I. QUANTUM MECHANICS OF ONE-DIMENSIONAL TWO-PARTICLE MODELS

II. A QUANTUM MECHANICAL TREATMENT OF INELASTIC COLLISIONS

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ABSTRACT

Part I

Solutions of Schrödinger's equation for systems of two particles bound in various stationary one-dimensional potential wells and repelling each other with a Coulomb force are obtained by the method of finite differences. The general properties of such systems are worked out in detail for the case of two electrons in an infinite square well. For small well widths (1-10 a. u.) the energy levels lie above those of the noninteracting particle model by as much as a factor of 4, although excitation energies are only half again as great. The analytical form of the solutions is obtained and it is shown that every eigenstate is doubly degenerate due to the "pathological" nature of the one-dimensional Coulomb potential. This degeneracy is verified numerically by the finite-difference method. The properties of the square-well system are compared with those of the free-electron and hard-sphere models; perturbation and variational treatments are also carried out using the hard-sphere Hamiltonian as a zeroth-order approximation. The lowest several finite-difference eigenvalues converge from below with decreasing mesh size to energies below those of the "best" linear variational function consisting of hard-sphere eigenfunctions. The finite-difference solutions in general yield expectation values and matrix elements as accurate as those obtained using the "best" variational function.

The system of two electrons in a parabolic well is also treated by finite differences. In this system it is possible to separate the center-of-mass motion and hence to effect a considerable numerical simplification. It is shown that the pathological one-dimensional Coulomb potential gives rise to doubly degenerate eigenstates for the parabolic well in exactly the same manner as for the infinite square well.

Part II

A general method of treating inelastic collisions quantum mechanically is developed and applied to several one-dimensional models. The formalism is first developed for nonreactive "vibrational" excitations of a bound system by an incident free particle. It is then extended to treat simple exchange reactions of the form A + BC → AB + C. The method consists essentially of finding a set of linearly independent solutions of the Schrödinger equation such that each solution of the set satisfies a distinct, yet arbitrary boundary condition specified in the asymptotic region. These linearly independent solutions are then combined to form a total scattering wavefunction having the correct asymptotic form. The method of finite differences is used to determine the linearly independent functions.

The theory is applied to the impulsive collision of a free particle with a particle bound in (1) an infinite square well and (2) a parabolic well. Calculated transition probabilities agree well with previously obtained values.

Several models for the exchange reaction involving three identical particles are also treated: (1) infinite-square-well potential surface, in which all three particles interact as hard spheres and each two-particle subsystem (i. e., BC and AB) is bound by an attractive infinite-square-well potential; (2) truncated parabolic potential surface, in which the two-particle subsystems are bound by a harmonic oscillator potential which becomes infinite for interparticle separations greater than a certain value; (3) parabolic (untruncated) surface. Although there are no published values with which to compare our reaction probabilities, several independent checks on internal consistency indicate that the results are reliable.

PREFACE

All of Part I of this work is concerned exclusively with the treatment and properties of one-dimensional (1-D) model systems. Also in Part II we have chosen 1-D models to illustrate the application of a quite general theory. Because of their mathematical tractability, 1-D analogues of real physical systems have long been studied with the hope of gaining insight into the real systems. Indeed, there has been published recently a book entitled "Mathematical Physics in One Dimension"*, in which are collected reprints of one-dimensional model studies.

On one hand, we must question the value of investigating models which indubitably suffer from a lack of three-dimensional effects. On the other hand, we may in particular cases adduce much evidence, perhaps empirical, that a one-dimensional model faithfully reflects the properties of interest in the real physical system under scrutiny. Whatever the case may be, it is clear that the study of one-dimensional models indirectly makes a significant contribution to our understanding of real systems. First, the appealing feature of 1-D models, i. e., their susceptibility to rigorous mathematical analysis, makes us wary of simplistic theories contrived merely to circumvent mathematical complexities inherent in the three-dimensional problem. Second, specific results of the 1-D treatment may suggest interpretations of confounding 3-D results or modifications in the theory which lead to a more satisfactory "picture". In this respect the study of one-dimensional models serves to sharpen our concept of reality.

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* "Mathematical Physics in One Dimension", ed. E. Lieb and D. Mattis (Academic Press, Inc., New York, 1966).

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I. QUANTUM MECHANICS OF ONE-DIMENSIONAL TWO-PARTICLE MODELS

A. Introduction

A classic example of a valuable one-dimensional (1-D) model is the simple free-electron model (FEM), in which the electrons move independently in a 1-D infinite square well. In spite of the relative success of this model, e. g., in its application to pi-electron spectra of conjugated molecules, a first obvious "improvement" is the inclusion of the 1-D Coulomb interaction among the electrons. The solution of our model gives wavefunctions, energies, and other properties for the two-electron case of this improved FEM and furthermore demonstrates how "physics" may get distorted in one-dimension.

In this part we solve, by the method of finite differences (FD), the Schrödinger wave equation for systems of two particles bound in various types of one-dimensional potentials and interacting with each other via a 1-D Coulomb potential $|x_1 - x_2|^{-1}$. For the case of two electrons in an infinite square well,[1] which we shall treat in detail, the energy levels lie higher than those of the noninteracting-particle model (FEM) by as much as a factor of 4; excitation energies are 50 to 70% greater. Most important, however, every eigenstate is doubly degenerate. This is a non-group-theoretically required degeneracy and is due to the "pathological" nature of the 1-D Coulomb potential which requires that the wavefunction vanish when the coordinates of the electrons are equal.

A central problem in the quantum theory of many-electron systems is to find approximate wavefunctions which accurately predict the properties of the system. Traditionally, one uses the variational principle to determine the "best" trial function of a given form. Often, however, this "best" trial function does not successfully predict other properties of the system more important to the chemist than total energy. To discover directly why this function fails it is necessary to examine the exact solution. For example, to study the effects of electron correlation in two-electron atoms, Kestner and Sinanoglu[2] and Tredgold and Evans[3] independently investigated the "exactly" soluble 3-D model consisting of two electrons bound in a parabolic well, but repelling each other with a Coulomb force. Although the model is not exactly soluble in the sense that the wavefunction may be written in closed form, the presence in the Hamiltonian of the attractive (nuclear-electron) parabolic terms allowed them to separate the Schrödinger equation in the center-of-mass coordinate system. As we shall see, the one-dimensional problem may be treated similarly. In fact, the solution of the 1-D relative equation is identical to the 3-D relative solution multiplied by the interelectron coordinate r_{12}. It is clear, however, that the FD method has the advantage of enabling one to study the effects of a wide variety of attractive (nuclear-electron) potentials on electron correlation, since it does not rely on the presence of a separable potential in the Hamiltonian.

A great deal of study has been given to the problem of electronic interaction in the FEM. Several authors have investigated the effect of including explicit interelectronic interaction (Coulomb) terms in the model Hamiltonian. Araki and

Araki[4] used a 2-D average over the 3-D Coulomb potential in a 1-D treatment of the cyanine dyes. In a similar manner, Huzinaga[5] re-examined the Platt model for the naphthalene molecule, including electron repulsion terms as 1-D averages over the 3-D potentials. Also, Ham and Ruedenberg[6] modified the free-electron network model by introducing the electron interaction terms as 2-D averages over the cross-section of the bond path. Finally, Olszewski[7] attempted a configuration interaction treatment of linear conjugated molecules using antisymmetrized 1-D free-electron molecular orbitals (ASFEMO).[8] The solution of our model suggests several alternative methods of treating linear conjugated molceules which do not involve taking averages over arbitrary cross sections or limits of 3-D expressions.

Bolton and Scoins,[9] concerned primarily with the solution of eigenvalue problems by the finite-difference method, have reviewed attempts to solve various two-variable Schrödinger equations. Although not particularly interested in electron correlation, they obtained for the "S-limit"[10] of the ground state of the helium atom a value of -2.65 a.u. (best value -2.879).[10, 11]

In the remaining sections of Part I we have two main purposes: first to obtain accurate energies, wavefunctions, and selected properties for the model system (IFEM) discussed above and then to consider the relevance of our results to more complicated and interesting systems. In Section II the IFEM is treated quantitatively. The analytical properties of the wavefunctions, including the "accidental" double degeneracies, in part 1; the FD method, uniqueness and convergence properties of FD eigenfunctions, eigenvalues, and matrix elements in part 2.

We also discuss numerical verification of the degeneracies in part 2. In part 3 the FD results are compared with approximate solutions obtained by the perturbation and variational methods. In Section C we apply the FD method to the problem of two electrons in a parabolic well, discussing how the accidental degeneracies arise analogously to those of the IFEM. Finally, in Section D we discuss the results and how they apply to more complicated one-dimensional models and also indicate how the FD method may be used to solve differential equations arising in the treatment of more "chemically" interesting three-dimensional problems such as the He atom.

B. Mathematical Treatment of the IFEM

1. General Considerations

The time-independent Schrödinger equation for the one-dimensional system of two electrons in an infinite square well is written in atomic units (a. u.) in the coordinate system $[x_1', x_2']$[12]

$$H'\psi(x_1', x_2') = E\psi(x_1', x_2') \ , \tag{1a}$$

$$H' = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1'^2} + \frac{\partial^2}{\partial x_2'^2}\right) + \frac{1}{|x_1' - x_2'|} , \tag{1b}$$

where $0 \leq x_1', x_2' \leq a$ and x_1' and x_2' denote the electron coordinates; a is the well width. Since the wavefunction must vanish outside the well, the boundary conditions on ψ in $[x_1', x_2']$ are:

$$\begin{aligned} \psi(x_1', 0) &\equiv 0 \\ \psi(x_1', a) &\equiv 0 \\ \psi(0, x_2') &\equiv 0 \\ \psi(a, x_2') &\equiv 0 \quad . \end{aligned} \tag{2}$$

These conditions require that $\psi(x_1', x_2')$ vanish on the boundary of a square of edge a (see Fig. Ia). The Schrödinger equation (1a) is invariant under transformation to the system $[x_1, x_2]$, defined by

$$\begin{aligned} x_1 &= x_1' - a/2 \\ x_2 &= x_2' - a/2 \, . \end{aligned}$$

However, the boundary conditions in $[x_1, x_2]$ are:

$$\begin{aligned} \varphi(x_1, - a/2) &\equiv 0 \\ \varphi(x_1, a/2) &\equiv 0 \\ \varphi(- a/2, x_2) &\equiv 0 \\ \varphi(a/2, x_2) &\equiv 0 \, . \end{aligned} \tag{3}$$

In the center-of-mass coordinate system $[X_1, X_2]$, where

$$X_1 = \frac{x_1 + x_2}{2}$$

$$X_2 = x_1 - x_2 ,$$

the Schrödinger equation becomes

$$-\frac{1}{4}\frac{\partial^2\Psi}{\partial X_1^2} - \frac{\partial^2\Psi}{\partial X_2^2} + \frac{\Psi}{|X_2|} = E\Psi , \tag{4}$$

with the corresponding boundary conditions

$$\begin{aligned} \Psi(X_1, \ 2X_1 + a) &= 0 \\ \Psi(X_1, \ 2X_1 - a) &= 0 \\ \Psi(X_1, \ -2X_1 - a) &= 0 \\ \Psi(X_1, \ -2X_1 + a) &= 0 \ . \end{aligned} \tag{5}$$

These conditions specify that the wavefunction vanish on the boundary of a rhombus, the edges of which are not coincident with coordinate surfaces in $[X_1, X_2]$ (see Fig. Ib).

In each of the coordinate systems there is a group of operators $\mathbb{E}$, $\mathbb{i}$, $\mathbb{R}_1$, $\mathbb{R}_2$ defining coordinate transformations which leave the Hamiltonian invariant. It is simplest to define these operators in $[x_1, x_2]$, although we shall express them later in the other systems. Thus $\mathbb{E}$ is the identity which takes the point (x_1, x_2) into itself, $\mathbb{i}$ is the inversion about (0, 0) taking (x_1, x_2) into $(-x_1, -x_2)$, $\mathbb{R}_1$ is the reflection about the diagonal $x_2 = x_1$ which transforms (x_1, x_2) into (x_2, x_1) and $\mathbb{R}_2$ is the reflection about the other diagonal which carries (x_1, x_2) into $(-x_2, -x_1)$. This group is isomorphic with the Vierergruppe,[13] in which all the elements are mutually commuting. Thus the group of the Schrödinger equation is Abelian and has only one-dimensional irreducible representations (i. r.). These are listed in Table I. Furthermore, since the exact eigenfunctions of the Hamiltonian must transform according to these i. r.'s, we conclude that all the eigenstates of our system are nondegenerate, i. e., there is no group-theoretically-required degeneracy.

Now consider the solution of the Schrödinger equation in the system $[X_1, X_2]$ by the method of separation of variables. To study the form of the components of the required solution, we substitute $\Psi(X_1, X_2) = \phi(X_1)\chi(X_2)$ into Eq. (4). A sum of such components will, of course, have to be used to satisfy the boundary conditions, Eq. (5). We obtain

$$\frac{1}{4}\frac{d^2\phi}{dX_1^2} + E_\phi \phi = 0 \tag{6a}$$

and

$$-\frac{d^2\chi}{dX_2^2} + \frac{\chi}{|X_2|} - E_\chi \chi = 0\,, \tag{6b}$$

where $E = E_\phi + E_\chi$. The general solution of Eq. (6a) may be written

$$\phi(X_1) = A_1 \cos k_\phi X_1 + A_2 \sin k_\phi X_1 \ , \tag{7}$$

where $k_\phi{}^2 = 4E_\phi$ and A_1 and A_2 are arbitrary constants.

In the region $X_2 > 0$, Eq. (6b) may be transformed into Kummer's equation

$$z \frac{d^2v}{dz^2} + (2 - z)\frac{dv}{dz} - (1 - \frac{1}{2k_\chi})v = 0 \ , \tag{8}$$

by the substitutions $\chi = X_2 e^{k_\chi X_2} v(z)$, $z = -2k_\chi X_2$, where $k_\chi{}^2 = -E_\chi$.[14] Since b in the general form of Kummer's equation is an integer in this case, namely 2, the two independent solutions are, in the notation of Slater[14]

$$v_1 = {}_1F_1(a,b;z) = \sum_{m=0}^{\infty} \frac{(a)_m}{(b)_m} \frac{z^m}{m!} \ ,$$

$$v_2 = \sum_{r=0}^{n-1} \frac{(a-n)_r}{(1-n)_r} \frac{z^{r-n}}{r!} + \sum_{r=0}^{\infty} \frac{(a-n)_{n+r}}{(1-n)_{n-1}(1)_{n+r}} \frac{z^{r-1}}{r!} \times \tag{9}$$

$$\left[\log z + \sum_{s=1}^{n+r-1} \frac{1}{(a+s-n-1)} - \sum_{s=1}^{r} \frac{1}{(s+n-1)} - \sum_{s=1}^{r-1} \frac{1}{s} \right] \ ,$$

where

$$a = 1 - \frac{1}{2k_\chi} ,$$

$$b = n + 1 = 2 ,$$

$$(\xi)_p = \xi(\xi + 1) \cdots\cdot (\xi+p-1) .$$

Thus for $X_2 > 0$ the <u>general</u> solution of the relative equation (6b) is

$$\chi_>(X_2) = X_2 e^{k_\chi X_2} \left\{B_1 v_1(-2k_\chi X_2) + B_2 v_2(-2k_\chi X_2)\right\} . \qquad (10a)$$

Similarly for $X_2 < 0$ the general solution takes the form

$$\chi_<(X_2) = CX_2 e^{-k_\chi X_2} \left\{B_1 v_1(2k_\chi X_2) + B_2 v_2(2k_\chi X_2)\right\} , \qquad (10b)$$

where the B's and C are arbitrary constants. We note that with the substitutions

$$\eta = \frac{1}{2\sqrt{\lambda}}$$

$$\rho = \sqrt{\lambda}\, X_2$$

$\lambda = E_\chi$, Eq. (6b) becomes

$$\frac{d^2\chi}{d\rho^2} + (1 - \frac{2\eta}{\rho})\,\chi = 0\,, \tag{11}$$

the Coulomb wave equation for states of zero angular momentum.[15] The general solution of the relative equation may thus be expressed as a sum of the regular and irregular Coulomb wavefunctions of order zero, F_0 and G_0, respectively

$$\chi = B_1F_0(\eta, \rho) + B_2G_0(\eta, \rho)\,.$$

The solution of the relative equation in the regions $X_2 < 0$ and $X_2 > 0$ is thus reasonably straightforward but, on account of the singularity in the Coulomb potential, it is not clear how the solutions should be joined at $X_2 = 0$. In order to ascertain the appropriate boundary conditions in the case of an infinite potential it is necessary to start with a finite potential V requiring continuity of the wavefunction and its gradient, and then to take the limit as V goes to infinity.[16] To resolve the joining problem at $X_2 = 0$ we consider a related simplified problem in which the "physics" is identical except that the boundary conditions arising from the stationary potential (the infinite square well) pose no difficulty. A suitable system is that of a particle of mass 1/2 which is repelled by a "truncated" Coulomb potential symmetric about the origin, but which is confined in an infinite square well. The Schrödinger equation is

$$-\frac{d^2\psi}{dx^2} + \frac{\psi}{|x| + \epsilon} = E\psi\,, \tag{12}$$

where $-a/2 \le x \le a/2$, a is the well width. We require that $\psi(-a/2) = \psi(+a/2) = 0$. Equation (12) is identical in form with Eq. (6b) and thus the <u>general</u> solution may be expressed

$$\psi = a\, F_0(\eta, \frac{y}{2\eta}) + bG_0(\eta, \frac{y}{2\eta}) , \tag{13}$$

where $y = x + \varepsilon$ for $x > 0$ and $y = -x + \varepsilon$ for $x < 0$. Since the potential $V = 1/(|x| + \varepsilon)$ is even under inversion of the coordinate x, the solutions ψ must be either even or odd under inversion. Hence, for the states of odd parity ψ must vanish at $y = \varepsilon$ and $\varepsilon \pm a/2$,

$$\psi_o(\varepsilon) = a_o\, F_0\,(\eta, \varepsilon/2\eta) + b_o\, G_0(\eta, \varepsilon/2\eta) = 0 \tag{14a}$$

$$\psi_o(\varepsilon + a/2) = a_o\, F_0(\eta, \frac{\varepsilon + a/2}{2\eta}) + b_o\, G_0(\eta, \frac{\varepsilon + a/2}{2\eta}) = 0\,. \tag{14b}$$

On the other hand, for the even states the first derivative must vanish at $y = \varepsilon$. Since $\psi(\varepsilon + a/2) = 0$ for the even states also, we have

$$\psi_e{}'(\varepsilon) = a_e\, F_0{}'(\eta, \varepsilon/2\eta) + b_e\, G_0{}'(\eta, \varepsilon/2\eta) = 0 \tag{15a}$$

$$\psi_e(\varepsilon + a/2) = a_e\, F_0(\eta, \frac{\varepsilon + a/2}{2\eta}) + b_e\, G_0(\eta, \frac{\varepsilon + a/2}{2\eta}) = 0\,. \tag{15b}$$

The eigenvalues $E = 1/4\eta^2$ are found for each ε from the requirement that the determinant of coefficients of the unknowns

a_o, b_o, a_e, b_e in the above equations vanish. We now consider the behavior of the solutions as ϵ becomes arbitrarily small, in the limit restoring the Coulomb potential. For the odd states b_o must be zero in the limit since $F_0(\eta, 0) = 0$ and $G_0(\eta, 0) \neq 0$. Thus, for the odd states

$$\psi_o = a_o F_0(\eta, \frac{x}{2\eta}) \quad x > 0$$

$$\psi_o = -a_o F_0(\eta, \frac{-x}{2\eta}) \quad x < 0 ,$$

where η is chosen such that F_0 vanishes at $y = a/2$ and a_o so that ψ_o is normalized.

For the even states, if Eq. (15a) is to be satisfied, b_e must become very small as ϵ approaches zero since G_0' diverges while F_0' remains finite. In the limit $\epsilon = 0$, we thus obtain for the even states

$$\psi_e = a_e F_0(\eta, \frac{x}{2\eta}) \quad x > 0$$

$$\psi_e = a_e F_0(\eta, \frac{-x}{2\eta}) \quad x < 0 ,$$

where η and a_e are chosen as before.

Apparently, the odd and even states are degenerate in pairs as are the one-dimensional hydrogen-atom eigenstates (except the ground state).[17] Also there is a required node for all states (actually the coalescing of two nodes for even states) at $x = 0$.

This result is equivalent to that obtained by initially eliminating G_0 on the basis of "physical" considerations. We suppose that ψ contains G_0. Then the expectation value of the Hamiltonian is

$$\langle \psi | H | \psi \rangle = \langle \psi | K_{op} | \psi \rangle + \langle \psi | V | \psi \rangle ,$$

where $\langle \psi | V | \psi \rangle$ contains a term

$$\int_{-a/2}^{+a/2} {G_0}^2 \frac{1}{|x|} \, dx .$$

Since G_0 is approximately constant in the neighborhood of the origin, the integrand diverges. We have

$$\int_{-a/2}^{a/2} {G_0}^2 \frac{1}{|x|} \, dx \simeq \lim_{\alpha \to 0} \left\{ \int_{-a/2}^{-\alpha} - \frac{1}{x} \, dx + \int_{\alpha}^{a/2} \frac{1}{x} \, dx \right\}$$

$$= 2 \lim_{\alpha \to 0} \ln \frac{a}{2\alpha} .$$

Hence $\langle \psi | V | \psi \rangle$ diverges logarithmically and since $\langle \psi | K_{op} | \psi \rangle > 0$, we find that the eigenvalue is infinite. Hence we eliminate G_0.

The discontinuity of the first derivative for the even wavefunctions is tolerable since the potential is singular there. The same sort of discontinuity is observed in the solutions of other one-dimensional problems which involve singular potentials, e. g., the particle in the box, hard spheres in a box, and the hydrogen atom.

Applying the results of this simplified problem [Eq. (12)] to the solution of the relative equation (6b), we set B_2, the coefficient of the irregular function v_2 in the general solution, equal to zero, thus obtaining

$$\chi(X_2) = B_1 X_2 e^{k_\chi |X_2|} v_1(-2k_\chi |X_2|) .$$

Finally, we have the complete general solution of the Schrödinger equation in $[X_1, X_2]$

$$\Psi(X_1, X_2) = \mathsf{S}_j (A_{1j}' \cos k_{\phi j} X_1 + A_{2j}' \sin k_{\phi j} X_1) \times \tag{16a}$$

$$[\, |X_2| e^{k_{\chi j} |X_2|} v_1(-2k_{\chi j} |X_2|) \,]$$

for the states symmetric under reflection about the line $X_2 = 0$, i.e., operation $\mathbb{R}_1$ of the symmetry group, and

$$\Psi(X_1, X_2) = \mathsf{S}_j (A_{1j}' \cos k_{\phi j} X_1 + A_{2j}' \sin k_{\phi j} X_1) \times \tag{16b}$$

$$[\, X_2 e^{k_{\chi j} |X_2|} v_1(-2k_{\chi j} |X_2|) \,]$$

for the states antisymmetric under this operation. Here $1/4\, k_{\phi j}^{\;2} - k_{\chi j}^{\;2} = E$, the A_{1j}' and A_{2j}' are arbitrary constants, and the S_j indicates a sum over the discrete spectrum of k and an integral over the continuum. In order to find the allowed eigenvalues and eigenfunctions we must impose the boundary conditions (5) in $[X_1, X_2]$. To simplify the discussion we consider only the totally symmetric eigenfunctions, i. e., those which transform according to the i. r. Γ_1, and therefore set $A_{2j}' = 0$ for all j. Thus, from Eqs. (16a) and (5)

$$\Psi(X_1, -2X_1 + a) = S_j A_{1j}' \cos k_j X_1 \left\{ |-2X_1 + a| e^{\sqrt{1/4\, k_j^2 - E}\, |-2X_1 + a|} \right.$$

$$\left. v_1(-2\sqrt{1/4\, k_j^2 - E}\, |-2X_1 + a|) \right\} = 0 \qquad (17)$$

for all X_1 for $0 \leq X_1 \leq a/2$. To further simplify the discussion we rewrite Eq. (17) as

$$\Psi(X_1, -2X_1 + a) = S_j A_j \phi_j(k_j; X_1) \chi_j(E, k_j; X_1) \, . \qquad (18)$$

The ϕ_j and χ_j may be expanded in power series as

$$\phi_j = \sum_{n=0}^{\infty} a_{jn}(k_j) X_1^{\,n} \qquad (19a)$$

$$\chi_j = \sum_{\ell=0}^{\infty} b_{j\ell}(E, k_j) X_1^{\,\ell} \, . \qquad (19b)$$

Now from Eqs. (18) and (19), we have

$$\Psi(X_1, -2X_1 + a) = \sum_{n=0}^{\infty} \sum_{\ell=0}^{n} S_j A_j a_{j\ell}(k_j) b_{j,\, n-\ell}(E, k_j) X_1^{\,n}. \tag{20}$$

Since the sum must vanish identically in the range $0 \leq X_1 \leq a/2$, the coefficient of each power of X_1 in the right member of Eq. (20) must vanish. We have thus

$$\sum_{\ell=0}^{n} S_j A_j a_{j\ell}(k_j) b_{j,\, n-\ell}(E, k_j) = 0, \quad n = 0, 1, 2, \ldots \tag{21}$$

In fact, since the spectrum of k is continuous, Eq. (21) represents an infinite set of coupled integral equations found to be highly intractable mathematically. Employing a discrete set of k and truncating the expansions in n and j, we obtain a finite set of equations in the unknowns A_j, which has a nontrivial solution only if the determinant of the coefficients of the A_j vanishes. This requirement allows one to determine the approximate eigenvalues E. We have investigated this method, but have encountered difficulties in choosing an appropriate set of k_j's and also in solving a rather unmanageable determinantal equation in E. We shall therefore defer further consideration of this approach until a later date and go on to discuss the more generally applicable and highly tractable finite-difference method.

2. The Finite-Difference Method

In the FD method the approximate solution of the Schrödinger equation (1a) is expressed as a set of numbers ψ_i which are the approximate values of the wavefunction of a finite set of grid (mesh) points in $[x_1', x_2']$. The set of grid points is divided into boundary points, at which the values of ψ_i are known, and interior points, at which the values of ψ_i are to be determined by solving the difference equation analogue of the Schrödinger equation

$$H_i \psi_i = \epsilon \psi_i, \quad i = 1, 2, \ldots M, \tag{22}$$

where H_i is the discretized Hamiltonian, ϵ is the discretized eigenvalue, and M is the number of interior points. A square mesh of size h is conveniently constructed as shown in Fig. IIa, where the boundary points are denoted by circles ○ and the interior points by dots ●. It is not necessary to construct a mesh over the whole square since, as we have shown above, all of the exact eigenfunctions vanish along the diagonal, being either symmetric or antisymmetric with respect to $\mathbb{R}_1$. The explicit form of the difference equation analogue (22) is found at each point of the mesh by expressing the partial derivatives in H in terms of ψ_i at neighboring points. Thus we consider mesh point $i \leq M$ and denote the neighboring points as i_1, i_2, i_3, and i_4 (Fig. IIb). The values ψ_{i_j} at neighboring points may be expanded in a Taylor's series as[18]

$$\psi_{i_1} = \psi_i + \left(\frac{\partial\psi}{\partial x_1'}\right)_i h + \left(\frac{\partial^2\psi}{\partial x_1'^2}\right)_i \frac{h^2}{2!} + \left(\frac{\partial^3\psi}{\partial x_1'^3}\right)_i \frac{h^3}{3!} + \left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_1} \frac{h^4}{4!} + \ldots$$

$$\psi_{i_3} = \psi_i - \left(\frac{\partial\psi}{\partial x_1'}\right)_i h + \left(\frac{\partial^2\psi}{\partial x_1'^2}\right)_i \frac{h^2}{2!} - \left(\frac{\partial^3\psi}{\partial x_1'^3}\right)_i \frac{h^3}{3!} + \left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_3} \frac{h^4}{4!} + \ldots.$$

Adding these equations and rearranging, we obtain

$$\left(\frac{\partial^2\psi}{\partial x_1'^2}\right)_i = \frac{\psi_{i_1} + \psi_{i_3} - 2\psi_i}{h^2} - \frac{h^2}{4!}\left[\left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_1} + \left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_3}\right] + \ldots.$$

A similar expression may be obtained for $(\partial^2\psi/\partial x_2'^2)_i$. For h small enough the bracketed terms may be neglected[19] so that the difference equation analogue becomes

$$\left(-4 - \frac{2h^2}{|x_{1i}' - x_{2i}'|}\right)\psi_i + \sum_{j=1}^{4} \psi_{i_j} = \lambda\psi_i, \quad i = 1, 2, \ldots M, \qquad (23)$$

where $\varepsilon = -\lambda/2h^2$. The set of equations (23) may be expressed more conveniently in matrix form as

$$\underset{\sim}{H}\,\underset{\sim}{\psi} = \lambda\,\underset{\sim}{\psi}, \qquad (24)$$

where $\underset{\sim}{H}$ is a real symmetric (Hermitian) matrix order M, $\underset{\sim}{\psi}$ is a column vector of the ψ_i, and λ is the modified eigenvalue. The structure of $\underset{\sim}{H}$ is, of course, determined by the mesh labeling shown in Fig. IIa. All the diagonal elements are negative and the off-diagonal elements are either 1 or 0. Since $\underset{\sim}{H}$ is Hermitian, its eigenvectors, which are approximations to the exact eigenfunctions, are orthogonal. Furthermore, the matrix $\underset{\sim}{R}_2$ which reflects $\underset{\sim}{\psi}$ across the diagonal $x_2' = -x_1' + a$ commutes with $\underset{\sim}{H}$ so that the FD eigenvectors have the same symmetry required of the exact eigenfunctions. Thus, the eigenvectors $\underset{\sim}{\psi}_{ws}$, formed over the <u>whole</u> square by joining the discretized solutions in the two <u>half</u>-squares such that $\underset{\sim}{\psi}_{ws}$ is of either even or odd parity, must transform according to the i.r.'s of the <u>Vierergruppe.</u>

a. <u>Uniqueness and convergence</u>

A symmetric nxn matrix always has n distinct (i.e., linearly independent) eigenvectors.[20] Furthermore, a Hermitian matrix can be diagonalized by a similarity transformation with a unitary matrix whose columns are the eigenvectors determined up to a phase factor.[21] Hence, we may conclude that for every mesh size h there is a set of distinct eigenvectors determined up to a constant factor, which we set by normalization.

Following the procedure of Bolton and Scoins[9] we consider whether the discretized eigenvalues, eigenfunctions, and matrix elements converge to the exact values in the limit as the mesh size h approaches zero. We assume that there exists a continuous function $\psi_c(x_1', x_2'; h)$ which satisfies the difference equation analogue (23) for all values of h and that $\psi_c(x_1', x_2'; h)$ and $\lambda(h)$, the discretized eigenvalue, may be expanded as follows in the intervals $0 \le x_1', x_2' \le a$, $0 \le h \le h_o$

$$\begin{aligned} \psi_c(x_1', x_2'; h) &= \sum_k \phi_k(x_1', x_2') h^k , \\ \lambda(h) &= h^2 \sum_\ell c_\ell \, h^\ell \ , \end{aligned} \tag{25}$$

or

$$\epsilon(h) = -\frac{1}{2} \sum_\ell c_\ell \, h^\ell ,$$

where the ϕ_k may be expanded in the complete orthonormal set of exact eigenfunctions. If the expansions (25) are substituted into Eq. (23), the value of ψ_c at neighboring grid points expanded in Taylor's series, and the coefficients of equal powers of h equated, one obtains

$$-\frac{1}{2}\left(\frac{\partial^2\phi_o}{\partial x_1'^2} + \frac{\partial^2\phi_o}{\partial x_2'^2}\right) + \frac{\phi_o}{|x_1' - x_2'|} = -\frac{c_o}{2}\ \phi_o \tag{26a}$$

$$-\frac{1}{2}\left(\frac{\partial^2\phi_1}{\partial x_1'^2} + \frac{\partial^2\phi_1}{\partial x_2'^2}\right) + \frac{\phi_1}{|x_1' - x_2'|} = -\frac{1}{2}(c_o\phi_1 + c_1\phi_o) \tag{26b}$$

$$\begin{aligned} -\frac{1}{2}\left(\frac{\partial^2\phi_2}{\partial x_1'^2} + \frac{\partial^2\phi_2}{\partial x_2'^2}\right) - \frac{1}{24}\left(\frac{\partial^4\phi_o}{\partial x_1'^4} + \frac{\partial^4\phi_o}{\partial x_2'^4}\right) + \frac{\phi_2}{|x_1' - x_2'|} &= \\ -\frac{1}{2}(c_o\phi_2 + c_1\phi_1 + c_2\phi_o) . \end{aligned} \tag{26c}$$

Since Eq. (26a) is just the Schrödinger equation, we see that ϕ_o is the exact eigenfunction and $E = -c_o/2$ the exact eigenvalue. Multiplying Eq. (26b) by ϕ_o and integrating over the range $0 \le x_1', x_2' \le a$, we obtain

$$\int_0^a \int_0^a \phi_o H \phi_1 dx_1' dx_2' = E \int_0^a \int_0^a \phi_o \phi_1 dx_1' dx_2' - \frac{c_1}{2} \int_0^a \int_0^a \phi_o^2 dx_1' dx_2' . \tag{27}$$

Since H is Hermitian and the ϕ_k real, the left member of Eq. (27) equals the first term of the right member and

$$-\frac{c_1}{2} \int_0^a \int_0^a \phi_o^2 dx_1' dx_2' = 0 .$$

Hence $c_1 = 0$. Thus from Eq. (26b) $\phi_1 \equiv 0$ or is a multiple of ϕ_o. We set $\phi_1 \equiv 0$, thus obtaining $c_3 = 0$ in a manner similar to that above. If we multiply Eq. (26c) by ϕ_o and integrate as before, we obtain eventually

$$c_2 = \frac{1}{12} \int_0^a \int_0^a \phi_o \left(\frac{\partial^4}{\partial x_1'^4} + \frac{\partial^4}{\partial x_2'^4} \right) \phi_o dx_1' dx_2' .$$

Thus we see that the error in the leading term of the discretized energy $\epsilon(h)$ is of order h^2

$$\epsilon(h) = E + c_2 h^2 + c_4 h^4 + \ldots$$

It can be shown that, under rather general conditions, as h tends to zero, the solutions of the difference equation approach the solution of the differential equation, i. e., the discretization error usually decreases as the mesh size is reduced. A small value of h will minimize the truncation error inherent in Eq. (23) but will increase the size of the matrix to be diagonalized. Although the eigenvalues of fairly large matrices of this type can be obtained quite accurately and economically,[11] it would be advantageous to avoid such large matrices. Since the difference between the eigenvalue at a given mesh size and the exact eigenvalue is a polynomial in h^2, one may use the Richardson extrapolation technique[22]: put a polynomial through the values obtained at various not-too-large mesh sizes and extrapolate to "zero" mesh size. Of course, this extrapolation process may be somewhat dangerous since it is necessary to employ mesh sizes sufficiently small to be certain that the extrapolant lies close to the true eigenvalue. Exactly how small a mesh size is required must be ascertained by investigation of specific cases. As we show below, there are several cogent reasons why our solutions should be reliable, e. g., agreement with variation and perturbation treatments, small differences between FD eigenvectors for mesh sizes differing by a factor of 2, and results obtained for the "S-limit" of the He atom using much smaller mesh sizes and including fourth-difference terms in the discretized Schrödinger equation.

Consider the matrix element of an operator M connecting states k and ℓ. We write

$$\langle k|M|\ell\rangle \simeq \langle\psi_{c_k}(x_1', x_2'; h)|M|\psi_{c_\ell}(x_1', x_2'; h)\rangle =$$

$$\int_o^a\int_o^a \psi_{c_k}(x_1', x_2'; h)M\psi_{c_\ell}(x_1', x_2'; h)dx_1'dx_2' \,. \tag{28a}$$

Substituting the expansion of Eq. (25) for $\psi_c(x_1', x_2'; h)$, we obtain

$$\langle\psi_{c_k}|M|\psi_{c_\ell}\rangle = \langle \sum_r \phi_{\ell_r} h^r|M| \sum_p \phi_{k_p} h^p\rangle$$

$$= \sum_r h^r\Big(\sum_{p=0}^{r} \langle\phi_{\ell_r}|M|\phi_{k,\,r-p}\rangle\Big)$$

$$= \langle\phi_{\ell_o}|M|\phi_{k_o}\rangle + (\langle\phi_{\ell_o}|M|\phi_{k_1}\rangle + \langle\phi_{\ell_1}|M|\phi_{k_o}\rangle)h$$

$$+ (\langle\phi_{\ell_o}|M|\phi_{k_2}\rangle + \langle\phi_{\ell_1}|M|\phi_{\ell_2}\rangle + \langle\phi_{\ell_2}|M|\phi_{k_o}\rangle)h^2$$

$$+ O(h^3)$$

$$= \langle k|M|\ell\rangle + O(h^2) \,. \tag{28b}$$

Hence as h approaches zero, the discretized matrix element approaches the exact value with error of order h^2, since $\phi_{j_1} \equiv 0$ for all j.

b. Method of solution of the finite difference equations

In order for the set of homogeneous equations (23) to have a nontrivial solution, the determinantal equation

$$|\underset{\sim}{H} - \lambda \underset{\sim}{I}| = 0$$

must hold, where $\underset{\sim}{I}$ is the M × M unit matrix. The eigenvalues λ are determined by solving this Mth degree equation. For large mesh sizes ($M \leq 4$), the roots may be found analytically. For $M > 4$ the problem is solved by diagonalization of $\underset{\sim}{H}$ by the Householder method on a computer. Symmetry serves as a useful check on the accuracy of eigenvectors for a given mesh size. Various approximations, $\epsilon_n(h) = -1/2h^2 \cdot \lambda_n(h)$, to a particular eigenvalue E_n are obtained for a series of values of h corresponding to M = 10, 15, 21, 28, 36, 45, 55, 66, and 78. To obtain an accurate estimate of the true eigenvalue E_n for a given state, we extrapolate to zero mesh size using the method of Richardson and Gaunt[22] as discussed above, which depends on the fact that the discretized eigenvalue is expressible as a series in even powers of h.

Matrix elements of operators $M(x_1', x_2')$, e.g., expectation values and transition moments, are approximated for a given mesh size h by

$$\langle i|M|j\rangle \simeq \sum_{k=1}^{M(h)} \psi_{ik} M_k(x_{1k}', x_{2k}')\psi_{jk} , \qquad (29)$$

where i and j denote the eigenstates connected by M, $M_k(x_{1k}', x_{2k}')$ is the FD analogue of the operator M at point k of the mesh; ψ's now have two subscripts, the first indicating the eigenstate and the second the mesh point. ψ_i's are normalized so that $\sum_{k=1}^{M} \psi_{ik}^2 = 1$. Of course, the matrix elements may be evaluated by more accurate numerical quadrature methods.[23] In a few cases examined these methods yielded values very little different from those calculated from the simpler expression (29). We note that if one wishes to compare eigenvectors corresponding to different mesh sizes, it is necessary to normalize the approximate eigenfunction over the half-square $x_1' \geq x_2'$. We do this below.

c. Results

Results of calculations performed for the case of a square well of width 4.00 a.u. are shown in Table II.

The eigenvectors corresponding to the eigenvalues ϵ_1, ϵ_2, etc. are, of course, approximations to the exact eigenfunctions ψ_{1ex}, ψ_{2ex}, etc. in the half-square $x_1' > x_2'$. Since the exact eigenstates are all doubly degenerate, we form the FD approximations over the whole square by joining the reflection of $\underset{\sim}{\psi}$ (or $-\underset{\sim}{\psi}$) in the half-square $x_1' < x_2'$ with $\underset{\sim}{\psi}$ in the half-square $x_1' > x_2'$. Thus we have doubly degenerate eigenstates whose approximate eigenfunctions are either symmetric or antisymmetric with respect to $\mathbb{R}_1$ and transform according to the i.r.'s listed in Table I. The symmetric states are denoted by a superscript + and the antisymmetric states by -. Figure III shows probability amplitude contours (obtained by linear interpolation) for $h = .50$ for the first three symmetric eigenstates of the 4.00 - a. u. well. A three-dimensional plot of the approximate symmetric FD ground-state eigenfunction is shown in Fig. IV. An indication of the relative accuracy of eigenvectors corresponding to different mesh sizes may be obtained by comparing eigenvectors generated from meshes whose sizes differ by a factor of 2, such that each point of the coarser mesh coincides with alternate points of the finer mesh. Such a comparison is made in Table III for the ground- and first excited-state eigenvectors (normalized over the half- square) and shows that the eigenfunction changes very little when the mesh size is halved. This is a commonly used method[24] of estimating the accuracy of a finite-difference solution. Usually if the difference between two solutions with quite different mesh sizes is small, one may feel justified in assuming that the error is small. Our results certainly indicate this.

In $[x_1, x_2]$ the matrix elements of $\vec{x} = x_1\vec{e}_1 + x_2\vec{e}_2$, where $\vec{e}_1$ and $\vec{e}_2$ are unit vectors, may be written

$$\langle i|\vec{x}|j\rangle_{ws} = \langle i|x_1|j\rangle_{ws}\vec{e}_1 + \langle i|x_2|j\rangle_{ws}\vec{e}_2, \tag{30}$$

where the subscript ws denotes that the integral is over the whole square. Each of these integrals may be broken up into two integrals, one over the lower half-square (lhs) where $x_1 > x_2$ and over the upper half-square (uhs). Thus

$$\langle i|x_1|j\rangle_{ws} = \langle i|x_1|j\rangle_{lhs} + \langle i|x_1|j\rangle_{uhs} \cdot \tag{31}$$

Now if both ψ_i and ψ_j are either symmetric or antisymmetric, $\psi_i \cdot \psi_j$ is symmetric about $x_1 = x_2$, whereas if only one is antisymmetric $\psi_i \cdot \psi_j$ is antisymmetric. Further, since x_1 in uhs at (x_2, x_1) is equal to x_2 in lhs at the reflected point (x_1, x_2), we can rewrite Eq. (31) as

$$\langle i | x_1 | j \rangle_{ws} = \langle i | x_1 \pm x_2 | j \rangle_{lhs} = \langle i | \pm x_2 + x_1 | j \rangle_{uhs}, \tag{32}$$

where the + sign holds if both i and j are symmetric or antisymmetric and the - if only one is antisymmetric. From Eq. (32) we deduce

$$\langle i | x_1 | j \rangle_{ws} = \frac{1}{2} \langle i | x_1 \pm x_2 | j \rangle_{ws} \cdot \tag{33}$$

In a similar manner,

$$\langle i | x_2 | j \rangle_{ws} = \frac{1}{2} \langle i | x_2 \pm x_1 | j \rangle_{ws} \tag{34}$$

with the same sign convention. If ψ_i and ψ_j transform according to the same i. r., then $\psi_i \cdot \psi_j$ transforms totally symmetrically (Γ_1). Then, since $(x_1 + x_2)$ transforms as Γ_3, the total integrand transforms as Γ_3. We conclude that $\langle i | x_1 | j \rangle = 0$ in $[x_1, x_2]$ or 2.0 in $[x_1', x_2']$. Table II confirms these group theoretical results. Furthermore, since $x_1^2 + x_2^2$ and $V = 1/|x_1 - x_2|$ both transform according to Γ_1, their expectation values do not vanish in general. However, all matrix elements of these operators connecting eigenstates of different symmetry must vanish.

Ground-state energies, extrapolated by Richardson's method from mesh sizes corresponding to M = 10, 15, 21, and 28, are plotted as a function of well width in Figure V. In particular we verify that the FD eigenfunctions satisfy the virial theorem approximately. For any system of particles interacting by Coulomb potentials the virial theorem is given by

$$2\langle K_{op}\rangle_{\eta=a} + \langle V\rangle_{\eta=a} = 2E_a - \langle V\rangle_{\eta=a} = -a\left(\frac{\partial E}{\partial \eta}\right)_{\eta=a}, \qquad (34a)$$

where E_a is the total energy, η is a scale factor, in our case the well width, and a is a particular value of η.[25] The quantity $-a(\partial E/\partial\eta)_{\eta=a}$, calculated using values of $(\partial E/\partial\eta)$ obtained by five-point interpolation, is tabulated in Table IV along with $2E_a - \langle V\rangle_{\eta=a}$. The increasing percentage error with well width is due to the fact that extrapolations for larger well widths are approximately as inaccurate as for smaller, yet the virial is decreasing with increasing well width.

d. Numerical verification of degeneracies

When the boundary condition along the diagonal $x_1' = x_2'$ is relaxed and a rectangular mesh with n(n + 1) interior points (arranged n + 1 horizontal by n vertical) constructed over the whole square such that no mesh point lies on the diagonal, near degeneracies occur in pairs, the eigenvector associated with the lesser of the two eigenvalues (see Table V) being symmetric with respect to $\underset{\sim}{R}_1$ and that associated with the greater being antisymmetric. The eigenvalues of the lowest four eigenstates (two lowest nearly degenerate pairs) of the 4.00 -a.u. well are listed in Table V as a function of n along with the Richardson extrapolants. We note that the eigenvalue for the lower state of the 1-2 pair converges less rapidly than the eigenvalue of the higher state, thus indicating that in the limit $n = \infty$ exact degeneracy would occur. We also note that the higher-state eigenvalue of neither pair is greater than the corresponding eigenvalue obtained from the half-square treatment. Probability amplitude contours (normalized over the whole-square) for the lowest nearly degenerate pair are pictured in Fig. VI. The heavy dark lines represent the approximate nodes. Note that the inversion $\mathbf{i}$ is the only operator transforming mesh points in lhs into mesh points in uhs, although the contours indicate that the other required symmetry is present.

3. Comparison of Results with Other Approximate Treatments

In order to compare the accuracy of the approximate eigenvalues and functions found by the FD method and also to assess the effects of inter-electronic interaction on the properties of the system, it is advantageous to consider some other perhaps less accurate approximations.

FEM. As a zeroth-order approximation we neglect the electronic interaction entirely. The Hamiltonian for the model system becomes simply that of two independent particles in an infinite square well, whose eigenvalues and associated eigenfunctions may be written in $[x_1', x_2']$

$$\phi_{FEM}(n, m; x_1', x_2') = \frac{2}{a} (\sin \frac{n\pi x_1'}{a} \sin \frac{m\pi x_2'}{a} \pm \sin \frac{m\pi x_1'}{a} \sin \frac{n\pi x_2'}{a})$$

$$E_{FEM}(n, m) = \frac{\pi^2}{2a^2} (n^2 + m^2) , \tag{35}$$

where the + and - signs hold when $n \neq m$. If one attempts to improve the FEM approximation by using the FEM Hamiltonian as an unperturbed Hamiltonian and including the 1-D Coulomb interaction as a perturbation, one finds that the integrals involved in the first-order corrections to the energies and wavefunctions diverge, since the integrand in $\int \psi_0 {}^* H' \psi_0 d\tau$ behaves as $1/|x_1' - x_2'|$ in the region of $x_1' = x_2'$. This suggests that we do perturbation theory on a system whose wavefunctions are required to vanish on $x_1' = x_2'$, i. e., a system in which a large part of interelectronic interaction has been accounted for. Such a system is that of two point hard spheres (HSM) in an infinite square well.

HSM. The HSM Hamiltonian is identical to the FEM Hamiltonian, except that the hard-sphere condition requires that the wavefunctions vanish on $x_1' = x_2'$, where the potential becomes infinite. Because of the singularity in the potential, every state is at least doubly degenerate (for the reasons discussed above in part 1 of section B). Further degeneracies occur for states $\phi_{HSM}(n, m)$ and $\phi_{HSM}(n', m')$ for which $n^2 + m^2 = n'^2 + m'^2$. These degeneracies are all "accidental" in the sense that they are not group-theoretically required. Thus the energy levels and wavefunctions (normalized over the half square) are:

$$E_{HSM}(n, m) = \frac{\pi^2}{2a^2} (n^2 + m^2) \tag{36a}$$

$$\phi^+_{HSM>}(n,m;x_1', x_2') = \frac{2}{a}(\sin\frac{n\pi x_1'}{a} \sin\frac{m\pi x_2'}{a} - \sin\frac{m\pi x_1'}{a} \sin\frac{n\pi x_2'}{a}),\ x_1' > x_2' \tag{36b}$$

$$\phi^+_{HSM<}(n,m;x_1', x_2') = \frac{-2}{a}(\sin\frac{n\pi x_1'}{a} \sin\frac{m\pi x_2'}{a} - \sin\frac{m\pi x_1'}{a} \sin\frac{n\pi x_2'}{a}),\ x_1' < x_2' \tag{36c}$$

$$\phi^-_{HSM}(n,m;x_1', x_2') = \frac{2}{a}(\sin\frac{n\pi x_1'}{a} \sin\frac{m\pi x_2'}{a} - \sin\frac{m\pi x_1'}{a} \sin\frac{n\pi x_2'}{a}), \tag{36d}$$

all x_1' and x_2', where $n \neq m$. From expressions (36) it is clear that

$$\phi^+_{HSM}(n,m;x_1', x_2') = \phi^+_{HSM}(n, m;x_2', x_1') \text{ and } \phi^-_{HSM}(n, m;x_1', x_2') = -\phi^-_{HSM}(n, m;x_2', x_1').$$

Using the HSM Hamiltonian as an unperturbed Hamiltonian, we calculate corrections to first- and second-order in the energies and to first-order in the wavefunctions for the first two symmetric eigenstates of the 4.00 - a.u. well (see Tables VI and VII). The first- and second-order corrections to the energy are given by the expressions

$$E_{nm}^{(1)} = \langle \phi^{+}_{HSM}(n, m) \left| \frac{1}{|x_1' - x_2'|} \right| \phi^{+}_{HSM}(n, m) \rangle \tag{37a}$$

$$E_{nm}^{(2)} = \sum_{\ell} \sum_{k > \ell} \langle \phi^{+}_{HSM}(n,m) \left| \frac{1}{|x_1'-x_2'|} \right| \phi^{+}_{HSM}(\ell,k) \rangle \langle \phi^{+}_{HSM}(\ell,k) \left| \frac{1}{|x_1'-x_2'|} \right|$$

$$\phi^{+}_{HSM}(n, m) \rangle \times \frac{1}{(E_{HSM}(n, m) - E_{HSM}(\ell, k))} . \tag{37b}$$

Although these integrals may be evaluated analytically (see Appendix), for the purposes of the present calculation they were done numerically by a Simpson's rule routine on a computer. The numerical and analytical results for selected integrals agree closely, as demonstrated by the small errors in integrals which vanish by group theory (see Table VII). The energies corrected to second-order in Table VI were calculated including the first ten terms of the sum (37b); matrix elements were evaluated from the first-order wavefunctions given by

$$\psi_{nm} = \phi^{+}_{HSM}(n, m) + \sum_{\ell=1}^{N-1} \sum_{k>\ell}^{N} \frac{1}{(E_{HSM}(n, m) - E_{HSM}(\ell, k))} \cdot$$

$$\langle \phi^{+}_{HSM}(\ell, k) \left| \frac{1}{|x_1'-x_2'|} \right| \phi^{+}_{HSM}(n, m) \rangle \; \phi^{+}_{HSM}(\ell, k) , \tag{38}$$

where N = 5. Properties involving the third eigenstate were not included since this state is of the same symmetry as the ground state.

We note that the double degeneracies due to the singularity in the hard sphere potential are not split since the perturbation operator $1/|x_1' - x_2'|$ does not connect symmetric and antisymmetric states.

The Ritz linear variation treatment employing an expansion in N HSM eigenfunctions is also carried out for the 4.00 - a.u. well. We express the variational function as

$$\phi_v = \sum_{nm} c_{nm} \phi^+_{HSM} (n, m; x_1', x_2') .$$

Since the ϕ^+_{HSM} form a complete orthonormal set, the requirement that $\langle \phi_v | H | \phi_v \rangle$ be stationary for first-order variations in the c_{nm} leads to the equations

$$\sum_{n=1}^{m-1} \sum_{m>n}^{N} c_{nm} \left\{ \langle \phi^+_{HSM}(n, m) | H | \phi^+_{HSM}(k, \ell) \rangle - \epsilon \delta_{nk} \delta_{m\ell} \right\} = 0$$

$$k = 1, 2, \ldots \ell - 1$$

$$\ell > k \; .$$

To find the eigenvalues ϵ, which are approximations to the true eigenvalues, we have diagonalized the H matrix by the Householder method on a computer. This is done for N = 1, 2, and 5 and the results are collected in Tables VI and VII. The energy $\langle \phi_{v1} | H | \phi_{v1} \rangle$ for the variational function

$$\phi_{v1} = x_1'(x_1' - a)x_2'(x_2' - a)(x_1' - x_2')$$

is also included in Table VI for comparison.

In order to compare the wavefunctions calculated by these various approximations, we expand the FD eigenfunctions in the complete orthonormal set of HSM eigenfunctions. The expansion coefficients for the ground state eigenfunction are listed in Table VII along with those of the HSM and the HSM perturbation and variational treatments. All of the wavefunctions are normalized over the half-square in $[x_1', x_2']$. We also compare some average properties predicted by these various approximations in Table VI. All matrix elements and expectation values are calculated for the states symmetric with respect to $\mathbb{R}_1$.

From Table VI we note that no variational function gives an energy less than the ground state FD eigenvalue. Furthermore, the "best" trial function, the 10-term HSM function, yields an energy about .5% above that of the extrapolated FD eigenvalue for the ground state. We conclude that the FD method is converging to the exact eigenvalue from below and gives a very good lower bound to the true eigenvalue. The energies determined by first-order perturbation theory on the HSM are very inaccurate, in general. It is clear that the first-order corrections to the energy are not small and hence we should not be surprised that first-order theory is inaccurate in this instance. However, the second-order corrections lower the energies nearly to those of the variational values, and higher-order corrections appear to be progressively less important. We note further that since the unperturbed energy is proportional to $1/a^2$ and the first-order correction to $1/a$ (see

Appendix), we would expect the accuracy of the first-order treatment to improve for smaller well widths.

Table VII indicates that, for the coefficients that do not vanish by group theory, i. e., c_{12}, c_{14}, c_{23}, c_{25}, and c_{34}, the 10-term HSM variational ground-state function agrees remarkably well with the $M = 78$ ($h = .285$) FD eigenfunction; matrix elements are also in close agreement. The HSM ground-state eigenfunction corrected to first-order by perturbation theory also agrees well with the FD treatment, although matrix elements do not compare as favorably.

C. Two Electrons in a Parabolic Well

The Schrödinger equation governing two electrons in a parabolic well is, in $[x_1, x_2]$

$$\left\{-\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) + \frac{1}{2}\varkappa(x_1^2 + x_2^2) + \frac{1}{|x_1 - x_2|}\right\}\psi = E\psi, \tag{39}$$

where x_1 and x_2 are the electron coordinates with respect to the center of force and $\varkappa$ is the force constant which determines how tightly the electrons are bound. In the center-of-mass system Eq. (39) is separable into the two ordinary differential equations

$$-\frac{1}{4}\frac{d^2\Gamma}{dX_1^2} + \varkappa X_1^2\Gamma = E_\Gamma\Gamma \tag{40a}$$

$$-\frac{d^2\Phi}{dX^2} + \frac{1}{4}\varkappa X_2^2\Phi + \frac{1}{|X_2|}\Phi = E_\Phi\Phi, \tag{40b}$$

where

$$E = E_\Gamma + E_\Phi .$$

We note that the group of the Schrödinger equation (39) is identical to that of Eq. (1a) for the infinite square well and hence we should be tempted to conclude, as before, that there are <u>no</u> degeneracies in the eigenstates of this system. However, comparing Eqs. (6b) and (40b) near $X_2 = 0$, we observe that the behavior of Φ is similar to that of χ and that similar arguments about joining the solutions for regions $X_2 < 0$ and $X_2 > 0$ at $X_2 = 0$ may be made. Hence we again have <u>accidental</u> double degeneracies.

To solve Eqs. (40) we note that $\psi = \Gamma(X_1)\Phi(X_2)$ must vanish rapidly enough for large values of X_1 and X_2 such that ψ is square integrable. Hence the boundary conditions in $[X_1, X_2]$ are

$$\lim_{X_1 \to \infty} \Gamma = 0 \tag{41a}$$

$$\lim_{X_2 \to \infty} \Phi = 0 \tag{41b}$$

such that Γ and Φ are separately square integrable. Eq. (40a) describes the motion of a harmonic oscillator of mass 2 and force constant 2κ, the eigenfunctions and eigenvalues of which are given by

$$\Gamma_n(\xi) = \left(\frac{\sqrt{\beta/\pi}}{2^n n!}\right)^{1/2} H_n(\xi) e^{-\xi^2/2} \tag{42a}$$

$$\xi = \sqrt{\beta}\, X_1$$

$$E_\Gamma(n) = \sqrt{2}\varkappa(n + 1/2)\ , \tag{42b}$$

where $H_n(\xi)$ is a Hermite polynomial.[26] Eq. (40b) cannot be solved by the power series method since it gives rise to an irreducible three-term recursion relation. Hence we use the method of finite differences.

The FD analogue of Eq. (40b) is easily obtained by a procedure similar to that followed in section B2 above. We divide the interval of interest, say $[0, a]$, into $M + 1$ equal subintervals as shown in Fig. VII. The value of $d^2\Phi/dX_2^{\,2}$ at point i is then found by using appropriate Taylor's series expansions about the neighboring points, of which there are only two now. Upon substituting the discretized expressions into Eq. (40b), we obtain

$$[-2 - (\frac{1}{4}\varkappa^2 x_i^{\,2} + \frac{1}{x_i})h^2]\Phi_i + \Phi_{i-1} + \Phi_{i+1} = \lambda\Phi_i\ , \tag{43}$$

$$i = 1, 2, \cdots, M,$$

where $\lambda = -\epsilon_\Phi h^2$, h is the mesh size, and ϵ_Φ is the discretized energy eigenvalue. We note that in Eq. (43) X_2 has been replaced by x_i, where the subscript i denotes the mesh point. In matrix form, Eq. (43) becomes

$$\underset{\sim}{H}\,\underset{\sim}{\Phi} = \lambda\,\underset{\sim}{\Phi}\,, \tag{44}$$

where $\underset{\sim}{H}$ is a M x M real symmetric tridiagonal matrix and $\underset{\sim}{\Phi}$ is the M-component column vector of approximate values of Φ at the mesh points. The eigenvectors and eigenvalues of $\underset{\sim}{H}$ are found by diagonalization by the Householder or Jacobi method. We note that in the FD treatment of Eq. (40b) much finer meshes may be used than in the treatment of Eq. (23). This is, of course, because Eq. (40b) involves only one independent variable whereas Eq. (23) involves two. Hence, for the same number of mesh points M and the same interval for each variable, the mesh size h is inversely proportional to $M + 1$ in Eq. (43) rather than to $1 + \sqrt{M}$ as in Eq. (23). As we shall see below, it is possible to obviate Richardson extrapolation by using fine enough meshes.

Uniqueness and convergence properties of the solutions of Eq. (44) may be proved in analogy to the proofs of section B2.

1. Results

We have solved Eq. (44) for $\varkappa = .320224$ and $a = 10.0$. This value of a is large enough that the value of the wavefunction at a is negligible compared to its maximum value. The eigenvalues as a function of mesh size are given in Table VIII for the first several eigensolutions of Eq. (44). Kestner and Sinanoglu[2] obtained the ground state energy and wavefunction for the three-dimensional problem also using $\varkappa = .320224$. They too separated variables in the center-of-mass system, obtaining equations analogous to Eqs. (40). Their relative wavefunction Φ_{ks} is related to ours by

$$\Phi(X_2) = r_{12}\Phi_{k-s}(r_{12}),$$

where Φ_{k-s} is a solution to their relative equation (6). The corresponding relative eigenvalue E_{k-s} is identical to ours. Solving their relative equation by the Hartree method, they obtained an eigenvalue $E_{k-s} = 1.384168$, which agrees well with the 1.384 which we estimate from Table VIII. Plots of our lowest several relative wavefunctions are shown in Fig. VIII.

D. Discussion

Consideration of two examples has demonstrated that the FD method can yield (1) accurate lower bounds to the true eigenvalues of a system of two particles interacting by a Coulomb potential, and also (2) discretized wavefunctions which give expectation values of accuracy comparable to that obtained using the "best" variational functions. In the solution of single-variable relative ordinary differential equations resulting from a separation of variables it is relatively easy to obtain convergence to 4 or 5 significant figures by using a fine enough mesh (see Table VIII).

The "accidental" double degeneracies found for the IFEM seem to be characteristic of linear one-dimensional systems of particles interacting by the Coulomb potential. For example, we have solved the problem of two electrons bound in a parabolic well and have observed the same double degeneracies arising. By arguments similar to those of section B1 we can show for the general case of an arbitrary binding potential that if the energy is to be finite, the wavefunctions must vanish at least as rapidly as $(x_1 - x_2)$ near $x_1 = x_2$. Hence, the general solutions in the region $X_2 > 0$ and $X_2 < 0$ can be joined to form either symmetric or antisymmetric wavefunctions by satisfying appropriate boundary conditions. An interesting corollary to this result is that for one-dimensional systems of two fermions interacting by Coulomb potentials, $S = 0$ and $S = 1$ states are degenerate, a conclusion in accord with Lieb and Mattis'[27] result: "If $S > S'$, the $E(S) > E(S')$ unless V is pathologic, in which case $E(S) \geq E(S')$," where $E(S)$ is the ground-state energy, S is the spin. The Coulomb potential is an example of a pathologic potential.

The pathological nature of the 1-D Coulomb potential has certainly "distorted" physics, since we know that in three-dimensional systems of two fermions, the $S = 0$ state is of lower energy than the $S = 1$ state. The Coulomb potential is too "strong" in one dimension. Hence, in order to apply our model to real systems, some modifications, or at least conventions, will have to be made. For example, our treatment above of the IFEM suggests at least two ways of handling the pi-electron system of linear conjugated molecules. One way is to expand a trial wavefunction as a linear combination of hard-sphere eigenfunctions and use the Ritz method to find the approximate eigenvalues and functions. This does not get rid of the degeneracies, but at least allows us to calculate the integrals in the Hamiltonian matrix. An alternative method is to assume that the electrons move on parallel lines so that the Coulomb potential $1/|x_{ij}|$ is replaced by $1/\sqrt{d^2 + x_{ij}^2}$, where d is distance between the lines. This modified potential corresponds to a 2-D average over a 3-D Coulomb potential.[28] The latter method has the advantage of no degeneracy, but the disadvantage that d cannot be known a priori.

Although we have been concerned in this part with the treatment of several examples of one-dimensional two-particle models, further work (yet in progress) has demonstrated the general utility of the FD method in the solution of real three-dimensional problems of more direct interest to chemists. As we mentioned above, it has been possible to obtain an accurate value for the "S-limit" of helium-like atoms.[11] Another application is the solution of second-order, inhomogeneous, partial differential equations resulting from the reduction of the N-electron first-order perturbation equation

$$(H_o - \varepsilon)\psi^{(1)} = (\varepsilon^{(1)} - V)\psi_o \qquad (45)$$

to a series of pair equations. Each of these pair equations correspond to a description of the motion of that pair in the field of the remaining electrons and is not coupled to other pair equations. Each pair function is associated with a pair energy and the second order correction to the energy is a sum over the various pair energies. The first order equation is obtained by varying $\tilde{\psi}_1$ in the expression

$$\tilde{\varepsilon}^{(2)} = \langle\tilde{\psi}_1|H_o - \varepsilon|\tilde{\psi}_1\rangle + 2\langle\tilde{\psi}_1|H_1 - \varepsilon^{(1)}|\psi_0\rangle \; . \qquad (46)$$

Hence, we can use Eq. (46) to determine an upper bound for the contribution of each pair energy to the second order correction.

We solve the pair equations by expanding the pair functions in a series of partial waves and then solving the resulting uncoupled partial-wave equations by the FD method. The discretized partial-wave solutions are fit to a convenient analytical expansion and the analytical expansion plugged back into Eq. (46) to obtain an upper bound for the contribution of each partial wave. This procedure has been applied to the He atom with encouraging results: using a mesh size of .25 a.u. we have obtained -0.12386, -0.02554, and-.00323 a.u. for the contributions to the second-order energy of the the $\ell = 0, 1,$ and 2 partial waves, respectively. These are to be compared to the $\ell = 0, 1,$ and 2 contributions of -0.12532, -0.02648, and -0.00389 obtained by Byron and Joachain[29] using a variational expansion of the form

$$\psi_1(\vec{r}_1, \vec{r}_2) = \frac{1}{4\pi} \sum_{\ell, m, n} C_{\ell mn} r_>^m r_<^n e^{-\frac{1}{2}\alpha r_>} e^{-\frac{1}{2}\beta r_<} P_\ell(\cos\theta_{12}) .$$

We are presently extending this method to more complicated atoms.

Acknowledgment. We thank Dr. David Cartwright for supplying the programs necessary to generate the three-dimensional graphs of Fig. IV.

E. Appendix

The first-order correction to the energy of hard-sphere state $\phi^{+}_{HSM}(n, m)$ is given by

$$E^{(1)}_{nm} = I = \int_{0}^{a} dx_1' \int_{0}^{x_1'} dx_2' \, \phi^{+}_{HSM}(n,m;x_1', x_2') \frac{1}{|x_1'-x_2'|} \phi^{+}_{HSM}(n,m;x_1', x_2'), \qquad (A-1)$$

since the integrand is symmetric with respect to R_1 and ϕ^{+}_{HSM} is normalized over the half-square. Making the changes of variables

$$x = \frac{\pi x_1'}{a}$$

$$y = \frac{\pi x_2'}{a} \qquad (A-2a)$$

and

$$\bar{x} = \frac{1}{2}(x + y)$$

$$\bar{y} = (x - y), \qquad (A-2b)$$

we obtain from Eq. (A-1)

$$I = 4 \cdot \frac{2}{a} \cdot \frac{2}{\pi} \int_{0}^{\pi} d\bar{y} \int_{\bar{y}/2}^{\pi/2} d\bar{x} \left\{ \sin \frac{n}{2}(2\bar{x} + \bar{y}) \sin \frac{m}{2}(2\bar{x} - \bar{y}) - \sin \frac{m}{2}(2\bar{x} + \bar{y}) \sin \frac{n}{2}(2\bar{x} - \bar{y}) \right\}^{2} \cdot \frac{1}{\bar{y}} . \qquad (A-3)$$

Hence, we see that $E^{(1)}_{nm}$ is proportional to $1/a$, the reciprocal of the well width. The integrand in Eq. (A-3) is expanded to obtain a sum of three terms, each term consisting of a product of four sines of arguments involving the sum of $\bar{x}$ and $\bar{y}$. These three terms may be further broken down by trigonometric identities into sums of products of sines and cosines. Thus

$$I = \frac{8}{a} \cdot \frac{2}{\pi} \int_{0}^{\pi} d\bar{y} \int_{\bar{y}/2}^{\pi/2} d\bar{x}\,(\bar{I}_1 + \bar{I}_2 + \bar{I}_3), \tag{A-4a}$$

where

$$\begin{aligned}
\bar{I}_1(n,m) = \frac{1}{4} \cdot \frac{1}{\bar{y}} \Big\{ & 1 - \cos n\bar{y} \cos 2n\bar{x} + \sin n\bar{y} \sin 2n\bar{x} \\
& - \cos m\bar{y} \cos 2m\bar{x} - \sin m\bar{y} \sin 2m\bar{x} \\
& + \frac{1}{2} \cos (n-m)\bar{y} \cos 2(n+m)\bar{x} - \frac{1}{2} \sin (n-m)\bar{y} \sin 2(n+m)\bar{x} \\
& + \frac{1}{2} \cos (n+m)\bar{y} \cos 2(n-m)\bar{x} - \frac{1}{2} \sin (n+m)\bar{y} \sin 2(n-m)\bar{x} \Big\}
\end{aligned} \tag{A-4b}$$

$$\begin{aligned}
\bar{I}_2(n,m) = -\frac{1}{2}\frac{1}{\bar{y}} \Big\{ & \cos 2n\bar{x} \cos 2m\bar{x} - \cos m\bar{y} \cos 2n\bar{x} - \cos n\bar{y} \cos 2m\bar{x} \\
& + \cos n\bar{y} \cos m\bar{y} \Big\}
\end{aligned}$$

$$\bar{I}_3(n,m) = \bar{I}_1(m,n) .$$

Carrying out the integrations over $\bar{x}$, we have

$$I = \frac{8}{a} \cdot \frac{1}{2\pi} \int_0^{\pi} d\bar{y} \left\{ \pi \left(\frac{\frac{1}{2} - \frac{1}{2} \cos (n+m)\bar{y}}{\bar{y}} \right) + \pi \left(\frac{\frac{1}{2} - \frac{1}{2} \cos (n-m)\bar{y}}{\bar{y}} \right) \right.$$

$$-1 + \left(\frac{1}{2n} - \frac{1}{4(n+m)} - \frac{1}{4(n-m)} \right) \frac{\sin 2n\bar{y}}{\bar{y}}$$

$$+ \left(\frac{1}{2m} - \frac{1}{4(n+m)} + \frac{1}{4(n-m)} \right) \frac{\sin 2m\bar{y}}{\bar{y}}$$

$$+ \left(\frac{1}{2(n+m)} - \frac{1}{2n} - \frac{1}{2m} \right) \frac{\sin (n+m)\bar{y}}{\bar{y}}$$

$$+ \left(\frac{1}{2(n-m)} - \frac{1}{2n} + \frac{1}{2m} \right) \frac{\sin (n-m)\bar{y}}{\bar{y}}$$

$$\left. + \cos n\bar{y} \cos m\bar{y} \right\} . \qquad \text{(A-5)}$$

The first two terms of Eq. (A-5) may be written in the form

$$\int_0^{\alpha} \frac{\sin^2 x}{x} \, dx = \frac{1}{2} (\ln \gamma + \log \alpha - \mathrm{Ci}(2\alpha)) , \qquad \text{(A-6)}$$

where γ is Euler's constant and Ci is the cosine integral.[30] The last term of Eq. A-5 vanishes since $n \neq m$. Thus we obtain finally

$$
\begin{aligned}
I = \frac{4}{\pi a} \Big\{ & \frac{\pi}{2} [\ln \gamma + \ln \frac{(n+m)\pi}{2} - \mathrm{Ci}\,(n+m)\pi\,] \\
& + \frac{\pi}{2} [\ln \gamma + \ln \frac{(n-m)\pi}{2} - \mathrm{Ci}\,(n-m)\pi] - \pi \\
& + (\frac{1}{2n} - \frac{1}{4(n+m)} - \frac{1}{4(n-m)}) \, \mathrm{Si}\,(2n\pi) \\
& + (\frac{1}{2m} - \frac{1}{4(n+m)} + \frac{1}{4(n-m)}) \, \mathrm{Si}\,(2m\pi) \\
& + (\frac{1}{2(n+m)} - \frac{1}{2n} - \frac{1}{2m}) \, \mathrm{Si}\,(n+m)\pi \\
& + (\frac{1}{2(n-m)} - \frac{1}{2n} + \frac{1}{2m}) \, \mathrm{Si}\,(n-m)\pi \Big\} , \qquad \text{(A-7)}
\end{aligned}
$$

where Si is the sine integral.

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TABLE I.

The Irreducible Representations of the *Vierergruppe*

	E	i	R_1	R_2
Γ_1	1	1	1	1
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1

TABLE II

Properties (in a. u.) as a Function of Mesh Size for a Well Width of 4.00.

Mesh size Property	.666	.571	.500	.444	.400	.363	.333	.300	.287	Extrapolated Values
ϵ_1	2.15726	2.19336	2.21718	2.23369	2.24558	2.25442	2.26118	2.26645	2.27064	2.28_1
ϵ_2	3.44520	3.59209	3.69108	3.76054	3.81102	3.84881	3.87779	3.90049	3.91859	3.96_4
ϵ_3	4.16623	4.34877	4.46940	4.55340	4.61417	4.65953	4.69426	4.72143	4.74307	4.79_7
$\langle 1^+\|x_1'\|1^+\rangle$	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.99_9
$\|\langle 1^+\|x_1'\|2^+\rangle\|$	.359	.362	.363	.364	.364	.364	.364	.364	.364	$.36_4$
$\|\langle 1^+\|x_1'\|3^+\rangle\|$	5.0×10^{-8}	9.0×10^{-8}	1.0×10^{-8}	4.5×10^{-8}	9.5×10^{-8}	15.0×10^{-8}	5.0×10^{-8}	15.0×10^{-8}	41.0×10^{-8}	-
$\langle 2^+\|x_1'\|2^+\rangle$	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.99_9
$\|\langle 2^+\|x_1'\|3^+\rangle\|$	.277	.304	.316	.322	.326	.329	.331	.332	.333	$.33_5$
$\langle 3^+\|x_1'\|3^+\rangle$	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.99_9
$\langle 1^+\|x_1'^2+x_2'^2\|1^+\rangle$	9.859	9.864	9.864	9.863	9.862	9.861	9.860	9.859	9.858	9.86
$\langle 2^+\|x_1'^2+x_2'^2\|2^+\rangle$	9.809	9.844	9.851	9.853	9.852	9.851	9.850	9.849	9.848	9.85
$\langle 3^+\|x_1'^2+x_2'^2\|3^+\rangle$	10.324	10.375	10.391	10.396	10.398	10.399	10.399	10.399	10.399	10.40
$\langle 1^+\|V\|1^+\rangle$	.6846	.6904	.6942	.6969	-	-	-	-	-	$.700_5$
$\langle 2^+\|V\|2^+\rangle$	.8337	.8489	.8593	.8665	-	-	-	-	-	$.876_1$
$\langle 3^+\|V\|3^+\rangle$	.7581	.7810	.7948	.8039	-	-	-	-	-	$.816_1$

TABLE III

Comparison of FD Ground- and First-Excited-State Eigenvectors for the 4.00-a.u. Well

State	Ground state		First excited state	
Mesh Size	.571	.286	.571	.286
Mesh Point				
1	.03821	.03751	.12456	.12663
2	.14178	.14177	.34840	.35116
3	.27866	.27775	.42171	.41246
4	.34600	.34196	.21740	.21612
5	.24750	.24260	0.0	0.0
6	.12818	.13129	.22911	.24444
7	.33380	.33811	.29243	.29746
8	.46116	.46084	0.0	0.0
9	.34602	.34196	- .21740	- .20612
10	.17995	.18162	0.0	0.0
11	.33380	.33810	- .29243	- .29746
12	.27866	.27775	- .42171	- .41246
13	.12818	.13129	- .22911	- .24444
14	.14178	.14177	- .34840	- .35116
15	.03821	.03751	- .12456	- .12663

TABLE IV

Verification of Virial Theorem for the IFEM

Well Width a	$(2E_a - \langle V \rangle_{\eta=a})$	$-a(\partial E/\partial \eta)_{\eta=a}$	% Error[b]
3.00	6.42	6.72	4.5
4.00	3.82	3.56	7.3
5.00	2.55	2.90	12.1

[b] Based on $a(\partial E/\partial \eta)_{\eta=a}$. See Eq. (34a).

TABLE V

Eigenvalues of the Lowest 4 Eigenstates for the 4.00-a.u. Well Obtained by the FD Treatment Over the Whole Square

Eigenstate	1	2	3	4
n				
6	2.03624	2.21361	3.37296	3.65420
7	2.06110	2.23207	3.44395	3.73663
8	2.08029	2.24502	3.49775	3.79488
9	2.09554	2.25446	3.53989	3.83759
10	2.10795	2.26154	3.57379	3.86983
11	2.11824	2.26699	3.60162	3.89476
Extrapolated	2.18	2.28	3.76	3.96

TABLE VI

Comparison of FD Results with Other Approximations for the 4.0-a.u. Well

Approximation	Eigen-state	Eigen-value	Matrix Element $\langle i\|x_1'\|1\rangle$	Matrix Element $\langle i\|x_1'\|2\rangle$	Matrix Element $\langle i\|x_1'\|3\rangle$	Expec-tation Value of $x_1'^2+x_2'^2$
Finite Difference (FD)	1	2.281	1.999	.364	$4. \times 10^{-7\dagger}$	9.86
(extrapolated to h=0)	2	3.964		1.999	.335	9.85
	3	4.798			1.999	10.40
Free-Electron Model	1	.61684	2.000	0.00	0.0	8.90
(FEM)	2	1.5421		2.000	0.0	10.16
	3	2.4674			2.00	10.26
Hard-Sphere Model	1	1.5421	2.000	.389	$3. \times 10^{-5\dagger}$	9.65
(HSM)	2	3.0842		2.000	.397	9.77
	3	4.0095			2.000	9.81
HSM Perturbation	1	2.291	2.043	.368	-	10.08
Treatment	2	4.036		2.034	-	10.01
	3	-			-	-
HSM Variational Treatment a) 1 function (n=1, m=2)	1	2.353	2.000	-	-	9.65
b) 2 functions (n=1, m=2;	1	2.353[a]	-	-	-	-
n=1, m=3)	2	4.097	-	-	-	-
c) 10 functions	1	2.298	2.000	.364	$3. \times 10^{-4\dagger}$	9.85
(n=1, m=2,... 5; n=2, m=3,... 5;	2	4.040	-	2.000	.336	9.84_9
n=3, m=4, 5; n=4, m=5)	3	4.887	-	-	2.000	10.40
Variational Function $x_1'(x_1'-a)x_2'(x_2'-a)(x_1'-x_2')$	1	2.382	-	-	-	-

[a] These values are identical with energies corrected to first-order.

† These elements vanish by group theory.

TABLE VII

Coefficients of Hard-Sphere Eigenfunctions in Expansions of Various Approximate Ground State Wavefunctions for the 4.00-a.u. Well

Approximation	Coefficients					
	C_{12}	$C_{13}^{\dagger}$	C_{14}	$C_{15}^{\dagger}$	C_{23}	$C_{24}^{\dagger}$
Finite Difference (M = 78)	.991	2.06×10^{-6}	3.67×10^{-2}	1.04×10^{-6}	- .124	7.70×10^{-7}
HSM	1.000	0.0	0.0	0.0	0.0	0.0
HSM Perturbation treatment	1.000	-1.49×10^{-5}	3.57×10^{-2}	-7.61×10^{-6}	- .135	-5.87×10^{-7}
HSM Variational treatment (10 functions)	.991	-1.44×10^{-5}	3.48×10^{-2}	-6.97×10^{-6}	- .123	1.41×10^{-6}

Approximation	C_{25}	C_{34}	$C_{35}^{\dagger}$	C_{45}
Finite Difference (M=78)	7.24×10^{-3}	-2.62×10^{-2}	2.86×10^{-8}	-1.01×10^{-2}
HSM	0.0	0.0	0.0	0.0
HSM Perturbation treatment	1.00×10^{-2}	-3.72×10^{-2}	1.74×10^{-6}	-1.56×10^{-2}
HSM Variational treatment (10 functions)	7.32×10^{-3}	-2.64×10^{-2}	1.91×10^{-6}	-1.05×10^{-2}

† These coefficients should vanish by group theory.

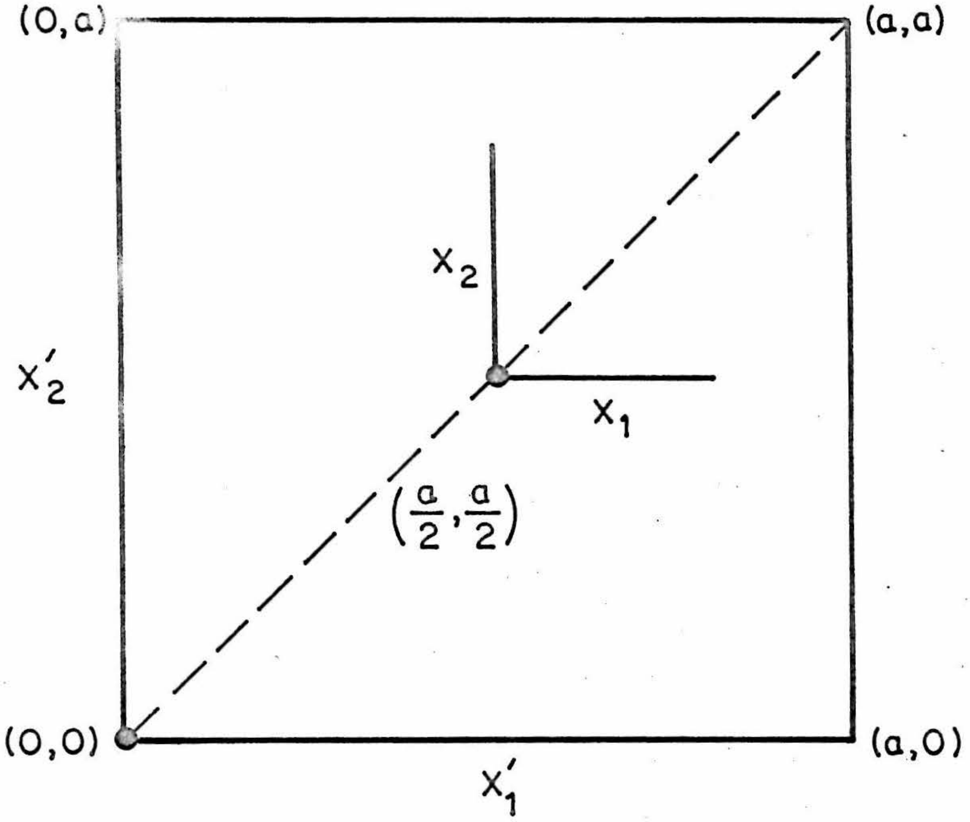
TABLE VIII

Eigenvalues as a Function of Mesh Size for the First Three Eigenstates of the Relative Eq. (40b) for Two Electrons in a Parabolic Well ($\varkappa = .320224$, $a = 10.0$)

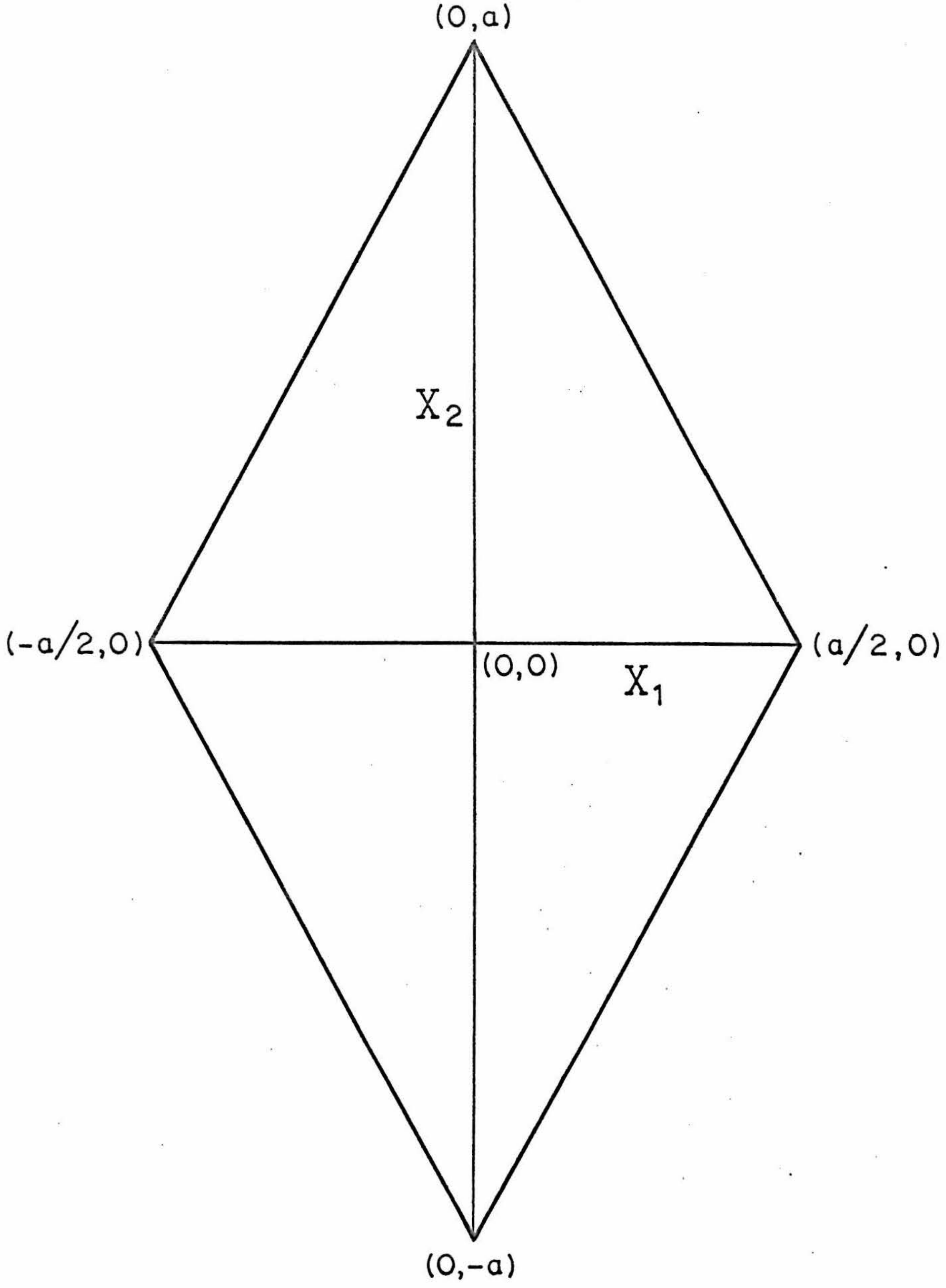
Eigenstate	1	2	3
Mesh size			
1.250	1.34210	2.24398	2.94878
.500	1.37784	2.42160	3.46717
.333	1.38135	2.43785	3.50787
.250	1.38258	2.44347	3.52185
.200	1.38314	2.44606	3.52828
.167	1.38344	2.44746	3.53175

Figure I

Boundary conditions on the wavefunctions in various coordinate systems. (a) Coordinate systems $[x_1', x_2']$ and $[x_1, x_2]$, in which the wavefunctions vanish on the edges of a square. (b) Center-of-mass coordinate system $[X_1, X_2]$, in which wavefunctions vanish on the edges of a rhombus.



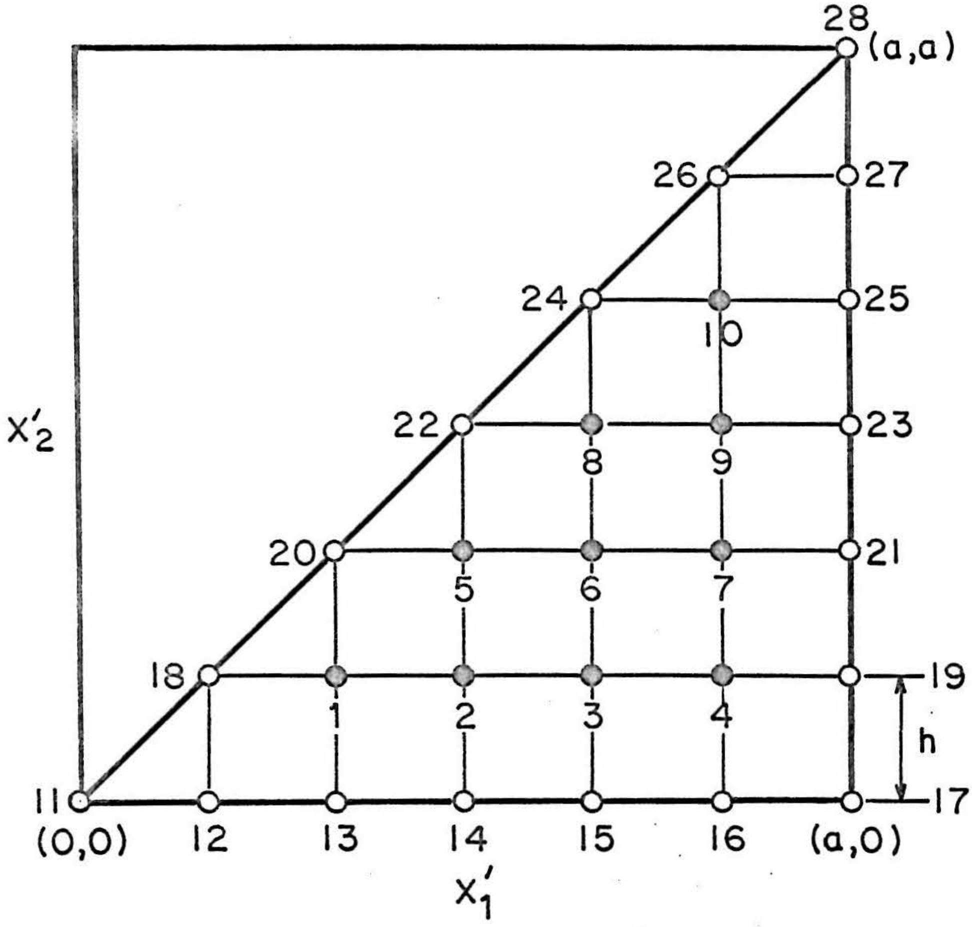
(a)



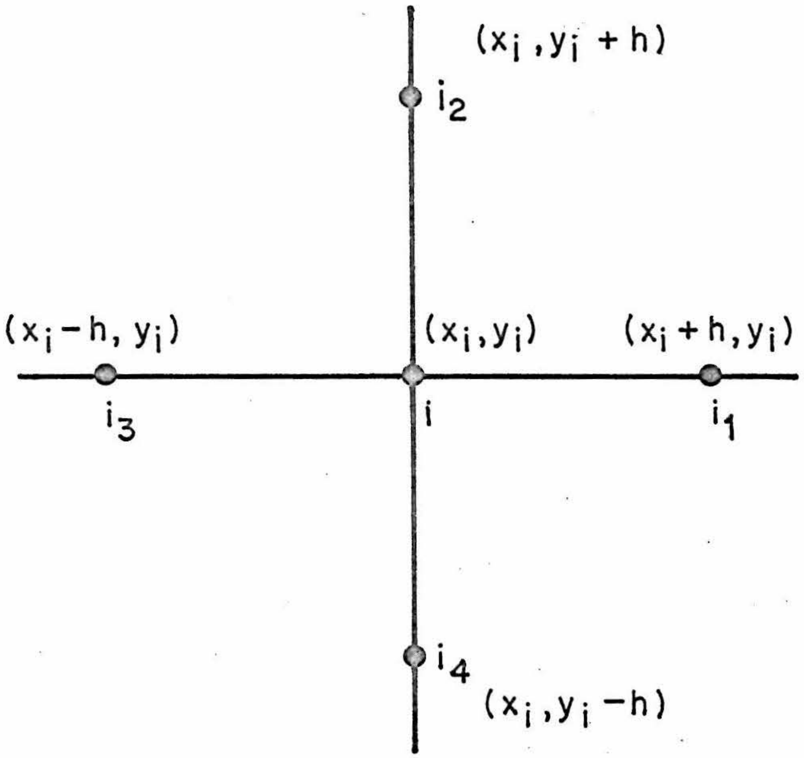
(b)

Figure II

Finite-difference mesh. (a) Square mesh of size $h = a/6$ (a is well width). (b) Enlargement of mesh of size h around point i.


28
(a,a)
26
27
24
25
10
22
23
8
9
X'_2
20
21
5
6
7
18
19
1
2
3
4
h
11
17
(0,0)
12
13
14
15
16
(a,0)
X'_1

(a)

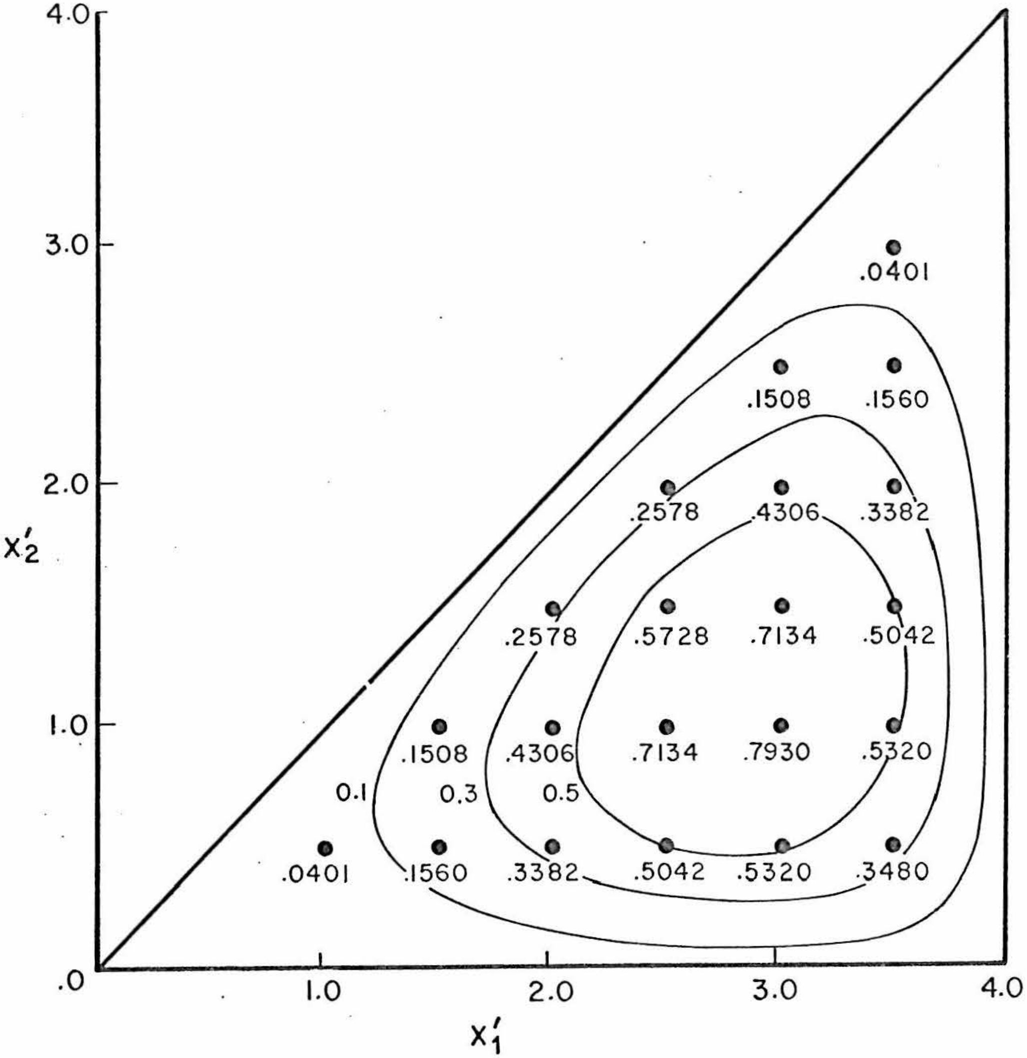


(b)

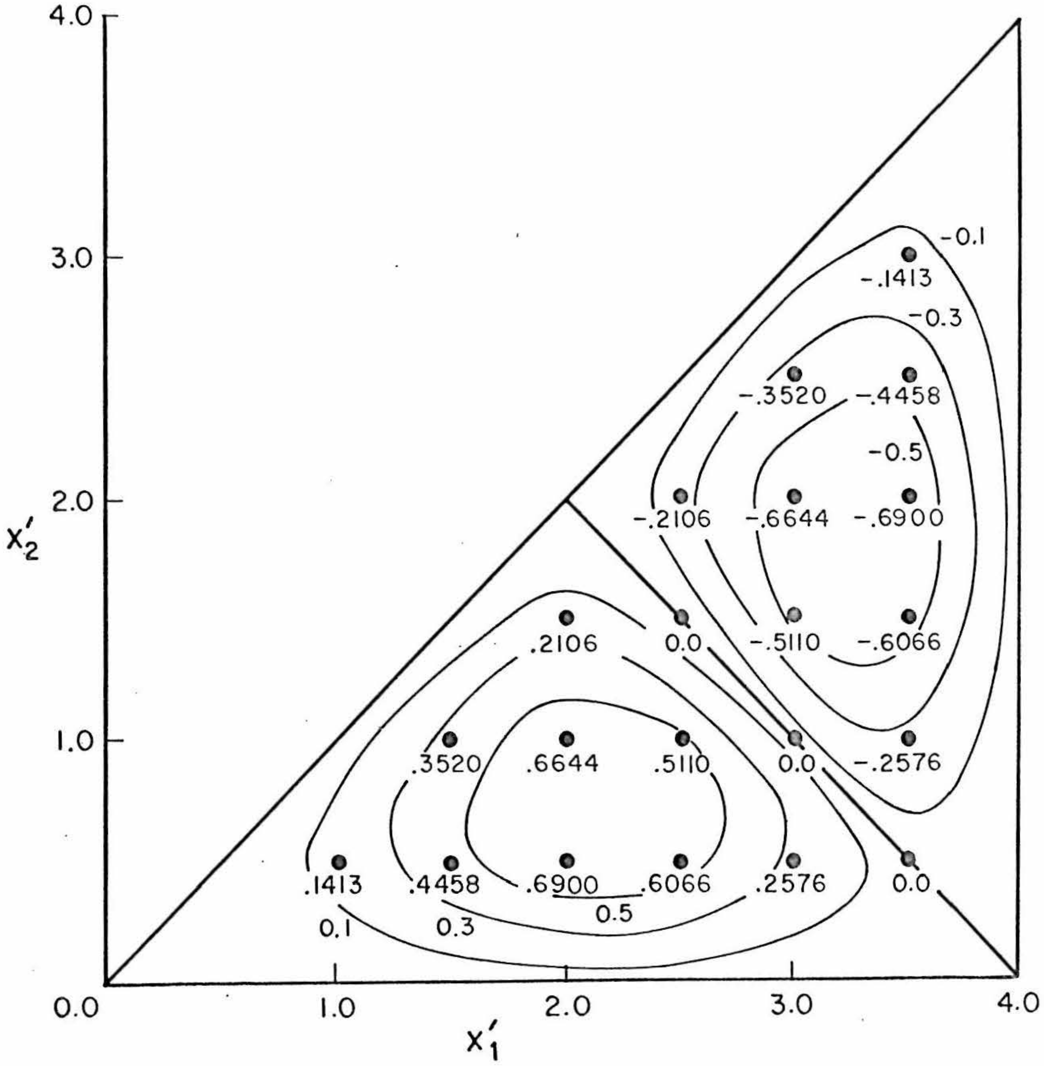
Figure III

Probability amplitude contours (normalized over the half-square) for the three lowest symmetric eigenstates of the 4.00-a.u. well determined by the FD method over the half-square. (a) Ground state $\psi_1^+(\Gamma_1)$. (b) First excited state $\psi_2^+(\Gamma_3)$. (c) Second excited state $\psi_3^+(\Gamma_1)$.

(a)

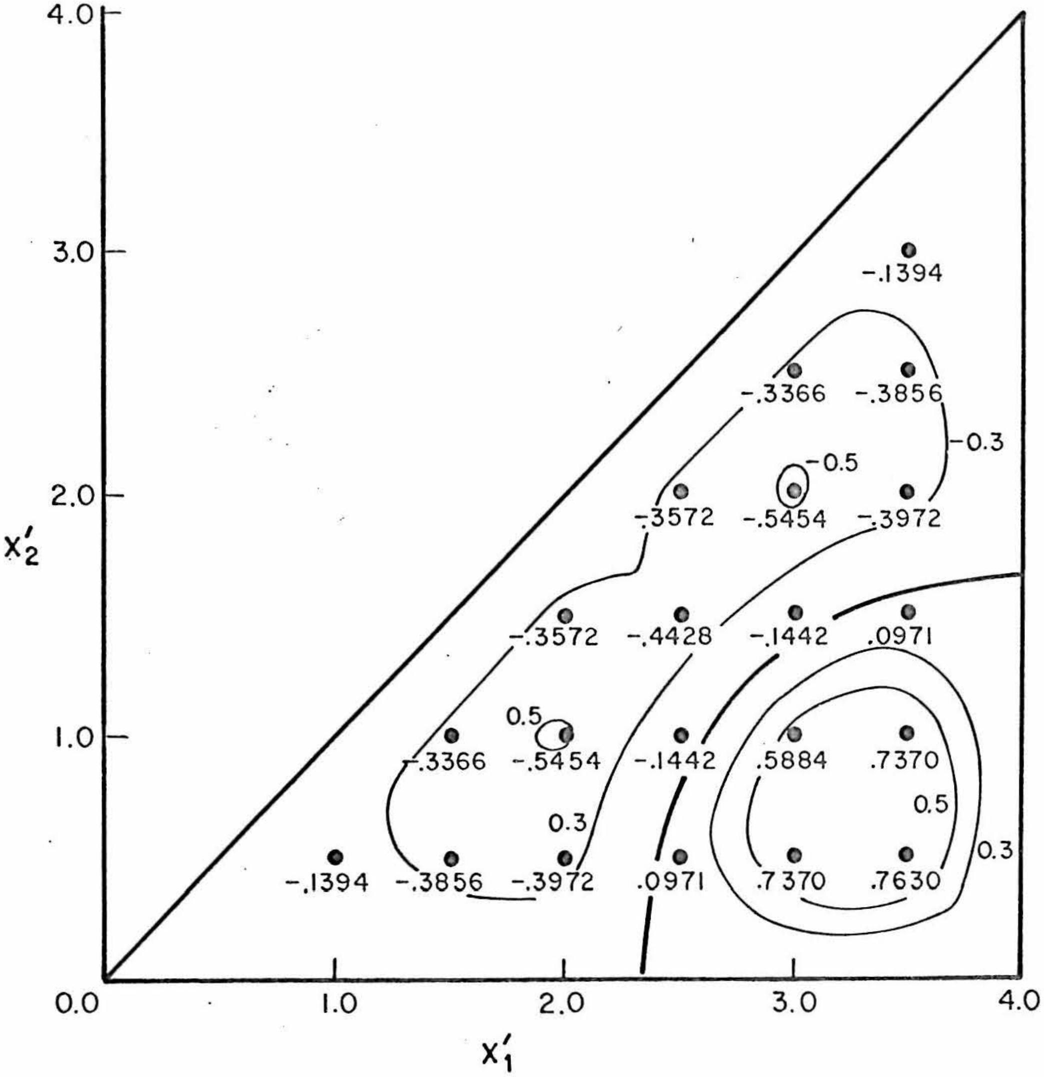

4.0
3.0
2.0
1.0
.0
1.0
2.0
3.0
4.0
x'_2
x'_1
.0401
.1508
.1560
.2578
.4306
.3382
.2578
.5728
.7134
.5042
.1508
.4306
.7134
.7930
.5320
0.1
0.3
0.5
.0401
.1560
.3382
.5042
.5320
.3480

(b)



4.0
3.0
2.0
1.0
0.0
1.0
2.0
3.0
4.0
x'_2
x'_1
-0.1
-.1413
-0.3
-.3520
-.4458
-0.5
-.2106
-.6644
-.6900
0.0
-.5110
-.6066
.2106
.3520
.6644
.5110
0.0
-.2576
.1413
.4458
.6900
.6066
.2576
0.0
0.5
0.1
0.3

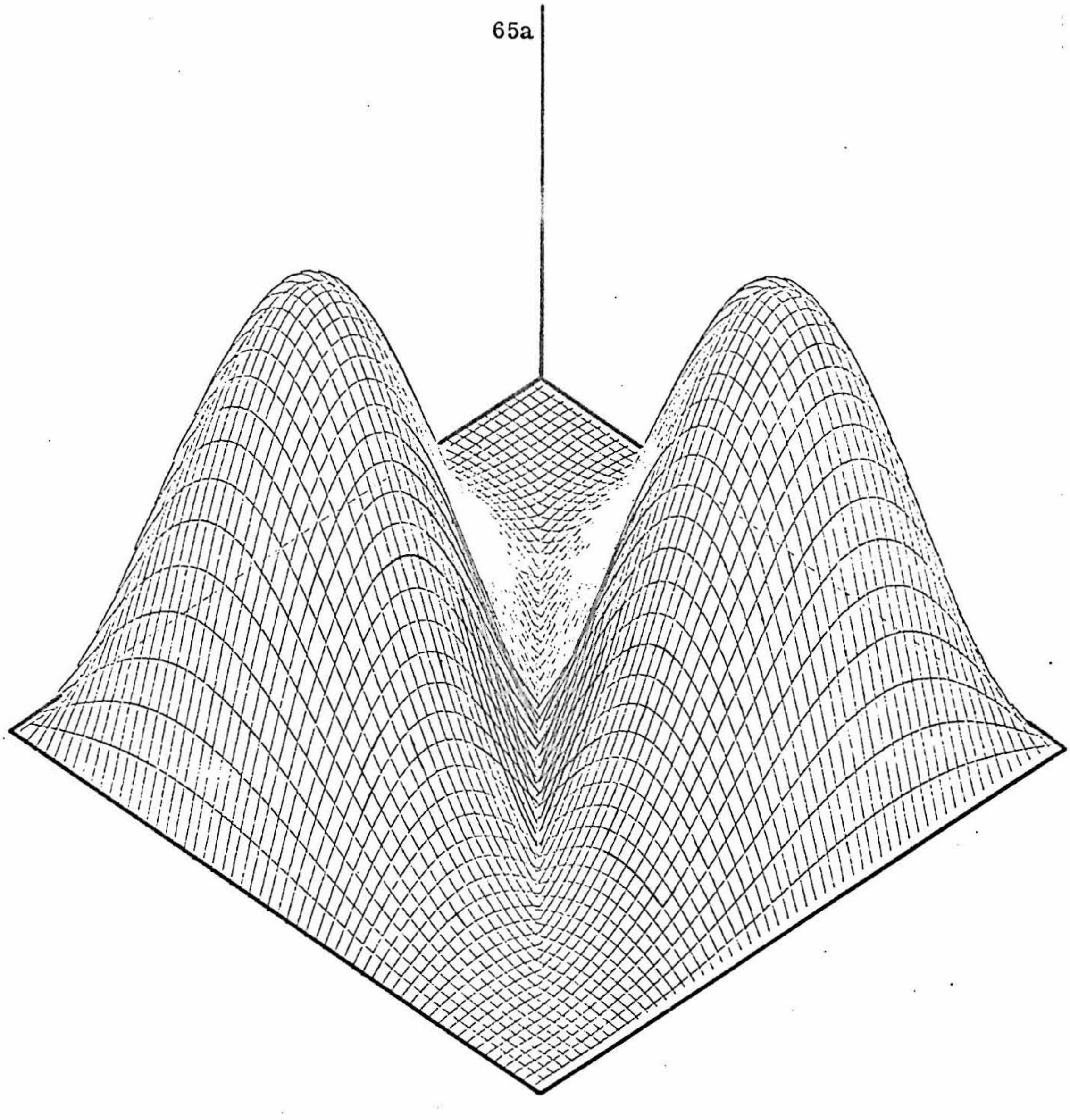
(c)



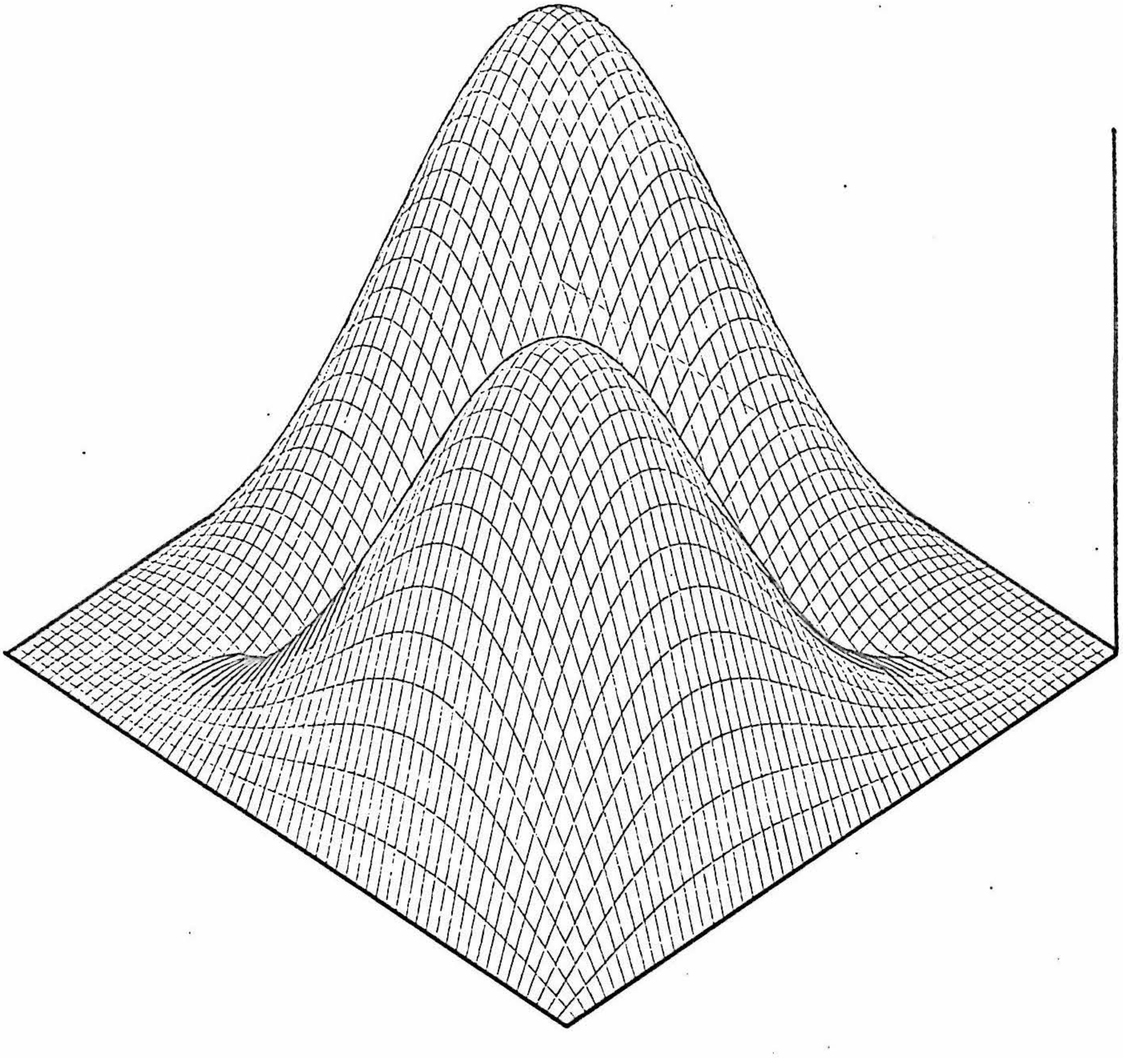
4.0
3.0
2.0
1.0
0.0
1.0
2.0
3.0
4.0
X'_2
X'_1
-.1394
-.3366
-.3856
-0.3
-0.5
-.3572
-.5454
-.3972
-.3572
-.4428
-.1442
.0971
0.5
-.3366
-.5454
-.1442
.5884
.7370
0.5
0.3
0.3
-.1394
-.3856
-.3972
.0971
.7370
.7630

Figure IV

Three-dimensional plots of symmetric FD ground state eigenvector for the 4.00-a.u. well (interpolated from M = 78).



(a)



(b)

Figure V

Ground-state eigenvalue as a function of well width for two electrons with (a) no interaction (FEM) (b) one-dimensional Coulomb potential (IFEM).

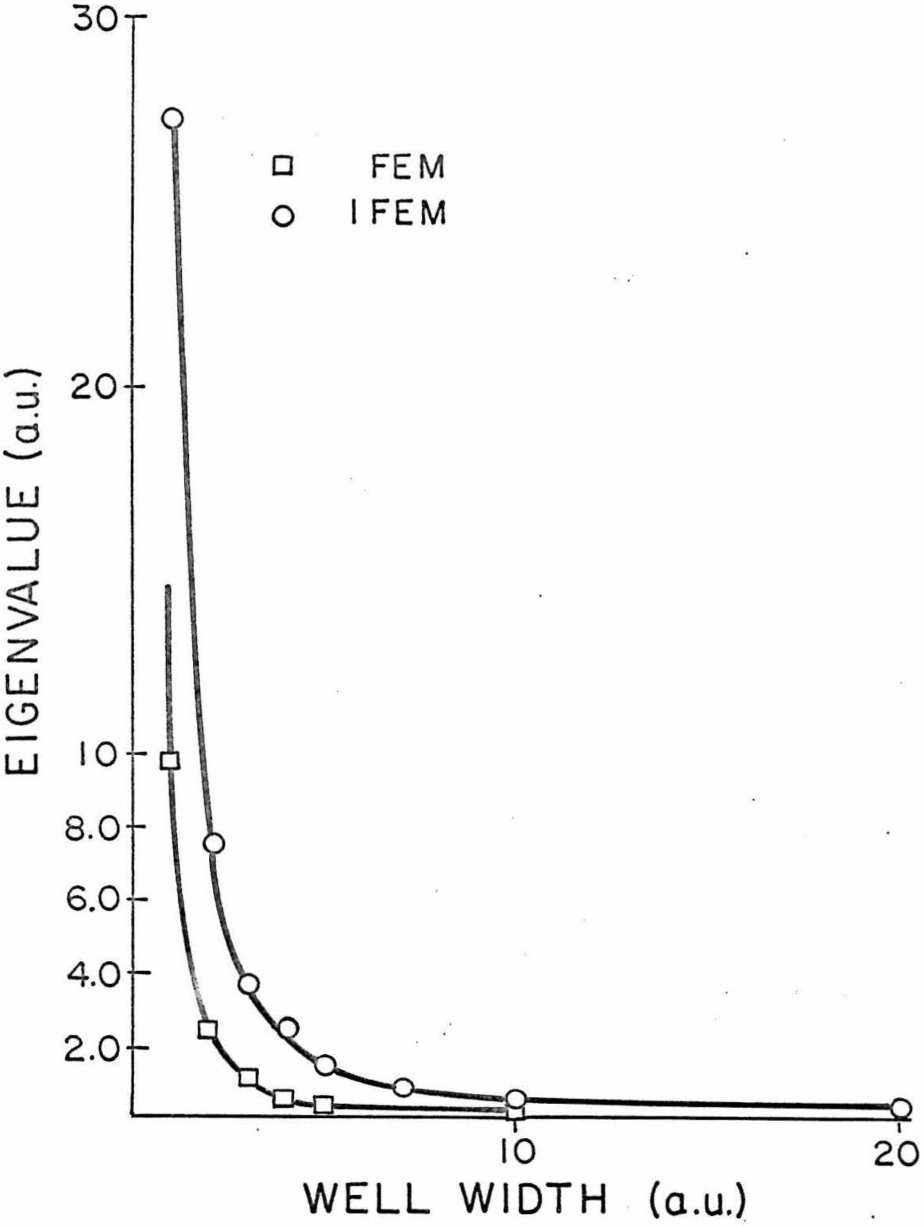
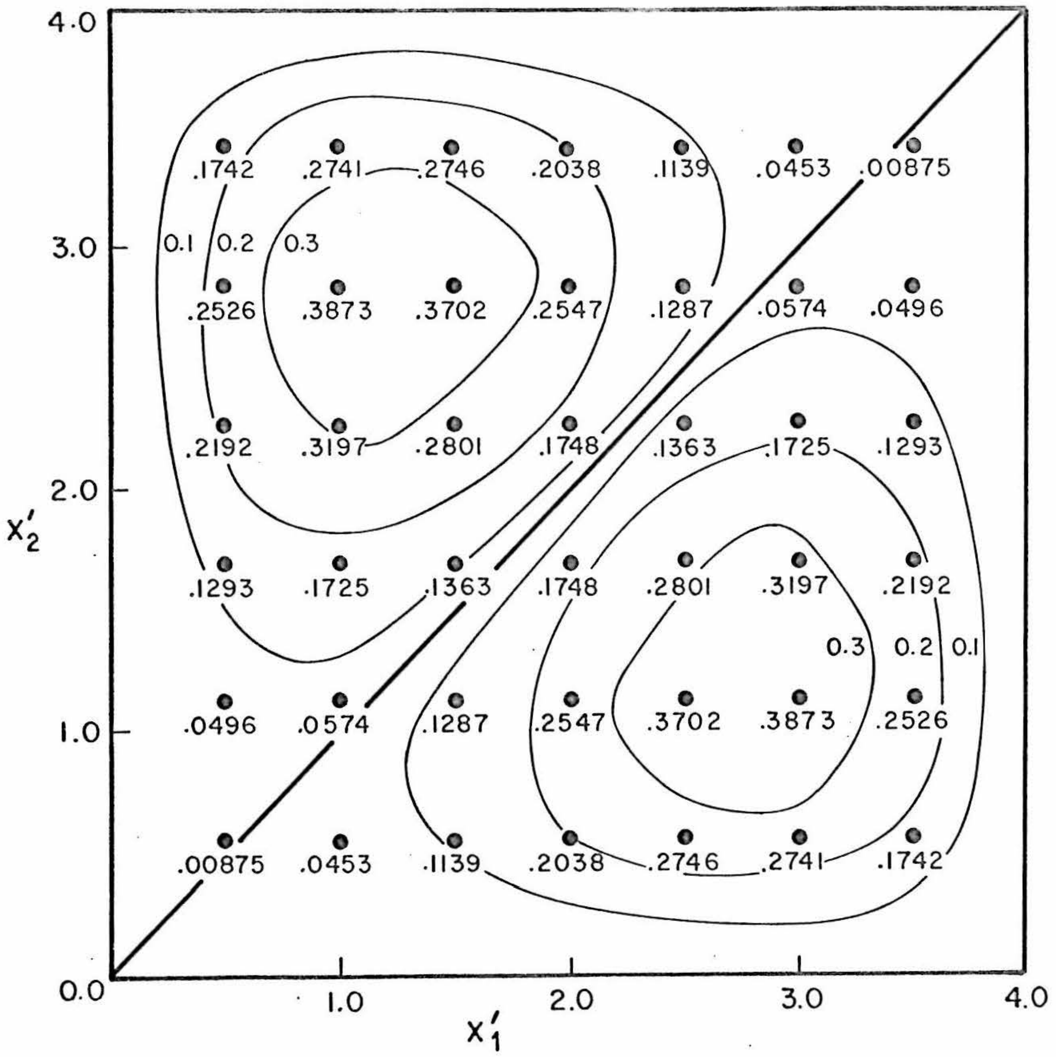

30
20
10
8.0
6.0
4.0
2.0
EIGENVALUE (a.u.)
□ FEM
○ IFEM
10
20
WELL WIDTH (a.u.)

Figure VI

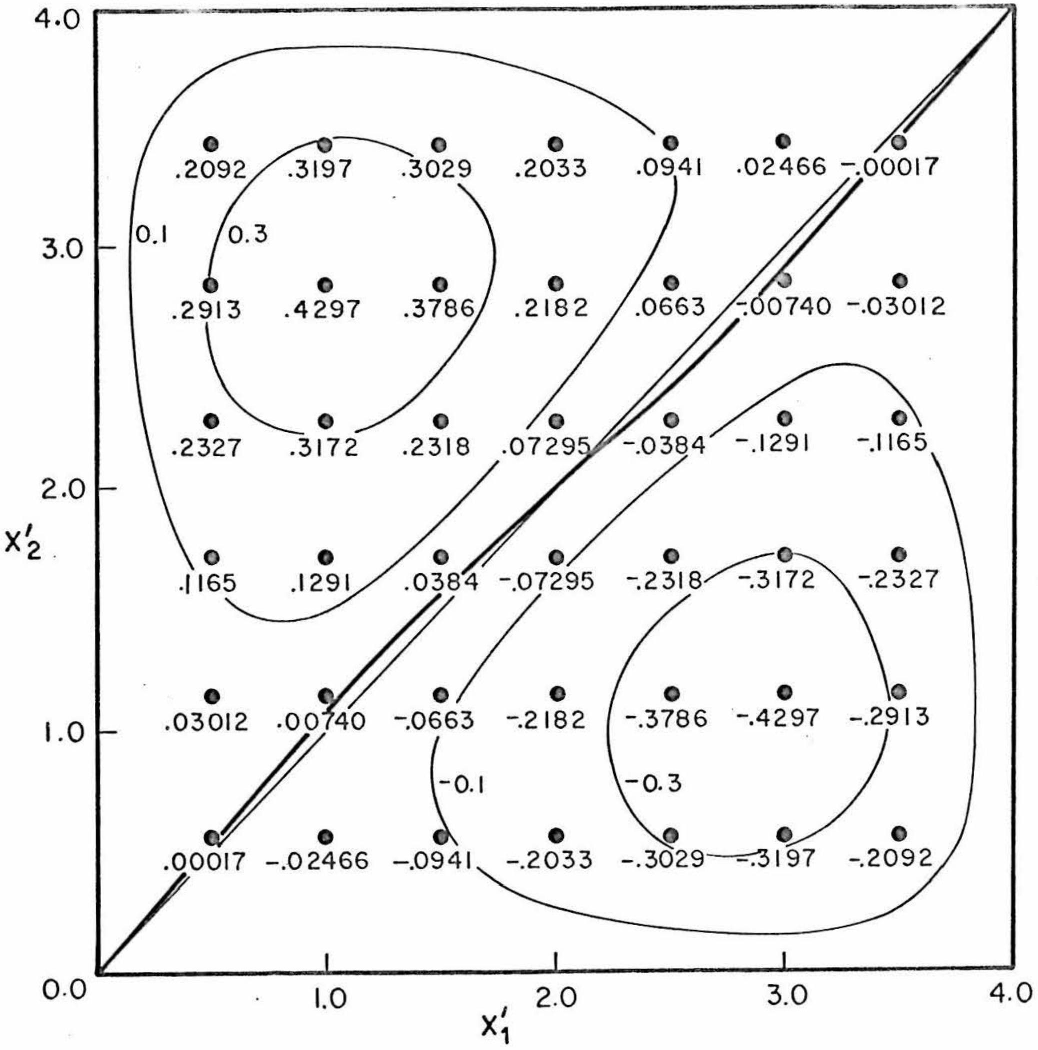
Probability amplitude contours (normalized over the whole square) for the lowest pair of nearly degenerate states of the 4.00-a.u. well. (a) Ground state (symmetric). (b) First excited state (antisymmetric).

(a)



4.0
3.0
2.0
1.0
0.0
1.0
2.0
3.0
4.0
X'_2
X'_1
0.1
0.2
0.3
0.3
0.2
0.1
.1742
.2741
.2746
.2038
.1139
.0453
.00875
.2526
.3873
.3702
.2547
.1287
.0574
.0496
.2192
.3197
.2801
.1748
.1363
.1725
.1293
.1293
.1725
.1363
.1748
.2801
.3197
.2192
.0496
.0574
.1287
.2547
.3702
.3873
.2526
.00875
.0453
.1139
.2038
.2746
.2741
.1742

(b)



4.0
3.0
2.0
1.0
0.0
1.0
2.0
3.0
4.0
X'_2
X'_1
0.1
0.3
-0.1
-0.3
.2092
.3197
.3029
.2033
.0941
.02466
-.00017
.2913
.4297
.3786
.2182
.0663
-.00740
-.03012
.2327
.3172
.2318
.07295
-.0384
-.1291
-.1165
.1165
.1291
.0384
-.07295
-.2318
-.3172
-.2327
.03012
.00740
-.0663
-.2182
-.3786
-.4297
-.2913
.00017
-.02466
-.0941
-.2033
-.3029
-.3197
-.2092

Figure VII

Illustration of finite-difference mesh (M = 19) used in the treatment of the relative equation (40b) for two electrons in a parabolic well.

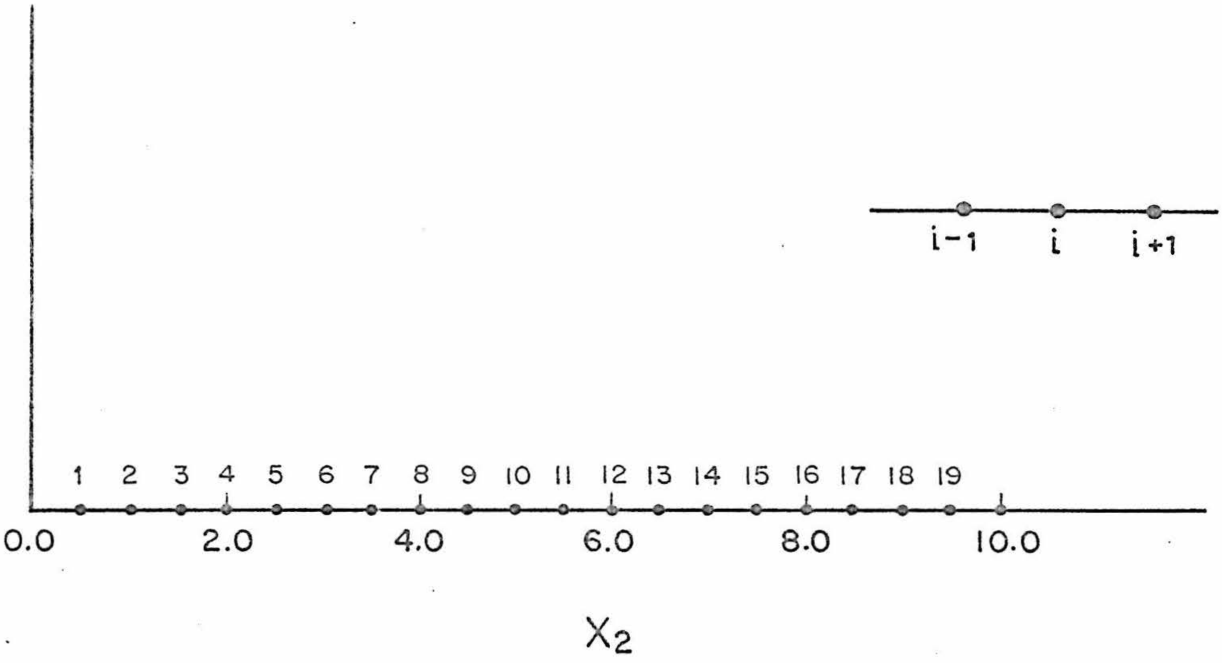
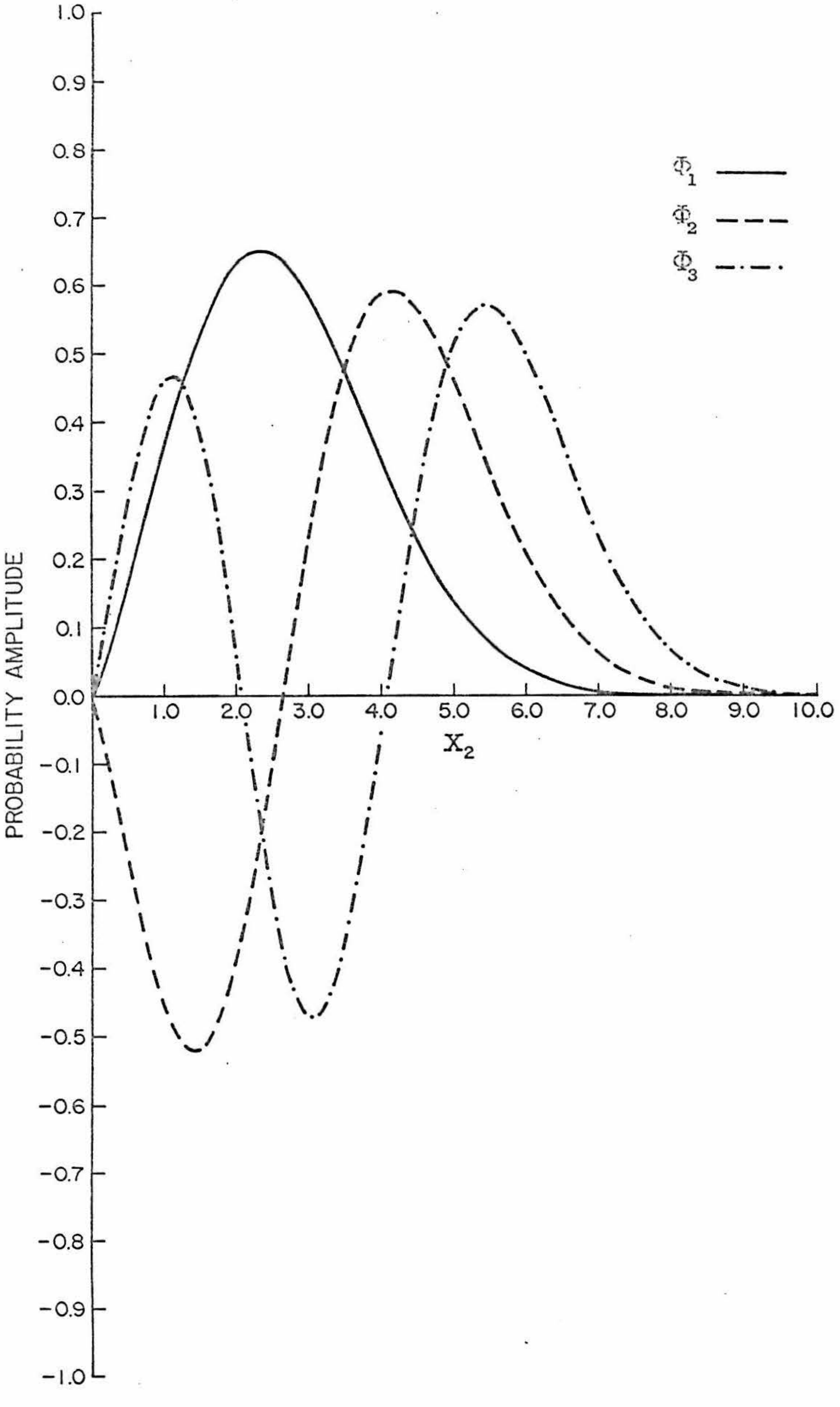

i-1
i
i+1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
0.0
2.0
4.0
6.0
8.0
10.0
X_2

Figure VIII

Plots of the lowest three FD eigenfunctions (normalized over half-space $X_2 > 0$) of the relative equation (40b) for two electrons in a parabolic well ($\varkappa = .320224$; $a = 10.0$).


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
PROBABILITY AMPLITUDE
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
X_2
Φ_1
Φ_2
Φ_3

II. A QUANTUM MECHANICAL TREATMENT OF INELASTIC COLLISIONS

A. Introduction

There exists a large volume of literature devoted to the theoretical study of energy transfer in the inelastic collision of composite particles. In particular, the problem of energy transfer between translational and vibrational and rotational degrees of freedom has received a great deal of attention. Takayanagi[1] has written a stellar review of the work done in this field.

A great proportion of the theoretical work has been done on colinear (one-dimensional) models representing the collision between an atom and a diatomic molecule or a solid surface or between two diatomic molecules. Although these models undoubtedly suffer from a neglect of three-dimensional effects of real space, it may be reasonably argued that the configuration allowing the most efficient transfer of energy is that in which the atoms are colinear. The model of a diatomic molecule, represented by a harmonic oscillator, being struck by an atom has been treated classically,[2,3] semiclassically,[4] and quantum mechanically by the method of distorted waves.[5,6]

Shuler and Zwanzig[7] have calculated numerically the quantum mechanical transition probabilities for the impulsive collision (colinear) of a free particle with a particle bound harmonically to a fixed equilibrium position, a problem mathematically equivalent to the atom-diatomic collision. Their method consists of expanding the total scattering wavefunction $\Psi(R, r)$ as a linear combination of products of the bound-state eigenfunctions of the oscillator and free-particle wavefunctions such that Ψ satisfies the Schrödinger equation describing the system. Now since the Schrödinger equation is separable, Ψ as expressed above automatically has the correct asymptotic form. The impulsive condition now requires that the $\Psi(R, r = R) \equiv 0$, i.e., that the wavefunction vanish whenever the particle coordinates are identical. Shuler and Zwanzig satisfied this requirement in a least-squares sense by expanding the $\Psi(R, R)$ in the complete orthonormal set of harmonic oscillator eigenfunctions, thereby obtaining an infinite set of simultaneous linear equations for the unknown expansion coefficients. Although the matrix corresponding to this set of equations is inherently ill-conditioned, Shuler and Zwanzig found that they could obtain transition probabilities which had converged to several significant figures by using successively larger finite matrices, i.e., by successively increasing the number of virtual channels in the expansion of Ψ. We have attempted to apply this method to the impulsive collision between two diatomic molecules. However, the number of equations in the truncated set increases as the square of the number of channels included in the expansion so that numerical instability sets in before the probabilities converge.

The Shuler-Zwanzig method has the clear disadvantage (in addition to numerical instability) that it is applicable only to impulsive collisions. Secrest and Johnson[8, 9] have recently developed an approximate method of treating inelastic collisions which is more generally applicable. Essentially their method involves a stepwise matching of the total scattering solutions for a portion of the interaction potential and an additional "slab" to obtain finally the total scattering wavefunction having the correct asymptotic form. To clarify this procedure, we look at the scattering of a one-dimensional plane wave incident upon a potential barrier. We can find the reflection and transmission coefficients by splitting up the barrier into "slabs". Suppose that we know the solutions ψ_1 and ψ_2 of the Schrödinger equations for slabs 1 and 2. We can then form a "partial" solution ψ for both slabs by requiring continuity of ψ and grad ψ at the point where the slabs join. This procedure is continued by matching this partial solution for slabs 1 and 2 with that for the next slab 3, and so on until the total scattering wavefunction Ψ is obtained. An analogous procedure may be employed to treat inelastic scattering except that in this case the matching is complicated somewhat by the fact that it is necessary to invert two matrices of order equal to the number of channels in the state expansion (or Green's function expansion) for Ψ.

Secrest and Johnson applied their method to the atom-diatomic collision problem, using various types of interaction potentials between the incident particle and the diatomic. In particular they were able to duplicate the results of Shuler and Zwanzig by approximating the hard-sphere interaction by a step potential +25 oscillator units high.

Chemical reactions constitute a special case of inelastic collisions. We wish to restrict our consideration to reactions which involve the collision of two composite particles to produce two new composite particles, e.g., exchange reactions. Furthermore, we shall consider only electronically adiabatic constrained linear encounters primarily because such a model is mathematically tractable (in contradistinction to the non-linear case). Also a vast amount of previous theoretical work in this area has been devoted to this model, presumably for the same reasons. It has been treated both classically[10, 11] and quantum mechanically.[12, 13] Mazur and Rubin[12] solved the time-dependent Schrödinger equation for a linear model exchange reaction using a specially prepared wave packet giving directly a momentum averaged reaction probability.

Mortensen and Pitzer[13] have treated the H_2, H exchange reaction by solving the time-independent Schrödinger equation using the Sato[14] potential surface and including "bending" corrections to take into account the effects of nonlinearity. They use the finite-difference method to solve the Schrödinger equation in the inseparable region, assuming a set of amplitudes and phases which determine the asymptotic form of the wavefunction. In the intermediate region between the inseparable and asymptotic regions they analyze the solution to obtain a new set of amplitudes and phases apparently differing little from the assumed set. These are then "corrected to the boundary using the WKB approximation". These corrected values are next used to obtain an improved finite-difference solution and the above process is repeated until convergence is obtained.

The principal purport of the present work is to develop a general method of treating the problem of energy transfer occurring in the inelastic collision of composite particles. Essentially the theory consists of constructing the total scattering wavefunction from a set of linearly independent solutions of the relevant Schrödinger equation, each solution of the set satisfying a different arbitrary boundary condition specified in the asymptotic region. We shall see that the method is capable of handling both nonreactive (e. g., vibrational excitation) and reactive (e. g., exchange reaction) collisions. After presenting the formalism for one-dimensional colinear models, we shall consider several specific examples of each type (i. e., nonreactive and reactive) of collision which demonstrate the utility of the method.

In section B we develop the general theory for vibrational excitations, using the atom-diatomic collision as an example. The determination of the set of linearly independent functions (χ_j) by the method of finite differences is the subject of section C., in which we also consider the "analysis" of the χ_j's into their separable components in the asymptotic region and also the convergence of the χ_j's and transition probabilities as a function of the mesh size. In section D we apply the theory to two problems in vibrational excitation: the impulsive collision of a free particle with a particle bound in (1) an infinite square well and (2) a parabolic well. In section E the general theory is extended to exchange reactions and then applied in section F to several models for exchange reactions involving three identical particles, of which the $H_2, H\cdot$ exchange reaction is the simplest physical realizable example. Finally in section G we shall discuss our results and indicate how the general theory might be modified to treat three-dimensional collisions.

B. General Theory

In order to clarify the presentation of the theory we shall consider the colinear atom-diatomic collision, which is depicted in Fig. I. If we let m_1, m_2, m_3 and x_1, x_2, x_3 denote the masses and coordinates of the three particles, respectively, we may write the time-independent Schrödinger equation for the system

$$\left\{-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2}-\frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2}-\frac{\hbar^2}{2m_3}\frac{\partial^2}{\partial x_3^2}+V_{12}'((x_2-x_1))\right.$$

$$\left.+\ V_I'((x_3-x_2))\right\}\Psi = E\Psi \ , \qquad (1)$$

where we have assumed that particles 1 and 2 are bound by the potential V_{12}' and that the incident particle (atom) 3 interacts only with particle 2 of the bound pair (diatomic).

In the center-of-mass coordinate system, defined by the following transformation,

$$X = (m_1x_1 + m_2x_2 + m_3x_3)/M$$

$$x' = x_3 - (m_1x_1 + m_2x_2)/m$$

$$y' = x_2 - x_1$$

$$M = m_1 + m_2 + m_3$$

$$m = m_1 + m_2$$

the Schrödinger equation (1) becomes

$$\left\{-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2\mu_{12,3}}\frac{\partial^2}{\partial x'^2}-\frac{\hbar^2}{2\mu_{12}}\frac{\partial^2}{\partial y'^2}+V_{12}'(y')+V_I'(x'-\frac{m_1}{m}y')\right\}\Psi=E\Psi, \tag{2}$$

where

$$\mu_{12,3}=\frac{m\cdot m_3}{M}$$

$$\mu_{12}=\frac{m_1m_2}{m}.$$

Since the potential energy does not depend on the center-of-mass coordinate X, we can separate variables in the Schrödinger equation (2) by making the substitution $\Psi=\chi_{CM}(X)\cdot\psi(x',y')$. The equation for the relative motion is then found to be

$$\left\{-\frac{\hbar^2}{2\mu}\frac{\partial^2\psi}{\partial x^2}-\frac{\hbar^2}{2\mu_{12}}\frac{\partial^2\psi}{\partial y^2}+V_{12}(y)+V_I(x-y)\right\}\cdot\psi=E_r\psi, \tag{3}$$

where

$$x' = (x+y_o)\frac{m_1}{m},$$

$$y' = y+y_o,$$

$$\mu = \frac{m_3m_1^2}{Mm},$$

$$V_{12}(y) = V_{12}'(y'-y_o),$$

$$V_I(x-y) = V_I'(\frac{m_1}{m}(x-y)),$$

$$E = E_{CM} + E_r ,$$

and y_o denotes the equilibrium separation of particles 1 and 2. We see from Eq. (3) that our problem is equivalent to that of a particle of mass μ_{12} oscillating about an equilibrium position y_o being struck by a particle of mass μ. Hence, we now can simplify our treatment by adopting this point of view.

In Fig. IIa is drawn the coordinate system for the system described by the Schrödinger equation (3). We shall assume that the bound particle has a discrete spectrum and that it is bound tightly enough that $\psi(x, y) \equiv 0$ for $|y| \geq a$. Furthermore, we assume that the interaction potential is weak enough that

$$V_I = 0 \text{ if } x > x_o, \quad x < x_o' .$$

The "cutoffs" x_o, x_o' thus specify the extent of what we shall refer to as the <u>inseparable</u> (or interaction) region (see Fig. IIb). Outside the interaction region, where the Schrödinger equation is separable, we seek a total scattering wavefunction of the form

$$\psi = e^{-ik_I x} \phi_I(y) + \sum_{m=1}^{N} R_m e^{+ik_m x} \phi_m(y) + O(e^{-\lambda x}), x > x_o \qquad (4a)$$

$$\psi = \sum_{m=1}^{N} T_m e^{-ik_m x} \phi_m(y) + O(e^{+\lambda x}), \ x < x_o' , \qquad (4b)$$

where the ϕ_m are eigenfunctions of the bound particle which satisfy

$$-\frac{\hbar^2}{2\mu_{12}}\frac{\partial^2\phi_m}{\partial y^2} + V_{12}(y)\,\phi_m = \epsilon_m\phi_m, \tag{4c}$$

and the exponentials are the corresponding free-particle wavefunctions, such that

$$\epsilon_m + \frac{\hbar^2 k_m^{\,2}}{2\mu} = E_r\,. \tag{4d}$$

From Eqs. (4) we see that there are N open channels, i. e., the incoming particle has sufficient energy to excite the bound particle to any of the lowest N eigenstates. In the asymptotic region $x > x_o$ the total scattering wavefunction ψ consists of an incoming wave of unit amplitude in channel I plus reflected waves of amplitudes R_m in the various open channels. In the other asymptotic region ψ given by Eq. (4b) consists of transmitted waves of amplitudes R_m in the various open channels. The terms $O(e^{-\lambda x})$ in Eq. (4a) and $O(e^{+\lambda x})$ in Eq. (4b) indicate contributions to ψ from virtual states, which are included for mathematical completeness as we shall see below. Physically, Eq. (4a) describes a free particle of momentum $\hbar k_I$ impinging on a particle initially in state I, exciting the bound particle to state m with a certain probability given by

$$P^{(R)}_{I \to m} = \frac{k_m}{k_I} |R_m|^2, \tag{5a}$$

and then reflecting back in the direction from which it came. Eq. (4b) corresponds to the incident particle's exciting the bound particle to state m with probability

$$P^{(T)}_{I \to m} = \frac{k_m}{k_I} |T_m|^2, \tag{5b}$$

and continuing on its path in the same direction. Relations (5a) and (5b) are obtained by identifying the transition probability $P_{I \to m}$ with the ratio of current scattered into channel m to incident current $\hbar k_I/m$ in channel I.

Conservation of current (flux) requires that

$$\sum_{m=1}^{N} \frac{k_m}{k_I} |R_m|^2 + \sum_{m=1}^{N} \frac{k_m}{k_I} |T_m|^2 = 1 , \tag{6}$$

a relation which serves as a useful check on numerical calculations of the transition probabilities. Another check is provided by time-reversal invariance, which, stated classically, means that a system executes its motion in reverse if time is allowed to run backward. In quantum scattering processes this means that $P_{i \to j} = P_{j \to i}$, i. e., the probability of a transition for state i to state j is equal to that for transition for state j to i. We now turn to the central problem - determination of the R_m and T_m.

The crux of the method, which has already been stated in the Introduction, is to find a set of linearly independent solutions χ_j of the Schrödinger equation, each solution of the set satisfying a <u>distinct</u> <u>arbitrary</u> boundary condition specified in the asymptotic regions $x < x_o'$, $x > x_o$. For example, we might set $\chi_j(x_o', y) = \phi_1(y)$, $\chi_j(x_o, y) = \phi_2(y)$. These conditions, along with those that $\chi_j(x, |y| \geq a) \equiv 0$, are sufficient to determine a unique solution of Schrödinger's equation. Although none of the solutions χ_j will have the correct asymptotic form, each may be expressed in the regions $x < x_o'$, $x > x_o$ as

$$\chi_j(x, y) = \sum_{\ell=1}^{N} [A_\ell^{(j)} e^{-ik_\ell x} + \bar{A}_\ell^{(j)} e^{+ik_\ell x}]\phi_\ell(y)$$

$$+ \sum_{\ell>N}^{\infty} [B_\ell^{(j)} e^{-k_\ell x} + \bar{B}_\ell^{(j)} e^{+k_\ell x}]\phi_\ell(y), \quad x > x_o \tag{7a}$$

$$\chi_j(x, y) = \sum_{\ell=1}^{N} [\alpha_\ell^{(j)} e^{-ik_\ell x} + \bar{\alpha}_\ell^{(j)} e^{+ik_\ell x}]\phi_\ell(y)$$

$$+ \sum_{\ell>N}^{\infty} [\beta_\ell^{(j)} e^{-k_\ell x} + \bar{\beta}_\ell^{(j)} e^{+k_\ell x}]\phi_\ell(y), \quad x < x_o', \tag{7b}$$

where

$$\frac{\hbar^2 k_\ell^2}{2\mu} + \epsilon_\ell = E_r .$$

We note that χ_j satisfies the wave equation (3). The first sum in each of Eqs. (7) is over the open channels, i. e., k_ℓ is pure real; the second is over all virtual (i. e., energetically inaccessible) channels for which k_ℓ is pure imaginary. We can regard χ_j as being expanded in the "complete" (for energy E_r) orthonormal set of eigenfunctions of the Hamiltonian without the interaction term V_I and this set must include the virtuals.

The coefficients $A_\ell^{(j)}$, $\overline{A}_\ell^{(j)}$, $B_\ell^{(j)}$, etc., may be found by taking the appropriate inner product with $\phi_\ell(y)$ and solving the resulting sets of simultaneous equations (see Appendix). Now the total scattering wavefunction ψ is constructed as a linear combination of the independent χ_j as

$$\psi = \sum_{j=1}^{\infty} C_j^{(I)} \chi_j , \tag{8}$$

such that ψ is everywhere a solution of the Schrödinger equation (3) and also satisfies the correct asymptotic conditions (4). Thus we must require

$$\sum_j C_j^{(I)} A_I^{(j)} = \delta_{I\ell} , \quad \ell \leq N \tag{9a}$$

$$\sum_j C_j^{(I)} \overline{B}_\ell^{(j)} = 0 , \quad \ell > N \tag{9b}$$

$$\sum_j C_j^{(I)} \overline{\alpha}_\ell^{(j)} = 0 , \quad \ell \leq N \tag{9c}$$

$$\sum_j C_j^{(I)} \beta_\ell^{(j)} = 0, \qquad \ell > N, \tag{9d}$$

where the superscript (I) on the $C_j^{(I)}$ denotes the incident state. Physically, Eq. (9a) states that there is only a single incoming wave incident from the right and Eq. (9c) that there are no waves incident from the left. Eqs. (9b) and (9d) require that there be no rising virtual components in either asymptotic region.

In practice we anticipate solving Eqs. (9) by truncating the expansions in ℓ and j to obtain a finite system of simultaneous linear equations. Suppose we retain a total of M states, N open and M-N virtual, in the ℓ expansion of Eq. (7). Then there are 2M Eqs. (9) so that we must determine 2M linearly independent χ_j's. If this is done, Eqs. (9) may be expressed more compactly in matrix form as

$$\underset{\sim}{A}\,\underset{\sim}{C} = \underset{\sim}{I}' , \tag{10}$$

where $\underset{\sim}{A}$ is a 2M × 2M matrix of the coefficients $A_\ell^{(j)}$, etc., $\underset{\sim}{C}$ is a 2M × N matrix of unknown coefficients $C_j^{(I)}$, and $\underset{\sim}{I}'$ is a 2M × N matrix consisting of a N × N unit matrix spanning the first N rows and a (2M-N) × N null matrix spanning the remaining. The column vectors of $\underset{\sim}{C}$ correspond to the various possible incident states I = 1, 2, ... N. Having obtained $\underset{\sim}{C}$ by solving Eq. (10), we can find the reflection and transmission coefficients by taking the product

$$\underset{\sim}{\bar{A}}\,\underset{\sim}{C} = \underset{\sim}{\bar{A}}\,\underset{\sim}{A}^{-1}\,\underset{\sim}{I}' , \tag{11}$$

where $\underset{\sim}{\overline{A}}$ is a N × 2M matrix of the coefficients $\overline{A}_\ell^{(j)}$, $\alpha_\ell^{(j)}$ corresponding to the relations

$$\sum_j C_j \overline{A}_\ell^{(j)} = R_\ell \qquad \ell \leq N \tag{12a}$$

$$\sum_j C_j \alpha_\ell^{(j)} = T_\ell \qquad \ell \leq N . \tag{12b}$$

C. Determination of the χ_j

Having developed the formalism of the method, we now turn to the central problem - determination of the set of linearly independent solutions χ_j. For this purpose we choose the method of finite differences, which has been discussed already in Part I. In this case, however, our task is considerably simpler since we do not have an eigenvalue problem. We have only to find the solution (discretized χ_j) of the simultaneous set of linear equations resulting from the discretization of the Schrödinger equation for a fixed energy E_r.

Substituting the expressions for the discretized partial derivatives derived in Part I, we obtain for the finite-difference analogue of the Schrödinger equation (3)

$$\left[2\left(\frac{1}{\mu} + \frac{1}{\mu_{12}}\right) + 2h^2(V_{12} + V_I - E)_i\right]\chi_i - \frac{1}{\mu}\left(\chi_{i_1} + \chi_{i_3}\right)$$

$$- \frac{1}{\mu_{12}}\left(\chi_{i_2} + \chi_{i_4}\right) = 0 , \quad i = 1, 2, \ldots Q , \tag{13}$$

where the points are numbered as shown in Fig. III and the subscripts on χ have the same significance as in Part I, i.e., the subscript j denoting the particular member of the linearly independent set has been suppressed. The set of equations (13) may be rewritten in matrix form as

$$\underset{\sim}{H}\,\underset{\sim}{\chi} = \underset{\sim}{b} \,. \tag{14}$$

$\underset{\sim}{H}$ is a <u>real</u> <u>symmetric</u> <u>band</u> matrix of order Q (the number of interior mesh points). The bandwidth, defined by the expression

$$\text{bandwidth} \equiv 2B - 1 \,,$$

where $H_{ij} = 0$ if $|i - j| \geq B$, is determined by the number of points across the well (i.e., the number of points which divide the range of the y variable in the finite-difference mesh), for the particular 5-point difference analogue which we are using. $\underset{\sim}{\chi}$ is the column vector of approximate values of χ_j at the grid points. $\underset{\sim}{b}$ is the column vector of the form

$$\begin{bmatrix} \chi(x < x_o', \frac{a}{n+1})/\mu \\ \chi(x < x_o', \frac{2a}{n+1})/\mu \\ \cdot \\ \cdot \\ \cdot \\ \chi(x < x_o', \frac{na}{(n+1)})/\mu \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \\ \chi(x > x_o, \frac{a}{n+1})/\mu \\ \chi(x > x_o, \frac{2a}{n+1})/\mu \\ \cdot \\ \cdot \\ \cdot \\ \chi(x > x_o, \frac{na}{(n+1)})/\mu \end{bmatrix} ,$$

where n is the number of points across the well. The form of $\underset{\sim}{b}$ corresponds to the non-zero boundary conditions at either end of the interaction region which occur as "off-diagonal" terms in the left member of Eq. (13).

1. Uniqueness and Convergence

The uniqueness of the solution of the finite-difference equations resulting from elliptic partial differential equations with Dirichlet boundary conditions has been discussed elsewhere.[15] We wish to consider further the explicit dependence of the convergence of the solutions χ_j and the transition probabilities upon the mesh size h. Employing the procedure of Part I, we assume that there exists a continuous function $\chi_c(x, y; h)$ such that χ_c satisfies the difference equation for all values of h and that χ_c may be expanded in a power series of the form

$$\chi_c(x, y; h) = \sum_k \xi_k(x, y)\, h^k \quad , \tag{15}$$

where the ξ_k may in turn be expanded in a complete set of linearly independent functions which are the exact solutions of Eq. (3).[16] Then χ_c must satisfy the difference equation analogue

$$\begin{aligned} &[2(\frac{1}{\mu} + \frac{1}{\mu_{12}}) + 2h^2(V_{12} + V_I)]\, \chi_c(x, y; h) \\ &- \frac{1}{\mu}\chi_c(x+h, y; h) - \frac{1}{\mu}\chi_c(x-h, y; h) - \frac{1}{\mu_{12}}\chi_c(x, y+h; h) \\ &- \frac{1}{\mu_{12}}\chi_c(x, y-h; h) = \epsilon\, \chi_c(x, y; h) \ , \end{aligned} \tag{16}$$

where

$$\epsilon = 2h^2 E_r \ .$$

Substituting Taylor's series expansions for χ_c into Eq. (16) gives

$$[2(\frac{1}{\mu} + \frac{1}{\mu_{12}}) + 2h^2 (V_{12} + V_I)] \ \chi_c(x, y; h)$$

$$- \frac{1}{\mu} \left\{\chi_c(x, y;h) + (\frac{\partial \chi_c}{\partial x})h + (\frac{\partial^2 \chi_c}{\partial x^2})\frac{h^2}{2!} + (\frac{\partial^3 \chi_c}{\partial x^3})\frac{h^3}{3!} + (\frac{\partial^4 \chi_c}{\partial x^4})\frac{h^4}{4!}\right\}$$

$$- \frac{1}{\mu} \left\{\chi_c(x, y; h) - (\frac{\partial \chi_c}{\partial x})h + (\frac{\partial^2 \chi_c}{\partial x^2})\frac{h^2}{2!} - (\frac{\partial^3 \chi_c}{\partial x^3})\frac{h^3}{3!} + (\frac{\partial^4 \chi_c}{\partial x^4})\frac{h^4}{4!}\right\}$$

$$- \frac{1}{\mu_{12}} \left\{\chi_c(x, y; h) + (\frac{\partial \chi_c}{\partial y})h + (\frac{\partial^2 \chi_c}{\partial y^2})\frac{h^2}{2!} + (\frac{\partial^3 \chi_c}{\partial y^3})\frac{h^3}{3!} + (\frac{\partial^4 \chi_c}{\partial y^4})\frac{h^4}{4!}\right\}$$

$$- \frac{1}{\mu_{12}} \left\{\chi_c(x, y; h) - (\frac{\partial \chi_c}{\partial y})h + (\frac{\partial^2 \chi_c}{\partial y^2})\frac{h^2}{2!} - (\frac{\partial^3 \chi_c}{\partial y^3})\frac{h^3}{3!} + (\frac{\partial^4 \chi_c}{\partial y^4})\frac{h^4}{4!}\right\}$$

$$= \epsilon \ \chi_c(x, y; h) \ . \tag{17}$$

Replacing χ_c with its expansion Eq. (15), making appropriate cancellations, and equating coefficients of equal powers of h, we obtain

$$\left\{ - \frac{1}{2\mu} \frac{\partial^2}{\partial x^2} - \frac{1}{2\mu_{12}} \frac{\partial^2}{\partial y^2} + V_{12} + V_I\right\} \xi_o = E_r \xi_o \tag{18a}$$

$$\left\{ -\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{1}{2\mu_{12}}\frac{\partial^2}{\partial y^2} + V_{12} + V_I \right\} \xi_1 = E_r \xi_1 \tag{18b}$$

$$\left\{ -\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{1}{2\mu_{12}}\frac{\partial^2}{\partial y^2} + V_{12} + V_I \right\} \xi_2 +$$

$$\left\{ -\frac{1}{24\mu}\frac{\partial^4}{\partial x^4} - \frac{1}{24\mu_{12}}\frac{\partial^4}{\partial y^4} \right\} \xi_o = E_r \xi_2 . \tag{18c}$$

Since ξ_o satisfies the Schrödinger equation and the boundary conditions we have that

$$\xi_o \equiv \chi \quad ,$$

the exact solution of the problem. Hence, the approximate finite difference function may be expressed as

$$\chi_c = \chi + h\xi_1 + h^2\xi_2 , \tag{19}$$

and χ_c approaches the exact solution as h approaches zero. Now the asymptotic form of χ_c may be written in analogy to Eq. (7) as

$$\chi_c = \sum_{\ell=1}^{N} [(A_{\ell o} + A_{\ell 1}h + \cdots)e^{-ik_\ell x} + (\overline{A}_{\ell o} + \overline{A}_{\ell 1}h + \cdots)e^{+ik_\ell x}]\phi_\ell$$

$$+ \sum_{\ell > N}^{N} [(B_{\ell o} + B_{\ell 1}h + \cdots)e^{-k_\ell x} + (\overline{B}_{\ell o} + \overline{B}_{\ell 1}h + \cdots)e^{+k_\ell x}]\phi_\ell ,$$

where the various channel coefficients have been expanded in powers of h. This is possible since the asymptotic form of each ξ_k can be expanded in the complete set of eigenfunctions of the Hamiltonian without the interaction term V_I. Corresponding to this approximate expansion of the χ_j our matrix equation (10) becomes

$$(\underset{\sim}{A}_o + \underset{\sim}{A}_1 h + \underset{\sim}{A}_2 h^2 + \cdots)(\underset{\sim}{c}_o + \underset{\sim}{c}_1 h + \underset{\sim}{c}_2 h^2 + \cdots) = \underset{\sim}{I}' . \qquad (20)$$

Identifying coefficients of equal powers of h on either side of Eq. (20), we find

$$\underset{\sim}{c}_o = \underset{\sim}{A}_o^{-1} \underset{\sim}{I}' \qquad (21a)$$

$$\underset{\sim}{c}_1 = -\underset{\sim}{A}_o^{-1} \underset{\sim}{A}_1 \underset{\sim}{c}_o , \qquad (21b)$$

etc. From Eq. (11) we see that the matrix of approximate amplitudes may be written

$$(\underset{\sim}{\bar{A}}_o + \underset{\sim}{\bar{A}}_1 h + \underset{\sim}{\bar{A}}_2 h^2 + \cdots)(\underset{\sim}{c}_o + \underset{\sim}{c}_1 h + \underset{\sim}{c}_2 h^2) =$$

$$\underset{\sim}{\bar{A}}_o \underset{\sim}{c}_o + (\underset{\sim}{\bar{A}}_o \underset{\sim}{c}_1 + \underset{\sim}{\bar{A}}_1 \underset{\sim}{c}_o) h + \cdots . \qquad (21c)$$

Thus the approximate transition probabilities determined by the finite-difference method approach the exact values as the mesh size tends to zero

$$P_{i \to j}(h) = (P_{i \to j})_o + (P_{i \to j})_1 h + (P_{i \to j})_2 h^2 + \cdots . \qquad (22)$$

This equation may be used to extrapolate to the exact transition probability $(P_{i \to j})_o$ analogously to the Richardson procedure used in Part I. We obtain values $P_{i \to j}(h_1)$, $P_{i \to j}(h_2)$, $P_{i \to j}(h_3)$, $\cdots$ at various not-too-large mesh sizes h_1, h_2, h_3 $\cdots$ and then fit a polynomial of the form of Eq. (22) through these points. We shall do this in several examples considered below. Alternatively, we may regard $P_{i \to j}(h)$ as a "mathematical transient" and apply the so-called $e_1^{\ m}$ transform to enhance the convergence of the sequence.[17] We shall also use this procedure.

2. Solution of Finite-Difference Equations

Depending on the extent of the interaction region and on the accuracy we demand of the transition probabilities, it may be necessary to solve very large systems of simultaneous equations (14). It turns out that for the examples we shall consider below it is necessary to solve up to 1500 simultaneous equations, the corresponding matrix $\underset{\sim}{H}$ having a bandwidth of 81. To accomplish this we have employed a highly accurate and efficient computer subroutine capable of handling large band matrices.[18] Originally devised by C. W. McCormick for treating large distributed elastic systems, the method is based on triangular resolution without interchanges.

The matrix $\underset{\sim}{H}$ is put into upper triangular form (i. e., zeros below the diagonal) by Gaussian elimination, taking the successive pivots along the principal diagonal. The upper triangular matrix is called $\underset{\sim}{U}$. If the successive multipliers are arranged in columns to form the matrix

$$\underset{\sim}{L} = \begin{bmatrix} 1 & 0 & 0 & & 0 \\ \ell_{21} & 1 & 0 & \cdots & 0 \\ \ell_{31} & \ell_{32} & & & \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & \cdot \\ \ell_{n1} & \ell_{n2} & & & 1 \end{bmatrix} ,$$

where the first column is composed of the multipliers $-a_{j1}/a_{11}$, $j = 2 \cdots n$ used to eliminate the first variable from the last $n - 1$ equations, and so on, the following relation holds

$$\underset{\sim}{L}\,\underset{\sim}{U} = \underset{\sim}{H} , \tag{23}$$

Hence, we can find the solution $\underset{\sim}{\chi}$ to Eq. (14) by solving

$$\underset{\sim}{L}\,\underset{\sim}{y} = \underset{\sim}{b} \tag{24a}$$

$$\underset{\sim}{U}\,\underset{\sim}{\chi} = \underset{\sim}{y} \tag{24b}$$

sequentially by back substitution. The method fails if the ith leading minor of $\underset{\sim}{H}$ is singular or nearly so, since the element ℓ_{ji} of $\underset{\sim}{L}$ depends on the reciprocal of this minor. Usually such a difficulty may be avoided by interchanging the rows or columns of $\underset{\sim}{H}$.

A great computational advantage of the triangular resolution scheme for band matrices is realized as reduced storage requirements and running times compared with conventional matrix inversion routines. This is so because at each stage of elimination only B rows of H need be contained in core, so B^2 locations are required for an unsymmetric matrix and about half as many for a symmetric matrix. McCormick has made provision for large matrices by using magnetic tapes to store $\underset{\sim}{H}$ and $\underset{\sim}{b}$. They are read into core in successive "blocks" and the resulting triangular matrices written on special magnetic tapes. Once the triangular resolution has been effected, the $\underset{\sim}{L}$ and $\underset{\sim}{U}$ matrices may be used to operate on as many right-hand side vectors $\underset{\sim}{b}$ as desired.

The solution may be improved iteratively to specified accuracy. This is done by solving Eqs. (24) to find a first approximation χ_o. Then a residual vector $\delta \underset{\sim}{b} = \underset{\sim}{b} - \underset{\sim}{b}_o$ is calculated using $\underset{\sim}{b}_o = \underset{\sim}{H} \chi_o$. A correction $\delta \underset{\sim}{\chi}_o$ to $\underset{\sim}{\chi}_o$ is calculated using Eqs. (24) with $\underset{\sim}{b}$ replaced by $\delta \underset{\sim}{b}$. This process is repeated until $|\frac{\delta\chi}{\chi}|$ is less than a specified number ϵ or until a specified maximum number of iterations have been carried out. For the FD equations one iteration is sufficient to obtain an accuracy of 1 part in 10^7.

3. Analysis of the χ_j

The integrals necessary in the determination of the expansion coefficients $A_\ell^{(j)}$, $\bar{A}_\ell^{(j)}$, etc. in Eq. (7) are of the form

$$\int_{-\infty}^{+\infty} \phi_k^* \chi_j \, dy = f_k^{(j)}(x)$$

where χ_j vanishes for $|y| \geq a$ (see Appendix). These integrals are evaluated approximately using an extended Simpson's rule, the general form of which is

$$\int_{y_o}^{y_{2n}} p(y)\, dy = \frac{h}{3}[f_o + 4 \sum_{j=0}^{n-1} f_{2j+1}$$

$$+ 2 \sum_{j=0}^{n-1} f_{2j} + f_{2n}] - \frac{nh^5}{90} p^{(4)}(\xi) \tag{25}$$

where h is the mesh size, 2n is the number of mesh points (including the end points) in the interval, and ξ is some value of y such that $y_o \leq \xi \leq y_{2n}$.[19] For selected χ_j, this method has yielded integrals accurate to 1 part in 10^8.

D. Application of the Theory to Vibrational Excitations

In this section we apply the theory to two one-dimensional (two-particle) models for vibrational excitations. We consider the impulsive (hard-sphere) collision of a free particle with a particle bound to a fixed center of force. A diagram of the coordinate system and appropriate boundary conditions is shown in Fig. IV. Note that transmission is not allowed in this case.

1. Infinite-Square-Well Binding Potential

The Schrödinger equation for this system is simply

$$-\frac{\hbar^2}{2m_A}\frac{\partial^2\psi}{\partial x^2}-\frac{\hbar^2}{2m_B}\frac{\partial^2\psi}{\partial y^2}=E_r\psi\ , \qquad (26)$$

where $x \geq y$ and $o \leq y \leq a$, a being the width of the square well. Making the substitutions $x = a/\pi\, x'$, $y = a/\pi\, y'$, and dividing through by $\hbar^2\pi^2/m_B a^2$, we obtain

$$\left\{-\frac{1}{2(m_A/m_B)}\frac{\partial^2}{\partial x'^2}-\frac{1}{2}\frac{\partial^2}{\partial y'^2}\right\}\psi = E'\psi \qquad (27)$$

where $E' = m_B a^2/\hbar^2\pi^2\ E$. The bound states of the well are described by eigenfunctions

$$\phi_n = \sqrt{2/\pi}\ \sin nx'\ ,$$

and eigenvalues

$$\epsilon_n = \frac{n^2}{2} \, .$$

Hence, we express energy conservation by the equation

$$E' = \frac{n^2}{2} + \frac{m_B}{m_A} \frac{a^2}{\pi^2} \frac{k_n^2}{2} \quad \text{for all } n, \tag{28}$$

where k_n is the wavenumber of the free particle. Transition probabilities have been obtained for two different total energies and the following parameters: $a = \pi$; $x_o = a$; $m_A/m_B = 1.0$. Fig. V shows a graph of transition probability v. s. (a/h - 1), the number of mesh points across the well, for a total energy of 2.25 units, i. e., two open channels. It was found necessary to include only one virtual channel in the state expansion for the range of mesh sizes considered. Adding one or two more virtuals did not change the transition probabilities before the fifth decimal place. Table I lists transition probabilities as a function of the mesh size together with e_1^m-extrapolated probabilities, which differ by ± .005 to ± .01 from values obtained for the finest mesh. For a total energy of 4.75 units (corresponding to three open channels) lists of transition probabilities are contained in Table II. Again it was necessary to retain only one virtual channel in the state expansion.

We observe from the tables that the sum check, i. e., $\sum_{j=1}^{N} P_{i \to j} = 1$, improves as we decrease the mesh size; also that the sum check for extrapolated values is better than that for the finest mesh. The same appears to be true of the check afforded by the time reversal requirement $P_{i\to j} = P_{j\to i}$.

2. Parabolic Binding Potential

For the collision of a free hard sphere with a hard-sphere oscillator we may write the Schrödinger equation as

$$[\, -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\varkappa(y - y_o)^2\,]\psi = E_r\psi. \tag{29}$$

In the coordinate system defined by

$$\xi = \left(\frac{M\omega}{\hbar}\right)^{1/2}(y - y_o)$$

$$\xi' = \left(\frac{M\omega}{\hbar}\right)^{1/2} x\,,$$

Eq. (29) becomes

$$[\, -\frac{1}{2}\frac{1}{\left(\frac{m}{M}\right)}\frac{\partial^2}{\partial \xi'^2} - \frac{1}{2}\frac{\partial^2}{\partial \xi^2} + \frac{1}{2}\xi^2\,]\psi = E'\psi, \tag{30}$$

where $E' = (\hbar\,\omega)^{-1}E$, $\varkappa = M\omega^2$, ω being the classical frequency of the oscillator. In these units the eigenstates of the oscillator are described by

$$\phi_n = \left(\frac{1}{2^n n! \pi^{1/2}}\right)^{1/2} H_n(\xi) e^{-\xi^2/2} \tag{31a}$$

$$\varepsilon_n = (n + 1/2) \;, \tag{31b}$$

where H_n is a Hermite polynomial. The energy conservation relation determining k_n, the free particle wavenumber, is given by

$$E_{K.E.} + (n + 1/2) = E'. \tag{32}$$

The χ_j's are determined by solving the Schrödinger equation (30) with the harmonic oscillator equilibrium position with $\xi_o = a/2$ and taking a large enough that the χ_j's are in fact small compared to their maximum value for $\xi > a/2$. Transition probabilities were determined for several total energies using the following set of parameters: $a = 10$; ξ_o' (cutoff in asymptotic region) = 10; $m/M = 1/2$. Table III contains the e_1^m-extrapolated transition probabilities for $E' = 1.75$. In this case there are two open channels and it was sufficient to include two virtuals in the state expansion. Table IV lists e_1^m-extrapolated transition probabilities for $E' = 2.75$, in which case there were three open and two virtual channels in the state expansion. In general we find that the sum and time-reversal checks improve as the mesh size decreases, the extrapolated values satisfying these requirements better than finest-mesh values. These results also agree with Shuler and Zwanzig's to ± .02.[7]

Observing that extrapolated values seem to differ from finest-mesh values by approximately ± .006, we have calculated transition probabilities in the range E' = 1.50 - 2.50 (two open and two virtual channels) using a mesh size $h = .3125$ (number of points across well = 31). The transition probability v.s. total incident energy curves (see Fig. VI) agree to ± .02 with previously calculated[7] curves, taking into account the extrapolation error and the error in reading the Shuler-Zwanzig curves.

From the preceding examples we see that transition probabilities for impulsive collisions may be obtained quite accurately using relatively crude meshes. Also, computing times for the solution of FD equations, which is really the rate determining step in the calculation, are relatively low. For example, for the impulsive free-particle-harmonic-oscillator collision the execution time is approximately linear in the bandwidth as shown by the curves in Fig. VII. These curves were obtained specifying a maximum of three iterations. However, it is possible to obtain solutions χ_j agreeing with the three-iteration solutions to 1 part in 10^7 requiring only one iteration, which consumes approximately one-third as much time. We note that these time estimates are independent of the nature of the interaction potential V_I or the total energy E_r.

E. Extension of the Theory to Exchange Reactions of the Type $A + BC \rightarrow AB + C$

Although the extension of the theory to exchange reactions is perhaps straightforward in principle (as most insoluble problems seem to be), some simplifications can be effected by choosing an appropriate coordinate system in which to determine the χ_j and to analyze them into their separable components in the asymptotic regions. To keep the presentation clear and simple we consider a colinear electronically adiabatic reaction (see Fig. VIII), for which the time-independent Schrödinger equation may be written as

$$\left\{ -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} - \frac{\hbar^2}{2m_3}\frac{\partial^2}{\partial x_3^2} + V_{123}\right\}\Psi = E\Psi, \quad (33)$$

where x_1, x_2, x_3 and m_1, m_2, m_3 are, respectively, the coordinates and masses of the three particles (atoms or molecular fragments) involved in the reaction. The potential V_{123} is a three-body potential, i. e., the total potential cannot be expressed simply as a sum of two-body potentials. This is so because, in the adiabatic approximation, the electron "clouds" of the three atoms interact with one another in a complicated fashion to produce an effective potential surface upon which the nuclei of the atoms move. Our task is to develop a quantum mechanical description of the motion of these nuclei on the potential surface which will allow us to predict the probability that for a given incident state (e. g., atom A impinging with a given relative kinetic energy upon pair BC bound in a given eigenstate) a reaction yielding products AB and C will occur.

In the following treatment we shall employ four distinct coordinate systems, which are labeled as in Part I. The three systems other than $[x_1, x_2, x_3]$ are defined by the following transformations:

(a) $[X, x_{12}, x_{23}]$,

$$X = (m_1x_1 + m_2x_2 + m_3x_3)/(m_1 + m_2 + m_3)$$

$$x_{12} = x_2 - x_1$$

$$x_{23} = x_3 - x_2 \; ; \qquad (34a)$$

(b) $[X, x, x_{12}]$,

$$X = \sum_{i=1}^{3} m_ix_i/M$$

$$x = x_3 - (m_1x_1 + m_2x_2)/(m_1 + m_2)$$

$$x_{12} = x_2 - x_1 \; ; \qquad (34b)$$

(c) $[X, x', x_{23}]$,

$$X = \sum_{i=1}^{3} m_ix_i/M$$

$$x' = x_1 - (m_2x_2 + m_3x_3)/(m_2 + m_3)$$

$$x_{23} = x_3 - x_2 \,. \tag{34c}$$

In these equations the symbols have their usual significance, i. e., x_1, x_2, x_3 are the particle coordinates in an arbitrary space-fixed reference frame, X is the coordinate of the center of mass in this frame, x_{12} and x_{23} are the interparticle separations, and x and x' are the coordinates of particles 3 and 1, respectively, with respect to the center of mass of the bound pair.

Since the potential is independent of X, we can separate the center-of-mass motion in each of the three coordinate systems defined above. Thus in $[X, x_{12}, x_{23}]$ the Schrödinger equation for the relative motion becomes

$$\left\{ - \frac{\hbar^2}{2\mu_{12}} \frac{\partial^2}{\partial x_{12}^2} - \frac{\hbar^2}{2\mu_{23}} \frac{\partial^2}{\partial x_{23}^2} + \frac{\hbar^2}{m_2} \frac{\partial^2}{\partial x_{12}\partial x_{23}} + V_{123} \right\} \psi = E_r \psi, \tag{35}$$

where

$$\mu_{12} = m_1m_2/m_1 + m_2$$

$$\mu_{23} = m_2m_3/m_2 + m_3 \;.$$

The coordinate system showing the interaction region and boundary conditions is sketched in Fig. IXa. We assume that each bound pair has a discrete spectrum and that $V_{123} = V_{12}$ when $x_{23} > x_{23}^{(0)}$, $V_{123} = V_{23}$ when $x_{12} > x_{12}^{(0)}$. These "cutoff" parameters define the inseparable region for the reaction in a manner analogous to x_o, x_o' for the case of nonreactive scattering. We also sketch the boundary conditions and inseparable region in the systems $[X, x, x_{12}]$ and $[X, x', x_{23}]$ (see Fig. IXb) since the asymptotic forms of ψ assume a simpler, more physically aesthetic appearance than in $[X, x_{12}, x_{23}]$.

We now wish to find a total wavefunction ψ satisfying the wave equation everywhere and having the following form in the asymptotic regions:

$$\psi(x, x_{12}) = e^{-ik_I x} \phi_I(x_{12}) + \sum_{m=1}^{N} R_m e^{+ik_m x} \phi_m(x_{12}),$$

$$x > x_o = \alpha x_{12} + x_{23}^{(0)} \tag{36a}$$

$$\psi(x', x_{23}) = \sum_{m=1}^{N'} T_m e^{+ik'_m x'} \bar{\phi}_m(x_{23}), \quad x' > x_o' = \beta x_{23} + x_{12}^{(0)} \tag{36b}$$

where

$$\alpha = m_1/(m_1 + m_2), \quad \beta = m_3/(m_2 + m_3), \text{ and}$$

where the ϕ_m and $\bar{\phi}_m$ are the bound-state eigenfunctions of the BC and AB subsystem, respectively, and the exponentials are the corresponding free-particle eigenfunctions. The energy conservation condition may be expressed as

$$\epsilon_{12}^{(I)} + \frac{\hbar^2 k_I^2}{2\mu_{12,3}} = \epsilon_{12}^{(m)} + \frac{\hbar^2 k_m^2}{2\mu_{12,3}} = \epsilon_{23}^{(m)} + \frac{\hbar^2 k_m'^2}{2\mu_{23,1}} , \qquad (37)$$

where

$$1/\mu_{12,3} = (\sum_{i=1}^{3} m_i)/(m_1 + m_2) \cdot m_3$$

$$1/\mu_{23,1} = (\sum_{i=1}^{3} m_i)/(m_2 + m_3) \cdot m_1 .$$

We may interpret the asymptotic behavior of ψ as given in Eqs. (36) analogously to that described by Eq. (4), i.e., the total stationary scattering wavefunction consists of an incident wave of unit amplitude in channel I plus scattered waves of various amplitudes in channels corresponding to reaction and reflection <u>without</u> reaction. Thus R_m is the amplitude for excitation of the BC subsystem to state m and reflection of A with relative momentum $\hbar k_m$. T_m is the amplitude for reaction to occur, producing AB in state m and ejecting C with relative momentum $\hbar k_m'$. The transition probabilities are expressed as

$$P_{I \to m}^{(R)} = \frac{k_m}{k_I} |R_m|^2 \qquad (38a)$$

$$P_{I \to m}^{(T)} = \frac{k_m'}{k_I} |T_m|^2 , \qquad (38b)$$

where $P^{(R)}_{I \to m}$ is the probability that the incoming particle A will excite subsystem BC from incident state I to excited state m and reflect, $P^{(T)}_{I \to m}$ is the probability that A will react with subsystem BC to form a new subsystem AB in eigenstate m. Relation (6), requiring conservation of flux, holds exactly in the case of exchange reactions also, thus providing a check on numerical computations.

As in the case of vibrational excitation, our primary goal is to obtain the R's and T's and we do this again by finding the appropriate linear combination of linearly independent solutions χ_j, each χ_j satisfying the wave equation (33) in addition to distinct arbitrary boundary conditions specified in the asymptotic regions. In $[X, x_{12}, x_{23}]$ each χ_j has the asymptotic form

$$\chi_j = \sum_{\ell=1}^{N} [A_\ell^{(j)} e^{-ik_\ell(\alpha x_{12} + x_{23})} + \bar{A}_\ell^{(j)} e^{+ik_\ell(\alpha x_{12} + x_{23})}] \phi_\ell(x_{12})$$

$$+ \sum_{\ell > N} [B_\ell^{(j)} e^{-k_\ell(\alpha x_{12} + x_{23})} + \bar{B}_\ell^{(j)} e^{+k_\ell(\alpha x_{12} + x_{23})}] \phi_\ell(x_{12}),$$

$$x_{23} > x_{23}^{(0)} \qquad (39a)$$

$$\chi_j = \sum_{\ell=1}^{N'} [\alpha_\ell^{(j)} e^{-ik_\ell'(\beta x_{23} + x_{12})} + \bar{\alpha}_\ell^{(j)} e^{+ik_\ell'(\beta x_{23} + x_{12})}] \bar{\phi}_\ell(x_{23})$$

$$+ \sum_{\ell > N'} [\beta_\ell^{(j)} e^{-k_\ell'(\beta x_{23} + x_{12})} + \bar{\beta}_\ell^{(j)} e^{+k_\ell'(\beta x_{23} + x_{12})}] \bar{\phi}_\ell(x_{23}),$$

$$x_{12} > x_{12}^{(0)}, \qquad (39b)$$

where N and N' are the number of open channels for subsystems BC and AB, respectively. The coefficients in the above expansions $A_\ell^{(j)}$, $\bar{A}_\ell^{(j)}$, etc. are found by truncating the expansion, taking inner products with the bound-state eigenfunctions, and solving the resultant set of simultaneous equations (see Appendix). The total wavefunction for the reaction may now be written

$$\psi = \sum_j c_j^{(I)} \chi_j , \tag{40}$$

such that ψ everywhere satisfies Eq. (33) and has the correct asymptotic forms [Eqs. (36)]. As before, we must have

$$\sum_j c_j^{(I)} \bar{A}_\ell^{(j)} = \delta_{I\ell} , \qquad \ell \leq N \tag{41a}$$

$$\sum_j c_j^{(I)} \bar{B}_\ell^{(j)} = 0 \qquad \ell > N \tag{41b}$$

$$\sum_j c_j^{(I)} \alpha_\ell^{(j)} = 0 , \qquad \ell \leq N' \tag{41c}$$

$$\sum_j c_j^{(I)} \bar{\beta}_\ell^{(j)} = 0 , \qquad \ell > N' , \tag{41d}$$

where the superscript I denotes the particular incident state. The physical interpretation of these equations is as follows: Eq. (41a) corresponds to the requirement that we have a monoenergetic beam of particles A from the right, Eq. (41c) to the fact that there are no particles C incident from the left; Eqs. (41b) and (41d) eliminate the rising virtual components in regions $x_{23} > x_{23}^{(0)}$ and $x_{12} > x_{12}^{(0)}$, respectively. Truncating the expansions in ℓ and j, we may obtain a finite system of simultaneous linear equations expressed in matrix form as

$$\underset{\sim}{A}\,\underset{\sim}{c} = \underset{\sim}{I}' , \tag{42}$$

where $\underset{\sim}{A}$ is the $(M + M') \times (M + M')$ matrix of coefficients $A_\ell^{(j)}$, etc., $\underset{\sim}{c}$ is the $(M + M') \times N$ matrix of $c_j^{(I)}$, and $\underset{\sim}{I}'$ is a $(M + M') \times N$ matrix consisting of the $N \times N$ unit matrix occupying the first N rows and a $(M + M' - N)$ null matrix the rest. M is the total number of BC channels and M' the total number of AB channels retained in the truncated state expansion (39). The amplitudes R_m and T_m are determined from

$$\underset{\sim}{\tau} \equiv \underset{\sim}{\bar{A}}\,\underset{\sim}{c} = \underset{\sim}{\bar{A}}\,\underset{\sim}{A}^{-1}\,\underset{\sim}{I}' , \tag{43}$$

where $\underset{\sim}{\bar{A}}$ is the $(N + N') \times (M + M')$ matrix of coefficients $\bar{A}_\ell^{(j)}$, $\bar{\alpha}_\ell^{(j)}$, $\underset{\sim}{c}$ is the matrix of $c_j^{(I)}$ determined from (42), and $\underset{\sim}{\tau}$ is the $NN' \times N$ matrix, the first N rows of which are the R_m, the next N' the T_m.

The χ_j may be determined most easily by the finite-difference method in the coordinate system $[X, x_{12}, x_{23}]$. Making the substitutions[20]

$$\left(\frac{\partial^2\chi}{\partial x_{12}\partial x_{23}}\right)_{i,j} = \frac{1}{4h^2}\left(\chi_{i+1,j+1} - \chi_{i+1,j+1} - \chi_{i-1,j+1} + \chi_{i-1,j-1}\right) + O(h^2) \quad (44a)$$

$$\left(\frac{\partial^2\chi}{\partial x_{12}^2}\right)_{i,j} = \frac{1}{h^2}\left(\chi_{i+1,j} - 2\chi_{i,j} + \chi_{i-1,j}\right) + O(h^2) \quad (44b)$$

$$\left(\frac{\partial^2\chi}{\partial x_{23}^2}\right)_{i,j} = \frac{1}{h^2}\left(\chi_{i,j+1} - 2\chi_{i,j} + \chi_{i,j-1}\right) + O(h^2)\,, \quad (44c)$$

we obtain for the discretized Schrödinger equation (Eq. (33))

$$-\frac{1}{\mu_{12}}\left(\chi_{i,j-1} + \chi_{i,j+1}\right) - \frac{1}{\mu_{23}}\left(\chi_{i-1,j} + \chi_{i+1,j}\right)$$

$$+\frac{1}{2m_2}\left(\chi_{i-1,j} - \chi_{i-1,j+1} - \chi_{i+1,j-1} + \chi_{i+1,j+1}\right)$$

$$+2\left[\frac{1}{\mu_{12}} + \frac{1}{\mu_{23}} + \hbar^{-2}\left(\left\{V_{123}\right\}_{i,j} - E_r\right)h^2\right]\chi_{i,j} = 0, \quad (45)$$

where the indices i and j denote the point of the mesh as shown in Fig. X. Again the subscript j of χ_j, denoting a particular member of the linearly independent set, has been dropped. We note that even though the Hamiltonian contains a mixed partial derivative in the kinetic term, this is not difficult to incorporate in the FD equations and does not ruin the symmetry or "bandedness" of the FD matrix, although the bandwidth increases. Furthermore, the boundary conditions are separable and it is easy to construct a uniform mesh, as we have seen in Fig. X.

It is possible to make arguments about uniqueness and convergence analogous to those given above in section C. We shall not review those here.

F. Application of the Theory to Exchange Reactions

We consider in this section two models for the exchange reaction involving three equivalent particles. Though the particles are equivalent, they are not indistinguishable since they cannot penetrate one another. We solve for the χ_j in $[X, x_{12}, x_{23}]$. Since V_{123} is symmetric about $x_{12} = x_{23}$, it is necessary to solve for only half as many χ_j's as usual. Suppose we include M channels in the truncated state expansion. Then, according to the development in section E, we need 2M linearly independent χ_j's. We find M of these using the following set of boundary conditions: $\chi_j(x_{12}, x_{23}^{(0)}) = \phi_j(x_{12})$, $\chi_j(x_{23}, x_{12}^{(0)}) \equiv 0$, $j = 1, 2, \cdots M$. For the remaining M we simply use the "reversed" set of conditions: $\chi_j(x_{12}, x_{23}^{(0)}) \equiv 0$, $\chi_j(x_{23}, x_{12}^{(0)}) = \phi_j$, $j = 1, 2, \cdots M$. But the χ_j's corresponding to the reversed conditions are identical to the first M χ_j's reflected through the line $x_{12} - x_{23} = 0$. Hence, it is necessary to determine only M χ_j's, i.e., to solve the FD equations only M times. We have done this for several model potential surfaces.

1. Infinite Square-Well Potential Surface

We consider first the simplest possible potential surface, i.e., $V_{123} \equiv 0$ inside the L-shaped reaction path and $V_{123} = \infty$ outside. Thus, each subsystem is bound by an infinite square well potential. Making the substitutions

$$x_{12} = \frac{a}{\pi} x_{12}'$$

$$x_{23} = \frac{a}{\pi} x_{23}'$$

in Eq. (32) and then multiplying both members by $(\hbar^2\pi^2/\mu_{12}a^2)^{-1}$, we obtain

$$\left\{-\frac{1}{2}\frac{\partial^2}{\partial x_{12}'^2} - \frac{1}{2}\frac{\partial^2}{\partial x_{23}'^2} + \frac{1}{(m_2/\mu_{12})}\frac{\partial^2}{\partial x_{12}'\partial x_{23}}\right\}\psi = E'\psi \tag{46}$$

where

$$E' = \frac{\mu_{12}a^2}{\hbar^2\pi^2} E_r .$$

The spectra of the two subsystems are discrete, the eigenfunctions and eigenvalues being given by

$$\phi_n = \sqrt{2/\pi}\ \sin n\, x_{12}'$$

$$\epsilon_{12}^{(n)} = n^2/2 \ , \quad \text{respectively.}$$

Energy conservation requires, as usual,

$$E' = \frac{n^2}{2} + \frac{\mu_{12}}{\mu_{12,3}} \frac{a^2}{\pi^2} \frac{k_n^2}{2} , \quad \text{where}$$

k_n is the free-particle wavenumber. Since the particles are identical, we have $m_2/\mu_{12} = 2$, $\mu_{12}/\mu_{12,3} = 3/4$. Transition probabilities have been determined for $E' = 2.125$ (two open channels), $a = \pi$, $x_{12}^{(0)} = x_{23}^{(0)} = \pi$. It was necessary to retain only two virtuals in the state expansion and five for the analysis of χ_j (see Appendix). Probabilities as a function of mesh size are given in Table V along with extrapolated values obtained using Eq. (22). Since probabilities for only four different mesh sizes were obtained, an accurate e_1^m extrapolation was not possible.

From Table V we observe that sum and time-reversal checks are good not only for individual mesh values but also for the extrapolated values. For examples, $P_{1 \to 2}^{(R)}$ and $P_{2 \to 1}^{(R)}$ differ by less than 2%, or .0006, and $P_{1 \to 2}^{(T)}$ and $P_{2 \to 1}^{(T)}$ by less than 3% (.0028).

2. Truncated Parabolic Potential Surface

A more realistic potential surface is described by the expressions

$$V_{123} = \frac{1}{2} \kappa (r_{12} - r_{120})^2 \qquad r_{23} > r_{23}^{(0)}, \quad 0 \leq r_{12} \leq a$$

$$V_{123} = \infty \qquad r_{23} > r_{23}^{(0)}, \quad r_{12} < 0, \quad r_{12} > a \qquad (47a)$$

$$V_{123} = \frac{1}{2}\,\kappa\left\{\left[(2r_{120} - r_{12})^2 + (2r_{230} - r_{23})^2\right]^{1/2} - r_{120}\right\}^2 ,$$

$$r_{12} < r_{12}^{(0)},$$

$$r_{23} < r_{23}^{(0)}$$

$$V_{123} = \infty \qquad r_{12}, r_{23} < 0 \tag{47b}$$

$$V_{123} = \frac{1}{2}\,\kappa(r_{23} - r_{230})^2 \qquad r_{12} > r_{12}^{(0)}, \quad 0 \le r_{23} \le a$$

$$V_{123} = \infty \qquad r_{12} > r_{12}^{(0)}, \quad r_{23} < 0,\ r_{23} > a, \tag{47c}$$

where $r_{120} = r_{230}$, the equilibrium separation of the two atoms of the equivalent subsystems. The potential surface described by Eqs. (47) is sketched in Fig. XI. In the asymptotic regions the potential is a truncated parabola. In the interaction region, it is generated by rotating a parabola centered at r_{120} about an axis at ($r_{12} = 2r_{120}$, $r_{23} = 2r_{230}$) perpendicular to the $r_{12} - r_{23}$ plane. With the substitutions

$$x_{12}' = \pi/a \;\, x_{12} \tag{48a}$$

$$x_{23}' = \pi/a \;\, x_{23} , \tag{48b}$$

the Schrödinger equation (32) becomes

$$\left\{-\frac{1}{2}\frac{\partial^2}{\partial x_{12}'^2}-\frac{1}{2}\frac{\partial^2}{\partial x_{23}'^2}+\frac{1}{2\gamma}\frac{\partial^2}{\partial x_{12}'\partial x_{23}'}+V_{123}'\right\}\psi = E'\psi , \qquad (49)$$

where

$$\gamma = m_2/2\mu_{12}$$

$$V_{123}' = (\hbar^2\pi^2/\mu_{12}a^2)^{-1}\, V_{123}$$

$$E' = (\hbar^2\pi^2/\mu_{12}a^2)^{-1}\, E_r ,$$

and a is the well width, i. e., truncation point. The eigenvalues and eigenfunctions of the truncated parabolic binding potential are determined using the Ritz linear variational method, expressing the trial wavefunction as a linear combination of particle-in-box eigenstates as

$$\phi_k(x_{12}) = \sqrt{2/\pi}\sum_{n=1}^{n_{max}} c_{kn} \sin n\, x_{12}' . \qquad (50)$$

Energy conservation requires, as usual,

$$(E_{K.E.})_n + \varepsilon_n = E' , \qquad (51)$$

where ε_n is the approximate eigenvalue associated with the nth eigenstate and $(E_{K.E.})_n$ is the corresponding energy of the free particle, either A or C. Since we are dealing with identical particles, the mass ratios are fixed as follows: $\mu_{12} = 1/2$; $\gamma = 1$. Reaction probabilities are given in Table VI for other system parameters arbitrarily fixed as follows: $\kappa = 10.0$; $a = \pi$; $E_r' = 5.00$; $n_{max} = 10$. For this particular energy there are two open channels; it was found sufficient to retain three virtuals in the asymptotic state expansions. The probabilities were calculated by analyzing the χ_j with values of x_{12}' or x_{23}' as far apart as possible in the asymptotic regions (see Appendix). As we can see from Table VI, the values seem to converge in a reasonable fashion, with sum and time-reversal checks improving as the mesh size decreases. Probabilities obtained by doing the χ_j analyzes at x_{12}' (x_{23}') values closer together differ little ($< 1\%$) from the values of Table VI. Also, including more functions in the variational trial function Eq. (50), i.e., taking $n_{max} > 10$, induces an insignificant change in the probabilities.

3. Untruncated Parabolic Surface

Certainly a more realistic potential surface is that described by Eqs. (47) without the truncation. In this case the binding potentials become "pure" parabolic in the asymptotic regions. In order to determine the χ_j we take the interaction region to be large enough that χ_j are negligibly small outside the L-shaped reaction path, requiring that $\chi_j \equiv 0$ outside this region (except, of course, in the asymptotic regions). Making the substitutions

$$\xi' = (\hbar/\mu_{12}\omega)^{-1/2} x_{12}$$

$$\xi = (\hbar/\mu_{12}\omega)^{-1/2} x_{23} ,$$

the Schrödinger equation (32) becomes

$$\left\{ -\frac{1}{2}\frac{\partial^2}{\partial \xi'^2} - \frac{1}{2}\frac{\partial^2}{\partial \xi^2} - \frac{1}{2}\left(-\frac{1}{\gamma}\right)\frac{\partial^2}{\partial\xi\partial\xi'} + V_{123}'\right\}\psi = E'\psi, \qquad (52)$$

where

$$\gamma = m_2/2\mu_{12}$$

$$E' = E_r/\hbar\omega$$

$$V_{123}' = V_{123}/\hbar\omega$$

$$\omega = \sqrt{\kappa/\mu}_{12} .$$

The eigenfunctions and eigenvalues of the bound states of the subsystem are given, with minor modifications, by Eqs. (31). Energy conservation may be expressed by

$$(E_{K.E.})_n + (n + 1/2) = E' , \qquad (53)$$

where, as usual, $(E_{K.E.})_n$ is the kinetic energy of the free particle, A or C. As before, since we are dealing with identical particles, the mass ratios are fixed as follows: $\mu_{12} = 1/2$, $\gamma = 1$. When we attempted to treat the reaction using the parameters $a = 10.0$, $E' = 1.75$ (two open channels), difficulties were encountered. The problem is summarized in Table VII, which lists probabilities obtained using a mesh size of .4165 (23 points across the well) and two virtual states. For this mesh size there are four pairs of values of ξ (or ξ') for which the analysis of χ_j may be carried out. Probabilities obtained using these various possible pairs are listed in the columns of Table VII. The first column corresponds to the ξ values farthest apart, the second column to ξ values next closest, etc. Clearly the various sets of probabilities disagree markedly. Column 2 seems to best satisfy sum and time reversal checks, although there is no obvious reason. We attribute this "instability" to the fact that the mesh is too coarse. For example, the finest mesh size attainable for $a = 10.0$ is $h = .325$ compared with $h = .157$ for the coarsest mesh used in the treatment of the truncated parabolic surface. One might reasonably expect an improvement using finer meshes. Addition of more virtuals in either the state expansion or χ_j analysis did not alter the columns of Table VII appreciably. Although there is no really sound reason to favor column 2, we would expect columns 3 and 4 to be more in error since the analysis matrix (see Appendix) may be ill-conditioned for ξ values too near one another.

G. Discussion

We have presented a quite general method for the quantum mechanical treatment of the inelastic collision of composite particles. The essential feature of the method consists of forming the complete stationary wavefunction describing the collision by taking a linear combination of members of a set of linearly independent functions, each member of the set satisfying the relevant Schrödinger equation in addition to an arbitrary boundary condition specified in the asymptotic region. We have shown that the functions of the linearly independent set may be found using the finite-difference method; that the finite-difference equations may be quickly and accurately solved by the McCormick subroutine.

Two examples of one-dimensional impulsive collisions have been treated and in one case, the free-particle-harmonic-oscillator collision, the results agree well with previously published results.

By a simple extension of the theory we have been able to treat an important special class of chemical reactions - exchange reactions. We have obtained very reasonable results for the reaction probabilities on several model potential surfaces for constrained linear electronically adiabatic encounters. As far as we know, this is the first direct quantum mechanical treatment of exchange reactions. The crucial feature of our method is that it avoids the difficulty of the usual state expansion

$$\psi = \sum_j \phi_j f_j , \qquad (54)$$

where ϕ_j are eigenfunctions of the initially bound pair BC and f_j are arbitrary functions of the coordinate of the incoming particle A relative to the center of mass of the bound pair. The difficulty is that the ϕ_j do not form a complete set over the whole reaction space and hence ψ cannot be everywhere expressed as in Eq. (54). In our method it is not necessary to expand the functions χ_j in any particular set, except in either asymptotic region where expansions (39) are valid.

The success of our method in the treatment of impulsive collisions indicates that it should be generally useful, although there are several difficulties. For long-range interaction potentials the FD equations must be solved over a large interaction region. For vibrational excitations, this may pose no problem, since, as we found for the free-particle-harmonic-oscillator collision, it may be possible to obtain convergence of transition probabilities using relatively crude meshes. However, from our results on the parabolic potential surface, it is clear that large interaction regions may lead to a type of "instability" or, at least, inconsistency in the treatment of exchange reactions. It may be possible to circumvent this difficulty by using a small interaction region, specifying the boundary condition in the "near asymptotic" region and then extending the solution into the asymptotic region by the WKB method (assuming the potential is essentially separable in the "near asymptotic" region).

A possibly very useful application of our method would be an investigation of a parametrized potential surface to determine which regions most influence reaction probabilities for a given incident total energy. Such a parametrized surface has been studied classically by Wall and Porter.[21] It would be interesting to compare our results with quantum mechanical approximations and with the classical results. This should give us an idea of the importance of quantum effects and conditions under which these other approximations are reliable.

It does not appear to be practical to apply our method directly to three-dimensional problems, since the number of FD equations increases as $(a/h - 1)^n$, where a is the range of each variable, h is the mesh size, and n is the number of variables. Thus, for a three-dimensional two-particle problem, one would be required to solve 10^6 simultaneous equations for $a = 10.0$ and $h = 10/11$, a very crude mesh. This is a formidable task even if the FD matrix is banded. However, it may be possible to solve the problem indirectly by using a state expansion of the form of Eq. (54). For instance, suppose we are interested in the collision of two diatomic molecules. Following Takayanagi's[1] formal treatment, we expand the total scattering wavefunction Ψ as

$$\Psi = \sum_{j\nu\lambda} f(j,\nu,\lambda|k_\lambda, R)R^{-1}\xi(j,\nu,\lambda|\theta,\phi,r_1,\theta_1,\phi_1,\chi_1,r_2,\theta_2,\phi_2,\chi_2) \tag{55}$$

where R is the distance between centers-of-mass of the molecules, ξ are vibrational-rotational functions for the free molecules, characterized by quantum numbers j, ν, and λ. We obtain an infinite set of coupled equations for the f's by making use of the orthonormality of the various factors in Ψ. These equations may be expressed as

$$\frac{\hbar^2}{2M}\left\{\frac{d^2}{dR^2} - \frac{j(j+1)}{R^2} + k_\lambda{}^2\right\} f(j, \nu, \lambda | k_\lambda, R) =$$

$$\sum_{j', \nu', \lambda'} V_{j\nu\lambda j'\nu'\lambda'} f(j', \nu', \lambda' | k_{\lambda'}, R) . \tag{56}$$

Our approach to the solution of this set of coupled equations would be as follows. Having truncated the expansion in j', ν', and λ', we would solve the FD equations to obtain sets of f's corresponding to independent boundary conditions specified in the asymptotic region. Then we would take an appropriate linear combination of these sets to satisfy the asymptotic condition on the total wavefunction Ψ. Unfortunately, the FD matrix is symmetric but unbanded. However, the total number of FD equations should be given by the product of the number of states retained in Eq. (56) by the number of mesh points, there being only one variable R. If one can tolerate a paucity of both mesh points and expansion states, it may be relatively easy to solve the coupled FD equations.

H. Appendix

If we multiply Eq. (7a) by $\phi_k{}^*$ and integrate with respect to y from $-\infty$ to ∞, we obtain (for $k \leq N$)

$$A_k^{(j)}e^{-ik_kx} + \bar{A}_k^{(j)}e^{+ik_kx} = \int_{-\infty}^{\infty} \phi_k{}^*(y)\chi_j(x, y)dy = f_k^{(j)}(x). \qquad \text{(A1)}$$

A similar equation involving the virtual coefficients $B_k^{(j)}$ and $\bar{B}_k^{(j)}$ may be obtained if $k > N$. Choosing two different values of x, say x_1 and x_2, in the asymptotic region $(x > x_o)$ gives us two simultaneous linear equations from which to determine $A_k^{(j)}$ and $\bar{A}_k^{(j)}$. We have, dropping the subscript k and superscript j,

$$A\ e^{-ikx_1} + \bar{A}\ e^{+ikx_1} = f(x_1) \qquad \text{(A2a)}$$

$$A\ e^{-ikx_2} + \bar{A}\ e^{+ikx_2} = f(x_2)\ , \qquad \text{(A2b)}$$

where the integrals f are evaluated using the extended Simpson's rule as discussed in section C. Eqs. (A2) can be solved trivially using Cramer's rule:

$$A = (f(x_1)e^{+ikx_2} - f(x_2)e^{+ikx_1})/(e^{-ik(x_1-x_2)} - e^{+ik(x_1-x_2)}) \qquad \text{(A3a)}$$

$$\bar{A} = (f(x_2)e^{-ikx_1} - f(x_1)e^{-ikx_2})/(e^{-ik(x_1-x_2)} - e^{+ik(x_1-x_2)}). \qquad \text{(A3b)}$$

Clearly from Eqs. (A3),

$$A^* = \bar{A} . \tag{A4}$$

Repeated evaluations of A and $\bar{A}$ using different pairs of values of x agree to 1 or 2% (depending on the mesh size) for the cases of vibrational excitation treated in section D.

We now consider the more complicated analysis of the χ_j for the case of exchange reactions. Upon multiplying Eq. (36a) by ϕ_k^* and integrating with respect to x_{12} over all space, we arrive at the following equation

$$\sum_{\ell=1}^{N} [I_{k\ell}(x_{23})A_\ell^{(j)} + I_{k\ell}^*(x_{23})\bar{A}_\ell^{(j)}] + \sum_{\ell>N} [H_{k\ell}(x_{23})B_\ell^{(j)} + G_{k\ell}(x_{23})\bar{B}_\ell^{(j)}] = g_k^{(j)}(x_{23}), \quad k = 1, 2, 3, \ldots, \tag{A5}$$

where

$$I_{k\ell} = \int_{-\infty}^{\infty} \phi_k^*(x_{12})\, \phi_\ell(x_{12})\, e^{-ik_\ell \alpha x_{12}}\, dx_{12} \cdot e^{-ik_\ell x_{23}}, \tag{A6a}$$

$$H_{k\ell} = \int_{-\infty}^{\infty} \phi_k^*(x_{12})\, \phi_\ell(x_{12})\, e^{-k_\ell \alpha x_{12}}\, dx_{12} \cdot e^{-k_\ell x_{23}}, \tag{A6b}$$

$$G_{k\ell} = \int_{-\infty}^{\infty} \phi_k^*(x_{12})\, \phi_\ell(x_{12})\, e^{+k_\ell \alpha x_{12}}\, dx_{12} \cdot e^{+k_\ell x_{23}}, \tag{A6c}$$

and

$$g_k^{(j)}(x_{23}) = \int_{-\infty}^{\infty} \phi_k^*(x_{12})\, \chi_j(x_{12}, x_{23})\, dx_{12} \,. \qquad (A6d)$$

We note that Eq. (A5) is, in fact, a set of simultaneous equations involving all the unknown coefficients. We solve this set of equations by truncating the expansions in ℓ and k and then adding successively more terms until convergence of the coefficients is achieved. If we retain n terms in the ℓ expansion, then we have n equations (obtained by taking inner products with ϕ_k, k = 1, 2, ... n) in 2n unknown, there being an "unbarred" and "barred" unknown for each of the n terms. Hence, we secure two equations per k by choosing two different values of x_{23}, as we did above. A similar analysis of χ_j for the $\alpha_\ell^{(j)}$, etc., may be carried out.

For the model exchange reactions discussed in section D we have found it necessary to take n equal to 5 or 6 (using a computer subroutine CSLECD which solves systems of equations with complex coefficients) for a four-channel (two open, two virtual) state expansion of χ_j. Analyses using different pairs of x_{23} (or x_{12}) values vary considerably depending on mesh size, as the examples treated in section F demonstrate.

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16. Let $\left\{\phi_i(E_r)\right\}$ be the set of *exact* solutions of the Schrödinger equation corresponding to linearly independent boundary conditions (labeled by index i) specified in the asymptotic region. Then this set $\left\{\phi_i(E_r)\right\}$ is complete in the sense that any "well-behaved" function, e.g., ξ_k, may be expanded as a linear combination of the $\phi_i(E_r)$.

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TABLE I

Transition Probabilities as a Function of Mesh Size for Impulsive Collision of Free Particle with Particle Bound in Infinite Square Well ($E' = 2.25$; Number of Virtuals = 1; $a = \pi$; $m_A/m_B = 1$)

Mesh size	$P_{1\rightarrow 1}$	$P_{1\rightarrow 2}$	$P_{1\rightarrow 1} + P_{1\rightarrow 2}$
.1745	.5468	.4463	.9931
.1571	.5498	.4446	.9944
.1428	.5521	.4433	.9954
.1309	.5538	.4423	.9961
.1208	.5552	.4415	.9967
Extrapolated value	.5606	.4387	.9993
	$P_{2\rightarrow 1}$	$P_{2\rightarrow 2}$	$P_{2\rightarrow 1} + P_{2\rightarrow 2}$
.1745	.4602	.5468	1.0070
.1571	.4557	.5499	1.0056
.1428	.4524	.5522	1.0046
.1309	.4500	.5539	1.0039
.1208	.4480	.5552	1.0032
Extrapolated value	.4399	.5607	1.0007

TABLE II

Transition Probabilities as a Function of Mesh Size for Impulsive Collision of a Free Particle with a Particle Bound in an Infinite Square Well ($E' = 4.75$; Number of Virtuals = 1; $a = \pi$; $m_A/m_B = 1$)

Mesh size	$P_{1\to1}$	$P_{1\to2}$	$P_{1\to3}$	$\sum P_{1\to i}$
.1745	.6126	.1281	.2470	.9877
.1571	.6121	.1304	.2475	.9900
.1428	.6115	.1325	.2477	.9917
.1309	.6108	.1345	.2477	.9930
.1208	.6103	.1362	.2477	.9942
Extrapolated value	.6072	.1466	.2477	1.0015
	$P_{2\to1}$	$P_{2\to2}$	$P_{2\to3}$	$\sum P_{2\to i}$
.1745	.1321	.6069	.2564	.9954
.1571	.1337	.6050	.2576	.9963
.1428	.1353	.6034	.2583	.9970
.1309	.1368	.6019	.2587	.9974
.1208	.1382	.6008	.2588	.9978
Extrapolated value	.1473	.5965	.2588	1.0026
	$P_{3\to1}$	$P_{3\to2}$	$P_{3\to3}$	$\sum P_{3\to i}$
.1745	.2681	.2698	.4796	1.0175
.1571	.2645	.2684	.4812	1.0141
.1428	.2617	.2673	.4827	1.0117
.1309	.2594	.2662	.4841	1.0097
.1208	.2575	.2652	.4855	1.0082
Extrapolated value	.2461	.2529	.5010[a]	1.0000

[a] This value is obtained by difference from $P_{3\to1}$, $P_{3\to2}$, since extrapolation on such rapidly varying values gave faulty results.

TABLE III

Extrapolated Transition Probabilities for Hard-Sphere-Harmonic Oscillator Collision (E = 1.75; Number of Virtuals = 2; a = 10.0; m/M = 1/2)

Final State Incident State	1	2
1	.4941	.5044
2	.5084	.4941

TABLE IV

Extrapolated Transition Probabilities for Hard-Sphere-Harmonic Oscillator Collision (E = 2.75; Number of Virtuals = 2; a = 10.0; m/M = 1/2)

Final State Incident State	1	2	3
1	.0014	.5903	.3981
2	.5988	.1595	.2414
3	.4059	.2480	.3506

TABLE V

Reaction Probabilities as a Function of Mesh Size for Square-Well Binding Potentials ($a = \pi$; $E' = 2.125$; Number of Virtual Channels = 2)

Mesh size	$P^{(R)}_{1\to 1}$	$P^{(R)}_{1\to 2}$	$P^{(T)}_{1\to 1}$	$P^{(T)}_{1\to 2}$	$\sum\limits_{T,R,i=1}^{2} P_{1\to i}$
.1571	.7673	.0249	.1178	.0859	.9959
.1308	.7590	.0267	.1208	.0911	.9976
.1122	.7539	.0279	.1225	.0943	.9986
.0982	.7509	.0286	.1237	.0965	.9997
Extrapolated value	.7404	.0306	.1264	.1042	1.0016
	$P^{(R)}_{2\to 1}$	$P^{(R)}_{2\to 2}$	$P^{(T)}_{2\to 1}$	$P^{(T)}_{2\to 2}$	$\sum\limits_{T,R,i=1}^{2} P_{2\to i}$
.1571	.0251	.4398	.0942	.4453	1.0054
.1308	.0268	.4429	.0960	.4369	1.0026
.1122	.0278	.4451	.0971	.4314	1.0014
.0982	.0284	.4466	.0978	.4277	1.0005
Extrapolated value	.0300	.4562	.1014	.4116	.9992

TABLE VI

Reaction Probabilities as a Function of Mesh Size for Truncated Parabolic Surface ($\varkappa = 10.0$; $E' = 5.0$; $a = \pi$; Number of Virtual Channels = 3)

Mesh size	$P^{(R)}_{1\to 1}$	$P^{(R)}_{1\to 2}$	$P^{(T)}_{1\to 1}$	$P^{(T)}_{1\to 2}$	$\sum\limits_{T,R,i} P_{1\to i}$
.1571	.0455	.1134	.6489	.1774	.9852
.1308	.0538	.1196	.6327	.1832	.9893
.1122	.0595	.1233	.6224	.1865	.9917
.0982	.0635	.1256	.6156	.1885	.9932
Extrapolated value	.0779	.1326	.5932	.1939	.9976

	$P^{(R)}_{2\to 1}$	$P^{(R)}_{2\to 2}$	$P^{(T)}_{2\to 1}$	$P^{(T)}_{2\to 2}$	$\sum\limits_{T,R,i} P_{2\to i}$
.1571	.1178	.4271	.2048	.2673	1.0170
.1308	.1230	.4177	.2022	.2688	1.0117
.1122	.1262	.4118	.2007	.2701	1.0088
.0982	.1282	.4079	.1997	.2712	1.0070
Extrapolated value	.1347	.3958	.1958	.2753	1.0016

TABLE VII

Transition Probabilities for the Untruncated Parabolic Surface ($a = 10.0$; $E_r' = 1.75$; $h = .4165$; Number of Virtual Channels = 2). The Columns Correspond to Various Analyses of χ_j as Discussed in Text

Transition Probability	1	2	3	4
$P^{(R)}_{1\to 1}$	.000667	.000611	.000915	.00103
$P^{(R)}_{1\to 2}$	.003135	.002430	.001429	.00840
$P^{(T)}_{1\to 1}$	.724909	.712349	.698335	.68557
$P^{(T)}_{1\to 2}$	.256870	.283050	.314947	.34546
$\sum_{R,T,i} P_{1\to i}$	.995581	.998440	1.015626	1.04146
$P^{(R)}_{2\to 1}$	.000306	.001567	.002316	.00268
$P^{(R)}_{2\to 2}$	.005751	.005947	.004405	.00277
$P^{(T)}_{2\to 1}$	.292969	.287198	.283838	.28214
$P^{(T)}_{2\to 2}$	.719046	.707013	.694846	.68384
$\sum_{R,T,i} P_{2\to i}$	1.018072	1.001725	.985405	.97143

Figure I

Diagram of the colinear collision of an atom (m_3) with a diatomic molecule (m_1 - m_2) showing relation between coordinate systems.

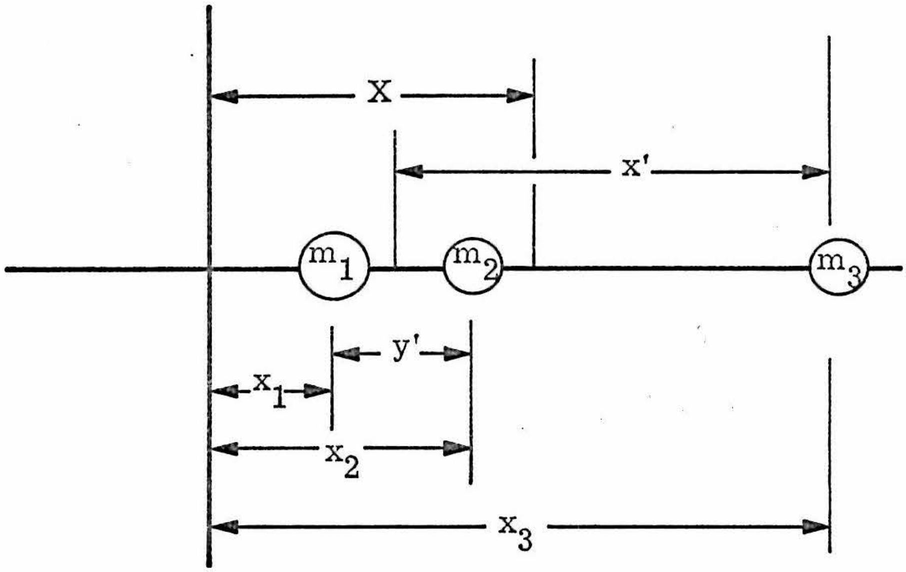
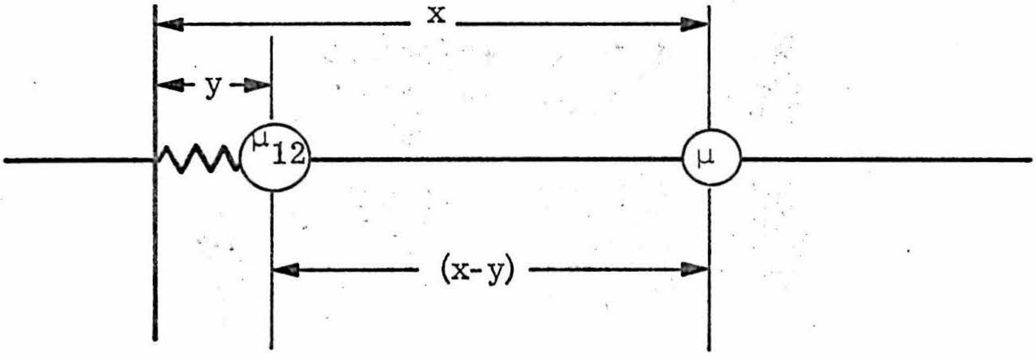
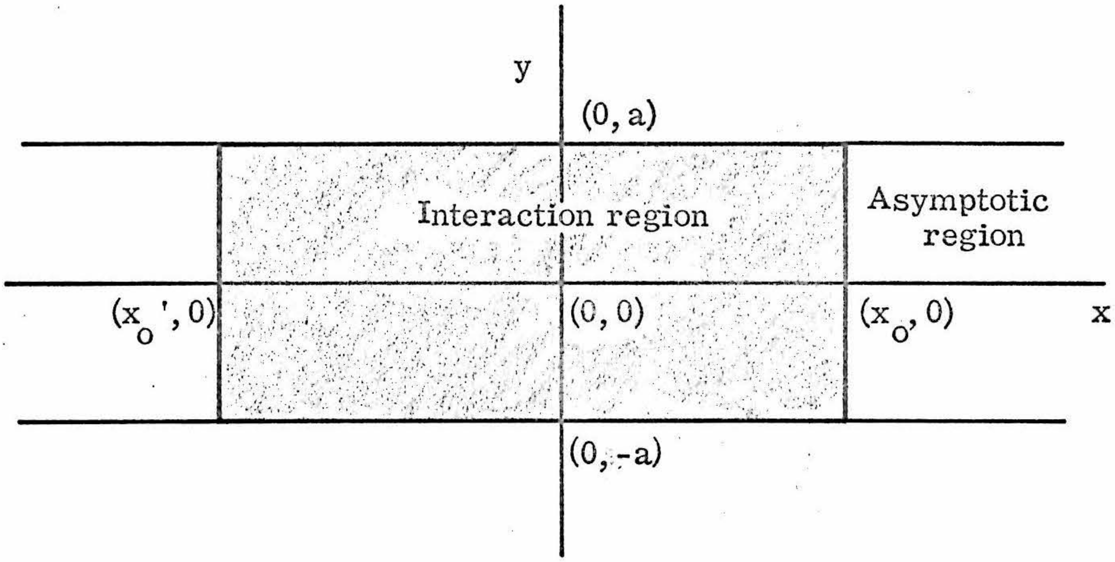

X
x'
m1
m2
m3
y'
x1
x2
x3

Figure II

(a) Diagram of a collision of a free particle with a particle bound to a fixed center of force. (b) Schematic showing boundary conditions and interaction (inseparable) region for collision diagrammed in (a).



(a)



(b)

Figure III

Finite-difference mesh used in the solution of the atom-diatomic collision problem.

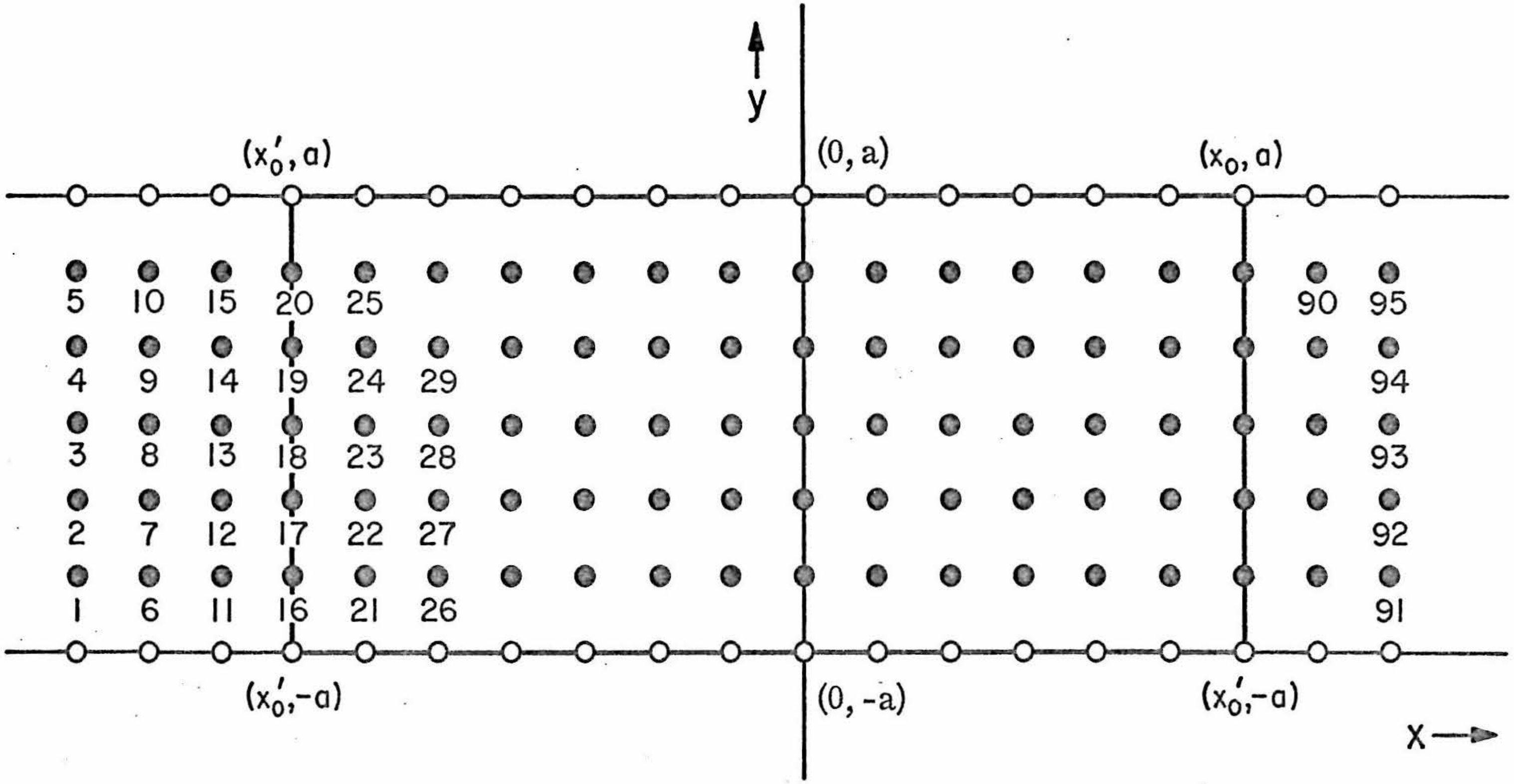
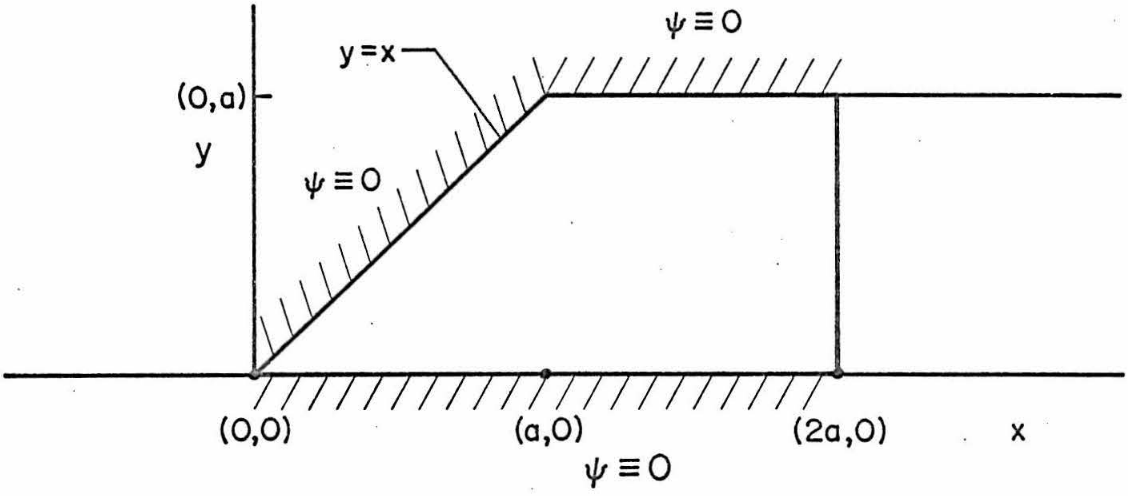

y
(x_0', a)
$(0, a)$
(x_0, a)
5
10
15
20
25
90
95
4
9
14
19
24
29
94
3
8
13
18
23
28
93
2
7
12
17
22
27
92
1
6
11
16
21
26
91
$(x_0', -a)$
$(0, -a)$
$(x_0', -a)$
X

Figure IV

Schematic of the coordinate system and boundary conditions for the impulsive collision of a free particle with a particle bound to a fixed equilibrium position.



ψ ≡ 0
y = x
(0,a)
y
ψ ≡ 0
(0,0)
(a,0)
(2a,0)
x
ψ ≡ 0

Figure V

Transition probability v. s. number of mesh points across the well (y' coordinate) for the impulsive collision of a particle bound in an infinite square well with a free particle (incident energy $E' = 2.25$; number of virtuals in state expansion $(N - M) = 1$; well width $a = \pi$; $m_A/m_B = 1$).

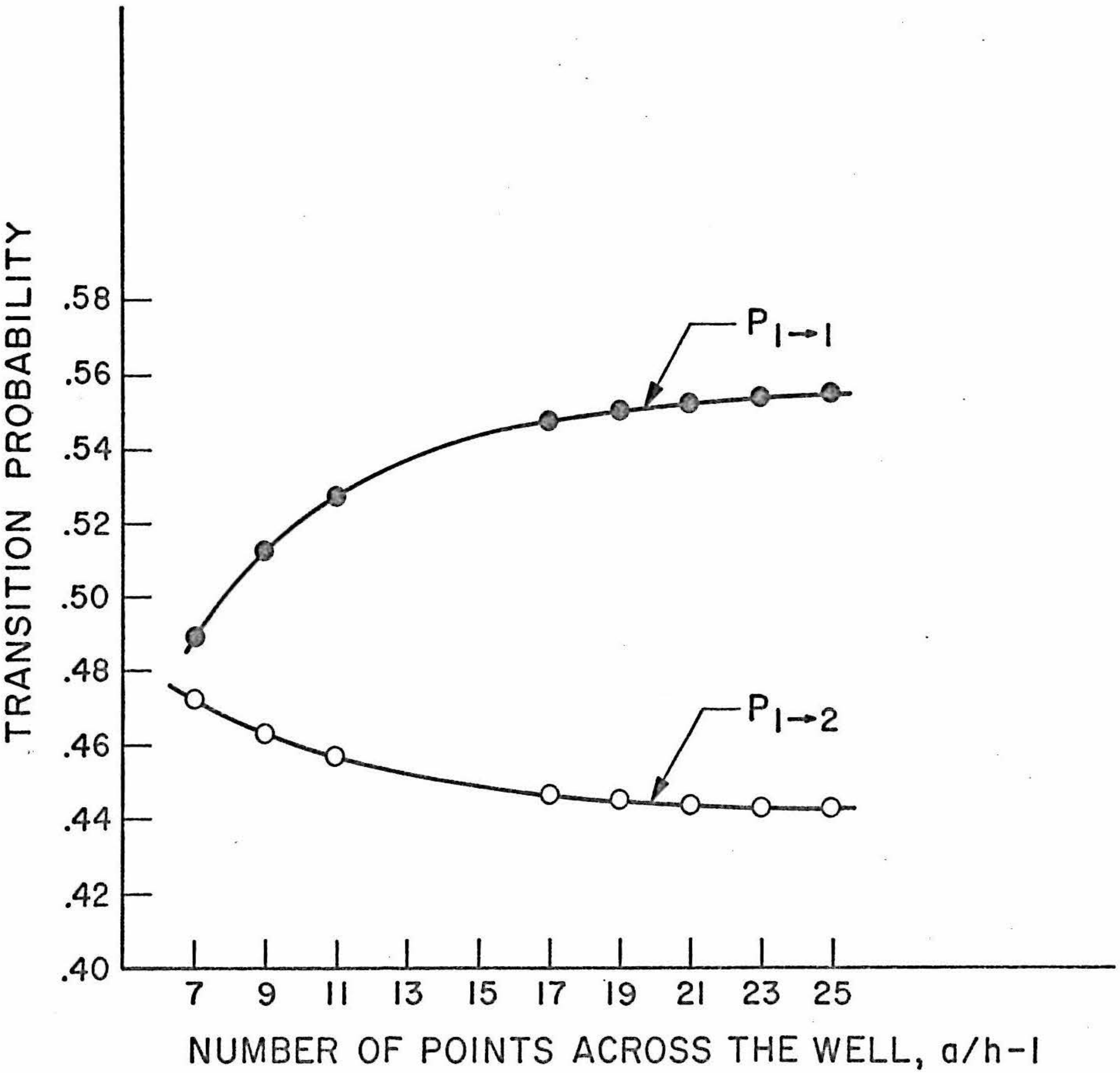

TRANSITION PROBABILITY
.58
.56
.54
.52
.50
.48
.46
.44
.42
.40
$P_{1\rightarrow 1}$
$P_{1\rightarrow 2}$
7
9
11
13
15
17
19
21
23
25
NUMBER OF POINTS ACROSS THE WELL, a/h-1

Figure VI

Transition probability v. s. total incident energy for the impulsive harmonic-oscillator-free-particle collision.

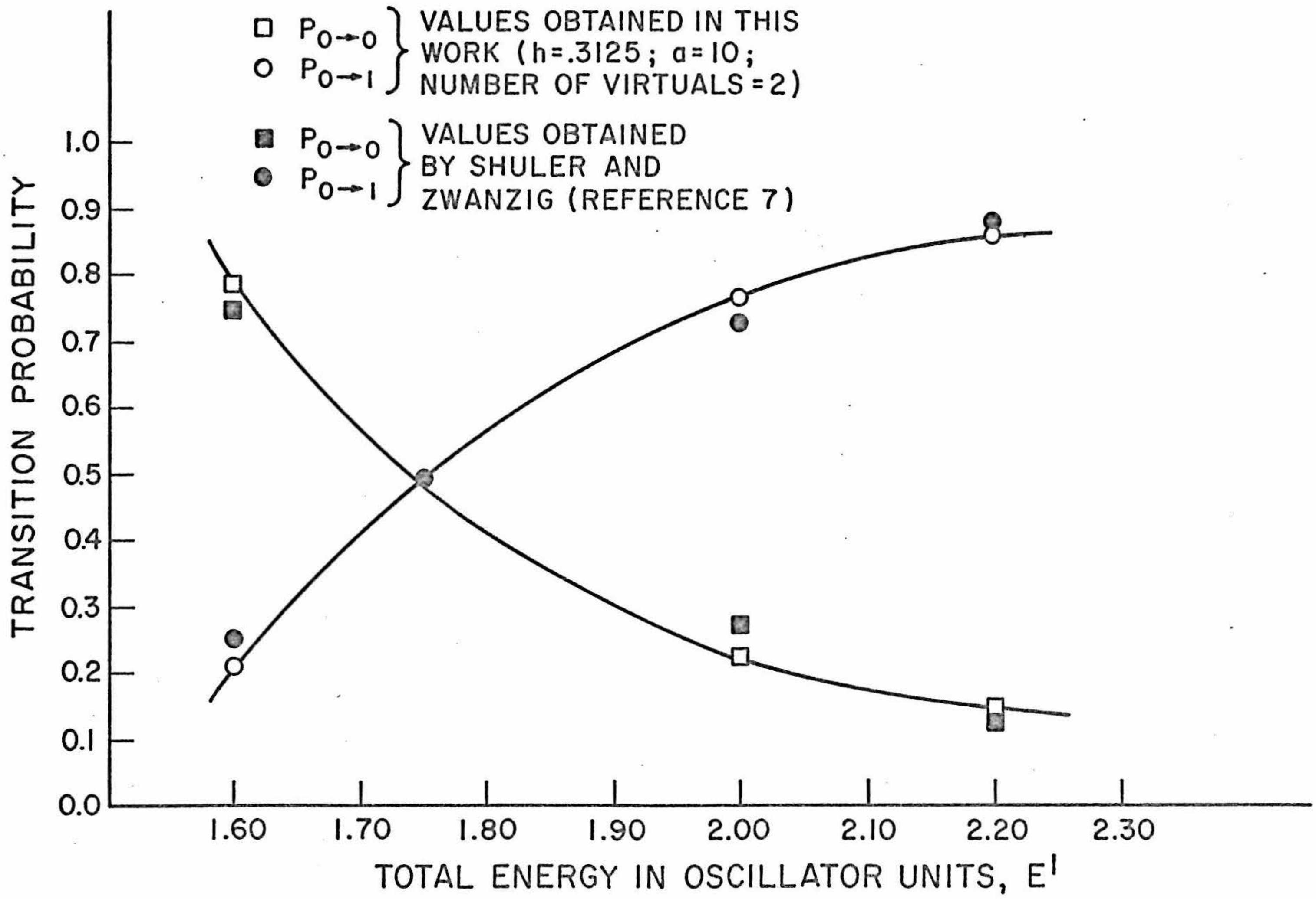

□ $P_{0\to 0}$
○ $P_{0\to 1}$
VALUES OBTAINED IN THIS WORK (h=.3125; a=10; NUMBER OF VIRTUALS=2)
■ $P_{0\to 0}$
● $P_{0\to 1}$
VALUES OBTAINED BY SHULER AND ZWANZIG (REFERENCE 7)
TRANSITION PROBABILITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1.60
1.70
1.80
1.90
2.00
2.10
2.20
2.30
TOTAL ENERGY IN OSCILLATOR UNITS, E'

Figure VII

Execution time v. s. number of mesh points across the well for the computation of transition probabilities in the impulsive harmonic-oscillator-free-particle collision.

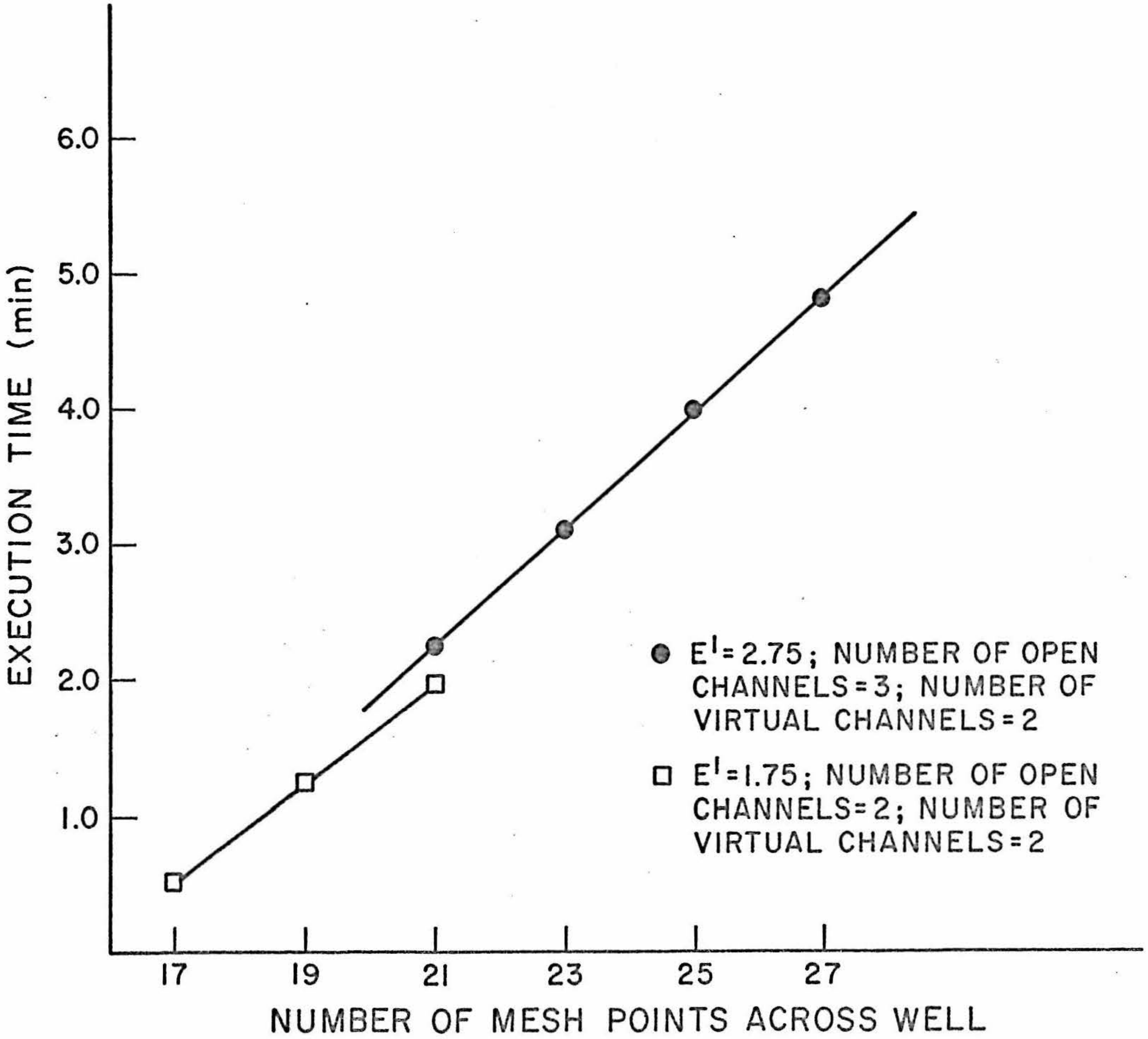

6.0
5.0
4.0
3.0
2.0
1.0
EXECUTION TIME (min)
17
19
21
23
25
27
NUMBER OF MESH POINTS ACROSS WELL
● $E^I = 2.75$; NUMBER OF OPEN CHANNELS = 3; NUMBER OF VIRTUAL CHANNELS = 2
□ $E^I = 1.75$; NUMBER OF OPEN CHANNELS = 2; NUMBER OF VIRTUAL CHANNELS = 2

Figure VIII

Diagram of exchange reaction $A + BC \rightarrow AB + C$.

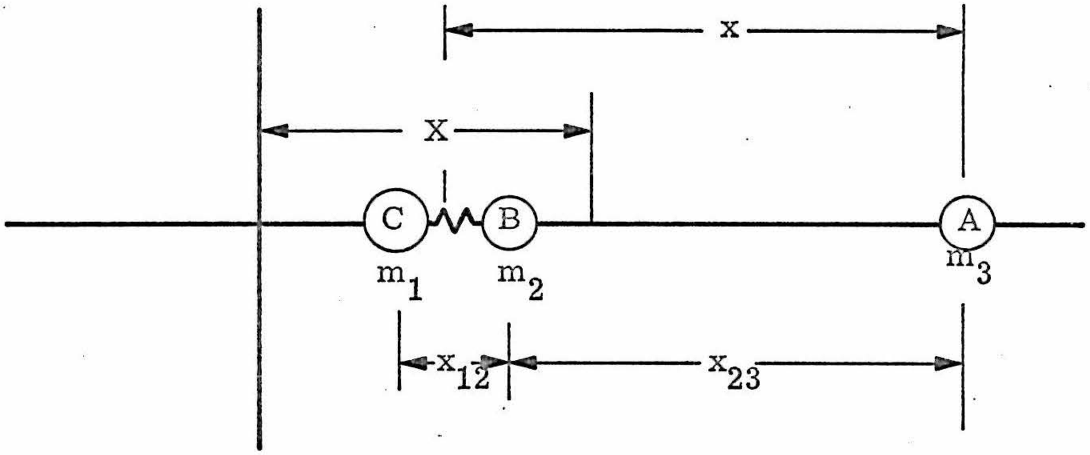
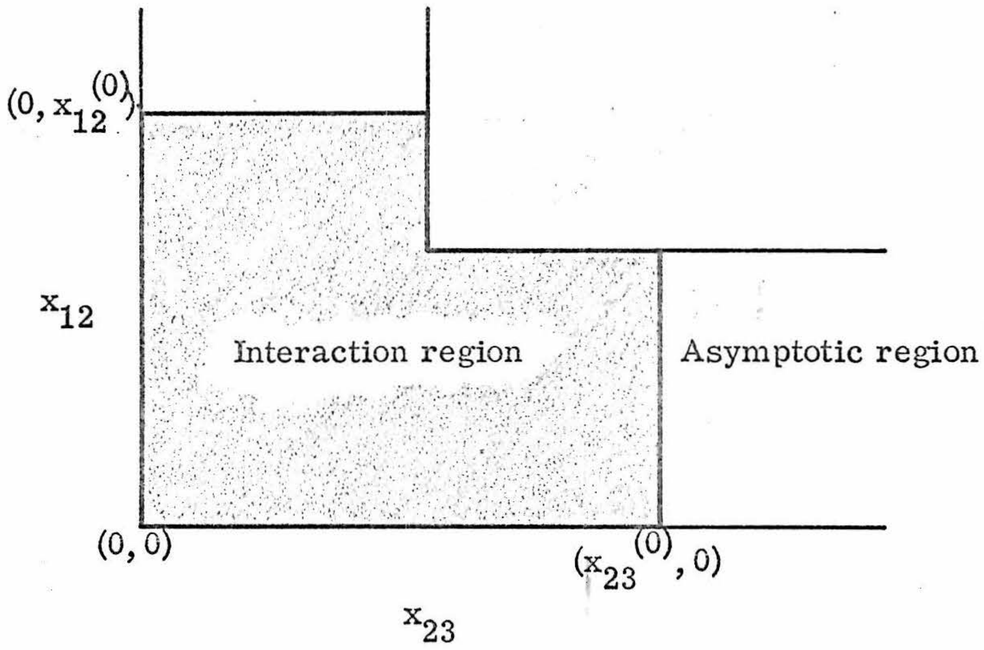
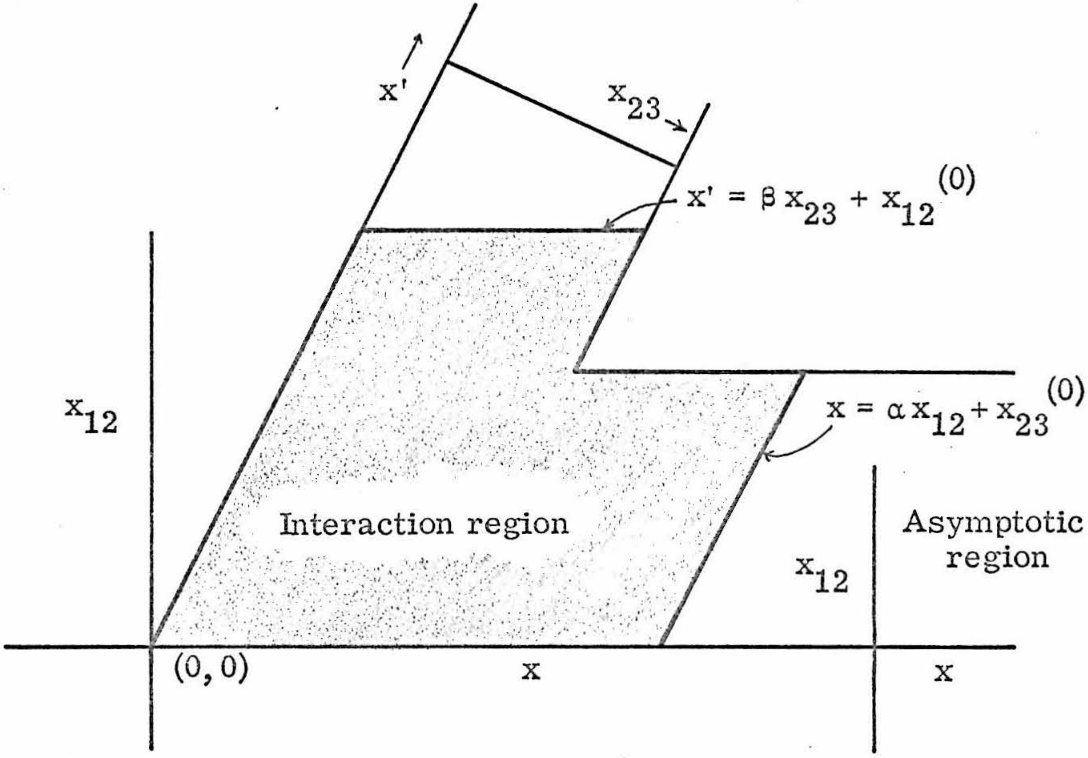

x
X
C
B
A
m$_1$
m$_2$
m$_3$
x$_{12}$
x$_{23}$

Figure IX

Coordinate systems used in the treatment of exchange reactions showing boundary conditions and the interaction region: (a) $[X, x_{12}, x_{23}]$; (b) $[X, x, x_{12}]$.


(0, $x_{12}^{(0)}$)
x_{12}
Interaction region
Asymptotic region
(0, 0)
($x_{23}^{(0)}$, 0)
x_{23}

(a)


x'
x_{23}
$x' = \beta x_{23} + x_{12}^{(0)}$
x_{12}
$x = \alpha x_{12} + x_{23}^{(0)}$
Interaction region
Asymptotic region
x_{12}
(0, 0)
x
x

(b)

Figure X

Finite-difference mesh used in the treatment of exchange reactions in the coordinate system $[X, x_{12}, x_{23}]$.

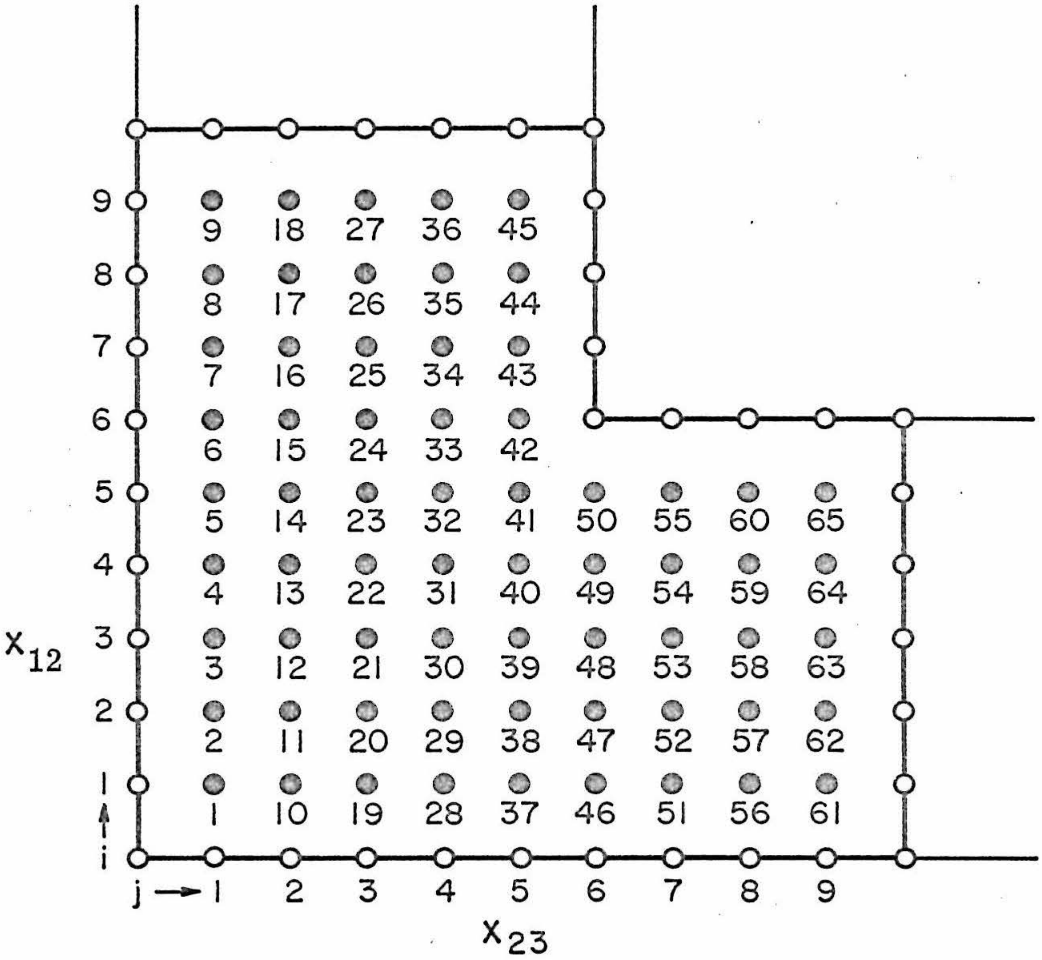
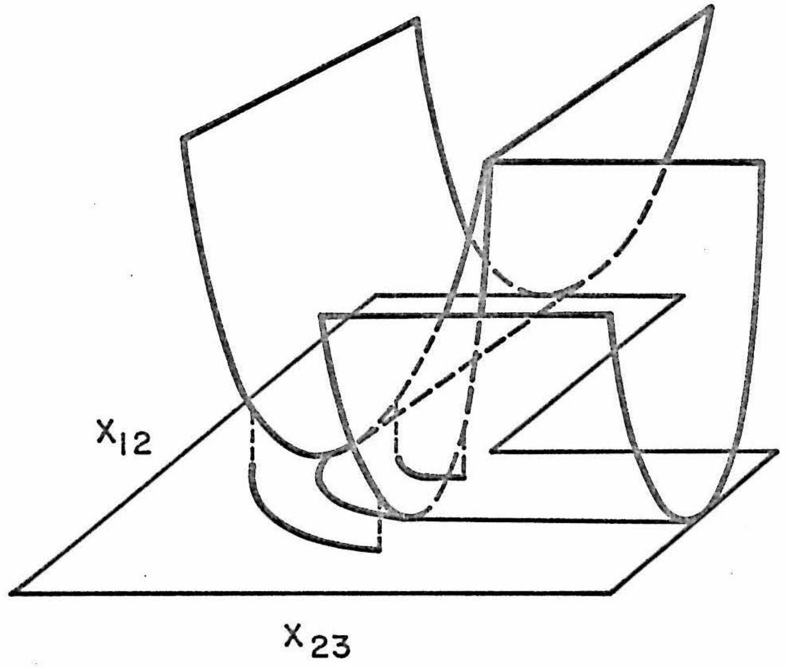

9
18
27
36
45
8
17
26
35
44
7
16
25
34
43
6
15
24
33
42
5
14
23
32
41
50
55
60
65
4
13
22
31
40
49
54
59
64
3
12
21
30
39
48
53
58
63
2
11
20
29
38
47
52
57
62
1
10
19
28
37
46
51
56
61
X_{12}
i
j
1 2 3 4 5 6 7 8 9
X_{23}

Figure XI

Sketch of truncated parabolic surface for model exchange reaction.


X_{12}
X_{23}

Abstract of Propositions

I. An improved model for physical adsorption on metal surfaces is presented and discussed. It is proposed that the model be tested by calculating heats of adsorption of nitrogen on three different copper crystal faces for which reliable experimental data are available.

II. An initial-value method of calculating quantum-mechanical transition probabilities for inelastic collisions is presented. A perturbation method for solving the coupled equations to various orders in a "cutoff" parameter is proposed.

III. A semiclassical theory of radiationless transitions is proposed. The theory views the relaxation of an electronically excited solute molecule as a transition between zero-order nonstationary states induced by a time-dependent perturbation caused by solute-solvent Coulomb interactions. The translational motion of the molecules is treated classically and the internal degrees of freedom quantum mechanically. Two model studies designed to compare the effect of various parameters of the classical motion on the transition probability are proposed.

IV. A method for treating the collisional transfer of energy between vibrational and electronic degrees of freedom is proposed. The central feature of the method, which remedies several defects of a previous treatment, is that it treats only the electronic motion of the vibrator adiabatically. This is believed to be a reasonable approximation since the vibrator is not undergoing a change of electronic state. It is proposed that the transition probabilities be found by the initial-value method outlined in Proposition II.

V. It is proposed that the relaxation (including reaction) of an initial distribution of reactant molecules among various quantum levels be investigated. The transition rates W_{nm} depend explicitly on concentration so that the relaxation equations are nonlinear. After outlining the general theory, we derive the relaxation equations for a displacement reaction and briefly discuss methods of solution.

Proposition I

An improved model for physical adsorption on metal surfaces is presented and discussed. It is proposed that the model be tested by calculating heats of adsorption of nitrogen on three different copper crystal faces for which reliable experimental data are available.

It seems apparent that not a great deal is understood about forces between isolated pairs of atoms and molecules and even less about the interaction of atoms and molecules with surfaces, wherein the interaction among large collections of particles complicates the problem. The particular case of physical adsorption on metal surfaces is of great interest. Gurney[1] has discussed the theory of electrical double layers in terms of one-dimensional systems of potential wells representing the metal and adsorbate. Gomer and Swanson[2] have recently elaborated on this model in conjunction with a theory of field desorption.

Lennard-Jones[3] had earlier viewed the van der Waals attraction of a molecule to a metal surface in terms of the interaction of instantaneous dipoles formed between the electrons and their images in the metal. Bardeen[4] and Margenau and Pollard[5], objecting that Lennard-Jones' model assumed instantaneous relaxation of the metal electrons and that it neglected their quantum-mechanical behavior, developed their respective models. Bardeen presented a general method for the approximate calculation of dispersion forces between two arbitrary systems. The method of Margenau and Pollard regards the metal as composed of polarizable volume elements and the total interaction of metal and molecule is expressed as a sum of dipole-dipole induced interactions over the volume of the metal.

All of the theories discussed above seem to suffer from the disadvantage of not considering the internal structure of the metal in detail, a factor which may be of considerable importance in the process of physical adsorption. It is therefore proposed that a new approach, which is based on an extant model for metals and which also explicitly takes into account the structure of the metal, be investigated. In the following paragraphs the general model will be discussed and then a specific proposal made to test the worth of the model.

As a zeroth-order approximation the Sommerfeld theory of metals will be assumed, in which one valence electron from each atom is in a non-localized state belonging to the metal as a whole and the remaining electrons are localized. It is further assumed that for the delocalized electrons the potential is zero inside the metal and infinite outside. Thus, for a metal in the shape of a cube of edge a, the wave function for the free-electron gas is given by

$$\psi_{FE} = A\left\{ \prod_{n_i \ell_i m_i} \sin\frac{n_i \pi x_i}{a} \sin\frac{\ell_i \pi y_i}{a} \sin\frac{m_i \pi z_i}{a} \right\} . \qquad (1)$$

Hence, the metal appears as a lattice of positive ions in a uniformly dense electron gas. This implies that an electric field will exist outside the metal which is non-uniform and depends on the structure of the lattice.

Consider an arbitrary array of lattice points in the half-space $z > 0$. For points $z < -\varepsilon < 0$, the electric field is given by

$$\vec{E}(\vec{r}) = \vec{E}^{-}(\vec{r}) + \vec{E}^{+}(\vec{r}) \tag{2a}$$

$$\vec{E}(\vec{r}) = \int \frac{\rho(\vec{r}\,')(\vec{r} - \vec{r}\,')\,dv'}{|\vec{r} - \vec{r}\,'|^{3}} + \sum_{j=1}^{N} \frac{e(\vec{r} - \vec{r}_j^{\,+})}{|\vec{r} - \vec{r}_j^{\,+}|^{3}}, \tag{2b}$$

where ρ is the electron density, $\vec{r}$ is the radius vector to the field point, and $\vec{r}_i^{\,+}$ is the radius vector locating the ith lattice point. Note that since ρ is constant the integral $\vec{E}^{-}(\vec{r})$ will be constant for a very large volume of metal. Therefore the variations in the surface electric field will be determined only by the positive lattice. For example, for a simple cubic lattice of $8n^3$ atoms, the z-component of the electric field will be given by

$$E_z^{+}(\vec{r}) = e \sum_{k=-n}^{n} \sum_{\ell=-n}^{n} \sum_{m=0}^{2n} \frac{(z - m\alpha)}{\left\{(x - k\alpha)^2 + (y - \ell\alpha)^2 + (z - m\alpha)\right\}^{3/2}}, \tag{3}$$

where α is the lattice spacing. Hence, it is seen that the field component perpendicular to the metal surface will vary as a function of the coordinates (x, y, z) of the field point in a manner that reflects the structure of the lattice. An atom or molecule in the vicinity of the surface will thus be polarized and the resulting dipole attracted toward the surface where it will reside in a region of lower energy. The properties of the adsorbed species and of the adsorption process may then be calculated using quantum and statistical mechanics.

It is suggested that this theory be applied to a specific case for which reasonably reliable experimental data are available. Rhodin[6] has reported results for the adsorption of nitrogen on very clean, regular copper crystal faces at coverages low enough that lateral interactions among the adsorbed molecules are negligible. He found that the heats of adsorption are -1800, -2000, -2200 cal/mole on the (100), (110), and (111) faces, respectively. As a zeroth-order approximation, the potential energy of a nitrogen molecule near the metal surface can be expressed as

$$V(\vec{r}) = V_{FI}(\vec{r}) + V_D(\vec{r}) + V_R(\vec{r}) \,. \tag{4}$$

$V_{FI}(\vec{r})$ is given by

$$V_{FI}(\vec{r}) = -\frac{1}{2}\alpha' |\vec{E}(\vec{r})|^2 \,, \tag{5}$$

and is the energy of interaction of the induced dipole with the electric field, V_D is the van der Waals attraction energy, and V_R is the repulsive interaction energy. V_{FI} can be broken down into the contribution of the lattice V_{FI}^+ and that of the electron gas V_{FI}^-. The dispersion and repulsive interactions of the molecule with the lattice may be approximated by the Lennard-Jones 6-12 potential.

Other applications of this model to the problem of the interactions of molecules with metal surfaces may be envisioned.[7] Also, there are several obvious (albeit perhaps difficultly incorporable) improvements, among which are, for example, (1) the requirement that there be fewer than one delocalized electron per metal atom, (2) the employment of a periodic, lattice-dependent potential, and (3) allowance for repulsion among the free electrons. Each of these "improvements" will affect the negative charge distribution in the metal and consequently the negative component of the surface electric field.

References

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7. Dr. James King of the Jet Propulsion Laboratory, California Institute of Technology, from discussions with whom inspiration for this proposition was largely derived, has used a model to explain the chromatographic separation of hydrogen isotopes on an alumina column (see J. King, Jr. and S. Benson, J. Chem. Phys. 44 1007 (1966)).

Proposition II

An initial-value method of calculating quantum-mechanical transition probabilities for inelastic collisions is presented. A perturbation method for solving the coupled equations to various orders in a "cutoff" parameter is proposed.

Reconsider the one-dimensional problem of the inelastic collision of a free particle with a particle bound to a fixed equilibrium position. Assume that the interaction potential V_I is slowly varying and that the interaction region is well localized (for reasons which will become clear below). We wish to solve the Schrödinger equation

$$H\Psi = E\Psi , \tag{1}$$

where

$$H = -\frac{\hbar^2}{2m_A}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_B}\frac{\partial^2}{\partial y^2} + V_B(y) + V_I(x, y), \tag{2}$$

and Ψ satisfies the asymptotic conditions

$$\Psi = e^{-ik_I x}\phi_I(y) + \sum_{m=1}^{N} R_m e^{+ik_m x}\phi_m(y) + O(e^{-\lambda x}),\quad x > x_o , \tag{3a}$$

$$\Psi = \sum_{m=1}^{N} T_m e^{-ik_m x}\phi_m(y) + O(e^{+\lambda x}),\qquad x < 0, \tag{3b}$$

and

$$E = \epsilon_I + \frac{\hbar^2 k_I^2}{2m_A} = \epsilon_m + \frac{\hbar^2 k_m^2}{2m_A} , \tag{4}$$

where we have assumed that the interaction region extends from $x = 0$ to $x = x_o$. The symbols in Eqs. (2) - (4) have the same significance as in Part II, i. e., A labels free-particle parameters, B labels bound-particle parameters, R_m is the amplitude for reflection in channel m, T_m the amplitude for transmission in channel m, N is the number of open channels, ϵ_m is the mth discrete eigenvalue of the bound particle, and k_m is the corresponding free-particle wavenumber.

The method of solution of the Schrödinger equation (1) is essentially that described in Part II. There is one important modification, however, and that involves the method of determination of the χ_j's.[1] We express the total scattering wavefunction Ψ as a linear combination of functions of a set, each member of the set satisfying linearly independent initial conditions in the asymptotic region $x < 0$. Denoting the members of this set by χ_j, we have

$$\Psi = \sum_j c_j \chi_j . \tag{5}$$

Now each χ_j is expressed as

$$\chi_j = \sum_{i=1}^{\infty} f_i^{(j)}(x)\,\phi_i(y) \quad , \tag{6}$$

where the ϕ_i are the bound-state eigenfunctions and $f_i^{(j)}(x)$ are arbitrary functions of x to be determined. The χ_j are found by solving the initial-value problem created by specifying the values and slopes of the $f_i^{(j)}$ corresponding to arbitrary initial conditions on χ_j. Now since each χ_j must satisfy the Schrödinger equation (1), we substitute Eq. (6) into Eq. (1) and take the inner product of both sides with ϕ_ℓ to obtain

$$\frac{d^2 f_\ell^{(j)}(x)}{dx^2} + \gamma k_\ell^2 f_\ell^{(j)}(x) - \sum_{i=1}^{M} \overline{u}_{\ell i}(x)\, f_i^{(j)}(x) = 0, \quad \ell = 1, 2, \ldots M \tag{7}$$

where

$$\overline{u}_{\ell i}(x) = \frac{2m_A}{\hbar^2} \int_{-\infty}^{\infty} \phi_\ell^* V_I(x, y)\,\phi_i\, dy$$

$$\gamma = m_A/m_B$$

$$k_\ell^2 = (E - \epsilon_\ell)\, 2m_A/\hbar^2 \quad .$$

We find the $f_i^{(j)}$ by solving the set of coupled equations (7), which we note has been truncated. If $\chi_j(x < 0, y) = e^{-ik_j x}\,\phi_j(y)$, then we have the following <u>initial</u> conditions on $f_i^{(j)}$:

$$f_i^{(j)}(0) = \delta_{ij} \tag{8a}$$

$$f_i^{(j)}(0) = -ik_j \, \delta_{ij}, \qquad j \leq N \tag{8b}$$

or

$$f_i^{(j)}(0) = \delta_{ij} \tag{9a}$$

$$f_i^{(j)}(0) = k_j \, \delta_{ij} \, , \qquad j > N \, . \tag{9b}$$

Inside the interaction region the various channels "couple" so that in the asymptotic region $x > x_o$, χ_j is expressible as

$$\chi_j = \sum_{i=1}^{N} (A_i^{(j)} e^{-ik_i x} + \bar{A}_i^{(j)} e^{+ik_i x}) \, \phi_i(y)$$

$$+ \sum_{i>N} (B_i^{(j)} e^{-k_i x} + \bar{B}_i^{(j)} e^{+k_i x}) \, \phi_i(y) \, , \tag{10}$$

where the coefficients $A_i^{(j)}$, $\bar{A}_i^{(j)}$, $B_i^{(j)}$, $\bar{B}_i^{(j)}$ are determined by requiring continuity of χ_j and grad χ_j at $x = x_o$. Thus for $i \leq N$

$$f_i^{(j)}(x_o) = A_i^{(j)} e^{-ik_i x_o} + \bar{A}_i^{(j)} e^{+ik_i x_o} \tag{11a}$$

$$f_i^{(j)}(x_o) = -ik_iA_i^{(j)}e^{-ik_ix_o} + ik_i\bar{A}_i^{(j)}e^{+ik_ix_o} , \qquad (11b)$$

from which the $A_i^{(j)}$ and $\bar{A}_i^{(j)}$ can be determined. Similar equations may be written for the virtual-channel coefficients. Since we choose only outgoing waves in the open channels and decaying virtual channels for our initial conditions, we need solve for only M (the total number of states retained in the state expansion of each χ_j) χ_j's. The equations determining c_j in Eq. (5) are

$$\sum_{j=1}^{M} c_j^{(I)} A_i^{(j)} = \delta_{Ii} \qquad j \leq N \qquad (12a)$$

$$\sum_{j=1}^{M} c_j^{(I)} \bar{B}_i^{(j)} = 0, \qquad j > N \quad . \qquad (12b)$$

These may be written more compactly as

$$\underset{\sim}{A}\ \underset{\sim}{c}^{(I)} = \underset{\sim}{I}' , \qquad (13)$$

where I denotes the incident state. The amplitudes $R_m^{(I)}$ and $T_m^{(I)}$ are given by

$$R_m^{(I)} = \sum_{j=1}^{M} c_j^{(I)} \bar{A}_m^{(j)} \qquad (14a)$$

$$T_m^{(I)} = c_m^{(I)} \quad . \tag{14b}$$

It now remains to solve the coupled set Eq. (7). If $\overline{u}_{\ell i}(x)$ is a smooth, slowly varying function and the interaction region is not too large, i. e., the interaction is of the nature of a perturbation, we may be able to obtain a rapidly convergent power series representation of $f_i^{(j)}$ in the interaction region. We expand $f_\ell^{(j)}$ and $\overline{u}_{\ell i}$ in a Taylor's series about $x = 0$ as follows

$$f_\ell^{(j)} = \sum_{n=0}^{\infty} a_n^{(j)}(\ell)\, x^n \tag{15a}$$

$$\overline{u}_{\ell i} = \sum_{n=0}^{\infty} d_n(\ell, i)\, x^n \quad . \tag{15b}$$

Substituting these expansions into Eq. (7), we obtain

$$\sum_{n=0}^{\infty} \left\{(n+2)(n+1)\, a_{n+2}^{(j)}(\ell) \pm \gamma k_\ell^{\,2}\, a_n^{(j)}(\ell)\right\} x^n$$

$$- \sum_{i=1}^{M} \Big(\sum_{n=0}^{\infty} a_n^{(j)}(i)\, x^n\Big)\Big(\sum_{m=0}^{\infty} d_m(\ell, i)\, x^m\Big) = 0, \ j = 1, 2, \ldots M \, , \tag{16}$$

where the + holds for $\ell \leq N$ and the - for $\ell > N$. Equating coefficients of equal powers of x gives

$$(m+2)(m+1)\, a_{m+2}^{(j)}(\ell) \pm \gamma k_\ell^2 a_m^{(j)}(\ell) - \sum_{i=1}^{M} \left\{ \sum_{k=0}^{m} a_k^{(j)}\, d_{m-k}(\ell, i) \right\} = 0 . \tag{17}$$

The initial conditions (8) and (9) determine $a_o^{(j)}(\ell)$ and $a_1^{(j)}(\ell)$. Thus

$$a_o^{(j)}(\ell) = \delta_{\ell j} \tag{18a}$$

$$a_1^{(j)}(\ell) = -ik_\ell\, \delta_{\ell j}\,, \qquad j \leq N \tag{18b}$$

or

$$a_o^{(j)}(\ell) = \delta_{\ell j} \tag{19a}$$

$$a_1^{(j)}(\ell) = k_\ell\, \delta_{\ell j}\,, \qquad j > N\ . \tag{19b}$$

From Eqs. (18) and (19) we can use the recursion relation (17) to find all the coefficients $a_m^{(j)}(\ell)$ successively.

Now we treat x_o as a parameter to obtain a "perturbation" expansion for the c_j's and transition probabilities. To see how this is possible, we solve Eqs. (11) to obtain

$$A_\ell^{(j)} = \frac{[ik_\ell f_\ell^{(j)}(x_o) - f_\ell'^{(j)}(x_o)]}{2ik_\ell} e^{+ik_\ell x_o} . \qquad (20)$$

Substituting the expansions

$$f_\ell^{(j)}(x_o) = \sum_{n=0}^{\infty} a_n^{(j)}(\ell)\, x_o^n$$

$$f_\ell'^{(j)}(x_o) = \sum_{n=0}^{\infty} (n+1) a_{n+1}^{(j)}(\ell) x_o^n$$

$$e^{ik_\ell x_o} = \sum_{n=0}^{\infty} \frac{(ik_\ell)^n}{n!} x_o^n$$

into Eq. (20) gives

$$A_\ell^{(j)}(x_o) = \frac{1}{2ik_\ell} \sum_{n=0}^{\infty} \left\{ \sum_{q=0}^{n} [ik_\ell a_q^{(j)}(\ell) - (q+1) a_{q+1}^{(j)}(\ell)] \frac{(ik_\ell)^{n-q}}{(n-q)!} \right\} x_o^n . \qquad (21a)$$

Similarly, we obtain

$$\mathrm{B}_{\ell}^{(j)}(x_o) = \frac{1}{2k_{\ell}} \sum_{n=0}^{\infty} \left\{ \sum_{q=0}^{n} [k_{\ell} a_q^{(j)}(\ell) + (q+1) a_{q+1}^{(j)}(\ell)] \cdot \frac{(-k_{\ell})^{n-q}}{(n-q)!} \right\} x_o^{\,n} , \tag{21b}$$

$$\overline{\mathrm{B}}_{\ell}^{(j)}(x_o) = \frac{1}{2k_{\ell}} \sum_{n=0}^{\infty} \left\{ \sum_{q=0}^{n} [k_{\ell} a_q^{(j)}(\ell) - (q+1) a_{q+1}^{(j)}(\ell)] \cdot \frac{(+k_{\ell})^{n-q}}{(n-q)!} \right\} x_o^{\,n} , \tag{21c}$$

and

$$\overline{\mathrm{A}}_{\ell}^{(j)}(x_o) = \frac{1}{2ik_{\ell}} \sum_{n=0}^{\infty} \left\{ \sum_{q=0}^{n} [ik_{\ell} a_q^{(j)}(\ell) + (q+1) a_{q+1}^{(j)}(\ell)] \cdot \frac{(-ik_{\ell})^{n-q}}{(n-q)!} \right\} x_o^{\,n} . \tag{21d}$$

Thus, we have the matrix elements of $\underset{\sim}{A}$ expressed as explicit functions of the "cutoff" parameter x_o. The matrix equation (13) for the $\underset{\sim}{c}^{(I)}$ may now be expressed as

$$(\underset{\sim}{A}_o + \underset{\sim}{A}_1 x_o + \underset{\sim}{A}_2 x_o^{\,2} \cdots)(\underset{\sim}{c}_o^{(I)} + \underset{\sim}{c}_1^{(I)} x_o + \underset{\sim}{c}_2^{(I)} x_o^{\,2} \cdots) = \underset{\sim}{I}' \tag{22}$$

The various "orders" of $\underset{\sim}{c}^{(I)}$ may be determined by identifying coefficients of equal powers of the "cutoff" parameter. Hence, we obtain the matrix equations

$$\underset{\sim}{A}_o \underset{\sim}{c}_o^{(I)} = \underset{\sim}{I}' \tag{23a}$$

$$\sum_{j=0}^{m} \underset{\sim}{A}_j \underset{\sim}{c}_{m-j}^{(I)} = \underset{\sim}{0} \ . \tag{23b}$$

We note from the expansions (21) that

$$A_{\ell o}^{(j)} = \frac{1}{2ik_\ell} [ik_\ell \, a_o^{(j)}(\ell) - a_1^{(j)}(\ell)] = \delta_{\ell j}$$

$$\bar{B}_{\ell o}^{(j)} = \frac{1}{2k_\ell} [k_\ell \, a_o^{(j)}(\ell) + a_1^{(j)}(\ell)] = \delta_{\ell j} \ ,$$

and thus $\underset{\sim}{A}_o$ is the M × M unit matrix. From Eqs. (23) we then obtain

$$\underset{\sim}{c}_o^{(I)} = \underset{\sim}{I}' \tag{24a}$$

$$\underset{\sim}{c}_1^{(I)} = - \underset{\sim}{A}_1 \underset{\sim}{c}_o^{(I)} \tag{24b}$$

$$\underset{\sim}{c}_2^{(I)} = (- \underset{\sim}{A}_2 + \underset{\sim}{A}_1^{\,2}) \underset{\sim}{c}_o^{(I)} \tag{24c}$$

$$\vdots$$

Expressing Eqs. (14) as a matrix equation, we can obtain the reflection and transmission amplitudes to various orders as follows:

$$(\underset{\sim}{\bar{A}}_o + \underset{\sim}{\bar{A}}_1 x_o + \underset{\sim}{\bar{A}}_2 x_o^{\,2} + \cdots)(\underset{\sim}{c}_o^{(I)} + \underset{\sim}{c}_1^{(I)} x_o + \underset{\sim}{c}_2^{(I)} x_o^{\,2} + \cdots) =$$

$$\underset{\sim}{R}_o^{(I)} + \underset{\sim}{R}_1^{(I)} x_o + \underset{\sim}{R}_2^{(I)} x_o^{\,2} + \cdots \tag{25a}$$

$$\underset{\sim}{T}^{(I)} = \underset{\sim}{c}_o^{(I)} + \underset{\sim}{c}_1^{(I)} x_o + \underset{\sim}{c}_2^{(I)} x_o^{\,2} + \cdots \; . \tag{25b}$$

In particular, if $x_o = 0$, i.e., there is no interaction, we observe that

$$\underset{\sim}{\bar{A}}_o \underset{\sim}{c}_o^{(I)} = \underset{\sim}{R}_o^{(I)} = 0 \tag{26a}$$

$$\underset{\sim}{T}^{(I)} = \underset{\sim}{c}_o^{(I)} \tag{26b}$$

which means that there is only a wave of unit amplitude transmitted in channel I and nothing reflected. Evidently, our formalism is correct in the limit $x_o = 0$. The hope is that we may obtain reasonably accurate approximations to the amplitudes for weak interactions V_I by including only a few powers of x_o in the expansions (24) and (25). The method has two possible advantages over the distorted wave method. The first is that it is possible to obtain analytic expressions for the amplitudes for arbitrary potentials. Second, each order of correction couples all the channels, both open and virtual, included in the state expansion for Ψ.

References

1. This initial-value method has been independently developed by Barnes *et al.*, (see L. Barnes, N. Lane, and C. Lin, Phys. Rev., **137**, 388 (1965)) and by Merle Riley at California Institute of Technology.

Proposition III

A semiclassical theory of radiationless transitions is proposed. The theory views the relaxation of an electronically excited solute molecule as a transition between zero-order nonstationary states induced by a time-dependent perturbation caused by solute-solvent Coulomb interactions. The translational motion of the molecules is treated classically and the internal degrees of freedom quantum mechanically. Two model studies designed to compare the effect of various parameters of the classical motion on the transition probability are proposed.

Several theories of radiationless transitions have been proposed.[1,2,3] Among those which consider explicitly the relation of solute molecules (guest) to environment (host, lattice), Robinson and Frosch's[2] and Gouterman's[3] are probably most prominent. Essentially Robinson and Frosch determine the rate of a radiationless transition by following the "decay" and "build-up" of the nonstationary initial and final states which are coupled by stationary perturbations. The most important of these stationary perturbations arise in the free molecule. Solute-solvent perturbations are not important except in special cases. Hence, the major role of the solvent is to serve as a collection of coupled oscillators into which the excitation energy ultimately flows as phonons.

Gouterman[3], in contrast to Robinson and Frosch, assumes that the solute-environment interaction is wholly responsible for inducing transitions between stationary electronic states of molecules. He develops a Hückel-type theory based on the analogy of the "phonon field" of the solvent to the photon field used in the semiclassical theory of radiative transitions. Expressing the time-dependent perturbation as

$$H'' = \sum_{\alpha} \eta_{\alpha} x_{\alpha} F_{\alpha} \cos(\omega t + \vec{\kappa} \cdot \vec{r}_{\alpha}) \ , \qquad (1)$$

where F_{α} is a force field set up by "phonon waves" (analogous to E_x) and η_{α} is a "coupling constant", he obtains expressions for the induced and spontaneous radiationless transition rates. These expressions involve Hückel-type constants, e. g., the coupling constants η_{α}.

It is proposed that a more realistic semiclassical model for radiationless transitions be investigated. Gouterman admits that his perturbation (1) is wrong, but he hopes to compensate for this error after the manner of Hückel theory by introduction of empirical parameters. The model we propose to investigate here takes full account of the proper solute-solvent interaction Hamiltonian in the same fashion as the semiclassical theory of radiative transitions. We now suppose that we have a solution of excited solute molecules which exist in any of a complete set of "stationary" excited states at time $t = 0$. The translational motion of the molecules is treated classically and the internal degrees of freedom quantum mechanically. We now look at a particular excited solute molecule. It is constantly colliding with solvent molecules which are creating an effective time-dependent perturbation through the Coulomb interactions of their charges with the electrons of the excited solute molecule. It is this time-dependent perturbation which we wish to consider causing radiationless transitions between the "stationary" states of the free-molecule. In a way, it appears that this is an extension of the Robinson-Frosch theory which involves transitions between nonstationary states induced by a stationary perturbation switched on at time $t = 0$. In fact, there exist no true stationary states of molecules in condensed media, although this approximation may not be unreasonable for gases. An alternative way of looking at the present theory is as follows. It takes into account the full Hamiltonian of the free molecule to calculate a complete set of zero-order nonstationary states. The states are nonstationary by virtue of solute-solvent time-dependent interactions. These time-dependent interactions which couple the initial and final nonstationary states are determined by the classical motion of individual molecules.

Of course, the time-dependent field which any particular molecule experiences is an incredibly complex function of time which depends on the velocities, impact parameters, and phases of many successive collisions. In condensed media the intermolecular correlations are important in determining the detailed nature of the time dependence. Hence, we should expect the radiationless transition rate to depend on the pressure and temperature as well as the molecular structure. In order to study the effects of these variables, it is proposed that several simplified models be investigated: (1) the binary collision of two hydrogen-like atoms; (2) the system of monatomic solute molecules imbedded in a monatomic solvent.

In Fig. 1 is depicted the collision of an excited hydrogen-like atom A (nuclear charge Z_A) and a ground-state hydrogen-like atom B (nuclear charge Z_B). Initially B is travelling toward A with velocity $\vec{v}$ and impact parameter b. For the present, we assume that the trajectory of B, calculated classically using an appropriate adiabatic intermolecular potential such as the Lennard-Jones 6-12, is such that we may neglect relativistic and exchange effects. The set of zero-order states is denoted by $\left\{\phi_n(\vec{r}_a) \cdot \psi_m(\vec{r}_b)\right\}$. The perturbation may be written

$$V(\vec{r}_a, \vec{r}_b, t) = - \frac{Z_B e^2}{|\vec{R}_{AB} - \vec{r}_a|} - \frac{Z_A e^2}{|\vec{R}_{AB} + \vec{r}_b|} + \frac{e^2}{|\vec{R}_{AB} + \vec{r}_b - \vec{r}_a|} + \frac{Z_A Z_B e^2}{R_{AB}}, \tag{2}$$

where $\vec{R}_{AB}$ is the radius vector from nucleus A (regarded as fixed in the x - y frame) to nucleus B, $\vec{r}_a$ is the radius vector from A to the electron on atom A, and $\vec{r}_b$ the radius vector from nucleus B to its electron. The time dependence enters in $R_{AB} = R_{AB}(t)$. Since the perturbation acts for only a finite time, i.e., the time of duration of the collision, the transition probability $P_{nm \to n'm'}$ is given by[4]

$$P_{nm \to n'm'} = \frac{1}{\hbar^2 \omega^2_{nm,n'm'}} \left| \int_{-\infty}^{\infty} \frac{\partial}{\partial t}(V_{nm,n'm'}) e^{+i\omega_{nm,n'm'}t} \, dt \right|^2, \tag{3}$$

where

$$V_{nm,n'm'}(t) = \langle \phi_{n'}(\vec{r}_a)\psi_{m'}(\vec{r}_b) | V(\vec{r}_a, \vec{r}_b, t) | \phi_n(\vec{r}_a)\psi_m(\vec{r}_b)\rangle ,$$

and

$$\omega_{nm,n'm'} = (E_{n'm'} - E_{nm})/\hbar .$$

E_{nm} is the eigenvalue associated with the stationary state $\phi_m(\vec{r}_a)\psi_n(\vec{r}_b)$. This model could be used to study the dependence of the transition rate on relative velocity and impact parameter.

Now for a system of molecules we have seen that the time-dependent perturbation is a much more complicated function. For dense media, especially, it is not a good approximation to assume that only binary collisions are important and that the interval between collisions is long compared to molecular rotation and vibration. We thus propose a model which allows for the complex correlations in a dense medium such as a liquid. We adopt a simplified model which consists of a dilute solution of excited monatomic solute molecules in a monatomic solvent. We assume that only the valence electrons of the solute need be considered. Also, the solvent molecules are not excited during solute-solvent collisions so that the electronic motion of the solvent can be treated adiabatically in calculating the perturbation. The complicated motion of the nuclei is found classically by integrating Newton's equations using an adiabatic intermolecular potential. Thus a single solute molecule A experiences a time-dependent perturbation of the form

$$V_A(\vec{r}_a, t) = \sum_{j=1}^{N} V_{Aj}(\vec{r}_a, \vec{R}_{Aj}(t)) , \tag{4}$$

where V_{Aj} is the time-dependent perturbation due to solvent molecule j, $\vec{R}_{Aj}(t)$ being its trajectory relative to the solute molecule. The radiationless transition probability $P_{n \to m}$ for the solute molecule to be deexcited from state n to state m is then given by^5

$$P_{n \to m} = \frac{1}{\hbar^2} \left| \int_0^t V_{mn}(t)\, e^{+i\omega_{mn} t} dt \right|^2 , \tag{5}$$

where

$$V_{mn}(t) = \langle \phi_m(\vec{r}_a) | V_A(\vec{r}_a, t) | \phi_n(\vec{r}_a) \rangle$$

$$\omega_{mn} = (E_m - E_n)/\hbar \quad .$$

This model should allow us to study the effect solvent-solvent and solvent-solute correlations on the transition probabilities in addition to the effects of temperature and pressure.

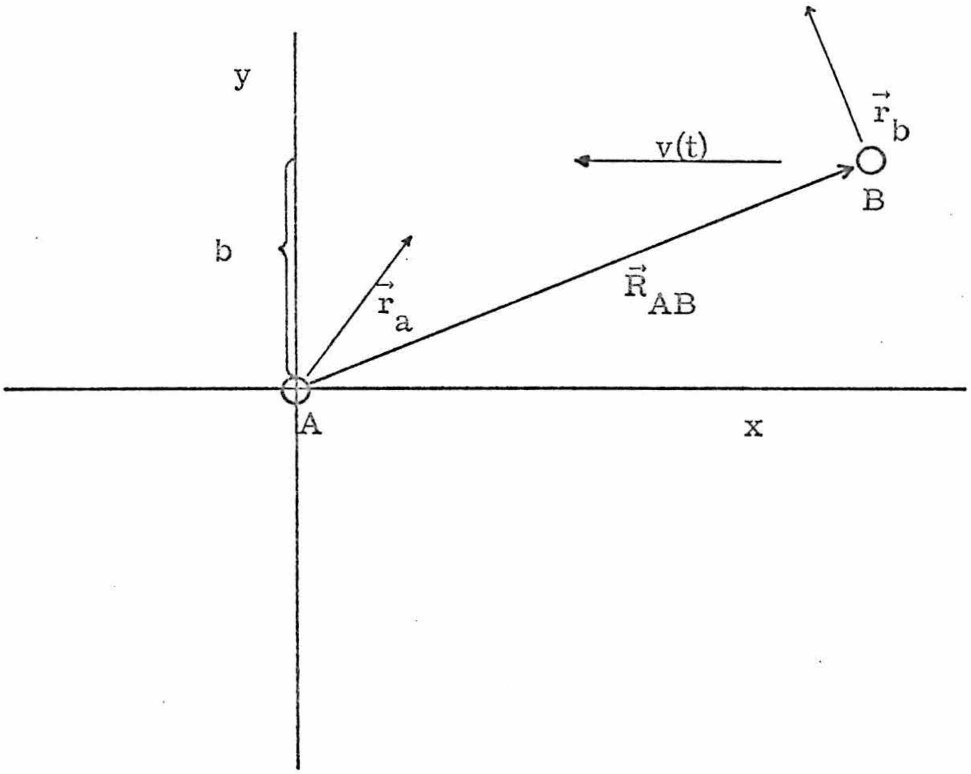

Figure I. The collision of two hydrogen-like atoms.

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Proposition IV

A method for treating the collisional transfer of energy between vibrational and electronic degrees of freedom is proposed. The central feature of the method, which remedies several defects of a previous treatment, is that it treats only the electronic motion of the vibrator adiabatically. This is believed to be a reasonable approximation since the vibrator is not undergoing a change of electronic state. It is proposed that the transition probabilities be found by the initial-value method outlined in Proposition II.

The treatment of collisional energy transfer between electronic and vibrational degrees of freedom is complicated by the fact that the interaction potential cannot be calculated in the adiabatic approximation, i. e., by assuming that electronic motion adjusts itself instantaneously to provide a surface upon which the nuclei move. Effectively, the surface changes discontinuously during the collision. We consider the <u>colinear</u> collision of a diatomic molecule BC with an atom A and desire to find the cross sections for the following reactions

$$A^* + BC \rightarrow A + BC^* \tag{1}$$

$$A + BC^* \rightarrow A^* + BC \tag{2}$$

$$A + BC \rightarrow A^* + BC^* \ . \tag{3}$$

Reaction (2) is a transfer of electronic excitation of atom A to vibrational excitation of molecule BC and reaction (2) vice versa. Reaction (3) is a collision in which translational energy is converted into electronic and/or vibrational energy. Dickens, Linnett, and Sovers[1] have calculated cross sections for electronic-vibrational transfer reactions of type (1) above using the Born and distorted-wave approximations. Unfortunately, they used a very approximate interaction potential of the form $V = V_1(\vec{r}) \cdot V_2(q) \cdot V_3(\vec{r}_1)$, where $\vec{r}$ is the vector distance between the centers of mass, q is the vibrational coordinate, and $\vec{r}_1$ the electronic coordinate. Apparently this form was chosen to simplify the integrals necessary in the calculation. For the various potential factors they used

$$V_1(\vec{r}) = V_o'' e^{-\alpha r} \tag{4a}$$

$$V_2(q) = e^{+\alpha q} \tag{4b}$$

$$V_3(\vec{r}_1) = (1 + \beta r_1) \ , \tag{4c}$$

where V_o'', α, and β are empirical constants. This corresponds to an exponential interaction between the incident atom A and the nearest atom of the diatomic, modulated by the electronic charge of A concentrated at r_1. They found that the cross sections were very sensitive to the empirical parameters. Furthermore, one would expect that the interaction potential would not be entirely repulsive and actually might be attractive similar to a Lennard-

Jones 6-12 potential. Also, with all the approximations, both mathematical (Born or distorted-wave) and physical (potential) it is not clear why the cross sections do not agree with experiment. For these several reasons it is proposed that reactions of type (1), (2), and (3) be treated rigorously within the framework of the initial-value method of Proposition II using a more physically realistic form for the interaction potential.

We consider the "colinear" collision of atom A with diatomic molecule BC (see Fig. I). The motion of the nuclei is restricted to a straight line, although each of the electrons has three-degrees of freedom. To illustrate the nature of the interaction potential, we choose A to be very simple, say a hydrogen atom. Then we wish to solve the following wave equation, expressed in the center-of-mass (of nuclei) system

$$\left\{-\frac{\hbar^2}{2\mu_{A,BC}}\nabla_r^2 + H_o - \frac{\hbar^2}{2\mu_{BC}}\nabla_y^2 + V_{BC}(y) + V_I(r, y, \vec{r}_a)\right\}\Psi = E\Psi, \tag{5}$$

where

$$r = \xi_A - (m_B\xi_B + m_C\xi_C)/(m_B + m_C)$$

$$y = \xi_C - \xi_B$$

$$\mu_{A,BC} = m_A \cdot (m_B + m_C)/(m_A + m_B + m_C)$$

$$\mu_{BC} = m_B m_C/(m_B + m_C)\ ,$$

H_o is the Hamiltonian of the electron a in the field of nucleus A, V_{BC} is the adiabatic binding potential of the diatomic BC, V_I the interaction potential, $\vec{r}_a$ the radius vector from the nucleus of A to its electron, and E the total energy. Hence, the interaction potential depends explicitly on the electronic and nuclear coordinates of A only and may be expressed as

$$V_I(r, y, \vec{r}_a) = \frac{Z_C Z_A e^2}{[r - \frac{m_B}{(m_B+m_C)} y]} + \frac{Z_B Z_A e^2}{[r + \frac{m_C}{(m_B+m_C)} y]} - Z_A e^2 \int \frac{\rho(y;\vec{r}_{BC})\ d\vec{r}_{BC}}{|\vec{r} + \vec{r}_{BC}|} + e^2 \int \frac{\rho(y;\vec{r}_{BC})\ d\vec{r}_{BC}}{|\vec{r} + \vec{r}_{BC} - \vec{r}_a|}, \tag{6}$$

where the first two terms are the nuclear repulsion terms, the third term is the interaction of nucleus A with the charge cloud about the diatomic, and the last term is the interaction of the electron about A with the diatomic charge cloud. If one wishes, he may take into account polarization of the diatomic by making $\rho(\vec{r}_{BC})$, the electronic density of BC, a function of r. Note that we have assumed that the diatomic behaves adiabatically and this does not seem unreasonable in view of the fact that its electronic state does not change during the collision. If the diatomic is not highly vibrationally excited, the approximation may be expected to be good.

To find the transition probabilities for the various reactions (1), (2), and (3), we expand the total scattering wave as

$$\Psi = \sum_{n} \sum_{m} f_{nm}(r) \chi_n(y) \psi_m(\vec{r}_a) \tag{7}$$

where χ_n is the nth vibrational eigenfunction of BC, ψ_m the mth electronic eigenfunction of atom A, and f_{nm} the corresponding arbitrary function of r, the asymptotic behavior of which is

$$\lim_{r\to\infty} f_{oo} = e^{-ik_{oo}r} + R_{oo} e^{+ik_{oo}r} \tag{8a}$$

$$\lim_{r\to\infty} f_{nm} = R_{nm} e^{+ik_{nm}r} , \tag{8b}$$

where f_{oo} is the incident channel function. Since the interaction V_I becomes infinite for $r \leq 0$, $f_{nm}(0) = 0$. The transition probability $P_{oo\to nm}$ is given as usual by

$$P_{oo\to nm} = \frac{k_{nm}}{k_{oo}} |R_{nm}|^2 , \tag{9}$$

where

$$\frac{\hbar^2}{2\mu_{A,BC}} k_{nm}^2 + \epsilon_n + \varepsilon_m = E . \tag{10}$$

In Eq. (10), which is an expression of energy conservation, ϵ_n and ε_m are, respectively, the vibrational and electronic eigenvalues and k_{nm} is the corresponding free-particle wavenumber. Substituting expansion (7) into Schrödinger equation (5) and taking the inner product with $\chi_{n'}(y)\,\psi_{m'}(\vec{r}_a)$, we obtain the set of coupled equations for the f_{nm},

$$(\nabla_r^{\,2} + k_{nm}^{\,2}) f_{n'm'} = \frac{2\mu_{A,BC}}{\hbar^2} \sum_{nm} V_{n'm'nm}(r) f_{nm}(r) , \qquad (11)$$

where

$$V_{n'm'nm} = \langle \chi_{n'}(y)\,\psi_{m'}(\vec{r}_a) | V_I(r, y, \vec{r}_a) | \chi_n(y)\,\psi_m(\vec{r}_a) \rangle .$$

The coupled set (11) may be solved by the method outlined in Proposition II or, if only a rough approximation is needed, the Born approximation or distorted wave method may be used. The integrals $V_{n'm'nm}$ will probably have to be calculated numerically.

For atoms A with more than one electron, we may wish to express the interaction potential and zero-order electronic eigenfunctions as functions involving all the electronic coordinates explicitly. Alternatively, we may treat just the valence electrons.

In summary, the salient feature of the proposed method is that it treats adiabatically those electrons whose motion is not greatly affected by the collision, i.e., the electrons associated with the diatomic and possibly with the core of a many electron atom A.

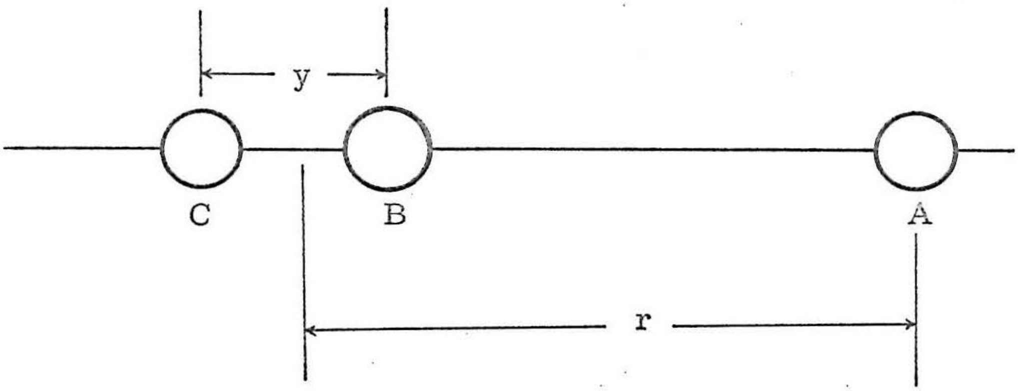

Figure I. Collision of an atom A with a diatomic molecule BC.

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Proposition V

It is proposed that the relaxation (including reaction) of an initial distribution of reactant molecules among various quantum levels be investigated. The transition rates W_{nm} depend explicitly on concentration so that the relaxation equations are nonlinear. After outlining the general theory, we derive the relaxation equations for a displacement reaction and briefly discuss methods of solution.

The standard theories of chemical kinetics, i.e., the collision theory and Eyring's absolute rate theory, assume that the velocities of the reactants are distributed according to the Maxwell-Boltzmann law throughout the course of the reaction. Montroll and Shuler[1] have reviewed various models of chemical reactions which allow for the disturbance of the initial equilibrium velocity distribution. Curtiss[2], Prigogine[3], and Takayanagi[4] have investigated the perturbation of an initial Maxwell velocity distribution by a chemical reaction. They developed a generalized Boltzmann equation which took account of (1) the energy change during reaction and (2) the loss of highly energetic molecules by reaction. Zwolinski and Eyring[5] described chemical reactions as occurring by collision-induced transitions from one set of quantum levels representing the reactant to another set representing the product. Equations governing the concentration of reactants and products in the various quantum levels as a function of time were derived and applied to test the validity of the equilibrium postulate of absolute rate theory. Kramers[6] postulated a Brownian-motion model in which reactant molecules gain sufficient energy by successive collisions to surmount a potential barrier (react).

Montroll and Schuler[1] have generalized the Zwolinski-Eyring approach to a stochastic model and have derived general mathematical expressions describing the relaxation of non-equilibrium initial distributions. They consider a large number of reactant molecules with quantized energy levels to be dilutely dispersed in a constant-temperature heat bath. By successive collision with heat bath molecules the reactants are stepwise excited to higher levels. Reaction is defined to occur when a molecule is excited into the (N + 1) "level", where it is in an unbound state. The model corresponds to unimolecular decomposition following activation. The equation governing the relaxation of some initial distribution is

$$\frac{dx_n}{dt} = \sum_{m \neq n}^{N} \left\{ W_{nm} x_m - W_{mn} x_n \right\}, \quad n = 1, 2, \ldots N, \tag{1}$$

where x_n is the concentration of reactant molecules in level n, W_{nm} is the transition probability per unit time per molecule. The first term corresponds to transitions from various levels m to level n, the second to transitions from level n to the other levels. The transition rates W_{nm} can be calculated quantum mechanically.

Widom[7], using classical mechanics, has derived a "continuous" version of the relaxation equations (1) in which the transition rate matrix $\underset{\sim}{W}$ is replaced by a kernel $k(x, y)$ and the summation by an integration.

A great deal of attention has been devoted to the relaxation of non-equilibrium distributions of harmonic oscillators diluted dispersed in a constant-temperature bath. Under these conditions, the W_{nm} are constant and the relaxation equations thus are linear. It is possible to obtain analytical expressions for the solutions of Eqs. (1).[1] However, for more general relaxation processes, e.g., reactions and nonconstant-temperature relaxations, the explicit dependence of W_{nm} on concentration, temperature and time must be taken into account. It is proposed that a model for reactions which incorporates these various dependencies be investigated. Below we shall derive the relaxation equations and consider the specific manner in which the transition rates depend on concentrations. Then we shall consider briefly the method of solution of the relaxation equations.

Since most complex reactions occur by a series of bimolecular reactions, we restrict our consideration here to such a reaction, realizing that we obtain the overall relaxation equation by "coupling" the bimolecular relaxation equations. Consider the displacement reaction

$$AB + C \overset{M}{\leftrightharpoons} BC + A, \tag{2}$$

in which, for simplicity, we assume that AB is a diatomic molecule with internal quantum levels 1, 2, ··· N, BC is a diatomic molecule with levels 1, 2, ··· N', and C and A are atoms possessing only translational kinetic energy. M denotes an "inert"low density gas solvent. It is inert in the sense that it cannot react with any of the reactants or products, although it can undergo inelastic collisions with any of them. The equations describing the relaxation (reaction) may be written

$$\frac{dx_{AB}(n,t)}{dt} = \sum_{m\neq n}^{N} \left\{W_{nm}\, x_{AB}(m,t) - W_{mn}\, x_{AB}(n,t)\right\}$$

$$+ \sum_{q=1}^{N'} \left\{U_{nq}\, x_{BC}(q,t) - U_{qn}\, x_{AB}(n,t)\right\} \qquad (3a)$$

$$\frac{dx_{BC}(n,t)}{dt} = \sum_{m\neq n}^{N'} \left\{\overline{W}_{nm}\, x_{BC}(m,t) - \overline{W}_{mn}\, x_{BC}(n,t)\right\}$$

$$+ \sum_{q=1}^{N} \left\{\overline{U}_{nq}\, x_{AB}(q,t) - \overline{U}_{qn}\, x_{BC}(n,t)\right\}, \qquad (3b)$$

$$\sum_{n=1}^{N} x_{AB}(n,t) + \sum_{n=1}^{N'} x_{BC}(n,t) = \sum_{n=1}^{N} x_{AB}(n,o) + \sum_{n=1}^{N'} x_{BC}(n,o)\,. \qquad (3c)$$

Eqs. (3a) and (3b) relate the rates of change of concentrations of various quantum levels of the reactants and products, while Eq. (3c) expresses conservation of matter. $x_{AB}(n,t)$ and $x_{BC}(n,t)$ are the concentrations of AB and BC in quantum level n at time t; W_{nm} is the transition probability per unit time per molecule from level m to level n of molecule AB and $\overline{W}_{nm}$ is the transition rate similarly defined for molecule BC; U_{nq} is the transition probability per unit time per molecule for transition from level q of BC to level n of AB and, similarly, $\overline{U}_{nq}$ is the transition rate for AB in level q going to BC in level n. Thus, the contribution of the first term of Eq. (3a) arises from nonreactive transitions among the levels of AB, while the second term corresponds to reactive transitions from levels of BC to levels of AB. Eq. (3b) has a similar interpretation.

Before considering solutions of Eqs. (3), we discuss the behavior of the transition rates W_{nm}, $\overline{W}_{nm}$, U_{nq}, $\overline{U}_{nq}$ in which the various consequences of our assumptions about the reaction conditions are manifested. A general expression for the transition rate T_{ij} is given by

$$T_{ij}=\sqrt{8/\pi}\,c(kT/\mu)^{1/2}\int_0^\infty \sigma_{ij}(E)(E/kT)^{1/2}\,e^{-E/kT}\,dE\,, \tag{4}$$

where T is the absolute temperature, μ is the reduced mass of the "collision complex" leading to the transition i → j, $\sigma_{ij}(E)$ is the cross section for transition i → j at relative kinetic energy E, and c is the concentration of molecules capable of forming a complex leading to the transition.[7] The derivation of Eq. (4) assumes that the relative translational motion of the molecules forming the complex is determined by an equilibrium velocity distribution at temperature T.

Now let us consider reaction (2) in which we begin with equal concentrations of AB and C in a dilute solution. Since AB - M and BC - M collisions are primarily responsible for nonreactive transitions among the quantum levels of AB and BC, W_{nm} and $\overline{W}_{nm}$ should remain constant if T remains constant. However, reactive transitions can occur only via collision complexes of the form AB - C or BC - A. Hence, from Eq. (4) we see that U_{nq} decreases in proportion to the concentration of C as the reaction (2) proceeds to the right. At the same time, the increasing concentration of A causes $\overline{U}_{nq}$ to increase. Thus, since the initial concentrations of AB and C are equal

$$x_C(t) = \sum_{n=1}^{N} x_{AB}(n, t) \tag{5a}$$

$$x_A(t) = \sum_{n=1}^{N'} x_{BC}(n, t) \;. \tag{5b}$$

Thus

$$U_{nq} = k_{nq}(T) \cdot \left[\sum_{m=1}^{N'} x_{BC}(m, t)\right] \tag{6a}$$

$$U_{qn} = k_{qn}(T) \cdot \left[\sum_{m=1}^{N} x_{AB}(m, t)\right] \tag{6b}$$

$$\overline{U}_{nq} = \overline{k}_{nq}(T) \cdot \left[\sum_{m=1}^{N} x_{AB}(m, t)\right] \tag{6c}$$

$$\overline{U}_{qn} = \overline{k}_{qn}(T) \cdot \left[\sum_{m=1}^{N'} x_{BC}(m, t) \right] , \tag{6d}$$

where $k_{ij}(T)$ is the temperature dependent factor which depends implicitly on the cross section also. Substitution of Eqs. (6) into Eq. (3a) for example, gives

$$\begin{aligned} \frac{dx_{AB}(n, t)}{dt} = & \sum_{m \neq n}^{N} \left\{ W_{nm} x_{AB}(m, t) - W_{mn} x_{AB}(n, t) \right\} \\ & + \sum_{q=1}^{N'} \left\{ k_{nq}(T) \left[\sum_{\ell=1}^{N'} x_{BC}(\ell, t) \right] x_{BC}(q, t) \right. \\ & \left. - \; k_{qn}(T) \cdot \left[\sum_{\ell=1}^{N} x_{AB}(\ell, t) \right] x_{AB}(n, t) \right\}, \quad n = 1, 2, \cdots N, \end{aligned} \tag{7}$$

which, together with the similar equations for dx_{BC}/dt, form a set of coupled, nonlinear first-order ordinary differential equations.

In most cases of interest, it will probably not be possible to obtain analytical expressions for the solutions of Eqs. (7). For initial distributions $\{x_{AB}(1, 0),\ x_{AB}(2, 0), \cdots,\ x_{BC}(N', 0)\}$ close to equilibrium, it is possible to use the equilibrium transition rates and obtain analytical expressions for the x_{AB} and x_{BC}. For initial distributions far from equilibrium, such as the one discussed above, it is necessary to solve Eqs. (7) numerically. For this purpose there are numerous computer subroutines available which are based on the Runge-Kutta method or various modifications.

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