MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2017

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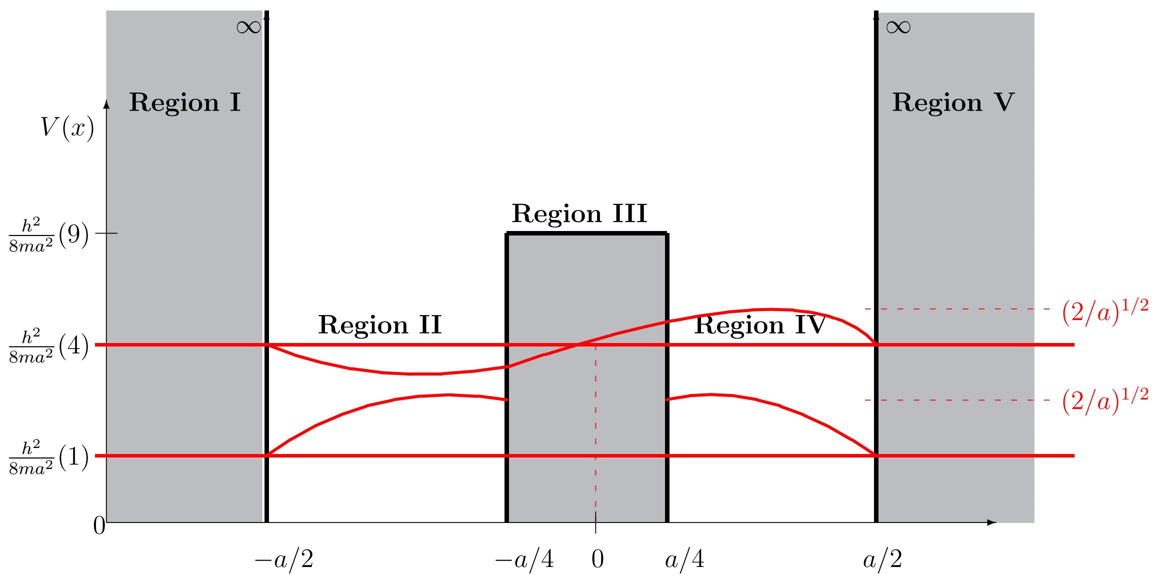
FIFTY MINUTE EXAMINATION I ANSWERS

Thursday, October 5

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 $\psi_1(0) = 0$?

No. ψ_1 cannot have a node and still be the lowest energy state.

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

Yes.

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

Yes, because ψ_1 is a symmetric function.

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 $\psi_2(0) = 0$?

Yes. ψ_2 must be antisymmetric and have a node at $x = 0$.

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

No.

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)	$e^{k_{\text{I}}x_{\text{I}}}$	
(ii)	$e^{-k_{\text{I}}x_{\text{I}}}$	
(iii)	sin kx or cos kx	
(iv)	$e^{ikx} + e^{-ikx}$	
(v)	$e^{ikx} - e^{-ikx}$	
(vi)	something else	**X**

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

Yes. $\psi_1(x)$ feels the barrier strongly, which results in an increase in energy so that $E_1 \gg E_1^{(0)}$.

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.

The E_2 level hardly feels the barrier. It is shifted only slightly to higher energy than $E_2^{(0)}$.

$$\left|E_2 - E_2^{(0)}\right| \ll \left|E_1 - E_1^{(0)}\right|$$

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 — These are the eigenvalues of ψ_1 and ψ_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?

$$\begin{aligned}\langle E\rangle &= \frac{1}{3}E_1 + \frac{2}{3}E_2\\ &= \left[\frac{h^2}{8ma^2}\right]\left[\frac{1}{3}\cdot 1 + \frac{2}{3}\cdot 4\right]\\ &= \left[\frac{h^2}{8ma^2}\right]\left[\frac{1}{3} + \frac{8}{3}\right]\\ &= \left[\frac{h^2}{8ma^2}\right][3]\end{aligned}$$

This value of $\langle E\rangle$ is between E_1 and E_2 and is the weighted average energy.

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

Consider the two potential energy functions:

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

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

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.

For V_1

$$p_E = \left[2m|V_0|\right]^{1/2}$$
$$n = \left(\frac{2}{h}\right)\int_{-a/2}^{a/2}\left[2m|V_0|\right]^{1/2} dx = \frac{\left[2m|V_0|\right]^{1/2} a}{h}$$

For V_2

$$p_E = \left[2m2|V_0|\right]^{1/2}$$
$$n = \left(\frac{2}{h}\right)\int_{-a/4}^{a/4}\left[2m2|V_0|\right]^{1/2} dx = \frac{\left[4m|V_0|\right]^{1/2} a/2}{h}$$

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%?

$$n(V_1) = 2^{1/2} n(V_2)$$

V_1, the wider well, has more levels than V_2, the deeper well. Width has larger fractional effect than depth.

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)?

There are four $\hat{\mathbf{a}}^\dagger$ and three $\hat{\mathbf{a}}$, therefore $v = v' + 1$. The integral is non-zero when $v - v' = +1$.

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!).

Starting from right-most factor in the operator, with $\psi_{v'=4}$ we have

$[(5)(4)(3)(2)(2)(3)(4)]^{1/2}$

↑ last ↑ first

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!).

The $v - v'$ selection rule is the same for Part **A** but the numerical value of the integral is different. Starting from the right, we have

$[(5)(5)(5)(5)(5)(5)(5)]^{1/2}$

↑ last ↑ first

which is larger than the value in Part **B**.

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

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

$$\left[\hat{\mathbf{a}},\hat{\mathbf{a}}^{\dagger}\right] = +1$$

$$\left[\hat{N},\hat{\mathbf{a}}\right] = \hat{N}\hat{\mathbf{a}} - \hat{\mathbf{a}}\hat{N} = \hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}}\hat{\mathbf{a}} - \hat{\mathbf{a}}\hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}}$$

$$= \hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}}\hat{\mathbf{a}} - \left(\left[\hat{\mathbf{a}},\hat{\mathbf{a}}^{\dagger}\right] + \hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}}\right)\hat{\mathbf{a}}$$

$$= -\left[\hat{\mathbf{a}},\hat{\mathbf{a}}^{\dagger}\right]\hat{\mathbf{a}} = -\hat{\mathbf{a}}$$

$$\left[\hat{N},\hat{\mathbf{a}}\right] = -\hat{\mathbf{a}}$$

OR

$$\left[\hat{N},\hat{\mathbf{a}}\right] = \hat{N}\hat{\mathbf{a}} - \hat{\mathbf{a}}\hat{N} = \left[\hat{\mathbf{a}}^{\dagger},\hat{\mathbf{a}}\right]\hat{\mathbf{a}} + \hat{\mathbf{a}}\hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}} - \hat{\mathbf{a}}\hat{\mathbf{a}}^{\dagger}\hat{\mathbf{a}}$$

$$= \left[\hat{\mathbf{a}}^{\dagger},\hat{\mathbf{a}}\right]\hat{\mathbf{a}} = \hat{\mathbf{a}}$$

$$\left[\hat{N},\hat{\mathbf{a}}\right] = -\hat{\mathbf{a}}$$

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

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

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

$$\hat{\mathbf{a}}\hat{\mathbf{a}}^\dagger = \left[\hat{\mathbf{a}},\hat{\mathbf{a}}^\dagger\right] + \hat{\mathbf{a}}^\dagger\hat{\mathbf{a}} = 1 + \hat{N}$$

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

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.

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

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

$$\hat{\mathbf{a}}\hat{\mathbf{a}}^\dagger = \hat{N} + 1$$

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

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

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

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

we want $\int \psi_v \hat{x}^2 \psi_v dx$, selection rule is $\Delta v = 0$

$$\langle \hat{x}^2 \rangle = \left[\frac{\hbar}{2\mu\omega}\right](2v+1)$$

$\langle \hat{x} \rangle = 0$ because selection rule is $\Delta v = \pm 1$

$$\sigma_x = \left[\frac{\hbar}{2\mu\omega}\right]^{1/2}(2v+1)^{1/2}$$

$$\hat{p}^2 = \left[\frac{\hbar\mu\omega}{2}\right]\left[-\widehat{\mathbf{a}^2}^{\dagger} - \hat{\mathbf{a}}^2 + 2\hat{N} + 1\right]$$

$$\langle \hat{p}^2 \rangle = \left[\frac{\hbar\mu\omega}{2}\right](2v+1)$$

$$\sigma_p = \left[\frac{\hbar\mu\omega}{2}\right]^{1/2}(2v+1)^{1/2}$$

Note that

$$\sigma_x\sigma_p = \left[\frac{\hbar}{2\mu\omega}\right]^{1/2}\left[\frac{\hbar\mu\omega}{2}\right]^{1/2} 2(v+1/2)$$

$$= \frac{\hbar}{2}\left[\frac{\mu\omega}{\mu\omega}\right]^{1/2} 2(v+1/2)$$

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

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

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

$$\frac{\widehat{p^2}}{2\mu} = \frac{\hbar\mu\omega}{4\mu}\left[(2v+1) - \hat{\mathbf{a}}^{\dagger 2} - \hat{\mathbf{a}}^2\right]$$

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

$$\frac{\hbar\mu\omega}{4\mu} = \frac{\hbar\omega}{4}$$

$\frac{k}{2}\left(\frac{\hbar`}{2\mu\omega}\right) = \frac{\hbar\omega}{4}$ because $(k/\mu) = \omega^2$

$$\hat{H} = \hbar\omega\left[\hat{N} + 1/2\right]$$

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, $\Psi(x,t)$.

$$\Psi(x,t) = c_0 e^{-i0.5\omega t}\psi_0 + c_1 e^{-i1.5\omega t}\psi_1 + c_2 e^{-i2.5\omega t}\psi_2$$

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: $2\cos\theta = e^{i\theta} + e^{-i\theta}$.]

We know the selection rule for $\hat{x}$ is $\Delta v = \pm 1$.

We know the selection rule for $\widehat{x^2}$ is $\Delta v = 0, \pm 2$.

$$\langle \hat{x} \rangle = \int \Psi^* \hat{x} \Psi dx = |c_0|^2 0 + |c_1|^2 0 + |c_2|^2 0$$
$$+ c_0 c_1 x_{01} e^{-i\omega t} + c_1 c_0 x_{10} e^{i\omega t}$$
$$+ c_1 c_2 x_{12} e^{-i\omega t} + c_2 c_1 e^{i\omega t}$$
$$+ c_0 c_2 0 + c_2 c_0 0$$

Thus $\langle \hat{x} \rangle = 2c_0 c_1 x_{01} \cos\omega t + 2c_1 c_2 x_{12} \cos\omega t$ because $x_{01} = x_{10}$ and $x_{12} = x_{21}$

$x_{21} = 2^{1/2} x_{10}$ could give additional simplification.

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

$$\left\langle \widehat{x^2} \right\rangle = \frac{\hbar}{2\mu\omega}\left[\underbrace{\hat{\mathbf{a}}^{\dagger 2} + \widehat{\mathbf{a}^2}}_{\text{these give } \cos 2\omega t} + \underbrace{2\hat{N} + 1}_{\text{this gives a } t\text{-independent term}} \right]$$

Some Possibly Useful Constants and Formulas

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

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

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

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

1 eV = 1.602×10^{-19} J $\quad\quad e = 1.602 \times 10^{-19}$ C

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

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

Free particle:

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

Particle in a box:

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

Harmonic oscillator:

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

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

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

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

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

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

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 $V(x_0)$:

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