MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2013

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FIFTY MINUTE EXAMINATION II

Write your name on this cover page. You may use a calculator. This exam consists of
a cover page, 3 questions, each followed by a blank page for calculations, and a page
of useful equations, a total of 13 pages. Please count them now!

Question	Possible Score	My Score
I	40	
II	40	
III	20	
TOTAL	100	

Name: _____

I. Short Answer Questions   **(40 Points)**

 A. (20 points) Rotational Spectrum of HCl

$$m_H = 1.0078 \text{ g/mol}$$
$$m_{35_{Cl}} = 34.9689 \text{ g/mol}$$
$$m_{37_{Cl}} = 36.9659 \text{ g/mol}$$
$$\mu(\text{H}^{35}\text{Cl}) = 0.97957 \text{ g/mol}$$
$$\mu(\text{H}^{37}\text{Cl}) = 0.98105 \text{ g/mol}$$
$$B_e(\text{H}^{35}\text{Cl}) = 10.593416 \text{ cm}^{-1}$$
$$\alpha_e(\text{H}^{35}\text{Cl}) = 0.3072 \text{ cm}^{-1}$$

 (i) (4 points) What physical property is required for the rotational spectrum of HCl to be observable?

 (ii) (4 points) What is the B_e value for H^{37}Cl?

 (iii) (7 points) What are the transition frequencies (in cm^{-1} units) of the $J = 1 \leftarrow J = 0$ transitions in H^{35}Cl and H^{37}Cl?

 (iv) (5 points) What is the difference (in cm^{-1} units) between the $J = 1 \leftarrow J = 0$ transition frequencies in H^{35}Cl for $v = 0$ and $v = 1$? The rotational constants depend on v, as specified by the equation

$$B(v) = B_e - \alpha_e(v + 1/2).$$

B. (12points) Harmonic Oscillator Plus Barrier or Well

$$\widehat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$\widehat{H}^{(1)} = V_0 \qquad -x_0 \le x \le x_0, \quad V_0 = 0 \quad |x| > x_0$$

$$E^{(0)}(v) = \hbar\omega(v + 1/2)$$

(i) (6 points) Does the second-order perturbation theory correction term, $E_v^{(2)}$, depend on the sign of V_0?

(ii) (6 points) Does perturbation theory predict that the energy levels of a harmonic oscillator plus a barrier ($V_0 > 0$) are different from those of a harmonic oscillator plus a well ($V_0 < 0$)? Explain your answer.

C. (8 points) Rigid Rotor

For a freely-evolving rigid rotor ($\widehat{H}$ is time-independent).

(i) (4 points) You find $\left\langle \hat{J}^2 \right\rangle_{t=0} = \hbar^2 3.000$. What does this imply about $\Psi(\theta, \phi, t = 0)$?

(ii) (4 points) Will $\left\langle \hat{J}^2 \right\rangle_t$ be time–dependent? Explain your answer.

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II. The Two–Level Problem: Bright and Dark States   (40 Points)

Consider the 2–level problem where

$$E_1^{(0)} = A + \Delta/2 \qquad (\Delta > 0)$$
$$E_2^{(0)} = A - \Delta/2$$
$$H_{12}^{(1)} = V \qquad (|V| \ll \Delta)$$
$$H_{11}^{(1)} = H_{22}^{(1)} = 0.$$

The eigen–energies and eigen–functions are

$$E_{\pm} = A \pm (\Delta/2 + V^2/\Delta)$$
$$\star \qquad \psi_+ = [1 - (V/\Delta)^2]^{1/2}\psi_1 + (V/\Delta)\psi_2$$
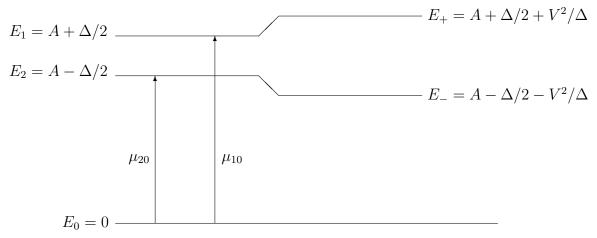$$\star \qquad \psi_- = -(V/\Delta)\psi_1 + [1 - (V/\Delta)^2]^{1/2}\psi_2$$
$$\psi_1 \text{ and } \psi_2 \text{ are normalized and orthogonal.}$$

The zero–order wave functions, expressed in terms of the eigenfunctions are

$$\star\star \qquad \psi_1^{(0)} = [1 - (V/\Delta)^2]^{1/2}\psi_+ - (V/\Delta)\psi_-$$
$$\star\star \qquad \psi_2^{(0)} = (V/\Delta)\psi_+ + [1 - (V/\Delta)^2]^{1/2}\psi_-$$

A.   (10 points) Show that ψ_+ and ψ_- in the $\star$ equations are normalized and orthogonal.

B. (10 points) Suppose that a laser is used to excite molecules from level 0 (at $E_0 = 0$) to the two–level system
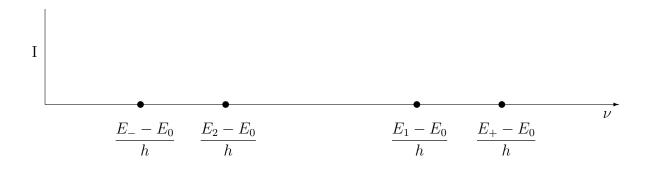
$$E_1 = A + \Delta/2$$

$$E_2 = A - \Delta/2$$

$$E_+ = A + \Delta/2 + V^2/\Delta$$

$$E_- = A - \Delta/2 - V^2/\Delta$$

μ_{20} μ_{10}

$$E_0 = 0$$

where $\mu_{10} \neq 0$ and $\mu_{20} = 0$.

Consider an experiment in which the total fluorescence intensity is recorded as the frequency of a long–pulse excitation laser is scanned through the frequency region that includes the $\frac{E_+ - E_0}{h}$ and $\frac{E_- - E_0}{h}$ eigenstate to eigenstate transition frequencies. This is called a "fluorescence excitation spectrum". The fluorescence intensity from the E_+ level is proportional to

$$I_{+0} \propto |\mu_{+0}|^2 \equiv \left| \int dx \psi_+^\star \hat{\mu} \psi_0 \right|^2 .$$

Sketch the observed fluorescence excitation spectrum and specify the relative intensities of the transitions in the spectrum.

I

                ν

$\frac{E_- - E_0}{h}$ $\frac{E_2 - E_0}{h}$ $\frac{E_1 - E_0}{h}$ $\frac{E_+ - E_0}{h}$

C. (20 points) Now consider short–pulse excitation of the two–level system from level E_0.

   (i) (3 points) Which zero–order level (level 1 or level 2) is "bright" and which is "dark"?

   (ii) (3 points) Based on your answer to part (i), what is $\Psi(x, t = 0)$?

   (iii) (4 points) Write an expression for $\Psi(x, t)$, following the prescription that the bright state produced at $t = 0$ must be expressed as a linear combination of the eigenstates, each with a phase factor $e^{-iE_{\pm}t/\hbar}$.

   (iv) (10 points) The observed fluorescence intensity will exhibit quantum beats where

$$I(t) \propto \left| \int dx\, \Psi^{\star}(x, t)\hat{\mu}\psi_0 \right|^2.$$

   Describe the features of this quantum beating signal.

   ⋆ Does the fluorescence intensity at $t = 0$, $I(t = 0)$, correspond to a maximum or minimum?

   ⋆ Are the oscillations observed at frequency

$$\frac{E_1 - E_2}{h} \qquad \text{or} \qquad \frac{E_+ - E_-}{h}$$

   or both?

   ⋆ What is the ratio of the intensity at the first minimum of $I(t)$ to that at the first maximum, $I_{\min}/I_{\max}$?

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III. VIBRATIONAL TRANSITION INTENSITIES   (20 Points)
AND ANHARMONIC INTERACTIONS

The intensities of vibrational absorption transitions are proportional to

$$I_{v',v''} \propto \left| \int dQ \psi_{v'}(Q)\hat{\mu}(\widehat{Q})\psi_{v''}(Q) \right|^2$$

where

$$\hat{\mu}(\widehat{Q}) = \mu_0 + \frac{d\mu}{dQ}\widehat{Q} + \frac{1}{2}\frac{d^2\mu}{dQ^2}\widehat{Q^2}$$

where, for a harmonic oscillator, the displacement from equilibrium (called $\hat{x}$ in the lecture notes)

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

and, for a harmonic oscillator

$$\int dQ \psi_{v-1}\hat{\mathbf{a}}\psi_v = v^{1/2}$$

$$\int dQ \psi_{v+1}\hat{\mathbf{a}}^\dagger\psi_v = (v+1)^{1/2}.$$

A. (5 points) What is the ratio of transition probabilities for the $v' = 1 \leftarrow v'' = 0$ fundamental transition to that for the $v' = 2 \leftarrow v'' = 1$ hot band?

B. (15 points) In OCS there are 3 normal modes and $\frac{\partial \mu}{\partial Q_i} \neq 0$ for normal modes num-
bered $i = 1, 2$, and 3. This means that there are allowed fundamental transitions
$(1, 0, 0) \leftarrow (0, 0, 0)$, $(0, 1, 0) \leftarrow (0, 0, 0)$, and $(0, 0, 1) \leftarrow (0, 0, 0)$ where each zero-order
vibrational level is denoted by (v_1, v_2, v_3). Suppose that there is an important anhar-
monic resonance, $k_{122}\widehat{Q}_1\widehat{Q}_2^2$.

  (i) (3 points) What are the selection rules for anharmonic interactions caused by
$k_{122}\widehat{Q}_1\widehat{Q}_2^2$?

$\Delta v_1 =$

$\Delta v_2 =$

$\Delta v_3 =$

  (ii) (3 points) Consider the anharmonic interaction between the $\psi^{(0)}_{(1,0,0)}$ and $\psi^{(0)}_{(0,2,0)}$
zero–order states:

$$
\begin{aligned}
V &\equiv \int dQ_1 dQ_2 dQ_3 \psi^{(0)}_{(1,0,0)}\widehat{Q}_1\widehat{Q}_2^2\psi^{(0)}_{(0,2,0)} \\
\Delta &\equiv E^{(0)}_{(0,2,0)} - E^{(0)}_{(1,0,0)} \\
E_+ - E_- &= \Delta + 2V^2/\Delta \\
\psi^{(0)}_{(1,0,0)} &= [1 - (V/\Delta)^2]^{1/2}\psi_+ - (V/\Delta)\psi_- \\
\psi^{(0)}_{(0,2,0)} &= (V/\Delta)\psi_+ + [1 - (V/\Delta)^2]^{1/2}\psi_- \\
\psi_+ &= [1 - (V/\Delta)^2]^{1/2}\psi^{(0)}_{(1,0,0)} + (V/\Delta)\psi^{(0)}_{(0,2,0)} \\
\psi_- &= -(V/\Delta)\psi^{(0)}_{(1,0,0)} + [1 - (V/\Delta)^2]^{1/2}\psi_{(0,2,0)}
\end{aligned}
$$

A short infrared pulse excites a coherent superposition of ψ_+ and ψ_-. What is
$\Psi(Q_1, Q_2, Q_3, t = 0)$?

  (iii) (5 points) The number operator $\widehat{N}_i = \hat{a}_i^\dagger \hat{a}_i$ tells us the number of quanta in the
i–th zero–order normal mode. What are the expectation values of $\widehat{N}_1$ and $\widehat{N}_2$ at
$t = 0$?

(iv) (4 points) Describe what you expect for the time evolution of $\left\langle \widehat{N}_1 \right\rangle$ and $\left\langle \widehat{N}_2 \right\rangle$ for the coherent superposition state excited by the short infrared pulse. Your description can be in words, pictures, or equations.

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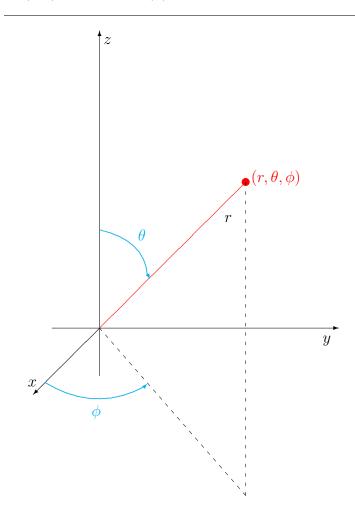
POSSIBLY USEFUL INFORMATION

The classical mechanical relationship between x and p is

$$p(x) = [2m(E - V(x))]^{1/2}.$$

For a harmonic oscillator with $V(x) = \frac{1}{2}kx^2$, when $x = 0$ and $E_v = \hbar\omega(v + 1/2)$

$$p_v(0) = [2\mu\hbar\omega(v + 1/2)]^{1/2}.$$

$\widehat{L}^2\psi_{L,M_L} = \hbar^2 L(L + 1)\psi_{L,M_L}$

$\widehat{L}_z\psi_{L,M_L} = \hbar M_L\psi_{L,M_L}$

$\widehat{L}_\pm\psi_{L,M_L} = \hbar[L(L + 1) - M_L(M_L \pm 1)]^{1/2}\psi_{L,M_L\pm 1}$

$E_{n\ell} = \frac{-\hbar c\Re}{n^2}$

$\widehat{H}^{\text{Zeeman}} = -\frac{\mu_B}{\hbar}B_z[\widehat{L}_z + 2\widehat{S}_z]$ (μ_B is the "Bohr magneton" and B_z is the magnetic field along the z–axis)

$\Psi_n(x, t) = e^{-iE_n t/\hbar}\psi_n(x)$

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