Science and Computers II: Project 4

Numerical Solution of the Schrödinger Equation

The Schrödinger equation for a one-dimensional simple harmonic potential is given by

$$\left(-\frac{\hbar}{2m}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right)\psi = E\psi \tag{1}$$

where $\hbar$ Planck's constant divided by 2π, k is the "spring constant" of the oscillator and E is the energy. There are a number of techniques one can use to numerically solve the one-dimensional Schrödinger equation. In this exercise you will find the eigenvalues and eigenvectors of a hydrogen atom vibrating in this potential.

When dealing with numerical solutions of equations like this, it is often useful to use *dimensionless variables* to eliminate very small numbers (such as $\hbar$) from the numerics. Equation (1) can be made dimensionless by letting

$$\begin{aligned}\hat{x} &= \left(\frac{mk}{\hbar^2}\right)^{\frac{1}{4}} x\\ \hat{E} &= \frac{2}{\hbar}\sqrt{\frac{m}{k}}E\end{aligned}$$

Demonstrate that $\hat{x}$ and $\hat{E}$ are dimensionless and show that when we transform to these variables equation (1) simplifies to

$$\frac{d^2\psi}{d\hat{x}^2}+\left(\hat{E}-\hat{V}\right)\psi = 0. \tag{2}$$

where $\hat{V}=\hat{x}^2$.

For physically acceptable solutions, i.e. those for which $|\psi|^2$ is integrable, we require $\psi \to 0$ as $\hat{x}\to\pm\infty$. This is only possible for certain values of $\hat{E}$ called eigenvalues.

Analytic solutions exist to equation (2) in the form

$$\psi = H_n(\hat{x})\exp\left(-\frac{\hat{x}^2}{2}\right)$$

where $n \geq 0$ is an integer and H_n are the Hermite polynomials defined by $H_0 = 1$, $H_1 = 2\hat{x}$ and the recurrence relation

$$H_{n+1} = 2\hat{x}H_n(\hat{x}) - 2nH_{n-1}(\hat{x})$$

The corresponding eigenvalues are

$$\hat{E}_n = 2n+1 \quad \text{where } n \geq 0 \text{ is an integer.}$$

For a general differential equation of the form

$$\frac{d^2}{dx^2}y(x) = f(x, y(x))$$

we can use an algorithm called *Numerov's Method* to integrate the equation. Starting from the Taylor expansion for $y(x_n)$ we get for the two sampling points adjacent to x_n

$$y_{n+1} = y(x_n + h) = y(x_n) + hy'(x_n) + \frac{h^2}{2!}y''(x_n) + \frac{h^3}{3!}y'''(x_n) + \frac{h^4}{4!}y''''(x_n) + \frac{h^5}{5!}y'''''(x_n) + \mathcal{O}(h^6)$$
$$y_{n-1} = y(x_n - h) = y(x_n) - hy'(x_n) + \frac{h^2}{2!}y''(x_n) - \frac{h^3}{3!}y'''(x_n) + \frac{h^4}{4!}y''''(x_n) - \frac{h^5}{5!}y'''''(x_n) + \mathcal{O}(h^6)$$

The sum of those two equations gives

$$y_{n-1} + y_{n+1} = 2y_n + h^2 y''_n + \frac{h^4}{12}y''''_n + \mathcal{O}(h^6)$$

We solve this equation for y''_n and replace it by the expression $y''_n = -f_n y_n$ which we get from the defining differential equation.

$$f_n y_n = \frac{1}{h^2}\left(2y_n - y_{n-1} - y_{n+1} + \frac{h^4}{12}y''''_n\right) + \mathcal{O}(h^4)$$

We take the second derivative of our defining differential equation and get

$$y''''(x) = -\frac{d^2}{dx^2}\left[f(x)y(x)\right]$$

We replace the second derivative $\frac{d^2}{dx^2}$ with the second order difference quotient and insert this into our equation for $f_n y_n$

$$f_n y_n = \frac{1}{h^2}\left(2y_n - y_{n-1} - y_{n+1} - \frac{h^4}{12}\frac{f_{n-1}y_{n-1} - 2f_n y_n + f_{n+1}y_{n+1}}{h^2}\right) + \mathcal{O}(h^4)$$

We neglect the terms of $\mathcal{O}(h^4)$ collect the terms for y_n and thus get

$$\left(1 + \frac{h^2}{12}f_{n+1}\right)y_{n+1} = \left(2 - \frac{h^2(12-2)}{12}f_n\right)y_n - \left(1 + \frac{h^2}{12}f_{n-1}\right)y_{n-1}$$

and so

$$y_{n+1} = \frac{\left(2 - \frac{5h^2}{6}f_n\right)y_n - \left(1 + \frac{h^2}{12}f_{n-1}\right)y_{n-1}}{1 + \frac{h^2}{12}f_{n+1}}$$

Therefore, since we can write the Schrödinger equation in the form

$$\frac{d^2\phi(x)}{dx^2} = f(x)\phi(x)$$

for a uniformly spaced set of grid points labeled $i = 0, 1, 2, \ldots$ with spacing h the value of ϕ at grid point $i+1$ is approximately related to the values at grid points i and $i-1$ by

$$\left(1 - \frac{h^2}{12}f_{i+1}\right)\phi_{i+1} = \left(2 + \frac{5}{6}h^2 f_i\right)\phi_i - \left(1 - \frac{h^2}{12}f_{i-1}\right)\phi_{i-1} \tag{3}$$

where f_i and ϕ_i are the values of $f(x)$ and $\phi(x)$ at $x = ih$.

We must think about where to start the integration and about the boundary conditions there. The obvious starting points are at $\hat{x} = 0$ or at $\hat{x} = \infty$ (or in practice some large value). Since $\hat{V}(\hat{x})$ is symmetric, solutions will fall into even or odd categories. If we start at $\hat{x} = 0$, convenient boundary conditions will be

$$\phi(0) = 1, \quad \frac{d\phi}{d\hat{x}} = 0 \qquad \phi \text{ even,}$$
$$\phi(0) = 0, \quad \frac{d\phi}{d\hat{x}} = 1 \qquad \phi \text{ odd.}$$

Note that you will only need values of ϕ at two grid points to start this calculation, but the boundary condition only provides values at one grid point. Values at a second point can be calculated using a Taylor series expansion

$$\phi(h) = \phi(0) + h\phi'(0) + \frac{h^2}{2}\phi''(0) + \frac{h^3}{6}\phi'''(0) + \frac{h^4}{24}\phi^{(4)}(0) + \cdots$$

where prime denotes differentiation with respect to $\hat{x}$. Show that this leads to

$$\begin{aligned}
\phi(h) &= \phi(0) + \frac{h^2}{2}f(0)\phi(0) + \frac{h^4}{24}\left[f''(0)\phi(0) + 2f'(0)\phi'(0) + f^2(0)\phi(0)\right] + \cdots \quad \text{even solutions,} \\
\phi(h) &= h\phi'(0) + \frac{h^3}{6}\left[f(0)\phi'(0) + f'(0)\phi(0)\right] + \cdots \quad \text{odd solutions.}
\end{aligned}$$

Note that for the harmonic oscillator, $f'(0) = 0$, even n corresponds to even solutions and odd n corresponds to odd solutions.

Write a program to integrate equation (1) from $\hat{x} = 0$ to some suitable upper bound $\hat{x}_1$ using the algorithm given in equation (3) and plot both the numerical results and the analytic solution. Your program should take $h, \hat{x}_1, n$ and $\hat{E}$ as input and should be able to deal with both even and odd n. You may find it convenient to write $f(\hat{x})$ and the Numerov algorithm as functions. Note that equation (1) is homogeneous and so a solution may be scaled by an arbitrary factor and still be a solution. As described above, the analytical and numerical solutions may have different scalings which must be allowed for when they are compared.

Choose $h = 0.05$ and $\hat{x} = 5$ initially. Explore the dependence of the solution on the value of $\hat{E}$ by running your program with $\hat{E} = 0.95, 1.0$ and 1.05.

Why does your numerical solution differ from the analytic solution for large $\hat{x}$?

Devise a method by which the eigenvalue $\hat{E} = 1$ can be obtained starting at a trial value of $\hat{E}$ reasonably near $\hat{E} = 1$. One possibility, by no means the best, is to look for the value of $\hat{E}$ which gives the smallest value of the wavefunction at $\hat{x}_1 = 5$. Thus starting from the first trial value proceed by small steps in the direction of $\hat{E}$ which reduces this value.

Compute also the solutions of $\hat{E}$ near $\hat{E} = 3, 5$ and 7.