Problem 01 - Schrödinger Equation with a step potential

For the step potential we discussed in class on Jan. 17, we decided that we could have different wavelengths on either side of the step but a single frequency. In this problem will examine this observation in a little more detail. As we discussed, such a wavefunction must be continuous, and its first derivative with respect to position must also be continuous, since the Schrödinger equation includes a second derivative with respect to position (a twice-differentiable function must be continuous and must have a continuous first derivative.) With the potential energy defined as

\[ V(x) = \begin{cases} 
0 & \text{for } x < 0 \\
1 & \text{for } x \geq 0 
\end{cases} \]

show that the following wavefunction solves the Schrödinger equation as long as

\[ \hbar \omega = \frac{\hbar^2 k_1^2}{2m} = \frac{\hbar^2 k_2^2}{2m} + 1 \]  

Also, work out the relationships between the coefficients \( A, B, \) and \( C \) such that the wavefunction is continuous and has a continuous first derivative over all of space (with \( k_1 \neq k_2 \)).
The potential energy is given as,

\[ V(x) = \begin{cases} 
0 & \text{for } x < 0 \\
1 & \text{for } x \geq 0 
\end{cases} \]  

(2)

Wave function,

\[ \psi(x, t) = \begin{cases} 
Ae^{i(k_1x - \omega t)} + Be^{-i(k_1x + \omega t)} & \text{for } x < 0 \\
Ce^{i(k_2x - \omega t)} & \text{for } x \geq 0 
\end{cases} \]  

(4)

a).

When \( x < 0 \):

Time Dependent Schrodinger Equation,

\[ i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi \]

Substitute \( \psi(x, t) = Ae^{i(k_1x - \omega t)} + Be^{-i(k_1x + \omega t)} \) to T.D.S.E \((V(x) = 0)\),

\[ -i^2 \hbar \omega \psi = -\frac{\hbar^2}{2m} \cdot i^2 \cdot k_1^2 \psi \]

\[ \hbar \omega = \frac{\hbar^2}{2m} k_1^2 \]

Therefore, when \( x < 0 \), \( \psi(x, t) = Ae^{i(k_1x - \omega t)} + Be^{-i(k_1x + \omega t)} \) solves T.D.S.E.

Similarly,

When \( x \geq 0 \):

Substitute \( \psi(x, t) = Ce^{i(k_2x - \omega t)} \) to T.D.S.E \((V(x) = 1)\),

\[ \hbar \omega = \frac{\hbar^2}{2m} k_2^2 + 1 \]
Therefore, when \( x \geq 0 \), \( \psi(x,t) = Ce^{i(k_2x - \omega t)} \) solves T.D.S.E.

b)

Apply the boundary conditions,

1) \( \psi_{1(x=0)} = \psi_{2(x=0)} \)

Therefore

At \( x = 0 \),

\[
\left[ Ae^{i(k_1x - \omega t)} + Be^{-i(k_1x + \omega t)} \right]_{(x=0)} = \left[ Ce^{i(k_2x - \omega t)} \right]_{(x=0)}
\]

\[
Ae^{-i\omega t} + Be^{-i\omega t} = Ce^{-i\omega t}
\]

\[
A + B = C \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (1)
\]

2) \( \left[ \frac{d\psi_1}{dx} \right]_{(x=0)} = \left[ \frac{d\psi_2}{dx} \right]_{(x=0)} \)

Therefore

At \( x = 0 \),

\[
iki_1(Ae^{-i\omega t} - Be^{-i\omega t}) = iki_2Ce^{-i\omega t}
\]

\[
k_1(A - B) = k_2C \quad \ldots \ldots \ldots \ldots \ldots \quad (2)
\]

From (1) and (2),

\[
B = \frac{(k_1 - k_2)A}{(k_1 + k_2)} \quad (k_1 \neq k_2)
\]

\[
C = \frac{2k_1A}{(k_1 + k_2)} \quad (k_1 \neq k_2)
\]
**Problem 02 – Bohr model**

Classical physics predicts that there is no stable orbit for an electron moving around a proton. What criterion did Niels Bohr and/or Louis de Broglie use to define special orbits that he/they assumed were stable? (it may help to read a general chemistry book)

**Solution:**

To explain why an electron does not spiral into the nucleus (which is what classical physics predicts) Bohr postulated that the electron is allowed to occupy only certain orbits of specific energies. Technically he said that the angular momentum of the electron is restricted to be an integer multiple of a constant (specifically the constant $\hbar$). For circular motion at constant speed the angular momentum (classically) is $rmv$ ($r=\text{orbital radius}$, $m=\text{mass}$, $v=\text{speed}$); thus the condition reads $rmv = n\hbar$ for integer $n$.

deBroglie argued that the specific orbits occur because the electron behaves like a standing wave, and so its wavelength must fit the circumference of the orbit exactly. In other words, the circumference must be an integer multiple of the wavelength.
Problem 3
Consider a particle in a one-dimensional box of length L in its lowest energy (ground) stationary state. Calculate the probability that the particle is

a – 3 marks) in the left half of the box
solution:
For the lowest energy state, we have
\[ \psi(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \] (1)
The probability density of this state is thus
\[ \frac{2}{L} \sin^2 \frac{\pi x}{L} \] (2)
You need to integrate this expression. Normally this integral is found in textbooks as
\[ \int \sin^2 x \, dx = \frac{1}{2} x - \frac{1}{4} \sin 2x \] (3)
Changing variables from \( x \) to \( u = \frac{\pi x}{L} \), we have
\[ \int_a^b \frac{2}{L} \sin^2 \frac{\pi x}{L} \, dx = \frac{2}{\pi} \int_{\pi a/L}^{\pi b/L} \sin^2 u \, du \] (4)
For \( a = 0 \) and \( b = L/2 \) we get a probability of 1/2. This makes sense because of symmetry – see Fig ??.

b – 3 marks) in the middle third of the box.
solution:
put \( a = L/3 \) and \( b = 2L/3 \) to get
\[ \frac{1}{3} + \frac{\sqrt{3}}{2\pi} \approx 0.609 \] (5)
This makes sense, because we know from the shape of the wavefunction in Fig. ?? that the answer must be more than 1/3.

c – 3 marks) Draw a picture of the wavefunction and associated probability for each of parts a) and b) and justify that your answers make sense in terms of these pictures.

Problem 4
Consider a particle in a one-dimensional box of length L in its first excited stationary state. Calculate the probability that the particle is
Consider a particle in a one-dimensional box of length $L$ in its first excited stationary state. Calculate the probability that the particle is

a – 2 marks) in the left half of the box

solution:

This time we can change variables from $x$ to $u = \frac{2\pi x}{L}$, giving

$$
\int_a^b \frac{2}{L} \sin^2 \left( \frac{2\pi x}{L} \right) dx = \frac{1}{\pi} \int_{2\pi a/L}^{2\pi b/L} \sin^2 u \, du
$$

Putting $a = 0$ and $b = L/2$ we get a probability of $1/2$. This makes sense because of symmetry (see Fig 1).

b – 2 marks) in the middle third of the box.
solution:
Putting \( a = L/3 \) and \( b = 2L/3 \) gives

\[
\frac{1}{3} - \frac{\sqrt{3}}{4\pi} \approx 0.1955 \quad (7)
\]

This makes sense, because we know from the shape of the wavefunction in Fig. 1 that the answer must be less than 1/3 due to the node at \( x = L/2 \).

\( \text{c – 2 marks} \) Draw a picture of the wavefunction and associated probability for each of parts a) and b) and justify that your answers make sense

Problem 5
Do problem 3-6 from your textbook (page 97)

Solution:
Following the book, we have the hexatriene length as \( 3 \times 135 + 2 \times 154 + 2 \times 77 = 867 \text{ pm} \).

With 6 \( \pi \) electrons the HOMO to LUMO transition is \( n = 3 \) to \( n = 4 \). This corresponds to the first electronic transition of

\[
\frac{\Delta E}{hc} = \frac{(6.626 \times 10^{-34} \text{Js})^2(4^2 - 3^2)}{8(9.109 \times 10^{-31} \text{kg})(867 \times 10^{-12} \text{m})^2(6.626 \times 10^{-34} \text{Js})(3.00 \times 10^8 \text{m/s})} \quad (8)
\]

\[
= 2.8 \times 10^6 \text{ m}^{-1} = 2.8 \times 10^4 \text{ cm}^{-1} \quad (9)
\]