Quantum Mechanics
Numerical solutions of the Schrödinger equation

- Integration of 1D and 3D-radial equations
- Variational calculations for 2D and 3D equations
- Solution using matrix diagonalization methods
- Time dependence
Brief review of quantum mechanics

In classical mechanics, a point-particle is described by its position $x(t)$ and velocity $v(t)$

- Newton’s equations of motion evolve $x,v$ as functions of time

In quantum mechanics, $x$ and $v$ cannot be precisely known simultaneously (the uncertainty principle). A particle is described by a wave function $\Psi(x,t)$

- the probability of the particle being in a volume $dx$ is

$$P(x, t)dx \propto |\Psi(x, t)|^2 dx$$

- The Schrödinger equation evolves $\Psi(x,t)$ in time
- There are energy eigenstates of the Schrödinger equation
  - for these, only a phase changes with time
  $$\Psi_n(x, t) = \Psi_n(x, 0)e^{-itE_n/\hbar}, \quad \hbar \approx 1.05 \cdot 10^{-34} Js$$

$\Rightarrow$ Finding the energy eigenstates (stationary states) is an important task
Stationary Scrodinger equation in three dimensions

\[-\frac{\hbar}{2m} \nabla^2 \Psi(\vec{x}) + V(\vec{x}) \Psi(\vec{x}) = E \Psi(\vec{x})\]

Spherical symmetric potentials; separable

\[\Psi_{L,L_z,n}(\vec{x}) = R_{L,n}(r)Y_{L,L_z}(\phi, \Theta) = \frac{1}{r} U_{L,n} Y_{L,L_z}(\phi, \Theta)\]

Radial wave function

\[\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{L(L + 1)\hbar^2}{2mr^2} + V(r) \right) U_{L,n}(r) = E_{L,n} U_{L,n}(r)\]

Similar to purely one-dimensional problems

\[-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) = E \Psi(x)\]
Numerov’s method (one dimension)

Stationary Schrödinger equation

\[-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{d x^2} + V(x) \Psi(x) = E \Psi(x)\]

Can be written as (also radial function in three dimensions)

\[\Psi''(x) = f(x) \Psi(x)\]

Discretization of space: \(\Delta_x\). Consider Taylor expansion

\[\Psi(\Delta_x) = \Psi(0) + \sum_{n=1}^{\infty} \frac{\Delta_x^n}{n!} \Psi^{(n)}(0)\]

Add expansions for \(\pm \Delta_x\)

\[\Psi(\Delta_x) + \Psi(-\Delta_x) = 2\Psi(0) + \Delta_x^2 \Psi''(0) + \frac{1}{12} \Delta_x^4 \Psi^{(4)}(0) + O(\Delta_x^6)\]

Second derivative determined by the Schrödinger equation

How to deal with the fourth derivative?
Central difference operator

\[ \delta g(0) = g(\Delta_x/2) - g(-\Delta_x/2) \]

\[ \delta^2 g(0) = \delta[\delta g(0)] = g(\Delta_x) - 2g(0) + g(-\Delta_x) \]

\[ g''(x) = \frac{1}{\Delta_x^2} \delta^2 g(x) + O(\Delta_x^2) \]

We can rewrite the previous equation

\[ \Psi(\Delta_x) + \Psi(-\Delta_x) = 2\Psi(0) + \Delta_x^2 \Psi''(0) + \frac{1}{12} \Delta_x^4 \Psi^{(4)}(0) + O(\Delta_x^6) \]

using the second central difference, giving

\[ \delta^2 \Psi(0) = \Delta_x^2 \Psi''(0) + \frac{1}{12} \Delta_x^4 \Psi^{(4)}(0) + O(\Delta_x^6) \]

Approximate the fourth derivative

\[ \Delta_x^4 \Psi^{(4)}(0) = \Delta_x^4 [\Psi''(0)]'' = \Delta_x^2 \delta^2 \Psi''(0) + O(\Delta_x^6) \]

leads to the general result

\[ \delta^2 \Psi(0) = \Delta_x^2 \Psi''(0) + \frac{1}{12} \Delta_x^2 \delta^2 \Psi''(0) + O(\Delta_x^6) \]
\[ \delta^2 \Psi(0) = \Delta_x^2 \Psi''(0) + \frac{1}{12} \Delta_x^2 \delta^2 \Psi''(0) + O(\Delta_x^6) \]

Schrodinger equation \( \Psi''(x) = f(x)\Psi(x) \) gives

\[ \delta^2 \Psi(0) = \Delta_x^2 f(0)\Psi(0) + \frac{1}{12} \Delta_x^2 \delta^2 [f(0)\Psi(0)] + O(\Delta_x^6) \]

More compact notation: \( g_n = g(n\Delta_x) \)

\[ \Psi_1 - 2\Psi_0 + \Psi_{-1} = \Delta_x^2 f_0 \Psi_0 + \frac{1}{12} \Delta_x^2 [f_1 \Psi_1 + f_{-1} \Psi_{-1} - 2f_0 \Psi_0] + O(\Delta_x^6) \]

Introduce function \( \phi_n = \Psi_n (1 - \Delta_x^2 f_n / 12) \)

\[ \phi_1 = 2\phi_0 - \phi_{-1} + \Delta_x^2 f_0 \Psi_0 + O(\Delta_x^6) \]

Fortran implementation

```
do n=2,nx
    q2=dx2*f1*psi(n-1)+2.d0*q1-q0
    q0=q1; q1=q2
    f1=2.d0*(potential(dx*dble(n))-energy)
    psi(n)=q1/(1.d0-dx2*f1)
enddo
```
Boundary-value problems

The Schrodinger equation has to satisfy boundary conditions

**quantization**, as not all energies lead to valid solutions

**Example: Particle in a box (infinite potential barrier)**

\[ V(x) = 0 \quad (|x| < 1), \quad V(x) = \infty \quad (|x| \geq 1) \]

Using \( \hbar = 1, m = 1 \)

\[ \Psi''(x) = 2[V(x) - E]\Psi(x) \]

Boundary conditions: \( \Psi(\pm 1) = 0 \)

\[ \Psi(x) = N \cos \left( n\pi x/2 \right), \quad (n \text{ odd}) \]

\[ \Psi(x) = N \sin \left( n\pi x/2 \right), \quad (n \text{ even}) \]

\[ E = \frac{\pi^2 n^2}{8} \]

How do we proceed in a numerical integration?
Choose valid boundary conditions at $x=-1$

$$\Psi(-1) = 0, \quad \Psi(-1 + \Delta x) = A$$

A is arbitrary (not 0); normalize after solution found

“Shooting method”

Pick an energy $E$

- Integrate to $x=1$
- Is boundary condition at $x=1$ satisfied?
- If not, adjust $E$, integrate again
- Use bisection to refine
**Solving an equation using bisection (general)**

We wish to find the zero of some function

\[ f(E) = 0 \]

First find \( E_1 \) and \( E_2 \) bracketing the solution

\[ f(E_1) < 0, \quad f(E_2) > 0 \]

Then evaluate the function at the mid-point value

\[ E_3 = \frac{1}{2}(E_1 + E_2) \]

Choose new bracketing values:

- if \( f(E_3) < 0 \), then \( E'_1 = E_3, \quad E'_2 = E_2 \)
- if \( f(E_3) > 0 \), then \( E'_1 = E_1, \quad E'_2 = E_3 \)

Repeat procedure with the new bracketing values - until \( f(E_3) < \epsilon \)
Bisection search for the ground state

- First find $E_1$, $E_2$ giving different signs at $x=+1$
- Then do bisection within these brackets
More complicated example:
Box with central Gaussian potential barrier

Ground state
Search
First excited state
Potential well with non-rigid walls

Looking for bound state; $\Psi(x \to \pm \infty) \to 0$

Asymptotic solution: $\Psi(x) = Ae^{\alpha x} + Be^{-\alpha x}$. $\alpha = \sqrt{2(V_\infty - E)}$

$A=0$ for $x>0$
$B=0$ for $x<0$

Use the asymptotic form for two points far away from the center of the well

Find $E$ for which the solution decays to 0 at the other boundary
Ground state search

Using criterion:
\[ \Psi(1) = \Psi(-1) \]