8   Vibrational Modes and Time-Dependent Quantum Mechanics

12/2:   1. Consider the molecule BeH_2.

   (a) How many degrees of freedom does the molecule possess?

   Answer. BeH_2 has three atoms, each of which is completely described by three coordinates. Thus, BeH_2 has $3N = \boxed{9}$ degrees of freedom.   □

   (b) For each degree of freedom, there is a normal mode of vibration. Enumerate each of the normal modes of vibration.

   Answer. Since BeH_2 is a linear molecule, it has $3N - 5 = 4$ vibrational degrees of freedom/normal modes. These are a singly degenerate symmetric stretch, a doubly degenerate bending mode (one mode in each of the two axes orthogonal to the principal axis), and a singly degenerate asymmetric stretch.   □

   (c) Which of these modes are IR active? Explain.

   Answer. The $\boxed{\text{asymmetric stretch}}$ and $\boxed{\text{bending modes}}$ are IR active since both are vibrations during which the dipole moment of the molecule varies. The symmetric stretch is IR inactive for the same reason.   □

   2. Using the worksheet "Normal Modes" with the Quantum Chemistry Toolbox for Maple, you will compute the optimized geometry and the vibrational normal modes of hypochlorous acid (or HOCl) using the electronic structure theory known as the Hartree-Fock method. After using the worksheet to perform the calculations and view the animations of the normal modes on your computer, answer the following questions.

   (a) In performing the geometry optimization of HOCl, what are the computed bond lengths and angle in the STO-3G basis set, and how do these bond lengths and angle compare to the experimental values?

   Answer. The computed bond lengths and angle are $\boxed{1.006\,\text{Å}}$, $\boxed{1.738\,\text{Å}}$, and $\boxed{100.158°}$, respectively. The $\boxed{\text{computed bond lengths are greater than the experimental bond lengths}}$, and the $\boxed{\text{computed bond angle is less than the experimental bond angle}}$; as per the NIST database, the experimental values are $0.964\,\text{Å}$, $1.689\,\text{Å}$, and $102.450°$, respectively.   □

   (b) Give the computed and experimental values of the three normal modes, and based on the computed animations, draw an illustrative sketch for each normal mode.

   Answer. The computed values are $\boxed{4165\,\text{cm}^{-1}}$ for the $O-H$ stretch, $\boxed{1535\,\text{cm}^{-1}}$ for the bend, and $\boxed{983\,\text{cm}^{-1}}$ for the $Cl-O$ stretch. The experimental values are $\boxed{3609\,\text{cm}^{-1}}$ for the $O-H$ stretch, $\boxed{1239\,\text{cm}^{-1}}$ for the bend, and $\boxed{724\,\text{cm}^{-1}}$ for the $Cl-O$ stretch.
   Sketches of the normal modes: □

(a) $O-H$ stretch.   (b) Bend.   (c) $O-Cl$ stretch
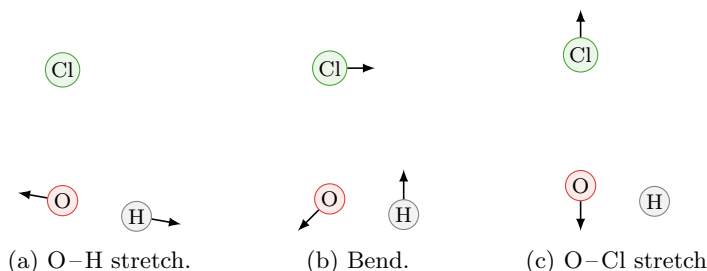
(c) Repeat parts (a) and (b) for the triatomic molecule sulfur dioxide (or SO_2) by changing at the top of the worksheet r_1 and r_2 to the experimental bond length of 1.43 Å, θ to 119°, and the atoms in the variable *molec* from H, O, and Cl to O, S, and O, respectively.

Proof. The computed bond lengths and angle are $\boxed{1.507\,\text{Å}}$, $\boxed{1.559\,\text{Å}}$, and $\boxed{108.633°}$, respectively. The $\boxed{\text{computed bond lengths are greater than the experimental bond lengths}}$, and the $\boxed{\text{computed bond angle is less than the experimental bond angle}}$; as per the NIST database, the experimental values are 1.432 Å, 1.432 Å, and 119.500°, respectively.

The computed values are $\boxed{1151\,\text{cm}^{-1}}$ for the asymmetric stretch, $\boxed{1126\,\text{cm}^{-1}}$ for the symmetric stretch, and $\boxed{462\,\text{cm}^{-1}}$ for the bend. The experimental values are $\boxed{1381\,\text{cm}^{-1}}$ for the asymmetric stretch, $\boxed{1168\,\text{cm}^{-1}}$ for the symmetric stretch, and $\boxed{526\,\text{cm}^{-1}}$ for the bend. Sketches of the normal modes: □

(a) Symmetric stretch.   (b) Asymmetric stretch.   (c) Bend.
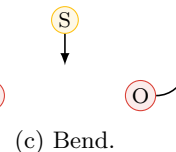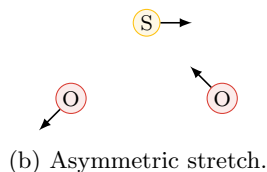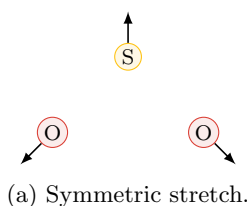
3. The wave functions of the harmonic oscillator may be categorized as being either even or odd. They are even when $\psi(-x) = \psi(x)$ and they are odd when $\psi(-x) = -\psi(x)$.

(a) Using this symmetry property, compute the probability for a transition from $n = 0$ to $n = 2$.

Answer. The probability for a transition from $n = 0$ to $n = 2$ is proportional to the transition dipole moment $(\mu_x)_{02}$, so we will compute that first. From the definition, we have that

$$(\mu_x)_{02} = \int_{-\infty}^{\infty} \psi_2^* \mu_x \psi_0 \, \mathrm{d}x$$
$$= \mu_0 \int_{-\infty}^{\infty} \psi_2^* \psi_0 \, \mathrm{d}x + \left(\frac{\mathrm{d}\mu}{\mathrm{d}x}\right)_0 \int_{-\infty}^{\infty} \psi_2^* x \psi_0 \, \mathrm{d}x$$

The left integral above can be evaluated via symmetry. First off, note that ψ_0 and ψ_2 are even functions. Additionally, taking the conjugate of ψ_2 does not change the fact that it's an even function, and nor does taking the product $\psi_2^* \psi_0$:

$$(\psi_2^* \psi_0)(-x) = \psi_2^*(-x)\psi_0(-x) = \psi_2^*(x)\psi_0(x) = (\psi_2^* \psi_0)(x)$$

Thus, making use of the even-ness of $\psi_2^* \psi_0$, we can determine that

$$\int_{-\infty}^{\infty} \psi_2^* \psi_0 \, \mathrm{d}x = \int_{-\infty}^{0} (\psi_2^* \psi_0)(x) \, \mathrm{d}x + \int_{0}^{\infty} (\psi_2^* \psi_0)(x) \, \mathrm{d}x$$
$$= -\int_{0}^{-\infty} (\psi_2^* \psi_0)(x) \, \mathrm{d}x + \int_{0}^{\infty} (\psi_2^* \psi_0)(x) \, \mathrm{d}x$$
$$= -\int_{0}^{\infty} (\psi_2^* \psi_0)(-x) \, \mathrm{d}x + \int_{0}^{\infty} (\psi_2^* \psi_0)(x) \, \mathrm{d}x$$
$$= -\int_{0}^{\infty} (\psi_2^* \psi_0)(x) \, \mathrm{d}x + \int_{0}^{\infty} (\psi_2^* \psi_0)(x) \, \mathrm{d}x$$
$$= 0$$

As to the other integral, we expand in terms of the harmonic oscillator wave functions, substitute $\xi = \sqrt{\alpha}x$, make use of the Hermite polynomial recursion formula

$$\xi H_n(\xi) = n H_{n-1}(\xi) + \tfrac{1}{2}H_{n+1}(\xi)$$

and invoke the orthogonality of the Hermite polynomials with respect to the weighting function $e^{-\xi^2}$ to get

$$\int_{-\infty}^{\infty} \psi_2^* x \psi_0 \, \mathrm{d}x = N_2 N_0 \int_{-\infty}^{\infty} x H_2(\sqrt{\alpha}x) H_0(\sqrt{\alpha}x) e^{-\alpha x^2} \, \mathrm{d}x$$

$$= \frac{N_2 N_0}{\alpha} \int_{-\infty}^{\infty} \xi H_2(\xi) H_0(\xi) e^{-\xi^2} \, \mathrm{d}\xi$$

$$= \frac{N_2 N_0}{\alpha} \int_{-\infty}^{\infty} [2H_1(\xi) + \tfrac{1}{2}H_3(\xi)] H_0(\xi) e^{-\xi^2} \, \mathrm{d}\xi$$

$$= 0$$

Therefore, the probability of the transition is zero since the overall transition dipole moment is equal to zero. □

(b) In general, what may be said regarding transitions between even states?

Answer. Transitions between even states are forbidden . □

(c) Are these results consistent with the more general selection rules derived in class?

Answer. Yes . In class, we derived that only transitions with $\Delta n = \pm 1$ may be allowed, so transitions between even states (with $\Delta n = \pm 2, \pm 4, \pm 6, \dots$) should certainly be forbidden. □

4. The molecule $^{39}\text{K}^{127}\text{I}$ has a microwave spectrum of equally-spaced lines.

(a) In a laboratory at the University of Chicago, the spacing is measured to be $3634\,\text{MHz}$. What is the bond length of $^{39}\text{K}^{127}\text{I}$?

Answer. From McQuarrie and Simon (1997), we know that

$$2B = 3.634 \times 10^9 \, \text{s}^{-1}$$

and that

$$2B = \frac{h}{4\pi^2 \mu R_e^2}$$

where R_e is the bond length. This combined with the fact that the reduced mass of $^{39}\text{K}^{127}\text{I}$ is

$$\mu = \frac{39 \cdot 127}{39 + 127} = 4.96 \times 10^{-26} \, \text{kg}$$

implies that

$$R_e = \sqrt{\frac{h}{4\pi^2 \mu \cdot 2B}}$$

$$\boxed{R_e = 3.05 \, \text{Å}}$$

□

(b) In the far infrared region, the molecule $^{39}\text{K}^{35}\text{Cl}$ has an intense line at $278.0\,\text{cm}^{-1}$. Compute the force constant and the period of vibration for $^{39}\text{K}^{35}\text{Cl}$.

Answer. From McQuarrie and Simon (1997), we know that

$$\tilde{\nu} = 2.780 \times 10^4 \, \text{m}^{-1}$$

and that

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where k is the force constant. This combined with the fact that the reduced mass of $^{39}\text{K}^{35}\text{Cl}$ is

$$\mu = \frac{39 \cdot 35}{39 + 35} = 3.06 \times 10^{-26} \, \text{kg}$$

implies that

$$k = 4\pi^2 c^2 \tilde{\nu}^2 \mu$$

$$\boxed{k = 84.0 \, \text{N/m}}$$

Additionally, we have that

$$T = 2\pi \sqrt{\frac{\mu}{k}}$$

$$\boxed{T = 1.20 \times 10^{-13} \, \text{s}}$$

$\square$

5. Using the worksheet "Molecular Spectroscopy" with the Quantum Chemistry Toolbox for Maple, you will compute the rotational spectra for the ground and first-excited states of hydrogen chloride HCl. You will compute the rotational spectra by two methods: (i) a normal-mode approximation in which the vibrational and rotational energies are modeled with the harmonic oscillator and the three-dimensional rigid rotor approximations, respectively, and (ii) an *ab initio* approximation in which the rovibrational Schrödinger equation is solved for the rovibrational energies with the potential energy curve computed by density functional theory (DFT). After using the worksheet to perform the calculations, answer the following questions.

   (a) What are the rovibrational energies in reciprocal centimeters of the P and R branches in the normal-modes approximation?

   Answer. We have

$P = 2694 \, \text{cm}^{-1}$	$R = 2733 \, \text{cm}^{-1}$
$P = 2674 \, \text{cm}^{-1}$	$R = 2753 \, \text{cm}^{-1}$
$P = 2654 \, \text{cm}^{-1}$	$R = 2772 \, \text{cm}^{-1}$
$P = 2634 \, \text{cm}^{-1}$	$R = 2792 \, \text{cm}^{-1}$
$P = 2615 \, \text{cm}^{-1}$	$R = 2812 \, \text{cm}^{-1}$

   $\square$

   (b) How does the spacing between rovibrational energies in part (a) change with J?

   Answer. The spacing $\boxed{\text{stays the same}}$. $\square$

   (c) What are the rovibrational energies of the P and R branches in the *ab initio* approximation?

Answer. We have

$P = 2552\,\mathrm{cm}^{-1}$
$P = 2481\,\mathrm{cm}^{-1}$
$P = 2408\,\mathrm{cm}^{-1}$
$P = 2333\,\mathrm{cm}^{-1}$
$P = 2256\,\mathrm{cm}^{-1}$

$R = 2689\,\mathrm{cm}^{-1}$
$R = 2753\,\mathrm{cm}^{-1}$
$R = 2816\,\mathrm{cm}^{-1}$
$R = 2875\,\mathrm{cm}^{-1}$
$R = 2932\,\mathrm{cm}^{-1}$

□

(d) How does the spacing between rovibrational energies in part (c) change with J?

Answer. On the P branch, the spacing increases as J increases. On the R branch, the spacing decreases as J decreases □

(e) Compute the wavelength of a photon required to excite a molecule from $n = 0$ and $J = 0$ to $n = 1$ and $J = 1$.

Answer. Using the *ab initio* approximation, the first listed R value corresponds to the desired $0, 0 \to 1, 1$ transition. Thus,

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{2.689 \times 10^5\,\mathrm{m}^{-1}}$$

$$\boxed{\lambda = 3.72 \times 10^{-6}\,\mathrm{m}}$$

□

(f) In what region of the electromagnetic spectrum does this energy lie?

Answer. It lies in the $\boxed{\text{infrared}}$ region. □

6. If the ground state and the excited state have a degeneracy of g_1 and g_2, respectively, the Einstein A coefficient is given by

$$A = \frac{16\pi^3 \nu^3 g_1}{3\epsilon_0 h c^3 g_2} |\mu|^2$$

where $|\mu|$ is the **transition dipole moment**. Consider the $1s \to 2p$ absorption of gaseous hydrogen $H_{(g)}$, which is observed at 121.8 nm. The radiative lifetime of the triply degenerate excited $2p$ state of $H_{(g)}$ is 1.6×10^{-9} s. Compute the value of the transition dipole moment for this transition.

Answer. The ground state as a singly degenerate s orbital and the excited state as a triply degenerate p orbital have degeneracies

$$g_1 = 1 \qquad\qquad g_2 = 3$$

The wavelength of light absorbed in the transition is

$$\lambda = \frac{c}{\nu} = 1.218 \times 10^{-7}\,\mathrm{m}$$

The radiative lifetime is

$$\tau_R = \frac{1}{A} = 1.6 \times 10^{-9}\,\mathrm{s}$$

Therefore, the transition dipole moment is

$$|\mu| = \sqrt{\frac{3\epsilon_0 h c^3 g_2 A}{16\pi^3 \nu^3 g_1}}$$

$$\boxed{|\mu| = 1.1 \times 10^{-29}\,\mathrm{C\,m}}$$

□

7. The He-Ne laser has a line at $3391.3\,\text{nm}$ from the $5s\,{}^1P_1 \to 3p\,{}^3P_2$ transition. In the *Table of Atomic Energy Levels* by Charlotte Moore, the energies of these levels are $166\,658.484\,\text{cm}^{-1}$ and $163\,710.581\,\text{cm}^{-1}$, respectively. Compute the wavelength of this transition, and explain why the result is not $3391.3\,\text{nm}$. (Hint: Consult Example 8-10 in McQuarrie and Simon (1997).)

8. Chemical lasers generate population inversions through chemical reactions. In the HF gas laser, the gaseous HF is produced by the reaction

$$\text{F}_{(g)} + \text{H}_{2\,(g)} \longrightarrow \text{HF}_{(g)} + \text{H}_{(g)}$$
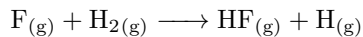
The major product of this reaction is $\text{HF}_{(g)}$ in the excited $n = 2$ vibrational state. The reaction creates a population inversion in which $N(n)$, the number of molecules in each vibrational state n, is much larger for $n = 2$ than $n = 0$ or $n = 1$. The output of the $\text{HF}_{(g)}$ laser corresponds to transitions between vibrational lines of the $n = 2 \to n = 1$ transition ($\lambda = 2.7 - 3.2\,\mu\text{m}$). Why isn't there any lasing action from $n = 2 \to n = 0$ even though there is a population inversion between these states?