# 5.61 Physical Chemistry

## Fall, 2017

Professor Robert W. Field

FIFTY MINUTE EXAMINATION II

Thursday, October 26

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Name: __________________________________________
I. $a^\dagger$ and $a$ Matrices \hspace{1cm} (20 POINTS)

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

$$
\begin{pmatrix}
\vdots \\
0 \\
\vdots \\
\end{pmatrix}
\
\begin{pmatrix}
\vdots \\
0 \\
\vdots \\
\end{pmatrix}
$$

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

$$
\begin{pmatrix}
\vdots \\
0 \\
\vdots \\
\end{pmatrix}
\
\begin{pmatrix}
\vdots \\
0 \\
\vdots \\
\end{pmatrix}
$$

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

$$
|v = 3\rangle =
\begin{pmatrix}
\vdots \\
\vdots \\
\vdots \\
\end{pmatrix}
\hspace{2cm} a^\dagger |v = 3\rangle =
\begin{pmatrix}
\vdots \\
\vdots \\
\vdots \\
\end{pmatrix}
$$

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

F. (3 points) Is $i(a^\dagger - a)$ Hermitian? If it is, use a matrix element relationship similar to what you used for part E.
II. The Road to Quantum Beats (41 POINTS)

Consider the 3-level H matrix

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

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

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

(i) \( E_{\tilde{10}} = \)

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

(iii) \( E_{-\tilde{10}} = \)

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

(i) \( \psi_{\tilde{10}} = \)
(ii) \( \psi_0 = \)

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

C. (5 points) Demonstrate the approximate relationship:
\[
\int \psi_{-10} \mathbf{H} \psi_{-10} \, dx = E_{-10}
\]
[HINT: normalize by dividing by \( \int \psi_{-10}^* \psi_{-10} \, dx \).]
D. (4 points) Use the results from part B to write the elements of the $T'$ matrix that non-degenerate perturbation theory promises will give a *nearly diagonal* 

$$\hat{H} = T'HT$$

matrix [do not normalize, and do not compute $T'HT$].

E. (6 points) Suppose, at $t = 0$, you prepare a state $\Psi(x, 0) = \psi_0^{(0)}(x)$. Use the correct elements of the $T'$ matrix to write $\Psi(x, 0)$ as a linear combination of the eigenstates, $\psi_{10}$, $\psi_0$, and $\psi_{-10}$ [HINT: the columns of $T$ are the rows of $T'$].:
F. (4 points) For the $\Psi(x,0) = c_{\frac{x}{10}} \psi_{\frac{x}{10}} + c_0 \psi_0 + c_{-\frac{x}{10}} \psi_{-\frac{x}{10}}$ initial state you derived in part E, write $\Psi(x, t)$ (do not normalize). If you do not believe your derived $c_{\frac{x}{10}}$, $c_0$, and $c_{-\frac{x}{10}}$ constants, leave them as symbols.
G. (10 points) Suppose you do an experiment that samples $\Psi(x,t)$ by detecting fluorescence exclusively from the zero-order $\psi_0^{(0)}$ character in $\Psi(x,t)$. This would be obtained from

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

$P_0(t)$ 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?
(Blank page for Calculations)
III. Inter-Mode Anharmonicity in a Triatomic Molecule (10 POINTS)

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

$$H^{(0)} = \frac{\hbar c}{\omega_1} (N_1 + 1/2) + \frac{\hbar c}{\omega_2} (N_2 + 1/2) + \frac{\hbar c}{\omega_3} (N_3 + 1/2)$$

$$H^{(1)} = k_{122} Q_1^2 Q_2^2 + k_{223} Q_2^2 Q_3^2$$

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 $H^{(1)}$? 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 $k_{223}$ term in $H^{(1)}$?

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 $k_{223}$ term contributes.

<table>
<thead>
<tr>
<th></th>
<th>Expression</th>
<th>X</th>
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<tbody>
<tr>
<td>(i)</td>
<td>$\omega_1 x_{e_1} (v_1 + 1/2)(v_2 + 1/2)$</td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>$\omega_2 x_{e_2} (v_2 + 1/2)(v_3 + 1/2)$</td>
<td></td>
</tr>
<tr>
<td>(iii)</td>
<td>$\omega_3 x_{e_23} (v_2 + 1/2)^2 (v_3 + 1/2)^2$</td>
<td>X</td>
</tr>
</tbody>
</table>
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.
(Blank page for Calculations)
IV. Your First Encounter with a Non-Rigid Rotor  

Your goal in this problem is to compute the \( \nu \)-dependence of the rotational constant of a harmonic oscillator.

Some equations that you will need:

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

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

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

Power series expansion:

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

thus

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

Some algebra yields

\[
\frac{Q}{R_e} = \left( \frac{B_e}{\omega_e} \right)^{1/2} (\hat{a} + \hat{a}^\dagger)
\]

(1)

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

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

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

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

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

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

What is $E_J^{(1)}$, as a function of $\hbar c, B_e, \omega_e, (\nu + 1/2)$, and $J(J + 1)$?

[HINT: $(a a + a a^\dagger) = (2N + 1)$.]
D. (5 points) From experiment we measure

\[ E_{J,\nu} = E_J^{(0)} + E_J^{(1)} = \hbar \omega_B J (J + 1) \]
\[ B_{\nu} = B_{\epsilon} - \alpha_{\epsilon} (\nu + 1/2), \quad B_{\nu+1} - B_{\nu} = -\alpha_{\epsilon}. \]

What is \( \alpha_{\epsilon} \) expressed in terms of \( \hbar \omega_B, B_{\epsilon}, \) and \( \omega_{\epsilon}? \)

E. (2 points extra credit) Does the sign you have determined by \( \alpha_{\epsilon} \) bother you?
Why?
V. Derivation of One Part of the Angular (10 POINTS) 
Momentum Commutation Rule

\[ \mathbf{\hat{L}} = \mathbf{\hat{r}} \times \mathbf{\hat{p}} = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix} = \hat{i} (yp_z - zp_y) - \hat{j} (xp_z - zp_x) + \hat{k} (xp_y - yp_z) \]  
(1)

\[ [x, p_x] = i\hbar \]  
(2)

\[ [L_x, L_y] = +i\hbar L_z \]  
(3)

Use equations (1) and (2) to derive equation (3).
(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} \\
\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{kg}^{-1} \text{m}^{-3} \\
c = 3.00 \times 10^8 \text{ m/s} \quad c = \lambda \nu \\
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} \\
E = h\nu \quad a_0 = 5.29 \times 10^{-11} \text{ m} \\
\rho = \frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ where } R_H = \frac{m_e^4}{8\varepsilon_0^2 h^3 c} = 109,678 \text{ cm}^{-1} \\
\varepsilon_0 c^2 = \frac{1}{8\pi^2} \\
E = \hbar^2 k^2 \\
\psi(x) = A\cos(kx) + B\sin(kx) \\
E_n = \frac{\hbar^2}{8ma^2} n^2 = E_1 n^2 \\
\psi(x) = \left( \frac{2}{a} \right)^{1/2} \sin\left( \frac{n\pi x}{a} \right) \quad n = 1, 2, \ldots \\
E_n = \left( n + \frac{1}{2} \right) \hbar \omega \quad \text{[units of } \omega \text{ are radians/s]} \\
\psi_0(x) = \left( \frac{a}{\pi} \right)^{1/4} e^{-ax^2/2}, \quad \psi_1(x) = \frac{1}{\sqrt{2}} \left( \frac{a}{\pi} \right)^{1/4} (2\alpha^{1/2} x) e^{-ax^2/2} \quad \psi_2(x) = \frac{1}{\sqrt{8}} \left( \frac{a}{\pi} \right)^{1/4} (4\alpha x^2 - 2) e^{-ax^2/2} \\
\hat{x} = \sqrt{\frac{m\omega}{\hbar}} \hat{x} \quad \hat{p} = \sqrt{\frac{1}{\hbar m\omega}} \hat{p} \quad \text{[units of } \omega \text{ are radians/s]} \\
a = \frac{1}{\sqrt{2}} \left( \hat{x} + i\hat{p} \right) \quad \frac{\hat{H}}{\hbar \omega} = a a^+ - \frac{1}{2} = a^+ a + \frac{1}{2} \quad \hat{N} = a^+ a \\
a^+ = \frac{1}{\sqrt{2}} \left( \hat{x} - i\hat{p} \right) \\
2\pi c\tilde{\omega} = \omega \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 \( \varepsilon \) where \( \varepsilon \) is very small, located at \( x_0 \), and height \( V(x) \):

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

Perturbation Theory

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

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

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

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

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