C455A –Quantum Chemistry and Spectroscopy
Exam 1
April 25, 2005
Exams will be collected at **9:30:00 am**
1 8.5x11" page of notes is allowed

-ALL ANSWERS MUST BE IN THE ANSWER BOXES
-CROSSED OUT/PARTIALLY ERASED WORK WILL BE IGNORED
-NO PARTIAL CREDIT ON NUMERICAL PROBLEMS WITHOUT A FORMULA
-NO PARTIAL CREDIT ON "PHYSICALLY IMPLAUSIBLE" ANSWERS UNLESS THE ERROR IS RECOGNIZED BY THE STUDENT

Your name: Key

Student ID#: ______________________

I have neither received not provided assistance of any kind on this exam.

Signature: ______________________

In the following, u and v are functions of x, and a and n and m are real numbers

$$\int u\,dv = uv - \int v\,du$$

$$\int x^n dx = \frac{x^{n+1}}{n+1} \text{ except } n=-1$$

$$\int \frac{dx}{x} = \ln x$$

$$\int e^{ax} dx = \frac{1}{a} e^{ax}$$

$$\int (\sin ax)\,dx = -\frac{1}{a} \cos ax$$

$$\int (\cos ax)\,dx = \frac{1}{a} \sin ax$$

$$\int (\sin^2 ax)\,dx = \frac{1}{2}x - \frac{1}{4a} \sin 2ax$$

$$\int (x \sin^2 ax)\,dx = \frac{x^2}{4} - \frac{\cos 2ax}{8a^2} - \frac{x \sin 2ax}{4a}$$

$$\int (\cos^2 ax)\,dx = \frac{1}{2}x + \frac{1}{4a} \sin 2ax$$

$$\int (x^2 \sin^2 ax)\,dx = \frac{1}{6}x^3 - \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right) \sin 2ax - \frac{1}{4a^2} x \cos 2ax$$

$$\int (x^2 \cos^2 ax)\,dx = \frac{1}{6}x^3 + \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right) \sin 2ax + \frac{1}{4a^2} x \cos 2ax$$

$$\int x^m e^{ax} dx = \frac{x^m e^{ax}}{a} - \frac{m}{a}\int x^{m-1} e^{ax} dx$$

$$\int \frac{e^{ax}}{x^m} dx = -\frac{1}{m-1}\frac{e^{ax}}{x^{m-1}} + \frac{a}{m-1}\int \frac{e^{ax}}{x^{m-1}} dx$$

$$\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cdot \sin\left(\frac{m\pi x}{a}\right) dx = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\cdot \cos\left(\frac{m\pi x}{a}\right) dx = \frac{a}{2}\delta_{nm}$$

$$\int_0^a \left[\sin\left(\frac{n\pi x}{a}\right)\right]\cdot\left[\cos\left(\frac{n\pi x}{a}\right)\right] dx = 0$$

$$\int_0^\pi \sin^2 mx\,dx = \int_0^\pi \cos^2 mx\,dx = \frac{\pi}{2}$$

$$\int_0^\infty \frac{\sin x}{\sqrt{x}} dx = \int_0^\infty \frac{\cos x}{\sqrt{x}} dx = \sqrt{\frac{\pi}{2}}$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \text{ (a > 0, n positive integer)}$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}} \text{ (a > 0, n positive integer)}$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \text{ (a > 0, n positive integer)}$$

$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}$$

$$\frac{d}{dx}\frac{u}{v} = \frac{1}{v}\frac{du}{dx} - \frac{u}{v^2}\frac{dv}{dx}$$

$$\frac{d}{dx}(u^n) = nu^{n-1}\frac{du}{dx}$$

$$\frac{d}{dx}\left(\frac{1}{u^n}\right) = -\frac{n}{u^{n+1}}\frac{du}{dx}$$

$$\frac{d}{dx}[f(u)] = \frac{d}{du}[f(u)]\cdot\frac{du}{dx}$$

$$\frac{d}{dx}(u^n v^m) = u^{n-1}v^{m-1}\left(nv\frac{du}{dx} + mu\frac{dv}{dx}\right)$$

$$\frac{d}{dx}(e^u) = e^u\frac{du}{dx}$$

$$\frac{d \sin x}{dx} = \cos x$$

$$\frac{d \cos x}{dx} = -\sin x$$

$$\frac{d \sin u}{dx} = \frac{du}{dx} \cos u$$

$$\frac{d \cos u}{dx} = -\frac{du}{dx} \sin u$$

$$\sin\alpha \sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$$

$$\cos\alpha \cos\beta = \frac{1}{2}\cos(\alpha-\beta) + \frac{1}{2}\cos(\alpha+\beta)$$

$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$

$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

Total Points: 100

Question 1: 15 /15

Question 2: 15 /15

Question 3: 35 /35

Question 4: 35 /35

Total: 100 / 100

Potentially Useful Information:

Workfunctions of Metals:

Li	2.3 eV
Ca	2.87 eV
Al	4.28 eV
Au	5.1 eV

Spin Operator / Eigenfunction Relations:

$$S_z\alpha = \frac{\hbar}{2}\alpha$$
$$S_z\beta = -\frac{\hbar}{2}\beta$$
$$S_y\alpha = i\frac{\hbar}{2}\beta$$
$$S_y\beta = -i\frac{\hbar}{2}\alpha$$
$$S_x\alpha = \frac{\hbar}{2}\beta$$
$$S_x\beta = \frac{\hbar}{2}\alpha$$
$$S^2\alpha = \frac{1}{2}(1+\frac{1}{2})\hbar^2\alpha$$
$$S^2\beta = \frac{1}{2}(1+\frac{1}{2})\hbar^2\beta$$

Values of Some Physical Constants

Constant	Symbol	Value
Atomic mass constant	amu	$1.660\ 5402 \times 10^{-27}$ kg
Avogadro constant	N_A	$6.022\ 1367 \times 10^{23}$ mol^{-1}
Bohr magneton	$\mu B = eh/2m_e$	$9.274\ 0154 \times 10^{-24}$ J · T^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0^2/r_e e^2$	$5.291\ 772\ 49 \times 10^{-11}$ m
Boltzmann constant	k_B	$1.380\ 658 \times 10^{-23}$ J · K^{-1}
		0.695 038 cm^{-1}
Electron rest mass	m_e	$9.109\ 3897 \times 10^{-31}$ kg
Gravitational constant	G	$6.672\ 59 \times 10^{-11}$ · m^3 · kg^{-1} · s^{-2}
Molar gas constant	R	8.3145101 J · K^{-1} · mol^{-1}
		0.083 1451 dm^3 · bar K^{-1} · mol^{-1}
		0.082 0578 dm^3 · atm K^{-1} · mol^{-1}
Molar volume, ideal gas		
(one bar, 0°C)		22.711 08L · mol^{-1}
(one atm, 0°C)		22.414 09 L · mol^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\ 7866 \times 10^{-27}$ J · T^{-1}
Permittivity of vacuum	ε_0	$8.854\ 187\ 816 \times 10^{-12}$ C^2 · J^{-1} · m^{-1}
	$4\pi\varepsilon_0$	$1.112\ 650\ 056 \times 10^{-10}$ C^2 · J^{-1} · m^{-1}
Planck constant	h	$6.626\ 0755 \times 10^{-34}$ J · s
	$\hbar$	$1.054\ 572\ 66 \times 10^{-34}$ J · s
Proton charge	e	$1.602\ 177\ 33 \times 10^{-19}$ C
Proton magnetogyric ratio	γ_p	$2.675\ 221\ 28 \times 10^{8}$ s^{-1} · T^{-1}
Proton rest mass	m_p	$1.672\ 6231 \times 10^{-27}$kg
Rydberg constant (Bohr)	$R_\infty = m_e e^4/8\varepsilon_0^2 h^2$	$2.179\ 8736 \times 10^{-23}$ J
		109 737.31534 cm^{-1}
Rydberg constant for H	R_H	109677.581 cm^{-1}
Speed of light in vacuum	c	299 792 458 m · s^{-1} (defined)
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k_B^4/15h^3c^2$	$5.670\ 51 \times 10^{-8}$ J · m^{-2} · K^{-4} · s^{-1}

Problem 1 (15 points)

1a). (5 pts) On a sunny day, solar radiation illuminates the ground with an intensity of approximately 900 W / m^2. If every photon that struck the field in Husky stadium (you may assume the field is 100 m long by 50 m wide) could be converted to electricity using a photovoltaic cell with 100% photon-to-electron conversion efficiency, *how much current would be generated*? (For simplicity, assume that all the photons from the sun are at the peak of ~500 nm).

$$900 \frac{\cancel{J}}{\cancel{m^2} s} \times (100\cancel{m} \times 50\cancel{m}) \times \frac{1 \text{ photon}}{3.98\times10^{-19}\cancel{J}} \times \frac{1e^-}{1 \text{ photon}} \times \frac{1.6\times10^{-19} C}{1 e^-} = 1.8\times10^{6} \frac{C}{s} = 1.8\times10^{6} A$$

$$E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34} J\cdot\cancel{s} \times 3\times10^{8} \cancel{m}/\cancel{s}}{500\times10^{-9} m} = 3.98\times10^{-19} J/\text{photon}$$

Answer 1A:

1.8×10^{6} Amps

1b) (5pts) A popular guest star on CSI and Law and Order, an electron microscope can acquire images with much higher resolution than a conventional optical microscope. The scanning electron microscope (SEM) in the Nanotech Center in Fluke Hall creates images with electrons that have been accelerated to energies of anywhere between
1 keV – 30 keV. *What is the range of electron wavelengths that are generated in the Fluke Hall SEM?* (on a side note: this microscope is a newer "field emission" model it creates its electron-beam by electric field-induced tunneling [but don't confuse it with a STM]!).

$$\lambda = \frac{h}{p} = \frac{6.626\times10^{-34} J\cdot s}{1.71\times10^{-23} kg\, m/s} = 3.88\times10^{-11} m$$

$$E = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mE} \qquad P_1 = \sqrt{2\times9.1\times10^{-31} kg (1000\times1.6\times10^{-19}) J} = 1.71\times10^{-23} kg\, m/s$$

using $1 eV = 1.6\times10^{-19} J$

$$P_{30} = \sqrt{2\times9.1\times10^{-31} kg (30{,}000\times1.6\times10^{-19})} = 9.34\times10^{-23} kg\, m/s$$

Answer 1B:

7.1×10^{-12} to 3.88×10^{-11} m

1c) (5pts) If a HeCd laser that emits 1 mW of 325 nm light is directed at a Ca surface, what is the maximum kinetic energy that will be measured for the ejected photoelectrons (in Joules)?

$$E_{phot} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34} J\cdot\cancel{s} \times 3\times10^{8} \cancel{m}/\cancel{s}}{325\times10^{-9} \cancel{m}} = 6.11\times10^{-19} J$$

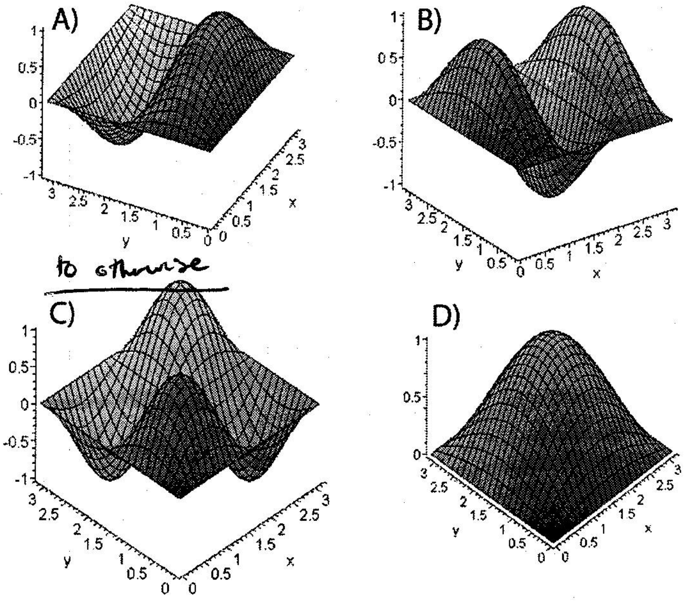
$$KE = E_{phot} - \phi = 6.11\times10^{-19} J - \left(2.87 eV\times1.6\times10^{-19}\frac{J}{eV}\right) = 1.52\times10^{-19} J$$

Answer 1C:

1.52×10^{-19} J

Problem 2) (15 Points)
On the right, the wave function $\psi(x,y)$ is plotted for a particle confined to a 2D square box in 4 different energy eigenstates (labeled A,B,C and D).

A) **(5)** Rank the states in order from *lowest to highest energy*. ***Explain your ranking with 1-2 sentences.***



2.5pts

$D < A < C < B$

+1 if C+B Switched

to otherwise

Sharper curvature - more nodes - implies higher energy. B+C have same # of nodal lines but since $E \propto n^2$ B must have higher E.

2.5pts

B) **(10)** If the particle placed in the box is an electron, and the units on the x and y graph axes are in Å, what is the energy **DIFFERENCE** between an electron in state "A" and an electron in state "C" (Express your answer in electron volts).

PC

box length = 3.1 Å per side ($L_x = L_y$)

+2 for 2D PIB formula

-1 for wrong units

for A $n_x = 1$, $n_y = 2$

for C $n_x = n_y = 2$

$$\Delta E = \frac{h^2}{8ml^2}\left[\left(n_{x_c}^2 + n_{y_c}^2\right) - \left(n_{x_A}^2 + n_{x_c}^2\right)\right]$$

$$= \frac{h^2}{8ml^2}\left[4+4-4-1\right] = \frac{3h^2}{8ml^2} = \frac{3\left(6.626\times10^{-34}\ J\cdot s\right)^2}{8\times9.1\times10^{-31}\ kg\times\left(3.1\times10^{-10}\ m\right)^2}$$

$$= 1.88\times10^{-18}\ J \times \frac{1\ eV}{1.6\times10^{-19}\ J}$$

$$= 11.8\ eV$$

12eV w/ sig figs

Problem 3) Hint the spin operators and eigenfunctions are on the exam cover. (35 points, 5/part)

A series of hydrogen atoms is prepared with identical spin functions (3 α + 2*i* β)

3a) If the spin function (3 α + 2*i* β) is normalized show that it is normalized. If not, normalize it. (5 points)

$|3|^2 + |2i|^2 = 13$ $\boxed{\text{not normalized}}$ +2.5

PC

+1 for $\int \psi^* \psi = 1$

$c^2 13 = 1$ $c = \frac{1}{\sqrt{13}}$ +2.5

$\frac{1}{\sqrt{13}}(3\alpha + 2i\beta)$ is normalized fxn

3b) Explicitly check if this function is an eigenfunction of the spin operator S_z If it is an eigenfunction, what is the eigenvalue?

$S_z \frac{(3\alpha + 2i\beta)}{\sqrt{13}} = \frac{1}{\sqrt{13}}\left(3\frac{\hbar}{2}\alpha + -\frac{\hbar}{2}2i\beta\right) \neq \text{Konstant}\left(\frac{3\alpha + 2i\beta}{\sqrt{13}}\right)$ +2.5

Not an eigenfunction +2.5

Note Students w/ typo on exam cover could get full credit for soln by properly -sing functions given

3c) Explicitly check if this function is an eigenfunction of the spin operator S^2? If it is an eigenfunction, what is the eigenvalue?

$S^2 \frac{(3\alpha + 2i\beta)}{\sqrt{13}} = \frac{1}{\sqrt{13}}\left(3\tfrac{1}{2}(1+\tfrac{1}{2})\hbar^2\alpha + 2i\tfrac{1}{2}(1+\tfrac{1}{2})\hbar^2\beta\right) = \tfrac{1}{2}(1+\tfrac{1}{2})\hbar^2\frac{(3\alpha + 2i\beta)}{\sqrt{13}}$ +2.5

$\boxed{\text{Yes}}$ $\boxed{\tfrac{1}{2}(1+\tfrac{1}{2})\hbar^2 \text{ is eigenvalue}}$

+2.5

3d) If a beam of atoms in this state (3 α + 2*i* β) were passed through an inhomogeneous magnetic field oriented along the z-axis (as in the Stern-Gerlach experiment), what would you expect to happen in the idealized case? (*be as quantitative as possible-i.e. what is the probability that a given atom will be measured as spin up or spin down?*). (5 points)

Beam is split into spin up + spin down components w/ prob:

$\left|\frac{3}{\sqrt{13}}\right|^2$ will be α (spin up) $= \frac{9}{13}$ ↑

$\left|\frac{2i}{\sqrt{13}}\right|^2$ will be β (spin down) $= \frac{4}{13}$ ↓

3e) What are the spin functions for each of the beams emerging from the magnet in 3d)? If these beams were each individually subjected to another pass through a magnet with a magnetic field identical to that from 3d) (inhomogeneous magnetic field along **z**-axis) what would happen? (*be as quantitative as possible for credit-i.e. what percentage of atoms emerge in each beam?*) (5 points)

α for spin up

β for spin down

α beam gives $|1|^2 = 100\%$ α spin up

β beam gives $|1|^2 = 100\%$ β spin down

neither beam is further split upon repeat measurement

3f) Pass the beams emerging from 3e through another experimental Stern-Gerlach setup, this time with the magnetic field at a right angle (oriented along x) to the first field. What happens? (*be as quantitative as possible for credit-i.e. what percentage of atoms emerge in each beam?*) (5 points)

$\alpha + \beta$ not eigenfunctions of S_x → x-field

splits α beam into "spin left" + "spin right" w/ 50% chance for each particle, same for β beam

3g) The measurement in 3f is equivalent to operating on the spin function with S_x. What are the normalized spin eigenfunctions for the hydrogen atoms emerging from the beam passing through the x-oriented field in 3f) (i.e. after measuring with S_x)?

Spin right $= \chi^+ = \dfrac{\alpha + \beta}{\sqrt{2}}$ ie. $S_x \chi^+ = \dfrac{S_x\alpha + S_x\beta}{\sqrt{2}} = \dfrac{\hbar}{2}\chi^+$

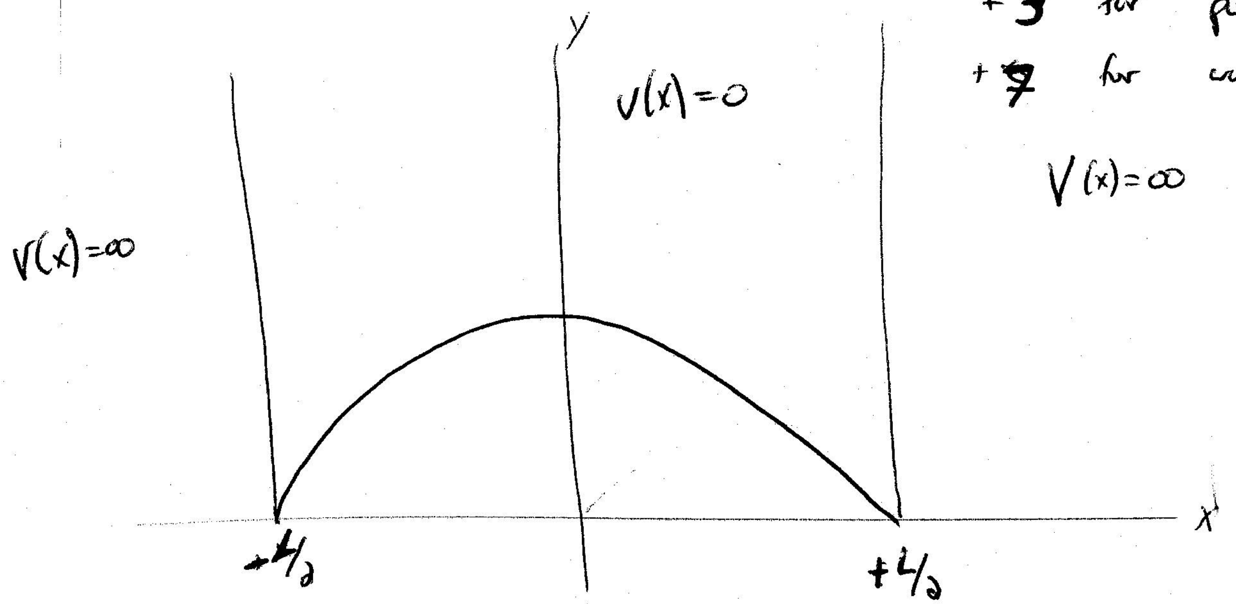
spin left $= \chi^- = \dfrac{\alpha - \beta}{\sqrt{2}}$ $S_x \chi^- = \dfrac{S_x\alpha - S_x\beta}{\sqrt{2}} = -\dfrac{\hbar}{2}\chi^-$

Problem 4) (35 points)
A particle is placed in the potential V(x) defined piecewise as: $V(x)=\infty$ for $x<-L/2$, $V(x)=0$ for $-L/2\le x\le L/2$ and $V(x)=0$ for $x > L/2$

4A) Graph this potential below. Notice that this potential is not exactly the same as the particle in an infinite box potential that we solved in lecture (it is shifted over so the wavefunctions we found will no longer satisfy the boundary conditions!). ***Include a sketch of the ground state wavefunction on your graph.*** (10 points)

+3 for potential (-1 not labelled)

+7 for wave fxn (points off if not centered + not zero at boundary)



4B) Guess a normalized wave function for the lowest energy eigenstate of this potential, *then verify that this wave function satisfies all requirements imposed on acceptable wave functions by their physical interpretation.* (10 points)

wave fxn

+3: $\psi_1(x) = \sqrt{\frac{2}{L}}\cos\left(\frac{\pi x}{L}\right)$ in box

$\psi_n(x) = 0$ elsewhere

$\psi_1\left(-\frac{L}{2}\right) = \psi_1\left(\frac{L}{2}\right) = \sqrt{\frac{2}{L}}\cos\left(\frac{\pi}{2}\right) = 0$

+3 so is continuous at boundary + single valued

$$\frac{2}{L}\int_{-L/2}^{L/2}\cos^2\left(\frac{\pi x}{L}\right)dx = \text{from table } \frac{2}{L}\left(\frac{1}{2}x + \frac{L}{4\pi}\sin\left(\frac{2\pi x}{L}\right)\right)\Bigg|_{-L/2}^{L/2} = \frac{2}{L}\left(\frac{L}{4} - \frac{-L}{4}\right) = 1$$ ✓

wave function is normalized +3

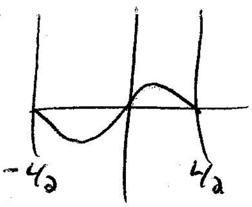
potential goes to ∞ so $\psi'(x)$ doesn't have to be continuous +1

4C/D CONTINUE ON NEXT PAGE

4C) What will the wave function for the first excited energy eigenstate of this potential be? Explain. (5 points) 5

$\cos\left(\frac{2\pi x}{L}\right)$ doesn't satisfy boundary condition! — but +1 pt for guess

So to add a node we chose (keeping same shape) $\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$ +5



✓

10 4D) Use your wave function from 4B to compute the probability of finding this particle in the region between x=L/4 and x=L/2 for the ground state (10 points)

$\psi(x) = \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right)$

$$P = \int_{L/4}^{L/2} \left(\sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right)\right)^2 dx$$ +5

+4 w/ wrong ψ if it's ψ from 2B

$$= \frac{2}{L}\int_{L/4}^{L/2} \cos^2 \frac{\pi x}{L} = \frac{2}{L}\left(\frac{1}{2}x + \frac{L}{4\pi}\sin\frac{2\pi x}{L}\right)\Bigg|_{L/4}^{L/2} \text{ (via table)}$$

$$= \frac{2}{L}\left(\frac{L}{4} + 0\right) - \frac{2}{L}\left(\frac{L}{8} + \frac{L}{4\pi}\sin\left(\frac{2\pi}{4}\right)\right)$$

$$= \frac{1}{2} - \left(\frac{1}{4} + \frac{1}{2\pi}\right) = .094$$

$$\boxed{\frac{1}{4} - \frac{1}{2\pi} = .091} \quad (.09085)$$

or +5