Notes on Discretization of Schrödinger equation

A. Bertoni, T. Serafini

April 14, 2009

Abstract

1 Notation

Let f be a functional $f : R^n \mapsto C$.

$$F = \bigtriangledown f = \mathrm{grad}(f) = (F_1, \cdots, F_n) = \left(\frac{\partial f}{\partial x_1}, \cdots, \frac{\partial f}{\partial x_n}\right)$$

$$div(F) = \bigtriangledown \cdot F = \frac{\partial F}{\partial x_1} + \cdots + \frac{\partial F}{\partial x_n}$$

$$\bigtriangledown^2 f = \bigtriangledown \cdot \bigtriangledown f = \frac{\partial^2 f}{\partial x_1^2} + \cdots + \frac{\partial^2 f}{\partial x_n^2}$$

2 Scrödinger equation

We want to solve the time-dependent Scrödinger equation on a domain with Dirichlet boundary conditons, starting from the wave function $\psi(0)$ at the initial time. The equation is:

$$i\hbar \frac{\partial}{\partial t}\psi(t) = H\psi(t)$$

where $H = -\frac{\hbar^2}{2m^*}\partial_x^2 + V(x)$. The equation can be rewritten as:

$$\frac{\partial \psi}{\partial t} = \beta \bigtriangledown G + v\psi \quad (1)$$

$$G = \bigtriangledown \psi \quad (2)$$

$$\psi \in D, \quad \psi = g \text{ on } \partial D$$

where $\beta = -\frac{1}{i\hbar}\frac{\hbar^2}{nm^*} = i\frac{\hbar}{2m^*}$ and $v = \frac{1}{i\hbar}V = -\frac{i}{\hbar}V$

3 Box Integration Method

We start by semidiscretizing the Scrödinger equation in the space. We work on a special case where the domain is a box and the dicretization grid is orthogonal and separable. For simplicity we are going to consider a 2D grid, but the discretization can easily be extedned to a higher dimensional domain.

Figure 1: Single box scheme

Let $D = [x_0, x_{n+1}] \times [y_0, y_{m+1}]$ be a quare domain. Let $x_0 < x_1 < \cdots < x_{n+1}$ and $y_0 < y_1 < \cdots < y_{m+1}$ be the coordinates of an orthogonal grid. We will have nm internal nodes in which the function ψ is unknown. The function $\psi(x, y, t)$ in the points where $x = x_0$ or $x = x_{n+1}$ or $y = y_0$ or $y = y_{m+1}$ is known thanks to the Dirichlet boundary contitions. We consider a vertex-centered Box Integration Method: this means that we divide the domain D into nm boxes $C_{ij} = [\frac{x_i - x_{i-1}}{2}, \frac{y_i - y_{i-1}}{2}] \times [\frac{x_{i+1} - x_i}{2}, \frac{y_{i+1} - y_i}{2}]$. If we call $a_i = x_i - x_{i-1}, \quad i = 1, \cdots, n+1$ and $b_j = y_j - y_{j-1}, \quad j = 1, \cdots, m+1$, a box C_{ij} has area $s_{ij} = \frac{a_i + a_{i+1}}{2} \frac{b_i + b_{i+1}}{2}$. In the Box Integration Method we integrate the equation on each box C_{ij}:

$$\int_{C_{ij}} \frac{\partial \psi}{\partial t} ds = \beta \int_{C_{ij}} \bigtriangledown G ds + \int_{C_{ij}} v\psi ds$$

The three integrals can be approximated as follow:

$$\int_{C_{ij}} \frac{\partial \psi}{\partial t} ds \approx s_{ij} \frac{d\psi}{dt}(x_i, y_j, t) \tag{3}$$

$$\int_{C_{ij}} v\psi ds \approx s_{ij}(v\psi)(x_i, y_j, t) \tag{4}$$

$$\int_{C_{ij}} \bigtriangledown G ds = \oint_{\partial C_{ij}} G\bar{\boldsymbol{n}} dl \approx (G_e \bar{\boldsymbol{n}}_e + G_n \bar{\boldsymbol{n}}_n + G_w \bar{\boldsymbol{n}}_w + G_s \bar{\boldsymbol{n}}_s) \tag{5}$$

where $\bar{\boldsymbol{n}}_e, \bar{\boldsymbol{n}}_n, \bar{\boldsymbol{n}}_w, \bar{\boldsymbol{n}}_s$ are the vectors normal to the four edges of the box, whose modulus is equal to the lenght of the edge (area of the surface in the 3D case), and G_e, G_n, G_w, G_s are gradients in the mid point of each edge, as shown in Figure.

Let $y \in R^{nm}$ be the space-discretized wave function: $y_{ij}(t) = \psi(x_i, y_i, t)$. For ease of notation, we sometimes repreent an element of y with a double index (y_{ij}): this implicitly means that we are accessing the element y_{im+j}, i.e. the vector y is a column-wise representation of the space-dicretization of ψ. Usign a centered difference formula, the gradient values can be aproximated from the y values on the nodes and the approximation of integral 5 becomes:

$$\frac{y_{i,j} - y_{i-1,j}}{a_i} \frac{b_j + b_{j+1}}{2} + \frac{y_{i,j} - y_{i+1,j}}{a_{i+1}} \frac{b_j + b_{j+1}}{2} + \frac{y_{i,j} - y_{i,j-1}}{b_j} \frac{a_i + a_{i+1}}{2} + \frac{y_{i,j} - y_{i,j+1}}{b_{j+1}} \frac{a_i + a_{i+1}}{2}$$

Let define

$$k_1 = \frac{b_j + b_{j+1}}{2a_i}, \qquad k_2 = \frac{b_j + b_{j+1}}{2a_{i+1}}$$

$$k_3 = \frac{a_i + a_{i+1}}{2b_j}, \qquad k_4 = \frac{a_i + a_{i+1}}{2b_{j+1}}$$

The approximation of integral 5 becomes:

$$(k_1 + k_2 + k_3 + k_4)y_{i,j} + k_1 y_{i-1,j} + k_2 y_{i+1,j} + k_3 y_{i,j-1} + k_4 y_{i,j+1}$$

If a box is on the boundary of the domain, some of the y terms of the summation are defined by the boundary conditions rather than being unknown. In this case we can group all these terms in one constant term. For example, if $(i, j) = (1, 1)$, then $y_{i-1,j}$ and $y_{i,j-1}$ are on the boundaries and the above expression becomes

$$(k_1 + k_2 + k_3 + k_4)y_{i,j} + k_2 y_{i+1,j} + k_4 y_{i,j+1} + d_{ij}$$

with $d_{ij} = k_1 y_{i-1,j} + k_3 y_{i,j-1}$.

In vector form, these summations can be represented as a scalar product $\boldsymbol{m}_{ij} y + d_{ij}$ with $\boldsymbol{m}_{ij} \in R^{nm}$ and $\boldsymbol{m}_{ij} = (0, \cdots, 0, k_1, 0, \cdots, 0, k_3, k_1 + k_2 + k_3 + k_4, k_4, 0, \cdots, 0, k_2, 0, \cdots, 0)$.

Thus, the Scrödinger equation can be approximately integrated on the box C_{ij} with

$$s_{ij} \frac{dy_{ij}}{dt}(t) = \beta \boldsymbol{m}_{ij} y(t) + s_{ij} v_{ij} y_{ij}(t) + \beta d_{ij}$$

Let $S = \text{diag}(s_{ij})$ and $M = \beta[\boldsymbol{m}_{ij}] + \text{diag}(s_{ij} v_{ij})$: the equation can be written in matrix form:

$$S \frac{d\boldsymbol{y}}{dt}(t) = M\boldsymbol{y}(t) + \beta \boldsymbol{d}$$

The time discretization of the above equation with the trapezoidal rule becomes:

$$S\boldsymbol{y}^{(n+1)} = S\boldsymbol{y}^{(n)} + \frac{M\Delta t}{2}(\boldsymbol{y}^{(n)} + \boldsymbol{y}^{(n+1)}) + \beta \Delta t \boldsymbol{d}$$

or equivalently

$$\left(S - \frac{M\Delta t}{2}\right) \boldsymbol{y}^{(n+1)} = \left(S + \frac{M\Delta t}{2}\right) y^{(n)} + \beta \Delta t \boldsymbol{d}$$