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Notes on numerical solutions of Schrödinger equation

Consider the following one-dimensional Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_n(x)=E_n\psi_n(x), \tag{1}$$

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,

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

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

$$\frac{d^2\psi_n(x)}{dx^2}\approx\frac{\psi_n(x+s)+\psi_n(x-s)-2\psi_n(x)}{s^2}+O(s^4). \tag{3}$$

This central difference approximation can be used to solve both bound state and scattering state solutions of the Schrodinger equation 1. For an 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 $0\le x\le X$ 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:

$$Mv_n=\lambda_n v_n, \tag{4}$$

where

$$M=\begin{pmatrix} b_1 & c_1 & 0 & 0 & .. \\ a_2 & b_2 & c_2 & 0 & .. \\ 0 & a_3 & b_3 & c_3 & .. \\ 0 & 0 & a_4 & b_4 & .. \\ .. & .. & .. & .. & .. \end{pmatrix}. \tag{5}$$

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 $i=1,2,3...N$. 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:

$$Mv_n = \lambda_n S v_n. \tag{6}$$

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

$$S = \begin{pmatrix} \beta_1 & \gamma_1 & 0 & 0 & .. \\ \alpha_2 & \beta_2 & \gamma_2 & 0 & .. \\ 0 & \alpha_3 & \beta_3 & \gamma_3 & .. \\ 0 & 0 & \alpha_4 & \beta_4 & .. \\ .. & .. & .. & .. & .. \end{pmatrix}. \tag{7}$$

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