quad (106)$$

and also obeys the energy conservation law [Eq. (90)]:

$$\frac{1}{2}m\dot{x}^{2}(t) + \operatorname{Re}\left\{\frac{[\underline{U}(t'',t)\underline{H}(x)\underline{U}(t,t')]}{\underline{U}_{\beta\alpha}(t'',t')}\beta\alpha\right\} = E$$
(107)

where E is measured in units of  $\hbar\omega$ , twice the zero-point energy of the oscillator. For the case studied here,  $\hbar\omega \sim 0.5$  eV. To obtain a transition probability for the  $\alpha \rightarrow \beta$  event at a total energy E one must simultaneously solve Eqs. (32) and (106). Equation (106) defines a classical trajectory  $\{x(t)\}$  for a particular event while Eq. (32) defines the response of the vibrational state to this time-dependent perturbation. The energy conservation law, Eq. (107), states that the translational motion initially (finally) recognizes a potential energy surface belonging to the  $\alpha$  th ( $\beta$  th) state of the oscillator, and that during the collision the energy surface switches over smoothly from one to the other.

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The translational motion in this theory is clearly coupled to the vibrational motion and the coupling is such that the path which the system follows is a path of least action.

The numerical solution of the semiclassical equations proceeds by three steps. First of all, it is necessary to calculate U(t,t'), which involves the solution of n sets of n coupled equations [Eq. (32)], where n is the number of vibrational states and where the translational motion is assumed to be known, either exactly or approximately. This solution is obtained using a fourth-order Runge-Kutta-Gill method previously developed for use in electronic excitation problems (28), with appropriate modifications in the definition of H(x). Secondly, we must determine the translational motion in such a way that it satisfies Eq. (106). This is accomplished by the algorithm discussed in Chapter III (Section B). Thirdly, we need to ensure that the vibrational basis set is complete. The aim of this calculation is to produce a precise semiclassical solution, and it is therefore necessary to increase the number of vibrational states until further increases no longer affect the transition probability. In practice, no more than 15 states were ever required. (Note that in the quantum mechanical calculation a similar problem is encountered (94,122).)

Of the three problems mentioned above, the most difficult one is the determination of the translational motion. The algorithm used to solve this problem proceeds as follows: one guesses an approximate energy surface for a particular event and solves an initial-value problem for  $\underline{U}(t",t')$  using the trajectory determined by this energy surface. This

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value of  $\underline{U}(t",t')$  is then used to determine an "improved" force law for translational motion, which allows one to calculate an "improved" value of  $\underline{U}(t'',t')$ , etc. Convergence to a boundary-value solution is obtained when two successive estimates of U(t",t') agree. The number of iterations required to produce good convergence varied considerably, depending on the nature of the event. For low energy elastic collisions as few as five iterations were often sufficient, while for other events convergence was never obtained (i.e. no solution to the semiclassical equations was found). Although the final transition probability for an event does not depend on the initial estimate of the energy surface, it is clear that the rate of convergence will depend on this choice. For elastic  $(0 \rightarrow 0)$ events we normally used the diabatic surface  $\frac{H}{-00}(x)$  to initiallize the calculation. For those inelastic events which converged quickly we continued to use  $\underline{H}_{00}(x)$  to initiallize the calculation even though it does not possess the correct long-range behaviour after the collision. Whenever convergence difficulties were encountered in an inelastic event we used a modified (velocity dependent) energy surface as an initial estimate. The velocity dependence was introduced in such a way that the kinetic energy lost exactly one (or two) quanta of energy during the collision. For these calculations the translational motion would behave as though it was following an energy surface which was monotonically switching over from the surface  $\underline{H}_{\alpha\alpha}(x)$  to the surface  $\underline{H}_{\beta\beta}(x)$  during the collision. The only effect of this velocity dependence is to provide a more sophisticated initial estimate of U(t'',t') and thus increase the rate of convergence of the algorithm. (A copy of the program used in this calc-

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ulation is given in Appendix II.)

We note, finally, that the converged boundary-value solution in this theory obeys detailed-balancing (15), but that the transition probabilities are not normalized in general.

Calculations were performed for the events  $0 \rightarrow 0$ ,  $0 \rightarrow 1$ , and  $0 \rightarrow 2$ , using parameters  $(m, \alpha)$  which correspond to the system He + H<sub>2</sub>. The transition probabilities are shown in Table II. The results were obtained by solving Eqs. (32) and (106) exactly, using a complete basis set in each case. They should therefore represent the best that can be obtained within a time-dependent semiclassical theory, as we have defined it. Figure 12 shows a comparison of our results and the exact calculation of Secrest and Johnson (94) for the  $0 \rightarrow 0$  and  $0 \rightarrow 1$  events. For the  $0 \rightarrow 0$ event we find that the semiclassical result (represented by dots) becomes progressively worse as the total energy is increased. We also found it increasingly difficult to obtain solutions to the semiclassical equations at high energies. This was due partly to the large basis set which was required and partly to the fact that the rate of convergence to a boundary-value solution became poorer at high energies. At a total energy E = 10we were unable to produce a solution. (The solution may in fact exist, but we could not find it.) Preliminary calculations which we performed at this energy indicated that at least 15 states would be required and that convergence to a boundary-value solution could be obtained only if extreme care was taken in the definition of the energy surface used to initiallize the iterative procedure. The energy surface which the translational motion recognizes during these elastic events is consistently

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Table II.

Vibrational transition probabilities for the events  $0 \rightarrow 0$ ,  $0 \rightarrow 1$ , and  $0 \rightarrow 2$  as a function of total energy E.

E	0 ~ 0	0 ÷ 1	0 ÷ 2
3.0	.941		
4.0	.812		
4.63		.111	
4.70		.132	
5.0	.621	.192	
6.0	.416	.325	
7.0	.242	.362	.100
8.0	.122	.309	.211
9.0	.054	.215	.265
10.0			.240

Figure 12.

Logarithm of the transistion probability as a function of total energy E for the events: a)  $0 \rightarrow 0$ , b)  $0 \rightarrow 1$ . The solid line in each case is the exact result of Secrest and Johnson (94). The dots are the semiclassical result. The dashed line in a) is obtained using the diabatic energy surface, as explained in the text.

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less repulsive than the diabatic surface  $\underline{H}_{00}(x)$ , and the atom therefore approaches the diatom more closely than one would expect (see Fig. 13). This leads to an increasingly complex behaviour of the evolution matrix U(t,t') during the collision, which in turn complicates the problem of converging to a boundary-value solution. It is interesting to note that the  $0 \rightarrow 0$  event at E = 10 is classically forbidden (114) in the S Matrix theory, and that our results become progressively worse as we approach this region of forbiddenness. For the  $0 \rightarrow 0$  event we have also performed calculations using a simpler theory in which the translational motion follows the diabatic energy surface  $\underline{H}_{00}(x)$ , while  $\underline{U}(t'',t')$  is calculated as usual, using a complete basis set. These results will be termed "diabatic", and are shown as a dashed line in Fig. 12(a). Surprisingly enough, the diabatic prediction yields better results at high energies than does the exact semiclassical theory, an indication that the semiclassical theory in its present form may not be as good as one would expect it to be. We also note that the present numerical results do not represent an improvement over the predictions of the ITFITS theory. (This applies to inelastic events as well as to the  $0 \rightarrow 0$  event.)

Transition probabilities for the  $0 \rightarrow 1$  event are shown in Fig. 12(b) and a typical energy surface for this event is shown in Fig. 13. (The energy surface for an inelastic event is a two-valued function of x, as discussed in Chapter III.) We find that our transition probabilities are best at energies between E = 5 and E = 8 and become progressively worse at higher or lower energies. At a total energy E = 10 we were unable to produce a solution (although it may exist) because of con-

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Figure 13.

Potential energy V(x,t) as a function of the translational coordinate x, where V(x,t) is given by Eq. (107). The three solid lines are for the following three events at a total energy E = 6: (1)  $0 \rightarrow 0$ , (2)  $0 \rightarrow 1$ , (3)  $1 \rightarrow 1$ . The dashed lines are the diabatic surfaces  $\underline{H}_{00}(x)$  and  $\underline{H}_{11}(x)$ . The potential energy surfaces at other impact energies show a similar behaviour.



vergence difficulties and also because of the size of the basis set which was required. In the low energy region of Fig. 12(b) a more thorough study of the behaviour of the solution was possible since only a small number of states were required. In this region we note that the transition probability drops very rapidly (relative to the exact result) as the energy is decreased below E = 5. Furthermore, we found that E = 4.63 was the lowest energy at which a solution could be obtained for this event. For energies below this value it was impossible to converge to a boundary-value solution. The behaviour of the algorithm for energies below 4.63 was the following: the sequence of successive approximations to the solution would initially appear to converge to a well defined result but would ultimately diverge away from this apparent solution. That is, the first ten (or so) iterations would show a convergent pattern while the next ten showed a divergent one. The behaviour was essentially independent of the initial estimate of the energy surface. We have therefore concluded that there is in fact no solution to our equations for energies below E = 4.63. To the best of our knowledge, this is not the fault of our particular numerical method for finding the solution, but is a case of complete disappearance of a solution regardless of which algorithm were used. It is interesting to note that the energy E = 4.63is very close to the energy at which the  $0 \rightarrow 1$  event becomes forbidden within the S Matrix theory (see below).

An inspection of the transition probabilities in Table II for the  $0 \rightarrow 2$  event shows a behaviour which is very similar to that obtained for the  $0 \rightarrow 1$  event; that is, the accuracy of the transition probabilities

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deteriorates in both the high energy and low energy limits. In summary, therefore, we find that for inelastic events there is an intermediate energy range in which our transition probabilities are relatively good (and in which we encounter no numerical difficulties), while at higher or lower energies they become progressively worse (while, at the same time, we encounter severe numerical difficulties); for elastic events there is a low energy region in which we obtain relatively good results and a high energy region in which our results again become worse. For both types of events, the energy range in which the semiclassical solution is reasonably good happens to be a region of classically allowed (114) events, with the result that whenever we attempt to approach a forbidden (114) region we encounter difficulties. The difficulties are partially numerical, in the sense that the computing time increases, and partially analytical, in the sense that the solution disappears entirely for the  $0 \rightarrow 1$  event at low energies. As a result, it is not possible to use this type of semiclassical theory for strongly forbidden (117,118) events, as previously hoped.

The main conclusion reached during this calculation is that the relationship between our theory and the real-trajectory version (114) of the S Matrix theory is much closer than anticipated. Within the (real-trajectory) S Matrix theory one can distinguish between classically allowed and classically forbidden events, and our numerical results imply that the semiclassical theory also recognizes this distinction, for reasons which are not entirely clear. In an attempt to compare our solutions more closely with the S Matrix solutions we have performed

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calculations using the equations which are appropriate to the real-trajectory version of that theory. The hamiltonian is given by (114)

$$H = P_{x}^{2}/2m + P_{y}^{2}/2 + L_{2y}^{2} + Ae^{-\alpha(x-y)} .$$
 (108)

Both x and y are treated as real classical variables and the classical equations of motion are solved (using the coordinates x and y instead of action-angle variables) with appropriate boundary conditions. For the event  $\alpha \rightarrow \beta$  the vibrational degree of freedom is given  $\alpha + \frac{1}{2}$  units of energy initially, and the initial phase of the oscillator is chosen in such a way that the final vibrational energy is  $\beta + \frac{1}{2}$  units. At any particular total energy E either zero or two solutions are found. The purpose of the calculation is two-fold: to find the exact energies at which an event becomes forbidden and to compare the translational trajectories obtained in the S Matrix theory and the semiclassical theory. We find that the energy at which the  $0 \rightarrow 0$  event becomes forbidden is between 8.0 and 8.05. The low energy limit of forbiddenness for the  $0 \rightarrow 1$  event is between 4.80 and 4.85, while the high energy limit is between 10.75 and 10.80. The high energy limits at which the S Matrix solution becomes forbidden do not agree very closely with the energies at which we encountered numerical difficulties in our theory, but this may be partly due to the fact that the collision problem at high energies is a strongly coupled one and we would expect differences between the two theories to become more pronounced as the coupling between vibration and translation increases. At low energies our semiclassical solution

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for the  $0 \rightarrow 1$  event disappears at E = 4.63 while the S Matrix solution becomes forbidden at E = 4.80. The agreement between these energies is sufficiently close to suggest that these two occurrences are related.

In order to compare the translational trajectories obtained in the two theories we have calculated the distances of closest approach in each case. These are the minimum values of x, at which the direction of translational motion is reversed. The S Matrix theory always yields two (or none) values for any particular event while our theory yields one (or none). Figure 14 shows these values of x as a function of E for the  $0 \rightarrow 0$  and  $0 \rightarrow 1$  events. The bottom dashed line in both Fig. 14(a) and Fig. 14(b) represents the absolute minimum distance of closest approach in the S Matrix theory. This is obtained by setting the potential energy V equal to the total energy E (where V =  $\frac{1}{2y}^2$  + Ae<sup>- $\alpha$ (x-y)</sup>), and by choosing y such that  $x_{\min}$  takes on the smallest possible value. The actual turning points in the S Matrix theory (solid lines in Fig. 14) are invariably greater than this minimum value. The top dashed line in Fig. 14(a) and the middle dashed line in Fig. 14(b) are the turning points which would be obtained if the translational trajectory moved along the diabatic surface  $\frac{H}{-00}(x)$ , which contains the zero-point energy of  $\frac{1}{2}$  unit. The top dashed line in Fig. 14(b) is the turning point obtained if the translational trajectory moves along  $\underline{H}_{11}(x)$ . For the  $0 \rightarrow 0$  event we find that at low energies both the S Matrix theory and the semiclassical theory yield values of  ${\tt x}_{\min}$  which agree closely with the diabatic prediction based on  $\frac{H}{-00}(x)$ . At high energies x min takes on values which are progressively lower than the diabatic predict-

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Figure 14.

Turning points in the semiclassical and S Matrix theories as a function of total energy E, for the events: a)  $0 \rightarrow 0$ , b)  $0 \rightarrow 1$ . Solid lines: S Matrix theory. Dots: semiclassical theory. The dashed lines are explained in the text.

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ion, indicating that the atom and diatom approach each other more closely than one would expect on the basis of a weak-coupling theory. The main feature of Fig. 14(a) is that the semiclassical and S Matrix theories predict essentially the same trend in  $x_{min}$  as a function of E, and that the semiclassical turning point is always very close to being an average value of the two S Matrix results whenever the event is allowed.

For the  $0 \rightarrow 1$  event, shown in Fig. 14(b), the turning points in the S Matrix theory form a closed contour within which almost all of the semiclassical results lie. At low energies (E = 4.63) the turning point in the semiclassical theory comes close to being an average value of the two diabatic predictions, based on  $\underline{H}_{00}(x)$  and  $\underline{H}_{11}(x)$ , while at high energies the turning points come close to the absolute minimum prediction given by the bottom dashed line in Fig. 14(b). The overall trend is essentially the same as for the  $0 \rightarrow 0$  event, except that the inelastic event is forbidden at both low and high energies. We find that the semiclassical turning point again lies close to the average value of the two S Matrix predictions, indicating that the relationship between the translational trajectories obtained in the two theories is quite close even though the vibrational motion is treated quite differently.

These comparisons serve to show that both the semiclassical theory and the real-trajectory version of the S Matrix theory encounter numerical and analytical difficulties at roughly the same energies. Furthermore, it is found that the translational trajectories in both cases show similar

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trends as a function of E. On the basis of these comparisons we have come to the conclusion that it is not likely that the present theory will ever yield better results than the real-trajectory version of the S Matrix theory, quite apart from the fact that it is much more difficult to work with in practice. This conclusion is somewhat more pessimistic than that which was recently formed by Pechukas and Davis (104). Clearly, one could improve the present theory by considering the possibility of using complex translational trajectories and by taking account of variations in the magnitude of  $\underline{U}_{\beta\alpha}(t",t")$  as the path varies about the classical path (15), but the improved theory would probably be too difficult to work with in practice.

A comparison of the conclusions reached in this chapter with those reached in Chapter III shows that both sets of conclusions are surprisingly similar. In Chapter III it was found that a multi-trajectory theory yielded better information (at least for elastic scattering) than did a single-trajectory theory, even though the single-trajectory theory treats electronic motion precisely, instead of using SLZ theory. In this chapter we have used a theory which treats vibrational motion completely quantum mechanically and have found that it is not as useful as the S Matrix theory which treats the dynamics of vibration classically. The multitrajectory curve-crossing theory and the S Matrix theory of vibrational excitation have one feature in common: they both develop approximate treatments of a quantum mechanical degree of freedom and as a result they are both able to produce a more detailed picture of the classical (translational) degree of freedom, in the sense that more than one solution

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is found to correspond to the same observable event. From a formal point of view both of these theories succeed in breaking the original path integral [Eq. (56)] up into smaller, more manageable, pieces and this seems to be the reason why they are so successful.

In conclusion, it should be noted that both the multi-trajectory curve-crossing theory and the real-trajectory version of the S Matrix theory can be regarded as special cases of the general theory discussed in Ref. (15) and Chapter III (Section A) of this document. Since the numerical results which we have produced using the general theory are not as encouraging as anticipated, we conclude that the real value of the general theory lies not so much in its ability to produce good numbers as it does in its ability to serve as a starting point in the development of more specialized approaches.

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Appendix I

## MATRIX ELEMENTS FOR THE H-Be++ CALCULATION

(This subroutine replaces the QUANTM subroutine used by Corrigall [Appendix II of Ref. (57)] for the proton-hydrogen calculation.)

SUBROUTINE QUANTM(T,R,B,DBT,ARG,DRT,PIE,FIRST) IMPLICIT COMPLEX\*16 (A-H, O-Z) REAL\*8 T,R,RINV,ANORM,XR1,XG1,XR2,XG2,XZ2,DEXP,DCOS,DSIN,DRT,TRM,Z XRG,G,Z,T1,C1,CNORM,JCL1(2),JCL2(2),JCL3(2),DJCL1(2),DJCL2(2),DJCL: X(2),X,G2,H11B,H11C,H11D,Z1,H11A,TRM2,TRM3,CCLASS,DSQRT DATA NDIM/2/ COMPLEX\*16 IMAG/(0.D00,1.D00)/,N(2,2),RESULT(2,2),B(2),DBT(2),PDBT X(2),NINV(2,2),H(2,2),PDNR(2,2),NE(2,2),VECT(2),BT(2),PDBR(2),PDHR( X2,2) EQUIVALENCE (NE(1,1), NINV(1,1), PDNR(1,1))LOGICAL\*4 FIRST TWO PHASE FACTORS ARE NOW EVALUATED PHPOS=DCOS(.15809D00\*T) + IMAG\*DSIN(.15809D00\*T) PHNEG=DCOS(.15809D00\*T) - IMAG\*DSIN(.15809D00\*T) RINV = 1.D00/RXR1 = DEXP(-R)IF (XR1 .LT. 1.D-20) XR1 = 0.D00 G = 1.3290D00Z = 3.6875D00T1 = G\*G - G\*Z + Z\*ZC1 = (G + Z)/3.D00CNORM = DSORT(3.D00\*G\*\*5/T1)XG1 = DEXP(-G\*R)IF (XG1 .LT. 1.D-20) XG1 = 0.D00XR2 = XR1\*XR1IF (XR2 .LT. 1.D-20) XR2 = 0.D00 XG2 = XG1 \* XG1IF (XG2 .LT. 1.D-20) XG2 = 0.D00XZ2 = DEXP(-2.D00\*Z\*R)IF (XZ2 .LT. 1.D-20) XZ2 = 0.D00CALC. OF J INTEGRALS AS PER COULSON 1941 X = 1.000 - G\*GTRM = (R\*X - 4.D00\*G)\*XG1 + G\*(R\*X + 4.D00)\*XR1JCL1(1) = 8.D00\*TRM/R/(X\*\*3)G2 = G + 2.D00\*ZX = 1.D00 - G2\*G2TRM = (R\*X - 4.D00\*G2)\*XZ2\*XG1 + G2\*(R\*X + 4.D00)\*XR1JCL1(2) = 8.D00\*TRM/R/(X\*\*3)X = G \* G - 1.000TRM = (-R\*X\*X + 4.D00\*X\*(1.D00 + R\*G\*G) - 24.D00\*G\*G)\*XR1TRM = TRM + (X\*X\*R\*R + 4.D00\*X\*(2.D00\*G\*R - 1.D00) + 24.D00\*G\*G)\*X XG1 JCL2(1) = 8.D00\*TRM/R/(X\*\*4)

C C C

С

C C

С

С

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С
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X = G2*G2 - 1.000
        TRM = (-R*X*X + 4.D00*X*(1.D00 + R*G2*G2) - 24.D00*G2*G2)*XR1
        TRM = TRM + (X*X*R*R + 4.D00*X*(2.D00*G*R - 1.D00) + 24.D00*G2*G2)
      X *XZ2*XG1
       JCL2(2) = 8.D00*TRM/R/(X**4)
 С
       X = 1.D00 - G*G
       TRM = 2.D00*XG1 - (2.D00 + R*X)*XR1
       JCL3(1) = 4.D00*TRM/R/X/X
 С
       X = 1.000 - G2*G2
       TRM = 2.D00 * XZ2 * XG1 - (2.D00 + R*X) * XR1
       JCL3(2) = 4.D00*TRM/R/X/X
 С
 С
       N MATRIX IS CALCULATED
 С
       N(1,1) = 1.000
       N(2,2) = N(1,1)
       TRM = CNORM*(JCL1(1) - C1*JCL2(1))
       N(1,2) = TRM*PHNEG
       N(2,1) = TRM*PHPOS
       IF (.NOT. FIRST) GO TO 35
       DO 20 I = 1, 2
  20
       BT(I) = DCONJG(B(I))
       CALL CDGMPD(N,B,VECT,NDIM,NDIM,1)
       CALL CDGMPD(BT, VECT, BNORM, 1, NDIM, 1)
       ANORM = BNORM
       ANORM = DSORT(ANORM)
       DO 30 I = 1, 2
 30
      B(I) = B(I) / ANORM
С
С
С
      EVALUATION OF H MATRIX (TOTAL)
С
С
      H11
С
 35
      CONTINUE
      H11B = G^{*}(G^{*}G - 2.D00^{*}G^{*}Z + 3.D00^{*}Z^{*}Z)/2.D00/T1
      H11C = G*G*(Z*Z - G*C)/T1
      H11D = G^{**3}/3.D00^{*}(G + Z)^{**2}/T1
      Ζ1
            = (1.D00 + Z) * (1.D00 - Z)
      H11A = 1.000 + 2.000 \times X22 + XG2
      H(1,1)=H11A*RINV+ 2.D00*Z*XZ2 + XG2*(H11B + H11C*R + H11D*R*R)
      H(1,1) = H(1,1) - .65809D00
С
С
      H22
С
      H(2,2)=4.D00*RINV+ 2.D00*((XZ2 - 1.D00)*RINV + Z*XZ2)
      H(2,2) = H(2,2) + 4.D00*((XR2 - 1.D00)*RINV + XR2)
```

```
TRM = (1.D00 - (1.D00 + Z*R)*XZ2)*RINV
       TRM2 = -(XZ2 - XR2)*2.D00*Z*RINV/Z1/Z1 + (XZ2 + Z*XR2)/Z1
       TRM2 = TRM2*Z*Z*Z/Z1
       TRM3 = -Z^*(XZ2 - XR2)*RINV/Z1
       TRM3 = Z*Z*Z*(TRM3 + XZ2)/Z1
       TRM = TRM - TRM2 - TRM3
       H(2,2) = H(2,2) + 2.D00*TRM - .5D00
 C
С
       H12
С
       CCLASS = 2.D00*(1.D00 + XZ2)*RINV + 2.D00*Z*XZ2
       TRM = CNORM*(JCL1(1) - C1*JCL2(1))
       TRM2 = CCLASS*TRM - 2.D00*CNORM*(JCL3(1) - C1*JCL1(1))
       TRM2 = TRM2 + 2.D00*CNORM*(-(Z - C1)*JCL1(2)-JCL3(2)+Z*C1*JCL2(2))
       TRM3 = -TRM/2.D00 + TRM2
       H(1,2) = TRM3*PHNEG
       H(2,1) = TRM3*PHPOS
С
С
       CALC. NE MATRIX
C
       DO 40 I=1,2
       NE(I, 1) = -N(I, 1) * .65809D00
 40
       NE(I,2) = -N(I,2) * .5D00
С
С
       CREATE N INVERSE
С
       CALL MOVEC (NINV (1,1),64, N(1,1))
       CALL CDMINV (NINV, NDIM, NDIM, DET)
С
С
      NOW CALCULATION OF PARTIAL DER. OF B W.R.T. T
С
      CALL CDGMPD (NINV, H, RESULT, NDIM, NDIM, NDIM)
      RESULT(1,1) = RESULT(1,1) + .65809D00
      RESULT(2,2) = RESULT(2,2) + .5D00
      CALL CDGMPD(RESULT, B, PDBT, NDIM, NDIM, 1)
      D0 60 I=1,2
 60
      PDBT(I) = -IMAG*PDBT(I)
С
С
      CALC. PIE (REQUIRE BTILDA)
С
      DO 70 I = 1,2
 70
      BT(I) = DCONJG(B(I))
      IF (.NOT. FIRST) GO TO 75
      CALL CDGMPD(H,B,VECT,NDIM,NDIM,1)
      CALL CDGMPD(BT,VECT,PIE,1,NDIM,1)
С
С
      CALC. TOTAL DER. OF B W.R.T. T
С
         1. PARTIAL DER. OF N W.R.T. R
С
```

75 CALL EXCLOR (PDNR (1, 1), 64, PDNR (1, 1))

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С С CALC. DER. OF J INTEGRALS С X = 1.000 - G\*GTRM=(-R\*R\*X+4.D00\*G\*R+4.D00)\*XG1-(R\*R\*X+4.D00\*R+4.D00)\*XR1 DJCL1(1) = 8.D00\*G\*TRM\*RINV\*RINV/(X\*\*3)С G2 = G + 2.D00\*ZX = 1.000 - G2\*G2TRM=(-R\*R\*X+4.D00\*G2\*R+4.D00)\*XZ2\*XG1-(R\*R\*X+4.D00\*R+4.D00)\*XR1 DJCL1(2) = 8.D00\*G2\*TRM\*RINV\*RINV/(X\*\*3)С X = G \* G - 1.000TRM=(R\*R\*X\*X-4.D00\*X\*(G\*G\*R\*R+R+1.D00)+24.D00\*G\*G\*(R+1.D00))\*XR1 TRM=TRM+(R\*R\*X\*X\*(1.D00-G\*R)-4.D00\*X\*(2.D00\*G\*G\*G\*R\*R-G\*R-1.D00)-X 24.D00\*G\*G\*(G\*R+1.D00))\*XG1 DJCL2(1) = 8.D00\*TRM\*RINV\*RINV/(X\*\*4)С X = G2\*G2 - 1.000TRM=(R\*R\*X\*X-4.D00\*X\*(G2\*G2\*R\*R+R+1.D00)+24.D00\*G2\*G2\*(R+1.D00))\* X XR1 TRM=TRM+(R\*R\*X\*X\*(1.D00-G2\*R)-4.D00\*X\*(2.D00\*G2\*G2\*R\*R-G2\*R-1.D00) X -24.D00\*G2\*G2\*(G2\*R+1.D00))\*XZ2\*XG1 DJCL2(2) = 8.D00\*TRM\*RINV\*RINV/(X\*\*4)С X = 1.000 - G\*GTRM=-2.D00\*(1.D00+G\*R)\*XG1+(2.D00\*(1.D00+R)+X\*R\*R)\*XR1 DJCL3(1) = 4.D00\*TRM\*RINV\*RINV/X/XС X = 1.000 - G2\*G2TRM=-2.D00\*(1.D00+G2\*R)\*XZ2\*XG1+(2.D00\*(1.D00+R)+X\*R\*R)\*XR1 DJCL3(2) = 4.D00\*TRM\*RINV\*RINV/X/X С TRM = CNORM\*(DJCL1(1) - C1\*DJCL2(1))PDNR(1,2) = TRM\*PHNEGPDNR(2,1) = TRM\*PHPOSCALL CDGMPD (PDNR, B, VECT, NDIM, NDIM, 1) CALL CDGMPD(BT,VECT,RES,1,NDIM,1) DO 80 I = 1,2PDBR(I) = -.5D00\*RES\*B(I)80 DBT(I) = PDBR(I)\*DRT + PDBT(I)С С С PARTIAL DER. OF E W.R.T. R С 1. PARTIAL DER. OF H W.R.T. R C H11 TRM = -H11A\*RINV\*RINV - (4.D00\*Z\*XZ2+2.D00\*G\*XG2)\*PINV TRM = TRM-4.D00\*Z\*Z\*XZ2-2.D00\*G\*(H11B+H11C\*R+H11D\*R\*R)\*XG2TRM = TRM + (H11C + 2.D00\*H11D\*R)\*XG2PDHR(1,1) = TRM

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С

```
H22
 TRM = -4.D00*RINV*RINV+2.D00*(-2.D00*Z*RINV*XZ2-RINV*RINV*(XZ2-1.I
X00) - 2.D00*Z*Z*XZ2)
 PDHR(2,2) = TRM+4.D00*(-2.D00*RINV*XR2-RINV*RINV*(XR2-1.D00)-2.D0(
X *XR2)
 TRM=-RINV*RINV+RINV*(2.D00*Z*(1.D00+Z*R)+RINV)*XZ2
 TRM2=-2.D00*Z*(-RINV*RINV*(XZ2-XR2)+RINV*(-2.D00*Z*XZ2+2.D00*XR2))
Х
   /Z1/Z1
 TRM2 = TRM2 - 2.D00*Z*(XZ2 + XR2)/Z1
 TRM2 = TRM2 * Z * Z * Z / Z 1
 TRM3=-Z*(-RINV*RINV*(XZ2-XR2)+RINV*(-2.D00*Z*XZ2+2.D00*XR2))/Z1
 TRM3 = Z*Z*Z*(TRM3 - 2.D00*Z*XZ2)/Z1
 TRM = TRM - TRM2 - TRM3
 PDHR(2,2) = PDHR(2,2) + 2.D00*TRM
H12
 TRM = CNORM*(DJCL1(1)-C1*DJCL2(1))*(-.5D00+CCLASS)
 CCLASS = -2.D00*RINV*RINV*(1.D00+XZ2)-4.D00*Z*RINV*XZ2-4.D00*Z*Z*Z
XZ2
 TRM = TRM + CCLASS*CNORM*(JCL1(1) - C1*JCL2(1))
 TRM = TRM - 2.D00*CNORM*(DJCL3(1) - C1*DJCL1(1))
TRM=TRM+2.D00*CNORM*(-(Z-C1)*DJCL1(2)-DJCL3(2)+Z*C1*DJCL2(2))
 PDHR(1,2) = TRM*PHNEG
PDHR(2,1) = TRM*PHPOS
CALL CDGMPD(H, PDBR, VECT, NDIM, NDIM, 1)
CALL CDGMPD (BT, VECT, PDER, 1, NDIM, 1)
CALL CDGMPD (PDHR, B, VECT, NDIM, NDIM, 1)
CALL CDGMPD(BT, VECT, RES, 1, NDIM, 1)
PDER = RES + PDER + DCONJG(PDER)
ARG = PDER
RETURN
END
```

С

С

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Appendix II

## COMPUTER PROGRAM FOR THE VIBRATIONAL EXCITATION CALCULATION

\* С С THIS PROGRAM-COLTRANS-VERSION 2 SIMULATES SEMI-CLASSICAL С SCATTERING OF AN ATOM OFF A VIBRATING DIATOMIC. С С С THE SYMBOL SET IS CHOSEN TO BE AS CLOSE TO NORMAL NOTATION AS С POSSIBLE. С REFER TO VARIOUS DOCUMENTATION IN PROGRAM AND IN MY POSS-С ESSION. С IMPLICIT REAL\*8(A-H, O-Z) С \* С С PROGRAMMER B.KUPPERS (A.P.PENNER) REAL\*8 ERRORX(1), ERRORY(1), ERRORZ(1), ERPX(1), ERPY(1), ERPZ(1), DELP X(1), DELPY(1), DELPZ(1), ALPHA(4)/.5D00, .292893218813453D00, X1.70710678118654D00,.16666666666666666667D00/,BETA(4)/.5D00, X.292893218813453D00,1.707106781186547D00,.5D00/,ANUMB(4)/2.D00,2\* X1.D00,2.D00/,VINIT(13,13) REAL\*4 TMINT, TCPU, TMTRM, TMACCM INTEGER STATEI, STATEF EQUIVALENCE (JN,L) DATA TOOLRB, TOOSB/1.D-07, 1.D-10/ DATA NLENG, NOPART/8,1/ DATA IWRITE/6/, NDIM/13/ COMPLEX\*16 U, PIE, USAVE (13, 13), UCOPY (13, 13), ERRORU (13, 13), TERM, X = UFIN(13)LOGICAL\*4 NTEST,FIRST С С FOLLOWING COMMON BLOCKS STORE С С THE POSITIONS AND MOMENTUM ARE STORED IN COMMON CORPRP.ALSO MASSE С COMMON /CORDRP/RX(1,3), RY(1,3), RZ(1,3), PX(1,3), PY(1,3), PZ(1,3), XTMASS(1) COMMON /RW/NORUN, TMINT, NOTHNG, TMTRM, TMACCM, TCPU COMMON /UMATRX/U(13,13,3) С С INITIAL INFORMATION READ BY READ ROUTINE С PARAMETERS С С TOOLRG IS MAXIMUM TOTAL ERROR FOR POSITIONS AND MOMENTA. С TOOSM IS MINIMUM TOTAL ERROR FOR POSITIONS AND MOMENTA. С NLENG LENGTH IN BYTES FOR ANY SET OF POSITIONS OR MOMENTA ALONG С A GIVEN AXIS С С С CALCULATE VINIT MATRIX C READ (5,2) STATEI, STATEF

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```
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```

```
2
       FORMAT(212)
       WRITE(6,9) STATEI, STATEF
       FORMAT( ' INITIAL STATE = ', 12, ' FINAL STATE = ', 12)
  9
       READ (5,3) ALPHAV, CONST
  3
       FORMAT (2D20.10)
       WRITE (6,4) ALPHAV, CONST
       FORMAT (///, ' ALPHA = ',D13.5,20X, ' B0 CONSTANT = ',D18.10)
  4
       DO 5 I = 1, NDIM
       READ (5,15) UFIN(I)
  15
       FORMAT(2D10.4)
       DO 5 J = 1,NDIM
 5
       VINIT(I,J) = 0.D00
       WRITE(6,16) (UFIN(I), I = 1, NDIM)
      FORMAT(/, ' UFIN = ',/,1X,12D11.4,/,1X,12D11.4,/,1X,2D11.4)
 16
С
С
      GENERATE MATRIX ELEMENTS OF VINIT USING RECURRENCE RELATION.
С
      ALPHA2 = ALPHAV/DSORT(2.D00)
      VINIT(1,1) = 1.0D00
       DO 21 I = 2,NDIM
       REALI = I - 1
      VINIT(1,I) = ALPHA2*VINIT(1,I-1)/DSORT(REALI)
 21
      DO 22 I = 2, NDIM
      REALI = I - 1
      REALI = DSQRT(REALI)
      DO 22 J = I, NDIM
      REALJ = J - 1
      REALJ = DSQRT(REALJ)
      VINIT(I,J) = (REALJ*VINIT(I-1,J-1) + ALPHA2*VINIT(I-1,J))/REALI
 22
      DO 7 I = 1, NDIM
      WRITE (6,6) (VINIT(I,J), J = 1, NDIM)
 6
      FORMAT (/////,6D20.10,/,4D20.10)
 7
      CONTINUE
      DO 8 I = 1, NDIM
      DO 8 J = 1, NDIM
      VINIT(I,J) = VINIT(I,J)*CONST
 8
С
      CALL ERRSET (208,256,-1,1,0,0)
   10 CALL READ (DELTAT, NOTRY, TIME, NWRIT, NTEST, JN2, EPREV, TEND, TOOLRG,
     XTOOSM)
      NCOUNT=0
      DO 11 I = 1, NDIM
      DO 11 J = 1,NDIM
      DO 11 K = 1,3
 11
      U(I,J,K) = (0.D00, 0.D00)
      DO 12 I = 1, NDIM
      DO 12 J = 1,3
 12
      U(I,I,J) = (1.D00,0.D00)
С
       TEST TO SEE IF PREVIOUSLY RUN. IF NOT GO TO STARTING BLOCK ( LABE
С
```

С 40) WHICH USES RUNGE -KUTTA BLOCK IN A SPECIAL FASHION FOR С TWO ITERATIONS. С IF (.NOT.NTEST) GO TO 50 JN1=JN2+1IF (JN1.GT.3) JN1=1 JN=JN1+1 IF (JN.GT.3) JN=1CALL MOVEC (UCOPY(1,1),2704,U(1,1,JN)) GO TO 70 \*\*\*\*\*\*\*\*\* С С С С С \$ NOTE \$ Ç MOVEC AND EXCLOR ARE IBM ASSEMBLER ROUTINES С MOVEC (INTO, NLEN, FROM) С MOVES NLENG BYTES FROM STARTING BYTE FROM INTO STARTING BYTE С INTO С THIS IS USED TO MOVE ARRAY CHUNKS. С С EXCLOR (INTO, NLENG, FROM) С EXCLUSIVE OR'S FROM ONTO INTO FOR A STRING NLENG BYTES LONG. С THIS IS USED TO ZERO OUT MATRIX. С С С DERIVATIVES OF POSITIONS AND MOMENTA JN1, JN2, SAVED. TEST TO SEE IF FIRST LOOP OF R.-K. AND APPROPRIATE POINT CALC. С С \*\*\*\*\*\*\*\*\*\*\*\*\* С С C С INTERVAL IS SHORTENED IF MOTION TOO LARGE-BACK STEP TO N-3 TIME С STEP AND P.C.RESTARTED. С LOSE TWO ITERATIONS SINCE POINTERJN3 HAS ALREADY BEEN SHIFTED. С 20 TIME=TIME-DELTAT NOTRY=NOTRY-1 DELTAT=DELTAT\*.5D00 NORUN=2\*NORUN-NOTRY WRITE (IWRITE, 160) DELTAT, NOTRY, NORUN NTEST=.FALSE. IF (DELTAT .LT.1.D-07) CALL EXIT С C FURTHEST BACK KNOWLEDGE STEP JN3 LOADED INTO R(I,1)SO TO START С IN RUNGE-KUTTA. С IF (JN2.EQ.1) GO TO 50 CALL MOVEC(RX(1,1),NLENG,RX(1,JN2)) CALL MOVEC(RY(1,1),NLENG,RY(1,JN2))

```
CALL MOVEC (RZ(1,1), NLENG, RZ(1, JN2))
      CALL MOVEC(PX(1,1),NLENG,PX(1,JN2))
      CALL MOVEC (PY(1,1), NLENG, PY(1, JN2))
      CALL MOVEC (PZ(1,1), NLENG, PZ(1, JN2))
      CALL MOVEC(U(1,1,1),2704,U(1,1,JN2))
      GO TO 50
С
С
      CALCULATION DONE TOO ACCURATELY-TRUNCATIONAND ROUND OFF ERROR OF
C
       SAME ORDER. LENGTHEN INTERVAL LOAD LAST CALC. R(I, JN) INTO R(I,
С
      ) AND RESTART WITH RUNGE KUTTA.
С
   30 DELTAT=DELTAT*2.D00
      NORUN=(NORUN+NOTRY)/2
   40 WRITE (IWRITE, 160) DELTAT, NOTRY, NORUN
      NTEST=.FALSE.
      IF (JN1.EQ.1) GO TO 50
      CALL MOVEC(RX(1,1),NLENG,RX(1,JN1))
      CALL MOVEC (RY(1,1), NLENG, RY(1, JN1))
      CALL MOVEC (RZ(1,1), NLENG, RZ(1, JN1))
      CALL MOVEC(PX(1,1),NLENG,PX(1,JN1))
      CALL MOVEC(PY(1,1),NLENG,PY(1,JN1))
      CALL MOVEC(PZ(1,1),NLENG,PZ(1,JN1))
      CALL MOVEC (U(1,1,1),2704,U(1,1,JN1))
 ************************
С
С
   *************************
С
С
      RUNGE-KUTTA BLOCK.
С
   50 JN2=1
      JN1=JN2
      JN=2
      CALL MOVEC (UCOPY (1,1), 2704, U(1,1, JN2))
      GO TO 70
   60 EPREV=E
      IF (NOTRY.EQ.0) GO TO 67
   65 NOTRY=NOTRY+1
      JN1=2
      JN=3
      NTEST=.TRUE.
      GO TO 90
С
С
        SET UP ENERGY TEST IF NOTRY=0
С
   67 TOOLRG=DABS (TOOLRB*E)
      TOOSM=DABS (TOOSB*E)
     WRITE (IWRITE, 170) E, TOOLRG, TOOSM
      GO TO 65
С
С
      FIRST STEP ERROR ARRAYS INITIALIZED TO ZERO
С
```

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70 CALL EXCLOR (ERRORX (1), NLENG, ERRORX (1)) CALL EXCLOR (ERRORY (1), NLENG, ERRORY (1)) CALL EXCLOR (ERRORZ (1), NLENG, ERRORZ (1)) CALL EXCLOR (ERPX (1), NLENG, ERPX (1)) CALL EXCLOR(ERPY(1), NLENG, ERPY(1)) CALL EXCLOR (ERPZ (1), NLENG, ERPZ (1)) CALL EXCLOR (ERRORU(1,1), 2704, ERRORU(1,1)) IF (.NOT.NTEST) GO TO 90 POINTERS ARE NOW CHANGED FOR POSITIONS OF MOMENTA AND POSITIONS 80 IHOLD=JN2 JN2=JN1 JN1=JN JN=IHOLD 90 CALL MOVEC (RX(1,JN), NLENG, RX(1,JN1)) CALL MOVEC(RY(1,JN),NLENG,RY(1,JN1)) CALL MOVEC (RZ(1,JN), NLENG, RZ(1,JN1))CALL MOVEC (PX(1, JN), NLENG, PX(1, JN1)) CALL MOVEC(PY(1,JN),NLENG,PY(1,JN1)) CALL MOVEC (PZ(1, JN), NLENG, PZ(1, JN1)) FIRST=.TRUE. NOW ACTUAL R. K. G. PROCEDURE DO 140 KK=1,4 IF (KK.EQ.2.OR.KK.EQ.4) TIME=TIME+.5D00\*DELTAT X=RX(1,JN)R=X CALL QUANTM (TIME, R, UCOPY, USAVE, DET, PIE, FIRST, VINIT, ALPHAV, UFIN, Х STATEI) DELPX(1) = -DETFINAL RESULT LOADED INTO A THEN ENERGY CALCULATED AND TESTED. IF (.NOT.FIRST) GO TO 110 TK=0.D00 DO 100 I=1,NOPART 100 TK=TK + PX(I,JN1) \* 2/(2.D00 \* TMASS(I))E=PIE+TK IF (.NOT.NTEST) GO TO 110 CALL MOVEC(U(1,1,JN1),2704,UCOPY(1,1)) ERROR=DABS (EPREV-E) IF (ERROR.GT.TOOLRG) GO TO 20 IF (ERROR.LT.TOOSM.AND.DELTAT.LT.1.9D00) GO TO 30

С

EPREV=E

C C C C C

C

C C

С

C C

С

С

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С С NOW NEW POSITIONS AND MOMENTA OF A PARTICULAR ITERATION CALCULATE C 110 ALP=ALPHA(KK) APP=3.D00\*ALP BET=BETA(KK) ANUM=ANUMB(KK) DO 120 I=1,NOPART TMASSI=TMASS(I) PXI=PX(I,L) XK=PXI/TMASSI ERROR=ERRORX(I) RX(I,L)=RX(I,L)+ALP\*(XK-ANUM\*ERROR)\*DELTAT ERRORX(I) = ERROR+APP\* (XK-ANUM\*ERROR) - BET\*XK DELP=DELPX(I) ERP=ERPX(I)PX(I,L)=PXI+ALP\*(DELP-ANUM\*ERP)\*DELTAT ERPX(I) = ERP+APP\* (DELP-ANUM\*ERP) - BET\*DELP 120 CONTINUE С С NEW A CALCULATED FOR A PARTICULAR ITERATION С DO 130 I=1,NDIM DO 130 J = 1, NDIM TERM=ALP\*(USAVE(I,J)-ANUM\*ERRORU(I,J)) UCOPY(I,J)=UCOPY(I,J)+TERM\*DELTAT 130 ERRORU(I,J)=ERRORU(I,J)+3.D00\*TERM-BET\*USAVE(I,J) FIRST=.FALSE. 140 CONTINUE С IF (.NOT.NTEST) GO TO 60 С NOW TIME INCREMENTED AND ITERATION COUNTERS AND TEST TO SEE IF С THERE IS TO BE PRINTOUT С NOTRY=NOTRY+1 NCOUNT=NCOUNT+1 IF (NCOUNT.LT.NWRIT) GO TO 80 CALL WRITE (NOTRY, TIME, JN1, DELTAT, E, TK, PIE, UFIN, STATEI, STATEF, \$10) NCOUNT=0 GO TO 80 160 FORMAT (1H0, 'TIME INTERVAL CHANGED TO', G15.8, ' AT STEP', 18, ' NUMB XR OF RUNS IS ', I10) 170 FORMAT(1H , 'INITIAL ENERGY IS ', D20.10,' WITH UPPER TOLERANCE ' XG20.10, ' AND LOWER TOLERANCE', G20.10, ' ON ENERGY'/) END SUBROUTINE QUANTM(T,R,U,DUT,ARC,PIE,FIRST,VINIT,ALPHAV,UFIN, X STATEI) IMPLICIT COMPLEX\*16 (A-H, O-Z) INTEGER STATEI REAL\*8 T, R, DEXP, ARG, DSORT, VINIT(13, 13), ALPHAV, E(13), XR,

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```
XREALI, DSIN, DCOS
       DATA NDIM/13/
       COMPLEX*16 IMAG/(0.D00,1.D00)/,U(13,13),DUT(13,13),V(13,13),
      Х
         PHASE, UFIN(13), UCOL(13), TEMP1(13, 13), TEMP2(13)
       LOGICAL*4 FIRST
       XR = DEXP(-ALPHAV*R)
       IF (XR .LT. 1.D-20) XR = 0.D00
С
C
       EVALUATION OF V MATRIX AND E VECTOR
С
       DO 5 I = 1, NDIM
       UCOL(I) = U(I, STATEI)
       REALI = I - 1
 5
       E(I) = 0.5D00 + REALI
       DO 6 I = 1, NDIM
 6
       V(I,I) = VINIT(I,I) * XR
       DO 7 I = 2,NDIM
       REALI = I - 1
       PHASE = DCOS(REALI*T) - IMAG*DSIN(REALI*T)
       INDIM = NDIM - I + 1
       DO 7 J = 1, INDIM
       V(J,I+J-1) = VINIT(J,I+J-1)*XR*PHASE
 7
       V(I+J-1,J) = DCONJG(V(J,I+J-1))
С
С
       CALCULATION OF TOTAL DER. OF B W.R.T. T
С
       CALL CDGMPD (V,U,DUT,NDIM,NDIM,NDIM)
       DO 11 I = 1, NDIM
       DO 11 J = 1, NDIM
 11
       \text{TEMP1}(I,J) = \text{DCONJG}(\text{DUT}(J,I))
       CALL CDGMPD (TEMP1, UCOL, TEMP2, NDIM, NDIM, 1)
      CALL CDGMPD (UFIN, TEMP2, EPERT, 1, NDIM, 1)
      EPERT = EPERT/UFIN(STATEI)
      DO 60 I=1, NDIM
      DO 60 J = 1, NDIM
 60
      DUT(I,J) = -IMAG*DUT(I,J)
C
С
      CALC. PIE
С
      IF (.NOT. FIRST) GO TO 75
      DO 20 I = 1, NDIM
      DO 20 J = 1, NDIM
 20
      \text{TEMP1}(I,J) = E(J) * \text{DCONJG}(U(J,I))
      CALL CDCMPD (TEMP1, UCOL, TEMP2, NDIM, NDIM, 1)
      CALL CDGMPD (UFIN, TEMP2, PIE, 1, NDIM, 1)
      PIE = PIE/UFIN(STATEI)
      PIE = PIE + EPERT
 75
      CONTINUE
С
С
      PARTIAL DER. OF E W.R.T. R
```

С

С

```
С
      ARG = -ALPHAV*EPERT
      RETURN
      END
      SUBROUTINE READ (DELTAT, NOTRY, TIME, NWRIT, NTEST, JN2, EO, TND, TOOLRG,
     XTOOSM)
С
С
      THIS SUBROUTINE READS THE INITIAL DATA FROM DISK AND CARDS
С
      TO START THE CALCULATION.
С
      IMPLICIT REAL*8(A-H, O-Z)
      COMPLEX*16 U,A(13,3)
      REAL*8 ZIP1(19)
      COMMON /UMATRX/U(13, 13, 3)
      DATA IREAD, IWRITE/5,6/, NDIM/13/
      REAL*4 TMTRM, TMACCM, TMINT, TCPU
      LOGICAL*4 NTEST, START/.TRUE./
      COMMON /CORDRP/RX(1,3), RY(1,3), RZ(1,3), PX(1,3), PY(1,3), PZ(1,3),
     XTMASS(1)
      EQUIVALENCE (ZIP1(1), RX(1,1))
      COMMON /RW/NORUN, TMINT, NREAD, TMTRM, TMACCM, TCPU
      IF (START) GO TO 20
   10 READ (IREAD, 130, END=70) NORUN, NREAD, NWRIT, TND
      READ (NREAD) JN2, NOTRY, NTEST, EO, TIME, DELTAT, TOOLRG, TOOSM
      READ (NREAD) ZIP1
      READ (NREAD) A
      READ (NREAD, END=30)
      WRITE (IWRITE,90) NREAD
      GO TO 70
   20 CALL $TRTM(TCPU)
С
      $TRTM STARTS THE CPU TIMER.
      READ (IREAD, 80) TMINT, TMTRM
      TMACCM=0.0
      START=.FALSE.
      GO TO 10
   30 IF (NOTRY.GE.NORUN) GO TO 10
      REWIND NREAD
      JN=JN2-1
      IF (JN2.E0.1) JN=3
      IF (.NOT.NTEST) JN=JN2
      WRITE (IWRITE, 120) DELTAT, (I, PX(I, JN), PY(I, JN), PZ(I, JN), TMASS(I),
     XRX(I,JN), RY(I,JN), RZ(I,JN), I=1,1)
      WRITE (IWRITE, 100)
                               (I,A(I,JN),I=1,NDIM)
      RETURN
   70 CALL EXIT
      RETURN
   80 FORMAT (2G10.0)
   90 FORMAT (1H
                   , 'ON READING DATA SET-ENDFILE MISSING', 15)
```

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```
,'B MATRIX'/(15,2G20.10))
  100 FORMAT (1H
                   ,7A4)
  110 FORMAT (1H
  120 FORMAT (1H1,28X, 'SEMICLASSICAL SCATTERING OF PROTON-HYDROGEN SYST
             ,31X, 'INITIAL TIME INTERVAL USED IN CALCULATION IS',D20.10
     XM'/1H
     X' A.U.'///1H ,53X,'INITIAL PARTICLE PARAMETERS'///1H
                                                                  , PARTICL
     X*', 6X, 'PX', 5X, '**', 6X, 'PY', 5X, '**', 6X, 'PZ', 5X, '**', 3X, 'TMASS', 5X,
     X**',6X,'RX',5X,'**',6X,'RY',5X,'**',6X,'RZ',5X,'*'/(1H ,2X,15,2X
     X7D15.8))
  130 FORMAT (110,215,D20.10)
      END
      SUBROUTINE WRITE (NOTRY, TIME, JN, DELTAT, E, TK, PIE, UFIN, STATEI, STATEF
     Х
       *)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER STATEI, STATEF
      REAL*8 ZIP1(19)
      COMMON /CORDRP/RX(1,3), RY(1,3), RZ(1,3), PX(1,3), PY(1,3), PZ(1,3),
     XTMASS(1)
      EQUIVALENCE (ZIP1(1), RX(1,1))
      LOGICAL*4 NTEST
      COMPLEX*16 U, PIE, UCHECK(13,13), UDAG(13,13), TEST(13,13), UFIN(13)
      COMMON /UMATRX/U(13, 13, 3)
      REAL*4 TMTRM, TMACCM, TCPU, TMINT, PHASE
      DATA IWRITE/6/, NOPART/1/, NDIM/13/
      COMMON /RW/NORUN, TMINT, NWRT, TMTRM, TMACCM, TCPU
   20 TIMN=TIME-DELTAT
      WRITE (IWRITE, 70) NOTRY, TIMN, (I, PX(I, JN), PY(I, JN), PZ(I, JN), RX(I, J
     X), RY(I, JN), RZ(I, JN), I=1, NOPART)
      R=RX(1,JN)
      WRITE(IWRITE,55) R
      DO 30 I=1, NDIM
      VA=CDABS(U(I,STATEI,JN))**2
С
С
      VA IS THE SQUARE OF THE MODULUS OF THE COEFFICIENTS.
С
   30 WRITE (IWRITE, 60) I, U(I, STATEI, JN), VA
      WRITE (IWRITE, 90) PIE, TK, E
      IF (NOTRY.LT.NORUN) GO TO 40
      WRITE(IWRITE, 50)
 50
      FORMAT(1H1)
      DO 52 I = 1,NDIM
      WRITE (IWRITE, 51) (U(I, J, JN), J = 1, NDIM)
 51
      FORMAT (///, 1X, 12D11.4, /, 1X, 12D11.4, /, 1X, 2D11.4)
 52
      CONTINUE
      DO 56 I = 1,NDIM
      DO 56 J = 1, NDIM
      UCHECK(I,J) = U(I,J,JN)
 56
      UDAG(J,I) = DCONJG(UCHECK(I,J))
      CALL CDGMPD (UDAG, UCHECK, TEST, NDIM, NDIM, NDIM)
      WRITE (IWRITE, 57)
 57
      FORMAT(1H1)
```

```
DO 59 I = 1,NDIM
   UFIN(I) = U(STATEF, I, JN)
   WRITE (IWRITE, 58) (TEST(I, J), J = 1, NDIM)
   FORMAT(1X,12D11.4,/,1X,12D11.4,/,1X,2D11.4,////)
   CONTINUE
   DO 100 I = 1,NDIM
   VA = CDABS(UFIN(I)) **2
   TEMP1 = UFIN(I)
   TEMP2 = (0.D00, -1.D00) * UFIN(I)
   PHASE = 180.D00/3.14159D00*DATAN(TEMP2/TEMP1)
   IF (TEMP1 .LT. 0.D00) PHASE = PHASE + 180.0
   IF (PHASE .LT. 0.0)
                          PHASE = PHASE + 360.0
   WRITE (6,101) UFIN(I), VA, PHASE
   FORMAT(/,1X,2D13.4,D20.4,F15.1)
   CONTINUE
   RETURN 1
40 CONTINUE
   RETURN
55 FORMAT(1H ,'*** THE INTERNUCLEAR SEPARATION R IS ', D20.10/1H ,1X,
  X'STATE * ',16X,'B MATRIX',16X,' ** ','B MODULUS SQUARED *')
60 FORMAT (1H ,15,3X,2G20.10,4X,G20.10)
```

70 FORMAT (1H0, 'RUN NUMBER', I10, 'AT T= ', D20.13, 'A.U.'/1H ,'OBJEC X \*',8X,'PX',8X,'\*',1X,'\*',8X,'PY',8X,'\*',1X,'\*',8X,'PZ',8X,'\*',1X X'\*',8X,'RX',8X,'\*',1X,'\*',8X,'RY',8X,'\*',1X,'\*',8X,'RZ',8X,'\*'/(1 X ,2X,I2,2X,6(1X,D20.13)))

90 FORMAT (1H ,10X,'\*\*\* TOTAL QUANTUM ENERGY ',2D20.10/1H ,10X,'\*\* X KINETIC ENERGY',D20.10,2X,'TOTAL ENERGY',D20.10) END

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58 59

101

100

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and like loiterers

on the fringes of a fair

we ogle the unobtainable

imagined mystery

Yet away around on the far side

like the stage door of a circus tent

is a wide wide vent in the battlements

where even elephants

waltz thru

- L. Ferlinghetti