Time Independent Schrödinger Equation (TISE)

In quantum mechanics, the TISE governs the energy states that are accessible to a system. The TISE is given by:

$$\hat{H}\psi = E\psi$$

$\hat{H}$: Hamiltonian ψ: wave fctn.
E: Energy

The Hamiltonian is just the QM operator that gives the energy, ie

$$\hat{H} = \text{kinetic} + \text{potential}$$

$$= \frac{p^2}{2m} + V(\text{coordinates}) = -\frac{\hbar^2}{2m}\nabla^2 + V$$

using the fact that the momentum operator $\vec{p} = -i\hbar\vec{\nabla}$. Hence the total equation is

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi .$$

Therefore, given a specific form of the potential energy V, the aim is to solve for the energy eigenstates $\phi(E)$ & wave fctn (ψ).

Consider the simple particle-in-a-box, where

$$V = V(x) = \begin{cases} \infty & x \le 0 \\ 0 & 0 < x < L \\ \infty & x \ge L \end{cases} \qquad (1 \text{ dimension})$$

Since the barriers of $V(x)$ are infinite, we ~~immediately~~ know that $\psi(0) = \psi(L) = 0$ & we need only focus on the range $0 \le x < L$. In this region, the TISE reduces to

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$$

rearranging, we obtain:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad \text{which we know has solution}$$

$$\frac{2mE}{\hbar^2} = k^2$$

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Using the boundary conditions, $\psi(0) = 0 \Rightarrow B = 0$

$$\psi(L) = 0 \Rightarrow \sin(kL) = 0$$

In summary then, the wave function or $k = \frac{n\pi}{L}$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

(note $\sqrt{\frac{2}{L}}$ comes from normalization condition).

and the energy states are $E_n = \frac{(n\pi\hbar)^2}{2mL^2}$

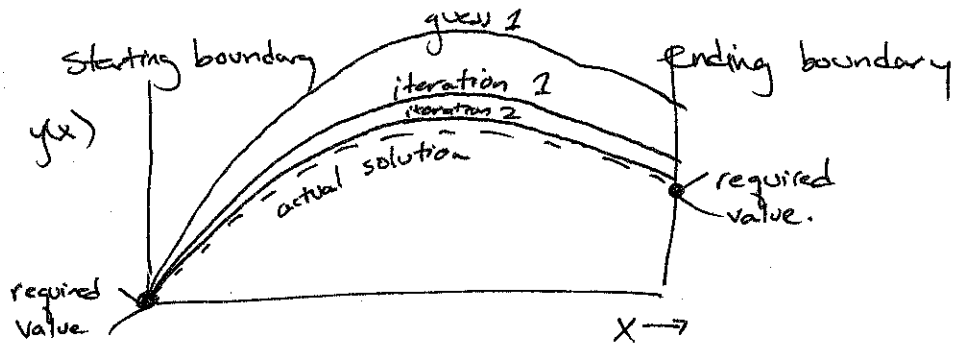
What if $V(x)$ is more complicated? What if it is so complicated we cannot analytically solve the problem?

Boundary Value Problems. (BVP)

BVP are problems like the TISE where we know values at some boundaries, & we want the solution in the interval between those boundaries. This is in contrast to initial value problems, where the initial state is completely specified & we want to integrate forward. An example of this is gravitional motion where we know all the initial positions & velocities.

For BVP, the information at the boundary is not sufficient to integrate forward — and so we must guess at the correct values, & then revise those guesses until the integrated value at the opposite boundary matches.

Pictorially, it is something like this:



This is the SHOOTING METHOD.

So we make some guess for parameters at the starting boundary, & the based on the error at the ending boundary we revise those parameteres. Hence the entire process reduces to making the difference between our solution at the boundary & the expected value $\rightarrow 0$ -- ie we are looking for zeros!

Let's formalize this..... consider the linear homogeneous case

$$y''(x) = v_1(x)\, y + v_2(x)\, y'$$

with boundary conditions $y(a) = y(b) = 0$.

Starting @ $y = a$, we can evaluate $v_1(a)$, $v_2(a)$, but we do not know y'! Hence we must make a guess for y'. Once we guess $y'(a)$, we may use some method to obtain $y(x+dx)$ based of the above equation, and eventually obtain $y(b)$. If $y(b) \neq 0$, we modify our guess for $y'(a)$ and repeat.

Let's make this specific to the TISE: (1-D)

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{2m}{\hbar^2}(E - V(x))\psi \quad \& \quad \psi(0) = \psi_0$$
$$\psi(L) = \psi_1 .$$

In this case, we do not know E, so we must make a guess for it & integrate from $x=0 \rightarrow x=L$. We have the correct solution when $\psi_{trial}(L) - \psi_1 = 0$ and so we simply need to do root finding of this function. To do this, start with a bracket method, ie, starting at energy E, step in intervals δE until the sign of $\psi_{trial}(L) - \psi_1$ changes. You know the correct solution is in the range $E \rightarrow E+\delta E$.

Next, use the bisection method to more accurately identify the exact vale of E.

Question: How do you integrate $\psi(x)$? Previously, we have always broken 2nd order ODE's into sets of coupled 1st order ODE's, & then use Euler, Runge-Kutta, etc. We could do that here, but instead we will use a 2nd order method, the Numerov-Cowling algorithm.

→ eg: Solve $\frac{\partial\psi}{\partial x} = \psi'$ $\frac{\partial\psi'}{\partial x} = \frac{-2m}{\hbar^2}(E-V(x))\psi$

Note that to obtain $\psi(x+dx)$, the method requires $\psi(x)$ & $\psi(x-dx)$ -- hence to start the algorithm you must be able to estimate the first iteration.

Numerov-Cowling algorithm

The Numerov-Cowling method (like the Euler method, Runge-Kutta, etc) is an algortihm for integrating ODE's; however, it is designed to integrate 2^{nd} order ODE's, unlike the other methods that we have discussed. Consider a 2^{nd} order ODE of the form

$$\frac{d^2y}{dx^2} = f(x, y). \tag{1}$$

If you expand $y(x+\delta)$ and $y(x-\delta)$ in Taylor series to 4^{th} order and sum the terms you obtain

$$\frac{y(x+\delta) + y(x-\delta) - 2y(x)}{\delta^2} = f(x, y) + \frac{d^4y}{dx^4}\frac{\delta^2}{12} + \mathcal{O}(\delta^4). \tag{2}$$

Since

$$\frac{d^2y}{dx^2} = f(x, y), \quad \frac{d^4y}{dx^4} = \frac{d^2f}{dx^2} \tag{3}$$

which we can express using the standard numerical second derivative

$$\frac{d^2f}{dx^2} = \frac{f(x+\delta) + f(x-\delta) - 2f(x)}{\delta^2}. \tag{4}$$

Substituting this into eq. (2) and rearranging we find that

$$y(x+\delta) = 2y(x) - y(x-\delta) + \frac{\delta^2}{12}[f(x+\delta, y(x+\delta)) + f(x-\delta, y(x-\delta)) + 10f(x, y)] + \mathcal{O}(\delta^6). \tag{5}$$

Hence the Numerov-Cowling method is a very accurate method of solving 2^{nd} order ODE's. The only problem is that $y(x+\delta)$ depends of $f(x+\delta, y(x+\delta))$, and so $y(x+\delta)$ is only implicitly defined. In other words, to determination of $y(x+\delta)$ depends on knowing the value of $y(x+\delta)$ – a very sticky situation.

Consider the special case where $f(x, y)$ is a linear function of y, *i.e.*

$$f(x, y) = g(x) \cdot y. \tag{6}$$

In this case, we can substitute into eq. (5) and obtain

$$y(x+\delta) = \frac{1}{1 - \frac{\delta^2}{12}g(x+\delta)}\left(y(x)\left[2 + \frac{5\delta^2}{6}g(x)\right] + y(x-\delta)\left[-1 + \frac{\delta^2}{12}g(x-\delta)\right]\right). \tag{7}$$

Hence if $f(x, y)$ is linear in y, the $y(x+\delta)$ is explicitly defined the algorithm becomes applicable to one of the most common classes of problems in physics. Note that even this special case, the first step must be calculated by some alternate method, since $y(x+\delta)$ depends on the values at both x and $x-\delta$.

One example where $f(x, y)$ a linear function is the one dimensional time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \tag{8}$$

where $V(x)$ is the potential energy. For this case, clearly the function

$$g(x) = \frac{2m}{\hbar^2}(V(x) - E). \tag{9}$$