1.5: Numerically Solving the Schrödinger Equation

Often the bound potentials that we encounter are complex, and the time-independent Schrödinger equation will need to be evaluated numerically. There are two common numerical methods for solving for the eigenvalues and eigenfunctions of a potential. Both methods require truncating and discretizing a region of space that is normally spanned by an infinite dimensional Hilbert space. The Numerov method is a finite difference method that calculates the shape of the wavefunction by integrating step-by-step across along a grid. The DVR method makes use of a transformation between a finite discrete basis and the finite grid that spans the region of interest.

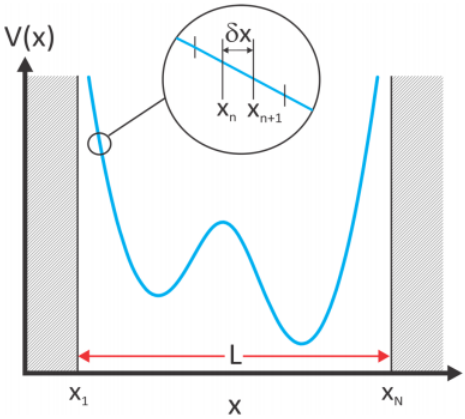

Figure 1.5.1: Selection and discretization of a space bounding the region for which the TISE will be solved numerically. A space of length L is discretized into N points separated by a spacing δx over which the potential varies slowly.

The Numerov Method

A one-dimensional Schrödinger equation for a particle in a potential can be numerically solved on a grid that discretizes the position variable using a finite difference method. The TISE is

$$[T+V(x)]\psi(x)=E\psi(x) \tag{1.5.1}$$

with

$$T=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \tag{1.5.2}$$

which we can write as

$$\psi''(x)=-k^2(x)\psi(x) \tag{1.5.3}$$

where

$$k^2(x)=\frac{2m}{\hbar^2}[E-V(x)]. \tag{1.5.4}$$

If we discretize the variable x, choosing a grid spacing δx over which V varies slowly, we can use a three point finite difference to approximate the second derivative:

$$f_i''\approx\frac{1}{\delta x^2}\left(f\left(x_{i+1}\right)-2f\left(x_i\right)+f\left(x_{i-1}\right)\right) \tag{1.5.5}$$

The discretized Schrödinger equation can then be written in the form

$$\psi\left(x_{i+1}\right)-2\psi\left(x_i\right)+\psi\left(x_{i-1}\right)=-k^2\left(x_i\right)\psi\left(x_i\right) \tag{1.5.6}$$

Using the equation for $\psi\left(x_{i+1}\right)$, one can iteratively solve for the eigenfunction. In practice, you discretize over a range of space such that the highest and lowest values lie in a region where the potential is very high or forbidden. Splitting the space into N points, chose the first two values $\psi\left(x_1\right)=0$ and $\psi\left(x_2\right)$x to be a small positive or negative number, guess E, and propagate iteratively to $\psi\left(x_N\right)$. A comparison of the wavefunctions obtained by propagating from x_1 to x_N with that obtained propagating from x_N to x_1 tells you how good your guess of E was.

The Numerov Method improves on Equation 1.5.6 by taking account for the fourth derivative of the wavefunction $\Psi^{(4)}$, leading to errors on the order $O\left(\delta x^6\right)$. Equation 1.5.5 becomes

$$f_i'' \approx \frac{1}{\delta x^2}\left(f\left(x_{i+1}\right)-2f\left(x_i\right)+f\left(x_{i-1}\right)\right)-\frac{\delta x^2}{12}f_i^{(4)} \tag{1.5.7}$$

By differentiating Equation 1.5.3 we know

$$\psi^{(4)}(x)=-\left(k^2(x)\psi(x)\right)'' \tag{1.5.8}$$

and the discretized Schrödinger equation becomes

$$\begin{aligned}\psi''\left(x_i\right) &= \frac{1}{\delta x^2}\left(\psi\left(x_{i+1}\right)-2\psi\left(x_i\right)+\psi\left(x_{i-1}\right)\right)+ \\ &\frac{1}{12}\left(k^2\left(x_{i+1}\right)\psi\left(x_{i+1}\right)-2k^2\left(x_{i+1}\right)\psi\left(x_i\right)+k^2\left(x_{i+1}\right)\psi\left(x_{i-1}\right)\right)\end{aligned}$$

This equation leads to the iterative solution for the wavefunction

$$\psi\left(x_{i+1}\right)=\frac{\psi\left(x_i\right)\left(2+\frac{10\delta x^2}{12}k^2\left(x_i\right)\right)-\psi\left(x_{i-1}\right)\left(1-\frac{\delta x^2}{12}k^2\left(x_{i-1}\right)\right)}{1-\frac{\delta x^2}{12}k^2\left(x_{i+1}\right)} \tag{1.5.9}$$

Discrete Variable Representation (DVR)

Numerical solutions to the wavefunctions of a bound potential in the position representation require truncating and discretizing a region of space that is normally spanned by an infinite dimensional Hilbert space. The DVR approach uses a real space basis set whose eigenstates $\varphi_i(x)$ we know and that span the space of interest—for instance harmonic oscillator wavefunctions—to express the eigenstates of a Hamiltonian in a grid basis (θ_j) that is meant to approximate the real space continuous basis $\delta(x)$. The two basis sets, which we term the eigenbasis (φ) and grid basis (θ), will be connected through a unitary transformation

$\Phi^{\dagger}\varphi(x)=\theta(x)\ \Phi\theta(x)=\varphi(x)$

For N discrete points in the grid basis, there will be N eigenvectors in the eigenbasis, allowing the properties of projection and completeness will hold in both bases. Wavefunctions can be obtained by constructing the Hamiltonian in the eigenbasis,

$H=T(\hat{p})+V(\hat{x})$, transforming to the DVR basis, $H^{DVR}=\Phi H\Phi$, and then diagonalizing.

Here we will discuss a version of DVR in which the grid basis is set up to mirror the continuous $|\mathcal{X}\rangle$ eigenbasis. We begin by choosing the range of x that contain the bound states of interest and discretizing these into N points (x_i) equally spaced by δx. We assume that the DVR basis functions $\theta_j\left(x_i\right)$ resemble the infinite dimensional position basis

$$\theta_j\left(x_i\right)=\sqrt{\Delta x}\delta_{ij} \tag{1.5.10}$$

Our truncation is enabled using a projection operator in the reduced space

$$P_N=\sum_{i=1}^{N}|\theta_i\rangle\langle\theta_i|\approx 1 \tag{1.5.11}$$

which is valid for appropriately high N. The complete Hamiltonian can be expressed in the DVR basis DVR

$$H^{DVR}=T^{DVR}+V^{DVR}. \tag{1.5.12}$$

For the potential energy, since $\{\theta_i\}$ is localized with $\langle\theta_i|\theta_j\rangle=\delta_{ij}$, we make the DVR approximation, which casts V^{DVR} into a diagonal form that is equal to the potential energy evaluated at the grid point:

$$V_{ij}^{DVR}=\langle\theta_i|V(\hat{x})|\theta_j\rangle\approx V\left(x_i\right)\delta_{ij} \tag{1.5.13}$$

This comes from approximating the transformation as $\Phi V(\hat{x})\Phi^{\dagger}\approx V\left(\Phi\hat{x}\Phi^{\dagger}\right)$.

For the kinetic energy matrix elements $\langle\theta_i|T(\hat{p})|\theta_j\rangle$, we need to evaluate second derivatives between different grid points. Fortunately, Colbert and Miller have simplified this process by finding an analytical form for the T^{DVR} matrix for a uniformly

gridded box with a grid spacing of Δx.

$$T_{ij}^{\mathrm{DVR}} = \frac{\hbar^2 (-1)^{i-j}}{2m\Delta x^2} \begin{Bmatrix} \pi^2/3 & i = j \\ 2/(i-j)^2 & i \neq j \end{Bmatrix} \tag{1.5.14}$$

This comes from a Fourier expansion in a uniformly gridded box. Naturally this looks oscillatory in x at period of δx. Expression becomes exact in the limit of $N \to \infty$ or $\Delta x \to 0$. The numerical routine becomes simple and efficient. We construct a Hamiltonian filling with matrix elements whose potential and kinetic energy contributions are given by Equations 1.5.13 and 1.5.14. Then we diagonalize H^{DVR}, from which we obtain N eigenvalues and the N corresponding eigenfunctions.

References

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