

APPLICATION OF THE FINITE-DIFFERENCE METHOD TO
THE SOLUTION OF SCHRÖDINGER'S EQUATION

by

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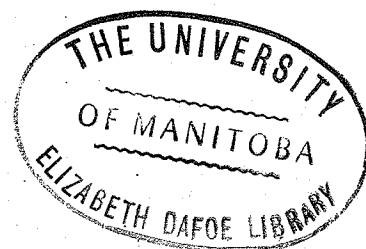
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TO THE PEOPLE

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PREFACE

This thesis is divided into three main sections; the first section being an old technique in mathematics, rewritten with some applications to quantum mechanics.

The non-uniform difference method in Chapter III was developed entirely by the author, but the iterative method in Chapter IV was mainly developed by Dr. R. Wallace.

ABSTRACT

The finite-difference method and some improved versions of the method are described. Their applications to quantum mechanics both in the solution of the Time Independent and the Time Dependent Schrödinger's equations are illustrated by examples such as the Harmonic Oscillator, the Hydrogen Atom, the Calculations of Phase Shifts in Electron Scattering, and the Transition Probability Calculations.

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CHAPTER I

INTRODUCTION

For a long time, atomic collision theory has been a major interest of both the physicists and the chemists. The influence of Rutherford's experiment on science is a classical example demonstrating the importance of this field.

After the birth of quantum mechanics, the pursuit for methods of calculating the absolute reaction rates theoretically was under way for a number of years. However, since the publication of "The Theory of Rate Processes"(1), little progress was achieved until the automatic high-speed electronic digital computer became available.

Numerous papers have been published since then, but it is not the purpose of this thesis to discuss them here. However, the "amplitude density functions" of Secrest and Johnson(2), the " δ -function of Locker(3), the "distorted-wave method" of Trindle and Illinger(4), and Gordon's(5) method for constructing wave functions for bound states and scattering are illustrative examples. Some of the methods used appear in the review of Rapp and Kassal(6).

The finite-difference method has been extensively employed by many authors to solve various problems; most of these are concerned with the Schrödinger's equation. It has been used to compute the dipole moment of iodine chloride by Glazer and Reiss(7). Using Liebmann iteration for the three-dimensional equation, Bartlett(8) gave a finite-difference solution for Helium. However, the accuracy of the method was low at that time. The partial-

wave expansion of the solution of the two-electron Schrödinger's equation was first employed by Luke, Meyrerott, and Clendenin(9) for the 3S state of Li^+ . The method has been recently improved by Winter, Laferrière, and McKoy(10). The finite-difference method has also been applied to the quantum mechanical treatment of inelastic collisions(11).

We are interested in the finite-difference method for the same reasons as those set out by these authors. It is straightforward in principle, adaptable to computer-programming, and applicable to many interesting problems. Despite the fact that no analytical expression can be obtained, it does not have the difficulties encountered in the infinite-series approach. Since only a few terms of the series can be included in practice, very often these terms are inadequate and erroneous results may arise. Many approximate methods or solutions in terms of basis functions have been proposed. It is increasingly more difficult to choose and apply them. For example, just for the anharmonic oscillator, there are Raleigh-Schrödinger perturbation method(12), JWKB method(13), elliptic functions(14), Gaussian basis functions(15), and many others.

Both the applications and the improvements of the method have been presented in this thesis. Since we cannot afford the time to calculate everything that interests us, we have to select a few well-known problems involving the

Schrödinger's equation. A one-dimensional harmonic oscillator is interesting as a starting example because it can illustrate the basic features of the finite-difference method. It has been used to represent a diatomic molecule in the theoretical study of energy transfer in the collision between an atom and a diatomic molecule(16). The interest in the harmonic oscillator also arises from the fact that it is possible to extend the method to treat the anharmonic oscillator, which has been used as a mathematical model in collision theory(17) as well as in field theory(18).

The second example chosen is the hydrogen atom. The obvious reason is that the solution of the Schrödinger's equation for the hydrogen atom(19) plays a very important role in modern chemistry. The original plan was to solve the three-dimensional equation explicitly. Even though it appears easy in principle, the MATLAN language programs did not turn out to be efficient, and the tremendous amount of computer time required discourages further calculations in that respect. At present, the partial-wave expansion method appears to demand less computer time.

Our interest in the three-dimensional problem brought us to the partial wave method. Instead of using it to calculate the hydrogen atom, we turned to the more interesting electron scattering problem. After Holtzmark(20), Robinson(21) has recently recalculated the phase shifts and the scattering cross-sections for the electron scattering

of rare gases by the method of numerical integration. The difference method has been used by Robertson(22) to calculate the phase shifts of some other systems, but his method has little improvement over the standard one. In this thesis, the method has been improved to tackle both the problems of the rapidly changing potential near the origin and the slowly vanishing potential at a large distance. The details will be found in Chapter III.

In order to treat the subject more thoroughly, a chapter on the solution of some problems in finite-difference form without the conventional finite-difference notations has been included in this thesis, although the author was primarily concerned with the calculations.

The ultimate goal of all these efforts is to understand the mechanism of chemical reactions in terms of mathematics. It is not the purpose of this thesis to create models and calculate trajectories and energy transfer from them, as will be found in the works of Pettitt and Corrigall(23). It tries to improve the numerical techniques of the finite-difference method in its application to the Schrödinger's equation.

CHAPTER II

REVIEW OF THE

FINITE-DIFFERENCE METHOD

A. INTERPOLATION FORMULA

To a certain degree, one can always have a numerical representation of a wave function at each co-ordinate point. The gradient at these points can be obtained by means of some interpolation formula. For example, the eigenvalues can be easily calculated by expressing the second derivative term in the Time Independent Schrödinger's equation of the Harmonic Oscillator in the form of the Backward Interpolation Formula of Gauss.

All the interpolation formula with divided differences are based on the mean-value theorem for the derivative, which states that if $f(x)$ is continuous for $a \leq x \leq b$ and $f'(x)$ is continuous for $a < x < b$, then $f(b) - f(a) = (b - a)f'(\xi)$ for at least one ξ such that $a < \xi < b$.

An extension of this theorem leads to the following basic definitions:

$$\begin{aligned}
 f(x) &= f(x_0) + (x - x_0)f'(x_0, x), \\
 f(x, x) &= f(x_0, x_1) + f(x - x_1)f'(x_0, x_1, x), \\
 &\dots\dots\dots \\
 f(x, x, \dots, x) &= f(x_0, \dots, x_n) + \\
 &\quad (x - x_n)f(x_0, \dots, x_n, x)
 \end{aligned}$$

where

$$f(x_0, x_1) = \frac{f(x_1) - f(x_0)}{x_1 - x_0} \quad \text{and}$$

$$f(x_0, \dots, x_k) = \frac{f(x_1, \dots, x_k) - f(x_0, \dots, x_{k-1})}{x_k - x_0}$$

By substituting these relations successively, starting from the last equation into the second last and working upwards, the Newton's Interpolation formula with divided differences can be shown equal to :

$$\begin{aligned} f(x) &= f(x_0) + (x - x_0)f(x_0, x_1) \\ &+ (x - x_0)(x - x_1)f(x_0, x_1, x_2) \\ &+ \dots + (x - x_0)\dots(x - x_{n-1})f(x_0, \dots, x_n) \\ &+ E(x) \end{aligned} \quad (I-2)$$

$$\text{where } E(x) = (x - x_0)\dots(x - x_n)f(x_0, \dots, x_n, x)$$

To simplify the calculation, the technique of finite-difference interpolation is employed where

$$x_{k+1} = x_k + h \quad \text{and}$$

$$\begin{aligned} \Delta f(x_k) &= f(x_{k+1}) - f(x_k) \\ &= (x_{k+1} - x_k)f(x_k, x_{k+1}) \\ &= h f(x_k, x_{k+1}) \end{aligned} \quad (I-3)$$

$$\begin{aligned}
 \Delta^2 f(x_k) &= h f(x_{k+1}, x_{k+2}) - h f(x_k, x_{k+1}) \\
 &= h f(x_k, x_{k+1}, x_{k+2}) (x_{k+2} - x_k) \\
 &= 2 h f(x_k, x_{k+1}, x_{k+2}) \quad (I-4)
 \end{aligned}$$

Carrying this to the r th term, we get

$$\begin{aligned}
 \Delta^r f(x_k) &= (r-1)! h^{r-1} f(x_{k+1}, \dots, x_{k+r}) \\
 &\quad - (r-1)! h^{r-1} f(x_k, \dots, x_{k+r-1}) \\
 &= (r-1)! h^{r-1} (x_{k+r} - x_k) f(x_k, \dots, x_{k+r}) \\
 &= r! h^r f(x_k, \dots, x_{k+r}) \quad (I-5)
 \end{aligned}$$

Substituting this into Newton's divided difference formula we can obtain

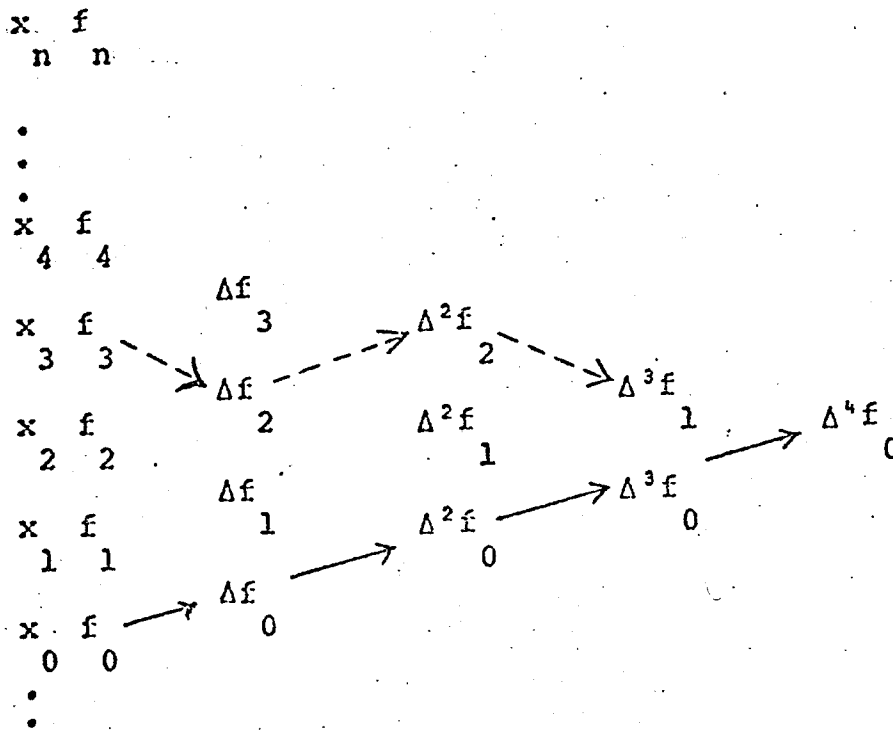
$$\begin{aligned}
 f(x) &= f_0 + (x - x_0) \frac{\Delta f_0}{1!h} \\
 &\quad + (x - x_0)(x - x_1) \frac{\Delta^2 f_0}{2!h^2} \\
 &\quad + \dots \\
 &\quad + (x - x_0)(x - x_1) \dots (x - x_{n-1}) \frac{\Delta^n f_0}{n!h^n} \\
 &\quad + E(x) \quad (I-6)
 \end{aligned}$$

where

$$E(x) = (x - x_0) \dots (x - x_n) \frac{f_0^{(n+1)}(\xi)}{(n+1)!}$$

and where ξ is in the interval occupied by x_0, \dots, x_n .

To familiarize with the difference formula, it is advantageous to set up a difference table and to understand the Sheppard's Zigzag Rule.



$$\Delta f_0 \text{ is equal to } f_1 - f_0$$

$$\Delta^2 f_0 \text{ is equal to } \Delta f_1 - \Delta f_0$$

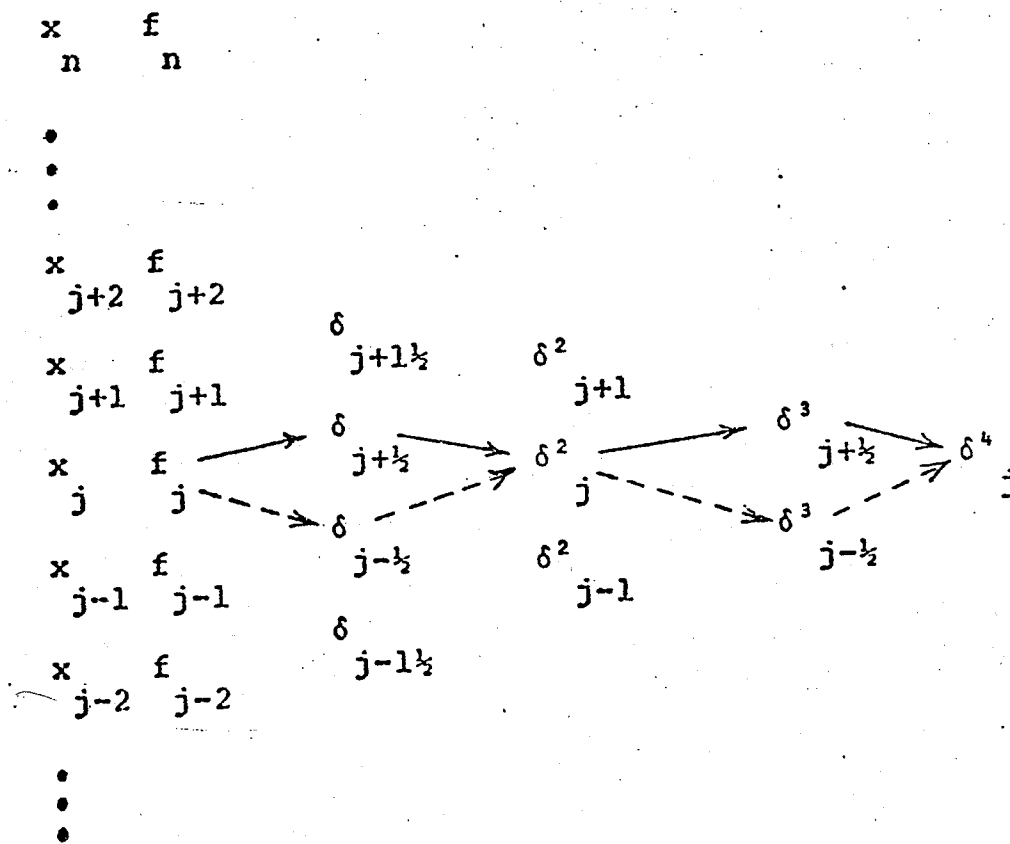
$$\dots \dots \dots$$

$$\Delta^n f_0 \text{ is equal to } \Delta^{(n-1)} f_1 - \Delta^{(n-1)} f_0$$

The direction of the solid arrow is in the forward direction and, therefore, the interpolation formula is called the Newton's forward formula.

If we want a better approximation for a particular

point, say x , it would be more desirable to take a zigzag difference path in the direction of the dotted arrows. Instead of calling them divided differences we prefer to call them central differences and we have a slightly different notation for them.



Interpolations following the path of the solid arrows and that of the dotted arrows are known respectively as the forward and backward formula of Gauss. The forward formula of Gauss may be written as

$$\begin{aligned}
 f(x) \cong & f_0 + (x - x_j) \frac{\delta f_{j+\frac{1}{2}}}{1!h} \\
 & + (x - x_j)(x - x_{j+1}) \frac{\delta^2 f_j}{2!h^2} \\
 & + (x - x_j)(x - x_{j+1})(x - x_{j-1}) \frac{\delta^3 f_{j+\frac{1}{2}}}{3!h^3} \\
 & + (x - x_j)(x - x_{j+1})(x - x_{j-1})(x - x_{j+2}) \frac{\delta^4 f_j}{4!h^4}
 \end{aligned}
 \tag{I-7}$$

Now we can find the first, second or higher order derivative from this formula.

$$\begin{aligned}
 f'(x) \cong & \frac{\delta f_{j+\frac{1}{2}}}{h} + (x - x_{j+1}) \frac{\delta^2 f_j}{2!h^2} + \\
 & (x - x_{j+1})(x - x_{j-1}) \frac{\delta^3 f_{j+\frac{1}{2}}}{3!h^3} + \\
 & (x - x_{j+1})(x - x_{j-1})(x - x_{j+2}) \frac{\delta^4 f_j}{4!h^4}
 \end{aligned}
 \tag{I-8}$$

For a uniform net, $(x - x_{j+1}) = -h$, $(x - x_{j-1}) = +h$,

and $(x - x_{j+2}) = -2h$.

Equation (I-8) can then be simplified to

$$h f'(x) \cong \delta f_{j+\frac{1}{2}} - \delta^2 f_j / 2 - \delta^3 f_{j+\frac{1}{2}} / 6 + \delta^4 f_j / 12 \quad (\text{I-9})$$

Similarly the second derivative can be simplified to

$$h^2 f''(x) \cong \delta^2 f_j - \delta^4 f_0 / 12 \quad (\text{I-10})$$

These approximations will now be applied to calculate some simple examples in quantum mechanics.

1. HARMONIC OSCILLATOR

The partial differential equation for the harmonic oscillator is

$$-\frac{1}{2} \frac{d^2}{dx^2} f(x) + \frac{1}{2} x^2 f(x) - Ef(x) = 0 \quad (I-11)$$

The wave function $\pi^{-1/4} \text{EXP}(-x^2/2)$ is a normalized solution of equation (I-11). Therefore the eigenvalue associated with this wavefunction can be found by integration.

$$E = \int_{-\infty}^{\infty} -f(x) \left(\frac{1}{2}\right) \frac{d^2}{dx^2} f(x) dx + \int_{-\infty}^{\infty} \frac{1}{2} x^2 f(x)^2 dx$$

$$= 0.5 \quad (I-12)$$

However, one can do a numerically equivalent calculation of equation (I-12) by means of the backward interpolation formula of Gauss and then integrate numerically.

The first derivative for the point x_3 can be written as

$$f'(x_3) = (f(x_1)/6 - f(x_2) + f(x_3)/2 + f(x_4)/3)/h \quad (I-13)$$

where h is the separation between x_1, x_2, x_3 and so on.

The second derivative can be easily calculated once the first derivatives of more than four points have been found.

In order to solve equation (1-11) with boundary conditions: $f(-A) = 0$ and $f(A) = 0$, one may employ the uniform net $x_j = -A + j h$, $j = 0, 1, \dots, j+1$ where the separation h is equal to $2A/(j+1)$ and A and $-A$ are the upper and lower bound for x . Then the differential equation can be replaced by some finite-difference equations of the form

$$L_h u_j + \epsilon u_j = 0, \quad j = 1, 2, \dots, j \quad (1-19)$$

with boundary conditions $u_0 = 0$ and $u_{j+1} = 0$. Here L_h is a "difference approximation" of the linear differential operator L , which for the present will be taken to be

$$L_h u_j = - (1/2h^2) \delta_j^2 u_j - (1/12) \delta_j^4 u_j + (1/2) x_j^2 u_j \quad (1-20)$$

where

$$\begin{aligned} \delta_j^2 u_j &= u_{j+1} - 2u_j + u_{j-1} \\ \delta_j^4 u_j &= \delta_{j+(1/2)}^3 - \delta_{j-(1/2)}^3 \\ &= \delta_{j+1}^2 - \delta_j^2 - \delta_j^2 + \delta_{j-1}^2 \\ &= \delta_{j+(3/2)} - 3\delta_{j+(1/2)} + 3\delta_{j-(1/2)} - \delta_{j-(3/2)} \\ &= u_{j+1} - 4u_{j+1} + 6u_j - 4u_{j-1} - u_{j-2} \quad (1-21) \end{aligned}$$

Therefore

$$\begin{aligned} L_h u_j &= + (1/24h^2) u_{j+2} - (2/3h^2) u_{j+1} \\ &\quad + (1/h^2) (1.25 + 0.5x^2 h^2) u_j \\ &\quad - (2/3h^2) u_{j-1} + (1/24h^2) u_{j+2} \quad (1-22) \end{aligned}$$

For a boundary limit of 5.0, that is, $A = 5.0$, and a matrix of order 90, the eigenvalues were calculated using both the linear interpolation (second order) and the fourth order Gauss interpolation. The first four eigenvalues are compared.

Table 1.1
THE FIRST FOUR EIGENVALUES OF
THE HARMONIC OSCILLATOR

SECOND ORDER	FOURTH ORDER
0.49962	0.499998
1.49811	1.499989
2.49508	2.499962
3.49054	3.499907

The diagonalization method used here to calculate the eigenvalues was originated by Jacobi and adapted by Von Neumann(24) for large computers. There are many other methods(25-28), but only the Jacobi method will be illustrated in the appendix.

The eigenvalues for other boundary limits and different matrix orders are also compared. They were all calculated using fourth order Gauss interpolation. The results are listed in the following page.

Table 1.2

EIGENVALUES FOR
BOUNDARY LIMIT 10.0

<u>ORDER OF MATRIX</u>	
41	81
0.49939	0.49996
1.49580	1.49972
2.48525	2.49901
3.46339	3.49753
4.42600	4.49498
5.36880	5.49107

Table 1.3

EIGENVALUES FOR
BOUNDARY LIMIT 5.0

<u>ORDER OF MATRIX</u>	
21	41
0.49939	0.49996
1.49580	1.49972
2.48525	2.49901
3.46339	3.49753
4.42601	4.49498
5.36886	5.49112

Table 1.4

EIGENVALUES FOR
BOUNDARY LIMIT 2.5

<u>ORDER OF MATRIX</u>		
11	21	41
0.50243	0.50288	0.50336
1.52427	1.52978	1.53610
2.59925	2.63663	2.67239
3.75256	3.90465	4.01910
4.99882	5.41361	5.66378
6.33835	7.20861	7.64867

Table 1.5

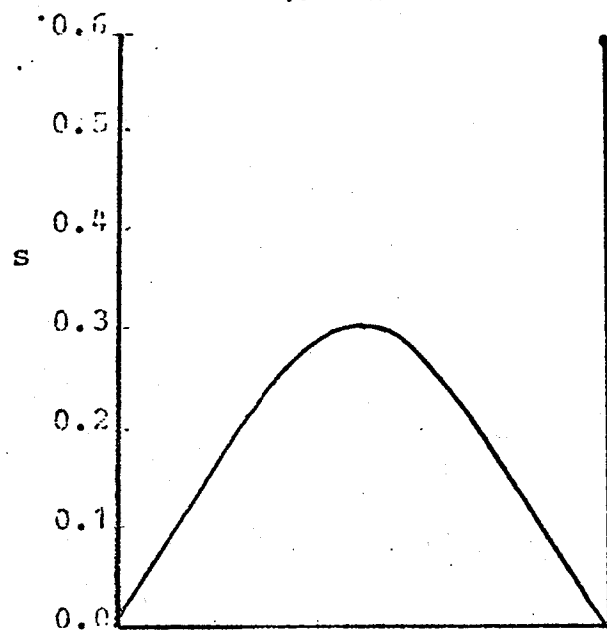
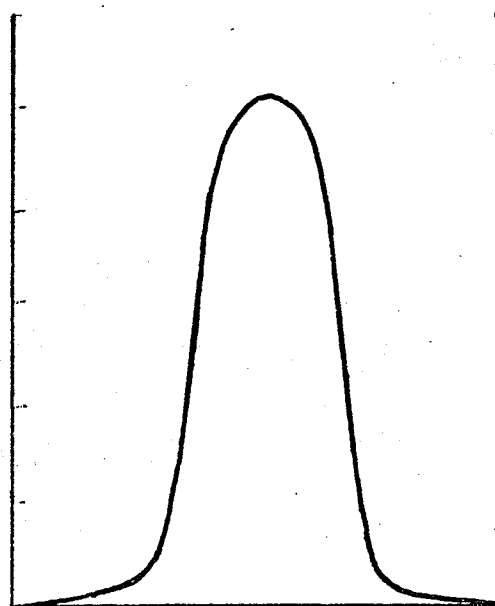
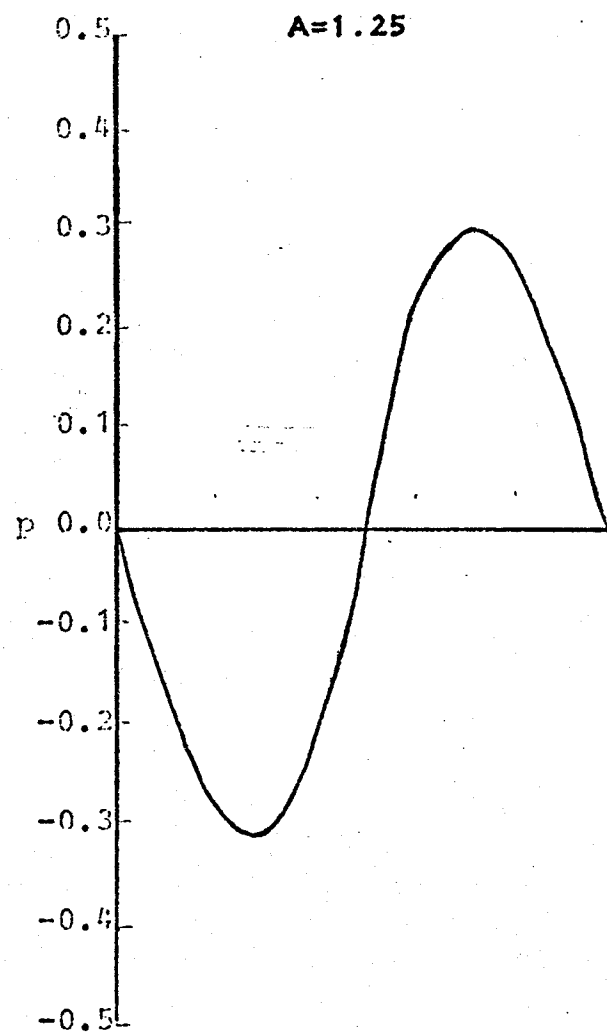
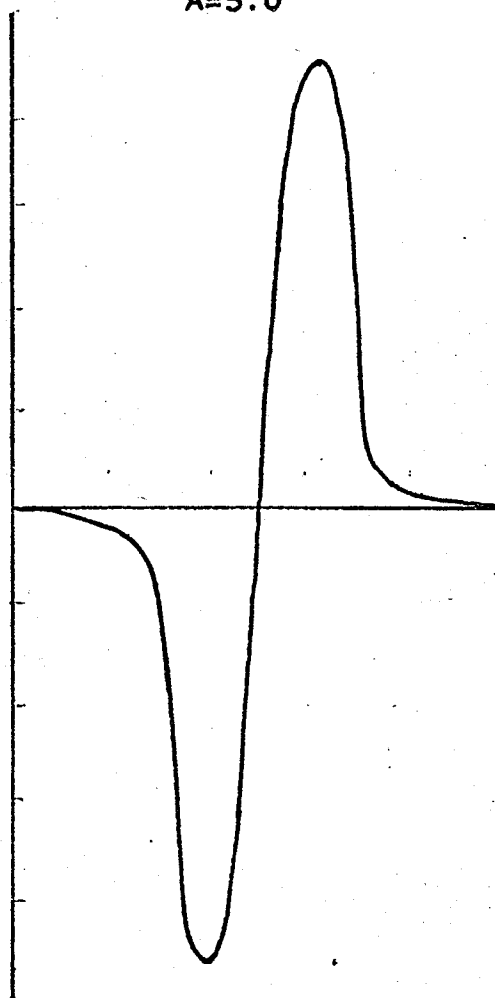
EIGENVALUES FOR
BOUNDARY LIMIT 1.25

<u>ORDER OF MATRIX</u>
21
0.78605
2.91445
6.24872
10.87199
16.78042
23.94203

Figure 1.

WAVEFUNCTIONS OF THE HARMONIC OSCILLATOR
WITH DIFFERENT BOUNDARY CONDITIONS *

*The IBM Scientific Subroutine Package has a program which calculates both the eigenvalues and the eigenfunctions. The program is based on Reference 24. To support the arguments in the discussion of this chapter, four of the eigenfunctions computed by the program were selected and drawn on the opposite page.

$A=1.25$  $A=5.0$  $A=1.25$  $A=5.0$ 

2. THE HYDROGEN ATOM

It is essentially the same as the harmonic oscillator except it is three dimensional with a slightly different wave function. The Schrödinger Equation is

$$\nabla^2 \psi - (1/r)\psi = E \psi \quad (\text{I-14})$$

where ψ is a function of x , y and z only. Therefore

$$\begin{aligned} & \left(-\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) + (1/\sqrt{x^2 + y^2 + z^2}) \psi(x, y, z) \\ & = E \psi(x, y, z) \end{aligned} \quad (\text{I-15})$$

The total energy is equal to

$$\begin{aligned} E = & \int \psi^*(x, y, z) \left(-\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) dx dy dz \\ & + \int \psi^*(x, y, z) (1/\sqrt{x^2 + y^2 + z^2}) \psi(x, y, z) dx dy dz \end{aligned} \quad (\text{I-16})$$

The integral is summed over all space and is equal to $\frac{1}{2}$ for the ground state wave function

$$\pi^{-1/2} \text{EXP}(-\sqrt{x^2 + y^2 + z^2}) \quad (\text{I-17})$$

Since it is symmetrical in all directions, one can replace (I-16) by

$$\begin{aligned} E = & (3/\pi) \left(\int \text{EXP}(-\sqrt{x^2 + y^2 + z^2}) \left(-\frac{\partial^2}{\partial x^2} \right) \text{EXP}(-\sqrt{x^2 + y^2 + z^2}) \right. \\ & \left. + (1/3) \int x^2 \text{EXP}(-2\sqrt{x^2 + y^2 + z^2}) \right) (dx)^3 \end{aligned} \quad (\text{I-18})$$

Then the rest of the calculations will be the same as in the case of the harmonic oscillator, except that one has

to calculate dE for each (y,z) pair and then sum them up.

The author wrote a program in MATLAN computer language, which is supposed to be able to handle large matrices with many built-in matrix operations. However, the language is really inefficient because it occupies 80K storage units just by itself. When the matrix is large, the Input-Output time required to transfer information back and forth from the discs (accessory memory unit linked to the computer) is even more than the actual computation time. It took the computer three hours to calculate equation (I-18) for a three dimensional matrix about the size of $100 \times 100 \times 100$. The calculated ground state energy differs from the theoretical value by one per cent. A much faster program can be written in FORTRAN and, therefore, the MATLAN program will not be given here.

To solve the eigenvalue problem of the hydrogen atom, all that is required is to transform equation (I-15) into finite-difference equations. With a second order Gauss interpolation, there will be seven terms instead of three, as there are six neighbouring points instead of two. The order of the matrix to be diagonalized is equal to n^3 , where n is the number of separations in one direction. A crude model of the hydrogen atom may be represented by twenty points in each direction, that is, sixteen thousand points altogether. To diagonalize a matrix of the order 16,000 is simply not feasible at present.

B. DISCUSSION

The results of the harmonic oscillator clearly demonstrate two facts. First, the wave function is quite well localized. The first few eigenvalues for a boundary limit of 5.0 are exactly the same as those for a boundary limit of 10.0; and differ from the theoretical value for infinite domain only in the fifth or sixth figure after the decimal. Secondly, the eigenvalues increase sharply as the boundary limit becomes too small. There is only an increase of 0.003 when the boundary limit decreases from 5.0 to 2.5, but an increase of 0.28 from 2.5 to 1.25.

The spherically symmetric wave functions of the hydrogen atom behave similarly to the harmonic wave functions. Since the hydrogen wave functions have been used in a number of standard texts(29) to explain the chemical properties of other atoms, we may relate these two properties to some commonly known phenomena, such as the localizability of many everyday objects and the incompressibility of many solids and liquids.

It was mentioned earlier that the finite-difference method has been applied to the solution of the three-dimensional Schrödinger's equation by many authors. In reference 10, they improved the technique by a square-root grid along with a transformation of the co-ordinates in the Schrödinger's equation. By including more partial waves,

they improved the S-limit result and obtained the G-limit ground state energy of helium atom to be -2.90351 a.u. as compared to the exact value of -2.90372 a.u.

Thus far, their calculations are limited to $(1s^2)^1S$ and $(1s2s)^3S$ states of helium and the $(1s^2)^1S$ state of hydride ion.

Although we did not go too far in the calculation of the hydrogen atom, it is very likely that the method suggested can be used in the future when a large enough computer will be available.

CHAPTER III

THE PARTIAL WAVE METHOD

A. THE THEORY OF THE SCATTERING OF A BEAM OF
PARTICLES BY A CENTRE OF FORCE

A stream of electrons moving from left to right with velocity v along the z -direction may be represented by the plane wave $\text{EXP}(ikz)$, where k is equal to $2\pi mv/h$, which corresponds to a flow of v electrons across unit area per unit time. The wave will be scattered by the atom situated at the origin, the asymptotic wave function at the point (r, θ, ϕ) being

$$\psi = e^{ikz} + r^{-1} e^{ikr} f(\theta) \quad (11-1)$$

where $f(\theta)^2 2\pi \sin\theta d\theta$ is the number of particles scattered between angles θ and $\theta + d\theta$.

The problem now is to solve the Schrödinger equation

$$\nabla^2 \psi + (k^2 - U(r))\psi = 0 \quad (11-2)$$

where $k = mv/\hbar$ and $U(r) = 2mV(r)/\hbar^2$. The equation can be solved in spherical polar co-ordinates. The general solution having axial symmetry is

$$\psi = \sum_{\ell=0}^{\infty} A_{\ell} P_{\ell}(\cos\theta) L_{\ell}(r) \quad (11-3)$$

where A_{ℓ} are arbitrary constants, $P_{\ell}(\cos\theta)$ is the ℓ th Legendre coefficient, and L_{ℓ} is any solution of

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dL_{\ell}}{dr} \right) + \left(k^2 - U(r) - \frac{\ell(\ell+1)}{r^2} \right) L_{\ell} = 0 \quad (11-4)$$

If we assume $U(r)$ has a pole not of higher order than r^{-1} , the equation has two independent solutions, one finite at the origin and the other infinite. In order that (11-3) shall have the asymptotic form (11-1), the wave

function must be everywhere finite. If we set $L_\ell = r^{-1}G_\ell(r)$, equation (11-4) reduces to

$$\frac{d^2 G_\ell}{dr^2} + (k^2 - U(r) - \frac{\ell(\ell+1)}{r^2})G_\ell = 0 \quad (11-5)$$

The solution for large r must be of the form

$$G_\ell = A \sin(kr + \epsilon)$$

where ϵ is a small angle.

The particular solution we want is

$$L_\ell(r) = (kr)^{-1} \sin(kr - (1/2)\ell\pi + \eta_\ell) \quad (11-6)$$

which is finite at the origin. η_ℓ is the phase shift. To find A_ℓ we have to take advantage of the fact that for all ℓ and large r ,

$$A_\ell L_\ell(r) - (2\ell + 1) i^\ell f_\ell(r) \approx C_\ell r^{-1} e^{ikr} \quad (11-7)$$

where C_ℓ is some constant, $f_\ell \approx (kr)^{-1} \sin(kr - (1/2)\ell\pi)$

for large r . Since $\sin(x) = (1/2i)(e^{ix} - e^{-ix})$, the left-hand side of equation (11-7) becomes

$$\begin{aligned} & (1/2)(ikr)^{-1}(A_\ell e^{i(kr - (1/2)\ell\pi + \eta_\ell)} - \\ & A_\ell e^{-i(kr - (1/2)\ell\pi + \eta_\ell)} - (2\ell + 1)i^\ell e^{i(kr - (1/2)\ell\pi)} \\ & + (2\ell + 1)i^\ell e^{-i(kr - (1/2)\ell\pi)}) \end{aligned} \quad (11-8)$$

Since the wave $(r)^{-1}e^{-ikr}$ is a wave moving towards the centre and hence the scattered wave should not contain any term of this type of wave function. Therefore,

$$A_\ell e^{-i\eta_\ell} - (2\ell + 1)i^\ell = 0$$

$$A_\ell = (2\ell + 1)i^\ell e^{i\eta_\ell} \quad (11-9)$$

Substituting this into equation (11-3), we get

$$\Psi = \sum_{\ell=0}^{\infty} (2\ell+1) i^{\ell} e^{i\eta_{\ell}} L_{\ell}(r) P_{\ell}(\cos\theta) \quad (11-10)$$

which is the sum of the incident wave and scattered wave at large r . From equation (11-1), the scattered wave is therefore obtained by subtracting the incident wave

$$\sum_{\ell=0}^{\infty} (2\ell+1) i^{\ell} P_{\ell}(\cos\theta) f_{\ell}(r) \text{ from equation (11-10).}$$

$$r^{-1} e^{ikr} f(\theta) = (2ikr)^{-1} e^{ikr} \times$$

$$\sum_{\ell=0}^{\infty} e^{-(1/2)\ell\pi i} (2\ell+1) i^{\ell} (e^{2i\eta_{\ell}} - 1) P_{\ell}(\cos\theta)$$

Since $e^{-(1/2)\ell\pi i} i^{\ell} = i^{\ell} \cos((1/2)\ell\pi) - i^{\ell+1} \sin((1/2)\ell\pi) = 1$ for all ℓ , therefore

$$f(\theta) = (2ik)^{-1} \sum_{\ell=0}^{\infty} (2\ell+1) (e^{2i\eta_{\ell}} - 1) P_{\ell}(\cos\theta) \quad (11-11)$$

The total elastic cross-section

$$Q = 2\pi \int_0^{\pi} |f(\theta)|^2 \sin\theta d\theta \quad \text{becomes}$$

$$Q = k^{-2} 4\pi \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2\eta_{\ell} \quad (11-12)$$

This method was first used by Rayleigh (30). It was first applied to the problem of the scattering of electrons by atoms by Faxén and Holtsmark (20).

The next three sections are concerned with the numerical solution of the phase shifts and the wave functions by the difference and the non-uniform difference methods, using only a three point approximation for the second

derivative with a refinement in the diagonal term adjusted from the knowledge of the approximate solution. This method, the author believes, is more sophisticated, faster, and more accurate than the difference method involving more than three points, as the number of storage requirements, together with the number of operations involved, increases many times in the latter. When ℓ is greater than zero, or the potential term changes quite rapidly near the origin, the non-uniform difference method is highly favoured.

B. SOLUTION OF THE DIFFERENCE EQUATIONS

As we have seen from the last chapter, the difference equations are essentially a set of linear simultaneous equations derived from the differential equation. This method has been applied by Robertson(22) to calculate phase shifts without much modification to improve the accuracy and the speed of computation.

For a three points approximation, we notice that we only get $(n-2)$ equations from n points and therefore two constants are necessary to determine a particular solution. These are sometimes referred to as boundary conditions. If we let the point by point representation of G_ℓ in equation (II-5) be $f_0, f_1, \dots, f_i, \dots, f_{n+1}$, we can find the particular solution for the boundary conditions: f_0 equal to zero as, according to Huygens' Principle, the atom may be regarded as the source of a secondary wave. The other condition is, that the maximum amplitude at a large distance be equal to one.

Since the second boundary condition is very inconvenient for the calculation of the wave function, as the asymptotic amplitude can only be found at the end of the computation, this means we must store up all the necessary information. Then we must return to the very beginning or proceed in the reverse direction, all of which involves a series of divisions which are too time consuming. For

example, we have a hundred thousand points on the curve, therefore, we need at least 800K bytes for storage in double precision mode. This is three or four times greater than the capacity of most computers. To avoid this difficulty, we take advantage of the approximate solution of equation (II-5) when r is small. If we differentiate $A r^{\ell+1}$ twice, we get

$$\frac{\ell(\ell+1)}{r^2} A r^{\ell+1}$$

and therefore $A r^{\ell+1}$ is a solution of equation (II-5) when r is small. From some of the calculations done, A is within a few order of magnitude greater or less than one, which, of course, also depends on the potential term. The magnitude of A can be most conveniently found by using the SCALING ROUTINE in the CALCOMP PLOTTING SYSTEM of IBM 360. That is, f_1 is set equal to $r^{\ell+1}$ initially, and we have to calculate the scaling factor of the plot of this function section by section because of storage problem. The scaling factor for a large distance is used to calculate the value of A . The wave function can then be plotted nicely.

The following will be a brief description of the method used to calculate the phase shifts and, a numerical representation of the wave function. We have

$$\frac{d^2}{dx^2} f_i \approx \frac{\frac{f_{i+1} - f_i}{h} - \frac{f_i - f_{i-1}}{h}}{h} = \frac{f_{i+1} - 2f_i + f_{i-1}}{h^2} \quad (\text{II-14})$$

Equation (11-5) is therefore approximately equal to a set of n equations of the form

$$f_{i-1} + (-2 + k^2 h^2 - U(r)h^2 - \frac{\ell(\ell+1)}{i^2}) f_i + f_{i+1} = 0 \quad (11-15)$$

where i runs from 1 to n . f_0 and f_1 are given as above. Of course the amplitude of the asymptotic wave will not be exactly equal to one; but if we want it to be exactly one, the whole function can always be multiplied by a constant.

Equation (11-15) can be rewritten in matrix form

$$\begin{bmatrix} c_1 & d_1 & & & \\ d_1 & c_2 & & & \\ & \ddots & \ddots & \ddots & \\ & & \ddots & \ddots & \\ & & & c_{n-1} & d_{n-1} \\ & & & d_{n-1} & c_n \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ \vdots \\ \vdots \\ f_{n-1} \\ f_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \\ -d_{n-1} f_{n+1} \end{bmatrix} \quad (11-16)$$

where $d = 1$ and $c_i = -2 + (k^2 - U(r) - \ell(\ell+1)/r_i^2) h^2$

One method used to find the phase shifts is to adjust h until the determinant goes to zero which then implies that f_{n+1} also becomes zero. Therefore $h(n+1)$ is the point where the wave function intercepts the axis and hence $\sin \eta_\ell$ can be found. Actually the determinant changes sign at that point. In practice this procedure is too time consuming and we cannot find the sign nor the absolute magnitude of the phase shifts.

Instead of finding the determinant, we proceed directly to solve the linear equations by the Gauss Elimination method, which is particularly easy in the case of a tridiagonal symmetric matrix. After the elimination process the diagonal terms usually become a series of negative numbers interposed by a few positive numbers. If c_i is positive, that means f_i and f_{i+1} have a different sign and, therefore, indicates the point where the wave intercepts the axis. A better approximation is that the wave intercepts the x-axis at the point $(i + 1/(1+c_i))h$. It can be proved, therefore, by considering the following diagram.

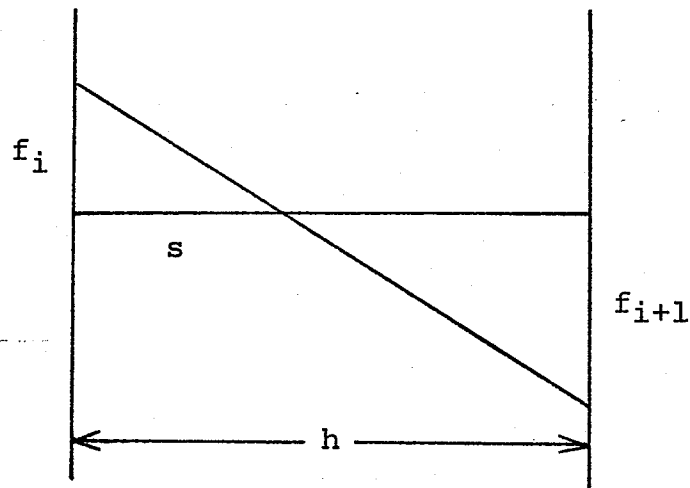


Figure 2. DIAGRAM TO DETERMINE THE POINT OF INTERSECTION.

We have $s/f_i = h/(f_i + f_{i+1})$ from the diagram.

Therefore $s = 1/(1+f_{i+1}/f_i)$. Since $c_i f_i = f_{i+1}$,
 $s = 1/(1 + c_i)$.

From the number of positive diagonal terms we can calculate the sign and the absolute magnitude of the phase shifts without any doubt. Due to the fact that the difference method is an approximate method, if h is not small enough, there is occasionally a sudden "spur" of the values of the phase shifts. This can be recognised by plotting the values of the phase shifts against the values of k and the curve should be smooth and should also tend to zero for large k . However, this problem does not occur in the non-uniform approach.

C. NON-UNIFORM DIFFERENCE METHOD

In solving equation (II-5), we can see that $1/r^2$ changes very rapidly near the origin but tapers off very slowly. It would only be natural to use a finer net near the origin and widen the separation as we move away from that point. Actually, the method the author developed, can be used to shorten or widen any region as desired. Although it might be used for general matrices, the calculations might be too tedious to allow for fast computation, even by the computer. For the same reason, the change of the separation from one region to the next should be either double or half. The example shown is a tridiagonal matrix. At each increment junction, we are in effect having a fourth diagonal element. The problem is to change it back to a tridiagonal matrix.

The outline is as follows:

In equation (II-16), instead of having a tridiagonal matrix, we have the following matrix:

$M(1) \quad S(1)$			
$S(1) \quad M(2) \quad S(2)$			
$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$			
$S(i-1) \quad M(i)$			$S(i)$
$S'(0)$	0	$M'(1) \quad S'(1)$	
$S'(1) \quad \cdot \quad \cdot \quad \cdot \quad \cdot$			
$S'(j-1) \quad M'(j)$			$S'(j)$
$S''(0)$	0	$M''(1)$	$\cdot \quad \cdot \quad \cdot$

To understand the difference method thoroughly, one must master the technique of transforming a differential equations like (II-5) into a set of difference equations similar to (II-15). The size of h is chosen arbitrarily. As long as h is constant within a set of equations, the solutions can be calculated easily by Gauss Elimination Process. Two sets of equations from the same differential equation with multiples of h can be related to each other through the "junction technique" developed by the author; it is actually very simple. There is nothing unusual about the first i equations, as the $(i+1)$ 'th equation is just one of those equations of the form (II-15), except h is double.

It may be rewritten as

$$f_{i-1} + (-2 + k^2(2h)^2 - U(r)(2h)^2 - \frac{\ell(\ell+1)}{i^2})f_{i+1} + f_{i+3} = 0$$

Once we relate one block of equation to the other, the others fall in line, and it is then just a matter of performing the Gauss Elimination Process after we set up the matrix.

To save storage space, certain symbols are used to store enough information for the following steps of calculation. Once these steps are completed, their values are replaced by new information, usually the newly calculated results. A simple matrix can illustrate how this is done.

$$\begin{array}{l}
\Rightarrow \left| \begin{array}{cccc} 1_{C2} & 1 & & \\ 1 & 2_{C2} & 1 & \\ & 1 & 3_{C2} & 1 \\ & 1 & 0 & M'(1) & 1 \\ & & 1 & M'(2) & 1 \end{array} \right| \Rightarrow \left| \begin{array}{cccc} 1 & 1_D (=1/1_{C2}) & & \\ 2_{C2} - 1_D & 1 & & \\ & 1 & 3_{C2} & 1 \\ & 1 & 0 & M'(1) & 1 \\ & & 1 & M'(2) & 1 \end{array} \right| \\
\\
\Rightarrow \left| \begin{array}{cccc} 1 & 1_D & & \\ & 1 & 2_D (=1/2_{C2} - 1_D) & \\ 1 & 3_{C2} & 1 & \\ & 1 & 0 & M'(1) & 1 \\ & & 1 & M'(2) & 1 \end{array} \right| \Rightarrow \left| \begin{array}{cccc} 1 & 1_D & & \\ & 1 & 2_D & \\ & & 1 & 3_D (=1/3_{C2} - 2_D) \\ 1 & 0 & M'(1) & 1 \\ & & 1 & M'(2) & 1 \end{array} \right| \\
\\
\Rightarrow \left| \begin{array}{cccc} 1 & 1_D & & \\ & 1 & 2_D & \\ & & 1 & 3_D \\ & & -2_D M'(1) & 1 \\ & & 1 & M'(2) & 1 \end{array} \right| \Rightarrow \left| \begin{array}{cccc} 1 & 1_D & & \\ & 1 & 2_D & \\ & & 1 & 3_D \\ & & 1 & M'(1)/-2_D & 1/-2_D \\ & & 1 & M'(2) & 1 \end{array} \right| \\
\\
\Rightarrow \left| \begin{array}{cccc} \cdot & & & \\ \cdot & 1 & 3_D & \\ 0 & (M'(1) + 2_D 3_D)/-2_D & 1/-2_D & \\ & 1 & & M'(2) & 1 \end{array} \right| \Rightarrow \left| \begin{array}{cccc} \cdot & & & \\ \cdot & 1 & 3_D & \\ 1 & 1/(M'(1) + 2_D 3_D) & & \\ 1 & & M'(2) & 1 \end{array} \right|
\end{array}$$

The symbol D is used in the computer and only one storage space is allocated for all these off-diagonal terms, as old values are not needed once a new D has been calculated. The same conditions apply to C2, which also represents all the M', M'' and so on.

The formula for i_D is therefore equal to

$$i_D = \frac{1}{\frac{i}{C2} - \frac{i-1}{D}} = \frac{1}{\frac{i}{M} - \frac{i-1}{D}} \quad \text{or}$$

$$\frac{i-1}{D} = \frac{i_D i_M - 1}{i_D} \quad (\text{II-27})$$

From the result obtained after Gauss Elimination, the effective D in the uniform difference method becomes

$$D = -\frac{i-1}{D} i_D = 1 - i_D i_M \quad (\text{II-28})$$

One way of choosing how many intervals should be allocated to each region is to double the separation when the first derivative of the function decreases approximately by a half. A simple function such as

$$0.4 \text{ EXP}(0.23262 \text{ } x) \quad (\text{II-29})$$

was found to be quite satisfactory. One restriction is that at least three intervals must be in each region.

For a clearer understanding of the process, one should refer to the program given in the appendix.

D. REFINEMENT OF THE METHOD

If the method were exact, the phase shift should be zero in the case where there is no potential term. Instead it was found that there is a positive phase shift roughly equal to $n(nk)^2/\pi$ where n is the number of half-waves from the origin. In order to check the calculation, we set

$$\begin{aligned} f_{i-1} &= \sin(k(x-h)) \\ f_i &= \sin(kx) \\ f_{i+1} &= \sin(k(x+h)) \end{aligned} \tag{II-17}$$

Therefore,

$$\begin{aligned} f''_i &= \frac{(\sin(kx+kh) - \sin(kx)) - (\sin(kx) - \sin(kx-kh))}{h^2} \\ &= \frac{2\sin(kx)\cos(kh) - 2\sin(kx)}{h^2} \\ &= - (4\sin^2(kh/2))/h^2 \end{aligned} \tag{II-18}$$

As hk tends to zero, $(4\sin^2(kh/2)/h^2)$ tends to $h^2k^2/h^2 = k^2$. Since the sine of an angle is always smaller than the angle itself, therefore a positive phase shift will result if k^2h^2 is used instead of $4\sin^2(kh/2)$ in equation (II-15) because the smaller the k , the bigger the wave length is.

After that substitution, another error is due to the precision of the computer. In the case where $\ell = 0$, $hk = 8 \times 10^{-4}$, the phase shift starts from 0.936×10^{-10} increasing steadily and the value at 200 waves from the

origin becomes 0.38×10^{-7} . This may be explained by the fact that IBM 360 double precision numbers have fifteen to sixteen significant figures, but the number of effective significant figures of $h^2 k^2$ after adding -2 will be reduced to seven or eight, and hence the estimated error in the phase shift will be of the order of 10^{-7} to 10^{-8} . However, for hk ten times bigger, we have a statistical error of $\pm 10^{-9}$ and sometimes even $\pm 10^{-10}$. This error is probably due to the straight line approximation in finding the intercept on the x -axis as described previously. Anyway, the non-uniform difference method described in the last section can get around this problem because only a very small region will have a very small hk value.

For ℓ not equal to zero, the phase shift tends to zero extremely slowly. For example, for $\ell = 1$, the phase shift at 200 wavelengths from the origin is still in the order of 10^{-4} . Even the non-uniform method is ineffective in this case. However, there are three ways to solve the problem, namely by graphical extrapolation is one way, and a power fit calculation is another. Finally, it is considered that by finding the theoretical correction by integration is superior to both.

$$\text{When } k^2 \gg \frac{\ell(\ell+1)}{r^2}$$

where r is the distance from the origin,

$$\left(k^2 - \frac{\ell(\ell+1)}{r^2}\right) = \left(k - \frac{(\ell(\ell+1))/r^2}{2k}\right)^2 \quad (11-19)$$

because

$$\frac{\left(\frac{\ell(\ell+1)}{r^2}\right)^2}{4k^2} \ll 1 \quad (11-20)$$

Since the first order correction of the phase shift

$$\Delta' \delta_\ell \approx \frac{\frac{\pi}{k'} - \frac{\pi}{k}}{\frac{\pi}{k}} \times \pi \quad \text{radians} \quad (11-21)$$

where $k' = k - \ell(\ell+1)/(2kr^2)$.

$$\text{Therefore } \Delta' \delta_\ell \approx \ell(\ell+1)\pi/(2k^2r^2) \quad \text{radians} \quad (11-22)$$

$$\text{Since } r^2 = \pi^2 N^2 / k^2 \quad (11-23)$$

where N is the number of half-waves from the origin plus $1/2$. The sum of the the first order corrections

$$\sum_N \Delta' \delta_\ell = \int_N^\infty \frac{\ell(\ell+1)}{2\pi N^2} dN = - \frac{\ell(\ell+1)}{2\pi N} \quad (11-24)$$

The sum of the second order corrections can be obtained similarly in noticing that

$$k'' = k - \frac{\ell(\ell+1)}{2kr^2} - \frac{1}{2k} \left(\frac{\ell(\ell+1)}{2kr^2} \right)^2 \quad (11-25)$$

$$\sum_N \Delta'' \delta_\ell = \int_N^\infty \frac{(\ell(\ell+1))^2}{8\pi^3 N^4} = - \frac{(\ell(\ell+1))^2}{24\pi^3 N^3} \quad (11-26)$$

Similarly, for a polarization term of s/r^4 , the sum of the first order corrections is $k^2 s / (6\pi^3 N^3)$. (11-26)

E. ELECTRON SCATTERING OF KRYPTON

Holtzmark(20) used a Hartree potential with polarization to calculate the phase shifts in the electron scattering of krypton. He used the method of numerical integration without a computer; therefore we cannot expect the calculation to be very accurate. Instead of just a forty point representation used by Holtzmark, the potential used here is a polynomial function. A polynomial regression program was used, but it was found that it had to be applied to at least four sections of the potential function in order to have a curve fitting reasonably well with all the points.

The effect of a small change (10%) in the polarization on the calculation of the phase shifts and hence the total cross-sections was studied. The results were plotted on Page 43. It was found that the greater polarization had a better result near the point of maximum total cross-section, and the smaller polarization at higher energy. This suggests that if the asymptotic potential decreases faster than a constant times r^{-4} , there may be results closer to the experimental values.

The angular distributions of electrons scattered elastically by krypton atoms were calculated for electrons of energy between 0.1 a.u. and 1.5 a.u. The method used will be found in the following page.

1. ANGULAR DISTRIBUTION

From equation (II-11), the scattering cross-section

$$d\sigma(\theta) = \frac{2\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \delta_{\ell} (P_{\ell}(\cos \theta))^2 \sin \theta d\theta \quad (\text{II-30})$$

The Legendre polynomials $P_{\ell}(\cos \theta)$ can be calculated by the recursive formula (26)

$$(n+1) P_{n+1}(x) = (2n+1) P_n(x) x - n P_{n-1}(x) \quad (\text{II-31})$$

$$\text{The total cross-section } \sigma(\theta) = \int_0^{\pi} d\sigma(\theta) \quad (\text{II-32})$$

For large ℓ , $\sin^2 \delta_{\ell}$ is very small. For example, the total cross-section does not increase more than 1% in summing over from $\ell=0$ to $\ell=9$ instead of to $\ell=4$.

The scattered intensity per unit solid angle can be obtained by dividing equation (II-30) by $0.5 \sin \theta d\theta$.

The results were plotted.

Figure 3.

TOTAL CALCULATED ELASTIC CROSS-SECTIONS
FOR ELECTRON-KRYPTON SCATTERING AND THE
EXPERIMENTALLY OBSERVED TOTAL CROSS-SECTIONS.

⊙ greater polarization = 22.0 r^{-4}

x smaller polarization = 20.0 r^{-4}

— experimental

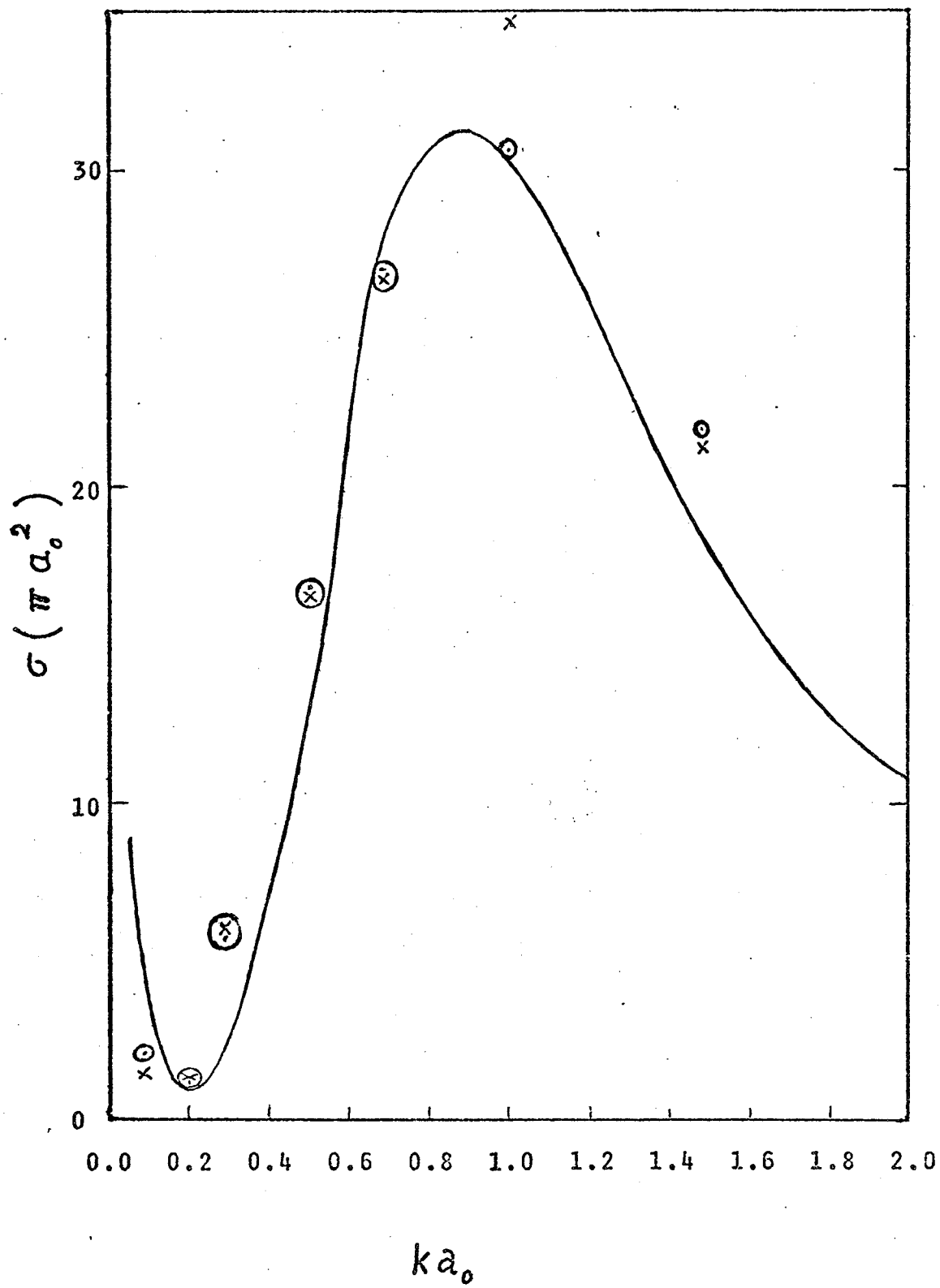


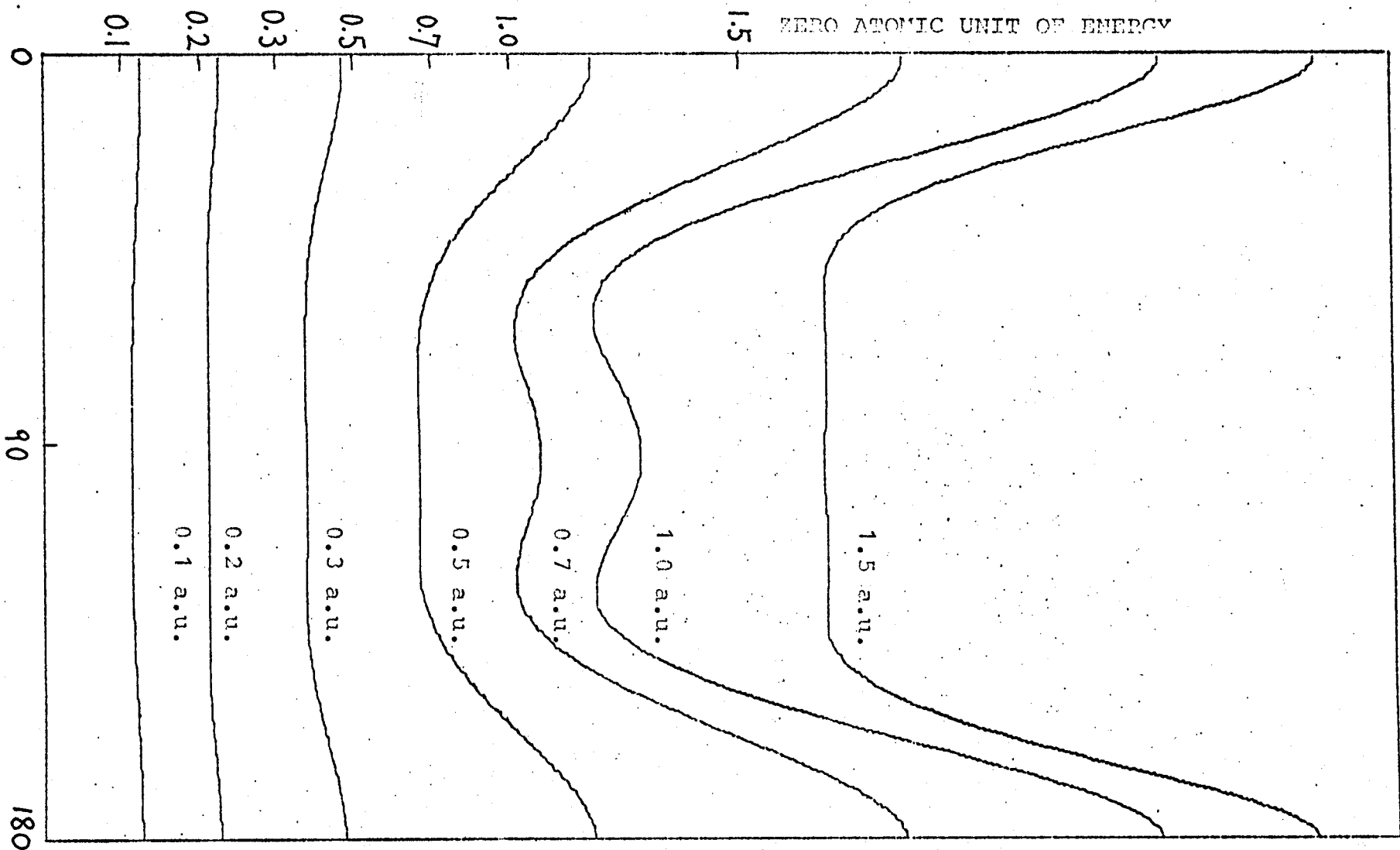
Figure 4.

CALCULATED ANGULAR DISTRIBUTIONS OF ELECTRONS

SCATTERED ELASTICALLY BY KRYPTON ATOM.

SCATTERED INTENSITY PER UNIT SOLID ANGLE (ARBITRARY UNITS)

ANGLE OF SHATTERING IN DEGREES



F. DISCUSSION

With a computer that can handle double precision numbers, seven to ten significant figures for the phase shift may be obtained through this improved version of the finite-difference method. It was found that the values of the phase shifts calculated by this method agree very well with those that appear on a standard text(31). Only in two cases did the values show a difference equal to π . If the criterion is that the phase shift should tend to zero as the velocity, and hence k , tends to infinity, the results calculated by this method are justified.

If the potential is simple enough, a program can be written for the Hewlett-Packard desk computer, which is capable of performing about one thousand cycles per minute in the Gauss Elimination Process for a spherical potential well.

A ten per cents change in the polarization potential results in a remarkable change in the calculated total scattering cross-sections of krypton. Therefore, if the potential is not exactly known, it is not easy to make a direct comparison with other methods. However, Holtzmark did not expect more than three significant figures in his results while Robinson claimed to have three to five significant figures. It is believed that this method should be superior in both respects of computer time and accuracy.

The problem we have solved is the determination of the phase shifts from a given differential equation, such as a Schrödinger's equation, with a given known $V(r)$ in our scattering problem. The inverse of the problem is commonly encountered in the field of nuclear collisions where the interaction law $V(r_1-r_2)$ between two colliding particles is not known from first principles. Although a method was described by Wu and Ohmura (32), as yet the usefulness of the method as a criterion for ascertaining η_l and $V(r)$, they said, is rather limited. The obvious procedure to check the $V(r)$ is to calculate the phase shifts from the potential found by their method.

Of course, one can resort to the numerical integration of the Schrödinger's equation, or some approximate methods, such as the Born approximation or the Variational methods. However, the difference method is very attractive because it is straightforward in principle and the accuracy can be increased readily by a finer mesh-size.

Recently, some work has been done to find a better polarization potential through the calculation of phase shifts(33). Therefore, this method is also useful in this area.

CHAPTER IV

TRANSITION PROBABILITY AND THE

TIME DEPENDENT SCHRÖDINGER EQUATION. *

* The ideas in this chapter are essentially those of Wallace(34). The author was primarily concerned with the calculations.

A. S-MATRIX THEORY

The time dependent Schrödinger equation,

$$H \Psi(t) = i\hbar \frac{\partial}{\partial t} \Psi(t) \quad (III-1)$$

with appropriate Hamiltonian operator H can be applied to electrons, atoms and many other systems, where relativistic effects are not significant. One way of solving it is to break up the Hamiltonian operator into an asymptotic part, H^0 , whose eigenstates are well known and a "perturbation" part, V , which is usually the potential. Therefore,

$$i\hbar \frac{\partial}{\partial t} |\Psi_e(t)\rangle = (H^0 + V) |\Psi_e(t)\rangle \quad (III-2)$$

Expanding in terms of a complete set of asymptotic states

$$1 = \sum_j |\psi_j\rangle \langle \psi_j| \quad (III-3)$$

$$i\hbar \frac{\partial}{\partial t} \sum_j |\psi_j(t)\rangle \langle \psi_j(t) | \Psi_e(t)\rangle \quad (III-4)$$

$$= H^0 \sum_j |\psi_j(t)\rangle \langle \psi_j(t) | \Psi_e(t)\rangle + \sum_j V |\psi_j(t)\rangle \langle \psi_j(t) | \Psi_e(t)\rangle$$

$$\text{Putting } \langle \psi_j(t) | \Psi_e(t)\rangle = c_j(t), \quad (III-5)$$

$$\text{we have } H^0 \sum_j c_j(t) \psi_j(t) = \sum_j E^0 c_j(t) \psi_j(t) \quad (III-6)$$

$$\therefore i\hbar \frac{\partial}{\partial t} \sum_j c_j(t) |\psi_j(t)\rangle = \sum_j E^0 c_j(t) |\psi_j(t)\rangle + V |\psi_j(t)\rangle c_j(t) \quad (III-7)$$

$$i\hbar \sum_j \dot{c}_j(t) |\psi_j(t)\rangle = \sum_j V |\psi_j(t)\rangle c_j(t) \quad (III-8)$$

$$i\hbar \dot{c}_k(t) = \sum_j c_j(t) \langle \psi_k(t) | V | \psi_j(t) \rangle \quad (III-9)$$

$$c_k(t) = c_k(t_0) + (i\hbar)^{-1} \sum_j \int_{t_0}^t c_j(\tau) \langle \psi_k(\tau) | V | \psi_j(\tau) \rangle d\tau \quad (III-10)$$

The evaluation of $c_k(t)$ by the finite difference method is easily derived by partitioning the time integration into sections,

$$\begin{aligned} c_k(t_{n+1}) = & (i\hbar)^{-1} \sum_j \int_{t_0}^{t_n} c_j(\tau) \langle \psi_k(\tau) | V | \psi_j(\tau) \rangle d\tau \\ & + (i\hbar)^{-1} \sum_j \int_{t_n}^{t_{n+1}} c_j(\tau) \langle \psi_k(\tau) | V | \psi_j(\tau) \rangle d\tau \\ & + c_k(t_0) \end{aligned} \quad (III-11)$$

$$c_k(t_{n+1}) = c_k(t_0) + (i\hbar)^{-1} \sum_j \int_{t_0}^{t_{n+1}} c_j(\tau) \langle \psi_k(\tau) | V | \psi_j(\tau) \rangle d\tau \quad (III-12)$$

Employing the first approximation to the integral, we obtain

$$c_k(t_{n+1}) = c_k(t_n) + (i\hbar)^{-1} \delta t \sum_j c_j(t_n) \langle \psi_k(t_n) | V | \psi_j(t_n) \rangle \quad (III-13)$$

In matrix form, this reads

$$\begin{aligned} \underline{c}(t + \delta t) &= \underline{c}(t) + (i\hbar)^{-1} \delta t \underline{D}(t) \underline{c}(t) \\ \underline{c}(t + \delta t) &= (\underline{1} + (i\hbar)^{-1} \delta t \underline{D}(t)) \underline{c}(t) \end{aligned} \quad (III-14)$$

A better approximation can be made by applying the Simpson Three Point Rule

$$a(t_{n+2}) = a(t_n) + (a(t_n) + 4a(t_{n+1}) + a(t_{n+2}))\delta t/3 \quad (III-15)$$

after the first two initial points.

Normalization at each cycle is actually not necessary because the process of normalization is a multiplication of a constant to a vector and the product of a series of constants is still a constant, and hence normalization can be done wherever chosen.

B. TRANSITION PROBABILITY

The transition probability from a given initial state $|i\rangle$ of the system to a given final state $|f\rangle$ per unit time can be defined as

$$w_{i \rightarrow f}(t) = |\langle f|U(t, t_0)|i\rangle|^2 \quad (III-16)$$

where $U(t, t_0)$ is the evolution operator defined by the relation

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle \quad (III-17)$$

Therefore the transition probability can be calculated if we can solve the time dependent Schrödinger equation in the chosen representation.

The conventional perturbation series approach to the problem can be found in a number of texts (35,36,37). $U(t, t_0)$ is expanded as an infinite series.

$$U(t, t_0) = U_0(t, t_0) + \sum_{n=1}^{\infty} U^n(t, t_0) \quad (III-18)$$

where

$$U^n(t, t_0) = (i\hbar)^{-1} \int_{t_0}^t d\tau_n \cdots d\tau_1 \{ \quad (III-19)$$

$$U_0(t, \tau_n) V(\tau_n) U_0(\tau_n, \tau_{n-1}) \cdots U_0(\tau_1, t_0) \}$$

The transition amplitude then becomes

$$\langle f|U(t, t_0)|i\rangle = \sum_n \langle f|U^n(t, t_0)|i\rangle \quad (III-20)$$

In practice, only the first few terms may be retained, resulting in an approximate formula which is only valid for short times. Even if one retains only the first nonvanishing term, the resulting expression is not necessarily simple since it may involve second and higher order terms

summing over complete states of operator products.

However, the finite difference method approach eliminates much of this difficulty.

As usual, $|\Psi(t)\rangle$ may be expanded in terms of some complete set of orthonormal basis functions:-

$$|\Psi(t)\rangle = \sum_j a_j(t) |\phi_j(t)\rangle \quad (III-21)$$

The Schrödinger equation reduces to the following well known equation for the coefficients $a(t)$,

$$i\hbar \frac{da_k(t)}{dt} = \sum_j a_j(t) V_{kj}(t) \quad (III-22)$$

$$\text{where } V_{kj}(t) = \langle \phi_k(t) | V | \phi_j(t) \rangle \quad (III-23)$$

$$a_f(t) = \langle \phi_f(t) | \Psi(t) \rangle = \langle \phi_f(t) | U(t, t_0) | \Psi(t_0) \rangle \quad (III-24)$$

$$\text{then } a_f(t) = \langle \phi_f(t) | U(t, t_0) | \phi_i(t_0) \rangle \quad (III-25)$$

if the initial state $|i\rangle = |\Psi(t_0)\rangle = |\phi_i(t_0)\rangle$.

Evaluation of the time dependent coefficients, i.e. solution of the set of equations (III-22), is therefore completely equivalent to calculating the complete transition amplitude.

The method of solving this set of equations was already given in the last section on S-matrix theory. By considering the perturbation series approach to the two-level system, the two methods can be compared. In this case equations (III-22) become

$$\begin{aligned} (i\hbar) \frac{da_1(t)}{dt} &= a_1(t)V_{11}(t) + a_2(t)V_{12}(t) \\ (i\hbar) \frac{da_2(t)}{dt} &= a_1(t)V_{21}(t) + a_2(t)V_{22}(t) \end{aligned} \quad (III-26)$$

If the initial states are $a_1(t_0) = 1$, $a_2(t_0) = 0$,

$$(i\hbar) \frac{da_1(t)}{dt} = V_{11}(t) \quad (III-27)$$

$$(i\hbar) \frac{da_2(t)}{dt} = V_{21}(t)$$

After rearranging and integrating,

$$a_1(t) = 1 + (i\hbar)^{-1} \int_{t_0}^t V_{11}(\tau) d\tau \quad (III-28)$$

$$a_2(t) = (i\hbar)^{-1} \int_{t_0}^t V_{21}(\tau) d\tau \quad (III-28b)$$

These are the first order perturbation expression which is only valid when $a_2(t)$ is negligible as compared to $a_1(t)$. However, the finite difference method is valid for any value of $a_2(t)$.

1. RAMAN SCATTERING

The second order expression for the transition probability for raman scattering was given by Wallace (38) (39) as follows:

$$w_{i \rightarrow f}^2(t) = \hbar^{-4} \left| \sum \left\{ \frac{V_{f2}(\omega_2) V_{vi}(\omega_1)}{\omega_2 + \omega_{vi}} + \frac{V_{fv}(\omega_1) V_{vi}(\omega_2)}{\omega_1 + \omega_{vi}} \right\} \right|^2 |f(t, \omega')| \quad (III-29)$$

where in this case $\omega' = \omega_{fi} + \omega_1 + \omega_2$.

For the sake of comparison, only one term will be retained in the summation over intermediate states, thus the process might be represented diagrammatically as follows,

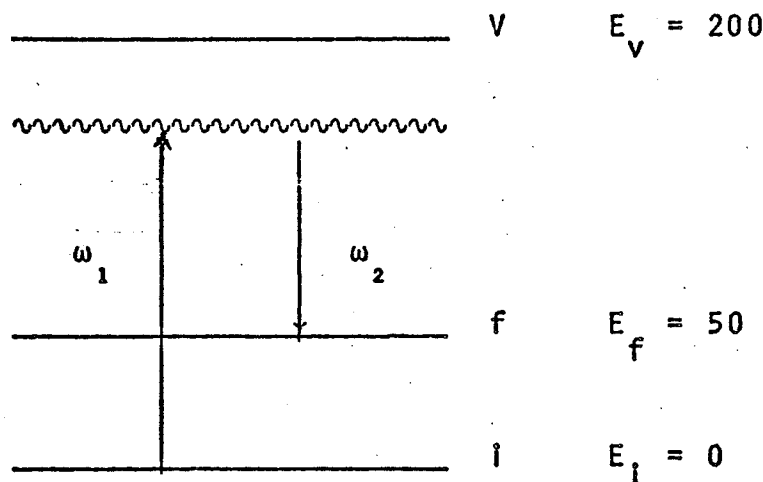


Figure 5. RAMAN SCATTERING

the energy levels shown being conveniently chosen. Putting $V_{fv} = V_{vi} = \beta$, $\hbar = 1$, then we have

$$w_{i \rightarrow f}^{(2)}(t) = \beta^4 \left| \frac{1}{200 + \omega_2} + \frac{1}{200 + \omega_1} \right|^2 f(t, \omega') \quad (III-30a)$$

In order to have energy conservation, $(\omega_2 - \omega_1)$ should be equal to $(E_f - E_i)$. With $\beta = 0.2$, $\omega_1 = -195$, and $\omega_2 = 145$,

$$w_{i \rightarrow f}^{(2)}(t) = 0.000066t^2 \quad (III-30b)$$

The plot of this function will be compared with the transition probability calculated by the difference method where

$$V(t) = v^\alpha e^{i\omega_1 t} + v^\beta e^{i\omega_2 t} \quad (III-31)$$

The \underline{D} -matrix is then

$$\underline{D} = \begin{bmatrix} 0 & 0 & v_{iv}^\alpha e^{i(\omega_1 - \omega_{vi})t} \\ 0 & 0 & v_{fv}^\alpha e^{i(\omega_1 - \omega_{vf})t} \\ v_{vi}^\alpha e^{i(\omega_{vi} + \omega_1)t} & v_{vf}^\alpha e^{i(\omega_{vf} + \omega_1)t} & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & v_{iv}^\beta e^{i(\omega_2 - \omega_{vi})t} \\ 0 & 0 & v_{fv}^\beta e^{i(\omega_2 - \omega_{vf})t} \\ v_{vi}^\beta e^{i(\omega_{vi} + \omega_2)t} & v_{vf}^\beta e^{i(\omega_{vf} + \omega_2)t} & 0 \end{bmatrix} \quad (III-32)$$

where, as before, we have assumed that $\hbar = 1$. etc. When we used the same data as the perturbation treatment, the transition probability was found to be smaller and the difference widened as time proceeded.

If $\omega_1 + \omega_{vi} \approx 0$, resonance raman scattering(42) occurs. The program for the resonance raman scattering is given in the appendix.

FIGURE 6.

TRANSITION PROBABILITIES FOR ORDINARY

RAMAN SCATTERING

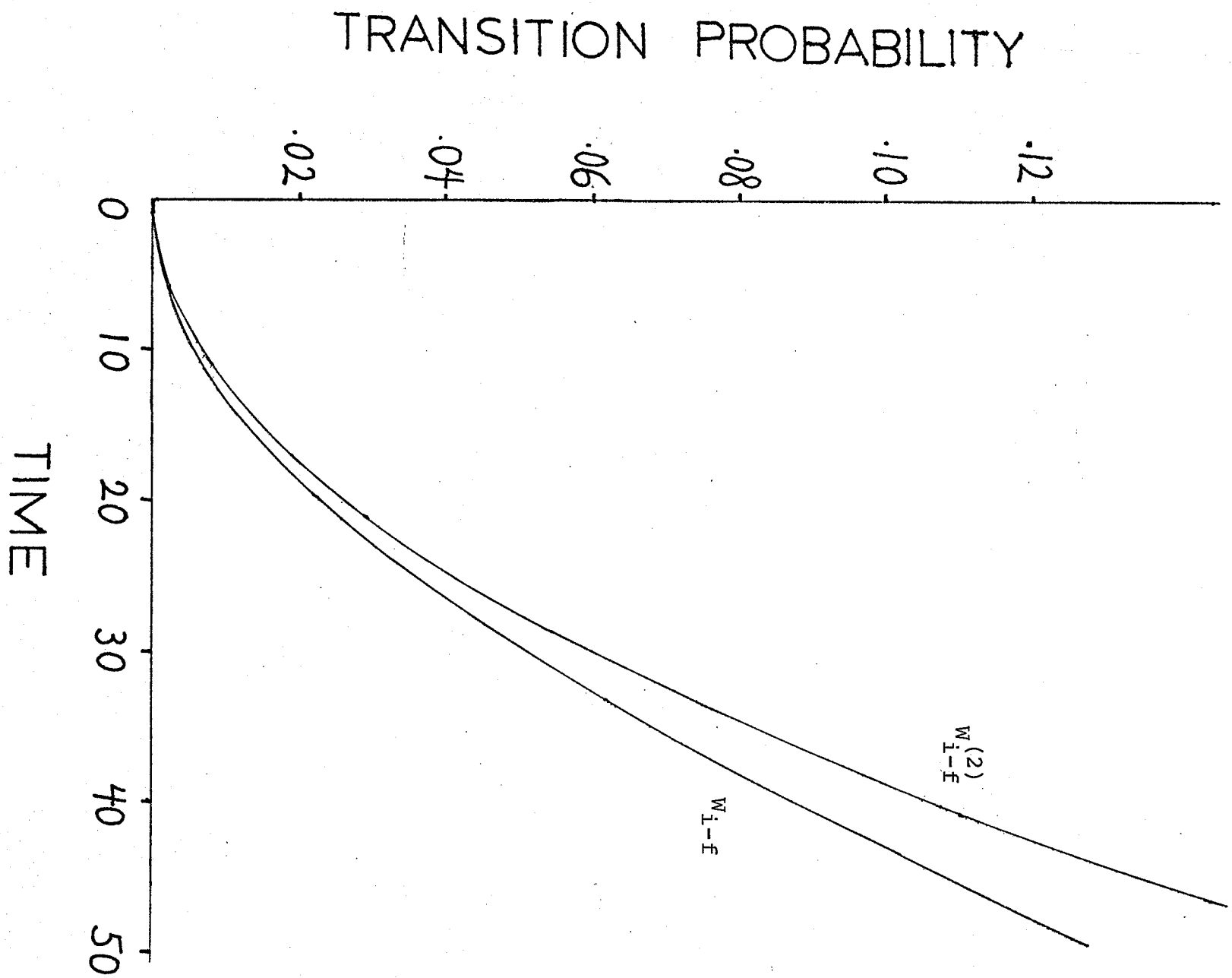
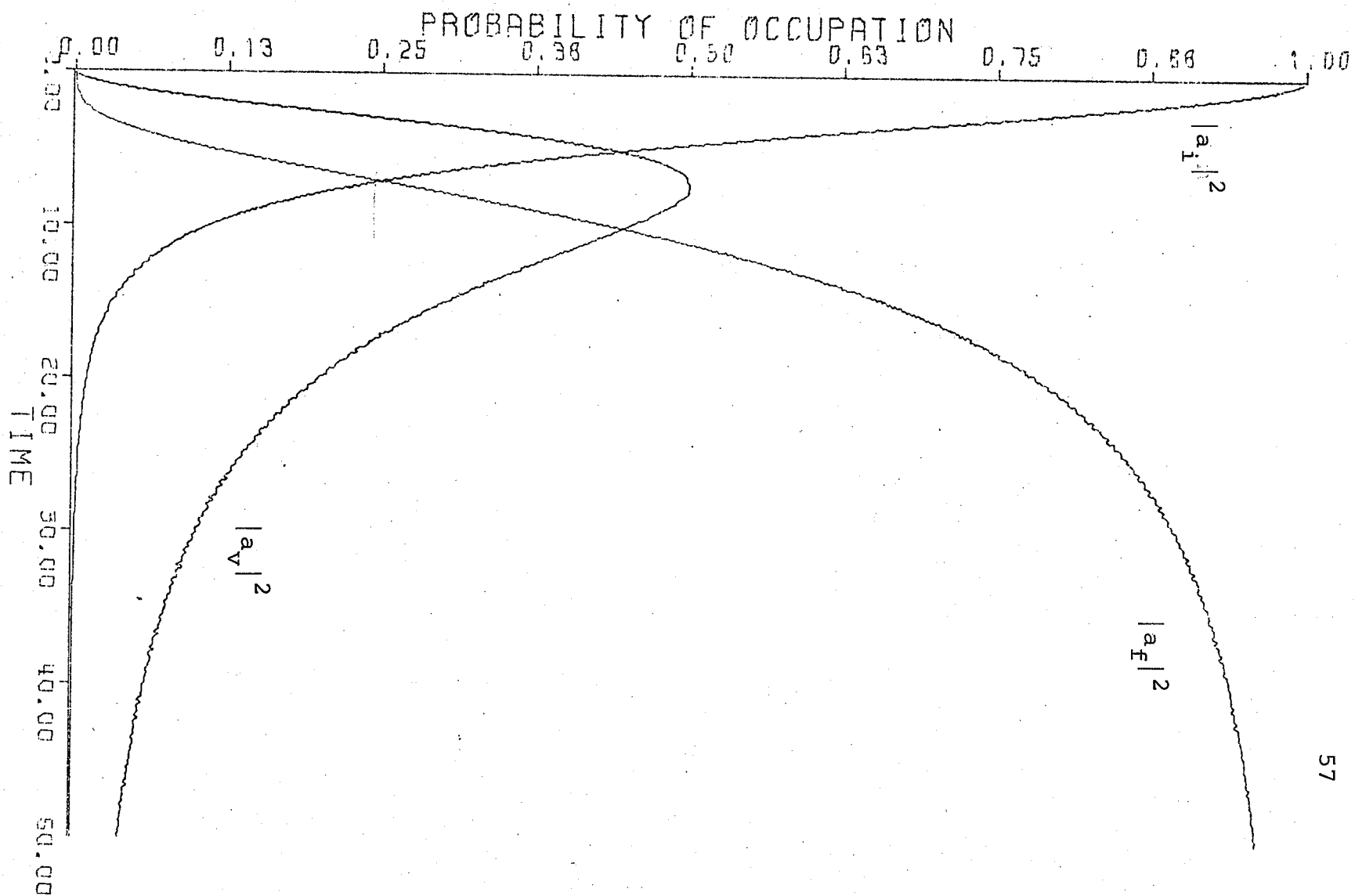


FIGURE 7

TIME DEPENDENCE OF OCCUPATION PROBABILITIES FOR STATES

INVOLVED IN RESONANCE RAMAN SCATTERING.



C. DISCUSSION

The calculation of transition probabilities in a finite-difference form has an advantage over its alternative perturbation-series approach. The formal expression has to be truncated at the first relevant non-vanishing term of the series in order to apply it in practice. It is fairly satisfactory for some simple cases but it cannot adequately describe important cases such as the amplitude for a low-energy collision, single and multiple resonances. A further disadvantage is that the calculated transition amplitudes are not ordinarily unitary.

The method described does not have these disadvantages. One of advantages is that the corresponding equations are equivalent to the corresponding perturbation-series expressions, but sums rather than products of operators are involved, and thereby, the computation time required is greatly reduced. However, analytic expressions cannot be written for the transition amplitudes.

CHAPTER V

CONCLUSION

We have seen in the last few chapters that the finite-difference method has been successfully applied to solve some interesting problems involving Schrödinger's equation. Almost always, whenever the solution of differential equations is required, this method can be used with certain modifications. It has been used quite often in the past and, it will be even more frequently used in the future, if the computer becomes more efficient and less expensive.

It should be very interesting to calculate the eigenvalues and eigenfunctions of the hydrogen atom and other systems and plot the electron density out on a three-dimensional net by the method described in Chapter II. It would be more straightforward than the well-known method of separation of the Schrödinger's equation in spherical polar co-ordinates, involving spherical harmonic functions.

Dynamic potentials obtained by methods similar to that of Corrigall, Kupper, and Wallace(40) may be used in phaseshift calculations. The validity of their method may be checked or improved by comparing the total cross-sections calculated and the experimental values.

It should be relatively simple to apply the nonperturbative approach to more complicated systems. It is a matter of evaluating more terms in the matrix.

Much of the work has been done in the direction of reducing storage requirements and manipulation steps.

The three-dimensional problem may be solved through the guide-line of Gordon(5) or the use of eikonal approximation of Chen and Watson(41). However, these methods tend to destroy the simplicity of the finite-difference approach.

APPENDIX A

THE JACOBI METHOD

The Jacobi method (1846) can only be applied to real symmetric matrices. The process is simply doing a series of matrix multiplications by a certain matrix on one side and its transpose on the other side until the off-diagonal elements become negligibly small. The matrix is simply

$$\underline{R}_k = \begin{matrix} & & & & p & & & q & & \\ \begin{matrix} p \\ q \end{matrix} & \begin{pmatrix} \ddots & \cdot & & 0 & 0 & 0 & 0 & 0 & 0 & \cdot & \cdot \\ & \ddots & \cdot & \cdot & 0 & 0 & 0 & 0 & 0 & \cdot & \cdot \\ & & \ddots & \cdot & 1 & 0 & 0 & 0 & 0 & \cdot & \cdot \\ & & & \ddots & 0 & \cos \theta & 0 & 0 & \sin \theta & 0 & \cdot \\ & & & & \ddots & 0 & 1 & 0 & 0 & 0 & \cdot \\ & & & & & \ddots & 0 & 0 & 1 & 0 & \cdot \\ & & & & & & \ddots & -\sin \theta & 0 & \cos \theta & 0 \\ & & & & & & & \ddots & 0 & 0 & 1 \\ & & & & & & & & \ddots & \cdot & \cdot \\ & & & & & & & & & \ddots & \cdot \\ & & & & & & & & & & \ddots \end{pmatrix} \end{matrix} \quad (1-26)$$

After multiplication of the three matrices,

$$\underline{A}_k = \underline{R}_k \underline{A}_{k-1} \underline{R}_k^T \quad (1-27)$$

$$\begin{aligned} a_{ip}^k &= a_{ip}^{(k-1)} \cos \theta + a_{iq}^{(k-1)} \sin \theta = a_{pi}^{(k)} \\ a_{iq}^k &= -a_{ip}^{(k-1)} \sin \theta + a_{iq}^{(k-1)} \cos \theta = a_{qi}^{(k)} \end{aligned} \quad \} i \neq p, q \quad (1-28)$$

$$a_{pp}^k = a_{pp}^{(k-1)} \cos^2 \theta + 2 a_{pq}^{(k-1)} \cos \theta \sin \theta + a_{qq}^{(k-1)} \sin^2 \theta$$

$$a_{qq}^k = a_{qq}^{(k-1)} \sin^2 \theta - 2 a_{pq}^{(k-1)} \cos \theta \sin \theta + a_{pp}^{(k-1)} \cos^2 \theta$$

$$\begin{aligned} a_{pq}^k &= (a_{qq}^{(k-1)} - a_{pp}^{(k-1)}) \cos \theta \sin \theta + a_{pq}^{(k-1)} (\cos^2 \theta - \sin^2 \theta) \\ &= a_{qp}^k \end{aligned} \quad (1-29)$$

In order to set $a_{pq}^{(k)}$ equal to zero, the following relationship must hold

$$\tan \theta = 2 a_{pq}^{(k-1)} / (a_{pp}^{(k-1)} - a_{qq}^{(k-1)}) \quad (1-30)$$

where $|\theta|$ must be less than or equal to $\pi/4$. If $a_{pp}^{(k-1)} = a_{qq}^{(k-1)}$, θ must be equal to $\pm\pi/4$ according to the sign of $a_{pq}^{(k-1)}$, \underline{R}_k matrix and its transpose can therefore be determined.

By squaring both sides of equation (1-28), one can easily prove that the sum of the squares of the off-diagonal elements excluding the (p,q) and (q,p) elements remains constant while $a_{pq}^{(k)} = a_{qp}^{(k)} = 0$ and therefore there is a net decrease in the sum of the squares of all the off-diagonal elements. After many cycles the off-diagonal terms will be be very small.

The eigenfunction can be found by subtracting $E h^2$ to each of the diagonal terms in (1-25) and then do a Gauss elimination with u_1 equal to an arbitrary constant.

APPENDIX B

COMPUTER PROGRAMS

PROGRAM II-1

ENERGY OF THE HARMONIC OSCILLATOR

C
C
C
C
C
C

THIS PROGRAM CALCULATES THE KINETIC AND POTENTIAL
ENERGY OF AN HARMONIC OSCILLATOR WHEN THE WAVE
FUNCTION IS GIVEN. THE METHOD IS GAUSS BACKWARD
INTERPOLATION AND THEN SUMMATION OVER ALL THE POINTS.

```

      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(803),Y(803),FDER(803),SDER(803)
      GAUSS(H,A,B,C,D)=(0.16666666666666667D+00*A -B
1  +0.5D+00*C +0.33333333333333333D+00*D)*H
1  FORMAT(I5,F15.10)
2  FORMAT(10X,I5,6F15.10)
      A =0.314159265358979D+01**(-0.25D+00)
      READ(5,1) N,DELTAD
      DO 40 M=1,3
      DH=0.5D+00*DELTAD
      D=-DELTAD*(N+1)/0.2D+01
      DI=0.1D+01/DELTAD
      SUMKE=0.0D+00
      SUMPE=0.0D+00
      DO 10 I=1,3
      D=D+DELTAD
      X(I)=D
10  Y(I)=A*DEXP(-D*D*0.5D+00)
      W2=Y(1)
      W3=Y(2)
      W4=Y(3)
      DO 20 I=4,6
      D=D+DELTAD
      X(I)=D
      W1=W2
      W2=W3
      W3=W4
      W4=A*DEXP(-D*D*0.5D+00)
      Y(I)=W4
20  FDER(I-1)=GAUSS(DI,W1,W2,W3,W4)
      U2=FDER(3)
      U3=FDER(4)
      U4=FDER(5)
      DO 30 I=7,N
      D=D+DELTAD
      X(I)=D
      W1=W2
      W2=W3
      W3=W4
      W4=A*DEXP(-D*D*0.5D+00)
      Y(I)=W4
      FDER(I-1)=GAUSS(DI,W1,W2,W3,W4)
      J=I-2
      U1=U2

```

```
U2=U3
U3=U4
U4=FDER(I-1)
HOLD=GAUSS(DI,U1,U2,U3,U4)
SDER(J)=HOLD
SUMKE=SUMKE-W2*HOLD*DH
SUMPE=SUMPE+X(J)*X(J)*W2*W2*DH
WRITE(6,2) J,X(J),Y(J),FDER(J),SDER(J),SUMKE,SUMPE
30 CONTINUE
DELTAD=DELTAD*0.5D+00
40 CONTINUE
CALL EXIT
END
```

PROGRAM III-1

PHASESHIFTS AND WAVEFUNCTION WITH PLOT

C
C
C

PROGRAM TO CALCULATE PHASESHIFTS AND WAVEFUNCTION

```

REAL*8 K,DK,H,P,R,C1,C2,D,DIAG,PI,LS,C,HOLD,LSOR,SINCL
REAL*8 DSQRT,DFLOAT,DSIN,DSIGN,NHFW,HK,LSOP,HFL,HAFPIL
REAL*8 POT,WAVEFN
DIMENSION DATAD(7)
DIMENSION IBUF(1000)
COMMON PI,HFL,LSOP,HAFPIL,C,D,LS,H,P,K,WAVEFN,
1 XARRAY(1002),YARRAY(1002),L,NR
1 FORMAT(I1,F9.4,F10.6,I2,D18.10,I10,F10.2,F10.5)
2 FORMAT('0',/,15X,' L = ',I2,' K = ',F9.4,/,15X,
1' INCREMENT OF K',F10.6,/,15X,
2' NUMBER OF INCREMENT OF K ',I2,/,15X,
3' INCREMENT OF DISTANCE H = ',D18.10,/,15X,
4' NUMBER OF INTERVAL IN LAST REGION = ',I10,/,
515X,' APPROXIMATE NUMBER OF HALF-WAVES DESIRED IN ',
6' FIRST REGION = ',F10.2)
3 FORMAT(/,15X,' K = ',F10.5,' SEPARATION H = ',D20.10)
4 FORMAT('1',7(/),15X,' SEPARATION = ',D20.12,/,15X,
1' NUMBER OF NONUNIFORM INTERVALS = ',I10,/,15X,
2' (L*L+L)*H*H/(R*R) = ',D20.12,/,15X,
3' H*H*K*K = ',D20.12)
5 FORMAT('0',//,20X,' DISTANCE',10X,' WAVENUMBER',8X,
1' PHASESHIFT')
6 FORMAT('1',7(/),15X,7A4)
PI=0.3141592653589793D+01
CALL PLOTS(IBUF,1000)
CALL PLOT(0.0,3.0,-3)
10 READ(5,1,END=60) L,K,DK,NK,H,N,NHFW,WAVEFN
CALL $DATE(DATAD)
WRITE(6,6) DATAD
WRITE(6,2) L,K,DK,NK,H,N,NHFW
LS=L*L+L
HFL=0.5D+00*L
LSOP=0.5D+00*LS/PI
HAFPIL=0.5D+00*PI*L
HK=H
DO 40 M=1,NK
CALL $DATE(DATAD)
WRITE(6,6) DATAD
WRITE(6,3) K,H
WRITE(6,5)
P=0.0D+00
C=0.0D+00
D=0.0D+00
N2=10
WAVEFN=-WAVEFN*(H*K)**(L+1)/
1 (-0.2D+01+H*H*K*K-LS+POT(H)*H*H)
NR=1
XARRAY(1)=0.0

```

```

YARRAY(1)=SNGL(WAVEFN)
CALL PLOT(9.0,0.0,-3)
XARRAY(1001)=0.0
XARRAY(1002)=1.5
YARRAY(1001)=-1.0
YARRAY(1002)=0.25
WRITE(6,7) XARRAY(1001),XARRAY(1002),YARRAY(1001),YARRAY(1002)
7 FORMAT(' SCALING FACTOR',4E17.10)
CALL AXIS(0.0,0.0,'DISTANCE IN ATOMIC UNITS',
1-24,6.0,0.0,XARRAY(1001),XARRAY(1002))
CALL AXIS(0.0,0.0,'WAVE FUNCTION',13,8.0,90.0,
1YARRAY(1001),YARRAY(1002))
CALL AXIS(0.0,4.0,1H,-1,6.0,0.0,XARRAY(1001),XARRAY(1002))
CALL AXIS(0.0,8.0,1H,+1,6.0,0.0,XARRAY(1001),XARRAY(1002))
CALL GAUSSE(N2,&50)
DO 20 I=8,1000
IF ( P .GT. NHFW) GO TO 30
SINCL=DSIN(0.5D+00*H*K)
SINCL=0.4D+01*SINCL*SINCL
D=0.1D+01-D*(-0.2D+01+SINCL-LS/(C*C))
H=0.2D+01*H
C=(C-0.1D+01)/0.2D+01
N2=INT(0.4*EXP(0.23262*I))+1
CALL GAUSSE(N2,&50)
20 CONTINUE
30 CONTINUE
DIAG=H*H*K*K
N2=IDINT(0.4D+00*DEXP(0.23262D+00*I)/0.23262D+00)
LSOR=LS/(C*C)
WRITE(6,4) H,N2,LSOR,DIAG
K=K+DK
H=HK
40 CONTINUE
50 GO TO 10
60 CALL PLOT(20.0,0.0,999)
CALL EXIT
END

```

C
C
C
C
C
C

WHEN THE WAVE FUNCTION CROSS THE AXIS, THE DIAGONAL
ELEMENT CHANGES SIGN AND THE SHIFT CAN THUS BE
CALCULATED.

```

SUBROUTINE GAUSSE(M,*)
REAL*8 C,D,H,DIAG,LS,P,R,SHIFT,PI,C2,K,LSOR,HS,HAFPII
REAL*8 SINCL,CORVAL,HFL,DFLOAT,DSQRT,DSIN,POT,WAVEFN
COMMON PI,HFL,LSOR,HAFPII,C,D,LS,H,P,K,WAVEFN,
1 XARRAY(1002),YARRAY(1002),L,NR
1 FORMAT(15X,D20.10,8X,F5.0,D20.10)
2 FORMAT('1',7(/),20X,'DISTANCE',10X,'WAVENUMBER',8X,

```



```

1 'PHASESHIFT')
7 FORMAT(' SCALING FACTOR',4E17.10)
HS=H*H
SINCL=DSIN(0.5D+00*H*K)
SINCL=0.4D+01*SINCL*SINCL
DO 50 I=1,M
C=C+0.1D+01
R=C*H
C2=-0.2D+01-D+SINCL-LS/(C*C)+POT(R)*HS
D=0.1 D+01/C2
WAVEFN=-C2*WAVEFN
NR=NR+1
XARRAY(NR)=SNGL(R)
YARRAY(NR)=SNGL(WAVEFN)
IF (NR .LT. 1000) GO TO 10
IF(R .GT. 10.0) RETURN 1
CALL SCALE(YARRAY,8.0,1000,1)
WRITE(6,7) YARRAY(1001),YARRAY(1002)
CALL LINE(XARRAY,YARRAY,1000,1,0,0)
NR=1
XARRAY(1)=XARRAY(1000)
YARRAY(1)=YARRAY(1000)
10 IF(C2) 50,20,60
60 P=P+0.1D+01
R=(C+0.1D+01/(0.1D+01+C2))*H
SHIFT=PI*P+HAFPI-L-K*R
CORVAL=LSOR/(P+HFL)
CORVAL=CORVAL+CORVAL*CORVAL/(0.6D+01*PI*(P+HFL))
SHIFT=SHIFT-CORVAL
IF (P .EQ. 1.2D+01) RETURN 1
WRITE(6,1) R,P,SHIFT
50 CONTINUE
20 RETURN
END
REAL FUNCTION POT*8(R)
REAL*8 R
POT=0.0D+00
RETURN
END

```

PROGRAM III-2

CALCULATION OF PHASESHIFTS IN THE

ELECTRON SCATTERING OF KRYPTON

C
C
C

MAIN PROGRAM TO CALCULATE PHASESHIFTS OF KRYPTON

```

REAL*8 C,D,H,NHFW,LS,P,R,SHIFT,PI,C2,K,LSOR,HS,HAFPIL
REAL*8 SINCL,HFL,POT,HK,DK
DIMENSION DATAD(7)
COMMON PI,HFL,LSOR,HAFPIL,C,D,LS,H,P,K,NHFW,R,HS,SINCL,L
1  FORMAT(F10.4,I2,D18.10,F10.5)
2  FORMAT(I1,F10.5)
3  FORMAT(/,15X,' K =',F10.5,' SEPARATION H =',D20.10)
4  FORMAT (/,15X,' LAST SEPARATION =',D20.12,/,15X,
1  ' NUMBER OF NONUNIFORM INTERVALS =',I10)
5  FORMAT(/,20X,'DISTANCE',10X,'WAVENUMBER',8X,
1  'PHASESHIFT')
6  FORMAT('1',5(/,15X,7A4,10X,'L =',I2)
CALL ERRSET(208,999,-1,1)
PI=0.3141592653589793D+01
10 READ(5,1,END=60) K,NK,H
HK=H
CALL $DATE(DATAD)
DO 40 M=1,NK
READ (5,2) L,NHFW
LS=L*L+L
HFL=0.5D+00*L
LSOR=0.5D+00*LS/PI
HAFPIL=0.5D+00*PI*L
WRITE(6,6) DATAD,L
WRITE(6,3) K,H
WRITE(6,5)
P=0.0D+00
C=0.0D+00
D=0.0D+00
N2=10
CALL GAUSSE(N2,&30)
DO 20 I=8,1000
D=0.1D+01-D*(-0.2D+01+SINCL-LS/(C*C)+POT(R)*HS)
H=0.2D+01*H
C=(C-0.1D+01)/0.2D+01
N2=INT(0.4*EXP(0.23262*I))+1
CALL GAUSSE(N2,&30)
20 CONTINUE
30 N2=IDINT(0.4D+00*DEXP(0.23262D+00*I)/0.23262D+00)
WRITE(6,4) H,N2
H=HK
40 CONTINUE
50 GO TO 10
60 Call EXIT
END

```

C
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WHEN THE WAVE FUNCTION CROSS THE AXIS, THE DIAGONAL
ELEMENT CHANGES SIGN AND THE SHIFT CAN THUS BE
CALCULATED.

C

```

SUBROUTINE GAUSSE(M,*)
REAL*8 C,D,H,NHFW,LS,P,R,SHIFT,PI,C2,K,LSOR,HS,HAFPII
REAL*8 SINCL,CORVAL,HFL,POT
COMMON PI,HFL,LSOR,HAFPII,C,D,LS,H,P,K,NHFW,R,HS,SINCL,L
1 FORMAT(15X,D20.10,8X,F5.0,D20.10)
2 FORMAT('1',7(/),20X,'DISTANCE',10X,'WAVENUMBER',8X,
1'PHASESHIFT')
HS=H*H
SINCL=DSIN(0.5D+00*H*K)
SINCL=0.4D+01*SINCL*SINCL
DO 50 I=1,M
C=C+0.1D+01
R=C*H
C2=-0.2D+01-D+SINCL-LS/(C*C)+POT(R)*HS
D=0.1D+C1/C2
10 IF(C2) 50,20,60
60 P=P+0.1D+01
R=(C+0.1D+01/(0.1D+01+C2))*H
SHIFT=PI*P+HAFPII-K*R
CORVAL=LSOR/(P+HFL)
CORVAL=CORVAL+CORVAL*CORVAL/(0.6D+01*PI*(P+HFL))
SHIFT=SHIFT-CORVAL
WRITE(6,1) R,P,SHIFT
IF (P .GE. NHFW) RETURN 1
50 CONTINUE
20 RETURN
END
REAL FUNCTION POT*8(R)
REAL*8 R,R2,R3,R4,R5,R6
R2=R*R
R3=R2*R
R4=R2*R2
R5=R3*R2
R6=R3*R3
IF (R .LE. 0.1D+00)
1POT=0.72D+02/R-0.3533881899D+03-0.1146350537D+04*R
2+0.1841818834D+06*R2-0.5279525462D+07*R3+0.7514265787D+08*R4
3-0.5397741491D+09*R5+0.1551005487D+10*R6
IF (R .GT. 0.1D+00 .AND. R .LE. 0.50D+00)
1POT=0.7625479807D+02/R-0.4572041792D+03+0.2635553926D+04*R
2-0.1121322713D+05*R2+0.2883189221D+05*R3
3-0.3943388899D+05*R4+0.2193604414D+05*R5
IF (R .GT. 0.5D+00 .AND. R .LE. 0.22D+01)
1POT=0.7554322115D+02/R-0.2689478423D+03+0.5138835010D+03*R
2-0.5786366144D+03*R2+0.3919502097D+03*R3
3-0.1567437242D+03*R4+0.3403842985D+02*R5-0.3090055427D+01*R6
IF (R .GT. 0.22D+01 .AND. R .LE. 0.70D+01)
1POT=-0.395482454D+02/R+0.8606638291D+02-0.6924502874D+02*R
2+0.2874593118D+02*R2-0.6815859726D+01*R3+0.9334986726D+00*R4
3-0.6882078619D-01*R5+0.2115934812D-02*R6
IF (R .GT. 0.7D+01) POT=0.20D+02/R4
RETURN
END

```

PROGRAM III-3 — —

TOTAL SCATTERING CROSS SECTIONS AND

THE ANGULAR DISTRIBUTION

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PROGRAM TO CALCULATE THE ANGULAR DISTRIBUTION OF
ELECTRON SCATTERING WHEN THE PHASESHIFTS AND THE
ENERGY ARE GIVEN

```

      IMPLICIT REAL*8(A-H,K,O-Z)
      REAL*4 YARRAY,XARRAY,ENERGY
      DIMENSION YARRAY(182),XARRAY(182),C(10),ANG(10)
      DIMENSION IBUF(2000),SINSQ(10),LABEL(10)
1  FORMAT(I5,F20.10)
2  FORMAT(8F10.5)
3  FORMAT(15X,I10,10X,F20.10)
4  FORMAT('1',/,10X,' N = ',I5,' K = ',F20.10,/,
1'          PHASESHIFT = ',(/,20X,F20.10))
5  FORMAT(20X,'TOTAL CROSS-SECTION ',D20.10)
      PI=0.3141592653589793D+01
      RADIAN=PI/0.18D+03
      CALL PLOTS(IBUF,2000)
      CALL PLOT(0.0,1.5,-3)
      CALL PLOT(5.0,0.0,-2)
      CALL PLOT(0.0,8.5,-2)
      CALL PLOT(-5.0,0.0,-2)
      CALL PLOT(0.0,-8.5,-2)
      XARRAY(181)=0.0
      XARRAY(182)=36.0
      YARRAY(181)=0.0
      YARRAY(182)=8.0
      NRUN=0
20 READ(5,1,END=40) N,K
      NRUN=NRUN+1
      READ(5,2) (ANG(I),I=1,N)
      WRITE(6,4) N,K,(ANG(I),I=1,N)
      KK=K*K
      ENERGY=13.595*SNGL(KK)
      THETA=-RADIAN
      DO 50 J=1,180
      XARRAY(J)=FLOAT(J)
50 CONTINUE
      SUM=0.0D+00
      DO 30 J=1,180
      THETA=THETA+RADIAN
      X=DCOS(THETA)
      DO 10 I=1,N
      SINP=DSIN(ANG(I))
      SINSQ(I)=SINP*SINP
      C(I)=((2*I-1)**2)*SINSQ(I)/KK
10 CONTINUE
      Z=0.1D+01
      CALL LEPSS(Y,X,Z,C,N)
      YARRAY(J)=SNGL(Y)
      Z=DSIN(THETA)
      CALL LEPSS(Y,X,Z,C,N)
      SUM=SUM+Y
30 CONTINUE
      SUM=SUM*RADIAN*0.5D+00
      WRITE(6,5) SUM

```

```

WRITE(6,3) (I,YARRAY(I),I=1,180)
IF (NRUN .LT. 7) GO TO 60
CALL PLOT(0.0,1.0,-3)
60 CALL PLOT(0.0,0.5,-3)
CALL LINE(XARRAY,YARRAY,180,1,0.0)
GO TO 20
40 CALL PLOT(20.0,0.0,999)
CALL EXIT
END

```

C
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COMPUTES THE VALUE OF AN N-TERM EXPANSION IN LEGENDRE
POLYNOMIALS SQUARE WITH COEFFICIENT VECTOR C FOR
ARGUMENT VALUE. Z IS A FIX CONSTANT COEFFICIENT.

```

SUBROUTINE LEPSS(Y,X,Z,C,N)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION C(1)
Y=C(1)*Z
IF(N-2) 1,3,3

```

C
C

```

INITIALIZATION
3 H0=0.1D+01
H1=X
DO 4 I=2,N
H2=X*H1
H2=H2-H0+H2-(H2-H0)/DFLOAT(I)
H0=H1
H1=H2
4 Y=Y+C(I)*H0*H0*Z
1 RETURN
END

```

PROGRAM IV-1

RESONANCE RAMAN SCATTERING WITH ONE INTERMEDIATE STATE

C
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C

PROGRAM TO CALCULATE OCCUPATION PROBABILITY
IN A RAMAN SCATTERING TRANSITION

```

      IMPLICIT REAL*8 (A-H,O-Z)
      COMPLEX*16 A,V(3),C(3),IMAGIN
      REAL*4 DATAD(7)
      COMMON A(3,3),IMAGIN,T,R
1     FORMAT(4F10.7)
2     FORMAT(10X,F15.5,3F15.10)
3     FORMAT(2I5,F20.10)
4     FORMAT(10X,'DELTAT',F20.10)
14    FORMAT('1',4(/),10X,7A4)
      IMAGIN=(0.0D+00,+0.1D+01)
50    CALL $DATE(DATAD)
      WRITE(6,14) DATAD
30    READ(5,3,END=999) N,M,DELTAT
      WRITE(6,4) DELTAT
      R=-0.2D+00*DELTAT
      DO 40 I=1,3
40    V(I)=0.0D+00
      V(1)=0.1D+01
      A(1,1)=0.1D+01
      A(2,2)=0.1D+01
      A(3,3)=0.1D+01
      A(1,2)=0.0D+00
      A(2,1)=0.0D+00
      T=-DELTAT
      DO 10 I=1,N
      DO 20 J=1,M
      T=T+DELTAT
      CALL CGEN
      CALL MULT(3,V,C)
      CALL NORM(V,3)
20    CONTINUE
      Z1=SQUARE(V(1))
      Z2=SQUARE(V(2))
      Z3=SQUARE(V(3))
      WRITE(6,2) T,Z1,Z2,Z3
      WRITE(7,1) T,Z1,Z2,Z3
10    CONTINUE
      GO TO 30
999   CALL EXIT
      END
      SUBROUTINE CGEN
      IMPLICIT REAL*8 (A-H,O-Z)
      COMPLEX*16 A,IMAGIN
      COMMON A(3,3),IMAGIN,T,R
      R1=0.5D+02*T
      R2=0.30D+03*T

```

```

R3=0.35D+03*T
R4=0.40D+03*T
A(1,3)=(DCOS(R4)+DCOS(R1))*IMAGIN+DSIN(R4)+DSIN(R1))*R
A(2,3)=(DCOS(R3)+0.1D+01)*IMAGIN+DSIN(R3))*R
A(3,2)=(DCOS(R2)+DCOS(R1))*IMAGIN+DSIN(R1)-DSIN(R2))*R
A(3,1)=(DCOS(R3)+0.1D+01)*IMAGIN-DSIN(R3))*R
RETURN
END
SUBROUTINE MULT(N,B,C)
C   MULTIPLY A VECTOR B BY A MATRIX A RESULTING VECTOR C
COMPLEX*16 A,B,C,SUM
COMMON A(3,3)
DIMENSION B(N),C(N)
DO 10 I=1,N
SUM=(+0.0D+00,+0.0D+00)
DO 20 J=1,N
20 SUM = SUM + A(I,J)*B(J)
10 C(I) = SUM
DO 30 I=1,N
30 B(I)=C(I)
RETURN
END
REAL FUNCTION SQUARE*8(ARG)
C   CALCULATE THE SQUARE OF THE NORM
COMPLEX*16 ARG,NIMAG
REAL*8 A,B
A=ARG
NIMAG=(0.0D+00,-0.1D+01)*ARG
B=NIMAG
SQUARE=A*A+B*B
RETURN
END
SUBROUTINE NORM(V,N)
C   NORMALIZE COMPLEX VECTOR V
COMPLEX*16 V,FACT,VAR
REAL*8 FACTOR,SUM,SQUARE
DIMENSION V(N)
SUM = +0.0D+00
DO 10 I=1,N
10 SUM=SUM+SQUARE(V(I))
FACTOR=SUM**(-0.5D+00)
DO 20 I=1,N
20 V(I) = FACTOR * V(I)
RETURN
END

```

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