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A New Method for the Numerical Solution of the Schrödinger Equation

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ABSTRACT

A new method for the numerical solution of the diffusion-type equation $H\psi = -\partial\psi/\partial\beta$ is presented for both infinite and bounded regions. When H is the Hamiltonian for a system of particles, a method closely related to the path integral technique is used to find an approximate form for the Green's function of this equation for small β. Iteration, using this Green's function as an integral operator, gives the solution for any β. Alternatively, the eigenvalues and eigenvectors of the corresponding integral equation are directly related to those of the Schrödinger equation. The technique is illustrated by its application to several one-dimensional problems including the hydrogen atom.

I. INTRODUCTION

In general it is a difficult problem to obtain the solution to equations of the form,

$$H\psi = -\frac{\partial\psi}{\partial\beta} \tag{1.1}$$

where H is a differential operator, satisfying certain boundary conditions, and β is a real parameter. Except in a few special cases where an exact solution actually exists, one usually has to resort to some approximation; for instance, in quantum mechanics, an approximate solution to the Schrödinger equation can be found by an approximation to the wave function, as in the variational or W.K.B. methods, by a perturbation expansion of the Hamiltonian, H, or ultimately by a numerical calculation.

There have been various attempts towards the solution of this class of problem, both formally by the development of a series solution for the corresponding operator, $e^{-\beta H}$, [ref. *1*, *2*], and numerically by the integration of the original equation. In a recent paper, Goldberg and Schwartz [ref. *3*, *4*] have given examples of the use of finite difference methods for the solution of (1.1). Their results indicate that it is possible to select appropriate difference equations which can lead to quite reasonable results, when H depends on one variable only. They have also suggested a technique for extending the difference method to more spatial variables, by approximating the operator, $e^{-\beta H}$. Baker et al. [ref. *5*] have used straightforward numerical integration to obtain the smallest eigenvalue of the operator H, for a system with three particles. Kalos [ref. *6*, *7*] has evaluated the strength of the potential required to produce a bound state of a three-body problem by considering an integral equation obtained by using the exact Green's function for the time independent Schrödinger equation. His results involve a multi-dimensional integral which he calculates by Monte-Carlo techniques.

In this paper we propose a new scheme for the numerical integration of Eq. (1.1), which has the advantage of an apparently simple extention to systems with many spatial variables. The method we have adopted involves the construction of an approximate form for the Green's function for Eq. (1.1), valid for small values of β, and then the application of an iterative procedure to obtain approximate solutions at large β. The solution involves the calculation of certain integral expressions, which result in greater numerical stability than the corresponding difference methods and in fact are valid in the very region these difference schemes become unstable. An important feature of the method is the possibility of treating systems of particles with hard cores and also cases where the potential has singularities. To illustrate the technique we have considered simple cases where an evaluation of the integrals by numerical quadratures is possible.

When the operator H is the Hamiltonian for a system of particles, and β is related to the temperature, the Green's function becomes the statistical density matrix for the system. An evaluation of this density matrix in terms of path integral expressions leads to the same results and indicates the values of β for which the approximation is valid. For large β, the solution of (1.1) approaches the ground state wave function of the system, while for small β it is possible to obtain an eigenvalue equation for the calculation of higher states. In this paper we have illustrated the method by a numerical computation of the ground state of the hydrogen atom, and a calculation of some higher eigenvalues by expanding the approximate form of the Green's function in terms of a complete set of eigenfunctions.

The theory is extended to bounded regions by obtaining an approximate form for the Green's function in terms of solutions of the equations which satisfy the boundary conditions separately. This procedure, which appears rather arbitrary at first sight, turns out to give the exact eigenfunctions for all β and an error in the eigenvalues of H which is small for small β.

II. General Theory

We consider the solution to Eq. (1.1) where the operator H can be written in the form,

$$H = H_0 + H_1, \tag{2.1}$$

where H_0, H_1 are differential operators with appropriate boundary conditions. We suppose that ψ satisfies the initial condition, written in coordinate representation as

$$\psi(\mathbf{x}, \beta = 0) = \psi_0(\mathbf{x}). \tag{2.2}$$

The solution to the operator equation (1.1) can be found in terms of the Green's function, which must satisfy the equation

$$HG(\mathbf{x}, \beta \mid \mathbf{x}_0, 0) = -\frac{\partial G(\mathbf{x}, \beta \mid \mathbf{x}_0, 0)}{\partial \beta}, \tag{2.3}$$

with the initial condition

$$G(\mathbf{x}, 0 \mid \mathbf{x}_0, 0) = \delta(\mathbf{x} - \mathbf{x}_0). \tag{2.4}$$

From Eq. (2.3), $G(\mathbf{x}, \beta \mid \mathbf{x}_0, 0)$ is the coordinate representation of the operator $\exp(-\beta H)$, i.e.

$$G(\mathbf{x}, \beta \mid \mathbf{x}_0, 0) = \langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle, \tag{2.5}$$

and the solution to eqn. (1.1) can be written as

$$\psi(\mathbf{x}, \beta) = \int \langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle \, \psi_0(\mathbf{x}_0) \, d\mathbf{x}_0, \tag{2.6}$$

where we have restricted the boundary conditions so that the surface terms in Eq. (2.6) vanish. Thus the solution for all β can be found if the Green's function can be formed. Usually this is a difficult, if not impossible problem, but we can obtain an approximation by expanding the exponential in Eq. (2.5). There are various ways in which this can be done, [*1*, *2*], but it is important to select an expansion which retains the symmetry properties of $e^{-\beta H}$. To do this we use a theorem due to Zassenhaus [*7*], which is closely related to the Baker–Hausdorff formulae.

Following Kumar [*8*], the "right-running" formula for the expansion of the exponential of the sum of two noncommuting operators can be written as

$$e^{-\beta/2(H_0+H_1)} = e^{-\frac{1}{2}\beta H_1} e^{-\frac{1}{2}\beta H_0} e^{\beta^2 c_2} e^{-\beta^3 c_3} \cdots \tag{2.7}$$

where

$$\begin{aligned} c_2 &= -\tfrac{1}{8}[H_1, H_0], \\ c_3 &= \frac{1}{48}[H_1, [H_1, H_0]] + \frac{1}{24}[H_0, [H_1, H_0]] \end{aligned} \tag{2.8}$$

and the coefficients of the terms of higher order in β consist of higher order commutator products of H_0 and H_1. Using a similar expression for the "left-running" formula, we have that,

$$\begin{aligned} e^{-\beta(H_0+H_1)} &= e^{-\beta/2(H_0+H_1)} e^{-\beta/2(H_0+H_1)} \\ &= e^{-\frac{1}{2}\beta H_1} e^{-\frac{1}{2}\beta H_0} e^{\beta^2 c_2} e^{-\beta^3 c_3} \cdots \times \cdots e^{-\beta^3 c_3} e^{-\beta^2 c_2} e^{-\frac{1}{2}\beta H_0} e^{-\frac{1}{2}\beta H_1} \end{aligned}$$

Hence, for small β, we have the approximation,

$$e^{-\beta H} \approx e^{-\frac{1}{2}\beta H_1} e^{-\beta H_0} e^{-\frac{1}{2}\beta H_1} + 2\beta^3 e^{-\frac{1}{2}\beta H_1} e^{-\frac{1}{2}\beta H_0} c_3 e^{-\frac{1}{2}\beta H_0} e^{-\frac{1}{2}\beta H_1} + O(\beta^4). \quad (2.10)$$

So that, to order β^2, we can write

$$\langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle \approx \int d\mathbf{x}_1 \int d\mathbf{x}_2 \langle \mathbf{x} \mid e^{-\frac{1}{2}\beta H_1} \mid \mathbf{x}_1 \rangle \langle \mathbf{x}_1 \mid e^{-\beta H_0} \mid \mathbf{x}_2 \rangle \langle \mathbf{x}_2 \mid e^{-\frac{1}{2}\beta H_1} \mid \mathbf{x}_0 \rangle \quad (2.11)$$

where $\langle \mathbf{x} \mid e^{-\beta H_0} \mid \mathbf{x}_0 \rangle$ and $\langle \mathbf{x} \mid e^{-\frac{1}{2}\beta H_1} \mid \mathbf{x}_0 \rangle$ are the Green's functions for the equations,

$$H_0 \chi = -\frac{\partial \chi}{\partial \beta} \quad (2.12)$$

and

$$\frac{1}{2} H_1 \xi = -\frac{\partial \xi}{\partial \beta},$$

with appropriate boundary conditions. If it is possible to obtain expressions for these Green's functions, the general solution to Eq. (1.1) can be written, for sufficiently small β, as

$$\psi(\mathbf{x}, \beta) \approx \int d\mathbf{x}_0 \int d\mathbf{x}_1 \int d\mathbf{x}_2 \langle \mathbf{x} \mid e^{-\frac{1}{2}\beta H_1} \mid \mathbf{x}_1 \rangle \langle \mathbf{x}_1 \mid e^{-\beta H_0} \mid \mathbf{x}_2 \rangle \langle \mathbf{x}_2 \mid e^{-\frac{1}{2}\beta H_1} \mid \mathbf{x}_0 \rangle \, \psi_0(\mathbf{x}_0). \quad (2.13)$$

To obtain the solution for larger values of β, we note, from Eq. (2.6), the exact relation for all N,

$$\begin{aligned} \psi(\mathbf{x}, N\beta) &= \int \langle \mathbf{x} \mid e^{-N\beta H} \mid \mathbf{x}_0 \rangle \, \psi_0(\mathbf{x}_0) \, d\mathbf{x}_0 \\ &= \int d\mathbf{x}_0 \int \cdots \int d\mathbf{x}_{N-1} \langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_1 \rangle \langle \mathbf{x}_1 \mid e^{-\beta H} \mid \mathbf{x}_2 \rangle \\ &\qquad \cdots \langle \mathbf{x}_{N-1} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle \, \psi_0(\mathbf{x}_0). \end{aligned} \quad (2.14)$$

Thus the solution at larger values of β can be obtained by choosing a sufficiently large N, such that $\beta' = \beta/N$ is small enough to enable each term in the integrand of (2.14) to be replaced by its approximate form Eq. (2.11).

For the purpose of numerical computation, the calculation of expression (2.13), a multi-dimensional integral, will in general be time-consuming, and in this paper, to illustrate the method, we have only considered cases where, in coordinate representation, $H_0 = H_0(\mathbf{x}, (\partial/\partial\mathbf{x}))$ and $H_1 = H_1(\mathbf{x})$.

Under these circumstances, using the orthogonality condition, $\langle \mathbf{x} \mid \mathbf{x}' \rangle = \delta(\mathbf{x} - \mathbf{x}')$, equation (2.13) becomes,

$$\psi(\mathbf{x}, \beta) \approx \int d\mathbf{x}_0 \, e^{-\frac{1}{2}\beta H_1(\mathbf{x})} \langle \mathbf{x} \mid e^{-\beta H_0} \mid \mathbf{x}_0 \rangle \, e^{-\frac{1}{2}\beta H_1(\mathbf{x}_0)} \psi_0(\mathbf{x}_0). \tag{2.15}$$

III. CONNECTION WITH STATISTICAL MECHANICS

In statistical mechanics, equation (1.1) is the Bloch equation for the statistical density matrix, $\rho(\mathbf{x}, \mathbf{x}_0, \beta)$ of a system with Hamiltonian H and temperature T, related to the parameter β through $\beta = 1/kT$, [*10*]. If we rewrite the Hamiltonian as the sum of the free particle Hamiltonian, H_0, plus the contribution from the potential, $V(\mathbf{x})$, we have from (2.14),

$$\rho(\mathbf{x}, \mathbf{x}_0, N\beta) = \int d\mathbf{x}_1 \int \cdots \int d\mathbf{x}_{N-1} \langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_1 \rangle \langle \mathbf{x}_1 \mid e^{-\beta H} \mid \mathbf{x}_2 \rangle \cdots \langle \mathbf{x}_{N-1} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle. \tag{3.1}$$

Using the approximation (2.11), for small β (i.e. large temperature)

$$\begin{aligned} \rho(\mathbf{x}, \mathbf{x}_0, N\beta) \approx \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_{N-1} \, & e^{-\frac{1}{2}\beta V(\mathbf{x})} \rho_0(\mathbf{x}, \mathbf{x}_1, \beta) \, e^{-\beta V(\mathbf{x}_1)} \rho_0(\mathbf{x}_1, \mathbf{x}_2, \beta) \\ & \cdots e^{-\beta V(\mathbf{x}_{N-1})} \rho_0(\mathbf{x}_{N-1}, \mathbf{x}_0, \beta) \, e^{-\frac{1}{2}\beta V(\mathbf{x}_0)}, \end{aligned} \tag{3.2}$$

where $\rho_0(\mathbf{x}, \mathbf{x}', \beta)$ is the free particle statistical density matrix

$$\rho_0(\mathbf{x}, \mathbf{x}', \beta) = \langle \mathbf{x} \mid e^{-\beta H_0} \mid \mathbf{x}' \rangle. \tag{3.3}$$

Expression (3.2) for the density matrix can be obtained by an evaluation of the path integral formula for this quantity; in the notation of Feynman and Hibbs [9] this is

$$\rho(\mathbf{x}, \mathbf{x}_0, N\beta) = \int \exp\left\{-\int_0^{N\beta} (H_0 + V) \, dt\right\} D\mathbf{x}(t) \tag{3.4}$$

where the integral represents a sum over all possible paths, commencing at $\mathbf{x}_0$, at the "time" 0, and finishing at $\mathbf{x}$, at "time", $N\beta$. As shown by Feynman, such a functional integral can be calculated as a limit, by breaking each path, $\mathbf{x}(t)$, into N piecewise straight paths, each of length β, and then taking the limit as $N \to \infty$. A semi-classical result is achieved by taking sufficiently small β. If one expands the integrals over the potential term using a trapezoidal rule, it is easily seen that (3.2) has the resultant form of an evaluation of (3.4), if on each straight section of the paths $V[\mathbf{x}(t)]$ does not differ too greatly from the mean, $\frac{1}{2}\{V(\mathbf{x}_i) + V(\mathbf{x}_{i+1})\}$, where $\mathbf{x}_i$ and $\mathbf{x}_{i+1}$ are the coordinates of the end points. Such a condition may be posed as the requirement that β be chosen sufficiently small, that

$$N\beta^3 V''(\xi) \ll 1, \tag{3.5}$$

where ξ "lies between" $\mathbf{x}_i$ and $\mathbf{x}_{i+1}$.

The iteration scheme suggested by Storer [*10*, *11*] for the evaluation of these path integral expressions, results in a density matrix appropriate to a system at a much lower temperature. Since the probability of a system being in a state other than the ground state decreases exponentially with the temperature, it is seen from (2.14) that repeated application of the operator, $\langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle$ to an arbitrary state function eventually produces the ground state wave function.

IV. APPLICATIONS

(a) The smallest eigenvalue of the operator H can be found by forming the following sequence of normalized functions, $\phi^{(N)}$, defined by the relations

$$\begin{aligned} \phi^{(0)}(\mathbf{x}, 0) &= \psi_0(\mathbf{x}) \\ \phi^{(N)}(\mathbf{x}, N\beta) &= \frac{\psi(\mathbf{x}, N\beta)}{[\int \psi^*(\mathbf{x}, N\beta)\, \psi(\mathbf{x}, N\beta)\, d\mathbf{x}]^{1/2}} \end{aligned} \tag{4.1}$$

where

$$\psi(\mathbf{x}, N\beta) = \int d\mathbf{x}_{N-1} \langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_{N-1} \rangle\, \phi^{(N-1)}(\mathbf{x}_{N-1}, (N-1)\beta).$$

Now if we expand the initial function $\psi_0(x)$ in a complete set of eigenfunctions of the operator H,

$$\psi_0(\mathbf{x}) = \sum_{i=0}^{\infty} a_i \psi^{(i)}(x) \tag{4.2}$$

where

$$H\psi^{(i)} = E_i \psi^{(i)} \qquad \text{and} \qquad a_i = \int \psi_0^*(\mathbf{x})\, \psi^{(i)}(\mathbf{x})\, d\mathbf{x},$$

it can easily be seen that the sequence $\lambda^{(N)}$, defined by

$$\lambda^{(N)} = \frac{\int \psi^*(\mathbf{x}, N\beta)\, \psi(\mathbf{x}, N\beta)\, d\mathbf{x}}{\int \psi^*(\mathbf{x}, N\beta)\, \phi^{(N-1)}(\mathbf{x}, (N-1)\beta)\, d\mathbf{x}} \tag{4.3}$$

$$= \frac{\sum_i |\, a_i\,|^2\, e^{-2N\beta E_i}}{\sum_i |\, a_i\,|^2\, e^{-(2N-1)\beta E_i}},$$

has the limit, $\lambda^{(N)} \to e^{-\beta E_0}$ as $N \to \infty$, where E_0 is the smallest eigenvalue of H. In the same limit, the sequence $\phi^{(N)}$ approaches the corresponding eigenfunction $\psi^{(0)}$.

As an example we consider the hydrogen atom, which is not a trivial numerical problem (even though an exact analytic solution is available) because of the singular behaviour of the potential near the origin. The Hamiltonian operator for the relative motion of the system is

$$H = -\frac{\partial^2}{\partial \mathbf{x}^2} + V(\mathbf{x}) \tag{4.4}$$

in units where the unit of length is the Bohr radius, $a_0 = \hbar^2/\mu e^2$ (μ is reduced mass of the electron), and the unit of energy is that of the ground state $E_0 = \hbar^2/2\mu a_0^2$. In these units $V(\mathbf{x}) = -2/|\,\mathbf{x}\,|$. Taking $H_0 = -\partial^2/\partial \mathbf{x}^2$, the Green's function for (2.12) can be written as

$$\langle \mathbf{x} \,|\, e^{-\beta H_0} \,|\, \mathbf{x}_0 \rangle = \frac{1}{(4\pi\beta)^{3/2}} \exp\{-(\mathbf{x} - \mathbf{x}_0)^2/4\beta\}. \tag{4.5}$$

Now equation (2.15), in spherical polar coordinates (r, θ, ϕ), becomes

$$\Phi(r, \beta) = \int_0^\infty dr_0 e^{-\frac{1}{2}\beta V(r)} \frac{1}{(4\pi\beta)^{1/2}} \times \left[\exp\left\{-\frac{(r - r_0)^2}{4\beta}\right\} - \exp\left\{-\frac{(r + r_0)^2}{4\beta}\right\}\right] e^{-\frac{1}{2}\beta V(r_0)} \Phi_0(r_0), \tag{4.6}$$

where $\Phi(r, \beta) = r\psi(r, \beta)$, and the integration over the polar coordinates in Eq. (4.6) has been carried out because, since $V = V(r)$, it is only necessary to consider ψ_0 as a function of r for the ground state.

By repeated application of the approximate form for the operator $e^{-\beta H}$ in Eq. (4.6), and appropriate normalization at each stage, we form the sequence (4.1). In this way we obtain an approximation to the limit of $\lambda^{(N)}$ (i.e. to E_0) and to the corresponding ground state wave function.

Numerically, the integrals can be evaluated using the trapezoidal rule, and the problem resembles the calculation of the largest eigenvalue of a matrix, whose elements tend to zero away from the diagonal, due to the limiting factors,

$\exp\{-(r - r_0)^2/4\beta\}$. Replacing the upper limit in the integration by a finite value, beyond which the ground state wave function becomes negligible (we took $10a_0$), and using a square grid with n points, each separated by a distance $\Delta(=10/n)$, Eq. (4.6) becomes

$$\Phi(r_i, \beta) = \sum_{j=1}^{n} \frac{\Delta}{(4\pi\beta)^{1/2}} e^{-\frac{1}{2}\beta V(r_i)}\{\exp(-\Delta^2(i-j)^2/4\beta) - \exp(-\Delta^2(i+j)^2/4\beta)\}$$
$$\times\, e^{-\frac{1}{2}\beta V(r_j)}\Phi_0(r_j), \tag{4.7}$$

where $r_i = i\Delta$, $1 \leqslant i \leqslant n$.

In evaluating Eq. (4.7) numerically a suitable value of β must be chosen. Basically β must be chosen sufficiently small so that the approximation (2.11) is valid. According to Eq. (2.10) we would require $\beta^3 \mid c_3\psi_0 \mid \ll 1$, or alternatively the less stringent condition (3.5) may be applied to give an order of estimate of β as

$$\beta^3 \ll \frac{1}{N\{V''\}_{\max}}. \tag{4.8}$$

On the other hand β must be chosen large enough so that, for a given separation Δ, the exponential terms do not decrease too rapidly as r differs from r_0. Taking $\Delta^2 \ll 4\beta$ seems to give a sufficient sample of the integrand in Eq. (4.6). It should be noted that this condition is the opposite of the well-known condition for the stability of the explicit time integration using difference schemes [*12*]. Hence one chooses the largest possible value of β in accordance with the condition (4.8), and then a value of Δ to sample the integrand sufficiently. For the hydrogen atom we have taken values of β and Δ for which $1 \ll 4\beta/\Delta^2 < 4/\Delta$.

In Fig. 1 we illustrate the convergence towards the ground state, starting with the initial function,

$$\begin{aligned} \Phi_0(r) &= 0.5 \qquad 0 \leqslant r \leqslant 5 \\ &= 0 \qquad\;\; 0 < r \leqslant 10 \end{aligned} \tag{4.9}$$

The corresponding eigenvalues are given in Table 1.

The apparently slow convergence to the ground state is a result of the choice of the initial function, and most of the calculations are concerned with producing the exponential behaviour of the tail for large r. However, the coresponding energy value (4.3), is given by the theory only to order β, and fewer iterations are needed for its convergence than for the wavefunction (correct to β^2). It is possible to improve the estimate for the ground state energy value by using the wave function together with the variational calculation i.e.

$$E_0' = \frac{\int \phi^{(N)}(\mathbf{x}, N\beta)\{H\phi^{(N)}(\mathbf{x}, N\beta)\}\, d\mathbf{x}}{\int \phi^{(N)}(\mathbf{x}, N\beta)\, \phi^{(N)}(\mathbf{x}, N\beta)\, d\mathbf{x}}, \tag{4.10}$$

where

$$H\phi^{(N)}(\mathbf{x}, N\beta) = -\int d\mathbf{x}_{N-1} \frac{\partial}{\partial\beta} \langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_{N-1}\rangle \, \phi^{(N-1)}(\mathbf{x}_{N-1}, (N-1)\beta).$$

Using the explicit form for $\langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_{N-1}\rangle$ for the hydrogen atom, i.e. as used in Eq. (4.6), we have evaluated the new ground state energy values E_0'. These are given in the last column of Table 1.

To take advantage of the faster convergence for larger values of β, the following procedure was adopted. Starting with a comparatively large value of β, and a

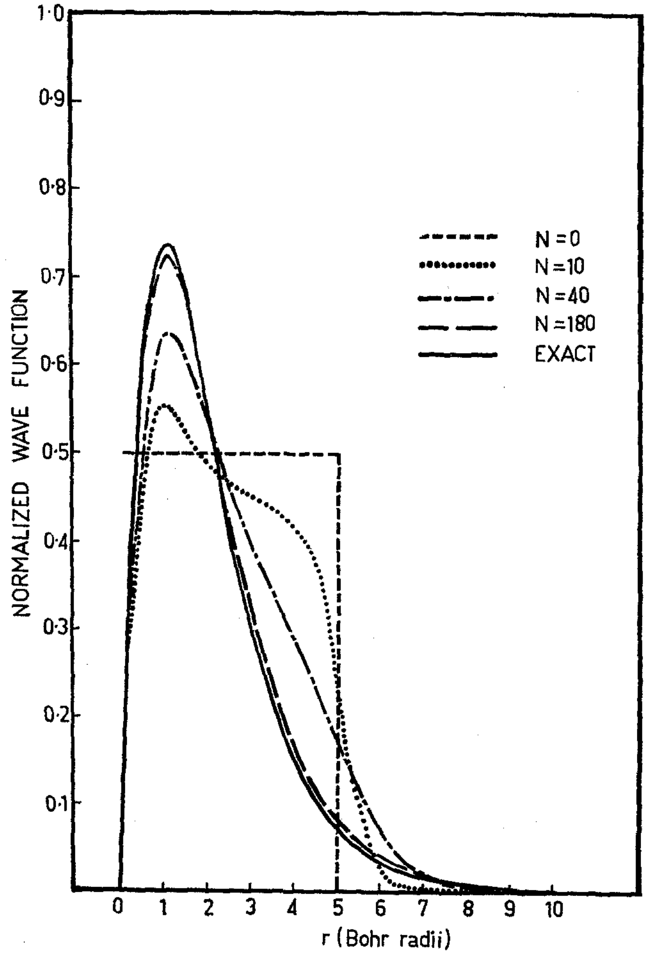

FIG. 1. Illustrating the convergence to the ground state for the hydrogen atom, using the initial approximation given in Eq. (4.9). $\beta = 0.02$, $n = 100$, $\Delta = 0.1$.

TABLE 1

CALCULATION OF THE GROUND STATE ENERGY OF THE HYDROGEN ATOM USING EQ. (4.13) AND EQ. (4.10) WITH $\beta = 0.02$ AND $\Delta = 0.1$

No. of iterations	Eigenvalue	E_0'
10	-0.8209	-0.8269
40	-0.9494	-0.9536
100	-0.9912	-0.9959
150	-0.9958	-1.0008
175	-0.9963	-1.0015
180	-0.9965	-1.0015
Exact	-1.0000	-1.0000

corresponding large Δ (small n) we iterated until successive energy values differed by less than 0.01 %. The new approximation to the ground state wave function was then transferred as the initial trial function to a new grid with twice as many points by defining the values at the new grid points by interpolation. Dividing β by 4 ensured the same value for $\Delta^2/4\beta$ and hence similar behaviour of the exponential factors. The results of these calculations, including the ground state energy values at each stage, and the number of iterations required on each grid for convergence are listed in Table 2. It is to be noticed that the effect of transferring to a finer grid is most apparent for small values of r, where the new grid samples the effect of the potential better. The values of the wavefunctions at various grid points are listed in Table 3.

The calculations were performed in this way to demonstrate the rapid

TABLE 2

TO SHOW THE RAPID INCREASE IN RATE OF CONVERGENCE BY USING A LARGE STARTING VALUE OF β

	Grid size etc.			Eigenvalue	No. of iterations needed for convergence
1	$n = 10$,	$\Delta = 1.0$,	$\beta = 2.0$	-0.9126	3
2	$n = 20$,	$\Delta = 0.5$,	$\beta = 0.5$	-0.9862	5
3	$n = 40$,	$\Delta = 0.25$,	$\beta = 0.125$,	-0.9924	3
4	$n = 80$,	$\Delta = 0.125$,	$\beta = 0.03125$,	-0.9954	2
5	$n = 160$,	$\Delta = 0.0625$,	$\beta = 0.0078125$,	-0.9978	5
6	$n = 320$,	$\Delta = 0.03125$,	$\beta = 0.001953125$,	-0.9983	1

TABLE 3

[illegible]

r	1	2	3	4	5	6	Exact
1	0.81263	0.68083	0.72362	0.72457	0.72603	0.73551	0.73575
2	0.44898	0.54122	0.54409	0.54614	0.54605	0.54154	0.54134
3	0.30296	0.31045	0.31078	0.31027	0.30992	0.29908	0.29872
4	0.18330	0.15725	0.15778	0.15741	0.15712	0.14683	0.14652
5	0.09821	0.07569	0.07502	0.07489	0.07475	0.06758	0.06738
6	0.04837	0.03556	0.03451	0.03438	0.03429	0.02985	0.02975
7	0.02293	0.01650	0.01562	0.01549	0.01543	0.01278	0.01278
8	0.01079	0.00754	0.00697	0.00688	0.00684	0.00526	0.00537
9	0.00505	0.00330	0.00296	0.00288	0.00284	0.00190	0.00222
10	0.00231	0.00124	0.00082	0.00057	0.00033	0.00009	0.00091

[a] For grid 6 the iteration was continued until the wavefunction remained constant to within 0.001 %.

convergence in energy values after only a small amount of computing time (about 5 minutes on IBM 1130). To obtain more accurate values for the energy, we can apply Eq. (4.10) to a more accurate wave function obtained by iterating several more times, or alternatively, by further reducing the value of β, and decreasing the size of the grid. Eventually, in the latter case, one would expect the behaviour of the Coulomb potential near $r = 0$ to begin to affect the results, thus providing some limit on the attainable accuracy. Alternatively one could use a Coulomb potential which is cut off at a small value of r and estimate the error that this procedure generates.

(b) The larger eigenvalues of H can be found from the solution of an eigenvalue equation obtained from Eq. (2.6) by expanding $\psi(\mathbf{x}, \beta)$ and $\psi_0(\mathbf{x}_0)$ in a complete set of eigenfunctions of H. Using Eq. (4.2) and

$$\psi(\mathbf{x}, \beta) = \sum_{i=0}^{\infty} a_i e^{-\beta E_i} \psi^{(i)}(\mathbf{x}), \tag{4.11}$$

Eq. (2.6) becomes

$$e^{-\beta E_i} \psi^{(i)}(\mathbf{x}) = \int \langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle \, \psi^{(i)}(\mathbf{x}_0) \, d\mathbf{x}_0 , \tag{4.12}$$

i.e. an integral equation for E_i and $\psi^{(i)}(\mathbf{x})$.

For example, the s state energy values of the hydrogen atom can be obtained by a solution of the equation

$$e^{-\beta E_s}\psi^{(s)}(r) = \int \rho(r, r_0, \beta)\, \psi^{(s)}(r_0)\, r_0^2\, dr_0\,, \tag{4.13}$$

where for small β

$$\rho(r, r_0, \beta) \approx \frac{1}{(4\pi\beta)^{1/2}}\, e^{-\frac{1}{2}\beta V(r)}\, \frac{1}{rr_0}\{\exp(-(r-r_0)^2/4\beta) - \exp(-(r+r_0)^2/4\beta)\}\, e^{-\frac{1}{2}\beta V(r_0)}. \tag{4.14}$$

Numerically this can be achieved by first expanding ρ and $\psi^{(s)}$ in orthogonal polynomials $\Phi_n(r)$, where

$$\int_0^\infty \Phi_n(r)\, \Phi_m(r)\, r^2\, dr = \delta_{mn}\,. \tag{4.15}$$

Writing

$$\rho(r, r_0, \beta) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A_{nm}\Phi_n(r)\, \Phi_m(r_0)$$

and

$$\psi^{(s)}(r) = \sum_{n=0}^{\infty} B_n^{(s)}\Phi_n(r),$$

Eq. (4.13) becomes,

$$e^{-\beta E_s} B_n^{(s)} = \sum_{m=0}^{\infty} A_{nm} B_m^{(s)}. \tag{4.16}$$

The energy values can now be obtained by finding the eigenvalues of the matrix A_{nm}. Obviously the closer the polynomials $\Phi_n(r)$ are chosen to the actual s state wavefunctions for the hydrogen atom, the nearer this matrix is to being diagonal. One can test this method by taking the actual s state wavefunctions,

$$\Phi_n(r) = \left(\frac{2}{n}\right)^{3/2} \frac{1}{\sqrt{2n^2(n!)^2}}\, e^{-r/n} L_n^{\,1}\left(\frac{2r}{n}\right). \tag{4.17}$$

where the $L_n^{\,1}$ are the associated Laguerre polynomials; then the energy values are given by

$$e^{-\beta E_n} = A_{nn} = \int_0^\infty r^2\, dr \int_0^\infty r_0^2\, dr_0 \Phi_n(r)\, \rho(r, r_0, \beta)\, \Phi_n(r_0). \tag{4.18}$$

Using the approximation (4.14) for small β, and evaluating the integrals numerically by Simpson's rule, we can calculate the higher energy values if we replace the upper limits of the integrals in Eq. (4.18) by finite values, chosen so that the corresponding polynomials are normalized to a sufficient accuracy according to Eq. (4.15).

Using an approximation for $\rho(r, r_0, \beta)$ produces errors in all the elements of the matrix A_{nm}, and the energy values calculated from the diagonal elements only will be inaccurate unless very small values of β are used. As before, such a requirement places a restriction on the choice of the grid spacing (Δ) needed for the evaluation of (4.18), because of the sharply peaked Gaussian expressions in (4.14). The situation is further complicated by the singular behaviour of the potential near the origin, particularly in the case of the ground state, where the wavefunction is large exactly where the approximation for $\rho(r, r_0, \beta)$ is likely to be bad.

If however, we choose β and Δ to satisfy simultaneously the conditions,

$$\beta/\Delta < 1 \qquad \text{and} \qquad \Delta^2/4\beta \ll 1,$$

we will be in a region where the approximation for $\rho(r, r_0, \beta)$ is good and also where the integrand in (4.18) is sampled sufficiently. By successively reducing the value of β and selecting a suitable value of Δ, it is possible to find acceptable results which are equally as good as those found using the best difference techniques.

In Table 4 we illustrate the effect of reducing the value of β/Δ (for fixed $\Delta^2/4\beta$) on the calculated values for the ground state of the hydrogen atom, while in Table 5 we have listed values obtained for the first four exicited s states.

The method is not limited to s states since we can expand the kernel, $\langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle$, of Eq. (4.12) in terms of Legendre polynomials, i.e. if

$$\langle \mathbf{x} \mid e^{-\beta H} \mid \mathbf{x}_0 \rangle = \sum_{l=0}^{\infty} \frac{(2l+1)}{4\pi} \rho_l(r, r_0, \beta) P_l(\cos\theta) \tag{4.19}$$

TABLE 4

GROUND STATE ENERGY VALUES FOR FIXED $\Delta^2/4\beta$ AND VARYING β/Δ OBTAINED BY THE METHODS OF §IV(b)[a]

β	Δ	β/Δ	$\Delta^2/4\beta$	E_0
0.5	0.25	2.0	0.03125	−1.22357
0.125	0.125	1.0	0.03125	−1.04512
0.03125	0.0625	0.5	0.03125	−1.00767
0.0089125	0.03125	0.25	0.03125	−1.00118
0.005	0.025	0.2	0.03125	−1.00064
0.0032	0.02	0.16	0.03125	−1.00035
0.00245	0.0175	0.14	0.03125	−1.00025

[a] The integrals were cut off at 20 Bohr radii.

TABLE 5

THE FIRST FOUR EXCITED s STATES OF THE HYDROGEN ATOM[a]

	β	Δ	β/Δ	$\Delta^2/4\beta$	Energy value	Exact energy value
E_1	0.00125	0.01	0.125	0.02	−0.250004	−0.250000
E_2	0.005	0.02	0.25	0.02	−0.111136	−0.111111
E_3	0.01125	0.03	0.375	0.02	−0.062532	−0.062500
E_4	0.02	0.04	0.5	0.02	−0.040036	−0.040000

[a] The integrals were cut off at 30, 60, 90, 120 Bohr radii respectively.

where $\cos\theta = (\hat{\mathbf{x}} \cdot \hat{\mathbf{x}}_0)$, then the higher angular states can be obtained by a solution of the equation (cf. Eq. (4.13))

$$e^{-\beta E_s}\psi_l^{(s)}(r) = \int \rho_l(r, r_0, \beta)\, \psi_l^{(s)}(r_0)\, r_0^{\,2}\, dr_0, \tag{4.20}$$

where for small β, [10], we approximate ρ_l by

$$\rho_l(r, r_0, \beta) \approx (4\pi\beta^3)^{-\frac{1}{2}}\, e^{-\frac{1}{2}\beta V(r)} \exp(-(r^2 + r_0^{\,2})/4\beta)\, i^{-l} j_l(irr_0/2\beta)\, e^{-\frac{1}{2}\beta V(r_0)}. \tag{4.21}$$

and j_l is the spherical Bessel function.

V. BOUNDED REGIONS

In contrast to the previous sections where we considered infinite or semi-infinite regions, in this section we consider a simple one-dimensional parabolic equation of the type (1.1), where $H = (\partial^2/\partial x^2) + V(x)$, with the two boundary conditions $\psi(x) = 0$ when $x \leqslant 0$ and also when $x \geqslant a$. The general solution for this case can be found in terms of the Green's function satisfying the equation,

$$\left[-\frac{\partial^2}{\partial x^2} + V(x)\right] G(x, \beta \mid x_0, 0) = -\frac{\partial G}{\partial \beta}(x, \beta \mid x_0, 0) \tag{5.1}$$

with the initial condition, $G(x, \beta \mid x_0, 0) = \delta(x - x_0)$ when $\beta = 0$, and the boundary conditions $G(x, \beta \mid x_0, 0) = 0$ when x or $x_0 = 0$ and when x or $x_0 = a$. Because of the symmetry which exists in the initial and boundary conditions between x and x_0, we could have written this equations as

$$\left[-\frac{\partial^2}{\partial x_0^{\,2}} + V(x_0)\right] G(x, \beta \mid x_0, 0) = -\frac{\partial G}{\partial \beta}(x, \beta \mid x_0, 0) \tag{5.2}$$

with the same initial and boundary conditions.

The fact that G must satisfy the boundary conditions at $x, x_0 = 0$ and $x, x_0 = a$ simultaneously is an awkward one for the application of our method because there exists no closed form for the corresponding equation with $V \equiv 0$. However, this difficulty can be eliminated, for we can show that we sacrifice no accuracy (at least as far as the eigenfunctions of H are concerned) if we satisfy each boundary condition separately, and define a new Green's function which is a composite of two functions, one satisfying the boundary conditions at x or $x_0 = 0$ and the other satisfying the boundary conditions at x or $x_0 = a$. Let us call $G_1(x, \beta \mid x_0, 0)$ the function which satisfies equation (5.1) with $G_1 = 0$ at x or $x_0 = 0$, and $G_2(x, \beta \mid x_0, 0)$ the function which satisfies equation (5.2) with $G_2 = 0$ at x or $x_0 = a$. If we now divide the square region $0 \leqslant x, x_0 \leqslant a$ into two parts by the line $x + x_0 = a$, we can define a composite Green's function $\tilde{G}(x, \beta \mid x_0, 0)$ by

$$\tilde{G}(x, \beta \mid x_0, 0) = G_1(x, \beta \mid x_0, 0) \qquad \text{for} \quad 0 \leqslant x + x_0 \leqslant a$$

and (5.3)

$$\tilde{G}(x, \beta \mid x_0, 0) = G_2(x, \beta \mid x_0, 0) \qquad \text{for} \quad a < x + x_0 \leqslant 2a.$$

The important feature of this definition is that $\tilde{G}(x, \beta \mid x_0, 0)$, regarded as the [redacted] $V(a - x)$. To show this, consider

$$I_n(x) = \int_0^a \tilde{G}(x, \beta \mid x_0, 0)\, \psi_n(x_0)\, dx_0$$

where $\psi_n(x_0)$ is an eigenfunction of H, with the corresponding eigenvalue E_n. Now

$$\begin{aligned}
&\left[-\frac{\partial^2}{\partial x^2} + V(x)\right] I_n(x) \\
&\quad = \int_0^{a-x} \left[-\frac{\partial^2}{\partial x^2} + V(x)\right] G_1(x, \beta \mid x_0, 0)\, \psi_n(x_0)\, dx_0 \\
&\quad + \int_{a-x}^{a} \left[-\frac{\partial^2}{\partial x^2} + V(x)\right] G_2(x, \beta \mid x_0, 0)\, \psi_n(x_0)\, dx_0 \\
&\quad + \frac{\partial}{\partial x}\{[G_1(x, \beta \mid a - x, 0) - G_2(x, \beta \mid a - x, 0)]\, \psi_n(a - x)\} \\
&\quad + \left\{\frac{\partial}{\partial x}[G_1(x, \beta \mid x_0, 0) - G_2(x, \beta \mid x_0, 0)]\right\}_{x+x_0=a} \psi_n(a - x).
\end{aligned}$$

Using (5.1) and (5.2), and integrating by parts, we can easily show that this reduces to,

$$\begin{aligned} HI_n(x) &= E_n I_n(x) \\ &\quad + \frac{\partial}{\partial x}\left[G_1(x, \beta \mid a - x, 0) - G_2(x, \beta \mid a - x, 0)\right] \psi_n(a - x) \\ &\quad + \left\{\frac{\partial}{\partial x}\left[G_1(x, \beta \mid x_0, 0) - G_2(x, \beta \mid x_0, 0)\right]\right\}_{x+x_0=a} \psi_n(a - x) \\ &\quad - \left\{\frac{\partial}{\partial x_0}\left[G_1(x, \beta \mid x_0, 0) - G_2(x, \beta \mid x_0, 0)\right]\right\}_{x+x_0=a} \psi_n(a - x). \qquad (5.4) \end{aligned}$$

Thus, provided $G_1(x, \beta \mid x_0, 0)$ and $G_2(x, \beta \mid x_0, 0)$ are continuous across the line $x + x_0 = a$ and the function $[G_1(x, \beta \mid x_0, 0) - G_2(x, \beta \mid x_0, 0)]$ is a symmetric function of x and x_0 when $x + x_0 = a$ ($V(x) = V(a - x)$ is a sufficient condition for this to be true), $I_n(x)$ is an (unnormalized) eigenfunction of the operator H with eigenvalue E_n, i.e.

$$\int_0^a \tilde{G}(x, \beta \mid x_0, 0)\, \psi_n(x_0)\, dx_0 = \tilde{g}_n \psi_n(x) \qquad (5.5)$$

However, the eigenvalues, $\tilde{g}_n$, of the kernel $\tilde{G}(x, \beta \mid x_0, 0)$ are not the same as those of the kernel $G(x, \beta \mid x_0, 0)$.

We have shown therefore that the exact eigenfunctions of the operator H, with two boundary conditions, can be found by looking for the eigenfunctions of the kernel $\tilde{G}(x, \beta \mid x_0, 0)$, which is defined as the composite of two functions which satisfy the boundary conditions separately. Once the eigenfunctions are known the eigenvalues can be obtained readily by variational or other techniques.

In order to use this analysis to calculate the solution to (1.1) in a bounded one-dimensional region, we make the approximation, as before,

$$G(x, \beta \mid x_0, 0) \approx e^{-\beta V(x)/2} G^{(0)}(x, \beta \mid x_0, 0)\, e^{-\beta V(x_0)/2} \qquad (5.6)$$

for sufficiently small β. Here $G^{(0)}(x, \beta \mid x_0, 0)$ is the solution of

$$\frac{\partial^2 G^{(0)}}{\partial x^2}(x, \beta \mid x_0, 0) = \frac{\partial G^{(0)}}{\partial \beta}(x, \beta \mid x_0, 0) \qquad (5.7)$$

with $G^{(0)}(x, \beta \mid x_0, 0) = 0$ at both x or $x_0 = a$, and $G^{(0)}(x, \beta \mid x_0, 0) = \delta(x - x_0)$ when $\beta = 0$. We could express $G^{(0)}(x, \beta \mid x_0, 0)$ as its eigenfunction expansion,

$$G^{(0)}(x, \beta \mid x_0, 0) = \sum_{n=0}^{\infty} e^{-\beta(n\pi/a)^2} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x_0}{a}\right) \qquad (5.8)$$

but it is essential to our iteration method to obtain a closed form for this expression, at least for small β.

Now,

$$G_1^{(0)}(x, \beta \mid x_0, 0) = \frac{1}{(4\pi\beta)^{1/2}} \{\exp(-(x - x_0)^2/4\beta) - \exp(-(x + x_0)^2/4\beta)\} \quad (5.9)$$

satisfies (5.7) with the correct boundary conditions at only $x = 0$ and $x_0 = 0$, and

$$G_2^{(0)}(x, \beta \mid x_0, 0) = \frac{1}{(4\pi\beta)^{1/2}} \{\exp(-(x - x_0)^2/4\beta) - \exp(-(x + x_0 - 2a)^2/4\beta)\} \quad (5.10)$$

satisfies equation (5.7) with the correct boundary conditions only at $x = a$ and $x_0 = 0$. Moreover (5.9) and (5.10) are continuous across the line $x + x_0 = a$, and the function $[G_1^{(0)}(x, \beta \mid x_0, 0) - G_2^{(0)}(x, \beta \mid x_0, 0)]$ is symmetric in x and x_0 throughout the region $0 \leqslant x, x_0 \leqslant a$. By the preceding arguments the composite Green's function,

$$\tilde{G}_0(x, \beta \mid x_0, 0) = \begin{cases} G_1^{(0)}(x, \beta \mid x_0, 0) & \text{for} \quad 0 \leqslant x + x_0 \leqslant a \\ G_2^{(0)}(x, \beta \mid x_0, 0) & \text{for} \quad a \leqslant x + x_0 \leqslant 2a \end{cases} \quad (5.11)$$

has the same eigenfunctions as $G^{(0)}(x, \beta \mid x_0, 0)$, and a direct calculation of the corresponding eigenvalue $\tilde{g}_n^{(0)}$, gives

$$\tilde{g}_n^{(0)} = e^{-\beta(n\pi/a)^2} \left[erf(y) + \frac{e^{-y^2}}{y\sqrt{\pi}} \int_0^{n\pi} e^{x^2/4y^2} \sin x \, dx \right] \quad (5.12)$$

where $y^2 = a^2/4\beta$ and erf (y) is the error function. Thus replacing $G^{(0)}(x, \beta \mid x_0, 0)$ by $\tilde{G}^{(0)}(x, \beta \mid x_0, 0)$ involves an error in the eigenvalue of $O(e^{-y^2})$, which is very small when $\beta \ll a^2$, and no error at all in the eigenfunction. Using this replacement in equation (5.6), we obtain the following expression for the Green's function of equation (5.1)

$$G(x, \beta \mid x_0, 0) \approx e^{-\beta V(x)/2} \tilde{G}^{(0)}(x, \beta \mid x_0, 0)\, e^{-\beta V(x_0)/2}, \quad (5.13)$$

which is accurate provided β is small enough, so that the higher order terms in Eq. (2.10) can be neglected. In general this would be a stronger requirement than $\beta < a^2$.

To illustrate these ideas we consider the effect on the energy values and the wavefunctions of a particle in a one-dimensional infinite well of width, a, caused by the presence of a repulsive barrier,

$$\begin{aligned} V(x) &= V_0 && a/4 \leqslant x \leqslant 3a/4 \\ &\quad 0 && 0 < x < a/4 \text{ and } 3a/4 < x < a \\ &+\infty && x \leqslant 0 \text{ and } x \geqslant a. \end{aligned} \quad (5.14)$$

The eigenvalues and eigenfunctions of the corresponding Hamiltonian operator can now be obtained using Eq. (4.12) in the form,

$$e^{-\beta E_s}\psi^{(s)}(x) = \int_0^a \rho(x, x', \beta)\, \psi^{(s)}(x')\, dx' \tag{5.15}$$

where the Green's function $\rho(x, x', \beta)$ is to be found from Eqs. (5.13), (5.11), (5.10), and (5.9).

Numerical estimates for the lowest N eigenfunctions and eigenvalues of this homogenous integral equation can be obtained by approximating the integral by an N point quadrature rule, thus replacing the integral equation by a set of N simultaneous equations in N unknowns [*13*, *14*]. Dividing $[0, a]$ into $N+1$ equal intervals, each of length $\Delta = a/(N+1)$, Eq. (5.15) becomes,

$$e^{-\beta E_s}\psi_i = \sum_{j=1}^{N} \rho_{ij}\psi_j \tag{5.16}$$

where

$$\psi_i = \psi(xi), \qquad \rho_{ij} = \Delta\rho(x_i, x_j', \beta)$$

and

$$x_i = i\Delta, \qquad i = 1, 2, \ldots, N.$$

The eigenvalues and eigenvectors of the matrix ρ_{ij} now furnish us with approximations to the lowest N eigenvalues and eigenfunctions of the operator ρ. These approximations improve as N is made larger.

For the simple one-dimensional problem we have chosen, we approximated the integrals by a trapezoidal rule with 50 grid points, thus obtaining values for the lowest 50 eigenvalues and eigenfunctions. Using $a = 2\pi$, $V_0 = 2.5$, we list in Table 6 the results for the first ten energy values (E_s), calculated from the eigenvalues of ρ_{ij}, together with the exact results evaluated from the original Schrödinger equation. It is expected that the last few eigenvalues would not be too accurate because the region is not sampled sufficiently for their determination. This is not a serious difficulty, however, as seen from the results in Table 6 for the thirtieth and fourtieth eigenvalues (E_{29}, E_{39}). As in the previous calculations in this paper, it should be realized that β must be chosen carefully because of its association with the grid spacing, Δ. In general this means that if more accurate results are required, the reduction in the size of β must be accompanied by an increase in N to ensure that the quadrature rule still samples the integrand sufficiently.

TABLE 6

ENERGY VALUES OF A PARTICLE IN A POTENTIAL WELL (DEFINED BY EQ. (5.14)) FOR DIFFERENT VALUES OF β; $N = 49$; $a = 2\pi$, $V_0 = 2.5$

β	0.05	0.01	0.0075	Exact
E_0	1.7573	1.7609	1.7910	1.7624
E_1	1.8898	1.8936	1.8937	1.8955
E_2	3.6133	3.6133	3.6133	3.6136
E_3	5.5037	5.5045	5.5045	5.5029
E_4	7.6713	7.6749	7.6750	7.6733
E_5	10.206	10.210	10.210	10.212
E_6	13.431	13.432	13.432	13.435
E_7	17.323	17.323	17.323	17.321
E_8	21.600	21.603	21.603	21.599
E_9	26.229	26.233	26.233	26.235
E_{29}	226.24	226.24	226.17	226.25
E_{39}	390.62	400.59	398.16	401.25

VI. DISCUSSION

Even though we have emphasized the quantum mechanical applications of this method it could be applied equally well to the numerical solution of diffusion problems, e.g. Fig. 1 privides a picture of the time development of the radial distribution of particles diffusing via Brownian motion in a Coulomb potential.

The method offers several advantages over the standard technique of replacing the basic differential equation by a difference equation. The error made in the replacement of the operator $e^{-\beta(H_0+V)}$ by $e^{-\beta/2V}e^{-\beta H_0}e^{-\beta/2V}$ depends only on the value of β and the magnitude of the derivatives of V; it is independent of any grid size. The "free-particle" problem is essentially solved by the explicit expression for $e^{-\beta H_0}$ whereas the relation between the "time" step β and the grid size Δ for difference schemes must be maintained ($\Delta^2 \geqslant \beta$) and both Δ and β must be small even with no potential present. The replacement of the differential equation by an integral equation seems to have eliminated any problem of stability and moreover the expression in terms of an integral equation leaves open the possibility of using methods, (e.g. as in §IV(a) and §V) other than integration by quadratures. A modification of this method using Monte-Carlo integration techniques is being developed by the authors and promises to give good results for problems involving many particles.

We have considered cases where the operator H is of the form $H = -(\partial^2/\partial x^2) + H_1$. Convergence can be improved if we absorb into H_0 as much of the variation in H_1 as possible; this will enable a larger value of β to be chosen.

However, this requires an explicit form for $\langle \mathbf{x} \mid e^{-\beta H_0} \mid \mathbf{x}_0 \rangle$. We give here the main forms for H_0 for which this can be done: For

$$H_0 = -\frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{r^2} \quad (r \geqslant 0) \tag{6.1}$$

$$\langle r \mid e^{-\beta H_0} \mid r_0 \rangle = 4\pi r r_0 (4\pi\beta)^{-3/2} \exp[-(r^2 + r_0^2)/4\beta]\, i^{-l} j_l(r r_0\, i/2\beta); \tag{6.2}$$

for

$$H_0 = -\frac{\partial^2}{\partial \mathbf{x}^2} + \omega^2 \mathbf{x}^2 (\text{harmonic oscillator}), \tag{6.3}$$

$$\begin{aligned} \langle \mathbf{x} \mid e^{-\beta H_0} \mid \mathbf{x}_0 \rangle &= [2\pi \sinh(2\omega\beta)/\omega]^{-3/2} \\ &\quad \times \exp\{-(\omega/2)\coth(2\omega\beta)(\mathbf{x}^2 + \mathbf{x}_0^2) + \omega \operatorname{cosech}(2\omega\beta)\mathbf{x} \cdot \mathbf{x}_0\}; \end{aligned} \tag{6.4}$$

and for

$$H_0 = -\frac{\partial^2}{\partial \mathbf{x}^2} - iB\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + B^2(x^2 + y^2)/4$$

$$(\text{particle in a magnetic field } B\hat{\mathbf{z}}), \tag{6.5}$$

$$\begin{aligned} \langle \mathbf{x} \mid e^{-\beta H_0} \mid \mathbf{x}_0 \rangle &= (4\pi\beta)^{-3/2} \frac{\beta B}{\sinh(\beta B)} \exp[-\{2i\beta B(x_0 y - y_0 x) \\ &\quad + \beta B \coth(\beta B)((x - x_0)^2 + (y - y_0)^2) + (z - z_0)^2\}/4\beta]. \end{aligned} \tag{6.6}$$

These expressions may be quite useful where the remaining part of the Hamiltonian is quite small.

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