# Numerical methods to solve the Time-Dependent Schrodinger Equation

Author : Samyak Jain

200260046

Supervisor : Professor Alok Shukla

July 2021

## 1 Introduction

Through this report I discuss the key concepts I covered in the SURP (Summer Undergraduate Research Program) 2021 under Professor Alok Shukla.
The main problem addressed in the project was to propagate a wave function forward in time, provided the initial wave function is given. The initial wave function can be either in terms of values at discrete points, or as a function of spatial coordinates.

## 2 Method of finite differences

The time dependent tdse in atomic units reads :

$$i\frac{\partial\psi}{\partial t} = -\frac{1}{2}\frac{\partial^2\psi}{\partial x^2} + V\psi$$

Let's say at t = 0, we are given the values of the wave function and the potential at $x_1 = a, x_2 = 2a.....x_n = na$ as $c_1, c_2...c_n$ and $V_1, V_2...V_n$.
We approximate the second order derivative at $x_j$ as

$$\frac{\partial^2 c_j}{\partial x^2} = \frac{c_{j+1} - 2c_j + c_{j-1}}{\Delta x^2} + O(\Delta x^2)$$

Assuming the boundary conditions to be zero, in matrix notation, this gives us :

$$i\frac{\partial\bar{\psi}}{\partial t} = -\frac{1}{2}A\bar{c} + \bar{V}\bar{\psi}$$

where

$$\bar{c} = \begin{bmatrix} c_1 \\ c_2 \\ . \\ . \\ . \\ c_n \end{bmatrix}$$

$$\bar{\psi} = \begin{bmatrix} \psi_1 \\ \psi_2 \\ . \\ . \\ . \\ \psi_n \end{bmatrix}$$

$\bar{V}$ is the diagonal matrix with entries as $V_1, V_2....V_n$

$A$ is the n*n matrix with all diagonal entries as 2 and all the super-diagonal and sub-diagonal entries as -1.

Therefore we have a set of n differential equations, which can be solved while using the initial conditions to propagate the wave-function forward in time.

# 3 Pseudo-spectral methods

These methods take advantage of the fact that the kinetic energy operator is linear in k-space. We have the same notations as before.
We use a discrete fourier-transform to transport our data points at t = 0 to k-space. Since $p$ and$k$ are related by

$$p = \bar{h}k$$

and in k-space, the kinetic energy operator ($D(k)$) for an electron is $\frac{p^2}{2}$ (in atomic units) we have :

$$i\frac{\partial \psi}{\partial t} = F^{-1}D_k F\bar{\psi} + \bar{V}\bar{\psi}$$

Here $D_k$ is the kinetic energy operator in the k-space. It takes the form of a diagonal matrix as diag($\frac{p^2}{2m}$). We transport our data back to k-space using an inverse fourier transform. These operations can be done using fft (fast fourier transform) in MATLAB.

# 4 Split-Operator method

For a time-independent hamiltonian, one can calculate $\psi(t)$ to be :

$$\psi(r, t + \Delta t) = e^{-iHt}\psi(r, t)$$

If the hamiltonian is time dependent, we can use the second order Magnus expansion to approximate the solution as :

$$\psi(r, t + \Delta t) = e^{-i\int_t^{t+\Delta t} H(t)dt}\psi(r, t)$$

The integral is approximated as $(H(t + \Delta t) - H(t))\Delta t$, which is second order accurate in time. In the split-operator method, we split the hamiltonian into T and V (the kinetic energy and potential energy matrices respectively), which do not necessarily commute. However we can approximate the equation as

$$\psi(r, t + \Delta t) = \psi(r, t)e^{-iT\Delta t/2}e^{-iV\Delta t}e^{-iT\Delta t/2}\psi(r, t)$$

Pairing this method with the pseudo-spectral method makes for an n-efficient method.

# 5 Multi-Projection Approach

The initial conditions required for this approach is the initial wavefunction $\psi_o$ and the Hamiltonian $H(t)$ as a function of time.
We split the hamiltonian into two parts :

$$H(t) = H_o + V(t)$$

We write the wave function at a time $t$ as a linear combination of eigen-functions of the initial hamiltonian :

$$\psi(t) = \Sigma C_j(t)e^{-iw_j t}W_j(t)$$

where $W_j$ are eigen-functions of the initial Hamiltonian with eigen-values $E_j$ and $w_j = \frac{E_j}{\hbar}$.
The analytical solution of the TDSE reads :

$$\psi(t_j) = e^{-i\int_{t_{j-1}}^{t_j} H(t)dt}\psi(t_{j-1})$$

We define :

$$\hat{H}_j = \frac{H(t_{j-1} + H(t_j)}{2}$$

And approximate the equation as :

$$\psi(t_j) = e^{-i\hat{H}_j\Delta t}\psi(t_{j-1})$$

For each $\hat{H}_j$, we define eigen-functions $W_k^j$ such that :

$$\hat{H}_j W_k^j = E_k^j W_k^j$$

If we know $psi(t_{j-1})$, we can calculate $\psi(t_j)$ as :

$$\psi(t_j) = \Sigma C_k^j e^{-iw_k^j \Delta t_j} W_j^k(r)$$

where we can calculate $C_k^j$ as :

$$C_k^j = \int \psi(t_{j-1}) W_k^{j^*} dr$$

Hence we can project the initial wave-function to any time by projecting it through multiple time-steps.

# 6 Time-Evolution operator and the The Cayley-Crank-Nicolson Algorithm

We define

$$\psi(t) = U(t, t_o)\psi(t_o)$$

Here $U(t, t_o)$ is the called as the time evolution operator. Plugging this into the TDSE, we get :

$$U(t, t_o) = 1 - i \int_{t_o}^{t} H(t) U(t, t_o) dt$$

This operator is unitary and we can derive the Cayley approximation of the Crank-Nicolson Algorithm :

$$(1 + i \int_{t+\frac{\Delta t}{2}}^{t+\Delta t} H(t')dt')\psi(t + \Delta t) = (1 - i \int_{t}^{t+\frac{\Delta t}{2}} H(t')dt')\psi(t)$$

Same as the finite differences method, we consider that we have the wave-function at different points in a grid at time $t_o$. We use the finite-difference approximation to define the hamiltonian matrix same as before :

$$H = \frac{A}{2} + diag(V_1(t), V_2(t)...V_n(t))$$

Here A is the matrix with diagonal entries as 2, subdiagonal and superdiagonal entries as 1. $V_i$ represents the velocity at the point $x_i$ in our grid as a function of time.
Defining

$$P^{(-)}(t, \frac{\Delta t}{2}) = I + i \int_{t+\frac{\Delta t}{2}}^{t+\Delta t} H(t')dt'$$

$$P^{(+)}(t, \frac{\Delta t}{2}) = I - i \int_{t}^{t+\frac{\Delta t}{2}} H(t')dt'$$

Representing the initial condition $\psi(t)$ as a column vector, we have :

$$P^{(-)}(t, \frac{\Delta t}{2})\psi(t + \Delta t) = P^{(+)}(t, \frac{\Delta t}{2})\psi(t)$$

Using this, one can project the wave-function forward by the time interval $\Delta t$. To simplify the calculation, one can approximate the integral by considering the hamiltonian to be constant for a single time step.

# 7 Bibliography


- Chen, C. Y. "A general procedure for solving the time-dependent Schrödinger equation." Journal of Physics A: Mathematical and General 35.31 (2002): 6589.
- Viklund, Lina, Louise Augustsson, and Jonas Melander. "Numerical approaches to solving the time-dependent Schrödinger equation with different potentials." (2016).
- Becerril, R., et al. "Solving the time-dependent Schrödinger equation using finite difference methods." Revista mexicana de física E 54.2 (2008): 120-132.
- Scientific Computing Department, STFC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK. (2020, June 2). Solving the Time-Dependent Schrödinger Equation. https://www.scd.stfc.ac.uk/SiteAssets/Pages/Solving-the-TDSE/Solving%20the%20TDSE%20.pdf