MASSACHUSETTS INSTITUTE OF TECHNOLOGY

**5.61 Physical Chemistry**
**Fall, 2017**

Professor Robert W. Field

FIFTY MINUTE EXAMINATION II

**Thursday, October 26**

| Question | Possible Score | Extra Credit | My Score |
|---|---|---|---|
| | | | |
| **I** | 20 | | |
| **II** | 41 | | |
| **III** | 10 | | |
| **IV** | 19 | 2 | |
| **V** | 10 | | |
| | | | |
| **Total** | 100 | 2 | |

Name:________________________________________________________________

# I. $\mathbf{a}^\dagger$ and a Matrices (20 POINTS)

**A.** (3 points) $\langle v+1|\mathbf{a}^\dagger|v\rangle = (v+1)^{1/2}$. Sketch the structure of the $\mathbf{a}^\dagger$ matrix below:

$$\mathbf{a}^\dagger = \begin{pmatrix} 0 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & 0 \end{pmatrix}$$

**B.** (3 points) Now sketch the **a** matrix on a similar diagram.

$$\mathbf{a} = \begin{pmatrix} 0 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & 0 \end{pmatrix}$$

**C.** (5 points) Now apply $\mathbf{a}^\dagger$ to the column vector that corresponds to $|v = 3\rangle$.

$$|v = 3\rangle = \begin{pmatrix} \\ \\ \\ \\ \end{pmatrix} \qquad \mathbf{a}^\dagger|v = 3\rangle = \begin{pmatrix} \\ \\ \\ \\ \end{pmatrix}$$

**D.** (3 points) Is $\mathbf{a}^\dagger$ Hermitian?

**E**. (3 points) Is ($\mathbf{a}^\dagger + \mathbf{a}$) Hermitian? If it is, demonstrate it by the relationship between matrix elements that is the definition of a Hermitian operator.

**F**. (3 points) Is $i(\mathbf{a}^\dagger - \mathbf{a})$ Hermitian? If it is, use a matrix element relationship similar to what you used for part **E**.

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# II. The Road to Quantum Beats **(41 POINTS)**

Consider the 3-level **H** matrix

$$\mathbf{H} = \hbar\omega\begin{pmatrix} 10 & 1 & 0 \\ 1 & 0 & 2 \\ 0 & 2 & -10 \end{pmatrix}$$

Label the eigen-energies and eigen-functions according to the dominant basis state character. The $\widetilde{10}$ state is the one dominated by the zero-order state with $E^{(0)} = 10$, $\tilde{0}$ by $E^{(0)} = 0$, and $-\widetilde{10}$ by $E^{(0)} = -10$.

**A**. (6 points) Use non-degenerate perturbation theory to derive the energies [HINT: $\mathbf{H}^{(0)}$ is diagonal, $\mathbf{H}^{(1)}$ is non-diagonal]:

(i) $E_{\widetilde{10}} =$

(ii) $E_{\tilde{0}} =$

(iii) $E_{-\widetilde{10}} =$

**B**. (6 points) Use non-degenerate perturbation theory to derive the eigenfunctions [HINT: do not normalize]

(i) $\psi_{\widetilde{10}} =$

(ii) $\psi_{\tilde{0}} =$

(iii) $\psi_{-\widetilde{10}} =$

**C**. (5 points) Demonstrate the *approximate* relationship: $\int \psi_{-\widetilde{10}} \mathbf{H} \psi_{-\widetilde{10}} dx \approx E_{-\widetilde{10}}$
[HINT: normalize by dividing by $\int \psi^*_{-\widetilde{10}} \psi_{-\widetilde{10}} dx$ .]

**D**. (4 points) Use the results from part **B** to write the elements of the $\mathbf{T}^{\dagger}$ matrix that non-degenerate perturbation theory promises will give a *nearly diagonal*

$$\tilde{\mathbf{H}} = \mathbf{T}^{\dagger}\mathbf{H}\mathbf{T}$$

matrix [do not normalize, and do not compute $\mathbf{T}^{\dagger}\mathbf{H}\mathbf{T}$].

**E**. (6 points) Suppose, at $t = 0$, you prepare a state $\Psi(x,0) = \psi_0^{(0)}(x)$. Use the correct elements of the $\mathbf{T}^{\dagger}$ matrix to write $\Psi(x,0)$ as a linear combination of the eigenstates, $\psi_{\widetilde{10}}, \psi_{\tilde{0}}$, and $\psi_{-\widetilde{10}}$
[HINT: the columns of $\mathbf{T}$ are the rows of $\mathbf{T}^{\dagger}$.]:

**F**. (4 points) For the $\Psi(x,0) = c_{\widetilde{10}}\psi_{\widetilde{10}} + c_{\tilde{0}}\psi_{\tilde{0}} + c_{-\widetilde{10}}\psi_{-\widetilde{10}}$ initial state you derived in part **E**, write $\Psi(x, t)$ (do not normalize). If you do not believe your derived $c_{\widetilde{10}}$, $c_{\tilde{0}}$, and $c_{-\widetilde{10}}$ constants, leave them as symbols.

**G**. (10 points) Suppose you do an experiment that samples $\Psi(x,t)$ by detecting fluorescence exclusively form the zero-order $\psi_0^{(0)}$ character in $\Psi(x,t)$. This would be obtained from

$$P_0(t) = \left|\int \Psi(x,t)\psi_0^{(0)} dx\right|^2$$

$P_0(t)$ will be modulated at several frequencies.

(i) What is the value of $P_0(0)$?

(ii) The contribution of the zero-order $\psi_0^{(0)}$ state to the observed fluorescence will be modulated at some easily predicted frequencies. What are these frequencies?

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# III. Inter-Mode Anharmonicity in a Triatomic Molecule (10 POINTS)

Consider a nonlinear triatomic molecule. There are three vibrational normal modes, as specific in $\mathbf{H}^{(0)}$ and two anharmonic inter-mode interaction terms, as specified in $\mathbf{H}^{(1)}$.

$$\frac{\mathbf{H}^{(0)}}{hc} = \tilde{\omega}_1\left(\mathbf{N}_1 + 1/2\right) + \tilde{\omega}_2\left(\mathbf{N}_2 + 1/2\right) + \tilde{\omega}_3\left(\mathbf{N}_3 + 1/2\right)$$

$$\mathbf{H}^{(1)} = k_{122}Q_1Q_2^2 + k_{2233}Q_2^2Q_3^2$$

**A**. (2 points) List *all* of the ($\Delta v_1$, $\Delta v_2$, $\Delta v_3$) *combined* selection rules for nonzero matrix elements of the $k_{122}$ term in $\mathbf{H}^{(1)}$? One of these selection rules is $(+1, +2, 0)$.

**B**. (2 points) List *all* of the ($\Delta v_1$, $\Delta v_2$, $\Delta v_3$) selection rules for nonzero matrix elements of the $k_{2233}$ term in $\mathbf{H}^{(1)}$?

**C**. (2 points) In the table below, in the last column, place an X next to the inter-mode vibrational anharmonicity term to which the $k_{2233}$ term contributes .

| | | |
|---|---|---|
| (i) | $\widetilde{\omega_e x_{e_{12}}}\left(v_1 + 1/2\right)\left(v_2 + 1/2\right)$ | |
| (ii) | $\widetilde{\omega_e x_{e_{23}}}\left(v_2 + 1/2\right)\left(v_3 + 1/2\right)$ | |
| (iii) | $\widetilde{\omega_e z_{e_{2233}}}\left(v_2 + 1/2\right)^2\left(v_3 + 1/2\right)^2$ | |

**D**. (2 points) Does the term you specified in part **C** depend on the sign of $k_{2233}$?

**E**. (2 points) Does the $k_{122}$ term in $\mathbf{H}^{(1)}$ give rise to any vibrational anharmonicity terms that are sensitive to the sign of $k_{122}$? Justify your answer.

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# IV. Your First Encounter with a Non-Rigid Rotor (19 POINTS)

Your goal in this problem is to compute the *v*-dependence of the rotational constant of a harmonic oscillator.

Some equations that you will need:

$$B(R) = \frac{\hbar^2}{4\pi c\mu} R^{-2} \quad , \quad B_e = \frac{\hbar^2}{4\pi c\mu} R_e^{-2}$$

$$\hat{\mathbf{Q}} \equiv R - R_e = \left[\frac{\hbar}{4\pi c\mu\omega_e}\right]^{1/2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)$$

$$\frac{1}{R^2} = \frac{1}{(\mathbf{Q} + R_e)^2} = \frac{1}{R_e^2}\left(\frac{\mathbf{Q}}{R_e} + 1\right)^{-2}$$

Power series expansion:

$$\frac{1}{R^2} = \frac{1}{R_e^2}\left[1 - 2\left(\frac{\mathbf{Q}}{R_e}\right) + 3\left(\frac{\mathbf{Q}}{R_e}\right)^2 - 4\left(\frac{\mathbf{Q}}{R_e}\right)^3 + \ldots\right],$$

thus

$$B(R) = B_e\left[1 - 2\left(\frac{\mathbf{Q}}{R_e}\right) + 3\left(\frac{\mathbf{Q}}{R_e}\right)^2 - \ldots\right].$$

Some algebra yields

$$\boxed{\frac{\mathbf{Q}}{R_e} = \left(\frac{B_e}{\omega_e}\right)^{1/2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)} \qquad (1)$$

where $\left(\frac{B_e}{\omega_e}\right) \approx 10^{-3}$, an excellent order-sorting parameter.

$$\boxed{\hat{\mathbf{H}}^{\text{ROT}} = hcB_e J(J+1)\left[1 - 2\left(\frac{B_e}{\omega_e}\right)^{1/2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger) + 3\left(\frac{B_e}{\omega_e}\right)(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^2 - \ldots\right]} \qquad (2)$$

**A**. (4 points) From boxed equation (2), what is $\hat{\mathbf{H}}^{(0)}$ ?

**B**. (4 points) What is $\hat{\mathbf{H}}^{(1)}$ ?

**C**. (6 points) $E_J = E_J^{(0)} + E_J^{(1)} + E_J^{(2)}$ .

What is $E_J^{(0)}$ , as a function of $hc$, $B_e$, and $J(J + 1)$?

What is $E_J^{(1)}$ , as a function of $hc$, $B_e$, $\omega_e$, $(v + 1/2)$, and $J(J + 1)$?
[HINT: $(\mathbf{a}^\dagger\mathbf{a} + \mathbf{a}\mathbf{a}^\dagger) = (2\mathbf{N} + 1)$.]

**D**. (5 points) From experiment we measure

$$E_{J,v} = E_J^{(0)} + E_{J,v}^{(1)} = hcB_v J(J+1)$$
$$B_v = B_e - \alpha_e (v+1/2), \qquad B_{v+1} - B_v = -\alpha_e .$$

What is $\alpha_e$ expressed in terms of $hc$, $B_e$, and $\omega_e$?

**E**. (2 points *extra credit*) Does the sign you have determined by $\alpha_e$ bother you? Why?

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# V. Derivation of One Part of the Angular Momentum Commutation Rule (10 POINTS)

$$\vec{\mathbf{L}} = \vec{\mathbf{r}}x\vec{\mathbf{p}} = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix} = \hat{i}\left(yp_z - zp_y\right) - \hat{j}\left(xp_z - zp_x\right) + \hat{k}\left(xp_y - yp_x\right) \quad (1)$$

$$\left[\mathbf{x},\mathbf{p}_x\right] = i\hbar \quad (2)$$

$$\left[\mathbf{L}_x,\mathbf{L}_y\right] = +\mathbf{i}\hbar\mathbf{L}_z \quad (3)$$

Use equations (1) and (2) to derive equation (3).

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## Some Possibly Useful Constants and Formulas

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

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

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

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

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

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

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

**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:**

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

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

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

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

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

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

**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 $\varepsilon$ where $\varepsilon$ is very small, located at $x_0$, and height $V(x_0)$:

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

**Perturbation Theory**

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)}$$

$$E_n^{(1)} = \int \psi_n^{(0)*} \widehat{H}^{(1)} \psi_n^{(0)} dx = H_{nn}^{(1)}$$

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{H_{nm}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left|H_{nm}^{(1)}\right|^2}{E_n^{(0)} - E_m^{(0)}}$$