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H3b Time dependent quantum mechanics

Here you are asked to implement and apply the split operator FFT method on various time-dependent quantum problems. You will consider both a scattering problem in one dimension and a so called curve-crossing problem.

Time evolution

In quantum mechanics the time evolution of the state vector is given by the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \tag{1}$$

This is the analogue of Newton's equation of motion in classical mechanics. Formally the solution can be written as

$$|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle \tag{2}$$

where the time-evolution operator $\hat{U}(t)$ is given by

$$\hat{U}(t) = \exp\left[-\frac{i}{\hbar}\hat{H}t\right] \tag{3}$$

In position representation the formal solution for the motion of a single particle 1 dimension can be written as

$$\begin{aligned}
\psi(x,t) &= \langle x|\psi(t)\rangle \\
&= \langle x|\hat{U}(t-t')|\psi(t')\rangle \\
&= \int dx'\langle x|\hat{U}(t-t')|x'\rangle\psi(x',t') \\
&\equiv \int dx' G(x,t;x',t')\psi(x',t')
\end{aligned} \tag{4}$$

where $G(x,t;x',t')$ is known as the propagator or the Green's function for the time-dependent Schrödinger equation. It is the amplitude for finding the particle at x at time t, if it was at x' at time t'. Multiplying $G(x,t;x',t')$ by $\psi(x',t')$ and integrating over x' gives the total amplitude for finding the particle at x at time t.

Wave packets

If a particle is localized at a specific position x the uncertainty in momentum will be infinite, and vice versa, a particle with definite value for the momentum will be completely delocalized in coordinate space. To describe particles which are reasonably well localized in coordinate space and at the same time has a fairly well defined momentum one has to use wave packets.

Consider a one-dimensional Gaussian wave packet which in coordinate space is given by

$$\langle x|\psi\rangle = (\frac{1}{\pi d^2})^{1/4} \exp\,[-\frac{(x-x_0)^2}{2d^2}] \exp\,[ip_0(x-x_0)/\hbar] \tag{5}$$

This function describes a particle localized around x_0, or more precisely, the probability density is a Gaussian centered around x_0 and with the width being equal to $\Delta x = d/\sqrt{2}$. The expectation value for the momentum is p_0, a particle moving in the positive x-direction, and the uncertainty in momentum is $\Delta p = \hbar/\sqrt{2}d$. The Gaussian wave packet fulfills the relation $\Delta x \Delta p = \hbar/2$, the lower limit set by Heisenberg's uncertainty relation, and it is therefore often called a minimum uncertainty wave packet.

Short-time propagators

In the general case the time-dependent Schrödinger equation has to be solved by numerical methods. A convenient approach is to introduce short-time propagators. This is done by decomposing the the time-evolution operator into a product of short-time propagators

$$\hat{U}(t_{tot}) = \prod_{n=1}^{N} \hat{U}(n\Delta t, (n-1)\Delta t) \tag{6}$$

with $t_{tot} = N\Delta t$. The time-evolution is then obtained by repeatedly applying the short-time propagator according to

$$|\psi(t+\Delta t)\rangle = \exp\,(-\frac{i}{\hbar}\hat{H}\Delta t)|\psi(t)\rangle \tag{7}$$

Cayley's form The short-time propagator in eqn (7) has to be approximated. The simplest scheme is to expand the propagator in a Taylor series, and to keep the first term only,

$$|\psi(t+\Delta t)\rangle = (1 - \frac{i}{\hbar}\hat{H}\Delta t)|\psi(t)\rangle \tag{8}$$

When this equation is discretized an explicit method is obtained. This means that $|\psi(t+\Delta t)\rangle$ can be calculated from what is known at the previous time-step. However, the method is unstable for any value of Δt because the eigenvalues of the operator, $(1 - i\epsilon_n \Delta t/\hbar)$, has the moduli greater than one, $\sqrt{1 + (\epsilon_n \Delta t/\hbar)^2} > 1$. The solution will grow in time. To obtain a stable method we write instead

$$\exp\,(\frac{i}{\hbar}\hat{H}\Delta t)|\psi(t+\Delta t)\rangle = |\psi(t)\rangle$$

and expand

$$(1 + \frac{i}{\hbar}\hat{H}\Delta t)|\psi(t+\Delta t)\rangle = |\psi(t)\rangle$$

or

$$|\psi(t+\Delta t)\rangle = \frac{1}{(1+\frac{i}{\hbar}\hat{H}\Delta t)}|\psi(t)\rangle \tag{9}$$

This is stable for any Δt because the moduli of the eigenvalues, $1/(1 - i\epsilon_n\Delta t/\hbar)$, for the operator are all smaller than one, $1/\sqrt{(1+(\epsilon_n\Delta t/\hbar)^2} < 1$. The solution does not increase uncontrolled but the method becomes implicit.

However, both operators in eqns (8) and (9) do not have the important unitary property of the exact evolution and the norm of the wave function will not be conserved. This is a major drawback. To obtain a unitary operator we make the following symmetric construction

$$\exp\,(\frac{i}{2\hbar}\hat{H}\Delta t)|\psi(t+\Delta t)\rangle = \exp\,(-\frac{i}{2\hbar}\hat{H}\Delta t)|\psi(t)\rangle$$

and expand to obtain Cayley's form (cf. chapter 19.2 in [1])

$$(1+\frac{i}{2\hbar}\hat{H}\Delta t)|\psi(t+\Delta t)\rangle = (1-\frac{i}{2\hbar}\hat{H}\Delta t)|\psi(t)\rangle$$

or

$$|\psi(t+\Delta t)\rangle = \frac{(1-\frac{i}{2\hbar}\hat{H}\Delta t)}{(1+\frac{i}{2\hbar}\hat{H}\Delta t)}|\psi(t)\rangle \tag{10}$$

This is unitary and therefore unconditionally stable. The error in the time propagation will only accumulate in the phase, not in the absolute value of the wave function. It is also second order accurate in time which is one more power compared with eqns (8) and (9).

By combining Cayley's form for the short-time propagator together with the finite difference approximation in evaluating the Hamiltonian acting on a state vector the so called Crank-Nicholson method is obtained.

Split operator FFT method A somewhat different approach has been developed based on a scheme where the short-time propagator is split into different parts. Consider the propagator in eqn (7). We split it into two parts according to

$$\exp\,(-\frac{i}{\hbar}(\hat{T}+\hat{V})\Delta t) = \exp\,(-\frac{i}{\hbar}\hat{T}\Delta t)\ \exp\,(-\frac{i}{\hbar}\hat{V}\Delta t) + O(\Delta t^2) \tag{11}$$

where the error is due to that $\hat{T}$ and $\hat{V}$ do not commute. This propagator is strictly unitary. Higher order accuracy can be obtained by making the following symmetric decomposition

$$\exp\,(-\frac{i}{\hbar}(\hat{T}+\hat{V})\Delta t) = \exp\,(-\frac{i}{2\hbar}\hat{T}\Delta t)\ \exp\,(-\frac{i}{\hbar}\hat{V}\Delta t)\ \exp\,(-\frac{i}{2\hbar}\hat{T}\Delta t)+O(\Delta t^3) \tag{12}$$

The Fourier method is then used to evaluate the propagators. By using the fast Fourier transform (FFT) technique the method becomes numerically very efficient.

For motion in one dimension one time-step is obtained from the following formula

$$\begin{aligned}\psi(x,t+\Delta t) &= \langle x|\exp(-\frac{i}{\hbar}\hat{T}\Delta t)\exp(-\frac{i}{\hbar}\hat{V}\Delta t)|\psi(t)\rangle \\ &= \int dx'\langle x|\exp(-\frac{i}{\hbar}\hat{T}\Delta t)|x'\rangle\exp(-\frac{i}{\hbar}V(x')\Delta t)\ \psi(x',t) \\ &= \int dp'\int dx'\langle x|p'\rangle\exp(-\frac{i}{\hbar}\frac{p'^2}{2m}\Delta t)\langle p'|x'\rangle\exp(-\frac{i}{\hbar}V(x')\Delta t)\ \psi(x',t) \\ &= \mathcal{F}^{-1}\left[\exp(-\frac{i}{\hbar}\frac{p'^2}{2m}\Delta t)\ \mathcal{F}\left[\exp(-\frac{i}{\hbar}V(x')\Delta t)\ \psi(x',t)\right]\right]\end{aligned}$$

where $\mathcal{F}$ denotes the Fourier transform. The coordinate space is discretized

$$x_j = x_0 + j\Delta x; \quad j = 0, ..., N-1$$

and the Fourier transform becomes discrete (cf. chapter 12.1 in [1])

$$\psi_m = \sum_{j=0}^{N-1}\exp(-ik_m x_j)\ \psi_j$$

where

$$k_m = (m - \frac{N}{2})\ \Delta k; \quad m = 0, ..., N-1$$

and

$$\Delta k = \frac{2\pi}{N\Delta x}$$

The method is implemented in the following way:

- The wave function $\psi_j(t)$ is given on a grid.
- It is multiplied by $\exp[-(i/\hbar)V_j\Delta t]$ and a discrete Fourier transform is performed.
- The Fourier transformed wave function is multiplied by $\exp[-(i/\hbar)(\hbar^2 k_m^2/2m)\Delta t]$ and an inverse discrete Fourier transform is performed.
- The wave function in coordinate space is now obtained at the next time step $\psi_j(t+\Delta t)$ and the procedure is repeated.

Typically the number of grid points is of the order 100 in each dimension. For a three dimensional problem this implies 10^6 grid points. Straightforward evaluation of the discrete Fourier transform leads to N^2 complex

multiplications (for each m you have to do N multiplications). Using a fast Fourier transform (FFT) routine (see chapter 12 in [1]) this number is reduced to $N \log_2 N$. The difference between N^2 and $N \log_2 N$ is immense. With $N = 10^6$ and with a Mflops (million floating points operations per second) computer we have that $N^2 \sim 10^6$ seconds $\sim$ 278 hours $\sim$ 12 days and $N \log_2 N \sim 20$ seconds, respectively.

Dynamics with electronic transitions

We have up to now considered the motion on a single potential energy surface. For instance, that could correspond to atomic motion on the adiabatic potential energy surface, the potential energy surface corresponding to the ground-state of the electronic degrees of freedom. Important quantum effects are then tunneling, interference and level quantization. Another important quantum effect is connected to electronic transitions to excited states. Within the Born-Oppenheimer approximation for separating the nuclear and electronic degrees of freedom these are excluded. When a transition between electronic states occurs, the forces experienced by the atoms changes, often dramatically. Proper incorporation of this effect is crucial in many physical, chemical and biological processes.

If two electronic states are relevant the state-vector has to include two components

$$|\psi(t)\rangle = \begin{bmatrix} |\psi_1(t)\rangle \\ |\psi_2(t)\rangle \end{bmatrix} \tag{13}$$

For motion in one-dimension the Hamiltonian $\hat{H} = \hat{T} + \hat{V}$ is generalized to a 2x2 matrix with

$$\hat{T} = \begin{bmatrix} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} & 0 \\ 0 & -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \end{bmatrix} \tag{14}$$

and

$$\hat{V} = \begin{bmatrix} V_{11}(x) & V_{12}(x) \\ V_{21}(x) & V_{22}(x) \end{bmatrix} \tag{15}$$

Here the diabatic representation is used and $V_{11}(x)$ and $V_{22}(x)$ are the two diabatic potential energy surfaces. The coupling between the two different surfaces is given by the nondiagonal terms.

An important model case that contains two electronic states is the so called *curve crossing* problem. It could for instance describe the neutral and ionic states for an atom approaching a solid surface. Close to the surface the ionic state may be lowest in energy while further away from the surface the neutral state is lower. At some distance these two diabatic curves then have to cross each other.

Consider for simplicity the following model system. In the diabatic representation the potential energy is given by the expressions

$$V_{11}(x) \;\; = \;\; a\,[2 - \exp(-x/b)], \quad x > 0$$

$$
\begin{aligned}
V_{11}(x) &= a\ \exp(x/b), \quad x < 0 \\
V_{22}(x) &= 2a - V_{11}(x) \\
V_{12}(x) &= V_{21}(x) = c\exp(-(x/d)^2)
\end{aligned}
$$

The two curves $V_{11}(x)$ and $V_{22}(x)$ cross each other at x=0. In the adiabatic representation, where $\hat{V}$ is diagonal, there will be a splitting around $x = 0$ between the ground state and the excited state. The magnitude of the splitting depends on the strength of the coupling $V_{12}(x)$. If the coupling strength is large the splitting is also large and the probability for a transition between the adiabatic states becomes small. An analytical expression for this transition probability has been derived under certain assumptions by Landau [2], Zener [3] and Stückelberg [4].

Task

1. Consider a hydrogen atom with mass m. Assume that it is described by a Gaussian wave packet

$$\psi(x) = (\frac{1}{\pi d^2})^{1/4} \exp[-\frac{(x-x_0)^2}{2d^2}] \exp[ip_0(x-x_0)/\hbar]$$

   with the width d=0.5 Å. The magnitude of the mean momentum p_0 is such that $p_0^2/2m = 0.1eV$. A suggestion is to use Å, fs and eV as units for length, time and energy, respectively. What are then m and $\hbar$ in these units? Determine the probability density $n(x) = |\psi(x)|^2$ and the corresponding density in momentum space numerically using a FFT routine. Compare with the analytical results and convince yourself that the Fourier transformation is done correctly. (2p)

2. Consider now the motion of the hydrogen atom in the previous exercise. Assume that it is moving as a free particle and determine the time-evolution numerically using the split-operator FFT method. Visualize your results. Determine the time-evolution of the width of the Gaussian wave packet both in real and momentum space. You can compare with the analytical results (see for instance Ref. [5] which is available electronically at the Chalmers library). (2p)

3. Consider now the scattering against a one-dimensional Eckart barrier described by the expression

$$V(x) = V_0 \cosh^{-2}(x/\alpha)$$

   using the Gaussian wave packet from the previous exercises. Assume that V_0=0.1 eV and consider two cases for the width, α=0.5 Å and α=2.0 Å. Solve the scattering problem using the split-operator FFT

method for three cases; $p_0^2/2m$=0.08 eV, 0.10 eV and 0.12 eV. Determine the following integrated probability densities

$$n_<(t) = \int_{-\infty}^{0} |\psi(x,t)|^2 dx$$

and

$$n_>(t) = \int_{0}^{\infty} |\psi(x,t)|^2 dx$$

which can be used to determine the transmission and reflection probabilities. Interpret your results. (4p)

4. Consider now the curve crossing problem and the model system described in the text. Use the following numbers for the parameters that enter in the potential: $a = 0.3$ eV, $b = 0.4$ Å, $d = 0.7$ Å. Consider two cases for the coupling strength: $c = 0.05$ eV and $c = 0.1$ eV, respectively. Determine the adiabatic states by diagonalizing the matrix $\hat{V}$ and plot your results both for the diabatic and adiabatic surfaces, for the two different coupling strength. If a *classical* particle is moving on the adiabatic ground state it will be reflected at the crossing point for energies $E < E_0$. How large is E_0 for the two different coupling strengths? (1p)

5. Consider now a quantum particle which is represented initially by a Gaussian wave-packet. Locate it to the left of the crossing point with momentum in the positive direction. Assume the mass to be given by the proton mass. Choose the width of the wave-packet such that the initial energy spread is about ± 10 % of the initial energy. Consider energies in the range $0 < E < 5a$. A quantum particle with $E < E_0$ can tunnel and there is a finite probability for transmission on the adiabatic ground state. For $E > E_0$ the probability for transmission is not unity due to non-classical reflection. The upper adiabatic state, the excited state, will also influence the motion of the quantum particle. For not too high energies it can be temporarily trapped in the crossing region and reflected back. At high energies there is also a large probability of transition to and transmission on the upper state.

   Propagate the wave-packet using the split operator fast Fourier transform technique. The following references can be useful when generalizing and implementing the method for a two state system [6, 7, 8]. Study the probabilities for the following processes: (i) transmission on the adiabatic ground state; (ii) reflection on the adiabatic ground state; and (iii) transmission on the upper adiabatic state, the excited state. Interpret your results! (7p)

References

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