

The Schrödinger equation and wave packets

The numerical solution of the time-dependent Schrödinger equation for a particle of mass m in one dimension

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi + V(x)\psi ,$$

is discussed in Section A.7.2.1 of Thijssen's book. This equation has the formal solution

$$\psi(x, t) = e^{-\frac{i}{\hbar} \mathcal{H} t} \psi(x, 0) , \quad \mathcal{H} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) = \mathcal{H}^\dagger ,$$

where $\mathcal{H}$ is the hermitian Hamiltonian operator. Note that the time evolution is *unitary*, which implies that probability is conserved:

$$\left(e^{-\frac{i}{\hbar} \mathcal{H} t} \right)^\dagger = \left(e^{-\frac{i}{\hbar} \mathcal{H} t} \right)^{-1} , \quad \int |\psi(x, t)|^2 dx = \int |\psi(x, 0)|^2 dx .$$

This can be compared a diffusion-type equation:

$$\frac{\partial}{\partial t} n(x, t) = D \frac{\partial^2}{\partial x^2} n(x, t) + C n(x, t) ,$$

which we encountered in Chapter 12. In contrast to the unitary time evolution of quantum mechanics, diffusion is characterized by *damped* evolution. A mode with wavenumber k is damped like $\sim \exp(-k^2 D t)$, whereas the wavefunction of a free particle with momentum $p = \hbar k$ and energy $E = p^2/(2m)$ behaves $\sim \exp(-i E t/\hbar)$.

We see by comparing the two equations that quantum mechanics of a free particle is mathematically equivalent to diffusion with an *imaginary* diffusion constant $D = i\hbar/(2m)$. The Schrödinger equation can also be considered to represent diffusion in imaginary time:

$$\frac{\partial \psi}{\partial (it)} = \frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} - \frac{1}{\hbar} V(x) \psi ,$$

as we saw in Chapter 12 on Quantum Monte Carlo methods.

Discretization using a Forward Time Centered Space (FTCS) Scheme

To solve this equation, we discretize space $x_j = (j-1)h - L/2$, $j = 1, 2, \dots, N$ in the spatial region $-L/2 \leq x \leq L/2$, and time $t_n = (n-1)\tau$, $n = 1, 2, \dots$, and define $\psi_j^n \equiv \psi(x_j, t_n)$ and $V_j \equiv V(x_j)$.

The discretized equation

$$i\hbar \frac{\psi_j^{n+1} - \psi_j^n}{\tau} = -\frac{\hbar^2}{2m} \frac{\psi_{j+1}^n + \psi_{j-1}^n - 2\psi_j^n}{h^2} + V_j \psi_j^n ,$$

can be solved *explicitly* for the solution at the next time step

$$\psi_j^{n+1} = \psi_j^n - \frac{i\tau}{\hbar} \left[-\frac{\hbar^2}{2m} \frac{\psi_{j+1}^n + \psi_{j-1}^n - 2\psi_j^n}{h^2} + V_j \psi_j^n \right] .$$

If we introduce the column vector of values of ψ

$$\Psi^n \equiv \begin{pmatrix} \psi_1^n \\ \psi_2^n \\ \vdots \\ \psi_N^n \end{pmatrix} ,$$

this equation can be written in matrix form

$$\Psi^{n+1} = \left(\mathbf{I} - \frac{i\tau}{\hbar} \mathbf{H} \right) \Psi^n .$$

Here $\mathbf{I}$ is the $N \times N$ unit matrix, and $\mathbf{H}$ is the discrete matrix representation of the Hamiltonian. Unfortunately, this scheme is *unconditionally unstable*. For example, if Ψ^1 happens to be an eigenvector

$$\mathbf{H}\Psi^1 = E\Psi^1 ,$$

then

$$\Psi^{n+1} = \left(1 - \frac{i\tau E}{\hbar}\right) \Psi^n = \left(1 - \frac{i\tau E}{\hbar}\right)^2 \Psi^{n-1} = \dots = \left(1 - \frac{i\tau E}{\hbar}\right)^n \Psi^1 ,$$

and the magnitude of the wavefunction

$$|\Psi^{n+1}| = \left(\sqrt{1 + \frac{\tau^2 E^2}{\hbar^2}}\right)^n |\Psi^1| \longrightarrow \infty , \quad \text{as } n \rightarrow \infty .$$

Backward Time Space Centered (BTCS) Implicit Differencing

If we choose to discretize the equation as follows

$$i\hbar \frac{\psi_j^{n+1} - \psi_j^n}{\tau} = -\frac{\hbar^2}{2m} \frac{\psi_{j+1}^{n+1} + \psi_{j-1}^{n+1} - 2\psi_j^{n+1}}{h^2} + V_j \psi_j^{n+1} ,$$

then it *cannot* be solved *explicitly* for the solution at the next time step because there are now three unknown quantities on the left hand side of

$$\psi_j^{n+1} + \frac{i\tau}{\hbar} \left[-\frac{\hbar^2}{2m} \frac{\psi_{j+1}^{n+1} + \psi_{j-1}^{n+1} - 2\psi_j^{n+1}}{h^2} + V_j \psi_j^{n+1} \right] = \psi_j^n .$$

We need more equations to find the unknowns $\Psi_j^{n+1}, \Psi_{\pm j}^{n+1}$. In fact we need to use all N equations, which can be written in matrix form

$$\left(\mathbf{I} + \frac{i\tau}{\hbar} \mathbf{H} \right) \Psi^{n+1} = \Psi^n ,$$

in order to obtain the solution at the next time step

$$\Psi^{n+1} = \left(\mathbf{I} + \frac{i\tau}{\hbar} \mathbf{H} \right)^{-1} \Psi^n .$$

It is easy to see that BTCS is *unconditionally stable* by considering an eigenvector of $\mathbf{H}$ with eigenvalue E :

$$\Psi^{n+1} = \left(1 + \frac{i\tau E}{\hbar}\right)^{-1} \Psi^n = \left(1 + \frac{i\tau E}{\hbar}\right)^{-2} \Psi^{n-1} = \dots = \left(1 + \frac{i\tau E}{\hbar}\right)^{-n} \Psi^1 ,$$

which implies that

$$|\Psi^{n+1}| = \left(\sqrt{1 + \frac{\tau^2 E^2}{\hbar^2}}\right)^{-n} |\Psi^1| \longrightarrow 0 , \quad \text{as } n \rightarrow \infty .$$

Unfortunately, this stability implies that probability is not conserved!

Symmetric Time Space Centered (STCS) Crank-Nicolson Differencing

This scheme averages the FTCS and BTCS formulas

$$\Psi^{n+1} = \Psi^n - \frac{i\tau}{2\hbar} \mathbf{H} (\Psi^n + \Psi^{n+1}) ,$$

which leads to the matrix solution

$$\Psi^{n+1} = \left(\mathbf{I} + \frac{i\tau}{2\hbar} \mathbf{H}\right)^{-1} \left(\mathbf{I} - \frac{i\tau}{2\hbar} \mathbf{H}\right) \Psi^n .$$

It is easy to see that this scheme is *unitary*

$$\Psi^{n+1} = \left[\frac{1 - \frac{i\tau E}{2\hbar}}{1 + \frac{i\tau E}{2\hbar}} \right]^n \Psi^1 ,$$

and conserves probability exactly:

$$|\Psi^{n+1}| = |\Psi^1| .$$

An additional advantage of this scheme is that it is one order of magnitude more accurate in time than FTCS or BTCS. Let us write the exact evolution operator for one time step τ schematically as

$$e^{-\frac{i}{\hbar}\mathcal{H}\tau} \equiv e^{-z} = 1 - z + \frac{z^2}{2} - \frac{z^3}{6} + \dots,$$

where $z = \mathcal{O}(\tau)$. The FTCS scheme corresponds to the following approximation

$$1 - z = e^{-z} + \mathcal{O}(\tau^2),$$

while BTCS corresponds to

$$\frac{1}{1+z} = 1 - z + z^2 - z^3 + \dots = e^{-z} + \mathcal{O}(\tau^2),$$

and the Crank-Nicolson scheme to

$$\frac{1}{1+\frac{z}{2}} \left(1 - \frac{z}{2}\right) = \left(1 - \frac{z}{2} + \frac{z^2}{4} - \frac{z^3}{8} + \dots\right) \left(1 - \frac{z}{2}\right) = 1 - z + \frac{z^2}{2} - \frac{z^3}{4} + \dots = e^{-z} + \mathcal{O}(\tau^3).$$

Sparse matrix methods for solving the Schrödinger equation

We have seen that solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi + V(x)\psi.$$

using the Crank-Nicolson algorithm is essentially a matrix inversion problem:

$$\Psi^{n+1} = \left(\mathbf{I} + \frac{i\tau}{2\hbar} \mathbf{H}\right)^{-1} \left(\mathbf{I} - \frac{i\tau}{2\hbar} \mathbf{H}\right) \Psi^n.$$

The standard Gaussian elimination techniques, see Appendix A, section A.8.1 of Thijssen's book, for solving a system of N linear equations for N unknowns, e.g., for finding the inverse of an $N \times N$ matrix, require $\mathcal{O}(N^3)$ operations. Assuming 10^6 operations per second, the CPU time required to evolve the initial wave packet through 1,000 time steps on a lattice with $N = 1,000$ points is 10^6 secs = 11.6 days. Clearly this is unacceptably long.

In fact, the discrete lattice Hamiltonian matrix $\mathbf{H}$ is a *sparse matrix*: most of its elements are zero, and the number of non-zero elements is $\mathcal{O}(N)$ and not $\mathcal{O}(N^2)$. There are very efficient algorithms for manipulation sparse matrices of particular types. These methods are discussed for example in Section 2.4 and Section 2.7 of *Numerical Recipes*.

Dirichlet Boundary Conditions: Tridiagonal Matrix

Let's examine the form of the matrix $\mathbf{H}$ in the case of homogeneous Dirichlet boundary conditions $\psi(\pm L/2, t) = 0$, which would be the appropriate choice for a particle in an infinitely deep potential well. Since the boundary values $\psi_{-1}^n = \psi_{N+1}^n = 0$, the discretized Laplacian operator acting on ψ takes the following form:

$$\left(\frac{\partial^2 \psi}{\partial x^2}\right)_j^n = \frac{1}{h^2} \begin{cases} \psi_2^n - 2\psi_1^n, & \text{for } j = 1 \\ \psi_{j-1}^n + \psi_{j+1}^n - 2\psi_j^n, & \text{for } 1 < j < N \\ \psi_{N-1}^n - 2\psi_N^n, & \text{for } j = N \end{cases}.$$

As an example, if $N = 5$, the form of $\mathbf{H}$ is

$$\mathbf{H}_{\text{Dirichlet}} = -\frac{\hbar^2}{2mh^2} \begin{pmatrix} -2 & 1 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & 1 & -2 \end{pmatrix} + \begin{pmatrix} V_1 & 0 & 0 & 0 & 0 \\ 0 & V_2 & 0 & 0 & 0 \\ 0 & 0 & V_3 & 0 & 0 \\ 0 & 0 & 0 & V_4 & 0 \\ 0 & 0 & 0 & 0 & V_5 \end{pmatrix}.$$

This matrix is *tridiagonal* in form.

Since most of the matrix elements of a large tridiagonal matrix $\mathbf{A}$ are zero, it should be possible to solve a linear equation

$$\mathbf{A}\vec{x} = \vec{b}$$

with much fewer than $\mathcal{O}(N^3)$ operations. The *Thomas algorithm* for doing this is discussed in Section A.8.1.2 of the textbook.

Periodic Boundary Conditions: Cyclic-Tridiagonal Matrix

In the case of *periodic* boundary conditions $\psi(x+L, t) = \psi(x, t)$, which would be appropriate to describe a particle confined to a ring of circumference L , $\psi_{-1}^n = \psi_N^n$ and $\psi_{N+1}^n = \psi_1^n$. In this case,

$$\left(\frac{\partial^2 \psi}{\partial x^2}\right)_j^n = \frac{1}{h^2} \begin{cases} \psi_N^n + \psi_2^n - 2\psi_1^n, & \text{for } j = 1 \\ \psi_{j-1}^n + \psi_{j+1}^n - 2\psi_j^n, & \text{for } 1 < j < N \\ \psi_{N-1}^n + \psi_1^n - 2\psi_N^n, & \text{for } j = N \end{cases}.$$

As an example, if $N = 5$, the form of $\mathbf{H}$ is

$$\mathbf{H}_{\text{Periodic}} = -\frac{\hbar^2}{2mh^2} \begin{pmatrix} -2 & 1 & 0 & 0 & 1 \\ 1 & -2 & 1 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 1 & -2 & 1 \\ 1 & 0 & 0 & 1 & -2 \end{pmatrix} + \begin{pmatrix} V_1 & 0 & 0 & 0 & 0 \\ 0 & V_2 & 0 & 0 & 0 \\ 0 & 0 & V_3 & 0 & 0 \\ 0 & 0 & 0 & V_4 & 0 \\ 0 & 0 & 0 & 0 & V_5 \end{pmatrix}.$$

A matrix of this type is said to be *cyclic-tridiagonal* in form.

A cyclic tridiagonal matrix is very close to being tridiagonal: only the two elements A_{1N} and A_{N1} differ from tridiagonal elements. The *Sherman-Morrison* formula can be used to obtain the solution of a linear equation involving a cyclic-tridiagonal matrix very efficiently in $\mathcal{O}(N)$ operations.