Name:

Chem 3322 test #1 solutions, out of 55 marks

I want complete, detailed answers to the questions. Show all your work to get full credit.

$$\text{indefinite integral}: \int \sin^2(ax)dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} \tag{1}$$

The classical wave equation in one dimension is

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{2}$$

The Schrödinger time dependent equation is, for $\psi(x,t)$

$$i\hbar\frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \tag{3}$$

The Schrödinger time independent equation is, for $\psi(x)$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{4}$$

The particle in a one dimensional box (of size L) energy levels are

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad \text{n} = 1, 2, 3, ... \tag{5}$$

energy levels of the particle on a ring of radius R:

$$E_n = \frac{n^2\hbar^2}{2mR^2} \qquad \text{n} = 0, 1, 2, ... \tag{6}$$

Speed of light = c = 3.0×10^8 m/s

electron mass = 9.11×10^{-31} kg. proton mass = 1.67×10^{-27} kg.

Avogadro's constant = $N_A = 6.022 \times 10^{23}$ mol^{-1}

Planck constants: h = 6.6262×10^{-34} Js and $\hbar = 1.05459 \times 10^{-34}$ Js

$\pi = 3.14159$

1 eV = 1.6022×10^{-19} J (electron volt to joule conversion)

mass conversion from amu to kg: 1.66×10^{-27} kg/amu

Relationship between the wavelength of a photon and its energy $\lambda = hc/E$

Problem 1 – **10 marks**

Recall that the normalized stationary state wavefunctions for the particle in a box model are given by

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{7}$$

and the energy levels are given by equation (5).

a) – 5 marks Sketch $\psi_n(x)$ for $n = 0$. Is this a valid wavefunction? Discuss.

Solution:

Since $\psi_0(x) = 0$ for all values of x, the probability density is zero everywhere, which is not valid since we are supposed to be modeling a particle.

b) – 5 marks Sketch $\psi_n(x)$ for $n = -1$. Is this a valid wavefunction? Discuss.

Solution:

Since $\psi_{-1}(x) = -\psi_1(x)$, this wavefunction is the negative of $\psi_1(x)$, and its probability density is identical to the $\psi_1(x)$ probability density. Therefore, $\psi_{-1}(x)$ is a different way, mathematically, to represent $\psi_1(x)$, and thus it corresponds to the ground state and is valid. This function also satisfies the boundary conditions, namely $\psi_{-1}(0) = 0 = \psi_{-1}(L)$.

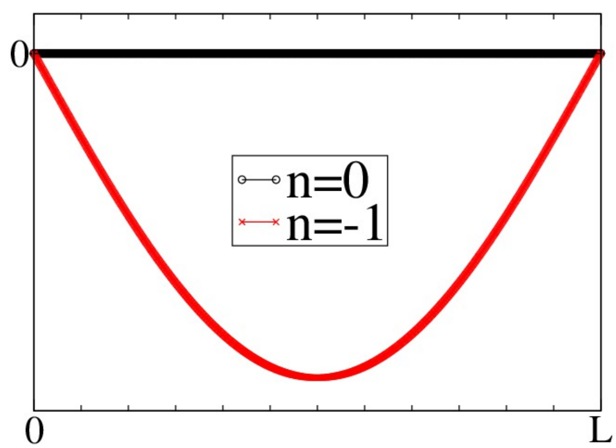

FIG. 1: $n = 0$ and $n = -1$ wavefunctions

<u>Problem 2</u> – 15 marks

The potential energy experienced by a quantum mechanical particle, and the total energy of the particle, are illustrated below. Sketch a valid wavefunction that is a solution to the TISE (Eq. 4 on page 1) across all of space, $x \in (-\infty, \infty)$. Be sure to carefully sketch what happens to the wavefunction when the potential energy abruptly changes. Also write down mathematical expressions to indicate what functions you have used in your sketch and how each region is different. Assume, as shown on the illustration, that $V_0 < E < V_1 < V_2$.

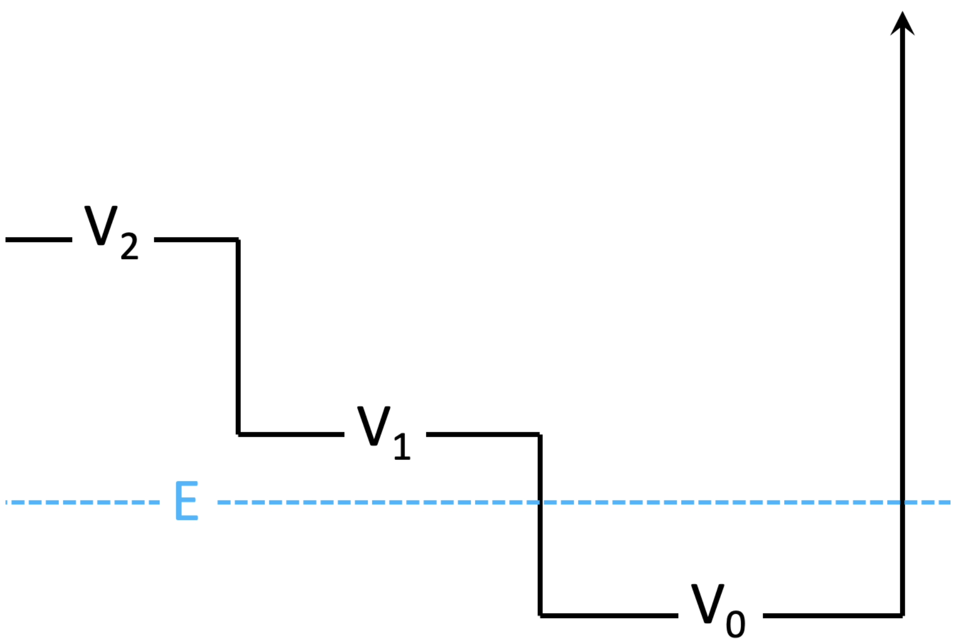

FIG. 2: Problem 2

Solution:

To the right of the V_0 region, $\psi(x) = 0$ since the potential is infinite. At the right hand edge of the V_0 region, we must have $\psi(x) = 0$ so that the wavefunction is continuous and matches the behavior to the right of the V_0 region. In the V_0 region the wavefunction has to be sin and/or cos. In the V_1 and V_2 regions the wavefunction has to be of exponential form. The constant in the exponential has to be larger in the V_2 region. And the wavefunction needs to be smooth at the places where the potential energy abruptly changes. A valid wavefunction is drawn below.

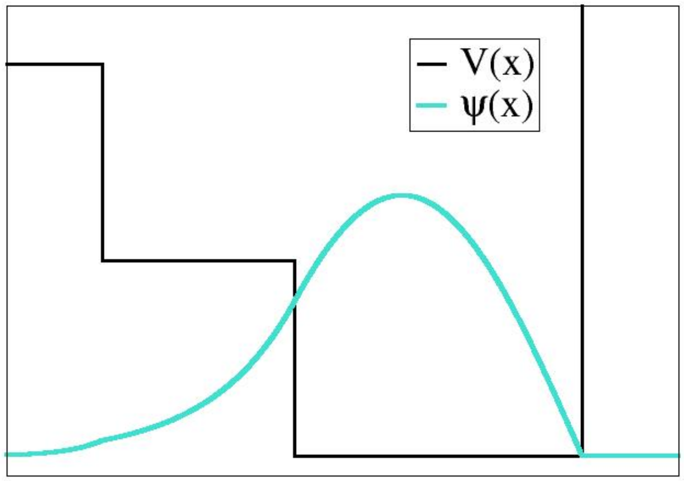

FIG. 3: Problem 2 solution

<u>Problem 3</u> – 10 marks

The one-dimensional particle in a box model can be applied to the π electrons in linear conjugated hydrocarbons. Consider butadiene, C_4H_6, which has 4 π electrons. The length of the conjugated backbone can be estimated as equal to two C=C bond lengths (2×135 pm) plus one C-C bond (154 pm) plus the distance of a carbon atom radius at each end (2×77 pm), giving a total distance of 578 pm. What is the longest wavelength of light that butadiene can absorb corresponding to an electronic excitation?

Solution: The HOMO to LUMO transition is $n = 2$ to $n = 3$. Looking at problems 3 and 4 of homework 4, we have

$$\lambda = \frac{8mL^2c}{h(3^2 - 2^2)} = 220 \text{ nm} \tag{8}$$

<u>Problem 4</u> – 5 marks

Explain the concept of tunneling in quantum mechanics. Include a sketch as part of your answer.

Solution:

When the particle energy is less than the barrier height, $E < V_0$, and the barrier is thin enough, the probability density does not decay to zero in the barrier region and therefore the particle can access both sides of the barrier. We can interpret this to mean that the particle can get from one side of the barrier to the other, through a region that is classically forbidden. In the sketch, the pink curves show the exponential decay that would occur if the other well was not present.

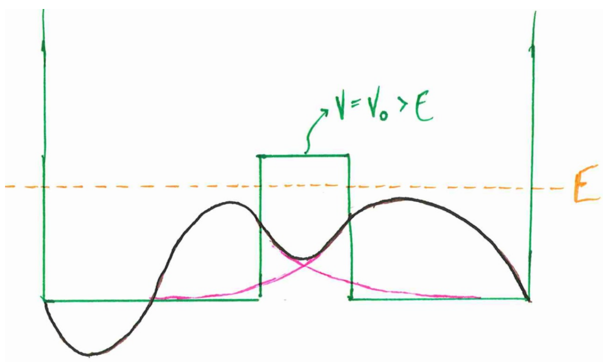

FIG. 4: tunneling

<u>Problem 5</u> – 15 marks

Recall that the wavefunction $\psi(x,t) = e^{i(kx-\omega t)}$ solves the classical wave equation (Eq. 2 on page 1), and also the Schrödinger time dependent equation (Eq. 3 on page 1) with $V(x) = 0$.

a) – 4 marks For each case (classical and quantum), work out the relationship between ω and k using the given wavefunction and the appropriate differential equation.

Solution:

First, note that

$$\frac{\partial \psi(x,t)}{\partial x} = \frac{\partial e^{i(kx-\omega t)}}{\partial x} = ik\psi(x,t) \tag{9}$$

and that

$$\frac{\partial \psi(x,t)}{\partial t} = \frac{\partial e^{i(kx-\omega t)}}{\partial t} = -i\omega\psi(x,t) \tag{10}$$

Putting $\psi(x,t)$ into equation (2) gives

$$(ik)^2\psi(x,t) = \frac{1}{v^2}(-i\omega)^2\psi(x,t) \tag{11}$$

This expression can be written as

$$k^2 = \frac{\omega^2}{v^2} \tag{12}$$

or

$$v = \omega/k \tag{13}$$

Putting $\psi(x,t)$ into equation (3) with $V(x) = 0$ gives

$$(i\hbar)(-i\omega)\psi(x,t) = -\frac{\hbar^2}{2m}(ik)^2\psi(x,t) \tag{14}$$

This expression can be written as

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \tag{15}$$

or

$$\omega = \frac{\hbar k^2}{2m} \tag{16}$$

b) – 1 mark Write this wavefunction $\psi(x,t)$ in separated form, namely as the product of a function of space and a function of time, $\psi(x,t) = f(x)g(t)$. Hint: recall that, in general, $e^{a+b} = e^a e^b$.

Solution:

We can use the fact that $e^{a+b} = e^a e^b$ to write

$$\psi(x,t) = e^{i(kx-\omega t)} = e^{ikx} e^{-i\omega t} \tag{17}$$

so that can identify $f(x) = e^{ikx}$ and $g(t) = e^{-i\omega t}$

c) – 5 marks Does $f(x)$ from part b solve the Schrödinger time independent equation (Eq. 4 on page 1) for the quantum mechanical particle in a box (which, of course, has $V(x) = 0$ in the box)?

Solution:

Using $f(x) = e^{ikx}$ in equation (4) with $V(x) = 0$ gives

$$-\frac{\hbar^2}{2m}(ik)^2 f(x) = E f(x) \tag{18}$$

so that this expression holds as long as

$$E = \frac{\hbar^2 k^2}{2m} \tag{19}$$

But equation (5) gives the particle in a box solutions as having

$$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \tag{20}$$

as the particle energy. Since n must be an integer, this implies that the expression $n = kL/\pi$ has to be an integer, which restricts the possible values of k. Namely, only particular values of k will correspond to a stationary state of the particle in a box. This is because the kinetic energy of the particle in a box is quantized.

d) – 3 marks For the quantum mechanical particle in a box, what are the boundary conditions and how did they arise (how did we get them)?

Solution:

The boundary conditions are $\psi(0) = \psi(L) = 0$. These arose from requiring that the wavefunction be continuous across all of space ($-\infty < x < \infty$), and by arguing that outside of the $0 < x < L$ range, $\psi(x) = 0$.

e) – 2 marks Does $f(x)$ from part b satisfy these boundary conditions?

Solution:

No. $f(0) = e^0 = 1$.