Bound states of one dimensional potential by Numerov method

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1 Introduction

One of the first topics encountered in the first course on quantum mechanics is the calculation of bound states. The texts illustrate the methods on one dimensional problems like wells and harmonic oscillator and then go on to discuss the three dimensional problems. The typical detailed examples presented are of spherically symmetric well and hydrogen atom. All this is done analytically using the machinery of differential equations. As it turns out the list of analytically solvable bound state problems is quite short. The more interesting real life problems involve potentials which are hard to treat analytically. One of the important areas in condensed matter physics and material science is the calculation of electronic structure. At a basic level this means obtaining the one electron energies and wave functions in a suitably chosen potential. It must be mentioned that in general a calculation of many body wave function for interacting electron systems is a non trivial and formidable task. The most common route is based on an elegant formulation of density functional theory proposed by noble prize winner W. Kohn. This formulation reduces the problem of interacting *many electrons* to that of finding *one electron* states in an effective potential. Thus we are back to our basic problem of finding bound states of a single particle in a potential. Quite clearly it is of considerable importance to develop tools to solve Schrödinger equation for a general potential. There are a variety of methods developed. In one dimensional problems it is most convenient to solve differential equation directly. In two or three dimensions the problem is more complicated. In such cases the potential is not spherically symmetric and it may be multi centered. An additional complication may be due to periodic nature of the potential leading to periodic boundary conditions. During the last thirty years or so many sophisticated techniques have been developed to attack general three dimensional bound state (or otherwise) problems. These include real space, grid based finite difference methods, use of various basis

functions, like Gaussian or plane waves. In this article we will discuss a very simple method used for one dimensional problems. The method will also be useful for spherically symmetric three dimensional potentials.

2 The one dimensional potentials

Let us consider the problem of finding bound state(s) of one dimensional attractive potential $V(x)$. Recall that in this case there will be at least one bound state. (Well, go ahead and prove it.) We are required to solve the Schrödinger equation ,

$$\left(-\frac{\hbar^2}{2m}\,\frac{d^2}{dx^2}\;+V(x)\right)\;\psi(x)\;=\;\epsilon\,\psi(x). \tag{1}$$

with the conditions,

1. $\psi(x) \rightarrow\; 0$ as $x \rightarrow\; \pm\infty$
2. $\int_{-\infty}^{+\infty} |\psi(x)|^2\, dx\;=\;1$
3. $\psi(x)$ and $\psi'(x)$ are continuous.

The first condition specifies the boundary condition and second one normalization. Typical examples are harmonic oscillator potential, various potential wells, Lennard Jones potential etc.

Before we proceed we chose convenient units. For the sake of concreteness let us chose following units. Unit of Length - Bohr radius a_0 i.e. $a_0 \;=\; 1$. Unit of mass - Electron mass i.e. $m \;=\; 1$ in addition we set $e^2 \;=\; 1$ where e is the electron charge and $\hbar \;=\; 1$. This makes unit of energy as 1 Hartree (27.2 electron volt). It must be emphasized that in every numerical problem proper units must be chosen to avoid occurrence of very small or very large numbers. This is because all the calculations are done with finite precision arithmetic. For example to use the value of $\hbar \;=\; 6.62 \times 10^{-34}$ Joule - second explicitly would be disastrous! The length scales relevant to problems involving electron in a potential are $\sim\; 10^{-8}$ cms. The choice used here is not unique. With these units the Schrödinger equation becomes,

$$\frac{d^2}{dx^2}\,\psi(x) - 2\;(V(x)-\epsilon)\;\psi(x)\;=\;0. \tag{2}$$

The potential $V(x)$ is now in Hartree.

3 Three dimensional spherically symmetric potentials

Let us now consider a case of spherically symmetric potential in three dimension. A typical example is that of hydrogen atom or in general single center Coulomb potential (electron in an atom) or a three dimensional well.Thus,

$$V(\vec{r}) \ = V(|\vec{r}|) = V(r).$$

It is well known that the Schrödinger equation ,

$$\left(-\frac{\nabla^2}{2} + V(\vec{r})\right) \ \psi(\vec{r}) \ = \ \epsilon\, \psi(\vec{r}), \tag{3}$$

can be reduced to one dimensional radial equation using spherical coordinates ($r,\ \theta,\ \phi$) with substitution

$$\psi(\vec{r}) = R_l(r)\ Y_{lm}(\theta, \phi),$$

where Y_{lm} is the spherical harmonics. The radial wave function satisfy,

$$-\frac{1}{2}\ \frac{d^2P}{dr^2} \ + \ \left[V(r) \ + \ \frac{l\ (l+1)}{2r^2}\right] \ P(r) \ = \ \epsilon P(r)$$

with $P(r) = r\ R(r)$ and

$$g(r) = V(r) + \frac{l\ (l+1)}{2r^2}.$$

We have

$$\frac{d^2P}{dr^2} \ - \ 2\ [g(r) \ - \ \epsilon]\, P(r) \ = \ 0. \tag{4}$$

The domain of solution is [0,∞] and $P(r) \rightarrow \ 0$ as $r \rightarrow 0$ and as $r \rightarrow \infty$.

$$4\pi \int_0^\infty \ |P(r)|^2 \ dr \ = \ 1$$

It can be seen that the one dimensional equation (2) and (4) are similar and share a common feature, namely both do not contain first order derivative term. Such equations are conveniently solved by using a powerful technique called *Numerov method.*

4 The Numerov Method

Consider a second order linear differential equation of the form,

$$y'' + Q(x)\, y \;=\; S(x) \tag{5}$$

Q and S are continuous function on the domain $[a,\ b]$. The equation is to be solved as a boundary value problem, i.e. $y(a)$ and $y(b)$ are given. We first discretize the interval using equal spaced points with step size say h. This is illustrated in Fig (1)

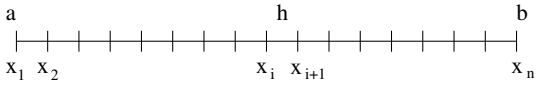

Figure 1: One dimensional discrete mesh

All the functions are specified on this mesh and this means the solution $y(x)$ is also obtained as discrete set of point on the mesh. Thus,

$$y(x) \;=\; y(x_i) \;=\; y_i$$

and the equation becomes

$$y_i'' \;+\; Q_i\, y_i \;-\; S_i \;=\; 0 \qquad\qquad \text{for all i.}$$

Next we derive the finite difference formula for the second derivative using Taylor series.

$$y(x+h) \;=\; y(x) \;+\; h\, y'(x) \;+\; \frac{h^2}{2}\, y''(x) \;+\; \frac{h^3}{6} y'''(x) \;+\; \frac{h^4}{24} y''''(x) \;+\; \cdots$$

Similarly,

$$y(x-h) \;=\; y(x) \;-\; h\, y'(x) \;+\; \frac{h^2}{2}\, y''(x) \;-\; \frac{h^3}{6} y'''(x) \;+\; \frac{h^4}{24} y''''(x) \;-\; \cdots$$

adding above we get,

$$y(x+h) \;+ y(x-h) \;=\; 2y \;+\; h^2\, y'' \;+\; \frac{h^4}{12} y'''' \;+ O(h^6).$$

Using discrete notation,

$$y_i'' = \frac{y_{i+1} \;+ y_{i-1} \;-\; 2y_i}{h^2} \;-\; \frac{h^2}{12} y'''' \;-\; O(h^4) \tag{6}$$

Thus the three point central difference formula for the second derivative is,

$$y_i{}'' = \frac{y_{i+1} + y_{i-1} - 2y_i}{h^2}$$

We can use equation (5) to explicitly calculate the third term in equation (6) involving y''''.

$$y_i'' = -\frac{d^2}{dx^2}\left[Q\,y - S\right]_i .$$

Using the central difference formula,

$$y_i'''' = -\frac{1}{h^2}\left[(Q_{i+1}y_{i+1} + Q_{i-1}y_{i-1} - 2Q_iy_i) - (S_{i+1} + S_{i-1} - 2S_i)\right] + O(h^2) \tag{7}$$

Substituting above equation in equation (6) we get,

$$\left(1 + \frac{h^2}{12}Q_{i+1}\right)y_{i+1} = 2\left(1 - \frac{5h^2}{12}Q_i\right)y_i - \left(1 + \frac{h^2}{12}Q_{i-1}\right)y_{i-1} + \frac{h^2}{12}\left(S_{i+1} + 10S_i + S_{i-1}\right) + O(h^6).$$

This is the desired relation. It can be seen that it is a recurrence relation connecting y_i, y_{i+1} and y_{i-1} : A three term relation. The error is of the order of h^6, which is one order smaller than 4^{th} order Runge Kutta. The scheme is efficient and accurate!

In the present case we do not have the source term , $S = 0$. Then the forward and the backward relations are ;

$$\left(1 + \frac{h^2}{12}Q_{i+1}\right)y_{i+1} = 2\left(1 - \frac{5h^2}{12}Q_i\right)y_i - \left(1 + \frac{h^2}{12}Q_{i-1}\right)y_{i-1}$$

$$\left(1 + \frac{h^2}{12}Q_{i-1}\right)y_{i-1} = 2\left(1 - \frac{5h^2}{12}Q_i\right)y_i - \left(1 + \frac{h^2}{12}Q_{i+1}\right)y_{i+1}$$

Once we have two values of the solution y_i at successive mesh points, we can generate the entire solution. The boundary conditions, along with the asymptotic nature of the function (if known) is used to specify these two required initial values. In fact, this initialization is potential specific and needs some thought.

Now we are ready to apply the method for the problem of bound states.

5 The Bound states by Numerov method

Consider a one dimensional potential,

$$\begin{aligned} V(x) &= -V_0 && -a \le x \le a \\ &= 0 && \text{otherwise.} \end{aligned}$$

as shown in the fig(2).

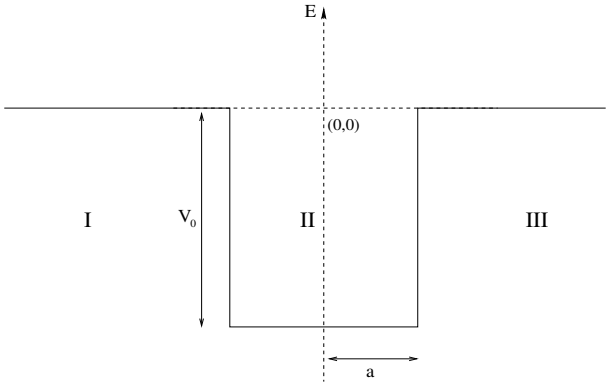

Figure 2: A potential well.

The differential equation to be solved is,

$$\frac{d^2}{dx^2}\,\psi(x) + \,2\,\left(\epsilon - V(x)\right)\,\psi(x) \;=\; 0. \tag{8}$$

with $\psi(x) \to 0$ as $x \to \pm\infty$

We note that the domain of solution is $[-\infty,\ \infty]$. However the solution is expected to decay outside the well and hence a suitable 'infinity' is chosen, say x_m and the problem solved on $[-x_m,\ x_m]$. The cut off x_m and the step size h are parameters which need to be adjusted to get desired accuracy.

It is important to recognize that finding bound states means finding a pair(s) (ϵ, ψ), which satisfies the Schrödinger equation along with the boundary conditions. Quite clearly this is a bit different than solving a differential equation since ϵ is unknown. There are three regions as shown in the fig (2). region I and III are classically forbidden where the wave function decays. In region I it is oscillatory.

A simple minded procedure would be to start with a trial energy ϵ_t say just above the bottom of the well $-V_0$. Then initialize wave functions in region I. i.e. $y_1 = 0.$ and $y_2 = c$, where c is a small constant. Then, use the forward recurrence relation to obtain the solution up to x_m. In the fig (3) we have shown solutions for a few different trial energy values obtained by using Numerov method. Although each of these is a solution, none of these qualifies to be an eigen function, since it does not satisfy the boundary condition in the region III. One simple way is to vary ϵ_t until we get a solution having desired boundary condition. Unfortunately this simple procedure does not work. It may be noted that in the classically forbidden region there are two

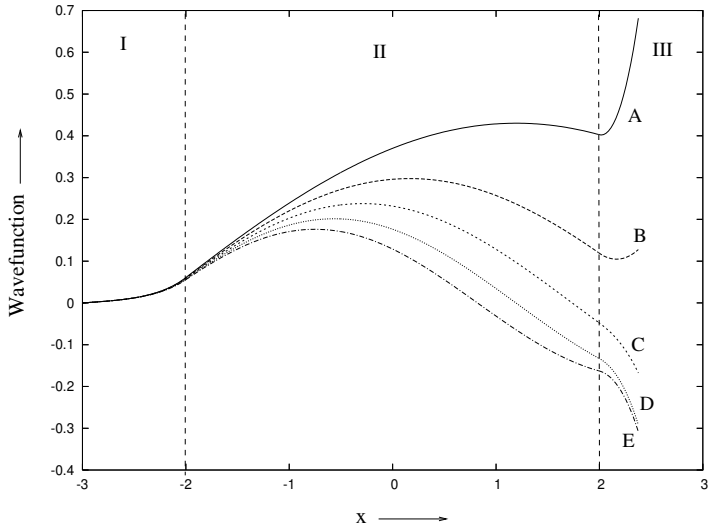

Figure 3: Typical solutions of the equation (8) by Numerov method. $V_0 = -1.5$ and $a = 2$. Note the changing nature of solutions in region III the eigen function is expected to lie between B and C. The lowest trial energy is 0.07 above V_0 (Curve E). The vertical dotted lines at ± 2 indicate the boundary of the potential well.

allowed solution one decaying and other growing. When we continue the solution in the region III from region II, large errors can creep in. This is because of admixture of the second undesired solution. This problem is not faced in the region I because we started with solution having only decaying component.Therefore the trick is to integrate the solution in the direction of increasing magnitude of the solution. We start the solution in region I from $-x_m$ and integrate to wards origin, we start another solution (with the same trial energy) in the classically forbidden region III from $+x_m$ and integrate to wards origin and match the solutions at a suitable chosen point. In the present case because of the symmetry, it could be origin. The matching is conveniently done by comparing the logarithmic derivative of both the solutions. If $\gamma = \frac{\psi'}{\psi}$ and if x_c is the matching point then a bound state is obtained by imposing a condition $\gamma_l = \gamma_r$ at $x = x_c$, where γ_l and γ_r are the logarithmic derivative of solutions starting from left and right regions respectively.

With these comment we are ready to put down the algorithm.

6 The Algorithm

Given the attractive square well potential to find the lowest eigenvalue (zero node solution),

- Initialize the parameters
  - potential parameters: V_0 and a.
  - mesh parameters: h and x_m.
  - accuracy δ for matching logarithmic derivatives.
  - state specification N i.e. ground state or higher ($N = 1, 2, ...$). Note this sets the parity in the present case. the number of nodes are $= N - 1$. We set $N = 1$.
  - Trial energy ϵ_t, and matching point $x_c (= 0)$.
- Begin iteration for finding eigenvalue
  - Set $\epsilon_l = \epsilon_t$.
  - Initialize y_1 and y_2 as $y_1 = 0$ and $y_2 =$ a small constant.
  - Use forward relation to obtain solution till x_c.
  - Calculate γ_l.
  - initialize y_n and y_{n-1} as $y_n = 0$ and $y_{n-1} =$ a small constant. Note : $x_n = x_m$, the rightmost point on the mesh.
  - Use backward relation and obtain γ_r at x_c.
  - Calculate $err = \gamma_l - \gamma_r$.
  - Increase trial energy until err changes sign. Denote this energy as ϵ_u. The eigenvalue is now bounded between ϵ_l and ϵ_u.
  - Use a suitable root finding algorithm e.g., bisection method, to find the energy ϵ_b so that $|err| \leq \delta$, the desired accuracy.
  - Match the values of left and right wave function at x_c and use the scale one of the wave functions to obtain a continuous eigenfunction.
  - Normalize the entire wave function.

Several comments are in order. We have initialized the functions at two points. In many cases it is possible to use known asymptotic form for accurate initialization. Can you improve upon the initialization that we have used ? What could be the best choice for matching points? For the symmetric well

we have chosen the origin. However this will pose problems for odd parity wave function since ψ will be zero at origin. A simple solution is to match $1/\gamma$. However in many cases it is most convenient to use classical turning point (i.e. the value at which function $[\epsilon - V(x)]$ changes its sign) for matching logarithmic derivatives. In the above algorithm we have implicitly assumed that the number of nodes of the function do not change for the energy interval ϵ_l to ϵ_u. In other words our search is restricted to energy region where the wave function has same number of nodes. This must be ensured explicitly in the program. Finally accuracy of the solution is dependent on the step size h and choice of x_m. These must be varied till the convergence in the energy is obtained. x_n will be different for different states.

The modifications required for a three dimensional problems are straight forward. In this case we would integrate from origin on wards and from 'infinity' in wards till the classical turning point. In addition the solution is obtained separately for each angular momentum. The initialization near the origin has to be carefully chosen depending upon the nature of the potential.

We end this article with the following question: How can you use Numerov method for calculating the scattering solution ($\epsilon \geq 0$) and corresponding phase shifts? In fact we invite reader to write a code to calculate phase shifts for three dimensional spherically symmetric potential well.