

THE UNIVERSITY OF MANITOBA

A GENERALIZED IMPACT PARAMETER MODEL APPLICABLE TO
CHEMICAL REACTIONS

by

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"Up the road, in his shack, the old man was sleeping again. He was still sleeping on his face and the boy was sitting by him watching him. The old man was dreaming about the lions."

Ernest Hemingway

TO THE LIONS

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I can sincerely say that I have had both an educational and an enjoyable stay at the University of Manitoba.

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ABSTRACT

The development of a semiclassical model for atomic and molecular collisions is discussed. The model treats the interaction forces explicitly so that no resort to model potentials need be made. Using this model a description of the collision throughout the entire region of interaction is possible. The equations of the model are solved numerically.

Preliminary calculations have been carried out on the simple system consisting of a proton colliding with a hydrogen atom. Studies were made at both low and high energies. At low energies, the model casts considerable doubt on the validity of the adiabatic approximation, and, in fact, on the assumption of any static model potential to describe a dynamic process such as a collision. At high energies, the model gives excellent agreement with experimental charge exchange cross sections, and adds to the controversy over an appropriate basis set for the description of high-energy p - H scattering.

The model is also applied to the "reverse" collision, the photodecomposition of H_2^+ . This allows an estimate of the lifetime of the excited intermediate state due to photon absorption and of the probability for decomposition.

The model is shown to be capable of generalization to many-centre reactions.

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Chapter I

INTRODUCTION

The study of chemistry is largely the study of molecular interactions, and molecular interactions may be described mathematically by the formalism of collision theory. Consequently one might expect, and indeed would find, that a good deal of research into the theoretical aspects of atomic and molecular processes has involved this formalism as a starting point[†] (1). Such approaches undeniably have proved fruitful in disclosing certain aspects of reactive molecular encounters, but they come no where near prescribing a "mechanism" for the reaction of interest. That is to say, although one may employ the results of collision theory to describe a given chemical reaction, the extent of our knowledge of the reaction is essentially limited to the calculation either of asymptotic final states or some perturbative expansion of the initial state into the interaction region. Neither of these pieces of information is too useful to the understanding of chemical reactions, the former because the asymptotic final states will tell one little of what occurred during the interaction in the way of rearrangement processes, and the latter because a perturbative expansion to any finite order is really an "initial value solution" only and this solution is therefore valid only when the initial conditions are maintained to

[†]Reference 1 contains a selective sampling of such research.

a high degree throughout the process (2), a situation obviously atypical of chemical reactions. Thus, from such approaches, one has no picture of the causal evolution of the reacting species, of the complexity of sub-processes which may constitute a chemical reaction.

Because of these difficulties recent years have seen a swing to what perhaps could be called "more realistic models" (3). Although the basic aim of these models is the understanding of the physical mechanism of chemical reactions, the impetus has been provided by the need for interpretation of molecular beam studies. Typical calculations of this type include the following two steps as a main framework:

- 1) the assumption of some potential energy surface describing the interaction between the species, and,
- 2) some form of trajectory calculation which is carried out to evaluate the angular distribution of products, cross sections for various processes, and the like.

Now the idea of a trajectory implies a semiclassical model in which the atoms or molecules move along classical trajectories determined by some potential (step 1).

Presuming that such a potential can be found, step 2 requires

the solution of the classical many-body problem which is quite feasible by present computer techniques. Now although the internal electronic structure of atoms and molecules certainly must be treated quantum-mechanically, there can be little argument with the treatment of the positions and momenta of an atom or molecule, as a whole, classically. Consequently such models have led to a simplification of the problem in this sense. The quarrel that the present author has with these "more realistic models" is that they have treated step 1 completely unrealistically. For example, common approaches to potentials are as follows:

- 1) if the system is sufficiently simple (for example, atom-atom collisions) the potential surface may be taken, for thermal collisions, to be the static (velocity independent) ground state potential energy surface or some analytic approximation to it.
- 2) for more complicated cases, some model potential (4), or even set of model potentials (5) may be assumed, the general characteristics of the process being described by this potential.

It is difficult to see how one can, if he accepts the idea of a model potential, achieve any more understanding of the details of a given process than he puts into the model

potential. Furthermore, the non-uniqueness of the results obtained by suitably choosing a variety of parameters is scarcely satisfactory and the assumption of a static potential energy surface as an interaction potential is unquestionably questionable.

It was this discontent with these semiclassical approaches to atomic and molecular collisions which initiated the research discussed in this manuscript. It was felt that a model could be developed which was capable not only of describing the state of the system completely throughout the interaction region but also of treating the interaction forces explicitly, with the result that the model would be entirely dynamic and no resort to static potential energy surfaces would be necessary. In this dissertation the development of such a model is discussed. It is important to note that although the model is developed in terms of a semiclassical picture, it is easily generalized to a fully quantum mechanical model by the use of some practical method to treat the various classical modes quantum mechanically (for example, a wave packet treatment of the translational states of the atoms). It is, however, also important to realize that a semiclassical picture of atomic and molecular collisions is quite justified due to the large masses of the interacting species.

Chapter II

A BRIEF DISCUSSION OF THE FORMALISM OF THE EVOLUTION OF A QUANTUM SYSTEM IN TIME[†]

[†] The ideas discussed in this chapter are essentially those of reference 6.

In attempting to obtain a model for molecular collisions which is useful at all stages of the interaction, one is in fact trying to solve the time-dependent Schrodinger equation at all times t . For this reason, a brief discussion of the formalism used in treating the time development of a quantum system is worthwhile as an orientation to the problem and to the futility of using conventional techniques such as time-dependent perturbation theory to obtain a solution. Since the development of the model in the following chapter is carried out in the Schrodinger picture, this will be the only mode of description discussed here.

The observable dynamical quantities of a quantum system are the expectation values of the various observables

$$\langle \Omega \rangle = \langle \Psi | \Omega | \Psi \rangle \quad (\text{II.1})$$

The Schrodinger picture assumes that the form of the operators Ω remains unchanged in time (unless Ω has an explicit time dependence) and that the state vector $|\Psi\rangle$ bears the time dependence. If the system is not subjected to observation during the time interval (t_0, t) , the state at time t , $|\Psi(t)\rangle$, is exactly specified by the state of the system at time t_0 , $|\Psi(t_0)\rangle$. This specification is made more precise by the postulate that the linear

superposition of states is preserved in the course of time. Consequently there is a linear correspondence between $|\Psi(t_0)\rangle$ and $|\Psi(t)\rangle$ which defines a time-translation operator $U(t, t_0)$:

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle. \quad (\text{II.2})$$

This operator is most commonly known as the evolution operator. Obviously it satisfies the initial condition

$$U(t_0, t_0) = 1, \quad (\text{II.3})$$

where 1 is the unit operator, and it also obeys the group property

$$U(t, t_0) = U(t, t_1)U(t_1, t_0). \quad (\text{II.4})$$

The evolution operator can be shown to be unitary as follows. From the group property it is apparent that

$$U(t_0, t_1)U(t_1, t_0) = 1, \quad (\text{II.5})$$

or,

$$U(t_1, t_0) = U^{-1}(t_0, t_1). \quad (\text{II.6})$$

(7)

Since, in the course of time development of the system, the normalization must not change,

$$\langle \Psi(t) | \Psi(t) \rangle = \langle \Psi(t_0) | U^\dagger(t, t_0) U(t, t_0) | \Psi(t_0) \rangle = \langle \Psi(t_0) | \Psi(t_0) \rangle ,$$

or,

$$U^\dagger(t, t_0) U(t, t_0) = 1 . \quad (\text{II.7})$$

Now multiplying (II.5) from the left by $U^\dagger(t_0, t_1)$ and using (II.7), one obtains

$$U(t_1, t_0) = U^\dagger(t_0, t_1) . \quad (\text{II.8})$$

Comparison of (II.6) and (II.8) shows that

$$U^{-1}(t_0, t_1) = U^\dagger(t_0, t_1) , \quad (\text{II.9})$$

which is the desired unitary property of U .

To obtain the differential operator equation satisfied by the evolution operator, one uses the group property in the form

$$U(t, t_0) = U(t, t - \delta t) U(t - \delta t, t_0) , \quad (\text{II.10})$$

where $t-\delta t$ is a time moment immediately preceding t . For small δt , $U(t, t-\delta t)$ is an infinitesimal unitary operator, and denoting its generator by $H(t)$, one can write[†]

$$U(t, t-\delta t) = 1 - \frac{i\delta t H(t)}{\hbar} . \quad (\text{II.11})$$

Substitution of (II.11) into (II.10) yields

$$\frac{U(t, t_0) - U(t-\delta t, t_0)}{\delta t} = -\frac{i}{\hbar} H(t) U(t-\delta t, t_0) ,$$

which, in the limit as $\delta t \rightarrow 0$, becomes

$$-i\hbar \partial_t U(t, t_0) + H(t) U(t, t_0) = 0 \quad (\text{II.12})$$

To make contact with the usual Schrodinger picture in terms of the state vector, it is only necessary to apply the operator equation (II.12) to the state vector $|\Psi(t_0)\rangle$ to obtain

$$i\hbar \partial_t |\Psi(t)\rangle = H(t) |\Psi(t)\rangle , \quad (\text{II.13})$$

[†] An infinitesimal unitary transformation T may be written as $T = 1 + i\epsilon G$, where G is the generator and ϵ is a real parameter. In equation (II.11) the parameter is $-\delta t$, and the factor \hbar^{-1} ensures that H has the dimension of energy.

which is the familiar time-dependent Schrodinger equation, the generator $H(t)$ being known as the Hamiltonian.

Thus to be in a position to calculate the various observables of the quantum system at any time t , it is necessary to be able to solve the time-dependent Schrodinger equation at all times. This is equivalent to a knowledge of the evolution operator $U(t, t_0)$ for all times t . Conventionally, solutions of the time-dependent Schrodinger equation are approximated by perturbation theory. This theory supposes that the Hamiltonian H is susceptible to resolution as

$$H(t) = H_0(t) + V(t) , \quad (\text{II.14})$$

where H_0 may be regarded as the Hamiltonian of a known approximate solution to the full problem, and V may be considered as a small perturbation. In such cases it is useful to set

$$U = U_0 U_I , \quad (\text{II.15})$$

where U_0 is the (known) solution of the operator equation

$$i\hbar \partial_t U_0 = H_0 U_0 , \quad U_0(t_0, t_0) = 1 . \quad (\text{II.16})$$

(10)

Substitution of equation (II.15) into the differential equation (II.12) for the full evolution operator, and multiplication of the resulting equation from the left by U_0^\dagger yields

$$i\hbar \partial_t U_I = U_0^\dagger (H U_0 - i\hbar \partial_t U_0) U_I . \quad (\text{II.17})$$

U_I is the solution of this equation satisfying the initial condition $U_I(t_0, t_0) = 1$. Thus, if one could obtain an expression for U_I , the full evolution operator U would be known. However, from the resolution of the Hamiltonian as in (II.14), equation (II.17) may be written as

$$i\hbar \partial_t U_I = (U_0^\dagger V U_0) U_I , \quad (\text{II.18})$$

and since V has an explicit dependence upon time, a closed solution for U_I is, in general, impossible. The solution, however, may be obtained formally by iteration. Recasting equation (II.18) as an integral equation incorporating the boundary condition, one obtains

$$U_I(t, t_0) = 1 + (i\hbar)^{-1} \int_{t_0}^t d\tau U_0^\dagger(\tau, t_0) V(\tau) U_0(\tau, t_0) U_I(\tau, t_0) . \quad (\text{II.19})$$

(11)

The zeroth approximation to U_I is then $U_I(t, t_0) = 1$. This leads to the first approximation

$$U_I(t, t_0) = 1 + (i\hbar)^{-1} \int_{t_0}^t d\tau U_0^\dagger(\tau, t_0) V(\tau) U_0(\tau, t_0) .$$

To obtain the second approximation, the first approximation is substituted for $U_I(\tau, t_0)$ in the right-hand side of (II.19), and so on to higher orders. This results in the following expansion for $U_I(t, t_0)$:

$$\begin{aligned} U_I(t, t_0) = & 1 + (i\hbar)^{-1} \int_{t_0}^t d\tau_1 U_0^\dagger(\tau_1, t_0) V(\tau_1) U_0(\tau_1, t_0) \\ & + (i\hbar)^{-2} \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 U_0^\dagger(\tau_2, t_0) V(\tau_2) U_0(\tau_2, t_0) U_0^\dagger(\tau_1, t_0) \times \\ & \qquad \qquad \qquad V(\tau_1) U_0(\tau_1, t_0) \\ & + \dots . \end{aligned} \tag{II.20}$$

Then from (II.15) and (II.20), the full evolution operator is given by

$$\begin{aligned} U(t, t_0) = & U_0(t, t_0) + (i\hbar)^{-1} \int_{t_0}^t d\tau_1 U_0(t, \tau_1) V(\tau_1) U_0(\tau_1, t_0) \\ & + (i\hbar)^{-2} \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 U_0(t, \tau_2) V(\tau_2) U_0(\tau_2, \tau_1) V(\tau_1) U_0(\tau_1, t_0) \\ & + \dots . \end{aligned} \tag{II.21}$$

Suppose now that H_0 is time-independent. This is usually the case for chemical collision problems, H_0 then corresponding to the various asymptotic channel Hamiltonians. Since H_0 is not dependent upon time, the solution of equation (II.16) is simply

$$U_0(t, t_0) = \exp[-iH_0(t-t_0)/\hbar] . \quad (\text{II.22})$$

Assuming that the state of the system at time t_0 is known, to find the value of the observable Ω on the system at time t it is necessary to use $U(t, t_0)$ as given by equation (II.21) to evolve the state of the system from t_0 to t . A simpler example as far as notation is concerned is that of the transition probability. Suppose that a complete set of eigenvectors of H_0 is the discrete set $|a\rangle$, $|b\rangle$, ..., $|k\rangle$, ..., and that the corresponding eigenvalues are E_a^0 , E_b^0 , ..., E_k^0 , Allowing the system to be in the eigenstate $|a\rangle$ at time t_0 , the probability of finding the system in state $|b\rangle$ at time t is given by

$$W_{a \rightarrow b} = |\langle b | U(t, t_0) | a \rangle|^2 . \quad (\text{II.23})$$

Since H is still explicitly dependent upon time, it is necessary to resort to the expansion (II.21) to obtain $U(t, t_0)$. The successive contributions to the transition

amplitude are as follows:

$$\langle b|U^{(0)}|a\rangle = 0, \quad (\text{II.24a})$$

$$\begin{aligned} \langle b|U^{(1)}|a\rangle = (i\hbar)^{-1} \int_{t_0}^t d\tau_1 e^{-iE_b^0(t-\tau_1)/\hbar} \langle b|V(\tau_1)|a\rangle \times \\ e^{-iE_a^0(\tau_1-t_0)/\hbar} \end{aligned} \quad (\text{II.24b})$$

$$\begin{aligned} \langle b|U^{(2)}|a\rangle = (i\hbar)^{-2} \sum_k \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 e^{-iE_b^0(t-\tau_2)/\hbar} \times \\ \langle b|V(\tau_2)|k\rangle e^{-iE_k^0(\tau_2-\tau_1)/\hbar} \langle k|V(\tau_1)|a\rangle e^{-iE_a^0(\tau_1-t_0)/\hbar} \end{aligned} \quad (\text{II.24c})$$

and so on. These increasing orders of approximation to the transition amplitude may be interpreted as follows:

- 1) to zeroth order there is no coupling and the system remains in the eigenstate $|a\rangle$.
- 2) to first order (equation(II.24b)), the system can be regarded as propagating from time t_0 to τ_1 under the influence of the evolution operator $U_0(t, \tau_1)$, its state at time τ_1 being $|a\rangle e^{-iE_a^0(\tau_1-t_0)/\hbar}$. At τ_1 the perturbation $V(\tau_1)$ causes transition to state $|b\rangle$.

From τ_1 to t the system remains in state $|b\rangle$, evolving according to U_0 .

- 3) to second order (equation(II.24c)), there is a transition at time τ_1 from $|a\rangle$ to an intermediate state $|k\rangle$, and again at time τ_2 from $|k\rangle$ to $|b\rangle$. At all other times the system evolves under U_0 .
- 4) by now it should be apparent that the third order contribution involves two intermediate states $|k\rangle$ and $|l\rangle$. Similarly the n -th order contribution involves $(n-1)$ virtual states.

Diagrammatically, these contributions to the transition amplitude may be depicted as shown in Figure 1.

The purpose for labouring through the above discussion was to indicate the extent of the validity of a perturbative solution to problems of chemical reactions. Physically this may be most easily understood by considering the general molecular reaction $A + B \rightarrow C + D$, as depicted schematically for the centre of mass frame in Figure 2. According to first-order perturbation theory, only the initial and final states are coupled by the interaction causing the reaction. However, in a chemical reaction, not only are the initial and final states usually spatially separated, but they are also frequently extremely dissimilar. Consequently, the overlap charge density between these states

Figure 1

Diagrammatic representation of the contributions to the
transition amplitude in perturbation theory.

(15)

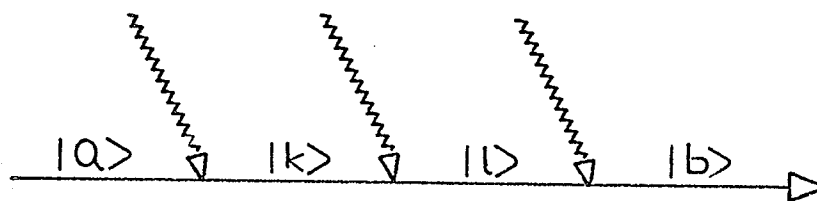
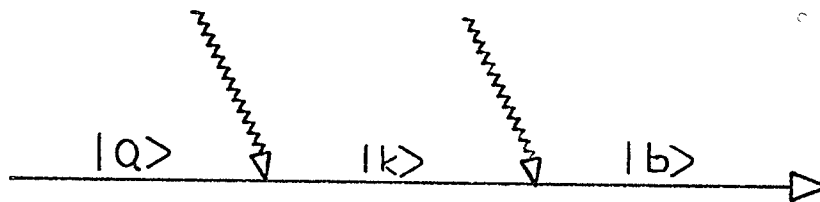
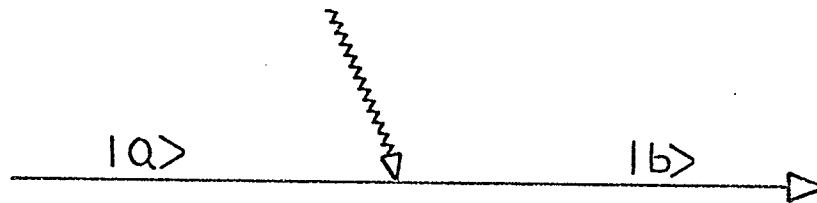
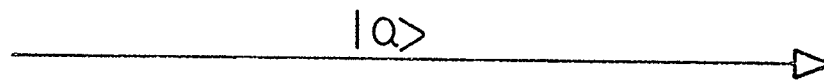
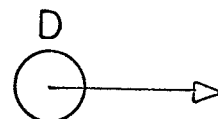
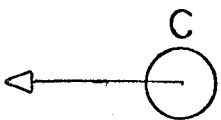
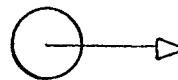
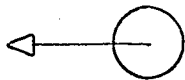
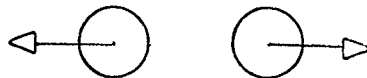
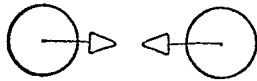
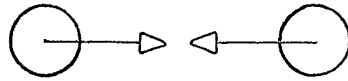
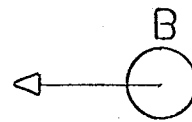
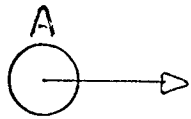


Figure 2

Schematic representation of a rearrangement collision
in the centre of mass frame.

(16)



is negligible, and the coupling $\langle f|V|i\rangle \approx 0$. Second-order perturbation theory couples the initial state to some intermediate state, and that state to the final state. The only states which will couple significantly to the initial state are those with neighbouring nuclear configurations and similar electronic states, but these same states will couple only negligibly to the final state for the same reason as initial-final state coupling. Similarly, states which couple strongly to the final state will not couple significantly to the initial state. Since chemical reactions are processes of large transition probability, or, equivalently, of strong coupling, an adequate description of the process can be achieved only with a sufficient number of intermediate states. In terms of the diagrammatic representation of perturbation theory used earlier, this would appear as shown in Figure 3. Obviously the required number of intermediate states is effectively infinite. This presents a completely intractable calculation.

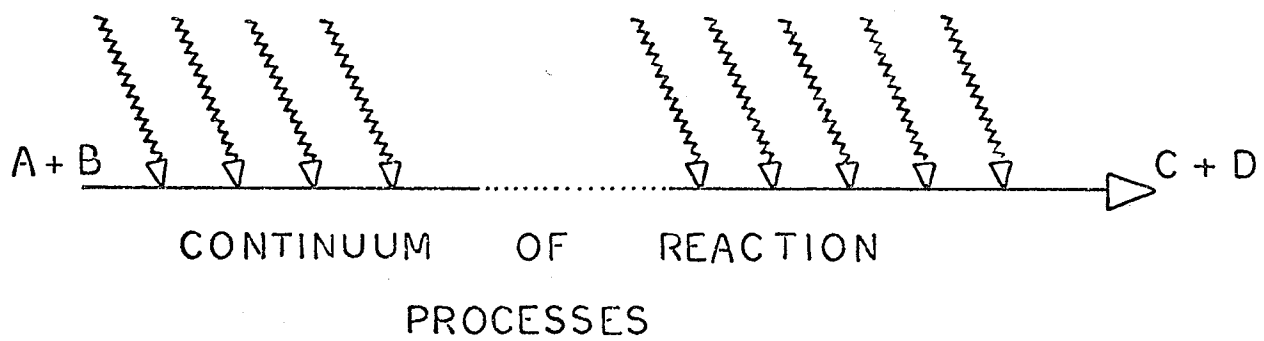
Mathematically, the validity of the approximation of equation (II.15) can be seen from equation (II.17) which is

$$i\hbar\partial_t U_I = U_0^\dagger (H U_0 - i\hbar\partial_t U_0) U_I .$$

Recall that U_0 is the solution to the equation $i\hbar\partial_t U_0 = H_0 U_0$.

Figure 3

Diagrammatic representation of the perturbation theory that would be required by a process of strong coupling.

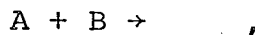


For the approximation to be justified, U_I must be an operator changing slowly with time, as is evident from equation (II.17), since in that case $(HU_0 - i\hbar\partial_t U_0)$ is small. However for any process of strong coupling, the right-hand side of equation (II.17) will be small asymptotically only, this region then being the only region in which a perturbative treatment may be used with any validity. When the colliding species are in the region of strong interaction, the right-hand side of (II.17) is large and the evolution operator U_I , and consequently U , changes rapidly in time. Thus, it is again apparent that a perturbative approach to processes of strong coupling would necessarily have to be of effectively infinite order to account for the rapid, significant changes occurring within the system. As a result, to solve the quantum mechanical equations for a model which purports to describe a system throughout the interaction region, it will be necessary to employ some method for solving the full differential (or integral) equation completely.

Chapter III

DEVELOPMENT OF THE GENERALIZED IMPACT PARAMETER MODEL

In developing the generalized impact parameter model within a semiclassical picture it is enough to consider the general two-centre reaction



where, at present, no specific statements need be made about the products of this reaction. Suffice it to say that there exist a variety of exit channels such as elastic scattering, charge exchange, molecular rearrangement, etc. Having obtained the equations of the model, one can easily show that it is capable of generalization to reactions involving three or more centres. This approach was thought to be the most straightforward since it was felt there would be no point to complicating the derivation of the basic equations by variables due to extra centres, especially since the equations for the two-centre process embody all the details of the model.

The model does not assume a static potential energy surface as an interaction potential. The atoms are considered as following classical trajectories determined by the interatomic potential, which is a dynamical variable in that it depends upon the internal states of the atoms, these states having an implicit dependence upon the velocities of the classical nuclei through their explicit

dependence on the time-dependent interatomic separation $R(t)$. The interaction between the atoms in this trajectory is the time-dependent coupling which leads to the various excitation and exchange processes constituting the mechanism of the reaction. Thus, all the changes occurring within the system are coupled. The derivation is carried out in atomic units in which the values of the electron mass and charge, and \hbar are unity.

A. The Quantum Mechanical Equations

If one does not suppose that the system is initially and finally in the same channel, the electronic Hamiltonian for the colliding species is capable of several resolutions of the form

$$H = H_0^C + V^C \quad (\text{III.1})$$

according to which channel is occupied. Since here the only resolutions of H considered will be those corresponding to the physical partitioning of the system, the Hamiltonians H_0^C are the asymptotic channel Hamiltonians, whose eigenvalue problems are presumed to be known,

$$H_0^C |\chi_j^C\rangle = E_j^C |\chi_j^C\rangle \quad (\text{III.2a})$$

$$\langle \chi_j^C | \chi_k^C \rangle = \delta_{jk} \quad (\text{III.2b})$$

The internal spatial coordinates of the asymptotic channel eigenfunctions $|\chi_j^C\rangle$ have been omitted to simplify the notation. Assuming that the state of the system can be expanded in terms of the complete sets of eigenfunctions of the asymptotic channel operators, one obtains

$$|\Psi\rangle = \sum_c \sum_j a_j^c(t) |\chi_j^c\rangle e^{-iE_j^c t} . \quad (\text{III.3})$$

Incorporation of the phase factors into the stationary eigenfunctions yields

$$|\Psi\rangle = \sum_c \sum_j a_j^c(t) |\phi_j^c(t)\rangle , \quad (\text{III.4})$$

where the time-dependent coefficients are given by

$$a_j^c(t) = \langle \phi_j^c(t) | \Psi \rangle . \quad (\text{III.5})$$

The operator

$$\Theta = \sum_c \sum_j |\phi_j^c(t)\rangle \langle \phi_j^c(t)| \quad (\text{III.6})$$

does not represent a resolution of the identity since, although the sets $\{\phi_j^c(t)\}$ are complete and orthonormal within their respective channels, the union of these sets, which is the basis on which the collision is being projected, is overcomplete and non-orthonormal. As a result, it is necessary to normalize the expansion (III.4) such that

$$|\Psi(R,t)\rangle = \bar{N}(R,t) \sum_c \sum_j a_j^c(t) |\phi_j^c(t)\rangle . \quad (\text{III.7})$$

The dependence of the normalization N on R and t can easily be shown as follows:

$$\langle \Psi(R, t) | \Psi(R, t) \rangle = 1 = \bar{N}^2 \sum_{c', c} \sum_{i, j} \tilde{a}_i^{c'}(t) \langle \phi_i^{c'}(t) | \phi_j^c(t) \rangle a_j^c(t) \quad (\text{III.8})$$

and denoting $\langle \phi_i^{c'}(t) | \phi_j^c(t) \rangle$ by $N_{ij}^{c'c}(R, t)$, the expression (III.8) becomes

$$1 = \bar{N}^2 \sum_{c', c} \sum_{i, j} \tilde{a}_i^{c'}(t) N_{ij}^{c'c}(R, t) a_j^c(t) , \quad (\text{III.9})$$

or, in matrix terms,

$$1 = \bar{N}^2 \underline{\tilde{a}}(t) \underline{N}(R, t) \underline{a}(t) . \quad (\text{III.10})$$

Thus, it is apparent that

$$\bar{N} = \bar{N}(R, t) = \{ \underline{\tilde{a}}(t) \underline{N}(R, t) \underline{a}(t) \}^{-1/2} . \quad (\text{III.11})$$

To keep the notation as simple as possible, the normalization $\bar{N}(R, t)$ may be incorporated into the coefficients $a_j^c(t)$ to yield

$$\begin{aligned} |\Psi(R, t)\rangle &= \sum_c \sum_j \{ \bar{N}(R, t) a_j^c(t) \} |\phi_j^c(t)\rangle \\ &= \sum_c \sum_j b_j^c(R, t) |\phi_j^c(t)\rangle . \end{aligned} \quad (\text{III.12})$$

The normalization requirement now becomes

$$\tilde{b}(R,t)N(R,t)b(R,t) = 1 . \quad (\text{III.13})$$

It is important to notice (as equation (III.13) shows) that normalization of the expansion only rescales the basis vectors; they are still non-orthogonal. This difficulty will be discussed in more detail at a later stage.

The purpose now is to obtain a solution to the time-dependent Schrodinger equation,

$$i\partial_t |\Psi(R,t)\rangle = H |\Psi(R,t)\rangle . \quad (\text{III.14})$$

To this end, the expansion (III.12) for the state vector is substituted into (III.14) to obtain

$$i\partial_t \sum_c \sum_j b_j^c(R,t) |\phi_j^c(t)\rangle = H \sum_c \sum_j b_j^c(R,t) |\phi_j^c(t)\rangle . \quad (\text{III.15})$$

Carrying out the differentiation, one has

$$\begin{aligned} i \sum_c \sum_j \{ \partial_t b_j^c(R,t) \} |\phi_j^c(t)\rangle + i \sum_c \sum_j b_j^c(R,t) \partial_t |\phi_j^c(t)\rangle \\ = \sum_c \sum_j b_j^c(R,t) H |\phi_j^c(t)\rangle , \end{aligned} \quad (\text{III.16})$$

or,

$$\begin{aligned} i \sum_c \sum_j \{ \partial_t b_j^c(R, t) \} | \phi_j^c(t) \rangle &= \sum_c \sum_j b_j^c(R, t) \{ H - i \partial_t \} | \phi_j^c(t) \rangle \\ &= \sum_c \sum_j b_j^c(R, t) \{ H - E_j^c \} | \phi_j^c(t) \rangle . \end{aligned} \quad (\text{III.17})$$

Multiplication across from the left by the bra $\langle \phi_i^{c'}(t) |$ yields

$$\begin{aligned} i \sum_c \sum_j \langle \phi_i^{c'}(t) | \phi_j^c(t) \rangle \{ \partial_t b_j^c(R, t) \} \\ = \sum_c \sum_j \langle \phi_i^{c'}(t) | H - E_j^c | \phi_j^c(t) \rangle b_j^c(R, t) . \end{aligned} \quad (\text{III.18})$$

Defining the matrix $\underline{H}(R, t)$ by

$$H_{ij}^{cc'}(R, t) = \langle \phi_i^{c'}(t) | H | \phi_j^c(t) \rangle , \quad (\text{III.19})$$

the set of coupled equations (III.18) becomes

$$i \underline{N}(R, t) \{ \partial_t \underline{b}(R, t) \} = \{ \underline{H}(R, t) - \underline{N}(R, t) \underline{E} \} \underline{b}(R, t) , \quad (\text{III.20})$$

or,

$$\partial_t \underline{b}(R, t) = -i \underline{N}^{-1}(R, t) \{ \underline{H}(R, t) - \underline{N}(R, t) \underline{E} \} \underline{b}(R, t) . \quad (\text{III.21})$$

The matrix \underline{E} is diagonal with its non-zero elements being the possible energy eigenvalues of the asymptotic channel states.

From the possible resolutions of H , one can write

$$\underline{H}(R,t) = \underline{N}(R,t)\underline{E} + \underline{V}(R,t) . \quad (\text{III.22})$$

\underline{V} is the matrix of the various channel perturbations between the various basis states. It is illustrative to write \underline{V} as follows:

$$\underline{V} = \begin{bmatrix} \underline{V}^{\alpha\alpha} & \underline{V}^{\alpha\beta} & \underline{V}^{\alpha\gamma} & \dots \\ \underline{V}^{\beta\alpha} & \underline{V}^{\beta\beta} & & \\ \underline{V}^{\gamma\alpha} & & & \\ \vdots & & & \\ \vdots & & & \end{bmatrix} . \quad (\text{III.23})$$

The various sub-matrices of \underline{V} can then be interpreted as follows:

- 1) a given diagonal block represents the perturbation within that channel coupling the states of that channel, for example, $\underline{V}^{\alpha\alpha}$ represents the perturbation V^{α} within channel α coupling the states of channel α ,

$V_{ij}^{\alpha\alpha}(R,t) = \langle \phi_i^\alpha(t) | V^\alpha | \phi_j^\alpha(t) \rangle$. The diagonal blocks are thus responsible for transitions occurring within the channels.

- 2) to interpret the off-diagonal blocks, consider a specific one such as $V^{\alpha\beta}$. This represents the perturbation V^β of channel β coupling the states of channel β to the states of channel α ,

$V_{ij}^{\alpha\beta}(R,t) = \langle \phi_i^\alpha(t) | V^\beta | \phi_j^\beta(t) \rangle$. Thus, transitions between the channels are determined by these off-diagonal blocks.

Now using (III.22), equation (III.21) becomes

$$\partial_t \underline{b}(R,t) = -i \underline{N}^{-1}(R,t) \underline{V}(R,t) \underline{b}(R,t) . \quad (\text{III.24})$$

At this point it is worthwhile to digress in order to consider the relationship between the above equation for the coefficient matrix $\underline{b}(R,t)$ and the evolution operator formulation of the problem. The coefficients in the expansion of the state vector are given by

$$b_j^C(R,t) = \langle \phi_j^C(t) | \Psi(R,t) \rangle . \quad (\text{III.25})$$

Since the derivation has been in the Schrodinger picture, one can write

$$|\Psi(R, t)\rangle = U(t, t_0) |\Psi(R, t_0)\rangle. \quad (\text{III.26})$$

Using this, the expression (III.25) for the coefficients becomes

$$\begin{aligned} b_j^c(R, t) &= \langle \phi_j^c(t) | U(t, t_0) | \Psi(R, t) \rangle \\ &= \langle \phi_j^c(t) | U(t, t_0) | \sum_{c'} \sum_k b_k^{c'}(R, t_0) | \phi_k^{c'}(t_0) \rangle \\ &= \sum_{c'} \sum_k \langle \phi_j^c(t) | U(t, t_0) | \phi_k^{c'}(t_0) \rangle b_k^{c'}(R, t_0). \end{aligned} \quad (\text{III.27})$$

Thus a solution of the partial differential equation (III.24) for the coefficient matrix $\underline{b}(R, t)$ at all times t would be equivalent to a determination of the matrix of the evolution operator of the full system, as long as the other variables upon which \underline{b} depends have no time dependence.

Since, in the present formulation, the interatomic separation R is time-dependent, the partial differential equation (III.24) must be replaced by the total differential equation

$$d_{\underline{t}} \underline{b}(R, t) = \partial_{\underline{t}} \underline{b}(R, t) + \{ \partial_{\underline{R}} \underline{b}(R, t) \} (dR/dt). \quad (\text{III.28})$$

The partial derivative of the matrix \underline{b} with respect to R is easily obtained as follows:

$$\begin{aligned}
 \partial_{\underline{R}} \underline{b}(R, t) &= \partial_{\underline{R}} \{ \bar{N}(R, t) \underline{a}(t) \} = \{ \partial_{\underline{R}} \bar{N}(R, t) \} \underline{a}(t) \\
 &= \{ \partial_{\underline{R}} \tilde{a}(t) \underline{N}(R, t) \underline{a}(t)^{-1/2} \} \underline{a}(t) \\
 &= -\frac{1}{2} \{ \tilde{a}(t) \underline{N}(R, t) \underline{a}(t) \}^{-3/2} \{ \tilde{a}(t) (\partial_{\underline{R}} \underline{N}) \underline{a}(t) \} \underline{a}(t) \\
 &= \{ \tilde{b} (\partial_{\underline{R}} \underline{N}) \underline{b} \} \underline{b} / 2 .
 \end{aligned}
 \tag{III.29}$$

$\partial_{\underline{R}} \underline{N}$ can be obtained from the matrix elements of \underline{N} , and dR/dt is simply related to the classical velocities of the atoms.

B. The Classical Equations

The classical equations of motion are most conveniently derived in the laboratory frame, in which the coordinates of the atoms may be denoted (x_1, y_1, z_1) and (x_2, y_2, z_2) . To obtain these equations one makes use of Hamilton's canonical equations (7),

$$\dot{q}_k = \partial \mathcal{H} / \partial p_k , \quad (\text{III.30a})$$

$$\text{and} \quad \dot{p}_k = -\partial \mathcal{H} / \partial q_k , \quad (\text{III.30b})$$

where p_k and q_k are, respectively, the generalized momentum and coordinate for the k -th particle, and \mathcal{H} is the total Hamiltonian function for the system. \mathcal{H} is defined by

$$\mathcal{H} = \sum_{j=1}^2 p_j^2 / 2m_j + \bar{E}(R, t) , \quad (\text{III.31})$$

where $\bar{E}(R, t)$ is the mean quantum mechanical energy given by

$$\begin{aligned} \bar{E}(R, t) &= \langle \Psi(R, t) | H | \Psi(R, t) \rangle \\ &= \underline{\tilde{b}}(R, t) \underline{H}(R, t) \underline{b}(R, t) \end{aligned} \quad (\text{III.32})$$

The fluctuations in \bar{E} are assumed to be small. Thus, Hamilton's equations become

$$\dot{q}_j = p_j/m_j \quad (\text{III.33a})$$

and
$$\dot{p}_j = -\partial \bar{E} / \partial q_j . \quad (\text{III.33b})$$

Thus, the mean quantum mechanical energy $\bar{E}(R,t)$ is the interatomic potential energy which determines the trajectories of the atoms. It is readily apparent that \bar{E} is a dynamical variable since, through its dependence on the coefficients $b_j^C(R,t)$, it has an implicit dependence upon the velocities of the classical particles.

Chapter IV

THE METHOD OF SOLUTION OF THE EQUATIONS

Having now developed the equations of the model, it only remains to obtain a solution to the set of equations consisting of

$$db/dt = \partial_{t^-} b + \partial_{R^-} b (dR/dt) , \quad (IV.1)$$

$$\dot{q}_j = p_j/m_j , \quad (IV.2)$$

and $\dot{p}_j = -\partial \bar{E} / \partial q_j . \quad (IV.3)$

Since it was desired to obtain a solution which was free of the previously mentioned faults of perturbation theory, it was decided to solve the equations numerically using the Runge-Kutta method (8). This method generates a fourth-order solution to a total differential equation. The computer program[†] was written to solve the equations simultaneously with momentum and total energy (classical plus quantum mechanical) conservation. Unitarity of the solutions was ensured by normalizing after each cycle of the Runge-Kutta process. Thus, from the initial positions, momenta, and state of the system, one obtains the initial

[†] The computer program is given in Appendix II in the form that it was set up to treat the specific physical examples discussed in the following chapter.

potential and kinetic (and therefore the total) energy; using this potential energy, the positions, momenta, and the coefficient matrix $\underline{b}(R,t)$ may be obtained at a time Δt later, this information then defining a new potential and kinetic energy. Proceeding in this iterative fashion, one may thus obtain all these quantities throughout the interaction region.

The accuracy of the calculations was controlled by using a variable step size Δt such that the total energy at a given iteration was equal to the total energy at the previous iteration within certain limits (which were varied according to the energy of the collision being considered). In all cases, energy conservation was sought to at least three significant figures. Further details of the numeric solution of the equations are to be found in the documentation within the program in Appendix II.

It perhaps should be mentioned here that equation (IV.3) presents no difficulty since, for example,

$$\dot{p}_{x_1} = -\partial \bar{E} / \partial x_1$$

can be written as

$$\dot{p}_{x_1} = -(\partial \bar{E} / \partial R) (\partial R / \partial x_1) ,$$

and,

$$\begin{aligned}\partial_{\underline{R}} \bar{E} &= \partial_{\underline{R}} (\tilde{\underline{b}} \underline{H} \underline{b}) \\ &= \tilde{\underline{b}} (\partial_{\underline{R}} \underline{H}) \underline{b} + \{ \tilde{\underline{b}} \underline{H} (\partial_{\underline{R}} \underline{b}) + (\partial_{\underline{R}} \tilde{\underline{b}}) \underline{H} \underline{b} \} .\end{aligned}\quad (\text{IV.4})$$

$\partial_{\underline{R}} \underline{H}$ can be obtained from the matrix elements of \underline{H} and the gradients of \underline{b} with respect to R are obtained numerically within the computer program. Since

$$R = \{ (x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 \}^{\frac{1}{2}} ,\quad (\text{IV.5})$$

one may calculate $\partial R / \partial x_1$, and therefore \dot{p}_{x_1} .

Chapter V

APPLICATION OF THE GENERALIZED IMPACT PARAMETER MODEL TO SOME PHYSICAL SYSTEMS

For the initial application of the generalized impact parameter model to physical systems it was thought best to choose simple systems. By simple systems it is meant systems for which the asymptotic channel eigenfunctions are known exactly so that the required matrix elements may be evaluated analytically. In this way one need not worry about numerical errors introduced through approximate evaluations of such matrix elements. Furthermore, simple systems have few degrees of freedom and, as such, give one some insight into the possibilities of applying the model to more interesting processes involving complex molecules and sustaining various possible exit channels. For these reasons, the collision of a proton with a hydrogen atom was chosen as a reasonable system on which to test the model.

Since one's first interest as a chemist lies in low energy processes ($\lesssim 10$ eV), a variety of calculations on proton-hydrogen atom scattering at low energies were performed. As an offshoot of this, a study was made of the photodecomposition of the simple molecule H_2^+ . Finally, recent years have seen considerable activity in high energy (that is, in the KeV range) scattering of a proton from a hydrogen atom. Thus, because we sought to compare the calculations of the model developed here with calculations performed by others and with experimental

results, a set of high energy calculations were obtained.

Before one proceeds to a discussion of these various calculations, a short orientation to the proton-hydrogen atom system is in order. To evaluate the matrix elements, a molecular coordinate system fixed on the nuclei was chosen. This coordinate system is shown in Figure 4. The problem reduces to two dimensions because of the symmetry about the internuclear line, and to one dimension for zero impact parameter collisions. Since the formation of three unbound particles is unlikely, the Hamiltonian for the system may be considered as capable of populating two exit channels. In the non-rearrangement channel (which is identical to the initial channel), the electron remains bound to the proton of the target atom (proton A). Denoting this channel as channel α , one has

$$H = H_0^\alpha + V^\alpha, \quad (V.1)$$

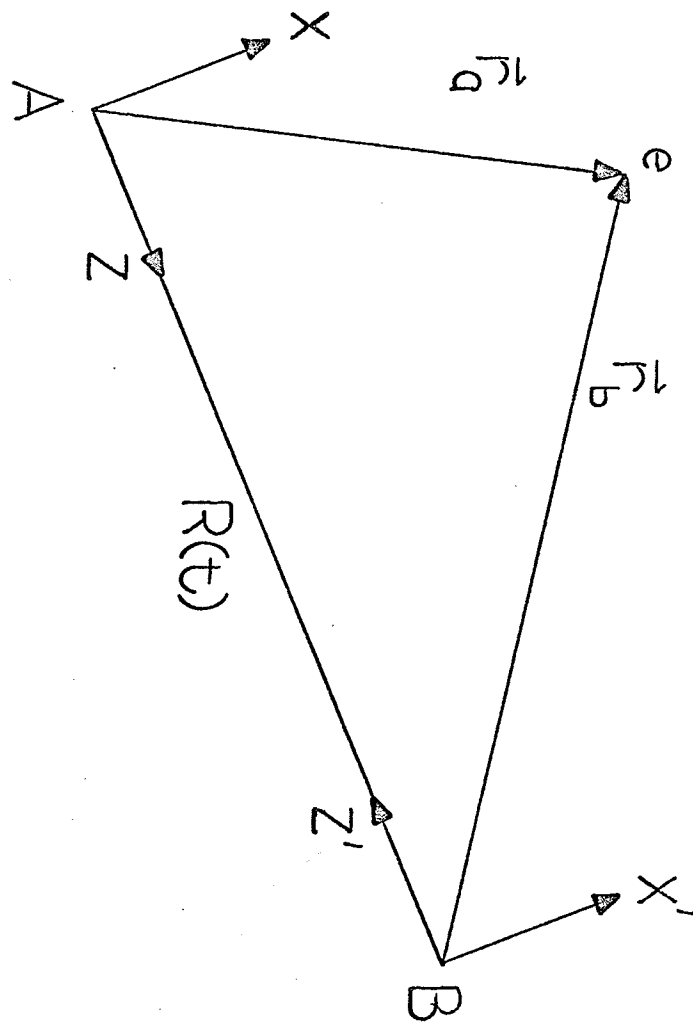
$$H_0^\alpha = -\frac{1}{2} \nabla^2 - \frac{1}{r_a}, \quad (V.2)$$

and
$$V^\alpha = \frac{1}{R} - \frac{1}{r_b}, \quad (V.3)$$

In the rearrangement channel (channel β), the electron is bound to the projectile proton (proton B). This leads to the resolution

Figure 4

The molecular coordinate system used in the evaluation
of the matrix elements.



$$H = H_0^\beta + V^\beta, \quad (V.5)$$

$$\text{with} \quad H_0^\beta = -\frac{1}{2} - \frac{1}{r_b}, \quad (V.6)$$

$$\text{and} \quad V^\beta = \frac{1}{R} - \frac{1}{r_a}, \quad (V.7)$$

These two channels include the possibility of the formation of H_2^+ as, for example, in a spiralling collision. For either channel, the set of eigenfunctions for the asymptotic channel Hamiltonian is the set of eigenfunctions for the hydrogen atom. Thus the union of two such sets is used as the basis on which to expand the state vector for the collision. The matrix elements of \underline{N} and \underline{V} were evaluated by conversion to elliptic coordinates in the usual manner. From these matrix elements, the matrix elements of \underline{H} can be obtained, and it is only straightforward differentiation to obtain the elements of the derivative matrices $\partial_{\underline{R}} \underline{N}$ and $\partial_{\underline{R}} \underline{H}$. These matrix elements are given in Appendix I.

A. Low Energy Proton-Hydrogen Atom Scattering

Since our present interest is in collisions at low energies ($\lesssim 10$ eV), it was considered that the hydrogenic orbitals $\{1s, 2s, 2p_z\}$ on each centre would be a sufficiently large set for this purpose. The orbitals $2p_x$ and $2p_y$ on each centre may be omitted by symmetry considerations.

It is well known from the general theory of scattering that the Schrodinger equation (or the corresponding integral equation) describing the scattering process may have several solutions depending upon how one chooses the asymptotic boundary conditions. This is borne out by test calculations which were carried out with the generalized impact parameter model largely to check the computer program. For example, if the initial asymptotic state is chosen to be the antisymmetric molecular function $1\sigma_u^*$,

$$\Psi(R=\infty, t=0) = (2)^{-1/2} \{ \phi_{1s}(A) - \phi_{1s}(B) \} , \quad (V.7)$$

and the atoms are directed toward each other with relative incident energy corresponding to 4 eV, it is found that the wave function $\Psi(R, t)$ always maintains the antisymmetric character with which it started. The dynamic potential energy surface for the collision turns out to be the same as the static potential energy surface of the $1\sigma_u^*$ molecular

state. This is easily understood in terms of the static molecular potential energy surfaces which are shown in Figure 5. (These surfaces were obtained by solving the time-independent Schrodinger equation on the above basis.) Since only antisymmetric states can contribute, it follows that the only potential energy surfaces which could influence that due to the $1\sigma_u^*$ state would be those due to the other antisymmetric states, all of which lie at sufficiently high energy to make a negligible contribution.

Similar results were obtained by starting out with a symmetric asymptotic molecular state,

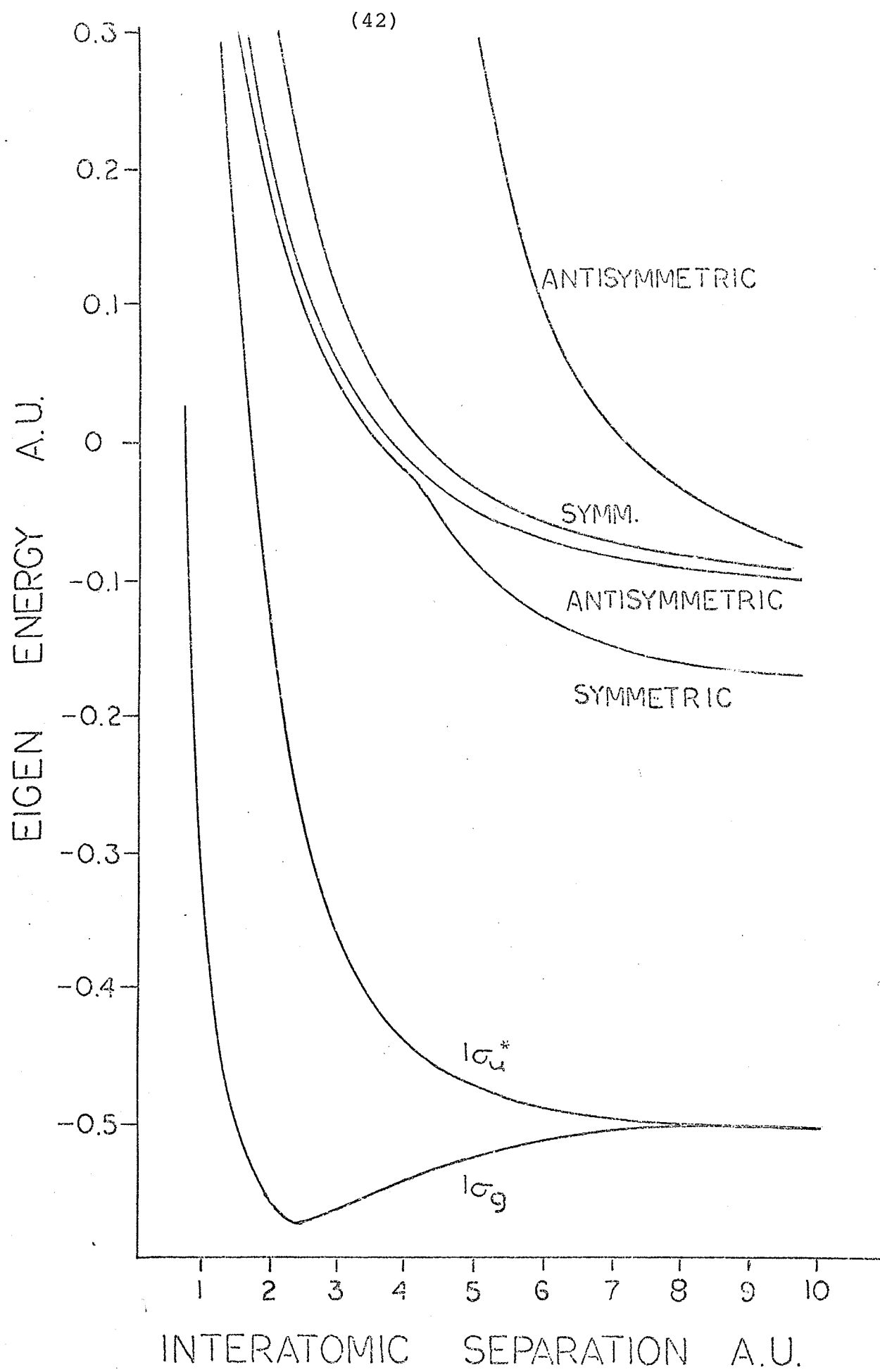
$$\Psi(R=\infty, t=0) = (2)^{-1/2} \{ \phi_{1s}(A) + \phi_{1s}(B) \} . \quad (V.8)$$

In this case, $\Psi(R, t)$ retains its symmetric character, the dynamic potential energy surface corresponding exactly with the static $1\sigma_g$ molecular potential energy surface, this being expected on grounds analogous to those applied to the antisymmetric collision.

The collision of a proton with a hydrogen atom corresponds to an asymmetric asymptotic state in which the electron is initially in, say, the $1s$ level of the target system. Therefore one might expect "conservation" of asymmetry in the process. In particular, since the asymptotic atomic state $\phi_{1s}(A)$, say, can be regarded as a

Figure 5

The molecular potential energy surfaces for H_2^+ .



linear combination of symmetric (V.8) and antisymmetric (V.7) molecular states,

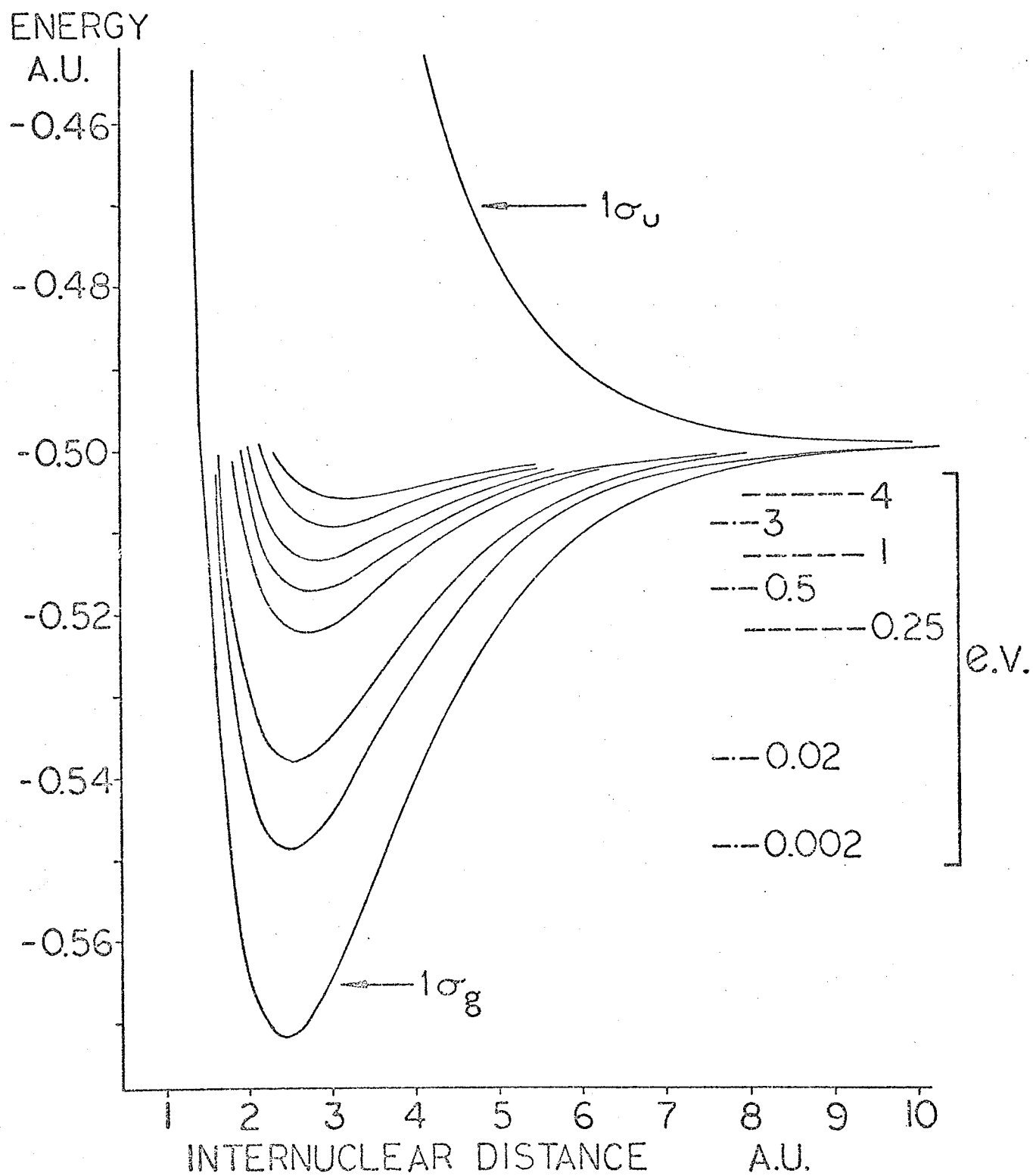
$$\phi_{1s}(A) = (2)^{-\frac{1}{2}} \{1\sigma_g(R = \infty) + 1\sigma_u^*(R = \infty)\} , \quad (V.9)$$

one should expect static potential energy surfaces due to both $1\sigma_g$ and $1\sigma_u^*$ to contribute. Equation (V.9) also suggests that caution should be exercised in choosing the initial state ($R = \text{finite}$) for numerical calculations since even small errors in this choice would cause the system initially to propagate along an erroneous potential energy surface. In practice this difficulty was overcome by minimizing the initial state of the target system with respect to energy and repeating the calculations using increasing values of the initial separation until the dynamic potential energy surface became independent of this separation. For these p - H collisions it was found that a suitable initial separation was in the range of 150 to 200 atomic units, and that at these separations the minimization process was essentially meaningless, the electron being effectively in the $1s$ level. Confidence in the validity of the results obtained was also reinforced by verifying the invariance of the calculations to time reversal. In this respect the accuracy proved to be remarkable in view of the extremely complicated behaviour of the electronic wave function, a point which will be discussed shortly.

The contribution of both $1\sigma_g$ and $1\sigma_u^*$ states to the scattering process is borne out by our calculations. Figure 6 portrays the dynamic potential energy surfaces for a variety of zero impact parameter collisions. As the incident energy decreases, the dynamic potential energy surfaces correlate more closely with the $1\sigma_g$ state. However, even for thermal (0.02 eV) and sub-thermal collisions, the dynamic potential energy surfaces are still significantly different from the static $1\sigma_g$ surface, as indeed one might expect from the above symmetry conservation arguments. This is quite interesting, since frequently low energy atomic and molecular collisions are approached theoretically via the adiabatic approximation (9). The heart of this approximation is that for low energy processes the colliding systems perturb each other so slowly and to such a small extent that their electronic wave functions go over smoothly into the static molecular eigenfunctions for the complete system. The potential energy surface for the interacting species is then taken to be the static molecular potential energy surface corresponding to the molecular state into which the system is assumed to go. From the results displayed in Figure 6, it would appear that this approximation really becomes valid only in the limit of an infinitely slow collision, in which the static and dynamic problems become equivalent.

Figure 6

The dynamic potential energy surfaces for the p - H
collision.



The differences between the static and dynamic approaches are even more obvious in the wave functions, or, more conveniently, in the electron densities. In the symmetric and antisymmetric collisions the electron density in one channel is the same as that in the other at any instant of time. On the other hand, the density for the p - H collision oscillates rapidly in the interaction region (resonant charge exchange) as depicted in Figure 7 for the rearrangement channel in a collision of typical energy.

A variety of calculations were carried out for non-zero impact parameters. The dynamic potential energy surfaces for these collisions were similar to those for zero impact parameter. The trajectories for these calculations are of interest, however, as they indicate the ability of the model to handle trajectories which are far from the usual linear-trajectory approximation normally employed in an impact parameter treatment. A typical trajectory is shown in Figure 8 corresponding to an impact parameter of 1 a.u. and incident energy of 0.5 eV. The coordinates refer to the laboratory frame. It can be seen how the initial and final interactions are attractive (corresponding to the outer region of the dynamic potential energy surface), the intermediate interaction being repulsive (corresponding to the inner region of the

Figure 7

Exemplary behaviour of the electron density during the
collision.

(47)

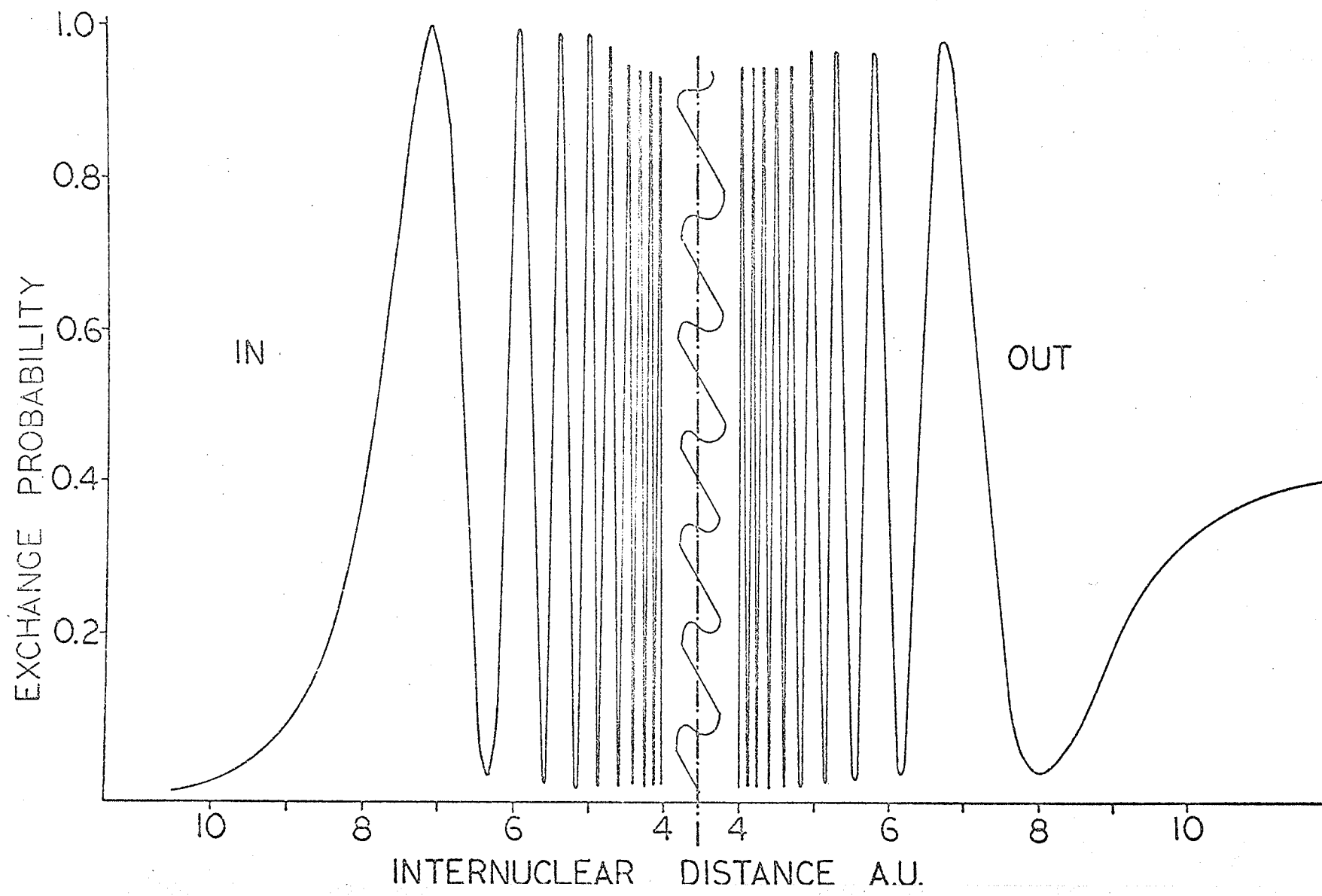
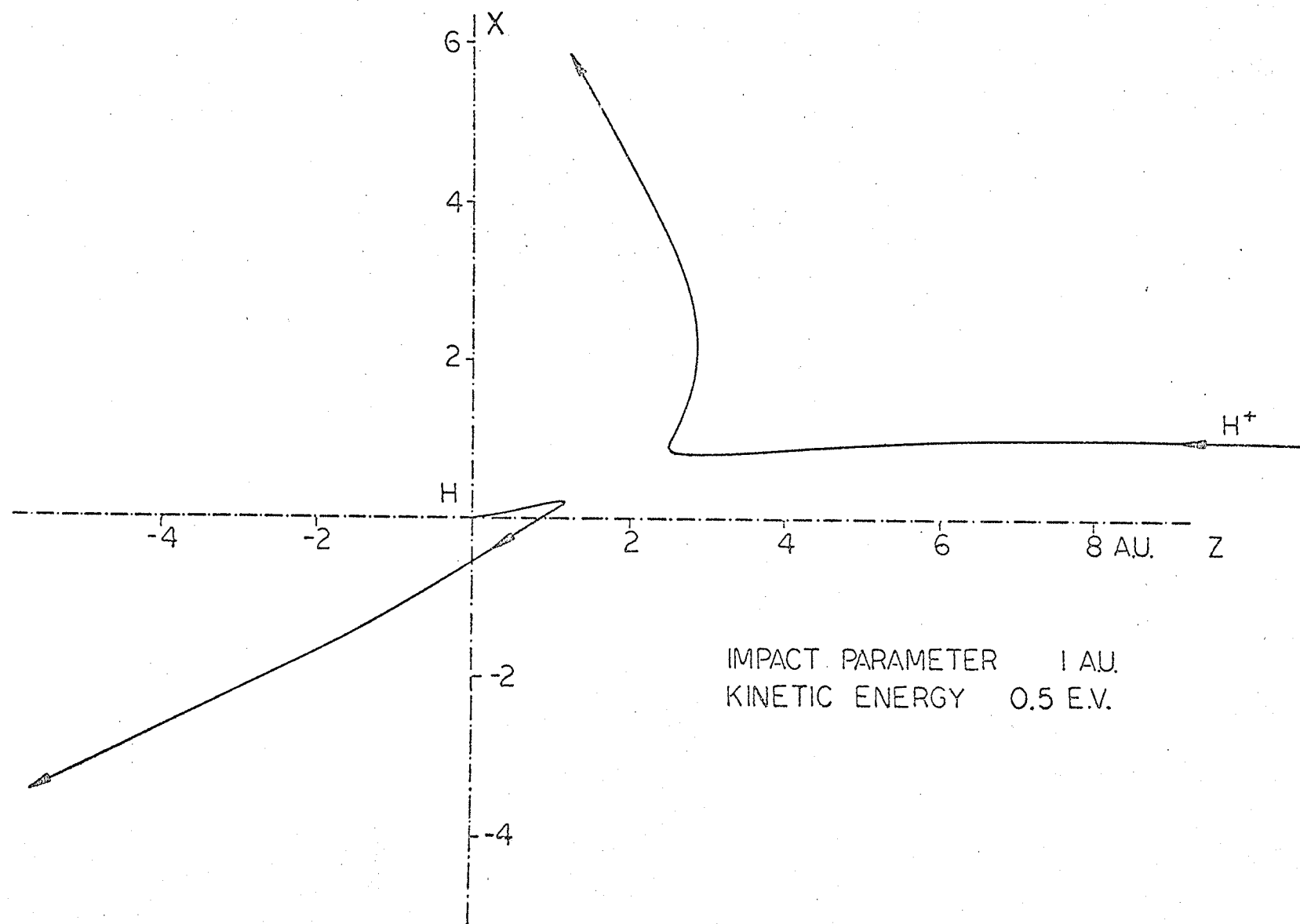


Figure 8

A typical trajectory produced by the generalized impact parameter model in low energy scattering. The coordinates refer to the laboratory frame.

(48)



potential energy surface).

The results that have been obtained here are especially simple, and, in general, one would not expect the same results for more complicated systems. For example, the dynamic potential energy surfaces shown in Figure 6 have the static $l\sigma_g$ and $l\sigma_u^*$ as lower and upper bounds, respectively. Consequently, it appears that, according to the generalized impact parameter model, it would be impossible to form H_2^+ by a low energy zero-impact parameter collision. However, for more complicated systems, there may be several molecular states lying at low enough energy so that the dynamic potential energy surfaces cross these stationary molecular levels. In such a case a collision can then be responsible for taking the system from one molecular level to another either in the same molecule or in a different molecule. The investigation of such collisions by the generalized impact parameter model should provide some interesting features of such processes as level crossing. Some possibilities for such an investigation will be discussed in Chapter VI.

B. Molecular Photodecomposition

In our treatment of low energy collisions, a discussion was made of symmetric and antisymmetric collisions. It should be realized that although these processes do not correspond to physical collisions, the antisymmetric collision, at least, is not entirely unphysical since it is closely equivalent to the reverse of the photodecomposition of H_2^+ . The realization of this prompted an application of our model to this photodecomposition process, the idea being to calculate the probability for molecular decomposition and the lifetime of the excited state resulting from photon absorption, both these quantities being unobtainable by time-dependent perturbation theory.

Using formal collision theory and partitioning the overall photodecomposition process into the constituent sub-processes of photon absorption and decomposition, it has been shown (10) that the transition probability for the complete process can be expressed as a correlated product of transition probabilities for these sub-processes, as follows:

$$w_{i \rightarrow f_1, f_2} = \frac{2\pi\delta(E_i - E_{f_1} - E_{f_2})}{\hbar} \frac{|\langle f_1, f_2 | T(\text{decomp}) | a \rangle|^2 |\langle a | T(\text{abs}) | i \rangle|^2}{(E_i - E_a)^2 + \Gamma_a^2/4},$$

T being the scattering operator. To use this expression, it is necessary to be in a position to calculate separately the probability for photon absorption, $|\langle a|T(\text{abs})|i\rangle|^2$, for molecular decomposition, $|\langle f_1, f_2|T(\text{decomp})|a\rangle|^2$, and the lifetime $t_a = (\Gamma_a)^{-1}$ of the intermediate state. Whereas the first of these may be evaluated by time-dependent perturbation theory, the last two cannot, since time-dependent perturbation theory is, as it has already been pointed out, applicable to processes of small probability only. However, the probability of molecular decomposition from an unstable state may be close to unity.

To apply the generalized impact parameter method to the photodissociation process it is necessary to know the state $|a\rangle$ to which the molecule is excited by photon absorption. In practice, $|a\rangle$ is a continuum eigenstate, and, strictly speaking, one should include all such states allowed by energy conservation. However, the sum over all such excited states may be approximated by the wavefunction for the antibonding molecular state if one invokes the Franck-Condon principle, which assumes that the nuclear configuration after excitation is the same as that just before. The application of the impact parameter method developed in this manuscript to the photodissociation process is equivalent to following the evolution of a system whose electronic state is initially the antisymmetric

molecular state $l\sigma_u^*$ corresponding to the nuclear coordinates R_0 , where R_0 is the equilibrium separation of the nuclei in the H_2^+ molecule. The asymptotic states resulting from the decomposition correspond to either ls_A or ls_B since the energy of the molecular state $l\sigma_u^*$ is insufficient to permit the formation of excited atomic states. Using the previously obtained solution of the stationary eigenvalue problem for H_2^+ , the equilibrium nuclear configuration R_0 and the eigenfunction of the state $l\sigma_u^*$ corresponding to this equilibrium separation were obtained (in the notation of the generalized impact parameter model this eigenfunction is $\underline{b}(R_0(t_0), t_0=0)$). Using this information as input for the computer program, the evolution of the molecular decomposition was followed.

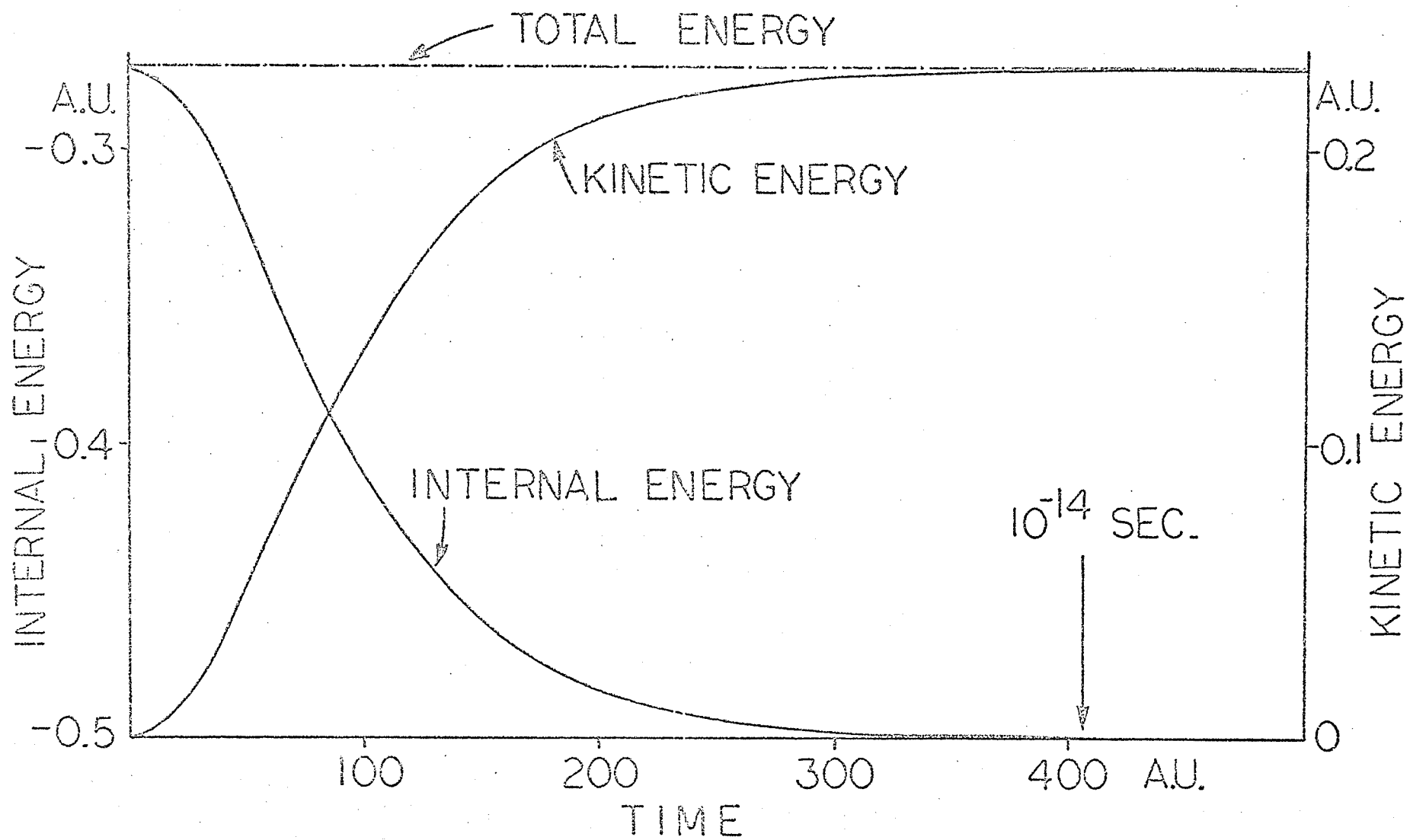
If the lifetime of the state $l\sigma_u^*$ is defined as the time during which the interaction between the fragmenting atoms is significant, this lifetime may be inferred from Figure 9 which shows the conversion of internal (or quantum mechanical energy) into the translational energy of the fragments. The lifetime of the state $l\sigma_u^*$ turns out to be of the order of 10^{-14} seconds. Since decay by decomposition is much faster than alternative relaxation processes such as spectroscopic emission, the probability of decomposition will be approximately unity.

Figure 9

Conversion of the internal energy of the molecule H_2^+ into
the translational energy of the fragments.

1 a.u. of time = 2.419×10^{-17} seconds

(53)

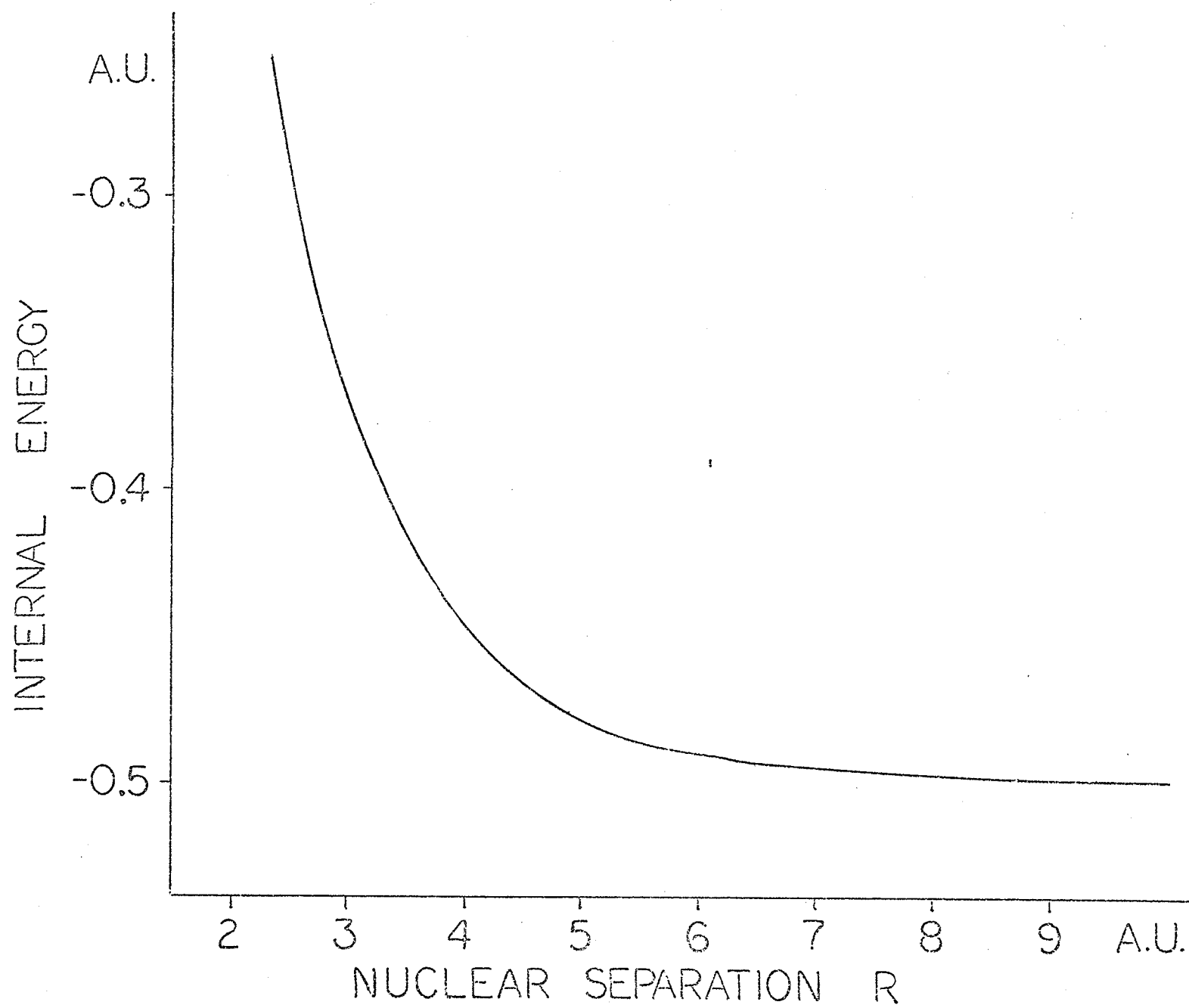


The internal energy as a function of internuclear distance is shown in Figure 10. Within numerical accuracy the curve corresponds to the static internal energy of the $1\sigma_u^*$ state. This is to be expected from the symmetry arguments of the previous section, the evolving state of the molecule remaining as the $1\sigma_u^*$ state since it can correlate only with antisymmetric states, of which there are none close to the $1\sigma_u^*$ in energy. As in the case of molecular collisions, one would not expect that the photodecomposition of more complex molecules, or, for that matter, asymmetric molecules, would be this simple.

Figure 10

The internal energy of the H_2^+ molecule as a function of the interatomic separation.

(55)



C. High Energy Proton-Hydrogen Atom Scattering

As was pointed out in the introduction to this chapter, there is currently quite considerable theoretical interest in high energy proton-hydrogen atom scattering. Such interest derives from the desire to be able to reproduce experimental observables for such collisions, specifically to be able to calculate accurate cross sections and exchange probabilities for such collisions. An application of the generalized impact parameter model to high energy proton-hydrogen atom encounters therefore allows comparison of this model with both experiment and models used by others.

At low relative velocities of incidence the translational energy of the electron can be neglected. However, for high energy encounters, the translational motion of the electron becomes quite significant. For example, at high relative velocities between the proton and the atom, the usual electronic eigenfunctions for the hydrogen atom do not satisfy the time-dependent Schrodinger equation even asymptotically. This was pointed out by Bates and McCarroll (11). These workers showed that the correct form for the basis set must be

$$\begin{aligned}
|\phi_j^c(t)\rangle &= |\chi_j^c\rangle \exp\{-i(E_j^c + \frac{v_{xj}^2}{8} + \frac{v_{yj}^2}{8} + \frac{v_{zj}^2}{8})t\} \\
&\times \exp(\bar{i}v_{xj}x/2)\exp(\bar{i}v_{yj}y/2)\exp(\bar{i}v_{zj}z/2) ,
\end{aligned}
\tag{V.11}$$

where $\{\chi_j^c\}$ is the set of stationary state eigenfunctions for the hydrogen atom and v_{xj} , v_{yj} , v_{zj} are the translational velocities of the electron in the x , y , z directions in state j . In practice, the subscript j on these velocities refers to the atomic centre only, but the above notation is simpler and results in the same interpretation. Actually the expression (V.11) is specifically for the centre of mass frame, which is the reference frame used for the high energy calculations reported here. The centre of mass frame was chosen because all other recent calculations of $p - H$ scattering have been obtained in this reference frame. Centre of mass collisions are easily accomplished in the generalized impact parameter model by starting the classical particles with equal and opposite velocities toward each other.

The only change that the modification (V.11) of the basis set makes, other than in the matrix elements, is that equation (III.24) for the partial derivative of \underline{b} with respect to time becomes

$$\partial_t \underline{b}(R,t) = -i \left[\underline{N}^{-1}(R,t) \underline{V}(R,t) - \underline{v} \right] \underline{b}(R,t) , \quad (V.12)$$

where the matrix \underline{v} is diagonal with its non-zero elements being $v_j^2/8$, where v_j is the translational velocity of the electron in state j .

Current research on the proton-hydrogen atom scattering system has been principally concerned with the search for a basis set appropriate to describe the collision. The reason for this trend is apparent from a short history of the research. Four years ago, Wilets and Gallaher (12) used a hydrogenic basis set modified in the manner of Bates and McCarroll. Their calculation used a linear-trajectory, constant-velocity approximation in which the classical particles were constrained to move in linear trajectories throughout the interaction, and the velocities of these particles were assumed to be constant. In comparing their calculated total electron exchange probabilities with the experiments of Helbig and Everhart (13), they found that the oscillations in their exchange probability as a function of energy were incorrect in both magnitude and phase. Since the validity of the linear-trajectory approximation had been investigated by Mittleman (14) and was found to be good down to about 200 eV, Wilets and Gallaher concluded that the errors in their calculations were due to the choice of the basis set. For this reason,

they repeated the calculation using a Sturmian basis set (15). This basis set, which purports to take account of the continuum, yielded total exchange probabilities which were in excellent agreement with experiment. Various cross sections were also reproduced quite well. However, the Sturmian functions were found to have poor convergence properties and did not represent the 2s level of hydrogen well. The search for a basis set continued. Cheshire (16) used a hydrogenic basis with variable nuclear charge, and subsequently Cheshire, Gallaher, and Taylor (17) have used a basis set consisting of both hydrogenic states and pseudo states (these pseudo states give strong overlap with the intermediate states of H_2^+ and as such simulate the molecular features of the collision at small atomic separations.)

It was felt by this author that perhaps all this investigation into the basis set could in fact be labelled as barking up the wrong tree, and that possibly the error in the original work of Wilets and Gallaher was indeed due to the assumption of linear trajectories and constant velocities in the interaction region. For this reason, it was thought worthwhile to perform some calculations of high energy p - H scattering using the same hydrogenic basis as Wilets and Gallaher, namely, the set $\{1s, 2s, 2p_z\}$ on each centre, but without the restriction of the linear-

trajectory, constant-velocity approximation. The generalized impact parameter method is ideally suited to this calculation.

In the way of practicalities, it should be noted that, at high energies, the classical particles approach each other quite closely in a zero impact parameter collision. This results in a very small step size Δt being necessary for energy conservation, and consequently in extremely long times for the calculations. Thus, some a priori decision is necessary as to what calculations would be the most useful. It was decided to choose some representative energy and perform a set of calculations over a range of impact parameters at this energy. This allows a determination of cross sections for the various processes occurring at this energy. It also allows one to obtain some idea of the variation of total electron exchange probability as a function of energy from calculations at some reasonably finite impact parameter and still compare with the experimental results of Helbig and Everhart (whose data is for scattering angles of the order of a degree). In this way the required computer time is minimized while very useful results are still obtained.

Thus, a series of calculations were performed over a range of impact parameters at 20 KeV. A plot of electron exchange probability versus impact parameter for 20 KeV is shown in Figure 11. From this figure it is seen that

Figure 11

Charge exchange probability versus impact parameter at 20KeV.

The scattering angle may be obtained from the asymptotic momenta after the collision. The scattering angle θ is

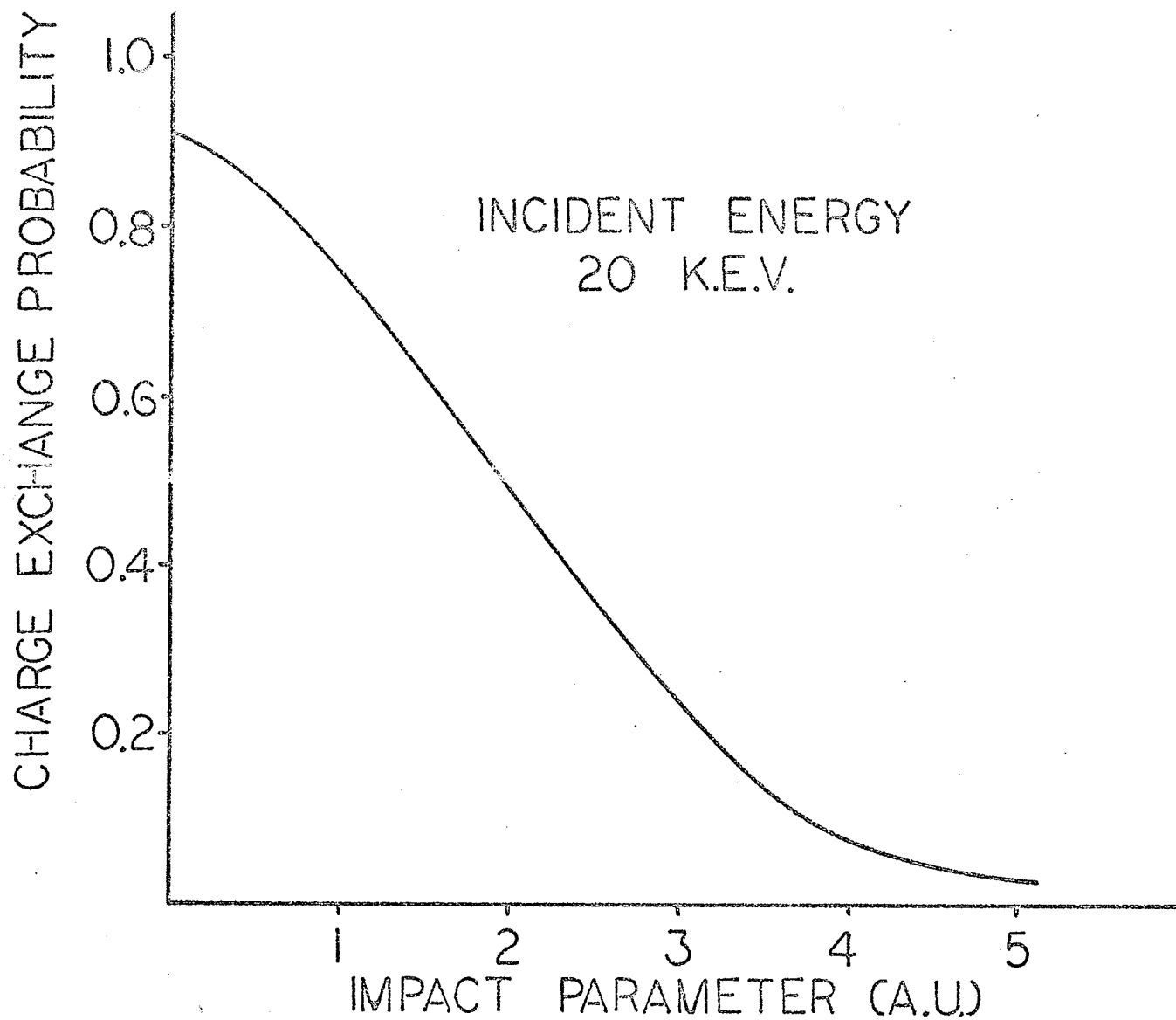
given below for several impact parameters:

$$\rho = 1.0 \text{ a.u.} \quad \theta = 0.036^\circ$$

$$\rho = 1.5 \text{ a.u.} \quad \theta = 0.012^\circ$$

$$\rho = 2.0 \text{ a.u.} \quad \theta = 0.004^\circ$$

$$\rho = 2.5 \text{ a.u.} \quad \theta = 0.001^\circ$$



the total exchange probability does not really become independent of impact parameter, but rather that the variation of these probabilities with impact parameter at small impact parameters becomes quite small. Exchange and excitation probabilities between various states at 20 KeV are shown in Figure 12.

From Figure 11 it is apparent that one would have to use very small impact parameters to obtain scattering angles of the order of degrees, and that the total exchange probabilities at these small impact parameters would not be significantly different from those at larger impact parameters as long as one is still working at a region where the rate of change of total exchange probability with impact parameter is small. Thus, a series of calculations at 2, 4, 8, 14, and 20 KeV were performed at reasonably small impact parameters (0.25 to 0.50 a.u.). The size of the impact parameter at a given energy was determined by repeating the calculation with decreasing impact parameters until the total exchange probability changed only slightly with impact parameter. The total exchange probability as a function of energy is shown in Figure 13. Also displayed in this figure are the experimental results of Helbig and Everhart and the results obtained in the original calculations of Wilets and Gallaher using the hydrogenic

Figure 12

Probability multiplied by impact parameter versus impact parameter at 20 KeV for the following processes:

—————	2p exchange
·—·—·—·	2p excitation
- - - - -	2s exchange
·········	2s excitation

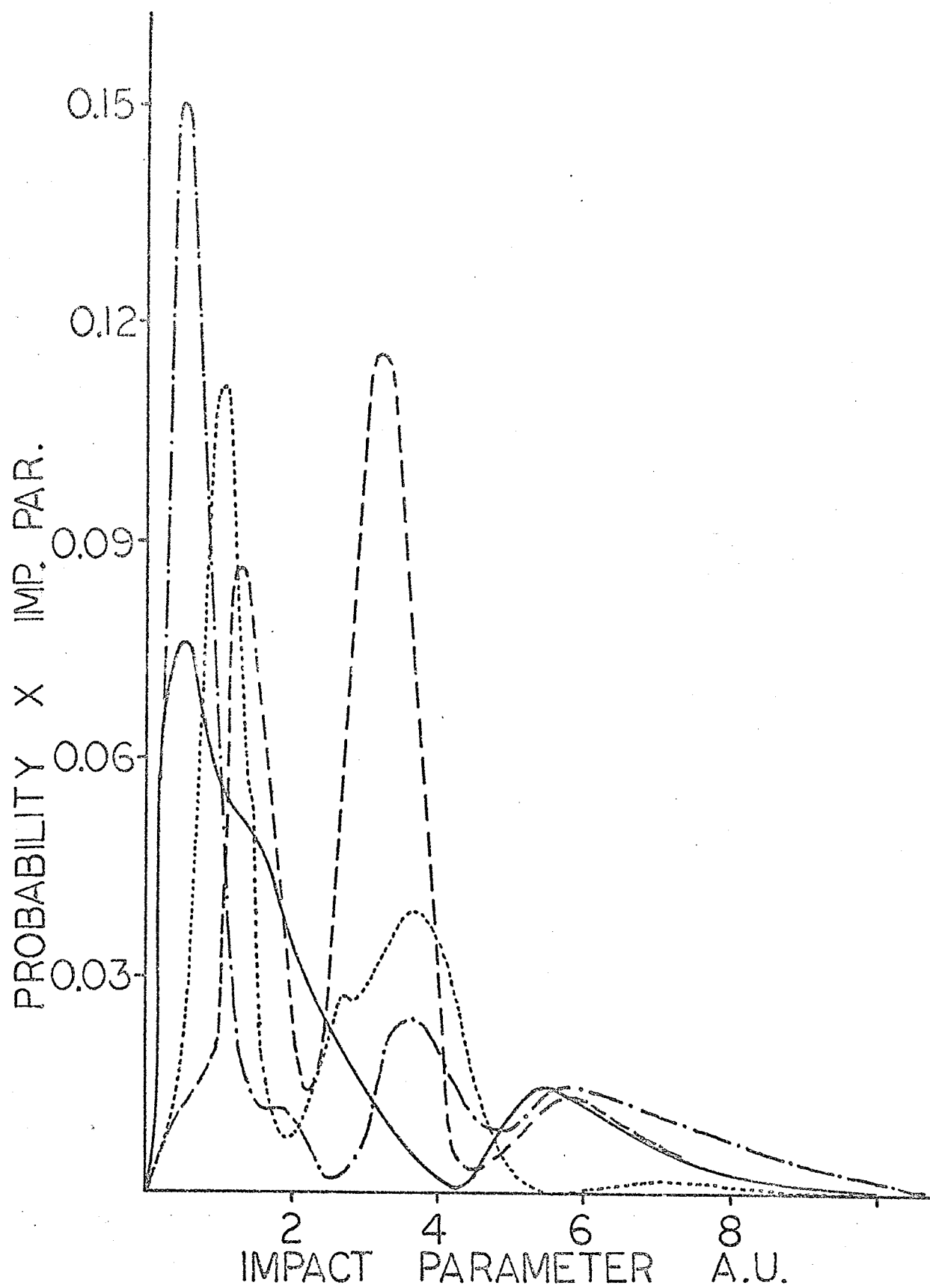
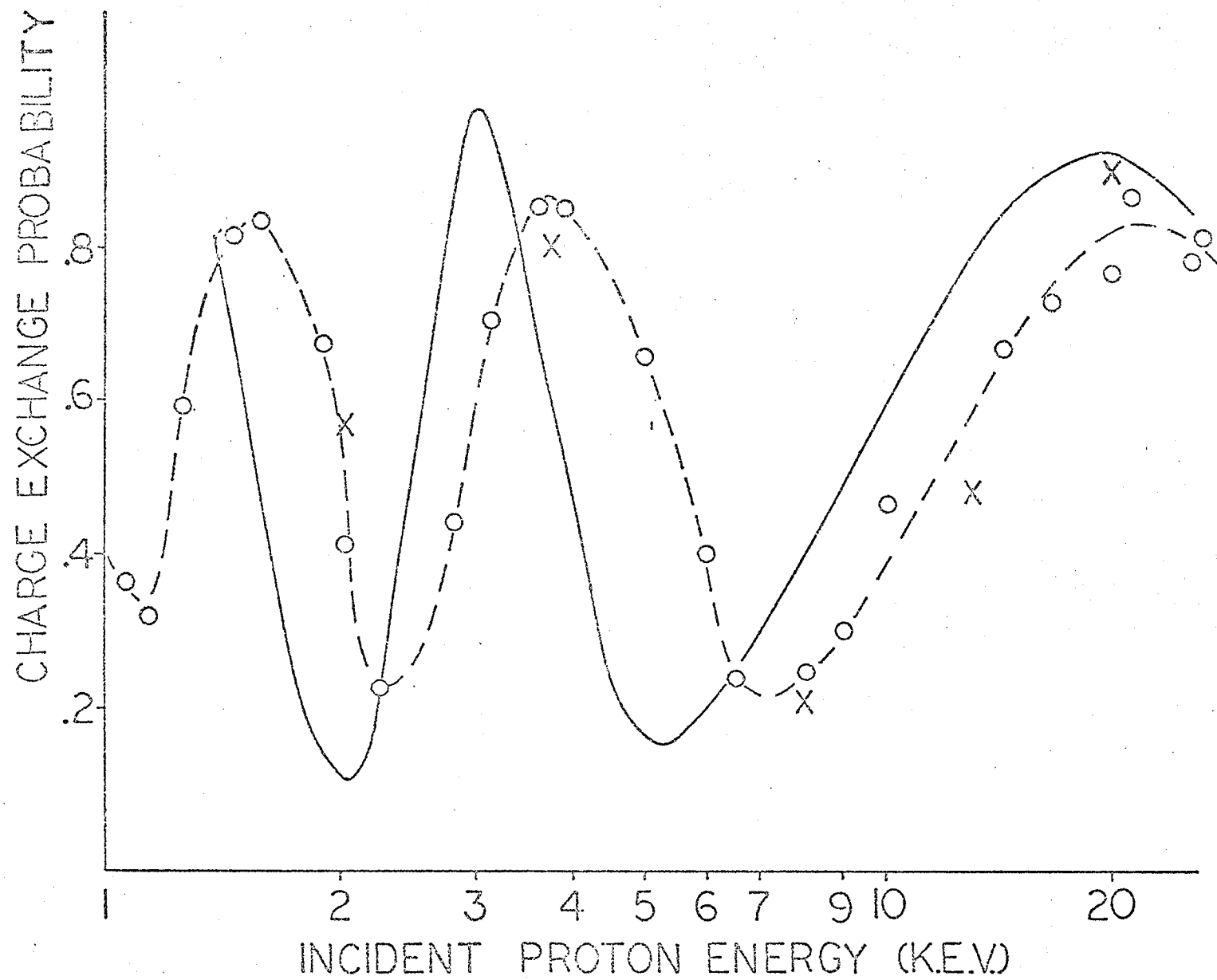


Figure 13

Electron exchange probability as a function of incident
proton energy:

- o -- curve through the experimental points of
Helbig and Everhart (13)
- the calculation of Wilets and Gallaher (12)
- X the generalized impact parameter calculation



basis set. The tremendous improvement of our results over the linear-trajectory, constant-velocity approximation is obvious. Since our calculations have used the same basis set as the Wilets and Gallaher calculation, one is at first led to the conclusion that the linear-trajectory, constant-velocity approximation is not valid. However, our same calculations indicate that not only are the trajectories effectively linear but the velocities along these trajectories are insignificantly different from their asymptotic values. Assuming that the numerical accuracy of the original Wilets and Gallaher calculation was sufficient, the only conclusion one can draw about the difference between the results of the linear-trajectory, constant-velocity approach and the generalized impact parameter approach lies in the difference in the physical natures of the two approaches. The linear-trajectory, constant-velocity approach is of course not an energy conserving approach, since, as the atoms approach, the internal energy of the atoms increases through excitation and exchange processes, the potential energy increases due to increasing interaction, but the kinetic energy of the atoms remains constant. However, in the generalized impact parameter approach the changes in the kinetic energy are coupled to the internal and potential energies (that is, to the quantum mechanical energy) so that there is overall energy.

conservation. Now although the changes in the kinetic energy represent only a small percentage of the total energy, the improper coupling of the various energies could still possibly be the proverbial straw that broke the camel's back.

The cross section for a given excitation or exchange process from the level i to the level f is defined as

$$\sigma_{i \rightarrow f} = 2\pi \int_0^\infty d\rho \rho P_{i \rightarrow f}(\rho, E_K) ,$$

where $P_{i \rightarrow f}(\rho, E_K)$ is the probability of excitation or exchange to the level f from the initial level i . This probability is defined as

$$P_{i \rightarrow f} = |b_f^c(R = \infty)|^2 ,$$

and is a function of impact parameter ρ and the incident proton energy E_K . $b_f^c(R = \infty)$ is the asymptotic coefficient of level f in channel c after the collision. From the 20 KeV calculations, cross sections for $2s$ and $2p_z$ excitation and $1s$, $2s$, and $2p_z$ exchange from the $1s$ level of the target atom were obtained. These are given in Table 1 along with other evaluations of the same quantities and experimental results. It is seen that our results are as good as, and in some cases, better than those obtained

Table 1

Excitation (D) and Charge Exchange (E) Cross Sections in Units of 10^{-17} cm^2 .

Process	Linear-Trajectory Approximation with			Generalized Impact Parameter Model	Experiment
	Hydrogenic Basis (12)	Pseudo-state Basis (17)	Sturmian Basis (15)		
2s (D)	1.076	0.943	1.3	3.400	-
2p _z (D)	1.816	3.425	4.6	3.577	4.5
1s (E)	38.730	41.400	40.0	47.950	-
2s (E)	3.327	3.760	3.6	4.002	4.2
2p _z (E)	1.085	1.633	3.2	2.531	3.1

The values for the hydrogenic and the pseudo-state bases are from a tabulation in reference 17; the experimental values are from the work of Stebbings et al (18), except for the value for 2s(E) which is from Figure 4 in reference 12.

using hydrogenic functions, Sturmians, etc., with the linear-trajectory, constant-velocity approximation.

As a general conclusion, it would appear that a hydrogenic basis is quite adequate for the description of the $p - H$ collision at high energies, provided that the coupling is treated properly. Furthermore, since the basis set used is quite small, it would seem that the high energy levels (both discrete and continuum) of hydrogen contribute to a small extent only to the evolution of the collision system. One should perhaps point out that the ability to follow the evolution of the collision throughout the interaction is also useful at high energies. For example, the charge density as a function of interatomic separation does not, at high energies, show the oscillatory behaviour which was seen at low energies. This indicates why simple perturbative approaches such as the Born approximation may be successful occasionally in the description of high energy processes, but certainly not in similar low energy reactions.

Chapter VI

GENERALIZATION OF THE MODEL AND A SURVEY OF POSSIBLE

APPLICATIONS TO PROCESSES INVOLVING COMPLEX MOLECULES

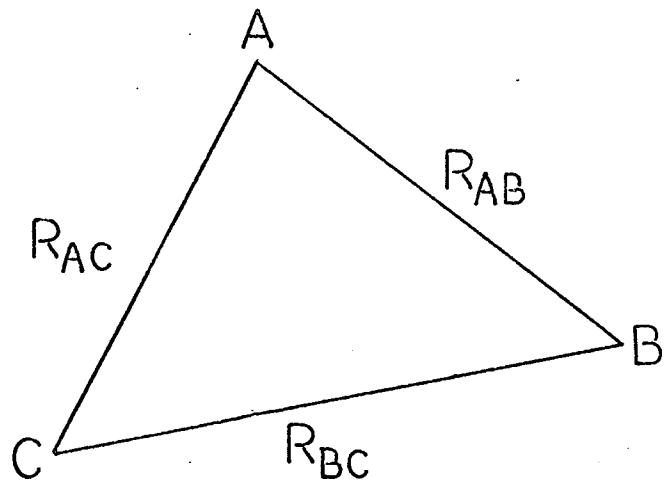
Although the generalized impact parameter model has brought forward several interesting features of the systems to which it has been applied in the research reported here, the real promise and purpose of the model lies in dealing with reactions of complex molecules. Because such reactions usually involve more than two centres, it is important to illustrate how easily the model may be generalized to many-centre reactions.

To this end, consider the application of the model to a general three-centre reaction. From such a discussion the extension to processes involving more centres is straightforward. For a three-centre reaction the interatomic separations may be denoted as in Figure 14. The only change that the extra centres will make in the quantum mechanical equations is in the evaluation of the required matrix elements. For three centres, the matrix elements may possibly be obtainable analytically, but for reactions involving more centres these elements will require numerical evaluation, unless the interactions can be treated pairwise, as will be illustrated in an example below. In any case, the matrix elements can be expressed in terms of the R_{ij} 's. For the three-centre reaction, there are three dynamic interatomic potentials which govern the classical motions of the atoms, just as the single potential does in the two-centre processes.

Figure 14

The coordinate system for a three-centre reaction.

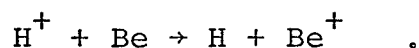
(70)



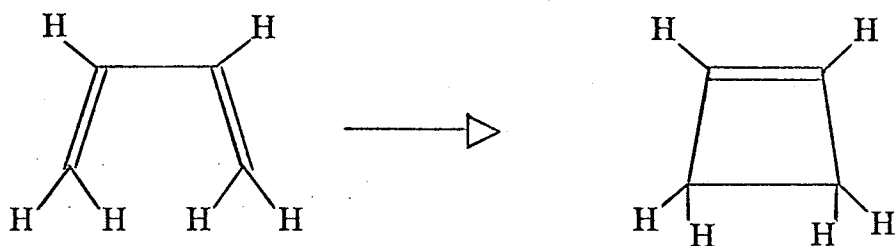
In an attempt to indicate the power of the model, several possibilities for research will be discussed here, the emphasis being on the ability of the model to predict a mechanism for a reaction. Although the required calculations may take large amounts of computer time, as a chemist one is more interested in the processes occurring during a specific collision than in obtaining macroscopic observable quantities, such as cross sections, which require a set of calculations. Consequently, only a few calculations may be needed to envisage a general mechanism. In any case, a single calculation would provide a vast amount of information as to electron densities and bond rearrangements occurring during the evolution of the collision. Such information could conceivably indicate why certain areas of a molecule are so-called "reactive sites" while others are not, why certain groups are eliminated during a reaction, etc.. The model should also be useful for studying hindered internal rotations within molecules, vibrational energy transfer, and so on.

As was pointed out in the discussion of low energy collisions in Chapter V, more complex reacting species, and indeed even simple asymmetric molecules, will show more complicated sub-processes in the course of their interactions. As an example, the phenomenon of level

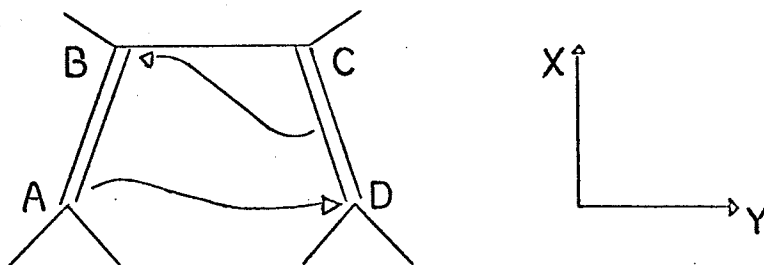
crossing was cited as a means for the collision to carry the system from one molecular state to another. This is certainly one possibility for study, and it could be accomplished using as simple a system as the collision of a proton with a beryllium atom,



Still another interesting possibility for study is the intramolecular rearrangement reaction



which is a symmetry conserving process. The conventional mechanism for such a process is



To apply the impact parameter model to such a process, the σ -bond framework could be set up in the following manner.

A basis set of hydrogenic orbitals consisting of $2s$, $2p_x$, $2p_y$, $2p_z$ (possibly with variable nuclear charge) could be chosen on each of the carbon atoms A, B, C, and D. The coefficients of such a basis set would initially correspond to sp^2 hybridization. The C-H σ -bond framework would then arise from overlap of one of the sp^2 orbitals with a $1s$ on the hydrogen. The π -bonds would be set up by overlap of the p_z orbitals. The atoms would all be treated classically and interactions such as those between neighbouring H atoms could be specified by some potential function. The calculation would then simply consist of feeding energy into the molecule and following the rearrangement. Before such a study could be attempted, it would be necessary to ascertain that the model could handle reasonably well changes in hybridization such as those occurring on centres A and D.

Of course, one could talk for great lengths about possible applications of such a model. Those discussed above are two of the more interesting of the possibilities which are planned for study by the research group this author has had the pleasure of working with for the past year and a half.

As a general conclusion to this manuscript it is only fair to mention the major drawback of the model, since this also suggests possibilities for future research in

this field. Of course the model is subject to the usual approximation of molecular quantum theory, namely, that the electrons are described by some truncated basis set. This is not a serious difficulty, however, as one can usually choose a sufficiently large basis and still remain within the realm of practical calculations. This has been borne out by the high energy calculations discussed in Chapter V. These calculations gave very good agreement with experimental results with only six states. The semi-classical approximation is also justifiable for atoms and molecules. The most serious approximation of the model is that which assumes the union of the asymptotic channel eigenfunctions as a basis set for the collision. Although these functions are renormalized, the set still remains overcomplete, and, in fact, can become grossly so in the regions of strong interaction when the particles are spatially in close proximity. This overcompleteness of the basis set results in the difficulty that, in general, the coefficient matrix \underline{b} is not unique. The solution to such a problem would be to project the collision on the eigenfunctions of a given channel of the reaction. As yet, however, no simple and satisfactory means has been found to accomplish this.

Appendix I

THE MATRIX ELEMENTS REQUIRED FOR THE PROTON-HYDROGEN

ATOM COLLISION

The matrix elements were evaluated by conversion to the elliptical coordinates (λ, μ, ϕ) . With reference to Figure 4, these coordinates are defined as follows:

$$\lambda = (r_a + r_b)/R ,$$

$$\mu = (r_a - r_b)/R ,$$

and ϕ is the azimuthal angle round the axis AB. The ranges of these three variables are

$$1 \leq \lambda \leq \infty ,$$

$$-1 \leq \mu \leq 1 ,$$

and

$$0 \leq \phi \leq 2\pi .$$

In atomic units, the basis functions are as follows:

$$\phi_{1s}(A) = (\pi)^{-\frac{1}{2}} \exp(-r_a) ,$$

$$\phi_{2s}(A) = (32\pi)^{-\frac{1}{2}} (2 - r_a) \exp(-r_a/2) ,$$

and

$$\phi_{2p_z}(A) = (32\pi)^{-\frac{1}{2}} r_a \exp(-r_a/2) \cos\theta .$$

Since the basis functions are orthonormal within the channels, only the cross-channel elements of the matrix \underline{N} need be evaluated. These elements are as follows:

$$\langle 1s(A) | 1s(B) \rangle = (1 + R + R^2/3) e^{-R}$$

$$\langle 2s(A) | 2s(B) \rangle = (1 + R/2 + R^2/12 + R^4/240) e^{-R/2}$$

$$\langle 2p_z(A) | 2p_z(B) \rangle = (-1 - R/2 - R^2/20 + R^3/60 + R^4/240) e^{-R/2}$$

$$\langle 1s(A) | 2s(B) \rangle = C\{(-64/R + 22 - 3R) + (64/R + 10) e^{-R/2}\} e^{-R/2}$$

$$\begin{aligned} \langle 1s(A) | 2p_z(B) \rangle = C\{ & (64/R^2 + 32/R - 16 + 3R) + (-64/R^2 - 64/R \\ & - 8) e^{-R/2}\} e^{-R/2} \end{aligned}$$

$$\langle 2s(A) | 2p_z(B) \rangle = -(R^3/120 + R^4/240) e^{-R/2}$$

where C is a constant whose numerical value is $\frac{32}{27\sqrt{2}}$.

For the matrix \underline{V} , the elements within the channels are as follows:

$$\langle 1s(A) | V | 1s(A) \rangle = (1 + 1/R) e^{-2R}$$

$$\langle 2s(A) | V | 2s(A) \rangle = (1/R + 3/4 + R/4 + R^2/8) e^{-R}$$

$$\begin{aligned} \langle 2p_z(A) | V | 2p_z(A) \rangle = & -12/R^3 + (12/R^3 + 12/R^2 + 7/R + 11/4 \\ & + 3R/4 + R^2/8) e^{-R} \end{aligned}$$

$$\langle 1s(A) | V | 2s(A) \rangle = D(2 + 3R) e^{-3R/2}$$

$$\langle 1s(A) | V | 2p_z(A) \rangle = D\{64/9R^2 + (-64/9R^2 - 32/3R - 8 - 3R) e^{-3R/2}\}$$

$$\langle 2s(A) | V | 2p_z(A) \rangle = 3/R^2 + (-3/R^2 - 3/R - 3/2 - 5R/8 - R^2/8) e^{-R}$$

where D is a constant whose numerical value is $-2(2)^{1/2}/27$.

The cross-channel elements of \underline{V} are as follows:

$$\langle 1s(A) | V | 1s(B) \rangle = (1/R - 2R/3) e^{-R}$$

$$\langle 2s(A) | V | 2s(B) \rangle = (1/R + 1/4 - R/24 + R^2/24 - R^3/160) e^{-R/2}$$

$$\langle 2p_z(A) | V | 2p_z(B) \rangle = (-1/R - 1/4 + 3R/40 + R^2/60 - R^3/160) e^{-R/2}$$

$$\begin{aligned} \langle 1s(B) | V | 2s(A) \rangle = & C\{(-64/R^2 + 8/R) + (64/R^2 + 24/R + 15/4) e^{-R/2}\} \\ & \times e^{-R/2} \end{aligned}$$

(78)

$$\langle 1s(A) | V | 2s(B) \rangle = C \{ (-64/R^2 + 32/R - 33/4 + 9R/8) + (64/R^2) e^{-R/2} \} \\ \times e^{-R/2}$$

$$\langle 1s(B) | V | 2p_z(A) \rangle = C \{ (64/R^3 + 48/R^2 - 8/R) + (-64/R^3 - 80/R^2 \\ - 24/R - 3) e^{-R/2} \} e^{-R/2}$$

$$\langle 1s(A) | V | 2p_z(B) \rangle = C \{ (64/R^3 + 24/R^2 + 12/R + 6 - 9R/8) \\ + (-64/R^3 - 56/R^2) e^{-R/2} \} e^{-R/2}$$

$$\langle 2s(B) | V | 2p_z(A) \rangle = 2s(A) | V | 2p_z(B) \\ = (-R/24 - 7R^2/240 + R^3/160) e^{-R/2}$$

The matrix elements of \underline{H} are obtained from the relation

$$\underline{H} = \underline{NE} + \underline{V} ,$$

where \underline{E} is the matrix

$$\begin{bmatrix} -0.5 & 0 & 0 & 0 & 0 & 0 \\ 0 & -0.125 & 0 & 0 & 0 & 0 \\ 0 & 0 & -0.125 & 0 & 0 & 0 \\ 0 & 0 & 0 & -0.5 & 0 & 0 \\ 0 & 0 & 0 & 0 & -0.125 & 0 \\ 0 & 0 & 0 & 0 & 0 & -0.125 \end{bmatrix}$$

The matrix elements of the derivative matrices $\partial_{\underline{R}} \underline{N}$ and $\partial_{\underline{R}} \underline{H}$ are simply obtained by differentiation of the elements of \underline{N} and \underline{H} with respect to R .

Appendix II

THE COMPUTER PROGRAM

PROGRAM INITIATE

 THIS PROGRAM INITIATES THE DATA ON DISK FOR THE MAIN PROGRAM

```

IMPLICIT REAL*8(A-H,O-Z)
COMMON /CORDRP/RX(2,3),RY(2,3),RZ(2,3),PX(2,3),PY(2,3),PZ(2,3),
XTMASS(2)

```

THE POSITIONS AND MOMENTA ARE DENOTED RX(I,J),RY(I,J),RZ(I,J), AND
 PX(I,J),PY(I,J),PZ(I,J) RESPECTIVELY. THE DIMENSION I REFERS TO
 THE PARTICLE NUMBER AND THE DIMENSION J REFERS TO ONE OF THE THREE
 SAVED ITERATIONS.

```

COMPLEX*16 A(6,3)

```

THE COEFFICIENT MATRIX B IS DENOTED A(I,J) WHERE THE DIMENSION I
 REFERS TO THE ASYMPTOTIC CHANNEL STATES AND THE DIMENSION J
 AGAIN REFERS TO ONE OF THE THREE SAVED ITERATIONS.

```

REAL*8 ZIP1(38),H(6),EVEC(9)
LOGICAL*4 NTEST/.FALSE./,AREAD
EQUIVALENCE (ZIP1(1),PX(1,1))
DATA IREAD,IWRITE/5,6/,JN2,NOTRY/1,0/
DATA NOPART,JN/2,1/

```

NOPART IS THE NUMBER OF CLASSICAL PARTICLES IN THE COLLISION.
 NOTRY IS THE NUMBER OF ITERATIONS PRESENTLY COMPLETED.

THE DATA IS READ AND THEN WRITTEN ON DISK

```

10 READ (IREAD,80,END=60) NWRT,DELTAT
   READ (IREAD,100) (PX(I,1),PY(I,1),PZ(I,1),TMASS(I),RX(I,1),RY(I,1),
   X,RZ(I,1),I=1,NOPART)

```

TEST WHETHER THE COEFFICIENT MATRIX IS READ AS DATA OR CALCULATED
 (BY A VARIATIONAL PROCEDURE TO OBTAIN A MINIMUM ENERGY STATE AS
 THE ASYMPTOTIC STATE).

```

READ (IREAD,130) AREAD,TIME
IF (.NOT.AREAD) GO TO 20

```

THE COEFFICIENTS ARE READ RATHER THAN BEING CALCULATED-THIS IS
 USED TO CONTINUE A CALCULATION. IT IS ALSO POSSIBLE TO CONTINUE A
 CALCULATION FROM A DISK WRITE UP OF THE NECESSARY DATA.


```

      READ (IREAD,99) (A(I,1),I=1,6)
      GO TO 50
20  RINV=1.D00/DSQRT((RX(1,1)-RX(2,1))**2+(RY(1,1)-RY(2,1))**2+(RZ(1,1)
      X)-RZ(2,1))**2)

```

```

      RINV IS JUST 1/R

```

```

      VARIATIONAL PROCEDURE IS USED TO OBTAIN THE MINIMUM ENERGY
      ASYMPTOTIC STATE.

```

```

      H(1)=-.5D00
      H(2)=0.D00
      H(3)=-.125D00
      H(4)=-.744935539026086D00*RINV*RINV
      H(5)=3.D00*RINV*RINV
      H(6)=-12.D00*RINV*RINV*RINV-.125D00
      CALL DEICHM(H,EVEC,3,0)
      EIG=H(6)

```

```

      EIG IS THE EIGEN ENERGY OF THE MINIMIZED ASYMPTOTIC STATE.

```

```

      THE COEFFICIENTS OF THE CALCULATED ASYMPTOTIC STATE ARE NORMALIZED

```

```

      ANORM=0.D00
      DO 30 I=1,3
      J=I+6
      A(I,1)=EVEC(J)
30  ANORM=ANORM+EVEC(J)**2
      ANORM=DSQRT(ANORM)
      DO 40 I=1,3

```

```

      THE NORMALIZED ASYMPTOTIC STATE IS

```

```

40  A(I,1)=A(I,1)/ANORM
      A(4,1)=(0.D00,0.D00)
      A(5,1)=(0.D00,0.D00)
      A(6,1)=(0.D00,0.D00)
50  WRITE (NWRT) JN2,NCTRY,NTEST,E0,TIME,DELTAT,TOOLRG,TOOSM

```

```

      E0 IS THE ENERGY CALCULATED ON THE FIRST ITERATION, DELTAT IS THE
      STEP SIZE BY WHICH THE TIME IS INCREMENTED.

```

```

      WRITE (NWRT) ZIP1
      WRITE (NWRT) A
      END FILE NWRT
      WRITE (IWRITE,70) NOPART,DELTAT,(I,PX(I,JN),PY(I,JN),PE(I,JN),
      XTMASS(I),RX(I,JN),RY(I,JN),RZ(I,JN),I=1,NOPART)
      WRITE (IWRITE,150) (I,A(I,1),I=1,6)

```

```

      IF (.NOT.AREAD) WRITE (IWRITE,140) EIG
      WRITE (IWRITE,120)
      GO TO 10
60  CALL EXIT
      RETURN
70  FORMAT (1H1,28X,'THE INITIAL DATA FOR THE SEMICLASSICAL SCATTERING
      XOF',I5,' NUCLEI  '/1H ,31X,'INITIAL TIME INTERVAL USED IN THE CAL
      XCULATION IS',D20.10,'A.U.'////1H ,53X,'INITIAL PARTICLE PARAMETER
      XS'////1H , 'PARTICLE*',6X,'PX',5X,'**',6X,'PY',5X,'**',6X,'PZ',5X,'
      X**',3X,'MASS',5X,'**',6X,'PX',5X,'**',6X,'PY',5X,'**',6X,'RZ',5X,
      X'*/(1H ,2X,I5,2X,7D15.8))
80  FORMAT (I5,D20.10)
90  FORMAT (4G20.10)
100 FORMAT (4G20.10/3G20.10)
110 FORMAT (1H ,7A4)
120 FORMAT (1H0,'THIS RUN FINISHED')
130 FORMAT (L1,4X,G20.10)
140 FORMAT (1H0,' THE EIGEN ENERGY WAS ',G20.10)
150 FORMAT (1H ,37X,'*',15X,'D MATRIX',15X,'*/(1H ,32X,I5,2G20.10))
      END

```

PROGRAM COLLISION

THIS PROGRAM SOLVES THE QUANTUM MECHANICAL AND THE CLASSICAL
EQUATIONS OF THE GENERALIZED IMPACT PARAMETER MODEL.

THE MAIN PROGRAM DEALS MOSTLY WITH THE CLASSICAL EQUATIONS.

```

      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 ERRORX(2),ERRORY(2),ERRORZ(2),ERRPX(2),ERRPY(2),ERRPZ(2),DELPX
      X(2),DELPY(2),DELPZ(2),ALPHA(4)/.5D00,.292893218813453D00,
      X1.70710678118654D00,.1666666666666667D00/,BETA(4)/.5D00,
      X.292893218813453D00,1.707106781186547D00,.5D00/,ANUMB(4)/2.D00,2*
      X1.D00,2.D00/

```

ALPHA, BETA, AND ANUMB ARE CONSTANTS FOR THE RUNGE-KUTTA PROCESS,
DELPX, DELPY, AND DELPZ ARE EFFECTIVELY MOMENTUM INCREMENTS, AND
THE REMAINDER OF THE ABOVE CHARACTERS ARE ERROR TERMS FOR THE
RUNGE-KUTTA PROCESS.

```

      REAL*4 TMINT,TCPU,TTERN,TMACCM

```

TMINT, TCPU, TTERN, AND TMACCM ARE USED FOR CONTROLLING THE
CPU TIME OF THE CALCULATION.

THE PHYSICAL TIME CONTROL IS IN THE RUNGE-KUTTA PROCESS.

EQUIVALENCE (JN,L)
 DATA TOOLRE,TOOSB/1.D-07,1.D-09/
 DATA NLENG,NOPART/16,2/
 DATA IWRITE/6/
 COMPLEX*16 A,PIL,ASAVE(6),ACOPY(6),ERRORA(6),TERM

ERRORA IS AN ERROR TERM FOR THE RUNGE-KUTTA PROCESS.

LOGICAL*4 NTEST,FIRST

TOOLRE AND TOOSB ARE USED TO ESTABLISH THE BOUNDS ON ENERGY CONSERVATION.

COMMON /CORDRP/PX(2,3),RY(2,3),RZ(2,3),PX(2,3),PY(2,3),PZ(2,3),
 XTHASS(2)

COMMON /RW/NORUN,TMINT,NOTHING,ENTRI,TNACCM,TCPU

NORUN IS THE NUMBER OF ALLOWED ITERATIONS. NOTHING IS A DUMMY ARGUMENT WHICH BECOMES A REAL ARGUMENT THROUGH THE COMMON BLOCKS OF SUBROUTINES READ AND WRITE.

COMMON /AMATRY/A(6,3)

THE INITIAL PARAMETERS ARE NOW READ BY SUBROUTINE READ.

10 CALL READ(DELTAT,NOTRY,TIME,NWRIT,NTEST,JN2,EPRFV,TEND,TOOLRG,
 XTOOSM)

TEND IS AN END PARAMETER ON THE TIME THE CALCULATION RUNS.

NCOUNT=0

TEST IF THE CALCULATION IS TO BE CONTINUED FROM A DISK DATA SET; IF NOT, STOP TO A STARTING BLOCK (LABEL 50) WHICH USES THE RUNGE-KUTTA PROCESS IN A SPECIAL FASHION FOR TWO ITERATIONS.

IF (.NOT.NTEST) GO TO 50
 JN1=JN2+1
 IF (JN1.GT.3) JN1=1
 JN=JN1+1
 IF (JN.GT.3) JN=1
 CALL MOVEC(ACOPY(1),96,A(1,JN))
 GO TO 70

MOVEC AND EXCLOR ARE IBM ASSEMBLER ROUTINES.

1) MOVEC (INTO,NLENG,FROM) MOVES 'NLENG' BYTES FROM STARTING
 BYTE 'FROM' INTO STARTING BYTE 'INTO'.
 THIS IS USED TO MOVE ARRAY CHUNKS.

2) EXCLOR (INTO,NLENG,FROM) EXCLUSIVE OR'S 'FROM' ONTO

'INTO' FOR A STRING 'NLENG' BYTES LONG. THIS IS USED TO
ZERO A MATRIX.

THE TIME INTERVAL IS SHORTENED IF THE ERROR IN THE ENERGY IS TOO
LARGE.

```
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
```

THE FURTHEST BACK ITERATION (STEP JN2) IS LOADED FOR THE
POSITIONS(I,1), THE MOMENTA(I,1), AND THE COEFFICIENT MATRIX(I,1)
TO RESTART THE RUNGE-KUTTA PROCESS.

```
IF (JN2.EQ.1) GO TO 50
CALL MOVEC(RX(1,1),NLENG,RX(1,JN2))
CALL MOVEC(RY(1,1),NLENG,RX(1,JN2))
CALL MOVEC(RZ(1,1),NLENG,RX(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(A(1,1),96,A(1,JN2))
GO TO 50
```

THE TIME INTERVAL IS LENGTHENED IF THE ENERGY CONSERVATION IS
GREATER THAN REQUIRED. THE LAST ITERATION (STEP JN) IS LOADED TO
RESTART THE RUNGE-KUTTA PROCESS. ACTUALLY THE JN1 ITERATION IS
LOADED SINCE THE ITERATION POINTERS HAVE ALREADY BEEN MOVED.

```
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,RX(1,JN1))
CALL MOVEC(RZ(1,1),NLENG,RX(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(A(1,1),96,A(1,JN1))
```

THE RUNGE KUTTA BLOCK FOLLOWS

```
50 JN2=1
```

```

JN1=JN2
JN=2
CALL MOVEC(ACOPY(1),96,A(1,JN2))
GO TO 70

```

```

60 EPREV=E

```

```

C
C   EPREV IS THE ENERGY AT THE PREVIOUS ITERATION.
C

```

```

IF(NOTRY.EQ.0) GO TO 67
65 NOTRY=NOTRY+1
JN1=2
JN=3
NTEST=.TRUE.
GO TO 90

```

```

C
C   THE ENERGY TEST IS SET UP IF NOTRY=0
C

```

```

67 TOOLRG=DABS(TOOLRE*E)
TOOSM=DABS(TOOSE*E)

```

```

C
C   TOOLRG AND TOOSM ARE THE ACTUAL BOUNDS ON THE ENERGY.
C

```

```

WRITE (IWRITE,170) E,TOOLRG,TOOSM
GO TO 65

```

```

C
C   THE FIRST STEP-THE ERROR ARRAYS ARE INITIALIZED TO ZERO.
C

```

```

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(ERRORA(1),96,ERRORA(1))
IF (.NOT.NTEST) GO TO 90

```

```

C
C   THE POINTERS FOR THE POSITIONS AND MOMENTA ARE NOW CHANGED.
C

```

```

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.

```

C NOW THE ACTUAL RUNGE-KUTTA PROCEDURE IS USED.

C
 DO 140 KK=1,4
 IF (KK.EQ.2.OR.KK.EQ.4) TIME=TIME+.5D00*DELTAT
 X=RX(1,JN)-RX(2,JN)
 Y=RY(1,JN)-RY(2,JN)
 Z=RZ(1,JN)-RZ(2,JN)
 R=DSQRT(X*X+Y*Y+Z*Z)
 RINV=1.D00/R
 PXI=PX(1,JN)/TMASS(1)-PX(2,JN)/TMASS(2)
 PYI=PY(1,JN)/TMASS(1)-PY(2,JN)/TMASS(2)
 PZI=PZ(1,JN)/TMASS(1)-PZ(2,JN)/TMASS(2)
 DRT=(X*PXI+Y*PYI+Z*PZI)*RINV

C
 C DRT IS THE DERIVATIVE OF R WITH RESPECT TO TIME.
 C

C-----
 C THESE QUANTITIES HAVE TO DO WITH THE TRANSLATIONAL ENERGY OF THE
 C ELECTRON AND ARE REQUIRED FOR HIGH-ENERGY CALCULATIONS ONLY.
 C

V1SQ=(PX(1,JN)**2+PY(1,JN)**2+PZ(1,JN)**2)/TMASS(1)**2
 V2SQ=(PX(2,JN)**2+PY(2,JN)**2+PZ(2,JN)**2)/TMASS(2)**2
 VSUMX=0.5D00*(PX(1,JN)/TMASS(1)+PX(2,JN)/TMASS(2))
 VSUMY=0.5D00*(PY(1,JN)/TMASS(1)+PY(2,JN)/TMASS(2))
 VSUMZ=0.5D00*(PZ(1,JN)/TMASS(1)+PZ(2,JN)/TMASS(2))
 VSX=VSUMX*X
 VSY=VSUMY*Y
 VSZ=VSUMZ*Z

C-----
 CALL QUANTM(TIME,R,ACOPY,ASAVE,DET,DRT,PIE,FIRST,V1SQ,V2SQ,VSUMX,
 XVSUMY,VSUMZ,VSX,VSY,VSZ,X,Y,Z)
 DELPX(1)=-X*DET*RINV
 DELPY(1)=-Y*DET*RINV
 DELPZ(1)=-Z*DET*RINV
 DELPX(2)=X*DET*RINV
 DELPY(2)=Y*DET*RINV
 DELPZ(2)=Z*DET*RINV

C
 C THE ENERGY IS CALCULATED AND TESTED AND THE NEW COEFFICIENT MATRIX
 C IS LOADED INTO A(1,JN1).
 C

IF (.NOT.FIRST) GO TO 110
 TK=0.D00
 DO 100 I=1,NOPART
 100 TK=TK+(PX(I,JN1)**2+PY(I,JN1)**2+PZ(I,JN1)**2)/(2.D00*TMASS(I))
 E=PIE+TK+(DCONJG(ACOPY(1))*ACOPY(1)+DCONJG(ACOPY(2))*ACOPY(2)+
 XDCONJG(ACOPY(3))*ACOPY(3))*V1SQ*.5D00+(DCONJG(ACOPY(4))*ACOPY(4)+
 XDCONJG(ACOPY(5))*ACOPY(5)+DCONJG(ACOPY(6))*ACOPY(6))*V2SQ*.5D00

C
 C TK IS THE KINETIC ENERGY, PIE IS THE QUANTUM MECHANICAL ENERGY, AND

```

C      E IS THE TOTAL ENERGY.
C
      IF (.NOT.NTEST) GO TO 110
      CALL MOVEC(A(1,JN1),96,ACOPY(1))
      ERROR=DABS(EPRIV-E)
      IF (ERROR.GT.TOOLRG) GO TO 20
      IF (ERROR.LT.TOOSM.AND.DLEAT.LT.20.D01) GO TO 30
      EPRIV=E
C
C      THE NEW POSITIONS AND MOMENTA OF A PARTICULAR ITERATION ARE
C      CALCULATED.
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)
      PYI=PY(I,L)
      PZI=PZ(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
      YK=PYI/TMASSI
      ERROR=ERRORY(I)
      RY(I,L)=RY(I,L)+ALP*(YK-ANUM*ERROR)*DELTAT
      ERRORY(I)=ERROR+APP*(YK-ANUM*ERROR)-BET*YK
      DELP=DELPY(I)
      ERP=ERPY(I)
      PY(I,L)=PYI+ALP*(DELP-ANUM*ERP)*DELTAT
      ERPY(I)=ERP+APP*(DELP-ANUM*ERP)-BET*DELP
      ZK=PZI/TMASSI
      ERROR=ERRORZ(I)
      RZ(I,L)=RZ(I,L)+ALP*(ZK-ANUM*ERROR)*DELTAT
      ERRORZ(I)=ERROR+APP*(ZK-ANUM*ERROR)-BET*ZK
      DELP=DELPZ(I)
      ERP=ERPZ(I)
      PZ(I,L)=PZI+ALP*(DELP-ANUM*ERP)*DELTAT
      ERPZ(I)=ERP+APP*(DELP-ANUM*ERP)-BET*DELP
120  CONTINUE
C
C      THE NEW COEFFICIENT MATRIX FOR A PARTICULAR ITERATION IS
C      CALCULATED.
C

```

```

DO 130 I=1,6
  TERM=ALP*(ASAVE(I)-ANUM*ERRORA(I))
  ACOPY(I)=ACOPY(I)+TERM*DELTAT
130 ERRORA(I)=ERRORA(I)+3.D00*TERM-BET*ASAVE(I)
  FIRST=.FALSE.
140 CONTINUE
  IF (.NOT.NTEST) GO TO 60
  NOTRY=NOTRY+1
  T=TCPU
  CALL $TPTM(T)
C
C  $TPTM STOPS THE CPU TIMER.
C
  IF ((T-TMACCM).LT.TMINT.AND.NOTRY.LT.NORUN) GO TO 150
  TMACCM=T
  CALL MOVEC (A(1,JN),96,ACOPY(1))
  CALL WPTDK (NOTRY,TIME,NTEST,JN2,JN1,EPREV,DELTAT,E,TK,PIE,TOOLRG,
XTOOSH,&10)
150 IF (TIME.LT.TEND) GO TO 80
  NCOUNT=NCOUNT+1
  IF (NCOUNT.LT.NWRIT) GO TO 80
  CALL WRITE (NOTRY,TIME,JN1,DELTAT,E,TK,PIE)
  NCOUNT=0
  GO TO 80
160 FORMAT (1H0,'TIME INTERVAL CHANGED TO',G15.2,' AT STEP',I3,' NUMBER
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,B,DBT,ARG,DRE,PIE,FIRST,V1SQ,V2SQ,VSUMX,
XVSUMY,VSUMZ,VSX,VSX,VSZ,X,Y,Z)
C
C  THIS SUBROUTINE PERFORMS MOST OF THE CALCULATIONS REQUIRED BY THE
C  QUANTUM MECHANICAL EQUATIONS.
C
  IMPLICIT COMPLEX*16 (A-H,O-Z)
  REAL*8 T,R,RINV,ANORM,EXR,EXR2,EXRH,DEXP,DCOS,DSIN,DRE,TRI,ARG
X,V1SQ,V2SQ,VDIF,VSUMX,VSUMY,VSUMZ,VSX,VSX,VSZ,X,Y,Z,VSUM,VAR
  DATA NDIM/6/
  COMPLEX*16 IMAG/(0.D00,1.D00)/,N(6,6),RESULT(6,6),B(1),DBT(1),PDBT
X(6),MINV(6,6),H(6,6),PDNR(6,6),HE(6,6),VECT(6),BT(6),PDBR(6),PDNR(
X6,6)
  EQUIVALENCE (NE(1,1),MINV(1,1),PDNR(1,1))
  LOGICAL*4 FIRST
  INTEGER*4 ONE/1/
C
C -----
C  THESE PHASE FACTORS ARE USED IN THE HIGH-ENERGY CALCULATIONS ONLY.
  VSUM=VSX+VSX+VSZ
  VDIF=T*(V1SQ-V2SQ)*.125D 00

```



```

PN=DCOS(VDIF)-IMAG*DSIN(VDIF)
PP=DCOS(VDIF)+IMAG*DSIN(VDIF)
PHP=DCOS(VSUM)+IMAG*DSIN(VSUM)
PIN=DCOS(VSUM)-IMAG*DSIN(VSUM)

```

```

C-----
PHPOS=DCOS(.375D00*T)+IMAG*DSIN(.375D00*T)
PHNEG=DCOS(.375D00*T)-IMAG*DSIN(.375D00*T)

```

```

C
C PHPOS AND PHNEG ARISE FROM THE TIME-DEPENDENCE OF THE BASIS
C FUNCTIONS.
C

```

```

RINV=1.D00/R
EXRH=DEXP(-.5D00*R)
IF (EXRH.LT.1.D-20) EXRH=0.D00
EXR=DEXP(-R)
IF (EXR.LT.1.D-20) EXR=0.D00
EXR2=DEXP(-2.D00*R)
IF (EXR2.LT.1.D-20) EXR2=0.D00

```

```

C
C THE MATRIX N IS CALCULATED.
C THE MATRIX N REPRESENTS OVERLAP WITHIN AND BETWEEN THE CHANNELS.
C WITHIN THE TWO CHANNELS N IS THE IDENTITY SINCE THE BASIS
C FUNCTIONS ARE ORTHONORMAL WITHIN THE REACTION CHANNELS.
C

```

```

CALL EXCLOR(N(1,1),576,N(1,1))
DO 10 I=1,6
10 N(I,I)=1.D00
N(1,4)=EXR*(1.D00+R+R*R*.3333333333333333D00)
N(4,1)=N(1,4)
TRM=0.8380524813D00*EXRH*(-3.D00*R+22.D00-64.D00/R+(10.D00+64.D00/
XR)*EXRH)
N(4,2)=TRM*PHNEG
N(1,5)=N(4,2)
N(2,4)=TRM*PHPOS
N(5,1)=N(2,4)
TRM=0.8380524813D00*EXRH*(3.D00*R-16.D00+32.D00/R+64.D00/(R*R)+(-
X8.D00-64.D00*(1.D00+1.D00/R)/R)*EXRH)
N(4,3)=TRM*PHNEG
N(1,6)=N(4,3)
N(3,4)=TRM*PHPOS
N(6,1)=N(3,4)
N(2,5)=EXRH*(1.D00+R*.5D00+R*R*.0833333333333333D00+R**4*
X.0041666666666667D00)
N(5,2)=N(2,5)
N(3,5)=-R*R*R*(2.D00+R)*EXRH*.0041666666666667D00
N(5,3)=N(3,5)
N(2,6)=N(3,5)
N(6,2)=N(3,5)
N(3,6)=EXRH*(-1.D00-R*.5D00-.05D00*R*R+R*R*R*.0166666666666667D00+R
X**4*.0041666666666667D00)

```

```

      N(6,3)=N(3,6)
      DO 15 I=1,3
      DO 15 J=4,6
      N(I,J)=N(I,J)*PP*PHP
15  N(J,I)=N(J,I)*PH*PHN
      IF (.NOT.FIRST) GO TO 35
      DO 20 I=1,6
20  BT(I)=DCONJG(B(I))

C
C      CDGMPD(A,B,C,DIM1,DIM2,DIM3) MULTIPLIES MATRIX A(DIM1,DIM2) BY
C      MATRIX B(DIM2,DIM3) TO GIVE MATRIX C(DIM1,DIM3).
C
      CALL CDGMPD(N,B,VECT,NDIM,NDIM,ONE)
      CALL CDGMPD(BT,VECT,BNORM,ONE,NDIM,ONE)

C
C      NORMALIZATION
C
      ANORM=BNORM
      ANORM=DSQRT(ANORM)
      DO 30 I=1,6
30  B(I)=B(I)/ANORM

C
C      THE MATRIX H IS EVALUATED. FIRST THE COULOMB INTEGRALS ARE
C      OBTAINED, THEN THE MATRIX NE AND THE INTERNUCLEAR REPULSION
C      ARE INCLUDED IN THE MATRIX H.
C      THE ELEMENTS WITHIN THE CHANNELS ARE AS FOLLOWS:
C
35  H(1,1)=-RINV+(1.D00+RINV)*EXR2
      H(4,4)=H(1,1)
      H(2,2)=-RINV+.25D00*(4.D00*RINV+3.D00+R+.5D00*R*R)*EXR
      H(5,5)=H(2,2)
      H(3,3)=-RINV-12.D00*RINV**3+((7.D00+(12.D00+12.D00*RINV)*RINV)*
      XRINV+2.75D00+.75D00*R+.125D00*R*R)*EXR
      H(6,6)=H(3,3)
      TRM=-.104756560175784D00*(2.D00+3.D00*R)*EXR*EXPH
      H(1,2)=PHNEG*TRM
      H(4,5)=H(1,2)
      H(2,1)=PHPOS*TRM
      H(5,4)=H(2,1)
      TRM=-.104756560175784D00*(7.111111111111111D00*RINV*RINV+(-(
      X10.66666666666667D00+7.111111111111111D00*RINV)*RINV-3.D00-3.D00*R)*
      XEXR*EXRH)
      H(1,3)=PHNEG*TRM
      H(4,6)=H(1,3)
      H(3,1)=PHPOS*TRM
      H(6,4)=H(3,1)
      H(2,3)=3.D00*RINV*RINV+(-(3.D00+3.D00*RINV)*RINV-1.5D00-.625D00*R-
      X.125D00*R*R)*EXR
      H(3,2)=H(2,3)
      H(5,6)=H(2,3)

```

H(6,5)=H(2,3)

THE CROSS-CHANNEL ELEMENTS ARE AS FOLLOWS:

H(4,1)=- (R+1.D00)*EXR
 H(1,4)=H(4,1)
 H(5,2)=- (R*.125D00+.25D00-.041666666666667D00*R*R+
 X.010416666666667D00*R*R*R)*EXRH
 H(2,5)=H(5,2)
 H(6,3)=-.03125D00*R*R*R*(.333333333333333D00-4.D00*RINV*RINV-3.D00
 X*RINV**3)*EXRH
 H(3,6)=H(6,3)
 TRM=-.8380524813D00*(5.25D00+10.D00*RINV*(-1.D00+EXRH)-1.125D00*R)
 X*EXRH
 H(4,2)=PHNEG*TRM
 H(1,5)=H(4,2)
 TRM=-.8380524813D00*(-3.D00+14.D00*RINV+(-3.75D00-14.D00*RINV)*
 XEXRH)*EXRH
 H(2,4)=PHPOS*TRM
 H(5,1)=H(2,4)
 TRM=-.8380524813D00*(1.125D00*R-3.D00+(4.D00+8.D00*RINV)*RINV-
 X8.D00*(1.D00+RINV)*RINV*EXRH)*EXRH
 H(4,3)=PHNEG*TRM
 H(1,6)=H(4,3)
 TRM=-.8380524813D00*(3.D00-8.D00*RINV*(1.D00+2.D00*RINV)+(3.D00+
 X16.D00*RINV*(1.D00+RINV))*EXRH)*EXRH
 H(6,1)=TRM*PHPOS
 H(3,4)=H(5,1)
 H(5,3)=-.015625D00*R*R*(1.333333333333333D00+2.666666666666667D00*
 XRINV-.666666666666667D00*R)*EXRH
 H(6,2)=H(5,3)
 H(3,5)=H(5,3)
 H(2,6)=H(5,3)

THE MATRIX NE IS CALCULATED.

DO 40 I=1,6
 NE(I,1)=-N(I,1)*.5D00
 NE(I,2)=-N(I,2)*.125D00
 NE(I,3)=-N(I,3)*.125D00
 NE(I,4)=-N(I,4)*.5D00
 NE(I,5)=-N(I,5)*.125D00
 40 NE(I,6)=-N(I,6)*.125D00

NOW THE TOTAL MATRIX H IS CALCULATED.

DO 37 I=1,3
 DO 37 J=4,6
 H(I,J)=H(I,J)*PP*PHP
 37 H(J,I)=H(J,I)*PN*PHN

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```

TRM=.471304520791033D00*R*EXR*EXRH
PDHR(1,2)=PINEG*TRM
PDHR(4,5)=PDHR(1,2)
PDHR(2,1)=PHPOS*TRM
PDHR(5,4)=PDHR(2,1)
TRM=-.104756560175784D00*(14.222222222222D00*RINV**3*(-1.D00+EXR*
XEXRH)+(RINV*(16.D00+RINV*21.333333333333D00)+9.D00+4.5D00*R)*EXR*
XEXRH)
PDHR(1,3)=PINEG*TRM
PDHR(4,6)=PDHR(1,3)
PDHR(3,1)=PHPOS*TRM
PDHR(6,4)=PDHR(3,1)
PDHR(2,3)=-6.D00*RINV**3+((3.D00+(6.D00+6.D00*RINV)*RINV)*RINV+
X.875D00+.375D00*R+.125D00*R*R)*EXR
PDHR(3,2)=PDHR(2,3)
PDHR(5,6)=PDHR(2,3)
PDHR(6,5)=PDHR(2,3)

```

THE CROSS-CHANNEL ELEMENTS ARE AS FOLLOWS:

```

PDHR(1,4)=R*EXR
PDHR(4,1)=PDHR(1,4)
PDHR(2,5)=-.208333333333333D-01*(-7.D00+2.5D00*R-.25D00*R*R)*EXRH*
XR
PDHR(5,2)=PDHR(2,5)
PDHR(3,6)=-.625D-01*(1.D00+R*(.5D00-R*.083333333333333D00))*EXRH*R
PDHR(6,3)=PDHR(3,6)
TRM=-.8380524813D00*EXRH*R*(.5625D00+(-3.75D00+(5.D00+10.D00*RINV)
X*RINV)*RINV-((10.D00+10.D00*RINV)*RINV)*RINV*EXRH)
PDHR(1,5)=PINEG*TRM
PDHR(4,2)=PDHR(1,5)
PDHR(2,4)=-PHPOS*.8380524813D00*EXRH*((1.5D00-(7.D00+14.D00*RINV)
X*RINV)*RINV+(3.75D00+(14.D00+14.D00*RINV)*RINV)*RINV*EXRH)*R
PDHR(5,1)=PDHR(2,4)
TRM=-.8380524813D00*EXRH*(-.5625D00+(2.625D00-(2.D00+(8.D00+16.D00
X*RINV)*RINV)*RINV)*RINV+8.D00*((1.D00+(2.D00+2.D00*RINV)*RINV)*
XRINV)*RINV*EXRH)*R
PDHR(1,6)=PINEG*TRM
PDHR(4,3)=PDHR(1,6)
PDHR(3,4)=-PHPOS*.8380524813D00*EXRH*((-1.5D00+(4.D00+(16.D00+
X32.D00*RINV)*RINV)*RINV)*RINV-(3.D00+(16.D00+(32.D00+32.D00*RINV)*
XRINV)*RINV)*RINV*EXRH)*R
PDHR(6,1)=PDHR(3,4)
PDHR(2,6)=R*EXRH*.520833333333333D-02*(-4.D00-8.D00*RINV+8.D00*R-R
X*R)
PDHR(5,3)=PDHR(2,6)
PDHR(3,5)=PDHR(2,6)
PDHR(6,2)=PDHR(2,6)
DO 82 I=1,3
DO 82 J=4,6

```

```

      PDHR(I,J)=PDHR(I,J)*PP*PHP
82 PDHR(J,I)=PDHR(J,I)*PN*PIN
      DO 33 I=1,3
      DO 33 J=4,6
      PDHR(I,J)=PDHR(I,J)+IMAG*VAR*H(I,J)
83 PDHR(J,I)=PDHR(J,I)-IMAG*VAR*H(J,I)
      DO 35 I=1,6
      RESULT(I,1)=-.5D00*PDNR(I,1)
      RESULT(I,2)=-.125D00*PDNR(I,2)
      RESULT(I,3)=-.125D00*PDNR(I,3)
      RESULT(I,4)=-.5D00*PDNR(I,4)
      RESULT(I,5)=-.125D00*PDNR(I,5)
85 RESULT(I,6)=-.125D00*PDNR(I,6)
      DO 90 I=1,6
      DO 90 J=1,6
90 PDHR(I,J)=PDHR(I,J)-N(I,J)*RINV*RINV+PDNR(I,J)*RINV+RESULT(I,J)

```

C

```

      CALL CDGMPD(H,PDER,VECT,NDIM,NDIM,ONE)
      CALL CDGMPD(BT,VECT,PDER,ONE,NDIM,ONE)
      CALL CDGMPD(PDHR,B,VECT,NDIM,NDIM,ONE)
      CALL CDGMPD(BT,VECT,RES,ONE,NDIM,ONE)
      PDLR=RES+PDER+DCONJG(PDER)
      ARG=PDER

```

C

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ARG IS THE PARTIAL DERIVATIVE OF THE INTERNAL ENERGY WITH
RESPECT TO R.

```

      RETURN
      END

```

SUBROUTINE READ(DELTAT,NOTRY,TIME,NWRIT,NTEST,JN2,BO,TND,TOOLRG,
XTOOSH)

C

C

C

C

THIS SUBROUTINE READS THE INITIAL DATA FROM DISK AND CARDS
TO START THE CALCULATION.

```

      IMPLICIT REAL*8(A-H,O-Z)
      COMPLEX*16 A
      REAL*8 ZIP1(36)
      COMMON /AMATRK/A(6,3)
      DATA IREAD,IWRITE/5,6/
      REAL*4 TINTRM,TMACCM,TMINT,TCPU
      LOGICAL*4 NTEST,START/.TRUE./
      COMMON /CORDRP/RX(2,3),RY(2,3),RZ(2,3),PX(2,3),PY(2,3),PZ(2,3),
      XTMAS(2)
      EQUIVALENCE (ZIP1(1),RX(1,1))
      COMMON /RW/NORUM,TMINT,NREAD,TINTRM,TMACCM,TCPU
      IF (START) GO TO 20
10 READ (IREAD,130,END=70) NORUM,NREAD,NWRIT,TND
      READ (NREAD) JN2,NOTRY,NTEST,BO,TIME,DELTAT,TOOLRG,TOOSH
      READ (NREAD) ZIP1

```

```

      READ (NREAD) A
      READ (NREAD,END=30)
      WRITE (IWRITE,90) NREAD
      GO TO 70
20  CALL $TRM(TCPU)
C
C      $TRM STARTS THE CPU TIMER.
C
      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.EQ.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=1,2)
      WRITE (IWRITE,100) (I,A(I,JN),I=1,6)
      RETURN
70  CALL EXIT
      RETURN
80  FORMAT (2G10.0)
90  FORMAT (1H , 'ON READING DATA SET-ENDFILE MISSING',I5)
100 FORMAT (1H , 'B MATRIX'/(I5,2G20.10))
110 FORMAT (1H , 7A4)
120 FORMAT (1H1,28X,'SEMICLASSICAL SCATTERING OF PROTON-HYDROGEN SYSTEM',
      XM'/1H ,31X,'INITIAL TIME INTERVAL USED IN CALCULATION IS',D20.10,
      X' A.U.'////1H ,53X,'INITIAL PARTICLE PARAMETERS'////1H , 'PARTICLE
      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,I5,2X,
      X7D15.8))
130 FORMAT (I10,2I5,D20.10)
      END
      SUBROUTINE WRITE(NOTRY,TIME,JN,DELTAT,E,TK,PIE)
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 ZIP1(38)
      COMMON /CORDRP/RX(2,3),PY(2,3),RZ(2,3),PX(2,3),PY(2,3),PZ(2,3),
      XTMASS(2)
      EQUIVALENCE (ZIP1(1),RX(1,1))
      LOGICAL*4 NTEST
      COMPLEX*16 A,PIE
      COMMON /AMATRX/A(6,3)
      REAL*4 TMTRM,TMACCM,TCPU,TMINT
      DATA IWRITE/6/,NOPART/2/
      COMMON /RW/NORUN,TMINT,MWRT,TMTRM,TMACCM,TCPU
20  TIMN=TIME-DELTAT
      WRITE (IWRITE,70) NOTRY,TIMN,(I,PX(I,JN),PY(I,JN),PZ(I,JN),RX(I,JN),
      X),RY(I,JN),RZ(I,JN),I=1,NOPART)

```



```

R=DSQRT((RX(1,JH)-RX(2,JH))**2+(RY(1,JH)-RY(2,JH))**2+(RZ(1,JH)-
X-RZ(2,JH))**2)

```

```

WRITE(IWRITE,55) R

```

```

DO 30 I=1,6

```

```

VA=CDABS(A(I,JH))**2

```

```

VA IS THE SQUARE OF THE MODULUS OF THE COEFFICIENTS.

```

```

30 WRITE (IWRITE,60) I,A(I,JH),VA

```

```

WRITE (IWRITE,90) PIE,TK,E

```

```

IF (NOTRY.GE.NORUN) GO TO 40

```

```

RETURN

```

```

ENTRY WRTEK(NOTRY,TIME,NTEST,JH2,JH,EO,DELTAT,E,TK,PIE,TOOLRG,
XTOOSM,*)

```

```

IF (NOTRY.GE.NORUN) GO TO 20

```

```

40 T=TCPU

```

```

CALL $TPTM(T)

```

```

IF ((TTERM-T).LT.1.0) CALL EXIT

```

```

WRITE (NWRT) JH2,NOTRY,NTEST,EO,TIME,DELTAT,TOOLRG,TCOSM

```

```

WRITE (NWRT) ZIP1

```

```

WRITE (NWRT) A

```

```

END FILE NWRT

```

```

WRITE(IWRITE,100)

```

```

IF (NOTRY.LT.NORUN) GO TO 50

```

```

WRITE (IWRITE,80)

```

```

RETURN 1

```

```

50 REWIND NWRT

```

```

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 ,I5,3X,2G20.10,4X,G20.10)

```

```

70 FORMAT (1H0,'RUN NUMBER',I10,' AT T= ',D20.13,' A.U./1H , 'OBJECT
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,'*',(1H
X ,2X,I2,2X,6(1X,D20.13)))

```

```

80 FORMAT (1H0,'THIS RUN FINISHED .')

```

```

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

```

```

100 FORMAT(1H , 'THE FOLLOWING DATA SET WRITTEN ON DISK')

```

```

END

```

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