

# DOING PHYSICS WITH MATLAB

## QUANTUM PHYSICS

### SCHRODINGER EQUATION

**Solving the one-dimensional Schrodinger Equation for bound states in a variety of potential wells using a matrix method that evaluates the eigenvalues and eigenfunctions**

Ian Cooper  
School of Physics, University of Sydney  
ian.cooper@sydney.edu.au

#### DOWNLOAD DIRECTORY FOR MATLAB SCRIPTS

The Matlab scripts are used to give the solution of the Schrodinger Equation for a variety of potential energy functions using a matrix method where the solution are the eigenvalues and eigenfunctions of the energy operator.

##### **se\_wells.m**

First m-script to be run when solving the Schrodinger Equation using the Matrix Method. Most of the constants and all the well parameters are declared in this file. You can select the type of potential well from the Command Window when the m-script is run. You alter the m-script code to change the parameters that characterize the wells and you can add to the m-script to define your own potential well. When this m-script is run it clears all variables and closes all open Figure Windows.

##### **se\_solve.m**

This m-script solves the Schrodinger Equation using the Matrix Method after you have run the m-script **se\_wells.m**. The eigenvalues and corresponding eigenvectors are found for the bound states of the selected potential well.

##### **se\_psi.m**

To be run after **se\_wells.m** and **se\_solve.m**. A graphical output displays the total energy, the potential energy function, kinetic energy function, eigenvector and probability distribution for a given quantum state.

### **se\_measurements.m**

To be run after **se\_wells.m** and **se\_solve.m**. Evaluates the expectation values for a set of dynamic quantities: the inherent quantum-mechanical uncertainties in measurements and gives a test of the Heisenberg uncertainty principle.

### **se\_orthonormal.m**

To be run after **se\_wells.m** and **se\_solve.m**. You can investigate the orthonormal characteristic of the eigenvectors (stationary state wavefunctions).

### **se\_infwell.m**

Used to test the accuracy of the Matrix Method. Compares the analytical and numerical results for an infinite square well potential of width 0.1 nm.

### **simpson1d.m**

Function to evaluate the area under a curve using Simpson's 1/3 rule.

### **Colorcode.m**

Function to return the appropriate colour for a wavelength in the visible range from 380 nm to 780 nm.

### **gaussian\_p.m**

Produces a graphical display of a Gaussian shaped potential well and the corresponding force graph.

## **Using the m-script to solve the Schrodinger Equation**

Run **se\_wells.m** then **se\_solve.m**

Then any of the following can be run to investigate the solution:

**se\_orthonormal.m** (orthonormal characteristic of wavefunctions)

**se\_psi.m** (displays energy functions and wavefunctions)

**se\_measurements.m** (calculation of expectation values)

## SCHRODINGER EQUATION

On an atomic scale, all particles exhibit a wavelike behavior. Particles can be represented by wavefunctions which obey a differential equation, the **Schrodinger Wave Equation** which relates spatial coordinates and time. You can gain valuable insight into quantum mechanics by studying the solutions to the one-dimensional time independent Schrodinger Equation.

A wave equation that describes the behavior of an electron was developed by Schrodinger in 1925. He introduced a wavefunction  $\Psi(x, y, z, t)$ . This is a purely mathematical function and does not represent any physical entity. An interpretation of the wave function was given by Born in 1926 who suggested that the quantity  $|\Psi(x, y, z, t)|^2$  represents the probability density of finding an electron. For the one dimensional case, the probability of finding the electron at time  $t$  somewhere between  $x_1$  and  $x_2$  is given by

$$(1) \quad \text{Prob}(t) = \int_{x_1}^{x_2} \Psi(x, t) \Psi^*(x, t) dx$$

where  $\Psi^*$  is the complex conjugate of the wavefunction  $\Psi$ . The value of  $\text{Prob}(t)$  must lie between 0 and 1 and so when we integrate over all space, the probability of finding the electron must be 1.

$$\int_{-\infty}^{+\infty} \Psi(x, t) \Psi^*(x, t) dx = 1$$

In this instance the wavefunction  $\Psi$  is said to be **normalized**.

We can see how the **time-independent Schrodinger Equation in one dimension** is plausible for a particle of mass  $m$ , whose motion is governed by a potential energy function  $U(x)$  by starting with the classical one dimensional wave equation and using the de Broglie relationship

$$\text{Classical wave equation} \quad \frac{\partial^2 \Psi(x, t)}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2} = 0$$

$$\text{Momentum (de Broglie)} \quad p = mv = \frac{h}{\lambda} = \hbar k$$

Kinetic energy	$K = \frac{1}{2} m v^2$
Total energy	$E = K(x) - U(x)$
Wavefunction	$\Psi(x, t) = \psi(x) e^{-i\omega t}$ periodic in time for $t$ coordinate

Combining the above relationships, the **time-independent Schrodinger Equation in one dimension** can be expressed as

$$(2) \quad -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + U(x) \psi(x) = E \psi(x)$$

Our goal is to find solutions of this form of the Schrodinger Equation for a potential energy function which traps the particle within a region. The negative slope of the potential energy function gives the force on the particle. For the particle to be bound the force acting on the particle is attractive. The solutions must also satisfy the **boundary conditions** for the wavefunction. The probability of finding the particle must be 1, therefore, the wavefunction must approach zero as the position from the trapped region increases. The imposition of the boundary conditions on the wavefunction results in a discrete set of values for the total energy  $E$  of the particle and a corresponding wavefunction for that energy, just like a vibrating guitar string which has a set of normal modes of vibration in which there is a harmonic sequence for the vibration frequencies.

The Schrodinger Equation can be solved analytically for only a few forms of the potential energy function. In this paper, we will consider a numerical approach to solving the Schrodinger Equation using a **matrix method** where the eigenvalues of a matrix gives the total energies of the particle and the eigenfunctions the corresponding wavefunctions.

## MATRIX METHOD

The one-dimensional time independent Schrodinger Equation can be expressed as

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

$$(3) \quad \left[ \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E\psi(x)$$

$$H\psi(x) = E\psi(x)$$

where the  $H$  is the Hamiltonian operator, which is the operator that corresponds to the total energy of the system. This is an **eigenvalue equation**. The action of the operator  $H$  on the function returns the original function multiplied by a constant which could be complex. This eigenvalue equation is generally satisfied by a particular set of functions  $\psi_1(x), \psi_2(x), \dots$ , and a corresponding set of constants  $E_1, E_2, \dots$ . These are the **eigenfunctions** and the corresponding **eigenvalues** of the operator  $H$ . The time independent Schrodinger Equation of a system is the energy eigenvalue equation of the system. An eigenfunction  $\psi_n(x)$  describes a state of definite energy  $E_n$ . When the energy of the system in this state is measured, the result will always be  $E_n$ . For the eigenfunction to represent physical sensible solutions, we require

$$\psi_n(x) \rightarrow 0 \quad \text{as} \quad x \rightarrow \pm\infty$$

so that the wavefunction can be normalized.

For atomic systems it is more convenient to measure lengths in nm (nanometers) and energies in eV (electron volts). We can use the scaling factors

$$\text{length: } L_{se} = 1 \times 10^{-9} \text{ to convert m into nm}$$

$$\text{energy: } E_{se} = 1.6 \times 10^{-19} \text{ to convert J into eV}$$

and so we can write equation (5) as

$$\left[ \left( \frac{-\hbar^2}{2m} \right) \left( \frac{1}{L_{se}^2 E_{se}} \right) \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E\psi(x)$$

$$(4) \quad \left[ C_{se} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E\psi(x) \quad \text{where} \quad C_{se} = \left( \frac{-\hbar^2}{2m} \right) \left( \frac{1}{L_{se}^2 E_{se}} \right)$$

$$H\psi(x) = E\psi(x)$$

Consider an electron in a potential well (see figure 1). For energy values below the top of the well, the physically acceptable solution of the time independent Schrodinger equation give a discrete set of energies which are the energy eigenvalues and corresponding to each eigenvalue there is the energy eigenfunction. Quantization of the energy levels of bound particles arises naturally from the time independent Schrodinger equation and the boundary conditions imposed for physically acceptable solutions. The spectral lines observed in atomic systems are the result of transitions between such energy levels.

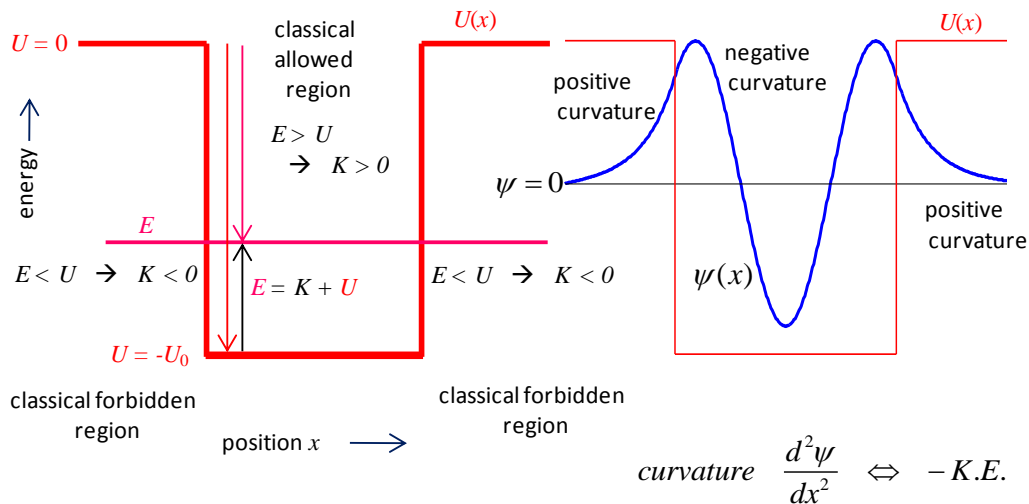


Fig. 1. Potential well defined by the potential energy function  $U(x)$ . The bound particle has total energy  $E$  and its wavefunction is  $\psi(x)$ .

These eigenstates  $\psi_n(x)$  represents stationary states and the total wavefunction can be expressed as

$$(5) \quad \Psi_n(x, t) = \psi_n(x) e^{-iE_n t / \hbar}$$

This is a state of definite energy, if the energy is measured then the value obtained will be  $E_n$ . It is called a stationary state, because the probability of locating a particle in an interval  $dx$  is time independent.

Many problems in physics reduce to solving an eigenvalue equation, for example, the vibrations of a violin string. The eigenvalues and eigenfunctions can be easily found using the Matlab command `eig`. The m-script `se_solve.m` is used to solve the Schrodinger equation using the Matrix Method. To solve equation (4), we first represent the continuous functions of  $x$  by sets of  $N$  discrete quantities expressed as vectors and

matrices. The discrete set of  $x$  values is represented by the vector  $|x_n\rangle$  the corresponding wavefunctions by the vector  $|\psi_n\rangle$ . The potential energy is given by a  $(N-2)\times(N-2)$  diagonal matrix  $[\mathbf{U}]$  with diagonal element  $U_n$ . A sample code `[se_solve.m]` for assigning the diagonal elements for  $[\mathbf{U}]$  is

```

...
U_matrix = zeros(N-2,N-2);
...
for c = 1 : N-2
U_matrix (c,c) = U(c);
end

```

Next, we have to represent the operator

$$\frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

as a matrix of size  $(N-2)\times(N-2)$ . From the definitions of the first and second derivatives of the function  $y(x)$ , we can approximate them by the equations

$$\left. \frac{dy}{dx} \right|_{x_{n-1/2}} \approx \frac{y_n - y_{n-1}}{\Delta x}$$

$$\left. \frac{d^2y}{dx^2} \right|_{x_n} \approx \frac{1}{\Delta x} \left( \left. \frac{dy}{dx} \right|_{x_{n+1/2}} - \left. \frac{dy}{dx} \right|_{x_{n-1/2}} \right) = \frac{y_{n+1} - 2y_n + y_{n-1}}{\Delta x^2}$$

Hence, the second derivative matrix for  $N = 6$  can be written as a  $4\times 4$  matrix

$$[\mathbf{SD}] = \frac{1}{\Delta x^2} \begin{bmatrix} -2 & 1 & 0 & 0 \\ 1 & -2 & 1 & 0 \\ 0 & 1 & -2 & 1 \\ 0 & 0 & 1 & -2 \end{bmatrix}$$

The SD matrix size is  $(N-2)\times(N-2)$  and not  $N\times N$  because the second derivative of the function can't be evaluated at the end points,  $n = 1$  and  $n = N$ . The kinetic energy matrix  $[\mathbf{K}]$  is then defined as

$$[\mathbf{K}] = C_{se} [\mathbf{SD}]$$

We can now define the **Hamiltonian matrix** as

$$[\mathbf{H}] = [\mathbf{K}] + [\mathbf{U}]$$

A sample code [[se\\_solve.m](#)] for the generating the Hamiltonian matrix is

```
% Make Second Derivative Matrix -----  
off = ones(num-3,1);  
SD_matrix = (-2*eye(num-2) + diag(off,1) + diag(off,-1))/dx2;  
  
% Make KE Matrix  
K_matrix = Cse * SD_matrix;  
  
% Make Hamiltonian Matrix  
H_matrix = K_matrix + U_matrix;
```

Therefore, the Schrodinger Equation in matrix form is

$$(6) \quad [\mathbf{H}]|\psi_n\rangle = E_n |\psi_n\rangle$$

This is an eigenvalue equation in matrix form where the action of the Hamilton matrix results in each value to be the vector  $|\psi_n\rangle$  being multiplied by a multiplied by the set of numbers  $E_n$ . The set of numbers  $E_n$  are called the **eigenvalues** and set of vectors  $|\psi_n\rangle$  are the **eigenvectors**.

This is a single Matlab function that finds both the eigenvalues and eigenvectors. The syntax of the command is

```
[e_funct, e_values] = eig(H)
```

where **e\_funct** is an  $(N-2)\times(N-2)$  matrix with the  $n^{\text{th}}$  column corresponding to the  $n^{\text{th}}$  eigenfunction and **e\_values** is a column vector for the  $N$  eigenvalues in increasing order. Only the negative values of **e\_values** are significant. To obtain the complete eigenvector we need to include the end points where  $\psi_n(x_{\min}) = \psi_n(x_{\max}) = 0$ . A sample Malab code [[se\\_solve.m](#)] to obtain the discrete set of eigenvalues and normalized eigenfunction is



```

% All Eigenvalues 1, 2, ... n where E_N < 0
flag = 0;
n = 1;
while flag == 0
    E(n) = e_values(n,n);
    if E(n) > 0, flag = 1; end;    % if
    n = n + 1;
end                                % while
E(n-1) = [];
n = n-2;

% Corresponding Eigenfunctions 1, 2, ... ,n: Normalizing the wavefunction
for cn = 1 : n
psi(:,cn) = [0; e_funct(:,cn); 0];
area = simpson1d((psi(:,cn) .* psi(:,cn))',xMin,xMax);
psi(:,cn) = psi(:,cn)/sqrt(area);
prob(:,cn) = psi(:,cn) .* psi(:,cn);
end                                % for

```

A potential well as shown in figure (2) has a minimum at  $x = 0$  and tends to zero away from the origin. A classical particle would be trapped by this potential well and oscillate to and fro about  $x = 0$  because the force on the particle is always directed towards origin for position since  $F = -dU/dx$ .

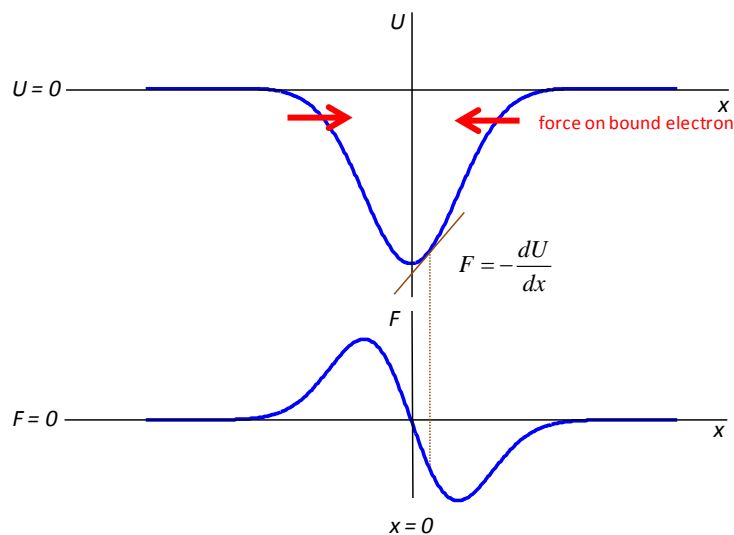


Fig. 2. A potential well which traps a particle because the force acting on the particle is always directed towards the origin. [guassian\_p.m annotation of figure done in MS Powerpoint].

We can solve the Schrodinger Equation (equation 6) for a variety of different potential energy functions. The m-script **SE\_wells.m** defines most of the constants and potential well parameters. Within the m-script you can change the code to modify the potential wells and add new potential wells. The first step in solving the Schrodinger Equation using the Matrix Method for a bound electron is to run the file **SE\_wells.m** and select the type of potential well. The default potentials include:

- 1 Square well
- 2 Stepped well
- 3 Double well
- 4 Sloping well
- 5 Truncated Parabolic well
- 6 Morse Potential well
- 7 Parabolic fit to Morse Potential
- 8 Lattice

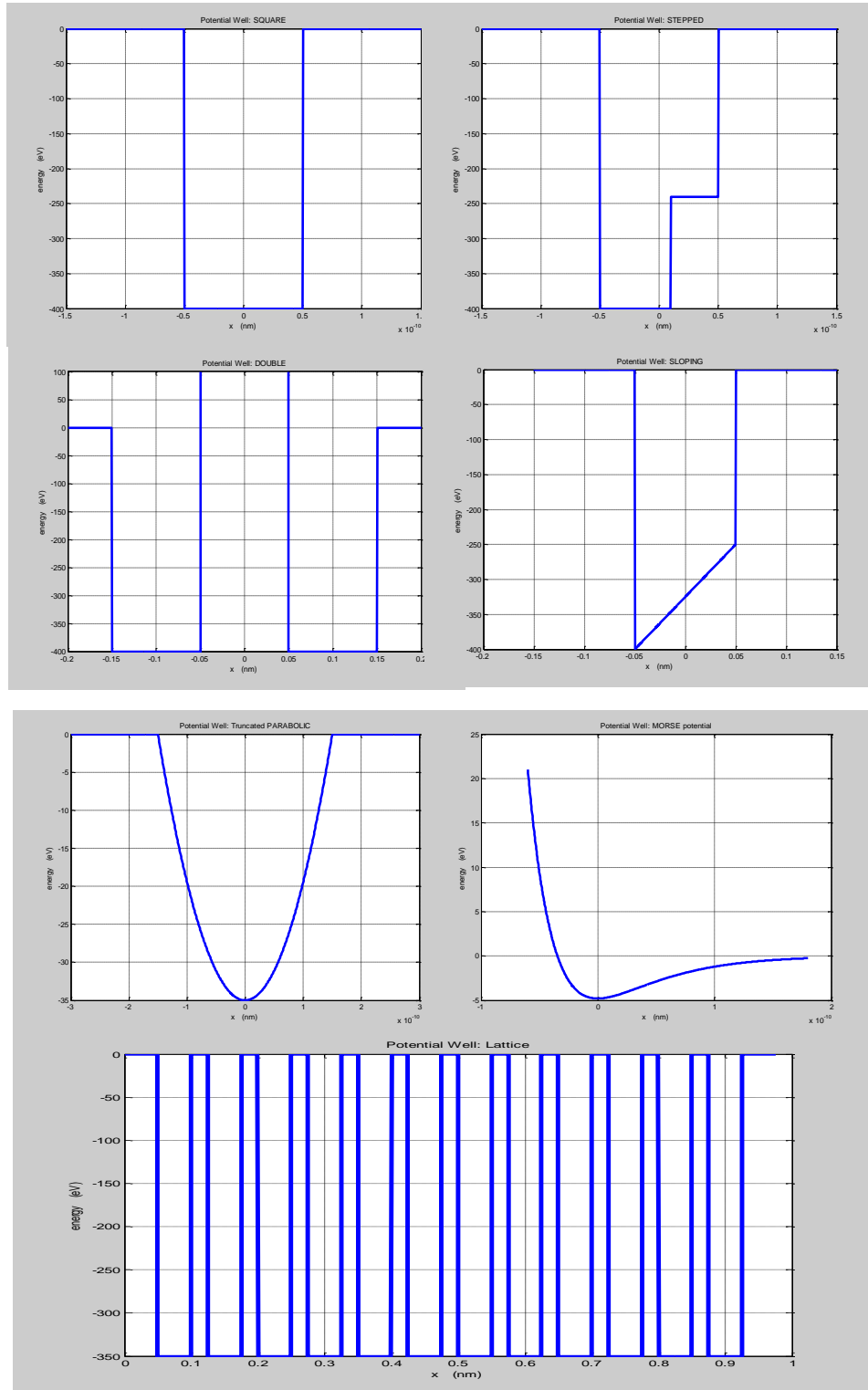


Fig. 3. Some of the default potential wells that can be generated using the m-script `se_wells.m`.

If you are not satisfied with the potential well that is displayed, you can change any of the parameters in the m-script `se_wells.m` and run it again. Then to solve the Schrodinger Equation run the m-script `se_solve.m`.

Consider a sloping potential well with input parameters set in `se_wells.m`

```
% Input parameters
num = 801;
xMin = -0.1; % default value = -0.1 nm
xMax = +0.1; % default value = + 0.1 nm
U1 = -1200; % Depth of LHS well: default = -1200 eV;
U2 = -200; % Depth of RHS well: default = -200 eV;
x1 = 0.05; % 1/2 width of well: default = 0.05 nm;
```

The solution of the Schrodinger Equation for this sloping potential well using `se_solve.m` provides the following information:

(1) The energy eigenvalues are displayed in the Command window

```
No. bound states found = 5
Quantum State / Eigenvalues En (eV)
1 -894.67
2 -624.3
3 -403.46
4 -203.93
5 -13.546
```

The energies are stored in the variable `E`. `E(1)` is the first energy level (ground state), `E(2)` is the second energy level, and so. The values can be displayed at any time in the Command Window by simply typing `E`

```
>> E
E =
-894.6664 -624.3014 -403.4580 -203.9267 -13.5456
```

- (2) A graph of the energy spectrum is shown in figure (4) for a sloping potential well

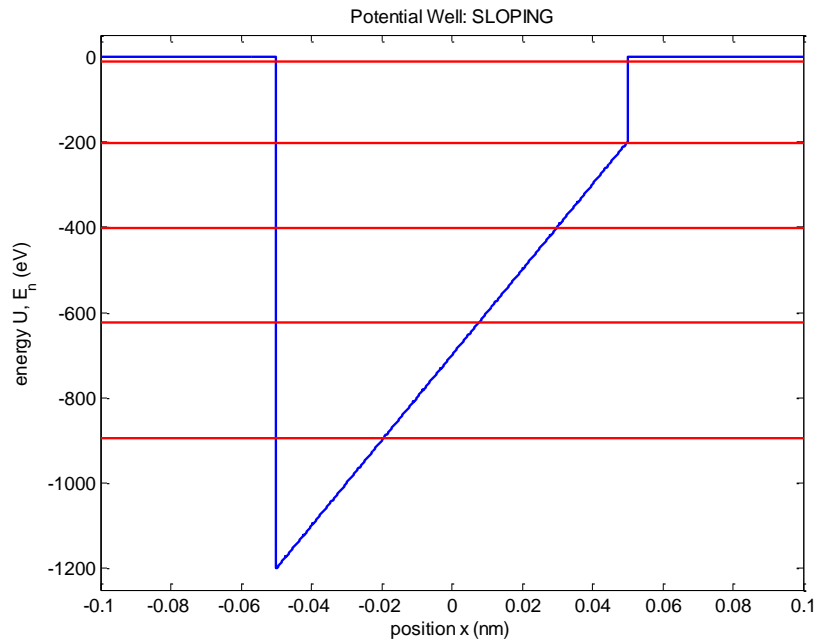


Fig. 4. The energy spectrum for a potential well produced by the m-script **se\_solve.m**.

- (3) The energy eigenvectors are given by the array **psi** with dimensions  $(num \times N)$  where *num* is the number of data points and *N* is the number of eigenvalues. For example, to display the eigenvector for quantum state  $n = 2$ , type **psi(:,2)** into the Command Window. A graphical display of the first 5 eigenvectors and corresponding probability density distributions are displayed in a Figure Window as shown in figure (5).

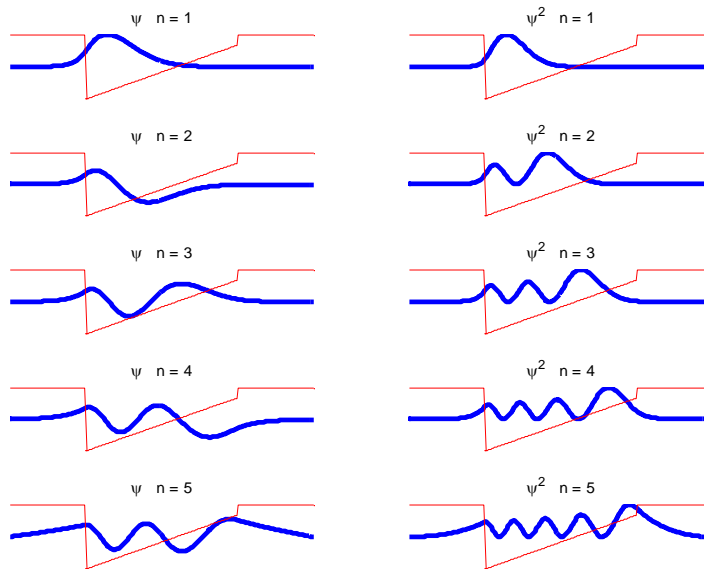


Fig. 5. The energy eigenvectors and probability distributions for sloping potential well. [[se\\_solve.m](#)].

To view a graphical display of an eigenvector and the probability density graphs for a given state, you can run the m-script [se\\_psi.m](#) from the Command Window. The graphical output for a sloping potential well for quantum state  $n = 3$  is shown in figure (6). Variations with position of the eigenvector  $\psi_n(x)$ ; probability density  $|\psi_n(x)|^2$ ; energies  $U(x)$ ,  $K(x)$ ,  $E$  are shown along with a probability cloud where each point displayed shows the position of the particle after a measurement is made on the system resulting in the collapse of the wavefunction.

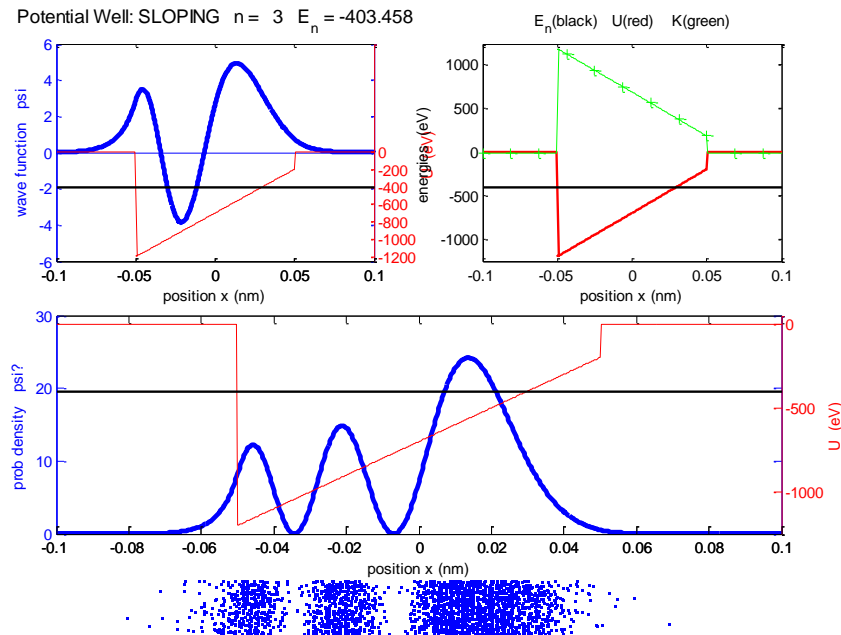


Fig. 6. The eigenvector, probability density and energy graphs for the quantum state  $n = 3$  of a particle trapped in a sloping potential well. `[se_psi.m]`.

We will again consider the sloping well. The sloping potential well represents an external electric field acting on the electron. Classically, the electron is subject to a very large force to the right at the left edge of the well and a force to the left along the sloping section with the magnitude of the force equal to the gradient of the slope ( $F = -dU / dx$ ). We could also view the potential as a quantum mechanical version of a particle sliding along a frictionless inclined plane with a high wall at the bottom. The classical motion of such a confined particle is that it would oscillate up and down the incline, having its largest kinetic energy at the bottom and decreasing kinetic energy the further up the incline. The particle would be moving most rapidly at the bottom of the incline and most slowly at the top. Therefore, it would spend less time at the bottom than at the top and this implies that it is more likely to find the particle at the top than at the bottom. Also the particle could be at rest at the bottom.

Figure (7) shows the quantum mechanical solution for the sloping well potential for the state  $n = 1$  (ground state). The results are very different from the classical predictions. The minimum energy of the particle is greater than zero. There is a non-zero probability of the electron being in a classically forbidden region ( $E_K < 0$ ), i.e., the electron can

penetrate the walls of the potential well and the most likely location to find the electron is towards the bottom and not at the top.

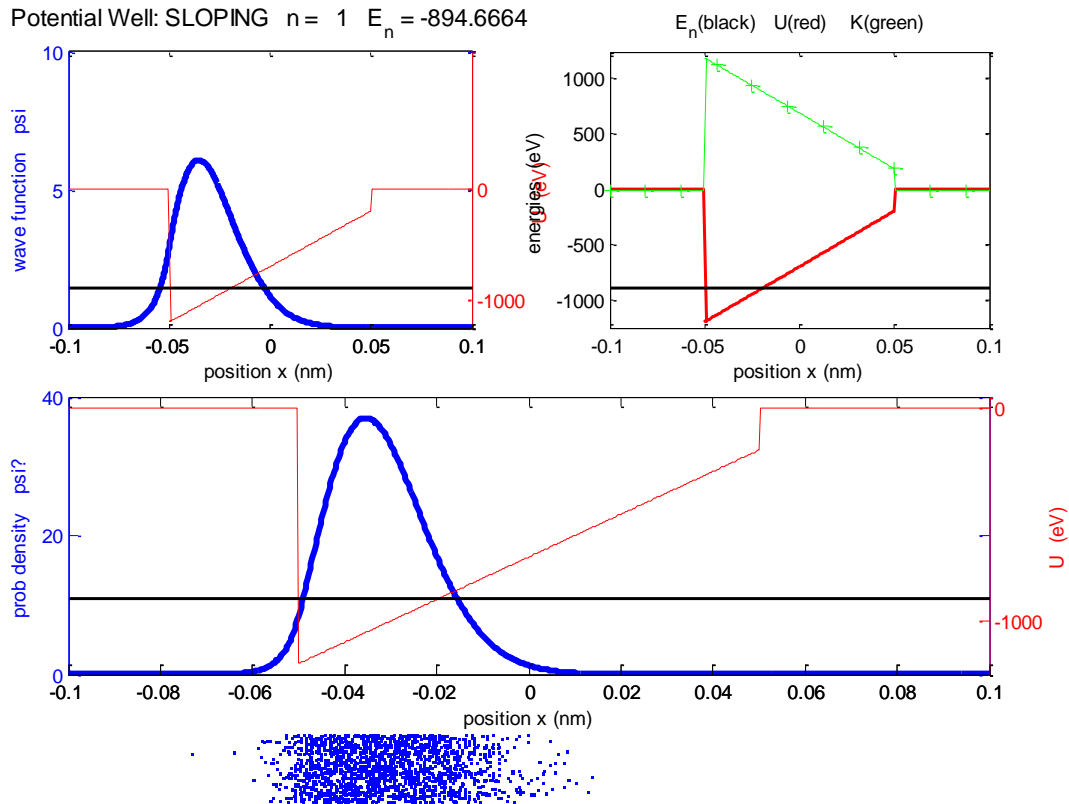


Fig. 7. The eigenvector, probability density and energy graphs for the quantum state  $n = 1$  (ground state) of a particle trapped in a sloping potential well. [se\_psi.m].

There are 5 bound states for the sloping potential well. As the quantum number  $n$  increases by 1, an additional hump of width in the order of half a wavelength is added to the shape of the wavefunction. For the state  $n = 1$  there is only 1 hump and the state  $n = 5$ , there are 5 humps. The characteristics of the highest bound state ( $n = 5$ ) is shown in Figure (8). This highly excited state has features more in-line with the classical picture. The particle is more likely to be found towards the top of the well where its kinetic energy is less. Since the particle moves at high speed at the bottom and less at the top, the wavelength of the wavefunction must be smallest near the bottom and increases towards the top. The ground state defies our classical expectations but the highly excited states are often in broad agreement with the classical picture. This is not so surprising since classical physics objects have very high quantum numbers. This idea is called the **correspondence principle**.



Measurements of the half-wavelengths can be made using the `ginput` command to measure the positions of the peaks and then the successive distances between the peaks of the probability density curve, for example,

```
z = ginput
z(5) - z(4)
```

The measured half-wavelengths [ 0.0184 0.0208 0.0241 0.0315 nm] from figure (8) increase from left to right, confirming the fact that the kinetic energy decreases with increasing wavelength increases since

$$p = \frac{h}{\lambda} \quad E_K = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

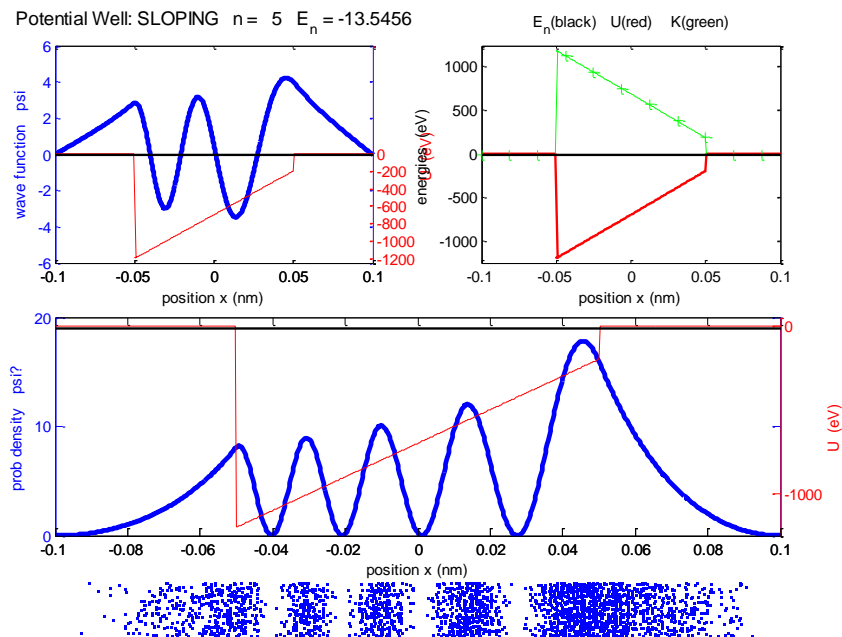


Fig. 8. The eigenvector, probability density and energy graphs for the excited state,  $n = 5$  of a particle trapped in a sloping potential well. `[se_psi.m]`.

## EXPECTATION VALUES

The quantum behavior of bound particles is becoming more important in electronic devices made using semiconductor materials such as silicon and gallium. The heart of such devices is a tiny structure called a **quantum dot** that consists of a speck of one semiconductor material (width  $\sim 1$  nm,  $\sim 100$ 's atoms) completely enclosed by a much larger semiconductor material. Some of the electrons in the tiny speck become detached from their parent atoms and behave as particles trapped in potential wells of 1 dimension (quantum wafer), 2 dimensions (quantum wire), or 3 dimensions (quantum dot). These particles are often referred to as particles in a box. The bound electrons have a discrete energy spectrum just like electrons bound in atoms. Quantum dots are often referred to as artificial atoms. The light emitting properties of quantum dots are used in solid state lasers such as DVD players, lighting systems, solar cells, fluorescent markers in biomedical applications. Our focus of finding the physically acceptable solutions of the Schrodinger Equation for bound particles is important to understanding real systems of increasing technological importance.

The wavefunction that describes a quantum state provides the most complete description that is possible of that state – it contains all the information we can possibly know about this quantum state. But the wavefunction is not something that can be measured and therefore has no physical meaning. The information we can get from the wavefunction is related only to the probabilities of the possible outcomes of measurements made on identical systems. Hence, there is an intrinsic and unavoidable indeterminism in the quantum world.

When a measurement is made on a quantum system, the wavefunction collapses, the state of the system after the measurement is not the same as the state before the measurement. The Schrodinger Equation does not describe this collapse of the wavefunction. So, for experiments designed to test the predictions of quantum mechanics, you can't do a sequence of measurements on a single system, rather, you start with a large number of identical systems all in the same state and then perform the same measurement of each system. Although each system is initially identical, the outcomes of

the measurements typically give a spread of results, for example, the measurement of the position of the electron in passing through an equivalent of a [double slit](#).

We will consider systems of a single electrons confined by a one dimensional potential wells. We already know that it is a simple matter to use the wavefunction to find the probability distribution for the position of the electron. However, we can extend this method to find the probability distributions of other measureable quantities such as position, momentum and energy. This information is contained in the shape of the wavefunction and we will show how this information can be extracted.

For the electron trapped in the sloping potential wells the solution of the Schrodinger Equation gave a set of energy eigenvalues and their corresponding eigenvectors ([stationary states](#)). The energy eigenvalues are the only allowed energies of the system. No matter what state the system is in, if we measure its energy, we always get one of the energy eigenvalues. These stationary states are special, because they are states of definite energy. So in this case, there is zero uncertainty in the measurements. If the system is described by a stationary state wavefunction  $\Psi_n(x,t)$  and we measure its energy, we will certainly get the result  $E_n$  for the energy eigenvalue.

The eigenvectors are said to be [orthonormal](#): (1) the eigenvector is [normalized](#) so that the probability is 1 of finding the electron, and (2) any two energy eigenvectors with different energy eigenvalues are [orthogonal](#) to each other. Mathematically this is stated as:

$$(7) \quad \int_{-\infty}^{+\infty} \psi_j^*(x) \psi_i(x) dx = \delta_{ji} \quad \text{Kronecker delta} \quad \delta_{ji} = \begin{cases} 1 & j = i \\ 0 & j \neq i \end{cases}$$

One meaning of the wavefunction is that its magnitude measures the [probability amplitude](#) of the particle being found at some point. If the wavefunction corresponds to an eigenfunction  $\Psi_n(x,t)$ , then the probability distribution  $prob_n(x)$  is independent of time and is given by

$$prob_n(x) = \psi_n^*(x) e^{\frac{iE_n t}{\hbar}} \psi_n(x) e^{-\frac{-iE_n t}{\hbar}} = \psi_n^*(x) \psi_n(x)$$

and the probability  $P_n$  of finding the particle between  $x_1$  and  $x_2$  is

$$P_n = \int_{x_1}^{x_2} \psi_n^*(x) \psi_n(x) dx$$

We can also calculate probability distributions for other observable quantities in a similar manner to above. The probability distribution is characterized by two measures – its **expectation value** (estimate of the mean value of the distribution) and its **uncertainty** (spread of values around the mean). Suppose that an observable quantity  $A$  has a discrete set of possible values  $a_1, a_2, \dots$ . Then, we can prepare  $N$  identical systems, all in the same state and measure the value of  $A$  in each system. In general, we will get a spread of results. The best estimate of the quantity  $A$  is its mean value  $\langle A \rangle$  and the standard deviation  $\Delta A$  can be used as a measure of the spread or uncertainty in the measurements. The expectation value of an observable  $A$  is the quantum-mechanical prediction for the mean value. In a stationary state described by the wavefunction  $\psi_n(x)$ , the expectation value of an observable  $A$  is given by

$$(8) \quad \langle A \rangle = \int_{-\infty}^{+\infty} \psi_n^*(x) \hat{A} \psi_n(x) dx$$

where  $\hat{A}$  is the quantum-mechanical operator corresponding to  $A$ . The operator is ‘sandwiched’ between the two wavefunction  $\psi_n^*(x)$  and  $\psi_n(x)$ , and for this reason we call the right hand side of equation (8) a *sandwich* integral. The first part of the integrand is called the **bra** ( $\psi_n^*(x)$ ) and the second part the **ket** ( $\hat{A} \psi_n(x)$ ). Some of the dynamical properties of a system that can be calculated are shown in Table 1.

<p><b>Total probability</b> <math>\hat{A} = 1</math></p> $1 = \int_{-\infty}^{+\infty} \psi_n^*(x) \psi_n(x) dx$	<p><b>Position</b> <math>\hat{A} = x</math></p> $\langle x \rangle = \int_{-\infty}^{+\infty} \psi_n^*(x) x \psi_n(x) dx$
<p><b>Momentum*</b> <math>\hat{A} = -i\hbar \frac{d}{dx}</math></p> $\langle p \rangle = \int_{-\infty}^{+\infty} \psi_n^*(x) \left( -i\hbar \frac{d}{dx} \right) \psi_n(x) dx$	<p><b>Kinetic Energy</b> <math>\hat{A} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}</math></p> $E_K = \int_{-\infty}^{+\infty} \psi_n^*(x) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \psi_n(x) dx$
<p><b>Potential Energy</b> <math>\hat{A} = U(x)</math></p> $E_P = \int_{-\infty}^{+\infty} \psi_n^*(x) U(x) \psi_n(x) dx$	<p><b>Total energy</b> <math>\hat{A} = H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x)</math></p> <p>where <math>H</math> is the Hamiltonian</p> $E = \int_{-\infty}^{+\infty} \psi_n^*(x) (H) \psi_n(x) dx$ $E = \int_{-\infty}^{+\infty} \psi_n^*(x) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right) \psi_n(x) dx$

Table 1. Operators and expectation value integrals for a range of dynamical quantities. \*Note: For the momentum, the integrand is imaginary, hence  $\langle p \rangle = 0$ .

The **standard deviation**  $\Delta A$  is used to describe the spread of the measurements about the mean value. It is measured by summing the square deviations from the mean and then taking the square root. For a system in a given state  $\psi_n(x)$ , the uncertainty of the observable  $A$  is defined by

$$(9) \quad \Delta A = \left\langle \left( A - \langle A \rangle \right)^2 \right\rangle^{1/2} = \left( \langle A^2 \rangle - \langle A \rangle^2 \right)^{1/2}$$

The fundamentals of quantum mechanics were worked out in a remarkably short period of time from 1925 to 1927. One of the fundamental consequences of quantum theory is the Heisenberg uncertainty principle. One form of the uncertainty principle is:

In any system, the uncertainties of position  $\Delta x$  and momentum component  $\Delta p_x$  obey the inequality

$$(10) \quad \Delta x \Delta p_x \geq \frac{\hbar}{2}$$

Hence, it is impossible to find a state in which a particle has both definite values for position and momentum. The classical picture of a particle following a well-defined trajectory is no longer valid. A system described by a wavefunction implies a spread of position and momentum values and that a narrow spread in one of these quantities is offset by a wide spread in the other. The uncertainty principle is sometimes interpreted in terms of the disturbance produced by a measurement, but, this is not correct. The uncertainty principle tells us about the indeterminacy that is inherent in a given state before the measurement is made.

When a system's wavefunction corresponds to one of its eigenfunctions  $\psi_n$ , the uncertainty in the total energy  $E_n$  is zero,  $\Delta E_n = 0$ . This is show by the following calculation, in which the operator for the total energy  $E$  is the Hamiltonian  $\hat{H}$  :

$$\begin{aligned}\hat{H}\psi &= E\psi \\ \langle E \rangle &= \int_{-\infty}^{+\infty} \psi_n^* \hat{H} \psi_n dx = E \int_{-\infty}^{+\infty} \psi_n^* \psi_n dx = E \\ \langle E \rangle^2 &= E^2 \\ \langle E^2 \rangle &= \int_{-\infty}^{+\infty} \psi_n^* \hat{H} \hat{H} \psi_n dx = E \int_{-\infty}^{+\infty} \psi_n^* \hat{H} \psi_n dx = E^2 \\ \Delta E &= \left( \langle E^2 \rangle - \langle E \rangle^2 \right)^{1/2} = \left( E^2 - E^2 \right)^{1/2} = 0\end{aligned}$$

In our models, the range of  $x$  values is restricted to the range,  $x_{Min}$  to  $x_{Max}$  and the wavefunction is forced to zero at these extreme values of  $x$ . So an expectation value is calculated as

$$(11) \quad \langle A \rangle = \int_{x_{Min}}^{x_{Max}} (bra) \times (ket) dx$$

The integral is evaluated numerically using Simpson's 1/3 rule by using the m-script **simpson1d.m**. The m-script **se\_measurements.m** can be used to evaluate the integrals in Table (1) and to evaluate the uncertainties.

Sample codes from the m-script **se\_measurements.m** to evaluate the expectation value for total energy and the uncertainty in position are:

```

% total energy – need to convert units in calculations
psi1 = gradient(Psi,x);
ket = - (hbar^2/(2*me*e))*gradient(psi1,x)(Lse^2*Ese) + (U.*Psi)';
braket = bra .* ket;
Eavg = simpson1d(braket,xMin,xMax);

% position x & uncertainty in position
ket = x .* Psi;
braket = bra .* ket;
xavg = simpson1d(braket,xMin,xMax);

ket = (x.^2) .* Psi;
braket = bra .* ket;
x2avg = simpson1d(braket,xMin,xMax);

deltax = sqrt(x2avg - xavg^2) * Lse;
        % length units nm to m

```

The m-script **se\_measurements.m** outputs numerical values of the integrals to the Command Window and graphical representations in a Figure Window (figure 9)). For example, the sloping well potential:

```

Quantum number, n = 3
Energy, E = -403.458 eV
Total Probability = 1
<x> = -0.000569644 nm
<x^2> = 0.000708057 nm^2
<ip> = -3.53767e-030 N.s
<ip^2> = 7.36845e-047 N^2.s^2
<U> = -655.895 eV
<K> = 252.787 eV
<E> = -403.107 eV
<K> + <U> = -403.107 eV

deltax = 2.66032e-011 m
deltap = 8.58397e-024 N.s
(dx dp)/hbar = 2.16456

```

From the above result, we can conclude the following:

- 1  $E = \langle E \rangle$  ignoring the slight difference in numerical values due to numerical inaccuracies in our modeling.
- 2  $\langle E \rangle = \langle K \rangle + \langle U \rangle$
- 3 The average position of the electron is slightly to the left of the origin.
- 4 The uncertainty principle is satisfied  $\frac{\Delta x \Delta p}{\hbar} = 2.2 > 0.5$ .
- 5 The expectation for momentum is complicated by the factor  $i$  and so we have to calculate  $\langle i p \rangle$  which is then a real quantity and from the results above, we can conclude that  $\langle i p \rangle = 0$ . No measurable physical quantity can be imaginary, hence the integral must be zero.

It is remarkable that a bound particle has definite set of discrete values for its total energy and this follows simply and directly from applying boundary conditions to a wavefunction that satisfies the Schrodinger Equation. At first, it seems surprising that the total energy has a set of unique values ( $\Delta E = 0$ ) but the momentum does not, since the uncertainty principle must be satisfied. But a classical vibrating string in a normal mode has a unique frequency of vibration while not possessing a unique wavelength as the transverse standing wave is sinusoidal along the string but is zero at and outside the fixed end points. However, the shape of the string inside and outside the fixed ends can be thought of a superposition of waves of different wavelengths with amplitudes and phases chosen so that the disturbance cancels everywhere except in the region between the end points. Therefore, the wavefunction can be thought of a superposition of different wavelengths and through the de Broglie relationship  $p = h / \lambda$ , the confined particle has a range of momentum.



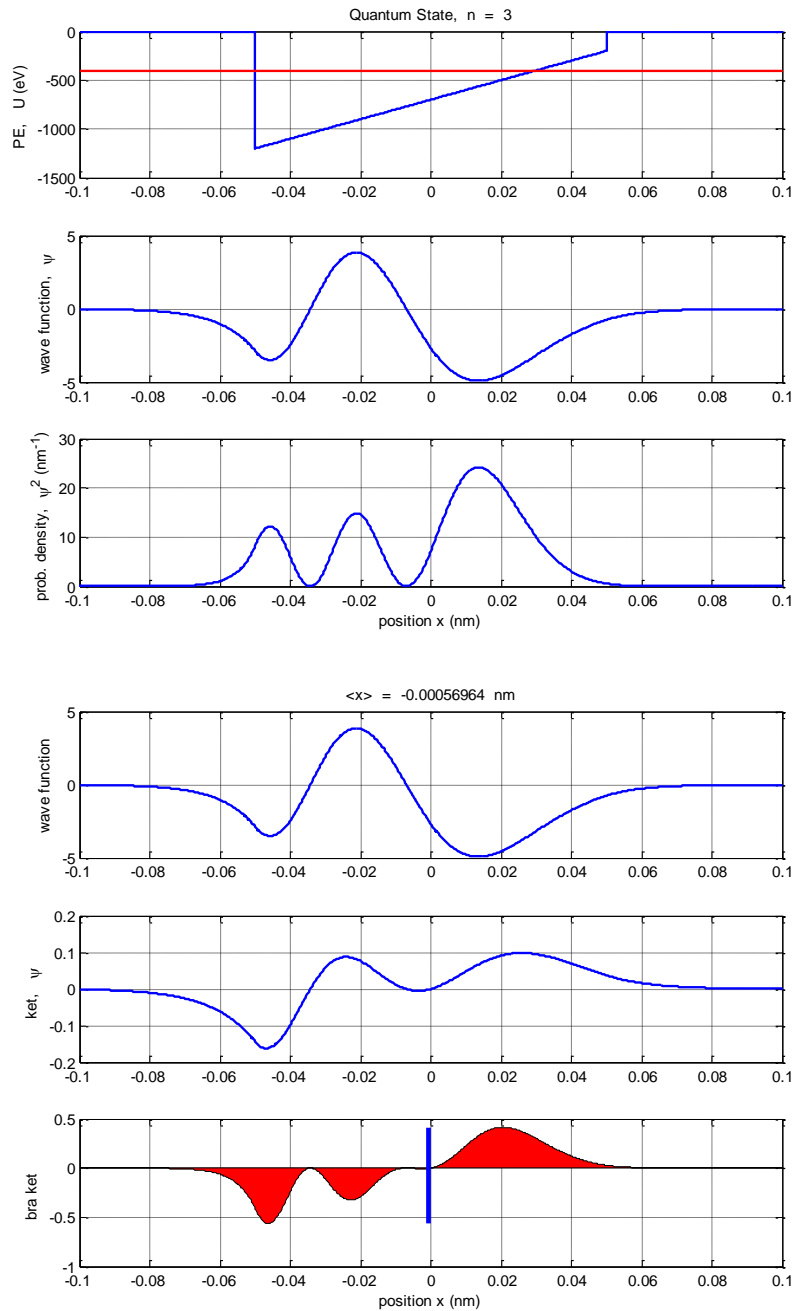


Fig. 9. The graphical output from the m-script `se_measurements.m` for the quantum state  $n = 3$  of a particle trapped in a sloping potential well. The lower graphs shows the bra (wavefunction), the ket and the area under the bracket curve representing the integral for the evaluation of the expectation value for position  $\langle x \rangle$ . The blue bar indicates the expectation value for position. You can modify the m-script `se_measurements.m` to produce graphical outputs for operators other than the position operator  $\hat{x}$ .

## ACCURACY OF THE NUMERICAL MODELLING

Numerical results may not always be accurate. Where possible you need to check that the results are OK. Firstly, you should always vary the number of points used in the modeling. In solving the Schrodinger Equation by the Matrix Method, the variable `num` which is set in the m-script `se_wells.m` determines the size of the vectors and arrays. Generally, if this number is too low the results are not accurate. You should start with a small number for `num` and increase it until there is a convergence in the results. If `num` is too large, then the execution time in running the m-scripts could be excessive and/or too much memory is used. Secondly, if possible you should compare the predictions of a numerical method with the known results predicted by analytical methods. The energy eigenvalues for an infinite square well can be easily found analytically, so we can compare those results with our numerical model.

Consider a system with an electron of mass  $m_e$  confined to a one dimensional region of length  $L$ . The potential well called an infinite square well has infinitely high walls which trap the particle, but the force on the electron is zero between the walls. The potential energy function and boundary conditions on the wavefunctions are

$$\begin{aligned}U(x) &= 0 & -L/2 \leq x \leq L/2 \\U(x) &= \infty & x < -L/2 \quad \text{and} \quad x > L/2 \\ \psi(-L/2) &= 0 & \psi(+L/2) = 0\end{aligned}$$

The classical predictions for such a system, is that the total energy of the trapped particle can have any positive value and since the potential energy inside the well is zero, the kinetic energy of the particle equals the total energy. The particle can have zero total energy (zero kinetic energy) and if its kinetic energy is greater than zero the particle will bounce back and forth between the impenetrable walls with constant speed. Increasing the energy simply increases the speed but no matter how great the speed, the particle can't be outside the walls, the region outside the walls is said to be classically forbidden.

The predictions of quantum mechanics are very different. In solving of the Schrodinger Equation it is found that the shape of the wavefunction inside the walls is sinusoidal and the wavefunction must be zero at the walls since the potential energy is infinite at each wall. Therefore, the only acceptable physical solutions are those wavefunctions where integer multiple of half-wavelengths of a sine curve fit into the distance  $L$  between the walls:

$$L = n \left( \frac{\lambda}{2} \right) \Rightarrow \lambda = \frac{2L}{n} \quad n = 1, 2, 3, \dots$$

The total energy  $E$  is related to the momentum  $p$  and the momentum related to a wavelength  $\lambda$  (de Broglie relationship) hence, we can determine an expression for the total energy as a function of  $n$  (principle quantum number) and the length  $L$

$$\lambda = \frac{2L}{n} \quad p = \frac{h}{\lambda} \quad E = \frac{p^2}{2m}$$

$$(12) \quad E_n = \left( \frac{h^2}{8mL^2} \right) n^2 \quad n = 1, 2, 3, \dots$$

This is a *momentous* result and very different from the predictions of classical physical. The principle quantum number  $n$  is restricted to integer values, therefore, the bound particle has only a discrete set of values for its total energy and these are the only possible values for the total energy of the system. The lowest value is  $n = 1$ , and the lowest allowed energy is  $E_1 = h^2 / (8mL^2) > 0$ . No particle in an infinite square well can have an energy lower than this, there is **no state of zero total energy**. This energy is called the **ground state energy**. If  $L \rightarrow \infty$  then the spacing between energy  $\Delta E \rightarrow 0$  which implies that the particle is behaving more like a free classical particle which can have any positive energy.

We can compare the predictions from the analytical model and the Matrix Method for an electron confined to an infinite square well potential of **width 0.1 nm**. To use the Matrix Method, modify m-script **se\_wells.m** to produce an infinite square well potential then run it:

Infinite square well parameters set in **se\_wells.m**

```
num = 801
```

```
Option 1 (case 1) square well
```

```
xMin = -0.05
```

```
xMax = +0.05
```

```
U1 = 0
```

Then run the m-script **se\_solve.m**. The screen output states that no eigenvalues are found. This is because the code is expecting negative values for the total energy. However, we can extract the required values for the total energy manually using the command **e\_values(mm,mm)** in the Command Window. Do this and record the first 10 eigenvalues for  $mm = 1, 2, \dots, 10$ . These values are stored in the m-script **se\_infwells.m**. Run the m-script **se\_infWells.m**. Note, when this file is run, all variables are cleared from the workspace. The file **se\_infWells.m** calculates the first 10 energy levels using equation (12), outputs the results to the Command Window and plots the numerical and analytical values in a Figure Window (figure 10):

n	E (eV)	Emm (eV)
1	37.74	37.69
2	150.95	150.74
3	339.64	339.17
4	603.80	602.97
5	943.44	942.13
6	1358.56	1356.60
7	1849.15	1846.50
8	2415.21	2411.70
9	3056.76	3052.30
10	3773.77	3768.10

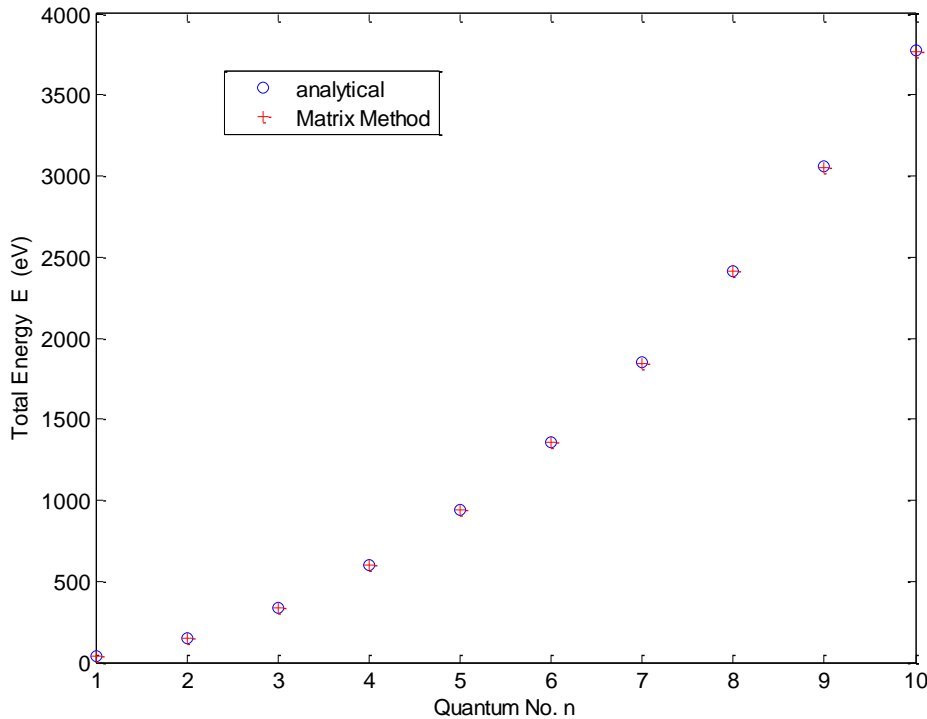


Fig. 10. The energy eigenvalues for an infinite square well of width 0.10 nm calculated from equation (12) and the Matrix Method using the m-scripts `se_wells.m` and `se_solve.m`. [`se_infWell.m`]

The discrepancy between the two sets of results is better than 0.2%. Therefore, we can have some confidence in the results from the Matrix Method for other potential well functions.

The wavefunctions for the infinite square well can be plotted after running `se_solve.m` by typing the following commands in the Command Window, for example, to display the eigenvector for the state  $n = 8$

```
plot(e_funct(:,8),'lineWidth',3)
axis off
```

Figure (11 show the eigenvectors for the first 10 quantum states of an infinite square well. The eigenfunction is zero outside the well and is of a sinusoidal shape inside the well. For the  $n^{\text{th}}$  state,  $n$  half-wavelengths of a sinusoidal curve fit into the width of the well. The shape of the wavefunction is the same as the shape of a vibrating guitar string for normal modes of vibration.

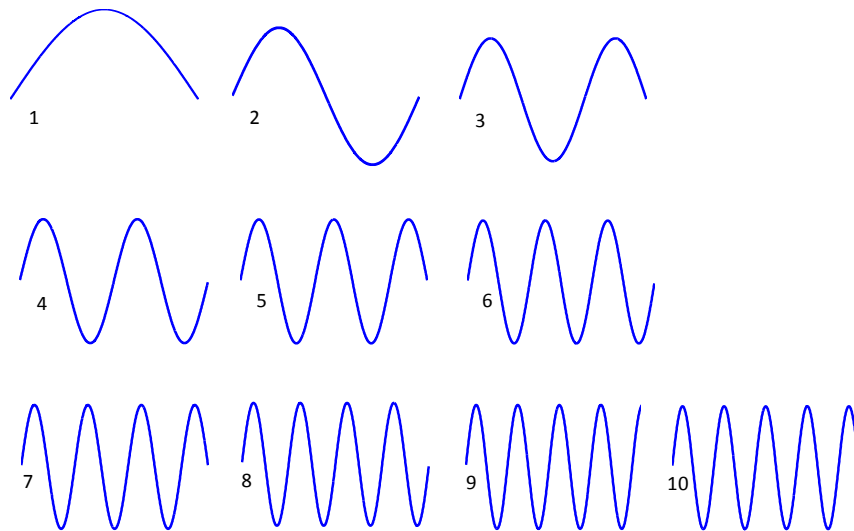


Fig. 11. The energy eigenvectors for an infinite square well for the first 10 quantum states. [[se\\_wells.m](#) [se\\_solve.m](#)]

When a potential well is of finite depth, the wavefunction extends into the classically forbidden region and so there is some probability of finding the particle outside the well which in classical terms is impossible. For a particular state of an infinite square well, the wavelength is constant (independent of  $x$ ). This is not the case when the potential inside the well changes with  $x$ , for example, the wavelength increases with decreasing potential in the sloping well (figures 8 & 9) and so the shape of the wavefunction is not simply sinusoidal.

## INVESTIGATIONS (Matrix Method)

There are many aspects of quantum behavior for bound states you can investigate by studying various potential wells with different parameters. A proven learning strategy that you can apply to gain a deeper understanding of quantum physics is called **POE**

**P**redict   **O**bserve   **E**xplain

For a given potential well, some of the **predictions** you could make are: number of bound states, approximate values of energy eigenvalues, spacing of energy levels, shape of wavefunction, number of half-wavelengths inside well, changes in half-wavelengths and size of exponential tails, the number of zero crossings of the wavefunction, and height of peaks in wavefunction. For example, in a square well the energy levels are more crowded towards the bottom of the well, in a parabolic well (shape bends away from  $x$ -axis) the energy levels are equally spaced and in the Morse potential well or a Coulomb shaped well (shape bends towards the  $x$ -axis) the energy levels are more crowded toward the top of the potential well.

After you have made your predictions, run the m-scripts and **observe** the results and compare them with your predictions.

Then, you explain the results you **observed** and rectify any discrepancies in the results and your predictions.

## 1 Infinite Square Well and Finite Square Well

- 1.1 Find the energy eigenvalues for various widths of an infinite square well and compare your results with theoretical values predicted by equation (12). For each state ( $n = 1, 2, \dots$ ) measure the wavelength  $\lambda$ , then using the de Broglie relationship ( $p = h / \lambda$ ), calculate the momentum of the electron and its kinetic energy ( $E_K = p^2 / 2m$ ). Compare the energy eigenvalues with the kinetic energy values. Repeat the calculations for different values of `num` (size of vectors and arrays). Can use the m-script `se_infwell.m`.
- 1.2 Find the energy eigenvalues for various square wells of different depths and widths. Observe the wavefunction and expectation values for different states. Check the orthonormal character of the wavefunctions [`se_orthonormal`]. Why does the wavelength of the eigenfunctions decrease as the quantum number  $n$  increases? Why is the kinetic energy of the electron in each eigenstate of a finite square well less than the value of its kinetic energy in an infinite square well of the same width? How does the number of zero crossing of the wavefunction vary with the quantum number  $n$ ? Comment on the curvature of the wavefunction inside and outside of the potential well and explain. Comment on the expectation values and is the Heisenberg Uncertainty Principle satisfied?
- 1.3 The simplest nuclear system is a `deuteron` - a single proton bound together with a single neutron by the attractive strong nuclear force. This system has only one bound state with a binding energy of 2.22 MeV near the top of the well. This is the ground state, there are no excited states. This is a three dimensional system, but we can model the strong nuclear force as a one-dimensional finite square well potential where the solution of the Schrodinger Equation gives the radial component of the wavefunction. Experiments on the scattering of high energy electrons from deuterons provides evidence of the existence of a strong repulsive core in the nuclear potential, this means that the particles avoid the centre of the deuteron, the proton and neutron can't get too close to each other, hence, the radial wavefunction must approach zero towards the centre. The mass of the bound particle is equal to the reduced mass of the system, hence



$$m = \frac{m_p m_n}{m_p + m_n} \quad m = (m_p + m_n) / 2$$

We can alter the code for the square well potential (**case 1**) to model the potential for the deuteron. The modifications are:

```
m = mp*mn/(mp+mn);   reduced mass - deuteron
xMin = 0             forces the wavefunction at the centre of the deuteron to be zero
x1 = 1.5e-6         width of square well in nm
xMax = 20*x1
U1 = -100e6        starting depth of square well in eV
```

Find the binding energy using **se\_solve.m**. Then, adjust the value of **U1** until the binding energy is about 2.2 MeV to find an estimate of the well depth. View the characteristics of the wavefunction using **se\_psi.m**. In the ground state, the eigenfunction describing the separation of the proton and neutron extends far beyond the confines of the well. From the Command Window determine the probability that the separation distance between the proton and neutron is greater than the width of the well using the function **simpson1d.m**:

Check that the function is normalized, use

```
simpson1d(prob(:,1)',xMin,xMax)   result should be 1.
```

The probability that the electron is found within the well, use

```
simpson1d(prob(1:min(find(x>=x1)),1)',0,x1)
```

to evaluate the integral  $\int_0^{x_1} \psi(x)\psi(x) dx = \int_0^{x_1} prob(x)dx$ . The statement

```
min(find(x>=x1))
```

finds the index of  $x$  for the edge of the well at  $x_1$ .

The probability density  $|\psi(x)|^2$  specifies the probability of finding the two nucleons in the deuteron with a separation in the vicinity of  $x$ .

Use **se\_measurements.m** to find the average separation distance.

One book quoted that the mean separation of the proton and neutron as  $4 \times 10^{-15}$  m (much larger than the width of the well) and that there was a 50% chance of finding the particles in the classical forbidden region. How do your results compare? Your results about probability imply that the attractive region for the only bound state is just barely strong enough to overcome the effect of the repulsive core and lead to binding. As a consequence, there is a high probability that the two nucleons in the deuteron have a separation larger than the range of nucleon forces. The values for `xMax`, `x1` and `U1` are not unique in giving the correct value for the binding energy. If you check different references, you will get different numbers quoted in each reference. Remember, that our model is a crude one, and the numbers are not necessary accurate but the model does give an insight to the deuteron nucleus.

## 2 Stepped Well (Asymmetrical Well)

- 2.1 Investigate the solutions of the Stepped Well for various widths and depths of the left and right sides of the well by modifying the code in `se_wells.m`

```
case 2
xMin = -0.15;    % default = -0.15 nm
xMax = +0.15;    % default = +0.15 nm
x1 = 0.1;        % Total width of well: default = 0.1 nm
x2 = 0.06;       % Width of LHS well: default = 0.06 nm;
U1 = -400;       % Depth of LHS well; default = -400 eV;
U2 = -200;       % Depth of RHS well (eV); default = -250 eV;
```

Set `U1 = -400`, `U2 = -200`, `x1 = 0.10` and `x2 = 0, 0.25x1, 0.50x1, 0.75x1, 1.00x1`

Set `x1 = -0.10`, `x2 = -0.05`, `U1 = -400` and `U2 = 0, 0.25U1, 0.50U1, 0.75U1, 1.00U1`

- 2.2 Investigate an asymmetrical well by commenting the line as shown below in the m-script for `se_wells.m` (case 2).

```
for cn = 1 : num
if x(cn) >= -x1/2,    U(cn) = U1; end; %if
if x(cn) >= -x1/2 + x2, U(cn) = U2; end; %if
%if x(cn) > x1/2,    U(cn) = 0; end; %if
% comment above line to give an asymmetrical well
end %for
```

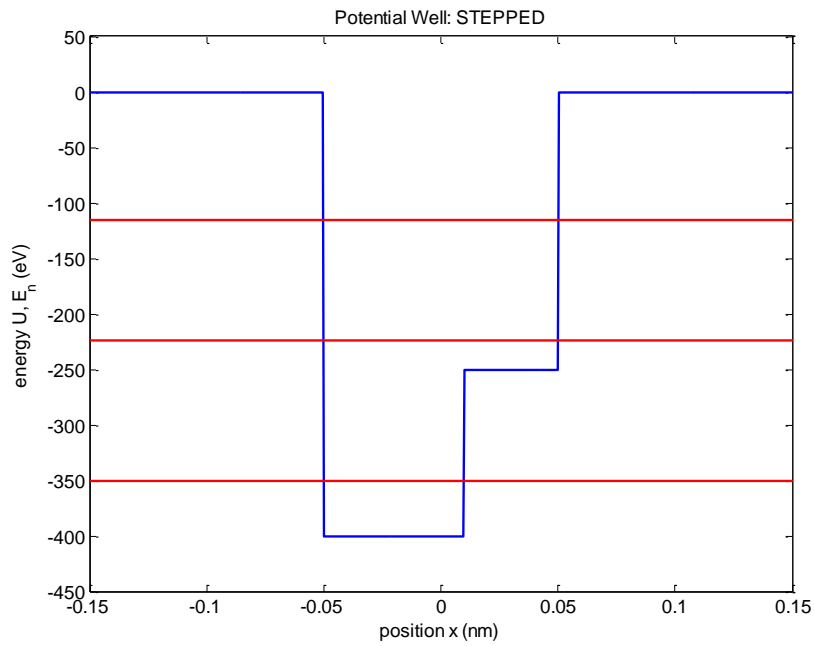


Fig. 12. The energy spectrum for a stepped well.  
[\[se\\_wells.m se\\_solve.m\]](#)

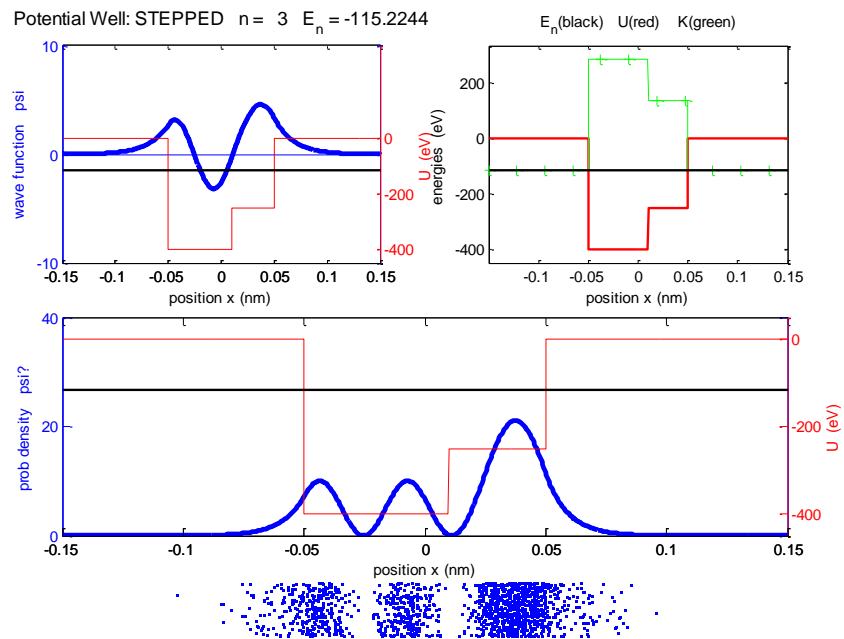


Fig. 13. The quantum state  $n = 3$  for a stepped well.  
[\[se\\_wells.m se\\_solve.m se\\_psi.m\]](#)

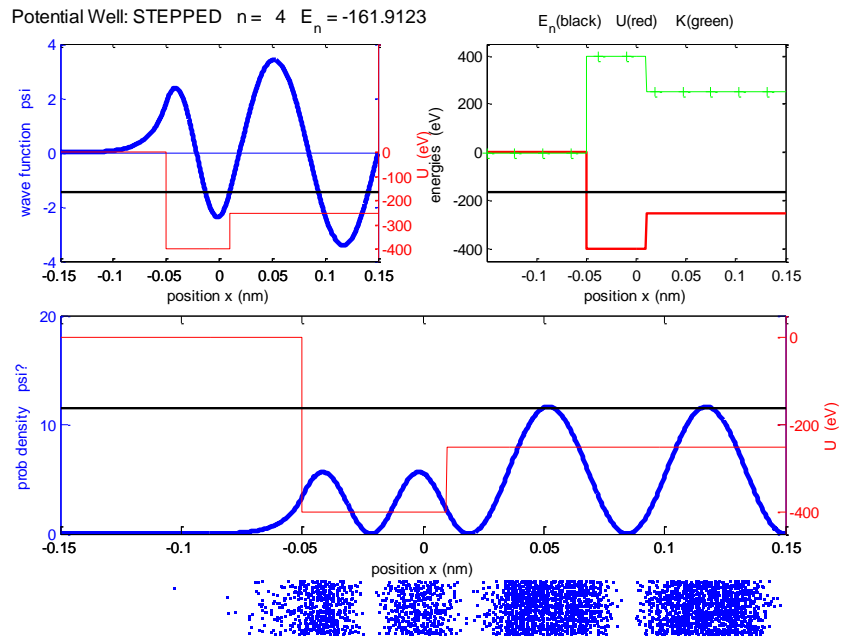


Fig. 14. The quantum state  $n = 4$  for an asymmetrical well. The total energy is greater than the potential on the left hand side of the well, therefore, the kinetic energy of the electron is positive with the electron no longer bound to the well and acts as a free particle.

[se\_wells.m se\_solve.m]

### 3 Double Well

3.1 Investigate the properties of double potential wells. Remember to employ the **POE** learning strategy. Start with the well parameters:

U1 = -400; % Depth of LHS well: default = -440 eV  
U2 = -400; % Depth of RHS well: default = -400 eV  
U3 = -300; % Depth of separation section: default = 100 eV  
x1 = 0.10; % width of LHS well: default = 0.10 nm  
x2 = 0.10; % Width of RHS well: default = 0.10 nm  
x3 = 0.10; % Width of separation section: default = 0.10 nm  
xEnd = 0.05; % parameters to define range for x-axis: default = 0.05 nm

Then, increase the height of the centre section of the well **U3** in steps of 50 to 200.

3.2 The results for the double well with **U3 = 200 eV** are:

Quantum State / Eigenvalues  $E_n$  (eV)  
1 -373.13  
2 -373.13  
3 -293.56  
4 -293.56  
5 -165.41  
6 -165.4  
7 -2.8576  
8 -2.7866

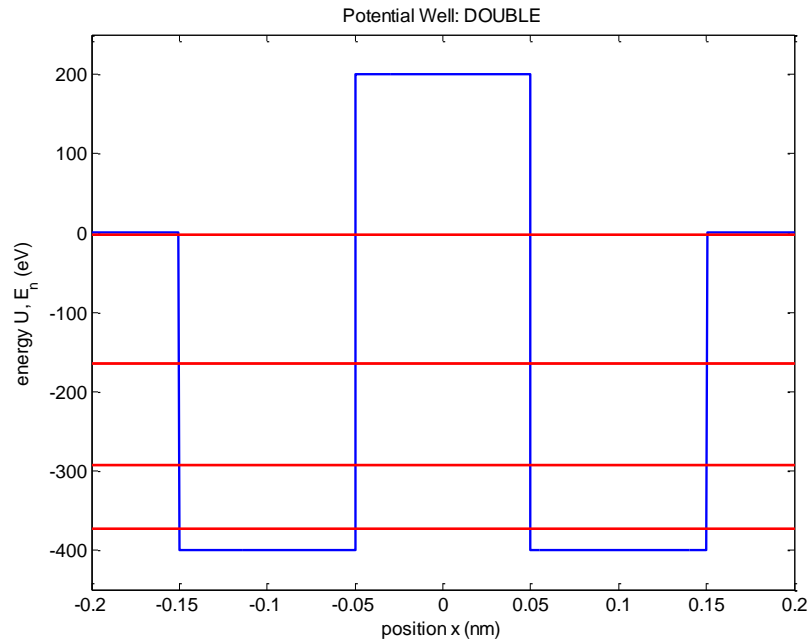


Fig. 15. The energy spectrum for the double well. Why do you only see 4 energy levels and not 8? [[se\\_wells.m](#) [se\\_solve.m](#)]

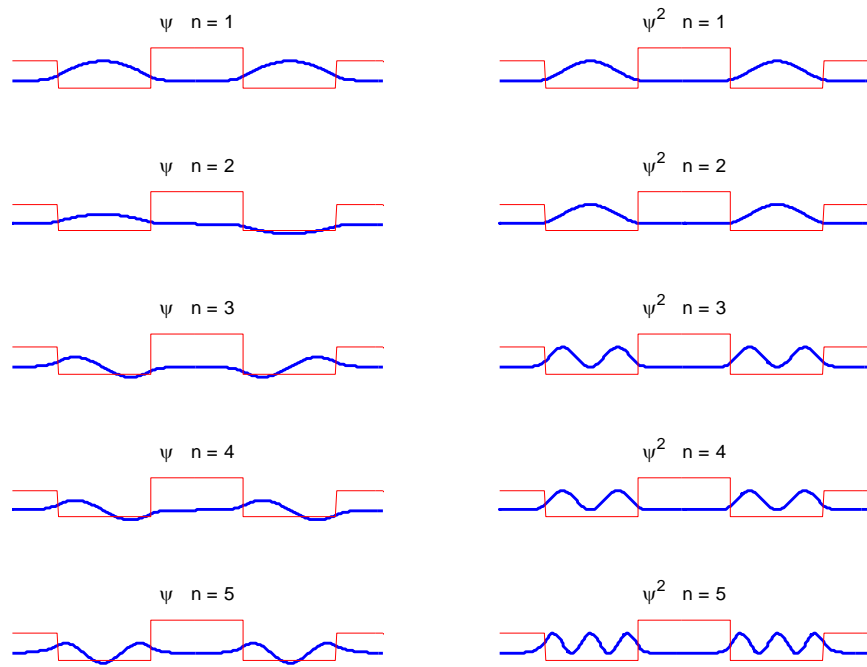


Fig. 16. The energy eigenvalues for the double well.  
`[se_wells.m se_solve.m]`

Explain the spacing of energy levels.

3.3 Investigate a well with a deep centre section, try  $U3 = -600$ .

## 4 Sloping Well

- 4.1 Investigate the properties of sloping potential wells. Remember to employ the **POE** learning strategy.

## 5 Truncated Parabolic Well

- 5.1 Investigate the properties of truncated parabolic potential wells. Remember to employ the **POE** learning strategy. What can you say about the spacing between energy levels?

- 5.2 The potential energy for a classical particle oscillating in a parabolic well (e.g. particle vibrating at the end of a spring executing simple harmonic motion) is

$$U(x) = \frac{1}{2} k_s x^2 \quad \text{where } k_s \text{ is the spring constant.}$$

The eigenstates for this system are the solutions of the Schrodinger Equation:

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k_s x^2 \right) \psi_n(x) = E_{sn} \psi_n(x)$$

The energy eigenvalues for this system known as the **quantum harmonic oscillator** are given by

$$E_{sn} = \left( n - \frac{1}{2} \right) \hbar \omega$$

where  $n = 1, 2, 3, \dots$  (N.B. most books have  $n = 0, 1, 2, 3, \dots$ )

The classical frequency of oscillation  $\omega$  for a particle of mass  $m$  is

$$\omega = \sqrt{\frac{k_s}{m}} \quad f = 2\pi \sqrt{\frac{k_s}{m}}$$

The Schrodinger Equation for our truncated parabolic well is

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U_1 \left( 1 - 4 \left( \frac{U_1}{x_1^2} \right) \right) \right) \psi_n(x) = E_{sn} \psi_n(x)$$

where  $U_1$  is the depth of the well and  $x_1$  is the full width of the well when  $U = 0$ .

Show that the spring constant  $k_s$  is related to the well parameters  $U_1$  and  $x_1$  by the relationship

$$k_s = \frac{8|U_1|}{x_1^2}$$

Run the m-script `se_wells.m` for the parabolic well (case 5) with the parameters:

```
xMin = -0.2; % default = -0. nm
xMax = +0.2; % default = +0.2 nm
x1 = 0.2; % width default = 0.2 nm;
U1 = -400; % well depth default = -400 eV;
```

and verify the following results.

$n$	Matrix Method $E_n$ (eV)	Theory $E_{sn} + U_1$	$E_{n+1} - E_n$
1	-360.92	-360.94	---
2	-282.77	-282.83	78.15
3	-204.68	-204.71	78.08
4	-127.09	-126.60	77.60
5	-52.272	-48.485	74.81

Explain why the discrepancies are larger for higher the quantum numbers.

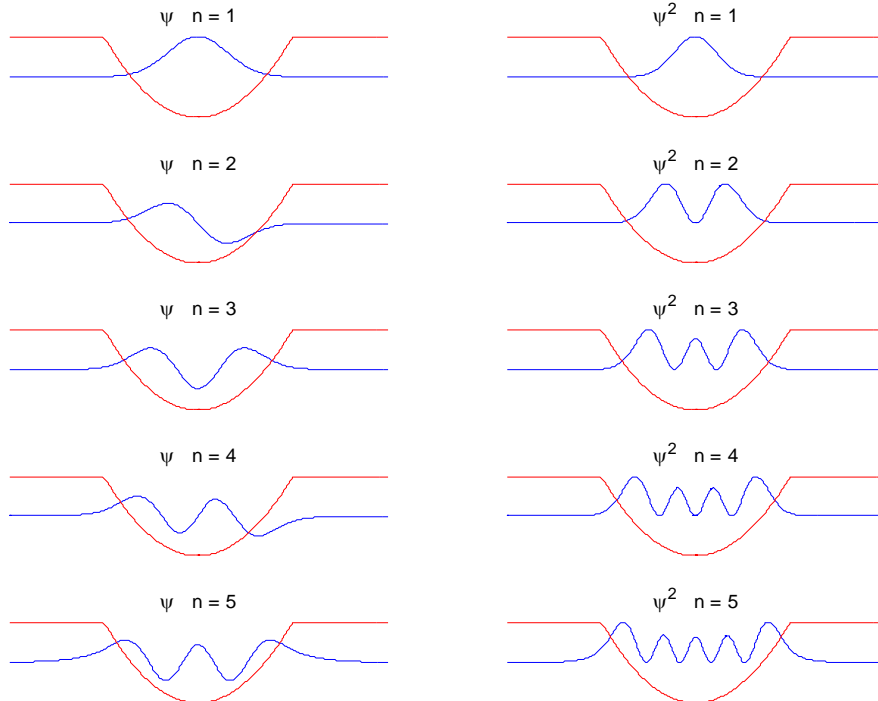


Fig. 17. The eigenfunctions and probability distributions for the harmonic oscillator.



Explain why the state  $n = 5$  in figure (17) is more like the classical prediction for the probability of locating the particle.

- 5.2 Repeat the above, for different well parameters. Run `se_measurements.m` and find the expectation values for a number of states. What is the significance for the state  $n = 1$  by considering the value for  $\Delta x \Delta p$  ?

## 6 Morse Potential Well

- 6.1 Investigate the properties of Morse parabolic potential wells. Remember to employ the **POE** learning strategy. What can you say about the spacing between energy levels?
- 6.2 The Morse potential is often used as the potential energy function for diatomic molecules. One form of the Morse potential is

$$U(x) = U_1 \left( 1 - \left( \exp\left( \frac{x_1 - x}{S} \right) - 1 \right)^2 \right)$$

where  $S$  is a positive constant which determines the width of the well and the maximum depth of the well is at  $x_1$ ,  $U(x_1) = U_1$ . Consider the Morse potential with parameters:

$U_1 = -1200$ ;  
 $x_0 = 0.08$ ;  
 $S = 0.075$ ;  
 $x_{\text{Min}} = 0$ ;  
 $x_{\text{Max}} = 0.3$ ;  
 $x_{\text{Max}} = 0.3$ ;

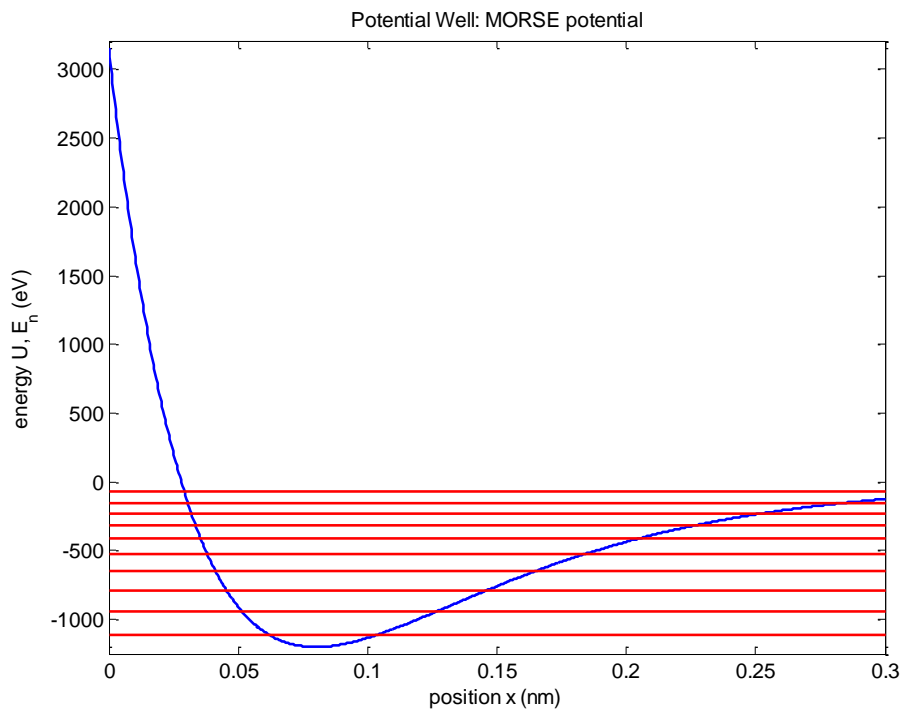


Fig. 18. The energy eigenvalues for the Morse potential.  
[se\_wells.m se\_solve.m]

Run the m-script `se_measurements.m` and record the expectation value for position. Comment on the spacing of the energy levels and explain why most materials expand upon heating.