CHM452: Problem Set 3

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This problem will guide you through the technical details and the computational implementation of the Split Operator (SO) Method. For the following you will need a good implementation of a Fast Fourier Transform (FFT). Numerical recipes has excellent FFT routines for Fortran and C++. FFT is also readily available in MATLAB. Note that the efficient use of FFT requires a grid with $N = 2^n$ points. Please provide your code with your solutions. Have fun and feel free to explore more than what the problem set asks you to do.

1. Fast Fourier Transform. We first need to learn how to do a FFT. To this end, consider a quantum mechanical wavepacket centered in space around x_0 of width $\sqrt{1/\alpha}$ and net momentum p_0

$$\Psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(x-x_0)^2/2} e^{ip_0(x-x_0)}. \tag{1}$$

   (i) Write a code to represent this wavepacket in a grid and plot it. Choose $x_0 = 0$ and $p_0 = 0$ in the range $x = (-20, 20)$ with $\alpha = 1$ and $\hbar = 1$. Numerically verify that it is normalized, and compute $\langle x \rangle$ and Δx. Contrast your numerical results with the analytical formulas for these basic quantities.

   (ii) Next consider the grid-based representation of this wavepacket in momentum space. Transformation from position to momentum representation is done through a Fourier Transform:

$$\Psi_0(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx e^{-ipx/\hbar} \Psi_0(x) \tag{2}$$

   The FT can be efficiently implemented in $\mathcal{O}(N \log(N))$ steps, when $\Psi_0(x)$ is represented on a grid with $N = 2^n$ points where n is an integer by using the FFT algorithm. By contrast, the implementation of the FT by quadrature integration would require $\mathcal{O}(N^2)$ steps.
   Write a code to represent the initial state $\Psi_0(x)$ in momentum space by applying the FFT algorithm to the grid representation of $\Psi_0(x)$ in the previous problem. Plot your result in the range $p = (-4, 4)$ and compare your output with the corresponding value obtained from the analytic Fourier transform obtained by using $\int dx \exp(-a_2 x^2 + a_1 x + a_0) = \sqrt{\pi/a_2} \exp(a_0 + a_1^2/(4a_2))$. Numerically verify that it is normalized, and compute $\langle p \rangle$ and Δp in momentum space. Contrast your numerical results with the analytical formulas for these basic quantities.

   (iii) Previously, we learned how to represent operators in a position grid. In particular, we worked out methods to express the kinetic energy in position representation in terms of a 3-point stencil and the DVR. Now that you have implemented a FFT, another possibility is to compute operators that are a function of the position operator $\hat{x}$ in position space, and compute the ones that are functions of the momentum operator $\hat{p}$ in momentum space. In this way, each class of operators will be represented by diagonal matrices and their computation is simple.
   Consider the initial state in (1) in a harmonic potential $V(\hat{x}) = \frac{1}{2} m\omega^2 (\hat{x} - x_0)^2$, with $x_0 = 0$, $p_0 = 0$, $\alpha = \omega m = 1$, and $m = \hbar = 1$. Write code to calculate the expectation value of the potential $V(\hat{x})$ operator in position representation and the kinetic energy operator $T = \langle \Psi_0 | \frac{\hat{p}^2}{2m} | \Psi_0 \rangle$ in momentum representation. Compute the expectation value of the energy and compare your result with the zero-point energy $E_0 = \omega/2$.

2. Single-Surface SO method. We now have all the essential elements to implement the split operator method.

   (i) Using the symmetric version of the evolution operator for a given time step

   $$\hat{U}(t+\Delta t,t) = e^{-i\hat{H}(t)\Delta t/\hbar} \approx e^{-i\hat{V}(t)\Delta t/2\hbar} e^{-i\hat{T}\Delta t/\hbar} e^{-i\hat{V}(t)\Delta t/2\hbar}, \tag{3}$$

   write a code that propagates the initial state $\Psi_0(x)$ in the harmonic potential above for 1000 time steps of $\Delta t = 0.1$ a.u. Use $x_0 = -2.5$, $p_0 = 0$. For each step compute the expectation value of the position $\hat{x}$, momentum $\hat{p}$ and Hamiltonian operator. Compare your calculations with the analytical solution for $\langle\hat{x}(t)\rangle$ and $\langle\hat{p}(t)\rangle$ for the Harmonic Oscillator. Plot the energy as a function of time and make sure that your method is conservative. Construct a movie of the wavepacket motion and make sure that everything makes sense. Provide the movie as part of your solution.

   This is how a single propagation time step from $t_k \to t_{k+1}$ should look like in your implementation:

   1. Represent $\Psi(x,t)$ and $e^{-iV(x,t)\Delta t/2\hbar}$ as a column (or row) array of numbers associated with a grid of N equally spaced coordinates $x_j = x_{\min} + (j-1)\Delta x$ with finite resolution $\Delta x = (x_{\max} - x_{\min})/(N-1)$.
   2. At time $t_k = k\Delta t$, apply the potential energy part of the Trotter expansion $e^{-iV(x,t_k)\Delta t/2\hbar}$ to $\Psi(x,t_k)$ by simple multiplication of array elements

   $$\tilde{\Psi}(x_j,t_k) = e^{-iV(x_j,t_k)\Delta t/2\hbar}\Psi(x_j,t_k) \tag{4}$$

   3. Fourier transform $\tilde{\Psi}(x_j,t_k)$ to obtain $\tilde{\Psi}(p_j,t_k)$, and represent the kinetic energy part of the Trotter expansion as an array of numbers $e^{-ip_j^2\Delta t/(2m\hbar)}$ associated with a grid of equally spaced momenta $p_j = \hbar j/(x_{\max} - x_{\min})$.
   4. Apply the kinetic energy part of the Trotter expansion $e^{-ip_j^2\Delta t/(2m\hbar)}$ to the Fourier transform $\tilde{\Psi}(p_j,t_k)$ by simple multiplication of array elements

   $$\tilde{\Psi}'(p_j,t_k) = e^{-ip_j^2\Delta t/(2m\hbar)}\tilde{\Psi}(p_j,t_k) \tag{5}$$

   5. Inverse Fourier transform $\tilde{\Psi}'(p_j,t_k)$ to obtain $\tilde{\Psi}'(x_j,t_k)$ on the grid of equally spaced coordinates x_j.
   6. Apply the potential energy part of the Trotter expansion $e^{-iV(x,t_k)\Delta t/2\hbar}$ to $\tilde{\Psi}'(x_j,t_k)$ by simple multiplication of array elements to obtain

   $$\Psi(x_j,t_{k+1}) = e^{-iV(x_j,t_k)\Delta t/2\hbar}\tilde{\Psi}'(x_j,t_k) \tag{6}$$

   (ii) Change the potential to that of a Morse oscillator $V(\hat{x}) = d(1-\exp(-a(\hat{x}-x_e)))^2$ with $x_e = 0$, $d = 8$ and $a = \sqrt{k/2d}$ where $k = m\omega^2$. Recompute the wave packet propagation with $x_0 = 0.5$ and $p_0 = 0$ for 1000 time steps with $\Delta t = 0.1$ a.u. For each step compute the expectation value of the position $\hat{x}$, momentum $\hat{p}$ operator and Hamiltonian, and plot their dynamics. Construct a movie of the wavepacket motion and provide it as part of your solution.

   (iii) Find the ground eigenstate of such Morse oscillator by propagation in imaginary time and renormalizing your solution every few time steps. Compare the final state that you obtained with this method with the ground eigenstate computed using the DVR method that you coded up for PS2.

   (iv) Simulate the propagation of a wavepacket with $x_0 = -5.5$ and initial momentum $p_0 = 2$ colliding with a barrier potential $V(x) = 3$ if $|x| < 0.5$ and $V(x) = 0$ otherwise. Hint: In order to avoid artificial recurrences you might need to add an absorbing imaginary potential $V_a(x) = i(|x| - 10)^4$ if $|x| > 10$ and $V_a(x) = 0$ otherwise. Construct a movie of the wavepacket motion.

3. Split Operator Method on Multiple Surfaces. The goal now is to generalize your implementation to the description of quantum dynamics on multiple coupled potential energy surfaces. For the sake of definitiveness, we will focus on a two-surface molecular Hamiltonian in interaction with a laser field $E(t)$

$$\hat{H}(t) = \frac{\hat{p}^2}{2m} + V_1(\hat{x})|1\rangle\langle 1| + V_2(\hat{x})|2\rangle\langle 2| + V_{12}(\hat{x},t)|1\rangle\langle 2| + V_{21}(\hat{x},t)|2\rangle\langle 1|. \tag{7}$$

As a model of the potential energy surfaces focus on the one-dimensional displaced harmonic oscillator model. In this model, the PES are harmonic potentials with minimum energy configurations that are displaced from one another. In this case, $V_1 = \frac{1}{2}K_1(x-x_1)^2$, $V_2 = \hbar\omega_0 + \frac{1}{2}K_2(x-x_2)^2$ where K_n $(n=1,2)$ is the force constant and x_n $(n=1,2)$ indicates the equilibrium nuclear geometry of the nth diabatic potential energy surface. The two surfaces are coupled via diabatic couplings λ_0 and photoexcitation. That is

$$V_{12} = \lambda_0 - \mu_{12}E(t). \tag{8}$$

Here μ_{12} is the transition dipole in the Condon approximation and $E(t)$ the electric field of light. As model parameters use $m = 86.65\,\text{eV}\cdot\text{fs}^2$, $\hbar\omega_0 = 0.44\,\text{eV}$, $K_{1,2} = 0.02\,\text{eV}$, $x_1 = -8.67$ and $x_2 = 5.62$, and $\lambda_0 = 0.19\,\text{eV}$. In this case, $\hbar = 0.6582$ eV fs.

The computational task is to implement the SO method to compute the time-dependent wavepacket

$$|\Psi(x,t)\rangle = \chi_1(x,t)|1\rangle + \chi_2(x,t)|2\rangle, \tag{9}$$

given the initial conditions $\chi_1(x,0)$ and $\chi_2(x,0)$. Here $\chi_i(x,t)$ is the time-dependent nuclear wavepacket component associated with the electronic state $|i\rangle$. In this problem, it is convenient to use the following Trotter expansion of the propagation operator:

$$\begin{aligned}
&\exp\left[-\frac{i}{\hbar}\begin{pmatrix} T+V_1 & V_{12} \\ V_{21} & T+V_2 \end{pmatrix}\Delta t\right] = \\
&\quad \exp\left[-\frac{i}{\hbar}\begin{pmatrix} T & 0 \\ 0 & T \end{pmatrix}\frac{\Delta t}{2}\right]\exp\left[-\frac{i}{\hbar}\begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}\Delta t\right]\exp\left[-\frac{i}{\hbar}\begin{pmatrix} T & 0 \\ 0 & T \end{pmatrix}\frac{\Delta t}{2}\right] \\
&\quad + O\left(\Delta t^3\right)
\end{aligned} \tag{10}$$

Note that the potential component, instead of the kinetic energy component, is in the middle.

The difficulty in using the SO method in this case is that the potential component is no longer diagonal. Therefore the coordinate space wavefunction has to be transformed into a representation in which the potential is diagonal. In general this can be done through numerical diagonalization. For two electronic states this can be performed analytically (Schwendner *et al.* Chem. Phys. Lett. **217**, 233 (1977)).

Let $\hat{U}$ be a unitary transformation that diagonalizes the potential component of the Hamiltonian. Since the V matrix is coordinate dependent, so is the transformation matrix $\hat{U}$. For two surfaces:

$$\begin{aligned}
&\exp\left[-\frac{i}{\hbar}\begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}\Delta t\right] \\
&= \hat{U}\exp\left[-\frac{i}{\hbar}\hat{U}^\dagger\begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}\hat{U}\Delta t\right]\hat{U}^\dagger = \hat{U}\begin{pmatrix} e^{-\frac{i}{\hbar}\lambda_1\Delta t} & 0 \\ 0 & e^{-\frac{i}{\hbar}\lambda_2\Delta t} \end{pmatrix}\hat{U}^\dagger \\
&= \exp\left[-\frac{i}{\hbar}(V_1+V_2)\frac{\Delta t}{2}\right]\left[\cos\left(\sqrt{D}\frac{\Delta t}{2\hbar}\right)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + i\frac{\sin\left(\sqrt{D}\frac{\Delta t}{2\hbar}\right)}{\sqrt{D}}\begin{pmatrix} V_2-V_1 & -2V_{12} \\ -2V_{21} & V_1-V_2 \end{pmatrix}\right]
\end{aligned} \tag{11}$$

where $D = 4|V_{21}|^2 + (V_1 - V_2)^2$.

(i) Verify the validity of Eq. (11).

(ii) Extend your split operator method to be able to deal with a two-surface Hamiltonian. As a first case, focus on the dynamics in the absence of a laser field ($E(t) = 0$) when the system is initially prepared in a superposition:

$$|\Psi(0)\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \otimes |\chi_0\rangle \tag{12}$$

where

$$\chi_0(x) = \left(\frac{1}{\pi}\right)^{\frac{1}{4}} e^{-(x-x_1)^2/2}. \tag{13}$$

Define your grid in the [-24.4, 35.6] range with $N = 512$ or 1024. Find an appropriate Δt to capture the dynamics. Check your dynamics by plotting the energy as a function of time, and making sure that your results are invariant with respect to the propagation time step, number of grid points and grid interval. Construct a movie of the resulting wavepacket evolution and characterize your dynamics by plotting the time-dependence of the nuclear wavepacket overlap $S_{12}(t) = |\langle\chi_1(x,t)|\chi_2(x,t)\rangle|^2$.

Qualitatively interpret your dynamics in terms of wavepacket motion in potential energy surfaces.

(iii) Now consider the case in which the molecule is prepared in the ground state and subsequently photoexcited. As an initial state, take the molecule to be prepared in the ground state of the ground diabatic surface:

$$|\Psi(0)\rangle = |1\rangle|\chi_0\rangle \tag{14}$$

Consider now excitation with a 10 fs laser pulse

$$E(t) = E_0 e^{-\frac{(t-t_c)^2}{t_w^2}} \cos(\omega(t - t_c)) \tag{15}$$

where E_0 is the laser amplitude, $t_w = 10\,\text{fs}$ and $t_c = 50\,\text{fs}$. The central frequency of the laser pulse is chosen to be at resonance with the vertical transition from the ground configuration, i,.e. $\hbar\omega = (V_2(x_1) - V_1(x_1)) = 2.48\,\text{eV}$. As laser amplitude use $E_0\mu_{12} = 0.2eV$.

Find an appropriate Δt to capture the dynamics. Check your dynamics by plotting the energy as a function of time, and making sure that your results are invariant with respect to the propagation time step, number of grid points and grid interval. Construct a movie of the resulting wavepacket evolution and characterize your dynamics by plotting the time-dependence of the nuclear wavepacket overlap $S_{12}(t) = |\langle\chi_1(x,t)|\chi_2(x,t)\rangle|^2$.

Qualitatively interpret your dynamics in terms of wavepacket motion in potential energy surfaces.