MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2017

Professor Robert W. Field

FIFTY MINUTE EXAMINATION I

Thursday, October 5

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<th>Possible Score</th>
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I. Tunneling and Pictures

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

The energy of the lowest level, E_n, n = 1 is near \( E_1^{(0)} = \left[ \frac{h^2}{8ma^2} \right] 9 \) 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 \( \psi_1 \)?
(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 \( \psi_2 \)?
(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.

<table>
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<tr>
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<th>( e^{ikx} )</th>
<th>( e^{-ikx} )</th>
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<tr>
<td>(i)</td>
<td>( e^{ikx} )</td>
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<td>(ii)</td>
<td>( e^{-ikx} )</td>
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<td>(iii)</td>
<td>( \sin kx ) or ( \cos kx )</td>
<td>( \sin kx ) or ( \cos kx )</td>
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<td>(iv)</td>
<td>( e^{ikx} + e^{-ikx} )</td>
<td>( e^{ikx} + e^{-ikx} )</td>
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<td>(v)</td>
<td>( e^{ikx} - e^{-ikx} )</td>
<td>( e^{ikx} - e^{-ikx} )</td>
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<td>(vi)</td>
<td>something else</td>
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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, \( |E_2 - E_2^{(0)}| \), larger or smaller than \( |E_1 - E_1^{(0)}| \)? Explain why.
(Blank page for Calculations)
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 \( \psi_1 \) and \( E_2 \) is the eigen-energy of \( \psi_2 \).

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?
(Blank page for Calculations)
III. Semiclassical Quantization  

(10 POINTS)

Consider the two potential energy functions:

\[ V_1 \begin{cases} 
|x| \leq a/2, & V_1(x) = -|V_0| \\
|x| > a/2, & V_1(x) = 0 
\end{cases} \]

\[ V_2 \begin{cases} 
|x| \leq a/4, & V_2(x) = -2|V_0| \\
|x| > a/4, & V_2(x) = 0 
\end{cases} \]

A. (5 points)  

The semi-classical quantization equation below

\[
\left( \frac{2}{\hbar} \right) \int_{x_{(E)}}^{x_{(E)}} p_E(x) dx = n
\]

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

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 \( X\% \)?
(Blank page for Calculations)
IV. Creation/Annihilation Operators (20 POINTS)

A. (2 points) Consider the integral

\[ \int_{-\infty}^{\infty} \psi(x)^* a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger \psi(x) \, dx. \]

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

\[ \int_{-\infty}^{\infty} \psi(x)^* a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger a^\dagger \psi(x) \, dx \]

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 \([\hat{N}, \hat{a}]\) starting from the definition of \(\hat{N}\).
V. $\langle x \rangle$, $\langle p \rangle$, $\sigma_x$, $\sigma_p$ and Time Evolution of a Superposition State  

(35 POINTS)

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

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

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

B. (5 points) Derive a similar expression for $\hat{p}^2$. (Be sure to combine $\hat{a}^\dagger \hat{a}$ and $\hat{a} \hat{a}^\dagger$ terms into an integer times $\hat{N}$ plus another integer.
C. (5 points) Evaluate $\sigma_x$ and $\sigma_p$. (Recall that $\sigma_x = \left[ \langle x^3 \rangle - \langle x \rangle^3 \right]^{1/2}$).

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

$$\hat{H} = \frac{\tilde{p}^2}{2\mu} + \frac{k\tilde{x}^2}{2} = \hbar \left[ \hat{N} + 1/2 \right].$$

(The contributions from $\hat{a}^2$ and $\hat{a}^\dagger$ 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 $c_0, c_1, c_2$ are real. Evaluate $\langle \hat{x} \rangle_t$ and show that $\langle x \rangle_t$ oscillates at angular frequency $\omega$. [HINT: $2\cos\theta = e^{i\theta} + e^{-i\theta}$.]

G. (5 points) Evaluate $\langle \hat{x}^2 \rangle_t$. Show that $\langle x^2 \rangle_t$ includes a contribution that oscillates at an angular frequency of $2\omega$. 
(Blank page for Calculations)
Some Possibly Useful Constants and Formulas

\[ h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \quad \hbar = 1.054 \times 10^{-34} \text{ J} \cdot \text{s} \]

\[ c = 3.00 \times 10^8 \text{ m/s} \quad \epsilon_0 = 8.854 \times 10^{-12} \text{Cs}^2\text{kg}^{-1}\text{m}^{-3} \]

\[ m_e = 9.11 \times 10^{-31} \text{ kg} \quad m_n = 1.67 \times 10^{-27} \text{ kg} \]

\[ 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \quad e = 1.602 \times 10^{-19} \text{ C} \]

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

\[ \bar{\nu} = \frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

where \( R_H = \frac{m_e^4}{8\epsilon_0^2\hbar^3 c} = 109,678 \text{ cm}^{-1} \)

**Free particle:**

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

**Particle in a box:**

\[ E_n = \frac{\hbar^2 n^2}{8ma^2} = E_1 n^2 \quad \psi(x) = \left( \frac{2}{a} \right)^{1/2} \sin \left( \frac{n\pi x}{a} \right) \quad n = 1, 2, \ldots \]

**Harmonic oscillator:**

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

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

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

\[ a = \frac{1}{\sqrt{2}} (\hat{x} + i\hat{p}) \quad \hat{H} = a^\dagger a + \frac{1}{2} = \frac{\hbar}{\hbar\omega} \quad \hat{N} = a^\dagger a \]

\[ a^\dagger = \frac{1}{\sqrt{2}} (\hat{x} - i\hat{p}) \quad 2\pi c\tilde{\omega} = \omega \quad [\text{units of } \tilde{\omega} \text{ are cm}^{-1}] \]
Semi-Classical

\[ \lambda = \frac{h}{p} \]

\[ p_{\text{classical}}(x) = \sqrt{2m(E - V(x))} \]

period: \( \tau = \frac{1}{\nu} = \frac{2\pi}{\omega} \)

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

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