Notes on numerical solutions of Schrödinger equation

Consider the following one-dimensional Schrödinger equation:

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

(1)

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 \( s \),

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

(2)

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

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

(3)

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:

\[
Mv_n = \lambda_n v_n,
\]

(4)

where

\[
M = \begin{pmatrix}
b_1 & c_1 & 0 & 0 & \ldots \\
a_2 & b_2 & c_2 & 0 & \ldots \\
0 & a_3 & b_3 & c_3 & \ldots \\
0 & 0 & a_4 & b_4 & \ldots \\
& & & & \ddots
\end{pmatrix}.
\]

(5)

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 \( O(s^4 \psi_{iv}(x)) \).
By keeping the next even term in the Taylor series expansion, one can derive a Numerov algorithm for this problem which takes the form:

\[ M v_n = \lambda_n S v_n. \]  

(6)

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

\[
S = \begin{pmatrix}
\beta_1 & \gamma_1 & 0 & 0 & \ldots \\
\alpha_2 & \beta_2 & \gamma_2 & 0 & \ldots \\
0 & \alpha_3 & \beta_3 & \gamma_3 & \ldots \\
0 & 0 & \alpha_4 & \beta_4 & \ldots \\
\ldots & \ldots & \ldots & \ldots & \ldots
\end{pmatrix}.
\]

(7)

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