Title: Numerov Date: 26.2.19

3 The quantum one-body problem

- You know the Numerov algorithm
- You can state the difference between
  - a scattering problem
  - an eigenvalue problem
- For a time-dependent problem you can give two possible approaches

3.1 The time-independent 1D Schrödinger equation

We start from the Schrödinger equation of last week

$$-\frac{\hbar^2}{2m}\partial_x^2\psi(x) + V(x)\psi(x) = E\psi(x).$$

As we saw, $\psi(x)$ is twice differentiable and square-integrable

$$\int dx\, |\psi(x)|^2 = 1.$$

In other words it lives in an infinite-dimensional Hilbert space. To approach this problem, we simply discretize space

$$x_n = n \cdot \Delta x \qquad n \in \mathbb{Z}$$

and we deal with $\psi_n = \psi(x_n)$.

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3.1.1. The Numerov algorithm

In principle, we could go for the standard route and rewrite ψ'' into a first order derivative of

$$\partial_x \begin{pmatrix} \psi \\ \psi' \end{pmatrix}$$

and use any known Runge-Kutta method. However, for the special problem of

$$\psi''(x) + k(x)\psi(x) = 0$$

with $k(x) = 2m[E - V(x)]/\hbar^2$ we can employ the Numerov algorithm:

$$\psi_{n\pm1} = \psi_n \pm \Delta x \psi_n' + \frac{\Delta x^2}{2}\psi_n'' \pm \frac{\Delta x^3}{6}\psi_n^{(3)} + \frac{\Delta x^4}{24}\psi_n^{(4)} + \frac{\Delta x^5}{120}\psi_n^{(5)} + O(\Delta x^6)$$

Adding ψ_{n+1} and ψ_{n-1} we find

$$\psi_{n+1} + \psi_{n-1} = 2\psi_n + (\Delta x)^2 \psi_n'' + \frac{(\Delta x)^2}{12}\psi_n^{(4)}$$

We now replace the fourth derivative by a finite difference second derivative of the second derivative:

$$\psi_n^{(4)} = \frac{\psi_{n+1}'' + \psi_{n-1}'' - 2\psi_n}{\Delta x^2}.$$

By further substituting $\psi'' \to -k(x)\psi(x)$ we obtain

$$\left[1+\frac{(\Delta x)^2}{12}k_{n+1}\right]\psi_{n+1} = 2\left[1-\frac{5(\Delta x)^2}{12}k_n\right]\psi_n - \left[1+\frac{(\Delta x)^2}{12}k_{n-1}\right]\psi_{n-1} + O(\Delta x^6)$$

which is locally of sixth order.

To start the above algorithm we need <u>two</u> initial values. How we chose them depends on the problem at hand. If $V(x) = V(-x)$ we know that wave functions either fulfill $\psi(x) = \psi(-x)$ or $\psi(x) = -\psi(-x)$ $\Rightarrow$ this implies that we can start either

- For even solutions $x_{n+1/2} = \left(n+\frac{1}{2}\right)\Delta x$ and we pick $\psi(x_{-1/2}) = \psi(x_{+1/2}) = 1$
- For odd solutions we know $\psi(0) = -\psi(0) = 0$ $\Rightarrow x_n = n\Delta x$ and $\psi(x_1) = 1$

For general problems we need different approaches. If $V(x) = 0$ for $|x| > a$ we can use the exact solution of the Schrödinger equation

$$\psi(-a) = 1, \qquad \psi(-a-\Delta x) = e^{-\Delta x\sqrt{2mE}/\hbar}.$$

In the most general case where $V(x) \neq 0$ for $x \to \infty$, we use $\psi(x_0) = 1$ and perform one Runge-Kutta step.

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3.1.2 The one-dimensional scattering problem

As we know that we essentially solve an eigenvalue problem, we will not necessarily find a solution with the Numerov algorithm. The easiest problems are scattering problems where we have solutions $\forall E > 0$ if $V(x) \to \alpha$ for $|x| \to \infty$. For the special case where $V(x) = 0$ outside $x \in [0, a]$ we use the Ansatz

$$\psi_L(x) = A e^{iqx} + B e^{-iqx} \qquad x < 0$$
$$\psi_R(x) = C e^{iqx} \qquad x > a$$

What remains to be done is to find A, B, C such that we match ψ_L & ψ_R to the solution we find numerically in $x \in [0, a]$.

The program goes as follows

- $C = 1$ and use $\psi_R(a)$ and $\psi_R(a + \Delta x)$ as starting values for a Numerov integration.
- Integrate backwards to $x = 0$
- Match ψ and ψ' to ψ_L at $x = 0$ to find A & B.

By doing so we find transmission and reflection coefficients: $R = |B|^2/|A|^2$,

$$T = 1/|A|^2 .$$

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3.1.3 Bound states

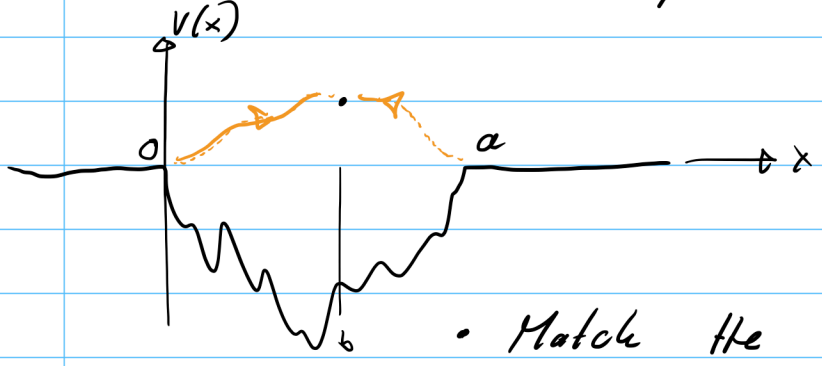
While we had a continuous spectrum for $E>0$ in the last section, we usually only have discrete $E<0$ solutions. We observe that for an arbitrary E $\psi(x \to \pm\infty)$ will diverge and hence is not square-integrable.

To address this numerically, we implement a *shooting method*:

- Start with a guess E.
- Integrate $\psi_E(x)$ from $x=0$ to $x_f \gg a$.
- Use a root solver to find $\psi_E(x_f) \approx 0$ as a function of E.

There is an issue with this approach: The divergences at $x \to \pm\infty$ introduce roundoff errors. To mitigate these we use the following procedure:

- Pick a starting point b and choose $E = V(b)$.
  $\Rightarrow \psi_E''(b) = 0$



- Integrate both from $a \to b$ and from $0 \to b$
- Match the two solutions and their derivatives at b (ψ'' is for free)

$$\Rightarrow \quad \psi_L(b) = \alpha \psi_R(b)$$
$$\psi_L'(b) = \alpha \psi_R'(b)$$

which reduces to

$$\frac{\psi_L'(b)}{\psi(b)} = \frac{\psi_R'(b)}{\psi_R(b)}$$

$\psi_{L/R}'$ we of course obtain from the finite differences. The last equation has to be solved with, e.g., a bisection method.

3.2 Higher dimensions

Higher dimensions require us to solve a PDE. A full coverage of how to do so with finite elements is a semester-filling endeavor. Here we only show a few tricks to avoid going there.

3.2.1 Factorization

In case $V(x,y,z) = V(x)V(y)V(z)$ we use the Ansatz

$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

which reduces the problem to three one-dimensional ones.

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3.2.2 Spherical symmetry

Another approach can be used if we have $V(\vec{x}) = V(|\vec{x}|) = V(r)$. We then use spherical harmonics

$$\psi_{\ell,m}(\vec{r}) = \frac{u(r)}{r} Y_{\ell m}(\vartheta, \varphi).$$

Inserted into the Schrödinger equation we obtain the following radial problem

$$\left[-\frac{\hbar^2}{2\mu} \partial_r^2 + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V(r) \right] u(r) = E u(r).$$

Here μ is the mass to avoid confusion with the index m of $Y_{\ell m}$. This one-dimensional Schrödinger equation has both the potential $V(r)$ and the centrifugal barrier

$$\frac{\hbar^2 \ell(\ell+1)}{r^2}$$

in it. Note that the centrifugal barrier is singular for $r \to 0$. Therefore, we should always start the Numerov algorithm at large r and integrate towards zero in order to accumulate the largest error only in the end.

3.2.3 Finite differences

If we cannot use any symmetries or factorizations we can still revert to the simplest solvers for PDEs:

finite differences. By going from differential operators to differences we turn the Schrödinger equation into a set of coupled equations. We begin with

$$\nabla^2\psi + 2m\left(E - V(\vec{x})\right)\psi = 0$$

and discretize space (i.e. turn the infinite dimensional Hilbert space into a finite one)

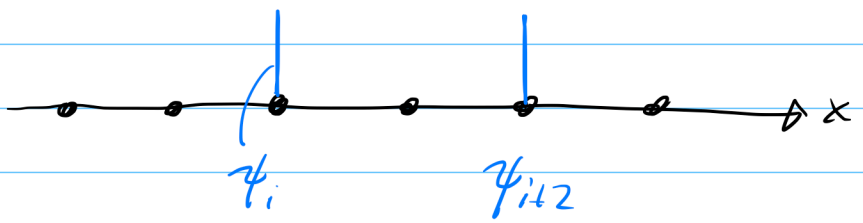
$$\frac{1}{\Delta x^2}\Big[\psi(x_{n+1}, y_n, z_n) + \psi(x_{n-1}, y_n, z_n) + \psi(x_n, y_{n+1}, z_n) + \psi(x_n, y_{n-1}, z_n) + \psi(x_n, y_n, z_{n+1}) + \psi(x_n, y_n, z_{n-1})\Big]$$

$$+ \left[2m\left(E - V(x_n, y_n, z_n)\right) - \frac{6}{\Delta x^2}\right]\psi(x_n, y_n, z_n) = 0$$

Solving these either for scattering problems, one *should use existing libraries*. The same holds true for the eigenvalue problems at $E<0$.

3.2.4 Variational approaches

By discretizing space we implicitly chose a basis in which we expand our problem: one of discrete delta-functions centred at the "sites" x_n:



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It is good for our numerical implementation that this basis is finite-dimensional. But is it the best discrete set of basis wave-functions?

In general we could write

$$|\phi\rangle = \sum_i a_i |u_i\rangle$$

where the $|u_i\rangle$'s are different from the discrete delta functions. We then write

$$E^* = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}.$$

It now becomes clear that discretization $x_n = n\Delta x$ was just one variational choice. To perform the minimization of E^* (assuming we are interested in the ground state) we write

$$H_{ij} = \langle u_i|H|u_j\rangle = \int dr\, u_i^*(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]u_j(\vec{r})$$

and for the overlaps

$$S_{ij} = \langle u_i|u_j\rangle = \int dr\, u_i^*(\vec{r})\, u_j(\vec{r}).$$

In other words, we allow ourselves to work with non-orthogonal basis functions. For a "standard" basis $S_{ij} = \delta_{ij}$. Minimizing E^* we find

$$\sum_j H_{ij} a_j = E^* \sum_k S_{ik} a_k$$

In compact notation we get

$$H\vec{a} = E^* S \vec{a}$$

"Normalizing" means we find U such that $U^\dagger S U = \mathbb{1}$. introducing $b = U^{-1} a$

$$H\vec{a} = E^* S \vec{a}$$
$$HU\vec{b} = E^* S U \vec{b}$$
$$U^\dagger H U \vec{b} = E^* U^\dagger S U \vec{b} = E^* \vec{b}$$

We now have to deal with a standard eigenvalue problem for $U^\dagger H U$.

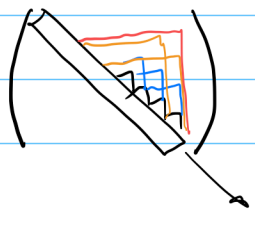
How do we chose the $|u_i\rangle$'s? Often it is good to use the eigenfunctions of a "close-by" problem. For example, for the anharmonic oscillator

$$H = \frac{1}{2}(p^2+q^2) + \lambda q^4$$

we would start from the solutions of the harmonic problem $\Rightarrow$

$$H = \frac{1}{2} + a^\dagger a + \lambda q^4 = \frac{1}{2} + a^\dagger a + \frac{\lambda}{4}(a^\dagger + a)^4.$$

You immediately see, that H in this basis has only 4- offdiagonal rows non-zero



$a^{\dagger 4}$ $a^{\dagger 2}$ $a^{\dagger 3}$ $a^\dagger$

For such sparse eigenvalue problems we can use efficient solvers.

3.2 The time-dependent Schrödinger equation

We are now switching to problems where we want to follow the time evolution of a given state $|\psi_0\rangle$.

3.2.1 Spectral methods

Clearly one one to go is to first solve the eigenvalue problem

$$H|\psi_n\rangle = E_n|\psi_n\rangle.$$

Using these solutions, we know that each individual one evolves as

$$|\psi_n(t)\rangle = e^{-iE_n t/\hbar}|\psi_n\rangle.$$

Now we only have to expand the initial state

$$c_n = \langle\psi_n|\psi_0\rangle$$

and we find

$$|\psi_0(t)\rangle = \sum_n e^{-iE_n t/\hbar} c_n |\psi_n\rangle.$$

3.2.2 Direct numerical integration

If the relevant Hilbert space is too big, the spectral method does not work. We can then just forward-integrate using the method of lines, where we either choose a set of basis functions or discretize the spatial derivatives we obtain a set of coupled ordinary differential equations (ODE's) which can be evolved for each point along the time line.

let's say H is the Hamiltonian matrix in a chosen basis set. We could be tempted to use a simple Euler forward scheme

$$|\psi(t_{n+1})\rangle = |\psi(t_n)\rangle - \frac{i\Delta t}{\hbar} H |\psi(t_n)\rangle.$$

However, this has two problems: (i) it is numerically unstable and (ii) it does not preserve the norm of the wave function $\langle\psi|\psi\rangle = 1$. Recall that the quantum evolution

$$\psi(\vec{x}, t+\Delta t) = e^{-iH\Delta t/\hbar}\psi(\vec{x}, t)$$

is unitary and hence preserves the norm of ψ! We should construct an approximate time evolution which itself is unitary. Instead of Taylor expanding

$$e^{-iH\Delta t/\hbar} \approx \mathbb{1} - \frac{i\Delta t}{\hbar} H + \dots$$

we write

$$e^{-iH\Delta t/\hbar} = \left(e^{iH\Delta t/2\hbar}\right)^{-1} e^{-iH\Delta t/2\hbar} =$$

$$\approx \left(1 + \frac{i\Delta t}{2\hbar} H\right)^{-1} \left(1 - \frac{i\Delta t}{2\hbar} H\right)$$

which is unitary! We don't want to invert H, however. So we could write

$$\left(1 + \frac{i\Delta t}{\hbar} H\right) \psi(\vec{x}, t+\Delta t) = \left(1 - \frac{i\Delta t}{\hbar} H\right) \psi(\vec{x}, t)$$

This implicit equation can be solved efficiently if we again make sure that H is zero a few off-diagonals away from the diagonal. i.e., we chose the right basis again!

3.2.3 The split operator method

A simpler trick can be used for systems where we have

$$H = \hat{T} + \hat{V}$$

where $\hat{T} = \frac{\hat{p}^2}{2m}$ is diagonal in Fourier space while $\hat{V} = V(\hat{r})$ is diagonal in direct space. We can then use

$$\tilde{\psi}(\vec{k}) = \frac{1}{\sqrt{2\pi}^d} \int_{-\infty}^{\infty} d\vec{x}\, \psi(\vec{x}) e^{-i\vec{x}\vec{k}}$$

$$\psi(\vec{x}) = \frac{1}{\sqrt{2\pi}^d} \int_{-\infty}^{\infty} d\vec{k}\, \tilde{\psi}(\vec{k}) e^{i\vec{k}\vec{x}}.$$

it is easy to check that

$$\hat{V}\,\psi(\vec{x}) = V(\vec{x})\,\psi(\vec{x}) \qquad \text{and}$$

$$\hat{T}\,\tilde{\psi}(\vec{k}) = \frac{|k|^2}{2m}\,\tilde{\psi}(\vec{k}).$$

In other words $\tilde{\psi}$ is indeed an eigenfunction to $\hat{T}$. We now split the time evolution as

$$e^{-\Delta t \hat{H}/\hbar} = e^{-i\Delta t \hat{V}/2\hbar}\, e^{-i\Delta t \hat{T}/\hbar}\, e^{-i\Delta t \hat{V}/2\hbar} + O(\Delta t^3)$$

The individual steps can be performed exactly

$$\left[e^{-i\Delta t \hat{V}/2\hbar}|\psi\rangle\right](x) = e^{-i\Delta t V(\vec{x})/2\hbar}\,\psi(\vec{x}),$$

$$\left[e^{-i\Delta t \hat{T}/\hbar}|\psi\rangle\right](k) = e^{-i\Delta t |k|^2\hbar/2m}\,\tilde{\psi}(\vec{k}).$$

To time evolve, we need $t = N\Delta t$ steps. Two consecutive real-space steps can be combined to one and we find

$$e^{-iH t/\hbar} = e^{-i\Delta t \hat{V}/2\hbar}\left[e^{-i\Delta t \hat{T}/\hbar}\, e^{-i\Delta t \hat{V}/\hbar}\right]^{N-1} e^{-i\Delta t \hat{T}/\hbar}\, e^{-i\Delta t \hat{V}/2\hbar}.$$

In practice we also discretize space (not just time) into P points of Δx spacing. In other words the Fourier transform becomes a discrete Fourier transform with P discrete $k_n = \frac{2\pi}{n} P$ values. Changing forth and back between x_n and k_n requires fast Fourier transforms which we write as $\mathcal{F}$.

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The discretized algorithm starts as:

$$\psi_1(\vec{x}) = e^{-i\Delta t V(\vec{x})/2\hbar}\,\psi_0(\vec{x})$$

$$\tilde{\psi}_1(\vec{k}) = \mathcal{F}\,\psi_1(\vec{x})$$

Now we propagate with full time steps:

$$\tilde{\psi}_{2n}(\vec{k}) = e^{-i2\Delta t\frac{\hbar k^2}{2m}}\,\tilde{\psi}_{2n-1}(\vec{k}),$$

$$\psi_{2n}(\vec{x}) = \mathcal{F}^{-1}\,\tilde{\psi}_{2n}(\vec{k}),$$

$$\psi_{2n+1}(\vec{x}) = e^{-i2\Delta t\,V(\vec{x})/\hbar}\,\psi_{2n+1}(\vec{x}),$$

$$\tilde{\psi}_{2n+1}(\vec{k}) = \mathcal{F}\,\psi_{2n+1}(\vec{x}).$$

At the very end, we add the last half-step

$$\psi_{2N+1}(\vec{x}) = e^{-i\Delta t\tilde{V}(\vec{x})/2\hbar}\,\psi_{2N}(\vec{x}).$$