MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2013

Professors Robert W. Field and Troy Van Voorhis

FIFTY MINUTE EXAMINATION I

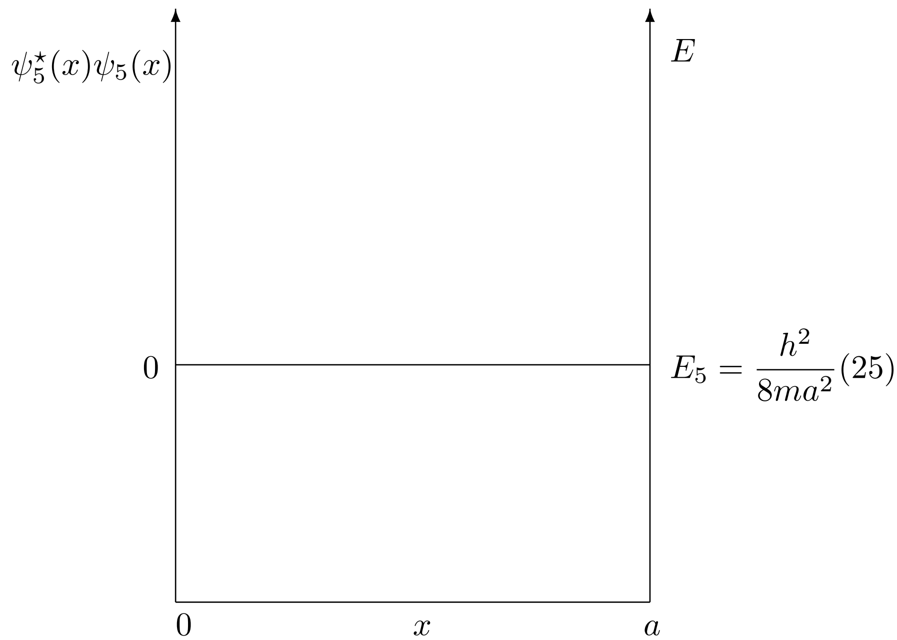
Write your name on this cover page. You may use a calculator and one 8.5 × 11" page (two-sided) of self-prepared notes. This exam consists of a cover page, 4 questions, each followed by a blank page for calculations, and one page of possibly helpful information: a total of 16 pages. Please count them now!

Question	Possible Score	My Score
I	26	
II	24	
III	20	
IV	30	
Total	100	

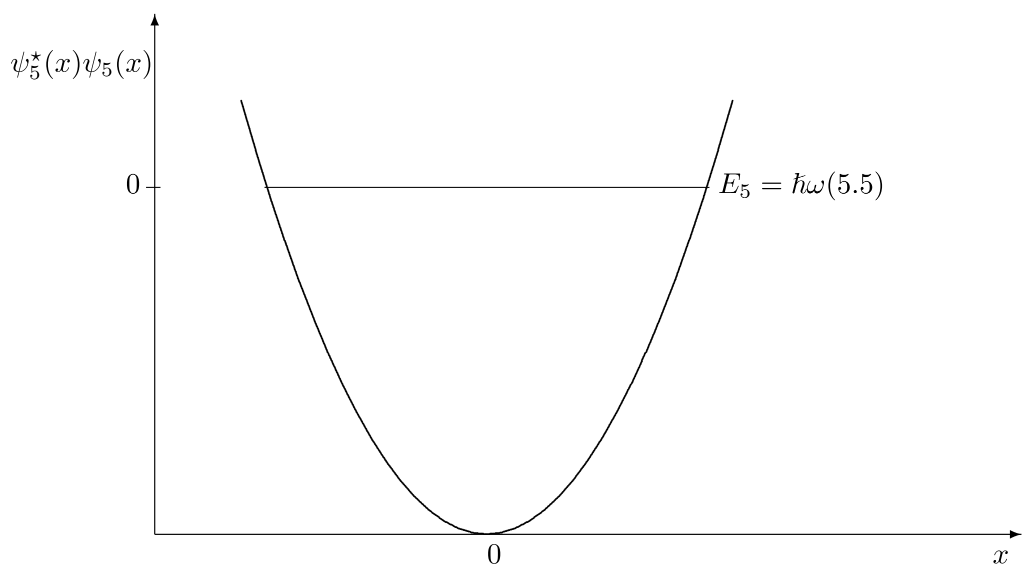
Name:____

I. Short Answer (26 points)

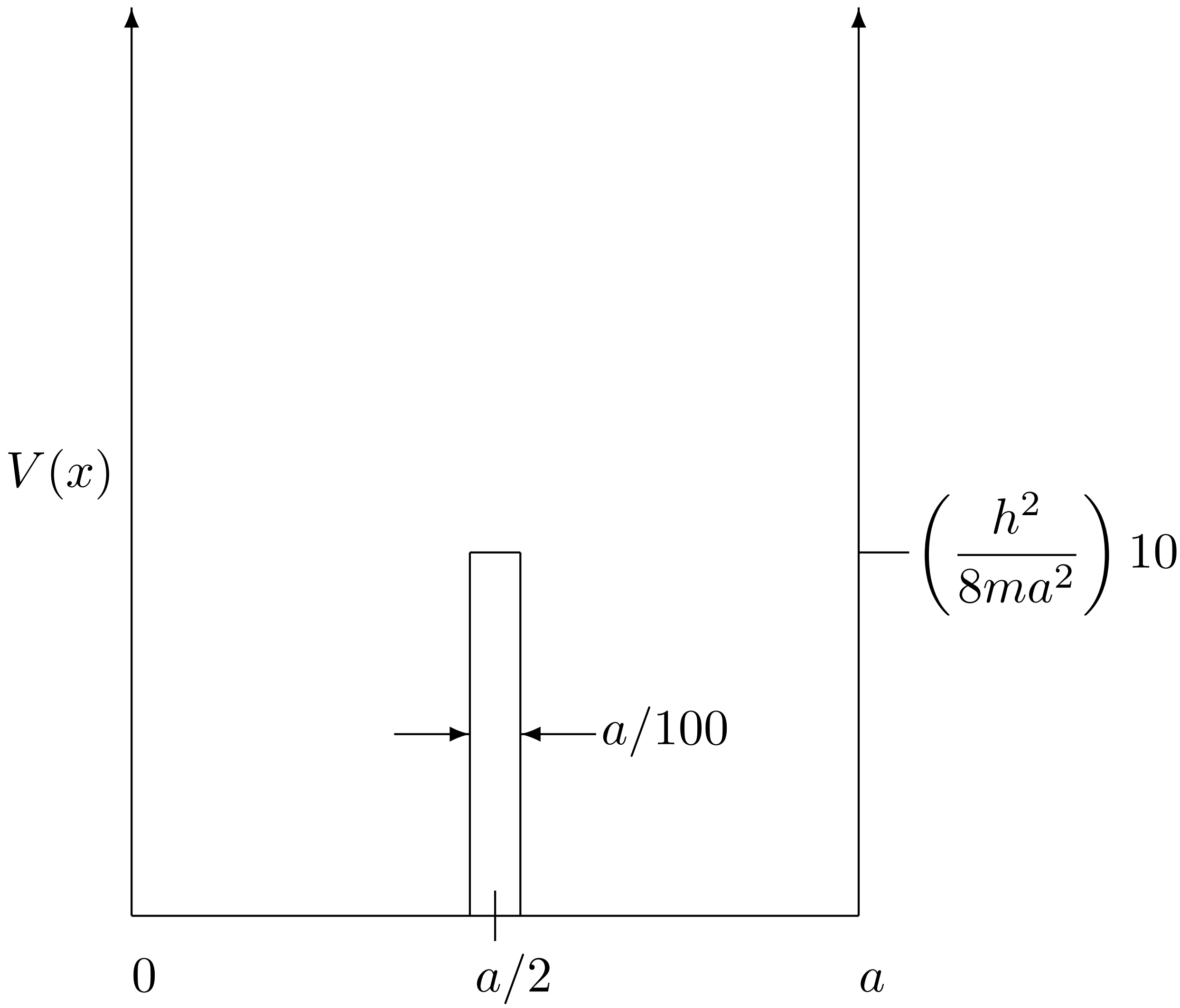
A. (5 points) Sketch $\psi_5^*(x)\psi_5(x)$ vs. x, where $\psi_5(x)$ is the n = 5 wavefunction of a particle in a box. Describe, in a few words, each of the essential qualitative features of your sketch.



B. (5 points) Sketch $\psi_5^*(x)\psi_5(x)$ vs. x, where $\psi_5(x)$ is the $v = 5$ wavefunction of a harmonic oscillator. Describe, in a few words, each of the essential qualitative features of this sketch.



C. (*i*) (3 points) *Sketch* $\psi_1(x)$ and $\psi_2(x)$ for a particle in a box where there is a small and thin barrier in the middle of the box, as shown on this V(x):

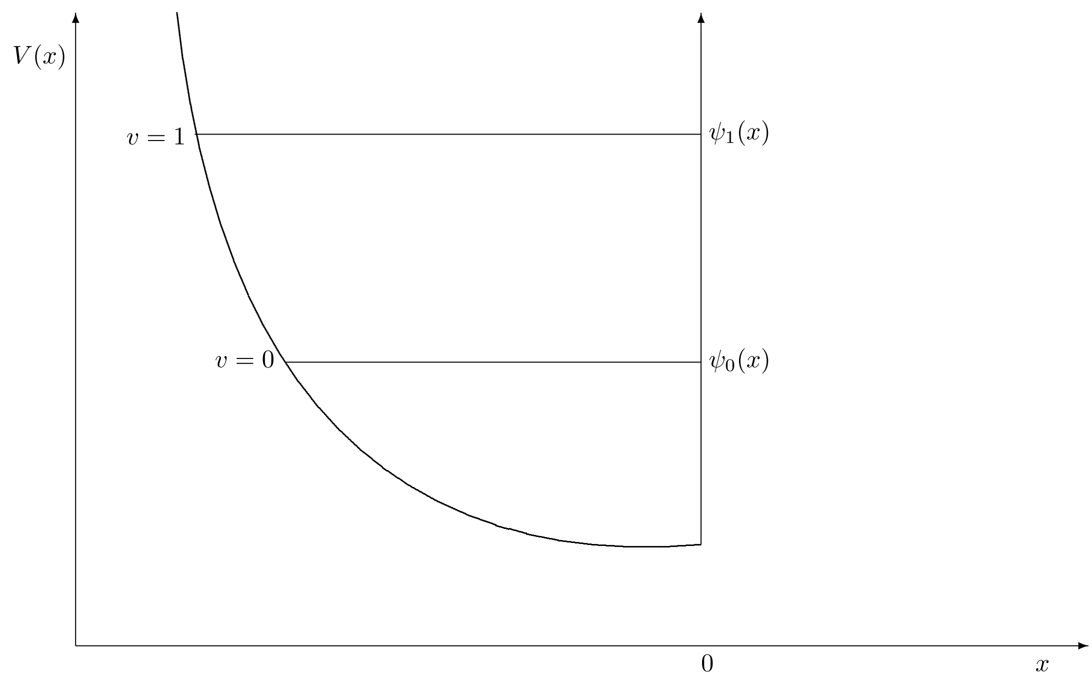


(*ii*) (2 points) Make a very approximate estimate of $E_2 - E_1$ for this PIB with a thin barrier in the middle. Specify whether $E_2 - E_1$ is *smaller than or larger than* $3\left(\frac{h^2}{8ma^2}\right)$, which is the energy level spacing between the $n = 2$ and n = 1 energy levels of a PIB without a barrier in the middle.

D. (5 points) Consider the half harmonic oscillator, which has $V(x) = \frac{1}{2}kx^2$ for $x < 0$ and $V(x) = \infty$ for $x \geq 0$. The energy levels of a full harmonic oscillator are

$$E(v) = \hbar\omega(v + 1/2)$$

where $\omega = [k/\mu]^{1/2}$. Sketch the $v = 0$ and $v = 1$ $\psi_v(x)$ of the half harmonic oscillator and say as much as you can about a general energy level formula for the half harmonic oscillator. A little speculation might be a good idea.



E. (6 points) Give exact energy level formulas (expressed in terms of k and μ) for a harmonic oscillator with reduced mass, μ, where

(***i***) $V(x) = \frac{1}{2}kx^2 + V_0$

(***ii***) $V(x) = \frac{1}{2}k\left(x - x_0\right)^2$

(***iii***) $V(x) = \frac{1}{2}k'x^2$ where $k' = 4k$

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II. PROMISE KEPT: FREE PARTICLE (24 points)

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_0$$

$$\psi(x) = ae^{ikx} + be^{-ikx}$$

A. (4 points) Is $\psi(x)$ an eigenfunction of $\hat{H}$? If so, what is the eigenvalue of $\hat{H}$, expressed in terms of $\hbar$, m, V_0, and k?

B. (4 points) Is $\psi(x)$ an eigenfunction of $\hat{p}$? Your answer must include an evaluation of $\hat{p}\psi(x)$.

C. (4 points) Write a complete expression for the *expectation value* of $\hat{p}$, without evaluating any of the integrals present in $\langle \hat{p} \rangle$.

D. (4 points) Taking advantage of the fact that

$$\int_{-\infty}^{\infty} dx e^{icx} = 0$$

compute $\langle \hat{p} \rangle$, the expectation value of $\hat{p}$.

E. (4 points) Suppose you perform a "click-click" experiment on this $\psi(x)$ where $a = -0.632$ and $b = 0.775$. One particle detector is located at $x = +\infty$ and another is located at $x = -\infty$. Let's say you do 100 experiments. What would be the fraction of detection events at the $x = +\infty$ detector?

F. (4 points) What is the expectation value of $\hat{H}$?

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III. $\hat{\mathbf{a}}$ AND $\hat{\mathbf{a}}^{\dagger}$ FOR HARMONIC OSCILLATOR (20 points)

$$\hat{\mathbf{a}}\psi_v = v^{1/2}\psi_{v-1}$$
$$\hat{\mathbf{a}}^{\dagger}\psi_v = (v+1)^{1/2}\,\psi_{v+1}$$
$$\hat{N}\psi_v = v\psi_v \qquad \text{where} \quad \hat{N} = \hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}}$$

A. (5 points) Show that $\left[\hat{\mathbf{a}}^{\dagger},\hat{\mathbf{a}}\right] = -1$ by applying this commutator to ψ_v.

B. (15 points) Evaluate the following expressions (it is not necessary to explicitly multiply out all of the factors of v).

(***i***) $\left(\hat{\mathbf{a}}^{\dagger}\right)^2 (\hat{\mathbf{a}})^5\,\psi_3$

(***ii***) $(\hat{\mathbf{a}})^5 \left(\mathbf{a}^{\dagger}\right)^2 \psi_3$

(***iii***) $\int dx \psi_3 \left(\mathbf{a}^{\dagger}\right)^3 \psi_0$

(***iv***) What is the selection rule for non-zero integrals of the following operator product $\left(\mathbf{a}^{\dagger}\right)^2 (\hat{\mathbf{a}})^5 \left(\hat{\mathbf{a}}^{\dagger}\right)^4$?

(***v***) $\left(\hat{\mathbf{a}}+\hat{\mathbf{a}}^{\dagger}\right)^2 = \hat{\mathbf{a}}^2 + \hat{\mathbf{a}}\hat{\mathbf{a}}^{\dagger} + \hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}} + \hat{\mathbf{a}}^{\dagger 2}$. Simplify using $\left[\hat{\mathbf{a}}^{\dagger},\hat{\mathbf{a}}\right] = -1$ to yield an expression containing $\hat{\mathbf{a}}^2 + \hat{\mathbf{a}}^{\dagger 2} +$ terms that involve $\widehat{N} = \hat{\mathbf{a}}^{\dagger}\mathbf{a}$ and a constant.

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IV. TIME-DEPENDENT WAVE EQUATION AND PIB SUPERPOSITION (30 POINTS)

For the harmonic oscillator

$$\hat{x} = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2}\left(\hat{\mathbf{a}}^{\dagger} + \hat{\mathbf{a}}\right)$$

$$\hat{p} = \left(\frac{\hbar\mu\omega}{2}\right)^{1/2} i\left(\hat{\mathbf{a}}^{\dagger} - \hat{\mathbf{a}}\right)$$

$$\widehat{N} = \hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}}$$

$$\delta_{ij} = \int dx \psi_i^*(x)\psi_j \text{, which means orthonormal } \{\psi_n\}$$

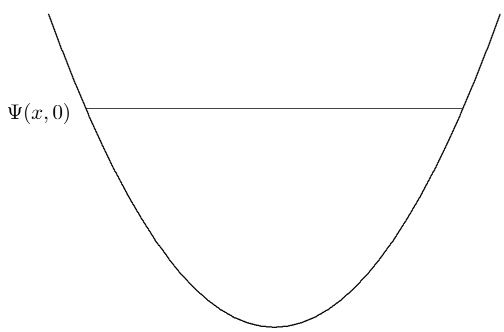
$$\widehat{H}\psi_n(x) = E_n\psi_n \qquad \text{eigenvalues } \{E_n\}$$

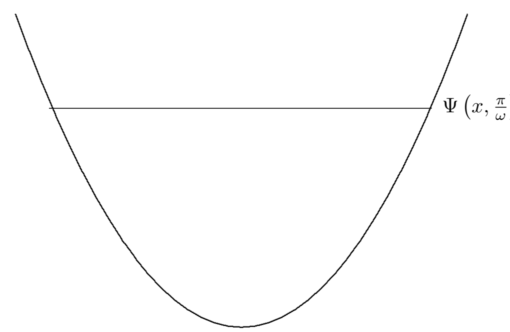
$$E_n = \hbar\omega\left(n + \tfrac{1}{2}\right)$$

Consider the time-dependent state

$$\Psi(x,t) = 2^{-1/2}\left[e^{-iE_0 t/\hbar}\psi_0(x) + e^{-iE_1 t/\hbar}\psi_1(x)\right]$$
$$= 2^{-1/2} e^{-iE_0 t/\hbar}\left[\psi_0(x) + e^{-i\hbar\omega t/\hbar}\psi_1\right]$$

A. (4 points) Sketch $\Psi(x,0)$ and $\Psi(x, t = \frac{\pi}{\omega})$.





B. (5 points) Compute $\int dx \Psi^*(x,t)\hat{N}\Psi(x,t)$.

C. (5 points) Compute $\left\langle \widehat{H} \right\rangle = \int dx \Psi^*(x,t)\widehat{H}\Psi(x,t)$ and comment on the relationship of $\left\langle \hat{N} \right\rangle$ to $\left\langle \widehat{H} \right\rangle$.

D. (4 points) Compute $\langle \hat{x} \rangle = \int dx \Psi^*(x,t)\hat{x}\Psi(x,t)$.

E. (4 points) Compute $\left\langle \hat{x}^2 \right\rangle$.

THIS PROBLEM IS CANCELLED, BUT YOU NEED TO USE THE ANSWER FOR THIS QUESTION IN PARTS F AND G. THE ANSWER IS:

$\left\langle \hat{x}^2 \right\rangle = \hbar / \mu\omega$

F. (4 points) Based on your answer to part **E**, evaluate $\left\langle \hat{V}(x) \right\rangle$.

G. (4 points) Based on your answer to parts **C** and **F**, evaluate $\left\langle \hat{T} \right\rangle$.

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Some Possibly Useful Definite Integrals and Constants

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2}[\pi/a]^{1/2}$$

$$\int_0^\infty xe^{-ax^2} dx = \frac{1}{2a}$$

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\pi^{1/2} a^{-3/2}$$

$h = 6.63 \times 10^{-34}$ J · s

$\hbar = 1.054 \times 10^{-34}$ J · s

$c = 3.00 \times 10^{8}$ m/s

$m_e = 9.11 \times 10^{-31}$ kg

$m_H = 1.67 \times 10^{-27}$ kg

$N_A = 6.022 \times 10^{23}$ mole^{-1}

$$\int_0^{2\pi/a} \sin^2 ax\, dx = \frac{1}{2}$$

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