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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 $0 \leq x \leq X$ into equal intervals with $X = (N+1)s$ and with N interior points.

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 $O(s^6\psi^{vi}(x))$.

For the case of a spherical atom, the wavefunction is assumed to take the form

$$\Psi_{nlm}(\mathbf{r}) = \frac{P_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}}), \tag{8}$$

where the radial function $P_{nl}(r)$ is determined by solving the radial Schödinger equation, which (dropping the nl indices can be written:

$$\frac{d^2P(r)}{dr^2} = A(r)P(r), \tag{9}$$

where

$$A(r) \equiv \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2}\left(V(r) - E\right). \tag{10}$$

Rather than solving the equation in matrix form as described above, it is generally found to be more efficient to solve for each eigenvalue E iteratively, using the Numerov algorithm to integrate inward and outward and matching at an intermediate point r_m. For this purpose, we can denote $P_i \equiv P(is)$. The recursion formula is given by

$$P_{i+1} = \left(-(1 - \frac{s^2}{12}A_{i-1})P_{i-1} + (2 + \frac{10s^2}{12}A_i)P_i \right) / (1 - \frac{s^2}{12}A_{i+1}). \tag{11}$$

For any given energy iteration, the correction to the energy eigenvalue can be estimated from the mismatch in the slope at the matching point:

$$\Delta E = \frac{1}{\mathcal{N}} \left(\left. \frac{\frac{dP}{dr}}{P} \right]_{\text{in}} - \left. \frac{\frac{dP}{dr}}{P} \right]_{\text{out}} \right), \tag{12}$$

where

$$\mathcal{N} \equiv \int_0^{r_m} |P(r)/P(r_m)|^2_{\text{out}} dr + \int_{r_m}^{\infty} |P(r)/P(r_m)|^2_{\text{in}} dr. \tag{13}$$