

# 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  $\mathbf{x}(t)$  and velocity  $\mathbf{v}(t)$

- 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**  $\Psi(\mathbf{x}, t)$

- 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  $\Psi(\mathbf{x}, t)$  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

Stationary Scrodinger equation in three dimensions

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

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 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

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

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

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

$$\phi_1 = 2\phi_0 - \phi_{-1} + \Delta_x^2 f_0 \Psi_0 + O(\Delta_x^6) \quad q2 = \phi_n$$

Fortran implementation

$$\text{psi}(n) = \Psi_n$$

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do n=2,nx
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  q2=dx2*f1*psi(n-1)+2.d0*q1-q0
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$$f1 = f_{n-1}$$

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  q0=q1; q1=q2
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```
  f1=2.d0*(potential(dx*double(n))-energy)
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```
  psi(n)=q1/(1.d0-dx2*f1)
```

```
enddo
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# 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:  $\Psi(\pm 1) = 0$

$$\begin{aligned} \Psi(x) &= N \cos(n\pi x/2), & (n \text{ odd}) \\ \Psi(x) &= N \sin(n\pi x/2), & (n \text{ even}) \end{aligned} \quad E = \frac{\pi^2 n^2}{8}$$

How do we proceed in a numerical integration?

Choose valid boundary conditions at  $x=-1$

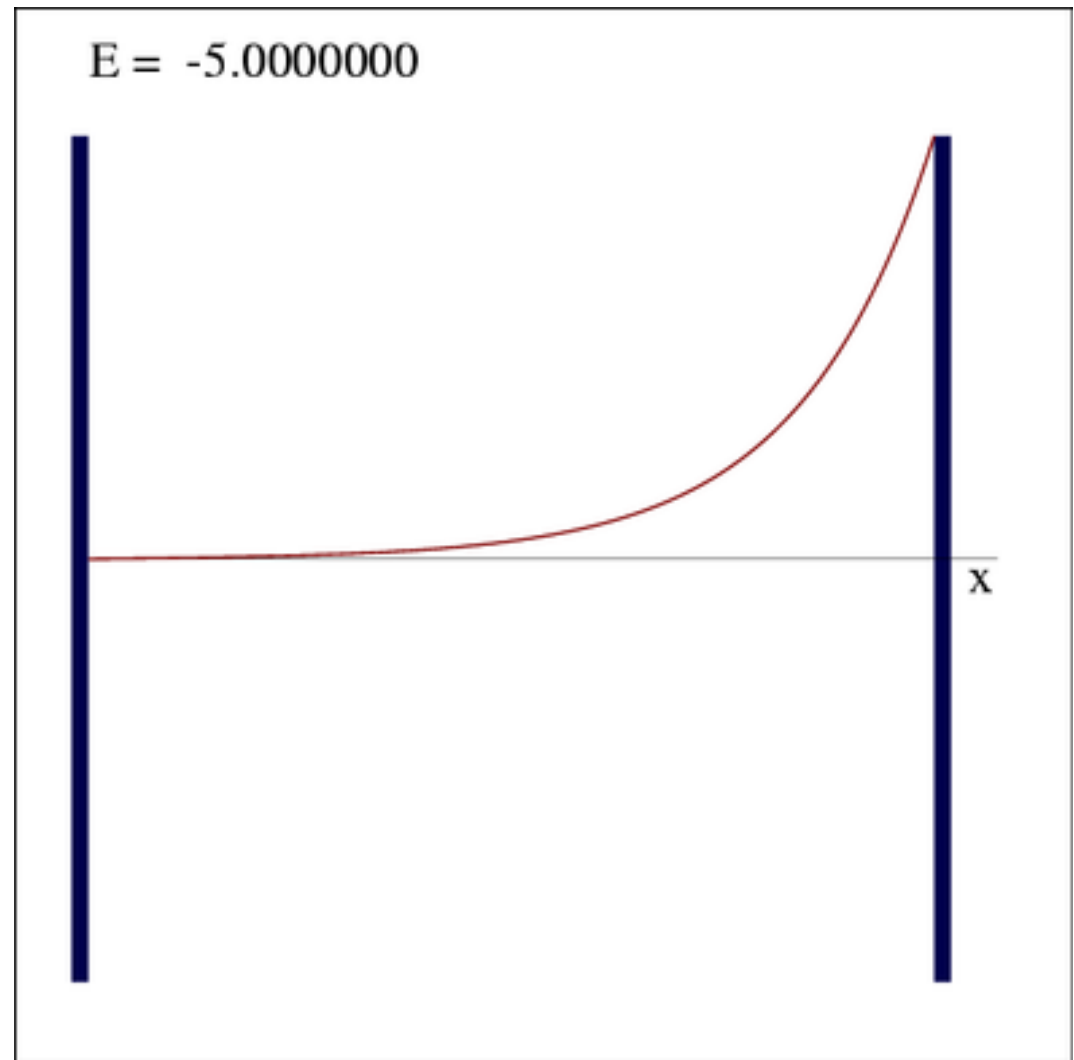
$$\Psi(-1) = 0, \quad \Psi(-1 + \Delta_x) = A$$

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:

$$\text{if } f(E_3) < 0, \text{ then } E'_1 = E_3, \quad E'_2 = E_2$$

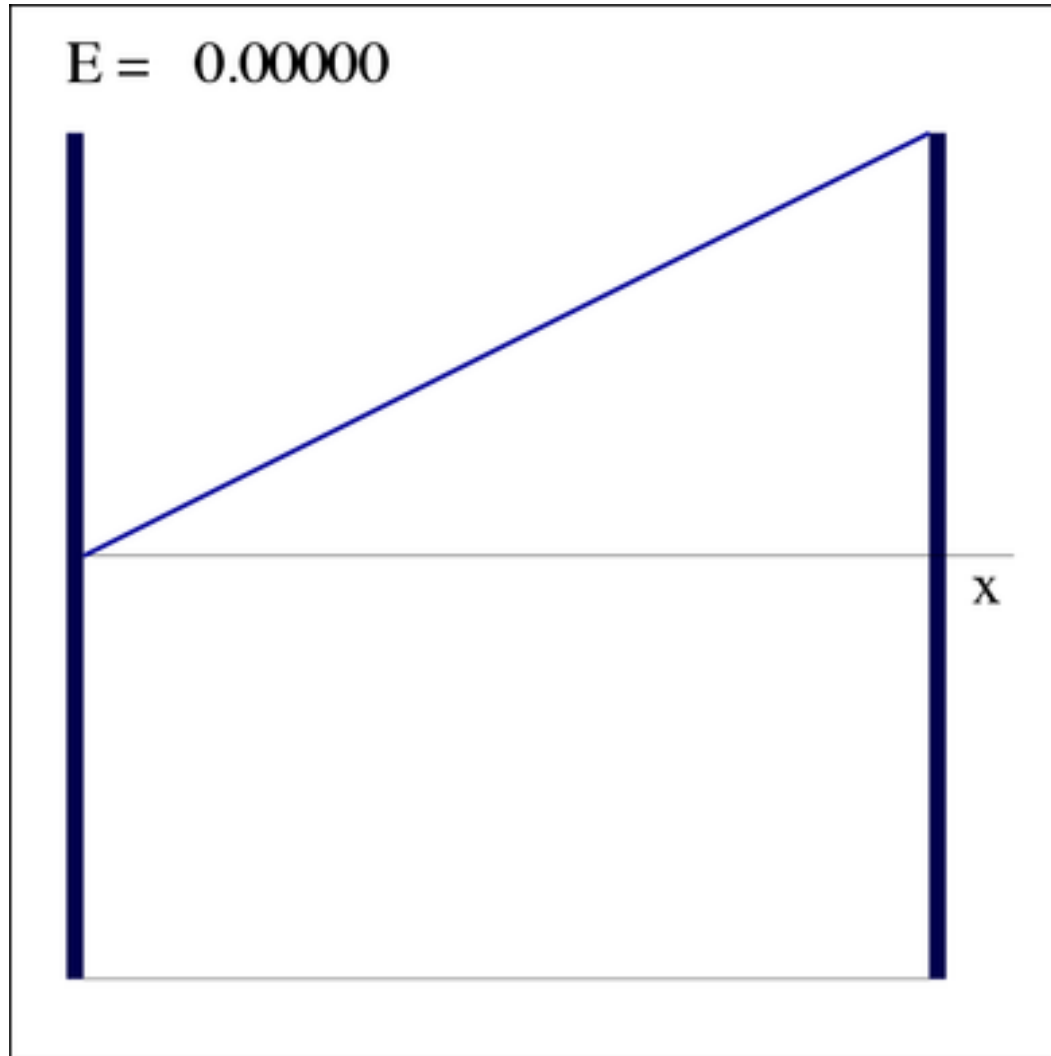
$$\text{if } f(E_3) > 0, \text{ then } E'_1 = E_1, \quad E'_2 = E_3$$

Repeat procedure with the new bracketing values

- until  $f(E_3) < \epsilon$

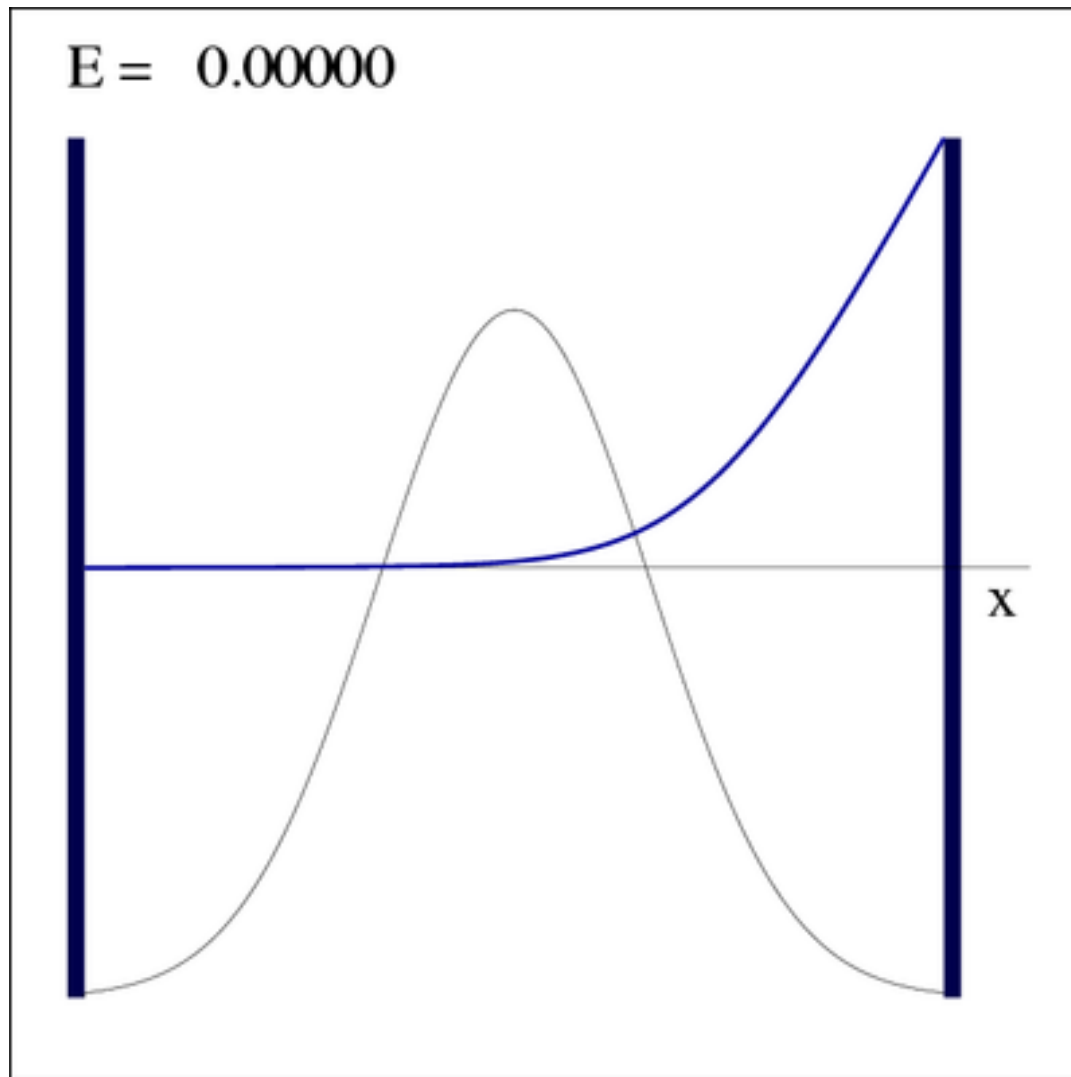
## Bisection search for the ground state

- First find  $E_1, E_2$  giving different signs at  $x=+1$
- Then do bisection within these brackets



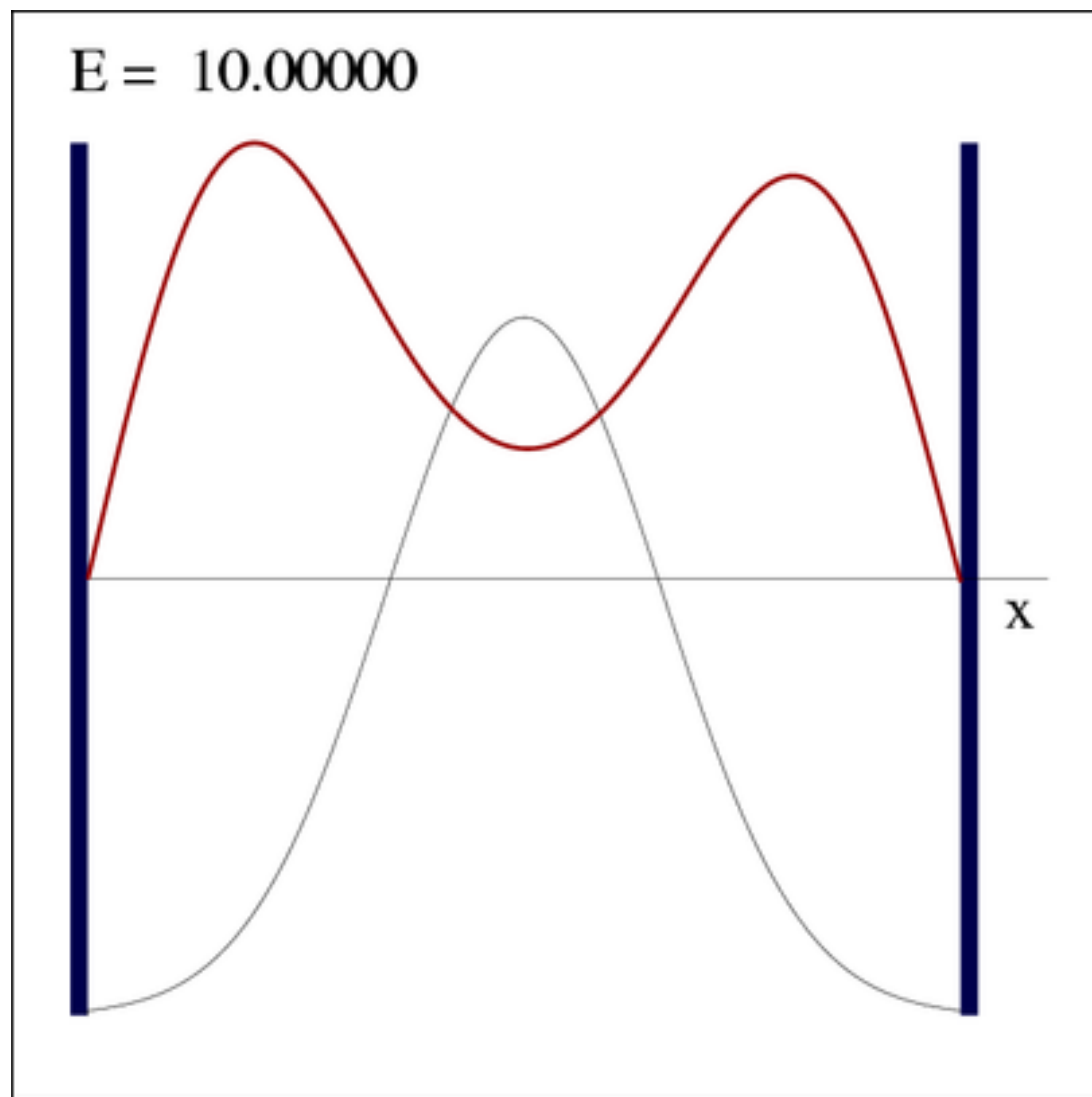
More complicated example:

Box with central Gaussian potential barrier



Ground state  
Search

First excited state



## Potential well with non-rigid walls

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

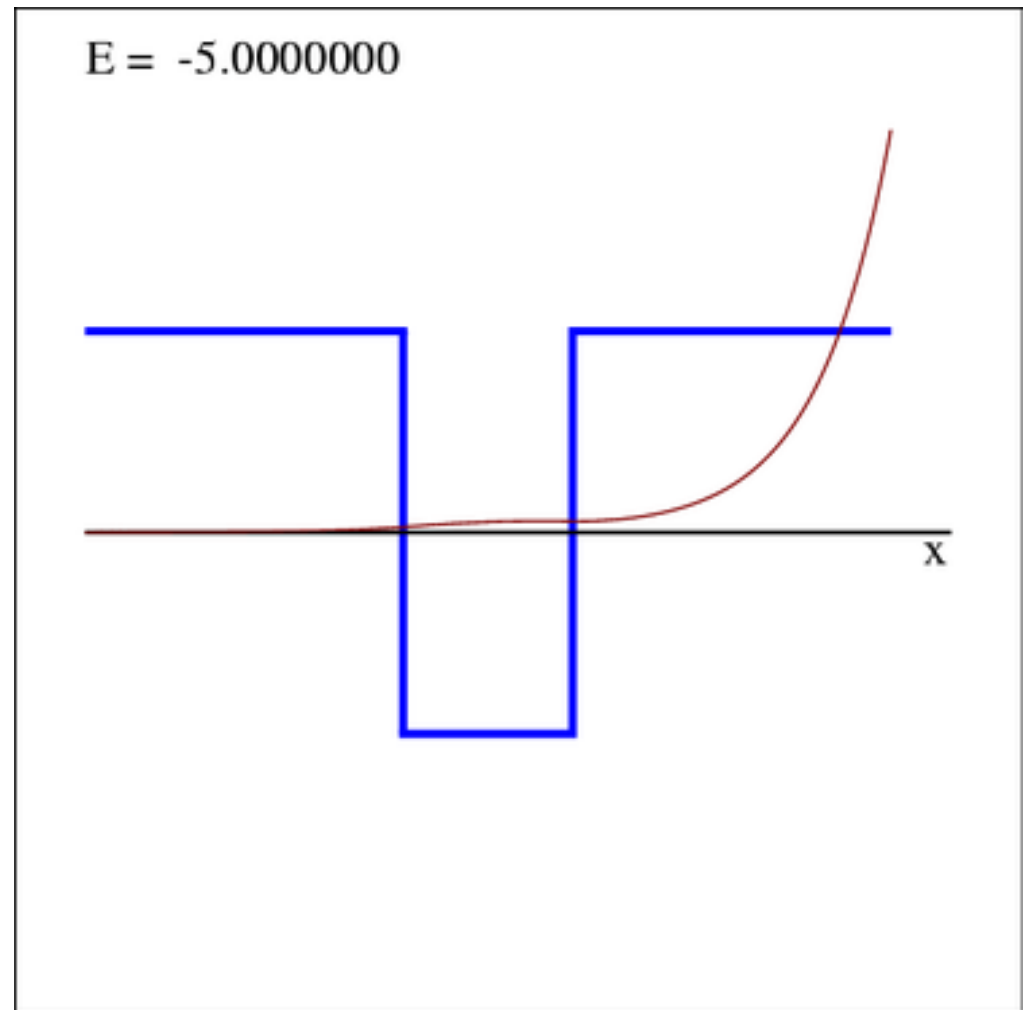
Asymptotic solution:  $\Psi(x) = Ae^{\alpha x} + Be^{-\alpha x}$ .  $\alpha = \sqrt{2(V_\infty - E)}$

$A=0$  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:

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

