MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2017

Professor Robert W. Field

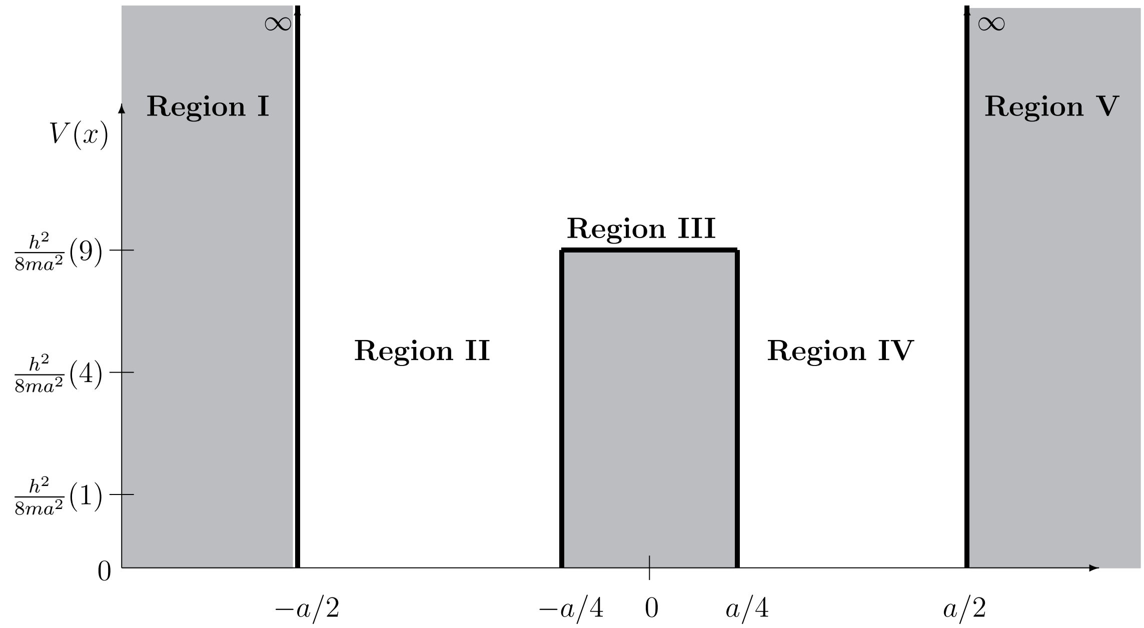
FIFTY MINUTE EXAMINATION I

Thursday, October 5

Question	Possible Score	My Score
I	25	
II	10	
III	10	
IV	20	
V	35	
Total	100	

Name:____

I. Tunneling and Pictures (25 POINTS)



$V(x) = \infty$	$\lvert x\rvert > a/2$	Regions I and V
$V(x) = 0$	$a/4 \le \lvert x\rvert \le a/2$	Regions II and IV
$V(x) = V_0 = \left[\frac{h^2}{8ma^2}\right]9$	$\lvert x\rvert < a/4$	Region III

The energy of the lowest level, E_n $n = 1$ is *near* $E_1^{(0)} = \left[\frac{h^2}{8ma^2}\right]$ and the second level, E_n $n = 2$, is *near* $E_2^{(0)} = \left[\frac{h^2}{8ma^2}\right]4$.

A. (8 points) Sketch $\psi_1(x)$ and $\psi_2(x)$ on the figure above. In addition, specify below the qualitatively most important features that your sketch of $\psi_1(x)$ and $\psi_2(x)$ must display *inside* Region III and *at the borders* of Region III.

B. (3 points) What do you know about $\psi_1(0)$ and $\left.\frac{d\psi_1}{dx}\right|_{x=0}$ *without solving* for E_1 and ψ_1?

(i) Is $\psi_1(0) = 0$?

(ii) Does $\psi_1(0)$ have the same sign as $\psi_1(a/2)$?

(iii) Is $\left.\frac{d\psi_1}{dx}\right|_{x=0} = 0$?

C. (3 points) What do you know about $\psi_2(0)$ and $\left.\frac{d\psi_2}{dx}\right|_{x=0}$ *without solving* for E_2 and ψ_2?

(i) Is $\psi_2(0) = 0$?

(ii) Is $\left.\frac{d\psi_2}{dx}\right|_{x=0} = 0$?

D. (3 points) In the table below, in the last column, place an X next to the mathematical form of $\psi_1(x)$ in Region III .

(i)	$e^{k\|x\|}$	
(ii)	$e^{-k\|x\|}$	
(iii)	$\sin kx$ or $\cos kx$	
(iv)	$e^{ikx} + e^{-ikx}$	
(v)	$e^{ikx} - e^{-ikx}$	
(vi)	something else	

E. (3 points) Does the exact E_1 level lie *above or below* $E_1^{(0)}$?

F. (5 points) For the exact E_2 level, is the energy difference, $\left|E_2 - E_2^{(0)}\right|$, larger or smaller than $\left|E_1 - E_1^{(0)}\right|$? Explain why.

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II. Measurement Theory (10 POINTS)

Consider the Particle in an Infinite Box "superposition state" wavefunction,

$$\psi_{1,2} = (1/3)^{1/2}\,\psi_1 + (2/3)^{1/2}\psi_2$$

where E_1 is the eigen-energy of ψ_1 and E_2 is the eigen-energy of ψ_2.

A. (5 points) Suppose you do one experiment to measure the energy of $\psi_{1,2}$
Circle the possible result(s) of your measurement:
(i) E_1
(ii) E_2
(iii) $(1/3)E_1 + (2/3)\,E_2$
(iv) something else.

B. (5 points) Suppose you do 100 identical measurements to measure the energies of identical systems in state $\psi_{1,2}$ What will you observe?

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III. Semiclassical Quantization **(10 POINTS)**

Consider the two potential energy functions:

V_1 $|x| \le a/2$, $V_1(x) = -|V_0|$
$|x| > a/2$, $V_1(x) = 0$

V_2 $|x| \le a/4$, $V_2(x) = -2|V_0|$
$|x| > a/4$, $V_2(x) = 0$

A. (5 points) The semi-classical quantization equation below

$$\left(\frac{2}{h}\right)\int_{x_-(E)}^{x_+(E)} p_E(x)dx = n$$

$$p_E = \left[2m\left(E - V(x)\right)\right]^{1/2}$$

describes the number of levels below E. Use this to compute the number of levels with energy less than 0 for V_1 and V_2.

B. (5 points) V_1 and V_2 have the same product of width times depth, V_1 is $(a)|V_0|$ and V_2 is $(a/2)(2|V_0|)$, but V_1 and V_2 have different numbers of bound levels. Which has the larger fractional effect, increasing the depth of the potential by X% or increasing the width of the potential by X%??

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IV. Creation/Annihilation Operators (20 POINTS)

A. (2 points) Consider the integral

$$\int_{-\infty}^{\infty} \psi(x)_v^* \widehat{a^\dagger}\,\widehat{a^\dagger}\,\widehat{a^\dagger}\,\widehat{a^\dagger}\,\hat{a}\hat{a}\hat{a}\psi(x)_{v'}\,dx\,.$$

For what values of $v - v'$ will the integral be non-zero (these are called selection rules)?

B. (4 points) Let $v' = 4$ and v be the value determined in part **A** to give a non-zero integral. Calculate the value of the above integral (DO NOT SIMPLIFY!).

C. (4 points) Now consider the integral

$$\int_{-\infty}^{\infty} \psi(x)_v^* \widehat{a^\dagger}\,\hat{a}\widehat{a^\dagger}\,\hat{a}\widehat{a^\dagger}\,\hat{a}\widehat{a^\dagger}\,\psi(x)_{v'}\,dx$$

Are the selection rules for $v' - v$ the same as in part **A**? Is the value of the non-zero integral for $v' = 4$ the same as in part **B**? If not, calculate the value of the integral (UNSIMPLIFIED!).

D. (10 points) Derive the commutation rule $\left[\hat{N},\hat{a}\right]$ starting from the definition of $\hat{N}$.

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V. $\langle x\rangle, \langle p\rangle, \sigma_x, \sigma_p$ and Time Evolution of a Superposition State (35 POINTS)

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

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

A. (5 points) Show that $\widehat{x^2} = \left[\frac{\hbar}{2\mu\omega}\right]\left(\hat{a}^2 + \widehat{a^\dagger}^2 + 2\hat{N} + 1\right)$.

B. (5 points) Derive a similar expression for $\widehat{p^2}$. (Be sure to combine $\widehat{a^\dagger}\hat{a}$ and $\hat{a}\widehat{a^\dagger}$ terms into an integer times $\hat{N}$ plus another integer.

C. (5 points) Evaluate σ_x and σ_p. (Recall that $\sigma_x = \left[\langle \widehat{x^2} \rangle - \langle \hat{x} \rangle^2\right]^{1/2}$).

D. (5 points) Show, using your results for $\widehat{x^2}$ and $\widehat{p^2}$, that

$\hat{H} = \frac{\widehat{p^2}}{2\mu} + \frac{k\widehat{x^2}}{2} = \hbar\omega[\hat{N} + 1/2]$. (The contributions from $\hat{a}^2$ and $\widehat{a^\dagger}^2$ exactly cancel.)

E. (5 points) For $\Psi(x, t=0) = c_0\psi_0 + c_1\psi_1 + c_2\psi_2$, write the time-dependent wavefunction, $\Psi(x,t)$.

F. (5 points) Assume that c_0, c_1, and c_2 are real. Evaluate $\langle \hat{x} \rangle_t$ and show that $\langle x \rangle_t$ oscillates at angular frequency ω. [HINT: $2\cos\theta = e^{i\theta} + e^{-i\theta}$.]

G. (5 points) Evaluate $\left\langle \widehat{x^2} \right\rangle_t$. Show that $\left\langle \widehat{x^2} \right\rangle_t$ includes a contribution that oscillates at an angular frequency of 2ω.

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Some Possibly Useful Constants and Formulas

$h = 6.63 \times 10^{-34}$ J · s $\hbar = 1.054 \times 10^{-34}$ J · s

$\varepsilon_0 = 8.854 \times 10^{-12} Cs^2 kg^{-1} m^{-3}$

$c = 3.00 \times 10^8$ m/s $c = \lambda\nu$ $\lambda = h/p$

$m_e = 9.11 \times 10^{-31}$ kg $m_H = 1.67 \times 10^{-27}$ kg

1 eV = 1.602 x 10^{-19} J $e = 1.602$ x 10^{-19} C

$E = h\nu$ $a_0 = 5.29$ x 10^{-11} m $e^{\pm i\theta} = \cos\theta \pm i\sin\theta$

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{where } R_H = \frac{me^4}{8\varepsilon_0^2 h^3 c} = 109{,}678 \text{ cm}^{-1}$$

Free particle:

$$E = \frac{\hbar^2 k^2}{2m} \qquad \psi(x) = A\cos(kx) + B\sin(kx)$$

Particle in a box:

$$E_n = \frac{h^2}{8ma^2} n^2 = E_1 n^2 \qquad \psi(0 \le x \le a) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right) \qquad n = 1, 2, \ldots$$

Harmonic oscillator:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad \text{[units of } \omega \text{ are radians}/s]$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}, \quad \psi_1(x) = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4}\left(2\alpha^{1/2}x\right)e^{-\alpha x^2/2} \quad \psi_2(x) = \frac{1}{\sqrt{8}}\left(\frac{\alpha}{\pi}\right)^{1/4}\left(4\alpha x^2 - 2\right)e^{-\alpha x^2/2}$$

$$\hat{\tilde{x}} \equiv \sqrt{\frac{m\omega}{\hbar}}\hat{x} \qquad \hat{\tilde{p}} \equiv \sqrt{\frac{1}{\hbar m\omega}}\hat{p} \quad \text{[units of } \omega \text{ are radians}/s]$$

$$\mathbf{a} \equiv \frac{1}{\sqrt{2}}\left(\hat{\tilde{x}} + i\hat{\tilde{p}}\right) \qquad \frac{\hat{H}}{\hbar\omega} = \mathbf{a}\mathbf{a}^\dagger - \frac{1}{2} = \mathbf{a}^\dagger\mathbf{a} + \frac{1}{2} \qquad \hat{\mathbf{N}} = \mathbf{a}^\dagger\mathbf{a}$$

$$\mathbf{a}^\dagger = \frac{1}{\sqrt{2}}\left(\hat{\tilde{x}} - i\hat{\tilde{p}}\right)$$

$$2\pi c\tilde{\omega} = \omega \qquad \text{[units of } \tilde{\omega} \text{ are cm}^{-1}]$$

Semi-Classical

$\lambda = h/p$

$p_{\text{classical}}(x) = [2m(E - V(x))]^{1/2}$

period: $\tau = 1/\nu = 2\pi/\omega$

For a *thin* barrier of width ε where ε is very small, located at x_0, and height $V(x_0)$:

$$H_{nn}^{(1)} = \int_{x_0-\varepsilon/2}^{x_0+\varepsilon/2} \psi_n^{(0)*} V(x) \psi_n^{(0)} dx = \varepsilon V(x_0) \left| \psi_n^{(0)}(x_0) \right|^2$$