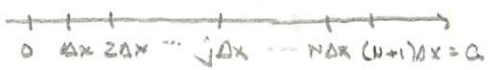
Finite Difference Approximation

For $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$ (*)

make a discrete grid in x:



$x_j = j\Delta x$

the projection of a continuous function, like $\psi(x)$ onto the grid is denoted

$$\psi_j \equiv \psi(x_j)$$

& by Taylor expansion:

$$\psi_{j\pm1} \equiv \psi(x_j \pm \Delta x) \approx \psi(x_j) \pm \Delta x\,\psi'(x_j) + \tfrac{1}{2}\Delta x^2 \psi''(x_j)$$
$$\pm \tfrac{1}{6}\Delta x^3 \psi'''(x_j) + O(\Delta x^4)$$

and.

$$\psi_{j-1} + \psi_{j+1} = 2\psi_j + \Delta x^2 \psi''(x_j) + O(\Delta x^4)$$

or

$$\left.\frac{d^2\psi(x)}{dx^2}\right|_{x=x_j} \approx \frac{\psi_{j-1} - 2\psi_j + \psi_{j+1}}{\Delta x^2} + O(\Delta x^2)$$

Using this approximation in (*) & projecting the entire eqn. onto the grid, we have:

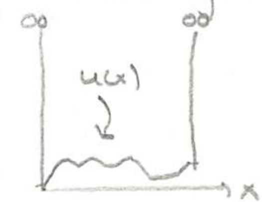
$$-\frac{\hbar^2}{2m}\frac{\psi_{j-1} - 2\psi_j + \psi_{j+1}}{\Delta x^2} + U_j\psi_j = E\psi_j$$

$j = 1 \longrightarrow n.$

What should we do about the endpoints? $\psi_0 = ?$ $\psi_{N+1} = ?$

Our boundary conditions are $\psi(\pm\infty) \longrightarrow 0$
we can imagine letting "$0 \leftarrow -\infty$", "$a \leftarrow \infty$" that's fine provided the potential is localized near $a/2$.

or, you can "immerse" your potential in an infinite square well



In either case, we have

$\psi(0) = \psi(a) = 0$, so

$\psi_0 = \psi_{N+1} = 0$

Then the $j=1$ eqn. reads:

$$-\frac{\hbar^2}{2m}\left(\frac{-2\psi_1 + \psi_2}{\Delta x^2}\right) + U_1\psi_1 = E\psi_1.$$

$j = 2 \longrightarrow N-2$

$$-\frac{\hbar^2}{2m}\left(\frac{\psi_{j-1} - 2\psi_j + \psi_{j+1}}{\Delta x^2}\right) + U_j\psi_j = E\psi_j \qquad (*)$$

& for $j = N$,

$$-\frac{\hbar^2}{2m}\left(\frac{\psi_{N-1} - 2\psi_N}{\Delta x^2}\right) + U_N\psi_N = E\psi_N.$$

let $\vec{\psi} \triangleq \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix}$, then we can write the set (*) as

$$\begin{pmatrix} \frac{\hbar^2}{m\Delta x^2}+U_1 & -\frac{\hbar^2}{2m\Delta x^2} & 0 & \\ -\frac{\hbar^2}{2m\Delta x^2} & \frac{\hbar^2}{m\Delta x^2}+U_2 & -\frac{\hbar^2}{2m\Delta x^2} & \\ 0 & -\frac{\hbar^2}{2m\Delta x^2} & \frac{\hbar^2}{m\Delta x^2}+U_3 & -\frac{\hbar^2}{2m\Delta x^2} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = E\vec{\psi}$$

call the matrix $\mathbb{H}$, then we have

$$\mathbb{H}\vec{\psi} = E\vec{\psi}$$

so we just want the eigenvalues & eigenvectors of the matrix $\mathbb{H}$.

This approach, which gives exact eigenvalues/vectors to an approximate problem, complements what we will do next, which is to find approximate eigenvalues/vectors to the exact problem.

Perturbation Theory

Suppose we know the states & energies for $\hat{H}^0$:

$$\hat{H}^0|\psi_j^0\rangle = E_j^0|\psi_j^0\rangle \quad w/ \langle\psi_j|\psi_k\rangle = \delta_{jk}$$

i.e. you have $\{|\psi_j^0\rangle\}_{j=0}^{\infty}$, $\{E_j^0\}_{j=0}^{\infty}$.

What you want is the set $\{|\psi_j\rangle\}_{j=0}^{\infty}$, $\{E_j\}_{j=0}^{\infty}$ such that

new piece

$$(\hat{H}^0 + \lambda\hat{H}')|\psi_j\rangle = E_j|\psi_j\rangle \qquad (*)$$

If we could solve this, we would, but in general, we cannot — so we try to approximate.

idea: take $|\psi_j\rangle = |\psi_j^0\rangle + \lambda|\psi_j^1\rangle + \lambda^2|\psi_j^2\rangle + \cdots$

$$E_j = E_j^0 + \lambda E_j^1 + \lambda^2 E_j^2 + \cdots$$

put in to (*) & collect in powers of λ:

$$(\hat{H}^0 + \lambda\hat{H}')(|\psi_j^0\rangle + \lambda|\psi_j^1\rangle + \cdots) = (E_j^0 + \lambda E_j^1 + \cdots)(|\psi_j^0\rangle + \lambda|\psi_j^1\rangle + \cdots)$$

at λ^0: $\hat{H}^0|\psi_j^0\rangle = E_j^0|\psi_j^0\rangle$ ✓

λ^1: $\hat{H}^0|\psi_j^1\rangle + \hat{H}'|\psi_j^0\rangle = E_j^1|\psi_j^0\rangle + E_j^0|\psi_j^1\rangle \quad (0)$

$\vdots$

For the λ^1 eqn, hit both sides w/ $\langle\psi_j^0|$

$$\langle\psi_j^0|\hat{H}^0|\psi_j^1\rangle + \langle\psi_j^0|\hat{H}'|\psi_j^0\rangle = E_j^1\underbrace{\langle\psi_j^0|\psi_j^0\rangle}_{=1} + E_j^0\langle\psi_j^0|\psi_j^1\rangle \quad (+)$$

remember that we are trying to find E_j^1 & $|\psi_j^1\rangle$, both of which appear in (+).

We can expand $|\psi_j^1\rangle$ in the basis $\{|\psi_j^0\rangle\}_{j=0}^{\infty}$

$$|\psi_j^1\rangle = \sum_{k=0}^{\infty} c_k |\psi_k^0\rangle ,$$

then:

$$\langle\psi_j^0|\psi_j^1\rangle = \sum_{k=0}^{\infty} c_k \underbrace{\langle\psi_j^0|\psi_k^0\rangle}_{=\delta_{jk}} = c_j$$

&

$$\hat{H}^0|\psi_j^1\rangle = \sum_{k=0}^{\infty} c_k \hat{H}^0|\psi_k^0\rangle = \sum_{k=0}^{\infty} c_k E_k^0|\psi_k^0\rangle$$

w/

$$\langle\psi_j^0|\hat{H}^0|\psi_j^1\rangle = \sum_{k=0}^{\infty} c_k E_k^0 \underbrace{\langle\psi_j^0|\psi_k^0\rangle}_{=\delta_{jk}} = c_j E_j^0$$

putting these back in (+) gives

$$\cancel{c_j E_j^0} + \langle\psi_j^0|\hat{H}^1|\psi_j^0\rangle = E_j^1 + \cancel{E_j^0 c_j}$$

we learn that

$$E_j^1 = \langle\psi_j^0|\hat{H}^1|\psi_j^0\rangle .$$

How about the eigenvector corrections: $\{|\psi_j^1\rangle\}_{j=0}^{\infty}$?

We can use (o) again - this time hit both sides w/ $\langle\psi_\ell^0|$ w/ $\ell \neq j$.

$$\underbrace{\langle\psi_\ell^0|\hat{H}^0|\psi_j^1\rangle}_{=c_\ell E_\ell^0} + \langle\psi_\ell^0|\hat{H}^1|\psi_j^0\rangle = E_j^1 \underbrace{\cancel{\langle\psi_\ell^0|\psi_j^0\rangle}}_{0\ \ell\neq j} + E_j^0 \underbrace{\langle\psi_\ell^0|\psi_j^1\rangle}_{=c_\ell}$$

so we have: $c_\ell(E_j^0 - E_\ell^0) = \langle\psi_\ell^0|\hat{H}^1|\psi_j^0\rangle$, &

$$c_\ell = \frac{\langle\psi_\ell^0|\hat{H}^1|\psi_j^0\rangle}{E_j^0 - E_\ell^0}$$

(assuming $E_j^0 \neq E_\ell^0$), & we need all the c_ℓ just to construct $|\psi_j^1\rangle$, & then we need $j = 0 \to \infty$.

$$|\psi_j^1\rangle = \sum_{\substack{\ell=0\\ \neq j}}^{\infty} \underbrace{\left(\frac{\langle\psi_\ell^0|\hat{H}^1|\psi_j^0\rangle}{E_j^0 - E_\ell^0}\right)}_{=c_\ell} |\psi_\ell^0\rangle .$$

This is "1st order" perturbation theory:

$$E_j \approx E_j^0 + E_j^1 = E_j^0 + \langle\psi_j^0|\hat{H}^1|\psi_j^0\rangle$$

$$|\psi_j\rangle \approx |\psi_j^0\rangle + |\psi_j^1\rangle = |\psi_j^0\rangle + \sum_{\substack{\ell=0\\ \neq j}}^{\infty} \left(\frac{\langle\psi_\ell^0|\hat{H}^1|\psi_j^0\rangle}{E_j^0 - E_\ell^0}\right)|\psi_\ell^0\rangle$$