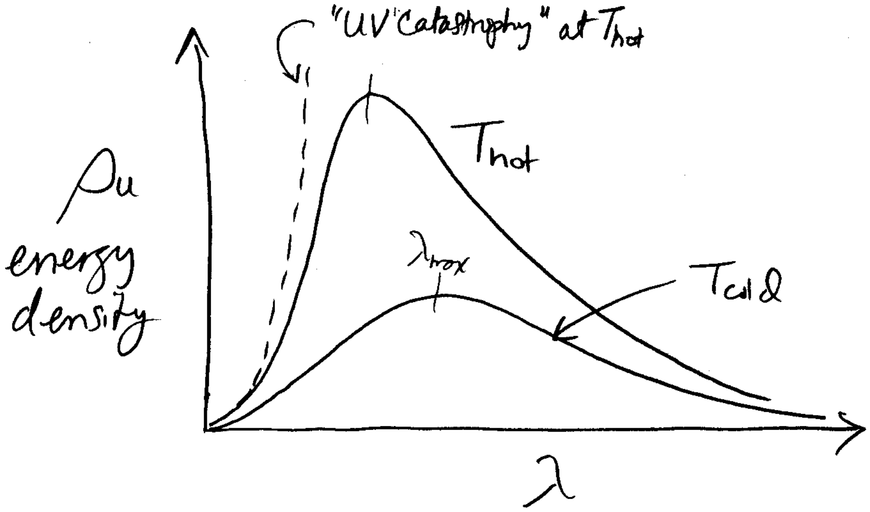
Name KEY

Student I.D.# ____________

1. (8 points) Consider the Black-Body Radiator. (a) Sketch the energy density per unit wavelength , versus λ, for a "hot" and "cold" body. (b) What is the "ultraviolet catastrophe" and how did Planch resolve this issue?

(a)



— as T increases λ_{max} decreases and the total energy radiated increases (as T^4).

(b) The classical theory of Rayleigh + Jeans assumed that cavity oscillators could store any amount of energy which led to the prediction that energy would be equally distributed among all modes (kT per mode). This equal distribution of energy, together with the fact that it is possible to fit many more standing waves of small λ into the cavity than large λ led to the prediction $\rho_u \propto \lambda^{-4} \Rightarrow$ i.e. $\rho_u \to \infty$ as $\lambda \to 0$, which was termed the "UV catastrophe".
Planck derived the proper $\rho_u(\lambda)$ by assuming that cavity modes could only take up energy in multiples of the quantum $h\nu = hc/\lambda$.

Name KEY

Student I.D.#

2. (6 points) Photoelectron experiments are conducted and it is found that light of 500 nm, which corresponds to (about) 2.5eV, is just sufficient to eject electrons from a pure metal surface. (a) What is the work function of the metal? (b) What would be observed if light with a wavelength of 800 nm is shined onto the same surface? (c) What do you expect to happen if light of wavelength 250 nm is shined on the metal surface?

(a) $W_0 = 2.5\text{eV}$ (or more accurately $W_0 = hc/\lambda_0$
$= 1.99 \times 10^{-25}\,\text{Jm}/5\times10^{-7}\,\text{m}$
$= 3.98\times10^{-19}\,\text{J} = 2.49\,\text{eV}$)

(b) for $\lambda = 800\,\text{nm}$ ($\lambda > \lambda_0$) no e would be ejected

(c) for $\lambda = 250\,\text{nm}$ ($\lambda < \lambda_0$) e will be ejected with excess (kinetic) energy in the amount $KE = \frac{hc}{\lambda} - W_0$

3. (6 points) Light of wavelength 2.82×10^{-6} m excited a certain harmonic oscillator from its ground to its first vibrational state. What is the wavelength of light that would accomplish this same excitation if the force constant of the oscillator were doubled? Explain your reasoning.

Harmonic oscillator energies are

$$\mathcal{E}_v = h\nu(v+\tfrac{1}{2}) \text{ with } \nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

and $v=0 \rightarrow v=1$ involves an energy difference

$$\Delta\mathcal{E} = h\nu$$

Light consisting of photons of this energy has a wavelength $\lambda = hc/\Delta\mathcal{E} = hc/\nu$

so $\lambda \propto \frac{1}{\nu} \propto \frac{1}{k^{1/2}}$. Wavelengths of the two oscillators are related by

$$\lambda_2/\lambda_1 = (k_1/k_2)^{1/2} \text{ so } \boxed{\lambda_2 = \left(\tfrac{1}{2}\right)^{1/2}\lambda_1 = 1.99\times10^{-6}\,\text{m}}$$

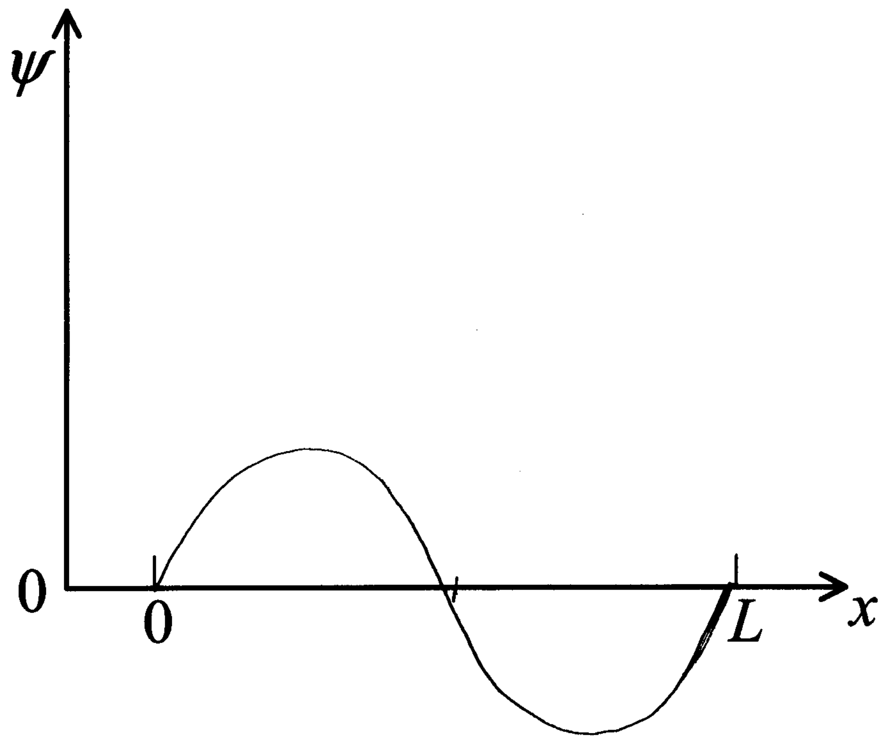
Name KEY

Student I.D.#

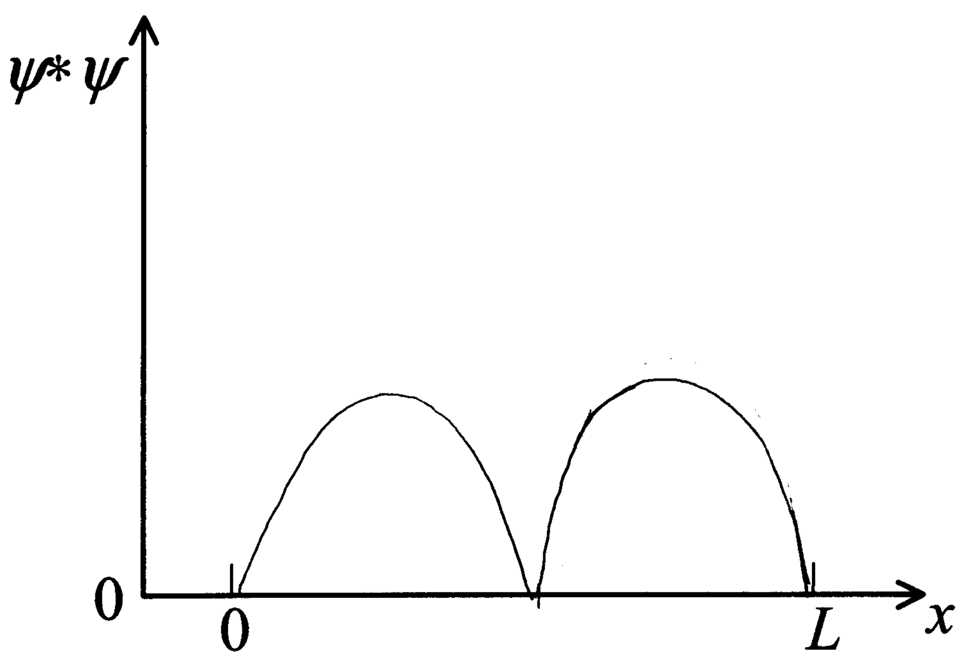
4. (27 points) Consider the 1st excited state (i.e. the 2nd lowest energy state) of a particle of mass m in a 1-dimensional box of length L. Coordinates are defined such that the box sides are at x=0 and x=L.

→ $n=2$ state

(a) (6 points) Sketch the wavefunction and the probability distribution of this state.



$(\sin\frac{2\pi x}{L})$



$(\sin^2\frac{2\pi x}{L})$

Name KEY

Student I.D.# ____________________

(b) (3 points) What is the expression for the normalized wavefunction?

$$\psi_2(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{2\pi x}{L}\right)$$

(c) (3 points) What is the expectation value (i.e. the average value) of the position $\langle x \rangle$?

$\langle x \rangle = L/2$ by symmetry

(d) (3 points) Is the most probable position equal to the expectation value? Explain.

No, the most probable positions occur at the maxima in $\psi^* \psi$ which are at $L/4$ and $3L/4$ here.

(e) (3 points) What integral is involved in calculating the mean-squared position $\langle x^2 \rangle$. Don't evaluate, just give the explicit expression required.

In general $\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x)\, x^2\, \psi(x)\, dx \Big/ \int_{-\infty}^{\infty} \psi^*(x)\psi(x)\, dx$

Here $\langle x^2 \rangle = \left(\frac{2}{L}\right) \int_0^L \sin^2\left(\frac{2\pi x}{L}\right) x^2\, dx$

(The denominator is unity for a normalized ψ.)

Name KEY

Student I.D.# ____________________

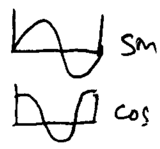
(f) (3 points) What integral is involved in determining the expectation value of the momentum <p>? Be explicit.

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx} \qquad \hat{p}\psi = \frac{\hbar}{i}\frac{2\pi}{L}\cos\left(\frac{2\pi}{L}x\right)$$

$$\langle p \rangle = \left(\frac{2}{L}\right)\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left(\frac{\hbar}{i}\frac{2\pi}{L}\right)\cos\left(\frac{2\pi x}{L}\right)dx$$

(g) (3 points) <p> = 0 for this state. How can one deduce this fact merely by examining the symmetry of the arguments of the integrand in part (g)?

The functions $\sin(2\pi x/L)$ and $\cos(2\pi x/L)$ are respectively antisymmetric and symmetric w.r.t. reflection about the center of the integral, $L/2$. Their product is antisymmetric and therefore the integral vanishes by symmetry.



(h) (3 points) Would the value p=0 ever be measured for a particle in this state? Explain.

No, the uncertainty principle requires that the momentum of a confined particle be non-zero.

(The values that could be observed for ψ_2 can be found by writing ψ_2 in terms of eigenfunctions of $\hat{p}$:

$$\psi_2 = \left(\frac{2}{L}\right)^{1/2}\left\{\frac{1}{2i}\left(e^{+2\pi i x/L} - e^{-2\pi i x/L}\right)\right\}$$

Possible values are the eigenvalues of $\hat{p}$ in this expansion

$$p = \pm\frac{2\pi\hbar}{L} = \pm h/\lambda\ )$$

Name KEY

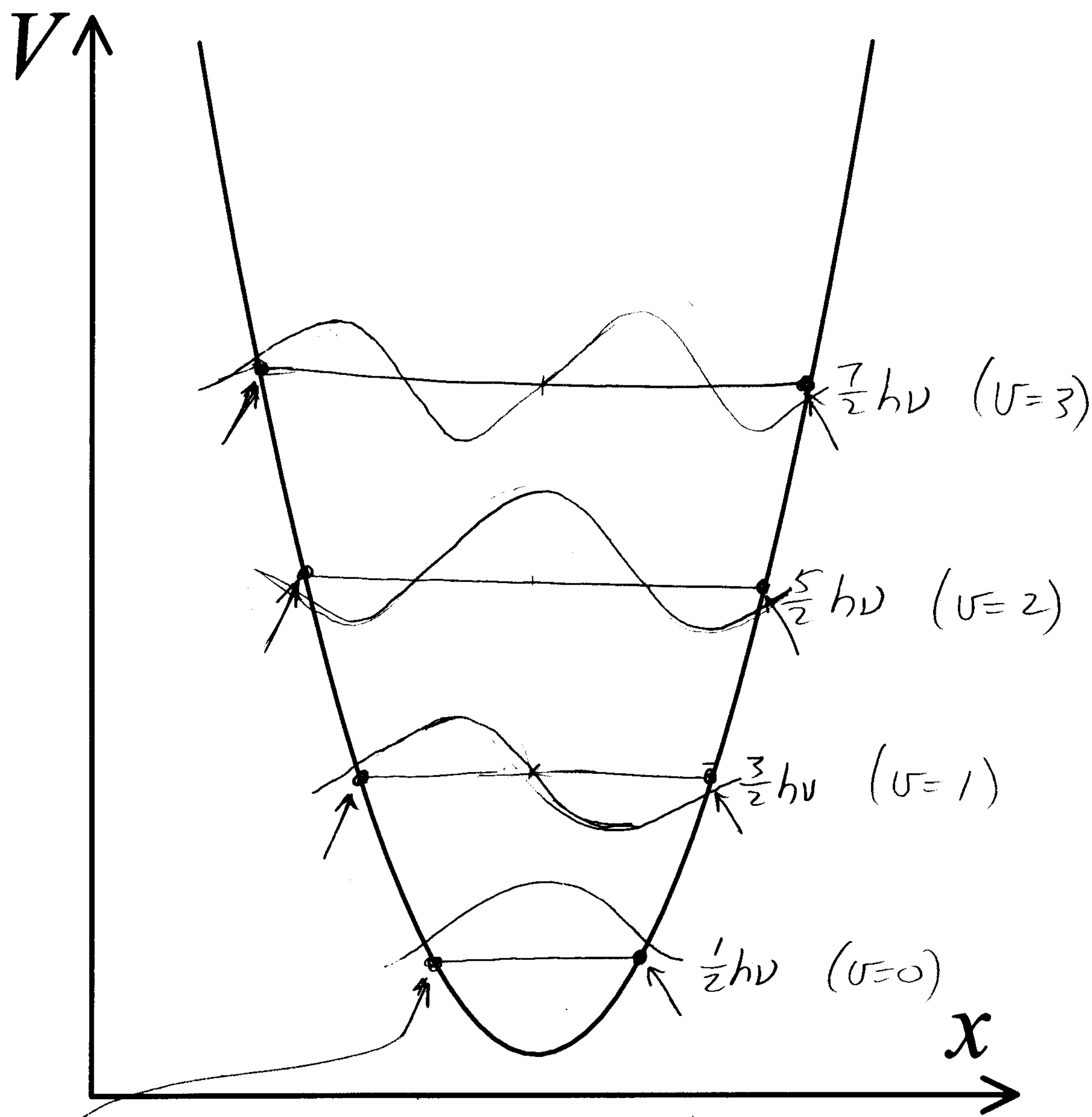
Student I.D.# ______

5. (21 points) Below is a plot of the potential $V(x)$ appropriate for a harmonic oscillator.

(a) (6 points) Draw horizontal lines on this plot to indicate the energies of the first four allowed quantum states and label them with their energies.

(b) (6 points) Plot $\psi(x)$ for all four states using the lines from part (a) to indicate ψ=0 for each state.

(c) (3 points) Indicate the classical turning points appropriate to each quantum energy.



arrows indicate classical turning points

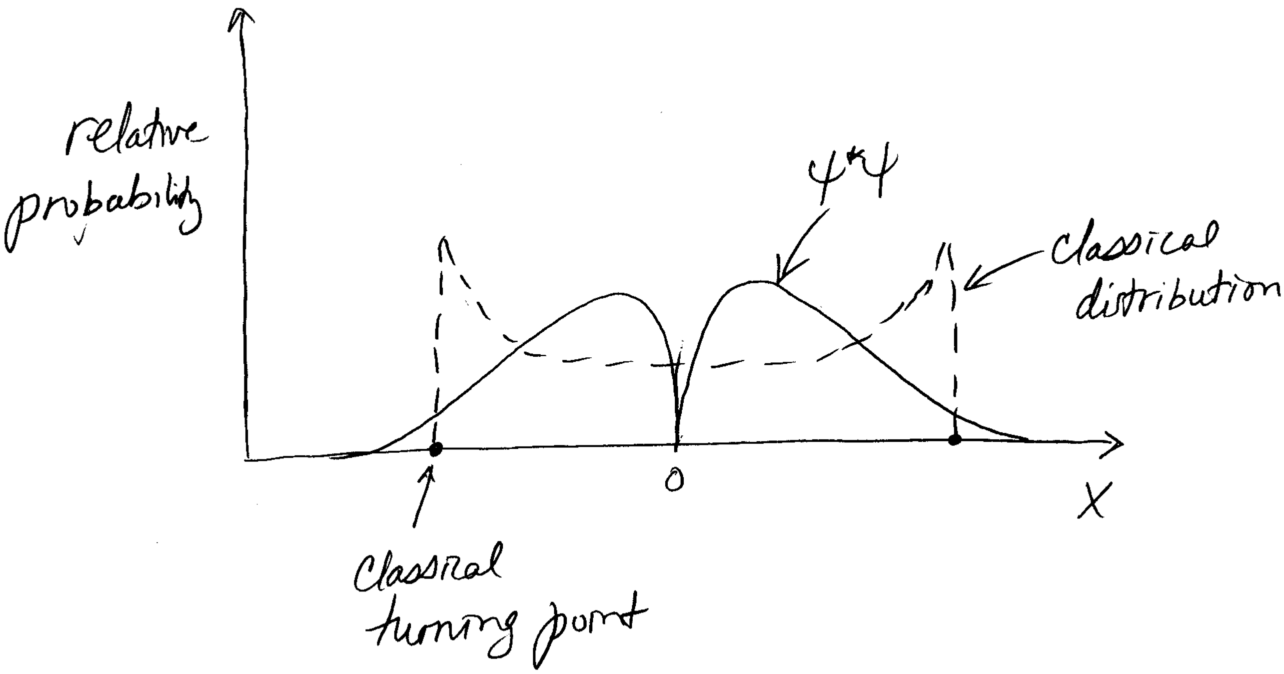
(note that ψ spills beyond these turning points but decays exponentially in the classically forbidden region).

Name KEY

Student I.D.# ______________________

(d) (6 points) On a separate graph with the classical turning points indicated, sketch the quantum mechanical probability density ($\psi^* \psi$) for the 1st excited state. On this same graph plot the probability distribution for a classical oscillator with the same energy. Clearly label your plots.

1st excited state is $v = 1$



Name KEY

Student I.D.#

6. (a) (3 points) Consider a particle on a sphere which has a quantum number $\ell = 7$. Determine the degeneracy of the energy level to which this state belongs. Explain.

The z component of angular momentum can take on values of $0, \pm 1, \pm 2, \ldots, \pm l$ which entails $2l+1$ distinct states. The degeneracy is thus $2l+1 = 15$ in the present case.

(b) (5 points) A particle moving on a sphere goes from $\ell = 5$ to $\ell = 6$. How much energy is absorbed? Express your answer in terms of the moment of inertia, I, and $\hbar$.

The energy of a state is given by $E_l = \frac{\hbar^2}{2I} l(l+1)$.

The energy difference involved here is then

$$\Delta E = \frac{\hbar^2}{2I}\left\{ l_2(l_2+1) - l_1(l_1+1)\right\}$$

$$= \frac{\hbar}{2I}\left\{ 6(7) - 5(6)\right\}$$

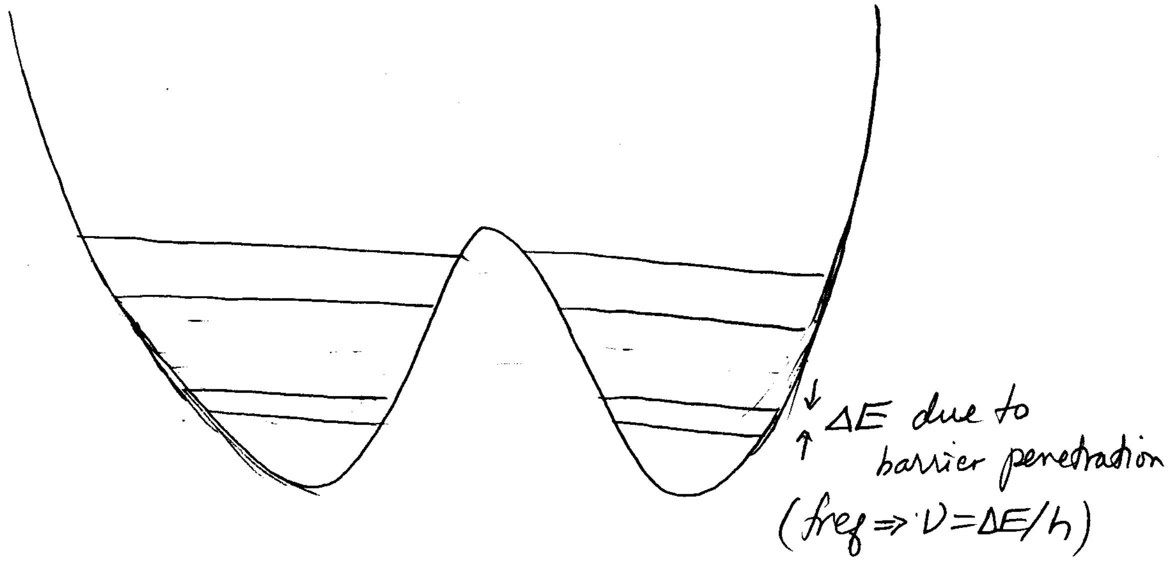
$$= \frac{6\hbar}{I}$$

Name KEY

Student I.D.# ____________

7. (9 points) (a) Sketch the potential energy curve for the ammonia molecule. Indicate the splitting of the vibrational levels that accounts for the inversion energies of NH_3 due to barrier penetration. (b) Discuss how you would expect the vibrational levels and splittings to differ to ND_3.

(a)



(b) All of the energy levels would decrease when H is replaced by D and the splittings would therefore also decrease.

Name KEY

Student I.D.# ______________________

$$\begin{array}{l} \underline{\quad} \; 6 \\ \uparrow\downarrow \; 5 \\ \uparrow\downarrow \; 4 \\ \uparrow\downarrow \; 3 \\ \uparrow\downarrow \; 2 \\ \uparrow\downarrow \; 1 \end{array}$$

8. (15 points) As shown by Kuhn (homework problem) a 1-D particle-in-a-box is a good model for mobile π electrons in linear dye molecules. Consider a system containing 10 π electrons in which each level in the box can hold no more than 2 electrons. The electronic transition responsible for the dye color corresponds to promotion of an electron from the highest filled to the lowest empty level, with the levels having initially been filled starting with the lowest.

(a) (9 points) Determine the wavelength of light absorbed by the dye assuming the length of the conjugated system to be 14Å = 1.4×10^{-9} m.

The transition is between PIB states $n=5 \rightarrow n=6$.

PIB energies are $E_n = \frac{h^2}{8mL^2} n^2$

$$\Delta E = \frac{h^2}{8mL^2} \Delta n^2 = \frac{(6.62 \times 10^{-34} J \cdot s)^2 \cdot 11}{8(9.11 \times 10^{-31} kg)(1.4 \times 10^{-9} m)^2}$$

$$= 3.37 \times 10^{-19} J$$

$$\lambda = \frac{hc}{\Delta E} = \frac{1.99 \times 10^{-25} J \cdot m}{3.37 \times 10^{-19} J} = 5.90 \times 10^{-7} m = 590 nm$$

(b) (3 points) Suppose that a second dye, having the same number of electrons but a length that is 10% shorter than the original, was prepared. Would this molecule absorb light that is redder or bluer than the original?

Increasing the "box" length decreases the PIB energies and energy spacings and would therefore cause an increase in λ or a red shift.

(c) (3 points) What is the ratio of wavelengths absorbed by the molecule of parts (a) and (b)?

$$\lambda_2 / \lambda_1 = \Delta E_1 / \Delta E_2 = (L_2/L_1)^2$$

$$= (1.1)^2 = 1.21$$