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The Fast Hankel Transform as a Tool in the Solution of the Time Dependent Schrödinger Equation

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A new method is presented for the solution of the time dependent Schrödinger equation, expressed in polar or spherical coordinates. The radial part of the Laplacian operator is computed using a Fast Hankel Transform. An algorithm for the FHT is described, based on the Fast Fourier Transform. The accuracy of the Hankel method is checked for the two- and three-dimensional harmonic oscillator by comparing with the analytical solution. The Hankel method is applied to the system $H + H_2$ with Delves hyperspherical coordinates and is compared to the Fourier method. © 1985 Academic Press, Inc.

1. INTRODUCTION

In recent years substantial research has been carried out on the numerical solution of partial differential equations. Equations like the Schrödinger equation [1], acoustic equation [2], elastic equation [3], Navier–Stokes equation [4], KDV-equation [5], and the diffusion equation [6] have great importance in physics and are the basis for modeling and simulation of actual experiments. Much of the progress in this field can be attributed to the Fourier or the pseudo spectral method [7] which enables a good representation of the Laplacian operator. This means a great reduction in grid size compared to finite difference methods. On the other hand the Fourier method is restricted to Cartesian coordinates, a rectangular grid, equidistant sampling points, and periodic boundary conditions. In many problems symmetry considerations decouple the problem, resulting in lower dimensionality and a different geometry, so that the Fourier method is not applicable. In this paper the use of the Fast Hankel Transform (FHT) will be demonstrated for the following cases: the solution of partial differential equations with radial or spherical symmetry and also an application with Delves hyperspherical coordinates.

The Hankel method is similar to the Fourier method in that it uses a double transform to calculate differential operators. In the FHT we calculate the radial part of the Laplacian operator. As can be expected the boundary conditions and the

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sampling points are the ones appropriate for the radial problem. Although this paper concentrates on the Schrödinger equation, the methods developed are applicable to other equations.

In quantum mechanics the state of the system is represented by the wave function ψ, and the time evolution is governed by the Schrödinger equation

$$i\frac{\partial\psi}{\partial t}=\mathbf{H}\psi, \tag{1.1}$$

where $\mathbf{H}$ is the Hamiltonian operator of the system and $\mathbf{H}=\mathbf{T}+\mathbf{V}$. $\mathbf{T}$ is the kinetic energy operator equal to $(-1/2m)\nabla^2$, where m is the mass and ∇^2 the Laplacian. $\mathbf{V}$ is the potential. (In this work atomic units are used in which $\hbar=1$ and the mass is given in units of the electron mass.)

The central idea behind the numerical solution is to discretize the space and time coordinates of the problem. The Hilbert space of square-integrable wave functions of the problem is thus represented by a new Hilbert space of square-integrable wave functions on the spatial grid. Hermitian operators in the original Hilbert space are represented as Hermitian operators in the discrete Hilbert space. Representing the potential operator $\mathbf{V}$ poses no problem since it is merely a local multiplication of $\psi(\mathbf{r}, t)$ by $\mathbf{V}(\mathbf{r}, t)$ and is represented as a multiplication at every grid point. The main problem is the representation of the kinetic energy operator $\mathbf{T}=-(1/2m)\nabla^2$, since it is nonlocal and cannot be represented as a local multiplication.

In Cartesian coordinates $\mathbf{T}$ is equivalent to a Fourier transform, followed by a multiplication by $-\mathbf{k}^2$ ($\mathbf{k}$ is the coordinate vector in momentum space), followed by an inverse Fourier transform. The representation of $\mathbf{T}$ in the discrete space is then the Discrete Fourier Transform followed by a local multiplication by $-\mathbf{k}^2$ and an inverse Discrete Fourier Transform. A fast algorithm to compute the Discrete Fourier Transform is the Fast Fourier Transform algorithm [8, 9].

The transform to momentum space in polar coordinates in the radial direction is the Hankel transform. A fast algorithm for the discrete approximation of the Hankel transform is demonstrated in this paper.

In polar coordinates the Laplacian operator is separated into radial and angular parts:

$$\nabla^2\psi=\left[\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right]\psi. \tag{1.2}$$

In spherical coordinates the Laplacian is

$$\nabla^2\psi=\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta}+\frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right]\psi. \tag{1.3}$$

The FHT is used to calculate the radial part of the Laplacian operator by applying a Hankel transform, multiplying by $-\mathbf{k}^2$ and applying the Hankel transform again.

For the time integration a second order explicit differencing method is used. As an alternative the semi-implicit Chebychev propagation method has also been used for the time propagation [10].

The paper is divided as follows: Section II describes the FHT and the calculation of the radial part of the Laplacian. Section III solves the Schrödinger equation numerically for examples which have analytical solutions. By this the accuracy of the method is checked. Section IV compares the method to results obtained on a square grid by the Fourier method. Section V gives the conclusions.

II. The FHT and Its Use in the Calculation of the Radial Part of the Laplacian

II.a. *The FHT Algorithm*

The Hankel transform of order v of a real or complex function f on the interval $(0, \infty)$ is defined by

$$\hat{f}(k) = \int_0^\infty r f(r)\, J_v(kr)\, dr \qquad \text{for } k > 0, \tag{2.1}$$

where J_v is the Bessel function of the first kind of order v. In this paper v is assumed to be real and nonnegative. The Hankel transform is its own inverse.

The calculation of the FHT is performed using a logarithmic change of variables, as described by Siegman [11] and Talman [12, 13]. An outline of the method is given below.

Substitution of $r = r_0 e^{-y}$ and $k = k_0 e^x$ in (2.1) gives

$$\hat{f}(k_0 e^x) = r_0^2 \int_{-\infty}^{\infty} e^{-2y} f(r_0 e^{-y})\, J_v(r_0 k_0 e^{x-y})\, dy. \tag{2.2}$$

The expression on the right-hand side is a convolution of the functions $e^{-2y} f(r_0 e^{-y})$ and $r_0^2 J_v(r_0 k_0 e^x)$, for which there exists an efficient convolution algorithm based on the Fast Fourier Transform (FFT, see [8, 9].)

The function f is sampled in N points, where N is a power of two. The variables x and y are discretized at equal distances δ: $x, y = j\delta$ for $j = 0, \ldots, N-1$. The discrete approximation of the Hankel transform of f is then given by

$$\hat{f}(k_0 e^{j\delta}) \approx r_0^2 \delta \sum_{m=0}^{N-1} e^{-2m\delta} f(r_0 e^{-m\delta})\, J_v(r_0 k_0 e^{(j-m)\delta}). \tag{2.3}$$

The use of the discrete (circular) Fourier transform to compute the continuous

(noncircular) convolution requires padding of the values of f with N zero's. This is done by setting

$$b_m = \begin{cases} 0 & \text{for } m = -N,\ldots,-1, \\ e^{-2m\delta} f(r_0 e^{-m\delta}) & \text{for } m = 0,\ldots, N-1, \end{cases} \tag{2.4}$$

and

$$c_j = r_0^2\, \delta J_\nu(r_0 k_0 e^{j\delta}) \qquad \text{for } j = -N,\ldots, N-1. \tag{2.5}$$

The resulting expression

$$a_j = \sum_{m=0}^{N-1} b_m c_{j-m} \qquad \text{for } j = -N,\ldots, N-1 \tag{2.6}$$

is a $2N$-term discrete circular convolution.

The well-known convolution theorem states that the Fourier transform of the convolution of b and c, $b * c$, equals the product of their Fourier transforms. Hence $b * c$ can be computed by performing $2N$-point FFTs on b and c, multiplying the results and performing an inverse FFT. The first N values of the result are discarded, and the N values $a_j = \hat{f}(k_0 e^{j\delta})$ for $j = 0,\ldots, N-1$ are the approximated values of the Hankel transform of f.

The Fourier transform of c is computed and stored in a table, thus saving computation time, when computing the Hankel transform many times with the same parameters.

II.b. *Choosing the Parameters*

The parameters N, δ, r_0, and k_0 have to be chosen according to certain criteria, as detailed below. The parameter $r_0 = r_{\max}$ is the maximum value of r in the r-domain. Let $r_{\min} = r_0 e^{-(N-1)\delta}$ be the minimum value of r. The parameter $k_0 = k_{\min}$ is the minimum value of k in the k-domain. Let $k_{\max} = k_0 e^{(N-1)\delta}$ be the maximum value of k.

The parameters δ, r_0, k_0 should be chosen such that the truncated intervals $(r_{\min}, r_{\max})$ and $(k_{\min}, k_{\max})$ contain the functions f (resp. $\hat{f}$) in the r- (resp. k-domain.) The values $r_{\max}$ and $k_{\max}$ are determined based on properties of f, where the accuracy that can be obtained depends on the space-bandwidth product $r_{\max} k_{\max}$.

One restriction while truncating is avoiding undersampling of the Bessel function $J_\nu(r_0 k_0 e^x)$. The Bessel function J_ν has zeros at distances approximately equal to π. For adequate sampling at least one sampling point between two successive zeros is required. This leads to

$$|r_0 k_0 (e^{(N-1)\delta} - e^{(N-2)\delta})| < \pi \tag{2.7}$$

or, approximately,

$$r_0 k_0 e^{(N-1)\delta}\, \delta < \pi, \tag{2.8}$$

which can be formulated as

$$r_{\max} k_{\max} \delta < \pi \tag{2.9}$$

giving a criterion for δ. As for the Bessel function the sampling of the function f should be sufficiently dense. The distance between two sampling points of f is $|e^{-m\delta} - e^{-(m+1)\delta}|$. This distance should be less than $\pi/k_{\max}$, the minimum distance between two zeros of f represented on the logarithmic grid. It is easily seen that this condition leads to the same criterion (2.9) for the adequate sampling of $f(r_0 e^{-y})$.

A rule of thumb for finding a minimum cut-off is given by the need to choose the first grid point closer to the origin than the minimum distance between two zeros of f represented on the grid

$$r_{\min} < \frac{\pi}{k_{\max}}. \tag{2.10}$$

II.c. *Computation of the Radial Part of the Laplacian*

The radial part of the 2-dimensional Laplacian operator in polar coordinates (r, φ) as given by eq. (1.2) is $(1/r)(\partial/\partial r)\, r(\partial/\partial r)$ and can be computed using the following theorem (cf. Sneddon [14].)

THEOREM. *Let* $\mathbf{L}_v$ *be the operator* $((1/r)(\partial/\partial r)\, r(\partial/\partial r)) - (v^2/r^2)$ *and* $\mathbf{H}_v$ *the Hankel transform of order* v, *then*

$$\mathbf{L}_v = \mathbf{H}_v(-k^2)\, \mathbf{H}_v. \tag{2.11}$$

Applying therefore the operator $(1/r)(\partial/\partial r)\, r(\partial/\partial r)$ is equivalent to applying a Hankel transform of order 0, multiplying by $-k^2$ and again applying a Hankel transform of order 0. A Hankel transform of order v can be used if terms of the form $-(v^2/r^2)$ are present. Such terms are introduced when symmetry considerations decouple a two- or three-dimensional problem.

For the computation of $\mathbf{L}_v \psi$ a total of four $2N$-point FFTs are performed. The number of arithmetic operations needed for this computation grows with N as $O(N \log N)$.

The case of spherical coordinates can be reduced to a case similar to the one described above. The radial part of the 3-dimensional Laplacian operator in spherical coordinates (r, ϑ, φ) is $(1/r^2)(\partial/\partial r)\, r^2(\partial/\partial r)$. Substitution of $\tilde{\psi}(r, \vartheta, \varphi, t) = r^{1/2}\psi(r, \vartheta, \varphi, t)$ leads to

$$\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\psi = r^{-1/2}\left[\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r} - \frac{1}{4r^2}\right]\tilde{\psi}, \tag{2.12}$$

the right-hand side of which can be computed using the FHT method with order $\frac{1}{2}$.

III. Examples for which Analytical Solutions Exist

III.a. *The Hankel Transform Method*

The numerical solution of the time dependent Schrödinger equation (1.1) is as follows:

The solution starts with an initial wave function ψ^0. ψ^1 is calculated from ψ^0 using a second order Runge–Kutta scheme. ψ is propagated in time by second order differencing. ψ^{n+1} is computed from its two predecessors by

$$\psi^{n+1} = \psi^{n-1} - 2i\,\Delta t\,\mathbf{H}\psi^n, \tag{3.1}$$

where Δt is the time step and ψ^n the wave function at time $t = n\,\Delta t$. The Hamiltonian of ψ is computed by $\mathbf{H}\psi = (-1/2m)\,\nabla^2\psi + \mathbf{V}\psi$. The radial part of the Laplacian of ψ is computed by using the FHT. If necessary, remaining terms of the Laplacian are computed by other methods (e.g., the Fourier method). The wave function ψ is discretized on a spatial grid. In the radial direction the spacing is logarithmic, as described in Section II.

For practical purposes limitations on computer time and memory have to be taken into account when determining the parameters, such as the spatial grid constants, the number of grid points, and the time step Δt. The procedure of chosing the parameters for the radial direction is as follows:

N, δ, and the truncation intervals $(r_{\min}, r_{\max})$ and $(k_{\min}, k_{\max})$ are chosen as in Section II.b. The value $k_{\max}$ can physically be interpreted as the maximum momentum $p_{\max}$ in the radial direction. The best value for $k_{\max}$ can either be calculated from physical data, or empirically found by performing an FHT. Equation (2.9) is equivalent to the physical uncertainty relation $p_{\max}\,\Delta r < \pi$.

The last parameter to be determined is the time step. If Δt is chosen too large the solution will grow exponentially out of bounds. The stability limit Δt_{crit} can be found empirically or estimated as described below. Artificial numerical dispersion is avoided when the time step is chosen as $\Delta t = 0.2\,\Delta t_{\text{crit}}$ (see [1].) An estimation of the stability limit can be derived as in [1], giving

$$\Delta t_{\text{crit}} \approx \frac{1}{(k_{\max}^2/2m) + V}, \tag{3.2}$$

where V is the maximum potential difference represented in the problem. (The above formula is valid for the case that only radial momentum is present, but it can easily be adjusted for other situations.)

III.b. *The Two-Dimensional Harmonic Oscillator*

The problem of the two-dimensional harmonic oscillator can be solved analytically. Comparison of the exact and the numerical solution is a check on the accuracy of the Hankel transform method. Two checks are performed: First, the (known) energy is compared to the approximated value $|\langle\psi\mathbf{H}\psi\rangle|$, where $\mathbf{H}$ is the

discrete Hamiltonian operator, the radial part of which is computed using the Hankel method. (Here the Dirac symbol $\langle fg \rangle$ denotes the scalar product of f and conjugate g integrated over the grid.) Second, an eigenfunction of the Hamiltonian is entered as an initial wave function and propagated in time. Since the wave function is stationary its discrete approximation should stay stationary in time and especially should have an overlap $|\langle \psi_t \psi_0 \rangle| = 1$ at all times during the propagation of the wave function.

Using a two-dimensional Cartesian coordinate system the problem could be solved by applying the Fourier transform method (Kosloff and Kosloff [1].) Since the problem has radial symmetry the use of polar coordinates reduces the dimensionality. In general the Hankel scheme will reduce the dimensionality for any radially symmetric potential.

The potential of the harmonic oscillator is

$$\mathbf{V}(r) = \mathbf{V}(r, \varphi) = \tfrac{1}{2} r^2. \tag{3.3}$$

The variables can be separated setting

$$\psi(r, \varphi, t) = R(r, t)\, e^{im\varphi}. \tag{3.4}$$

The time dependent Schrödinger equation (1.1) then reduces to

$$\left[-\frac{1}{2} \left[\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} - \frac{m^2}{r^2} \right] + \mathbf{V}(r) \right] R(r, t) = i \frac{\partial R}{\partial t}(r, t) \tag{3.5}$$

(the mass is 1.) The eigenfunctions of the harmonic oscillator are

$$\psi_{nm}(r, \varphi) = N_{nm} e^{-r^2/2} r^{|m|} L^{|m|}_{(n-|m|)/2}(r^2)\, e^{im\varphi}, \tag{3.6}$$

where $n = 0, 1, 2, \ldots$, and $m = -n, -n+2, \ldots, n-2, n$. The $N_{n,m}$ are normalization constants, and the L_n^m are the generalized Laguerre polynomials (see Abramowitz and Stegun [11].) The energy eigenvalues are

$$E_n = n + 1 \qquad \text{for } n = 0, 1, 2, \ldots. \tag{3.7}$$

The eigenfunctions and eigenvalues satisfy

$$\mathbf{H} \psi_{nm} = E_n \psi_{nm}. \tag{3.8}$$

The discrete Hamiltonian is checked by comparing the exact energy E_n with the approximated value $|\langle \psi_{nm} \mathbf{H} \psi_{nm} \rangle|$.

The second check of the method is done by taking an eigenfunction as initial wave function and integrating it in time. If the discrete wave function is stationary then the overlap $|\langle \psi^n \psi^0 \rangle|^2$ should stay equal to unity, during the integration of the wave function.

Table I shows the energy, overlap, and norm for several values of the quantum

TABLE I

Accuracy of the Hankel Transform Method for the Two-dimensional Harmonic Oscillator after 10,000 Time Steps ($\Delta t = 0.0001$, $N = 128$)

Quantum numbers		Order of	Truncation intervals				Maximum relative error (in 10^{-6})		
n	m	FHT	r_{min}	r_{max}	k_{min}	k_{max}	Energy	Overlap	Norm
0	0	0	0.00001	4	0.00001	4	1.0	0.9	0.4
1	1	0	0.03	4.5	0.11	16.5	1000	2,600	1.4
1	1	1	0.03	4.5	0.11	16.5	0.7	1.8	0.9
2	0	0	0.00005	5	0.00005	5	0.6	1.2	0.5
2	2	0	0.05	6	0.05	6	0.7	1.0	0.5
3	1	0	0.02	4.8	0.0625	15	1200	11,000	1.0
3	1	1	0.02	4.8	0.0625	15	1.9	1.5	0.8
3	3	0	0.025	6.5	0.04	10.4	1.0	3.1	0.7
4	0	0	0.00005	5	0.00005	5	0.7	8.8	0.5
4	2	0	0.02	6	0.02	6	0.8	1.5	1.1
4	4	0	0.04	8	0.035	7	1.0	2.3	1.2

numbers n and m. For most functions an accuracy of 10^{-6} can be achieved, during an integration period up to one atomic time unit. The required truncation intervals depend on the properties of ψ_{nm} and can be found empirically, for example by plotting ψ and $\hat{\psi}$ as in Fig. 1. For optimal accuracy the intervals should contain as much as possible of ψ and $\hat{\psi}$, while satisfying (2.9) and (2.10). A uniform time step $\Delta t = 0.0001$ was chosen for all functions.

The term $-(m^2/r^2)$ in Eq. (3.5), which entered the equation because of the separation (3.4), can either be included in the computation of the effective potential (when using an FHT of order 0), or in the computation of the Laplacian (when using an FHT of order m). Table I contains examples of both methods and indicates that the last method is preferable.

Results for several values of n and m were obtained using a Hankel transform of order 0. If $\psi(r)$ converges slowly to 0 for $r \to 0$ and $m \neq 0$, then the singularity at 0 of $-(m^2/r^2)$ disturbs the computation. This is clearly visible in the case $m = 1$, where the Hamiltonian and hence the energy are not represented very accurately, resulting in a steadily decreasing overlap. Using a Hankel transform of order 1 improves the accuracy very much.

In all cases the method conserves norm and energy almost within the accuracy of the computer.

III.c. *The Three-Dimensional Harmonic Oscillator*

The potential of the three-dimensional harmonic oscillator is

$$\mathbf{V}(r) = \mathbf{V}(r, \vartheta, \varphi) = \tfrac{1}{2}r^2. \tag{3.9}$$

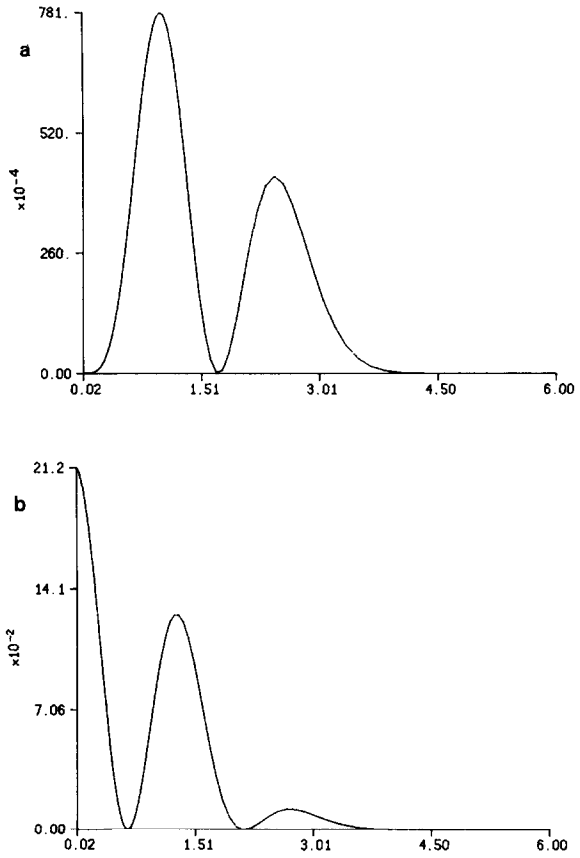

FIG. 1. (a) The square absolute value of the eigenfunction ψ_{42} of the two-dimensional harmonic oscillator (atomic units). (b) The square absolute value of the Hankel transform of ψ_{42}.

The variables can be separated setting

$$\psi(r, \vartheta, \varphi, t) = R(r, t)\, Y_l^m(\vartheta, \varphi), \tag{3.10}$$

where Y_l^m is a spherical harmonic function. The time dependent Schrödinger equation (1.1) then reduces to

$$\left[-\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right] + \mathbf{V}(r)\right] R(r, t) = i\frac{\partial R}{\partial t}(r, t) \tag{3.11}$$

(the mass is 1.) The eigenfunctions of the harmonic oscilator are

$$\psi_{klm}(r, \vartheta, \varphi) = N_{kl} e^{-r^2/2} r^l L_{k/2}^{l+1/2}(r^2)\, Y_l^m(\vartheta, \varphi), \tag{3.12}$$

where $k = 0, 2, 4,...$, $l = 0, 1, 2,...$, and $m = -l, -l+1,..., l$. The N_{kl} are normalization constants, and the L_k^l are the generalized Laguerre polynomials (see Abramowitz and Stegun [11].) The energy eigenvalues are

$$E_{kl} = k + l + \frac{3}{2} \qquad \text{for } k = 0, 2, 4,..., \text{ and } l = 0, 1, 2,.... \tag{3.13}$$

The eigenfunctions and eigenvalues satisfy

$$\mathbf{H}\psi_{klm} = E_{kl}\psi_{klm}. \tag{3.14}$$

The integration was done after replacing ψ by $r^{1/2}\psi$ in the computation of the Laplacian, as described in Section II.c.

Table II shows the energy, overlap, and norm for several values of the quantum numbers k and l. Like in the two-dimensional case an accuracy of 10^{-6} can be achieved for most wave functions.

The terms $-l(l+1)/r^2$ from eq. (3.11) and $(-1/4r^2)$ from the substitution (2.12) give together a term $-(l+\frac{1}{2})^2/r^2$. When using a Hankel transform of order 0, the singularity at 0 of this term disturbs the computation for wave functions $\psi(r)$ which do not converge fast to 0 for $r \to 0$. This can be observed for $l = 0$ and, to some lesser extent, for $l = 1$. The difficulty can be solved by using a Hankel transform of higher order. In Table II this is done for $l = 0$, with the same parameters, so that the two methods can be compared.

TABLE II

Accuracy of the Hankel Transform Method for the Three-Dimensional Harmonic Oscillator after 10,000 Time Steps ($\Delta t = 0.0001$, $N = 128$)

Quantum number		Order of	Truncation intervals				Maximum relative error (in 10^{-6})		
k	l	FHT	r_{min}	r_{max}	k_{min}	k_{max}	Energy	Overlap	Norm
0	0	0	0.008	4.5	0.024	13.5	16000	46000	1.4
0	0	0.5	0.008	4.5	0.024	13.5	0.6	1.1	0.7
0	1	0	0.02	4.4	0.075	16.5	29	85	0.9
2	0	0	0.007	4.8	0.0185	12.69	11000	92000	0.8
2	0	0.5	0.007	4.8	0.0185	12.69	0.7	1.8	0.8
0	2	0	0.06	8	0.07	9.33	67	20	0.5
2	1	0	0.025	5	0.075	15	48	525	0.7
0	3	0	0.025	6.5	0.04	10.4	1.1	1.1	1.2
4	0	0	0.009	5.3	0.02	11.78	10000	150000	0.5
4	0	0.5	0.009	5.3	0.02	11.78	0.7	1.3	1.2
2	2	0	0.025	5.5	0.06	13.2	1.1	16	0.6
0	4	0	0.05	9	0.04	7.2	0.8	1.7	0.5

From the results of Tables I and II the general conclusion may be drawn that it is preferable to include terms of the form $-(v^2/r^2)$ in the computation of the Laplacian, using a Hankel transform of order v.

IV. Comparision with a Fourier Method Solution for the Reaction $H + H_2$

The Fourier method on a rectangular grid has been used before to simulate collinear reactive collisions $A + BC \rightarrow AB + C$ [16]. In such a simulation an initial wave function is entered, representing the asymptotic position of an atom A far away moving in the direction of a molecule BC consisting of two atoms B and C, which are vibrating close together. The wave function is propagated in time and the reaction products are examined after enough time has elapsed. The fact that a reaction has taken place is represented by the configuration of A and B close together and C far away. The potential is represented as a function of the interatomic distances R_{AB} and R_{BC}.

The kinetic energy operator in the coordinates (R_{AB}, R_{BC}) is not separable. To separate the kinetic energy operator it is customary to transform to mass-weighted (skewed) coordinates [17]. The mass-weighted coordinates are then used as the basis for the Fourier method, which needs a rectangular grid. Examining the potential in these coordinates it is found that a large portion of the grid is devoted to coordinate values for which no dynamical configuration of the three atoms can exist. (See Fig. 3.) It is therefore desirable to transform to polar coordinates for which only allowable configurations are represented, i.e., configurations which have an angle between 0 and the skewing angle φ_{max}. These mass-weighted polar coordinates (r, φ) are called Delves hyperspherical coordinates. Recently it has been shown that these coordinates have computational advantages in describing triatomic collinear collisions [18] and potential energy surfaces [19]. The Hankel method allows a direct calculation of the reactive collision in these coordinates.

In this section a reactive collision is simulated using both rectangular and Delves hyperspherical coordinates. In the case of rectangular coordinates the Fourier method [16] is used and in the case of hyperspherical coordinates the Hankel method is used for the radial part and a modified Fourier method for the angular part.

The system chosen is the reaction of a hydrogen atom with a hydrogen molecule $H + H_2 \rightarrow H_2 + H$, which has a skewing angle of $\varphi_{max} = 60°$. The potential, which is shown in Fig. 2, was adopted from the work of Agmon and Levine [20]. As the initial wave packet a Gaussian wave was chosen for the translation of the atom towards the molecule and a $v = 0$ wave for the intramolecular vibration (for details see [16].) This initial wave packet was propagated for 1500 atomic time units (atu) using both methods. For the Fourier method a grid of 64×64 was used. For the Hankel method the grid contained 128×64 points.

The Hankel method for the system $H + H_2 \rightarrow H_2 + H$ was applied as described in Section III.a. A few additional details for this specific case are given below.

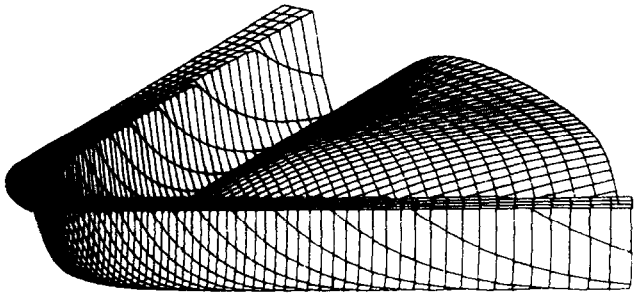

FIG. 2. Perspective view of the potential surface of the system $H + H_2$. The grid has logarithmic spacing in the radial direction. The grid points are at equal distances in the angular direction, from 0° up to the skewing angle 60°.

The wave function ψ was discretized on a two-dimensional grid, with $N_r = 128$ points for the radial direction and $N_\varphi = 64$ points, at equal distances from 0–60°, for the angular direction. The logarithmic step width δ for the radial direction was chosen as in Section II. The step width in the angular direction is $\Delta\varphi = (\pi/3)/(N_\varphi - 1)$. The resulting discretization was

$$\psi_{jk} = \psi(r = r_j = r_{\min} e^{j\delta},\ \varphi = \varphi_k = k\,\Delta\varphi) \tag{4.1}$$

for $j = 0, 1, \ldots, N_r - 1$ and $k = 0, 1, \ldots, N_\varphi - 1$.

The Laplacian of ψ, $\nabla^2\psi$ has radial and angular parts (Eq. (1.2).) For every angle φ_k the radial part $(1/r)(\partial/\partial r)\, r(\partial/\partial r)\,\psi$ was computed using the Hankel method. For every radius r_j the angular part $(1/r_j^2)(\partial^2/\partial\varphi^2)\,\psi$ was computed using the Fourier method and multiplying by $1/r_j^2$. The terms were added at every point giving the Laplacian.

The truncation interval of the Hankel transform in the r-domain was chosen as $r_{\min} = 0.2$, $r_{\max} = 10$. In the transform domain the choice was $k_{\min} = 0.17$ and $k_{\max} = 8.5$.

The time step was chosen as $\Delta t = 0.5$. The time step, as stated in III.a., is influenced by the maximum potential difference represented on the grid. To keep the time step reasonable the potential, which has a minimum value of -0.1744 was set to 0 for values greater than 0. A second factor that influences the time step is the maximum momentum represented on the grid. This momentum $k_{\max} = \pi/(\Delta x^2)$ is inversely proportional to the square of the distance between grid points. For the angular part of the Laplacian $(1/r_j^2)(\partial^2/\partial\varphi^2)$ the grid distance between points gets smaller when r approaches the origin. This means that very high momentum values are represented on the grid in the angular direction close to the origin. The maximum value of represented angular momentum is chosen as 31.5 and points of the Hankel transform of ψ for k-values beyond this are set to zero. This means that the cut-off in angular momentum is a function of r.

The parameters of the Fourier method solution were: $\Delta x = 0.125$, $\Delta y = 0.125$, and $\Delta t = 1$.

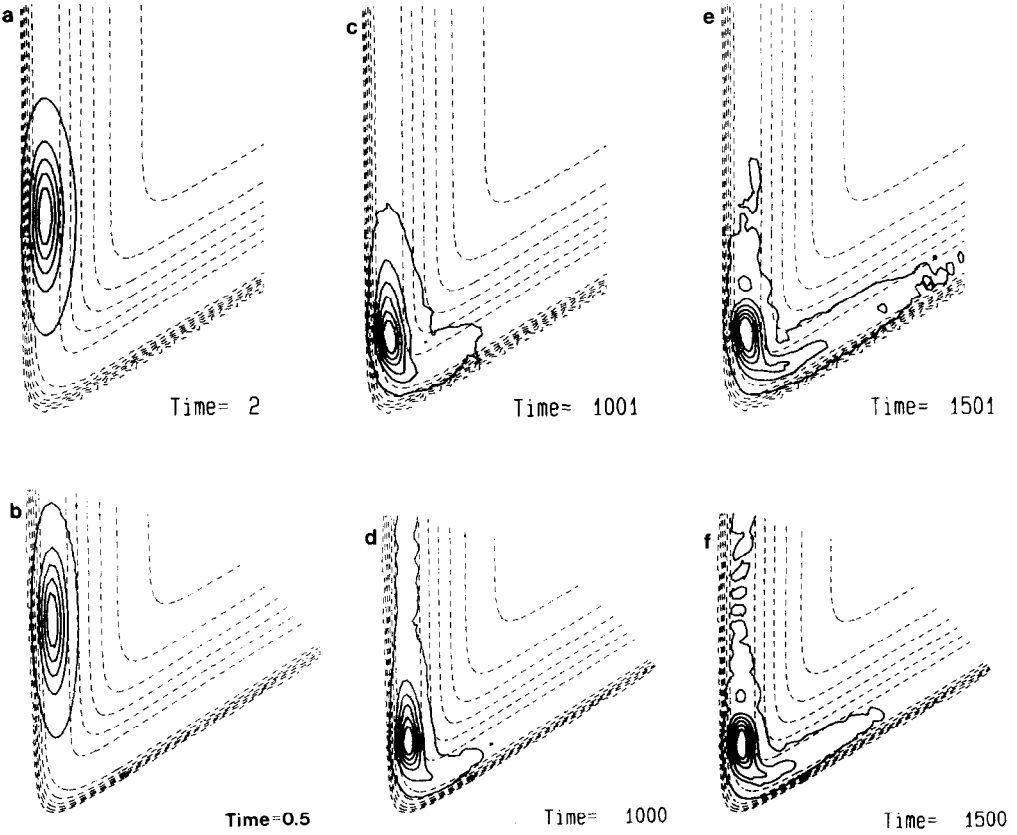

FIG. 3. Snapshots of the square absolute value of the wave function for the $H + H_2$ system. The energy is $E = -0.157$ and the initial vibration is $v = 0$. The continuous line is the contour of equal probability of the wave function and the dashed line is the contour of the potential surface. (a), (c), (e) are snapshots at time $t = 2$, 1001, 1501 of the wave function propagated by the Fourier method. (b), (d), (f) are snapshots at time $t = 0.5$, 1000, 1500 of the wave function propagated by the Hankel method. Contour lines of the normalized wave function are at 0.03, 0.31, 0.60, 0.88, 1.16. Contour lines of the potential are at -0.147, -0.120, -0.092, -0.065, -0.037, -0.010.

The initial wave packet that was used in both methods was placed at 6.5 a.u. from the origin, having a translational width of 1.5 and a momentum of 4.0 towards the origin. The vibrational level was the ground level.

Figure 3 compares the propagated wave function for both methods. It can be seen that the center of the wave packet propagates at the same rate for both methods. Figure 4 shows a stereoscopic view of the wave packet at time $t = 1500$. An additional comparison of the propagation for both methods was made by computing the overlap of the wave packet propagated by the hybrid Hankel/Fourier method and the wave packet propagated by the Fourier method. To do this the

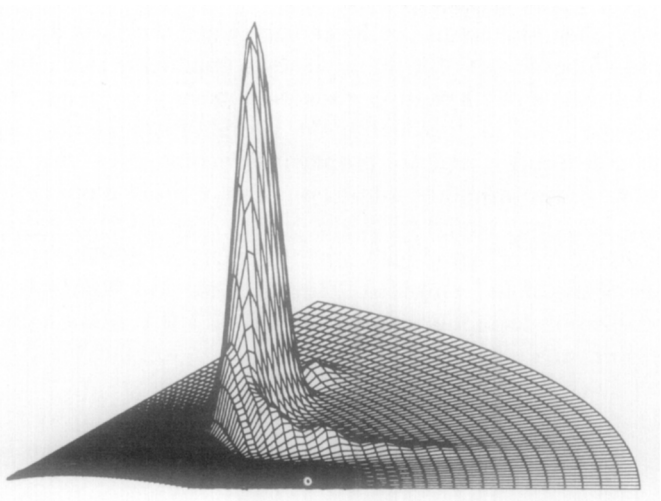

FIG. 4. Perspective view of the wave function at time $t = 1500$, after propagation by the Hankel method.

wave packet of the Fourier method was interpolated and transferred to the radial grid, where the overlap was computed. The result should stay close to unity during the entire integration. At $t = 0$ the overlap was 0.9999, at $t = 1000$ it was 0.9732, and at $t = 1500$ it was 0.9577.

A typical time step for the Fourier method on a 128×64 grid takes 11 sec on a VAX 750 computer, whereas a typical time step of the Hankel method takes 26 sec. A comparison of the efficiency of both methods for the system $H + H_2$ shows that they are of the same order of efficiency, where the Fourier method is superior. It can be expected that for different systems which have small skewing angles and where the coupling between the radial and angular parts is weak as in the system $Cl + HI$, the Hankel method will be superior.

V. CONCLUSIONS

In this work an extension of the Fourier or the pseudo spectral method for the solution of the time dependent Schrödinger equation was presented. The main goal was to demonstrate the flexibility of a pseudo spectral method to be adapted to different geometries and therefore different differential operators.

Two main conclusions can be drawn from this work. First, higher accuracy is achieved when as much as possible of the Hamiltonian is included in the operator which is calculated by the transform. In this case this means using a higher order FHT to include the $(-v^2/r^2)$ term.

Second, using a different geometry causes the spacing of the sampling points to be nonequidistant. In this method stability of the time integration depends on the

spatial geometry, therefore changing the geometry can seriously affect the time step Δt. Tapering, i.e., filtering out of high frequency components can solve this problem.

At this point a review of alternatives should be made. An obvious alternative is to use a large basis-set and to diagonalize the Hamiltonian, finding eigenvalues and eigenfunctions and using these to propagate in time. For the radial part the polynomials of Laguerre would be an obvious choice. For comparable accuracy the number of basis functions would be of the order of the number of grid points used in the Hankel method. For two-dimensional problems a few hundred to a few thousand basis functions would be needed. From a numerical point of view the CPU-time of diagonalization techniques grows as $O(N^3)$, where N is the number of basis functions. As compared to this the numerical effort of the Fourier and Hankel methods grows as $O(N \log N)$, where N is the number of grid points. In addition to this, when energy is increased the number of basis functions grows at least linearly, so CPU-time of diagonalization methods grows as $O(E^3)$. However, for the Fourier and Hankel methods the number of grid points increases proportional to the increase in momentum (hence as $O(E^{1/2})$) and the time step decreases as $O(E^{-1})$, therefore the numerical effort grows as $O(E^{3/2})$.

Summarizing, for small systems and low energy diagonalization methods are superior, since the minimum number of grid points required will be much larger than the number of basis functions. When increasing dimensionality and energy there is a point where the spectral methods take over and become more efficient.

Eventually the decision to use the FHT method depends on the existence of alternatives. For the exploitation of radial symmetry in a spectral method there is no alternative and the Hankel method is superior since it reduces dimensionality. It has been shown above that in the case of Delves hyperspherical coordinates the Hankel method provides a viable alternative to other methods.

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