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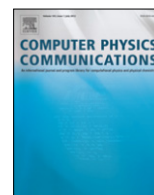
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Program for quantum wave-packet dynamics with time-dependent potentials[☆]

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ABSTRACT

We present a program to simulate the dynamics of a wave packet interacting with a time-dependent potential. The time-dependent Schrödinger equation is solved on a one-, two-, or three-dimensional spatial grid using the split operator method. The program can be compiled for execution either on a single processor or on a distributed-memory parallel computer.

Program summary

Program title: wavepacket

Catalogue identifier: AEQW_v1_0

Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AEQW_v1_0.html

Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland

Licensing provisions: Standard CPC licence, <http://cpc.cs.qub.ac.uk/licence/licence.html>

No. of lines in distributed program, including test data, etc.: 7231

No. of bytes in distributed program, including test data, etc.: 232209

Distribution format: tar.gz

Programming language: C (iso C99).

Computer: Any computer with an iso C99 compiler (e.g. gcc [1]).

Operating system: Any.

Has the code been vectorized or parallelized?: Yes, parallelized using MPI. Number of processors: from 1 to the number of grid points along one dimension.

RAM: Strongly dependent on problem size. See text for memory estimates.

Classification: 2.7.

External routines: fftw [2], mpi (optional) [3]

Nature of problem:

Solves the time-dependent Schrödinger equation for a single particle interacting with a time-dependent potential.

Solution method:

The wave function is described by its value on a spatial grid and the evolution operator is approximated using the split-operator method [4, 5], with the kinetic energy operator calculated using a Fast Fourier Transform.

Unusual features:

Simulation can be in one, two, or three dimensions. Serial and parallel versions are compiled from the same source files.

[☆] This paper and its associated computer program are available via the Computer Physics Communication homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/00104655>).

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Running time:

Strongly dependent on problem size. The example provided takes only a few minutes to run.

References:

- [1] <http://gcc.gnu.org>
- [2] <http://www.fftw.org>
- [3] <http://www.mpi-forum.org>
- [4] M.D. Feit, J.A. Fleck Jr., A. Steiger, Solution of the Schrödinger equation by a spectral method, J. Comput. Phys. 47 (1982) 412–433.
- [5] M.D. Feit, J.A. Fleck Jr., Solution of the Schrödinger equation by a spectral method II: vibrational energy levels of triatomic molecules, J. Chem. Phys. 78 (1) (1983) 301–308.

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1. Introduction

Quantum wave-packet dynamics, that is, the evolution of the spatial distribution of a quantum particle, is an important part of the simulation of many quantum systems. It can be used for studying problems as diverse as scattering, surface adsorption, and laser control, just to name a few.

We propose here a general-purpose program to solve the spatial part of the time-dependent Schrödinger equation (TDSE), aimed particularly at a quantum particle interacting with a time-dependent potential. Our interest mainly concerns such applications as laser control of quantum systems [1,2], but the program can be used with any user-supplied potential function.

The program is based on the split-operator method [3–6], which has successfully been used to solve the time-dependent Schrödinger equation in many different settings, from the calculation of vibrational bound states (see, e.g., [5]) and the simulation of high-power laser–matter interactions (see, e.g., [7]), to the laser control of chemical reactions (see, e.g., [8]). The method can also be applied to Schrödinger-like equations, such as the Gross–Pitaevskii [9] and Dirac [10] equations.

2. Numerical approach

2.1. Split-operator method

In this section, we present a detailed description of the split-operator method to solve the time-dependent Schrödinger equation. While everything presented here can be found in the original works developing the method [3–6], we think it useful to review all the elements necessary to understand the inner workings of the program.

We consider the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi(t) = \hat{H} \psi(t), \quad (1)$$

with \hat{H} the Hamiltonian for the motion of a particle interacting with an external time-dependent potential $V(t)$, i.e.,

$$\hat{H} = \hat{K} + \hat{V} = \frac{\hat{P}^2}{2m} + V(t), \quad (2)$$

where \hat{K} and \hat{V} are the kinetic and potential energy operators, respectively, \hat{P} is the momentum operator, and m the mass of the particle. (The same Hamiltonian is obtained for a vibrating diatomic molecule, where the spatial coordinate is replaced by the internuclear distance, and the potential $V(t)$ is the sum of the internal potential energy and an external, time-dependent potential, as will be shown in Section 4.1.)

The formal solution to Eq. (1) is given by the time evolution operator \hat{U} , itself a solution of the time-dependent Schrödinger equation [11],

$$i\hbar \frac{\partial}{\partial t} \hat{U} = \hat{H} \hat{U}, \quad (3)$$

such that, given an initial wave function at time t_0 , $\psi(t_0)$, the solution at any time t is obtained from

$$\psi(t) = \hat{U}(t, t_0) \psi(t_0). \quad (4)$$

As the Hamiltonian is time dependent, we have that [12]

$$\begin{aligned} \hat{U}(t, t_0) &= \hat{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t \hat{H}(t') dt' \right] \\ &= \hat{T} \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t [\hat{K} + \hat{V}(t')] dt' \right\}. \end{aligned} \quad (5)$$

In Eq. (5), the time-ordering operator \hat{T} ensures that the Hamiltonian is applied to the wave function in order of increasing time, as in general the Hamiltonian does not commute with itself at a different time, i.e., $[\hat{H}(t), \hat{H}(t')] \neq 0$ iff $t \neq t'$ [11,13]. By considering a small time increment Δt , we can do without the time-ordering operator by considering the approximate short-time evolution operator [13],

$$\hat{U}(t + \Delta t, t) = \exp \left\{ -\frac{i}{\hbar} \int_t^{t+\Delta t} [\hat{K} + \hat{V}(t')] dt' \right\}. \quad (6)$$

We are concerned here with time-dependent potentials that also have a spatial dependence, $\hat{V} \equiv V(\mathbf{x}, t)$, such as those produced by ion traps or focused laser pulses, such that $\hat{V} \equiv V(\mathbf{x}, t)$, in which case \hat{K} and \hat{V} do not commute. For two non-commuting operators \hat{A} and \hat{B} , $e^{\hat{A}+\hat{B}} \neq e^{\hat{A}}e^{\hat{B}}$, but the split-operator method [4,5] allows the approximation of the evolution operator with minimal error,

$$\begin{aligned} \hat{U}(t + \Delta t, t) &= \exp \left[-\frac{i\Delta t}{2\hbar} \hat{K} \right] \exp \left[-\frac{i}{\hbar} \int_t^{t+\Delta t} \hat{V}(t') dt' \right] \\ &\quad \times \exp \left[-\frac{i\Delta t}{2\hbar} \hat{K} \right] + O(\Delta t^3). \end{aligned} \quad (7)$$

Using the midpoint formula [14] for the integral of the potential,

$$\int_t^{t+\Delta t} f(t') dt' = f(t + \Delta t/2) \Delta t + O(\Delta t^3), \quad (8)$$

we get

$$\begin{aligned} \hat{U}(t + \Delta t, t) &\approx \exp \left[-\frac{i\Delta t}{2\hbar} \hat{K} \right] \exp \left[-\frac{i\Delta t}{\hbar} V \left(t + \frac{\Delta t}{2} \right) \right] \exp \left[-\frac{i\Delta t}{2\hbar} \hat{K} \right], \end{aligned} \quad (9)$$

where the global error is $O(\Delta t^3)$. The choice of the order of the operators \hat{K} and \hat{V} in the above equations is arbitrary, but the choice

we make here allows for a faster execution in the majority of cases, i.e., when the intermediate value of the wave function is not needed at all time steps. We can then link together n consecutive time steps into

$$\begin{aligned} \hat{U}(t + n\Delta t, t) &= \hat{U}(t + n\Delta t, t + [n - 1]\Delta t) \hat{U}(t \\ &+ [n - 1]\Delta t, t + [n - 2]\Delta t) \times \cdots \times \hat{U}(t + \Delta t, t) \\ &= \exp \left[-\frac{i\Delta t}{2\hbar} \hat{K} \right] \exp \left[-\frac{i\Delta t}{\hbar} \hat{V} \left(t + \frac{2n - 1}{2} \Delta t \right) \right] \\ &\times \left\{ \prod_{j=n-1}^1 \exp \left[-\frac{i\Delta t}{\hbar} \hat{K} \right] \right. \\ &\times \left. \exp \left[-\frac{i\Delta t}{\hbar} \hat{V} \left(t + \frac{2j - 1}{2} \Delta t \right) \right] \right\} \exp \left[-\frac{i\Delta t}{2\hbar} \hat{K} \right], \quad (10) \end{aligned}$$

where two sequential operations of \hat{K} are combined into one. The same is not possible with \hat{V} due to its time dependence.

We choose to discretize the problem on a finite spatial grid, i.e., $\mathbf{x} = (x, y, z)$ is restricted to the values

$$\begin{aligned} x_i &= x_{\min} + i\Delta x, \quad i = 0, \dots, n_x - 1, \\ y_j &= y_{\min} + j\Delta y, \quad j = 0, \dots, n_y - 1, \\ z_k &= z_{\min} + k\Delta z, \quad k = 0, \dots, n_z - 1, \end{aligned} \quad (11)$$

where the number of grid points (n_x, n_y, n_z) are (integer) parameters, as is the size of the grid, with bounds $x \in [x_{\min}, x_{\max}]$ and where

$$\Delta x = \frac{x_{\max} - x_{\min}}{n_x - 1}, \quad (12)$$

with equivalent expressions in y and z .

The problem now becomes that of calculating the exponential of matrices K and V , which is only trivial for a diagonal matrix [15]. In the original implementation of the split-operator method [4,5], this is remedied by considering that while the matrix for \hat{V} is diagonal for a spatial representation of the wave function, \hat{K} is diagonal in momentum space. By using a Fourier transform (here represented by the operator \mathcal{F}) and its inverse (\mathcal{F}^{-1}), we can write

$$\exp \left[-\frac{i\Delta t}{2\hbar} \hat{K}(\mathbf{x}) \right] \psi(\mathbf{x}) = \mathcal{F}^{-1} \exp \left[-\frac{i\Delta t}{2\hbar} \hat{K}(\mathbf{p}) \right] \mathcal{F} \psi(\mathbf{x}), \quad (13)$$

where, considering that $\hat{K} = \hat{p}^2/2m$,

$$\hat{K}(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}, \quad (14)$$

$$\hat{K}(\mathbf{x}) = -\frac{\hbar^2}{2m} \nabla^2, \quad (15)$$

since the operators transform as $-i\hbar\nabla \Leftrightarrow \mathbf{p}$ when going from position to momentum space [11]. Eq. (13) is efficiently implemented numerically using a Fast Fourier Transform (FFT) [16]. After the forward transform, the momentum grid, obtained from the wave vector $\mathbf{k} = \mathbf{p}/\hbar$, is discretized according to [16]

$$\begin{aligned} p_{x,i} &= 2\pi\hbar \frac{i}{n_x\Delta x}, \quad i = -\frac{n_x}{2}, \dots, \frac{n_x}{2}, \\ p_{y,j} &= 2\pi\hbar \frac{j}{n_y\Delta y}, \quad j = -\frac{n_y}{2}, \dots, \frac{n_y}{2}, \\ p_{z,k} &= 2\pi\hbar \frac{k}{n_z\Delta z}, \quad k = -\frac{n_z}{2}, \dots, \frac{n_z}{2}. \end{aligned} \quad (16)$$

Care must be taken to associate the appropriate momentum value to each element of the Fourier-transformed wave function, considering the order of the output from FFT routines [16]. Algorithm 1 summarizes the split-operator method as presented here.

Algorithm 1: Main algorithm for the split-operator method.

```

Initialize  $\psi(t = 0)$ 
for  $j \leftarrow 1$  to  $n_t/n_{\text{print}}$  do
     $\tilde{\psi}(\mathbf{p}) \leftarrow \mathcal{F} \psi(\mathbf{x})$ 
    Multiply  $\tilde{\psi}(\mathbf{p})$  by  $\exp \left[ -\frac{i\Delta t}{2\hbar} \frac{\mathbf{p}^2}{2m} \right]$ 
     $\psi(\mathbf{x}) \leftarrow \mathcal{F}^{-1} \tilde{\psi}(\mathbf{p})$ 
    for  $i \leftarrow 1$  to  $n_{\text{print}} - 1$  do
        Multiply  $\psi(\mathbf{x})$  by  $\exp \left[ -\frac{i\Delta t}{\hbar} V(\mathbf{x}, t) \right]$ 
         $\tilde{\psi}(\mathbf{p}) \leftarrow \mathcal{F} \psi(\mathbf{x})$ 
        Multiply  $\tilde{\psi}(\mathbf{p})$  by  $\exp \left[ -\frac{i\Delta t}{2\hbar} \frac{\mathbf{p}^2}{2m} \right]$ 
         $\psi(\mathbf{x}) \leftarrow \mathcal{F}^{-1} \tilde{\psi}(\mathbf{p})$ 
    end
    Multiply  $\psi(\mathbf{x})$  by  $\exp \left[ -\frac{i\Delta t}{\hbar} V(\mathbf{x}, t) \right]$ 
     $\tilde{\psi}(\mathbf{p}) \leftarrow \mathcal{F} \psi(\mathbf{x})$ 
    Multiply  $\tilde{\psi}(\mathbf{p})$  by  $\exp \left[ -\frac{i\Delta t}{2\hbar} \frac{\mathbf{p}^2}{2m} \right]$ 
     $\psi(\mathbf{x}) \leftarrow \mathcal{F}^{-1} \tilde{\psi}(\mathbf{p})$ 
    Calculate observables  $\langle \hat{A} \rangle \equiv \langle \psi(\mathbf{x}) | \hat{A} | \psi(\mathbf{x}) \rangle$ 
end
    
```

2.2. Parallel implementation

We consider now the implementation of the algorithm described above on a multi-processor architecture with distributed memory. The “natural” approach to parallelizing the problem is to divide the spatial grid, and therefore the wave function, among the processors. Each processor can work on its local slice of the wave function, except for the Fourier transform, which requires information across slices. This functionality is pre-built into the parallel implementation of the FFT package FFTW [17], of which we take advantage. The communications themselves are implemented using the Message Passing Interface (MPI) library [18,19].

For a 3D (or 2D) problem, the wave function is split along the x direction, with each processor having a subset of the grid in x , but with the full extent in y and z . To minimize the amount of communication after the forward FFT, we use the intermediate transposed function, where the split is now along the y dimension. The original arrangement is recovered after the backward function, so this is transparent to the user of our program. In addition, FFTW offers the possibility of performing a 1D transform in parallel, which we also implement here.

The only constraint this imposes on the user is that a 1D problem may only be defined along x , and a 2D problem in the xy -plane (in order to simplify the concurrent implementation of serial and parallel versions, this constraint also applies to the serial version). In addition to the total number of grid points along x , n_x , each processor has access to $n_{x,\text{local}}$, the number of grid points in x for this processor, along with $n_{x,0}$, the corresponding initial index. In other words, each processor has a grid in x defined by

$$x_i = x_{\min} + (i + n_{x,0}) \Delta x, \quad i = 0, \dots, n_{x,\text{local}}, \quad (17)$$

with the grids in y and z still defined by Eq. (11).

3. User guide

3.1. Summary of the steps for compilation and execution

Having defined the physical problem to be simulated, namely by setting up the potential $V(\mathbf{x}, t)$ and initial wave function $\psi(\mathbf{x})$,

$t = 0$), the following routines must be coded (see Section 3.2 for details):

- `initialize_potential`
- `potential`
- `initialize_wf`
- `initialize_user_observe` (can be empty)
- `user_observe` (can be empty).

The files containing these functions must include the header file `wavepacket.h`. The program can then be compiled according to the instructions in Section 3.3.

A parameter file must then be created, see Section 3.4. The program can then be executed using a command similar to `wavepacket parameters.in`

3.2. User-defined functions

The physical problem that is actually simulated by the program depends on two principal elements, the time-dependent potential $V(\mathbf{x}, t)$ and the initial wave function $\psi(\mathbf{x}; t = 0)$. In addition, the user may be interested in observables that are not calculated by the main program (the list `a` which is given in Section 3.4). The user must supply functions which define those elements, which are linked to at compile time. How these functions are declared and what they are expected to perform is described in what follows, along with the data structure that is passed to those functions.

3.2.1. Data structure *parameters*

The data structure `parameters` is defined in the header file `wavepacket.h`, which must be included at the top of the users own C files to be linked to the program. A variable of type `parameters` is passed to the user's functions, and contains all parameters the main program is aware of and that are useful/necessary for the execution of the tasks of the user-supplied routines. The structure reads

```
typedef struct
{
    /* Parameters and grid */
    int size, rank;
    size_t nx, ny, nz, n, nx_local, nx0, n_local;
    double x_min, y_min, z_min, x_max, y_max, z_max, dx, dy, dz;
    double *x, *y, *z, *x2, *y2, *z2;
    double mass, dt, hbar;
} parameters;
```

where the different variables are:

- `size`: Number of processors on which the program is running.
- `rank`: Rank of the local processor, with a value in the range $[0, \text{size} - 1]$. In the serial version, the value is therefore `rank = 0`. (Note: All input and output to/from disk is performed by the processor of rank 0.)
- `nx`, `ny`, `nz`: Number of grid points along x , y , and z , respectively. In the parallel version, this refers to the full grid, which is then split among the processors. For a one or two-dimensional problem, `ny` and/or `nz` should be set to 1. (x is always the principal axis in the program.) For best performance, these should be set to a product of powers of small prime integers, e.g., $nx = 2^i 3^j 5^k 7^l$.

See the documentation of FFTW for more details [20].

- `n` = `nx` \times `ny` \times `nz`.
- `nx_local`: Number of grid points in x on the local processor, see Section 2.2. In the serial version, `nx_local` = `nx`.
- `nx0`: Index of the first local grid point in x , see Section 2.2. In the serial version, `nx0` = 0.
- `x_min`, `y_min`, `z_min`, `x_max`, `y_max`, `z_max`: Values of the first and last grid points along x , y , and z .
- `dx`, `dy`, `dz`: Grid spacings Δx , Δy , and Δz , respectively, see Eq. (12).

- `x`, `y`, `z`: Arrays of size `nx_local`, `ny`, and `nz`, respectively, containing the value of the corresponding coordinate at the grid point.
- `x2`, `y2`, `z2`: Arrays of size `nx_local`, `ny`, and `nz`, respectively, containing the square of the value of the corresponding coordinate at the grid point.
- `mass`: Mass of the particle.
- `dt`: Time step Δt of the time evolution, see Eq. (6).
- `hbar`: Value of \hbar , Planck's constant over 2π , in the proper units. (See Section 3.4.)

3.2.2. Initializing the potential

In the initialization phase of the program, before the time evolution, the function

```
void
initialize_potential (const parameters params, const int argv,
                    char ** const argc);
```

is called, with the constant variable `params` containing all the values specified in Section 3.2.1. `argv` and `argc` are the variables relating to the command line arguments, as passed to the main program:

```
int
main (int argv, char **argc);
```

This function should perform all necessary pre-calculations and operations, including reading from a file additional parameters, for the potential function. The objective is to reduce as most as possible the time necessary for a call to the `potential` function.

3.2.3. Potential function

The function

```
double
potential (const parameters params, const double t,
          double * const pot);
```

should return the value of the potential $V(\mathbf{x}, t)$, for all (local) grid points at time t , in the array `pot`, of dimension `pot[nx_local][ny][nz]`.

3.2.4. Initial wave function

The initial wave function $\psi(\mathbf{x}, t = 0)$ is set by the function

```
void
initialize_wf (const parameters params, const int argv,
              char ** const argc, double complex *psi);
```

where `psi` is a 3D array of dimension `psi[nx_local][ny][nz]`. If the wave function is to be read from a file, users can make use of the functions `read_wf_text` and `read_wf_bin`, described in Section 3.2.6.

3.2.5. User-defined observables

In addition to the observables that are built in, which are described in Section 3.4, users may define additional observables, such as the projection of the wave function on eigenstates.

The function

```
void
initialize_user_observe (const parameters params, const int argc,
                       char ** const argv);
```

is called once at the beginning of the execution. It should perform all operations needed before any call to `user_observe`. The arguments passed to the function are the same as those of `initialize_potential`, see Section 3.2.2.

During the time evolution, every `nprint` time step, the function

```
void
user_observe (const parameters params, const double t,
              const double complex * const psi);
```

is called, with the current time t and wave function `psi`.

Table 1

Recognized parameters to be found in the parameter file. Parameters with no default value must be present, with the exception of those indicated as *none**

Key	Value type	Description	Default value
units	double	System of units used, SI or atomic units (AU)	AU
mass	double	m , mass of the particle	<i>none</i>
nx	size_t	n_x , number of grid points in x	<i>none</i>
ny	size_t	n_y , number of grid points in y	1
nz	size_t	n_z , number of grid points in z	1
x_min	double	Value of the first grid point along x	<i>none</i>
x_max	double	Value of the last grid point along x	<i>none</i>
y_min	double	Value of the first grid point along y	0 (<i>none</i> if $n_y > 1$)
y_max	double	Value of the last grid point along y	y_{\min} (<i>none</i> if $n_y > 1$)
z_min	double	Value of the first grid point along z	0 (<i>none</i> if $n_z > 1$)
z_max	double	Value of the last grid point along z	z_{\min} (<i>none</i> if $n_z > 1$)
dt	double	Time step Δt	<i>none</i>
nt	unsigned int	Number of time steps	<i>none</i>
nprint	unsigned int	Interval of the calculation of the observables	(See text)
results_file	char	Output file name for observables	results
wf_output_text	char	File name for output of final wave function in text format	<i>none</i> *
wf_output_binary	char	File name for output of final wave function in binary format	<i>none</i> *

The printing out of the results, as well as the eventual opening of a file, are to be performed within these user-supplied functions. In a parallel implementation, only the processor of rank 0 should be responsible for these tasks, and proper communication must be set up to ensure the full result is available to this processor.

Note that these functions *must* be present in the source file that will be linked with the main program, even if additional observables are not desired. In this case, the function body can be left blank.

3.2.6. Useful functions

A series of functions declared in the header file `wavepacket.h` and that are part of the main program are also available for use within the user-defined functions described above.

- double
norm (const parameters params,
const double complex * const psi);
calculates $\sqrt{\langle \text{psi} | \text{psi} \rangle}$.
- double complex
integrate3D (const parameters params,
const double complex * const f1,
const double complex * const f2);
given $f_1 \equiv f_1$ and $f_2 \equiv f_2$, calculates
$$\langle f_1 | f_2 \rangle = \int_{z_{\min}}^{z_{\max}} \int_{y_{\min}}^{y_{\max}} \int_{x_{\min}}^{x_{\max}} f_1^* f_2 \, dx \, dy \, dz.$$

(Correct results are also obtained for 1D and 2D systems.)
- double
expectation1D (const parameters params, const int dir,
const double * const f,
const double complex * const psi);
given $f(\xi) \equiv f$ and $\psi \equiv \text{psi}$, calculates
$$\langle \psi | f(\xi) | \psi \rangle = \int_{z_{\min}}^{z_{\max}} \int_{y_{\min}}^{y_{\max}} \int_{x_{\min}}^{x_{\max}} \psi^* f(\xi) \psi \, dx \, dy \, dz,$$

where $\xi = x, y, z$ for $\text{dir} = 1, 2, 3$, respectively.
- void
read_wf_bin (const parameters params,
const char * const wf_bin,
double complex * const psi);

opens the file with filename `wf_bin` and reads the wave function into `psi`. The file must be in a binary format, as written when the keyword `wf_output_binary` is present in the parameter file, see Section 3.4. In the parallel version, the file is read by the processor of rank 0, and each processor is assigned

its local part of the wave function of size `psi[nx_local][ny][nz]`.

- void
distribute_wf (const parameters params,
double complex * const psi_in,
double complex * const psi_out);

given the wave function `psi_in[nx][ny][nz]` located on the processor of rank 0, returns in `psi_out[nx_local][ny][nz]` the local part of the wave function on each processor. Intended only to be used in the parallel version, the function will simply copy `psi_in` into `psi_out` in the serial version.

- void
abort ()

terminates the program. This is the preferred method for exiting the program (e.g., in case of error) in user-supplied routines, especially in the parallel version.

3.3. Compiling the program

A sample makefile is supplied with the program, which should be straightforward to adapt to one's needs. Without a makefile, a typical command-line compilation would look something like

```
gcc -O3 -std=c99 -o wavepacket wavepacket.c user_defined.c \
-lfftw3 -lm
```

where the file `user_defined.c` contains all the routines specified in Section 3.2.

By default, the compiling will produce the serial version of the program. To compile the MPI parallel version requires defining the macro `MPI`, i.e., by adding `-DMPI` as an argument to the compiler (through `CFLAGS` in the makefile). In addition, MPI libraries must be linked to, including `-lfftw3_mpi`.

3.4. Parameter file

When executing the program, it will expect the first command-line argument to consist of the name of the parameter file. This file is expected to contain a series of statements of the type '`key = value`', each on a separate line. The order of these statements is not important, and blank lines are ignored, but white space must separate *key* and *value* from the equal sign. Note that the program does not check for duplicate keys, such that the last value found will be used (except for the key output, see below). Table 1 presents the keys recognized by the program. If a key listed with a default value of "*none*" is absent from the parameter file, the program will print out a relevant error message and the execution will be aborted. The

Table 2
Values of some atomic units [21].

Atomic unit	Symbol	SI value
Length	a_0	$0.529\,177\,210\,92 \times 10^{-10}$ m
Time		$2.418\,884\,326\,502 \times 10^{-17}$ s
Mass	m_e	$9.109\,382\,91 \times 10^{-31}$ kg
Energy	E_h	$4.359\,744\,34 \times 10^{-18}$ J

key units can take the value SI if the *Système International* set of units is desired (kg, m, s), with AU (the default) corresponding to atomic units, where $\hbar = m_e = e = 1$, with m_e and e the mass and the charge of the electron, respectively. Some equivalences between the two sets are given in Table 2. All parameters with units (mass, grid limits, time step) must be consistent with the set of units chosen.

In addition, the output of the program is controlled by a series of flags, set in the same fashion as above, with the key output and value equal to the desired flag. A list of valid flags is given in Table 3. These values will be printed out in the file designated by the `results_file` key, for the initial wave function and every `nprint` iteration of the time step Δt . The program will abort with an error message if `nprint > nt`. Note that if `nt mod nprint ≠ 0`, the values for the final wave function will not be calculated. The key `nprint` needs only be present if any of the output flags is set.

3.5. Memory usage

Calculating the exact memory usage is a bit tricky, but as the main use of memory is to store the wave function and some work arrays, we can estimate a minimum amount of memory necessary according to the grid size. Considering that a double precision real takes up 8 bytes of memory, the program requires at least

$$40 \frac{(n_x n_y n_z)}{n_{\text{proc}}} + 56 \left(\frac{n_x}{n_{\text{proc}}} + n_y + n_z \right)$$

bytes per processor, where $n_{\text{proc}} \equiv \text{size}$ is the number of processors used. This value holds when the autocorrelation function is not calculated; otherwise, the initial wave function must be stored and the factor 40 above changes to 56. Obviously, this estimate does not include any memory allocated within user-supplied routines.

4. Sample results

4.1. Laser excitation of vibration

As a first example, let us consider a vibrating diatomic molecule, with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \tilde{V}(r), \quad (18)$$

for a wave function $\tilde{\psi}(r, \theta, \phi, t)$ in spherical coordinates, with m the reduced mass and $\tilde{V}(r)$ the molecular potential [11]. We neglect here the rotation of the molecule, and only look at the radial part of the wave function, $\tilde{\psi}(r, t)$. Setting $\psi \equiv r\tilde{\psi}$, and substituting x for r , we get the one-dimensional Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x, t) \right] \psi(x, t), \quad (19)$$

which is the one-dimensional equivalent of Eq. (1) with Hamiltonian Eq. (2) and with the full potential $V(x, t)$ taken as a sum of the molecular potential $\tilde{V}(x)$ and the coupling of the molecule to a laser pulse, $V_L(x, t)$. We note that recovering an operator of the form d^2/dx^2 is a very special case obtained here for a diatomic molecule,

Table 3
Recognized output flags.

Flag	Description
<code>norm</code>	Norm, $\sqrt{\langle \psi \psi \rangle}$
<code>energy</code>	Energy, $E = \langle \psi \hat{H} \psi \rangle$
<code>x_avg</code>	Average position in x , $\langle x \rangle = \langle \psi x \psi \rangle$
<code>y_avg</code>	Average position in y , $\langle y \rangle = \langle \psi y \psi \rangle$
<code>z_avg</code>	Average position in z , $\langle z \rangle = \langle \psi z \psi \rangle$
<code>sx</code>	Width in x , $\langle x^2 \rangle - \langle x \rangle^2$
<code>sy</code>	Width in y , $\langle y^2 \rangle - \langle y \rangle^2$
<code>sz</code>	Width in z , $\langle z^2 \rangle - \langle z \rangle^2$
<code>autocorrelation</code>	Autocorrelation function, $ \langle \psi(0) \psi(t) \rangle ^2$
<code>user_defined</code>	User-defined observables (see Section 3.2.5)

and that in general the kinetic energy operator for the internal motion of a molecule can be quite different, such that this program may not be used to study the internal dynamics of molecules in general.

For the molecular potential, we take a Morse potential [22,23],

$$\tilde{V}(x) = D \left[1 - e^{-a(x-x_e)} \right]^2, \quad (20)$$

and from the data of Ref. [24], we derive the parameters for $^{12}\text{C}^{16}\text{O}$ in the ground electronic state:

$$m = 12498.10$$

$$D = 0.4076$$

$$a = 1.230211$$

$$x_e = 2.1322214$$

with $m = m_C m_O / (m_C + m_O)$ the reduced mass, and all values expressed in atomic units (see Table 2).

Using a classical model for the laser field and the dipole approximation, the laser–molecule coupling is given by [25]

$$V_L(x, t) = \mu(x) \mathcal{E}(t), \quad (21)$$

where $\mu(x)$ is the dipole moment of the molecule and $\mathcal{E}(t)$ the electric field of the laser. We approximate the internuclear-separation-dependent permanent dipole moment of the molecule as the linear function

$$\mu(x) = \mu_0 + \mu' (x - x_e), \quad (22)$$

with the values (in atomic units) $\mu = -0.1466$ and $\mu' = -0.948$ [26]. For the laser pulse, we take

$$\mathcal{E}(t) = \mathcal{E}_0 f(t) \cos(\omega t) \quad (23)$$

with \mathcal{E}_0 and ω the amplitude and frequency of the field, respectively, and the envelope function

$$f(t) = \begin{cases} \sin^2 \left(\pi \frac{t}{t_f - t_i} \right) & \text{if } t_i \leq t \leq t_f \\ 0 & \text{otherwise.} \end{cases} \quad (24)$$

In this sample simulation, we take the following values (in atomic units):

$$\mathcal{E}_0 = 1.69 \times 10^{-3}$$

$$\omega = 9.8864 \times 10^{-3}$$

$$t_i = 0$$

$$t_f = 41341.37.$$

This corresponds to a 1 ps pulse at an irradiance of 10^{11} W/cm², resonant with the $v = 0 \rightarrow v = 1$ transition.

Using a DVR method [27], we precomputed the first five vibrational eigenstates ϕ_v of the Morse potential for $^{12}\text{C}^{16}\text{O}$ on a grid of 4000 points, from $x = 1.5 \times 10^{-3}$ a.u. to 6 a.u.. The data, stored in file `CO_vib.txt`, are read when the wave function is initialized

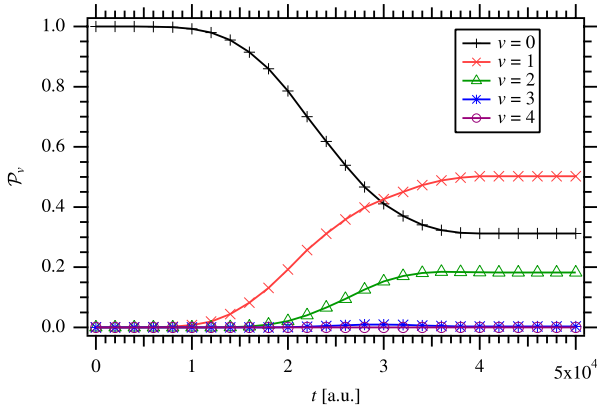


Fig. 1. Projection of the time-dependent vibrational wave function of the CO molecule, interacting with a resonant laser pulse, on the first five vibrational eigenstates.

in the function `initialize_wf`, and the initial wave function is set to $\psi(x, t = 0) = \phi_0(x)$. The function `user_observe` is programmed to calculate the projection of the wave function on the first five eigenstates, i.e.,

$$\mathcal{P}_v(t) \equiv |\langle \phi_v | \psi(t) \rangle|^2. \quad (25)$$

Using the same grid as the one described above for the calculation of the vibrational states, we run the simulation for 500 000 time steps of length $\Delta t = 0.1$ a.u., and calculate the projection of the wave function on the vibrational eigenstates every 20 000 time steps. the result is shown in Fig. 1.

4.2. Atomic ion in a Paul trap

Let us now consider the three-dimensional problem of the motion of a charged atomic ion in a Paul trap [28–30]. These create a time-dependent quadrupolar field allowing, under the right conditions, the confinement of an ion.

The electric potential inside a Paul trap is of the form [29,30]

$$\Phi(x, t) = \frac{U_0 + V_0 \cos \Omega t}{2d^2} (r^2 - 2z^2), \quad (26)$$

where U_0 is a static electric potential, V_0 the amplitude of an ac potential of frequency Ω , and $r^2 \equiv x^2 + y^2$. The scale factor d is obtained from $d^2 = r_0^2 + 2z_0^2$, with r_0 the radial distance from the center of the trap to the ring electrode and z_0 the axial distance to an end cap (see Refs. [29,30] for more details). Considering an atomic ion of charge Ze , where e is the elementary charge [21], we get the potential energy

$$V(\mathbf{x}, t) = Ze\Phi(x, t). \quad (27)$$

For the simulation, we consider conditions similar to those of Refs. [31,32] and take a $^{138}\text{Ba}^+$ ion, $m = 137.905232$ u = $2.28997005 \times 10^{-25}$ kg [33], in a trap with characteristics:

$$U_0 = 0 \text{ V}$$

$$V_0 = 200 \text{ V}$$

$$\Omega = 2\pi \times 18 \text{ MHz}$$

$$r_0 = 1.6 \times 10^{-3} \text{ m}$$

$$z_0 = r_0/\sqrt{2}.$$

The initial state is taken as a Gaussian wave packet,

$$\psi_i(x, y, z) = \left(\frac{2}{\pi}\right)^{3/4} \prod_{\xi=x,y,z} \frac{1}{\sqrt{\sigma_\xi}} \exp\left[\frac{i}{\hbar} p_{\xi 0} (\xi - \xi_0)\right] \times \exp\left[-\frac{(\xi - \xi_0)^2}{\sigma_\xi^2}\right], \quad (28)$$

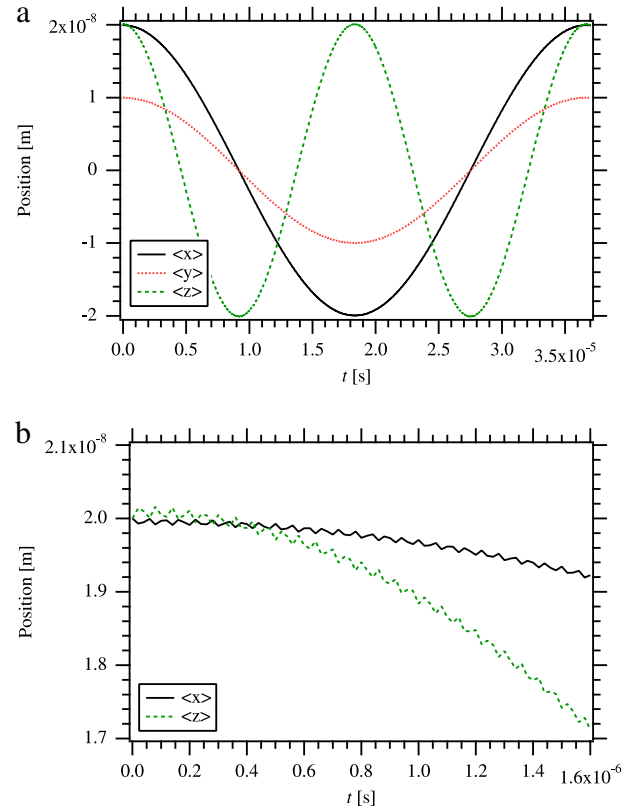


Fig. 2. (a) Sample trajectory of the wave packet of a Ba^+ ion in a Paul trap. The simulation is carried in three dimensions, and the expectation value of the position is plotted individually for each Cartesian coordinate. (b) Enlargement of panel (a), evidencing the micromotion of the ion at the frequency of the trapping potential.

and we set

$$x_0 = z_0 = 2 \times 10^{-8} \text{ m}$$

$$y_0 = 1 \times 10^{-8} \text{ m}$$

$$p_{x0} = 1 \times 10^{-27} \text{ kg m s}^{-1}$$

$$p_{y0} = p_{z0} = 0$$

$$\sigma_x = \sigma_y = 7.342 \times 10^{-8} \text{ m}$$

$$\sigma_z = 5.192 \times 10^{-8} \text{ m}.$$

Using $n_x = n_y = n_z = 512$ grid points, with the grid defined from -1×10^{-6} m to 1×10^{-6} m along each Cartesian coordinate, we run the simulation for $n_t = 18\,500$ time steps of length $\Delta t = 2 \times 10^{-9}$ s, measuring the wave function every 10 time steps. The resulting trajectory of the ion is shown in Fig. 2.

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