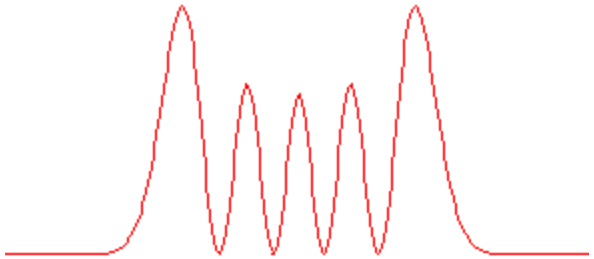
EP547 Computational Methods in QM

Topic 14

Schrödinger Equation



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Eigenvalue Problems

Eigenvalue problems are a special class of boundary value problems that are common in physics and engineering problem contexts involving:

$\Rightarrow$ Vibration

$\Rightarrow$ Elasticity

$\Rightarrow$ Quantum Mechanics etc.

We have seen that a Linear system equations can be written as in matrix form:

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix}$$

or

$$\mathbf{Ax = b}$$

For homogeneous systems, we have:

$$\mathbf{Ax = 0}$$

An eigenvalue problem is typically expressed as:

$$\begin{pmatrix} a_{11}-\lambda & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22}-\lambda & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn}-\lambda \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

where λ is known as *eigenvalue* and **x** as *eigenvector*.
The equation may also be written as

$$(\mathbf{A} - \lambda\mathbf{I})\mathbf{x} = \mathbf{0}$$

One way to get non-trivial solution is based on getting λ values from the equation

$$\det(\mathbf{A} - \lambda\mathbf{I}) = 0$$

Matlab provides a simple way to get eigenvalues and eigenvectors of a square matrix:

```
>> A = [1 2; 3 4];
>> [evec, lambda] = eig(A)

evec =
   -0.8246   -0.4160
    0.5658   -0.9094

lambda =
   -0.3723         0
         0    5.3723
```

Schrödinger Equation

- Schrödinger Equation (SE) is a one of the good example for an eigenvalue problem.

- We will generally consider numerical solution to the one dimensional and time independent problems. Therefore, SE for this case is:

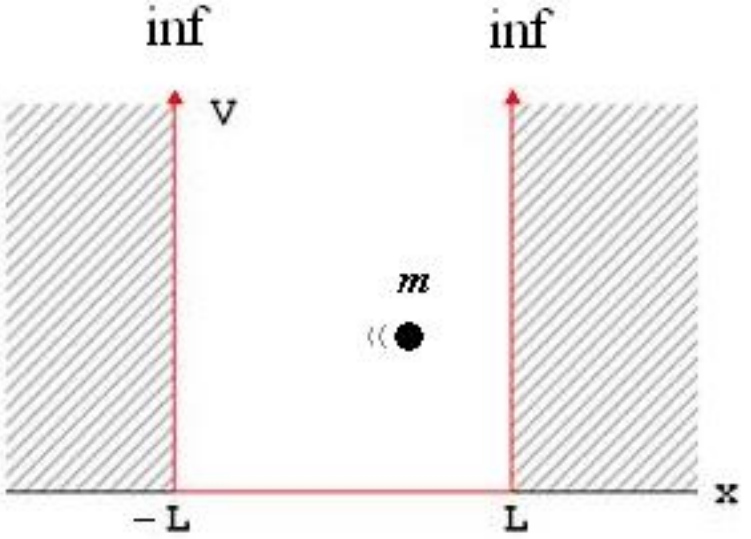
$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}+V(x)\Psi=E\Psi$$

- For simplicity, we will also consider that $\hbar=m=1$

$$-\frac{1}{2}\frac{d^2\Psi}{dx^2}+V(x)\Psi=E\Psi$$

- *Here the problem is to solve energy E and WaveFunction Ψ at the same time*!
- There are a few number of numerical solution method for the SE. *We will use a finite difference matrix method*.

A Particle in an Infinite Well



Analytical solution:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8mL^2} \quad n = 1,2,3,...$$

$$\Psi_n = \frac{1}{\sqrt{L}} \cos\left(\frac{n\pi x}{2L}\right) \quad \text{if } n \text{ is odd}$$

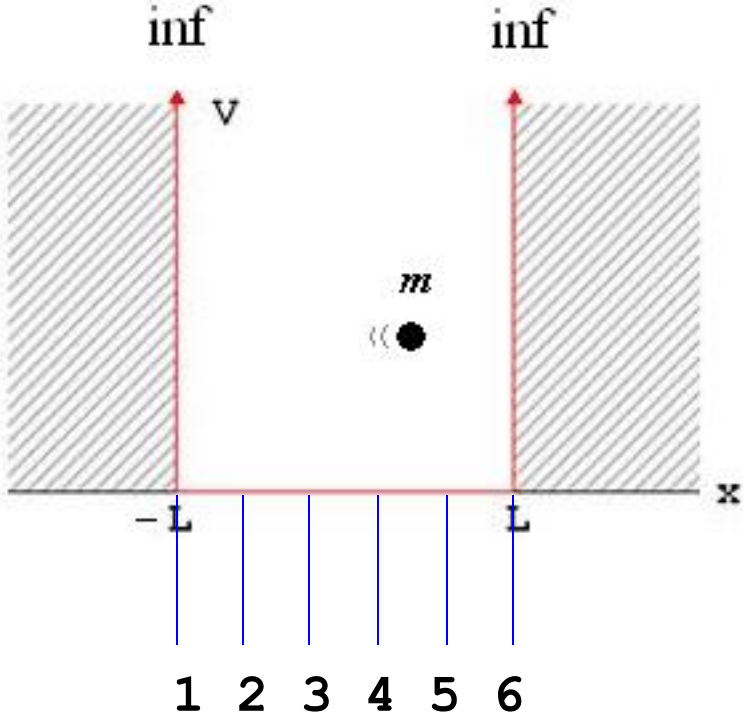
$$\Psi_n = \frac{1}{\sqrt{L}} \sin\left(\frac{n\pi x}{2L}\right) \quad \text{if } n \text{ is even}$$

Note that for $\hbar = m = L = 1$ we have

$$E_n = \frac{\pi^2 n^2}{8} \approx 1.2337 n^2$$

n	E
1	1.2337
2	4.9348
3	11.1033
4	19.7392
5	30.8425
6	44.4132
.	.
.	.

Numerical solution using finite difference method:



$$-\frac{1}{2}\frac{d^2\Psi}{dx^2}+V(x)\Psi=E\Psi$$

$$-\frac{1}{2}\frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{(\Delta x)^2}+V_i\Psi_i\approx E\Psi_i$$

or

$$\Psi_{i+1}=2\Psi_i-\Psi_{i-1}-2(\Delta x)^2(E-V_i)\Psi_i$$

$$\Psi(-L)=\Psi_1=0$$

or

$$\Psi(+L)=\Psi_6=0$$

$$\left(\frac{1}{(\Delta x)^2}+V_i-E\right)\Psi_i-\frac{1}{2(\Delta x)^2}\Psi_{i-1}-\frac{1}{2(\Delta x)^2}\Psi_{i+1}=0$$

$$\Delta x=\frac{2L}{5}$$

Matrix form:

$$\begin{pmatrix} \frac{1}{(\Delta x)^2}+V_2-E & -\frac{1}{2(\Delta x)^2} & 0 & 0 \\ -\frac{1}{2(\Delta x)^2} & \frac{1}{(\Delta x)^2}+V_3-E & -\frac{1}{2(\Delta x)^2} & 0 \\ 0 & -\frac{1}{2(\Delta x)^2} & \frac{1}{(\Delta x)^2}+V_4-E & -\frac{1}{2(\Delta x)^2} \\ 0 & 0 & -\frac{1}{2(\Delta x)^2} & \frac{1}{(\Delta x)^2}+V_5-E \end{pmatrix} \begin{pmatrix} \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

For L = 1 (dx = 2/5 = 0.4) and free particle (Vi = 0)

$$\begin{pmatrix} 6.250-E & -3.125 & 0 & 0 \\ -3.125 & 6.250-E & -3.125 & 0 \\ 0 & -3.125 & 6.250-E & -3.125 \\ 0 & 0 & -3.125 & 6.250-E \end{pmatrix} \begin{pmatrix} \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

```
% infwell-minimal.m  (minimal form)
% Matlab solution for a free particle in an infinite well
% See also: http://www1.gantep.edu.tr/~bingul/ep475/src/
 L = 1.0;    % well width
 n = 5;      % number of parts
 dx = 2*L/n;
 A = zeros(n-1);
 for i=1:n-1
    for j=1:n-1
      if i==j+1 | i==j-1
          A(i,j) = -0.5/dx^2;
      end
    end
    A(i,i) = 1.0/dx^2;
 end
 A  % print matrix
[wfn E] = eig(A);
 x = -L+dx:dx:L-dx;
 fprintf('*** Energy eigenvalues upto n = %d ***\n',n);
 for i=1:n-1
    fprintf('n=%2d --> E=%15.4f\n',i,E(i,i));
    plot(x,wfn(:,i));
    pause(1);
 end
```

Results for n = 5

```
>> infwell;

A =

    6.2500   -3.1250         0         0
   -3.1250    6.2500   -3.1250         0
         0   -3.1250    6.2500   -3.1250
         0         0   -3.1250    6.2500

*** Energy eigenvalues upto n = 5 ***
n= 1 --> E=          1.1936
n= 2 --> E=          4.3186
n= 3 --> E=          8.1814
n= 4 --> E=         11.3064
```

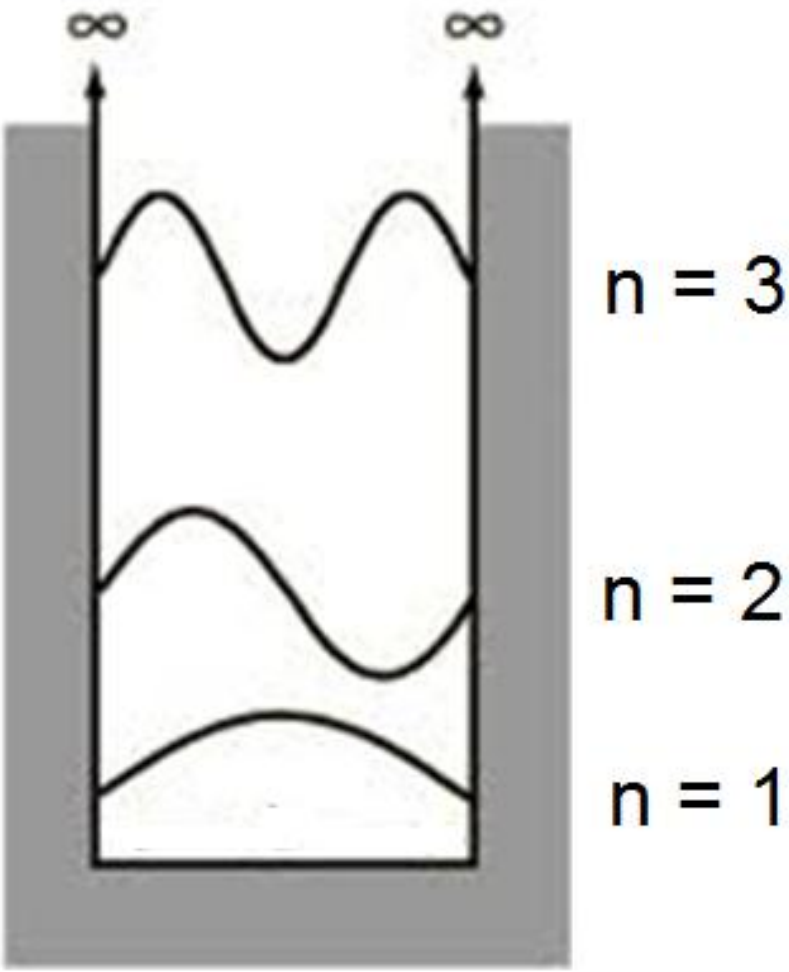
Results for n = 50

```
>> infwell;
*** Energy eigenvalues upto n = 50 ***
n= 1 --> E=          1.2333
n= 2 --> E=          4.9283
n= 3 --> E=         11.0705
n= 4 --> E=         19.6355
n= 5 --> E=         30.5897
n= 6 --> E=         43.8897
n= 7 --> E=         59.4831
n= 8 --> E=         77.3083
n= 9 --> E=         97.2950
n=10 --> E=        119.3644
n=11 --> E=        143.4292
n=12 --> E=        169.3946
.
.
.
```

Results for n = 500

```
>> infwell;
*** Energy eigenvalues upto n = 500 ***
n= 1 --> E=          1.2337
n= 2 --> E=          4.9347
n= 3 --> E=         11.1030
n= 4 --> E=         19.7382
n= 5 --> E=         30.8400
n= 6 --> E=         44.4080
n= 7 --> E=         60.4416
n= 8 --> E=         78.9402
n= 9 --> E=         99.9031
n=10 --> E=        123.3295
n=11 --> E=        149.2184
n=12 --> E=        177.5687
.
.
.
```

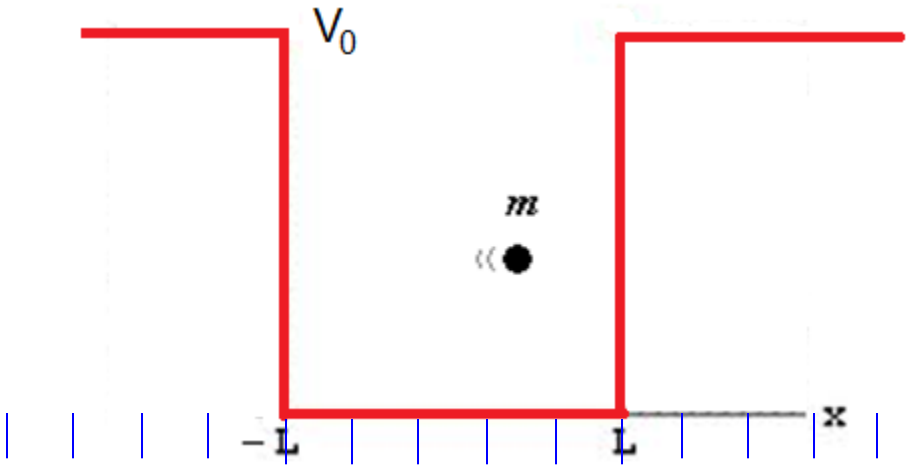
Wave functions



Eigenvalues

n	E
1	1.2337
2	4.9348
3	11.1033
4	19.7392
5	30.8425
6	44.4132
.	.
.	.
.	.

A Particle in a Finite Square Well



Depending on value of V0 we can extend the limits of the SE.

For bound states ($E < V0$) we can integrate the SE within the range (say) [-5L, 5L]. Here we may assume that the wave function vanishes at the boundaries.

$$\Psi(-5L) = \Psi(+5L) = 0$$

$$\Delta x = \frac{10L}{n}$$

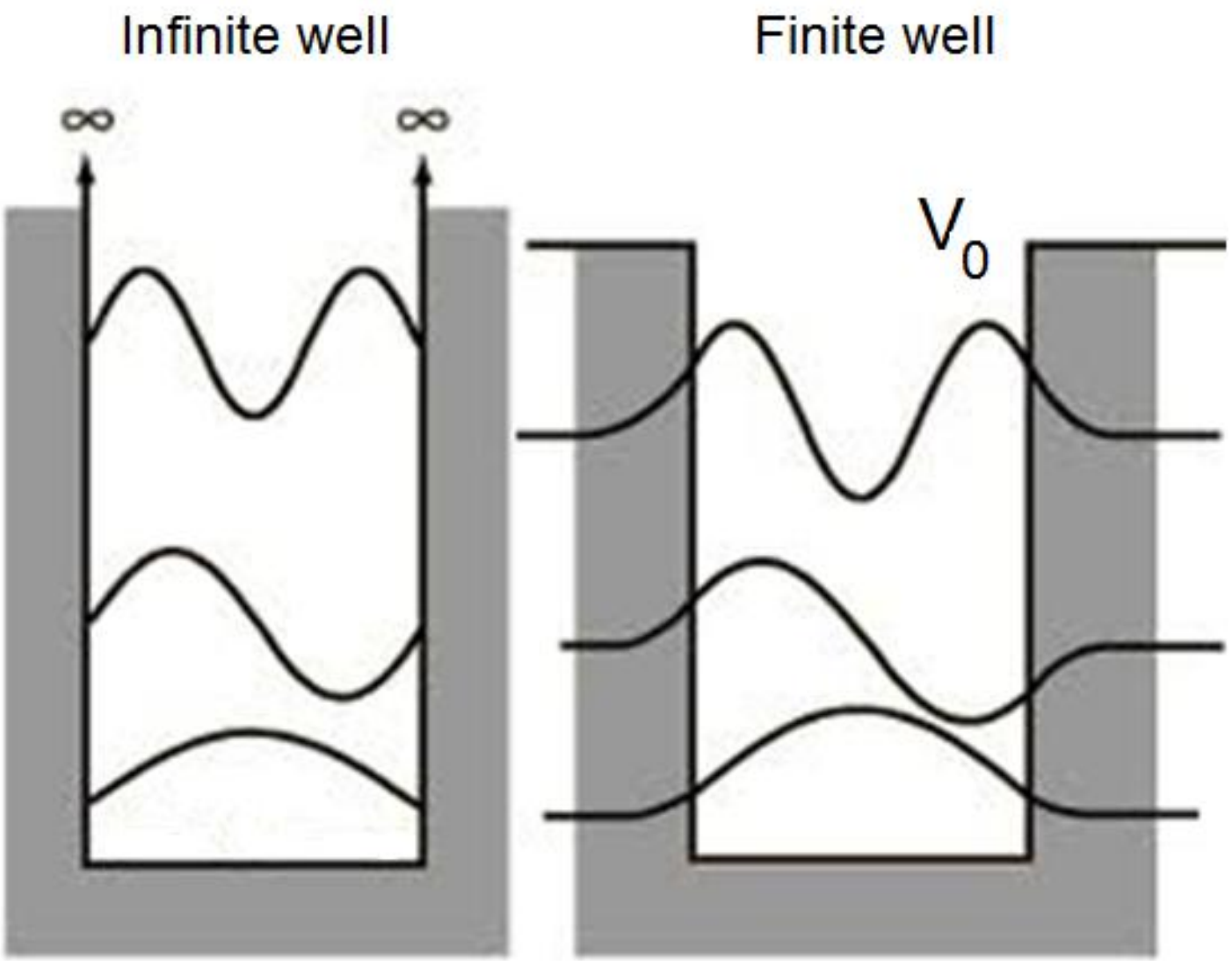
We need a small modification for the **`infwell.m`**.

You can find the computer implementation sqrwell.m at:
http://www1.gantep.edu.tr /~bingul/ep475/src/

Results for n = 500

```
>> sqrwell;
*** Energy eigenvalues for bound states ***
n= 1 --> E=          1.0149
n= 2 --> E=          4.0516
n= 3 --> E=          9.0839
n= 4 --> E=         16.0596
n= 5 --> E=         24.8787
n= 6 --> E=         35.3246
n= 7 --> E=         46.6655
```

Wavefunctions



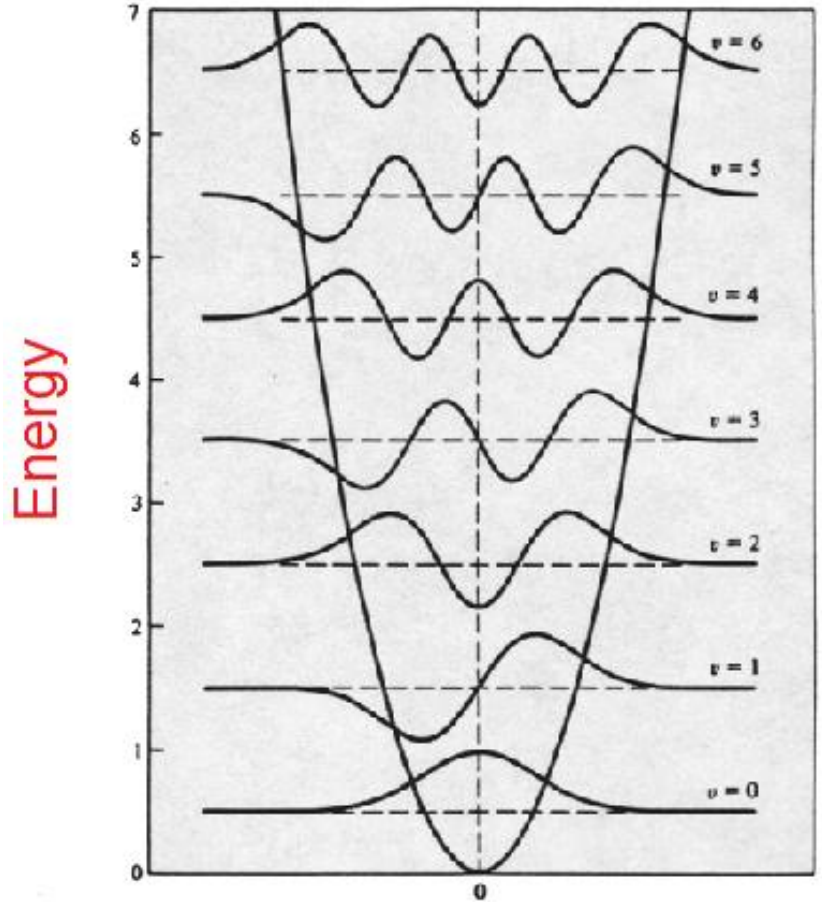
Simple Harmonic Oscillator

Hamiltonian of the particle:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

Energy eigenvalues:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \ldots.$$



Wavefunctions

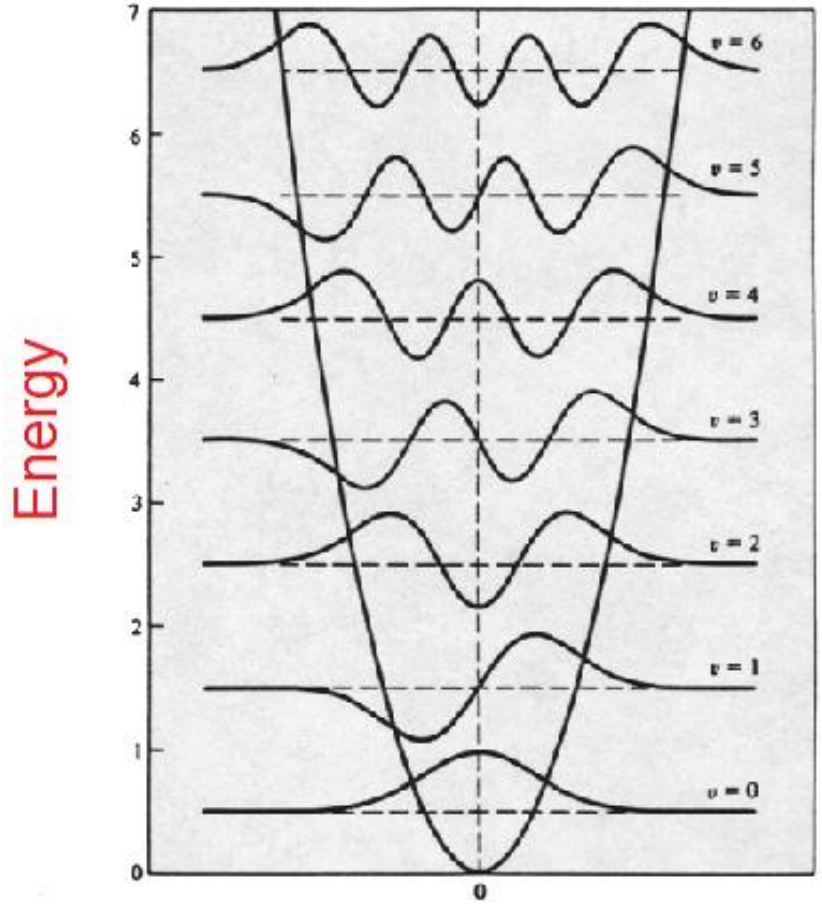
$$\psi_n(x) = \sqrt{\frac{1}{2^n\, n!}} \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \cdot e^{-\frac{m\omega x^2}{2\hbar}} \cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$

$$H_n(x) = (-1)^n e^{x^2}\frac{d^n}{dx^n}\left(e^{-x^2}\right)$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \ldots .$$

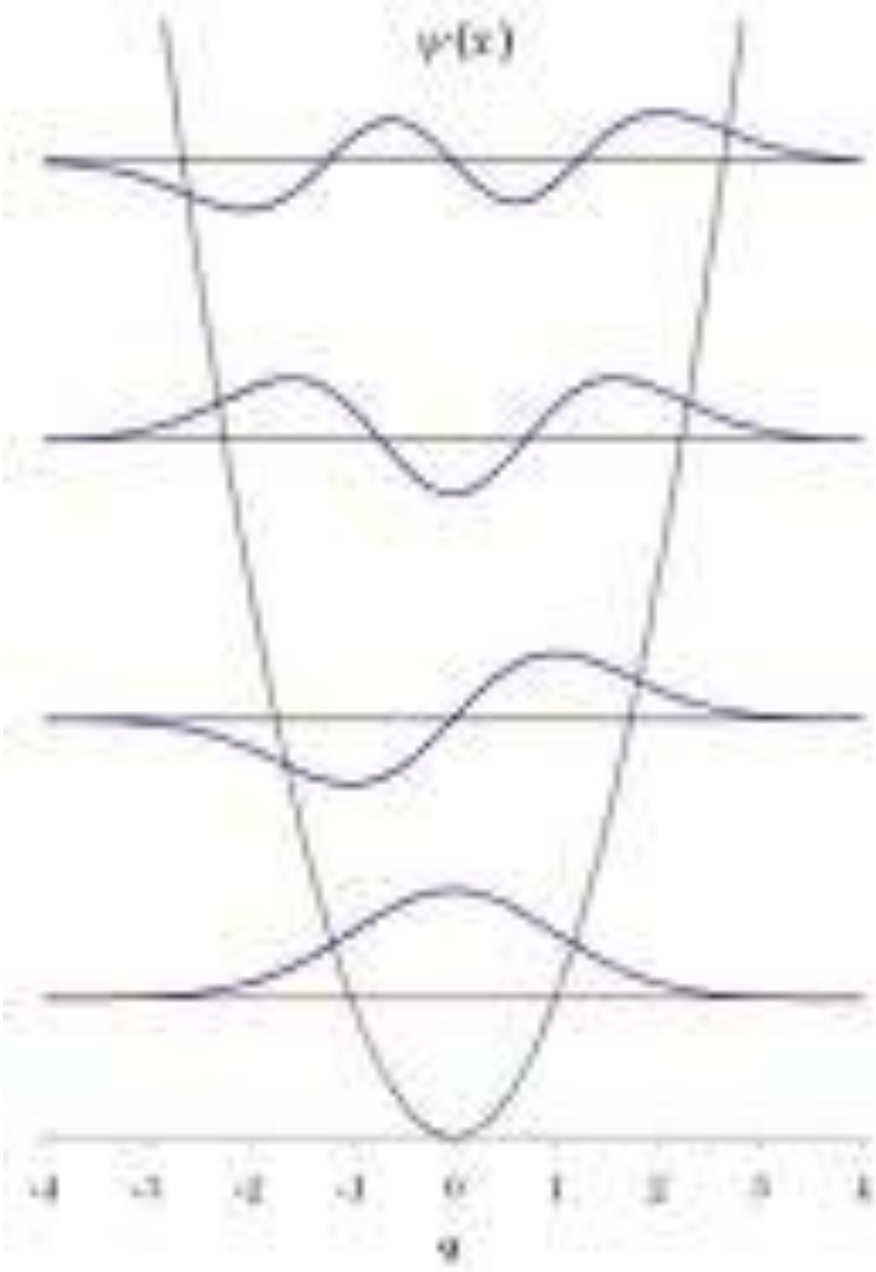
For *hbar* = *w* = *m* =1:

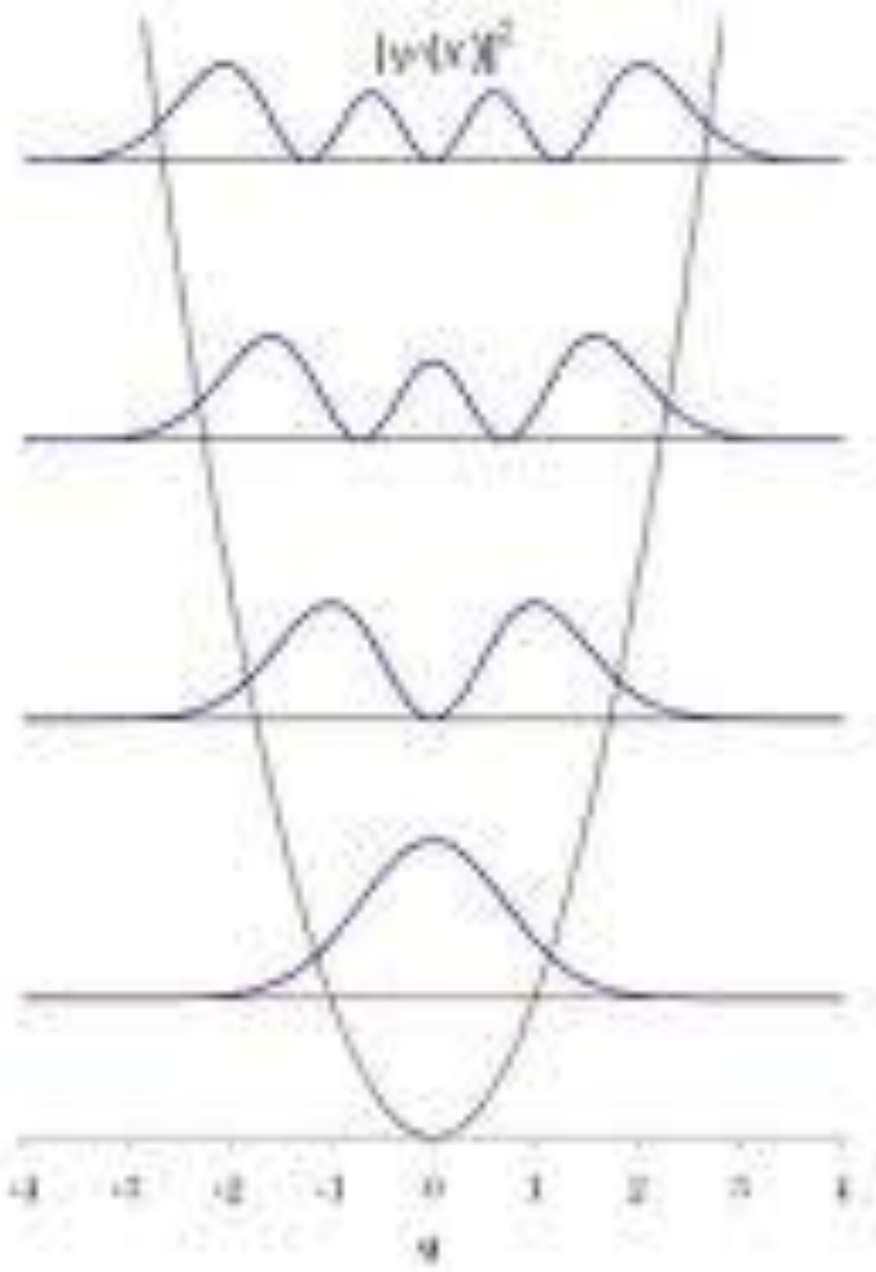
n	E
0	0.5
2	1.5
3	2.5
4	3.5
5	4.5
6	5.5
.	.
.	.



Results for n = 500

```
>> harmonic;
*** Energy eigenvalues for first 10 states ***
n= 1 --> E=      0.5000
n= 2 --> E=      1.4998
n= 3 --> E=      2.4995
n= 4 --> E=      3.4990
n= 5 --> E=      4.4983
n= 6 --> E=      5.4975
n= 7 --> E=      6.4966
n= 8 --> E=      7.4954
n= 9 --> E=      8.4941
n=10 --> E=      9.4927
```

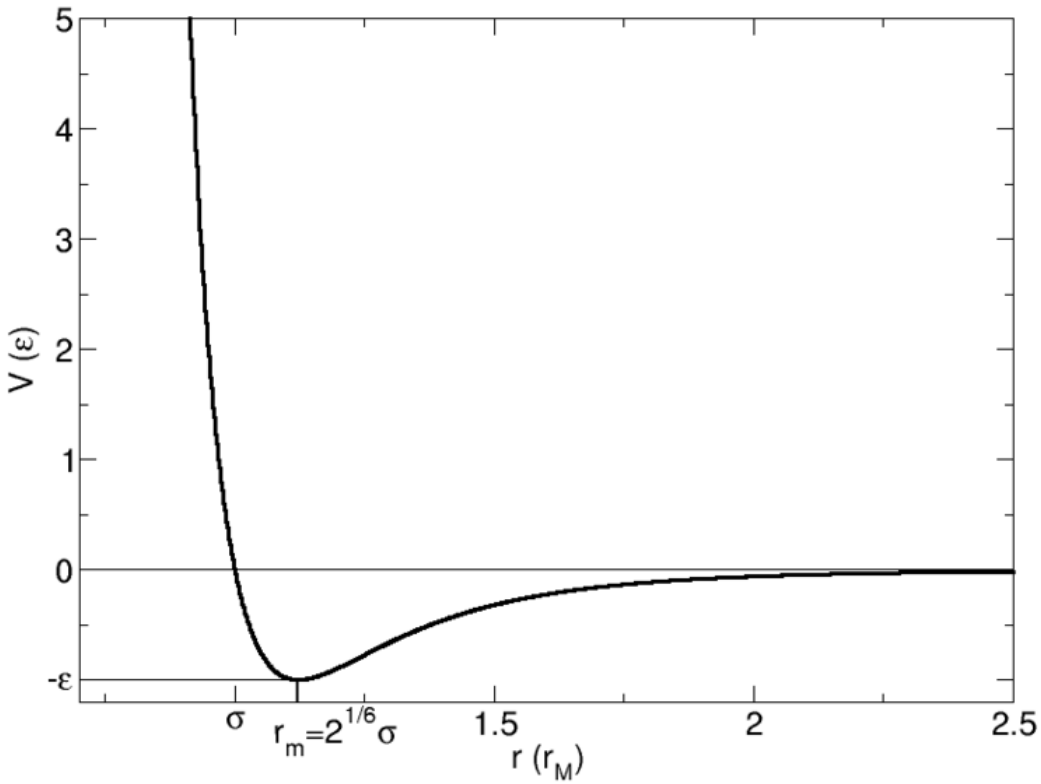

ψ(x)
q


|ψ(x)|²
q

Lennard-Jones Potential

The Lennard-Jones potential is a mathematically simple model that approximates the interaction between a pair of neutral atoms or molecules:

$$V_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

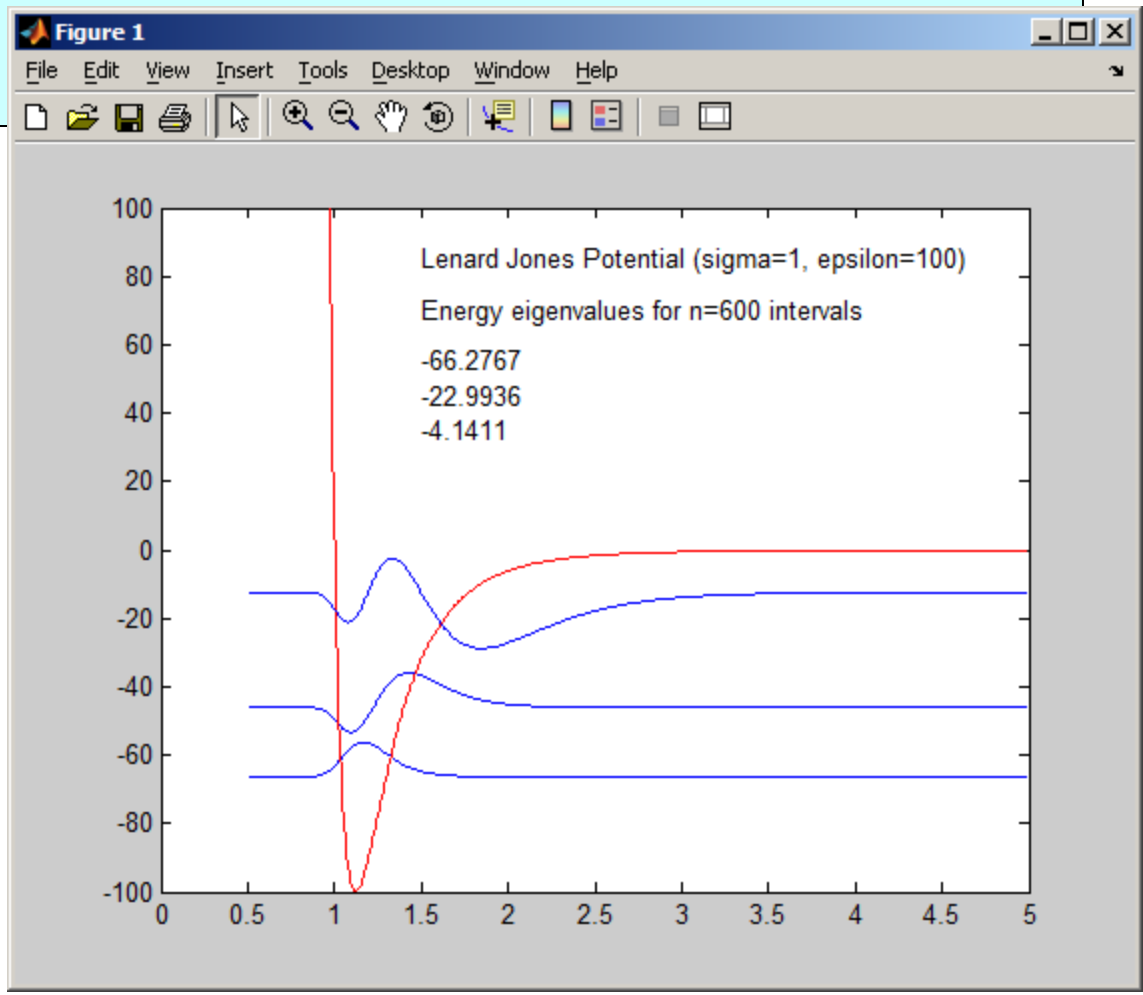


Note that there is no analytical solution for the SE:

$$-\frac{1}{2}\frac{d^2\Psi}{dr^2} + V_{LJ}\Psi = E\Psi$$

Sample run for n = 600 parts, sigma = 1 and epsilon = 100

```
>> LenardJones;
*** Energy eigenvalues for bound states ***
n= 1 --> E=   -66.2767
n= 2 --> E=   -22.9936
n= 3 --> E=    -4.1411
```



2D & 3D Problems for SE

Consider a 2D problem and assume that we break up space into a lattice of points with $\Psi(i, j)$ being the value of the wavefunction at location (i, j) on the lattice. SE $\hbar = m = 1$

$$-\frac{1}{2}\left[\frac{d^2\Psi}{dx^2}+\frac{d^2\Psi}{dy^2}\right]+V(x,y)\Psi = E\Psi$$

or

$$-\frac{1}{2}\left[\frac{\Psi(i+1, j)+\Psi(i-1, j)-2\Psi(i, j)}{\Delta x^2}\right]$$

$$-\frac{1}{2}\left[\frac{\Psi(i, j+1)+\Psi(i, j-1)-2\Psi(i, j)}{\Delta y^2}\right]$$

$$+V(i, j)\Psi(i, j) = E\Psi(i, j)$$

For $dx = dy = h$, the last finite difference equation can be written in matrix form as:

$$\begin{pmatrix} \frac{1}{h^2}+V_{22}-E & -\frac{1}{2h^2} & 0 & \cdots \\ -\frac{1}{2h^2} & \frac{1}{h^2}+V_{23}-E & -\frac{1}{2h^2} & \cdots \\ 0 & -\frac{1}{2h^2} & \frac{1}{h^2}+V_{24}-E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \Psi_{12} \\ \Psi_{12} \\ \Psi_{13} \\ \cdot \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \cdot \\ \vdots \end{pmatrix}$$

Using the matrix method for finding eigenvalues and vectors is not easy task and requires large amount of computer time.

e.g. if there are 50 grid elements we have

* a 2500x2500 matrix to deal with in 2D (50 MB RAM)
* a 125000x125000 matrix to deal with in 3D (125 GB RAM)

Alternative Methods to Solve SE

Finite Difference Method for solving boundary value and eigenvalue problems are time and memory consuming.

There are alternative methods to solve Schrödinger Equation:

- Shooting Method
  good at symmetric potentials

- Matching Method
  good at all potentials & 1D problems

- Variational Method
  good at all potentials & dimensions but for ground state only

See web page for the example programs.

Shooting Method

- Schrödinger Equation (m=h-bar=1)

$$-\frac{1}{2}\frac{d^2\Psi}{dx^2}+V(x)\Psi=E\Psi$$

- This equation is similar to many other second order differential equations, with one interesting twist, the energy, E, is also unknown.

- The numerical solution of this equation must determine both psi(x) and E.

- When the potential is symmetric, one can use the symmetry to an advantage. Namely, the wave functions can be written as purely odd or purely even functions of x.

- An even parity solution at x=0 requires

$$\psi(0) = 0 \qquad \psi'(0) = 1$$

- An odd parity solution at x=0 requires

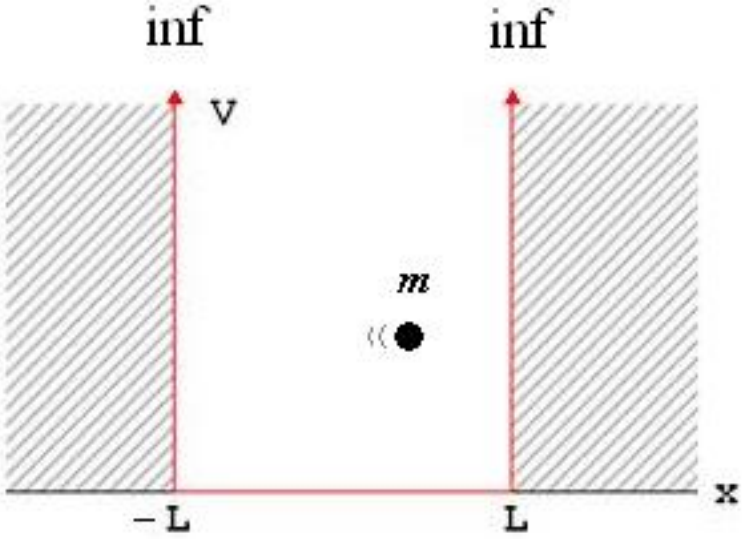
$$\psi(0) = 1 \qquad \psi'(0) = 0$$

The method of solution for

$$\frac{d^2\psi}{dx^2} = 2(V(x) - E)\psi$$

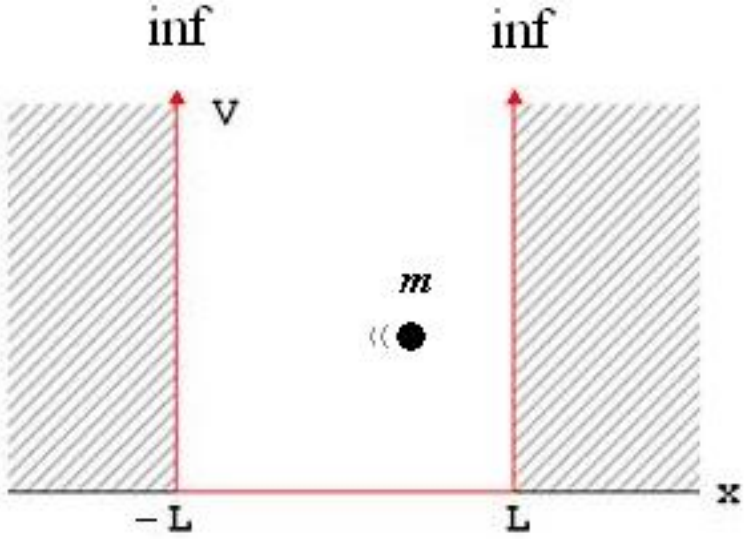
is to pick a values of E, propagate the solutions (for a given parity) to large x to determine if they match the boundary condition at large x. If they do not, adjust the value of E and try again.

Infinite Well:



$$\frac{d^2\psi}{dx^2} = -2E\psi$$

$$\psi(0) = 0 \qquad \psi'(0) = 1$$




```
% Shooting method for a particle in an infini
% Cromer-Euler solution
L      = 1;     % well width
n      = 1000;  % number of parts
dx     = L/n;
parity = 1;
E      = 1;    % energy estmiate
dE     = 0.1;
Enew   = E - dE;
psinew = 0;
while 1
      x=0; psi=1-parity; z=parity;
      for i=1:n
          z = z - 2*E*psi*dx;
          psi = psi + z*dx;
          x = x + dx;
      end
      if psi*psinew<0, dE = -dE/2; end
      E = E + dE;
      psinew = psi;
      if abs(E-Enew)<1.0e-6, break; end
      Enew = E;
      fprintf('Parity = %d and Energy = %f\n',parity, E);
end
```

References:

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Hahn B., Valentine D.T. (2007)

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[8]. http://en.wikipedia.org/wiki/Lenard-Jones_potential