Notes on numerical solutions of Schrödinger equation

Consider the following one-dimensional Schrödinger equation:

\[
\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi_n(x) = E_n \psi_n(x),
\]

where \(V(x)\) is a given potential function, and \(E_n\) is the energy eigenvalue associated with the eigenfunction \(\psi_n(x)\). This can either represent a bound state or a continuum state. One basic approach to developing accurate numerical approximations to the solution of these equations is to use a Taylor’s series expansion to relate the behavior of \(\frac{d^2 \psi_n(x)}{dx^2}\) to \(\psi_n(x')\) for points \(x'\) in the neighborhood of \(x\). Note that for any small distance \(s\),

\[
\psi_n(x \pm s) = \psi_n(x) \pm s \frac{d \psi_n(x)}{dx} + \frac{s^2}{2} \frac{d^2 \psi_n(x)}{dx^2} \pm \frac{s^3}{3} \frac{d^3 \psi_n(x)}{dx^3} + \frac{s^4}{4} \frac{d^4 \psi_n(x)}{dx^4} \ldots
\]

This means that if \(s\) is small, we can approximate the second derivative according to

\[
\frac{d^2 \psi_n(x)}{dx^2} \approx \frac{\psi_n(x + s) + \psi_n(x - s) - 2\psi_n(x)}{s^2} + O(s^4).
\]

This central difference approximation can be used to solve both bound state and scattering state solutions of the Schrödinger equation 1. For an example suppose the we have a bound state problem with the boundary conditions \(\psi_n(0) = \psi_n(X) = 0\) We then divide the interval \(0 \leq x \leq X\) into \(N\) intervals with \(X = (N + 1)s\).

Then we can use Eq. (3) to replace the kinetic energy operator. The Schrödinger Equation then takes the form of a tri-diagonal eigenvalue problem:

\[
M v_n = \lambda_n v_n,
\]

where

\[
M = \begin{pmatrix}
b_1 & c_1 & 0 & 0 & \ldots \\
c_2 & b_2 & c_2 & 0 & \ldots \\
0 & c_3 & b_3 & c_3 & \ldots \\
0 & 0 & a_4 & b_4 & \ldots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\]

The diagonal elements are \(b_i = 2 + s^2[2mV(is)/\hbar^2]\) and the off-diagonal elements are \(a_i \equiv c_i \equiv -1\). Here it is assumed that \(X\) is divided into \(N\) intervals with \(X = (N + 1)s\). \(v_n\) represents a vector of \(N\) coefficients \(\{\psi_n(is)\}\), with \(i = 1, 2, 3 \ldots N\). The energy eigenvalues are given by \(\lambda_n = s^2[2mE_n/\hbar^2]\). One can show that the error of this numerical procedure is of order \(O(s^4\psi_n(x))\).
By keeping the next even term in the Taylor series expansion, one can derive a Numerov algorithm for this problem which takes the form:

$$Mv_n = \lambda_n Sv_n.$$  \hspace{1cm} (6)

Here $M$ is a tridiagonal matrix having the same form as above, and $S$ is a positive definite tridiagonal matrix having the form:

$$S = \begin{pmatrix}
\beta_1 & \gamma_1 & 0 & 0 & \ldots \\
\alpha_2 & \beta_2 & \gamma_2 & 0 & \ldots \\
0 & \alpha_3 & \beta_3 & \gamma_3 & \ldots \\
0 & 0 & \alpha_4 & \beta_4 & \ldots \\
& & & & \ddots
\end{pmatrix}.$$  \hspace{1cm} (7)

In this expression, $\beta_i \equiv 10/12$ and $\alpha_i \equiv \gamma_i \equiv 1/12$, while $b_i \equiv 2 + \frac{10}{12} s^2 [2mV(is)/h^2]$, $a_i \equiv -1 + \frac{1}{12} s^2 [2mV((i-1)s)/h^2]$, and $c_i \equiv -1 + \frac{1}{12} s^2 [2mV((i+1)s)/h^2]$. One can show that the error of this numerical procedure is of order $O(s^6 \psi'(x))$. 