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Solving the Schrödinger equation using the finite difference time domain method

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Abstract

In this paper, we solve the Schrödinger equation using the finite difference time domain (FDTD) method to determine energies and eigenfunctions. In order to apply the FDTD method, the Schrödinger equation is first transformed into a diffusion equation by the imaginary time transformation. The resulting time-domain diffusion equation is then solved numerically by the FDTD method. The theory and an algorithm are provided for the procedure. Numerical results are given for illustrative examples in one, two and three dimensions. It is shown that the FDTD method accurately determines eigenfunctions and energies of these systems.

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1. Introduction

Microscopic dynamics for non-relativistic quantum systems are described by the Schrödinger equation. To apply the Schrödinger equation for a specified problem, one needs to solve a differential equation with a boundary condition and to determine eigenvalues and eigenfunctions of that problem. Only relatively few idealized problems have exact analytical solutions. In general numerical methods are needed. One such method is the diffusion Monte Carlo (DMC) method [1–4]. This method is based on the equivalency of the Schrödinger equation to the diffusion equation. A random walk method is used to solve the diffusion equation. This method can be implemented in a variety of ways and is applicable for determining both ground states and excited states [3, 4].

Recently, the finite difference time domain (FDTD) method has been applied for solving the Schrödinger equation [5, 6]. In this FDTD method, the Schrödinger equation is discretized using central finite difference in time and in space. In order to obtain solutions, one needs to perform two simulations using an initial impulse function. In first simulation, one determines

the impulse response of the problem which is then Fourier transformed to obtain the eigenvalues or eigenfrequencies. In second simulation, one uses these eigenfrequencies to obtain the eigenfunctions by a discrete Fourier transform.

In principle, the FDTD method can yield all the eigenvalues and eigenfunctions of the problem. However, if one is only interested in the ground state of a system, there is a simple method to obtain it, instead of the two-simulation procedure of FDTD method. In this paper, a single-simulation method for finding the ground state of a system is presented. We also show that this single simulation can be used to get excited states. The formulation of our method is similar to the DMC method, except that the diffusion equation is solved by using the FDTD method. This approach is very attractive since it can provide not only the ground states but also the excited states. Although simple and efficient, use of the FDTD method has been limited. Some examples of its use are given in [5–10] for one- to three-dimensional problems. However, in all of these papers [8–10], to obtain the excited states, one must repeat the simulations using different initial wavefunction for every excited state. The single-simulation procedure we propose to obtain the ground states as well as the excited states, to our knowledge, has not been done previously. The purpose of this paper is to demonstrate the applicability and the accuracy of this single-simulation FDTD method to obtain the ground states and the excited states for a variety of typical examples of a single particle in one-, two- and three-dimensional potential wells.

The accuracy of our proposed method depends on the procedure used to solve the diffusion equation and on the numerical integration to obtain the eigenenergies. In this paper, the explicit finite difference scheme and an easily programmed trapezoidal rule integration are used due to simplicity. We will show that this produces enough accuracy for applications in new practical problems such as occur in nanostructures or other low symmetry quantum systems. The method is validated for a variety of typical cases where highly accurate results are known in the literature for comparison. For an example, the ground-state energy of the double-well potential in one dimension is accurate to three parts in 180 000. The accuracy in any instance can be improved by reducing the mesh grid and increasing the cell size. The accuracy can also be improved by using the alternating direction implicit (ADI) method as in [8–10].

The rest of this paper is divided into the following sections. The formulation of the FDTD method and numerical algorithm are presented in section 2. The numerical results and discussions are given in section 3 and the conclusions are summarized in section 4.

2. Theory

The time-dependent Schrödinger equation for a particle having mass m in a potential $V(x, y, z)$ is

$$i\hbar \frac{\partial}{\partial t} \psi(x, y, z, t) = \hat{H} \psi(x, y, z, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z) \right] \psi(x, y, z, t). \quad (1)$$

The solution of equation (1) can be expanded in terms of eigenfunctions of the form

$$\psi(x, y, z, t) = \sum_{n=0}^{\infty} c_n \varphi_n(x, y, z) \exp(-iE_n t / \hbar) \quad (2)$$

where $\{c_n\}$ are expansion coefficients. The eigenfunctions $\varphi_n(x, y, z)$ and energies E_n are obtained by solving the time-independent Schrödinger equations,

$$\hat{H} \varphi_n(x, y, z) = E_n \varphi_n(x, y, z). \quad (3)$$

By introducing Wick rotational transformation from real time to imaginary time, $\tau = it$, and using units with $\hbar = 1$ and $m = 1$ we then have

$$\frac{\partial}{\partial \tau} \psi(x, y, z, \tau) = \frac{1}{2} \nabla^2 \psi(x, y, z, \tau) - V(x, y, z) \psi(x, y, z, \tau) \quad (4)$$

and

$$\psi(x, y, z, \tau) = \sum_{n=0}^{\infty} c_n \varphi_n(x, y, z) \exp(-E_n \tau). \quad (5)$$

2.1. Ground state

From equation (5) we note that for imaginary time τ much larger than the inverse excitation energy, the wavefunction $\psi(x, y, z, \tau)$ is dominated by the lowest energy state, i.e. the ground state E_0 .

$$\lim_{\tau \rightarrow \infty} \psi(x, y, z, \tau) \approx c_0 \varphi_0(x, y, z) \exp(-E_0 \tau). \quad (6)$$

Therefore, one can determine the ground state by solving equation (4) numerically. This is done by performing a simulation with an initial function $\psi(x, y, z, t = 0)$ and observing the evolution of the initial function. As long as the initial wavefunction can be expanded as in equation (5) and contains the ground-state function (i.e. $c_0 \neq 0$ in equation (5)), after sufficient simulation time, the wavefunction $\psi(x, y, z, \tau)$ will approach the ground-state limit.

Utilizing the ground-state wavefunction, the energy is then computed by

$$E_0 = \frac{\langle \varphi_0 | \hat{H} | \varphi_0 \rangle}{\langle \varphi_0 | \varphi_0 \rangle} = \frac{\int \varphi_0^* \hat{H} \varphi_0 d^3x}{\int |\varphi_0|^2 d^3x}. \quad (7)$$

In order to perform time-domain simulation numerically, one needs to discretize equation (4) using finite difference scheme. A notation $\psi^n(i, j, k) = \psi(i \Delta x, j \Delta y, k \Delta z, n \Delta t)$ (where Δt , Δx , Δy and Δz are the temporal and spatial spacing) is used in this paper. The time derivative in equation (4) is discretized by using the forward finite difference scheme given by

$$\frac{\partial \psi(x, y, z)}{\partial \tau} \approx \frac{[\psi^{n+1}(i, j, k) - \psi^n(i, j, k)]}{\Delta \tau}. \quad (8)$$

The spatial derivative is approximated by the central finite difference scheme given by

$$\begin{aligned} \frac{1}{2} \nabla^2 \psi(x, y, z) - V(x, y, z) \psi(x, y, z) &\approx \frac{1}{2\Delta x^2} [\psi^n(i+1, j, k) - 2\psi^n(i, j, k) \\ &+ \psi^n(i-1, j, k)] + \frac{1}{2\Delta y^2} [\psi^n(i, j+1, k) - 2\psi^n(i, j, k) + \psi^n(i, j, k-1)] \\ &+ \frac{1}{2\Delta z^2} [\psi^n(i, j, k+1) - 2\psi^n(i, j, k) + \psi^n(i, j, k-1)] \\ &- \frac{1}{2} V(i, j, k) [\psi^n(i, j, k) + \psi^{n+1}(i, j, k)]. \end{aligned} \quad (9)$$

Using equations (8) and (9), equation (4) becomes

$$\begin{aligned} \psi^{n+1}(i, j, k) &= \alpha \psi^n(i, j, k) + \beta \left[\frac{\Delta \tau}{2\Delta x^2} [\psi^n(i+1, j, k) - 2\psi^n(i, j, k) + \psi^n(i-1, j, k)] \right. \\ &+ \frac{\Delta \tau}{2\Delta y^2} [\psi^n(i, j+1, k) - 2\psi^n(i, j, k) + \psi^n(i, j, k-1)] \\ &\left. + \frac{\Delta \tau}{2\Delta z^2} [\psi^n(i, j, k+1) - 2\psi^n(i, j, k) + \psi^n(i, j, k-1)] \right] \end{aligned} \quad (10)$$

where the coefficients α and β are given by

$$\alpha = \frac{\left[1 - \frac{\Delta\tau}{2} V(i, j, k)\right]}{\left[1 + \frac{\Delta\tau}{2} V(i, j, k)\right]} \quad (11)$$

$$\beta = \frac{1}{\left[1 + \frac{\Delta\tau}{2} V(i, j, k)\right]}. \quad (12)$$

Using the Von Neumann stability analysis [11], it can be shown that for a stable simulation the time step Δt must satisfy a stability condition given by

$$\Delta\tau \leq \frac{1}{\left[\frac{1}{\Delta x^2} + \frac{1}{\Delta y^2} + \frac{1}{\Delta z^2}\right]}. \quad (13)$$

In order to have all of the eigenstates contained in the initial trial wavefunction, a random function is used in the simulation. However, if only one energy state is required, then the convergence of the simulation can be improved by using an initial wavefunction that is close to the final wavefunction.

In each step, the energy is computed by using equation (7) and is approximated numerically by

$$E_0 = \frac{1}{\sum_{i,j,k} \psi(i, j, k)^2} \sum_{i,j,k} \{V(i, j, k)\psi(i, j, k)^2 \\ - \psi(i, j, k)[\psi(i+1, j, k) - 2\psi(i, j, k) + \psi(i-1, j, k)]/2\Delta x^2 \\ - \psi(i, j, k)[\psi(i, j+1, k) - 2\psi(i, j, k) + \psi(i, j-1, k)]/2\Delta y^2 \\ - \psi(i, j, k)[\psi(i, j, k+1) - 2\psi(i, j, k) + \psi(i, j, k-1)]/2\Delta z^2\}. \quad (14)$$

In this method, it is convenient to truncate at a finite outermost boundary. In this paper, the outermost boundary condition is taken to be $\psi(x, y, z, \tau)_{\text{boundary}} = 0$. This boundary condition at a finite distance does not affect the results significantly provided that the simulation space is large enough such that the wavefunction has already decayed to small values at the boundary.

Equation (10) is used iteratively to evolve the wavefunction for a sufficient time such that the ground state is obtained as the final wavefunction. Since the final wavefunction $\psi_0(x, y, z, \tau)$ is proportional to $\exp(-E_0\tau)$, the magnitude of the final wavefunction may generally be quite small. However, we can rescale the wavefunction by a constant factor in every iteration step such that the final wavefunction does not have a small magnitude.

2.2. Excited states

To obtain the excited states of a system, we first do a simulation with an initial wavefunction to obtain the unnormalized ground state $\psi(x, y, z, \tau = \text{large})$ given by equation (6) after large simulation time. One can then redo the simulation with a new initial wavefunction, which has the ground-state component removed, to obtain the first excited state. The new initial wavefunction $\psi_{\text{new}}(x, y, z, \tau = 0)$ is given by

$$\psi_{\text{new}}(x, y, z, \tau = 0) = \psi(x, y, z, \tau = 0) - c_0\varphi_0(x, y, z) \quad (15)$$

where $\psi_{\text{new}}(x, y, z, \tau = 0)$ is the initial wavefunction for obtaining the first excited state, $\psi(x, y, z, \tau = 0)$ is the initial wavefunction, $\varphi_0(x, y, z)$ is the normalized ground-state wavefunction given by $\varphi_0(x, y, z) = N\psi(x, y, z, \tau = \text{large})$ (where N is a normalizing factor) and the coefficient c_0 is given by

$$c_0 = \langle \psi(\tau = 0) | \varphi_0 \rangle = \int \psi^*(x, y, z, \tau = 0)\varphi_0(x, y, z) d^3x. \quad (16)$$

Therefore, equation (5) becomes

$$\psi_{\text{new}}(x, y, z, \tau) = \sum_{n=1}^{\infty} c_n \varphi_n(x, y, z) \exp(-E_n \tau). \quad (17)$$

Similarly as previous analysis, we can note from equation (17) that for large τ the wavefunction $\psi(x, y, z, \tau)$ is dominated by its lowest energy component, i.e. the excited state E_1 :

$$\lim_{\tau \rightarrow \infty} \psi_{\text{new}}(x, y, z, \tau) \approx c_1 \varphi_1(x, y, z) \exp(-E_1 \tau). \quad (18)$$

Therefore, the simulation performed with the new initial wavefunction equation (15) will yield the excited state after sufficient time. This is expected since there is no contribution from the ground-state wavefunction. As discussed in the previous section, provided that in equation (17) the coefficient c_1 is non-zero, i.e. $c_1 \neq 0$, the final wavefunction is guaranteed to be first excited state. If the coefficient $c_1 = 0$, then the next lowest energy state with non-zero $c_n \neq 0$ will be obtained. The first excited state can be obtained by a simulation with a different new initial wavefunction. By doing successively recursive simulations we can obtain all the eigenvalues and eigenfunctions of a system.

However, there is a more efficient way to obtain the eigenvalues and eigenfunctions.

Instead of redoing the simulation for every excited state, one can also obtain the excited states using only one simulation provided that the evolutions of wavefunctions are saved for enough number of times and that the initial wavefunction contains contributions from all the required excited states. Using the saved wavefunctions, one can do post-processing to obtain all the excited states. To demonstrate how one can get the excited states from the saved wavefunctions, let us denote the saved wavefunction at simulation time τ_i as $\psi_0(x, y, z, \tau_i)$ (where subscript 0 denotes the first saved wavefunctions). From equation (5), we have

$$\psi_0(x, y, z, \tau_i) = \sum_{n=0}^{\infty} c_n \varphi_n(x, y, z) \exp(-E_n \tau_i). \quad (19)$$

For long enough simulation time τ , only the ground-state contribution remains large so that we can approximate equation (19) as

$$\lim_{\tau_i \rightarrow \infty} \psi_0(x, y, z, \tau_i) \approx c_0 \varphi_0(x, y, z) \exp(-E_0 \tau_i). \quad (20)$$

After renormalization of equation (20), equation (15) is then used to remove the ground-state contribution from all the saved wavefunctions. Let us denote the resulting wavefunctions as $\psi_1(x, y, z, \tau_i)$ which is given by

$$\psi_1(x, y, z, \tau_i) = \psi_0(x, y, z, \tau_i) - \alpha_i \varphi_0(x, y, z) = \sum_{n=1}^{\infty} c_n \varphi_n(x, y, z) \exp(-E_n \tau_i) \quad (21)$$

where $\alpha_i = \langle \psi_0(\tau_i) | \varphi_0 \rangle$.

We note that the new wavefunctions $\psi_1(x, y, z, \tau_i)$ provide an evolution containing only the excited states' wavefunctions. This evolved wavefunction approaches the first excited state as the time increases. Hence,

$$\lim_{\tau_i \rightarrow \infty} \psi_1(x, y, z, \tau_i) \approx c_1 \varphi_1(x, y, z) \exp(-E_1 \tau_i). \quad (22)$$

We can repeat this procedure to obtain all the excited states. The iterative procedure is summarized in steps as follows:

- (1) Do a simulation using an initial wavefunction for long enough time such that the total energy has converged and save the wavefunction $\psi_{k=0}(x, y, z, \tau_i)$ in every N iterations (where N is chosen in order to reduce the number of saved wavefunctions).

- (2) Determine the normalized eigenstate $\varphi_{k=0}$ and its energy.
- (3) Remove the contribution of the eigenstate φ_k from the wavefunctions $\psi_k(x, y, z, \tau_i)$ to obtain new wavefunctions $\psi_{k+1}(x, y, z, \tau_i)$.
- (4) Get φ_{k+1} from the wavefunctions $\psi_{k+1}(x, y, z, \tau_i)$.
- (5) Replace k with $k + 1$ and repeat steps 3 and 4 to obtain all the excited states' energies and eigenfunctions.

We can use a similar method for multi-run procedures. Instead of using the saved wavefunctions, the wavefunctions are computed on the fly and the wavefunctions are orthogonalized to the lower energy states at every step of the simulations.

Our procedures have advantages over the traditional FDTD method since we use only real-valued wavefunctions rather than complex wavefunctions and the simulation is faster and the Fourier transformation is not required. Moreover, the required computer memory is smaller since there is no requirement to hold variables for the discrete Fourier transform.

3. Applications and discussion

3.1. One-dimensional infinite square well

As a first simple example, let us consider a one-dimensional infinite square well with a width $a = 1$ (where $V(x) = 0$ for $0 < x < 1$ and $V(x) = \infty$ for $x > 1$ and $x < 0$). The eigenfunctions of this problem are

$$\psi_n(x) = \begin{cases} \sqrt{2} \sin(n\pi x), & \text{inside the well} \\ 0, & \text{outside the well} \end{cases} \quad (23)$$

and the energies are

$$E_n = \frac{(n\pi)^2}{2}. \quad (24)$$

The infinite well is achieved by using a condition that the wavefunction must be zero at the boundary, i.e., $\psi(0) = \psi(1) = 0$.

The simulation is performed using parameters as follows: $\Delta x = 0.01$, $\Delta \tau = \Delta x^2/5$. The initial random wavefunction used is given in figure 1. The first eight energy eigenvalues are shown in figure 2 as a function of the number of iterations. The convergence is good and the method is very stable even beyond 6000 iterations. The resulting wavefunctions for ground state and four excited states are shown in figure 3. It is clear from figures 2 and 3 that the numerical results are in excellent agreement with the theoretical results. To get higher excited states with comparable accuracy one must decrease Δt and Δx .

3.2. Anharmonic oscillator

Anharmonic oscillator potentials occur frequently in many non-relativistic quantum systems and are also of interest for some aspects of quantum field theory. General analytical solutions are not available for such problems and numerical methods are essential. We will consider the particular case of a double-well anharmonic oscillator which can describe structural phase transitions, tunnelling of protons in hydrogen-bonded systems and other systems with inversion symmetry. The potential is given by

$$V(x) = (x^2 - 2)^2. \quad (25)$$

The numerical results found using similar parameters as in the previous square well problem are given in table 1 for the energies. For comparison we quote the energies obtained by a different method in [12]. The agreement is good.

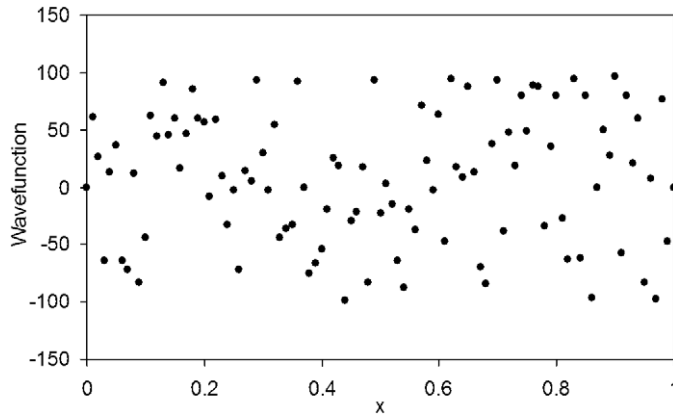


Figure 1. An initial random wavefunction used in an FDTD simulation.

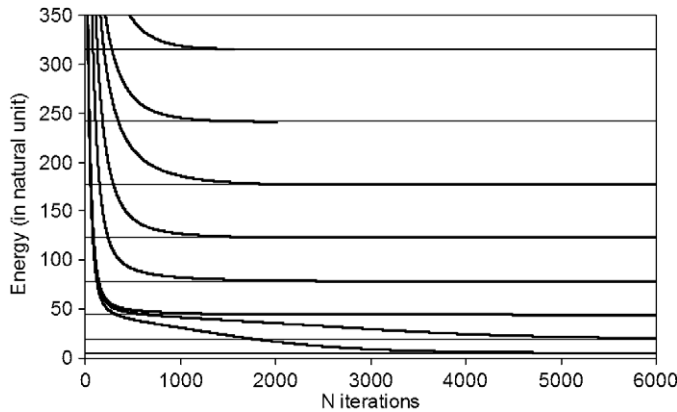


Figure 2. Variation of the energy eigenvalues as a function of the number of iterations for eight energy states. Note that the horizontal lines are the theoretical energies, equation (24).

Table 1. Comparison of the FDTD numerical results with values from [12].

Results from	Ground state energy	First excited energy	Second excited energy	Third excited energy
FDTD	1.800 78	1.896 46	4.370 50	5.573 0
Reference [12]	1.800 81	1.896 50	4.370 47	5.573 3

3.3. Two- and three-dimensional infinite square well

The previous examples concern a particle moving in a one-dimensional space. We now consider examples in two and three dimensions. Again we begin with infinite square wells; a square and a cube with unit side length of $a = 1$. The eigenfunctions of the two-dimensional well are

$$\psi_{n_x, n_y}(x) = \begin{cases} 2 \sin(n_x \pi x) \sin(n_y \pi y), & \text{inside the square} \\ 0, & \text{outside the square} \end{cases} \quad (26)$$

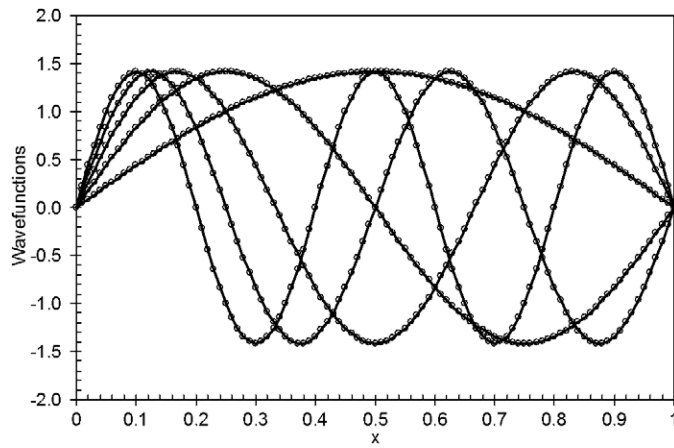


Figure 3. Comparison of numerical normalized wavefunctions (circles) with the theoretical wavefunctions (solid lines) for the ground state and the first four excited states of square well potential.

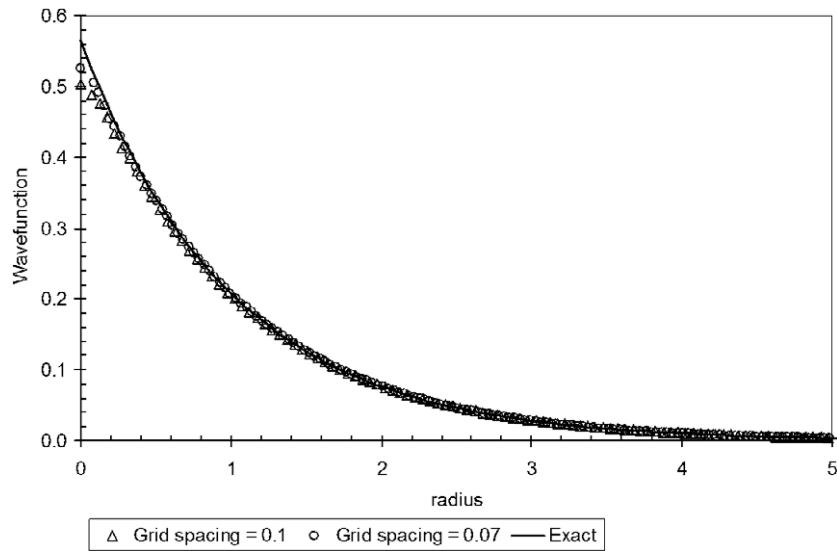


Figure 4. Comparison of numerical normalized ground-state wavefunction (triangles for grid spacing = 0.1 and circles for grid spacing = 0.07) with the theoretical wavefunction (solid line) of hydrogen atom.

and the energies are

$$E(n_x, n_y) = \frac{(n_x^2 + n_y^2)\pi^2}{2}. \tag{27}$$

Similarly for three-dimensional well, the eigenfunctions are

$$\psi_{n_x, n_y, n_z}(x) = \begin{cases} \sqrt{8} \sin(n_x \pi x) \sin(n_y \pi y) \sin(n_z \pi z), & \text{inside the box} \\ 0, & \text{outside the box} \end{cases} \tag{28}$$

Table 2. Comparison of the numerical results with exact values of energy eigenvalues for two- and three-dimensional square well.

Results from	Ground state energy	First excited energy	Second excited energy
2D			
FDTD	9.866	24.646	39.427
Equation (27)	9.870	24.674	39.478
3D			
FDTD	14.800	29.580	44.359
Equation (29)	14.804	29.608	44.413

and the energies are

$$E(n_x, n_y, n_z) = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2}{2}. \quad (29)$$

We note that the ground states ψ_{11} and ψ_{111} are not degenerate. However, the first excited states are doubly degenerate in two dimensions $E(2, 1) = E(1, 2)$ and triply degenerate in three dimensions $E(2, 1, 1) = E(1, 2, 1) = E(1, 1, 2)$. The degenerate states cannot all be determined by only one simulation. We need to perform the same number of simulations as the number of degenerate states with different initial wavefunctions. After performing the simulations, one can use Gram–Schmidt procedures to obtain orthonormal wavefunctions.

Similar to the previous simulation, the parameters used in this section are as follows: $\Delta x = \Delta y = \Delta z = 0.02$, $\Delta \tau = \Delta x^2/20$. The lowest three eigenvalues found using these parameters are given in table 2.

This demonstrates the effectiveness of the FDTD method for general dimension for potentials which have a lower bound. We next consider a series of examples involving the interaction of a charged particle with fixed point charges.

3.4. A two-dimensional potential

The potential generated at the interface between a semiconductor and an insulator in quasi-two-dimensional nanostructure devices can confine the motion of electrons to the plane of the interface. In suitable atomic units, the interaction between an electron in the (x, y) plane and an ionized impurity at a fixed distance d from the plane is

$$V(x, y) = \frac{-1}{\sqrt{x^2 + y^2 + d^2}}. \quad (30)$$

In the simulation, the potential is shifted by $V_0 = 1/d$ in order to increase the rate of convergence of the simulation. The energies of states can then be obtained by subtracting the same V_0 from the result of the simulation.

The parameters used for this simulation in atomic unit are as follows: $\Delta x = \Delta y = \Delta z = 0.2$, $\Delta \tau = \Delta x^2/10$, $d = 1$. The simulation space has side length of 40.0. The numerical results for the bound state energies are shown in table 3.

Note that this potential can also be regarded as a particular form of anharmonic oscillator. We are not aware of exact results for this problem.

Table 3. The numerical results for the two-dimensional potential given by equation (30).

Results from	Ground state energy	First excited energy	Second excited energy
FDTD	-0.4342	-0.1740	-0.1210

3.5. Hydrogen atom

To demonstrate the usefulness of the FDTD method in atomic problems, we first consider the hydrogen atom in free space which has an analytical solution for comparison. Other examples such as hydrogen molecule ion and helium atom can also be solved using this method. The hydrogenic potential in atomic units is

$$V(x, y, z) = \frac{-1}{r} = \frac{-1}{\sqrt{x^2 + y^2 + z^2}}. \quad (31)$$

The singular Coulomb potential (31) becomes very large when the denominator is small. To remove potential numerical errors at small r , equation (31) is truncated such that the minimum potential is $-V_0$. Then, the truncated potential is shifted by V_0 in order to increase convergence of the simulation. The modified potential is given by

$$V(x, y, z) = \begin{cases} \frac{-1}{r} + V_0 & \text{for } r > \frac{1}{V_0} \\ 0 & \text{for } r < \frac{1}{V_0}. \end{cases} \quad (32)$$

The energies of states can then be obtained by subtracting V_0 from the result of the simulation. The error due to this truncation at small r is negligible for sufficiently small $1/V_0$. This can be checked and, if desired, the correction can be computed explicitly by first-order perturbation theory.

The parameters used for this simulation in atomic unit are as follows: $\Delta x = \Delta y = \Delta z = 0.1$, $\Delta \tau = \Delta x^2/4$, $V_0 = 1/\Delta x$. The simulation box has side length of 20.0. Using these simulation parameters, only the two lowest energy states can be determined accurately. The numerical results for the energies of the ground state and the first excited state are -0.496 and -0.121 , in a good agreement with the exact energies -0.5 and -0.125 . The resulting ground-state wavefunction is shown in figure 4. The resulting first excited state wavefunction cannot be compared to the theoretical wavefunction since the numerical wavefunction contains 2s and 2p states. It is noted in figure 4 that small errors are shown in the wavefunction near the origin due to the truncation potential and the finite mesh size used in the FDTD method. The results can be improved by using smaller grid size. As an example by keeping the same side length of the simulation box and using smaller grid spacing $\Delta x = \Delta y = \Delta z = 0.07$ the ground state and the first excited state are -0.498 and -0.121 . This shows an improvement for the ground-state energy but no improvement for the first excited state. This is due to the fact that the size of the simulation box is accurate only for the ground state. It is noted in figure 4 that there is also an improvement in the wavefunction near the origin when smaller grid spacing is used. The size of the simulation box must be increased to obtain the higher excited states.

Table 4. Comparison of the numerical results with values from [13, 14].

Results from	Ground state energy	First excited energy	Second excited energy
<i>d</i> = 0			
FDTD	-0.1252	1.5693	3.3115
References [13, 14]	-0.1250	1.5760	3.3275
<i>d</i> = 1.0			
FDTD	0.1255	1.4227	1.7545
Reference [13]	0.1276	1.4281	Not given

3.6. Confined hydrogen atom

The properties of atoms under intense pressure or otherwise confined in atomic traps or quantum dots are of interest for a variety of reasons. As a last example of the versatility of the FDTD method, we consider a hydrogen atom confined in an infinite spherical well of radius r_c and displaced from the centre of the sphere. Using similar procedure as previous problem, the potential of this problem is defined by

$$V(x, y, z) = \begin{cases} \frac{-1}{\sqrt{x^2 + y^2 + (z-d)^2}} + V_0 & \text{for } \frac{1}{V_0} < r < r_c \\ 0 & \text{for } r < \frac{1}{V_0} \text{ and } \infty & \text{for } r > r_c \end{cases} \quad (33)$$

where the distance r is given by $r = \sqrt{x^2 + y^2 + z^2}$ and d is a distance from the centre of the confining sphere.

The infinite well confinement condition is achieved by setting the value of $\psi(x, y, z)$ to zero at $r = r_c$. The parameters used for this simulation in atomic units are as follows: $\Delta x = \Delta y = \Delta z = 0.04$, $\Delta \tau = \Delta x^2/20$, $V_0 = 1/\Delta x$ and $r_c = 2$. Results for the ground state and the first two excited states energy eigenvalues computed using the FDTD method are given in table 4. The numerical results show good agreement with the theoretical results obtained by very different methods in [13, 14].

We note that spherical symmetry of the confining well plays no special simplifying role. Cubical or other confinement geometries are treated with equal ease.

4. Conclusions

We have presented a numerical method for solving the Schrödinger equation for single particle systems. The method determines the eigenvalues and the eigenfunctions for general potentials and dimension. The Schrödinger equation is transformed to imaginary time τ , similar to the diffusion Monte Carlo method. However, rather than simulating the solution of a diffusion equation by Monte Carlo, we solve the Schrödinger equation by the FDTD method. Starting from a randomly generated initial trial function, an iterative algorithm was given to obtain the ground-state eigenvalue and eigenfunction in the limit of large τ . Excited states can be obtained by repeating the simulation with a revised trial function. Alternatively, we show that rather than repeating simulations for each excited state, the excited states can be obtained from only a single simulation provided that the evolution of the initial wavefunction is saved for enough time steps and that the initial trial function contains contributions from all the required

excited states. This single-simulation procedure is an efficient numerical method for obtaining excited states.

Although the single-simulation procedure has significant advantages, there are two cautionary notes. Since this version of the FDTD method depends on the saved wavefunctions, which have limited precision, the higher excited states can be prone to numerical error. For the three-dimensional problems studied we found that the single-simulation procedure is highly reliable only for the three to five lowest energy states. A second general cautionary note is that computer files for the saved wavefunctions become very large as the number of grid points increases, particularly for the wavefunctions for three-dimensional problems. The single-simulation procedure is then limited by the size of saved files. In such situations, the multi-simulation procedure is preferable.

In summary, an efficient and stable algorithm has been given for the accurate solution of the Schrödinger equation. Numerical results have been given for a variety of typical illustrative examples in one, two and three dimensions.

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