Eigenvalue problem of the Schrödinger equation via the finite-difference time-domain method

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We present a very efficient scheme to calculate the eigenvalue problem of the time-independent Schrödinger equation. The eigenvalue problem can be solved via an initial-value procedure of the time-dependent Schrödinger equation. First, the time evolution of the wave function is calculated by the finite-difference time-domain method. Then the eigenenergies of the electron system can be obtained through a fast Fourier transformation along the time axis of the wave function after some point. The computing effort for this scheme is roughly proportional to the total grid points involved in the structure and it is suitable for large scale quantum systems. We have applied this approach to the three-dimensional GaN quantum dot system involving one million grid points. It takes only 7 h to calculate the confined energies and the wave functions on a standard 2-GHz Pentium 4 computer. The proposed approach can be implemented in a parallel computer system to study more complex systems.

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It is essential in condensed matter physics to solve the time-independent Schrödinger equation and obtain the eigenenergies and the corresponding eigenwave functions. The electric and optical properties of the material are determined by the eigenvalues and eigenwave functions of the electrons involved. The eigenvalue problem of the Schrödinger equation usually leads to a matrix whose rank corresponds to the dimensionality of the system in question. An accurate description of a three-dimensional system involves handling matrices of the order of 10^6. The requirement of 100 grid points in each of the three directions to map a simple quantum dot (QD) results in a total of one million grid points (N), with N^2 matrix elements and the numerical effort scales as N^3. The problem therefore cannot be solved by means of direct matrix diagonalization [1–3]. The eigenvalue problem of a large system usually relies on iteration techniques or variational techniques in a subspace, e.g., the generalized Davidson algorithm (GDA) [1,4], the Lanczos method, and the related recursion methods [2,5,6]. The Lanczos method is the most common technique for this kind of problem and it works well when the ground state or few extreme eigenvalues are desired. However, there are a number of difficulties in using these methods, e.g., loss of orthogonality among the states due to finite-precision arithmetic, occurrence of spurious eigenvalues, and ghost states. To avoid these problems, an orthogonalization of the basis set in a larger subspace is required, but this would be costly in terms of storage memory and computing time which limits the variety of the system being less than 50 000 [1,2,7].

Glutsch *et al.* studied the susceptibility of the electron system and introduced a very efficient way to calculate the optical response via an initial-value procedure. A number of electron systems in external optical/electric field were explored successfully and the absorption spectra were obtained although the eigenenergies and wave functions could not be calculated explicitly [7–10].

In this paper, we propose to use an initial-value scheme to directly solve the eigenvalues of the Schrödinger equation. We start with an initial wave function and calculate the evolution according to the time-dependent Schrödinger equation with proper boundary conditions by the finite-difference time-domain (FDTD) method. We find that the wave function evolves quickly to a stationary state and the eigenvalues of the electron system can be given by the fast Fourier transformation (FFT) along the time axis, as well as the eigenwave functions. In principle, all the required eigenvalues can be given simultaneously. On the other hand, a number of trial wave functions and a shift of energy are needed in the Lanczos and GDA methods, and only one eigenvalue at one time can be dealt with therefore more computing effort is needed to calculate a large number of eigenvalues. The initial-value procedure is very efficient and the computing effort is roughly proportional to the total grid points N and there is no need to use any parameter. More importantly, the scheme can be implemented in a parallel computer [10]. It is therefore suitable to calculate the eigenvalues of a large-scale electron system. The initial-value procedure has been applied to the Schrödinger equation in the past. For example, the wave-packet propagation method has been used to study dynamical features in atoms and molecules [11,12] and coherent tunnelling in quantum wells (QW's) [13,14]. Here we use the FDTD method in the calculation of the eigenvalue problem for the Schrödinger equation. We describe the details of this method. An example of the calculation of the confined states in a $GaN/Al_xGa_{1-x}N$ QD structure is also given to demonstrate the efficiency of the approach.

We first look at the stationary Schrödinger equation:

$$H\phi_n(r) = E_n\phi_n(r), \tag{1}$$

where H is the time-independent Hamiltonian, E_n is the eigenenergy, $\phi_n(r)$ is the corresponding eigenwave function, n is the index for different states and its integer number for confined states.

We look at this problem again but in the time domain. The wave function including the time variable t for any stationary state can be written as

$$\Psi(r,t) = \sum_{n=1}^{N_l} a_n\phi_n(r)\exp\left(-i\frac{E_n}{\hbar}t\right), \tag{2}$$

where a_n is constant. It is easy to see that this function satisfies the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t}\Psi(r,t) = H\Psi(r,t). \tag{3}$$

At any position, e.g., r, we carry out a Fourier transform on the general wave function $\Psi(r,t)$,

$$F(\Psi(r,t)) = \int_{-\infty}^{+\infty} dt e^{i\omega t} \sum_{n=1}^{N_l} a_n \phi_n(r) \exp\left(-i\frac{E_n}{\hbar}t\right)$$
$$= \sum_{n=1}^{N_l} a_n \phi_n(r)\, \delta(\omega - \omega_n), \tag{4}$$

where $\omega_n = E_n/\hbar$. The Fourier transformed spectrum is comprised of a series of delta functions in the frequency domain ω (or energy domain $\hbar\omega$). The eigenenergies of the confined states can be easily obtained by the standard FFT routine if $\Psi(r,t)$ is known. The corresponding coefficients give the eigenfunctions if we do the FFT at every point. The only question remaining is how to calculate the time-dependent function $\Psi(r,t)$. Therefore the eigenvalue problem of the stationary Schrödinger equation becomes an initial-value problem of the time-dependent Schrödinger equation which is relatively easier.

For a very large-scale system, we may not be able to do the FFT because of the very large amount of computer memory required. We propose an alternative way of calculating the eigenwave function $\phi_n(r)$. Assuming there is only a limited number (N_l) of states occurring (usually no more than 50), we can store the time-dependent wave function $\Psi(r,t)$ at M_l different time steps t_m for each spacial point ($m = 1,2,\ldots,M_l \geqslant N_l$). Then, we have

$$\Psi(r,t_m) = \sum_{n=1}^{N_l} a_n \phi_n(r) \exp\left(-i\frac{E_n}{\hbar}t_m\right), \tag{5}$$

where E_n are known from the Fourier transform spectrum. The above equation then is a simple linear equation for $\phi_n(r)$. Defining a matrix T with element

$$T_{mn} = \exp(-it_m E_n/\hbar), \quad m = 1-M_l, \quad n = 1-N_l, \tag{6}$$

the eigenfunctions $\phi_a = \{a_n\phi_n(r)\}$ can be obtained by

$$\phi_a = T^{-1}\Psi, \quad \Psi = \{\Psi(r,t_m), \quad m = 1,2,\ldots,M_l\}. \tag{7}$$

$M_l = N_l$ is assumed in the above, otherwise T^{-1} should be regarded as the least square algorithm. The eigenwave functions $\phi = \{\phi_n(r),\ n = 1-N_l\}$ can be obtained by applying Eq. (7) at each point, and the coefficients a_n can be eliminated by normalization.

We study a GaN/$Al_{0.2}Ga_{0.8}N$ QW where the width $W = 5$ nm, the effective masses m^* are taken as $0.2m_e$ and $0.22m_e$ in the confined region and the barrier region, respectively. To demonstrate the suitability of this method, we assume the confining potential as

$$V(z) = 369.8[1-\cos(\pi z/W)]^2 \text{ meV}, \quad |z| < W/2. \tag{8}$$

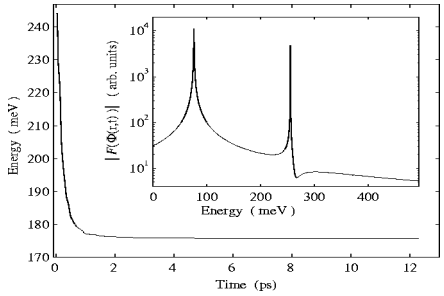

FIG. 1. The total energy evolution of the system in the GaN QW. The inset shows the Fourier spectrum of the time-dependent wave function after ~10 ps.

It is also sketched in Fig. 2. We choose a simple initial wave function from an infinitive QW, e.g.,

$$\Psi(z,0) = \begin{cases} \frac{1}{\sqrt{2W}}\left[\cos\left(\frac{\pi}{2W}z\right) + \sin\left(\frac{\pi}{W}z\right)\right], & |z| < W/2 \\ 0, & |z| > W/2. \end{cases}$$

The Schrödinger equation (3) can be rewritten as [15,16]

$$\exp\left(i\frac{\Delta t}{2\hbar}H\right)\Psi(r,t+\Delta t) = \exp\left(-i\frac{\Delta t}{2\hbar}H\right)\Psi(r,t), \tag{9}$$

where Δt is the time step. For a one-dimensional QW system, we use the Cayley formula [13,14],

$$\left(1+i\frac{\Delta t}{2\hbar}H\right)\Psi(z_k,t_j) = \left(1-i\frac{\Delta t}{2\hbar}H\right)\Psi(z_k,t_{j-1}), \tag{10}$$

where $\Delta t = t_j - t_{j-1}$ and the Hamiltonian H is

$$H = -\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} + V(z). \tag{11}$$

The effective mass Hamiltonian is a tridiagonal matrix after discretization [17] and a stretching-grid mesh is used. Equation (10) is unconditionally stable from the von Neumann analysis and it is solved by the LU factorization method. The condition $(1+Hi\Delta t/2\hbar)\Psi = 0$ is set at the outside boundary which is suitable for the confined states.

We first check the time evolution of the total energy defined as $E(t) = \langle\Psi(r,t)|H|\Psi(r,t)\rangle$ $(t>0)$. The results in Fig. 1 show that the total energy evolves very quickly in the first picosecond and changes very little after a few ps, indicating that the system becomes stationary within a few ps. The time to approach the stationary state also depends on the boundary conditions. After about 10 ps, the FFT is carried out on the $\Psi(r,t)$ along the time axis at several randomly selected points. The magnitude of the transformed spectrum is shown in the inset of the Fig. 1. The results show that there are two confined states, the ground level at 76.15 meV and the second level at 255.8 meV. The time transformation method described by Eq. (7) has been used to calculate the eigenwave functions and the results are shown in Fig. 2. The

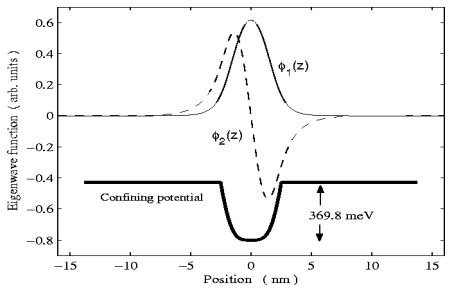

FIG. 2. The eigenwave functions of the confined states (ϕ_1 and ϕ_2) in the GaN QW. The confining potential has also been shown by a thick solid line.

results show that the ground level is symmetric and the second level is antisymmetric as expected. Those results are confirmed by other conventional methods. The intensity for each peak in the spectrum is finite as the integration limit in the FFT has to be truncated. The accuracy of the calculations depends on the time limit in the FFT, but it can be improved easily as the truncation error of Eq. (9) is as $o(\Delta t^3)$. Further details will be given elsewhere.

The FFT technique was used before by some groups to study the optical response of electron systems. Glutsch *et al.* applied FFT to the polarization [7,10] to study the optical response of the electrons. They calculated absorption spectra in semiconductors [7–10], but cannot provide direct information on the eigenstates.

We apply our method to a three-dimensional (3D) system to check the suitability and efficiency. We combine the Douglas-Rachford/alternating direction implicit (ADI) method [18] and split-operator (SO) [19] method to solve Eq. (9). We separate the 3D Hamiltonian into two parts and expand the operator $\exp(i2\beta H)$ as follows:

$$\begin{aligned}\exp(i2\beta H) &= \exp[i2\beta(H_x+H_y)+i2\beta H_z] \\ &\simeq \exp[i\beta(H_x+H_y)]\exp(i2\beta H_z) \\ &\quad \times \exp[i\beta(H_x+H_y)] \\ &\simeq [1+i\beta(H_x+H_y)](1+i2\beta H_z) \\ &\quad \times [1+i\beta(H_x+H_y)], \end{aligned} \tag{12}$$

where $\beta = \pm\Delta t/4\hbar$, $H_x \sim \partial^2/\partial x^2$, $H_y \sim \partial^2/\partial y^2$, and $H_z \sim \partial^2/\partial z^2$. The two-dimensional operator $1+i\beta(H_x+H_y)$ in

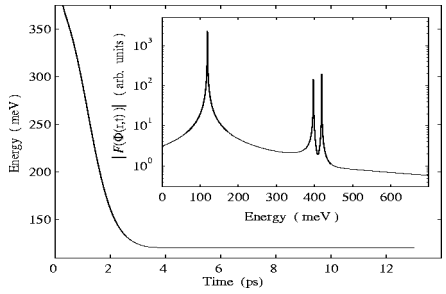

FIG. 3. The total energy evolution of the system in the GaN QD with SSS symmetry. The inset shows the Fourier spectrum of the wave function after it becomes stationary.

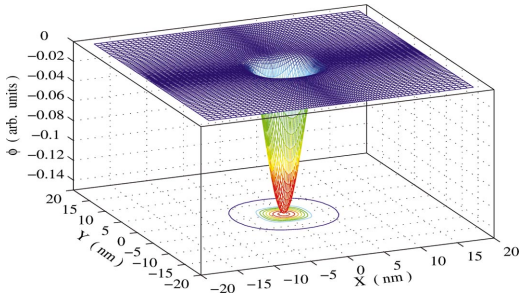

FIG. 4. (Color) Eigenwave function in the X-Y plane ($Z=0$) of the second SSS eigenstate in the GaN QD.

the above can be solved by the standard ADI method. The von Neumann analysis gives the stable condition as

$$[1/(m_x^*\Delta x^2)+1/(m_y^*\Delta y^2)]\hbar\Delta t \leqslant 16\sqrt{2}. \tag{13}$$

The accuracy of Eq. (12) is much better compared with the standard SO scheme.

We have used this modified method in the simulation of a $6\times6\times6$-nm^3 GaN/$Al_{0.3}Ga_{0.7}N$ QD. The QD is at the center of the structure. The grid cell $\Delta\times\Delta y\times\Delta z \simeq 1.8\times1.8\times1.8$ Å at the center, and it is gradually stretched to $10\times10\times10$ Å at the outside boundary. The total grid points are $\sim10^6$. The time step Δt is 0.15 fs, the effective masses are taken as $m_x^*, m_y^* = 0.21m_e$, and $m_z^* = 0.24m_e$, for the alloy in the barrier region. The confining potential is assumed as ($W=6$ nm and $V_0=554.7$ meV),

$$V_0\{1-[\cos(\pi x/W)\cos(\pi y/W)\cos(\pi z/W)]^{1/3}\}^4. \tag{14}$$

To save CPU time, we have used a symmetric condition for the wave functions because of the symmetric confining potential. SSS indicates symmetric wave function in X, Y, and Z directions, SSA indicates symmetric in X and Y directions and antisymmetric in the Z direction. There is a total of 17 confined levels, 6 of them are double degenerate (dd) while the spin degeneracy is excluded. Three eigenstates at 119.9, 400.7, and 421.6 (dd) meV appear in the Fourier spectrum with the SSS symmetry, while two eigenstates at 230.7 and 526.5 (dd) meV appear with the SSA symmetry. In Fig. 3 we show the total energy evolution of the system with the SSS symmetry. The results in Fig. 3 show that the total energy evolves quickly to a constant with a very small fluctuation, and the system becomes stationary in a few ps. The

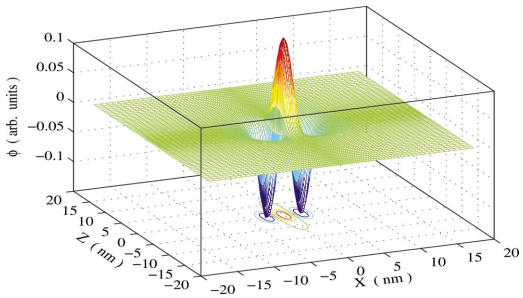

FIG. 5. (Color) Wave function in the X-Z plane ($Y=0$) of the second SSS eigenstate in the GaN QD.

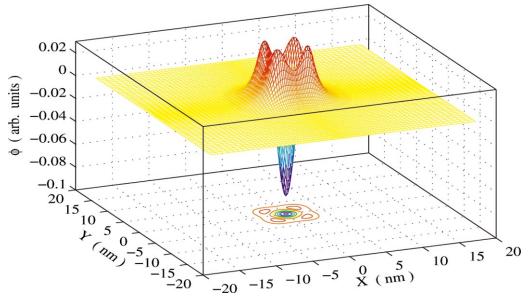

FIG. 6. (Color) Wave function in the X-Y plane ($Z=1.9$ nm off the middle) of the second SSA eigenstate in the GaN QD.

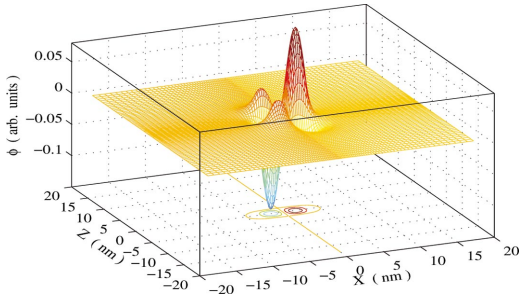

FIG. 7. (Color) Wave function in the X-Z plane ($Y=0$) of the second SSA eigenstate in the GaN QD.

inset in Fig. 3 shows the energy spectrum from the FFT of the time-dependent wave functions after a few ps. We have calculated all 17 eigenwave functions by Eq. (7). Some of them are shown below. Figures 4 and 5 show the eigenfunction of the second SSS eigenstate in the X-Y plane and X-Z plane, respectively. The contours are also shown at the bottom of these figures. Figures 6 and 7 show the wave function of the second SSA eigenstate in the X-Y plane and the X-Z plane, respectively. Notice that Eq. (5) can be treated as a group of nonlinear equations for E_n which is easily solved by the least square method to improve the accuracy. Combining with the FFT, we are able to obtain all the results in 7 h on a 2-GHz Pentium 4 PC with RAM of 768 MB. The typical orthogonality value $\langle \phi_i | \phi_j \rangle$ is 10^{-6} indicating the accuracy of our calculation.

In conclusion, we have demonstrated that the initial-value procedure can be used to calculate the eigenvalue problem of the Schrödinger equation. Using the FDTD method, we have calculated the eigenenergies and the eigenwave functions of the confined states in GaN/$Al_xGa_{1-x}N$ QW and QD systems. The computing effort is roughly proportional to the total grid points involved in the structure. The algorithm can be easily implemented in a parallel computing system and therefore is suitable to simulate a larger system or more realistic model. Many-body problems can be reduced to a set of self-consistent single-particle equations under the density functional theory [20]. We expect that our method can be used to calculate electronic structures in atoms, molecules, clusters, and localized states in semiconductors. It should also be applicable in first principles or pseudomethods to study the band structures in condensed matter systems.

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