I. Short Answer Questions (40 Points)

A. (20 points) Rotational Spectrum of HCl

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

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

A permanent electric dipole moment is required for observation of a pure rotation (microwave) spectrum. [A dipole derivative, \( \frac{d\mu}{dR} \), is required for observation of a vibrational spectrum.]

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

The \( B_e \) value for \( \text{H}^{37}\text{Cl} \) is

\[
B_e(\text{H}^{37}\text{Cl}) = \frac{\mu(\text{H}^{35}\text{Cl})}{\mu(\text{H}^{37}\text{Cl})} B_e(\text{H}^{35}\text{Cl})
\]
\[
= \frac{0.97957}{0.98105} \times 10.593416 \\
= 10.57743 \text{ cm}^{-1}
\]
(iii) (7 points) What are the transition frequencies (in cm\(^{-1}\) units) of the \(J = 1 \leftrightarrow J = 0\) transitions in \(\text{H}^{35}\text{Cl}\) and \(\text{H}^{37}\text{Cl}\)?

The \(J = 1 \leftrightarrow J = 0\) transitions are at \(\sim 2B_e\)

\[
\begin{align*}
\text{H}^{35}\text{Cl} & : 2(10.593416) = 21.186832 \text{ cm}^{-1} \\
\text{H}^{37}\text{Cl} & : 2(10.57743) = 21.15486 \text{ cm}^{-1}
\end{align*}
\]

+2 extra credit if the calculation was for the \(v = 0\) level where \(2\alpha_e\) was subtracted from the values above.

+1 additional credit if concern was expressed for the difference between \(\alpha_e\) for \(\text{H}^{35}\text{Cl}\) vs. \(\text{H}^{37}\text{Cl}\).

(iv) (5 points) What is the difference (in cm\(^{-1}\) units) between the \(J = 1 \leftrightarrow J = 0\) transition frequencies in \(\text{H}^{35}\text{Cl}\) for \(v = 0\) and \(v = 1\)?

The rotational constants depend on \(v\), as specified by the equation

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

For \(\text{H}^{35}\text{Cl}\) the \(J = 1 \leftrightarrow 0\) transitions are

\[
\begin{align*}
\text{for } v = 0 & : 2 \left[ 10.593416 - \frac{1}{2}(0.3072) \right] \text{ cm}^{-1} \\
\text{and } v = 1 & : 2 \left[ 10.593416 - \frac{3}{2}(0.3072) \right] \text{ cm}^{-1}
\end{align*}
\]

Full credit given for

\[
\nu_{v=0} - \nu_{v=1} = 2(0.3072) = 0.6144 \text{ cm}^{-1}.
\]
B. (12 points) Harmonic Oscillator Plus Barrier or Well

\[ \hat{H}^{(0)} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \]

\[ \hat{H}^{(1)} = V_0 \quad -x_0 \leq x \leq x_0, \quad V_0 = 0 \quad |x| > x_0 \]

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

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

The value of \( E^{(2)}_v \) does not depend on the sign of \( V_0 \) because \( E^{(2)}_v \propto V_0^2 \).

(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.

**YES** perturbation theory does predict a very substantial difference between the energy levels for \( V_0 > 0 \) vs. \( V_0 < 0 \) because

\[ E^{(1)}_v = \int_{-x_0}^{x_0} d\tau \psi_v^* V_0 \psi_v \propto 2x_0 V_0. \]

C. (8 points) Rigid Rotor

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

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

If \( \langle J^2 \rangle_{t=0} = \hbar^2 3.000 \) the system cannot be in an eigenstate of \( \hat{J}^2 \). The eigenvalues are

\[ J \int d\tau \psi^* \hat{J}^2 \psi \]

\[ 0 \quad 0 \hbar^2 \]

\[ 1 \quad 2 \hbar^2 \]

\[ 2 \quad 6 \hbar^2 \]

One way to achieve \( \langle J^2 \rangle_{t=0} = \hbar^2 3.00 \) is for

\[ \psi(\theta, \phi) = \left( \frac{3}{4} \right)^{1/2} \psi_{2,M} + \left( \frac{1}{4} \right)^{1/2} \psi_{3,M} \]

because

\[ \left( \frac{3}{4} \right)^2 + \left( \frac{1}{4} \right) 6 = 3. \]

There are many other ways to arrive at this value of \( \langle J^2 \rangle \).
(ii) (4 points) Will $\langle J^2 \rangle_t$ be time-dependent? Explain your answer.

The $J = 2$ and $J = 3$ eigenstates of $\hat{J}^2$ have different energies, so the minimum criterion for time-dependence of an expectation value is met. However the selection rule for $\hat{J}^2$ is $\Delta J = 0$. Thus there is no contribution to $\langle J^2 \rangle_t$ from a cross term between $\psi_{2,M}$ and $\psi_{3,M'}$ regardless of the values of $M$ and $M'$. 
II. The Two–Level Problem: Bright and Dark States

Consider the 2–level problem where

\[ E_{1}^{(0)} = A + \Delta/2 \quad (\Delta > 0) \]
\[ E_{2}^{(0)} = A - \Delta/2 \]
\[ H_{12}^{(1)} = V \quad (|V| \ll \Delta) \]
\[ H_{11}^{(1)} = H_{22}^{(1)} = 0. \]

The eigen–energies and eigen–functions are

\[ E_\pm = A \pm (\Delta/2 + V^2/\Delta) \]

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

ψ₁ and ψ₂ are normalized and orthogonal.

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

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

A. (10 points) Show that ψ₊ and ψ₋ in the * equations are normalized and orthogonal.

\[ \int d\tau \psi_+^* \psi_+ = [1 - (V/\Delta)^2] + (-V/\Delta)^2 = 1 \]
\[ \int d\tau \psi_-^* \psi_- = (V/\Delta)^2 + [1 - (V/\Delta)^2] = 1 \]
\[ \int d\tau \psi_+^* \psi_- = (V/\Delta)[1 - (V/\Delta)^2]^{1/2} - (V/\Delta)[1 - (V/\Delta)^2]^{1/2} = 0. \]

B. (10 points) Suppose that a laser is used to excite molecules from level 0 (at \( E_0 = 0 \)) to the two–level system

\[ E_1 = A + \Delta/2 \]
\[ E_2 = A - \Delta/2 \]
\[ E_+ = A + \Delta/2 + V^2/\Delta \]
\[ E_- = A - \Delta/2 - V^2/\Delta \]
\[ \mu_{20} \]
\[ \mu_{10} \]
\[ E_0 = 0 \]
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 $\frac{E_+ - E_0}{\hbar}$ and $\frac{E_- - E_0}{\hbar}$ eigenstate to eigenstate transition frequencies. This is called a “fluorescence excitation spectrum”. The fluorescence intensity from the $E_+$ level is proportional to

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

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

I was trying to trick you by labeling the frequency axis for both actual and zero–order frequencies. The transitions occur between the actual energy levels

$$\frac{E_- - E_0}{\hbar} \quad \text{and} \quad \frac{E_+ - E_0}{\hbar} .$$

The intensities of transitions into the + and − eigenstates are proportional to the fractional character of the bright state in each eigenstate. The bright state is $\psi_1$ because $\mu_{10} \neq 0$ and $\mu_{20} = 0$.

In $\psi_+$ fractional character of $\psi_1$ is $[1 - (V/\Delta)]^2$.

In $\psi_-$ fractional character of $\psi_1$ is $(\frac{V}{\Delta})^2$.

A basic assumption of perturbation theory is $|V| \ll |\Delta|$.

Any answer that shows

$$\frac{I_{E_- - E_0}}{\hbar} < \frac{I_{E_+ - E_0}}{\hbar}$$

gets full credit.
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”?

| Level 1 is bright because $\mu_{10} \neq 0$. |
| Level 2 is dark because $\mu_{20} = 0$. |

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

\[
\Psi(x, t = 0) = \psi_1^{(0)}(x) = [1 - (V/\Delta)^2]^{1/2}\psi_+ - (V/\Delta)\psi_-
\]

(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 $e^{-iE/t/\hbar}$.

\[
\Psi(x, t) = [1 - (V/\Delta)^2]^{1/2}e^{-iE_+/\hbar}\psi_+ - (V/\Delta)e^{-iE_-/\hbar}\psi_-
\]

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

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

Describe the features of this quantum beating signal.

One prepares a coherent superposition of $\psi_+$ and $\psi_-$ at $t = 0$, as shown in (iii) above because one prepares the bright zero–order state.

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

$\text{The fluorescence intensity is maximum at } t = 0.$

* Are the oscillations observed at frequency

\[
\frac{E_1 - E_2}{h} \quad \text{or} \quad \frac{E_+ - E_-}{h}
\]

or both?

$\text{The oscillations occur at frequency } \frac{E_+ - E_-}{h}. \text{ Full credit for } \frac{E_+ - E_-}{h} \text{ but that is angular frequency, } \omega, \text{ rather than the ordinary frequency, } \nu.$
What is the ratio of the intensity at the first minimum of $I(t)$ to that at the first maximum, $I_{\text{min}}/I_{\text{max}}$?

This can be algebraically complicated without a trick. The QB intensities are maximum at

$$2\pi n = \frac{E_+ - E_-}{\hbar} t_{\text{max}}$$

$$t_{\text{max}} = n \left( \frac{2\pi \hbar}{E_+ - E_-} \right)$$

For the minima, we require

$$t_{\text{min}} = \left( 2n + \frac{1}{2} \right) \frac{\hbar}{E_+ - E_-}$$

so for the earliest minimum

$$t_{\text{min}} = \frac{1}{2} \frac{2\pi \hbar}{E_+ - E_-}$$

$$\Psi(x, t_{\text{min}}) = e^{-iE_+ t_{\text{min}}/\hbar} \left[ [1 - (V/\Delta)^2]^{1/2} \psi_+ - (V/\Delta) e^{i(E_+ - E_-) t_{\text{min}}/\hbar} \psi_- \right]$$

$$e^{i(E_+ - E_-) t_{\text{min}}/\hbar} = e^{i\pi} = -1$$

$$\Psi(x, t_{\text{min}}) = e^{-iE_+ t_{\text{min}}/\hbar} \left[ [1 - (V/\Delta)^2]^{1/2} \psi_+ + (V/\Delta) \psi_- \right]$$

$$\text{term in } [ \quad ] = [1 - (V/\Delta)^2]^{1/2} [1 - (V/\Delta)^2]^{1/2} \psi_1$$

$$+ [1 - (V/\Delta)]^{1/2} V/\Delta \psi_2$$

$$- (V/\Delta)^2 \psi_1 + (V/\Delta) [1 - (V/\Delta)^2]^{1/2} \psi_2$$

$$= \left[ 1 - 2(V/\Delta) \right] \psi_1 + 2(V/\Delta) [1 - (V/\Delta)^2]^{1/2} \psi_2$$

bright

dark

So intensity at $t_{\text{min}}$ is $[1 - 2(V/\Delta)^2]^2 \mu_{10}^2$ and at $t_{\text{max}}$ it is $\mu_{10}^2$. 
III. VIBRATIONAL TRANSITION INTENSITIES AND ANHARMONIC INTERACTIONS

The intensities of vibrational absorption transitions are proportional to

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

where

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

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

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

and, for a harmonic oscillator

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

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?

\[ \int dQ \psi_{v+1}^* \hat{Q} \frac{d\mu}{dQ} \psi_v \propto (v + 1)^{1/2} \]

Transition intensity is \( \propto v \) of higher state

\[ \frac{I_{2-1}}{I_{1-0}} = 2. \]

B. (15 points) In OCS there are 3 normal modes and \( \frac{\partial \mu}{\partial Q_i} \neq 0 \) for normal modes numbered \( i = 1, 2, \) 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 anharmonic resonance, \( k_{122} \hat{Q}_1 \hat{Q}_2 \).

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

\[ \Delta v_1 = \pm 1 \]
\[ \Delta v_2 = \pm 2, 0 \]
\[ \Delta v_3 = 0 \]

\( \hat{Q}_1 \) selection rule is \( \Delta v_1 = \pm 1 \)
\( \hat{Q}_2^2 \) selection rule is \( \Delta v_2 = 0, \pm 2 \)
\( \hat{Q}_3^0 \) selection rule is \( \Delta v_3 = 0 \)
(ii) (3 points) Consider the anharmonic interaction between the $\psi^{(0)}_{(1,0,0)}$ and $\psi^{(0)}_{(0,2,0)}$ zero-order states:

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

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

This is a vibrational transition. The $\psi^{(0)}_{(1,0,0)}$ state is bright (vibrational fundamental) and the $\psi^{(0)}_{(0,2,0)}$ state is dark (vibrational overtone).

\[
\Psi(Q_1, Q_2, Q_3, t = 0) = \psi^{(0)}_{(1,0,0)}
\]

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

at $t = 0$

\[
\langle \hat{N}_1 \rangle_{t=0} = 1, \langle \hat{N}_2 \rangle_{t=0} = 0.
\]
(iv) (4 points) Describe what you expect for the time evolution of $\langle \hat{N}_1 \rangle$ and $\langle \hat{N}_2 \rangle$ for the coherent superposition state excited by the short infrared pulse. Your description can be in words, pictures, or equations.

$\langle \hat{N}_1 \rangle_t$ oscillates at

$$\omega_{+-} = \frac{E_+ - E_-}{\hbar} = \frac{\Delta + 2V^2/\Delta}{\hbar}$$

It is at its maximum value of 1.00 at $t = 0$.

It is at its minimum value of $1.00 - \delta$ at

$$t_{\text{min}} = \frac{1}{2} \frac{\hbar}{E_+ - E_-}.$$  

$\langle \hat{N}_2 \rangle_t = 0$ at $t = 0$

$$= 2\delta \quad \text{at} \quad t_{\text{min}} = \frac{1}{2} \frac{\hbar}{E_+ - E_-}.$$  

$\delta$ is small, so it could be calculated as in problem II.C (iv).

$$d = 4(V/\Delta)^2[(V/\Delta)^2 - 1]$$
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 $E_v = \hbar\omega(v + 1/2)$

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

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

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

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

$$E_{nl} = \frac{\hbar\omega R}{n^2}$$  

$$\hat{H}_{\text{Zeeman}} = -\frac{\mu_B}{\hbar}B_z[\hat{L}_z + 2\hat{S}_z] \quad (\mu_B \text{ is the “Bohr magneton” and } B_z \text{ is the magnetic field along the } z\text{-axis})$$  

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