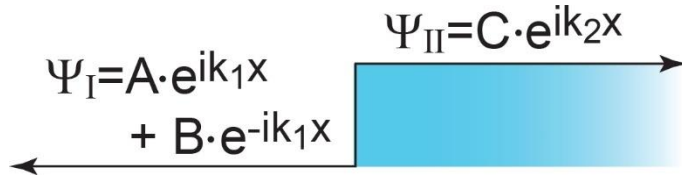# Chem 542 Problem Set 2

1. The step barrier from the first problem set:

can be modeled using the following Matlab code:

```
clear all;
syms B C k1 k2
eqn1= 1+B == C;
eqn2=i*k1-i*k1*B==i*k2*C;
[F,U] = equationsToMatrix([eqn1, eqn2], [B, C]);
X = linsolve(F,U)
```

As per what we did in class and the previous homework set, we can set A=1 and thus the code above solves for the coefficients B and C. The solutions are as expected:

`(k1 - k2)/(k1 + k2)` and `(2*k1)/(k1 + k2)`

These allow us to calculate various parameters and plot the wavefunctions using the following code. Note that two wavefunctions are plotted in Figure 1a (one above and anther below the barrier), while the reflection $|B|^2$ and transmission $|C|^2$ in Figure 1b.

```
clear all;

%define constants
h=1.05e-34; m=9.1e-31; V=1.6e-19; nm=1e-9; i=sqrt(-1);
%the energy varies from 0 to 2X times the potential
for j=1:200
energy(j)=j*V/100;
k1=sqrt(2*m*energy(j)/h/h);        %the wavevectors
k2=sqrt(2*m*(energy(j)-V)/h/h);
b(j)=(k1 - k2)/(k1 + k2);          %the wavefunction coefficients
c(j)=(2*k1)/(k1 + k2);
ref(j)=b(j)*conj(b(j));            %percent reflection
trans(j)=c(j)*conj(c(j));          %percent transmission?
    %calculates the wavefunction over 2000 points at every energy
    for k=1:2000
        xax(k)=(k-1000)/500*nm;    %the position in meters
        wf(k,j)=exp(i*k1*xax(k))+b(j)*exp(-i*k1*xax(k));
        if (xax(k)>=0)             %if right of the barrier at x=0
            wf(k,j)=c(j)*exp(i*k2*xax(k));
        end;
    end;
end;
%plots the wavefunctions, above and below the barrier, with an offset for
%clarity
```

```
plot(xax,wf(:,50),'b'); hold on; plot(xax,wf(:,150)+3,'r'); figure;
plot(energy,ref,'b'); hold on; plot(energy,trans,'r');
```
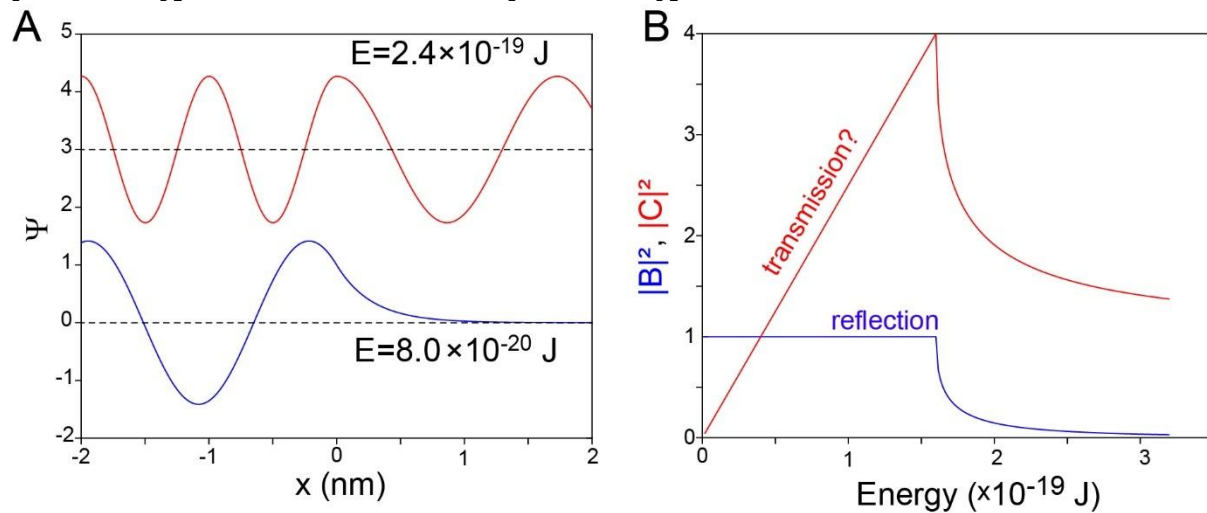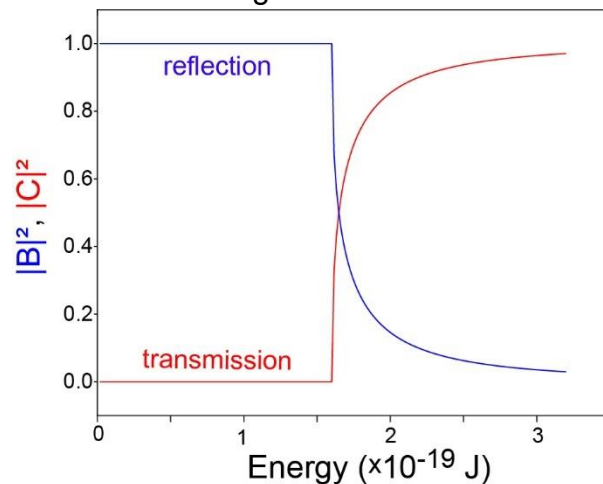

Whups! While the wavefunctions look correct, and the reflection $|B|^2$ is ok, it turns out that $|C|^2$ is not quite equal to the transmission! This is because particles are moving more slowly in region II since there is less kinetic energy available. This can be accounted for by the ratio of the wavevectors. Consequently, the percent transmission is actually: $\frac{k_2}{k_1}|C|^2$. Please modify the code with this information and submit a figure displaying the correct reflection and transmission.
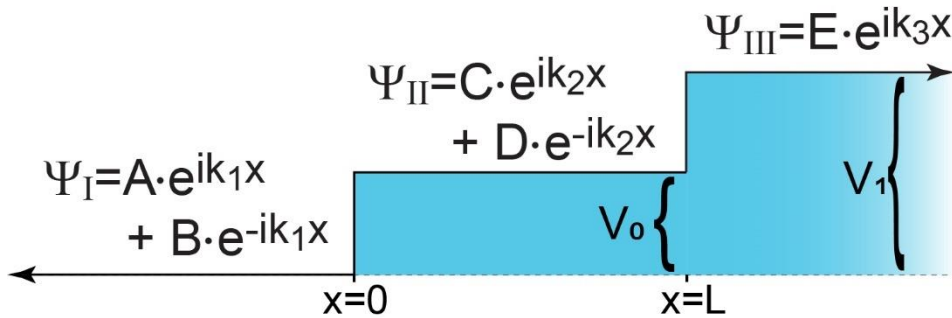
Answer: The code should be altered as so:

```
trans(j)=(k2/k1)*c(j)*conj(c(j)); %takes care of the flux
```

And here is the figure:

2. The multiple step barrier is described as so:

$\Psi_{III} = E \cdot e^{ik_3 x}$

$\Psi_{II} = C \cdot e^{ik_2 x} + D \cdot e^{-ik_2 x}$

$\Psi_I = A \cdot e^{ik_1 x} + B \cdot e^{-ik_1 x}$

V_1

V_0

x=0   x=L

a. Please use Matlab to solve for B and E, and then calculate the reflection and transmission as a function of energy above the barrier; of course provide your code for full credit. I suggest using a 1 eV barrier for V_0, 2 eV for V_1, and a step length of at least L=1 nm or greater.

b. Please experiment with the effects of L and the potential energies on the transmissions and reflections and describe what you see.

Answer. a.

```
clear all;
syms B C D E k1 k2 k3 L
eqn1=1+B == C+D;
eqn2=k1-k1*B==k2*C-k2*D;
eqn3=C*exp(i*k2*L)+D*exp(-i*k2*L)==E*exp(i*k3*L);
eqn4=k2*C*exp(i*k2*L)-k2*D*exp(-i*k2*L)==k3*E*exp(i*k3*L);
[H,U] = equationsToMatrix([eqn1, eqn2, eqn3, eqn4], [B, C, D, E]);
X = linsolve(H,U)

clear all;
%define constants
h=1.05e-34; m=9.1e-31; V1=1.6e-19; V2=2*1.6e-19; L=3.5e-9; i=sqrt(-1);
for j=1:1000
    energy(j)=j*V1/100;   %the energy varies from 0 to 10 times the potential
    k1=sqrt(2*m*energy(j)/h/h);
    k2=sqrt(2*m*(energy(j)-V1)/h/h);
    k3=sqrt(2*m*(energy(j)-V2)/h/h);
    b(j)=(k1*k2 + k1*k3 - k2*k3 + k2^2*exp(L*k2*2i) - k2^2 +
k1*k2*exp(L*k2*2i) - k1*k3*exp(L*k2*2i) - k2*k3*exp(L*k2*2i))/(k1*k2 + k1*k3
+ k2*k3 - k2^2*exp(L*k2*2i) + k2^2 + k1*k2*exp(L*k2*2i) - k1*k3*exp(L*k2*2i)
+ k2*k3*exp(L*k2*2i));
    c(j)=(2*k1*(k2 + k3))/(k1*k2 + k1*k3 + k2*k3 - k2^2*exp(L*k2*2i) + k2^2 +
k1*k2*exp(L*k2*2i) - k1*k3*exp(L*k2*2i) + k2*k3*exp(L*k2*2i));
    d(j)=(2*k1*exp(L*k2*2i)*(k2 - k3))/(k1*k2 + k1*k3 + k2*k3 -
k2^2*exp(L*k2*2i) + k2^2 + k1*k2*exp(L*k2*2i) - k1*k3*exp(L*k2*2i) +
k2*k3*exp(L*k2*2i));
    e(j)=(4*k1*k2*exp(L*k2*1i)*exp(-L*k3*1i))/(k1*k2 + k1*k3 + k2*k3 -
k2^2*exp(L*k2*2i) + k2^2 + k1*k2*exp(L*k2*2i) - k1*k3*exp(L*k2*2i) +
k2*k3*exp(L*k2*2i));
    trans(j)=(k3/k1)*e(j)*conj(e(j));
```
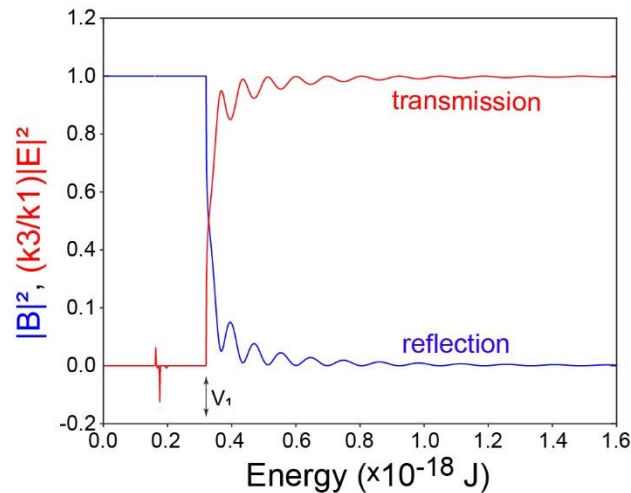
```
    ref(j)=b(j)*conj(b(j));
end;
plot(energy,ref,'b'); hold on; plot(energy,trans,'r');
```
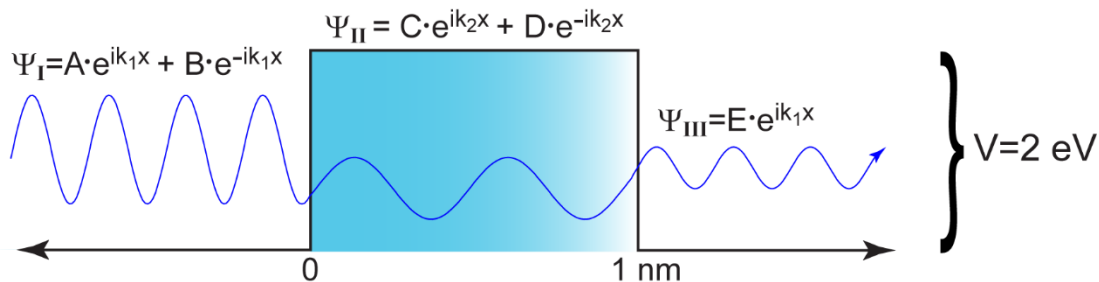
Here is a figure of the reflection and transmission, using a rather long step length of L=3.5 nm. This is plotted out to 10 eV.

b. You tend to get more resonances with increasing L and increasing potential energies.

3. The single barrier problem in a 1-dimensional scattering problem is set up as so:

Can you use Matlab to plot transmission ($|E|^2=E^*E$) vs energy for an electron impinging upon a 1 nm ($=1\times10^{-9}$ m), 1 eV ($=1.6\times10^{-19}$ J) barrier as a function of energy, from 0 J to 10 eV ($=16\times10^{-19}$ J)? Once successful please send me your code as well as the figure.

Answer.

```
clear all;
syms B C D E k1 k2 L
eqn1= 1+B == C+D;
eqn2=i*k1-i*k1*B==i*k2*C-i*k2*D;
eqn3=C*exp(i*k2*L)+D*exp(-i*k2*L)==E*exp(i*k1*L);
eqn4=i*k2*C*exp(i*k2*L)-i*k2*D*exp(-i*k2*L)== i*k1*E*exp(i*k1*L);
[F,U] = equationsToMatrix([eqn1, eqn2, eqn3, eqn4], [B, C, D, E]);
```

```
X = linsolve(F,U)

h=1.05e-34; m=9.1e-31; L=1e-9; V=2*1.6e-19; i=sqrt(-1);
for j=1:10000
energy(j)=j*1.6e-19/1000;
k1=sqrt(2*m*energy(j)/h/h);
k2=sqrt(2*m*(energy(j)-V)/h/h);

T(j)=conj((4*k1*k2*exp(-L*k1*1i)*exp(L*k2*1i))/(2*k1*k2 - k1^2*exp(L*k2*2i) -
k2^2*exp(L*k2*2i) + k1^2 + k2^2 + 2*k1*k2*exp(L*k2*2i)))*(4*k1*k2*exp(-
L*k1*1i)*exp(L*k2*1i))/(2*k1*k2 - k1^2*exp(L*k2*2i) - k2^2*exp(L*k2*2i) +
k1^2 + k2^2 + 2*k1*k2*exp(L*k2*2i));
end;
plot(energy/1.6e-19,T);
```

4. Now do the same from question 1 using the following potential energy surface. For this problem plot the transmission ($|T|^2 = T^*T$) as a function of energy from 0 J to 10 eV. Also send me your program.
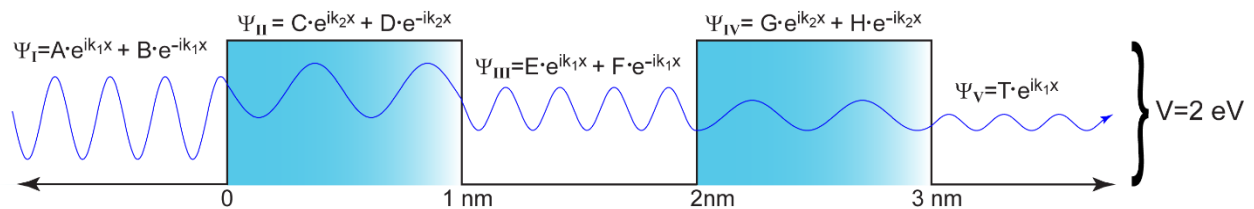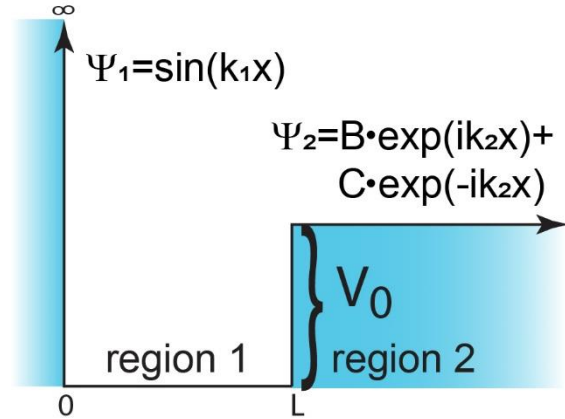

*Hint:* it should look like this:
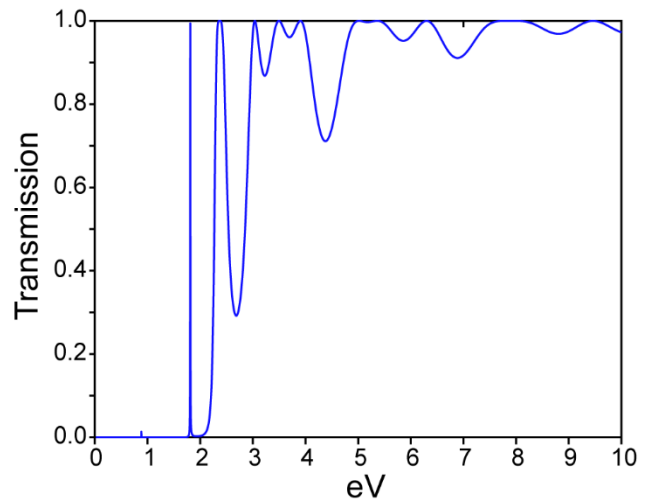
Answer.
Basically provided in the question.

5. Here we will learn an important lesson about quantum. We will perform a series of calculations on the half-infinite well shown here. We will do the calculations correctly, yet, we will nonetheless get a false result as described below.

$\Psi_1 = \sin(k_1 x)$
$\Psi_2 = B \cdot \exp(ik_2 x) + C \cdot \exp(-ik_2 x)$
V_0
region 1   region 2
0   L

We will use the same approach as on the last few questions to examine the wavefunctions for which the energy is less than the potential (i.e. $E < V_0$). We will specifically model an electron in a 1 nm trap, with a $V_0 = 1$ eV barrier to the right of the trap and an infinite barrier to the left. Note that this makes the wavefunction in region 1 a sine wave. You should be good enough at coding Matlab now to solve for the coefficients B and C.

Now, here is the problem. Matlab provides a solution for B and C as a function of k_1 and k_2, which are themselves functions of energy. However, when you write your code to visualize the wavefunctions at different energies (see below for a snippet to get you started) you get the following:
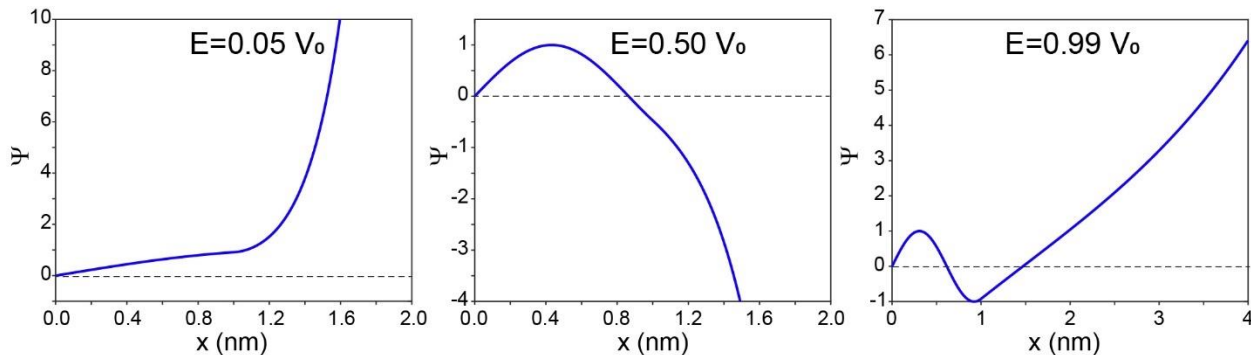
Clearly these wavefunctions are not well behaved- they are flying off to infinity either upwards or downwards, and they should rather go to 0 past x=1 nm, where the 1 eV barrier kicks in.

Here is the question: why is this happening? We did the calculations correctly, but wavefunctions can't just fly off to ±∞ like this! Please send me your code to repeat the above example wavefunctions, and then try to resolve this issue. ***Hints:*** there is a misinterpretation on how to do this calculation correctly. Perhaps if you plot wavefunctions as just the right energies there won't be a problem?

Here is a bit of Matlab code for visualizing wavefunctions- note that it isn't complete.

```matlab
h=1.05e-34; m=9.1e-31; L=1e-9; V=2*1.6e-19; i=sqrt(-1);
for j=1:100
energy(j)=j*V/100;
k1=sqrt(2*m*energy(j)/h/h);
k2=…
a(j)=…);
b(j)=…);
    for k=1:2000
        xax(k)=(k-1)/500*L;
        wf(k,j)=sin(k1*xax(k));
        if (xax(k)>=L)
            wf(k,j)=a(j)*exp(i*k2*xax(k))+b(j)*exp(-i*k2*xax(k));
        end;
    end;
end;
```
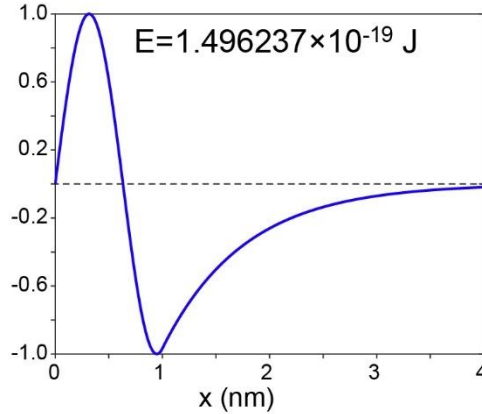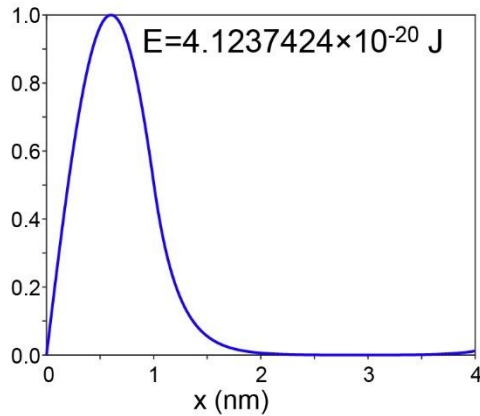
Answer:
There is my own code:
```matlab
clear all;
syms A B k1 k2 L
eqn1= sin(k1*L)==A*exp(i*k2*L)+B*exp(-i*k2*L);
eqn2= k1*cos(k1*L)==i*k2*A*exp(i*k2*L)-i*k2*B*exp(-i*k2*L);
[F,U] = equationsToMatrix([eqn1, eqn2], [A, B]);
X = linsolve(F,U)

h=1.05e-34; m=9.1e-31; L=1e-9; V=2*1.6e-19; i=sqrt(-1);
for j=1:2000
    energy(j)=j*1.6e-19/1000;
    k1=sqrt(2*m*energy(j)/h/h);
    k2=sqrt(2*m*(energy(j)-V)/h/h);
    a(j)=-(exp(-L*k2*1i)*(k1*cos(L*k1) + k2*sin(L*k1)*1i)*1i)/(2*k2);
    b(j)=(exp(L*k2*1i)*(k1*cos(L*k1) - k2*sin(L*k1)*1i)*1i)/(2*k2);
    fun1(j)=cot(k1*L); fun2(j)=-sqrt(V/energy(j)-1);
    for k=1:2000
        xax(k)=(k-1)/500*L;
        wf(k)=sin(k1*xax(k));
        if (xax(k)>=L)
            wf(k,j)=a(j)*exp(i*k2*xax(k))+b(j)*exp(-i*k2*xax(k));
        end;
    end;
end;
```

The problem is that there are only certain energies allowed for the bound states. You can't just calculate a wavefunction for any energy, or you might get irreverent behavior like in the examples. For this model system the bound energies are 4.1237424×10^{-20} J and 1.496237×10^{-19} J, and the wavefunctions look like:

Top-left plot: E=4.1237424×10⁻²⁰ J, x-axis labeled x (nm)
Top-right plot: E=1.496237×10⁻¹⁹ J, x-axis labeled x (nm)

6. For a 1D potential of the form:

$$V(x) = -\frac{\hbar^2}{2m}\Omega\delta(x)$$

where Ω is a real and positive number. The energies for bound states must be negative, can you find their wavefunctions?

Hint, you should consider wavefunctions in region I and II as having less energy than V. As a result, which wavefunction is appropriate, e^{ikx} or e^{-kx}? Also:

$$\lim_{\varepsilon\to 0}\int_{-\varepsilon}^{\varepsilon}\psi(x)\cdot\partial x = 0$$

as the area under the wavefunction must be finite.

Answer: We start with $\psi_I = Ae^{kx}$ and $\psi_{II} = Be^{-kx}$. As usual:

$\psi_I(0) = \psi_{II}(0)$ and $\frac{\partial\psi_I(0)}{\partial x} = \frac{\partial\psi_{II}(0)}{\partial x}$ which means $A = B$ and $Ak = -Ak$.

Next thing to do is to set up the S.E. and integrate it once:

$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi - \frac{\hbar^2}{2m}\Omega\delta(x)\psi = E\psi$ or better yet:

$$\frac{\partial^2}{\partial x^2}\psi(x) + \Omega\cdot\delta(x)\cdot\psi(x) = -\frac{2m}{\hbar^2}E\cdot\psi(x)$$

This rearranges as:

$$\frac{\partial^2}{\partial x^2}\psi(x) = \left\{-\frac{2m}{\hbar^2}\cdot E - \Omega\cdot\delta(x)\right\}\psi(x)$$

We first integrate from the left to the right over a range ε that we will let go to 0:

$$\int_{-\varepsilon}^{\varepsilon} \frac{\partial^2}{\partial x^2} \psi(x) \cdot \partial x = \frac{\partial \psi(+\varepsilon)}{\partial x} - \frac{\partial \psi(-\varepsilon)}{\partial x} = \frac{\partial \psi_I(0)}{\partial x} - \frac{\partial \psi_{II}(0)}{\partial x} = 2Ak$$

where we used the fact that the wavefunction $\psi(x)$ to the left of 0 is ψ_I and to the right is ψ_{II}. This allows us to know that:

$$\int_{-\varepsilon}^{\varepsilon} \left\{ -\frac{2m}{\hbar^2} \cdot E - \Omega \cdot \delta(x) \right\} \psi(x) \cdot \partial x = -\frac{2m}{\hbar^2} \int_{-\varepsilon}^{\varepsilon} E\psi(x) \cdot \partial x - \int_{-\varepsilon}^{\varepsilon} \Omega \cdot \delta(x) \cdot \psi(x) \cdot \partial x$$

Using the definition of a Dirac delta function means $\int_{-\varepsilon}^{\varepsilon} \Omega \cdot \delta(x) \cdot \psi(x) \cdot \partial x = \Omega \cdot \psi(0)$

Therefore we now know that $\Omega \cdot \psi(0) = 2Ak$. Since $\psi(0) = A$ then we are left with:

$\frac{\Omega}{2} = k$, which means that the wavefunctions are:

$$\psi_I = A \cdot e^{\frac{\Omega}{2} \cdot x}$$

and

$$\psi_{II} = A \cdot e^{-\frac{\Omega}{2} \cdot x}$$

7. Let's say you have two unnormalized wavefunctions, left and right of the origin defined as:

If x<0: $\psi_I = Ne^{\frac{\Omega}{2} \cdot x}$ and if x>0: $\psi_{II} = Ne^{-\frac{\Omega}{2} \cdot x}$

What is the proper normalization constant N?

Answer:

We assume that the wavefunction is symmetric, meaning that:

$$\int_{0}^{\infty} \psi^*(x) \cdot \psi(x) \partial x = N^2 \int_{0}^{\infty} e^{-\frac{\Omega}{2} \cdot x} e^{-\frac{\Omega}{2} \cdot x} \partial x = N^2 \int_{0}^{\infty} e^{-\Omega \cdot x} \cdot \partial x = \frac{1}{2}$$

Since $\int_0^\infty e^{-\Omega \cdot x} \cdot \partial x = -\frac{1}{\Omega} e^{-\Omega \cdot x} \Big|_0^\infty = \frac{1}{\Omega}$ we know then that $N^2 \frac{1}{\Omega} = \frac{1}{2}$ and therefore $N = \sqrt{\frac{\Omega}{2}}$

8. There is a branch of quantum mechanics called matrix mechanics. This is due to the fact that you can have eigenvalue equations in matrix form. Let's say that we have an operator:

$$\widehat{\Omega} = \begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}$$

and an eigenfunction of that operator: $\Phi = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$.

a. Can you show that:

$$\widehat{\Omega}\Phi = \omega\Phi$$

where $\omega = 0.9$? **Hint:** you might have to look up how to multiply a matrix by a column vector in Google. Also here is a useful identity: $\begin{bmatrix} -\omega \cdot a \\ \omega \cdot a \end{bmatrix} = \omega \begin{bmatrix} -a \\ a \end{bmatrix}$.

b. The eigenvalue equation $\widehat{\Omega}\Phi = \omega\Phi$ can be expressed as:

$$(\widehat{\Omega} - \omega)\Phi = 0$$

such that, as in the previous example:

$$\widehat{\Omega} - \omega = \begin{bmatrix} 1 - \omega & 0.1 \\ 0.1 & 1 - \omega \end{bmatrix}$$

There is a theorem in mathematics that the eigenvalues ω of $\widehat{\Omega}\Phi = \omega\Phi$ can be found by:

$$det(\widehat{\Omega} - \omega) = 0$$

where det is the determinant. Can you show that solving:

$$det \begin{bmatrix} 1 - \omega & 0.1 \\ 0.1 & 1 - \omega \end{bmatrix} = 0$$

for ω provides a quadratic equation that allows you to solve ω? Of course you will find two values, one of which is 0.9 as in pt. a. What is the other one? **Hint:** $det \begin{bmatrix} a & b \\ c & d \end{bmatrix} = ad - cb$, and, the roots of a quadratic equation: $ax^2 + bc + c = 0$ are $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$.

c. Can you show that the eigenfunction $\Phi = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$ of $\widehat{\Omega} = \begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}$ has an eigenvalue $\omega = 1.1$?

Answer a.:

$$\widehat{\Omega}\Phi = \begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}\begin{bmatrix} -1 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 \times -1 + 0.1 \times 1 \\ 0.1 \times -1 + 1 \times 1 \end{bmatrix} = \begin{bmatrix} -0.9 \\ 0.9 \end{bmatrix} = 0.9 \begin{bmatrix} -1 \\ 1 \end{bmatrix}$$

b. The determinant is:

$$det \begin{bmatrix} 1 - \omega & 0.1 \\ 0.1 & 1 - \omega \end{bmatrix} = (1 - \omega)^2 - 0.1 \times 0.1 = 0$$

Expanding the first term yields:

$$\omega^2 - 2\omega + 1 - 0.01 = \omega^2 - 2\omega + 0.99 = 0$$

The roots of $\omega^2 - 2\omega + 0.99 = 0$ using $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$, where a=1, b=-2 and c=0.99:

$$\frac{2 \pm \sqrt{4 - 3.96}}{2} = 1 \pm 0.1 = 0.9, 1.1$$

Thus the other eigenvalue is 1.1

c. If we solve as before:

$$\begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}\begin{bmatrix} 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 \times 1 + 0.1 \times 1 \\ 0.1 \times 1 + 1 \times 1 \end{bmatrix} = \begin{bmatrix} 1.1 \\ 1.1 \end{bmatrix} = 1.1 \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$