# Quantum Mechanics
# Numerical solutions of the Schrodinger 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 Schrodinger 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

Time dependent Scrodinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = H\Psi(x,t)$$ -> stationary $$H\Psi(x) = E\Psi(x)$$

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

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

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 Schrodinger equation

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

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 Schrodinger 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

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

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

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

Julia implementation

```
for n=2:nx
  phi2=dx2*fn1*psi(n-1)+2*phi1-phi0
  phi0=phi1; phi1=phi2
  fn1=2*(potential(dx*n)-energy)
  psi(n)=phi1/(1-dx2*fn1)
end
```

# 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)

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

Using $\hbar = 1, m = 1$

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

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

$$\Psi(x) = N\cos(n\pi x/2), \quad (n \text{ odd})$$
$$\Psi(x) = N\sin(n\pi x/2), \quad (n \text{ even})$$

$$E = \frac{\pi^2 n^2}{8}$$

How do we proceed in a numerical integration?

Choose valid boundary conditionas at x=-1

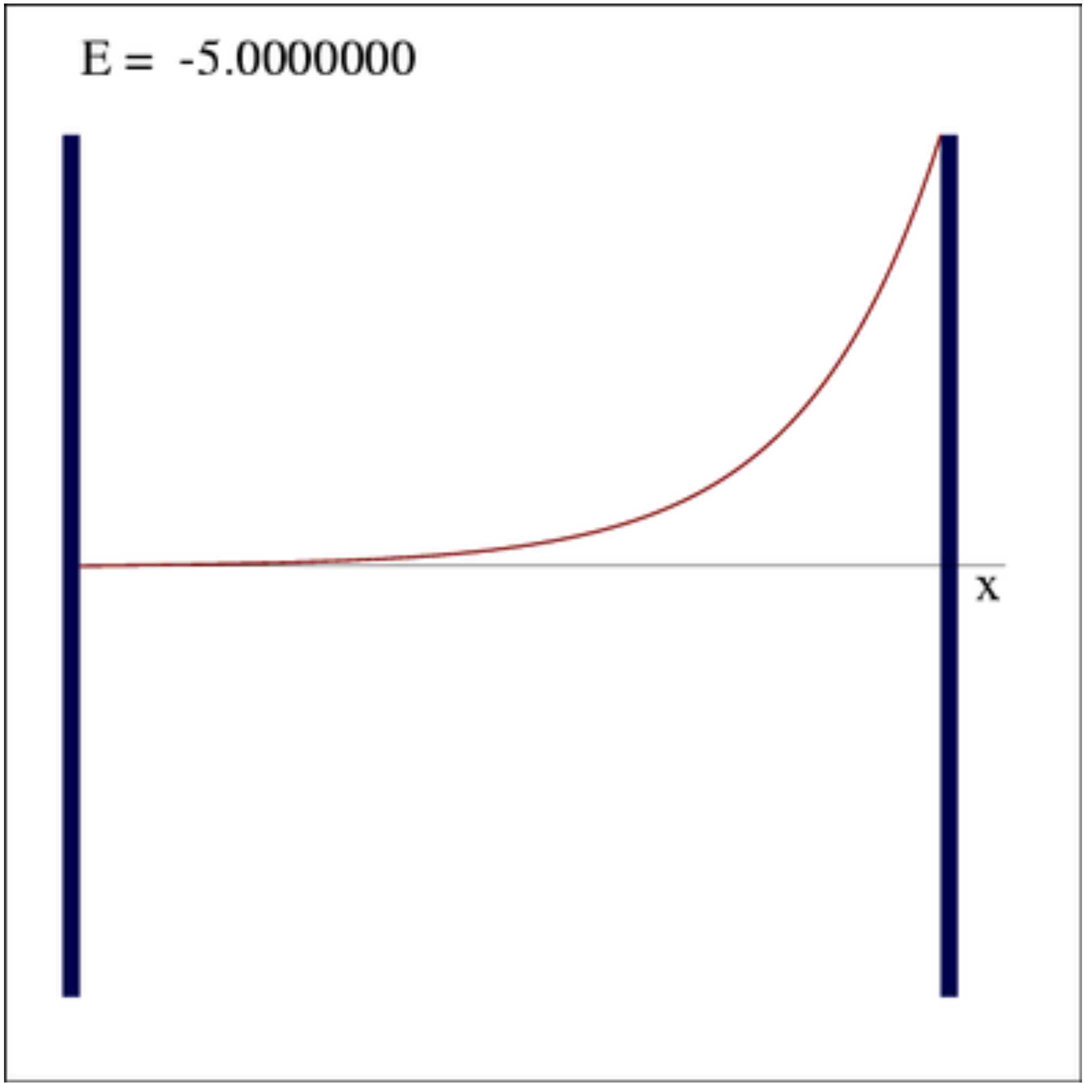
$$\Psi(-1) = 0, \quad \Psi(-1+\Delta_x) = A$$

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:

$$\text{if } f(E_3) < 0, \text{ then } E_1' = E_3, \ E_2' = E_2$$

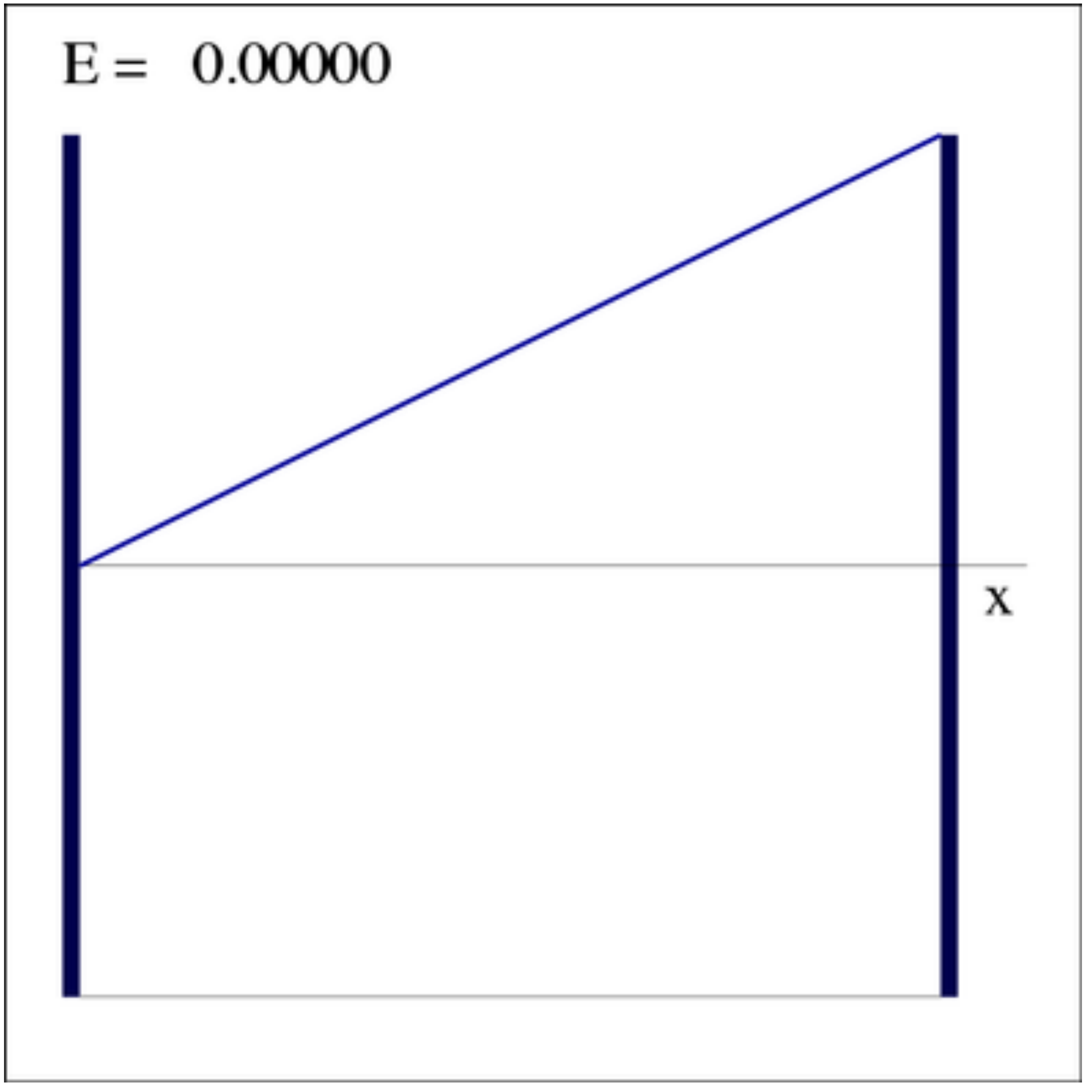
$$\text{if } f(E_3) > 0, \text{ then } E_1' = E_1, \ E_2' = E_3$$

Repeat procedure with the new bracketing values

- until $f(E_3) < \epsilon$

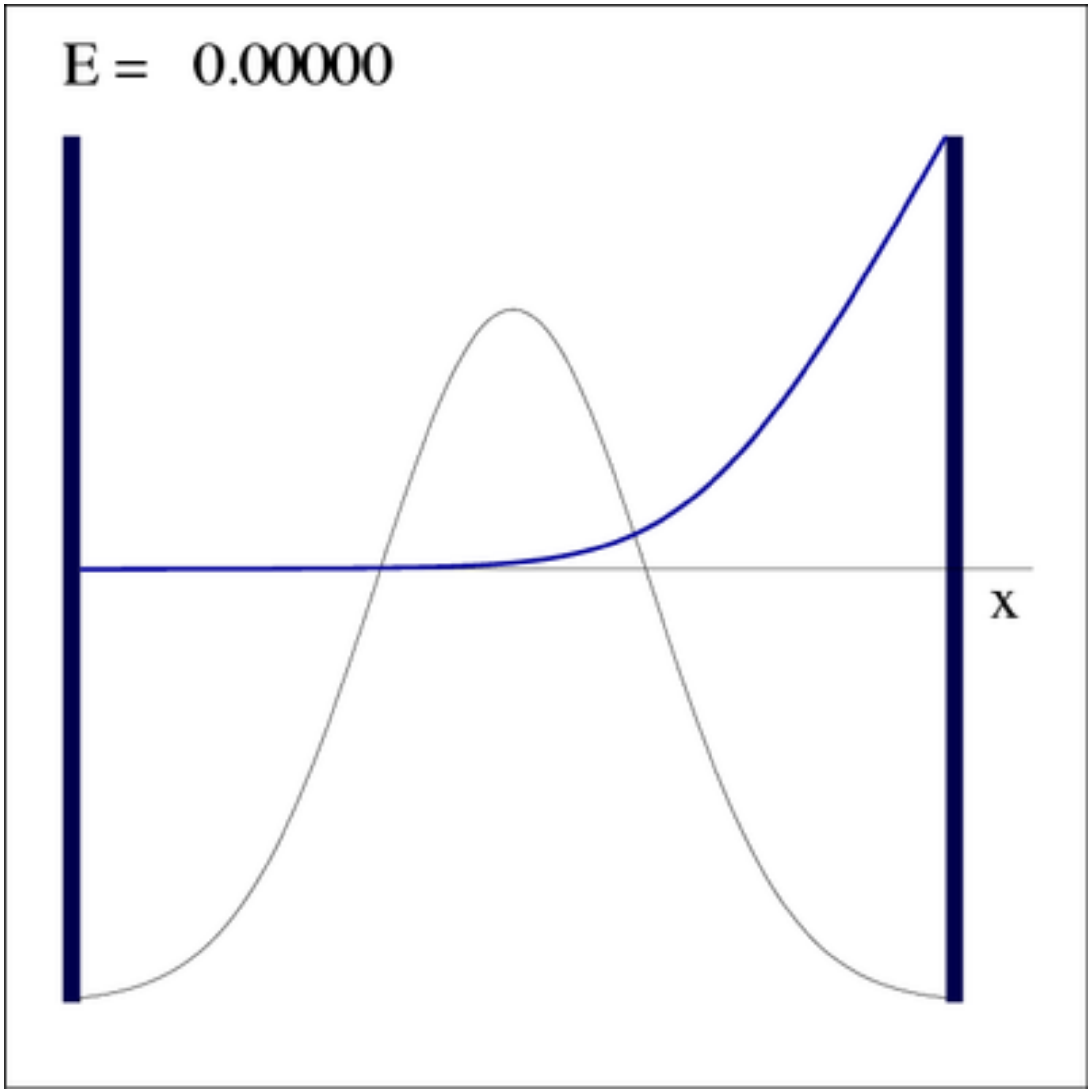
Bisection search for the ground state

- First find E1, E2 giving different signs at x=+1
- Then do bisection within these brackets



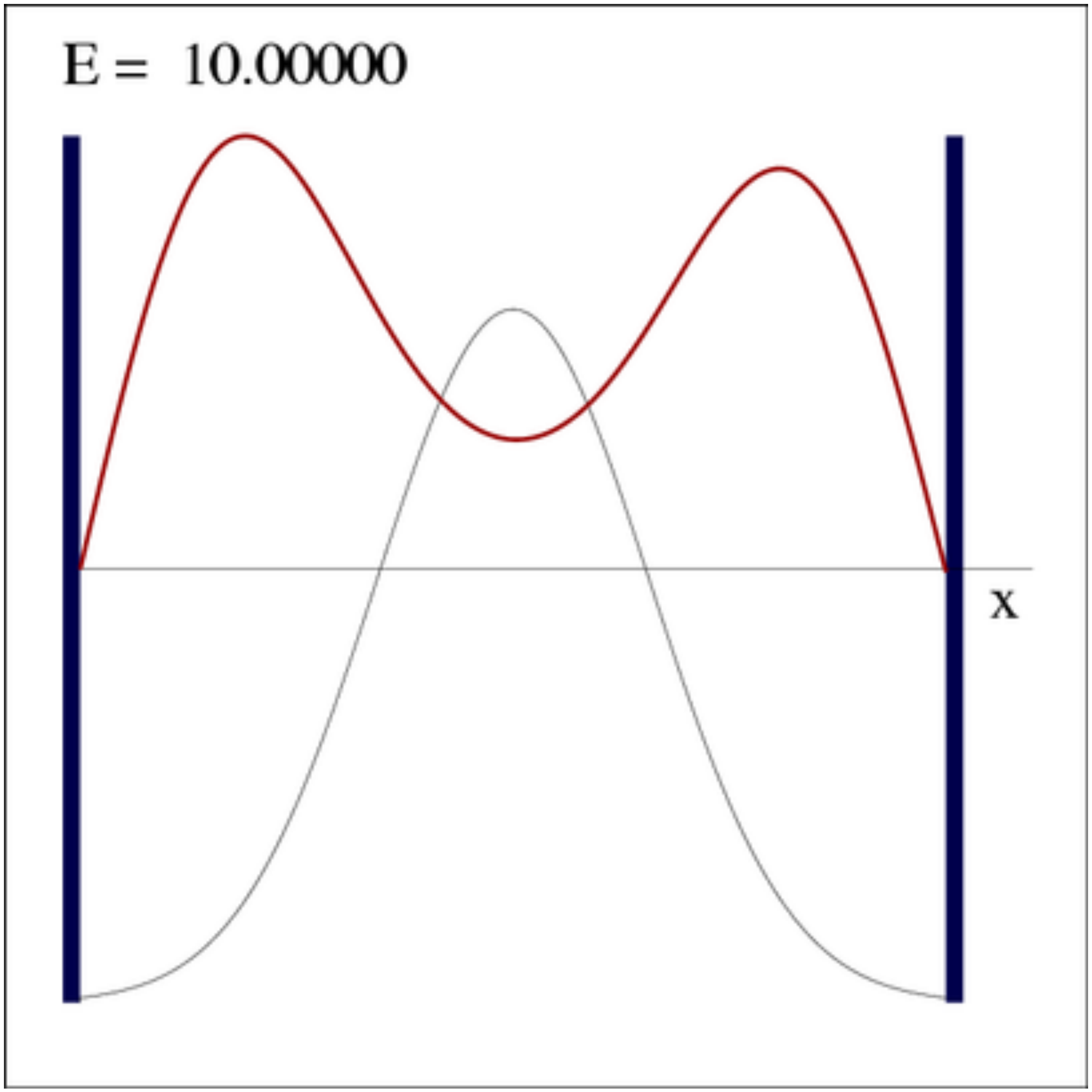
More complicated example:

Box with central Gaussian potential barrier




Ground state
Search

First excited state



# Potential well with non-rigid walls

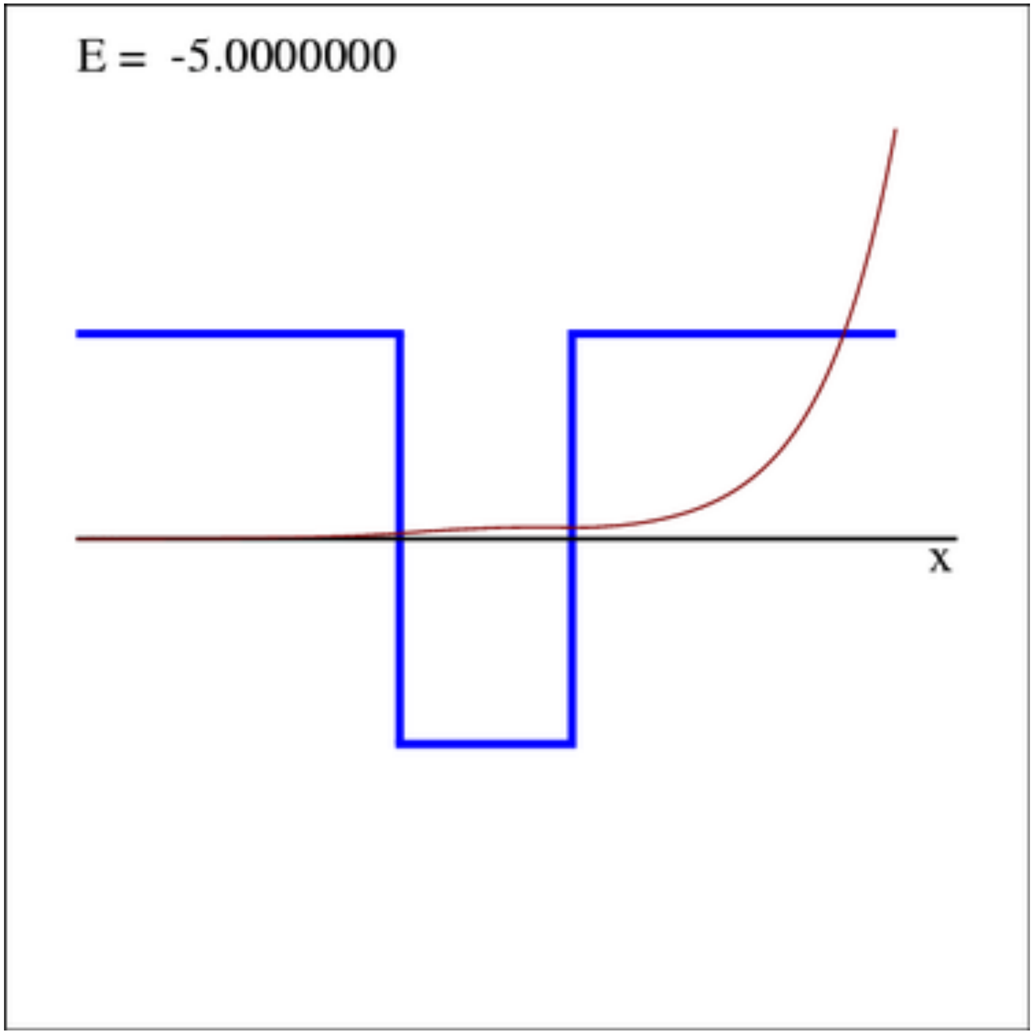
Looking for bound state; $\Psi(x \to \pm\infty) \to 0$

Asymptotic solution: $\Psi(x) = A\mathrm{e}^{\alpha x} + B\mathrm{e}^{-\alpha x}.\ \ \alpha = \sqrt{2(V_\infty - E)}$

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:

$$\Psi(1) = \Psi(-1)$$