C455A –Quantum Chemistry and Spectroscopy
Exam 1
April 26, 2004
Exams will be collected at 9:30:00 am SHARP
1 8.5x11" page of notes is allowed

-ALL ANSWERS MUST BE IN THE ANSWER BOX
-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

Your name:____

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

$$\int u\,dv = uv - \int v\,du$$
$$\int x^n dx = \frac{x^{n+1}}{n+1} \text{ except } n=-1$$
$$\int \frac{dx}{x} = \ln x$$
$$\int e^{ax} dx = \frac{1}{a} e^{ax}$$
$$\int (\sin ax)\,dx = -\frac{1}{a}\cos ax$$
$$\int (\cos ax)\,dx = \frac{1}{a}\sin ax$$
$$\int (\sin^2 ax)\,dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax$$
$$\int (x \sin^2 ax)\,dx = \frac{x^2}{4} - \frac{\cos 2ax}{8a^2} - \frac{x \sin 2ax}{4a}$$
$$\int (\cos^2 ax)\,dx = \frac{1}{2}x + \frac{1}{4a}\sin 2ax$$
$$\int (x^2 \sin^2 ax)\,dx = \frac{1}{6}x^3 - \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax - \frac{1}{4a^2}x\cos 2ax$$
$$\int (x^2 \cos^2 ax)\,dx = \frac{1}{6}x^3 + \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax + \frac{1}{4a^2}x\cos 2ax$$
$$\int x^m e^{ax} dx = \frac{x^m e^{ax}}{a} - \frac{m}{a}\int x^{m-1} e^{ax} dx$$
$$\int \frac{e^{ax}}{x^m} dx = -\frac{1}{m-1}\frac{e^{ax}}{x^{m-1}} + \frac{a}{m-1}\int \frac{e^{ax}}{x^{m-1}} dx$$
$$\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cdot\sin\left(\frac{m\pi x}{a}\right)dx = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\cdot\cos\left(\frac{m\pi x}{a}\right)dx = \frac{a}{2}\delta_{mn}$$
$$\int_0^a \left[\sin\left(\frac{n\pi x}{a}\right)\right]\cdot\left[\cos\left(\frac{n\pi x}{a}\right)\right]dx = 0$$
$$\int_0^\pi \sin^2 mx\,dx = \int_0^\pi \cos^2 mx\,dx = \frac{\pi}{2}$$
$$\int_0^\infty \frac{\sin x}{\sqrt{x}}dx = \int_0^\infty \frac{\cos x}{\sqrt{x}}dx = \sqrt{\frac{\pi}{2}}$$
$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad (a > 0, \text{ n positive integer})$$
$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}} \quad (a > 0, \text{ n positive integer})$$
$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2\,a^{n+1}} \quad (a > 0, \text{ n positive integer})$$
$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}$$
$$\frac{d}{dx}\frac{u}{v} = \frac{1}{v}\frac{du}{dx} - \frac{u}{v^2}\frac{dv}{dx}$$
$$\frac{d}{dx}(u^n) = nu^{n-1}\frac{du}{dx}$$
$$\frac{d}{dx}\left(\frac{1}{u^n}\right) = -\frac{n}{u^{n-1}}\frac{du}{dx}$$
$$\frac{d}{dx}[f(u)] = \frac{d}{du}[f(u)]\cdot\frac{du}{dx}$$
$$\frac{d}{dx}(u^n v^m) = u^{n-1}v^{n-1}\left(nv\frac{du}{dx} + mu\frac{dv}{dx}\right)$$
$$\frac{d}{dx}(e^u) = e^u\frac{du}{dx}$$
$$\frac{d\sin x}{dx} = \cos x$$
$$\frac{d\cos x}{dx} = -\sin x$$
$$\frac{d\sin u}{dx} = \frac{du}{dx}\cos u$$
$$\frac{d\cos u}{dx} = -\frac{du}{dx}\sin u$$
$$\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$$
$$\cos\alpha\cos\beta = \frac{1}{2}\cos(\alpha-\beta) + \frac{1}{2}\cos(\alpha+\beta)$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

Total Points: 100

Question 1:_________/16

Question 2:_________/35

Question 3:_________/13

Question 4:_________/36

Total: _____________/

Potentially Useful Information:

Workfunctions of Metals:

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

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	$\mu B = eh/2m_e$	$9.274\,0154 \times 10^{-24}$ $J \cdot T^{-1}$
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	$1.380\,658 \times 10^{-23}$ $J \cdot K^{-1}$
		$0.695\,038$ cm^{-1}
Electron rest mass	m_e	$9.109\,3897 \times 10^{-31}$ kg
Gravitational constant	G	$6.672\,59 \times 10^{-11} \cdot m^3 \cdot kg^{-1} \cdot s^{-2}$
Molar gas constant	R	8.3145101 $J \cdot K^{-1} \cdot mol^{-1}$
		$0.083\,1451$ $dm^3 \cdot bar\,K^{-1} \cdot mol^{-1}$
		$0.082\,0578$ $dm^3 \cdot atm\,K^{-1} \cdot mol^{-1}$
Molar volume, ideal gas		
(one bar, 0^0C)		$22.711\,08 L \cdot mol^{-1}$
(one atm, 0^0C)		$22.414\,09$ $L \cdot mol^{-1}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,7866 \times 10^{-27}$ $J \cdot T^{-1}$
Permittivity of vacuum	ε_0	$8.854\,187\,816 \times 10^{-12}$ $C^2 \cdot J^{-1} \cdot m^{-1}$
	$4\pi\varepsilon_0$	$1.112\,650\,056 \times 10^{-10}$ $C^2 \cdot J^{-1} \cdot m^{-1}$
Planck constant	h	$6.626\,0755 \times 10^{-34}$ $J \cdot s$
	$\hbar$	$1.054\,572\,66 \times 10^{-34}$ $J \cdot s$
Proton charge	e	$1.602\,177\,33 \times 10^{-19}$ C
Proton magnetogyric ratio	γ_p	$2.675\,221\,28 \times 10^8$ $s^{-1} \cdot T^{-1}$
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	$299\,792\,458$ $m \cdot s^{-1}$ (defined)
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k_B^4/15h^3c^2$	$5.670\,51 \times 10^{-8}$ $J \cdot m^{-2} \cdot K^{-4} \cdot s^{-1}$

(16 Points)

Problem 1 The Quantum Mechanics of TV Watching and Beer Drinking

Homer Simpson sits in front of the TV drinking a Duff beer.

1a) In the TV electrons are accelerated from rest through a potential of ~30,000 V before striking the screen. What is the wavelength of an electron in Homer's TV?

1a: wavelength=

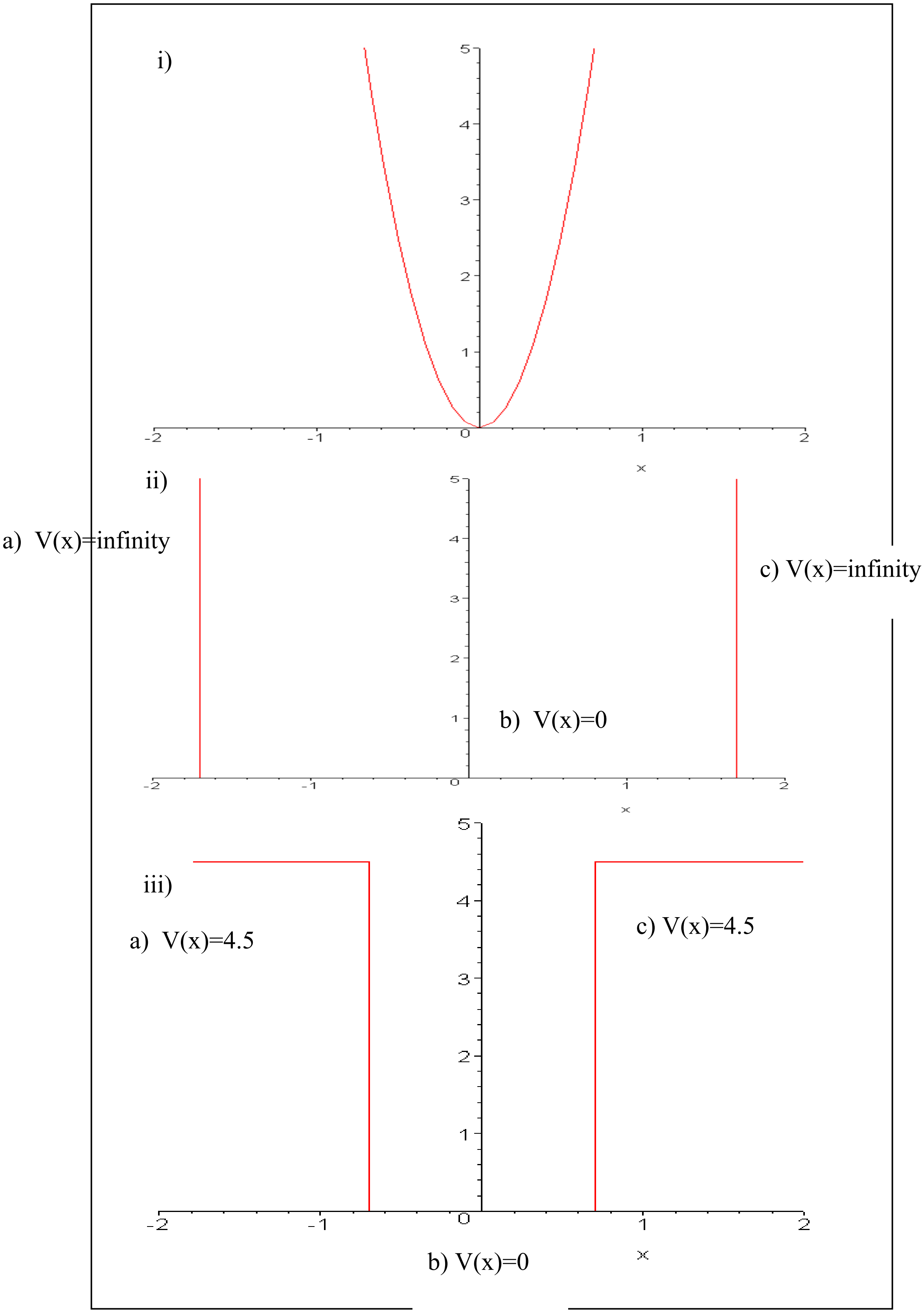
1b) Once the ethanol in the beer makes its way to Homer's liver, the alcohol dehydrogenase enzyme begins the reversible oxidation of the alcohol to an aldehyde. The rate-limiting step in this oxidation is the transfer of a hydride from the alcohol to the cofactor nicotinamide adenine dinucleotide (NAD). Although Homer doesn't understand what she's talking about, Lisa hypothesizes that hydride tunneling plays an important role in the rate of this reaction. Propose an experiment to test Lisa's hypothesis, and explain the results of this experiment in the event that (as is widely believed) hydride tunneling is indeed an important component of this reaction. You should use **equations,** but not necessarily calculations, to justify your explanation of the experiment and its results.

(2 points) 1c) Rank the following types of electromagnetic radiation in order from lowest to highest energy per photon:

visible
infrared
ultraviolet
microwave
x-ray

Problem 2 (35 Points)

2) An electron is placed into each of the following 1-D potential wells (i.e. the y-value represents the potential as a function of position along the x-axis):



2-continued

2) An electron is placed into each of the 1-D potential wells on the previous page, the axes labels are in arbitrary units, but are the same scale for each graph. You should assume all lines continue to infinity in their present functional shapes. If any question is not possible to determine with the information provided *then explain why not*.

2a) In which potential will the electron have the **smallest** zero point (ground state) energy? Explain/interpret your answer.

2a: potential #

2b) In which potential is the probability of finding the electron at x=0 going to be the **largest**? Explain. How would you calculate the probability of finding the particle between x=-infinity and x=0 in this potential? (write down an expression for this probability as an integral, calling the wave function ψ). Evaluate this integral (it shouldn't require a lot of math) to find the probability.

2b: potential #

2b: probability=

2c) For which potential could we find solutions to the time-independent Schrödinger equation that correspond to an electron with a well defined momentum? Explain, including an equation showing what the wave-function of a particle with a well defined momentum (value of $+d$) would be.

2d) Show, by explicit application of the x-momentum operator, p_x, that the wavefunction you wrote down in equation 1c is an eigenfunction of the operator p_x. What is the eigenvalue?

2e) If the units on the x-axis of the graphs are in nanometers, what energy (in eV) of photon would be needed to excite an electron from the ground to the first excited state in potential *ii* ?

2e:

Problem 3 (14 points)

(For the problems below, assume that all photoelectrons that could possibly be emitted are emitted, and that 100% of these emitted electrons are measured as a current).

3a) What is the photocurrent (in Amps) that would be expected if 1 μW of power from the 458 nm line of an Ar^+ laser was directed at a photocathode made of Lithium?

3a:

3b) What is the photocurrent (in Amps) that would be expected if 1 mW of power from the 325 nm line of an HeCd laser was directed at a photocathode made of Gold?

3b:

Problem 4 (36 points)

4) A particle is placed in a potential of the form:

$$V(x) = \tfrac{1}{2}bx^2$$

in a state where the wave function of the particle, ϕ, is given by the equation:

$$\phi = \psi_1 + i(\psi_3) + 2\psi_5 + (1-3i)(\psi_7)$$

(Here ψ_n represents the n$^{\text{th}}$ normalized energy eigenfunction of a Harmonic Oscillator with spring constant *b,* and energy E_n as given by the formula for a harmonic oscillator)

$\phi = \psi_1 + i(\psi_3) + 2\psi_5 + (1-3i)(\psi_7)$ (repeated here for your convenience)

4a) Is this wavefunction normalized? If not, normalize it. If it is normalized, then explicitly demonstrate this fact. If you decide the wave function isn't normalized, write the final normalized wavefunction as $A\phi$, where A is the normalization constant.

4a-i: YES (normalized)
NO (not normalized)

4a-ii:

4b) If many harmonic oscillators were prepared in states identical to ϕ and their energies were measured, what would the result of the energy measurements look like? Calculate **both** the average (expectation) value of the measured energies, and draw a labeled histogram showing the specific statistical distribution of the results (or, if this is impossible to determine, explain why).

$\phi = \psi_1 + i(\psi_3) + 2\psi_5 + (1-3i)(\psi_7)$ (repeated here for your convenience)

4c) A ***single*** quantum harmonic oscillator is placed in the state ϕ described above. The energy value of this system is measured and found to equal $\frac{1}{2}\hbar\omega$ (with $\omega = \sqrt{\frac{b}{\mu}}$, μ = reduced mass of the system). What is the probability that a ***second*** measurement of the energy on this ***same*** oscillator yields E=$\frac{1}{2}\hbar\omega$? Write down the wavefunction that describes the system ***after*** the second measurement. Explain.

4c-i: probability

4c-ii: wavefunction

4d) Find <x> (the average [expectation] value of the position) for a particle in the state ϕ. *You must set up and go through the required integral rather than just stating an answer*. (Hint: I would find it odd if you did not recognize the answer before completing the calculation.)