ENERGY TRANSFER IN MOLECULAR COLLISIONS

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Merle Eugene Riley

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ABSTRACT

Two general, numerically exact, quantum mechanical methods have been developed for the calculation of energy transfer in molecular collisions. The methods do not treat electronic transitions because of the exchange symmetry of the electrons. All interactions between the atoms in the system are written as potential energies.

The first method is a matrix generalization of the invariant imbedding procedure,[17, 20] adapted for multi-channel collision processes. The second method is based on a direct integration of the matrix Schrödinger equation, with a re-orthogonalization transform applied during the integration.

Both methods have been applied to a collinear collision model for two diatoms, interacting via a repulsive exponential potential. Two major studies were performed. The first was to determine the energy dependence of the transition probabilities for an H_2 on H_2 model system. Transitions are possible between translational energy and vibrational energy, and from vibrational modes of one H_2 to the other H_2. The second study was to determine the variation of vibrational energy transfer probability with differences in natural frequency of two diatoms similar to N_2.

Comparisons were made to previous approximate analytical solutions of this same problem. For translational to vibrational energy transfer, the previous approximations were not adequate. For vibrational to vibrational energy transfer of one vibrational quantum, the approximations were quite good.

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1. INTRODUCTION

1.1 Background

Theoretical studies in the natural sciences are aimed at an understanding of the physical world, but in many cases the problems are unsolvable because of unknown laws of physical behavior, or because of mathematical complexity alone. For the latter instances, one might try two approaches: to do an approximate treatment of a real physical system, or to do an exact treatment of a simpler model system which has some important features in common with the real one. The former approach frequently contains errors which are difficult to estimate or bound; one may become lost in trying to attribute significance to the results. The model problem may bear little resemblance to the real one, or may contain only one of several crucial features.

In this work, we have developed and applied two theoretical quantum mechanical methods to the problem of energy transfer between various modes of molecular motion during collision processes. We do not handle chemical reactions in the normal sense, nor deal with non-adiabatic electronic motion. The concept of a model enters our discussion because we present calculations for collinear collision processes. The methods we use are perfectly general for three-dimensional problems, but the computational time is prohibitive. It is our belief that an accurate treatment of a collinear model is of more worth than an approximate result for the real three-dimensional problem. This is not to say that the real problem is not under investigation and calculation by our methods; it is indeed.

Early theoretical studies of vibrational, rotational, and translational energy transfer in collisions were based on approximate analytical solutions to the quantum mechanical and classical equations of motion. The method of Zener,[1] later to become known as the distorted wave method, and the Born approximation are leading examples of approximate solutions to quantum mechanical collision problems based on first order perturbation theory. A very comprehensive survey of nearly all of the theoretical work on atom-diatom and diatom-diatom scattering prior to 1965 may be found in Takayanagi's reviews.[2,3] Macroscopic phenomena and experimental data in the area are discussed in Herzfeld and Litovitz.[4]

Before entering into the development of our theoretical methods and the results of calculations, we present an outline of formal scattering theory. The reason is two-fold: to state some important distinctions between quantum mechanics and classical mechanics in an understandable fashion, and to display some of the subtle mathematics necessary for the treatment of a relatively simple physical process.

1.2 Quantum Scattering Theory

1.2.1 The scattering process

The classical picture of the scattering process is intuitively simple. One projects a beam of particles with uniform cross sectional density and flux at a target consisting of particles of such low density that they do not interact with each other nor cause significant multiple scattering. Detectors measure the various numbers of particles and states emanating from the collision region. If all of the target lies within the beam, then the flux per unit solid angle of a species $\underset{\sim}{\alpha}'$ coming from the collision region, divided by the incident flux per unit area of species $\underset{\sim}{\alpha}$, and by the number of target particles, defines the laboratory differential cross section for the species $\underset{\sim}{\alpha}'$, $\sigma_{\underset{\sim}{\alpha}\underset{\sim}{\alpha}'}(\theta, \varphi)$. $\underset{\sim}{\alpha}$ and $\underset{\sim}{\alpha}'$ are written as vectors since they may contain several parameters: type of particle, momentum, internal states, etc.

Quantum mechanical scattering is just as simple in principle as classical scattering. The previous paragraph applies to either picture. However, the mathematical treatment of quantum scattering theory is very involved. The book by Goldberger and Watson[5] is a recommended text for the rigorous development of the theory, especially chapters 3, 4, 5, and 11. The papers of Faddeev[6, 7] are also necessary, along with some references contained therein. Perhaps it is of worth to mention that we use scattering theory in a contrary way. The raison d'etre of scattering theory is to understand the interactions and mechanisms involved in fundamental processes; however, we are ascribed the problem of calculating the results of scattering experiments, given the total Hamiltonian of the interacting systems.

1.2.2 Postulates of quantum mechanics

In effect, all physics is defined by measurements. If we have a machine that produces a definite physical state, that state is defined by the production process. Other machines measure certain physical properties, that is, they detect physical states. Consider three machines A, B, and C. A produces a set of states, labeled a_i, at time t_1; C detects states (which might be the same ones that A produces), labeled c_k, at time t_3. We define $Pc_k t_3, a_i t_1$ to be the probability that a_i prepared at t_1 is in state c_k at t_3. If machine C is "complete", then $\sum_k Pc_k t_3, a_i t_1 = 1$. If C does measure the same states that A produces, it is obvious from physical continuity that

$$\lim_{t_3 \to t_1} P c_k t_3, a_i t_1 \to \delta_{ik}$$

since c_i is equal to a_i. Suppose that at some intermediate time t_2 between t_1 and t_3 we use machine B to measure states produced by A. We label the states which B measures b_j, and we assume they are complete. Once B has detected a state b_j at t_2, we know that the state exists, and hence that it has been produced. We might have observed from the beginning that state preparation and detection are the same process. In classical mechanics, the three measurement procedures we have described obey the following law:

$$\sum_{b_j} P c_k t_3, b_j t_2 \, P b_j t_2, a_i t_1 = P c_k t_3, a_i t_1 \qquad 1\text{-}1$$

because the intermediate knowledge gained from the B measurements does not affect the development of the states prepared by A. Quantum mechanics does not assume 1-1 is true; rather, the concept of amplitude $\langle c_k, t_3 | a_i, t_1 \rangle$ is introduced, so that the probability of an event is related to the modulus of that amplitude:

$$P c_k t_3, \ a_i t_1 = |\langle c_k, t_3 | a_i, t_1 \rangle|^2 . \qquad 1\text{-}2$$

A postulate of quantum mechanics is that

$$\sum_{b_j} \langle c_k, t_3 | b_j, t_2 \rangle \langle b_j, t_2 | a_i, t_1 \rangle = \langle c_k, t_3 | a_i, t_1 \rangle \qquad 1\text{-}3$$

replaces 1-1 as the addition law for states. Suppose that we calculate a set of amplitudes $\langle c_k, t_3 | b_j, t_2 \rangle$, $\langle b_j, t_2 | a_i, t_1 \rangle$, $\langle c_k, t_3 | a_i, t_1 \rangle$ from some law of motion. If these satisfy 1-2 and 1-3, as they must, then any change in phase of the form,

$$\langle b_j, t_2 | a_i, t_1 \rangle \rightarrow e^{-i\beta_j(t_2)} \langle b_j, t_2 | a_i, t_1 \rangle e^{i\alpha_i(t_1)} \qquad 1\text{-}4$$

also satisfies 1-2 and 1-3. In order to make amplitudes unique, certain conventions concerning these phases must be adopted.[8] Having adopted such conventions, nearly all of which are related to invariance laws and transformations on the physical system, we are prepared to discuss the time dependent Schrödinger equation, which is the law of motion for quantum systems. We set out to develop a scheme for the calculation of the quantities measured in scattering experiments, that is, differential cross sections. The following parallels in essence chapter 5 of Goldberger and Watson.[5]

1.2.3 Quantum equations of motion for scattering

Our scattering system has a total Hamiltonian H, independent of time. In the remote past before the collision occurs, certain parts of H associated to the interaction V between incident and target particles are negligibly small because of the large distance between these particles. This affects a separation of H into $K_c + V_c$, where we use the label c to refer to possible different separations, called arrangement channels.[9] For example, the three-body system A, B, and C can be separated into (A, B) + C, (A, C) + B, and (B, C) + A, where (,) denotes a bound state of that pair with the remaining particle very far away. The Schrödinger equation is:

$$i\hbar \frac{\partial \Psi^{WP}_{c,a}(t)}{\partial t} = H \Psi^{WP}_{c,a}(t) \qquad 1\text{-}5$$

where $\Psi^{WP}_{c,a}(t)$ is a state vector $|c, a, t\rangle$ that coincided in the remote past with a prepared state wave packet (WP) $\Phi^{WP}_{c,a}(t)$:

$$\Psi^{WP}_{c,a}(t) \underset{t \to -\infty}{=} \Phi^{WP}_{c,a}(t) \ . \qquad 1\text{-}6$$

Let us use α to denote both of the labels c and a for prepared states. Analogously, we use β for the combined detected state labels, c' and a'. The prepared state is a narrow wave packet superposition of energy eigenstates of K_c:

$$\Phi_\alpha^{WP}(t) = \sum_a A_a \chi_\alpha e^{-iE_\alpha t/\hbar} \qquad 1\text{-}7$$

where

$$i\hbar \frac{\partial(\chi_\alpha e^{-iE_\alpha t/\hbar})}{\partial t} = E_\alpha(\chi_\alpha e^{iE_\alpha t/\hbar})$$

$$1\text{-}8$$

$$K_c \chi_\alpha = E_\alpha \chi_\alpha \; .$$

It is customary to refer to the different internal states of an arrangement channel as channels. Thus, $\chi_\alpha \equiv \chi_{c,a}$ has both arrangement channel and channel labels. The χ_α have infinite norms - they are plane wave states. They have orthonormal properties within the same arrangement channel, but not in general:

$$\langle \chi_{\alpha'} | \chi_\alpha \rangle = \delta(a, a') \qquad \text{for } c = c' \qquad 1\text{-}9$$

$$\langle \chi_{\alpha'} | \chi_\alpha \rangle \neq \delta(a, a') \qquad \text{for } c \neq c' \; . \qquad 1\text{-}10$$

We use either the large box normalization or the delta function process for the translational coordinates of the χ_α. If $\Phi_\alpha^{WP}(t)$ is normed to 1 (it is square integrable), $\Psi_\alpha^{WP}(t)$ is normed to 1 for all time since $\langle \Psi_\alpha^{WP}(t) | \Psi_\alpha^{WP}(t) \rangle$ is independent of time. The probability of detecting a state $| \beta, t_1 \rangle$ after the collision has occurred is just:

$$P_{\alpha\beta}(t_1) = |\langle \Phi_\beta^{WP}(t) \,|\, \Psi_\alpha^{WP}(t_1)\rangle|^2 \qquad 1\text{-}11$$

where t_1 is in the remote future, $\Phi_\beta^{WP}(t)$ is a wave packet superposition of eigenstates of $K_{c'}$. Expression 1-11 is almost useless, for the simple reason of transient wave packet behavior. The probability is a strong function of the relative positions of the maximum density of $\Phi_\beta^{WP}(t)$ and the same for the outgoing scattered part of $\Psi_\alpha^{WP}(t)$. If they are out of phase, there is no contribution to the integral in 1-11. A solution is to sum 1-11 over all phases of final state detection, effectively:

$$P_{\alpha\beta} = |\sum_{t_2} \langle \Phi_\beta^{WP}(t_1 - t_2) | \Psi_\alpha^{WP}(t_1)\rangle|^2 \qquad 1\text{-}12$$

for $\quad t_1 \to \infty$

and $\quad t_1 - t_2 >> 0$

assuming that the collision occurs about $t = 0$. It is reasonable that we should work with time-dependent quantities, since the scattering process as described in 1.2.1 is not time-dependent, nor is the differential cross section. We seek to develop a time-independent formalism for the calculation of cross sections.

1. 2. 4 Development of time-independent expressions for the wave function

The direct approach to the removal of time from expressions such as 1-11 would be to relax the wave packet form of $\Phi_\alpha^{WP}(t)$ so that the symbolic solution for $\Psi_\alpha^{WP}(t)$:

$$\Psi_\alpha^{WP}(t) = e^{-iH(t-\tau)/\hbar}\,\Phi_\alpha^{WP}(\tau) \qquad 1\text{-}13$$

(where $e^{-iH(t-\tau)/\hbar}$ is the evolution operator, defined by the power series expansion of the exponential) is properly defined for $\Phi_\alpha^{WP}(\tau)$ being replaced by $\chi_\alpha e^{-iE_\alpha\tau/\hbar}$:

$$\Psi_\alpha(t) = e^{-iH(t-\tau)/\hbar}\,\chi_\alpha e^{-iE_\alpha\tau/\hbar} \; . \qquad 1\text{-}14$$

Because of the non-square integrable nature of $\chi_\alpha e^{-iE_\alpha\tau/\hbar}$, this equation is not a valid relation.[10] Instead of removing "WP" from 1-13 immediately, let us suppose that $\Psi_\alpha^{WP}(t)$ has evolved from a superposition of channel states prepared at different past times τ_i:[11]

$$\Psi_\alpha^{WP}(t) = e^{-iHt/\hbar}\sum_i A_i e^{iH\tau_i/\hbar}\,\Phi_\alpha^{WP}(\tau_i) \; . \qquad 1\text{-}15$$

Taking a continuous distribution of these times, we have:

$$\Psi_{\alpha}^{WP}(t) = \int_{-\infty}^{0} d\tau \; A(\tau)\, e^{-iH(t-\tau)/\hbar} \; \Phi_{\alpha}^{WP}(\tau) \quad . \qquad 1\text{-}16$$

$A(\tau)$ is chosen to be the weighting function $\eta e^{\eta\tau}$,[11] so $\int_{-\infty}^{0} d\tau \, \eta e^{\eta\tau} = 1$ for any positive, non-zero η. Our new solution is a function of the η parameter:

$$\Psi_{\alpha}^{WP(\eta)}(t) = \int_{-\infty}^{0} d\tau \, \eta e^{\eta\tau} \; e^{-iH(t-\tau)/\hbar} \; \Phi_{\alpha}^{WP}(\tau) \; . \qquad 1\text{-}17$$

Now, if we remove the wave packet form of each $\Phi_{\alpha}^{WP}(\tau)$, replacing them with $\chi_{\alpha} e^{-iE_{\alpha}\tau/\hbar}$, we find:

$$\Psi_{\alpha}^{(\eta)}(t) = \int_{-\infty}^{0} d\tau \, \eta e^{\eta\tau} \, e^{-iHt/\hbar} \; e^{iH\tau/\hbar} \; \chi_{\alpha} e^{-iE_{\alpha}\tau/\hbar} \qquad 1\text{-}18$$

can be symbolically integrated in τ:

$$\Psi_{\alpha}^{(\eta)}(t) = e^{-iHt/\hbar} \; \frac{-i\eta}{(H - E_{\alpha})1/\hbar \; - \; i\eta} \; \chi_{\alpha} \quad . \qquad 1\text{-}19$$

Define $\psi_{\alpha}^{(\eta)} = e^{iHt/\hbar} \; \Psi_{\alpha}^{(\eta)}(t)$, so $\psi_{\alpha}^{(\eta)} = \Psi_{\alpha}^{(\eta)}(0)$. From 1-19 we have

$$\psi_{\alpha}^{(\eta)} = \frac{-i\eta}{(H - E_{\alpha})/\hbar \; - \; i\eta} \; \chi_{\alpha} \quad . \qquad 1\text{-}20$$

The important result is that we have a well defined equation (1-20) for any non-zero η, without the necessity of writing the prepared state as a wave packet. The solution of 1-20 is $\Psi_\alpha^{(\eta)}(0)$, from which we could construct $\Psi_\alpha^{(\eta)}(t) = e^{-iHt/\hbar}\psi_\alpha^{(\eta)}(0)$; however, this latter time evolution away from $t = 0$ is not needed, as we will later discuss.

Rewriting 1-20:

$$-i\eta\,\chi_\alpha = ((H - E_\alpha)/\hbar - i\eta)\psi_\alpha^{(\eta)} \tag{1-21}$$

or $$\psi_\alpha^{(\eta)} = \chi_\alpha + \frac{(H - E_\alpha)/\hbar}{i\eta}\,\psi_\alpha^{(\eta)} \tag{1-22}$$

and substituting 1-20 into the RHS of 1-22,

$$\psi_\alpha^{(\eta)} = \chi_\alpha + \frac{(H-E_\alpha)/\hbar}{i\eta}\,\frac{-i\eta}{(H-E_\alpha)/\hbar - i\eta}\,\chi_\alpha \tag{1-23}$$

or, $$\psi_\alpha^{(\eta)} = \chi_\alpha + \frac{1/\hbar}{(E_\alpha - H)/\hbar + i\eta}\,V_c\,\chi_\alpha \tag{1-24}$$

using the fact that $(H - E_\alpha)\chi_\alpha = (H - K_c)\chi_\alpha = V_c\,\chi_\alpha$. From 1-20, we can use the operator identity, $A^{-1} - B^{-1} \equiv A^{-1}(B - A)B^{-1}$, with $A = (H - E_\alpha)/\hbar - i\eta$ and $B = (K' - E_\alpha)/\hbar - i\eta$ and obtain the equation:

$$\psi_\alpha^{(\eta)} = \frac{i\eta}{(E_\alpha - K')/\hbar + i\eta}\chi_\alpha + \frac{1}{(E_\alpha - K')/\hbar + i\eta}(H - K')/\hbar\,\psi_\alpha^{(\eta)}. \qquad 1\text{-}25$$

If $K' = K_c$, $\frac{i\eta}{(E_\alpha - K_c)/\hbar + i\eta}\chi_\alpha = \frac{i\eta}{i\eta}\chi_\alpha = \chi_\alpha$, and we have:

$$\psi_\alpha^{(\eta)} = \chi_\alpha + \frac{1/\hbar}{(E_\alpha - K_c)/\hbar + i\eta} V_c\,\psi_\alpha^{(\eta)}. \qquad 1\text{-}26$$

Thus far, all of our time-independent solutions depend on the parameter η. From 1-21, we take the limit $\eta \to 0$:

$$0 = (H - E_\alpha)/\hbar\;\psi_\alpha^{(0)} \qquad 1\text{-}27$$

and see that $\psi_\alpha^{(0)}$ is a solution to the time-independent Schrödinger equation. Thus, we have arrived at a defining formula for the solution in terms of the plane wave incident state:

$$\psi_\alpha^{(0)} = \lim_{\eta \to 0}\left(\frac{-i\eta}{(H - E_\alpha)/\hbar - i\eta}\right)\chi_\alpha\;. \qquad 1\text{-}28$$

All of equations 1-20 through 1-26 could now be written in terms of $\psi_\alpha^{(0)}$ and a limiting $\eta \to 0$ symbol on the operators alone. Now we develop the interpretation of cross sections from the time-independent solutions.

1.2.5 Cross sections, transition rates, and probability

Our original statement regarding cross sections in 1.2.1 is formulated:

$$\sigma_{\underset{\sim}{\alpha}\underset{\sim}{\alpha}'}(\theta,\varphi) = \frac{F_{\underset{\sim}{\alpha}'}}{F_{\underset{\sim}{\alpha}}\, n} \qquad \text{1-29}$$

where $F_{\underset{\sim}{\alpha}'}$ is the detected flux per solid angle of species $\underset{\sim}{\alpha}'$, $F_{\underset{\sim}{\alpha}}$ is the incident flux of $\underset{\sim}{\alpha}$ per unit area normal to beam, and n is the number of target particles. We now re-interpret $F_{\underset{\sim}{\alpha}'}/n$ as the transition rate per target particle into final state $\underset{\sim}{\alpha}'$ and angle θ,φ. The angles θ and φ are hereafter included in the final state label $\underset{\sim}{\alpha}'$. The incident flux is the incident beam velocity multiplied by the beam density, or equivalently, the incident velocity divided by the volume per incident particle. For a single scattering event, the transition rate is the time derivative of the detection probability, which we now examine.

Previously, we wrote down the probability of detection using conventional wave packet states (1-11 and 1-12) and noted the resulting problem of transients. Our equation 1-12 is closely connected to the "beam feeder" state, 1-18, of Gell-Mann and Goldberger, which is also designed to remove transients.[11] Using 1-18 for the time-dependent solution evolved from initial state α, we have the probability, depending parametrically on η, of detecting state β:

$$P_{\alpha\beta}^{(\eta)}(t) = |f_{\alpha\beta}^{(\eta)}(t)|^2/N_{\alpha}^{(\eta)} \qquad \text{1-30}$$

where,

$$f_{\alpha\beta}^{(\eta)}(t) = \langle \chi_\beta e^{-iE_\beta t/\hbar} | \Psi_\alpha^{(\eta)}(t) \rangle \qquad 1\text{-}31$$

$$N_\alpha^{(\eta)} = \langle \Psi_\alpha^{(\eta)}(t) | \Psi_\alpha^{(\eta)}(t) \rangle \ . \qquad 1\text{-}32$$

The hermiticity of H insures that $N_\alpha^{(\eta)}$ does not depend on time. Since the prepared state depends on η, the $P_{\alpha\beta}^{(\eta)}(t)$ dependence on η is not unphysical. Having established a relation of cross sections to transition rates via time rate of change of probability, we cannot immediately take the $\eta \to 0$ limit of $P_{\alpha\beta}^{(\eta)}(t)$, for we see:

$$f_{\alpha\beta}^{(0)}(t) = \langle \chi_\beta e^{-iE_\beta t/\hbar} | e^{-iHt/\hbar} \psi_\alpha^{(0)} \rangle \qquad 1\text{-}33$$

using 1-27,

$$f_{\alpha\beta}^{(0)} = \langle \chi_\beta | \psi_\alpha^{(0)} \rangle \, e^{i(E_\beta - E_\alpha)t/\hbar} \qquad 1\text{-}34$$

and, therefore, $P_{\alpha\beta}^{(0)}(t)$ does not depend on time. We compute the transition rate before taking the $\eta \to 0$ limit, and find a meaningful answer. It so happens that we will only need the transition rate at $t = 0$, the collision time. From 1-30,

$$\dot{P}_{\alpha\beta}^{(\eta)}(0) = \frac{1}{N_\alpha^{(\eta)}} \, 2\mathrm{Re} \left\{ [f_{\alpha\beta}^{(\eta)}(0)]^* \, \dot{f}_{\alpha\beta}^{(\eta)}(0) \right\} \qquad 1\text{-}35$$

where the dot symbol denotes the time derivative. We evaluate $\dot{f}^{(\eta)}_{\alpha\beta}(0)$ from 1-31:

$$\dot{f}^{(\eta)}_{\alpha\beta}(0) = \frac{d}{dt} \langle \chi_\beta e^{-iE_\beta t/\hbar} \,|\, e^{-iHt/\hbar} \psi^{(\eta)}_\alpha \rangle_{t=0} \qquad 1\text{-}36$$

which will simplify to:

$$\dot{f}^{(\eta)}_{\alpha\beta}(0) = \frac{-i}{\hbar} \langle (H - E_\beta)\chi_\beta \,|\, \psi^{(\eta)}_\alpha \rangle$$

$$= \frac{-i}{\hbar} \langle \chi_\beta \,|\, V_{c'} \psi^{(\eta)}_\alpha \rangle \ . \qquad 1\text{-}37$$

The last expression serves as a definition for a transition matrix:

$$\mathcal{T}^{(\eta)}_{c,a;c',a'} = \frac{1}{\hbar} \langle \chi_{c',a'} \,|\, V_{c'} \psi^{(\eta)}_{c,a} \rangle \qquad 1\text{-}38$$

which will later appear in a reduced form in the connection of cross sections with properties of time-independent wave functions. From 1-31 again; using the equality of $\Psi^{(\eta)}_\alpha(0)$ and $\psi^{(\eta)}_\alpha$:

$$f^{(\eta)}_{\alpha\beta}(0) = \langle \chi_\beta \,|\, \psi^{(\eta)}_\alpha \rangle \ . \qquad 1\text{-}39$$

Replacing $\psi^{(\eta)}_\alpha$ with its equivalent defined in 1-25 (with $K' = K_{c'}$, $H = K_{c'} + V_{c'}$):

$$f^{(\eta)}_{\alpha\beta}(0) = \frac{i\eta}{(E_\alpha - E_\beta)/\hbar + i\eta}\langle\chi_\beta|\chi_\alpha\rangle + \frac{1/\hbar}{(E_\alpha - E_\beta)/\hbar + i\eta}\langle\chi_\beta|V_c, \psi^{(\eta)}_\alpha\rangle. \qquad 1\text{-}40$$

Physically, we know that $E_\beta = E_\alpha$ because of energy conservation; this would tend to indicate that the last term in 1-40 is singular as $\eta \to 0$. However, we always retain detected and prepared energies as independent variables for mathematical convenience. Combining 1-35, 1-37, 1-38, and 1-40, we have:

$$\dot{P}^{(\eta)}_{\alpha\beta}(0) = \frac{1}{N^{(\eta)}_\alpha}\, 2\mathrm{Re}\left\{\frac{-\eta}{(E_\alpha - E_\beta)/\hbar - i\eta}\langle\chi_\beta|\chi_\alpha\rangle^{*}\, \mathcal{T}^{(\eta)}_{\alpha\beta} - i\,\frac{|\mathcal{T}^{(\eta)}_{\alpha\beta}|^2}{(E_\alpha - E_\beta)/\hbar - i\eta}\right\}. \qquad 1\text{-}41$$

Letting $A_{\alpha\beta} = \langle\chi_\beta|\chi_\alpha\rangle\, \mathcal{T}^{(\eta)}_{\alpha\beta}$, we have:

$$N^{(\eta)}_\alpha\, \dot{P}^{(\eta)}_{\alpha\beta}(0) = \frac{-\eta}{(E_\alpha - E_\beta)^2/\hbar^2 + \eta^2}\left[(E_\alpha - E_\beta)/\hbar\,(A_{\alpha\beta} + A^{*}_{\alpha\beta}) + i\eta(A_{\alpha\beta} - A^{*}_{\alpha\beta})\right]$$

$$+ \frac{2\eta}{(E_\alpha - E_\beta)^2/\hbar^2 + \eta^2}\,|\mathcal{T}^{(\eta)}_{\alpha\beta}|^2 . \qquad 1\text{-}42$$

Here it is mathematically convenient to integrate over a narrow band of detected state energies, knowing that any detector will accept a range of final state kinetic energies. This allows the use of the limiting definition of the delta function:[12]

$$\lim_{\eta \to 0} \int_{E_\alpha - \Delta_1}^{E_\alpha + \Delta_2} dE_\beta\, \frac{\eta\, g(E_\beta)}{(E_\alpha - E_\beta)^2/\hbar^2 + \eta^2} = \pi\hbar\, g(E_\alpha) \qquad 1\text{-}43$$

for any continuous function $g(E_\beta)$ and Δ_1, Δ_2 positive reals. Representing the narrow band sum by $\sum_{a'}$, we can show that:

$$\lim_{\eta \to 0} N_\alpha^{(\eta)} \sum_{a'} \dot{P}_{\alpha\beta}^{(\eta)}(0) = N_\alpha^{(0)} \sum_{a'} \dot{P}_{\alpha\beta}^{(0)}(0)$$

$$= \lim_{\eta \to 0} \sum_{a'} \frac{2\pi}{\hbar} \delta(E_\alpha - E_\beta) |\mathcal{T}_{\alpha\beta}^{(\eta)}|^2 \quad . \tag{1-44}$$

Since, under the $\lim_{\eta \to 0}$ symbol and the sum $\sum_{a'}$, the first term in the RHS of 1-42 vanishes. The delta function indicates that the only physically observed transitions are those in which $E_\beta = E_\alpha$.

The relation between η and the physical properties of the system have not been discussed. $1/\eta$ is the effective duration in time of the prepared wave "train".[13] Consequently, the box normalization volume V must be large enough to contain the wave train throughout the scattering process. That is:[13]

$$V^{1/3}/v \gg 1/\eta \tag{1-45}$$

where v is the velocity of the incident beam. Taking the $\eta \to 0$ limit in $\mathcal{T}_{\alpha\beta}^{(\eta)}$ must allow for $V \to \infty$, and it is necessary to remove any normalization volume dependence. We investigate this now. Consider the case of two particles in either initial or final state; the un-normalized plane waves are $\underline{\chi}_\alpha$, whose integral over a volume V is proportional to V^2:

$$\langle \underline{\chi}_\alpha | \underline{\chi}_\alpha \rangle_V \sim V^2 \ . \qquad \text{1-46}$$

This implies that the box normalized solutions χ_α are inversely proportional to V:

$$\chi_\alpha \sim 1/V \qquad \text{1-47}$$

because $\langle \chi_\alpha | \chi_\alpha \rangle_V = 1$.

If we are in the barycentric subspace, there is no center-of-mass motion of the pair, leaving one integration for two particles:

$$\langle \underline{\chi}_\alpha | \underline{\chi}_\alpha \rangle_V \sim V$$

and $\chi_\alpha \sim V^{-1/2}$ 1-48

so that $\langle \chi_\alpha | \chi_\alpha \rangle_V = 1$.

For the case of n free particles in state χ_α, in the barycentric subspace,

$$\chi_\alpha \sim V^{-\frac{n-1}{2}} \ . \qquad \text{1-49}$$

The most general circumstance to concern us here is to have two particles in the prepared state and $n \geq 2$ in the final state. Note that a particle may consist of several bound components. Examining the definition of $\mathcal{T}^{(\eta)}_{\alpha\beta}$, 1-38, we see that the localized nature of $V_{c'}$ makes the integral proportional to the normalization factors in χ_β and $\psi^{(\eta)}_\alpha$, for a sufficiently large box. The normalization of $\psi^{(\eta)}_\alpha$ is seen from 1-26 to be the same as χ_α. Allowing for two particles in χ_α and n in χ_β, we expect:

$$\mathcal{T}^{(\eta)}_{\alpha\beta} \sim \frac{1}{V^{1/2}} \frac{1}{V^{\frac{n-1}{2}}} = V^{-n/2} \;. \qquad \text{1-49}$$

We now define a reduced transition matrix $T^{(\eta)}_{\alpha\beta}$, introducing a Kronecker delta to conserve total momentum. Let the labels $\underset{\sim}{P}_\alpha$ and $\underset{\sim}{P}_\beta$ denote total initial and total final momenta:

$$\mathcal{T}^{(\eta)}_{\alpha\beta} = \frac{(2\pi)^{3n/2}}{V^{n/2}} \, \delta_{\underset{\sim}{P}_\alpha, \underset{\sim}{P}_\beta} \, T^{(\eta)}_{\alpha\beta} \,. \qquad \text{1-50}$$

Introducing 1-50 into 1-44, remembering that the sum over a' is only on final momenta, not internal particle states:

$$N^{(0)}_\alpha \sum_{a'} \dot{P}^{(0)}_{\alpha\beta}(0) = \lim_{\eta \to 0} \sum_{a'} \frac{2\pi}{\hbar} \, \delta(E_\alpha - E_\beta) \, \frac{(2\pi)^{3n}}{V^n}$$

$$\delta_{\underset{\sim}{P}_\alpha \underset{\sim}{P}_\beta} \, | T^{(\eta)}_{\alpha\beta} |^2 \;. \qquad \text{1-51}$$

The sum over momentum states is converted to an integral over the n-1 independent conjugate momenta, $\underset{\sim}{k}_j$, of the n particles in that final state, using the prescription[14]

$$\sum_{a'j} \rightarrow \frac{V}{(2\pi)^3} \int d^3k_i$$

where a'j is the label for momentum $\underset{\sim}{k}_j$. Resulting:

$$N_\alpha^{(0)} \sum_{a'} \dot{P}_{\alpha\beta}^{(0)}(0) = \lim_{\eta \rightarrow 0} \frac{(2\pi)^4}{\hbar V} \int d^3k_1 \cdots d^3k_{n-1}$$

$$\delta(E_\alpha - E_\beta)\, \delta_{\underset{\sim}{P}_\alpha \underset{\sim}{P}_\beta} \, |T_{\alpha\beta}^{(\eta)}|^2 \; . \qquad \text{1-52}$$

Rather than use $\delta_{\underset{\sim}{P}_\alpha \underset{\sim}{P}_\beta}$, we write $\delta^3(\underset{\sim}{P} - \underset{\sim}{P}')$, where $\underset{\sim}{P}$ and $\underset{\sim}{P}'$ are the initial and final total momenta and then we must restore integration over all n final momenta of the n particles. Then 1-52 is written:

$$N_\alpha^{(0)} \sum_{a'} \dot{P}_{\alpha\beta}^{(0)}(0) = \lim_{\eta \rightarrow 0} \frac{(2\pi)^4}{\hbar V} \int d^3k_1 \cdots d^3k_n$$

$$\delta(E_\alpha - E_\beta)\, \delta^3(\underset{\sim}{P} - \underset{\sim}{P}') \, |T_{\alpha\beta}^{(\eta)}|^2 \, . \qquad \text{1-53}$$

Three questions remain concerning the $\eta \rightarrow 0$ limit. The first is answered in that $N_\alpha^{(0)}$ remains as 1 because of the box normalization of χ_α.[14] The second is answered in that $\dot{P}_{\alpha\beta}^{(0)}(0)$ is our needed transition rate. It may be shown[15] that

$\dot{P}^{(\eta)}_{\alpha\beta}(t)$ is accurately given by $\dot{P}^{(\eta)}_{\alpha\beta}(0)$ for $\eta t << 1$. The remaining observation is that $T^{(\eta)}_{\alpha\beta}$ is regular in the double limit $V \to \infty$, $\eta \to 0$ with the condition presented in 1-45.[12] The transition rate, $dT_{\alpha\beta}$, into an element, $\prod_{j=1}^{n} d^3k_j$, of momentum space is found from 1-53 by restricting integrations to a volume element:

$$dT_{\alpha\beta} \equiv \frac{(2\pi)^4}{\hbar V} \delta(E_\alpha - E_\beta)\,\delta^3(\underset{\sim}{P} - \underset{\sim}{P}')\,|T^{(0)}_{\alpha\beta}|^2 \prod_{j=1}^{n} d^3k_j. \qquad 1\text{-}54$$

Dividing this by the incident beam flux will give us the differential cross section. As observed in the text following 1-29, the incident flux is equal to the beam velocity v divided by the volume per particle. The volume per particle is just the normalization volume V by definition. Finally, we have the differential cross section for scattering into the final state β in the element $\prod_{j=1}^{n} d^3k_j$ of momentum space:

$$\sigma_{\alpha\beta} = \frac{(2\pi)^4}{\hbar v} \delta(E_\alpha - E_\beta)\,\delta^3(\underset{\sim}{P} - \underset{\sim}{P}')\,|T^{(0)}_{\alpha\beta}|^2 \left(\prod_{j=1}^{n} d^3k_j\right). \qquad 1\text{-}55$$

Up to this point, we have presented a method by which one could formally solve for the physically observed cross sections from the Schrödinger equation. Since this method is never used in practice, it is more a proof of physical validity than a calculational tool.

1.2.6 In and out states, scattering matrix

Referring back to our time-dependent description of scattering, we assumed that $\Psi_\alpha(t)$ was prepared in an approximate eigenstate of K_c in the past, and at some future time we take the integral $\langle \Phi_\beta(t) \mid \Psi_\alpha(t) \rangle$ to obtain the amplitude $f_{\alpha\beta}(t)$ of detecting state β. We equally well might have asked, why not use the Schrödinger equation of motion and find the state that becomes an approximate eigenstate of $K_{c'}$ (the one detected) and take the amplitude integral in the remote past with the prepared state ? The corresponding treatment for this problem parallels the previous discussion. Note that we are not talking about time-reversal invariance here. We use a minus sign to refer to the new solutions. In the future, we require:

$$\Psi_\beta^{-WP}(t) \underset{t \to \infty}{=} \Phi_\beta^{WP}(t) \qquad (1\text{-}6) \qquad 1\text{-}56$$

where the equation reference in parantheses gives the analogous previous one. Developing a time-independent equation of motion, we use the superposition of channel eigenstates prepared at different future times:

$$\Psi_\beta^{-(\eta)}(t) = \int_0^\infty d\tau\, \eta\, e^{-\eta\tau}\, e^{-iHt/\hbar}\, e^{iH\tau/\hbar}\, \chi_\beta e^{-iE_\beta \tau/\hbar} \qquad 1\text{-}57$$

$$(1\text{-}18)$$

where η is positive real. Letting $\psi_\beta^{-(\eta)} = e^{iHt/\hbar}\, \Psi_\beta^{-(\eta)}(t)$, we do the symbolic integration of 1-57 and obtain:

$$\psi_\beta^{-(\eta)} = \frac{i\eta}{(H - E_\beta)/\hbar + i\eta}\, \chi_\beta \; . \qquad (1\text{-}19) \qquad 1\text{-}58$$

From which one can show:

$$(H - E_\beta)\, \psi_\beta^{-(0)} = 0 \qquad (1\text{-}27) \qquad 1\text{-}59$$

$$\psi_\beta^{-(\eta)} = \chi_\beta + \frac{1/\hbar}{(E_\beta - H)/\hbar - i\eta}\, V_{c'}\, \chi_\beta \qquad (1\text{-}24) \qquad 1\text{-}60$$

$$\psi_\beta^{-(\eta)} = \chi_\beta + \frac{1/\hbar}{(E_\beta - K_{c'})/\hbar - i\eta}\, V_{c'}\, \psi_\beta^{-(\eta)} \quad (1\text{-}26) \qquad 1\text{-}61$$

taking the $\eta \to 0$ limit, we have:

$$\psi_\beta^{-(0)} = \chi_\beta + \lim_{\eta \to 0} \left[\frac{1/\hbar}{(E_\beta - K_{c'})/\hbar - i\eta} \right] V_{c'}\, \psi_\beta^{-(0)} . \qquad 1\text{-}62$$

The sole distinction between these and the previous time-independent solutions is the sign coefficient of η. Let us characterize the previous solutions with a + sign, and write:

$$\psi_\alpha^{\pm(0)} = \chi_\alpha + \lim_{\eta \to 0} \left[\frac{1/\hbar}{(E_\alpha - K_c)/\hbar \pm i\eta} \right] V_c\, \psi_\alpha^{\pm(0)} \qquad 1\text{-}63$$

where α and c denote initial or final state labels. It is customary to refer to + solutions as "out" states and - solutions as "in" states.

Our previous expression, 1-31, for the amplitude of going from α to β can be written:

$$f^{(\eta)}_{\alpha\beta}(t) = \langle e^{iHt/\hbar} \chi_\beta e^{-iE_\beta t/\hbar} \mid \psi^{+(\eta)}_\alpha \rangle . \qquad 1\text{-}65$$

The latter matrix element can be given a meaning if we form a wave packet of the β eigenstates, in particular, we form a superposition of outgoing states detected at different times, as prescribed by 1-57, resulting in a new amplitude:

$$f^{(\eta)(\eta')}_{\alpha\beta} = \langle e^{iHt/\hbar} \Psi^{-(\eta')}_\beta(t) \mid \psi^{+(\eta)}_\alpha \rangle \qquad 1\text{-}66$$

the bra part has been defined as $\psi^{-(\eta')}_\beta$ before, so:

$$f^{(\eta)(\eta')}_{\alpha\beta} = \langle \psi^{-(\eta')}_\beta \mid \psi^{-(\eta)}_\alpha \rangle \qquad 1\text{-}67$$

$f^{(\eta)(\eta')}_{\alpha\beta}$ is thus independent of time. The limiting value of 1-67 defines a new quantity, the scattering matrix or S matrix:

$$\lim_{\substack{\eta \to 0 \\ \eta' \to 0}} f^{(\eta)(\eta')}_{\alpha\beta} = S_{\alpha\beta} = \langle \psi^{-(0)}_\beta \mid \psi^{+(0)}_\alpha \rangle . \qquad 1\text{-}68$$

The unitarity relation for $S_{\alpha\beta}$ may be shown from 1-68, assuming $\psi^{-(0)}_\alpha$ and $\psi^{+(0)}_\beta$ are separately complete sets of states. It may be shown[16] from the defining equations for $\psi^{-(\eta)}_\beta$ and $\psi^{+(\eta)}_\alpha$ that:

$$S_{\alpha\beta} = \delta_{\alpha\beta} - \frac{2\pi i}{\hbar^2}\, \delta(E_\beta - E_\alpha)\, \langle (H - E_\beta)\chi_\beta \mid \psi_\alpha^{+(0)} \rangle$$

$$= \delta_{\alpha\beta} - \frac{2\pi i}{\hbar^2}\, \delta(E_\beta - E_\alpha)\, \langle \psi_\beta^{-(0)} \mid (H - E_\alpha)\chi_\alpha \rangle \,. \qquad \text{1-69}$$

We define:

$$\mathcal{T}^{+}_{\alpha\beta} = \frac{1}{\hbar}\, \langle\, (H - E_\beta)\chi_\beta \mid \psi_\alpha^{+(0)} \,\rangle$$

$$\mathcal{T}^{-}_{\alpha\beta} = \frac{1}{\hbar}\, \langle \psi_\beta^{-(0)} \mid (H - E_\alpha)\chi_\alpha \,\rangle \qquad \text{1-70}$$

and note that $\mathcal{T}^{+}_{\alpha\beta}$ is the $\eta \rightarrow 0$ limit of our previous $\mathcal{T}^{(\eta)}_{\alpha\beta}$ as defined in 1-37 and 1-38. Although $S_{\alpha\beta}$ is zero for $E_\alpha \neq E_\beta$, the $\mathcal{T}^{\pm}_{\alpha\beta}$ matrices have no such restriction.

1.2.7 Uniqueness of time-independent solutions

Even though we had pretended that all of the previous relationships of scattering cross sections to our time-independent equations and the time-dependent Schrödinger equation were unique, there is a possible flaw present. It lies in the development of the time-independent solution. Rewriting 1-26 and 1-61 together:

$$\psi_\alpha^{\pm(\eta)} = \chi_\alpha + \frac{1/\hbar}{(E_\alpha - K_c)/\hbar \pm i\eta}\, V_c\, \psi_\alpha^{\pm(\eta)} . \qquad \text{1-71}$$

Define $G_\alpha(\pm\eta) \equiv \frac{1/\hbar}{(E_\alpha - K_c)/\hbar \pm i\eta}$, this is referred to as the resolvent of the operator $(E_\alpha - K_c) \pm i\eta\hbar$. In a coordinate representation, it is also called the Green's function. The limiting case of 1-71 is

$$\psi_\alpha^{\pm(0)} = \chi_\alpha + \lim_{\eta \to 0} [G_\alpha(\pm\eta)] V_c \psi_\alpha^{\pm(0)}. \qquad 1\text{-}72$$

Suppose we solve 1-71 by the method of successive approximations, better known as a Born expansion or iteration method. This gives the formal solution:

$$\psi_\alpha^{\pm(\eta)} = \sum_{n=0}^{\infty} (G_\alpha(\pm\eta) V_c)^n \chi_\alpha \ . \qquad 1\text{-}73$$

The only other possible solution to 1-71 would occur when there is a solution ${}_0\psi_\alpha^{\pm(\eta)}$ to the homogeneous equation:

$${}_0\psi_\alpha^{\pm(\eta)} = G_\alpha(\pm\eta)\, V_c\, {}_0\psi_\alpha^{\pm(\eta)} \ . \qquad 1\text{-}74$$

This additional solution could be added to $\psi_\alpha^{\pm(\eta)}$, so that $\psi_\alpha^{\pm(\eta)} + {}_0\psi_\alpha^{\pm(\eta)}$ would solve 1-71. However, for finite η there are no solutions to 1-74 acceptable in their physical behavior, as may be seen from its Schrödinger equation analog:

$$[(E_\alpha - K_c)/\hbar \pm i\eta]\, {}_0\psi_\alpha^{\pm(\eta)} = 1/\hbar\ V_c\ \psi_\alpha^{\pm(\eta)} \qquad 1\text{-}75$$

or $$(K_c + V_c - (E_\alpha \mp i\eta\hbar))\, {}_0\psi_\alpha^{\pm(\eta)} = 0 \, . \qquad \text{1-76}$$

For any finite η the imaginary part of the eigenvalue of $K_c + V_c$, $\equiv H$, results in an exponential divergence of ${}_0\psi_\alpha^{\pm(\eta)}$ as some of the relative coordinates tend to infinity. This is easily realized from the behavior of a simple plane wave, e^{ikx}, when $k = \sqrt{E_\alpha \pm i\eta\hbar}$.

The trouble arises in that we do not use equations with finite η's for solving the Schrödinger equation; we use the limiting form 1-72. 1-72 has the Born expansion:

$$\psi_\alpha^{\pm(0)} = \sum_{n=0}^{\infty} \Big(\lim_{\eta \to 0} [G_\alpha(\pm\eta)]\, V_c \Big)^n \chi_\alpha \qquad \text{1-77}$$

and the homogeneous counterpart to 1-74:

$${}_0\psi_\alpha^{\pm(0)} = \lim_{\eta \to 0} [G_\alpha(\pm\eta)]\, V_c \; {}_0\psi_\alpha^{\pm(0)} \qquad \text{1-78}$$

which has the Schrödinger analog:

$$(K_c + V_c - E_\alpha)\; {}_0\psi_\alpha^{\pm(0)} = 0 \, . \qquad \text{1-79}$$

Equation 1-79 has no complex eigenvalue term, so it is not guaranteed to possess only unacceptable solutions. Thus the actual equation used to solve for $\psi_\alpha^{\pm(0)}$ (1-72) may have other bounded solutions besides the one with the correct form for scattering. Faddeev[6, 7] found the correct equation defining the unique solution for three particle scattering in the $\eta \to 0$ limit. It is important to realize that only exchange scattering and rearrangement cause difficulties with the equations we have presented here. The reason is that we have only one arrangement channel in energy transfer problems, and the equation 1-72 is unique. Translated into every man's language, it means that the resolvent, $\lim_{\eta \to 0} G_\alpha(\pm\eta)$, when written in the coordinate representation as a Green's function, contains sufficient specifications on the asymptotic form of $\psi_\alpha^{\pm(0)}$ to make it unique. For scattering into different arrangement channels, we must use the Faddeev equations.[6,7] Further discussion along this line is found in the text.

1.2.8 Relation of S matrix to the asymptotic form of the wave function

Consider 1-72 for a single arrangement channel collision and the out state only, omitting the superscripts on $\psi_\alpha^{\pm(0)}$:

$$\psi_\alpha = \chi_\alpha + \lim_{\eta \to 0} \left[\frac{1/\hbar}{(E_\alpha - K_\alpha)/\hbar + i\eta} \right] V_c \, \psi_\alpha . \qquad 1\text{-}80$$

Suppose that we insert the complete set of β channel states between the resolvant and V_c, using $I = \sum_\beta |\chi_\beta\rangle\langle\chi_\beta|$ as the identity:

$$|\psi_\alpha\rangle = |\chi_\alpha\rangle + \lim_{\eta \to 0} \left[\frac{1/\hbar}{(E_\alpha - K_\alpha)/\hbar + i\eta} \right] \sum_\beta |\chi_\beta\rangle\langle\chi_\beta| V_c \psi_\alpha\rangle \qquad 1\text{-}81$$

or $$|\psi_\alpha\rangle = |\chi_\alpha\rangle + \sum_\beta \lim_{\eta\to 0} \left[\frac{1}{(E_\alpha - K_\alpha)/\hbar + i\eta}\right]|\chi_\beta\rangle\, \mathcal{T}^{(0)}_{\alpha\beta}. \qquad 1\text{-}82$$

$\mathcal{T}^{(0)}_{\alpha\beta}$ was defined in 1-38; we write the $\eta \to 0$ limit here. Since $|\chi_\beta\rangle$ is in the channel c (same as $|\chi_\alpha\rangle$), $|\chi_\beta\rangle$ is an eigenfunction of the K_α operator, resulting in the equation:

$$|\psi_\alpha\rangle = |\chi_\alpha\rangle + \sum_\beta \lim_{\eta\to 0} \frac{1}{(E_\alpha - E_\beta)/\hbar + i\eta}\, |\chi_\beta\rangle\, \mathcal{T}^{(0)}_{\alpha\beta}. \qquad 1\text{-}83$$

The $\sum_\beta$ represents a sum over internal channel states and integration over all momenta. Further examination is not possible without a better knowledge of $\mathcal{T}^{(0)}_{\alpha\beta}$ behavior. Let us work with the collinear collision of two composite particles, in which case the barycentric volume dependence of $\mathcal{T}^{(0)}_{\alpha\beta}$ is $2\pi/L$, where L is the box normalization length. We replace $\mathcal{T}^{(0)}_{\alpha\beta}$ with the reduced transition matrix:

$$\mathcal{T}^{(0)}_{\alpha\beta} = \frac{2\pi}{L}\, \delta_{P_\beta P_\alpha}\, T^{(0)}_{\alpha\beta}. \qquad 1\text{-}84$$

In the coordinate representation we write:

$$|\chi_\alpha\rangle = e^{ik_1^\alpha x_1}\, e^{ik_2^\alpha x_2}\, \varphi_a(r) \qquad 1\text{-}85$$

where x_1 and x_2 are the coordinates of the composite particles, and r is all of their internal coordinates. Introducing 1-84 into

1-83, the $\delta_{P_\beta P_\alpha}$ eliminates the part of the $\sum_\beta$ over total momentum, leaving one sum over momentum states and a sum over internal particle states. The remaining sum over momentum states is converted to an integration over momentum using the prescription:

$$\sum_i \rightarrow \frac{L}{2\pi} \int dk_i \, .$$

Using b for the internal state labels, we have:

$$\psi_\alpha(x_1, x_2, r) = e^{ik_1^\alpha x_1} e^{ik_2^\alpha x_2} \varphi_a(r)$$

$$+ \sum_b \int dk \frac{1}{(E_\alpha - E_\beta)/\hbar + i\eta} e^{ik_1^\beta x_1} e^{ik_2^\beta x_2} \varphi_b(r)$$

$$T_{\alpha\beta}^{(0)}(k_1^\alpha, k_2^\alpha, a; k_1^\beta, k_2^\beta, b) \qquad \text{1-86}$$

(k defined below).

Where $E_\alpha = \frac{\hbar^2 (k_1^\alpha)^2}{2 m_1} + \frac{\hbar^2 (k_2^\alpha)^2}{2 m_2} + W_a$, E_β is a similar expression with α and a replaced with β and b, $k_1^\beta + k_2^\beta = k_1^\alpha + k_2^\alpha$, and W_a and W_b are the internal energies of $\varphi_a(r)$ and $\varphi_b(r)$. The $\eta \rightarrow 0$ limit is understood. If we use the center-of-mass variables, defined by:

$$X = (m_1x_1 + m_2x_2)/(m_1 + m_2) \qquad x = x_2 - x_1$$

$$K^0 = k_1^\alpha + k_2^\alpha = k_1^\beta + k_2^\beta$$

$$k = m_1k_2^\beta/(m_1 + m_2) - m_2k_1^\beta/(m_1 + m_2)$$

$$k^\alpha = m_1k_2^\alpha/(m_1 + m_2) - m_2k_1^\alpha/(m_1 + m_2)$$

$$\mu = m_1m_2/(m_1 + m_2)$$

expression 1-86 will reduce to:

$$\psi_\alpha(x, r) = e^{ik^\alpha x}\,\varphi_a(r) + \sum_b \int_{-\infty}^{\infty} dk\, \frac{1}{(E_\alpha - E_\beta)/\hbar + i\eta}$$

$$e^{ikx}\,\varphi_b(r)\, T^{(0)}_{\alpha\beta}(K^0,\ k^\alpha,\ a;\ K^0,\ k,\ b) \qquad \text{1-87}$$

with $$E_\alpha - E_\beta = \frac{\hbar^2(k^\alpha)^2}{2\mu} + W_a - \frac{\hbar^2k^2}{2\mu} - W_b.$$

We have already removed the total center-of-mass motion, e^{iK^0X}, from 1-87 and written $T^{(0)}_{\alpha\beta}$ as a function of the K^0, k momentum arguments rather than k_1 and k_2. The plane wave states $e^{ik^\alpha x}$ and e^{ikx} are here box normalized on the momentum scale:

$$\frac{1}{L}\int_0^L e^{-ikx}\, e^{ik'x}\, dx \sim \delta(k - k')\,.$$

If we are counting energy levels of plane waves, we wish that

$$\frac{1}{L}\int_0^L \frac{e^{-ikx}}{N}\frac{e^{ik'x}}{N}\,dx \sim \delta\left(\frac{\hbar^2 k^2}{2\mu} - \frac{\hbar^2 k'^2}{2\mu}\right) = \frac{\delta(k - k')}{\hbar^2 k/\mu} .$$

This results in a $\sqrt{k}$ factor under each plane wave later. The integral in 1-87 is of the form:

$$I = \hbar \int_{-\infty}^{\infty} dk \frac{e^{ikx}}{\left(Z_0 - \frac{\hbar^2 k^2}{2\mu}\right) + i\eta\hbar} T^{(0)}_{\alpha\beta}(K^0, k^\alpha, a;\ K^0, k, b) . \qquad 1\text{-}88$$

The behavior of $T^{(0)}_{\alpha\beta}$ in the large positive imaginary region of the complex k plane determines if we can close a contour around the top half of the plane. Certainly the most favorable circumstance for doing this occurs for large x, for then $e^{ikx} \to e^{-\lambda x}$, $\lambda = \mathrm{Imag}\,[k]$. We evaluate 1-88 as mentioned, using the first-order pole at $k = +\sqrt{Z_0 + i\eta\hbar}\ \sqrt{2\mu/\hbar^2}$ for the residue, and obtain, with η now zero:

$$\underset{x \to \infty}{I} = -2\pi i\hbar \frac{e^{i\sqrt{Z_1}\,x}}{2\sqrt{Z_1}\,(\hbar^2/2\mu)} T^{(0)}_{\alpha\beta}(K^0, k^\alpha, a;\ K^0, \sqrt{Z_1}, b) \qquad 1\text{-}89$$

where $Z_1 = Z_0(2\mu/\hbar^2)$. Replacing Z_0 by its implied equality in 1-87 and combining 1-87 and 1-88, we have:

$$\psi_\alpha(x, r) \underset{x \to \infty}{=} \frac{e^{ik^\alpha x}}{\sqrt{k^\alpha}} \varphi_a(r) + \sum_b \varphi_b(r)\, e^{ik^\beta x}/\sqrt{k^\beta}$$

$$\left[-2\pi i \frac{\mu}{\hbar k^\beta} T^{(0)}_{\alpha\beta} (K^0, k^\alpha, a;\ K^0, k^\beta, b) \right] \qquad 1\text{-}90$$

where $k^\beta = + \sqrt{(k^\alpha)^2 + (W_a - W_b) 2\mu/\hbar^2}$. The factor $\hbar k^\beta/\mu$ is the relative velocity of the particles in the final state. Let us take the relation of the S matrix to the transition matrix:[16]

$$S_{\alpha\beta} = \delta_{\alpha\beta} - 2\pi i \hbar\, \delta(E_\beta - E_\alpha)\, \mathcal{T}^{(0)}_{\alpha\beta} \qquad 1\text{-}91$$

and sum over energy states. Knowing the prescription for summing over momentum states:

$$\sum_i \to \frac{L}{2\pi} \int dk_i$$

we infer that a sum over energy states is:

$$\sum_i \to \frac{L}{2\pi} \int \frac{dk_i}{dE_i}\, dE_i \,.$$

Suppose that we sum over a unit energy range, then 1-91 becomes:

$$S_{\alpha\beta} = \delta_{\alpha\beta} - 2\pi i \hbar \frac{1}{dE/dK} \frac{L}{2\pi} \mathcal{T}^{(0)}_{\alpha\beta} \qquad 1\text{-}92$$

where $E_\alpha = E_\beta = E$. We see from 1-84 that:

$$S_{\alpha\beta} = \delta_{\alpha\beta} - 2\pi i\hbar \frac{1}{dE/dk} \delta_{P_\alpha P_\beta} T^{(0)}_{\alpha\beta} . \qquad 1\text{-}93$$

From the expression following 1-87, we find $dE_\beta/dk = \hbar^2 k^\beta/\mu$, because $E_\beta = \hbar^2 k^{\beta 2}/2\mu + W_b$. Under the sum in 1-90, $P_\alpha = P_\beta$, so we may insert 1-93 directly into 1-90 and have the result:

$$\psi_\alpha(x, r) \underset{x \to \infty}{=} \frac{e^{ik^\alpha x}}{\sqrt{k^\alpha}} \varphi_a(r) + \sum_b \varphi_b(r) \frac{e^{ik^\beta x}}{\sqrt{k^\beta}} (S_{\alpha\beta} - \delta_{\alpha\beta}) . \qquad 1\text{-}94$$

Thus, we have fulfilled our goal of relating the asymptotic form (x assumed large) of the scattering wave function to the S matrix. All of which was to show that it is not necessary to solve for $T^{(0)}_{\alpha\beta}$ or $S_{\alpha\beta}$ from their defining relations (i. e. : 1-38 and 1-91). Rather they may be obtained from the asymptotic form of the time-independent wavefunction.

2. INVARIANT IMBEDDING

The mathematical technique known as invariant imbedding has been applied to ordinary, second-order differential equations. Treatments have been given for the one-dimensional neutron diffusion problem[17] and the radial Schrödinger equation for elastic scattering.[18] The general procedure is as follows: introduce a parameter r into a problem that we wish to solve; for every value of this parameter r, our problem has a solution $S(r)$. For some value of r, say r_0, we know the solution $S(r_0)$; the actual problem requires the solution for a value $r = r_1$. Then, if we can find the total derivative of $S(r)$ with respect to r, or equivalently, the function f such that:

$$\frac{d}{dr} S(r) = f(r, S(r)) \qquad 2\text{-}1$$

we can integrate $S(r)$ from r_0 to r_1 and obtain the solution $S(r_1)$ directly.

2.1 Review of One-Dimensional Invariant Imbedding

For illustration of the method and one very important means of deriving $dS(r)/dr$ for scattering problems, we consider the Schrödinger equation for a particle in one-dimension scattered by a potential, commonly referred to as a barrier reflection and transmission problem.

2.1.1 Non-singular potentials

Consider any one-dimensional potential U(x) that is finite everywhere and tends to zero faster than $1/|x|$ for large positive and negative x. Without loss of generality, we suppose that U(x) vanishes outside the finite interval O to L. The Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + U(x)\,\psi(x) = E\,\psi(x)\,. \qquad 2\text{-}2$$

Outside the interval from O to L, the solutions of 2-2 are linear combinations of the plane waves, e^{ikx} and e^{-ikx}, where $k = \sqrt{2mE}/\hbar$. Ae^{ikx} defines a beam of free particles of flux $A^*A\hbar k/m$ moving in the positive x direction with momentum $\hbar k$. Be^{-ikx} defines another beam of flux $B^*B\hbar k/m$ with momentum $\hbar k$ moving in the negative x direction. The transmission (reflection) probability is the ratio of transmitted (reflected) flux to the flux incident upon the barrier. The scattering state solutions to 2-2 are made unique by specifying the asymptotic form of $\psi(x)$. For this one-dimensional problem, there are two linearly independent solutions, these corresponding to a beam incident from either the right or the left. We choose to have the beam incident from the right, and require that all parts of $\psi(x)$ in the asymptotic region, except the incident wave, be waves moving away from the potential. That is, we want an out state solution as defined in part 1. Thus:

$$x \geq L: \quad \psi(x) = e^{-ikx} + Re^{ikx}$$

2-3

$$x \leq O: \quad \psi(x) = e^{-ikx} + Te^{-ikx} \quad .$$

R is the reflection amplitude, 1 + T is the transmission amplitude; the flux ratios and probabilities are respectively, $|R|^2$ and $|1+T|^2$. Let $U(x) = \hbar^2/2m \; V(x)$. In terms of it, 2-2 can be written in the simpler form

$$- \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = k^2 \psi(x) \quad . \qquad 2\text{-}4$$

Together, 2-3 and 2-4 uniquely specify our solution. As an alternative, we can write the integral equation for $\psi(x)$ incorporating both of these:[19]

$$\psi(x) = e^{-ikx} + \int_{-\infty}^{\infty} \frac{e^{ik|x-x'|}}{2ik} V(x') \psi(x') dx' \quad . \qquad 2\text{-}5$$

Note that the limits on the integral could have been from O to L since the integrand vanishes outside this range. The S matrix for this simple problem is completely defined only if we have the solution incident from the left. Let the analogous transmitted and reflected amplitudes be T' + 1 and R'. Then:

$$\underset{\sim}{S} = \begin{pmatrix} 1 + T & R' \\ R & 1 + T' \end{pmatrix} \quad . \qquad 2\text{-}6$$

We now introduce our invariant imbedding parameter r; it is a cutoff in the potential V(x) at x = r. Define a new potential containing the cutoff as a parameter:

$$\begin{aligned} x \le r: &\quad V(x, r) = V(x) \\ x > r: &\quad V(x, r) = 0 \;. \end{aligned} \qquad 2\text{-}7$$

This cut potential could also be represented with the help of a Heaviside unit step function H(s), defined by:

$$\begin{aligned} s \ge 0: &\quad H(s) = 1 \\ s < 0: &\quad H(s) = 0 \;. \end{aligned} \qquad 2\text{-}8$$

So in terms of it we have

$$V(x, r) = V(x)\, H(r-x) \;. \qquad 2\text{-}9$$

The derivative of H(s) with respect to s is the definition of the delta function:

$$\frac{d}{ds} H(s) = \delta(s) \;. \qquad 2\text{-}10$$

From 2-10 and 2-9, we see

$$\frac{\partial V(x, r)}{\partial r} = V(x) \frac{\partial H(r-x)}{\partial r} = V(x)\, \delta(r-x) \qquad 2\text{-}11$$

this will be used later. The solution of the Schrödinger equation, or the integral equation, with $V(x, r)$ as a potential is itself a function of r, $\psi(x, r)$. We define $\psi(x, r)$ from the integral equation:

$$\psi(x, r) = e^{-ikx} + \int_{-\infty}^{\infty} \frac{e^{ik|x-x'|}}{2ik} V(x', r)\psi(x', r)dx' \qquad 2\text{-}12$$

or, because of the vanishing of $V(x, r)$:

$$\psi(x, r) = e^{-ikx} + \int_{0}^{r} \frac{e^{ik|x-x'|}}{2ik} V(x')\psi(x', r)dx' \ . \qquad 2\text{-}13$$

The asymptotic form of $\psi(x, r)$ can be obtained from 2-13,

$$\begin{aligned} x \geq r: &\quad \psi(x, r) = e^{-ikx} + R(r)e^{ikx} \\ x \leq 0: &\quad \psi(x, r) = e^{-ikx} + T(r)e^{-ikx} \end{aligned} \qquad 2\text{-}14$$

where:

$$\begin{aligned} R(r) &= \frac{1}{2ik} \int_{0}^{r} e^{-ikx'} V(x') \psi(x', r)dx' \\ T(r) &= \frac{1}{2ik} \int_{0}^{r} e^{ikx'} V(x') \psi(x', r)dx' \ . \end{aligned} \qquad 2\text{-}15$$

It is helpful to point out that $\psi(x, L)$ equals the $\psi(x)$ given by 2-5, since, when $r = L$, $V(x, L)$ is $V(x)$ and $\psi(x, L)$ is the solution of $V(x)$.

We now take the partial derivative of either equation 2-12 or 2-13 with respect to r:

$$\frac{\partial\psi(x,r)}{\partial r} = \frac{1}{2ik}\, e^{ik|x-r|}\, V(r)\, \psi(r,r) + \int_0^r \frac{e^{ik|x-x'|}}{2ik}\, V(x')\, \frac{\partial\psi(x',r)}{\partial r}\, dx' \,. \qquad 2\text{-}16$$

We have used either the delta function property of $\partial V(x, r)/\partial r$ or the rule for differentiating with respect to the upper limit of an integral, depending on whether we used equation 2-12 or 2-13. Having 2-16, which is valid for all x and r, we restrict the range of x and remove the absolute value sign from the inhomogeneous term. This gives an integral equation defining the solution $\partial\psi(x, r)/\partial r$ on the interval $x \leq r$:

$$x \leq r \quad \frac{\partial\psi(x,r)}{\partial r} = e^{-ikx}\left(\frac{1}{2ik}\, e^{ikr}\, V(r)\, \psi(r,r)\right) + \int_0^r \frac{e^{ik|x-x'|}}{2ik}\, V(x')\, \frac{\partial\psi(x',r)}{\partial r}\, dx' \,. \qquad 2\text{-}17$$

Note that the inhomogeneous term in 2-17 is the same as that of 2-13 multiplied by a function of r. In fact, the solution of 2-17 for $x \leq r$ is this same function of r times the solution of 2-13:

$$x \leq r \quad \frac{\partial \psi(x, r)}{\partial r} = \left(\frac{1}{2ik} e^{ikr} V(r) \psi(r, r)\right) \psi(x, r) . \qquad 2\text{-}18$$

This may be verified by substitution of 2-18 into 2-17, which furnishes 2-13, or by noting that if $\varphi(x)$ is a solution of the integral equation

$$\varphi(x) = \chi(x) + \int K(x, x') \, \varphi(x') \, dx'$$

then $A\varphi(x)$ is a solution of the integral equation obtained by replacing $\chi(x)$ with $A\chi(x)$:

$$A\varphi(x) = A\chi(x) + \int K(x, x') \, A\varphi(x') \, dx' .$$

From 2-14 we obtain:

$$x \geq r \quad \frac{\partial \psi(x, r)}{\partial r} = \frac{dR(r)}{dr} e^{ikx} \qquad 2\text{-}19$$

and

$$\psi(r, r) = e^{-ikr} + R(r) e^{ikr} . \qquad 2\text{-}20$$

Setting $x = r$ in 2-18 and 2-19 and equating the resulting expressions for $\partial \psi(x, r)/\partial r|_{x=r}$, we get:

$$\frac{dR(r)}{dr} e^{ikr} = \frac{1}{2ik} e^{ikr} V(r) \left(e^{-ikr} + R(r) e^{ikr}\right)^2 . \qquad 2\text{-}21$$

Letting $S(r) = e^{2ikr}\ R(r)$ and simplifying 2-21, we have:

$$\frac{dS(r)}{dr} = 2ik\ S(r) + \frac{1}{2ik}\ V(r)\ (1 + S(r))^2\ . \qquad \text{2-22}$$

Thus, we have constructed a relation of the form $dS(r)/dr = f(r, S(r))$, where $S(r)$ is related to the reflection amplitude $R(r)$. Equation 2-22 cannot be integrated unless we know $S(r)$ for some initial value of r; that is, we need a starting condition for the integration. This occurs at $r = 0$, for there the cutoff in $V(x)$ has eliminated the whole potential: $V(x, 0) = 0$. The solution $\psi(x, 0)$ is just e^{-ikx} everywhere, i. e., there is no scattering. We immediately see that $R(0) = 0$ and $T(0) = 0$. The solution for the actual, complete potential $V(x)$ is found at $r = L$, for there $V(x, L) = V(x)$ and $R(L)$ is the reflection amplitude of $\psi(x)$ as defined in 2-3.

The complete invariant imbedding problem which is equivalent to the Schrödinger equation with proper asymptotic conditions is therefore:

$$S(0) = e^{2ikr}\ R(0) = 0$$

$$\frac{dS(r)}{dr} = 2ik\ S(r) + \frac{1}{2ik}\ V(r)(1 + S(r))^2 \qquad \text{2-23}$$

$$P(\leftarrow, \rightarrow) = |S(L)|^2$$

where $P(\leftarrow, \rightarrow)$ is the reflection probability (as defined after 2-3) of a state incident from the right ($\leftarrow$), scattering back to the right

($\rightarrow$). The transmission probability $P(\leftarrow,\leftarrow)$ is just $1 - P(\leftarrow,\rightarrow)$, because $P(\leftarrow,\rightarrow) + P(\leftarrow,\leftarrow) = 1$. There is a more fundamental procedure for calculating $P(\leftarrow,\leftarrow)$. Briefly, we have from 2-14:

$$\psi(r,r) = e^{-ikr} + R(r)e^{ikr}$$

$$x \leq 0: \quad \frac{\partial\psi(x,r)}{\partial r} = \frac{dT(r)}{dr}\, e^{-ikx} \, . \qquad 2\text{-}24$$

Substituting 2-24 and 2-14 into 2-18 with x set equal to zero gives:

$$\frac{dT(r)}{dr} = \frac{1}{2ik} e^{ikr}\, V(r)(e^{-ikr} + R(r)e^{ikr}) \cdot (1 + T(r)) \qquad 2\text{-}25$$

or

$$\frac{dT(r)}{1+T(r)} = \frac{1}{2ik}\, V(r)\ (1 + S(r))\, dr \ . \qquad 2\text{-}26$$

Knowing that $T(0) = 0$, we integrate 2-26 from 0 to L directly:

$$\int_0^L \frac{dT(r')}{1+T(r')} = \frac{1}{2ik} \int_0^L V(r')(1 + S(r')dr' \ . \qquad 2\text{-}27$$

The LHS of 2-27 is just $\ln(1 + T(L))$, so:

$$T(L) = \exp\left(\frac{1}{2ik} \int_0^L V(r')(1 + S(r'))dr'\right) - 1 \ . \qquad 2\text{-}28$$

Therefore the transmission amplitude can be computed from a definite integral of $S(r)$, which can be obtained as we integrate 2-23. It is interesting to show that the solutions 2-28 and 2-23 conserve probability, as we know they must. Defining transmission and reflection probabilities as a function of r:

$$P(\leftarrow,\leftarrow;\ r) = |1 + T(r)|^2$$

$$P(\leftarrow,\rightarrow;\ r) = |R(r)|^2 \qquad \text{2-29}$$

where we used expression 2-28 to define $T(r)$ by integrating from 0 to r rather than 0 to L. We must show:

$$P(\leftarrow,\rightarrow;\ r) + P(\leftarrow,\leftarrow;\ r) = 1\ . \qquad \text{2-30}$$

Since we know $T(0) = R(0) = 0$, it is obvious from 2-29 that 2-30 is true at $r = 0$. It is now sufficient to show that the derivative of 2-30 with respect to r is zero. Substituting the definition of $T(r)$ into 2-30, introducing $R(r) = e^{2ikr}\ S(r)$, and simplifying:

$$\exp\left(\frac{1}{2ik}\int_0^r V(r')\,(S(r') - S^*(r'))dr'\right) + S^*(r)\,S(r) = 1\ . \qquad \text{2-31}$$

This equality is in doubt everywhere except at $r = 0$. Putting $S^*(r)\ S(r)$ on the RHS and taking the logarithm:

$$\frac{1}{2ik}\int_0^r V(r')\,(S(r') - S^*(r'))dr' = \ell n(1 - S^*(r)\,S(r)) \,. \qquad 2\text{-}32$$

Again this holds at $r = 0$. Taking the derivative of both sides and using 2-22 reduces the derivatives of the RHS and LHS of 2-32 to an identity. Thus, we can prove that 2-32 is an equality for all r, proving 2-30 for the same.

2.1.2 Singular potentials

If the potential in our one-dimensional problem tends to infinity in some region, we call that potential singular. The solutions to singular problems usually fall into two classes, regular and irregular. This will be discussed later; the present discussion is based on an impenetrable potential, which always has regular and irregular type solutions. By definition, we know that:

$$\begin{aligned} P(\leftarrow,\leftarrow) &= 0 \\ P(\leftarrow,\rightarrow) &= 1 \end{aligned} \qquad 2\text{-}33$$

for any such one-dimensional potential. There is no reason to calculate these numbers, per se, but if one is interested in the phase of the scattered wave, it must be obtained directly from the amplitude $R(r)$, which cannot be determined from the modulus. For example, in the elastic scattering of a particle by a spherical potential (in three dimensions), the radial

Schrödinger equation for each partial wave is similar to equation 2-22 with $V(x)$ substituted by the effective potential $V_{eff}(x) = V(x) + \ell(\ell + 1)/x^2$. The phase shift is determined from $R(r)$ or $S(r)$ as r becomes sufficiently large.

Let our impenetrable potential have the properties:

$$x \geq L \quad V(x) = 0 \tag{2-34}$$

$$x << 0 \quad V(x) - k^2 >> 0 \,. \tag{2-35}$$

The cut potential is defined the same as before:

$$V(x, r) = V(x)\, H(r - x) \,. \tag{2-36}$$

The integral equation for $\psi(x)$ is the same as 2-5, and the integral equation defining $\psi(x, r)$ is the same as 2-12. One might question the propriety of using $G_0 = e^{ik|x-x'|}/2ik$ as the free particle Green's function for a potential that does not allow the asymptotic $(x << x')$ e^{-ikx} state to the left. However, this Green's function is correct, for one can continuously deform a potential allowing transmitted states into one which does not allow transmission. The same Green's function must be used at each stage of the deformation. We clarify this as follows: consider $V(x)$ to be a potential satisfying 2-34 and 2-35. Introduce the modified potential $V_a(x) = V(x)\, H(x - a)$; for $x < a$, $V_a(x) = 0$. Because of this, $V_a(x)$ is always penetrable in principle and we must use the given form of G_0. However, as a approaches large negative values (deformation of $V_a(x)$), we will find by calculation that penetration drops toward zero. Since we do not use a deformed $V(x)$ explicitly, we have taken the limit $a \to -\infty$. Only if the potential contained an infinite barrier at a certain point $x = x_0$, would we use

$$G_0(x, x') = \begin{cases} -\frac{1}{k} e^{ik(x-x_0)} \sin k\,(x' - x_0) & x \geq x' \\ -\frac{1}{k} \sin k\,(x - x_0) e^{ik(x'-x_0)} & x \leq x' \,. \end{cases} \qquad \text{2-37}$$

Everything in our previous derivation of the invariant imbedding equation is the same for our new potential (2-34 and 2-35) except the starting point and starting condition. Looking at $V(x, r)$, we see that the cut potential appears as a very high barrier at r if r is sufficiently far to the left. Select an $r = r_0$ such that:

$$V(x, r_0)|_{x \leq r_0} >> k^2 \,.$$

We know the exact solution for an infinite barrier at r_0:

$$\psi(x, r_0) = \begin{cases} e^{-ikx} + e^{ikx}(-e^{-2ikr_0}) & x \geq r_0 \\ 0 & x \leq r_0 \,. \end{cases} \qquad \text{2-38}$$

We can also write down the exact solution for the barrier potential, $\underline{V}(x, r_0) = \begin{cases} 0 & x > r_0 \\ V(r_0) & x \leq r_0 \end{cases}$ as:

$$\underline{\psi}(x, r_0) = \begin{cases} e^{-ikx} + e^{ikx}\left(-e^{-2ikr_0}\frac{1 + ik/\lambda}{1 - ik/\lambda}\right) & x \geq r_0 \\ e^{\lambda x}\left(-e^{-\lambda r_0} e^{-ikr_0}\frac{2ik/\lambda}{1 - ik/\lambda}\right) & x \leq r_0 \end{cases} \qquad 2\text{-}39$$

where $\lambda = \sqrt{V(r_0) - k^2}$. The usual condition here is that our potentials are uniformly increasing as we move to negative x; therefore

$$V(x, r_0)|_{x \leq r_0} \geq V(r_0, r_0) = V(r_0) >> k^2 . \qquad 2\text{-}40$$

Suppose we use the starting condition $R(r_0) = -e^{-2ikr_0}$ for the invariant imbedding equation. This would be exact if we had an infinite barrier at r_0, as seen from 2-38. It is intuitively obvious that the phase shift error indicated by a comparison of 2-38 and 2-39 is greater than the phase shift error in the actual solution to 2-40, because the actual solution penetrates less than solution 2-39. As r_0 moves to the left, λ becomes large and the solution 2-39 approaches 2-38. We have thus shown how to make the starting condition $R(r_0) = -e^{-2ikr_0}$, or $S(r_0) = -1$, arbitrarily accurate by choosing r_0 sufficiently deep in the high, classically inaccessable, region of the potential. In terms of the solution 2-39, the phase shift error is approximately k/λ when $S(r_0) = -1$ is used. To test the actual error development in solving a problem, we integrated the invariant imbedding equation:

$$\frac{dS(r)}{dr} = iS(r) - ie^{-r}(1 + S(r))^2 \qquad 2\text{-}41$$

which corresponds to the Schrödinger equation:

$$-\frac{d^2\varphi(x)}{dx^2} + e^{-x}\varphi(x) = (1/2)^2\varphi(x) \qquad 2\text{-}42$$

describing scattering from a repulsive exponential barrier e^{-x}. The numerical stability and error damping properties of the equation are remarkable; we used several different starting points and integration step sizes. The variation in the solution as the starting point is moved farther back into the potential is shown in Figure 1. Note that the relative error in the starting condition does not build up, but decreases as we progress out of the region of high potential. Since e^{-x} does not vanish anywhere to the right, integration is continued until the phase of R is constant. In conclusion, we may begin our integration at some likely point r_0, calculate R outside the potential, choose another r_0 less than the previous, and calculate R again. If no significant change in R is found, we conclude that the starting conditions were adequate.

2.2 Multi-channel Invariant Imbedding

Consider one of the simpler non-separable Schrödinger equations,

$$H\psi = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + H_0(y) + V_I(x, y)\right)\psi(x, y) = E\,\psi(x, y)\;. \qquad 2\text{-}41$$

$H_0(y)$ is a Hamiltonian operator in the coordinate space of y and $V_I(x, y) \neq g(x) + f(y)$. We assume $H_0(y)$ has a complete discrete set of eigenstates $\varphi_n(y)$ with eigenvalues W_n:

$$H_0(y)\,\varphi_n(y) = W_n\,\varphi_n(y) \,. \tag{2-42}$$

The $\varphi_n(y)$ are orthonormal; later we will discuss the assumption of discreteness. Equation 2-41 might describe the collinear scattering problem of an atom of mass m striking another atom of mass M which is bound in a harmonic well. The incident atom does not interact with the well, but only with the bound atom through the interaction potential $V_I(x, y)$. The explicit form of $H_0(y)$ would be:

$$H_0(y) = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\,k\,y^2 \tag{2-43}$$

and the $\varphi_n(y)$ are harmonic oscillator wavefunctions. For a fixed E, there is a set of solutions to 2-41 which are linearly independent and have asymptotic behavior describing different kinds of scattering events. We label these $\psi^i(x, y)$, where i denotes the state of the bound particle before the collision. In other words, in the asymptotic form of $\psi^i(x, y)$ there is only one term corresponding to a plane wave moving toward the bound particle. It is $\varphi_i(y)e^{-ik_ix}$, where $k_i = +\sqrt{\frac{2m}{\hbar^2}(E - W_i)}$. The imaginary unit i is not to be confused with the state label i. We have assumed that $V_I(x, y)$ vanishes sufficiently rapidly as $x \to \infty$

that, for large x, we may write $\psi(x, y)$ as a linear combination (L. C.) of a complete set of solutions to $H - V_I$:

$$(H - V_I)\chi_n = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + H_0(y)\right)\chi_n = E\chi_n \,. \tag{2-44}$$

We see that these solutions are products of the separated solutions:

$$\chi_n^{\pm} = \varphi_n(y)\, e^{\pm ik_n x} \,. \tag{2-45}$$

So, for large x:

$$\psi^i(x, y) = \text{L. C.}\left\{\chi_n^{\pm}\right\} = \text{L. C.}\left\{\varphi_n(y)e^{\pm ik_n x}\right\} \,. \tag{2-46}$$

The $\chi_n^{\pm}$ are our channel states; they are the solutions of $H - V_c = K_c$ as discussed in the introduction.

2.2.1 Multi-channel integral equation

In analogy to our previous one-dimensional work, we want to convert 2-41 to integral equation form, incorporating the correct asymptotic conditions for scattering, i. e.: a unit incident wave striking a state i of the bound system, and outgoing waves after the collision. We also must require that $\psi(x, y)$ be a regular solution, not diverging anywhere. Scaling 2-41, we write:

$$H\psi^{i}(x, y) = \left(-\frac{1}{m}\frac{\partial^{2}}{\partial x^{2}} + H_{0}(y) + V_{I}(x, y)\right)\psi^{i}(x, y) = E\,\psi(x, y). \qquad 2\text{-}47$$

Knowing the channel solutions:

$$H_{0}(y)\,\varphi_{n}(y) = W_{n}\,\varphi_{n}(y)$$

$$2\text{-}48$$

$$(H - V_{I} - E)\chi_{n}^{\pm}(x, y) = 0$$

we want to construct the total Green's function or resolvent for the operator $H - V_{I} - E$, defined by:

$$(H - V_{I} - E)\,G(x, y; x', y') = \delta(x-x')\,\delta(y-y') \qquad 2\text{-}49$$

with the outgoing wave condition:

$$G(x, y; x', y')\big|_{x > x'} = \text{L. C.}\left\{g_{n}(x', y')\,\chi_{n}^{+}(x, y)\right\}. \qquad 2\text{-}50$$

The solution is:[19]

$$G(x, y; x', y') = -\sum_{n=0}^{\infty}\varphi_{n}(y)\,\varphi_{n}^{*}(y')\,\frac{m}{2ik_{n}}\,e^{ik_{n}|x - x'|}\,. \qquad 2\text{-}51$$

It is easy to prove 2-51 satisfies 2-49:

$$(H - V_I - E)\, G(x, y;\; x', y')$$

$$= - \sum_{n=0}^{\infty} \left(- \frac{1}{m} \frac{\partial^2}{\partial x^2} + H_0(y) - E\right) \varphi_n(y) \varphi_n^*(y') \frac{m}{2ik_n} e^{ik_n|x-x'|}$$

$$= - \sum_{n=0}^{\infty} \left(- \frac{1}{m} \frac{\partial^2}{\partial x^2} + W_n - E\right) \varphi_n(y) \varphi_n^*(y') \frac{m}{2ik_n} e^{ik_n|x-x'|} .$$

Now we must find what the second derivative does:

$$- \frac{1}{m} \frac{\partial^2}{\partial x^2} \left(\frac{m}{2ik_n} e^{ik_n|x-x'|} \right)$$

$$= - \frac{1}{2ik_n} \frac{\partial^2}{\partial x^2} \left(H(x-x') e^{ik_n(x-x')} + H(x'-x) e^{ik_n(x'-x)}\right)$$

$$= - \frac{1}{2ik_n} \frac{\partial}{\partial x} \left(ik_n\, H(x-x') e^{ik_n(x-x')} - ik_n\, H(x'-x) e^{ik_n(x'-x)}\right)$$

$$= - \frac{1}{2} \left(ik_n\, H(x-x') e^{ik_n(x-x')} + ik_n\, H(x'-x) e^{ik_n(x'-x)} + 2\,\delta(x-x')\right)$$

$$= - \delta(x-x') - \frac{ik_n}{2} e^{ik_n|x-x'|} .$$

Inserting this into the previous gives:

$$(H - V_I - E)\, G(x, y;\ x', y')$$

$$= - \sum_{n=0}^{\infty} (W_n - E)\, \varphi_n(y)\, \varphi_n^*(y')\, \frac{m}{2ik_n}\, e^{ik_n|x-x'|}$$

$$+ \sum_{n=0}^{\infty} \varphi_n(y)\, \varphi_n^*(y')\, \left(\delta(x-x') + \frac{ik_n}{2}\, e^{ik_n|x-x'|}\right)$$

$$= \sum_{n=0}^{\infty} \varphi_n(y)\, \varphi_n^*(y')\, \delta(x-x')$$

since $(W_n - E)\frac{m}{2ik_n} = + \frac{k_n^2}{m}\frac{m}{2ik_n} = + \frac{k_n}{2i}$, and the exponential terms in the above sums cancel exactly. The completeness relation says that

$$\sum_{n=0}^{\infty} \varphi_n(y)\, \varphi_n^*(y') = \delta(y-y') .$$

This completes the proof of 2-49. Writing 2-47 as:

$$(H - V_I - E)\, \psi^i = - V_I\, \psi^i \qquad 2\text{-}52$$

we see that

$$\psi^{i}(x, y) = \chi_i^-(x, y) - \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \; G(x, y; x', y') V_I(x', y') \psi^{i}(x', y') \qquad \text{2-53}$$

is equivalent to 2-52 and has the desired asymptotic properties for scattering, namely:

$$\psi^{i}(x, y) \underset{x \to \infty}{=} \varphi_i(y) e^{-ik_i x} + \sum_{n=0}^{\infty} c_n^i \varphi_n(y) e^{ik_n x} \qquad \text{2-54}$$

where

$$c_n^i = \frac{m}{2ik_n} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \; \varphi_n(y') e^{-ik_n x'} \; V_I(x', y') \psi^{i}(x', y'). \qquad \text{2-55}$$

The transition probability of the bound system from an initial state i to a final state n is just the ratio of the flux of the free particles in the final outgoing state to the flux of the incident state:

$$P_{i,n} = | c_n^i |^2 \frac{k_n}{k_i} . \qquad \text{2-56}$$

A further point should be mentioned: not all of the $\chi_n^{\pm}$ correspond to states that are physical observables. Whenever n is sufficiently large such that $W_n > E$, k_n is a positive imaginary number and $e^{ik_n x}$ is a decaying exponential of zero flux. These are referred to as virtual channel states. The inclusion of these in the Green's function expansion or a state expansion of the wavefunction is necessary for completeness. Their omission from a calculation could affect the values of $P_{i,n}$ significantly.

2.2.2 Matrix form of integral equation

Having our multi-channel integral equation, 2-53, we do an expansion of $\psi^i(x,y)$ in the eigenstates of $H_0(y)$:

$$\psi^i(x,y) = \sum_{n=0}^{\infty} f_n^i(x)\,\varphi_n(y) \qquad 2\text{-}57$$

where the $f_n^i(x)$ are unknown functions. Substituting 2-57 into 2-53 and taking inner products with the members of $\varphi_n(y)$ gives a coupled set of integral equations for the $f_n^i(x)$. To simplify our algebraic manipulations, define the matrices:

$$(\underset{\sim}{F}(x))_{nm} = f_n^m(x)$$

$$(\underset{\sim}{K})_{nm} = k_n \delta_{nm} \qquad (e^{i\underset{\sim}{K}x})_{nm} = e^{ik_n x}\,\delta_{nm}$$

$$(\underset{\sim}{V}(x))_{nm} = \int_{-\infty}^{\infty} dy\, \varphi_n^*(y) V_I(x,y)\, \varphi_m(y) \qquad 2\text{-}58$$

where we count rows and columns beginning with 0 because our sums begin at 0. Having these defined, the coupled set of integral equations may be written:

$$\underset{\sim}{F}(x) = e^{-i\underset{\sim}{K}x} + \int_{-\infty}^{\infty} dx' \, \frac{m}{2i\underset{\sim}{K}} e^{i\underset{\sim}{K}|x-x'|} \, \underset{\sim}{V}(x') \, \underset{\sim}{F}(x') \, . \qquad 2\text{-}59$$

The asymptotic form of $\underset{\sim}{F}(x)$ may be written down from this equation.

2.2.3 Derivation of multi-channel invariant imbedding equation

The invariant imbedding parameter r is again a cutoff in the potential, but only in the x coordinate of the interaction. Define the parametrized potential:

$$V_I(x, y, r) = V_I(x, y) \, H(r-x) \qquad 2\text{-}60$$

with

$$\frac{\partial V_I(x, y, r)}{\partial r} = V_I(x, y) \, \delta(r-x) \, . \qquad 2\text{-}61$$

The matrix form is simply:

$$\underset{\sim}{V}(x, r) = \underset{\sim}{V}(x) \, H(r-x) \, . \qquad 2\text{-}62$$

Our parametrized solution is defined by:

$$\underset{\sim}{F}(x, r) = e^{-i\underset{\sim}{K}x} + \int_{-\infty}^{\infty} dx' \, \frac{m}{2i\underset{\sim}{K}} e^{i\underset{\sim}{K}|x-x'|} \, \underset{\sim}{V}(x', r) \, \underset{\sim}{F}(x', r). \qquad 2\text{-}63$$

Attention is immediately called to the formal similarity of 2-63 to the one-dimensional analog 2-12 . The construction of the invariant imbedding equivalent to 2-59 parallels the one-dimensional problem. It is helpful to keep in mind that the j'th column of $\underset{\sim}{F}(x, r)$ relates to a particular scattering state $\psi^j(x, y, r)$, and that the i'th row relates to the i'th terms in the state expansions of these ψ^j, i. e., $f_i^j(x, r)\, \varphi_i(y)$. From 2-63, noting that the upper limit on the integral is effectively r:

$$x \geq r \qquad \underset{\sim}{F}(x, r) = e^{-i\underset{\sim}{K}x} + e^{i\underset{\sim}{K}x} \, \underset{\sim}{R}(r) \qquad 2\text{-}64$$

where

$$\underset{\sim}{R}(r) = \frac{m}{2i\underset{\sim}{K}} \int_{-\infty}^{r} dx' \, e^{-i\underset{\sim}{K}x'} \, \underset{\sim}{V}(x', r) \, \underset{\sim}{F}(x', r) \ . \qquad 2\text{-}65$$

The matrix elements of $\underset{\sim}{R}(r)$ give us the transition probabilities $P_{i,f}(r)$ for the cutoff interaction. For sufficiently large r, these are the transition probabilities for the whole interaction $V_I(x, y)$:

$$P_{i,f} = |(\underset{\sim}{R}(r))_{f,i}|^2 \, \frac{k_f}{k_i} \ , \text{ for } r \text{ large.} \qquad 2\text{-}66$$

Our interaction $\underset{\sim}{V}_I$ does not allow the incident particle to pass through the bound one; this eliminates the necessity for including transmitted flux. Taking the partial derivative of 2-63 with respect to r:

$$\frac{\partial \underset{\sim}{F}(x,r)}{\partial r} = \frac{m}{2i\underset{\sim}{K}} e^{i\underset{\sim}{K}|x-r|} \underset{\sim}{V}(r,r)\, \underset{\sim}{F}(r,r)$$

$$+ \frac{m}{2i\underset{\sim}{K}} \int_{-\infty}^{\infty} dx' \, e^{i\underset{\sim}{K}|x-x'|} \underset{\sim}{V}(x',r) \frac{\partial \underset{\sim}{F}(x',r)}{\partial r} . \tag{2-67}$$

$\underset{\sim}{V}(r,r)$ is just $\underset{\sim}{V}(r)$ as defined in 2-58. Restricting the range of x in 2-67, and placing the effective upper limit r on the integral, we have:

$$x \leq r \qquad \frac{\partial \underset{\sim}{F}(x,r)}{\partial r} = \frac{m}{2i\underset{\sim}{K}} e^{-i\underset{\sim}{K}x + i\underset{\sim}{K}r} \underset{\sim}{V}(r)\, \underset{\sim}{F}(r,r)$$

$$+ \frac{m}{2i\underset{\sim}{K}} \int_{-\infty}^{r} dx' \, e^{i\underset{\sim}{K}|x-x'|} \underset{\sim}{V}(x',r) \frac{\partial \underset{\sim}{F}(x',r)}{\partial r} . \tag{2-68}$$

Because $\underset{\sim}{K}$ and $e^{i\underset{\sim}{K}x}$ are diagonal, $e^{-i\underset{\sim}{K}x + i\underset{\sim}{K}r} = e^{-i\underset{\sim}{K}x} e^{i\underset{\sim}{K}r}$, and these diagonal matrices commute. We re-write the inhomogeneous term (first term on RHS above) of 2-68:

$$e^{-i\underset{\sim}{K}x} \left[\frac{m}{2i\underset{\sim}{K}} e^{i\underset{\sim}{K}r} \underset{\sim}{V}(r)\, \underset{\sim}{F}(r,r) \right]$$

and note that it is a function of r times the inhomogeneous term of 2-63. Using the same method as presented in the one-dimensional section, we conclude:

$$x \leq r \quad \frac{\partial \underset{\sim}{F}(x,r)}{\partial r} = \underset{\sim}{F}(x,r)\left[\frac{m}{2i\underset{\sim}{K}}\, e^{i\underset{\sim}{K}r}\, \underset{\sim}{V}(r)\, \underset{\sim}{F}(r,r)\right] . \qquad 2\text{-}69$$

It must be remembered that non-diagonal matrices do not, in general, commute. From 2-64:

$$x \geq r \quad \frac{\partial \underset{\sim}{F}(x,r)}{\partial r} = e^{i\underset{\sim}{K}x}\, \frac{d\underset{\sim}{R}(r)}{dr}$$

and 2-70

$$\underset{\sim}{F}(r,r) = e^{-i\underset{\sim}{K}r} + e^{i\underset{\sim}{K}r}\, \underset{\sim}{R}(r) \; .$$

Setting x = r in 2-69 and 2-70 and equating the resulting expression for $\left.\frac{\partial \underset{\sim}{F}(x,r)}{\partial r}\right|_{x=r}$ gives:

$$e^{i\underset{\sim}{K}r}\, \frac{d\underset{\sim}{R}(r)}{dr} = \left(e^{-i\underset{\sim}{K}r} + e^{i\underset{\sim}{K}r}\, \underset{\sim}{R}(r)\right) \frac{m}{2i\underset{\sim}{K}}\, e^{i\underset{\sim}{K}r}\, \underset{\sim}{V}(r)$$

$$\left(e^{-i\underset{\sim}{K}r} + e^{i\underset{\sim}{K}r}\, \underset{\sim}{R}(r)\right) \qquad 2\text{-}71$$

where we used the expression in 2-70 for $\underset{\sim}{F}(r,r)$. Let us define $\underset{\sim}{S}(r)$ as a new dependent function:

$$\underset{\sim}{S}(r) = e^{i\underset{\sim}{K}r}\, \underset{\sim}{R}(r)\, e^{i\underset{\sim}{K}r} \; . \qquad 2\text{-}72$$

Using this and the commutation property of diagonal matrices, 2-72 becomes:

$$\frac{d\underset{\sim}{S}(r)}{dr} = i\underset{\sim}{K}\underset{\sim}{S}(r) + i\underset{\sim}{S}(r)\underset{\sim}{K}$$

$$+ (\underset{\sim}{I} + \underset{\sim}{S}(r))\frac{m}{2i\underset{\sim}{K}}\underset{\sim}{V}(r)(\underset{\sim}{I} + \underset{\sim}{S}(r)) \ . \qquad 2\text{-}73$$

Either 2-71 or 2-73 is the invariant imbedding equation. The transition probabilities are related to the moduli of the $\underset{\sim}{S}(r)$ and $\underset{\sim}{R}(r)$ matrix elements:

$$P_{i,f}(r) = |(\underset{\sim}{R}(r))_{fi}|^2 \frac{k_f}{k_i} = |(\underset{\sim}{S}(r))_{fi}|^2 \frac{k_f}{k_i} \ . \qquad 2\text{-}74$$

As r becomes large, $P_{i,f}(r)$ approaches $P_{i,f}$, the transition probability for the uncut interaction $V_I(x, y)$. We have derived everything except the proper initial condition to begin the integration. It was stated previously that $V_I(x, y)$ precluded penetration; more specifically we require that, for some $r = r_0$:

$$V_B(y) + V_I(x, y, r_0) >> E \qquad \text{for } x \le r_0 \qquad 2\text{-}75$$

where V_B is the binding potential in $H_0(y)$. 2-75 is simply the requirement that there exist an r_0 such that the part of x, y configuration space to the "left" of r_0 is energetically forbidden. We approximate the cut potential $V_I(x, y, r_0)$ by an infinite barrier:

$$V_I^{\infty}(x, y, r_0) = \begin{cases} 0 & x > r_0 \\ \infty & x < r_0 \end{cases} \qquad 2\text{-}76$$

and obtain the solutions to the Schrödinger equation for V_I^{∞}:

$$\underset{\sim}{F}^{\infty}(x, r_0) = \begin{cases} e^{-i\underset{\sim}{K}x} + e^{i\underset{\sim}{K}x}\left(-e^{-2i\underset{\sim}{K}r_0}\right) & x \geq r_0 \\ 0 & x \leq r_0 \,. \end{cases} \qquad 2\text{-}77$$

These solutions possess no inelastic transitions, i. e., they are diagonal, consisting of an incident wave and a reflected wave in the same channel. The starting condition for the integration of 2-71 is $\underset{\sim}{R}(r_0) = e^{-2i\underset{\sim}{K}r_0}$. Using 2-72, we see that the starting condition for 2-73 is

$$\underset{\sim}{S}(r_0) = -\underset{\sim}{I} \qquad 2\text{-}78$$

which we assume is accurate to order $\sqrt{E/(V_{nn}(r_0)-E)}$, the error introduced by the penetration of the n'th channel incident wave into the high, but finite, cutoff interaction. In practice, we need to carry through convergence tests on the answers, P_{if}, as we move the starting point farther into the impenetrable region of $V_I(x, y)$. This completes our detailed description of the multi-channel invariant imbedding procedure.

2.3 Properties of the Invariant Imbedding Equation

The most important feature of the invariant imbedding method is that the asymptotic boundary condition of a unit incident wave and outgoing scattered waves has been built into the equation itself. Previously, only the integral equation had this property. The regularity boundary condition on the Schrödinger equation serves to determine the initial starting condition for integration of the first-order equation.

Our derivation of the multi-channel invariant imbedding equation is more general than we have implied. For simplicity, we have taken the H_0 part of the total Hamiltonian H to depend on one scalar coordinate y. However, we may define that y to represent several coordinates, so that the eigenfunctions of H_0 are described by several quantum numbers, $n_1, n_2, \ldots,$ the set of which is represented by n. If we order these indices consistently throughout the derivation, we obtain the same final result. Note that $\varphi_n(y)$ might be $\varphi_{n_1, n_2, n_3}(y_1, y_2, y_3)$ as long as they are complete, orthonormal, and discrete. The necessity of discreteness will be discussed later.

We must mention here that a previous derivation of the multi-channel invariant imbedding method was found after our work was completed. The other work was of the same general applicability as ours, but arrived at by a different procedure.[20]

3. INTEGRATION OF THE SCHRODINGER EQUATION

Any numerical method of calculation should have checks; the immediate answer for an alternative method to invariant imbedding is found in a direct integration of the Schrödinger equation itself. This procedure is the most fundamental of all calculations in scattering theory.

3.1 One-dimensional Theory

3.1.1 Non-singular potential

Integration of the one-dimensional scaled Schrödinger equation:

$$-\frac{d^2\varphi(x)}{dx^2} + V(x)\,\varphi(x) = k^2\varphi(x) \qquad 3\text{-}1$$

to find a solution conforming to prescribed asymptotic conditions could be accomplished as follows. We know that any solution of 3-1 may be formed from a linear combination of two linearly independent solutions. The theory of Sturm-Liouville equations is applicable,[21] so we know that solutions are linearly independent if their Wronskian, which is a constant, does not vanish. Let $\varphi_1(x)$ and $\varphi_2(x)$ be two solutions to 3-1; if, at any point x_0, the Wronskian is not zero:

$$W(\varphi_1(x),\ \varphi_2(x))\big|_{x=x_0} \neq 0 \qquad 3\text{-}2$$

or

$$\frac{\frac{d\varphi_1(x)}{dx}}{\varphi_1(x)} \neq \frac{\frac{d\varphi_2(x)}{dx}}{\varphi_2(x)} \qquad \text{at } x = x_0$$

then $\varphi_1(x)$ and $\varphi_2(x)$ are independent and we may form a correct scattering solution by taking a linear combination of them. In order to obtain $\varphi_1(x)$ and $\varphi_2(x)$ by numerical integration, we choose function and slope boundary conditions at some x_0:

$$\varphi_1(x_0) = c_1, \; \frac{d\varphi_1(x)}{dx}\bigg|_{x=x_0} = s_1$$

$$\varphi_2(x_0) = c_2, \; \frac{d\varphi_2(x)}{dx}\bigg|_{x=x_0} = s_2 \qquad 3\text{-}3$$

such that 3-2 is satisfied, namely:

$$\frac{s_1}{c_1} \neq \frac{s_2}{c_2} \qquad 3\text{-}4$$

and integrate away from the point x_0. This determines numerical solutions of 3-1 for all x that are assured of linear independence. To form the correct scattering solution, one analyzes $\varphi_1(x)$ and $\varphi_2(x)$ in the asymptotic regions, obtaining coefficients:

$$\varphi_1(x) \underset{x \text{ large}}{=} a_1 e^{-ikx} + b_1 e^{ikx}$$

$$\varphi_2(x) \underset{x\ \text{large}}{=} a_2 e^{-ikx} + b_2 e^{ikx} \qquad 3\text{-}5$$

and

$$\varphi_1(x) \underset{x\ \text{small}}{=} c_1 e^{-ikx} + d_1 e^{ikx}$$

$$\varphi_2(x) \underset{x\ \text{small}}{=} c_2 e^{-ikx} + d_2 e^{ikx} \quad . \qquad 3\text{-}6$$

Suppose we want a unit incident wave from the right and outgoing waves from the barrier $V(x)$ (we have assumed $V(x)$ is penetrable):

$$\varphi(x) \underset{x\ \text{large}}{=} e^{-ikx} + Re^{ikx}$$

$$\varphi(x) \underset{x\ \text{small}}{=} Te^{-ikx} \, . \qquad 3\text{-}7$$

The scattering solution $\varphi(x)$ is a linear combination of $\varphi_1(x)$ and $\varphi_2(x)$:

$$\varphi(x) = A\varphi_1(x) + B\varphi_2(x) \, . \qquad 3\text{-}8$$

For large x, we see that 3-5, 3-7, and 3-8 imply:

$$1 = Aa_1 + Ba_2$$

$$R = Ab_1 + Bb_2 \ . \qquad \text{3-9}$$

For small x, 3-6, 3-7, and 3-8 imply:

$$0 = Ad_1 + Bd_2$$

$$T = Ac_1 + Bc_2 \ . \qquad \text{3-10}$$

Together, 3-9 and 3-10 may be solved for A and B in terms of the coefficients. R and T are then found from these.

3.1.2 Singular potentials

If $V(x)$ tends to infinity in some region, for x either finite or infinite, we know that 3-1 has two types of solutions, which are classified as regular and irregular. The regular solution tends to zero as $V(x) \to \infty$, whereas the irregular solution diverges in that region. Proper solutions of 3-1 must be regular. A thorough treatment of singular potentials has been given by Kemble.[22] Suppose that $V(x)$ is singular at x_1. If we pick boundary conditions like 3-3 at $x_0 \neq x_1$, we will find in general that $\varphi_1(x)$ and $\varphi_2(x)$ each contain components of irregular solutions. We would then have to take an appropriate linear combination of $\varphi_1(x)$ and $\varphi_2(x)$ which eliminates the divergent parts. Rather than doing this, it is more practical to begin the integration near the singular point x_1, using function and slope values corresponding to a regular solution, and integrating out of the singular region of $V(x)$. This necessitates finding only one solution instead of two. The correct asymptotic behavior at infinity is produced by multiplying the solution by an overall normalization constant. If we do not know the form of the regular solution of $V(x)$ near x_1, we can approximate it with arbitrarily good accuracy by modifying $V(x)$. Suppose $V(x) = e^{-x}$, then the singular point x_1 is at $-\infty$. The form of the regular solution of 3-1 is known for this potential, but it is not as simple as one would like. Our procedure is to define a new potential:

$$V'(x) = \begin{cases} V(x) = e^{-x} & x \geq r \\ V = V(r) >> k^2 & x \leq r \end{cases} \qquad 3\text{-}11$$

which differs from the actual one only in the very high regions of $V(x)$. For $x \leq r$, the regular solution to the modified problem is $e^{\lambda x}$, $\lambda = +\sqrt{V(r) - k^2}$. At $x = r$, we choose the boundary conditions:

$$\begin{aligned} \varphi(x)\Big|_{x=r} &= e^{\lambda r} \\ \frac{d\varphi(x)}{dx}\Big|_{x=r} &= \lambda e^{\lambda r} \end{aligned} \qquad 3\text{-}12$$

and integrate into the asymptotic region. Note that any starting boundary conditions of the form:

$$\varphi(x)\big|_{x=r} = A$$

$$\frac{d\varphi(x)}{dx}\Big|_{x=r} = \lambda A \qquad 3\text{-}13$$

would only change the solution by an overall normalization constant. An alternative approach could be to define $V''(x)$ such that:

$$V''(x) = \begin{cases} V(x) & x \geq r \\ \infty & x < r \end{cases} \qquad 3\text{-}14$$

where $V(r) >> k^2$, and let:

$$\varphi(r) = 0$$

$$\frac{d\varphi(x)}{dx}\Big|_{x=r} = A \ . \qquad 3\text{-}15$$

In any case, we expect the solutions to the modified potential to approach the regular solution of $V(x)$ as the modification approaches the singular point.

3.1.3 Re-normalization procedure

Suppose we are integrating the equation:

$$-\frac{d^2\varphi(x)}{dx^2} + e^{-x}\varphi(x) = \varphi(x) \qquad 3\text{-}16$$

by starting at $x = -3$, using $\varphi(-3) = 1$ and $\varphi'(-3) = d\varphi(x)/dx|_{x=-3} = \sqrt{19} \cong \sqrt{e^3 - 1}$. At $x = -3$, the potential is 20 times the energy. The solution $\varphi(x)$ will increase by several orders of magnitude as we progress towards large x; this is to be expected, for the proper regular solution is decaying to zero inside the potential. If we had chosen starting conditions $\varphi(-3) = 10^{-5}$, $\varphi'(-3) = \sqrt{19} \times 10^{-5}$, we might have found that $\varphi(x)$ is of order 1 for large x. Instead of trying to guess a priori the correct order of magnitude for $\varphi(x)$ at -3 to give $\varphi(x)$ of order 1 as x becomes large, we could renormalize $\varphi(x)$ at selected points during the integration. Using $\varphi(-3) = 1$, $\varphi'(-3) = \sqrt{19}$, we might find that $\varphi(-2) = 100$; consequently we divide $\varphi(-2)$ by 100 and $\varphi'(-2)$ by 100 and use these as new starting conditions at $x = -2$. Both function and derivative must be divided by the same number, otherwise we are doing more than changing the overall normalization of the wavefunction. This renormalization procedure is of no practical utility unless numbers are becoming so large that computer overflow occurs.

3.2 Direct Integration of Multi-channel Schrödinger Equation

We will find it convenient to work with matrix notation here that is almost identical to the previous development of the matrix integral equation for multi-channel scattering. There are some slight differences in definitions, so the process will be quickly repeated.

3.2.1 Matrix Schrödinger equation

We begin with the scaled (dimensionless) form:

$$H\psi^{i} = (-\frac{1}{\mu}\frac{\partial^{2}}{\partial x^{2}} + H_{0}(y) + V_{I}(x,y)\,\psi^{i} = E\,\psi^{i} \qquad 3\text{-}17$$

where $H_0(y)$ has a complete, discrete spectrum of eigenstates. Label i denotes the initial state of the system prior to collision; as mentioned previously, both y and i may be regarded as symbols for several coordinates and quantum numbers. Using the solutions of

$$\begin{aligned} H_{0}(y)\,\varphi_{n}(y) &= W_{n}\,\varphi_{n}(y) \\ \langle \varphi_{n}(y) \,|\, \varphi_{m}(y) \rangle &= \delta_{nm} \end{aligned} \qquad 3\text{-}18$$

as an expansion basis for ψ^i, we have:

$$\psi^{i}(x,y) = \sum_{n=0}^{\infty} f_{n}^{i}(x)\;\varphi_{n}(y)\,. \qquad 3\text{-}19$$

3-19 is substituted into 3-17 and inner products are taken with members of the set of $\varphi_m(y)$. This gives a coupled set of differential equations for the $f_n^i(x)$, which may be written in matrix form. Defining:

$$(\underset{\sim}{F}(x))_{nm} = f_n^m(x)$$

$$(\underset{\sim}{K})_{nm} = k_n\,\delta_{nm} = +\sqrt{\mu(E-W_n)}\,\delta_{nm} \tag{3-20}$$

$$(\underset{\sim}{V})_{nm} = \mu \int_{-\infty}^{\infty} dy\, \varphi_n^*(y)\, V_I(x,y)\, \varphi_m(y)$$

we have

$$-\frac{d^2}{dx^2}\,\underset{\sim}{F}(x) + \underset{\sim}{V}(x)\,\underset{\sim}{F}(x) = \underset{\sim}{K}^2\,\underset{\sim}{F}(x)\quad . \tag{3-21}$$

Note that the matrices "count" rows and columns the same way that the sums are written, i. e., from zero. We will assume $V_I(x, y)$ does not allow penetration; then we are interested only in the asymptotic form of $\underset{\sim}{F}(x)$ for large positive x, orienting the system so that the incident flux comes in from the right. The scattering solutions that we wish to calculate must have the asymptotic form:

$$\underset{\sim}{F}(x) \underset{x\to\infty}{=} e^{-i\underset{\sim}{K}x} + e^{i\underset{\sim}{K}x}\,\underset{\sim}{R} \tag{3-22}$$

where $\underset{\sim}{R}$ is the matrix of amplitudes from which we calculate the transition probabilities:

$$P_{if} = |(\underset{\sim}{R})_{fi}|^2 \frac{k_f}{k_i} . \qquad 3\text{-}23$$

The object of our effort is to find the $\underset{\sim}{R}$ matrix as specified in 3-22.

3.2.2 Transformation of scattering states

Suppose for the moment that we have a complete set of linearly independent regular solutions to 3-17:

$$\chi^j(x, y) \qquad j = 0, 1, 2, \ldots .$$

These satisfy everything but the correct asymptotic form for scattering. Expand:

$$\chi^j(x, y) = \sum_{i=0}^{\infty} g_i^j(x)\ \varphi_i(y) \qquad 3\text{-}24$$

and define:

$$(\underset{\sim}{G}(x))_{ij} = g_i^j(x) . \qquad 3\text{-}25$$

In the region of large x, 3-17 is separable, so we know that:

$$\chi^j(x,y) \underset{x\to\infty}{=} \sum_{n=0}^{\infty} a_n^j \, e^{-ik_n x} \varphi_n(y)$$

$$+ \sum_{n=0}^{\infty} b_n^j \, e^{ik_n x} \varphi_n(y) \ . \qquad 3\text{-}26$$

Define:

$$(\underset{\sim}{A})_{ij} = a_i^j \qquad (\underset{\sim}{B})_{ij} = b_i^j \ . \qquad 3\text{-}27$$

The above four equations tell us that

$$\underset{\sim}{G}(x) \underset{x\to\infty}{=} e^{-i\underset{\sim}{K}x} \underset{\sim}{A} + e^{i\underset{\sim}{K}x} \underset{\sim}{B} \ . \qquad 3\text{-}28$$

$\underset{\sim}{G}(x)$ is a solution of 3-21, but does not have the behavior required for scattering. The correct solutions $\psi^i(x,y)$ are expressible as linear combinations of the $\chi^j(x,y)$:

$$\psi^i(x,y) = \sum_{j=0}^{\infty} d_j^i \, \chi^j(x,y) \ . \qquad 3\text{-}29$$

Inserting expansions 3-19 and 3-24 into 3-29, using definitions 3-20 and 3-25, we write the matrix equivalent of 3-29:

$$\underset{\sim}{F}(x) = \underset{\sim}{G}(x) \, \underset{\sim}{D} \qquad 3\text{-}30$$

where $(\underset{\sim}{D})_{ij} = d^j_i$. For large x, we use 3-22 and 3-28 in 3-30 and obtain

$$e^{-i\underset{\sim}{K}x} + e^{i\underset{\sim}{K}x}\underset{\sim}{R} \underset{x\to\infty}{=} (e^{-i\underset{\sim}{K}x}\underset{\sim}{A} + e^{i\underset{\sim}{K}x}\underset{\sim}{B})\underset{\sim}{D} \qquad 3\text{-}31$$

which implies:

$$\underset{\sim}{I} = \underset{\sim}{A}\,\underset{\sim}{D} \qquad \underset{\sim}{R} = \underset{\sim}{B}\,\underset{\sim}{D}$$

or

$$\underset{\sim}{R} = \underset{\sim}{B}\,\underset{\sim}{A}^{-1}\,. \qquad 3\text{-}32$$

Thus, once we have found a complete regular set of solutions to the Schrödinger equation, it is easy to examine their asymptotic behavior and form a correct set of scattering solutions. We see that $\underset{\sim}{A}^{-1}$ is the correct linear transformation that relates $\underset{\sim}{G}(x)$ and $\underset{\sim}{F}(x)$, because, from 3-32, $\underset{\sim}{D} = \underset{\sim}{A}^{-1}$:

$$\underset{\sim}{F}(x) = \underset{\sim}{G}(x)\,\underset{\sim}{A}^{-1}\,. \qquad 3\text{-}33$$

Our problem is now to determine the $\chi^j(x, y)$ solutions, or equivalently $\underset{\sim}{G}(x)$.

3.2.3 Determination of regular solutions

Consider the numerical procedure to determine any $\underset{\sim}{G}(x)$ solution; again we must choose function and slope conditions at some x_0 to uniquely determine $\underset{\sim}{G}(x)$ for all x. Suppose:

$$\underset{\sim}{G}(x_0) = \underset{\sim}{C}$$
$$\left.\frac{d\,\underset{\sim}{G}(x)}{dx}\right|_{x=x_0} = \underset{\sim}{S} \qquad 3\text{-}34$$

then equation 3-21 enables us to integrate away from x_0 and determine $\underset{\sim}{G}(x)$. The fact that the Schrödinger equation 3-21 is written with $\underset{\sim}{F}(x)$ as a dependent function is immaterial; both $\underset{\sim}{F}(x)$ and $\underset{\sim}{G}(x)$ are solutions. The integration is straight-forward, but we must accomplish two things: (1) insure that the χ^j, corresponding to columns j in $\underset{\sim}{G}(x)$, are linearly independent, and (2) satisfy the regularity requirement on χ^j so that they do not diverge in the singular region of the interaction V_I. We need the following theorems.

Theorem I. For any solution $\underset{\sim}{G}(x)$, if the columns of $\underset{\sim}{G}(x)|_{x=x_1}$ are linearly independent, then the functions χ^j are linearly independent for all x and y.

Proof. Let us assume that two of the χ^j, χ^n and χ^m, are linearly dependent. This means that there exist c_n and c_m such that:

$$0 = c_n \chi^n(x, y) + c_m \chi^m(x, y) \qquad \text{for all } x \text{ and } y \qquad 3\text{-}35$$

or

$$0 = c_n g_i^n(x) + c_m g_i^m(x) \qquad \text{for all } x \text{ and } i \qquad 3\text{-}36$$

because the $\varphi_i(y)$ are linearly independent. 3-36 implies that the columns n and m of $\underset{\sim}{G}(x)|_{x=x_1}$ are dependent, in violation of our hypothesis. The theorem is true by contradiction. QED

Theorem II. For any solution $\underset{\sim}{G}(x)$, if the columns of $\left.\frac{d\underset{\sim}{G}(x)}{dx}\right|_{x=x_1}$ are linearly independent, then the functions χ^j are linearly independent for all x and y.

Proof. Again, suppose that χ^n and χ^m were dependent. This implies that:

$$0 = c_n g_i^n(x) + c_m g_i^m(x) \qquad \text{for all } x \text{ and } i \qquad 3\text{-}37$$

$$0 = c_n \frac{dg_i^n(x)}{dx} + c_m \frac{dg_i^m(x)}{dx} \qquad \text{for all } x \text{ and } i\,. \qquad 3\text{-}38$$

The latter violates the hypothesis for $x = x_1$, so the theorem is true by contradiction. QED

Consequently, it is a simple matter to insure the independence of our $\underset{\sim}{G}(x)$ column vectors; we simply choose starting function and slope conditions as in 3-34, with either or both of $\det(\underset{\sim}{C}) \neq 0, \det(\underset{\sim}{S}) \neq 0$.

The regularity requirement is accomplished either by beginning the integration near the singular region with a regular asymptotic form, or by modifying the interaction potential in a region that has negligible effect on the regular wavefunctions. For problems of interest, we must do the latter, since we do not know the behavior of the regular solutions analytically. It is difficult to place bounds on the effect that a modification of V_I has on the solutions or the transition probabilities. Intuitively one knows that, as the modification moves farther into the classically forbidden region of the interaction, the solutions to the modified problem approach the correct solutions of the unmodified problem. Examining the whole Schrödinger equation, with $H_0(y) = T_0(y) + V_0(y)$, where $V_0(y)$ is the binding potential of the bound system:

$$(-\frac{1}{\mu}\frac{\partial^2}{\partial x^2} + T_0(y) + V_0(y) + V_I(x, y))\psi^i = E\,\psi^i \qquad 3\text{-}39$$

we place the modification in V_I such that

$$V_0(y) + V_I(x_1, y) >> E \qquad 3\text{-}40$$

for x_1 in the modified region. The same concept was used in the starting conditions for the invariant imbedding formalism.

The regularity requirement on $\psi^i(x, y)$ and $\chi^j(x, y)$ is ultimately expressed on $f^i_j(x)$ and $g^i_j(x)$. The easiest modification to place on $V_I(x, y)$ is an infinite barrier at $x = x_0$. Then we might use in 3-34:

$$\underset{\sim}{G}(x_0) = 0$$

$$\left.\frac{d\underset{\sim}{G}(x)}{dx}\right|_{x=x_0} = \underset{\sim}{I} \ . \qquad 3\text{-}41$$

Another modification is to make $\underset{\sim}{V}(x)$ diagonal for $x < x_0$:

$$(\underset{\sim}{V}'(x))_{ij} = \begin{cases} (\underset{\sim}{V}(x))_{ij} & x > x_0 \\ (\underset{\sim}{V}(x_1))_{ij}\,\delta_{ij} & x \le x_0 \end{cases} \qquad 3\text{-}42$$

and use

$$\underset{\sim}{G}(x_0) = \underset{\sim}{I}$$

$$\left.\frac{d\,\underset{\sim}{G}(x)}{dx}\right|_{x=x_0} = \underset{\sim}{\lambda} \qquad 3\text{-}43$$

where $(\underset{\sim}{\lambda})_{ij} = \sqrt{(\underset{\sim}{V}(x_1))_{ii} - k_i^2}\;\delta_{ij}$. Having a diagonal potential enables us to decouple the system of equations implied by 3-21 in the $x \le x_0$ region. The regular diagonal solution of the modified problem 3-42 is:

$$x \le x_0 \quad \underset{\sim}{G}(x) = e^{\underset{\sim}{\lambda}(x-x_0)} \qquad 3\text{-}44$$

from which we observed 3-43.

This completes a tentative scheme of solution, but it is not generally useful because of a hidden difficulty that arises in practice. In the next section we will explain this problem and the method of re-orthogonalization used to circumvent the difficulty.

3. 3 Method of Re-orthogonalization for Matrix Schrödinger Equation

3. 3. 1 Tendency to linear dependence

Integration of the matrix equation,

$$-\frac{d^2\underset{\sim}{G}(x)}{dx^2} + \underset{\sim}{V}(x)\ \underset{\sim}{G}(x) = \underset{\sim}{K}^2\ \underset{\sim}{G}(x) \qquad \text{3-45}$$

reveals the same general increase in magnitude of the solution as we progress out of the interaction as was observed for the one-dimensional problem in 3. 1. 3. Again this is no real difficulty, but, in addition, a new feature is observed which precludes solution of the whole problem. It turns out that the $\underset{\sim}{G}(x)$ solution, when put in the form $e^{-i\underset{\sim}{K}x}\ \underset{\sim}{A} + e^{i\underset{\sim}{K}x}\ \underset{\sim}{B}$ for large x, produces very ill-conditioned[23] matrices $\underset{\sim}{A}$ and $\underset{\sim}{B}$. We will define the term immediately. Our starting conditions for integration absolutely guarantee linear independence of the χ^j solutions, but we know nothing more definite than that.

An operational definition of an ill-conditioned matrix is that it is more difficult to achieve a given numerical accuracy in the inverse than one would expect on the basis of size alone. Many matrix systems have been investigated by Todd,[24] who decided that the measure of ill-conditioning was the magnitude of the ratio of the largest to the smallest eigenvalue, called the condition number. Consider the example,

$$\underset{\sim}{A} = \begin{pmatrix} a & a+\varepsilon \\ b & b-\varepsilon \end{pmatrix} .$$

The eigenvalues of $\underset{\sim}{A}$ are $a + b$ and $-\varepsilon$; as ε becomes small, or a and b large, the condition number $|(a + b)/\varepsilon|$ increases. One could picture the increase in condition number as the columns of $\underset{\sim}{A}$ tending toward linear dependence. In the limit of dependent columns, $\det(\underset{\sim}{A}) = 0$, but it is not necessary for the determinent to be near zero for $\underset{\sim}{A}$ to be ill-conditioned. For example, if $a = b = 10^6$ and $\varepsilon = 1$, $\det(\underset{\sim}{A}) = -2 \times 10^6$ and $|(a + b)/\varepsilon| = 2 \times 10^6$. Here we will set up a different definition of ill-conditioning, based on the concepts of linear independence of vectors. Consider any matrix $\underset{\sim}{C}$ as a collection of column vectors $\underset{\sim}{c}_j$:

$$\underset{\sim}{C} = (\cdots \underset{\sim}{c}_i \cdots \underset{\sim}{c}_j \cdots) . \qquad 3\text{-}46$$

Project out of $\underset{\sim}{c}_j$ the component of $\underset{\sim}{c}_i$ contained in it, leaving $\underset{\sim}{c}_j(i)$:

$$\underset{\sim}{c}_j(i) = \underset{\sim}{c}_j - \frac{\underset{\sim}{c}_i \cdot \underset{\sim}{c}_j}{\sqrt{\underset{\sim}{c}_i \cdot \underset{\sim}{c}_i}\sqrt{\underset{\sim}{c}_j \cdot \underset{\sim}{c}_j}} \underset{\sim}{c}_i . \qquad 3\text{-}47$$

If the norm of $\underset{\sim}{c}_j(i)$, $\|\underset{\sim}{c}_j(i)\|$, is small compared to the norm of $\underset{\sim}{c}_j$, we say that $\underset{\sim}{c}_i$ and $\underset{\sim}{c}_j$ are nearly linearly dependent. If for any or all pairs, i and j, of columns in a matrix $\underset{\sim}{c}$ we observe that $\|\underset{\sim}{c}_j(i)\| / \|\underset{\sim}{c}_j\|$ is small, the matrix is ill-conditioned by our definition. This is what we observe in the $\underset{\sim}{A}$ and $\underset{\sim}{B}$ of the asymptotic form of $\underset{\sim}{G}(x)$ (3-28) and in the columns of $\underset{\sim}{G}(x)$ itself at any point in the asymptotic region when we directly integrate the matrix Schrödinger equation as prescribed in 3. 2 .

Let us follow the behavior of two columns, $\underset{\approx}{g}_i(x)$ and $\underset{\approx}{g}_j(x)$, of $\underset{\sim}{G}(x)$ using 3-43 as starting conditions. At the starting point $\|\underset{\approx}{g}_i(x_0)\|$, $\|\underset{\approx}{g}_j(x_0)\|$, and $\|\underset{\approx}{g}_j(i)\|$ are all 1 because $\underset{\sim}{G}(x_0) = \underset{\sim}{I}$. As we progress out of the potential by integrating 3-21 (with $\underset{\sim}{G}(x)$), $\|\underset{\approx}{g}_i(x)\|$ and $\|\underset{\approx}{g}_j(x)\|$ both become large, but $\|\underset{\approx}{g}_j(i)\|$ remains small, so that the ratio $\|\underset{\approx}{g}_j(i)\| / \|\underset{\approx}{g}_j\|$ becomes small. In other words, we do not observe a corresponding rise in magnitude of the degree of linear independence, defined by $\|\underset{\approx}{g}_j(i)\|$, to compensate for the increase in magnitude of the $\underset{\approx}{g}_i$ vectors. This is the observed phenomenon which prevents the calculation of $\underset{\sim}{A}^{-1}$, needed in 3-32 for the transition amplitude evaluation. In table 1 we give the numerical data illustrating the above discussion.

3. 3. 2 Re-orthogonalization procedure

In section 3. 1. 3 we described the re-normalization of solutions to the one-dimensional Schrödinger equation; it involved an operation on $\varphi(x)$ at various points during the integration. The reason for that discussion was to lead into the method of re-orthogonalization which follows.

For purposes of numerical integration, we break 3-45 into the two first order equations:

$$\frac{d\,\underset{\sim}{G}'(x)}{dx} = (\underset{\sim}{V}(x) - \underset{\sim}{K}^2)\,\underset{\sim}{G}(x)$$

$$\frac{d\,\underset{\sim}{G}(x)}{dx} = \underset{\sim}{G}'(x) \qquad 3\text{-}48$$

which are equivalent in all ways to 3-45. We remember that $\underset{\sim}{G}(x)$ relates to the $\chi^j(x, y)$ solutions. Suppose we retain $N + 1$ terms in the state expansions; then our matrix solution is $(N+1) \times (N+1)$ in size, and the sums run from zero to N. Beginning with boundary conditions like 3-43 at x_0, we use 3-48 to integrate to x_1; there we have $\underset{\sim}{G}(x_1)$ and $\underset{\sim}{G}'(x_1)$ on hand as arrays of numbers. These also define the $\chi^j(x, y)$ at x_1 by means of 3-24:

$$\chi^j(x_1, y) = \sum_{i=0}^{N} g_i^j(x_1)\,\varphi_i(y)$$

$$\left.\frac{\partial\chi^j(x, y)}{\partial x}\right|_{x=x_1} = \sum_{i=0}^{N} g_i'^j(x_1)\,\varphi_i(y) \qquad 3\text{-}49$$

where $g_i'^j(x) \equiv \frac{d}{dx}\, g_i^j(x)$. Since the χ^j are independent solutions, we may form a new linearly independent set by taking linear combinations of the $\chi^j(x, y)$. Let the new set be $\xi^i(x, y)$:

$$\xi^i(x, y) = \sum_{j=0}^{N} c_j^i\, \chi^j(x, y)\,. \qquad 3\text{-}50$$

Expand:

$$\xi^{i}(x, y) = \sum_{j=0}^{N} h_{j}^{i}(x)\, \varphi_{j}(y) \tag{3-51}$$

and define the new matrices:

$$\begin{aligned} (\underset{\sim}{H}(x))_{nm} &= h_{n}^{m}(x) \\ \underset{\sim}{H}'(x) &= \frac{d}{dx} \underset{\sim}{H}(x) \\ (\underset{\sim}{C})_{nm} &= c_{n}^{m} \;. \end{aligned} \tag{3-52}$$

Combining 3-49, 3-50, and 3-51, we see that

$$\underset{\sim}{H}(x) = \underset{\sim}{G}(x)\, \underset{\sim}{C} \tag{3-53}$$

and

$$H'(x) = \underset{\sim}{G}'(x)\, \underset{\sim}{C} \;. \tag{3-54}$$

Thus, transforming from the basis χ^{j} to the basis ξ^{i} is equivalent to multiplication of the solution $\underset{\sim}{G}(x)$ on the right by a constant matrix $\underset{\sim}{C}$. The transformed solutions are $\underset{\sim}{H}(x)$. At the point x_1, we had our old solutions as $\underset{\sim}{G}(x_1)$ and $\underset{\sim}{G}'(x_1)$. The transformed solutions at x_1 have function and slope values as given by 3-53 and 3-54:

$$\underset{\sim}{H}(x_1) = \underset{\sim}{G}(x_1)\,\underset{\sim}{C} \qquad 3\text{-}55$$

$$\underset{\sim}{H}'(x_1) = \underset{\sim}{G}'(x_1)\,\underset{\sim}{C}\ . \qquad 3\text{-}56$$

We have not yet specified $\underset{\sim}{C}$. Naturally, it must not be singular or we could not claim the basis $\xi^i(x, y)$ was independent. What is desired is to find a transformation $\underset{\sim}{C}$ that will remove the tendency of $\underset{\sim}{G}$ to linear dependence. We opt to this by minimizing the ill-conditioning of $\underset{\sim}{H}(x_1)$, which is $\underset{\sim}{G}(x_1)\,\underset{\sim}{C}$. This minimum of ill-conditioning occurs when $\underset{\sim}{h}_j(i)$ (defined as in 3-47) is $\underset{\sim}{h}_j$ for all i and j, $i \neq j$. The obvious matrix having this property is the identity, $\underset{\sim}{I}$. All that is required is that the columns $\underset{\sim}{h}_j$ of $\underset{\sim}{H}(x_1)$ be orthogonal. Choosing $\underset{\sim}{C}$ such that:

$$\underset{\sim}{I} = \underset{\sim}{H}(x_1) = \underset{\sim}{G}(x_1)\,\underset{\sim}{C} \qquad 3\text{-}57$$

implies:

$$\underset{\sim}{C} = (\underset{\sim}{G}(x_1))^{-1}\ . \qquad 3\text{-}58$$

Consequently, from 3-55 and 3-56,

$$\begin{aligned} \underset{\sim}{H}(x_1) &= \underset{\sim}{I} \\ \underset{\sim}{H}'(x_1) &= \underset{\sim}{G}'(x_1)(\underset{\sim}{G}(x_1))^{-1} \end{aligned} \qquad 3\text{-}59$$

and from 3-53 and 3-54

$$\begin{aligned} \underset{\sim}{H}(x) &= \underset{\sim}{G}(x)\,(\underset{\sim}{G}(x_1))^{-1} \\ \underset{\sim}{H}'(x) &= \underset{\sim}{G}'(x)\,(\underset{\sim}{G}(x_1))^{-1}. \end{aligned} \tag{3-60}$$

The particular transformation evident in 3-60 has raised the conditioning of $\underset{\sim}{H}(x_1)$ to the optimum value. Accepting this, we use 3-59 as starting conditions to begin integration at x_1. If the columns of $\underset{\sim}{H}(x)$ again tend toward linear dependence, we repeat the process described at another point x_2, and so on as necessary. In practice, we repeat the "re-orthogonalization" transform (defined by 3-59) at regular intervals throughout the range of integration in x. A more efficient procedure would be to examine the trend toward dependence and re-orthogonalize only as often as necessary.

3.3.3 Discussion of re-orthogonalization

First of all, the succession of transformations applied to the original solution $\underset{\sim}{G}(x)$ still leaves a set of linearly independent solutions to the Schrödinger equation which are regular. The crucial point is that we examined the solutions that we were integrating and performed a transformation on them to remove a property that was developing. If we had waited until the whole integration had been performed, we would have found that this property precluded solution. At intermediate stages of integration, we can apparently rectify the bad property as it appears in small doses. To be more quantitative, let the succession of solutions be denoted by $\underset{\sim}{G}_{(i)}(x)$:

$$\begin{aligned} \underset{\sim}{G}_{(1)}(x) &= \underset{\sim}{G}_{(0)}(x)(\underset{\sim}{G}_{(0)}(x_0))^{-1} \\ \underset{\sim}{G}_{(2)}(x) &= \underset{\sim}{G}_{(1)}(x)(\underset{\sim}{G}_{(1)}(x_1))^{-1} \end{aligned} \tag{3-61}$$

and so on

where x_i denotes the points at which we applied the re-orthogonalization transform. One can show by induction that 3-61 implies:

$$\underset{\sim}{G}_{(n+1)}(x) = \underset{\sim}{G}_{(0)}(x)(\underset{\sim}{G}_{(0)}(x_n))^{-1} \tag{3-62}$$

and, either by an analogous induction process, or directly from 3-62:

$$\underset{\sim}{G}'_{(n+1)}(x) = \underset{\sim}{G}'_{(0)}(x)(\underset{\sim}{G}_{(0)}(x_n))^{-1} \quad . \tag{3-63}$$

Now, if we had continued with the solution $\underset{\sim}{G}_{(0)}(x)$ into the asymptotic region, we would have tried to determine $\underset{\sim}{B}_{(0)}\underset{\sim}{A}^{-1}_{(0)}$ from:

$$\underset{\sim}{G}_{(0)}(x) \underset{x\to\infty}{=} e^{-i\underset{\sim}{K}x}\underset{\sim}{A}_{(0)} + e^{i\underset{\sim}{K}x}\underset{\sim}{B}_{(0)} \tag{3-64}$$

as prescribed in 3-32. Using re-orthogonalization, we determine $\underset{\sim}{B}_{(n)}\,\underset{\sim}{A}^{-1}_{(n)}$ from:

$$\underset{\sim}{G}_{(n)}(x) \underset{x\to\infty}{=} e^{-i\underset{\sim}{K}x}\,\underset{\sim}{A}_{(n)} + e^{i\underset{\sim}{K}x}\,\underset{\sim}{B}_{(n)}\,. \qquad 3\text{-}65$$

Whether or not it is obvious, $\underset{\sim}{B}_{(0)}\underset{\sim}{A}_{(0)}^{-1} = \underset{\sim}{B}_{(n)}\underset{\sim}{A}_{(n)}^{-1}$, simply because the correct scattering solution is unique. The advantage in 3-65 is that the numerical solution is feasible, while it is observed not to be for 3-64 with the problems we have considered. One can show from 3-62, 3-64, and 3-65 that:

$$\begin{aligned} \underset{\sim}{A}_{(n)} &= \underset{\sim}{A}_{(0)}(G_{(0)}(x_{n-1}))^{-1} \\ \underset{\sim}{B}_{(n)} &= \underset{\sim}{B}_{(0)}(G_{(0)}(x_{n-1}))^{-1}. \end{aligned} \qquad 3\text{-}66$$

When we invert $A_{(n)}$, we have already "built in" the inverse of an ill-conditioned matrix, $G_{(0)}(x_{n-1})$.

3.3.4 Relation to Ricatti equation

If one repeats the process of re-normalization (3.1.3) of the one-dimensional Schrödinger equation at every increment of integration, one can construct a differential equation for the completely re-normalized solution. Starting with

$$-\frac{d^2\varphi(x)}{dx^2} + V(x)\,\varphi(x) = k^2\varphi(x)\,. \qquad 3\text{-}67$$

Define $\frac{d\varphi(x)}{dx} = \varphi'(x)$, so 3-67 may be written:

$$\frac{d\varphi'(x)}{dx} = (V(x) - k^2)\varphi(x)$$

$$\frac{d\varphi(x)}{dx} = \varphi'(x) \ . \tag{3-68}$$

Let the re-normalized solution be $\bar{\varphi}(x)$ and the re-normalized derivative be $\bar{\varphi}'(x)$. Then:

$$\bar{\varphi}(x + \Delta x) = \frac{\varphi(x + \Delta x)}{\varphi(x + \Delta x)} = 1$$

$$\bar{\varphi}'(x + \Delta x) = \frac{\varphi'(x + \Delta x)}{\varphi(x + \Delta x)} \ . \tag{3-69}$$

From 3-68, in incremental form,

$$\varphi'(x + \Delta x) = \varphi'(x) + \Delta x(V(x) - k^2)\varphi(x)$$

$$\varphi(x + \Delta x) = \varphi(x) + \Delta x\,\varphi'(x) \ . \tag{3-70}$$

Substituting 3-70 into the last expression in 3-69, we have:

$$\bar{\varphi}'(x + \Delta x) = \Delta x\frac{(V(x) - k^2)\varphi(x)}{\varphi(x) + \Delta x\varphi'(x)} + \frac{\varphi'(x)}{\varphi(x) + \Delta x\varphi'(x)} \ . \tag{3-71}$$

Dividing the fractions, keeping only order Δx and larger, we have:

$$\bar{\varphi}'(x + \Delta x) = \Delta x(V(x) - k^2) + \frac{\varphi'(x)}{\varphi(x)} \left(1 - \Delta x \frac{\varphi'(x)}{\varphi(x)}\right) . \qquad 3\text{-}72$$

The expression $\varphi'(x)/\varphi(x)$ is just $\bar{\varphi}'(x)$, the re-normalized derivative at x. So, from 3-72:

$$\bar{\varphi}'(x + \Delta x) = \bar{\varphi}'(x) + \Delta x(V(x) - k^2) - \Delta x (\bar{\varphi}'(x))^2 . \qquad 3\text{-}73$$

Dividing both sides of 3-73 by Δx and taking the limit $\Delta x \to 0$, we have:

$$\frac{d\bar{\varphi}'(x)}{dx} = V(x) - k^2 - (\bar{\varphi}'(x))^2 . \qquad 3\text{-}74$$

From the first of 3-69:

$$\frac{d\bar{\varphi}(x)}{dx} = 0 . \qquad 3\text{-}75$$

The starting conditions are,

$$\begin{aligned} \bar{\varphi}(x) &= 1 \\ \bar{\varphi}'(x) &= \lambda \end{aligned} \qquad 3\text{-}76$$

deduced from 3-13 and 3-69. Equation 3-74 is just the Ricatti equation,[25] which might have been obtained from 3-67 by the dependent variable transformation: $\bar{\varphi}'(x) = \frac{d\varphi(x)}{dx} / \varphi(x)$. In exact analogy to this analysis, one could find that the incrementally re-orthogonalized matrix equation,

$$-\frac{d^2 \underset{\sim}{G}(x)}{dx^2} + \underset{\sim}{V}(x)\,\underset{\sim}{G}(x) = \underset{\sim}{K}^2\,\underset{\sim}{G}(x) \qquad 3\text{-}77$$

can be converted to the matrix Ricatti system:

$$\begin{aligned} \frac{d}{dx}\,\underset{\sim}{\bar{G}}(x) &= 0 \\ \frac{d}{dx}\,\underset{\sim}{\bar{G}}'(x) &= \underset{\sim}{V}(x) - \underset{\sim}{K}^2 - (\underset{\sim}{\bar{G}}'(x))^2 \end{aligned} \qquad 3\text{-}78$$

with starting conditions:

$$\begin{aligned} \underset{\sim}{\bar{G}}(x_0) &= \underset{\sim}{I} \\ \underset{\sim}{\bar{G}}'(x_0) &= \underset{\sim}{\lambda} \end{aligned} \qquad 3\text{-}79$$

based on 3-43.

We do not use equation 3-74 because it diverges periodically in the region where $V(x) < k^2$. This is obvious from $\bar{\varphi}'(x) = \frac{d\varphi(x)}{dx} / \varphi(x)$, because the Schrödinger equation solutions for impenetrable barrier problems have the asymptotic form $\varphi(x) \underset{x \to \infty}{\to} \sin(kx + \delta)$; consequently, $\bar{\varphi}'(x) \underset{x \to \infty}{\to} k \cot(kx + \delta)$ and this diverges periodically in the asymptotic region. The same behavior is expected of $\underset{\sim}{\bar{G}}'(x)$ for analogous reasons. One might use the Ricatti equation in high regions of $V(x)$, i. e., $V(x) > k^2$, and switch to the Schrödinger equation thereafter. The efficiency of this method has not been examined.

4. RESTRICTIONS ON THE GENERALITY OF OUR METHODS

As derived in sections 2. and 3., we have restricted our multi-channel invariant imbedding and re-orthogonalization methods to the case where $H_0(y)$ has a complete, discrete spectrum of eigenstates. Thus, we have eliminated dissociation and reactive scattering from consideration, i. e., where the initial arrangement channel $A + (B, C)$ could end up as $(A, B) + C$, $(A, C) + B$, or $A + B + C$. This notation is explained in 1. 2. 3. In this section we examine the reasons for the restriction to single arrangement channel scattering and give the attempts to overcome it.

4. 1 Dissociation

Consider a system allowing dissociation: $H_0(y)$ has a complete set of discrete and continuum eigenstates, $\varphi_n(y)$ and $\varphi_k(y)$, respectively. We assume $V_I(x, y)$ does not have enough binding character to form bound states. The expansion of the total wavefunction in eigenstates of $H_0(y)$ must be written as

$$\psi(x, y) = \sum_n f_n(x)\,\varphi_n(y) + \int dk\, f_k(x)\,\varphi_k(y) \qquad 4\text{-}1$$

and the resolvent of $H - V_I - E$ (defined in 2. 2. 1) must be expressed as

$$G(x, y;\; x', y') = -\sum_n \varphi_n^*(y)\, \varphi_n(y')\, \frac{e^{ik_n|x - x'|}}{2ik_n}$$

$$- \int dk'\, \varphi_{k'}^*(y)\, \varphi_{k'}(y)\, \frac{e^{ik(k')|x - x'|}}{2ik(k')} . \qquad 4\text{-}2$$

Thus, neither the invariant imbedding nor re-orthogonalization methods would have a discrete matrix system of equations. Moreover, the matrix elements of V_I between the continuum states of $H_0(y)$ are singular. A possible resolution is to use the "eigen-differential" method of Kemble,[26] replacing the continuous spectrum of $H_0(y)$ by a discrete one having square integrable properties. This is equivalent to using a large, but finite, box normalized system. Since we must attempt to extrapolate to the continuum limit, this procedure requires extensive investigation into convergence properties. We should add that the continuum is only a serious problem when it is accessible, or almost so, as a final state. Otherwise, we approximate $H_0(y)$ with a Hamiltonian having nearly the same low energy eigenstates, but with no continuum. This has been done in our diatom Hamiltonians, where we assume the binding potential is a harmonic well rather than a more realistic potential allowing dissociation at high energies.

4.2 Reactive Scattering

For reactive scattering, $H_0(y)$ must have a continuum and $V_I(x, y)$ must be able to form bound states. The asymptotic form of $\psi(x, y)$ must allow for bound states in the initial arrangement channel A + (B, C), and for bound states in the other arrangement channel (A, B) + C. We assume (A, C) + B does not exist for simplicity of discussion. The expansions 4-1 and 4-2 are still valid, since the whole spectrum of $H_0(y)$ is complete, but the continuum solutions of $H_0(y)$ are being used to form the bound states of V_I in the arrangement channel (A, B) + C. This necessitates the use of continuum expansions and restricts the re-orthogonalization method as was previously discussed in 4.1 .

Our use of the resolvent of $H - V_I - E$ was to construct the integral equation incorporating the asymptotic scattering conditions on $\psi(x, y)$. A new and serious difficulty arises when we use 4-2 as for the resolvent in reactive scattering, since it does not contain the explicit form of the outgoing states in the arrangement channel (A, B) + C. Faddeev[6, 7] has resolved this by using two (or more) resolvents in a coupled system of integral equations. Together, the resolvents contain all of the necessary asymptotic behavior of the whole solution. The hope is that we can use the Faddeev system with only discrete terms in the resolvent expansions (like 4-2) and obtain a discrete matrix system that our methods will handle.

4.2.1 The multi-arrangement channel integral equation

Eyges[27] has worked with three-body systems and developed a formalism incorporating the salient features of Faddeev's theory. The following is based on both approaches. Consider a collinear system of three bodies, A, B, and C, in the barycentric subspace with two arrangement channels: (A, B) + C and A + (B, C). There are two coordinate systems appropriate, one for each arrangement. When A is removed to infinity, we have channel states:

$$\chi^{\pm}_{1n}(x_1, y_1) = e^{\pm ik_{1n}x_1}\,\varphi_{1n}(y_1) \tag{4-3}$$

where y_1 is the separation of B and C, and x_1 is the distance of A from the center of mass of (B, C). $\varphi_{1n}(y_1)$ are the bound state eigenfunctions of (B, C). When C is removed to infinity, we have the channel states:

$$\chi^{\pm}_{2n}(x_2, y_2) = e^{\pm ik_{2n}x_2}\,\varphi_{2n}(y_2) \tag{4-4}$$

where y_2 is the separation of A and B, and x_2 is the distance of C from the center of mass of (A, B). $\varphi_{2n}(y_2)$ are the (A, B) bound states. k_{1n} and k_{2n} are determined from energy conservation. The total wavefunction ψ is now written as $\psi^1 + \psi^2$, where ψ^1 is localized in the configuration space spanned by 4-3 and ψ^2 in that spanned by 4-4. Thus, we may expand:

$$\begin{aligned} \psi^1 &= \sum_n f^1_n(x_1)\,\varphi_{1n}(y_1) \\ \psi^2 &= \sum_n f^2_n(x_2)\,\varphi_{2n}(y_2)\ . \end{aligned} \tag{4-5}$$

The sums run over the bound states of (B, C) and (A, B) respectively. So far we have done no more than assume a two-basis expansion in bound states was sufficient for the total wavefunction:

$$\psi = \psi^1 + \psi^2 = \sum_n f_n^1(x_1)\, \varphi_{1n}(y_1) + \sum_n f_n^2(x_2)\, \varphi_{2n}(y_2) \qquad 4\text{-}6$$

which is very reasonable as long as the total energy is low enough to prevent dissociation.

Channel states 4-3 and 4-4 are, respectively, the solutions of:

$$\begin{aligned} (H - V_{AB} - E)\, \chi_{1n}^{\pm} &= 0 \\ (H - V_{BC} - E)\, \chi_{2n}^{\pm} &= 0 \end{aligned} \qquad 4\text{-}7$$

where we assume there are only the two pair potentials, V_{AB} and V_{BC}, present in the total Hamiltonian H. The Schrödinger equation is:

$$(H - E)\, \psi = 0 \,. \qquad 4\text{-}8$$

Introducing $\psi^1 + \psi^2$ for ψ, and rearranging some potential terms:

$$(H - E)\psi^1 + (H - E)\psi^2 = 0 \qquad 4\text{-}9$$

or

$$(H - V_{AB} - E)\psi^1 + (H - V_{BC} - E)\psi^2 = -V_{AB}\psi^1 - V_{BC}\psi^2. \qquad 4\text{-}10$$

We write 4-10 as the sum of the two equations:

$$\begin{aligned} (H - V_{AB} - E)\psi^1 &= -V_{BC}\,\psi^2 \\ (H - V_{BC} - E)\psi^2 &= -V_{AB}\,\psi^1 \end{aligned} \qquad 4\text{-}11$$

which defines ψ^1 and ψ^2 (4-10 only defines the sum $\psi^1 + \psi^2$). The resolvents of $H - V_{AB} - E$ and $H - V_{BC} - E$ are known:[19]

$$G^1(x_1, y_1; x_1', y_1') = \langle x_1, y_1|\,\frac{1}{H - V_{AB} - E}\,|x_1', y_1'\rangle$$

$$= -\sum_n \varphi_{1n}(y_1)\,\varphi_{1n}^*(y_1')\,\frac{e^{ik_{1n}|x_1 - x_1'|}}{2ik_{1n}}$$

$$G^2(x_2, y_2;\; x_2', y_2') = \langle x_2, y_2|\,\frac{1}{H - V_{BC} - E}\,|x_2', y_2'\rangle$$

$$= -\sum_n \varphi_{2n}(y_2)\,\varphi_{2n}^*(y_2')\,\frac{e^{ik_{2n}|x_2 - x_2'|}}{2ik_{2n}} \qquad 4\text{-}12$$

where we have used the outgoing form, retaining only bound states. The integral equations equivalent to 4-11 with correct scattering asymptotic forms for an incident wave in channel state χ^{-}_{1i} are:

$$\psi^1_i = \chi^{-}_{1i} - \iint d\tau' \, G^1 \, V_{BC} \, \psi^2_i$$

$$\psi^2_i = - \iint d\tau' \, G^2 \, V_{AB} \, \psi^1_i \, . \qquad 4\text{-}13$$

Faddeev writes his equations in terms of the two-body T operators. Knowing operator identities of the form $G^{\alpha}V_{\alpha} = G_0 T_{\alpha}$, we see that 4-13 is the same as his result.

We now have the differential equation 4-8, into which we could substitute expansion 4-6, and try to obtain a matrix differential equation for the $f^1_n(x_1)$ and $f^2_n(x_2)$ functions. Because of the two coordinate systems present, the kinetic energy operators act on the unknown functions and the bound state solutions $\varphi_{1n}(y_1)$ and $\varphi_{2n}(y_2)$. This is just restating the fact that φ_{1n} and φ_{2n} are eigenfunctions of different Hamiltonians. The simple fact is that we cannot set up a matrix differential like 3-21 for the system. System 4-13, however, has an appeal that deserves investigation.

4.2.2 Matrix form of re-arrangement integral equations

Using expansions 4-5 for ψ^1 and ψ^2 (with i to label initial state), and expansions 4-12 for G^1 and G^2, we write 4-13 as:

$$\sum_n f_n^{1i}(x_1)\,\varphi_{1n}(y_1) = e^{-ik_{1i}x_1}\,\varphi_{1i}(y_1)$$

$$+\int dx_1'\int dy_1'\sum_\ell \varphi_{1\ell}(y_1)\,\varphi_{1\ell}^*(y_1')\,\frac{e^{ik_{1\ell}|x_1-x_1'|}}{2ik_{1\ell}}$$

$$V_{BC}(y_1')\sum_m f_m^{2i}(x_2')\,\varphi_{2m}(y_2')$$

and

$$\sum_n f_n^{2i}(x_2)\,\varphi_{2n}(y_2) = \int dx_2'\int dy_2'\sum_\ell \varphi_{2\ell}(y_2)$$

$$\varphi_{2\ell}^*(y_2')\,\frac{e^{ik_{2\ell}|x_2-x_2'|}}{2ik_{2\ell}}\,V_{AB}(y_2')\sum_m f_m^{1i}(x_1')\,\varphi_{1m}(y_1') \qquad 4\text{-}14$$

where, under the integral, we know that $x_1' = x_1'(x_2', y_2')$ and $y_1' = y_1'(x_2', y_2')$ and the inverse coordinate relation also. These equations are simplified as follows: (1) Take inner products of the first equation in 4-14 with the functions $\varphi_{1j}(y_1)$; this generates a coupled set of equations without the sum over n and ℓ present. Do the same for the second equation with $\varphi_{2j}(y_2)$, giving another coupled set. (2) Substitute the expression resulting from the latter for $f_j^{2i}(x_2)$ into the RHS of the former equation, giving one coupled system for the $f_j^{1i}(x_1)$ unknowns:

$$f_j^{1i}(x_1) = e^{-ik_{1i}x_1}\,\delta_{ij} + \int dx_1' \int dx_1''$$

$$\frac{e^{ik_{1j}|x_1-x_1'|}}{2ik_{1j}} \sum_m V_{jm}(x_1', x_1'')\, f_m^{1i}(x_1'') \qquad 4\text{-}15$$

where:

$$V_{jm}(x_1', x_1'') = \int dy_1' \int dy_1''\, \varphi_{1j}(y_1')\, V_{BC}(y_1')$$

$$\left[\sum_\ell \varphi_{2\ell}(y_2')\, \varphi_{2\ell}^*(y_2'')\, \frac{e^{ik_{2\ell}|x_2' - x_2''|}}{2ik_{2\ell}} \right]$$

$$V_{AB}(y_2'')\, \varphi_{1m}(y_1'') \; . \qquad 4\text{-}16$$

In these we have changed from the $\int dx_2'' \int dy_2''$ integration to $\int dx_1'' \int dy_1''$. In 4-16, one must know that $x_2 = x_2(x_1, y_1)$ and $y_2 = y_2(x_1, y_1)$ as mentioned earlier. In matrix form, 4-15 is expressed as:

$$\underset{\sim}{F}'(x_1) = e^{-i\underset{\sim}{K}_1 x_1} + \int dx_1' \int dx_1''$$

$$\frac{1}{2i\underset{\sim}{K}_1}\, e^{i\underset{\sim}{K}_1|x_1-x_1'|}\, \underset{\sim}{V}(x_1', x_1'')\, \underset{\sim}{F}^1(x_1'') \; . \qquad 4\text{-}17$$

The scalar analog to this would be:

$$f(x) = e^{-ikx} + \int dx' \int dx'' \frac{e^{ik|x-x'|}}{2ik} V(x', x'') f(x''). \qquad 4\text{-}18$$

If we cannot invariantly imbed 4-18, there is little hope of doing so for 4-17. We have no proof that it is impossible to construct a first order differential equation equivalent to 4-18, but the previous potential cutoff method does not work because of the non-local "potential", $V(x', x'')$. Let us examine this. The Schrödinger-like equation for 4-18 is:

$$-\frac{d^2 f(x)}{dx^2} + \int dx' \, V(x, x') \, f(x') = k^2 f(x) . \qquad 4\text{-}19$$

The potential term says that the value at x depends on $f(x)$ over, possibly, all space. 4-19 is an integro-differential equation with no assurance of a pure differential equivalent. All physical potentials are local, as $V(x, x')$ would be if it were $V(x, x') \, \delta(x-x')$.

There are several ways of introducing cutoffs into 4-18: in x', in x'', or in both x' and x''. None of these enable one to perform the same treatment as done in section 2. to develop the invariant imbedding equation. One simply cannot relate the amplitudes to the derivatives of the amplitudes with respect to the cutoff parameter.

5. NUMERICAL TESTING OF THE MULTI-CHANNEL METHODS

There are several means available to check the accuracy of our calculations. Since all of these are used to some extent, the implications of each are discussed here.

First, there are the properties of time-reversal and normalization of probability.[19] Time reversal necessitates that the probability of going from state i to state j, P_{ij}, be the same as the probability of going from state j to state i, P_{ji}, at the same total energy. Probability, by definition, necessitates that the sum of the individual probabilities of going to all possible final states from a given initial state is 1. In the methods we use, all P_{ij} are calculated independently; by examining how well our results obey the laws:

$$P_{ij} = P_{ji} \tag{5-1}$$

$$\sum_{\text{all } j} P_{ij} = 1 \tag{5-2}$$

we have an internal test of accuracy for any calculation. This test, as will be pointed out later, serves mainly as an estimate of integration error.

The second accuracy check is to compare results with calculations performed by other people. This does not enable one to check the accuracy of any new results of course. However, one can re-solve the old problems by the new methods and compare the results, or simply use both old and new methods on some problem that can be solved by both.

The third check lies in our possession of two methods based on different fundamental theories. We actually developed the re-orthogonalization method to check the results of invariant imbedding. Throughout the remainder of the text, invariant imbedding will be referred to as II, and the re-orthogonalization method as DRILL, from Direct Reduction of ILL-conditioning. In a more specific sense, these code names refer to calculations performed by the computer programs written by the author to implement those methods.

5.1 Hard-sphere Interaction Model

A model problem in which the interaction potential $V_I(x, y)$ is replaced with a hard-sphere interaction can be solved with good numerical accuracy for a limited class of inelastic scattering problems. The interaction is not treated as a potential, but is used as a boundary condition on the wavefunction. Suppose there is only one internal coordinate y of $H_0(y)$ and the interaction is a function of the separation of the incident particle and the bound particle. Our hard-sphere interaction is defined as:

$$V_I^{HS}(x, y) = V_I^{HS}(x-y) = \begin{cases} 0 & x \geq y \\ \infty & x < y \,. \end{cases} \qquad 5\text{-}3$$

The boundary condition on the wavefunction is that:

$$\psi(x, y)\big|_{x=y} = 0 \,. \qquad 5\text{-}4$$

The scaled Schrödinger equation is (see 5. 2. 1 for the procedures of obtaining this form from the equation written in natural units):

$$(H_0(y) - \frac{1}{m}\frac{\partial^2}{\partial x^2} + V_I^{HS}(x-y) - E)\,\psi^i(x, y) = 0 \qquad 5\text{-}5$$

where i labels a particular incident state. For $x \geq y$, the equation is separable into product solutions, so $\psi^i(x, y)$ is expressible as a linear combination of these:

$$x \geq y \qquad \psi^i(x, y) = \sum_n (c_n^i e^{-ik_n x} \varphi_n(y) + d_n^i e^{ik_n x} \varphi_n(y)) \qquad 5\text{-}6$$

where $\varphi_n(y)$ are the known orthonormal eigenfunctions of $H_0(y)$:

$$H_0(y)\,\varphi_n(y) = W_n\,\varphi_n(y)$$

$$\langle \varphi_n(y) \mid \varphi_m(y) \rangle = \delta_{nm} \qquad 5\text{-}7$$

$$n, m = 0, 1, 2, \cdots$$

and,

$$k_n = +\sqrt{m(E - W_n)} \qquad 5\text{-}8$$

$$n = 0, 1, 2, \cdots .$$

The asymptotic conditions required for scattering (unit incident wave and outgoing scattered waves) demand that

$$x \geq y \quad \psi^i(x,y) = e^{-ik_i x}\varphi_i(y) + \sum_{n=0}^{N-1} d_n^i\, e^{ik_n x}\varphi_n(y). \qquad 5\text{-}9$$

Then the excitation probabilities are given by

$$P_{if} = |d_f^i|^2\; k_f/k_i \; . \qquad 5\text{-}10$$

We have taken N terms in 5-9, so the sum terminates at N - 1, having begun at n = 0. Boundary condition 5-4 furnishes a unique determination of the d_n^i amplitudes. Combining 5-4 and 5-9:

$$\psi^i(x,y)\big|_{x=y} = 0 = e^{-ik_i y}\varphi_i(y) + \sum_{n=0}^{N-1} d_n^i\, e^{ik_n y}\varphi_n(y) \; . \qquad 5\text{-}11$$

Since the RHS of 5-11 is in the space spanned by the eigenfunctions of $H_0(y)$, we take inner products of both sides of this equation with $\varphi_j(y)$ and obtain the coupled system of linear equations:

$$0 = \langle\varphi_j(y)|\, e^{-ik_i y}\varphi_i(y)\rangle + \sum_{n=0}^{N-1} d_n^i\, \langle\varphi_j(y)|\, e^{ik_n y}\varphi_n(y)\rangle \qquad 5\text{-}12$$

$$j = 0, 1, 2, \cdots N\text{-}1 .$$

By using as many $\varphi_j(y)$ as there are terms retained in the state sum (N), 5-12 contains a sufficient number of equations to determine the d_n^i, $i, n = 0, 1, 2, \cdots N-1$. Defining matrices:

$$(\underset{\sim}{U})_{ij} = \langle \varphi_i(y) | e^{ik_j y} \varphi_j(y) \rangle$$

$$(\underset{\sim}{D})_{ij} = d_i^j \qquad i, j=0, 1, 2, \cdots, N-1 \qquad \text{5-13}$$

we can write 5-12 as the matrix equation:

$$0 = \underset{\sim}{U}^* + \underset{\sim}{U}\,\underset{\sim}{D} \qquad \text{5-14}$$

since the $\varphi_j(y)$ are real. The solution for the unknown involves inverting $\underset{\sim}{U}$:

$$\underset{\sim}{D} = -\underset{\sim}{U}^{-1}\underset{\sim}{U}^* . \qquad \text{5-15}$$

From $\underset{\sim}{D}$ one calculates the transition probabilities as prescribed in 5-10. A particular case of this model, in which the binding potential of the target was harmonic, has been treated by Shuler and Zwanzig.[28] The same problem was also investigated by Secrest and Johnson.[19]

Our formalisms do not allow for the incorporation of a hard-sphere interaction explicitly. However, we can use instead a very high, infinitely thick, square barrier:

$$V_I^{SB}(x-y) = \begin{cases} 0 & x \geq y \\ V^{SB} & x < y \end{cases} \qquad 5\text{-}16$$

or, using the Heaviside step function:

$$V_I^{SB}(x-y) = V^{SB}\,H(y-x) \ . \qquad 5\text{-}17$$

As V^{SB}, the height of the barrier, becomes large compared to the total energy E, the solutions of the hard-sphere model and the square barrier model should become identical.

5.1.1 Square well binding potential

There are two potentials which facilitate analytic handling of the bound states $\varphi_n(y)$ and furnish simple expressions for the $V_I^{SB}(x-y)$ matrix elements. These are the infinite square well and the harmonic oscillator potentials. Consider the square well first. Since we are only using this for a comparison of methods, we use the scaled equations directly without any reference to physical dimensions.

Our target particle is bound in a square well of scaled width π, and is struck by another particle of scaled mass m interacting with it via a hard-sphere interaction. The incident particle does not interact with the square well. Figure 2 presents a diagram of the collinear collision and a configuration space outline of the potentials. The bound particle eigenfunctions are $2/\pi \sin((n+1)y)$, $n = 0, 1, \ldots,$ with scaled energies $(n+1)^2$; the scaled wavenumbers of the incident particle are $+\sqrt{m(E - (n+1)^2)}$. For channels such that $(n+1)^2 > E$, the wavenumbers are positive imaginary and these virtual channels decay exponentially as x becomes large. The $\underset{\sim}{U}$ matrix (5-13) is given by:

$$(\underset{\sim}{U})_{ij} = \frac{2}{\pi} \int_0^{\pi} dy \sin((i+1)y)\, e^{ik_j y} \sin((j+1)y) \,. \qquad 5\text{-}18$$

For a given total scaled energy E and mass m, we solve 5-15 for increasing numbers, N, of states in the expansion 5-9 until convergence is achieved for the probabilities P_{ij}. The number of states in expansion 5-9 is the dimension of the square matrix $\underset{\sim}{U}$. It so happens that $\underset{\sim}{U}$ is a very ill-conditioned[23] matrix; one can seldom obtain $\underset{\sim}{U}^{-1}$ for N larger than 10.

II (invariant imbedding) was compared to this hard-sphere model. The matrix elements of the interaction potential, $V_I^{SB}(x-y)$, are:

$$(\underset{\sim}{V}(x))_{ij} = \frac{2}{\pi} \int_0^{\pi} \sin((i+1)y)\, V^{SB}\, H(y-x) \sin((j+1)y)dy \qquad 5\text{-}19$$

$$i, j = 0, 1, 2, \ldots$$

or:

$$(\underset{\sim}{V}(x))_{ij} = \begin{cases} V^{SB}\,\delta_{ij} & x \le 0 \\ \frac{2}{\pi} V^{SB} \int_x^{\pi} \sin((i+1)y)\,\sin((j+1)y)dy & 0 \le x \le \pi \\ 0 & \pi \le x \end{cases} \qquad 5\text{-}20$$

$$i, j = 0, 1, 2, \ldots \,.$$

Having these, we integrate 2-73 and obtain the probabilities from II. The convergence of the state expansion in II must also be tested, as well as the effective barrier height V^{SB}.

Figure 3 presents the convergence of the probabilities for the scaled parameters: E = 4.5, m = MASS = 1.0. There are two open channels at this total energy. V^{SB} is taken to be 70, which is about 16 times the total energy. In figure 3, ERROR is the Romberg integrator error control, explained in Appendix A. The hard-sphere interaction model (referred to as a Shuler-Zwanzig (S-Z) model because they first used it)[28] takes less than 1 sec per calculation of a set of probabilities for a fixed total energy and about 10 states in the state expansion. II takes on the order of 1'40" for a total number of states, N = 4, and with ERROR = 10^{-6}. The S-Z model converges very slowly as N is increased; it is so slow that the ill-conditioning of $\underset{\sim}{U}$ prevents accurate solution for N larger than 10 or 11. II converges much more rapidly. The slow convergence of the S-Z probabilities as a function of N, $P_{ij}(N)$, encouraged an effort to extrapolate the $P_{ij}(N)$ to the limit $P_{ij}(\infty)$.

The expression

$$P_{ij}(N) = P_{ij}(\infty) + \frac{1}{(N)^{\alpha}} A \qquad 5\text{-}21$$

furnished a good empirical fit to the calculated $P_{ij}(N)$. α and A also depend on i and j; they are obtained by guessing α and testing the consistency of the predicted $P_{ij}(\infty)$ for pairs $P_{ij}(N)$, $P_{ij}(N+1)$. Usually an α of 1 or 2 would be sufficient to give a consistent $P_{ij}(\infty)$ for all $P_{ij}(N)$ calculated. See Appendix B. The S-Z results do not obey time reversal as well as II; in figure 3 (and figures 4 and 5, to be discussed) P_{ij} and P_{ji} are given separately. For II, they coincide to better than 6 digits.

Figure 4 depicts the same problem as figure 3, except for the higher energy, E = 8.5. There are still only two open channels. The same observations hold for these results as for figure 3. Here we see a much faster convergence for the S-Z method however.

Figure 5 is for the higher energy E = 10.5, where three channels are open. For II, the P_{ij} and P_{ji} coincide to graphical accuracy. Here we show the effect of the square barrier height, V^{SB}, on the II calculated probabilities. The effect is small, even when V^{SB} is less than 5 times the total energy.

In conclusion we summarize the important observations: (1) II gives the same results as the completely independent S-Z method, to well within the inherent accuracy limitations of that method. (2) II is about 2 or 3 orders of magnitude slower than the S-Z hard-sphere interaction method, but the reason is that the Π method is much more general than the S-Z one, which is only applicable to hard-sphere interactions and uses that property explicitly as a boundary condition. (3) Π converges much faster than the S-Z method as the number of states retained in the expansion is increased.

5.1.2 Harmonic oscillator binding potential

Shuler and Zwanzig's[28] results for the excitation of a particle in a harmonic well by a hard-sphere collision are available. Secrest and Johnson[19] repeated the same calculations and confirmed the results. We did calculations for the same values of the parameters used by these authors with the Π method. This gives a completely external check on the method. The bound state eigenfunctions of $H_0(y) = -\partial^2/\partial y^2 + y^2$ are:

$$\varphi_n(y) = \frac{1}{\sqrt{2^n\, n!\, \sqrt{\pi}}}\, H_n(y)\, e^{-y^2/2} \qquad 5\text{-}22$$

$$n = 0, 1, 2, \ldots .$$

$H_n(y)$ are the Hermite polynomials. The eigenvalues are $2n + 1$:

$$H_0(y)\, \varphi_n(y) = (2n + 1)\, \varphi_n(y) \qquad 5\text{-}23$$

and the corresponding incident particle wavenumbers are given by

$$k_n = +\sqrt{m(E - (2n + 1))} \qquad 5\text{-}24$$

$$n = 0, 1, 2, \ldots .$$

The matrix elements of the infinitely thick square barrier are:

$$\begin{aligned}(\underset{\sim}{V}(x))_{nm} &= \int_{-\infty}^{\infty} \varphi_n(y)\, V^{SB}\, H(y-x)\, \varphi_m(y) dy \\ &= V^{SB} \int_{x}^{\infty} \varphi_n(y)\, \varphi_m(y)\, dy .\end{aligned} \qquad 5\text{-}25$$

Expression 5-25 is not easy to evaluate efficiently. One could do a numerical quadrature for every x, but instead we related all of the elements of $\underset{\sim}{V}(x)$ to simple analytic forms, some of which contained the error function. This is explained in Appendix C. Tables 2 and 3 give the comparison of II with the same problems solved by Secrest and Johnson and by Shuler and Zwanzig. The results again confirm the accuracy of II, within the limitations imposed by reading the published graphs.

We should mention that the Romberg integrator error control enables us to satisfy time reversal and the probability sum to 1 (5-1 and 5-2) as well as desired for a given problem simply by specifying a lower ERROR value. In table 2, for example, $P_{00} + P_{01} + P_{02} = 1.0000$ for 1 virtual state. Never are the sums in error by more than ± .0001. Time reversal was obeyed to the same accuracy (not shown). If we had integrated with a larger error bound, the integration would have been faster but less accurate. Table 3 gives all of the probability elements of a lower energy problem to demonstrate the accuracy of the Romberg integrator. If one examines the time reversal and normalization of probability relations (5-1 and 5-2) for data in table 3, it turns out that they are true to 6 or 7 decimal digits for both the two and three virtual state calculations. However, each individual probability is not that accurate, as they are changing in the second or third decimal place as more virtuals are included.

5.2 Comparison of DRILL and II with Published Soft Atom on Diatom Calculations

The method developed by Secrest and Johnson (S-J) appeared in publication[19] while we were developing our multi-channel theories. We used their results as a final check on both of our methods, the II (invariant imbedding) and DRILL (re-orthogonalization). The problem considered is the following: an atom A of mass m_A collides collinearly with a diatom BC, whose atoms have masses m_B and m_C, respectively. We label BC so that A collides with B. The bond between B and C is approximated by a harmonic bond with a force constant k_{BC}. The interaction between A and B is a repulsive exponential function of the separation, $\xi_A - \xi_B$. This interaction is chosen for mathematical simplicity, and because of its previous use in the distorted wave[29] and semiclassical time-dependent perturbation[30] solutions for the same problem.

5. 2. 1 Transformations on the Schrödinger equation

In laboratory coordinates, the Schrödinger equation is:

$$\left(- \frac{\hbar^2}{2m_C} \frac{\partial^2}{\partial \xi_C^2} - \frac{\hbar^2}{2m_B} \frac{\partial^2}{\partial \xi_B^2} + \frac{1}{2} k_{BC}(\xi_B - \xi_C - \xi_{EQ})^2 \right.$$

$$\left. - \frac{\hbar^2}{2m_A} \frac{\partial^2}{\partial \xi_A^2} + e^{-(\xi_A - \xi_B)/L} - \varepsilon\right)\psi^i(\xi_A, \xi_B, \xi_C) = 0 \qquad 5\text{-}26$$

where ε is the total energy, L is the length parameter that characterizes the range and steepness of the interaction, and ξ_{EQ} is the equilibrium separation of BC. Let us apply the following transformations: (1) remove the center-of-mass energy from ε, (2) measure energies in units of the ground state (zero point) energy of BC, and (3) measure length in units of $(\hbar^2/\mu_{BC}\, k_{BC})^{1/4}$. The resulting scaled equation is:

$$\left(- \frac{\partial^2}{\partial y^2} + y^2 - \frac{1}{m} \frac{\partial^2}{\partial x^2} + e^{-\alpha(x-y)} - E\right) \psi^i(x, y) = 0 \qquad 5\text{-}27$$

where y is the scaled separation of BC, x is the scaled distance of A from the center of mass of BC, and α is proportional to the reciprocal of a scaled L. See S-J[19] for details. The three scaled quantities m, α, and E now characterize our problem. The eigenfunctions of $H_0(y) = -\partial^2/\partial y^2 + y^2$ are the solutions defined in 5-22. The interaction matrix elements are:

$$
\begin{aligned}
(\underset{\sim}{V}(x))_{nm} &= \langle \varphi_n(y) | e^{-\alpha(x-y)} | \varphi_m(y) \rangle \\
&= e^{-\alpha x} \langle \varphi_n(y) | e^{\alpha y} | \varphi_m(y) \rangle \ .
\end{aligned}
\qquad \text{5-28}
$$

Thus, we need not evaluate $\underset{\sim}{V}(x)$ for every x, we only need evaluate the exponential $e^{-\alpha x}$ since it factors out. The matrix elements $\langle \varphi_n(y) | e^{\alpha y} | \varphi_m(y) \rangle$ are evaluated only once in any given integration. Since some references[31] for these elements are in error, we give the correct analytic form here:

$$
\begin{aligned}
&\langle \varphi_n(y) | e^{\alpha y} | \varphi_m(y) \rangle \\
&= \frac{1}{\sqrt{2^n\, n!\, \sqrt{\pi}}} \frac{1}{\sqrt{2^m\, m!\, \sqrt{\pi}}} \int_{-\infty}^{\infty} e^{-y^2} e^{\alpha y} H_n(y)\, H_m(y) dy \\
&\underset{n \geq m}{=} \sqrt{\frac{m!}{n!}} \left(\frac{\alpha}{\sqrt{2}}\right)^{n-m} e^{\alpha^2/4} \sum_{\ell=0}^{m} \frac{n!(\alpha^2/2)^{\ell}}{(m-\ell)!(n+\ell-m)!\ell!} \ .
\end{aligned}
\qquad \text{5-29}
$$

5.2.2 Testing of II and DRILL with atom on diatom problem

There are four variations in this problem with either II or DRILL that can effect the agreement with the published results. They are: (1) position of starting point for integration,

(2) position of stopping point for same, (3) number of states retained in the state expansions, and (4) the integration error. Our practice has been to vary these until our own calculations indicate convergence has been achieved to some prescribed accuracy, and then to compare the results to other calculations.

It turns out that these four preceding variations are almost independent in their effects. The integrator error is easiest to examine: we test the probability sum to one and time reversal conditions on our results. Let us define δ and ϵ as:

$$\delta = \max_{i} \left| \sum_{j} P_{ij} - 1 \right|$$

$$\epsilon = \max_{i,j} \left| (P_{ij} - P_{ji}) \right| . \qquad 5\text{-}30$$

This makes δ and ϵ the maximum errors observed in the sum and time reversal; δ and ϵ turn out to be of the same magnitude and vary directly with the local truncation error control on the Romberg integrator.

The starting point variation must be checked by repeating calculations until the individual probabilities no longer change as we move the starting point farther back into the classically inaccessible region of the interaction. A rule of thumb observation is that the starting point is adequate when the diagonal elements of $\underset{\sim}{V}(x)$ are 10 times larger than the total energy at that point.

The stopping point may be checked during any integration by temporarily stopping, calculating the probabilities, then integrating farther, re-calculating probabilities and checking for consistency. The long tail of the repulsive exponential interaction causes significant effects until the diagonal elements of $\underset{\sim}{V}(x)$ are less than 1/5,000 of the total energy E.

The convergence of the state expansions is the all-important remaining topic. For the atom or diatom problems, we can always increase the total number of states, N, until the probabilities do not change. This increase in dimension of our matrix equations, however, causes a large increase in computational time. One can easily reason that matrix multiplication and inversion times increase as the cube of the dimension, simply because N^3 multiplications are involved in one matrix multiplication, and roughly that in an inversion. We will discuss this shortly.

Figure 6 shows the convergence of DRILL for a solution of 5-27 with $E = 4.9455$, α = ALPHA = .2973, m = MASS = 1.25. There are two open channels. The top graph of figure 6 indicates that two virtual channels are sufficient for an accuracy of 1% in P_{01}, because adding one more channel changed P_{01} by less than that amount. The lower graph shows the variation of P_{01} with the starting point, using two virtual channels. A starting point of -10.0 gives P_{01} to 1% also. The results presented in figure 6 converge to a P_{01} of 0.87×10^{-4}. This should be 1.12×10^{-4} as given in table 4; we had used in our preliminary calculations an expression[31] for 5-29 that was in error by a small amount. The error does not affect the convergence properties we are testing, and it was corrected shortly after the calculations in figure 6 were performed.

Table 4 gives the II results for the same problem: E = 4.9455, MASS = 1.25, ALPHA = 0.2973. The published results of S-J are also given for comparison.

Table 5 gives DRILL results for the problem $E = 6.0$, $MASS = 0.2$, $ALPHA = 0.114$. Here there are three open channels.

In figure 7 we make a comparison of execution times (ET) on the Caltech IBM 7040-7094 for DRILL and II running under various conditions. The important feature is the variation of ET with total number of states, N. The previously mentioned fact that matrix multiplication times increase as the cube of the dimension shows up in a near cubic dependence of ET on N for similar ERROR control. The dependence of ET on ERROR can be seen from the DRILL calculations at $N = 4$. The execution time is almost perfectly linear in -log(ERROR). The relative speed of DRILL and II can also be checked; II requires almost four times the ET of DRILL for $N = 4$, $ERROR = 10^{-8}$. The starting point is seen to make only a small effect in total ET. We should add that DRILL and II give equally accurate results when the same number of states are retained (matrix systems of same dimension) and the integrator ERROR control is the same. We observed earlier that DRILL was four times faster than II.

Table 6 represents an effort to speed up the calculations, maintaining the minimum acceptable accuracy of about 1% in the individual probabilities. Section (a) is the standard double precision (16 decimal digits) Romberg integrator with DRILL. $ERROR = 10^{-4}$ was found to give a reasonable 1% error for all P_{ij}, measured from the time reversal average $(P_{ij} + P_{ji})/2$. Conversion to single precision arithmetic (8 decimal digits) reduced the ET by 1/3 and gave the same probabilities to 4 or more significant figures. This is mentioned in section (b).

Section (c) of table 6 results from the use of a 5'th order Adams-Moulton predictor integrator with a Runge-Kutta starter.[33] The step size, h, was increased from .035 to .37 over the range of integration according to:

$$h \approx \frac{1.1}{3 + e^{-\alpha x}} \, . \tag{5-31}$$

The integrator performed 30 integrations of size h, stopped, evaluated a new h from 5-31, repeated another 30 integrations, evaluated another h, and so on. $e^{-\alpha x}$ is proportional to the elements of $\underset{\sim}{V}(x)$. The guess was that a smaller step size was needed in the range of x where the off-diagonal elements of $\underset{\sim}{V}(x)$ were large and strongly coupling the system of differential equations (represented by $\underset{\sim}{F}(x)$ in section 4.) that we are integrating. When the elements of $\underset{\sim}{V}(x)$ become small, the system of equations become uncoupled and a larger step size is tolerable. This executed rapidly, reducing ET to 1'28". Section (d) is the results of S-J and an estimate of their computational time on an IBM 7040-7094 of 1'45".[32]

In conclusion, we have no difficulty obtaining agreement with the published calculations of either Shuler and Zwanzig or Secrest and Johnson. Only the latter authors have a method of the same general nature as our methods. The long range problem of computation time arises here, since calculations with, say, hundreds of states retained in either II or DRILL are out of the question if they must be done in minutes rather than hours on the computer. We feel that our methods have advantages over the method of S-J, both in an analytical and computational sense. This cannot be discussed here, especially since the computational comparisons have not been thorough or perhaps fair. As to analytical comparisons, we will only say that the S-J method is more akin to II than DRILL. S-J calculate with a set of equations that, if one takes the limiting differential form, become the invariant imbedding equations.

6. COLLINEAR DIATOM ON DIATOM COLLISIONS

The previous calculations have involved the excitation of a bound target system by an incident structureless particle. Energy transfer occurs between kinetic translational motion and the vibrational energy of the target; for atom or diatom systems with realistic soft interactions, the probability of this transfer is quite small. However, when two diatoms collide, not only is translational to vibrational (T-V) energy conversion possible, but also transfer of vibrational energy from one diatom to the other (V-V) with differing degrees of translational contribution can occur. It is expected that the probabilities of these V-V transfers may be large. In our investigation of this problem, we will present more details than previously given in section 5. for the numerical testing of the methods. In particular, we will give all of the explicit scaling transformations of the Schrödinger equation.

6.1 Scaling and Coordinate Transformations

Consider a collinear collision configuration between two diatoms, AB and CD, interacting via a function of the separation of the nearest end atoms B and C. Let us call CD the target, and AB the incident projectile. The laboratory coordinates of A, B, C, and D are ξ_A, ξ_B, ξ_C, and ξ_D; their masses are m_A, m_B, m_C, and m_D respectively. The Schrödinger equation for this system is:

$$\left(-\frac{\hbar^2}{2m_D}\frac{\partial^2}{\partial\xi_D^2}-\frac{\hbar^2}{2m_C}\frac{\partial^2}{\partial\xi_C^2}-\frac{\hbar^2}{2m_B}\frac{\partial^2}{\partial\xi_B^2}-\frac{\hbar^2}{2m_A}\frac{\partial^2}{\partial\xi_A^2}\right.$$

$$\left.+V_{CD}(\xi_C-\xi_D)+V_{AB}(\xi_A-\xi_B)+V_I(\xi_B-\xi_C)-\varepsilon\right)$$

$$\psi(\xi_A,\xi_B,\xi_C,\xi_D) = 0 \qquad 6\text{-}1$$

where V_{AB} and V_{CD} are the binding potentials of AB and CD, and V_I is the interaction potential. We want to convert to the barycentric (stationary center of mass) system and use the internal coordinates of AB and CD. The new coordinates are:

$$x = \xi_A-\xi_B \qquad y = \xi_C-\xi_D$$

$$r = \frac{m_A\xi_A+m_B\xi_B}{m_A+m_B}-\frac{m_C\xi_C+m_D\xi_D}{m_C+m_D}$$

$$R = (m_A\xi_A+m_B\xi_B+m_C\xi_C+m_D\xi_D)/M \qquad 6\text{-}2$$

where $M = m_A+m_B+m_C+m_D$. In these variables 6-1 becomes:

$$\left(-\frac{\hbar^2}{2\mu_{CD}}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2\mu_{AB}}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} + V_{CD}(y)\right. \qquad \text{6-3}$$

$$\left. + V_{AB}(x) + V_I(r - \gamma_{AB}x - \gamma_{CD}y) - \mathcal{E}\right)\psi(x, y, r, R) = 0$$

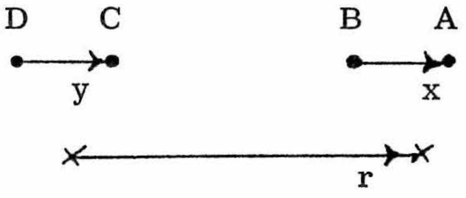
where the reduced masses and mass ratios are

$$\mu_{AB} = \frac{m_A\, m_B}{m_A + m_B}, \qquad \mu_{CD} = \frac{m_C\, m_D}{m_C + m_D}$$

$$\mu = \frac{(m_A + m_B)(m_C + m_D)}{M}$$

$$\gamma_{AB} = \frac{m_A}{m_A + m_B}, \qquad \gamma_{CD} = \frac{m_D}{m_C + m_D}\ . \qquad \text{6-4}$$

Note the arrangement of the new coordinates implied by 6-2:



r is the distance from the center of mass (COM) of CD to the COM of AB. We remove the energy of motion of the COM of the whole system, and keep the internal part only. Define:

$$E = \mathcal{E} - T_{COM} \, . \qquad 6\text{-}5$$

This enables us to factor out the R dependent part of the wave function as given in 6-3:

$$\psi(x, y, r, R) = \psi(x, y, r) e^{iK_{COM}R} \qquad 6\text{-}6$$

where $T_{COM} = \hbar^2 K_{COM}^2/2M$. $\hbar K_{COM}$ is the momentum of the whole system.

We now introduce harmonic bonds into AB and CD with force constants k_{AB} and k_{CD}. The equilibrium separations are x_{eq} and y_{eq}. Combining 6-5 and 6-6 and introducing the harmonic oscillator potentials:

$$\Big(-\frac{\hbar^2}{2\mu_{CD}} \frac{\partial^2}{\partial y^2} + \frac{1}{2} k_{CD}(y - y_{eq})^2 - \frac{\hbar^2}{2\mu_{AB}} \frac{\partial^2}{\partial x^2}$$

$$+ \frac{1}{2} k_{AB}(x - x_{eq})^2 - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2}$$

$$+ V_I(r - \gamma_{AB}x - \gamma_{CD}y) - E\Big) \psi(x, y, r) = 0 \, . \qquad 6\text{-}7$$

The reduced oscillator coordinates for CD and AB are defined as:

$$\bar{y} = \left(\frac{\mu_{CD}k_{CD}}{\hbar^2}\right)^{1/4} (y - y_{eq})$$

$$\bar{x} = \left(\frac{\mu_{AB}k_{AB}}{\hbar^2}\right)^{1/4} (x - x_{eq}) \; . \qquad \text{6-8}$$

The frequencies are

$$\omega_{AB} = (k_{AB}/\mu_{AB})^{1/2}$$

$$\omega_{CD} = (k_{CD}/\mu_{CD})^{1/2} \; . \qquad \text{6-9}$$

Introducing 6-8 and 6-9 into the Schrödinger equation 6-7, it becomes:

$$\left(- \frac{1}{2} \hbar \, \omega_{CD}\left(- \frac{\partial^2}{\partial \bar{y}^2} + \bar{y}^2\right) - \frac{1}{2} \hbar \, \omega_{AB}\left(- \frac{\partial^2}{\partial \bar{x}^2} + \bar{x}^2\right)\right.$$

$$+ \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V_I(r - \gamma_{AB}x - \gamma_{CD}y)$$

$$\left. - E\right) \psi(\bar{x}, \bar{y}, r) = 0 \; . \qquad \text{6-10}$$

We choose to use a repulsive exponential interaction between B and C. This simplifies somewhat the evaluation of the matrix elements of the interaction, and enables us to make direct comparisons of our calculations with previous approximate treatments of the same problem. We have therefore,

$$V_I(\xi_B - \xi_C) = V_0 e^{-(\xi_B - \xi_C)/L} \qquad 6\text{-}11$$

where L is the characteristic length that determines the steepness of the interaction. We can ignore any translational displacement in the argument of V_I that corresponds to a shift in the origin of our r coordinate. Suppose we have $\psi(x, y, r)$, the solution to 6-7 with interaction $V_I(r - \gamma_{AB}x - \gamma_{CD}y)$. Then the solution of 6-7 with interaction $V_I(r - r_0 - \gamma_{AB}x - \gamma_{CD}y)$ is just $\psi(x, y, r - r_0)$. This may be shown directly by replacing r with a new coordinate s and transforming the Hamiltonian. We then define $s = r - r_0$. The asymptotic forms of the correct scattering solutions of $\psi(x, y, r)$ and $\psi(x, y, r - r_0)$ can differ only by phases of the form $e^{i\varphi(r_0)}$ as $r \to \infty$ (see equation 6-33). Since these phases become unity when the probability modulus is taken, there is no change in the results. For a particular physical problem, we would choose V_0 such that the incident particle and the target do not penetrate. However, because of the collinear model and the subsequent invariance of the solution under a change in the r origin, we see that constant positive factors multiplying $e^{-(\xi_B - \xi_C)/L}$ can be taken into the exponent as an irrelevant displacement. Any V_0, for example, can be included in the argument of the interaction as $\ln(V_0)$. This is peculiar to exponential interactions, of course. The argument of V_I in 6-10 is

$$r - \gamma_{AB} x - \gamma_{CD} y \qquad 6\text{-}12$$

which, by 6-8, converts to:

$$r - \gamma_{AB} \left(\frac{\hbar^2}{\mu_{AB} k_{AB}} \right)^{1/4} \bar{x} - \gamma_{CD} \left(\frac{\hbar^2}{\mu_{CD} k_{CD}} \right)^{1/4} \bar{y}$$

$$- \gamma_{AB}\, x_{eq} - \gamma_{CD}\, y_{eq} \,. \qquad 6\text{-}13$$

For the reasons we gave prior to 6-12, we may ignore $- \gamma_{AB}\, x_{eq}$ $- \gamma_{CD}\, y_{eq}$ in 6-13. Let:

$$\bar{E} = E / \left(\frac{1}{2} \hbar\, \omega_{CD} \right)$$

$$\bar{\omega}_{AB} = \left(\frac{1}{2} \hbar\, \omega_{AB} \right) / \left(\frac{1}{2} \hbar\, \omega_{CD} \right) = \omega_{AB} / \omega_{CD}$$

$$\bar{r} = \frac{1}{\gamma_{CD}} \left(\frac{\mu_{CD}\, k_{CD}}{\hbar^2} \right)^{1/4} r \,. \qquad 6\text{-}14$$

Thus, energy is measured in units of the ground state energy (zero point) of CD, and the separation $\bar{r}$ is measured in units of the reduced oscillator length of CD times the mass ratio γ_{CD}. Substituting 6-14 into 6-10, using the exponential interaction, gives:

$$\Big(\Big(-\frac{\partial^2}{\partial \bar{y}^2} + \bar{y}^2\Big) + \bar{\omega}_{AB}\Big(-\frac{\partial^2}{\partial \bar{x}^2} + \bar{x}^2\Big)$$

$$+\frac{\hbar}{\mu\omega_{CD}}\,\frac{1}{\gamma_{CD}^2}\,\Big(\frac{\mu_{CD}\,k_{CD}}{\hbar^2}\Big)^{1/2}\frac{\partial^2}{\partial \bar{r}^2}$$

$$+\Big(\frac{V_0}{\frac{1}{2}\hbar\omega_{CD}}\Big)\exp\Big(-\frac{1}{L}\gamma_{CD}\Big(\frac{\hbar^2}{\mu_{CD}k_{CD}}\Big)^{1/4}(\bar{r}-\bar{y}-\bar{\beta}\,\bar{x})\Big)-\bar{E}\Big)$$

$$\psi(\bar{x},\ \bar{y},\ \bar{r}) = 0 \qquad 6\text{-}15$$

where:

$$\bar{\beta} = \frac{\gamma_{AB}}{\gamma_{CD}}\Big(\frac{\mu_{CD}\,k_{CD}}{\mu_{AB}\,k_{AB}}\Big)^{1/4} = \frac{m_C}{m_B}\Big(\frac{\mu_{AB}}{\mu_{CD}}\Big)^{1/2}\frac{1}{(\bar{\omega}_{AB})^{1/2}}\ . \qquad 6\text{-}16$$

The factor multiplying $\partial^2/\partial\bar{r}^2$ can be simplified; we note that

$$\frac{\hbar}{\mu\omega_{CD}}\,\frac{1}{\gamma_{CD}^2}\Big(\frac{\mu_{CD}\,k_{CD}}{\hbar^2}\Big)^{1/2} = \frac{\mu_{CD}}{\mu}\Big(\frac{m_C + m_D}{m_D}\Big)^2$$

$$= \frac{m_C\,M}{(m_A + m_B)m_D}\ . \qquad 6\text{-}17$$

Let us define an effective dimensionless mass $\bar{m}$ by

$$\bar{m} = \frac{(m_A + m_B)m_D}{m_C M} \qquad 6\text{-}18$$

and a dimensionless reciprocal characteristic length by

$$\bar{\alpha} = \frac{1}{L} \frac{m_D}{m_C + m_D} \left(\frac{\hbar^2}{\mu_{CD} k_{CD}}\right)^{1/4} . \qquad 6\text{-}19$$

We set $V_0/(\frac{1}{2} \hbar \omega_{CD}) = 1$, since this factor could be taken into the argument of the exponential as an irrelevant displacement. Combining 6-15, 6-17, 6-18, and 6-19, we have the scaled, dimensionless Schrödinger equation for the internal motion of the system:

$$((- \frac{\partial^2}{\partial \bar{y}^2} + \bar{y}^2) + \bar{\omega}_{AB}(- \frac{\partial^2}{\partial \bar{x}^2} + \bar{x}^2) - \frac{1}{\bar{m}} \frac{\partial^2}{\partial \bar{r}^2}$$

$$+ \exp(- \bar{\alpha} (\bar{r} - \bar{y} - \bar{\beta} \bar{x})) - \bar{E}) \psi(\bar{x}, \bar{y}, \bar{r}) = 0 . \qquad 6\text{-}20$$

The dimensionless parameters $\bar{E}$, $\bar{\alpha}$, $\bar{m}$, $\bar{\beta}$, and $\bar{\omega}_{AB}$ are related to the physical parameters consisting of all the masses, the force constants, the interaction length, and the total energy. From here onward, we drop the bars over these and the scaled coordinates, and the AB from $\bar{\omega}_{AB}$.

6.2 Explicit Relations

The dimensionless form of the H_0 part of our total Hamiltonian is

$$H_0(x, y) = -\frac{\partial^2}{\partial y^2} + y^2 + \omega(-\frac{\partial^2}{\partial x^2} + x^2) . \qquad 6\text{-}21$$

Here we have two internal coordinates in H_0, and we also need two quantum numbers to label the H_0 eigenfunctions. The orthonormal solutions of

$$H_0(x, y)\, \varphi_{ij}(x, y) = W_{ij}\, \varphi_{ij}(x, y)$$

$$i, j = 0, 1, 2, \ldots \qquad 6\text{-}22$$

are products of harmonic oscillator wavefunctions as defined in 5-22. We now establish the following convention: the left index in a pair, ij, refers to CD with internal coordinate y, and the right index to AB with internal coordinate x:

$$\varphi_{ij}(x, y) = \varphi_i(y)\, \varphi_j(x)$$

$$i, j = 0, 1, 2, \ldots \qquad 6\text{-}23$$

and

$$W_{ij} = (2i + 1) + \omega(2j + 1)$$

$$i, j = 0, 1, 2, \ldots \qquad 6\text{-}24$$

The wavenumbers of the relative motion associated with coordinate r are defined as

$$k_{ij} = +\sqrt{m(E - W_{ij})}$$

$$i, j = 0, 1, 2, \ldots \qquad 6\text{-}25$$

The matrix elements of the interaction potential are:

$$\langle \varphi_{nm}(x, y) | e^{-\alpha(r - y - \beta x)} | \varphi_{n'm'}(x, y) \rangle$$

$$= e^{-\alpha r} \langle \varphi_n(y) | e^{\alpha y} | \varphi_{n'}(y) \rangle$$

$$\cdot \langle \varphi_m(x) | e^{\alpha\beta x} | \varphi_{m'}(x) \rangle \; . \qquad 6\text{-}26$$

The analytic expression for each of the matrix elements in the product was given in 5-29. We now have all of the elements that go into a DRILL or II calculation. In addition to the previous variations in starting point, stopping point, and so on, we must choose the number of states retained in each of the two state expansions for the two different systems, AB and CD. In DRILL, we must choose N and M in:

$$\psi^{n_0 m_0}(x, y, r) = \sum_{n=0}^{N-1} \sum_{m=0}^{M-1} f_{nm}^{n_0 m_0}(r)\, \varphi_n(y)\, \varphi_m(x) \qquad 6\text{-}27$$

where $f_{nm}^{n_0 m_0}(r)$ are the unknown functions of the separation. Labels n_0 and m_0 denote a particular initial state of the system. For convenience of discussion, it is helpful to relate the dual index nm uniquely to one number. Once we have chosen an N and M (the number of states of CD and AB included in the expansion) we can do this as follows. Let $i = i(n, m)$ be:

$$i = n + N \cdot m \qquad 6\text{-}28$$

$$\begin{aligned} n &= 0, 1, 2, \ldots\ N-1 \\ m &= 0, 1, 2, \ldots\ M-1 \\ i &= 0, 1, 2, \ldots, N \cdot M-1 \ . \end{aligned}$$

This is sometimes referred to as converting a matrix to a super-vector; the essence is the unique relation of any pair nm to one index i.

The matrix elements of the interaction are now expressed in matrix form:

$$\begin{aligned} (\underset{\sim}{V}(r))_{ij} &= (\underset{\sim}{V}(r))_{i(n, m)\ j(n', m')} \\ &= m\ \langle \varphi_{nm}(x, y) |\, e^{-\alpha(r-y-\beta x)} \,| \varphi_{n'm'}(x, y) \rangle \ . \end{aligned} \qquad 6\text{-}29$$

Similarly the unknown matrix of solutions is given by:

$$(\underset{\sim}{F}(r))_{ij} = (\underset{\sim}{F}(r))_{i(n,\,m)\,j(n',\,m')} = f_{nm}^{n'm'}(r) \tag{6-30}$$

and the wavenumber matrix:

$$(\underset{\sim}{K})_{ij} = (\underset{\sim}{K})_{i(n,\,m)\;j(n',\,m')} = k_{nm}\,\delta_{nn'}\,\delta_{mm'}\,. \tag{6-31}$$

Consequently the re-orthogonalization method (DRILL) is based on integration of the matrix system (see 3-48):

$$\frac{d}{dr}\,\underset{\sim}{F}'(r) = (\underset{\sim}{V}(r) - \underset{\sim}{K}^2)\,\underset{\sim}{F}(r)$$

$$\frac{d}{dr}\,\underset{\sim}{F}(r) = \underset{\sim}{F}'(r) \tag{6-32}$$

which is equivalent to the coupled system of differential equations obtained by substituting 6-27 into 6-20 and taking inner products with $\varphi_{n'm'}(x, y)$. Note that 6-32 does not have a mass factor; it was absorbed into the definition of $\underset{\sim}{V}(r)$ in 6-29, and $\underset{\sim}{K}$ in 6-25, rather than left in front of d/dr.

The asymptotic form of $\underset{\sim}{F}(r)$ for large separation, where $\underset{\sim}{V}(r)$ tends to zero, is:

$$\underset{\sim}{F}(r) \underset{r \to \infty}{=} e^{-i\underset{\sim}{K}r}\,\underset{\sim}{A}' + e^{i\underset{\sim}{K}r}\,\underset{\sim}{B}'\,. \tag{6-33}$$

This is obtained by integrating 6-32 into the asymptotic region; $\underset{\sim}{A}'$ and $\underset{\sim}{B}'$ are to be determined from the solution. Since this is rather obscure, we will give the actual procedure of analyzing $\underset{\sim}{F}(r)$ at large r.

6.3 State Analysis for DRILL Method

At some point r_1 in the asymptotic region, our numerical solution will consist of the two matrices of numbers, $\underset{\sim}{F}(r_1)$ and $\underset{\sim}{F}'(r_1)$. The latter is the derivative matrix, as seen from 6-32. Equating these to the expressions defined by 6-33 gives

$$\underset{\sim}{F}(r_1) = e^{-i\underset{\sim}{K}r_1}\,\underset{\sim}{A}' + e^{i\underset{\sim}{K}r_1}\,\underset{\sim}{B}'$$

$$\underset{\sim}{F}'(r_1) = i\underset{\sim}{K}\left(-e^{-i\underset{\sim}{K}r_1}\,\underset{\sim}{A}' + e^{i\underset{\sim}{K}r_1}\,\underset{\sim}{B}'\right) \qquad \text{6-34}$$

therefore we have $2 \cdot N \cdot M$ equations to solve for the $2 \cdot N \cdot M$ unknowns $\underset{\sim}{A}'$ and $\underset{\sim}{B}'$. Actually we wish to find $\underset{\sim}{B}'\underset{\sim}{A}'^{-1}$, the matrix of transition amplitudes (3-32), from which we determine the transition probabilities (3-23) according to:

$$P_{n_0 m_0 \to nm} = P_{i(n_0,\, m_0) f(n,\, m)} = P_{if}$$

$$= \left| \left(\underset{\sim}{B}'\,\underset{\sim}{A}'^{-1} \right)_{fi} \right|^2 \frac{k_{f(n,\, m)}}{k_{i(n_0,\, m_0)}} \qquad \text{6-35}$$

in which we use the notation implied by 6-28. Rather than calculating the exponentials $e^{\pm i\underset{\sim}{K}r_1}$ present in 6-34, we may write the asymptotic form of $\underset{\sim}{F}(r)$ as

$$\underset{\sim}{F}(r) \underset{r\to\infty}{=} e^{-i\underset{\sim}{K}(r - r_1)}\underset{\sim}{A} + e^{i\underset{\sim}{K}(r - r_1)}\underset{\sim}{B} \,. \qquad 6\text{-}36$$

At $r = r_1$, $\underset{\sim}{F}(r)$ and $\underset{\sim}{F}'(r)$ would be:

$$\underset{\sim}{F}(r_1) = \underset{\sim}{A} + \underset{\sim}{B}$$

$$\underset{\sim}{F}'(r_1) = i\underset{\sim}{K}(-\underset{\sim}{A} + \underset{\sim}{B}) \,. \qquad 6\text{-}37$$

From 6-36, we see that the transformation $\underset{\sim}{A}^{-1}$, applied to $\underset{\sim}{F}(x)$, gives the asymptotic form

$$\underset{\sim}{F}(r)\,\underset{\sim}{A}^{-1} \underset{r\to\infty}{=} e^{-i\underset{\sim}{K}(r - r_1)} + e^{i\underset{\sim}{K}(r - r_1)}\underset{\sim}{B}\,\underset{\sim}{A}^{-1} \qquad 6\text{-}38$$

or

$$\underset{\sim}{F}(x)\,\underset{\sim}{A}^{-1} e^{-i\underset{\sim}{K}r_1} \underset{r\to\infty}{=} e^{-i\underset{\sim}{K}r} + e^{i\underset{\sim}{K}r}\, e^{-i\underset{\sim}{K}r_1}\underset{\sim}{B}\,\underset{\sim}{A}^{-1} e^{-i\underset{\sim}{K}r_1} \,. \qquad 6\text{-}39$$

The reason for writing 6-38 and 6-39 was to show that the probabilities calculated from 6-33 and 6-39 are the same (they involve a phase change in the definitions $\underset{\sim}{A}$ and $\underset{\sim}{B}$). Expression 6-35 gives P_{if} based on 6-33. From 6-39, the probabilities are

$$P_{if} = |(e^{-i\underset{\sim}{K}r_1} \underset{\sim}{B}\,\underset{\sim}{A}^{-1} e^{-i\underset{\sim}{K}r_1})_{fi}|^2 \frac{k_f}{k_i} . \qquad 6\text{-}40$$

Since k_n is real for open channels, and these are the only observed ones, the exponentials in 6-40 cancel when the modulus is taken. Consequently,

$$P_{if} = |(\underset{\sim}{B}\,\underset{\sim}{A}^{-1})_{fi}|^2 \frac{k_f}{k_i} . \qquad 6\text{-}41$$

We have just shown that $\underset{\sim}{B}\,\underset{\sim}{A}^{-1}$, determined from 6-37, which was based on asymptotic behavior 6-36, is the correct expression to use for determining P_{if}. The reason for avoiding 6-33 was to eliminate the computation of several exponentials at point r_1. Let us proceed with the numerical calculation of P_{if} from 6-37. Solving for $\underset{\sim}{A}$ and $\underset{\sim}{B}$:

$$2\underset{\sim}{B} = \underset{\sim}{F}(r_1) - i\underset{\sim}{K}^{-1}\,\underset{\sim}{F}'(r_1)$$

$$2\underset{\sim}{A} = \underset{\sim}{F}(r_1) + i\underset{\sim}{K}^{-1}\,\underset{\sim}{F}'(r_1) \ . \qquad 6\text{-}42$$

$\underset{\sim}{F}$ and $\underset{\sim}{F}'$ are real, $\underset{\sim}{K}$ is real for open channels and pure positive imaginary for virtual channels. Since we desire to use only real arithmetic, we define:

$$\underset{\sim}{K}^{R} = \mathrm{Re}\,(\underset{\sim}{K})$$

$$\underset{\sim}{\lambda} = \mathrm{Imag}\,(\underset{\sim}{K})$$

$$\underset{\sim}{K} = \underset{\sim}{K}^{R} + i\,\underset{\sim}{\lambda}\;. \qquad 6\text{-}43$$

The inverses are defined as

$$\underset{\sim}{\lambda}^{-1} = -\mathrm{Imag}\,(\underset{\sim}{K}^{-1})$$

$$(\underset{\sim}{K}^{R})^{-1} = \mathrm{Re}\,(\underset{\sim}{K}^{-1})$$

$$(\underset{\sim}{K})^{-1} = (\underset{\sim}{K}^{R})^{-1} - i\,\underset{\sim}{\lambda}^{-1}\;. \qquad 6\text{-}44$$

So, from 6-42,

$$2\,\underset{\sim}{B} = \underset{\sim}{F}(r_1) - \underset{\sim}{\lambda}^{-1}\,\underset{\sim}{F}'(r_1) - i(\underset{\sim}{K}^{R})^{-1}\,\underset{\sim}{F}'(r_1)$$

$$2\,\underset{\sim}{A} = \underset{\sim}{F}(r_1) + \underset{\sim}{\lambda}^{-1}\,\underset{\sim}{F}'(r_1) + i(\underset{\sim}{K}^{R})^{-1}\,\underset{\sim}{F}'(r_1)\;. \qquad 6\text{-}45$$

From the known real matrices $\underset{\sim}{F}(r_1)$ and $\underset{\sim}{F}'(r_1)$, we form:

$$\underset{\sim}{F}^{+} = \underset{\sim}{F}(r_1) + \underset{\sim}{\lambda}^{-1}\, \underset{\sim}{F}'(r_1)$$

$$\underset{\sim}{F}^{-} = \underset{\sim}{F}(r_1) - \underset{\sim}{\lambda}^{-1}\, \underset{\sim}{F}'(r_1)$$

$$\underset{\sim}{D} = (\underset{\sim}{K}^{R})^{-1}\, \underset{\sim}{F}'(r_1)\,. \qquad 6\text{-}46$$

Therefore the expressions 6-45 for $\underset{\sim}{A}$ and $\underset{\sim}{B}$ may be written as:

$$\underset{\sim}{B} = \frac{1}{2}(\underset{\sim}{F}^{-} - i\,\underset{\sim}{D})$$

$$\underset{\sim}{A} = \frac{1}{2}(\underset{\sim}{F}^{+} + i\,\underset{\sim}{D}) \qquad 6\text{-}47$$

from which we wish to calculate

$$\underset{\sim}{C} = \mathrm{Re}\,(\underset{\sim}{C}) + i\ \mathrm{Imag}(\underset{\sim}{C}) = \underset{\sim}{B}\,\underset{\sim}{A}^{-1}\,. \qquad 6\text{-}48$$

After considerable algebraic manipulation, one can use 6-47 to reduce 6-48 to:

$$\mathrm{Re}(\underset{\sim}{C}) = (\underset{\sim}{F}^{-} - \underset{\sim}{D}(\underset{\sim}{F}^{+})^{-1}\,\underset{\sim}{D})\,(\underset{\sim}{F}^{+} + \underset{\sim}{D}(\underset{\sim}{F}^{+})^{-1}\,\underset{\sim}{D})^{-1}$$

$$\mathrm{Imag}(\underset{\sim}{C}) = -(\underset{\sim}{D} + \underset{\sim}{F}^{-}\,(\underset{\sim}{F}^{+})^{-1}\,\underset{\sim}{D})(\underset{\sim}{F}^{+} + \underset{\sim}{D}(\underset{\sim}{F}^{+})^{-1}\,\underset{\sim}{D})^{-1}\,. \qquad 6\text{-}49$$

The numerical operations are now explicit: (1) Use $\underset{\sim}{F}(r_1)$ and $\underset{\sim}{F}'(r_1)$ to form $\underset{\sim}{F}^{+}$, $\underset{\sim}{F}^{-}$, and $\underset{\sim}{D}$ according to 6-46. (2) Invert $\underset{\sim}{F}^{+}$.

(3) Form expression $\underset{\sim}{F}^{+} + \underset{\sim}{D}(\underset{\sim}{F}^{+})^{-1}\underset{\sim}{D}$. (4) Invert this. (5) Construct the real and imaginary parts of $\underset{\sim}{C}$ by matrix multiplication as prescribed in 6-49. Transition probabilities are obtained from the moduli of the $\underset{\sim}{C}$ elements, i. e., $(\mathrm{Re}(\underset{\sim}{C})_{ij})^2 + (\mathrm{Imag}(\underset{\sim}{C})_{ij})^2$, multiplied by the flux normalizing factor k_i/k_j, according to 6-41.

6. 4 II Adaption for Diatom on Diatom Problem

The invariant imbedding problem has been set up in principle with 6-29 and 6-31, except that we do not include the mass factor m in the definition of $\underset{\sim}{V}(r)$ (see 2-58). The probabilities are obtained directly from the moduli of the asymptotic form of $\underset{\sim}{S}(r)$ (2-74):

$$P_{n_0 m_0\ nm} = P_{i(n_0, m_0)\ f(n,m)} \underset{r\to\infty}{=} |(S(r))_{fi}|^2 \frac{k_f}{k_i} . \qquad 6\text{-}50$$

As there is possible confusion on the nature of the invariant imbedding independent variable, we state the following: In the derivation of the II equation, the coordinate r used in the cutoff disappeared and the cutoff point r_0, which is a variable, effectively took its place. The II differential equation has the cutoff point r_0 as the independent variable; we treat this cutoff point, however, as if it were really the original coordinate r.

6.5 Translational Energy Dependence of Energy Transfer Probabilities in H_2 on H_2 Collisions

The number of physical systems that we could study is almost unlimited. After some trial calculations, we limited most of our investigations to two tasks. One was to find the energy dependence of H_2 on H_2 transition probabilities, and the other was to determine the variation of vibration to vibration (V-V) energy transfer probability with frequency ratio $\omega (\omega = \omega_{AB}/\omega_{CD}$, see 6-14) for N_2 on N_2-like collisions. H_2 on H_2 will be treated first.

6.5.1 Parameters for the H_2 on H_2 system

The dimensionless parameters E, m, α, β, and ω are calculated as follows. Since both H_2 molecules have the same frequency, $\omega = 1$ (6-14), and $\beta = 1$ also (6-16). m is seen to be 1/2 from 6-18. E is simply the total energy measured in units of the zero point energy of H_2 (6-14). The remaining parameter is α, which is the hardest to choose, because there is no accurate physical measurement that can determine this interaction constant. Secrest and Johnson[19] uniformly used $L = 0.2$ Å for all atom on diatom calculations, regardless of the identity of the species. For H_2 on H_2 we happened to choose $L = .212$ Å, which is a slightly softer interaction. This L converts to $\alpha = .2973$ when the physical parameters for H_2 are substituted in 6-10.[44] For calculational and comparison purposes, the scaled parameters are more significant than the physical ones, because the analytical methods to which we compare our calculations can also be put into our dimensionless system. Consequently α is exactly .2973 in our computations, and L can be calculated from this number using 6-19.

6.5.2 Previous approximate analytical solutions to diatom on diatom collision problem

There have been no previous numerical calculations on this problem. As the physical process is very fundamental and interesting, previous workers have utilized some of the perturbation methods of quantum mechanics and obtained analytic solutions to the identical collinear, exponential interaction, harmonic oscillator model we are solving. We summarize these now.

6.5.2.1 Distorted wave solution

Takayanagi[36] has used the distorted wave (DW) method on the diatom-diatom problem, generalizing previous studies of atom-diatom collisions.[1, 29] Essentially, DW treats the off-diagonal solutions in $\underset{\sim}{F}(r)$ (6-32) as perturbations on the zero-order diagonal solutions, which may be obtained analytically. In our dimensionless parameters, the result[36] is:

$$P^{DW}_{n_0m_0 \to nm} = (V_{n_0n}(\alpha))^2 \, (V_{m_0m}(\alpha\beta))^2 \, \frac{1}{4\pi^2}$$

$$\sinh(q_{n_0m_0}) \sinh(q_{nm})$$

$$\cdot \left(\frac{q^2_{n_0m_0} - q^2_{nm}}{\cosh(q_{n_0m_0}) - \cosh(q_{nm})} \right)^2 \qquad \text{6-51}$$

where $q_{ij} = \frac{2\pi k_{ij}}{\alpha}$ and

$$V_{ij}(x) = \int_{-\infty}^{\infty} e^{-y^2} \bar{H}_i(y)\, \bar{H}_j(y)\, e^{xy}\, dy \qquad 6\text{-}52$$

are the same matrix elements evaluated previously in 6-26. For exact resonance energy transfer, involving no change in translational energy, $q_{n_0 m_0} = q_{nm}$. We must use L'Hopital's rule for evaluating the indeterminexte form 0/0 which results from 6-51. Consider the ratio:

$$R = \frac{q^2_{n_0 m_0} - q^2_{nm}}{\cosh(q_{n_0 m_0}) - \cosh(q_{nm})} \qquad 6\text{-}53$$

and assume $q_{n_0 m_0}$ is the variable approaching q_{nm}:

$$\lim_{q_{n_0 m_0} \to q_{nm}} R = \frac{2\, q_{nm}}{\sinh(q_{nm})}\,. \qquad 6\text{-}54$$

Substituting 6-54 into 6-51, we get the expression for exact resonance transfer (ERT):

$$P^{ERT,\,DW}_{n_0 m_0\, nm} = (V_{n_0 m_0}(\alpha))^2 (V_{nm}(\alpha\beta))^2 \frac{4}{\alpha^2} (k_{nm})^2. \qquad 6\text{-}55$$

This shows that DW predicts a linear dependence of ERT probabilities on relative kinetic energy. For (0, 1) to (1, 0) transfers in a homonuclear system, we use the known forms of $V_{01}(\alpha)$ and $V_{10}(\alpha\beta)$ (5-29) and obtain

$$P^{ERT,\,DW}_{(0,\,1)(1,\,0)} = \frac{\alpha^2}{2}\, e^{\alpha^2/2}\, \frac{(\alpha\beta)^2}{2}\, e^{(\alpha\beta)^2/2}\, \frac{4}{\alpha^2}\, (k_{1,\,0})^2 . \qquad 6\text{-}56$$

Since $\beta = 1$ for identical diatoms, using 6-25 and 6-24, we get:

$$P^{ERT,\,DW}_{(0,\,1)(1,\,0)} = e^{\alpha^2}\, \alpha^2\, m\,(E - 4)\, . \qquad 6\text{-}57$$

E-4 is just the relative kinetic energy in units of $1/2\, \hbar\, \omega_{H_2}$. Mies[37] has published a corrected DW treatment which indicates that the term e^{α^2} in 6-57 should be neglected.

6. 5. 2. 2 Time-dependent quasi-classical perturbation method

Rapp and Englander-Golden[38] have studied diatom on diatom collisions in the framework of the time-dependent quasi-classical (TD-QC) perturbation method. For ERT processes, their result is, in our units:

$$P^{ERT,\,TD\text{-}QC}_{(0,\,1)(1,\,0)} = \sin^2(k_{01}\, \alpha\, e^{\alpha^2/2})\, . \qquad 6\text{-}58$$

Expanding sin in a power series and retaining the first term gives the DW result, 6-57, when we introduce $(k_{01})^2 = m(E - 4)$. This shows that both DW and TD-QC are consistent to the lowest orders in α, which is assumed small compared to unity.

6.5.3 Exact two state solution at exact resonance

Retaining only two states (say (0, 1) and (1, 0)) in the state expansion of the Schrödinger equation, we obtain:

$$\left(\frac{d^2}{dx^2} + k^2\right)f = e^{-\alpha x}(V_{00}(\alpha)V_{11}(\alpha\beta)f + V_{01}(\alpha)V_{10}(\alpha\beta)g)$$

$$\left(\frac{d^2}{dx^2} + k^2\right)g = e^{-\alpha x}(V_{11}(\alpha)V_{00}(\alpha\beta)g + V_{10}(\alpha)V_{01}(\alpha\beta)f) \qquad 6\text{-}59$$

where $k = k_{01} = k_{10}$ and $f = f(x) = f_{01}^{01}(x)$, $g = g(x) = f_{10}^{01}(x)$. 6-59 is the system 6-32 written out for a two by two system of equations, considering only the incident state (0, 1). We take $\beta = 1$ (identical diatoms) so that, using:

$$V_0 = V_{01}(\alpha)\, V_{10}(\alpha) = (V_{01}(\alpha))^2$$

$$V = V_{00}(\alpha)\, V_{11}(\alpha) \qquad 6\text{-}60$$

6-59 may be written:

$$\left(\frac{d^2}{dx^2} + k^2\right) \begin{pmatrix} f \\ g \end{pmatrix} = e^{-\alpha x} \begin{pmatrix} V & V_0 \\ V_0 & V \end{pmatrix} \begin{pmatrix} f \\ g \end{pmatrix} . \qquad \text{6-61}$$

If the diagonal potential elements were not equal ($\beta \neq 1$), we would apply a unitary transform and diagonalize 6-61. For the present case, we add and subtract the components of 6-61 to obtain the de-coupled system:

$$\left(\frac{d^2}{dx^2} + k^2\right) (f + g) = e^{-\alpha x}(V + V_0)(f + g)$$

$$\left(\frac{d^2}{dx^2} + k^2\right)(g - f) = e^{-\alpha x}(V - V_0)(g - f) . \qquad \text{6-62}$$

The solution to equations of this form was obtained by Zener.[1] Let $f + g = R^+(x)$, $g - f = R^-(x)$, then the regular solutions are:

$$R^+(x) = A\, K_{iq}\left(\frac{2}{\alpha} \quad V + V_0 \quad e^{-\frac{1}{2}\alpha x}\right)$$

$$R^-(x) = B\, K_{iq}\left(\frac{2}{\alpha} \quad V - V_0 \quad e^{-\frac{1}{2}\alpha x}\right)$$

$$\text{with } \; q = \frac{2k}{\alpha} . \qquad \text{6-63}$$

The asymptotic form as x → ∞ can be shown to be:[40]

$$R^+(x) \underset{x\to\infty}{=} A\,\delta(\gamma_+^* e^{ikx} - \gamma_+ e^{-ikx})$$

$$R^-(x) \underset{x\to\infty}{=} B\,\delta(\gamma_-^* e^{ikx} - \gamma_- e^{-ikx}) \qquad \text{6-64}$$

where $\delta = \frac{\pi}{2\sin(i\pi q)}$, $\gamma_\pm = \left(\frac{V \pm V_0}{\alpha}\right)^{iq} \frac{1}{iq\Gamma(iq)}$. Scattering conditions require that:

$$f(x) \underset{x\to\infty}{=} e^{-ikx} + R\,e^{ikx}$$

$$g(x) \underset{x\to\infty}{=} T\,e^{ikx} \; . \qquad \text{6-65}$$

If we represent f and g in terms of $R^+(x)$ and $R^-(x)$, 6-65 allows us to determine R and T in terms of A and B, which are uniquely determined also by 6-65. That is:

$$f = \frac{1}{2}(R^+(x) - R^-(x))$$

$$g = \frac{1}{2}(R^+(x) + R^-(x)) \; . \qquad \text{6-66}$$

Using 6-64 and 6-66 and comparing to 6-65, we find that:

$$B = \frac{1}{\delta\gamma_-}, \quad A = -\frac{1}{\delta\gamma_+} . \qquad 6\text{-}67$$

This enables us to calculate R and T,

$$R = -\frac{1}{2}\left(\frac{\gamma_+^*}{\gamma_+} + \frac{\gamma_-^*}{\gamma_-}\right)$$

$$T = -\frac{1}{2}\left(\frac{\gamma_+^*}{\gamma_+} - \frac{\gamma_-^*}{\gamma_-}\right) \qquad 6\text{-}68$$

and their moduli from the definition of $\gamma_\pm$:

$$|T|^2 = \sin^2\left(\frac{k}{\alpha}\ell n\left(\frac{V+V_0}{V-V_0}\right)\right)$$

$$|R|^2 = 1 - |T|^2 . \qquad 6\text{-}69$$

Using matrix elements defined in 6-26,

$$P^{ETS}_{(0,1)(1,0)} = \sin^2\left(\frac{k}{\alpha}\ell n\left(\frac{1+\alpha^2/2}{1-\alpha^2/2}\right)\right) \qquad 6\text{-}70$$

where ETS stands for Exact Two State. An expansion of ℓn gives, correct to $0(\alpha^5)$, :

$$P^{ETS}_{(0,1)(1,0)} = \sin^2\left(\frac{k}{\alpha}\alpha^2\right) = \sin^2(k_{01}\,\alpha). \qquad 6\text{-}71$$

This is similar to the TD-QC result. After we developed this ETS solution, we found that it had been obtained previously[39] but was apparently unknown to the authors of reference 38.

6.5.4 Results and discussion of H_2 on H_2 calculations

We did a series of calculations for the H_2 on H_2 system at different total energies, using the parameters prescribed in 6.5.1, namely: α = ALPHA = .2973 (corresponding[44] to an L of .212 Å), ω = OMEGA = 1.0, and masses of the atoms MA = MB = MC = MD = 1.0 (since only the mass ratios enter the calculation of β and m).

The starting point for integration, XST, was determined using DRILL calculations at E = 4.9455, ERROR = 10^{-5}, and an N = 2, M = 2 state expansion. The change in the probabilities as we moved from XST = -15 (table 7(a)) back to XST = -18 (table 7(b)) was insignificant. The ERROR control of 10^{-5} gave roughly six digit "sum to one" and time reversal accuracies. An increase in N and M to N = 3, M = 3 gave probabilities and execution time ET listed in table 7(c). For diatom on diatom problems, ET increases as the cube of N · M, since we have an N · M by N · M dimension matrix system. We did not try to confirm this by several expansions, as was presented in figure 7 for the atom on diatom problem, but it appears to be true for all the cases we have done. The larger probabilities have changed by little more than 5% in going from table 7(a) to table 7(c), but we choose to use N = 3, M = 3 in our series of calculations for H_2 on H_2 to maintain the more accurate results for the smaller probabilities. The II method was compared to DRILL also. The II results given in table 8 are for the identical problem solved by DRILL in table 7(a), with the same starting point and ERROR control. The results agree, helping to confirm both answers. Because our II program requires considerably more computation time, we use DRILL for the major studies on all diatom-diatom problems.

Tables 9(a) through 9(g) give our series of calculations for the H_2 on H_2 problem. In figures 8 and 9 we plot the more interesting of these and the DW results from Takayanagi's formula 6-51. Figure 8 contains the probabilities for translational to vibrational (T-V) energy conversions. The DW results are too large by an order of magnitude for one quantum T-V excitations. DW is even more seriously in error for two quantum T-V processes (not shown), in exact analogy to the conclusions in atom or diatom studies.[19]

Figure 9 displays the vibrational to vibrational (V-V) energy transfer probabilities. Here the DW is very accurate for one quantum transfers, but too small by a factor of 100 for the two quantum $(0, 2) \rightarrow (2, 0)$ process. The result of Mies[37] indicates that the exponential term in 6-57 should be omitted. This brings the DW expression for ERT processes (6-57) into better agreement with the ETS (6-71) solutions at low incident kinetic energies. Figure 9 shows that Mies' corrected DW method does give a better slope at the $(0, 1) \rightarrow (1, 0)$ threshold.

Apparently the $(0, 1) \rightarrow (1, 0)$ DW result is very accurate because the ETS method is valid when only those two channel states dominate in the expansion of the wavefunction. We have seen that DW and ETS are nearly identical at low energies. At high energies, we know that the DW result is grossly in error because it exceeds a probability of unity. The TD-QC result, which will be used later, may also base its accuracy for (0, 1) → (1, 0) on the dominance of the wavefunctions by those channels.

The plots in figures 8 and 9 have total energy on the abscissa. To obtain incident relative kinetic energies (KE) for the initial state (n_0, m_0) at a total energy E, we subtract off the initial internal energies from E, leaving

$$KE = E - (2n_0 + 1) - \omega(2m_0 + 1) \qquad 6\text{-}72$$

measured in units of the zero point energy of H_2. From this one can easily calculate the kinetic energy, and velocity, before the collision. For H_2 on H_2, the frequency ratio ω is 1, in later discussions, ω is not unity.

6.6 N_2 on N_2-like Collisions

As we see from figures 8 and 9, V-V processes are considerably more probable than T-V processes in H_2 on H_2 collisions (assuming our model for the system). The collision of two identical diatoms is a special case of an almost infinite spectrum of problems in which the diatoms are different. It would be profitable to study the dependence of V-V probabilities and T-V probabilities on mass ratios, diatom frequencies, and interaction parameters. This is too extensive a task; computational time is prohibitive and the significance of the results might be confusing. We chose to investigate the dependence of the transition probabilities (particularly the V-V transfer) on differences in natural frequency of the colliding diatoms. To effect a frequency difference without bringing in an additional dependence on masses, we vary the ratio of the force constants k_{AB}/k_{CD} and keep the masses unchanged.

6.6.1 Parameters for N_2 on N_2-like system

We constructed a model for a collision between an N_2 molecule and another N_2-like molecule with the same atomic masses, but varying force constant, k'. We chose the interaction parameter L to be 0.2 Å. This is done solely because of its previous use in numerical scattering problems.[19] As was mentioned previously, no accurate knowledge of L has been obtained from experiment. This L converts[44] to $\alpha = .113$ in our dimensionless system of parameters (6-19). We take ALPHA $= \alpha = .113$ as the exact parameter in our computations. The masses in AU are MA = MB = MC = MD = 14.0. Since the masses always appear as ratios in the evaluation of m and β, the units have no effect. Our independent parameter to be varied is ω = OMEGA = $k_{AB}/k_{CD} = k'/k_{N_2}$. We keep a constant incident relative kinetic energy of one zero point (ground state) vibration energy of N_2 for the incident state (0, 1). This may be shown to be a velocity of 1.42×10^5 cm/sec in the laboratory system.

6.6.2 Results and discussion of N_2 on N_2-like system

Our series of calculations covered the range of ω from .6 to 1.2. These are given in tables 11(a) through 11(j) with the correct total energy to give the initial relative kinetic energy of 1 (ground state units) for initial state (0, 1). These calculations were run with DRILL, using ERROR = 10^{-5}, XST = -40, and N = 2, M = 2. The starting point produced no significant change when moved back to -45 at OMEGA = 1. The use of only four states in the expansion of the wavefunction was sufficient for the $P_{(0,1)\to(1,0)}$ probabilities. We ran N = 3, M = 3 at $\omega = .85$ (corresponding to table 11(c)) and obtained results shown in table 10. The N = 2, M = 2 expansion was of sufficient accuracy for our $P_{01\to 10}$ probabilities.

Figure 10 displays the variation in $P_{(0,1)\to(1,0)}$ with ω. We evaluated the DW formula (6-51) and the TD-QC formula, given by;[38] in our units:

$$P^{\text{TD-QC}}_{(0,1)\to(1,0)} = \sin^2(k_{0,1}\alpha e^{\alpha^2/2})\,\text{sech}^2\left(\frac{\omega - 1}{\alpha k_{0,1}}\right) \qquad 6\text{-}73$$

for a diatom-diatom collision with all atomic masses the same. The DW result was much better than the TD-QC far away from $\omega = 1$. The TD-QC is symmetrical about $\omega = 1$, and the exact curve is not. The full width of the resonant peak is .15 at half height. The peak height is .0063, and occurs at $\omega = 1$.

Again, we attribute the excellent agreement of DW and TD-QC to the dominance of channel states (0, 1) and (1, 0) in the wavefunction. The ETS solution does not help us here, except at $\omega = 1$. We have taken advantage of the two state dominance, in fact, by keeping only the first two states for each diatom in our calculations. This gives us a total of four states, but we are solving for the incident channel (1, 0) also.

There are two points to be made in summary of this section. The first is that we have demonstrated the accuracy of the distorted wave method for V-V one quantum energy transfer in our two model systems. Perhaps the DW method will prove adequate for more general problems in near-resonant energy transfer. Of course, if T-V processes are more important for the systems, DW is inadequate.

The second point is the strong dependence of V-V processes on natural frequencies of the colliding species. Although DW had predicted this, (accurately it turns out) the fact is seldom mentioned.

APPENDIX A

The Romberg integrator we have used is rather novel, so the following pages give a listing of the program. This Fortran IV version was translated from Algol by Mr. Robert Deverill of the Booth Computing Center at Caltech. The "in press" reference in the explanitory section is reference 34 of the text. This reference contains the Algol program. In the listing here, the maximum dimension of the dependent vector integrated by DIFSYS is set at 10. We enlarged this to 200.

```
$IBFTC DED      DECK
      SUBROUTINE DIFSYS(F,N,H,X,Y,EPS,S,NEWH)
C
C**********************************************************************
C
C       F IS THE NAME OF A SUBROUTINE CALLED BY 'CALL F(X,Z,DZ)' WHICH
C            STORES IN THE VECTOR DZ THE N COMPONENTS OF THE DERIVATIVE
C            DZ/DX ACCORDING TO THE DIFFERENTIAL EQUATION WHICH IS BEING
C            SOLVED, DZ/DX=F(X,Z).
C       X, Z, AND DZ MUST BE DOUBLE PRECISION.
C
C       N IS THE ORDER OF THE SYSTEM OF DIFFERENTIAL EQUATIONS.
C       N MUST BE NO GREATER THAN MAXORD WHICH IS SET BELOW.
      DATA MAXORD/10/
      DIMENSION YA(10),YL(10),YM(10),DY(10),DZ(10),DT(10,7)
      DIMENSION YG(8,10),YH(8,10)
C
C       H IS THE BASIC STEP SIZE.
      DOUBLE PRECISION H
C
C       X AND Y(VECTOR) ARE THE INITIAL VALUES.
      DOUBLE PRECISION X,Y
      DIMENSION Y(N)
C
C       EPS AND S(VECTOR) ARE THE ERROR BOUNDS.
C       DABS(EPS) SHOULD BE NO SMALLER THAN 1.0D-13.
      DOUBLE PRECISION EPS,S
      DIMENSION S(N)
C
C       NEWH IS A FLAG WHICH IS SET EQUAL TO .TRUE. IF THE STEP SIZE USED
C            USED BY DIFSYS IS DIFFERENT FROM THE STEP SIZE H GIVEN IN THE
C            PARAMETER LIST.  NEWH IS SET EQUAL TO .FALSE. OTHERWISE.
      LOGICAL NEWH
C
C**********************************************************************
C
      DOUBLE PRECISION YA,YL,YM,DY,DZ,DT,D,YG,YH
      DIMENSION D(7)
      INTEGER R,SR
      LOGICAL KONV,BO,BH
      LOGICAL EPSERR
      DATA EPSERR/.FALSE./
      DOUBLE PRECISION E,A,EC,G,B,U,V,C,TA,B1
      IF(N.GT.0.AND.N.LE.MAXORD) GO TO 1
      WRITE(6,100)
  100 FORMAT(28H0ORDER TOO LARGE FOR DIFSYS.)
      STOP
    1 E=DABS(EPS)
      IF(E.GE.1.0D-13) GO TO 2
      IF(EPSERR) GO TO 102
      EPSERR=.TRUE.
      WRITE(6,101)
  101 FORMAT(51H0ERROR LIMIT TOO SMALL FOR DIFSYS.  WE USE 1.0D-13.)
  102 E=1.0D-13
C
C**********************************************************************
C
C             EACH CALL OF DIFSYS PERFORMS ONE INTEGRATION STEP OF THE
C       EQUATION DY/DX=F(X,Y) ACCORDING TO THE METHOD OF R. BULIRSCH AND
C       J. STOER (NUMERISCHE MATHEMATIK, IN PRESS).  THE STEP SIZE WILL
C       BE LESS THAN OR EQUAL TO H.  THE PROGRAM TAKES THE FIRST OF THE
```

```
C     NUMBERS H, H/2, H/4, .... AS STEP SIZE FOR WHICH NO MORE THAN 9
C     EXTRAPOLATION STEPS ARE NEEDED TO OBTAIN A SUFFICIENTLY ACCURATE
C     RESULT.  IF THE STEP SIZE USED IS DIFFERENT THAN THE STEP SIZE
C     GIVEN IN THE PARAMETER LIST, THEN THE LOGICAL FLAG NEWH WILL BE
C     SET EQUAL TO .TRUE., OTHERWISE IT WILL BE SET EQUAL TO .FALSE..
C     X AND Y ARE THE INITIAL VALUES FOR THE STEP TO BE COMPUTED.  AFTER
C     LEAVING THE SUBROUTINE, THE ORIGINAL VALUES OF THE PARAMETERS X
C     AND Y WILL HAVE BEEN REPLACED BY X+H' AND Y(X+H'), RESPECTIVELY,
C     WHERE H' IS THE STEP SIZE ACTUALLY USED.  IN ADDITION THE STEP
C     SIZE WILL HAVE BEEN CHANGED AUTOMATICALLY TO AN ESTIMATED OPTIMAL
C     STEP SIZE FOR THE NEXT INTEGRATION STEP.  THE ARRAY S AND THE
C     CONSTANT EPS ARE USED TO CONTROL THE ACCURACY OF THE COMPUTED
C     VALUES.  THE SUBROUTINE IS LEFT, IF FOR ALL I=1, 2, ...., N TWO
C     SUCCESSIVE VALUES FOR Y(I) DIFFER AT MOST BY AN AMOUNT EPS*S(I).
C     EPS SHOULD NOT BE SMALLER THAN 1.0D-13.  FOR THE FIRST INTEGRA-
C     TION STEP IT IS ADVISABLE TO SET S(I)=0.0.  BEFORE RETURN TO THE
C     CALLING PROGRAM, THE ARRAY S WILL HAVE HAD ITS CONTENTS MODIFIED
C     SO THAT S(I)=MAX(S(I),ABS(Y(I,X)), WHERE THE MAXIMUM IS TAKEN OVER
C     THE INTEGRATION INTERVAL (X,X+H').
C
C***********************************************************************
C
    2 CALL F(X,Y,DZ)
      BH=.FALSE.
      NEWH=.FALSE.
      DO 3 I=1,N
    3 YA(I)=Y(I)
    4 A=X+H
      FC=1.5
      BO=.FALSE.
      M=1
      R=2
      SR=3
      JJ=-1
      DO 1000 J1=1,10
      J=J1-1
      D(2)=2.25
      IF(BO) D(2)=4.0/D(2)
      D(4)=4.0*D(2)
      D(6)=4.0*D(4)
      KONV=J.GT.2
      IF(J.LE.6) GO TO 5
      L=6
      D(7)=64.0
      FC=0.6*FC
      GO TO 6
    5 L=J
      D(L+1)=M*M
    6 M=2*M
      G=H/DBLE(FLOAT(M))
      B=2.0*G
      IF(BH.AND. J.LT.8) GO TO 7
      KK=(M-2)/2
      M=M-1
      DO 8 I=1,N
      YL(I)=YA(I)
    8 YM(I)=YA(I)+G*DZ(I)
      IF(M.LE.0) GO TO 9
      DO 10 K=1,M
      CALL F(X+G*DBLE(FLOAT(K)),YM,DY)
      DO 11 I=1,N
```

```
      U=YL(I)+B*DY(I)
      YL(I)=YM(I)
      YM(I)=U
      U=DABS(U)
   11 S(I)=DMAX1(U,S(I))
      IF(K.NE.KK.OR.K.EQ.2) GO TO 10
      JJ=JJ+1
      DO 12 I=1,N
      YH(JJ+1,I)=YM(I)
   12 YG(JJ+1,I)=YL(I)
   10 CONTINUE
      GO TO 9
    7 DO 13 I=1,N
      YM(I)=YH(J+1,I)
   13 YL(I)=YG(J+1,I)
    9 CALL F(A,YM,DY)
      DO 14 I=1,N
      V=DT(I,1)
      DT(I,1)=0.5*(YM(I)+YL(I)+G*DY(I))
      C=DT(I,1)
      TA=C
      IF(L.LE.0) GO TO 15
      DO 16 K=1,L
      B1=D(K+1)*V
      B=B1-C
      U=V
      IF(B.EQ.0.0) GO TO 17
      B=(C-V)/B
      U=C*B
      C=B1*B
   17 V=DT(I,K+1)
      DT(I,K+1)=U
   16 TA=U+TA
   15 IF(DABS(Y(I)-TA).GT.F*DABS(S(I))) KONV=.FALSE.
   14 Y(I)=TA
      IF(KONV) GO TO 18
      D(3)=4.0
      D(5)=16.0
      BO=.NOT.BO
      M=R
      R=SR
 1000 SR=2*M
      BH=.NOT.BH
      NEWH=.TRUE.
      H=0.5*H
      GO TO 4
   18 H=FC*H
      X=A
      RETURN
      END
```

APPENDIX B

The use of extrapolation formula 5-21 will be explained and illustrated for the hard-sphere, square well data shown in figures 3 and 4. Repeating 5-21:

$$P_{ij}(N) = P_{ij}(\infty) + \frac{1}{(N)^{\alpha}} A . \qquad \text{B-1}$$

This formula says that the error found by using N states in a state expansion, rather than the complete set, is of the order of $1/(N)^{\alpha}$. Suppose we have calculated probabilities for two different expansions with N and M states:

$$\varphi(N) = \varphi(\infty) + \frac{1}{(N)^{\alpha}} A$$

$$\varphi(M) = \varphi(\infty) + \frac{1}{(M)^{\alpha}} A \qquad \text{B-2}$$

where φ represents any particular probability P_{ij}. Eliminating A between B-2, and solving for $\varphi(\infty)$:

$$\varphi(\infty) = \frac{\varphi(N)\,(N)^{\alpha} - \varphi(M)\,(M)^{\alpha}}{(N)^{\alpha} - (M)^{\alpha}} . \qquad \text{B-3}$$

Our simple procedure (which might be improved; see final paragraph in this appendix) is to guess an α and use our calculated values of $\varphi(N)$ to solve for $\varphi(\infty)$. Each pair of calculated $\varphi(N)$ defines $\varphi(\infty)$ for a given α. We check the consistency of the predicted $\varphi(\infty)$ for all pairs and repeat the whole procedure for a new α if needed.

Example #1. The complete table of P_{00} and P_{11} values obtained by the S-Z method for the problem presented in figure 3 is as follows:

Total number of states, N	$\varphi(N) = P_{00}(N) = P_{11}(N)$
4	.4806
5	.5104
6	.5262
7	.5357
8	.5418
9	.5461
10	.5496

Using $\alpha = 1$, we solve for $\varphi(\infty)$ from B-3 using adjacent pairs in the above table:

Pair used	$\varphi(\infty)$
4, 5	.5700
5, 6	.5736
6, 7	.5737
7, 8	.5723
8, 9	.5719
9, 10	.5741

The $\varphi(\infty)$ predictions are consistent within .572 ± .002. This is adequate for our needs so no further improvements on α were tried. The $P_{01}(\infty) = P_{10}(\infty)$ extrapolation is required to be $1 - P_{00}(\infty)$.

Example #2. The complete table of P_{00} and P_{11} values corresponding to the S-Z solution presented in figure 4 are:

Total number of states, N	$\varphi(N) = P_{00}(N) = P_{11}(N)$
4	.8636
5	.8337
6	.8231
7	.8181
8	.8153
9	.8136
10	.8125
11	.8122

An extrapolation based on $\alpha = 1$ gave:

Pair used	$\varphi(\infty)$
4, 5	.7739
5, 6	.7913
6, 7	.7981
7, 8	.8013
8, 9	.8034
9, 10	.8048
10, 11	.8098

The predicted $\varphi(\infty)$ are not very consistent. Using $\alpha = 2$, and letting the label N be the number of virtual states rather than the total number present gave a better result:

Pair used	$\varphi(\infty)$
4,5	.8098
5,6	.8095
6,7	.8092
7,8	.8089
8,9	.8089
9,10	.8089
10,11	.8111

The extrapolations are consistent to .8094 ± .0005 neglecting the 10, 11 pair result. The latter is questionable because of inaccuracies in obtaining the inverse of the ill-conditioned matrix $\underset{\sim}{U}$ (5-15) for large dimension.

The foregoing treatment is unique in its simplicity. The sole object was to demonstrate that the S-Z results can be drastically improved in spite of the slow rate of convergence (see figure 3) and the limiting of state expansions by ill-conditioning. It would be easy to use a higher order (more parameters) error formula and do least squares fitting to the $P_{ij}(N)$ for several N. This destroys the simple nature of the extrapolation and was not thought to be worthwhile.

APPENDIX C

The matrix elements defined in 5-25 are

$$\int_{x}^{\infty} \varphi_n(y)\, \varphi_m(y)\, dy \qquad \text{C-1}$$

$$n, m = 0, 1, 2, \ldots$$

where $\varphi_n(y)$ are the normalized eigenfunctions of 5-23. Let:

$$I_{nm}(x) = \delta_{nm} - \int_{x}^{\infty} \varphi_n(y)\, \varphi_m(y)\, dy$$

$$= \int_{-\infty}^{x} e^{-y^2}\, \bar{H}_n(y)\, \bar{H}_m(y)\, dy\,. \qquad \text{C-2}$$

$\bar{H}_n(y)$ are the normalized Hermite polynomials defined by

$$\bar{H}_n(y) = \frac{1}{\sqrt{2^n n!\, \sqrt{\pi}}}\, H_n(y)$$

$$H_n(y) = (-1)^n e^{y^2} \left(\frac{d}{dy}\right)^n (e^{-y^2})\,. \qquad \text{C-3}$$

The first few are

$$H_0(y) = 1, \quad H_1(y) = 2y$$

$$\bar{H}_0(y) = \frac{1}{\sqrt[4]{\pi}}, \quad \bar{H}_1(y) = \frac{\sqrt{2}}{\sqrt[4]{\pi}}\, y\,. \qquad \text{C-4}$$

We know that the derivative of these polynomials is given by

$$\frac{d}{dy} H_n(y) = 2n\, H_{n-1}(y) \quad \text{for } n > 0\,. \qquad \text{C-5}$$

Also, from C-2 we see that

$$I_{nm}(x) = I_{mn}(x)\,. \qquad \text{C-6}$$

Substitution of C-3 into C-2 gives:

$$I_{nm}(x) = \int_{-\infty}^{x} e^{-y^2} \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} (-1)^n e^{y^2} \left(\frac{d}{dy}\right)^n (e^{-y^2}) \bar{H}_m(y) dy. \qquad \text{C-7}$$

Let us integrate this by parts for n and m > 0:

$$I_{nm}(x) = \left[\frac{1}{\sqrt{2^n n! \sqrt{\pi}}} (-1)^n \left(\frac{d}{dy}\right)^{n-1} (e^{-y^2})\, \bar{H}_m(y) \right]_{-\infty}^{x}$$

$$- \int_{-\infty}^{x} \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} (-1)^n \left(\frac{d}{dy}\right)^{n-1} (e^{-y^2}) \frac{d\, \bar{H}_m(y)}{dy}$$

$$= \left[- \frac{1}{\sqrt{2n}} e^{-y^2} \overline{H}_{n-1}(y) \overline{H}_m(y) \right]_{-\infty}^{x}$$

$$+ \sqrt{\frac{m}{n}} \int_{-\infty}^{x} e^{-y^2} \overline{H}_{n-1}(y) \overline{H}_{m-1}(y) \, dy \, . \qquad \text{C-8}$$

Therefore:

$$I_{nm}(x) = - \frac{1}{\sqrt{2n}} e^{-x^2} \overline{H}_{n-1}(x) \overline{H}_m(x)$$

$$+ \sqrt{\frac{m}{n}} \; I_{n-1,\, m-1}(x) \, . \qquad \text{C-9}$$

This recursion relation enables us to reduce the calculation of any $I_{nm}(x)$ to $I_{0M}(x)$, $I_{N0}(x)$, or $I_{00}(x)$. Consider first the evaluation of $I_{00}(x)$:

$$I_{00}(x) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{x} e^{-y^2} \, dy \qquad \text{C-10}$$

from C-2 and C-4. The error function, erf(x), is:[35]

$$\mathrm{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{0}^{x} e^{-y^2} \, dy \quad \text{for } x \geq 0 \qquad \text{C-11}$$

$$\mathrm{erf}(-x) \;=\; -\mathrm{erf}(x) \qquad \text{for } x \geq 0 \;. \qquad \text{C-12}$$

In terms of erf(x):

$$I_{00}(x) \;=\; \frac{1}{2}\,(1 + \mathrm{erf}(x)) \qquad \text{all } x\;. \qquad \text{C-13}$$

To compute erf(x), we used an approximation[35] such that the absolute error was less than 1.5×10^{-7} for all x. Having calculated a particular $I_{00}(x)$ from C-13, we obtain all needed $I_{nn}(x)$ by means of C-9. Integrals of the form $I_{0N}(x) = I_{N0}(x)$ are treated as follows:

$$I_{0m}(x) = \frac{1}{\sqrt{2^m m!\sqrt{\pi}}}\;\frac{1}{\sqrt[4]{\pi}}\int_{-\infty}^{x} e^{-y^2}\,H_m(y)\,dy$$

$$= \frac{1}{\sqrt{2^m m!\pi}}\int_{-\infty}^{x} e^{-y^2}\,(-1)^m\,e^{y^2}\,\left(\frac{d}{dy}\right)^m (e^{-y^2})\,dy$$

$$= \frac{1}{\sqrt{2^m m!\pi}}\,(-1)^m\int_{-\infty}^{x}\left(\frac{d}{dy}\right)^m (e^{-y^2})\,dy$$

$$= \frac{1}{\sqrt{2^m m!\pi}}\,(-1)^m\left[\left(\frac{d}{dy}\right)^{m-1}(e^{-y^2})\right]_{-\infty}^{x}$$

$$= -\frac{1}{\sqrt{2m\sqrt{\pi}}}\,e^{-x^2}\;\bar{H}_{m-1}(x)\;. \qquad \text{C-14}$$

Using C-4, we have:

$$I_{0m}(x) = -\frac{1}{\sqrt{2m}} \bar{H}_0(x) \bar{H}_{m-1}(x) e^{-x^2} . \qquad \text{C-15}$$

The normalized Hermite polynomials are calculated for each x from the recursion relation:

$$\bar{H}_{n+1}(x) = \frac{\sqrt{2}\, x}{\sqrt{n+1}} \bar{H}_n(x) - \frac{\sqrt{n}}{\sqrt{n+1}} \bar{H}_{n-1}(x) \qquad \text{C-16}$$

beginning with $\bar{H}_0(x) = 1/\sqrt[4]{\pi}$, $\bar{H}_1(x) = \frac{\sqrt{2}\, x}{\sqrt[4]{\pi}}$.

To evaluate the required matrix elements (C-1) at point x, we first generate all needed $\bar{H}_n(x)$ from C-16. We then calculate $I_{00}(x)$ from C-13 and use C-9 to get all $I_{nn}(x)$ diagonal elements. All remaining elements are obtained from C-15 using C-9.

APPENDIX D

Some of the authors work was directed toward the problem of dissociation induced by high energy collisions. There are no quantum mechanical methods suited for this problem in atomic and molecular scattering. An untested method based on the impulse approximation is proposed as a means of obtaining approximate cross sections for dissociation processes.

Consider the following problem: Let atom #2 with mass m_2 bound in a fixed potential V_2 be struck by atom #1 with mass m_1. Interaction of 1 (atom #1) and 2(atom #2) is given by $V_{12}(|\underset{\sim}{x}_1 - \underset{\sim}{x}_2|)$ and 1 does not interact with V_2; m_2 has bound states $\varphi_n(\underset{\sim}{x}_2)$, binding energies w_n, and continuum states $\varphi^{\pm}_{\underset{\sim}{\ell}}(\underset{\sim}{x}_2)$ with energy $\hbar^2 \ell^2/2m_2$. The exact scattering amplitude for transition from incident state $\varphi_0(\underset{\sim}{x}_2)\, e^{i\underset{\sim}{k}_0 \cdot \underset{\sim}{x}_1}$ to final state $\varphi^-_{\underset{\sim}{\ell}_f}(\underset{\sim}{x}_2)\, e^{i\underset{\sim}{k}_f \cdot \underset{\sim}{x}_1}$ is given by:[41]

$$T(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f, \underset{\sim}{k}_f) = \int d^3x_1 \int d^3x_2\, \varphi^{-*}_{\underset{\sim}{\ell}_f}(\underset{\sim}{x}_2)\, e^{-i\underset{\sim}{k}_f \cdot \underset{\sim}{x}_1}$$

$$\times\, V_{12}(|\underset{\sim}{x}_1 - \underset{\sim}{x}_2|)\, \psi^0_{\underset{\sim}{k}_0}(\underset{\sim}{x}_1, \underset{\sim}{x}_2), \qquad \text{D-1}$$

where $\psi^0_{\underset{\sim}{k}_0}$ is the solution to the Lippman-Schwinger equation:

$$\psi^0_{\underset{\sim}{k}_0} = \varphi_0\, (\underset{\sim}{x}_2)\, e^{i\underset{\sim}{k}_0 \cdot \underset{\sim}{x}_1} - G_0\, (V_2 + V_{12})\, \psi^0_{\underset{\sim}{k}_0} \qquad \text{D-2}$$

or the Schrödinger equation:

$$[-\hbar^2/2m_i \nabla^2_{\underset{\sim}{x_1}} - \hbar^2/2m_2 \nabla^2_{\underset{\sim}{x_2}} + V_2(\underset{\sim}{x_2}) + V_{12}(|\underset{\sim}{x_1} - \underset{\sim}{x_2}|)]\, \psi^0_{\underset{\sim}{k_0}} = E^T \psi^0_{\underset{\sim}{k_0}} \tag{D-3}$$

with $E^T = \hbar^2 k_0^2/2m_1 - w_0$ and the correct asymptotic boundary conditions on $\psi^0_{\underset{\sim}{k_0}}$. The impulse approximation is developed as follows.[41] We must approximate $\psi^0_{\underset{\sim}{k_0}}$, as it is the solution to the whole problem, which is unknown to us. Introduce:

$$g_0(\underset{\sim}{K}) = 1/(2\pi)^3 \int d^3x_2 e^{-i\underset{\sim}{K}\cdot\underset{\sim}{x_2}}\, \varphi_0(\underset{\sim}{x_2})$$

$$g_{\underset{\sim}{\ell_f}}(\underset{\sim}{K}) = 1/(2\pi)^3 \int d^3x_2 e^{-i\underset{\sim}{K}\cdot\underset{\sim}{x_2}}\, \varphi^-_{\underset{\sim}{\ell_f}}(\underset{\sim}{x_2})$$

which are the momentum representations of the states $n = 0$ and $\underset{\sim}{\ell_f}$ of particle 2. Interpret $g_0(\underset{\sim}{K})$ as the amplitude of 2 to have momentum $\hbar\underset{\sim}{K}$ before 1 collides. Now, we can find exactly the state $\chi_{\underset{\sim}{k_0},\underset{\sim}{K}}(\underset{\sim}{x_1}, \underset{\sim}{x_2})$ representing the scattering of 1 with incident wave vector $\underset{\sim}{k_0}$ from 2 with wave vector $\underset{\sim}{K}$. $\chi_{\underset{\sim}{k_0},\underset{\sim}{K}}$ would describe the collision exactly if 2 were a free particle with momentum $\hbar\underset{\sim}{K}$. The impulse approximation consists in replacing $\psi^0_{\underset{\sim}{k_0}}$ by $\int d^3K\, g_0(\underset{\sim}{K})\, \chi_{\underset{\sim}{k_0},\underset{\sim}{K}}(\underset{\sim}{x_1}, \underset{\sim}{x_2})$. This averages the two particle scattering states over the momentum distribution of the bound particle, but does not account for the presence of V_2 except in producing the momentum distribution $g_0(\underset{\sim}{K})$ of 2. The impulse approximation to $T(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f, \underset{\sim}{k}_f)$ is:

$$\begin{aligned} T^{I}(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f, \underset{\sim}{k}_f) &= \int d^3K\, g^*_{\underset{\sim}{\ell}_f}(\underset{\sim}{K}')\, g_0(\underset{\sim}{K}) \\ &\quad \times \int d^3x_1 \int d^3x_2 \exp(-i\underset{\sim}{k}_f \cdot \underset{\sim}{x}_1 - i\underset{\sim}{K}' \cdot \underset{\sim}{x}_2) \\ &\quad \times V_{12}(|\underset{\sim}{x}_1 - \underset{\sim}{x}_2|)\, \chi_{\underset{\sim}{k}_0 \underset{\sim}{K}}(\underset{\sim}{x}_1, \underset{\sim}{x}_2). \end{aligned} \tag{D-4}$$

If we introduce the center of mass and internal coordinates of the 1, 2 subsystem; namely,

$$\underset{\sim}{r} = \underset{\sim}{x}_1 - \underset{\sim}{x}_2, \quad \underset{\sim}{R} = \frac{m_1 \underset{\sim}{x}_1 + m_2 \underset{\sim}{x}_2}{m_1 + m_2} \ ,$$

then the integral $\int d^3x_1 \int d^3x_2$ becomes:

$$\begin{aligned} I = \int d^3R \int d^3 r \exp(&-i\underset{\sim}{k}_f \cdot \underset{\sim}{R} - i\underset{\sim}{k}_f \cdot \underset{\sim}{r}\, \frac{m_2}{m_1 + m_2} - i\underset{\sim}{K}' \cdot \underset{\sim}{R} \\ &+ i\underset{\sim}{K}' \cdot \underset{\sim}{r}\, \frac{m_1}{m_1 + m_2} \times V_{12}(r)\, e^{i(\underset{\sim}{k}_0 + \underset{\sim}{K}) \cdot \underset{\sim}{R}}\, \varphi_{\underset{\sim}{k}_{INT}}(\underset{\sim}{r}). \end{aligned}$$

$\varphi_{\underset{\sim}{k}_{INT}}(\underset{\sim}{r})$ is the scattering state $\chi_{\underset{\sim}{k}_0 \underset{\sim}{K}}$ with the center of mass motion of 1 and 2, $e^{i(\underset{\sim}{k}_0 + \underset{\sim}{K}) \cdot \underset{\sim}{R}}$, factored out. Also, $\underset{\sim}{k}_{INT} = m_2 \underset{\sim}{k}_0 - m_1 \underset{\sim}{K}/(m_1 + m_2)$, the relative (internal) wave vector. Performing the d^3R integral, we have:

$$I = (2\pi)^3 \delta^3 (\underset{\sim}{k}_0 + \underset{\sim}{K} - \underset{\sim}{k}_f - \underset{\sim}{K}')$$

$$\times \int d^3 r \exp(-i \frac{m_2 \underset{\sim}{k}_f - m_1 \underset{\sim}{K}'}{m_1 + m_2} \cdot \underset{\sim}{r}) V_{12}(r) \varphi_{\underset{\sim}{k}_{INT}}(\underset{\sim}{r}).$$

Recognizing $\int d^3 r \, e^{-i\underset{\sim}{v} \cdot \underset{\sim}{r}} V_{12}(r) \varphi_k(r)$ as $f_{12}(\underset{\sim}{k}, \underset{\sim}{v})$, the scattering amplitude of particles 1 and 2, we finally write:

$$T^I(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f, \underset{\sim}{k}_f) = \int d^3K \, g^*_{\underset{\sim}{\ell}_f}(\underset{\sim}{K}') \, g_0(\underset{\sim}{K})$$

D-5

$$\times (2\pi)^3 \delta^3 (\underset{\sim}{k}_0 + \underset{\sim}{K} - \underset{\sim}{k}_f - \underset{\sim}{K}') f_{12}(\frac{m_2 \underset{\sim}{k}_0 - m_1 \underset{\sim}{K}}{m_1 + m_2}, \frac{m_2 \underset{\sim}{k}_f - m_1 \underset{\sim}{K}'}{m_1 + m_2}).$$

Note that the delta function conserves momentum in the 1, 2-subsystem and thus restricts the contribution of f_{12} to on-shell[42] scattering in the subsystem. Because we are calculating an inelastic three-body process, it would be necessary to use off-shell[42] two-body amplitudes to allow the all-over scattering event to conserve energy. Since it is impossible to find off-shell amplitudes without solving integral equations, we will use the calculable on-shell amplitude as a first approximation to the off-shell:

$$f_{E=\hbar^2 k_0^2/2m}(\underset{\sim}{K}, \underset{\sim}{K}') \approx f(kk_0,\ k'k_0);$$

k denotes a unit vector with direction $\underset{\sim}{K}$. This has been done in the literature in other circumstances.[42]

Since the bound state function $g_0(\underset{\sim}{K})$ is peaked at magnitudes of $\underset{\sim}{K}$ much smaller than $\underset{\sim}{k}_0$, we neglect $\underset{\sim}{K}$ in the first argument of f_{12}. Now we define $\hbar \underset{\sim}{q}_1$ as the momentum transfer to 1, and $\hbar \underset{\sim}{q}_2$ as the momentum imparted to 2. If 2 were free, $\underset{\sim}{q}_2 = -\underset{\sim}{q}_1$, but we want to account better for the binding effect of V_2 by letting $\underset{\sim}{q}_2 = -\ m_2/m_2^* \underset{\sim}{q}$, so that $\hbar^2 q_2^2/2m_2 = \hbar^2 q_1^2/2m_2^*$. m_2^* is an effective mass which controls the energy and momentum imparted to 2 during the collision. Letting $\underset{\sim}{q}_1 = \underset{\sim}{k}_f - \underset{\sim}{k}_0$, we have:

$$T^I(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f, \underset{\sim}{k}_f) = \int d^3K' \int d^3K\ g^*_{\underset{\sim}{\ell}_f}(\underset{\sim}{K}')\, g_0(\underset{\sim}{K}) \times (2\pi)^3 \delta^3(\underset{\sim}{K} - \underset{\sim}{K}' - \underset{\sim}{q}_1)\, f_{12}\left(\frac{m_2}{m_1+m_2}\underset{\sim}{k}_0,\ \frac{m_2}{m_1+m_2}\left(\underset{\sim}{k}_f - \frac{m_1}{m_2}\underset{\sim}{K}'\right)\right). \tag{D-6}$$

In order to transfer an effective $\underset{\sim}{q}_2$ to the bound particle rather than $-\underset{\sim}{q}_1$, we must replace $\underset{\sim}{q}_1$ in the δ function. The result is:

$$T^{I*}(\mathbf{k}_0, \boldsymbol{\ell}_f, \mathbf{k}_f) = \int d^3K' \, g^*_{\boldsymbol{\ell}_f}(\mathbf{K}') \, g_0(\mathbf{K}' - m_2/m_2^* \, \mathbf{q}_1)$$

$$\times \, f_{12}\left(\frac{m_2}{m_1 + m_2} \mathbf{k}_0, \frac{m_2}{m_1 + m_2} (\mathbf{k}_f - m_1/m_2 \, \mathbf{K}')\right) . \qquad \text{D-7}$$

Here f_{12} appears off-shell, because we have not insured that $\mathbf{k}_0^2 = |\mathbf{k}_f - m_1/m_2 \, \mathbf{K}'|^2$. However, we invoke our on-shell approximation and have:

$$T^{I*}(\mathbf{k}_0, \boldsymbol{\ell}_f, \mathbf{k}_f) = \int d^3K' \, g^*_{\boldsymbol{\ell}_f}(\mathbf{K}') \, g_0(\mathbf{K}' - m_2/m_2^* \, \mathbf{q}_1)$$

$$\times \, f_{12}\left(\frac{m_2}{m_1 + m_2} \mathbf{k}_0, \frac{m_2}{m_1 + m_2} (\mathbf{k}_0 + \mathbf{q}_1)\right) \qquad \text{D-8}$$

where

$$q_1 = 2k_0 \sin(\theta/2) .$$

If we are not detecting the scattered flux of 1, but are interested in the production of continuum states of particle 2, then we sum (integrate) over all the final states of 1, or equivalently, over the momentum transfer $\mathbf{q}_1$:

$$T^{I*}(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f) = \int d^3q_1 \, \delta(k_0^2 - |\underset{\sim}{k}_0 + \underset{\sim}{q}|^2) \int d^3K' \, g^*_{\underset{\sim}{\ell}_f}(\underset{\sim}{K}')$$

D-9

$$\times \; g_0(\underset{\sim}{K}' - \; m_2/m_2^* \, \underset{\sim}{q}_1) \, f_{12}(\frac{m_2}{m_1 + m_2} \underset{\sim}{k}_0, \frac{m_2}{m_1 + m_2} (\underset{\sim}{k}_0 + \underset{\sim}{q}_1))$$

or rather, with $k_f = k_0$:

$$T^{I*}(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f) = \int d(\underset{\sim}{k}_0 \cdot \underset{\sim}{k}_f) \int d^3K' \, g^*_{\underset{\sim}{\ell}_f}(\underset{\sim}{K}') \, g_0[\underset{\sim}{K}' - \; m_2/m_2^* \, (\underset{\sim}{k}_f - \underset{\sim}{k}_0)]$$

$$\times \; f_{12}(\frac{m_2}{m_1 + m_2} \underset{\sim}{k}_0, \frac{m_2}{m_1 + m_2} \underset{\sim}{k}_f). \quad \text{D-10}$$

Equation D-10 implies integration over the angular space spanned by $\underset{\sim}{k}_0 \cdot \underset{\sim}{k}_f$.

Another form of D-10 is:

$$T^{I*}(\underset{\sim}{k}_0, \underset{\sim}{\ell}_f) = \int d(k_0 \cdot k_f \int d^3z \, \varphi^{-*}_{\underset{\sim}{\ell}_f}(z)$$

D-11

$$\times \; \exp[-i \; m_2/m_2^* \, (\underset{\sim}{k}_f - \underset{\sim}{k}_0) \cdot \underset{\sim}{z}] \, \varphi_0(\underset{\sim}{z}) \, f_{12}(\frac{m_2}{m_1 + m_2} \underset{\sim}{k}_0, \frac{m_2}{m_1 + m_2} \underset{\sim}{k}_f).$$

The essence of these expressions is the presence of m_2^*, the effective mass. By correlating with energy transfer in simple linear systems, and possibly making m_2^* dependent on the angle between $\underset{\sim}{q}_1$ and $\underset{\sim}{z}$, $(\underset{\sim}{k}_f - \underset{\sim}{k}_0) \cdot \underset{\sim}{z}$, in D-11, we might carry out this quadrature to determine realistic dissociation probabilities for atom-molecule collisions. A shielding-effect correction for the multicenter scattering in our problem is appropriate because heavy atoms are not significantly diffracted by the molecule.[43]

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$x = -7.9$

$$\begin{pmatrix} .133E{-5} & .164E{-7} & .741E{-8} & .303E{-8} \\ .164E{-7} & .135E{-5} & .178E{-7} & .728E{-8} \\ .741E{-8} & .178E{-7} & .137E{-5} & .199E{-7} \\ .303E{-8} & .728E{-8} & .199E{-7} & .139E{-5} \end{pmatrix}$$

$x = -.59$

$$\begin{pmatrix} .516 & .105E\ 1 & .192E\ 1 & .264E\ 1 \\ .172E\ 1 & .351E\ 1 & .641E\ 1 & .879E\ 1 \\ .688E\ 1 & .141E\ 2 & .256E\ 2 & .350E\ 2 \\ .268E\ 2 & .549E\ 2 & .100E\ 3 & .139E\ 3 \end{pmatrix}$$

$x = 10.2$

$$\begin{pmatrix} .573E\ 2 & .117E\ 3 & .215E\ 3 & .298E\ 3 \\ .220E\ 3 & .451E\ 3 & .824E\ 3 & .114E\ 4 \\ .150E\ 4 & .306E\ 4 & .560E\ 4 & .776E\ 4 \\ .150E\ 6 & .308E\ 6 & .564E\ 6 & .782E\ 6 \end{pmatrix}$$

$x = 23.2$

$$\begin{pmatrix} .155E\ 3 & .319E\ 3 & .583E\ 3 & .808E\ 3 \\ .601E\ 3 & .123E\ 4 & .225E\ 4 & .312E\ 4 \\ .417E\ 4 & .855E\ 4 & .156E\ 5 & .217E\ 5 \\ .202E\ 8 & .414E\ 8 & .758E\ 8 & .105E\ 9 \end{pmatrix}$$

Development of linear dependence during the integration of the Schrödinger matrix equation for the atom on diatom problem defined by: E = 4.9455, MASS = 1.25, ALPHA = .2973, 2 open channels, 2 virtual channels. See section 5.2.2 of the text for definition of these parameters.

Table 1

	Number of virtual states in II.			Extrapolated II.	Estimates from Secrest and Johnson.[19]
	1	2	3		
P_{00}	.0085	.0048	.0044	.0043	.01 ± .007
P_{01}	.7014	.6695	.6525	.63	.62 ± .02
P_{02}	.2901	.3257	.3430	.36	.36 ± .02
P_{11}	.0987	.1301	.1474	.16	not given
P_{12}	.1998	.2004	.2001	.2002	.20 ± .02
P_{22}	.5101	.4740	.4569	.44	.42 ± .02
ET:	2'39"	4'59"	7'45"		

Convergence of II state expansion for the hard-sphere, harmonic oscillator problem: E = 5.5, MASS = 0.5, 3 open channels. II uses V^{SB} = 35.0, ERROR = 10^{-6}.

Table 2

	Number of virtual states in II.		Estimates from Shuler and Zwanzig.[28]
	2	3	
P_{00}	.83683646	.85905178	.87 ± .02
P_{01}	.16316352	.14094795	.11 ± .02
P_{10}	.16316352	.14094786	not given
P_{11}	.83683646	.85905178	not given

ET: 2'36" 5'00"

Convergence of II state expansion for the hard-sphere, harmonic oscillator problem: $E = 4.5$, MASS = 0.5, 2 open channels. II uses $V^{SB} = 35.0$, ERROR = 10^{-6}.

Table 3

Double precision Romberg integrator, ERROR = 10^{-6}, 2 virtual channels.

$$\begin{pmatrix} .99988912 & .00011236 \\ .00011236 & .99988769 \end{pmatrix}$$

Results of Secrest and Johnson.

$$\begin{pmatrix} ...... & .000112 \\ .000112 & .... \end{pmatrix}$$

Comparison of II with Secrest and Johnson's published data for the atom on diatom problem: E = 4.9455, MASS = 1.25, ALPHA = .2973, 2 open channels.

Table 4

Double precision Romberg integrator, ERROR = 10^{-6}, 2 virtual channels.

$$\begin{pmatrix} .99929335 & .70665095\text{E-}3 & .90223809\text{E-}9 \\ .70664643\text{E-}3 & .99928825 & .51047324\text{E-}5 \\ .90223315\text{E-}9 & .51047396\text{E-}5 & .99999489 \end{pmatrix}$$

Results of Secrest and Johnson.

$$\begin{pmatrix} \text{......} & .706\text{E-}3 & .903\text{E-}9 \\ .706\text{E-}3 & \text{......} & .511\text{E-}5 \\ .903\text{E-}9 & .511\text{E-}5 & \text{......} \end{pmatrix}$$

Comparison of DRILL with Secrest and Johnson's published data for the atom on diatom problem: E = 6.0, MASS = 0.2, ALPHA = 0.114, 3 open channels.

Table 5

(a) Double precision Romberg integrator, ERROR = 10^{-4}, ET = 4' 3".

$$\begin{pmatrix}
.6309 & .3192 & .4899E-1 & .2440E-2 & .3181E-4 & .4383E-7 \\
.3176 & .3036 & .3370 & .4412E-1 & .1100E-2 & .2485E-5 \\
.4754E-1 & .3287 & .3193 & .2790 & .1730E-1 & .7153E-4 \\
.2420E-2 & .4400E-1 & .2853 & .5077 & .1622 & .1549E-2 \\
.3154E-4 & .1097E-2 & .1769E-1 & .1622 & .7876 & .3157E-1 \\
.4342E-7 & .2477E-5 & .7313E-4 & .1549E-2 & .3157E-1 & .9668
\end{pmatrix}$$

(b) Single precision Romberg integrator, operating under the same conditions, gave almost identical results, with ET = 2'40".

(c) Single precision 5'th order Adams-Moulton integrator, with a step size increasing from 0.035 to 0.37 over the range of integration. ET = 1'28".

$$\begin{pmatrix}
.6318 & .3170 & .4849E-1 & .2491E-2 & .3346E-4 & .4938E-7 \\
.3173 & .3018 & .3351 & .4479E-1 & .1127E-2 & .2563E-5 \\
.4854E-1 & .3352 & .3150 & .2837 & .1760E-1 & .7280E-4 \\
.2492E-2 & .4478E-1 & .2836 & .5056 & .1620 & .1548E-2 \\
.3347E-4 & .1126E-2 & .1759E-1 & .1619 & .7877 & .3158E-1 \\
.4799E-7 & .2566E-5 & .7274E-4 & .1547E-2 & .3157E-1 & .9668
\end{pmatrix}$$

(d) Results of Secrest and Johnson. ET estimate: 1'45".

$$\begin{pmatrix}
..... & .317 & .486E-1 & .250E-2 & ..... & ..... \\
.317 & ..... & .335 & .447E-1 & & \\
..... & & & & & \\
..... & & & & & \\
..... & & & & & \\
..... & & & & &
\end{pmatrix}$$

Comparison of DRILL with Secrest and Johnson's published data for the atom on diatom problem: E = 12.8365, MASS = 1/13, ALPHA = .1287, 6 open channels and 1 virtual. The **i**,j element gives the probability of transition from state i to j.

Table 6

	(0,0)	(1,0)	(0,1)
(0,0)	.99964181	.00017906	.00017906
(1,0)	.00017913	.96133468	.03848623
(0,1)	.00017913	.03848623	.96133468

System: H_2 on H_2, E = 4.9455, ALPHA = .2973, OMEGA = 1.0, MA = MB = MC = MD = 1.0, N = 2, M = 2.

Integration: DRILL with double precision Romberg integrator, ERROR = 10^{-5}, XST = -15.0 , ET = 33".

Table 7(a)

	(0,0)	(1,0)	(0,1)
(0,0)	.99964327	.00017746	.00017746
(1,0)	.00017928	.96133686	.03848478
(0,1)	.00017928	.03848478	.96133686

System: H_2 on H_2, E = 4.9455, ALPHA = .2973, OMEGA = 1.0, MA = MB = MC = MD = 1.0, N = 2, M= 2.

Integration: DRILL with double precision Romberg integrator, ERROR = 10^{-5}, XST = -18.0, ET = 37".

Table 7(b)

	(0,0)	(1,0)	(0,1)
(0,0)	.99890878	.00054626	.00054626
(1,0)	.00054496	.95824503	.04120936
(0,1)	.00054496	.04120936	.95824503

System: H_2 on H_2, E = 4.9455, ALPHA = .2973, OMEGA = 1.0,
MA = MB = MC = MD = 1.0, N = 3, M = 3.

Integration: DRILL with double precision Romberg integrator,
ERROR = 10^{-5}, XST = -15.0, ET = 4'39".

Table 7(c)

	(0,0)	(1,0)	(0,1)
(0,0)	.99966844	.00017906	.00017906
(1,0)	.00017906	.96133274	.03848814
(0,1)	.00017906	.03848814	.96133274

System: H_2 on H_2, E = 4.9455, ALPHA = .2973, OMEGA = 1.0, MA = MB = MC = MD = 1.0, N = 2, M = 2.

Integration: II with double precision Romberg integrator, ERROR = 10^{-5}, XST = -15.0, ET = 2'33".

Table 8

	(0,0)	(1,0)	(0,1)
(0,0)	.99999662	.00000172	.00000172
(1,0)	.00000166	.99589831	.00410000
(0,1)	.00000166	.00410000	.99589831

All of the calculations presented in tables 9(a) through 9(g) are for an energy dependent study of the H_2 on H_2 system: ALPHA = .2973, OMEGA = 1.0, MA = MB = MC = MD = 1.0, N = 3, M = 3. The integrations were done using DRILL with the double precision Romberg integrator, ERROR = 10^{-5}, XST = -15.0.

E = 4.1   ET = 4'58"

Table 9(a)

	(0,0)	(1,0)	(0,1)
(0,0)	.99984320	.00007892	.00007892
(1,0)	.00007789	.97883120	.02109040
(0,1)	.00007789	.02109040	.97883120

E = 4.5   ET = 4'40"

Table **9(b)**

	(0,0)	(1,0)	(0,1)
(0,0)	.99870050	.00064976	.00064976
(1,0)	.00064975	.95559070	.04375955
(0,1)	.00064975	.04375955	.95559070

E = 5.0   ET = 4'46"

Table 9(c)

	(0,0)	(1,0)	(0,1)
(0,0)	.99538051	.00231001	.00231001
(1,0)	.00230948	.92964395	.06804631
(0,1)	.00230948	.06804631	.92964395

E = 5.5   ET = 4'54"

Table 9(d)

	(0,0)	(1,0)	(2,0)	(0,1)	(1,1)	(0,2)
(0,0)	.98717897	.00641025	.35 E -8	.00641025	.15 E -7	.35 E -8
(1,0)	.00641076	.89464854	.00000111	.09893784	.00000195	.56 E -7
(2,0)	.35 E -8	.00000111	.99216035	.56 E -7	.00782153	.00001695
(0,1)	.00641075	.09893784	.56 E -7	.89464854	.00000195	.00000111
(1,1)	.15 E-7	.00000195	.00782153	.00000195	.98435303	.00782153
(0,2)	.35 E -8	.56 E-7	.00001695	.00000111	.00782153	.99216035

E = 6.1 ET = 5'10"

Table 9(e)

	(0,0)	(1,0)	(2,0)	(0,1)	(1,1)	(0,2)
(0,0)	.96524878	.01736563	.00000189	.01736563	.00002238	.00000189
(1,0)	.01735943	.83569857	.00015178	.14591555	.00082601	.00004553
(2,0)	.00000189	.00015181	.92214656	.00004553	.07607607	.00157122
(0,1)	.01735943	.14591555	.00004553	.83569857	.00082601	.00015178
(1,1)	.00002238	.00082604	.07608993	.00082604	.84615957	.07608993
(0,2)	.00000189	.00004553	.00157122	.00015181	.07607607	.92214656

E = 7.0   ET = 5'29"

Table 9(f)

	(0,0)	(1,0)	(2,0)	(0,1)	(1,1)	(0,2)
(0,0)	.93437993	.03258572	.00001808	.03258572	.00039713	.00001808
(1,0)	.03260094	.77253625	.00044386	.18748031	.00653283	.00041256
(2,0)	.00001805	.00044417	.86225658	.00041269	.13170388	.00516479
(0,1)	.03260094	.18748031	.00041256	.77253625	.00653283	.00044386
(1,1)	.00039743	.00653411	.13170397	.00653410	.72312793	.13170397
(0,2)	.00001805	.00041269	.00516479	.00044417	.13170388	.86225658

E = 7.9 ET = 5'33"

Table 9(g)

	(0,0)	(1,0)	(0,1)
(0,0)	1.00000000	.44 E -11	.338 E -8
(1,0)	.43 E -11	.99957560	.00042439
(0,1)	.337 E -8	.00042439	.99957560

System: N_2 on N_2, E = 4.55, ALPHA = .113, OMEGA = .85, MA = MB = MC = MD = 14.0, N = 3, M = 3.

Integration: DRILL with double precision Romberg integrator, ERROR = 10^{-5}, XST = -40.0, ET = 11'47".

Table 10

(0,0)	.99999999	.11 E -11	.41 E -8
(1,0)	.47 E -7	1.00000000	.35 E -8
(0,1)	.20 E -7	.14 E -8	.99999999

All of the calculations presented in tables 11(a) through 11(j) are for the frequency ratio (OMEGA) study of the N_2 on N_2-like system: ALPHA = .113, MA = MB = MC = MD = 14.0, N = 2, M = 2, and an incident relative kinetic energy of 1 for the initial state (0,1). We list the total E and ET individually. ERROR and XST are 10^{-5} and -40.0 for all results in this series.

OMEGA = 0.6

E = 3.8 ET = 1'3"

Table 11(a)

	(0,0)	(1,0)	(0,1)
(0,0)	.99999995	.20 E -8	.18 E -7
(1,0)	.54 E -8	.99992649	.00007352
(0,1)	.18 E -6	.00007351	.99992643

OMEGA = 0.8

E = 4.4 ET = 1'1"

Table 11(b)

	(0,0)	(1,0)	(0,1)
(0,0)	1.00000000	.63 E -9	.42 E -10
(1,0)	.18 E -10	.99956567	.00043419
(0,1)	.80 E -9	.00043447	.99956567

OMEGA = 0.85

E = 4.55 ET = 1'3"

Table 11(c)

	(0,0)	(1,0)	(0,1)
(0,0)	1.00000000	.65 E -9	.55 E -9
(1,0)	.33 E -8	.99821700	.00178268
(0,1)	.13 E -8	.00178332	.99821700

OMEGA = 0.9

E = 4.7 ET = 1'6"

Table 11(d)

	(0,0)	(1,0)	(0,1)
(0,0)	1.00000000	.26 E -11	.10 E -10
(1,0)	.60 E -10	.99439627	.00560383
(0,1)	.29 E -12	.00560363	.99439627

OMEGA = 0.97

E = 4.91 ET = 1'10"

Table 11(e)

	(0,0)	(1,0)	(0,1)
(0,0)	1.00000000	.17 E -10	.17 E -10
(1,0)	.57 E -8	.99369823	.00630177
(0,1)	.57 E -8	.00630177	.99369823

OMEGA = 1.0

E = 5.0 ET = 1'7"

Table 11(f)

	(0,0)	(1,0)	(0,1)
(0,0)	1.00000000	.13 E -10	.53 E -8
(1,0)	.93 E -10	.99435696	.00564320
(0,1)	.30 E -10	.00564288	.99435696

OMEGA = 1.03

E = 5.09   ET = 1'10"

Table 11(g)

	(0,0)	(1,0)	(0,1)
(0,0)	.99999812	.00000044	.00000009
(1,0)	.00000008	.99778400	.00220314
(0,1)	.00003176	.00222860	.99778246

OMEGA = 1.1

E = 5.3 ET = 1'5"

Table 11(h)

	(0,0)	(1,0)	(0,1)
(0,0)	.99999999	.00000004	.11 E -9
(1,0)	.27 E -8	.99920441	.00079618
(0,1)	.15 E -7	.00079499	.99920442

OMEGA = 1.15

E = 5.45 ET = 1'16"

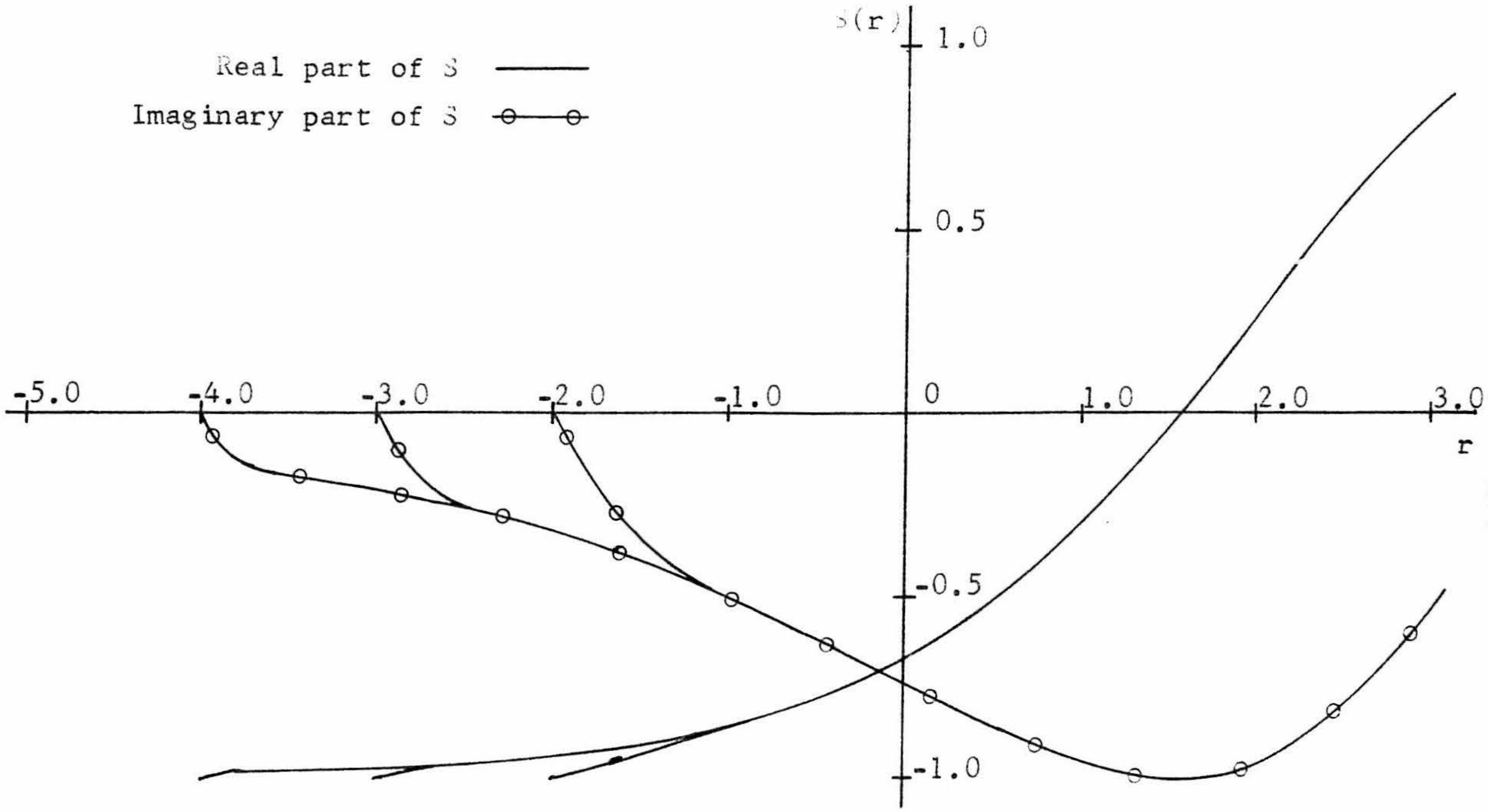
Table 11(i)

	(0,0)	(1,0)	(0,1)
(0,0)	1.00000000	.26 E -9	.88 E -12
(1,0)	.65 E -10	.99974685	.00025287
(0,1)	.69 E -12	.00025342	.99974685

OMEGA = 1.2

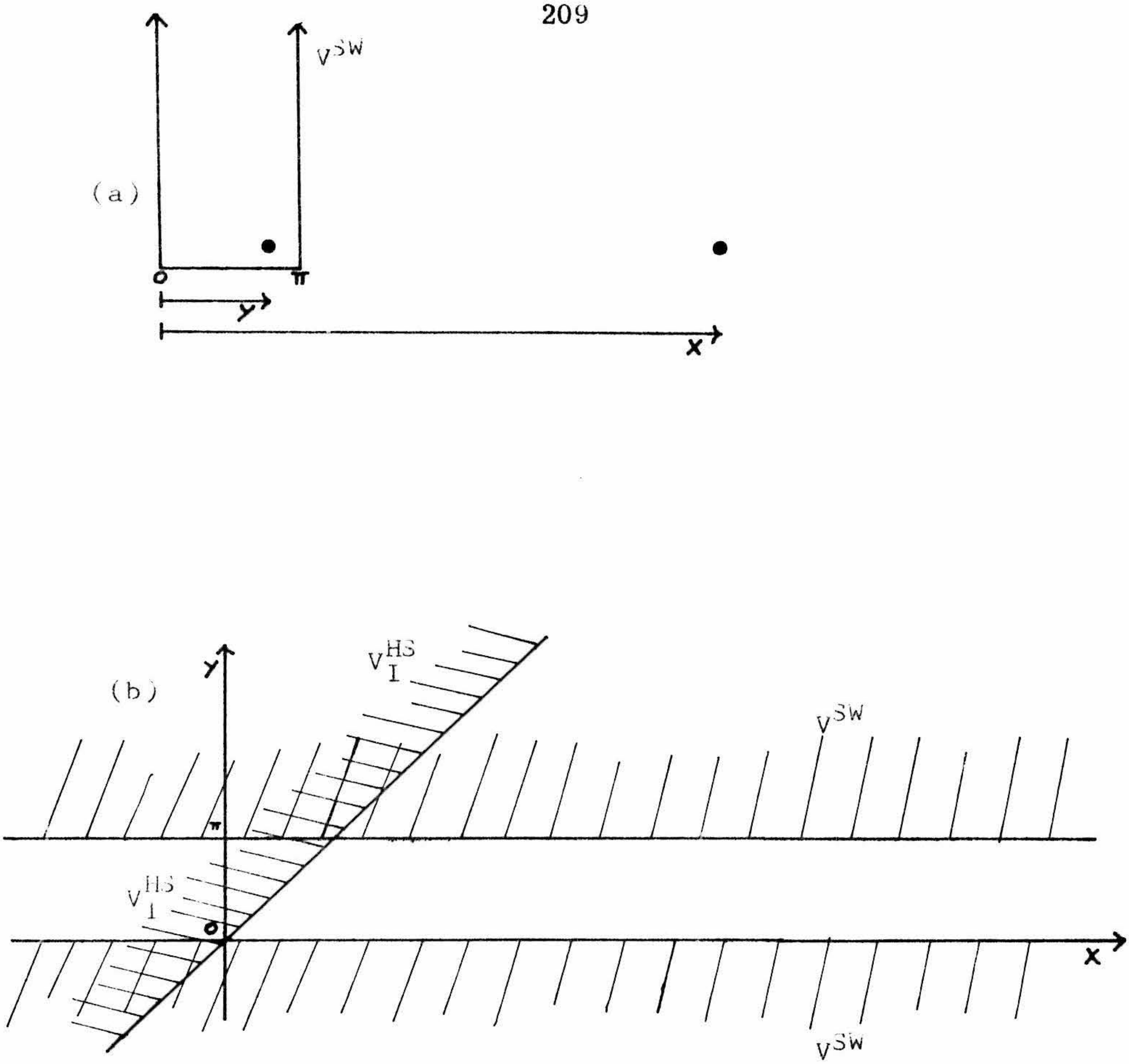
E = 5.6 ET = 1'16"

Table 11(j)



Integration of $dS(r)/dr = iS(r) - i\,e^{-r}(1 + S(r))^2$ with starting condition $S(r_o) = -1$. Three solutions are shown, corresponding to the starting points $r_o =$ -2, -3, and -4. At $r = 2$, the solutions differ at most by 1 part in 1000.

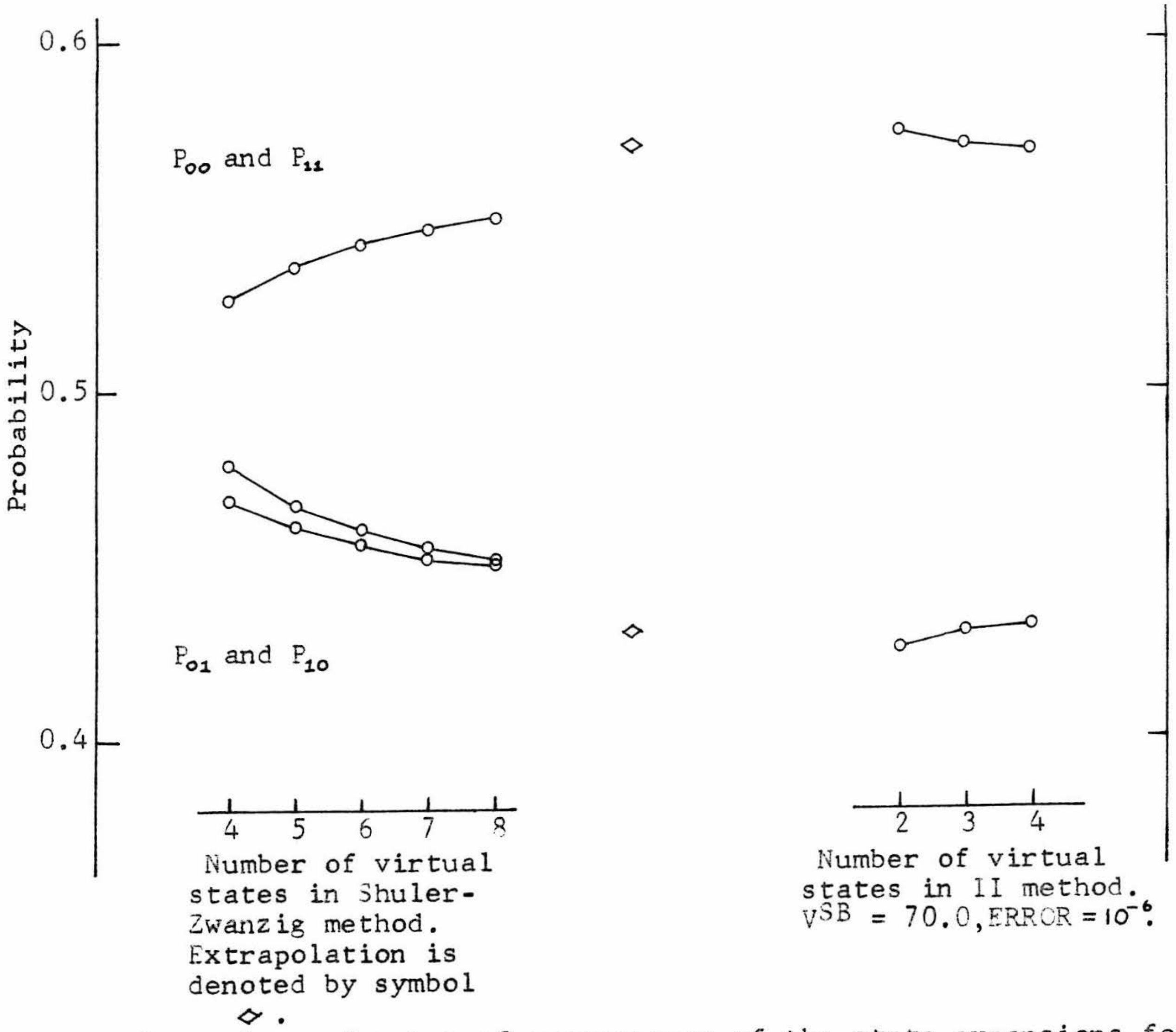
Figure 1



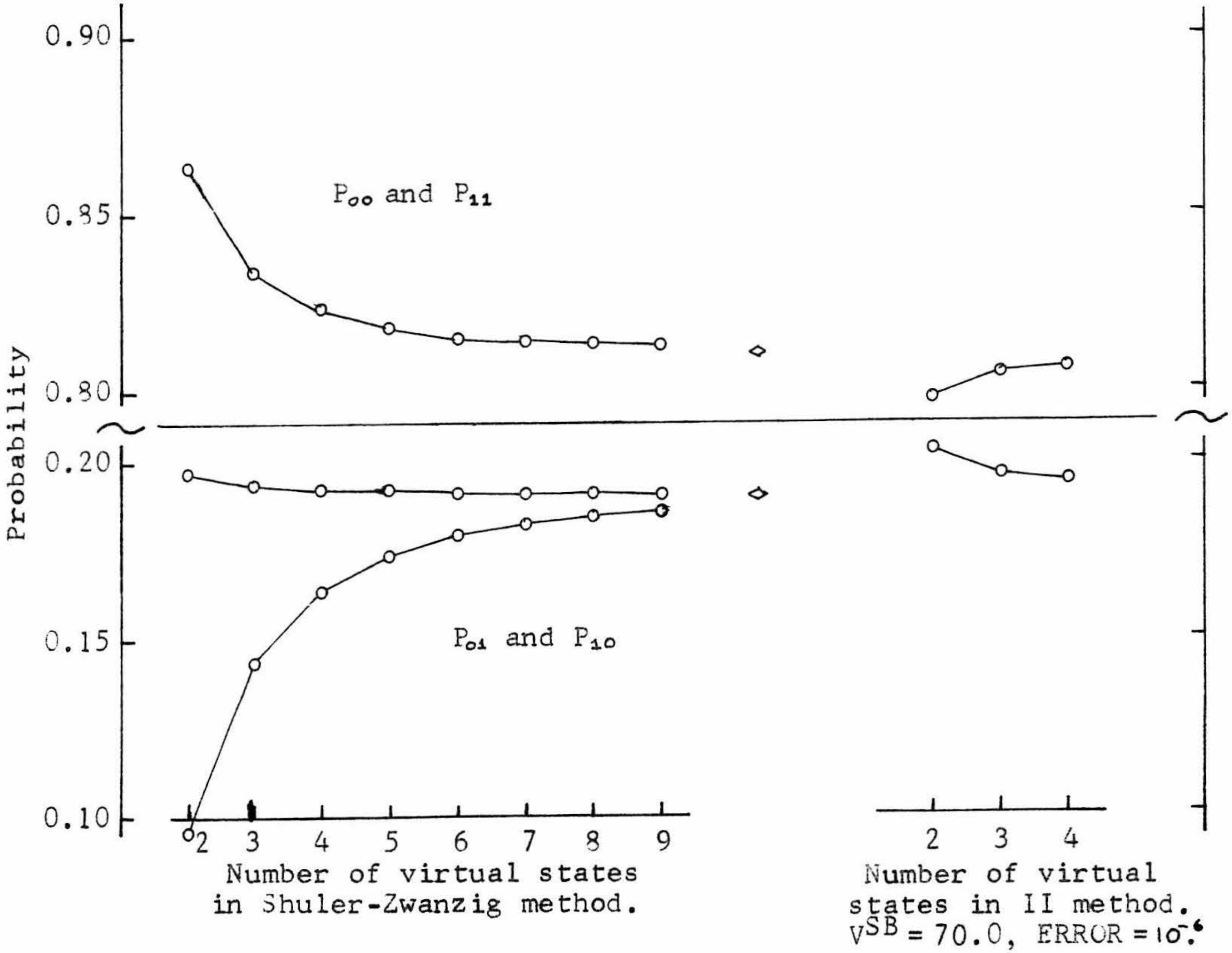
(a) Diagram of collinear collision of particle in an infinite square well, V^{SW}, with incident particle.

(b) Configuration space outline of potentials. Potential is infinite for $y \leq 0$ and $y \geq \pi$ in hatched areas labeled V^{SW}. For $x \leq y$, the V_I^{HS} interaction region is likewise infinite in the S-Z model, but a high square barrier in our calculations.

Figure 2



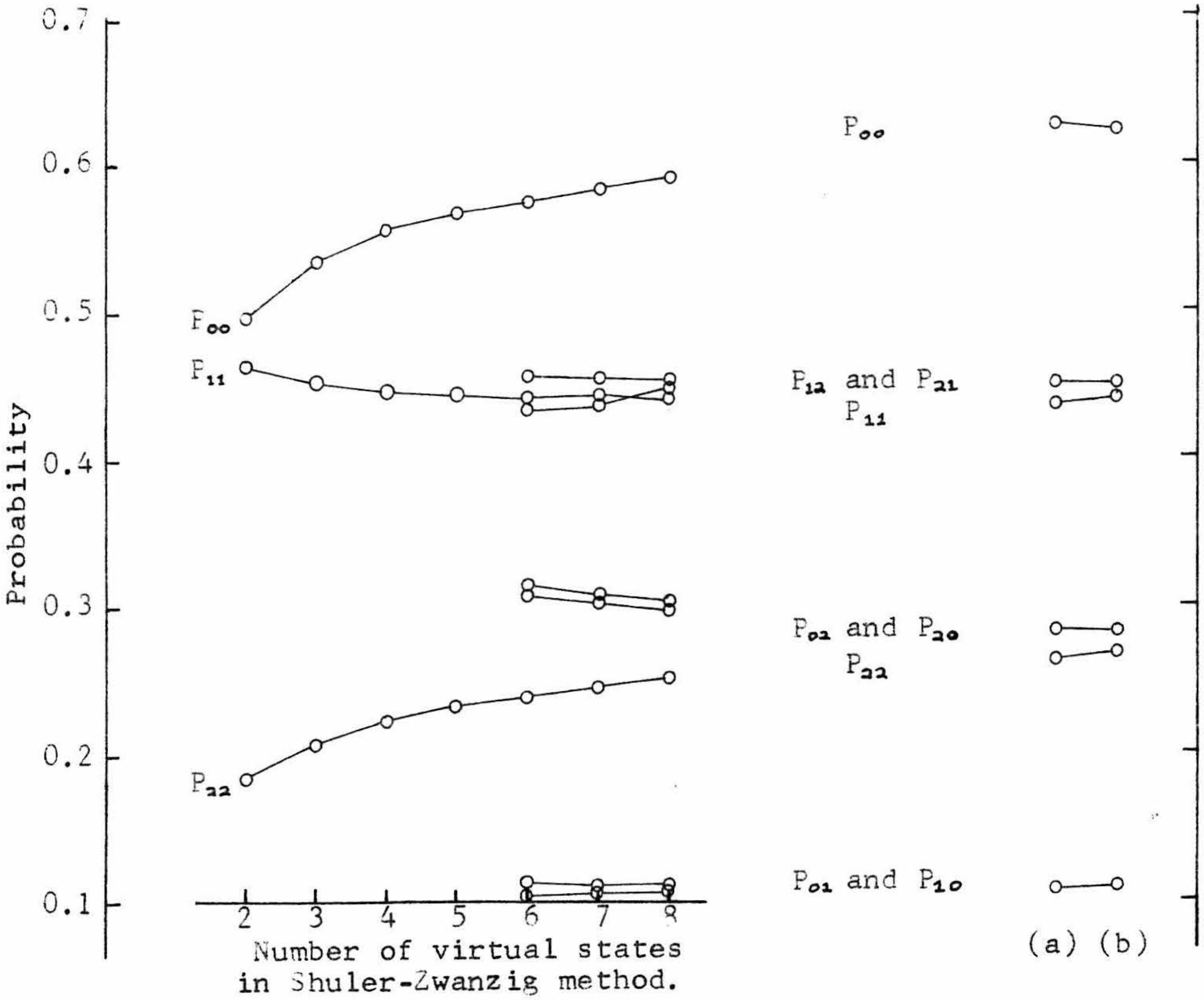
Comparison of rates of convergence of the state expansions for the hard-sphere, square well problem: E = 4.50, MASS = 1.0, 2 open channels.
Figure 3



Symbol ◇ denotes extrapolation.

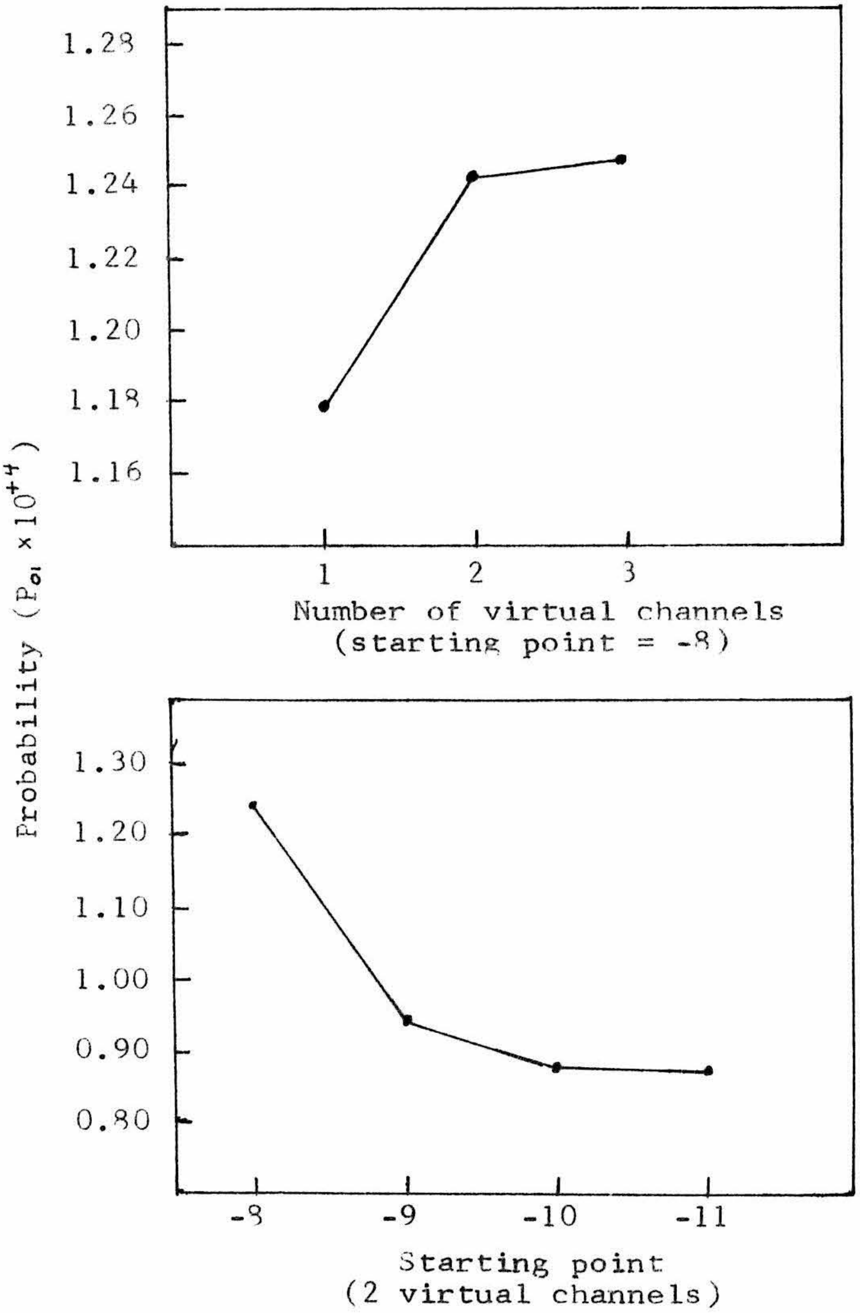
Comparison of rates of convergence of the state expansions for the hard-sphere, square well problem: E = 8.50, MASS = 1.0, 2 open channels.

Figure 4



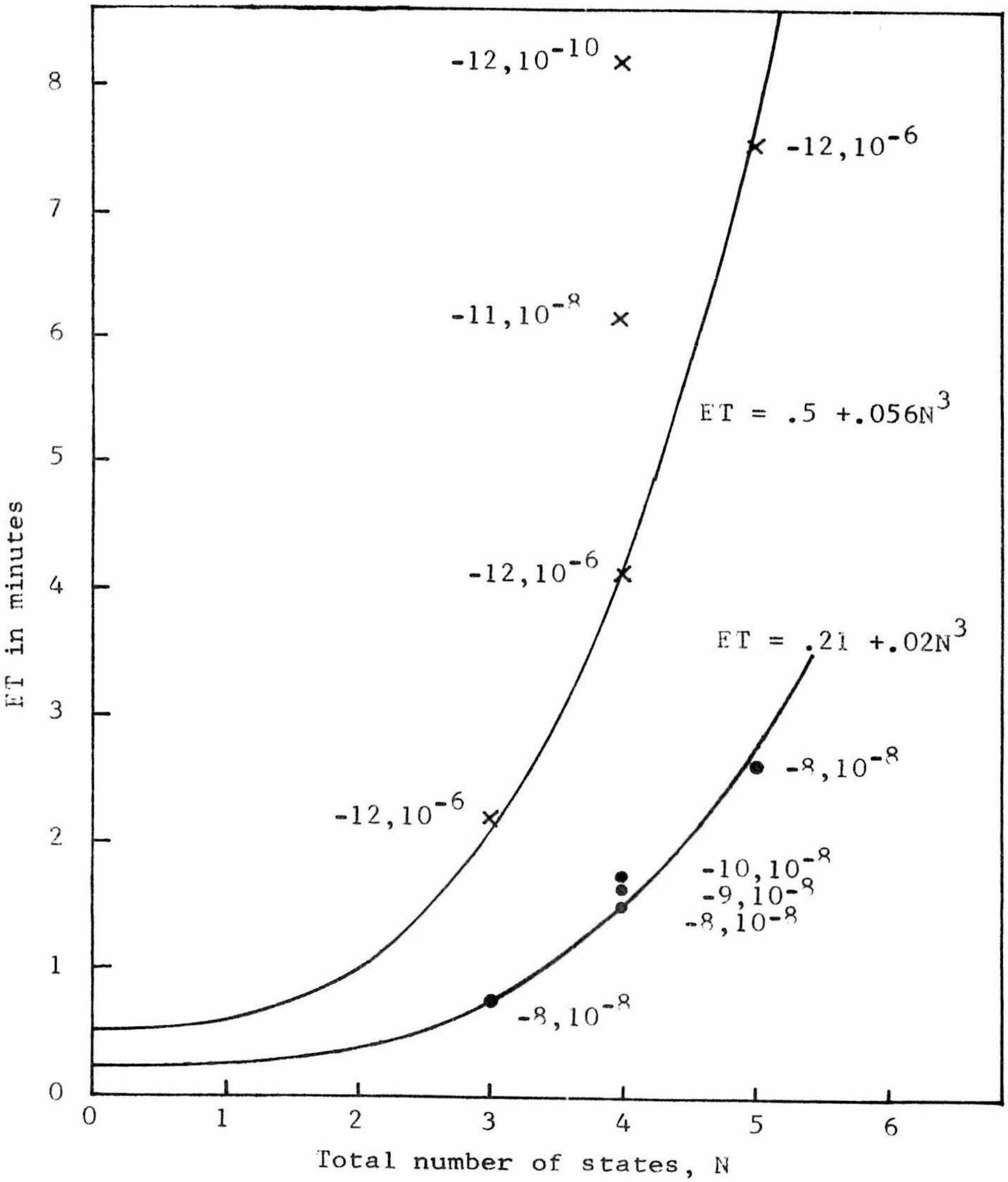
Comparison of II with the Shuler-Zwanzig method for the hard-sphere, square well problem: E = 10.5, MASS = 1.0, 3 open channels. (a) is II with V^{SB} = 50.0 and 2 virtual states. (b) is II with V^{SB} = 70.0 and 2 virtual states.

Figure 5



Convergence of DRILL as number of channels and starting point are varied. E = 4.9455, 2 open channels. Data converges to 0.87×10^{-4} because of an error in the potential matrix evaluation. See text for a discussion of this.

Figure 6



Comparison of execution times (ET) of II (x) and DRILL (•) for the atom on diatom problem: E = 4.9455, MASS = 1.25, ALPHA = .2973, 2 open channels. The numbers paired by a comma are the starting point and ERROR control: XST,ERROR.

Figure 7

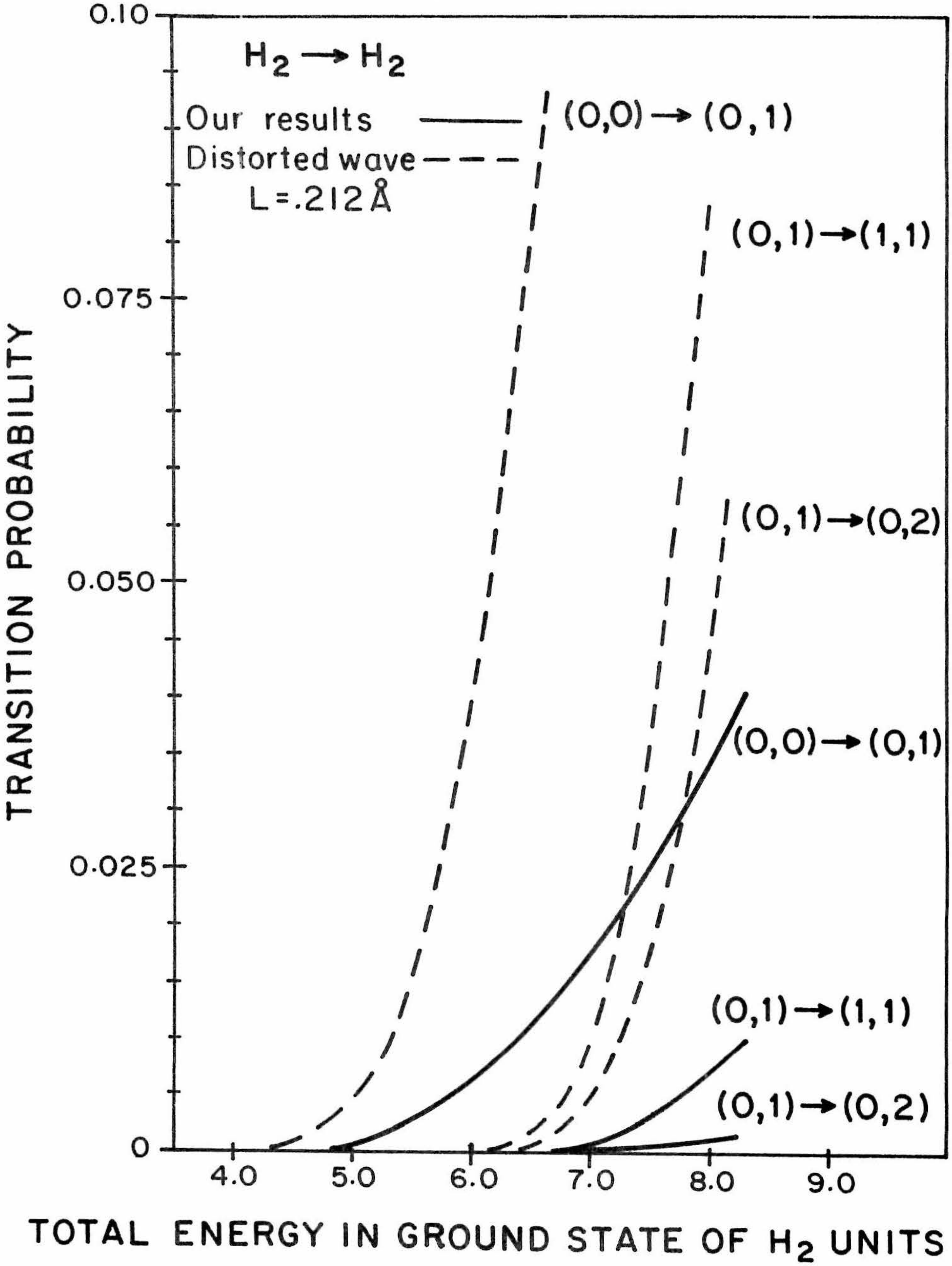

$H_2 \rightarrow H_2$
Our results
Distorted wave
L=.212Å
(0,0)→(0,1)
(0,1)→(1,1)
(0,1)→(0,2)
(0,0)→(0,1)
(0,1)→(1,1)
(0,1)→(0,2)
TRANSITION PROBABILITY
0.10
0.075
0.050
0.025
0
4.0
5.0
6.0
7.0
8.0
9.0
TOTAL ENERGY IN GROUND STATE OF H_2 UNITS

Figure 8

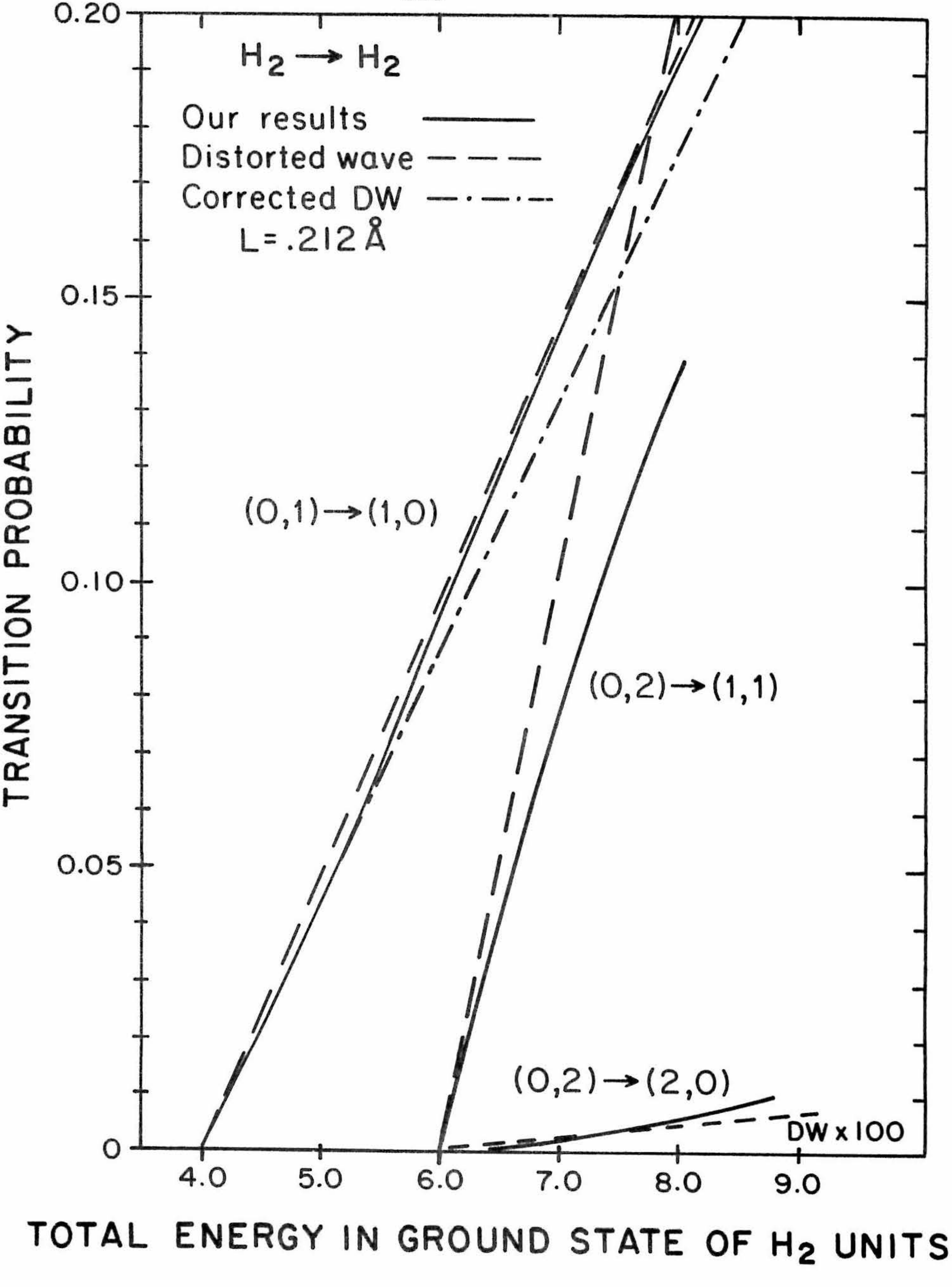

$H_2 \rightarrow H_2$
Our results
Distorted wave
Corrected DW
L=.212 Å
(0,1)→(1,0)
(0,2)→(1,1)
(0,2)→(2,0)
DW x 100
TRANSITION PROBABILITY
0.20
0.15
0.10
0.05
0
4.0
5.0
6.0
7.0
8.0
9.0
TOTAL ENERGY IN GROUND STATE OF H_2 UNITS

Figure 9

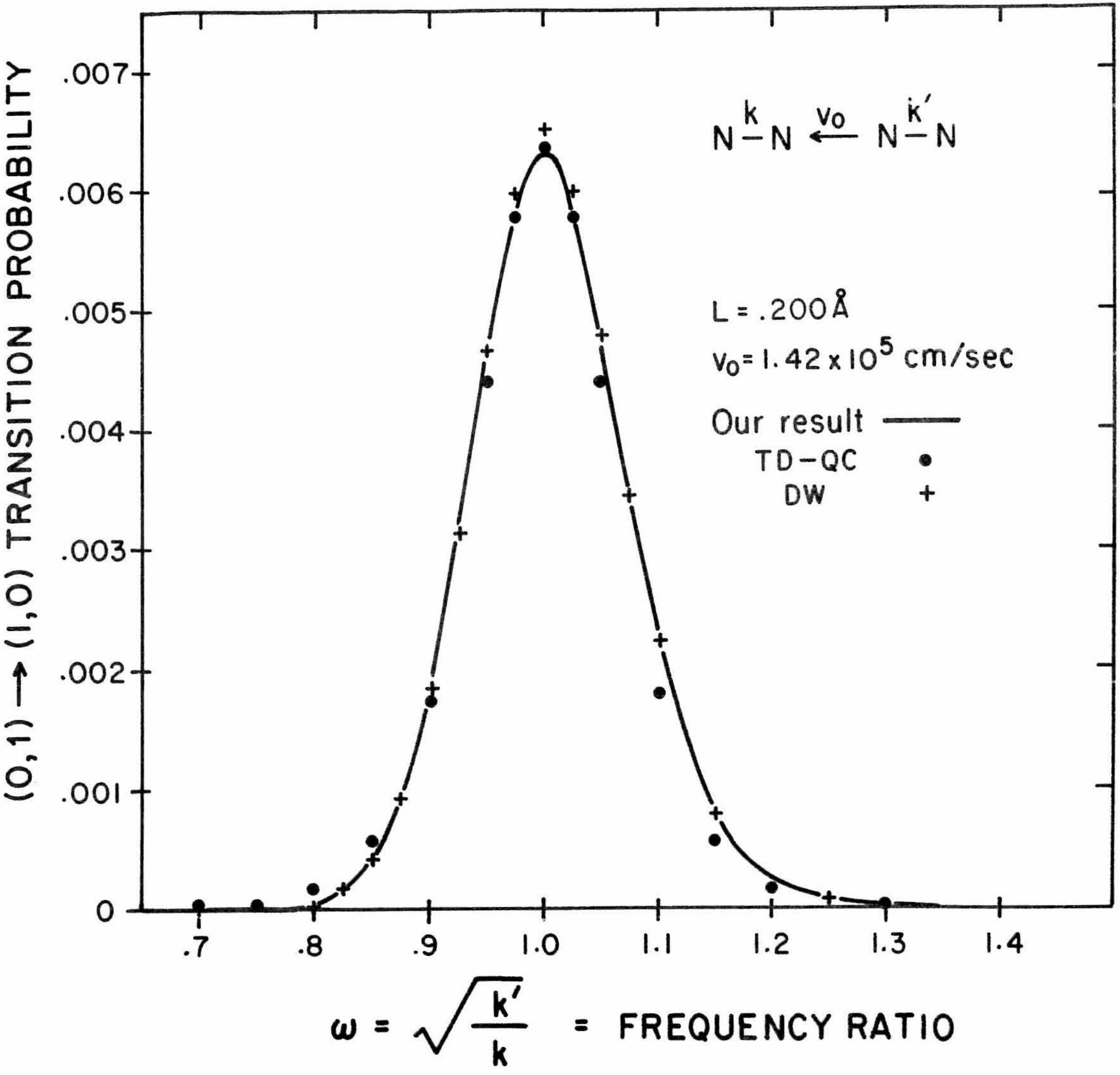

$N \overset{k}{-} N \xleftarrow{v_0} N \overset{k'}{-} N$
L = .200 Å
$v_0 = 1.42 \times 10^5$ cm/sec
Our result
TD-QC ●
DW +
(0,1) ⟶ (1,0) TRANSITION PROBABILITY
.007
.006
.005
.004
.003
.002
.001
0
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
$\omega = \sqrt{\frac{k'}{k}}$ = FREQUENCY RATIO

Figure 10

LISTING OF COMPUTER PROGRAMS

#1. II for the diatom on diatom problem. Main deck is II2, followed by subroutines DS3(double precision Romberg integrator), OUT(subroutine to print out probabilities at periodic intervals during integration), and XDR(evaluates derivative from the invariant imbedding differential equation).

#2. DRILL for the diatom on diatom problem. Main deck, IT2, only. Program uses BNDINV matrix inversion (given next) and DS3 integrator. The derivative of the Schrödinger equation is called from DS3. This derivative subroutine is similar to DR2 (given later), but is in double precision arithmetic.

#3. BNDINV double precision matrix inversion.

#4. Takayanagi's distorted wave evaluation for diatom on diatom problem.

#5. DRILL for atom on diatom problem in single precision arithmetic. Main deck is SP5, which contains the formula for increasing the step size of the integrator. Following are the subroutines: DR2(evaluation of the derivative of the matrix Schrödinger equation), INS(single precision matrix inversion), and AM5(5'th order predictor Adams-Moulton integrator).

#1.

```
$IBFTC II2       LIST,REF,DECK
      DOUBLE PRECISION F,KV(10),X,XST,XSTOP,ERROR,ALPHA,XPREV,
     1 H,Y(200),S(200),MASS,W,NNLAG(10,10),AB(10,10),CD(10,10),DELOUT
     2  ,OMEGA,MA,MB,MC,MD ,BETA
       DIMENSION ITENSR (5,5)
      LOGICAL FLAG
       COMMON KV,ALPHA,NNLAG, AB,CD,    NOPEN,NOPPO,NTOT
C       CD IS TARGET    E IN GS UNITS
      READ(5,1001) E,ALPHA,XST,XSTOP,H,ERROR,OMEGA,MA,MB,MC,MD,DELOUT
 1001 FORMAT(D16.8)
 1005 FORMAT(2I4)
      READ(5,1005) NTOTAB,NTOTCD
      MASS=(MA+MB)*MD/MC/(MA+MB+MC+MD)
      BETA=MC/MB*DSQRT(MA*MB*(MC+MD)/(MC*MD*(MA+MB)*OMEGA))
       NTOT=NTOTAB*NTOTCD
      IK=0
      DO 101 I=1,NTOTAB
      DO 101 J=1,NTOTCD
      S(I)=S(I)
      S(J)=S(J)
       XPREV=MASS*(E-DBLE(FLOAT(2*J-1))-OMEGA*DBLE(FLOAT(2*I-1)))
       IF(XPREV.LT.0.0D0) GO TO 101
       IK=IK+1
       ITENSR (I,J)=IK
        KV(IK)=DSQRT(XPREV)
       WRITE(6,102) IK,J,I
  101 CONTINUE
       NOPEN=IK
       NOPPO=IK+1
       NOVIRT=NTOT - NOPEN
  102 FORMAT(13H0MATRIX INDEX,I2,X,18HREFFERS TO CD STATE,I2,X,
     2  12HAND AB STATE,I2)
        DO 103 I=1,NTOTAB
       DO 103 J=1,NTOTCD
      S(J)=S(J)
      S(I)=S(I)
       XPREV=MASS*(E-DBLE(FLOAT(2*J-1))-OMEGA*DBLE(FLOAT(2*I-1)))
       IF(XPREV.GT.0.0D0) GO TO 103
       IK=IK+1
       ITENSR (I,J)=IK
       KV(IK)=DSQRT(-XPREV)
       WRITE(6,102) IK,J,I
  103 CONTINUE
       WRITE(6,450) (KV(I),I=1,NTOT)
  450 FORMAT(4D16.8)
      DO 3 I=1,NTOT
      IF(KV(I).LE.1.0D-04) GO TO 1006
       GO TO 3
 1006 WRITE(6,1007)
 1007 FORMAT(32H0FREE PARTICLE K LESS THAN 1.D-4)
        STOP
    3 CONTINUE
C    COMPUTE POTENTIAL MATRIX
C  EVALUATION OF LAGUERRE POLYNOMIALS IN ALSQ/2. AND NORM FACTORS
       DOUBLE PRECISION FACT(20),T,TT,ALSQ,FE
      FACT(1)=1.0D0
      FACT(2)=1.0D0
      DO12 I=2,19
   12 FACT(I+1)= FLOAT(I)*FACT(I)
      ALSQ=ALPHA*ALPHA
```

```
      FF=DEXP(ALSQ/4.0D0)*MASS/2.0D0
      DO 6 N=1,NTOT
      DO 6 M=1,N
       T=0.0
       DO 14 L=1,M
      ML=M-L+1
      NML=N-M+L
      TT=FACT(N  )/(FACT(ML)*FACT(NML)*FACT(L))*(ALSQ/2.0D0)**(L-1)
      IF(TT.LE.1.0D-12) GO TO 200
   14 T=T+TT
  200   CD  (N,M)=DSQRT(FACT(M)/FACT(N)/2.0D0**(N-M))*ALPHA**(N-M)*T*FF
    6  CD(M,N)= CD(N,M)
       ALSQ=ALPHA*ALPHA*BETA*BETA
      FF=DEXP(ALSQ/4.0D0)
      DO 66N=1,NTOT
      DO 66M=1,N
       T=0.0
       DO 141L=1,M
      ML=M-L+1
      NML=N-M+L
      TT=FACT(N  )/(FACT(ML)*FACT(NML)*FACT(L))*(ALSQ/2.0D0)**(L-1)
      IF(TT.LE.1.0D-12) GO TO 2008
  141 T=T+TT
 2008 AB    (N,M)=DSQRT(FACT(M)/FACT(N)/2.0D0**(N-M))*
     1 (ALPHA*BETA)**(N-M)*T*FF
   66  AB(M,N)= AB(N,M)
      DO 600 I=1,NTOTAB
      DO 600 J=1,NTOTAB
      DO 600 L=1,NTOTCD
      DO 600 M=1,NTOTCD
       IK= ITENSR (I,L)
      IKK= ITENSR (J,M)
  600 MNLAG(IK,IKK) = CD(L,M)*AB(I,J)
       WRITE(6,450) ((MNLAG(I,J),J=1,NTOT),I=1,NTOT)
       EXTERNAL F
      LOGICAL NEWH
       DO 5 I=1,200
      Y(I)=0.0
    5 S(I)=0.0
      WRITE(6,1100) E,MASS,ALPHA,NOPEN,NOVIRT,XST,          XSTOP,ERROR
 1100 FORMAT(9H0ENERGY =,D16.8/6HMASS =,D16.8/7HALPHA =,D16.8/
     119HNO OF OPEN CHANNELS,I4,10X,24HNO VIRTUAL CHANNELS USED,I4/
     218HXST AND XSTOP ARE ,2D16.8/13HLOCAL ERROR =,D16.8)
       XPREV=XST
      X=XST
      N=2*NTOT*NTOT
    7 CALL DIFSYS(F,N,H,X,Y,ERROR,S,NEWH,FLAG)
      IF(X.GE.XPREV+DELOUT) CALL OUTPUT(X,Y,H,NOPEN,KV,XPREV,NTOT)
      IF(FLAG) STOP
      IF(X.GE.XSTOP) GO TO 8
      GO TO 7
    8  STOP
       END
$IBFTC DS3       LIST,REF,DECK
      SUBROUTINE DIFSYS(F,NE,H,X,Y,EPS,S,NEWH,FLAG)
       DATA MAXORD/200/
      DATA ISET/1000/
      N=NE
       INTDEX=0
       DIMENSION YA(200),YL(200),YM(200),DY(200),DZ(200),DT(200,7),
     1  YG(8,200),YH(8,200)
```

```
      DOUBLE PRECISION H
      DOUBLE PRECISION X,Y
      DIMENSION Y(NE)
      DOUBLE PRECISION EPS,S
      DIMENSION S(NE)
      LOGICAL FLAG
      LOGICAL NEWH
      FLAG = .FALSE.
      DOUBLE PRECISION YA,YL,YM,DY,DZ,DT,D,YG,YH
      DIMENSION D(7)
      INTEGER R,SR
      LOGICAL KONV,BO,BH
      LOGICAL EPSERR
      DATA EPSERR/.FALSE./
      DOUBLE PRECISION E,A,FC,G,B,U,V,C,TA,B1
      IF(N.GT.0.AND.N.LE.MAXORD) GO TO 1
      WRITE(6,100)
  100 FORMAT(28H0ORDER TOO LARGE FOR DIFSYS.)
      STOP
    1 E=DABS(EPS)
      IF(E.GE.1.0D-13) GO TO 2
      IF(EPSERR) GO TO 102
      EPSERR=.TRUE.
      WRITE(6,101)
  101 FORMAT(51H0ERROR LIMIT TOO SMALL FOR DIFSYS.  WE USE 1.0D-13.)
  102 E=1.0D-13
    2 CALL F(X,Y,DZ)
      INTDEX=INTDEX+1
      BH=.FALSE.
      NEWH=.FALSE.
      DO 3 I=1,M
    3 YA(I)=Y(I)
    4 A=X+H
      FC=1.5D0
      BO=.FALSE.
      M=1
      R=2
      SR=3
      JJ=-1
      DO 1000 J1=1,10
      J= J1-1
       D(2)=2.25D0
      IF(BO) D(2)=4.0/D(2)
      D(4)=4.0*D(2)
      D(6)=4.0*D(4)
      KONV=J.GT.2
      IF(J.LE.6) GO TO 5
      L =6
      D(7)=64.0
      FC=0.6D0*FC
      GO TO 6
    5 L=J
      D(L+1)=M*M
    6 M=2*M
      G=H/DBLE(FLOAT(M))
      B=2.0*G
      IF(BH.AND. J.LT.8) GO TO 7
      KK=(M-2)/2
      M=M-1
      DO 8 I=1.N
      YL(I)=YA(I)
```

```
    8 YM(I)=YA(I)+G*DZ(I)
      IF(M.LE.0) GO TO 9
      DO 10 K=1,M
      CALL F(X+G*DBLE(FLOAT(K)),YM,DY)
      INTDEX=INTDEX+1
      DO 11 I=1,N
      U=YL(I)+B*DY(I)
      YL(I)=YM(I)
      YM(I)=U
      U=DABS(U)
      IF(YA(K).GE.0.0) GO TO 11
   11 S(I)=DMAX1(U,S(I))
      IF(K.NE.KK.OR.K.EQ.2) GO TO 10
      JJ=JJ+1
      DO 12 I=1,N
      YH(JJ+1,I)=YM(I)
   12 YG(JJ+1,I)=YL(I)
   10 CONTINUE
      GO TO 9
    7 DO 13 I=1,N
       YM(I)=YH(J+1,I)
   13 YL(I)=YG(J+1,I)
    9 CALL F(A,YM,DY)
      INTDEX=INTDEX+1
      DO 14 I=1,N
      V=DT(I,1)
      DT(I,1)=0.5*(YM(I)+YL(I)+G*DY(I))
      C=DT(I,1)
      TA=C
      IF(L.LE.0) GO TO 15
      DO 16 K=1,L
      B1=D(K+1)*V
      B=B1-C
      U=V
      IF(B.EQ.0.0) GO TO 17
      B=(C-V)/B
      U=C*B
      C=B1*B
   17 V=DT(I,K+1)
      DT(I,K+1)=U
   16 TA=U+TA
   15 IF(DABS(Y(I)-TA).GT.E*DABS(S(I))) KONV=.FALSE.
   14 Y(I)=TA
      IF(KONV) GO TO 18
      D(3)=4.0
      D(5)=16.0
      BO=.NOT.BO
      M=R
      R=SR
 1000 SR=2*M
      BH=.NOT.BH
      NEWH=.TRUE.
      H=0.5*H
      IF(INTDEX.GE.ISET) GO TO 2000
      GO TO 4
   18 H=FC*H
      X=A
      RETURN
 2000 WRITE(6,2001) INTDEX
      FLAG = .TRUE.
 2001 FORMAT(30HONO CONVERGENCE ACHIEVED AFTER,I6,2X,5HCALLS)
```

```
       RETURN
       END
$IBFTC OUT      LIST,REF,DECK
      SUBROUTINE OUTPUT(X,Y,H,NOPEN,KV,XPREV,NTOT)
      DOUBLE PRECISION X,Y(200),H,KV(10),P(10,10),DEL
       DO 1 I=1,NOPEN
       DO 1 J=1,NOPEN
       DEL=0.0
      IF(I.EQ.J) DEL=1.0D0
       IK=I+(J-1)*NTOT
       IKK=NTOT*NTOT + IK
    1 P(I,J)=((Y(IK)-DEL)**2+Y(IKK)**2)*KV(J)/KV(I)
      WRITE(6,2000)X,H
 2000 FORMAT(4H0 X=,D16.8,8X,19HROMBERG STEP SIZE =,D16.8)
      WRITE(6,2001) ((P(I,J),J=1,NOPEN),I=1,NOPEN)
 2001 FORMAT(12H0P(I,J) AT X/(6D16.8))
      XPREV=X
      RETURN
       END
$IBFTC XDR      LIST,REF,DECK
      SUBROUTINE F(X,Y,DY)
      DOUBLE PRECISION X,Y(200),DY(200),KV(10),NNLAG(10,10),AB(10,10),
     1 CD(10,10),TR(10,10),TI(10,10),V(10,10),EEEX,
     2 DUDR, DUDI, DUM ,ALPHA
       COMMON KV,ALPHA,NNLAG, AB,CD,    NOPEN,NOPPO,NTOT
C    PUT VECTOR INTO MATRIX FORM
      DO 1 J=1,NTOT
      DO 1 I=1,NTOT
      IK=I+(J-1)*NTOT
      IKK=IK+ NTOT*NTOT
      TR(I,J)= Y(IK)
    1 TI(I,J)= Y(IKK)
C     COMPUTE POTENTIAL MATRIX WITH 1/K INCLUDED
      EEEX=DEXP(-ALPHA*X)
       DO 4 I=1,NTOT
      DO 4 J=1,NTOT
    4 V(I,J)=NNLAG(I,J)*EEEX/KV(J)
C    COMPUTE AB AND CD INTERMEDIATES
      DO 11 I=1,NTOT
      DO 11 J=1,NTOT
      AB(I,J)=0.0
       CD(I,J)=0.0
      DO 12 K=1,NOPEN
      AB(I,J)=AB(I,J) + V(I,K)*TR(K,J)
   12 CD(I,J)=CD(I,J) + V(I,K)*TI(K,J)
      DO 13 K=NOPPO,NTOT
      AB(I,J)=AB(I,J) + V(I,K)*TI(K,J)
   13 CD(I,J)=CD(I,J) - V(I,K)*TR(K,J)
   11 CONTINUE
C   COMPLETE DERIVATIVE CALCULATION
      DO 14 I=1,NTOT
      DO 14 J=1,NTOT
       DUM=0.0
      IF(I.EQ.J) DUM=2.0D0
      IF(I.LE.NOPEN.AND.J.LE.NOPEN) GO TO 15
      IF(I.LE.NOPEN.AND.J.GT.NOPEN) GO TO 16
      IF(I.GT.NOPEN.AND.J.LE.NOPEN) GO TO 17
C REMAINING LOGICAL CHOICE IS FOR I.GT.NOPEN.AND.J.GT.NOPEN,DO NOW
      DUDR=-(KV(I)+KV(J))*TR(I,J)   + KV(I)*DUM
      DUDI= -(KV(I)+KV(J))*TI(I,J)
      GO TO 18
```

```
15 DUDR= -(KV(I)+KV(J))*TI(I,J)
   DUDI= (KV(I)+KV(J))*TR(I,J)    - DUM*KV(I)
   GO TO 18
16 DUDR=-KV(I)*TI(I,J) -KV(J)*TR(I,J)
   DUDI=  KV(I)*TR(I,J) -KV(J)*TI(I,J)
    GO TO 18
17 DUDR= -KV(I)*TR(I,J)  -KV(J)*TI(I.J)
   DUDI= -KV(I)*TI(I,J)  + KV(J)*TR(I,J)
18 CONTINUE
   DO 19 K=1,NTOT
   DUDR=DUDR + TR(I,K)*CD(K,J)  + TI(I,K)*AR(K,J)
19 DUDI=DUDI + TI(I,K)*CD(K,J) - TR(I,K)*AR(K,J)
   IK= I +(J-1)*NTOT
    IKK= IK+ NTOT*NTOT
    DY(IK)= DUDR
14 DY(IKK)= DUDI
   RETURN
    END
```

#2.

```
$IBFTC IT2      DECK
      DOUBLE PRECISION C(200),ENERGY,MASS,X,V(10,10),ALPHA,KSQED(10),
     1 XST,XSTOP,H,ERROR,C1(10,10),C2(10,10),X1,X2,A(10,10),B(10,10),
     2 DUM,CS1,SS1,CS2,SS2,MAT(50,10),DET,EPSIL,RR(10,10),RI(10,10),
     3 CHI(10,10),PSI(10,10),PROB ,S(200)
     4 ,MA,MB,MC,MD,OMEGA,BETA
      LOGICAL NEWH,FLAG
      COMMON V,ALPHA,KSQED,NTOT
C       CD IS TARGET     E IN GS UNITS
      READ(5,1001) ENERGY,ALPHA,XST,XSTOP,H,ERROR,OMEGA,MA,MB,MC,MD
 1001 FORMAT(D16.8)
      MASS=(MA+MB)*MD/MC/(MA+MB+MC+MD)
      BETA=MC/MB*DSQRT(MA*MB*(MC+MD)/(MC*MD*(MA+MB)*OMEGA))
      READ(5,1005) NTOTAB,NTOTCD
 1005 FORMAT(2I4)
       NTOT=NTOTAB*NTOTCD
C    SUPERMATRICES CYCLE THROUGH CD STATES FIRST
      DO 1 I=1,NTOTAB
       DO 1 J=1,NTOTCD
      IK =J+(I-1)*NTOTCD
    1 KSQED(IK)=MASS*(ENERGY-DBLE(FLOAT(2*J-1))-OMEGA*DBLE(
     1  FLOAT(2*I-1)))
C INITIALIZE  C MATRIX
      NNN=2*NTOT*NTOT
       DO 2 I=1,NNN
    2 C(I)= 0.0
       DO 3 I=1,NTOT
      IK=I+(I-1)*NTOT
        IKK=IK+NTOT*NTOT
       C(IK)= 1.0D 0
    3 C(IKK)= DSQRT(DEXP(-ALPHA*XST) *MASS)
C    COMPUTE POTENTIAL MATRIX
C  EVALUATION OF LAGUERRE POLYNOMIALS IN ALSQ/2. AND NORM FACTORS
       DOUBLE PRECISION FACT(20),T,TT,ALSQ,EE
      FACT(1)=1.0D0
      FACT(2)=1.0D0
      DO12 I=2,19
   12 FACT(I+1)= FLOAT(I)*FACT(I)
      ALSQ=ALPHA*ALPHA
      EE=DEXP(ALSQ/4.0D0)*MASS/2.0D0
      DO 6 N=1,NTOT
      DO 6 M=1,N
       T=0.0
       DO 14 L=1,M
      ML=M-L+1
      NML=N-M+1
      TT=FACT(N )/(FACT(ML)*FACT(NML)*FACT(L))*(ALSQ/2.0D0)**(L-1)
      IF(TT.LE.1.0D-12) GO TO 200
   14 T=T+TT
  200 CHI   (N,M)=DSQRT(FACT(M)/FACT(N)/2.0D0**(N-M))*ALPHA**(N-M)*T*EE
    6 CHI(M,N)=CHI(N,M)
       ALSQ=ALPHA*ALPHA*BETA*BETA
      EE=DEXP(ALSQ/4.0D0)
      DO 66N=1,NTOT
      DO 66M=1,N
       T=0.0
       DO 141L=1,M
      ML=M-L+1
      NML=N-M+1
      TT=FACT(N )/(FACT(ML)*FACT(NML)*FACT(L))*(ALSQ/2.0D0)**(L-1)
```

```
      IF(TT.LE.1.0D-12) GO TO 2008
  141 T=T+TT
 2008 PSI   (N,M)=DSQRT(FACT(M)/FACT(N)/2.0D0**(N-M))*
     1 (ALPHA*BETA)**(N-M)*T*FE
   66 PSI(M,N)=PSI(N,M)
      DO 600 I=1,NTOTAB
      DO 600 J=1,NTOTAB
      DO 600 L=1,NTOTCD
      DO 600 M=1,NTOTCD
      IK=L+(I-1)*NTOTCD
      IKK=M+(J-1)*NTOTCD
  600 V(IK,IKK)=CHI(L,M)*PSI(I,J)
C      BEGIN INTEGRATION
       EXTERNAL F
      DO 15 I=1,NNN
   15 S(I)=0.0D0
      X=XST
      NCYC= 0
    5 CALL DIFSYS(F,NNN,H,X,C,ERROR,S,NEWH,FLAG)
       IF(FLAG) STOP
      WRITE(6,1007) X
 1007 FORMAT(5H0X = ,D16.8)
      IF(X.GE.XSTOP.AND.NCYC.EQ.0) GO TO 314
       IF(NCYC.EQ.1) NCYC = 2
      GO TO 315
  314 DO 316 I=1,NTOT
      DO 316 J=1,NTOT
  316 V(I,J)= 0.0
      NCYC=1
  315 CONTINUE
      IF(NCYC.NE.0) GO TO 401
       EPSIL=0.0
       DO 400 I=1,NTOT
       DO 400 J=1,NTOT
       IK=I+(J-1)*NTOT
       IKK=IK+NTOT*NTOT
       PSI(I,J)=C(IKK)
  400  MAT(I,J) = C(IK)
       CALL BNDINV(MAT,NTOT ,DET,EPSIL,ITEST)
      WRITE(6,1010) ITEST
       IF(ITEST.NE.0) STOP
        DO 500 I=1,NTOT
       DO 500 J=1,NTOT
        DUM= 0.0
       IF(I.EQ.J) DUM = 1.0D0
       IK=I+(J-1)*NTOT
       IKK=IK+NTOT*NTOT
       C(IK)=DUM
        C(IKK)=0.0
       DO 500 K=1,NTOT
  500 C(IKK) = C(IKK) + PSI(I,K)*MAT(K,J)
  401 CONTINUE
       IF(NCYC.LT.2) GO TO 5
C STORE E-F IN RI, E+F IN B, A
      DO 20 I=1,NTOT
       DO 20 J=1,NTOT
      IF(KSQED(I).LE.0.0D0) GO TO 610
       DUM=DSQRT(KSQED(I))
        IK=I+(J-1)*NTOT
       IKK=IK+NTOT*NTOT
       RI(I,J)=C(IK)
```

```
        B(I,J)=C(IK)
       A(I,J)=C(IKK)/DUM
        GO TO 20
 610    DUM=DSQRT(-KSQED(I))
         IK=I+(J-1)*NTOT
        IKK=IK+NTOT*NTOT
         RI(I,J)= C(IK)-C(IKK)/DUM
        B(I,J)=C(IK) + C(IKK)/DUM
       A(I,J) =0.0
   20 CONTINUE
        DO 22 I=1,NTOT
        DO 22  J=1,NTOT
   22 MAT(I,J)=B(I,J)
        CALL BNDINV(MAT,NTOT ,DET,EPSIL,ITEST)
 1010 FORMAT(1H0,7HITEST =,I4)
       WRITE(6,1010) ITEST
        IF(ITEST.NE.0) STOP
        DO 50 I=1,NTOT
        DO 50 J=1,NTOT
        RR(I,J)=MAT(I,J)
        PSI(I,J)=0.0
        DO 50 K=1,NTOT
   50 PSI(I,J)=PSI(I,J) + MAT(I,K)*A(K,J)
        DO 70 I=1,NTOT
        DO 70 J=1,NTOT
       CHI(I,J)=0.0
         DO 60 K=1,NTOT
   60 CHI(I,J)=CHI(I,J) + A(I,K)*PSI(K,J)
   70 MAT(I,J)=B(I,J)   + CHI(I,J)
        CALL BNDINV(MAT,NTOT ,DET,EPSIL,ITEST)
       WRITE(6,1010) ITEST
        IF(ITEST.NE.0) STOP
        DO 23 I=1,NTOT
        DO 23 J=1,NTOT
        B(I,J) = 0.0
        DO 23 K=1,NTOT
   23 B(I,J)=B(I,J) + RI(I,K)*PSI(K,J)
        DO 24 I=1,NTOT
        DO 24 J=1,NTOT
        PSI(I,J) = B(I,J)
   24 B(I,J)=RI(I,J)
       WRITE(6,1206) ENERGY,ALPHA,XST,XSTOP,ERROR,OMEGA,MA,MB,MC,MD
 1206 FORMAT(1H0/8HENERGY =D16.8/8HALPHA   =D16.8/8HXST     =D16.8
     1  /8HXSTOP   =D16.8/8HERROR   =D16.8/8HOMEGA   =D16.8/
     2     23HMA, MB, MC, AND MD ARE 4D16.8)
       WRITE(6,1207) NTOTAB,NTOTCD
 1207 FORMAT(1H0/22HNTOTAB AND NTOTCD ARE 2I4)
          DO 90 I=1,NTOT
       DO 90 J=1,NTOT
       IF(KSQED(I).LE.0.0D0) GO TO 90
       IF(KSQED(J).LE.0.0D0) GO TO 90
        RR(I,J)=0.0
        RI(I,J)=0.0
        DO 80 K=1,NTOT
        RI(I,J)=RI(I,J) -(A(I,K) +PSI(I,K))*MAT(K,J)
   80   RR(I,J)=RR(I,J) + (B(I,K)-CHI(I,K))*MAT(K,J)
       PROB=(RI(I,J)*RI(I,J)+RR(I,J)*RR(I,J))*DSQRT(KSQED(I)/KSQED(J))
       WRITE(6,1000) J,I,PROB
 1000 FORMAT(1H0,2I4,10X,D16.8)
   90 CONTINUE
        STOP
```

END

#3.

```
$IBFTC BNDINV  DECK
CBNDINV
C     DOUBLE PRECISION MATRIX INVERSION SUBROUTINE
C
C     CALLING SEQUENCE  CALLBNDINV(A,N,DETERM,EPSIL,ITEST)
C     A IS ORIGINAL MATRIX (REPLACED BY A-INVERSE AT END OF PROGRAM)
C     EL IS AN N BY N ARRAY USED ONLY FOR WORKING STORAGE
C     N  IS DIMENSION OF MATRIX
C     DETERM IS LOCATION OF DETERMINANT
C     EPSIL IS USED TO TEST WHETHER MATRIX IS SINGULAR.
C           IF,AFTER TRIANGULARIZING THE MATRIX, THE RATIO OF THE
C           SMALLEST TO LARGEST DIAGONAL ELEMENT IS LESS THEN EPSIL
C           THE MATRIX IS CONSIDERED SINGULAR. IF ONE SETS EPSIL=0.
C           THE ROUTINE WILL USE EPSIL=1.E-8
C     ITEST IS AN ERROR INDICATOR.
C           IF ITEST = 0  ALL WENT WELL
C           IF ITEST = 1  MATRIX WAS FOUND TO BE SINGULAR
C           IF ITEST =-1  OVERFLOW OR DIVIDE CHECK OCCURED,
C           OR N LESS THAN 2
C
C     MAIN PROGRAM MUST CONTAIN DOUBLE PRECISION DIMENSION STATEMT FOR
C
      SUBROUTINE BNDINV(A,N,DETERM,EPSIL,ITEST)
      DOUBLE PRECISION A, EL, D, DSQRT, C, S, DETERM
      DIMENSION A(50,50),EL(50,50)
      COMMON/BNDCOM/EL
      IF(N .LT. 2) GO TO 140
      CALL SLITET(2,INDSNL)
      CALL OVERFL(K000FX)
      CALL DVCHK (K000FX)
C
C     SET EL = IDENTITY MATRIX
      DO30I=1,N
      DO 10 J = 1, N
   10 EL(I,J)=0.D0
   30 EL(I,I) = 1.D0
C
C     TRIANGULARIZE A, FORM EL
      N1 = N - 1
      M=2
      DO50J=1,N1
      DO45I=M,N
      IF(A(I,J) .EQ. 0.D0) GO TO 45
      D = DSQRT(A(J,J)*A(J,J) + A(I,J)*A(I,J))
      C=A(J,J)/D
      S=A(I,J)/D
   38 DO39K=J,N
      D=C*A(J,K)+S*A(I,K)
      A(I,K)=C*A(I,K)-S*A(J,K)
      A(J,K)=D
   39 CONTINUE
      DO40K=1,N
      D=C*EL(J,K)+S*EL(I,K)
      EL(I,K)=C*EL(I,K)-S*EL(J,K)
      EL(J,K)=D
   40 CONTINUE
   45 CONTINUE
   50 M=M+1
      CALL OVERFL(K000FX)
       GO TO(140,51),K000FX
C
```

```
C       CALCULATE DETERMINANT
   51 DETERP=A(1,1)
      DO52I=2,N
   52 DETERP=DETERP*A(I,I)
      DETERM = DETERP
      CALL OVERFL(K000FX)
       GO TO(140,520),K000FX
C
C       IS MATRIX SINGULAR
  520 E = A(1,1)
      F = A(1,1)
      DO58I=2,N
      IF(ABS(F) .LT. ABS(A(I,I))) F = A(I,I)
      IF(ABS(E) .GT. ABS(A(I,I))) E = A(I,I)
   58 CONTINUE
      EPSILP=EPSIL
      IF(EPSILP .LE. 0.) EPSILP = 1.E-8
      IF(ABS(E/F) .LT. EPSILP) GO TO 130
C
C       INVERT TRIANGULAR MATRIX
      J = N
      DO100J1=1,N
      CALL SLITE (2)
      I=J
      DO90I1=1,J
      CALL SLITET(2,K000FX)
       GO TO(70,75),K000FX
   70 A(I,J)=1.0D0/A(I,I)
      GOTO90
   75 KS=I+1
      D=0.D0
      DO80K=KS,J
   80 D=D+A(I,K)*A(K,J)
      A(I,J)=-D/A(I,I)
   90 I=I-1
  100 J=J-1
      CALL OVERFL(K000FX)
       GO TO(140,103),K000FX
  103 CALL DVCHK (K000FX)
       GO TO(140,105),K000FX
C
C       PREMULTIPLY EL BY INVERTED TRIANGULAR MATRIX
  105 M=1
      DO120I=1,N
      DO118J=1,N
      D=0.D0
      DO107K=M,N
  107 D=D+A(I,K)*EL(K,J)
      EL(I,J)=D
  118 CONTINUE
  120 M=M+1
      CALL OVERFL(K000FX)
       GO TO(140,123),K000FX
C
C       RECOPY EL TO A
  123 DO124I=1,N
      DO124J=1,N
  124 A(I,J)=EL(I,J)
      ITEST = 0
  126 IF(INDSNL .EQ. 1) CALL SLITE (2)
      RETURN
```

```
C
  130 ITEST=1
      GOTO126
  140 ITEST=-1
      GOTO126
       END
```

#4.

```
$IBFTC DW       DECK
       DOUBLE PRECISION Q(5,5),CHI(5,5),PSI(5,5)
      DOUBLE PRECISION ENERGY,ALPHA,MA,MB,MC,MD,OMEGA,MASS,BETA,
     1   PI,X,Y,Z,XX,YY,PROB   ,DELE,EMAX
      READ(5,1001) ENERGY,ALPHA,MA,MB,MC,MD,OMEGA,DELE,EMAX
       READ(5,1005) NTOTAB,NTOTCD
 1001 FORMAT(D16.8)
 1005 FORMAT(2I4)
      MASS=(MA+MB)*MD/MC/(MA+MB+MC+MD)
    5 BETA=MC/MB*DSQRT(MA*MB*(MC+MD)/(MC*MD*(MA+MB)*OMEGA))
       PI=3.1415927
C    COMPUTE POTENTIAL MATRIX
C  EVALUATION OF LAGUERRE POLYNOMIALS IN ALSQ/2. AND NORM FACTORS
       DOUBLE PRECISION FACT(20),T,TT,ALSQ,EE
      FACT(1)=1.0D0
      FACT(2)=1.0D0
      DO12 I=2,19
   12 FACT(I+1)= FLOAT(I)*FACT(I)
      ALSQ=ALPHA*ALPHA
      EE=DEXP(ALSQ/4.0D0)
      DO 6 N=1,NTOTCD
      DO 6 M=1,N
       T=0.0
       DO 14 L=1,M
      ML=M-L +1
      NML=N-M+L
      TT=FACT(N )/(FACT(ML)*FACT(NML)*FACT(L))*(ALSQ/2.0D0)**(L-1)
      IF(TT.LE.1.0D-12) GO TO 200
   14 T=T+TT
  200 CHI  (N,M)=DSQRT(FACT(M)/FACT(N)/2.0D0**(N-M))*ALPHA**(N-M)*T*EE
    6 CHI(M,N)=CHI(N,M)
       ALSQ=ALPHA*ALPHA*BETA*BETA
      EE=DEXP(ALSQ/4.0D0)
      DO 66N=1,NTOTAB
      DO 66M=1,N
       T=0.0
       DO 141L=1,M
      ML=M-L +1
      NML=N-M+L
      TT=FACT(N )/(FACT(ML)*FACT(NML)*FACT(L))*(ALSQ/2.0D0)**(L-1)
      IF(TT.LE.1.0D-12) GO TO 2008
  141 T=T+TT
 2008 PSI  (N,M)=DSQRT(FACT(M)/FACT(N)/2.0D0**(N-M))*
     1 (ALPHA*BETA)**(N-M)*T*EE
   66 PSI(M,N)=PSI(N,M)
    4 CONTINUE
       WRITE(6,1007) ENERGY
 1007 FORMAT(9H0ENERGY =,D16.8)
      DO 1 I=1,NTOTCD
      DO 1 J=1,NTOTAB
      X=ENERGY-DBLE(FLOAT(2*I-1))-OMEGA*DBLE(FLOAT(2*J-1))
       IF(X.LE.0.0D0) GO TO 1
       Q(I,J) = DSQRT(MASS*X)*2.0D0*PI/ALPHA
    1 CONTINUE
       DO 2 I=1,NTOTCD
       DO 2 J=1,NTOTAB
       DO 2 K=1,NTOTCD
       DO 2 L=1,NTOTAB
      IF(I.EQ.K.AND.J.EQ.L) GO TO 2
      XX=ENERGY-DBLE(FLOAT(2*I-1))-OMEGA*DBLE(FLOAT(2*J-1))
```

```
      YY=ENERGY-DBLE(FLOAT(2*K-1))-OMEGA*DBLE(FLOAT(2*L-1))
       IF(XX.LE.0.0D0.OR.YY.LE.0.0D0) GO TO 2
       X=DEXP(Q(I,J))
       Y=DEXP(Q(K,L))
       Z=(X+1.0D0/X-Y-1.0D0/Y)*(1.0D0/Y+1.0D0/(X*X*Y)
     1      -1.0D0/X -1.0D0/(X*Y*Y))
       PROB = (CHI(I,K)*PSI(J,L))**2/4.0D0/PI/PI*(Q(I,J)**2-Q(K,L)**2)
     1  **2 *(1.0D0-1.0D0/X**2)*(1.0D0-1.0D0/Y**2)/Z
       WRITE(6,3) I,J,K,L,PROB
    3 FORMAT(21H0PROB OF TRANS FROM (,I1,1H,,I1,6H) TO (I1,1H,,I1,
     15H) IS ,D16.8)
    2 CONTINUE
      IF(ENERGY.GE.EMAX) STOP
       ENERGY=ENERGY+DELE
       GO TO 4
       END
```

#5.

```
$IBFTC SP5     DECK
      REAL              C(200),ENERGY,MASS,X,V(10,10),ALPHA,KSQED(10),
     1 XST,XSTOP,H,ERROR,C1(10,10),C2(10,10),X1,X2,A(10,10),B(10,10),
     2 DUM,CS1,SS1,CS2,SS2,MAT(50,10),DET,EPSIL,RR(10,10),RI(10,10),
     3 CHI(10,10),PSI(10,10),PROB ,S(200)
       LOGICAL NEWH,FLAG
       COMMON V,ALPHA,KSQED,NTOT
C    HO AND EXP REPULSIVE, E IN GS UNITS
      READ(5,1001) ENERGY,MASS,ALPHA,XST,XSTOP,H,ERROR
 1001 FORMAT(E16.8)
      READ(5,1005) NTOT
 1005 FORMAT(I4)
      READ(5,1001) HFIN,RATIO,HOVRV
       DO 1  I=1,NTOT
    1 KSQED(I)=MASS*(ENERGY-     (FLOAT(2*I-1)))
      ISET=0
    4 ISET=ISET+ 1
      IF(KSQED(ISET).GT.0.0) GO TO 4
       NOPEN=ISET - 1
C INITIALIZE  C MATRIX
      NNN=2*NTOT*NTOT
       DO 2  I=1,NNN
    2 C(I)=  0.0
       DO 3  I=1,NTOT
      IK=I+(I-1)*NTOT
        IKK=IK+NTOT*NTOT
       C(IK)= 1.0E 0
    3 C(IKK)=   SQRT( EXP(-ALPHA*XST))*1.0E 0
C    COMPUTE POTENTIAL MATRIX
C   EVALUATION OF LAGUERRE POLYNOMIALS IN ALSQ/2. AND NORM FACTORS
      REAL               FACT(20),T,TT,ALSQ,EE
      FACT(1) = 1.0E0
      FACT(2) = 1.0E0
      DO12 I=2,19
   12 FACT(I+1)= FLOAT(I)*FACT(I)
      ALSQ=ALPHA*ALPHA
      EE= EXP(ALSQ/4.0E0)
      DO 6 N=1,NTOT
      DO 6 M=1,N
       T=0.0
       DO 14 L=1,M
      ML=M-L+1
      NML=N-M+L
      TT=FACT(N  )/(FACT(ML)*FACT(NML)*FACT(L))*(ALSQ/2.0E0)**(L-1)
      IF(TT.LE.1.0E -7) GO TO 200
   14 T=T+TT
  200      V(N,M)= SQRT(FACT(M)/FACT(N)/2.0E0**(N-M))*ALPHA**(N-M)*T*EE
    6 V(M,N)=V(N,M)
C     BEGIN INTEGRATION
      REAL CRP(50,1)
      NDOT = NNN + 1
      X = XST
      X1 = XST
      C(NDOT) = XST
      LSET = 0
       DOUBLE PRECISION DC(200),Q(200)
    5 CALL AM5(C,DC,H,Q,NNN,LSET,X)
       X = C(NDOT)
      IF(X.GE.(X1+ERROR)) GO TO 315
       GO TO 401
```

```
    315 CONTINUE
         WRITE(6,1007) H
        WRITE(6,1007) X
 1007   FORMAT(1H0,F16.8)
         DO 400 I=1,NTOT
         DO 400 J=1,NTOT
         IK=I+(J-1)*NTOT
         IKK=IK+NTOT*NTOT
         PSI(I,J)=C(IKK)
   400   MAT(I,J) = C(IK)
        CALL MATINV(MAT,NTOT,CRP,0,DET)
          DO 500 I=1,NTOT
         DO 500 J=1,NTOT
          DUM= 0.0
         IF(I.EQ.J) DUM = 1.0
         IK=I+(J-1)*NTOT
         IKK=IK+NTOT*NTOT
         C(IK)=DUM
          C(IKK)=0.0
         DO 500 K=1,NTOT
  500   C(IKK) = C(IKK) + PSI(I,K)*MAT(K,J)
        X1 = X1 + ERROR
        LSET = 0
         H = HOVRV/(HEIN+EXP(-ALPHA*X))
        ERROR= RATIO*H
   401  CONTINUE
        IF(X.LE.XSTOP) GO TO 5
C STORE F-F IN RI, F+F IN R, A
         DO 20 I=1,NOPEN
         DUM= SQRT(KSQED(I))
         DO 20 J=1,NTOT
          IK=I+(J-1)*NTOT
         IKK=IK+NTOT*NTOT
         RI(I,J)=C(IK)
         R(I,J)=C(IK)
   20   A(I,J)=C(IKK)/DUM
         NRMP=NOPEN+1
         DO 21 I=NRMP,NTOT
         DUM= SQRT(-KSQED(I))
         DO 21 J=1,NTOT
          IK=I+(J-1)*NTOT
         IKK=IK+NTOT*NTOT
          RI(I,J)= C(IK)-C(IKK)/DUM
         R(I,J)=C(IK) + C(IKK)/DUM
   21   A(I,J) =0.0
         DO 22 I=1,NTOT
         DO 22 J=1,NTOT
   22   MAT(I,J)=R(I,J)
        CALL MATINV(MAT,NTOT,CRP,0,DET)
 1010   FORMAT(1H0,7HITEST =,I4)
         DO 50 I=1,NTOT
         DO 50 J=1,NTOT
         RR(I,J)=MAT(I,J)
         PSI(I,J)=0.0
         DO 50 K=1,NTOT
   50   PSI(I,J)=PSI(I,J) + MAT(I,K)*A(K,J)
         DO 70 I=1,NTOT
         DO 70 J=1,NTOT
        CHI(I,J)=0.0
          DO 60 K=1,NTOT
   60   CHI(I,J)=CHI(I,J) + A(I,K)*PSI(K,J)
```

```
   70 MAT(I,J)=B(I,J)   + CHI(I,J)
      CALL MATINV(MAT,NTOT,CRP,0,DET)
       DO 23 I=1,NTOT
       DO 23 J=1,NTOT
       B(I,J) = 0.0
       DO 23 K=1,NTOT
   23 B(I,J)=B(I,J) + RI(I,K)*PSI(K,J)
       DO 24 I=1,NTOT
       DO 24 J=1,NTOT
       PSI(I,J) = B(I,J)
   24 B(I,J)=RI(I,J)
        DO 90 I=1,NOPEN
      DO 90 J=1,NOPEN
       RR(I,J)=0.0
       RI(I,J)=0.0
       DO 80 K=1,NTOT
       RI(I,J)=RI(I,J) -(A(I,K) +PSI(I,K))*MAT(K,J)
   80  RR(I,J)=RR(I,J) + (B(I,K)-CHI(I,K))*MAT(K,J)
      PROB=(RI(I,J)*RI(I,J)+RR(I,J)*RR(I,J))* SQRT(KSQED(I)/KSQED(J))
   90 WRITE(6,1000) J,I,PROB
 1000 FORMAT(1H0,2I4,10X,F16.8)
       STOP
       END
$IBFTC DR2      DECK
      SUBROUTINE F(X,C,DC)
      REAL               X,C(200),DC(200),DEL,Z  ,ALPHA,KSQED(10),V(10,10)
       COMMON V,ALPHA,KSQED,NTOT
      Z= EXP(-ALPHA*X)
       DO 1 I=1,NTOT
       DO 1 J=1,NTOT
      C(J)=C(J)
      IK=I+(J-1)*NTOT
      IKK=IK+NTOT*NTOT
      DC(IK)=C(IKK)
      DC(IKK)=0.0
      DO11 K=1,NTOT
      DEL=0.0
      IF(I.EQ.K) DEL=1.0
      KIK= K+(J-1)*NTOT
   11 DC(IKK)=DC(IKK) + (V(I,K)*Z -KSQED(I)*DEL)*C(KIK)
    1 CONTINUE
       NDOT=2*NTOT*NTOT+1
       DC(NDOT)=1.0
        RETURN
       END
$IBFTC INS      DECK
      SUBROUTINE MATINV(A,N,B,M,DETERM)
C
C     MATRIX INVERSION WITH ACCOMPANYING SOLUTION OF LINEAR EQUATIONS
C
       DIMENSION A(50,50),B(50,1),INDEX(50,2),PIVOT(50),IPIVOT(50)
C THE FOLLOWING STATEMENT(S) HAVE BEEN MANUFACTURED BY THE TRANSLATOR T
C   COMPENSATE FOR THE FACT THAT EQUIVALENCE DOES NOT REORDER COMMON---
C     DIMENSION IPIVOT(20), A(20,20), B(20,1), INDEX(20,2), PIVOT(20)
C     COMMON PIVOT, INDEX, IPIVOT
      EQUIVALENCE (IROW,JROW), (ICOLUM,JCOLUM), (AMAX, T, SWAP)
C
C     INITIALIZATION
C
   10 DETERM=1.0
   15 DO 20 J=1,N
```

```
   20 IPIVOT(J)=0
   30 DO 550 I=1,N
C
C       SEARCH FOR PIVOT ELEMENT
C
   40 AMAX=0.0
   45 DO 105 J=1,N
   50 IF (IPIVOT(J)-1) 60, 105, 60
   60 DO 100 K=1,N
   70 IF (IPIVOT(K)-1) 80, 100, 740
   80 IF (ABS (AMAX)-ABS (A(J,K))) 85, 100, 100
   85 IROW=J
   90 ICOLUM=K
   95 AMAX=A(J,K)
  100 CONTINUE
  105 CONTINUE
      IF(AMAX .EQ. 0.) GO TO 760
  110 IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1
C
C       INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
C
  130 IF (IROW-ICOLUM) 140, 260, 140
  140 DETERM=-DETERM
  150 DO 200 L=1,N
  160 SWAP=A(IROW,L)
  170 A(IROW,L)=A(ICOLUM,L)
  200 A(ICOLUM,L)=SWAP
  205 IF(M) 260, 260, 210
  210 DO 250 L=1, M
  220 SWAP=B(IROW,L)
  230 B(IROW,L)=B(ICOLUM,L)
  250 B(ICOLUM,L)=SWAP
  260 INDEX(I,1)=IROW
  270 INDEX(I,2)=ICOLUM
  310 PIVOT(I)=A(ICOLUM,ICOLUM)
  320 DETERM=DETERM*PIVOT(I)
C
C       DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
  330 A(ICOLUM,ICOLUM)=1.0
  340 DO 350 L= 1,N
  350 A(ICOLUM,L)=A(ICOLUM,L)/PIVOT(I)
  355 IF(M) 380, 380, 360
  360 DO 370 L=1,M
  370 B(ICOLUM,L)=B(ICOLUM,L)/PIVOT(I)
C
C       REDUCE NON-PIVOT ROWS
C
  380 DO 550 L1=1,N
  390 IF(L1-ICOLUM) 400, 550, 400
  400 T=A(L1,ICOLUM)
  420 A(L1,ICOLUM)=0.0
  430 DO 450 L=1,N
  450 A(L1,L)=A(L1,L)-A(ICOLUM,L)*T
  455 IF(M) 550, 550, 460
  460 DO 500 L=1,M
  500 B(L1,L)=B(L1,L)-B(ICOLUM,L)*T
  550 CONTINUE
C
C       INTERCHANGE COLUMNS
C
```

```
  600 DO 710 I=1,N
  610 L=N+1-I
  620 IF (INDEX(L,1)-INDEX(L,2)) 630, 710, 630
  630 JROW=INDEX(L,1)
  640 JCOLUM=INDEX(L,2)
  650 DO 705 K=1,N
  660 SWAP=A(K,JROW)
  670 A(K,JROW)=A(K,JCOLUM)
  700 A(K,JCOLUM)=SWAP
  705 CONTINUE
  710 CONTINUE
  740 RETURN
  760 DETERM = 0.
      RETURN
       END
$IBFTC AM5      LIST,REF,DECK
       SUBROUTINE AM5(Y,DY,DX,Q,NTEM,L,X)
      REAL              A(4),B(4),C(4),AMPC(5),AMCC(5),ARRAY(6,200),
     1 SAVY(200),SAVDY(200),Y(200),DY(200),DX,Q(200),VAR,CVAR,ACST,
     2 R,HVAR,HCVAR,X
      DATA A,B,C/0.5E+0,0.292893219E+0,0.170710678E+01,0.166666667E+0,
     1 2.0E+0,2*1.0E+0,2.0E+0,-0.5E+0,-0.292893219E+0,-0.170710678E+01,
     2-0.5E+0/,AMPC/-0.111059154E+0,0.672667758E+0,-0.170633622E+01,
     3 ,0.233387889E+01,-0.185246668E+01/,AMCC/-0.132540853E-01,
     4 0.969406561E-01,-0.310403612E+0,0.575992137E+0,-0.713555105E+0/
     5  ,VAR,CVAR,ACST/0.297013889E+01,0.107658730E+01,0.293141049E+0/
      N=NTEM+1
      IF (L) 4,1,3
    1 DO 2 J=1,N
    2  Q(J)=0.0E+0
      HVAR=DX*VAR
      HCVAR=DX*CVAR
    3 L=L+1
   15 DO 7 J=1,4
      X=Y(N)
     CALL F(X,Y,DY)
      DO 7 I=1,N
      DY(I)=DX*DY(I)
      R=A(J)*(DY(I)-B(J)*Q(I))
      Y(I)=Y(I)+R
    7 Q(I)=Q(I)+3.0    *R+C(J)*DY(I)
   14 X=Y(N)
      CALL F(X,Y,DY)
      IF (L-6) 5,6,6
    6 L=-1
      RETURN
    5 DO 8 J=1,N
    8 ARRAY(L,J)=DY(J)
      RETURN
    4 DO 10 J=1,N
      SAVDY(J)=DY(J)
      ARRAY(6,J)=SAVDY(J)
      DO 9 I=1,5
    9 ARRAY(6,J)=ARRAY(6,J)+AMPC(I)*ARRAY(I,J)
   10 Y(J)=ARRAY(6,J)*HVAR+Y(J)
      X=Y(N)
     CALL F(X,Y,DY)
      DO 12 J=1,N
     ARRAY(1,J)=ARRAY(2,J)
     ARRAY(2,J)=ARRAY(3,J)
     ARRAY(3,J)=ARRAY(4,J)
```

```
      ARRAY(4,J)=ARRAY(5,J)
   12 ARRAY(5,J)=SAVDY(J)
      RETURN
       END
```

PROPOSITION I

R. N. Doremus has investigated the optical absorption spectra of small gold and silver particles formed in glass.[1,2] The experimental results are compared to the calculations of Mie,[3] using measured bulk values of the dielectric constants and electrical conductivities of gold and silver in Mie's equation:

1.
$$\gamma = \frac{18\pi NV n_0^3 \epsilon_2}{\lambda[(\epsilon_1 + 2n_0^2)^2 + \epsilon_2^2]} .$$

γ is the absorption coefficient for N/cm^3 spherical particles in a medium having refractive index n_0. V is the volume of each particle. ϵ_1 and ϵ_2 are the real and imaginary parts of the metal's dielectric constant, and λ is the wavelength of the light in the medium surrounding the particles. This relation has been derived under the assumptions: 1) that the diameter of the particles is much smaller than the wavelength of the light, 2) that the particles scatter light independently, and 3) that no multiple scattering occurs. The latter placing some restriction on the number density for a given sample.

Assuming that free electrons are responsible for the dielectric properties of a metal, one determines the dielectric constant from:[4]

2.
$$\epsilon = \epsilon_0 - \left(\frac{4\pi N_e e^2 \lambda^2}{(2\pi c)^2 m_e}\right) + i\left(\frac{4\pi N_e^2 e^4 \lambda^3}{(2\pi c)^3 m_e^2 \sigma}\right)$$

where ϵ_0 is a frequency independent constant, N_e is the number density of free electrons, σ is the d. c. conductivity, λ is the wavelength of light, m_e is the electron mass, and e is the electronic charge.

Doremus used the combined form of 1. and 2. :

$$\text{3.}\qquad \gamma = \frac{9\pi N V n_0^3\, c}{\sigma}\; \frac{\lambda^2}{(\lambda_m^2 - \lambda^2)^2 + \lambda^6/\lambda_a^2}$$

where $\lambda_m^2 = \lambda_c^2(\epsilon_0 + 2n_0^2),\ \lambda_c^2 = \dfrac{(2\pi c)^2 m_e}{4\pi N_e\, e^2},\ \lambda_a = \dfrac{2\lambda_c^2\,\sigma}{c}$

to predict the optical absorption of the metal sols and to compare with his measurements. The maximum absorption occurs at $\lambda = \lambda_m$, and the height and peak width at half height are given by:

$$\text{4.}\qquad \gamma_m = \frac{36\pi N V n_0^3\,\sigma}{(\epsilon_0 + 2n_0^2)^2 c}\quad \frac{\lambda_m^2}{\lambda_a} = \frac{(\epsilon_0 + 2n_0^2)\,c}{2\sigma}\quad .$$

Doremus prepared the gold and silver sols in glass of the composition 71. 5% SiO_2, 23% Na_2O, 4% Al_2O_3, and 1% ZnO. .02 to .1% CeO_2 was added as a nucleating agent for the Au or Ag, which was introduced as chloride and irradiated to form atomic metal. Heating at 400°C to 630°C caused diffusion and growth of metal particles. Investigation showed that the particle size could be controlled to about 25% in radius, and that the particles were nearly spherical. The spectrometer had a sample furnace so that spectra could be taken at temperatures up to 500°C.

Here some of the pertinent results are summarized: For Ag, the location of the absorption peak agreed with the prediction from Mie's equation (1.) using the bulk dielectric values. The band shape agreed with the free electron theory (equation 3.). The band width was inversely proportional to the particle radius, agreeing with a free electron model (equation 4.) if one uses $\sigma = N_e e^2 R/mu$ as an estimate of the d. c. conductivity when the particle radius R is small compared to the electron mean free path.[5] u = electron velocity at Fermi level. For Au, the particles seemed to fall into two groups according to size. Those 85 Å to 200 Å diameter had ϵ_1 almost the same as bulk Au, but ϵ_2 was considerably greater. This is determined from 1.. The absorption peak at .525 was unaffected by particle radius down to 85 Å. This does not agree with the free electron model. For particles below 85 Å, the peak was proportional to diameter, in agreement with the free electron model for particles with dimensions smaller than the mean free path. It was observed that the peak broadened with increasing temperature for all sizes of particles.

It is proposed that inclusion and/or diffusion of impurities into the metal particles from the surrounding glass has occurred. The presence of impurities would necessitate a recomparison of the observed absorption spectra with the predictions of the free electron model. The impurities would affect the conductivity of the metal and the dielectric constant. Possible impurities are the components of the glass, Na_2O, SiO_2, Al_2O_3, ZnO, and CeO_2, trapped larger fragments, or even unanalyzed parts of the glass structure.

The effects of impurities can only be estimated. Doremus discounts the presence of them, but states that metallic crystal imperfections might occur and cause difficulty before the particles were annealed. The effect of impurities on the Au and Ag metal would be: 1) the free electron model mean free path would be smaller than the particles' dimensions, 2) the d. c. conductivity would be lowered, and 3) the imaginary part of the dielectric constant would be proportionally larger.[4]

The relevance of impurities to the conclusions of Doremus' work are the following: 1) the 85 Å Au particle diameter, below which the absorption peak height was proportional to the diameter, would indicate an electron path that has been effectively reduced to 85 Å. The electron mean free path in Au at 0°C is 410 Å.[5] 2) For Au and Ag, band widths calculated from bulk dielectric constants were less than one tenth of those observed. The free electron model predicts a band width inversely proportional to conductivity. A decrease in conductivity by a factor of ten in 4. would raise the band width by that amount. 3) The discrepancy between the ϵ_2 for small particles and bulk (ϵ_2 particle/ϵ_2 bulk ranges from 5 to 25) would be lessened if impurities lowered the electron mean free path.

It appears that one cannot determine the amount of impurities in the particles directly. However, one can measure the electrical effect of possible diffusion into Au and Ag layers. By preparing pure 50-200 Å thick layers of Au or Ag on glass of the composition used by Doremus and nearly identical layers on pure silica, one can compare the electrical conductivity as a function of temperature. Because of the similarity of silica and glass, a difference in the conductivity of the samples would be attributed to components in the glass. Pure silica diffusion would not be detected however. Techniques for preparing metal films may be found in reference 6.

If the experiment revealed a definite effect of glass composition on the metals' electrical properties, then the validity of the free electron model predictions may be reconsidered.

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PROPOSITION II

One might classify quantum mechanical descriptions of interactions into analytical, perturbation, and semiclassical methods. All of these involve numerical analysis, but not as an explicit means of solution. High speed computers have made it possible to attack simple or simplified problems in quantum mechanics at a fundamental level. Consider the simple Schrödinger equation:

1. $$\frac{\hbar}{i}\,\frac{\partial\psi(x,t)}{\partial t} = \frac{\hbar^2}{2m}\,\frac{\partial^2\psi(x,t)}{\partial x^2}\ .$$

ψ is a complex scalar and may be broken into $Re^{i\varphi}$ or $\varphi_R + i\varphi_I$ where R, φ, φ_R, φ_I are real. Using the latter, we have:

2. $$\frac{\partial\varphi_R}{\partial t} = -\frac{\hbar}{2m}\,\frac{\partial^2\varphi_I}{\partial x^2}$$

$$\frac{\partial\varphi_I}{\partial t} = \frac{\hbar}{2m}\,\frac{\partial^2\varphi_R}{\partial x^2}\ .$$

These are two real, coupled differential equations, which are of parabolic form. The general spirit of numerical differential equation solving is to replace derivatives by differences and, in the case of parabolic equations, advance from an initial given solution $\psi = \psi(x, t_0)$ to a later time in finite time increments. For example, the equations 2. become the difference equations:[1]

$$n = \cdots -2,\ -1,\ 0,\ 1,\ 2,\ \cdots$$

3.

$$\frac{\varphi_R(n\Delta x,\ t+\Delta t) - \varphi_R(n\Delta x,\ t)}{\Delta t} = -\frac{\hbar}{2m}\,\frac{\varphi_I((n+1)\Delta x, t) - 2\varphi_I(n\Delta x, t) + \varphi_I((n-1)\Delta x, t)}{(\Delta x)^2}$$

$$\frac{\varphi_I(n\Delta x,\ t+\Delta t) - \varphi_I(n\Delta x,\ t)}{\Delta t} = \frac{\hbar}{2m}\,\frac{\varphi_R((n+1)\Delta x, t+\Delta t) - 2\varphi_R(n\Delta x, t+\Delta t) + \varphi((n-1)\Delta x, t+\Delta t)}{(\Delta x)^2}$$

if we divide the x coordinate into a point mesh $x_n = n\Delta x$ and the time into intervals $t_k = k\Delta t$. For convenience, let $\varphi_{A_\ell}^{k} = \varphi_A(\ell\Delta x, k\Delta t)$. The solution at time $t = t_k + \Delta t$ is obtained from the solution at t_k by rearranging equations 3. :

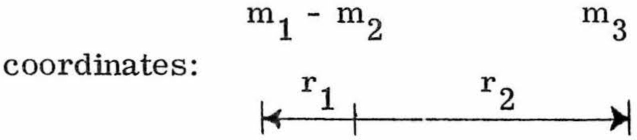
4.

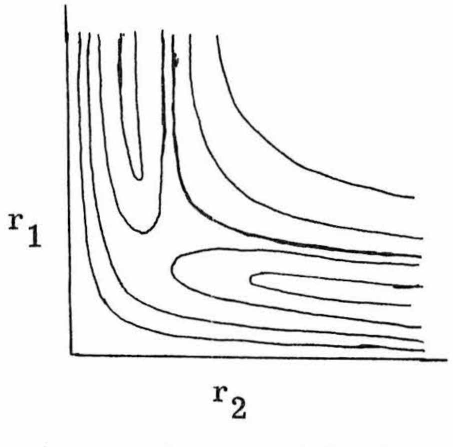
$$\varphi_{R_\ell}^{k+1} = \varphi_{R_\ell}^{k} - \frac{\Delta t}{(\Delta x)^2}\left(\frac{\hbar}{2m}\right)\left\{\varphi_{I_{\ell+1}}^{k} - 2\,\varphi_{I_\ell}^{k} + \varphi_{I_{\ell-1}}^{k}\right\}$$

$$\varphi_{I_\ell}^{k+1} = \varphi_{I_\ell}^{k} + \frac{\Delta t}{(\Delta x)^2}\left(\frac{\hbar}{2m}\right)\left\{\varphi_{R_{\ell+1}}^{k+1} - 2\,\varphi_{R_\ell}^{k+1} + \varphi_{R_{\ell-1}}^{k+1}\right\}.$$

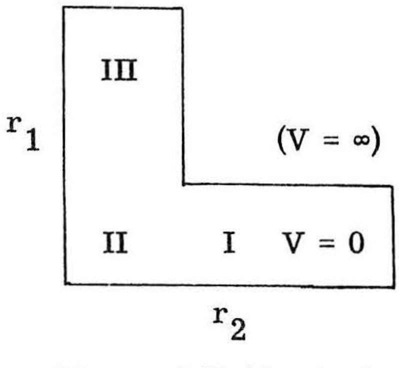
Note that $\varphi_{I_\ell}^{k+1}$ is computed from the differences of $\varphi_R(x,t)$ at $(k+1)\,\Delta t$, not $k\Delta t$. This was found necessary for stability of this particular difference scheme.[1] Finite difference methods involve problems of convergence and stability;[2] a general discussion of this will not be given here, but may be found in references 2 and 3. Specific conditions on Schrödinger's equation in one space variable are discussed in references 1 and 4.

Mazur and Rubin computed the collision induced reaction probability of a system representing H_2 and H in the following manner.[1] They approximated the potential interaction surface by an "L"-shaped region in coordinate space with zero potential within the bounds of the region. The wavefunction was kept zero at the boundaries of the "L".





"Actual" Potential Surface



Mazur & Rubin Analog

The Schrödinger equation for the interaction in center-of-mass coordinates, r_1 and r_2,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2}\left\{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\frac{\partial^2}{\partial r_1^2} + \left(\frac{1}{m_2}+\frac{1}{m_3}\right)\frac{\partial^2}{\partial r_2^2} - \frac{2}{m_2}\frac{\partial^2}{\partial r_1 \partial r_2}\right\}\psi + V(r_1, r_2)\psi \qquad \underline{5.}$$

was put into difference form with $m_1 = m_2 = m_3$ and with $V(r_1,r_2) = 0$. The initial state was in region I of the "L". Iteration showed the packet to move into region II and then divide, part entering region III. The probability of reaction was computed from the probability density of the wave in III, before reflection from the far end changes the character of the solution. The wave packet at time zero was separable: $\psi(r_1, r_2, 0) = \varphi(r_1)\theta(r_2)$, with $\varphi(r_1)$ a sine wave representing the lowest vibrational state and $\theta(r_2)$ a wave moving to the left with a momentum distribution corresponding to thermal averaging of H atoms at a given temperature. The results are discussed by Mazur and Rubin.

It is proposed that numerical difference solutions for potential interactions are feasible for better models than those with only boundary conditions as used by Mazur and Rubin. Specifically, the stability of the difference method will be demonstrated for a Schrödinger equation in two space variables of a modified form of 5..

Equation 5. is written as:

$$\frac{\partial\psi}{\partial t} = A\frac{\partial^2\psi}{\partial r_1^2} + 2B\frac{\partial^2\psi}{\partial r_1\partial r_2} + C\frac{\partial^2\psi}{\partial r_2^2} + V'(r_1, r_2)\psi \tag{6.}$$

where: $A = \frac{i\hbar}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)$, $B = \frac{-i\hbar}{2m_2}$, $C = \frac{i\hbar}{2}\left(\frac{1}{m_2} + \frac{1}{m_3}\right)$, $V' = \frac{V}{i\hbar}$.

And the difference analog is formed:

$$\begin{aligned}\frac{\psi^{k+1}_{\ell,m} - \psi^{k-1}_{\ell,m}}{2\Delta t} &= \frac{A}{(\Delta r_1)^2}\left(\psi^k_{\ell+1,m} - 2\psi^k_{\ell,m} + \psi^k_{\ell-1,m}\right)\\ &+ \frac{B}{2\Delta r_1\Delta r_2}\left(\psi^k_{\ell+1,m+1} - \psi^k_{\ell-1,m+1} - \psi^k_{\ell+1,m-1} + \psi^k_{\ell-1,m-1}\right)\\ &+ \frac{C}{(\Delta r_2)^2}\left(\psi^k_{\ell,m+1} - 2\psi^k_{\ell,m} + \psi^k_{\ell,m-1}\right) + V'(\ell\Delta r_1, m\Delta r_2)\psi^k_{\ell,m}\end{aligned} \tag{7.}$$

where: $\psi^k_{\ell,m} = \psi(\ell\Delta r_1, m\Delta r_2, k\Delta t)$

$\ell = 1, 2, \ldots, N \quad m = 1, 2, \ldots, N \quad k = 1, 2, \ldots.$

The time difference is chosen to be symmetric; also it is found necessary to replace the potential function by a constant, $V' \to V_c$. This was done in the stability analysis of one space dimensional

Schrödinger equations.[4] This is a restrictive assumption to make, but the author could find no alternative.

Just as the Hamiltonian operator has eigenfunctions, the difference equation analog has also. These are of the form $e^{i\pi k_1 \ell \Delta r_1} e^{i\pi k_2 m \Delta r_2}$. Let

8. $$\psi^k_{\ell, m} = T_k e^{i\pi k_1 \ell \Delta r_1} e^{i\pi k_2 m \Delta r_2} = T_k \varphi_{\ell, m}$$

where T_k depends only on the index k. Placing 8. into 7. and simplifying:

9. $$\frac{T_{k+1} - T_{k-1}}{2\Delta t} \varphi_{\ell, m} = 2 \left[\frac{A}{(\Delta r_1)^2} (\cos \pi k_1 \Delta r_1 - 1) \right.$$

9. $$\left. + \frac{B}{\Delta r_1 \Delta r_2} \sin \pi k_1 \Delta r_1 \sin \pi k_2 \Delta r_2 + \frac{C}{(\Delta r_2)^2} (\cos \pi k_2 \Delta r_2 - 1) + V_c \right] T_k \varphi_{\ell, m} .$$

Letting 4Δt [above quantity in brackets] = Λ, and canceling the $\varphi_{\ell, m}$,

10. $$T_{k+1} - T_{k-1} = \Lambda T_k$$

an iterative equation for the quantities T_k, k = 1, 2, · · · . This equation has solutions:[4, 5]

$$\underline{11.}\qquad T_k = c_1 \rho_1^k + c_2 \rho_2^k$$

where ρ_1 and ρ_2 are the roots of

$$\underline{12.}\qquad \rho^2 - 1 = \Lambda \rho .$$

One may substitute 11. into 10. and use 12. to confirm the solutions. c_1 and c_2 are constants related to the initial solution.

Now, if the maximum of $|\rho_1|$ and $|\rho_2|$ is greater than 1, we see from $T_k = c_1\rho_1^k + c_2\rho_2^k$ that T_k will increase in absolute value as k becomes large. If max $|\rho_1|, |\rho_2| < 1$, then T_k decreases. If max $|\rho_1|, |\rho_2| = 1$, then T_k is bounded. Thus, the k'th iteration at mesh point (ℓ, m), $\psi_{\ell,m}^k = T_k \varphi_{\ell,m}$, will grow unbounded in absolute value unless we can restrict max $|\rho_1|, |\rho_2| \leq 1$. Assuming the stability of the differential equation itself, that condition is the generally accepted criterion for stability, and consequently of convergence. The reverse is not true however. The above result possibly is derived easier via the route of Gerschgorin's theorem. For usage of this, see references 1, 2, and 6.

Solving 12. for ρ gives the two roots:

$$\underline{13.}\qquad \rho_1 = \frac{1}{2}\Lambda + \left[\frac{\Lambda^2}{4} + 1\right]^{1/2} \qquad \rho_2 = \frac{1}{2}\Lambda - \left[\frac{\Lambda^2}{4} + 1\right]^{1/2} .$$

Replacing Λ by its defined value, and A, B, and C from 6. by their values, and then requiring $|\rho_1|$ and $|\rho_2| \leq 1$ shows that max $|\rho_1|, |\rho_2| = 1$. This is true when:

14. $$\Delta t \left| \frac{\hbar\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}{(\Delta r_1)^2}(1-\cos\pi k_1\Delta r_1) + \frac{\hbar\,\frac{1}{m_2}}{\Delta r_1\Delta r_2}\sin\pi k_1\Delta r_1\,\sin\pi k_2\Delta r_2 + \frac{\hbar\left(\frac{1}{m_2}+\frac{1}{m_3}\right)}{(\Delta r_2)^2}(1-\cos\pi k_2\Delta r_2) + \frac{2V_c}{\hbar} \right| < 1 .$$

The result is similar to that for the one-dimensional case.[4] We may simplify this for specific cases. For example, if $m_1 = m_2 = m_3 = m$ and $\Delta r_1 = \Delta r_2 = \Delta r$, we get:

15. $$\frac{\Delta t}{(\Delta r)^2} < \frac{\frac{1}{8}\,m/\hbar}{1 + \frac{V_c m}{4\hbar^2}(\Delta r)^2} \qquad V_c > 0 .$$

This has in effect only demonstrated stability for constant potential. It follows from the derivation that the stability criterion applies to a regionally constant potential in the r_1 and r_2 coordinate surface. The stability of the difference method near a discontinuity in a sectionally constant potential is unknown. However, Mazur and Rubin calculated one-dimensional square barrier penetrations and got difference equation <u>vs</u> exact solution agreement to within ten percent.[1] What should be known is a stability criterion for a functional potential, but only estimates or trial and error tests seem available. Regardless, the stability of the difference method can be insured for some two-dimensional problems and estimated for the rest with reasonable judgment.

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PROPOSITION III

Integral equations of the first kind appear regularly in physics and chemistry. They are of the form:

1. $$y(x) = \int_a^b f(t)\, K(t, x)\, dt$$

where $f(t)$ is an unknown function, and is to be determined. Let us assume here that $y(x)$ is known by measurement at a set of points $x_1, x_2, \cdots, x_N$. Each measurement inherently contains error, so let m_i represent the measured value of $y(x_i), i=1, \cdots, N$. The problem is to obtain a function $f(t)$ which gives a best fit of all y_i to the m_i, where y_i is:

2. $$y_i = \int_a^b f(t)\, K(t, x_i)\, dt \, .$$

This proposition intends to show that a Gaussian least squares fit of the y_i (defined above) to the measured m_i furnishes a direct and preferable means of obtaining an approximate solution to the integral equation. The function $f(t)$ is assumed expandable in a series of linearly independent functions, $\varphi_j(t)$:

3. $$f(t) = \sum_{j=1}^{n} c_j \varphi_j(t) \qquad n \leq N \, .$$

Introducing 3. into 2. :

4. $$y_i = \sum_{j=1}^{n} c_j \int_a^b \varphi_j(t)\, K(t, x_i)\, dt \;.$$

The known integral $\int_a^b \varphi_j(t)\, K(t, x_i) dt$ is now labeled Φ_{ji} and is a constant.

We wish to minimize the sum of squared differences of y_i and m_i with respect to the unknown expansion coefficients $c_1, \cdots, c_n$, and thereby determine them. Let

5. $$S(c_1, \cdots, c_n) = \sum_{\nu=1}^{N} \frac{(m_\nu - y_\nu)^2}{\sigma_\nu^2} = \sum_{\nu=1}^{N} \frac{1}{\sigma_\nu^2} \left[m_\nu - \sum_{j=1}^{n} c_j\, \Phi_{j\nu} \right]^2 \;.$$

The σ_ν are weight factors related to the reliability of the measurement. The function $S(c_1, \cdots, c_n)$ has a unique minimum given by the solution of the normal equations:[1]

6. $$0 = \frac{1}{2} \frac{\partial S(c_1, \cdots, c_n)}{\partial c_\rho} = \sum_{\nu=1}^{N} \frac{1}{\sigma_\nu^2} \left[m_\nu - \sum_{j=1}^{n} c_j\, \Phi_{j\nu} \right] [\, - \Phi_{\rho\nu}\,] \;.$$

The solution may be written in compact matrix form if we define:

$$\underset{\sim}{c} = \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ c_n \end{pmatrix} \quad \underset{\sim}{m} = \begin{pmatrix} m_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ m_N \end{pmatrix} \quad \Lambda = \begin{pmatrix} 1/\sigma_1^2 & & & & 0 \\ & 1/\sigma_2^2 & & & \\ & & \ddots & & \\ 0 & & & & 1/\sigma_N^2 \end{pmatrix}$$

$$\Phi = \begin{pmatrix} \Phi_{11} & \cdots & \Phi_{1N} \\ \vdots & & \vdots \\ \Phi_{n1} & \cdots & \Phi_{nN} \end{pmatrix}$$

7\. So: $$\underset{\sim}{c} = (\Phi \Lambda \Phi^T)^{-1} (\Phi \Lambda \underset{\sim}{m}) \ .$$

If one has a two variable integral equation of the form:

8\. $$y(x^1, x^2) = \int_a^b \int_c^d f(t^1, t^2) \, K(t^1, t^2, x^1, x^2) \, dt^1 \, dt^2$$

and measured data: m_{ij}, $i=1,\cdots,N$, $j=1,\cdots,N$, then an expansion of $f(t^1,t^2)$ as $\sum_{\nu=1}^{n} c_\nu \varphi_\nu(t^1,t^2)$ results in:

9. $$y_{ij} = y(x_i^1, x_j^2) = \sum_{\nu=1}^{n} c_\nu \int_a^b \int_c^d \varphi_\nu(t^1, t^2) K(t^1, t^2, x_i^1, x_j^2) dt^1\, dt^2 .$$

A least squares fit of y_{ij} to m_{ij} requires the minimization of equation 10. with respect to the c_ν. Let

$$\Phi_{\nu ij} = \int_a^b \int_c^d \varphi_\nu(t^1, t^2) K(t^1, t^2, x_i^1, x_j^2)\, dt^1\, dt^2$$

10. $$S(c_1, \cdots, c_n) = \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\sigma_{ij}^2} [m_{ij} - y_{ij}]^2$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\sigma_{ij}^2} \left[m_{ij} - \sum_{\nu=1}^{n} c_\nu \Phi_{\nu ij} \right]^2 .$$

The normal equations are:

11. $$\sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\sigma_{ij}^2} m_{ij} \Phi_{\rho ij} = \sum_{\nu=1}^{n} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\sigma_{ij}^2} \Phi_{\nu ij} \Phi_{\rho ij} c_\nu$$

$$\rho = 1, 2, \cdots, n .$$

Define $$M_{\rho\nu} = \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\sigma_{ij}^2} \Phi_{\nu ij} \Phi_{\rho ij}$$

$$V_\rho = \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{m_{ij}}{\sigma_{ij}^{2}} \Phi_{\rho ij} .$$

Then 11. may be written as:

$$\text{12.} \qquad \sum_{\nu=1}^{n} M_{\rho\nu} c_\nu = V_\rho \qquad\qquad \underset{\sim}{c} = M^{-1} \underset{\sim}{V}$$

where $\underset{\sim}{c}$ is the coefficient vector and $\underset{\sim}{V}$ is an n component column vector.

The advantages of this method of solving integral equations are: 1) knowledge of the relative and overall accuracy of the measurements can be weighted into the solution through the weight factors σ_i or σ_{ij}. 2) An a priori knowledge of the form of the unknown function may allow one to use a minimal number of terms in its expansion. 3) Random errors in measurements are usually Gaussian distributed, implying that a least squares fit is the best way to remove them. Non-random instrument errors, for example, should be analyzed by other means.[2]

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PROPOSITION IV

Simple collision theory predicts the following reaction rate - cross section relationship for structurely averaged gas phase processes:[1]

1. $$\underline{k}(T) = \frac{1}{(\pi\mu)^{1/2}} \left(\frac{2}{kT}\right)^{3/2} \int_0^\infty dE\, Ee^{-E/kT}\, C(E)\,.$$

It would be desirable to take measured rate data[2] and solve for C(E), the total energy-dependent reaction cross section, but this is very difficult because of the nature of Laplace transform inversion. We discuss some approaches and propose a method that converts a maximal amount of information contained in k(T) into C(E). We avoid making use of any particular reaction theory to indicate forms of C(E) or k(T).

Method 1. We have the measured information $\underline{k}_n = \underline{k}(T_n)$ taken at the temperatures T_n. We wish to calculate C(E) at a series of points E_m. Since C(E) appears under an integral, we approximate it by a series of delta functions and have:

2. $$C(E) \approx \sum_m C_m\, \delta(E - E_m)$$

3. $$\underline{k}_n = \frac{1}{(\pi\mu)^{1/2}} \left(\frac{2}{kT_n}\right)^{3/2} \sum_m E_m e^{-E_m/kT_n} C_m\,.$$

Choosing as many points in E as we have points in T, we have a linear system of algebraic equations to solve for the unknowns. This effectively necessitates the inversion of the matrix $K_{nm} = e^{-E_m/kT_n}$. It turns out that this system is very ill-conditioned,[3] as are nearly all direct attempts of this nature.

Method 2. If one examines the overlapping part of $E\,e^{-E/kT}$ and C(E) (which contributes to the integral in 1.), one notices that the distribution function overlaps C(E) progressively more for higher temperatures. Reaction rates are measurable only within certain ranges because of physical limitations. This means that we will not have k(T) measurements for temperatures such that the distribution overlaps C(E) greatly or very little. In any case, the rate constant arises from the near-threshold part of C(E). Only if C(E) increased exponentially would the overlap of C(E) at energies far above threshold contribute to k(T). We want to avoid inversion of the Laplace transform type integral in 1.; this can be done by the following: choose an expansion for C(E) in some set of functions such that 1. can be integrated, resulting in an expansion for k(T). Conversely, we could expand k(T) in a series such that 1. is term by term analytically invertable; then we have a series for C(E). This is not so wonderful, for we are just replacing the difficulty of inverting the transform with fitting a series of functions to the measured data. One of the best expansions for C(E) near threshold is a simple power series. For convenience, we expand the product EC(E), including a threshold step function, $H(E-E_0)$, to make C(E) vanish at the threshold E_0. Also, a non-integer power is included. Let:

4. $$EC(E) = H(E-E_0)(E-E_0)^{\alpha} \sum_{n=0}^{\infty} C_n (E - E_0)^n \quad .$$

For $\alpha > -1$, we can substitute 4. into 1. and obtain:[4]

5. $$\underline{k}(T) = \frac{1}{(\pi\mu)^{1/2}} \left(\frac{2}{kT}\right)^{3/2} e^{-E_0/kT} (kT)^{\alpha+1} \sum_{n=0}^{\infty} C_n \Gamma(n+\alpha+1)(kT)^n \quad .$$

This is a power series in T about $T = 0$, times an exponential factor. If we could determine the set of numbers E_0, C_0, $C_1, \cdots$, C_N by fitting 5. to the rate measurements for some finite number of terms in the expansion 5., then we would have an expansion for $C(E)$ via 4.. Wray[5] has measured Ar + O_2 dissociation rate data. This is not bimolecular, but we use his published forms of $\underline{k}(T)$ to illustrate the method and pitfalls. The analytic forms are given as

6. $$\frac{1}{T} e^{-E_0/kT}$$

and

7. $$\frac{1}{(T)^{1/2}} e^{-E_0/kT} \quad .$$

Our inversion procedure gives the cross section forms:

8. $$H(E - E_0) \frac{1}{E} \frac{1}{(E - E_0)^{1/2}}$$

from 6., and

9. $$H(E - E_0) \frac{1}{E}$$

from 7.. The first is singular at $E = E_0$. We believe that this gives credence to the second form, although one must remember that we are determining $C(E)$ from an integral and the singular form is a good solution in the sense that it gives 6. when inserted into 1..

If we had expanded $EC(E)$ in dimensionless arguments:

10. $$EC(E) = H\left(\frac{E - E_0}{E_0}\right)\left(\frac{E - E_0}{E_0}\right)^{\alpha} \sum_{n=0}^{\infty} \bar{C}_n \left(\frac{E - E_0}{E_0}\right)^n$$

we would have obtained:

11. $$\underline{k}(T) = \frac{1}{(\pi\mu)^{1/2}} \left(\frac{2}{kT}\right)^{3/2} e^{-E_0/kT} \left(\frac{kT}{E_0}\right)^{\alpha + 1} \cdot \sum_{n=0}^{\infty} \bar{C}_n \, \Gamma(n + \alpha + 1) \left(\frac{kT}{E_0}\right)^n .$$

For measurements of $\underline{k}(T)$ at the lowest possible temperatures, $kT/E_0 << 1$; therefore,

12. $$\underline{k}(T) \approx \frac{1}{(\pi\mu)^{1/2}} \left(\frac{2}{kT}\right)^{3/2} \left(\frac{kT}{E_0}\right)^{\alpha+1} e^{-E_0/kT} \, \bar{C}_0 \, \Gamma(\alpha + 1) \, .$$

Implying,

13. $$\frac{d}{d(1/kT)} [\ell n(\underline{k}(T) \, (kT)^{1/2 - \alpha}] = -E_0$$

for kT small.

This is a best determination of E_0, with α chosen to make the logarithmic derivative as constant as possible. The remaining parameters $\bar{C}_0$, $\bar{C}_1$, $\cdots$ are to be determined by doing a least squares fit of the power series in kT/E_0 to the reduced data:

14. $$\underline{k}(T) \, (\pi\mu)^{1/2} \left(\frac{kT}{2}\right)^{3/2} \left(\frac{E_0}{kT}\right)^{\alpha+1} e^{E_0/kT}$$

at the measured temperatures T_i. The envisioned difficulty is that we do not know rate constants at low enough temperatures to justify 13. accurately, this then interferes with the determination of the $\bar{C}_i$ constants from 14.. A more thorough analysis would involve a non-linear least squares fit of E_0, α, $\bar{C}_0$, $\bar{C}_1$, $\cdots$ with error estimations.

Method 3. We propose the following scheme be investigated and compared to the results of Method 2.. We assume a definite threshold exists at some E_0, so let:

15. $$EC(E) = H(E - E_0) \, P(E - E_0)$$

where $H(E - E_0)$ is the unit step function. Then 1. becomes:

16. $$\underline{k}(T) = \frac{1}{(\pi\mu)^{1/2}} \left(\frac{2}{kT}\right)^{3/2} e^{-E_0/kT} \int_0^\infty P(E')e^{-E'/kT}\, dE'$$

where $E' = E - E_0$ has been introduced. $P(E')$ is the unknown function to be determined, along with the threshold E_0. Suppose that the rate data has been measured over some range of temperature from T_1 to T_2. Over this range, we want to fit the data to an expansion of $\underline{k}(T)$ in a series of functions whose inverse Laplace transforms, $\underline{L}^{-1}$, are known. It so happens that

17. $$\underline{k}(T) = e^{-E_0/kT} (kT)^{\alpha} \sum_{n=0} A_n \left(\frac{T - T_0}{T_0}\right)^n$$

has exact inverse transforms for certain α's.[4] We are free to choose T_0. Placing T_0 in the interval from T_1 to T_2 centers the power series in 17. about a point in the midst of our rate measurements. This is important for a power series fit in which successive terms are to be converging rapidly to the function. Equating 16. and 17. gives:

18. $$(kT)^{\alpha+3/2} \sum_{n=0} A_n \left(\frac{T - T_0}{T_0}\right)^n = \frac{1}{(\pi\mu)^{1/2}} 2^{3/2} \int_0^\infty dE' P(E')e^{-E'/kT}$$

which has the solution for P(E'), obtained by using known L^{-1} transforms,[4] for $\alpha = -1/2$:

19. $$P(E') = \sum_{n=0} A_n \frac{(\pi\mu)^{1/2}}{2^{3/2}} L_n\left(\frac{E'}{kT_0}\right)$$

where $L_n(x)$ is the Laguerre polynomial:

20. $$L_n(x) = \sum_{m=0}^{n} (-1)^m \binom{n}{n-m} \frac{1}{m!} x^m \, .$$

The predictions and behavior of this method have not been tested; we propose to do this. The major formal result is the introduction of a series expanded about an arbitrary point in the temperature scale. This enables one to obtain a better and more rapidly convergent fit to the rate data. One must investigate the convergence of 19. as more terms are included in the fit to k(T) in 17..

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PROPOSITION V

Invariant imbedding[1, 2] furnishes a powerful means of converting certain types of quantum mechanical problems, defined by the second-order Schrödinger equation with asymptotic boundary conditions, into first-order initial value problems. The procedure has never been formalized or tested for the solution of the bound state Schrödinger equation by conversion to a first-order initial value problem. We will show that the standard perturbation theory for bound systems leads directly to a first-order differential equation for the eigenvalues and eigenfunctions.

For any one-dimensional bound system, the orthonormal eigenfunctions and eigenvalues are determined from

<u>1.</u> $$H\psi_n = E_n \psi_n$$

by requiring square-integrability of the solutions. If we add a perturbation ΔH to H, the first order changes in E_n and ψ_n are:[3]

<u>2.</u> $$\Delta E_n = \langle \psi_n | \Delta H | \psi_n \rangle$$

<u>3.</u> $$\Delta\psi_n = \sum_{n' \neq n} \psi_{n'} \frac{\langle \psi_{n'} | \Delta H | \psi_n \rangle}{E_n - E_{n'}}$$

with normalization of <u>3.</u>:

$$\langle \psi_n + \Delta\psi_n | \psi_m + \Delta\psi_m \rangle = \delta_{nm}$$

4.

$$+ 0(\langle \psi_n | \Delta H | \psi_m \rangle)^2 .$$

Suppose we wish to determine the solutions of the scaled Schrödinger equation:

5. $$(-\frac{1}{2}\frac{d^2}{dx^2} + V(x))\,\psi_n(x) = E_n\,\psi_n(x) \quad .$$

Assume we know the solutions to some simpler problem:

6. $$(-\frac{1}{2}\frac{d^2}{dx^2} + V^0(x))\,\psi_n^0(x) = E_n^0\,\psi_n^0(x) \quad .$$

Introduce a parameter x_0 into $V(x)$ so that:

$$V(x,\ x_0)\Big|_{x_0 = 0} = V^0(x)$$

7.

$$V(x,\ x_0)\Big|_{x_0 = L} = V(x) \quad .$$

This parameter carries the parameterized potential $V(x, x_0)$ from $V^0(x)$ to $V(x)$ as x_0 goes from 0 to L. For any value of x_0, we define the solution to the potential $V(x, x_0)$ to be $\psi(x, x_0)$:

8. $$\left(-\frac{1}{2}\frac{d^2}{dx^2} + V(x, x_0)\right)\psi_n(x, x_0) = E_n(x_0)\,\psi_n(x, x_0) \;.$$

The eigenvalues are naturally dependent on x_0. We see from 7., and 5. and 6., that the "boundary conditions" on the variation of x_0 are:

9. $$\psi_n(x, 0) = \psi_n^0(x), \qquad E_n(0) = E_n^0$$

because, when $x_0 = 0$, 8. is the same as 6.. Likewise, when $x_0 = L$, 8. is the same as 5.:

10. $$\psi_n(x, L) = \psi_n(x), \qquad E_n(L) = E_n \;.$$

We have set up x_0 as an invariant imbedding parameter,[1] but lack the differential equation which describes the change in the $\psi_n(x, x_0)$ as x_0 changes. Suppose we know the $\psi_n(x, x_0)$ solutions and the $E_n(x_0)$ for a particular x_0. An incremental increase in x_0 changes the potential:

11. $$V(x, x_0 + \Delta x_0) = V(x, x_0) + \Delta x_0 \frac{\partial V(x, x_0)}{\partial x_0} \;.$$

The last term in 11. is a perturbation of the variety used in 2. and 3.. Equation 8. tells us that the first order changes in $\psi_n(x, x_0)$ and $E_n(x_0)$ due to the first order change in $V(x, x_0)$ are

$$\Delta E_n(x_0) = E_n(x_0 + \Delta x_0) - E_n(x_0)$$

12.

$$= \langle \psi_n(x, x_0) | \Delta x_0 \frac{\partial V(x, x_0)}{\partial x_0} | \psi_n(x, x_0) \rangle$$

$$\Delta \psi_n(x, x_0) = \psi_n(x, x_0 + \Delta x) - \psi_n(x, x_0)$$

13.

$$= \sum_{n' \neq n} \psi_{n'}(x, x_0) \frac{\langle \psi_{n'}(x, x_0) | \Delta x_0 \frac{\partial V(x, x_0)}{\partial x_0} | \psi_n(x, x_0) \rangle}{E_n(x_0) - E_{n'}(x_0)} .$$

If we expand the $\psi_n(x, x_0)$ in an orthonormal set $\varphi_n(x)$:

14.

$$\psi_n(x, x_0) = \sum_m c_{nm}(x_0) \varphi_m(x)$$

then

15.

$$\frac{\partial \psi_n(x, x_0)}{\partial x_0} = \sum_m \frac{d c_{nm}(x_0)}{dx_0} \varphi_m(x) .$$

Using 14. and 15., we can write the differential forms of 12. and 13., taking the limit $\Delta x_0 \to 0$,

16. $$\frac{dE_n(x_0)}{dx_0} = \langle \psi_n(x, x_0)| \frac{\partial V(x, x_0)}{\partial x_0} | \psi_n(x, x_0) \rangle$$

and

17. $$\frac{dc_{nm}(x_0)}{dx_0} = \sum_{n' \neq n} c_{n'm}(x_0) \frac{\langle \psi_{n'}(x, x_0)| \frac{\partial V(x, x_0)}{\partial x_0} | \psi_n(x, x_0)\rangle}{E_n(x_0) - E_{n'}(x_0)} .$$

Or, using only the $\varphi_n(x)$ basis and the $c_{nm}(x_0)$ functions:

18. $$\frac{dE_n(x_0)}{dx_0} = \sum_{\ell} \sum_{m} c^*_{n\ell}(x_0) V_{\ell m}(x_0) \; c_{nm}(x_0)$$

and

19. $$\frac{dc_{nm}(x_0)}{dx_0} = \sum_{n' \neq n} c_{n'm}(x_0) \frac{\sum_{k} \sum_{\ell} c^*_{n'k}(x_0) V_{k\ell}(x_0) c_{n\ell}(x_0)}{E_n(x_0) - E_{n'}(x_0)}$$

where

20. $$V_{ij}(x_0) = \langle \varphi_i(x)| \frac{\partial V(x, x_0)}{\partial x_0} | \varphi_j(y)\rangle .$$

If we had chosen the basis $\varphi_n(x)$ to be $\psi_n^0(x)$, the initial conditions on 18. and 19. would be:

21.
$$E_n(0) = E_n^0$$
$$c_{nm}(0) = \delta_{nm}$$

so that $\psi_n(x, 0) = \psi_n^0(x)$. This is seen from expansion 14.. The first-order (refering to the derivative, not an approximation) system 18. and 19., together with initial conditions 21., enable us to integrate from $x_0 = 0$ to $x_0 = L$. At $x_0 = L$, the expansion 14. gives us the wavefunctions $\psi_n(x, L)$, which are the desired solutions of $V(x, L) = V(x)$. The energies $E_n(L)$ are the eigenvalues E_n of 5.. Thus, we have completed the setting up of a first-order system equivalent to the second-order Schrödinger equation.

Before seriously investigating the utility of this method, one should try to integrate system 18. and 19. for a simple problem to determine if the highly non-linear and coupled nature of the system leads to numerical difficulties. We have done the following: The known solutions $\varphi_n(x) = \psi_n^0(x)$ were taken to be the eigenfunctions of an infinite square well with ends at 0 and π:

22. $$\psi_n^0(x) = (2/\pi)^{1/2} \sin(n+1)x$$

23. $$E_n^0 = (n+1)^2/2$$

for $n = 0, 1, 2, \cdots$.

We desired to calculate the solutions to a harmonic well centered at $\pi/2$:

24. $$V(x) = \frac{25}{2}(x - \pi/2)^2 .$$

Of course the solutions and energies are known:

25. $$\psi_n(x) = \frac{1}{(2^n n! \sqrt{\pi})^{1/2}} H_n(\sqrt{5}(x - \tfrac{\pi}{2})) e^{-\frac{5(x-\pi/2)^2}{2}}$$

26. $$E_n = 5(n + 1/2)$$

$$n = 0, 1, 2, \cdots .$$

For the parameterized potential we used:

27. $$V(x, x_0) = V_{SQ} + \frac{25}{2}(x - \frac{\pi}{2})^2 H(x_0 - x)$$

where $H(x_0 - x)$ is the unit Heaviside step function and V_{SQ} represents the infinite square well potential. From 27., using the definition of the delta function,

28. $$\frac{\partial V(x, x_0)}{\partial x_0} = \frac{25}{2}(x_0 - \frac{\pi}{2})^2 \delta(x_0 - x) .$$

Substituting this into 20. along with 22. gives:

29. $$V_{ij}(x_0) = \frac{25}{\pi} \sin(i+1)\,x_0 \sin(j+1)\,x_0\,(x_0 - \frac{\pi}{2})^2 .$$

We must integrate 18. and 19. to $x_0 = \pi$, for there the basis functions $\varphi_n(x)$ vanish. At this point our solutions should solve the potential:

30. $$V(x, \pi) = V_{SQ} + \frac{25}{2}\,(x - \frac{\pi}{2})^2$$

which is an infinite square well with a parabolic bottom. Using a first-order integrator and a 10 state expansion in the $\varphi_n(x)$ basis, we obtained the following eigenvalues:

TABLE 1

n	Infinite Square Well	Calculated	Pure Harmonic Oscillator
0	0.5	2.55	2.5
1	3.0	7.87	7.5
2	4.5	13.48	12.5
3	8.0	19.32	17.5
4	12.5	25.22	22.5
5	18.0	31.16	27.5
6	24.5	37.39	32.5
7	32.0	44.30	38.5
8	40.5	54.49	43.5
9	50.0	62.36	48.5

The ground state is accurate to 2%; a better integrator might improve on this. The system of equations indicated no unstable behavior, a favorable indication that the method is practical to solve in general. A few comments must be made about the results in table 1. As n becomes large, the bound particle sees more of the infinite square walls of V_{SQ}. The parabola in the bottom of V_{SQ} only influences the lower energy states. For n larger than 4 the spacing of the calculated eigenvalues is roughly that of the square well.

We propose that this novel method of solving bound state problems be further investigated, especially on higher dimensional problems (via state expansions), and compared to the variational method in speed and accuracy.

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