5.80 Small-Molecule Spectroscopy and Dynamics
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**Problem Set #1 ANSWERS**

1. (a) Make the necessary conversions in order to fill in the table:

| | | | | |
|---|---|---|---|---|
| Wavelength (Å) | 420 | | | |
| Wavenumber ($cm^{-1}$) | | 100 | | |
| Energy (J) | | | | |
| Energy (kJ/mole) | | | 490 | |
| Frequency (Hz) | | | | $8.21 \times 10^{13}$ |

**Answer:**

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{\lambda[\text{Å}] \cdot 10^{-10} m\text{Å}^{-1}} \cdot \frac{10^{-2} m}{1 \text{ cm}} = \frac{10^{8} \text{ cm}^{-1}}{\lambda[\text{Å}]}$$

$$E = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34} Js \cdot 2.998 \cdot 10^{8} ms^{-1}}{\lambda[\text{Å}] \cdot 10^{-10} m\text{Å}^{-1}}$$

$$= \frac{1.988 \cdot 10^{-15} J}{\lambda[\text{Å}]}$$

$$E = \frac{1.988 \cdot 10^{-15} J/\text{photon}}{\lambda[\text{Å}]} \cdot 6.022 \cdot 10^{23} \text{ photon/mole} \cdot 10^{-3} kJ/J$$

$$= \frac{1.197 \cdot 10^{6} \text{ kJ/mole}}{\lambda[\text{Å}]}$$

$\nu = \dfrac{c}{\lambda}$; $\nu$ is **not** angular frequency, but the reciprocal of the period of oscillation

$$= \frac{2.998 \cdot 10^{8} \; ms^{-1}}{\lambda[\text{Å}] \cdot 10^{-10} m\text{Å}^{-1}} = \frac{2.998 \cdot 10^{18} \text{ Hz}}{\lambda[\text{Å}]}$$

(b) Name the spectral region associated with each of the last four columns of the table.

**Answer:**

| Name for region of the spectrum | XUV | Far IR | UV | Mid IR |
|---|---|---|---|---|
| wavelength/Å | 420 | $1.00 \cdot 10^{6}$ | 2440 | $3.65 \cdot 10^{4}$ |
| wavenumber/$cm^{-1}$ | $2.38 \cdot 10^{5}$ | 100 | 40900 | 2740 |
| energy/J | $4.73 \cdot 10^{-18}$ | $1.99 \cdot 10^{-21}$ | $8.14 \cdot 10^{-19}$ | $5.44 \cdot 10^{-20}$ |
| energy/kJ $mole^{-1}$ | 2850 | 1.20 | 490 | 32.8 |
| frequency/Hg | $7.14 \cdot 10^{-15}$ | $3.00 \cdot 10^{12}$ | $1.23 \cdot 10^{15}$ | $8.21 \cdot 10^{13}$ |

2. A 100-W tungsten filament lamp operates at 2000 K. Assuming that the filament emits like a blackbody, what is the total power emitted between 6000 Å and 6001 Å? How many photons per second are emitted in this wavelength interval?

**Answer:** This problem makes use of the Stefan-Boltzman Law, $I = \sigma T^4$. You can either derive it (problem 8a) or look it up.
100 W tungsten filament lamp operating at 2000 K.
What is the total power emitted between 6000 Å and 6001 Å?
We can calculate this quantity by integrating the Planck function from 6000 Å to 6001 Å, and comparing that the value of the Planck function integrated over all $\lambda$'s.

$$\text{Power} = \frac{\int_{\nu_1}^{\nu_2} \rho(\nu, T) d\nu}{\int_0^\infty \rho(\nu, T) d\nu} \times 100W; \nu_1 = \frac{c}{6001\text{Å}}, \nu_2 = \frac{c}{6000\text{Å}}.$$

$\rho(\nu, T)$ is approximately constant between 6000 Å and 6001 Å.
$d\nu = -\frac{c}{\lambda^2} d\lambda,\ d\nu \simeq \frac{c}{\lambda^2}|\Delta\lambda|$
$\int_{\nu_1}^{\nu_2} \rho(\nu, T) d\nu \simeq \overline{\rho}\Delta\nu$
$\overline{\rho} \simeq \frac{8\pi h}{c^3}\overline{\nu}^3 e^{-\frac{h\overline{\nu}}{kT}}, h\overline{\nu} \gg kT$
$\int_0^\infty \rho(\nu, T) = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1} d\nu$
let $x = \frac{h\nu}{kT},\ d\nu = \frac{h}{kT} d\nu$

$$\int_0^\infty \rho(\nu, T) d\nu = \frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx$$
$$= \frac{8\pi h}{c^3}\left(\frac{\pi^4}{15}\right)\left(\frac{kT}{h}\right)^4 \text{ Stefan-Boltzman Law}$$

$$\frac{\overline{\rho}\Delta\nu}{\int_0^\infty \rho(\nu) d\nu} = \frac{\overline{\nu}^3 e^{-\frac{h\overline{\nu}}{kT}}\Delta\nu}{\frac{\pi^4}{15}\left(\frac{kT}{h}\right)^4} = \frac{(4.996 \times 10^{14} s^{-1})^3 (1.611 \times 10^5)^{-1} (8.326 \times 10^{+10} s^{-1})}{(6.494)(4.168 \times 10^{13} s^{-1})^4}$$
$$= 3.29 \times 10^{-6}$$

$$3.29 \times 10^{-6} \times 100W = 329\ \mu W$$
$$= \frac{3.29 \times 10^{-6} J s^{-1}}{3.313 \times 10^{-19} J \text{ photon}^{-1}}$$
$$= 9.93 \times 10^{12} \text{ photons } s^{-1}$$

3. (a) What is the magnitude of the electric field for the beam of a 1−mW helium-neon laser with a diameter of 1 mm?

**Answer:** Use Bernath (1.4b) $E = 27.4 I^{1/2} = 988$ V/m

(b) How many photons per second are emitted at 6328 Å?

**Answer:**

$$\begin{aligned} 1\ mW &= 1 \times 10^{-3} Js^{-1} @\ 6328\ \text{Å} \\ &= 1 \times 10^{-3} Js^{-1} \Big/ \left[ \frac{1.988 \times 10^{-15}\ \text{J photon}^{-1}}{6328} \right] \\ &= 3.18 \times 10^{15}\ \text{photons s}^{-1} \end{aligned}$$

(c) If the laser linewidth is 1 kHz, what temperature would a blackbody have to be to emit the same number of photons from a equal area over the same frequency interval as the laser?

**Answer:** The HeNe beam has $d = 1mm$, $A = \left(\frac{\pi}{4}\right) mm^2 = 0.785 mm^2$. For calculation of $T_{bb}$, $A = A_{\text{HeNe}} = 0.785 mm^2$.

$A \int I(\nu, T) d\nu \simeq A\rho(6328\text{Å}, T)\frac{c}{4}\Delta\nu = 1mW$

$\rho(6328\text{Å}, T) = \frac{8\pi h}{\lambda^3}\left[e^{\frac{h\nu}{kT}\frac{1}{\lambda}} - 1\right]^{-1}$

$A\rho(\lambda, T)\frac{c}{4}\Delta\nu = P$

$\frac{A}{P}\frac{8\pi h}{\lambda^3}\frac{c}{4}\Delta\nu = e^{\frac{h\nu}{k\lambda}\frac{1}{T}} - 1$

$$\begin{aligned} \frac{0.785 \times 10^{-6} m^2}{1 \times 10^{-3} Js^{-1}} \times \frac{(8\pi)6.626 \times 10^{-34} Js}{(6.328 \times 10^{-7} m)^3} \times \frac{3.000 \times 10^8 ms^{-1}}{4} \times 10^3 s^{-1} &= \frac{A}{P}\frac{8\pi}{\lambda^3}\frac{hc}{4} \\ &= 396 \end{aligned}$$

$e^x \simeq 1 + x, x \ll 1$

$\frac{hc}{h\lambda}\frac{1}{T} \simeq 3.86 \times 10^{-6}$

$$\begin{aligned} T &= \frac{6.626 \times 10^{-34} Js \times 3.00 \times 10^8 ms^{-1}}{1.381 \times 10^{-23} JK^{-1} \times 6.328 \times 10^{-7} m} \times \frac{1}{3.86 \times 10^{-6}} \\ &= 5.89 \times 10^9 K \end{aligned}$$

4. The lifetime of the $3^2P_{3/2} \rightarrow 3^2S_{1/2}$ transition of the Na atom at 5890 Å is measured to be 16 ns.

Na $3^2P_{3/2} \leftarrow 3^2S_{1/2}$   $\lambda = 5890$ Å, $\tau = 16$ ns

(a) What are the Einstein *A* and *B* coefficients for the transition?

**Answer:** The radiative lifetime of the state is related to the Einstein spontaneous emission coefficients

$$\tau_i^{-1} = \sum_j A_{ij}$$

The $3^2P_{3/2}$ state can radiate only to $3^2S_{1/2}$ (the ground state), so

$$A = \frac{1}{\tau} = \frac{1}{16ns} = 6.3 \times 10^7 s^{-1}$$

From Eq. (1.22)

$$B = \frac{\lambda^3 A}{8\pi h} = \frac{(5.890 \times 10^{-7} m)^3}{8\pi 6.626 \times 10^{-34} Js(16 \times 10^{-9} s)}$$
$$= 7.67 \times 10^{20} J^{-1} m^3 s^{-2}$$

(b) What is the transition dipole moment in debye?

**Answer:** from Eq. (1.52)

$$A_{10} = \frac{16\pi^3 \nu^3}{3\epsilon_0 hc^3}\mu_{10}^2 = 3.136 \times 10^{-7} \tilde{\nu}^3 \mu_{10}^2 \qquad \tilde{\nu} = [\text{cm}^{-1}]$$
$$\mu_{10}^2 = \frac{1}{16 \times 10^{-4}} \frac{1}{3.136 \times 10^{-7}} \left(\frac{5890\text{ Å}}{10^8\text{Å cm}^{-1}}\right)^{-3} = 40.7\ D^2$$
$$|\mu_{10}| = 6.38\ D$$

(c) What is the peak absorption cross section for the transition in Å$^2$, assuming that the linewidth is determined by lifetime broadening?

**Answer:** Lorentzian line profile is due to only lifetime broadening

$$g(\nu - \nu_0)$$
$$g(0) = \frac{4}{\gamma}; \gamma = \frac{1}{\tau_{sp}}$$
$$g(0) = 4\tau_{sp}$$

**Answer: 4c, continued**
From Eq. (1.57)

$$\sigma = \frac{A\lambda^2 g(\nu-\nu_{10})}{8\pi} = \frac{\lambda^2 g(\nu-\nu_{10})}{8\pi\tau_{sp}}; A = \frac{1}{\tau_{sp}}$$

$$\sigma_{\max} = \frac{\lambda^2 4\tau_{sp}}{8\pi\tau_{sp}} = \frac{\lambda^2}{2\pi}; \nu = \nu_0$$

$$= \frac{(5.890\times10^{-5}\text{ cm})^2}{2\pi} = 5.52\times10^{-10}\text{cm}^2$$

5. (a) For Na atoms in a flame at 2000 K and 760 Torr pressure calculate the peak absorption cross section (at line center) for the $3^2P_{3/2} - 3^2S_{1/2}$ transition at 5890 Å. Use 30 MHz/Torr as the pressure-broadening coefficient and the data in Problem 4.

**Answer:** Na atoms, $T = 2000$K, $p = 760$ torr.
Calculate peak absorption cross-section for $3^2P_{3/2} - 3^2S_{1/2}$ 5890Å.

$$\Delta\nu_{1/2} = (30\text{ MHz/torr})p$$

$$= \frac{30\text{MHz}}{\text{torr}}(760\text{ torr})(29979\text{ MHz/cm}^{-1})^{-1}$$

$$= 0.76\text{ cm}^{-1}$$

From Eq. (1.75), for a Lorentzian lineshape

$$\Delta\nu_{1/2} = \frac{\gamma}{2\pi} \quad ; \quad \gamma = 2\pi\Delta\nu_{1/2}$$

From Eq. (1.57),

$$\sigma_{\max} = \frac{A\lambda^2 g(0)}{8\pi} = \frac{A\lambda^2}{2\pi\gamma}, \quad g(0) = \frac{4}{\gamma}$$

$$= \frac{A\lambda^2}{(2\pi)^2\Delta\nu_{1/2}} = \frac{1}{16\times10^{-9}s}\frac{(5.890\times10^{-5}\text{cm})^2}{(2\pi)^2(22900\times10^6 s^{-1})}$$

$$= 2.41\times10^{-13}\text{cm}^2$$

(b) If the path length in the flame is 10 cm, what concentration of Na atoms will produce an absorption ($I/I_0$) of $1/e$ at line center?

**Answer:** $N_1 \approx 0$, $N_0 \approx N$ $\quad \frac{N}{N_0} = \frac{4}{2} e^{-\frac{169.78}{1340}} = 1.0 \times 10^{-5}$

$$\ln\left(\frac{I}{I_0}\right) = -\sigma N \ell = -1$$

$$N = [2.41 \times 10^{-13} \text{cm}^2 \times 10\text{cm}]^{-1} = 4.15 \times 10^{11} \text{ cm}^{-3}$$

(c) Is the transition primarily Doppler or pressure broadened?

**Answer:**

$$\Delta\tilde{\nu}_0 = 7.1 \times 10^{-7} \tilde{\nu}_0 \left(\frac{T}{M}\right)^{1/2}$$
$$\tilde{\nu}_0 = 16978 \text{ cm}^{-1}$$
$$T = 2000\ K$$
$$M = 23 \text{ amu}$$
$$\Delta\tilde{\nu}_0 = 0.11 \text{ cm}^{-1}$$

This compares to the pressure broadened linewidth of 0.76 $\text{cm}^{-1}$, as determined in part (a). The transition is primarily pressure broadened.

**NOTE:** lifetime broadening contributes $< 0.001 \text{ cm}^{-1}$ to homogeneous broadening. The fact that $\frac{\Delta\tilde{\nu}_L}{\Delta\tilde{\nu}_D} \simeq 7$ means that the cross-section calculated in part (a) is slightly overestimated.

(d) Convert the peak absorption cross section in $\text{cm}^2$ to the peak molar absorption coefficient $\epsilon$.

**No Answer given**

6. For Ar atoms at room temperature (20°C) and 1–Torr pressure, estimate a collision frequency for an atom from the van der Waals radius of 1.5 Å. What is the corresponding pressure-broadening coefficient in MHz/Torr?

**Answer:** Collision rate was determined using equations from P. W. Atkins, Physical Chemistry, 2nd edition.
From Bernath, Eq. (1.79)

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} \quad ; \quad T_2 \text{ is the average time between collisions}$$

$$T_2 = z^{-1} \quad ; \quad z = \text{collision rate}$$

$$z = \sqrt{2}\sigma\bar{c}\frac{N}{V}$$

$$\sigma = \pi r^2 = \pi[1.5\times 10^{-8}\text{cm}]^2 = 7.07\times 10^{-16}\text{cm}^2$$

$$\bar{c} = 14551\left(\frac{T}{M}\right)^{1/2} \text{cm } s^{-1} = 3.80\times 10^4 \text{cm } s^{-1}$$

$$\frac{N}{V} = \frac{p}{RT} = \left[\frac{\text{p/torr}}{\text{T/K}}\right]\times\frac{1\text{torr}\times\frac{1}{760}\text{ atm torr}^{-1}\times 10^{-3}\ell\text{cm}^{-3}}{1\,K\times 0.08206\,\ell\text{ atm mole}^{-1}K^{-1}}6.022\times 10^{23}\text{ molecules}\cdot\text{mole}^{-1}$$

$$= 9.656\times 10^{18}\left(\frac{p}{T}\right)\text{ molecules cm}^{-3}$$

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$$\Delta\nu_{1/2} = \frac{1}{\pi\, T_2} = \frac{z}{\pi} = \left[\frac{1}{\pi}\sqrt{2}(\pi r^2)14551\left(\frac{T}{M}\right)^{1/2}\frac{9.656\times 10^{18}}{T}\right]p$$

$$= \sqrt{2}(1.5\times 10^{-8}\text{cm})^2\left(\frac{293}{40}\right)^{1/2} 14551\frac{9.656\times 10^{18}}{293}p$$

$$= 0.41\text{ MHz/torr}\times\text{ p/torr}$$

7. Solve the following set of linear equations using matrix methods

$$4x - 3y + z = 11$$
$$2x + y - 4z = -1$$
$$x + 2y - 2z = 1.$$

**Answer:**

$$\begin{bmatrix} 4 & -3 & 1 \\ 2 & 1 & -4 \\ 1 & 2 & -2 \end{bmatrix}\boldsymbol{x} = \begin{bmatrix} 11 \\ -1 \\ 1 \end{bmatrix}$$

**Answer: #7, continued**

$$\mathbf{A}\boldsymbol{x} = \boldsymbol{b}$$
$$\boldsymbol{x} = \mathbf{A}^{-1}\boldsymbol{b}$$

The difficult part of this problem is calculating $\mathbf{A}^{-1}$. Bernath, Eq. (3.28) $(\mathbf{A}^{-1})_{ij} = \frac{M_{ji}}{|\mathbf{A}|}$

$$\begin{aligned}
|\mathbf{A}| &= 4\begin{vmatrix}1 & -4\\ 2 & -2\end{vmatrix} - (-3)\begin{vmatrix}2 & -4\\ 1 & -2\end{vmatrix} + (1)\begin{vmatrix}2 & 1\\ 1 & 2\end{vmatrix}\\
&= 4[-2-(-8)] + 3[-4-(-4)] + [4-1]\\
&= 27
\end{aligned}$$

$$M_{11} = (-1)^2\begin{vmatrix}1 & -4\\ 2 & -2\end{vmatrix} = 6$$

$$M_{12} = (-1)^3\begin{vmatrix}2 & -4\\ 1 & -2\end{vmatrix} = 0$$

$$M_{13} = (-1)^4\begin{vmatrix}2 & 1\\ 1 & 2\end{vmatrix} = 3$$

$$M_{21} = (-1)^3\begin{vmatrix}-3 & 1\\ 2 & -2\end{vmatrix} = -4$$

$$M_{22} = (-1)^4\begin{vmatrix}4 & 1\\ 1 & -2\end{vmatrix} = -9$$

$$M_{23} = (-1)^5\begin{vmatrix}4 & -3\\ 1 & 2\end{vmatrix} = -11$$

$$M_{31} = (-1)^4\begin{vmatrix}-3 & 1\\ 1 & -4\end{vmatrix} = 11$$

$$M_{32} = (-1)^5\begin{vmatrix}4 & 1\\ 2 & -4\end{vmatrix} = 18$$

$$M_{33} = (-1)^6\begin{vmatrix}4 & -3\\ 1 & 1\end{vmatrix} = 10$$

$$\mathbf{A}^{-1}\boldsymbol{b} = \frac{1}{27}\begin{bmatrix}6 & -4 & 11\\ 0 & -9 & 18\\ 3 & -11 & 10\end{bmatrix}$$

$$\mathbf{A}^{-1}\boldsymbol{b} = \frac{1}{27}\begin{bmatrix}6 & -4 & 11\\ 0 & -9 & 18\\ 3 & -11 & 10\end{bmatrix}\begin{bmatrix}11\\ -1\\ 1\end{bmatrix} = \begin{bmatrix}3\\ 1\\ 2\end{bmatrix}$$

$$\boldsymbol{x} = \begin{bmatrix}3\\ 1\\ 2\end{bmatrix}$$

8. (a) Find the eigenvalues and normalized eigenvectors of the matrix

$$\mathbf{A} = \begin{pmatrix} 2 & 4-i \\ 4+i & -14 \end{pmatrix}.$$

**Answer:** It will be much easier to find the eigenvalues and eigenvectors if we rewrite **A** as follows:

$$\begin{aligned} \mathbf{A} &= \begin{bmatrix} \epsilon^\circ & V^\star \\ V & -\epsilon^\circ \end{bmatrix} \quad + \begin{bmatrix} \overline{\epsilon} & 0 \\ 0 & \overline{\epsilon} \end{bmatrix} \\ & \qquad \mathbf{B} \qquad\quad + \quad \overline{\epsilon}\mathbf{I} \\ \overline{\epsilon} &= \frac{1}{2}(2-14) \quad = -6 \\ \epsilon^\circ &= 8 \\ V^\star V = |V|^2 &= (4+i)(4-i) = 17 \end{aligned}$$

Eigenvalues of **A** are found by solving $det[\mathbf{B} - E\mathbf{I}] = 0$ and adding $\overline{\epsilon}$

$$\begin{aligned} det[\mathbf{B} - E\mathbf{I}] &= (\epsilon^\circ - E)(-\epsilon^\circ - E) - |V|^2 = 0 \\ E^2 &= (\epsilon^\circ)^2 + |V|^2 \\ E &= \pm 9 \quad , \quad \overline{\epsilon} = -6 \end{aligned}$$

The eigenvalues of **A** are +3 and −15. Determine the eigenvectors of **A** by substituting the appropriate values of $\epsilon$ into $\mathbf{A} - \epsilon\mathbf{I}$

$$\epsilon_1 = +3 \qquad \mathbf{A} - \epsilon_1\mathbf{I} = \begin{bmatrix} -1 & 4-i \\ 4+i & -17 \end{bmatrix}$$

Normalize it to unit length

$$\epsilon_1 = +3, \boldsymbol{u}_1 = \frac{1}{\sqrt{18}} \begin{bmatrix} 4-i \\ 1 \end{bmatrix}$$

$$\epsilon_2 = -15 \qquad \mathbf{A} - \epsilon_2\mathbf{I} = \begin{bmatrix} 17 & 4-i \\ 4+i & 1 \end{bmatrix}$$

Same as for $\epsilon_1$, but

$$\epsilon_2 = -15, \boldsymbol{u}_2 = \frac{1}{\sqrt{18}} \begin{bmatrix} -1 \\ 4+i \end{bmatrix}$$

(b) Construct the matrix **X** that diagonalizes **A** and verify that it works.

**Answer:** **X**, which diagonalizes **A**, consists of the column vectors $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$.

$$\mathbf{X}^{-1}\mathbf{A}\mathbf{X} = \mathbf{\Lambda}$$
$$\mathbf{X} = \frac{1}{\sqrt{18}}\begin{bmatrix} -1 & 4-i \\ 4+i & 1 \end{bmatrix}$$
$$\mathbf{X}^{-1} = \mathbf{X} = (\mathbf{X}^{\star})^T$$

Let $a = 4 + i$, $a^{\star} = 4 - i$, $a^{\star}a = 17$

$$\begin{aligned}
\mathbf{X}^{-1}\mathbf{A}\mathbf{X} &= \frac{1}{18}\begin{bmatrix} -1 & a^{\star} \\ a & 1 \end{bmatrix}\begin{bmatrix} 2 & a^{\star} \\ a & -14 \end{bmatrix}\begin{bmatrix} -1 & a^{\star} \\ a & 1 \end{bmatrix} \\
&= \frac{1}{18}\begin{bmatrix} -1 & a^{\star} \\ a & 1 \end{bmatrix}\begin{bmatrix} 15 & 3a^{\star} \\ -15a & 3 \end{bmatrix} \\
&= \frac{1}{18}\begin{bmatrix} -15(1+17) & 0 \\ 0 & 3(17+1) \end{bmatrix} = \begin{bmatrix} -15 & 0 \\ 0 & 3 \end{bmatrix}
\end{aligned}$$

**X** diagonalizes **A**.

9. Given the matrices **A** and **B** as

$$\mathbf{A} = \begin{pmatrix} -\frac{1}{3} & \sqrt{\frac{2}{3}} & \frac{\sqrt{2}}{3} \\ \sqrt{\frac{2}{3}} & 0 & \frac{1}{\sqrt{3}} \\ \frac{\sqrt{2}}{3} & \frac{1}{\sqrt{3}} & -\frac{2}{3} \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} \frac{5}{3} & \frac{1}{\sqrt{6}} & -\frac{1}{3\sqrt{2}} \\ \frac{1}{\sqrt{6}} & \frac{3}{2} & \frac{1}{2\sqrt{3}} \\ -\frac{1}{3\sqrt{2}} & \frac{1}{2\sqrt{3}} & \frac{11}{6} \end{pmatrix}.$$

Show that **A** and **B** commute. Find their eigenvalues and eigenvectors, and obtain a unitary transformation matrix **U** that diagonalizes both **A** and **B**.

**Answer:**

**A**=

| | | |
|---|---|---|
| −.33333 | .81650 | .47140 |
| .81650 | .00000 | .57735 |
| .47140 | .57735 | −.66667 |

**B**=

| | | |
|---|---|---|
| 1.66667 | .40825 | −.23570 |
| .40825 | 1.50000 | .28868 |
| −.23570 | .28868 | 1.83333 |

**Answer: #9, continued**

COMMUTATOR (**AB** − **BA**) :

| | | |
|---|---|---|
| .00000 | .00000 | .00000 |
| .00000 | .00000 | .00000 |
| .00000 | .00000 | .00000 |

MATRIX BEFORE DIAGONALIZATION:

| | $\|1\rangle$ | $\|2\rangle$ | $\|3\rangle$ |
|---|---|---|---|
| $\langle 1\|$ = | 1.66667 | .40825 | −.23570 |
| $\langle 2\|$ = | .40825 | 1.50000 | .28868 |
| $\langle 3\|$ = | −.23570 | .28868 | 1.83333 |

EIGENVALUES AND EIGENVECTORS:

| | # 1 | # 2 | # 3 |
|---|---|---|---|
| Value: | 1.0000 | 2.0000 | 2.0000 |
| Vector: | | | |
| $\langle 1\|$ = | .57735 | −.70711 | .40825 |
| $\langle 2\|$ = | .22116 | −.34588 | −.91184 |
| $\langle 3\|$ = | .78597 | .61674 | −.04331 |

MATRIX BEFORE DIAGONALIZATION:

| | $\|1\rangle$ | $\|2\rangle$ | $\|3\rangle$ |
|---|---|---|---|
| $\langle 1\|$ = | −.33333 | .81650 | .47140 |
| $\langle 2\|$ = | .81650 | .00000 | .57735 |
| $\langle 3\|$ = | .47140 | .57735 | −.66667 |

EIGENVALUES AND EIGENVECTORS:

| | # 1 | # 2 | # 3 |
|---|---|---|---|
| Value: | −1.0000 | −1.0000 | −1.0000 |
| Vector: | | | |
| $\langle 1\|$ = | −.22217 | −.34509 | .91190 |
| $\langle 2\|$ = | .78569 | −.61718 | −.04214 |
| $\langle 3\|$ = | .57735 | .70711 | −.40825 |

10. Obtain eigenvalues and eigenvectors of the matrix

$$\mathbf{H} = \begin{pmatrix} 1 & 2\alpha & 0 \\ 2\alpha & 2+\alpha & 3\alpha \\ 0 & 3\alpha & 3+2\alpha \end{pmatrix}$$

to second order in the small parameter $\alpha$.

**Answer:**

$$\mathbf{H} = \begin{bmatrix} 1 & 2\alpha & 0 \\ 2\alpha & 2+\alpha & 3\alpha \\ 0 & 3\alpha & 3+2\alpha \end{bmatrix}$$

$$\mathbf{H} = \mathbf{H}^\circ + \mathbf{H}'$$

$$\mathbf{H}^\circ = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3 \end{bmatrix} \quad , \quad \mathbf{H}' = \alpha \begin{bmatrix} 0 & 2 & 0 \\ 2 & 1 & 3 \\ 0 & 3 & 2 \end{bmatrix}$$

Energy corrected to second order:

$$E_i = E_i^\circ + \langle i|\mathbf{H}'|i\rangle + \sum_{i \neq j} \frac{|\langle i|\mathbf{H}'|j\rangle|^2}{E_i^\circ - E_j^\circ}$$

$$\langle 1|\mathbf{H}'|1\rangle = 0$$
$$\langle 1|\mathbf{H}'|2\rangle = 2\alpha$$
$$\langle 1|\mathbf{H}'|3\rangle = 0$$
$$\langle 2|\mathbf{H}'|2\rangle = \alpha$$
$$\langle 2|\mathbf{H}'|3\rangle = 3\alpha$$
$$\langle 3|\mathbf{H}'|3\rangle = 2\alpha$$

$$E_1 = 1 + 0 + \frac{(2\alpha)^2}{1-2} = 1 - 4\alpha^2$$

$$E_2 = 2 + \alpha + \left\{ \frac{(2\alpha)^2}{2-1} + \frac{(3\alpha)^2}{2-3} \right\} = 2 + \alpha - 5\alpha^2$$

$$E_3 = 3 + 2\alpha + \frac{(3\alpha)^2}{3-2} = 3 + 2\alpha + 9\alpha^2$$

$$|i\rangle = |i\rangle^\circ + \sum_{i \neq j} \frac{H_{ij}}{E_i^\circ - E_j^\circ} |j\rangle^\circ$$

$$|1\rangle = |1\rangle^\circ - 2\alpha\,|2\rangle^\circ$$
$$|2\rangle = |2\rangle^\circ + 2\alpha\,|1\rangle^\circ - 3\alpha\,|3\rangle^\circ$$
$$|3\rangle = |3\rangle^\circ + 3\alpha\,|2\rangle^\circ$$

**Answer: # 10, continued**
Checking orthogonality:

$$\langle 1|2\rangle = 0$$
$$\langle 1|3\rangle = -6\alpha^2 \quad ; \quad \alpha \ll 1, \text{so approaches zero}$$
$$\langle 2|3\rangle = 0$$

11. A particle of mass $m$ is confined to an infinite potential box with potential

$$V(x) = \begin{cases} \infty, & x < 0, x > L, \\ k\left(1 - \frac{x}{L}\right), & 0 \le x \le L. \end{cases}$$

Calculate the ground and fourth excited-state energies of the particle in this box using first-order perturbation theory. Obtain the ground and fourth excited-state wavefunctions to first order, and sketch their appearance. How do they differ from the corresponding unperturbed wavefunctions?

**Answer:** Particle of mass $m$ confined a perturbed square well potential.

$$\psi_n^\circ(x) = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi}{L}x$$
$$V(x) = \begin{cases} \infty, & x < 0, x > L \\ k\left(1 - \frac{x}{L}\right), & 0 \le x \le L \end{cases}$$
$$\mathbf{H}' = k\left(1 - \frac{x}{L}\right)$$

$$\langle\psi_n^\circ|\mathbf{H}'|\psi_n^\circ\rangle = k - \frac{k}{L}\left(\frac{2}{L}\right)\left(\frac{L}{n\pi}\right)^2 \int_0^{n\pi} x\sin^2 x dx$$
$$= k - \frac{2k}{(n\pi)^2}\frac{(n\pi)^2}{4} = \frac{1}{2}k$$
$$\langle\psi_n^\circ|\mathbf{H}'|\psi_m^\circ\rangle = k\,\langle\psi_n^\circ|\psi_m^\circ\rangle - \frac{2k}{L^2}\int_0^L x\left(\sin\frac{n\pi}{L}x\right)\left(\sin\frac{m\pi}{L}x\right)dx$$

$\sin A \sin B = \frac{1}{2}[\cos(A-B) - \cos(A+B)]$

$$\langle\psi_n^\circ|\mathbf{H}'|\psi_m^\circ\rangle = \frac{-k}{L^2}\left[\int_0^L x\cos\frac{(n-m)\pi}{L}xdx - \int_0^L x\frac{\cos(n+m)}{L}xdx\right]$$
$$= \frac{-k}{L^2}\left[\frac{L^2}{(n-m)^2\pi^2}\int_0^{(n-m)\pi} x\cos xdx - \frac{L^2}{(n+m)^2\pi^2}\int_0^{(n+m)\pi} x\cos xdx\right]$$

$n \pm m = \text{even}$, $\langle\psi_n^\circ|\mathbf{H}'|\psi_m^\circ\rangle = 0$

**Answer: #11, continued**

$n \pm m$ = odd,

$$\langle\psi_n^\circ|\mathbf{H}'|\psi_m^\circ\rangle = \frac{+2k}{\pi^2}\left[\frac{1}{(n-m)^2} - \frac{1}{(n+m)^2}\right] = \frac{2k}{\pi^2}\left[\frac{4nm}{(n+m)^2(n-m)^2}\right]$$

$$\langle\psi_1^\circ|\mathbf{H}'|\psi_2^\circ\rangle = \frac{2k}{\pi^2}\left(\frac{8}{9}\right)$$

$$\langle\psi_1^\circ|\mathbf{H}'|\psi_4^\circ\rangle = \frac{2k}{\pi^2}\left(\frac{16}{225}\right)$$

$$\langle\psi_4^\circ|\mathbf{H}'|\psi_3^\circ\rangle = \frac{2k}{\pi^2}\left(\frac{48}{49}\right)$$

$$\langle\psi_4^\circ|\mathbf{H}'|\psi_3^\circ\rangle = \frac{2k}{\pi^2}\left(\frac{80}{81}\right)$$

$$\langle\psi_4^\circ|\mathbf{H}'|\psi_7^\circ\rangle = \frac{2k}{\pi^2}\left(\frac{112}{1089}\right)$$

$\Delta n \geq 3$ perturbations contribute extraordinarily little relative to $\Delta n = 1$

$$\begin{aligned} E_1 &= E_1^\circ + \langle\psi_1^\circ|\mathbf{H}'|\psi_1^\circ\rangle \\ &= \alpha + \frac{1}{2}k \qquad ; \alpha = \frac{h^2}{8mL^2} \\ E_4 &= E_4^\circ + \langle\psi_4^\circ|\mathbf{H}'|\psi_4^\circ\rangle \\ &= 16\alpha + \frac{1}{2}k \end{aligned}$$

To first order

$$|\psi_1\rangle = \left|\psi_1^\circ\right\rangle - \frac{2k}{\pi^2\alpha}\left(\frac{8}{27}\right)\left|\psi_2^\circ\right\rangle$$

$$|\psi_4\rangle = \left|\psi_4^\circ\right\rangle + \frac{2k}{\pi^2\alpha}\left[\left(\frac{48}{343}\right)\left|\psi_3^\circ\right\rangle - \left(\frac{80}{729}\right)\left|\psi_5^\circ\right\rangle\right]$$

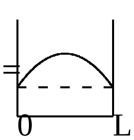
We can rewrite the $\psi$'s in terms of a single parameter, $\beta$

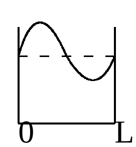
$$|\psi_1\rangle = \left|\psi_1^\circ\right\rangle - 0.296\beta\left|\psi_2^\circ\right\rangle$$

$$|\psi_4\rangle = \left|\psi_4^\circ\right\rangle + 0.140\beta\left|\psi_3^\circ\right\rangle - 0.110\beta\left|\psi_5^\circ\right\rangle$$

$$|\beta| \ll 1 \qquad ; \qquad \beta = \frac{2k}{\pi^2\alpha}$$

Establishing the qualitative effect on $|\psi_1\rangle$ is simple

$\left|\psi_1^\circ\right\rangle =$ 

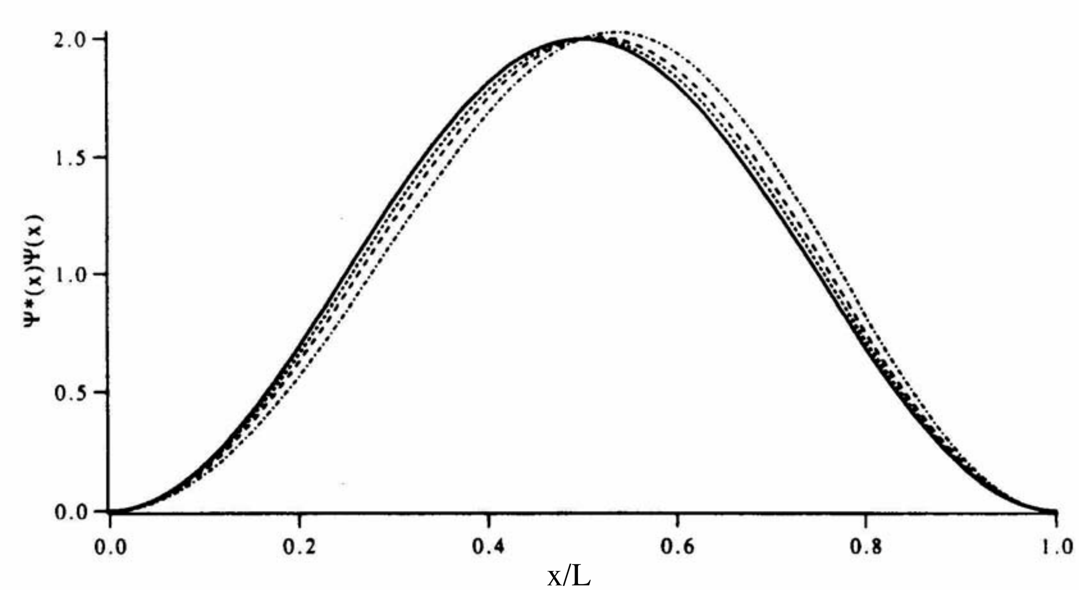

, $\left|\psi_1^\circ\right\rangle =$ 


Mixing in $-0.296\beta\left|\psi_2^\circ\right\rangle$ makes $|\psi_1\rangle$ asymmetric, with a slightly increased probability of finding the particle on "L–side" of the well.

**Answer: #11, continued**

$n \pm m$ = odd,

$$|\psi_1\rangle = |\psi_1^\circ\rangle - 0.296\beta\,|\psi_2^\circ\rangle$$
$$\beta = 0, 0.05, 0.1, 0.2$$




$$|\psi_4\rangle = |\psi_4^\circ\rangle + 0.140\beta\,|\psi_3^\circ\rangle - 0.110\beta\,|\psi_5^\circ\rangle$$
$$\beta = 0, 0.2, 0.5, 1$$