Problem Set 5 Solutions

1. How many vibrational modes do the following molecules or ions possess? [Hint: Drawing Lewis structures may be useful in some cases.]

In all of the cases, there will be \(3N-6\) vibrations for nonlinear molecules (or ions) and \(3N-5\) vibrations for linear molecules (or ions).

a.) \(\text{CH}_4\)

\(\text{CH}_4\) is a nonlinear molecule; therefore, it has \(3\times5-6 = 9\) vibrational modes.

b.) \(\text{HCN}\)

\(\text{HCN}\) is a linear molecule from the Lewis structure shown below.

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{N}
\end{array}
\]

Therefore, \(\text{HCN}\) possesses \(3\times3-5 = 4\) vibrational modes.

c.) \(\text{NH}_3\)

\(\text{NH}_3\) is a nonlinear molecule; therefore, it has \(3\times4-6 = 6\) vibrational modes.

d.) \(\text{NO}_3^-\)

\(\text{NO}_3^-\) is a nonlinear molecular ion; therefore, it has \(3\times4-6 = 6\) vibrational modes. [Note that \(\text{NO}_3^-\) is a planar molecule, not a linear molecule.]
2. Consider the molecule $\text{N}_2\text{O}$, with connectivity N-N-O.

a.) Is the molecule linear or nonlinear? How many vibrational modes does $\text{N}_2\text{O}$ possess?

$\text{N}_2\text{O}$ is a linear molecule (you can predict that from the Lewis dot structure, shown below).

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{O}
\end{array}
\]

Since $\text{N}_2\text{O}$ is linear, the number of vibrational modes is $3N - 5$, where $N$ is the number of atoms.

Thus, $\# \text{ modes} = 3 \times 3 - 5 = 4 \text{ modes}$.

b.) Describe the vibrational modes of $\text{N}_2\text{O}$.

(1) N-N stretch
(2) N-O stretch
(3, 4) degenerate N-N-O bends

Note here that the two stretching vibrations are not labeled as 'symmetric' and 'antisymmetric'. This is because for a molecule such as $\text{N}_2\text{O}$, the two bonds are not identical and therefore no symmetry combinations exist. In contrast, the two bonds in molecules such as $\text{H}_2\text{O}$ or $\text{SO}_2$ are identical, and so the stretching vibrations occur as symmetric and antisymmetric combinations.

c.) For $\text{N}_2\text{O}$, determine which of the vibrational modes are IR active.

(1) N-N stretch - IR active
(2) N-O stretch - IR active
(3, 4) degenerate N-N-O bends - IR active

The dipole moment changes in all three of the vibrations; therefore, all are IR active. A gas phase IR spectrum is available from NIST, showing the IR absorption peaks for the three IR active modes (at about 590, 1290, and 2220 cm$^{-1}$, for the bends, N-O stretch, and N-N stretch, respectively), as well as several overtone and combination bands. The spectrum is reproduced below for your information.
3. Consider the molecule NO$_2$, with connectivity O-N-O.

a.) Is the molecule linear or nonlinear? How many vibrational modes does NO$_2$ possess?

NO$_2$ is a nonlinear molecule (you again can predict that from the Lewis dot structure for one resonance contributor, shown below).

Since NO$_2$ is nonlinear, the number of vibrational modes is $3N - 6$, where $N$ is the number of atoms.

Thus, # modes = 3*3 - 6 = 3 modes.

b.) Describe the vibrational modes of NO$_2$.

(1) N-O symmetric stretch
(2) N-O antisymmetric stretch
(3) O-N-O bend

c.) For NO$_2$, determine which of the vibrational modes are IR active.

(1) N-O symmetric stretch - IR active
(2) N-O antisymmetric stretch - IR active
(3) O-N-O bend - IR active

As for water (which has a similar bent structure), the dipole moment changes in all three of the vibrations; therefore, all are IR active.

4. Consider the formaldehyde molecule, H$_2$CO.

a.) How many vibrational modes does formaldehyde possess?

Since formaldehyde is nonlinear, the number of vibrational modes is $3N - 6$, where $N$ is the number of atoms.

Thus, # modes = 3*4 - 6 = 6 modes.

b.) Describe the vibrational modes of formaldehyde (simple sketches may help).

(1) symmetric C-H stretch
(2) antisymmetric C-H stretch
(3) C-O stretch
(4) H-C-H bend (also referred to as the CH$_2$ scissors mode)
(5) CH$_2$ in-plane rock
(6) CH$_2$ out-of-plane bend (also referred to as the CH$_2$ wagging mode)
The first three modes listed above are similar to those we have seen before. Many times sketches of the vibrational modes use arrows to indicate the direction of motion of the atoms. Typical sketches of this type are included below for each of the vibrational modes of formaldehyde.

![Sketches of vibrational modes]

Note that for the last sketch, corresponding to the CH$_2$ out-of-plane wag, the plus and minus signs indicate that the atom comes out of the plane of the molecule (+) or goes back into the plane (–).

c.) For formaldehyde, list the vibrational modes that are IR active.

All the modes are IR active. Each one leads to a change in the dipole moment (either a change in magnitude or a change in direction).
5.) The molecule hydrogen peroxide, \( \text{H}_2\text{O}_2 \), is a nonplanar molecule with an H-O-O-H torsional angle of about 120 degrees.

a.) **How many vibrational modes does \( \text{H}_2\text{O}_2 \) have?**

Since \( \text{H}_2\text{O}_2 \) is nonlinear, the number of vibrational modes is \( 3N-6 \), where \( N \) is the number of atoms.

Thus, \( \# \text{ modes} = 3 \times 4 - 6 = 6 \) modes.

b.) **Describe the vibrational modes of \( \text{H}_2\text{O}_2 \) (simple sketches may help).**

(1) symmetric O-H stretch
(2) antisymmetric O-H stretch
(3) O-O stretch
(4) symmetric O-O-H bend
(5) antisymmetric O-O-H bend
(6) H-O-O-H torsional vibration

Sketches of the vibrational modes are shown below.

![Sketches of vibrational modes](image)

C.) **List which vibrational modes are IR active.**

(1) symmetric O-H stretch - IR active
(2) antisymmetric O-H stretch - IR active
(3) O-O stretch - IR active (There is only a very small change in the dipole moment, so it is okay if you stated that this mode was not IR active.)
(4) symmetric O-O-H bend - IR active
(5) antisymmetric O-O-H bend - IR active
(6) H-O-O-H torsional vibration - IR active
The ground state wavefunction of the harmonic oscillator is \( \psi_0(x) = N e^{-\alpha x^2/2} \). Determine the normalization constant \( N \).

The normalization constant \( N \) is defined by the equation

\[
N = \frac{1}{\left[ \int_{-\infty}^{\infty} \psi^\dagger(x) \psi(x) \, dx \right]^{1/2}}.
\]

Substituting the form of the wavefunction,

\[
\int_{-\infty}^{\infty} \psi^\dagger(x) \psi(x) \, dx = \int_{-\infty}^{\infty} e^{-\alpha x^2} \, dx.
\]

From the handout on integrals,

\[
\int_{0}^{\infty} e^{-bx^2} \, dx = \frac{1}{2} \left( \frac{\pi}{b} \right)^{1/2}.
\]

This is for only half the range. Since the function is an even function,

\[
\int_{-\infty}^{\infty} e^{-bx^2} \, dx = \left( \frac{\pi}{b} \right)^{1/2}.
\]

Then, making the substitution that \( b = \alpha \), the integral becomes

\[
\int_{-\infty}^{\infty} \psi^\dagger(x) \, \psi(x) \, dx = \int_{-\infty}^{\infty} e^{-\alpha x^2} \, dx = \left( \frac{\pi}{\alpha} \right)^{1/2}.
\]

Substitution into the normalization equation becomes

\[
N = \frac{1}{\left[ \int_{-\infty}^{\infty} \psi^\dagger(x) \, \psi(x) \, dx \right]^{1/2}} = \frac{1}{\left( \frac{\pi}{\alpha} \right)^{1/2}}.
\]

So,

\[
N = \left( \frac{\alpha}{\pi} \right)^{1/4}.
\]
7. The first excited state wavefunction of the harmonic oscillator is given by \( \psi_1(x) = N \cdot 2\sqrt{\alpha} \cdot x e^{-\alpha x^2/2} \), where \( \alpha = \left( \frac{\mu k}{\hbar^2} \right)^{1/2} \). Show that this function is an eigenfunction of the harmonic oscillator Hamiltonian operator and determine the energy eigenvalue. Here, \( N \) is the normalization constant and \( \mu \) is the reduced mass.

In order to show that the function is an eigenfunction, we start by operating the Hamiltonian operator on it,

\[
\hat{H} \psi_1(x) = \left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \right\} N \cdot 2\sqrt{\alpha} \cdot x e^{-\alpha x^2/2}
= -\frac{2N\sqrt{\alpha} \hbar^2}{2\mu} \frac{d^2}{dx^2} \left( x e^{-\alpha x^2/2} \right) + \frac{k}{2} 2N\sqrt{\alpha} \cdot x^3 e^{-\alpha x^2/2}.
\]

Evaluating the first derivative,

\[
\frac{d}{dx} \left( x e^{-\alpha x^2/2} \right) = e^{-\alpha x^2/2} - \alpha x^2 e^{-\alpha x^2/2}
= e^{-\alpha x^2/2} \left( 1 - \alpha x^2 \right).
\]

Evaluating the second derivative,

\[
\frac{d^2}{dx^2} \left( x e^{-\alpha x^2/2} \right) = \frac{d}{dx} \left[ e^{-\alpha x^2/2} \left( 1 - \alpha x^2 \right) \right]
= -2\alpha x e^{-\alpha x^2/2} - \alpha x \left( 1 - \alpha x^2 \right) e^{-\alpha x^2/2}
= -\alpha x e^{-\alpha x^2/2} \left( 3 - \alpha x^2 \right).
\]

Substituting into the Hamiltonian equation,

\[
\hat{H} \psi_1(x) = -\frac{2N\sqrt{\alpha} \hbar^2}{2\mu} \left\{ -\alpha x e^{-\alpha x^2/2} \left( 3 - \alpha x^2 \right) \right\} + \frac{k}{2} 2N\sqrt{\alpha} \cdot x^3 e^{-\alpha x^2/2}
= \left\{ \frac{\hbar^2 \alpha}{2\mu} \left( 3 - \alpha x^2 \right) + k \frac{x^2}{2} \right\} \psi_1(x).
\]
Using the definition of $\alpha$,

\[
\hat{H} \psi_1(x) = \left( \frac{\hbar^2 \alpha}{2 \mu} \right) \left( 3 - \alpha x^2 \right) + \frac{k}{2} x^2 \psi_1(x)
\]

\[
= \left\{ 3 \left( \frac{\hbar^2}{2 \mu} \right) \left( \frac{\mu k}{\hbar^2} \right)^{1/2} - \left( \frac{\hbar^2}{2 \mu} \right) \left( \frac{\mu k}{\hbar^2} \right) x^2 + \frac{k}{2} x^2 \right\} \psi_1(x)
\]

\[
= \left\{ \frac{3}{2} \hbar \left( \frac{k}{\mu} \right)^{1/2} - \frac{k}{2} x^2 + \frac{k}{2} x^2 \right\} \psi_1(x)
\]

\[
= \frac{3}{2} \hbar \left( \frac{k}{\mu} \right)^{1/2} \psi_1(x)
\]

Next, the definition of the harmonic frequency can be used,

\[
\nu_0 = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}
\]

Substituting,

\[
\hat{H} \psi_1(x) = \frac{3}{2} \frac{\hbar}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \psi_1(x),
\]

or

\[
\hat{H} \psi_1(x) = \frac{3}{2} \nu_0 \psi_1(x).
\]

Thus, we see that the function $\psi_1(x)$ is an eigenfunction of the Schrödinger equation for the harmonic oscillator. Since $\hat{H} \psi_1(x) = E_1 \psi_1(x)$, the energy eigenvalue must be given by

\[
E_1 = \frac{3}{2} \nu_0.
\]
8. Recall that two functions \( f(x) \) and \( g(x) \) are said to be orthogonal if

\[
\int_{-\infty}^{\infty} f^*(x) \, g(x) \, dx = 0.
\]

Show that the ground state (\( \nu=0 \)) and first excited state (\( \nu=1 \)) wavefunctions of the harmonic oscillator are orthogonal.

For the two functions to be orthogonal, we must show that

\[
\int_{-\infty}^{\infty} \psi_0^*(x) \, \psi_1(x) \, dx = 0.
\]

The harmonic oscillator functions for the ground and first excited states are

\[
\psi_0(x) = N_0 e^{-\alpha x^2/2} \quad \text{and} \quad \psi_1(x) = 2N_1 \sqrt{\alpha} x e^{-\alpha x^2/2}.
\]

Substituting,

\[
\int_{-\infty}^{\infty} \psi_0^*(x) \, \psi_1(x) \, dx = 2N_0 N_1 \sqrt{\alpha} \int_{-\infty}^{\infty} x \, e^{-\alpha x^2} \, dx.
\]

From the handout on integrals,

\[
\int_{0}^{\infty} x \, e^{-bx^2} \, dx = \frac{1}{2b}.
\]

This is for only half the range. Since the function is an odd function,

\[
\int_{-\infty}^{\infty} x \, e^{-bx^2} \, dx = 0.
\]

Then, the orthogonality integral is

\[
\int_{-\infty}^{\infty} \psi_0^*(x) \, \psi_1(x) \, dx = 2N_0 N_1 \sqrt{\alpha} \int_{-\infty}^{\infty} x \, e^{-\alpha x^2} \, dx = 0.
\]

Therefore, the two functions are orthogonal.
9. Determine the average value of the position for the ground state of the harmonic oscillator.

The expectation value of position is defined as

\[ \langle x \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi \, dx. \]

The wavefunction for the ground state of the harmonic oscillator is

\[ \psi_0(x) = N_0 e^{-\alpha x^2/2}, \]

where the normalization constant \( N_0 \) is given by

\[ N_0 = \left( \frac{\alpha}{\pi} \right)^{1/4}. \]

Substituting into the expression for the expectation value,

\[
\langle x \rangle = \int_{-\infty}^{\infty} \psi^* (\hat{x}) \psi \, dx \\
= \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} x e^{-\alpha x^2/2} \, dx \\
= \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2} \, dx.
\]

This integral is the same one evaluated in Problem 8, and it was shown to be 0. Therefore,

\[ \langle x \rangle = 0. \]
10. Determine the average value of the momentum for the ground state of the harmonic oscillator.

The expectation value of momentum for normalized wavefunctions is defined as

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* (x) \hat{p}_x \psi(x) \, dx .$$

The wavefunction for the ground state of the harmonic oscillator is

$$\psi_0(x) = N_0 e^{-\alpha x^2 / 2} ,$$

where the normalization constant $N_0$ is given by

$$N_0 = \left( \frac{\alpha}{\pi} \right)^{1/4} .$$

Substituting into the expression for the expectation value,

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* (x) \hat{p}_x \psi(x) \, dx = -i \hbar \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2 / 2} \frac{d}{dx} e^{-\alpha x^2 / 2} \, dx .$$

In the last expression above, the definition of the momentum operator,

$$\hat{p}_x = -i \hbar \frac{d}{dx} ,$$

has been used. Now, evaluating the derivative,

$$\frac{d}{dx} e^{-\alpha x^2 / 2} = -\alpha x e^{-\alpha x^2 / 2} .$$

Substituting, the expectation value becomes

$$\langle p_x \rangle = i \alpha \hbar \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2} \, dx .$$

This integral has already been shown to be 0. Therefore,

$$\langle p_x \rangle = 0 .$$
11. What are the most probable positions for the ground and first excited states of the harmonic oscillator?

To determine the most probable value, the maximum in the probability density must be determined. A maximum in a function can be found by setting the derivative equal to zero.

**Ground State**

The wavefunction for the ground state of the harmonic oscillator is

\[ \psi_0(x) = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2 / 2}, \]

and so the probability density is

\[ \psi_0^* (x) \psi_0 (x) = \psi_0^2 (x) = \left( \frac{\alpha}{\pi} \right)^{1/2} e^{-\alpha x^2}. \]

Setting the derivative equal to zero,

\[ \frac{d}{dx} \psi_0^* (x) \psi_0 (x) = 0 \]
\[ \left( \frac{\alpha}{\pi} \right)^{1/2} \frac{d}{dx} e^{-\alpha x^2} = 0 \]
\[ \left( \frac{\alpha}{\pi} \right)^{1/2} \left( -2 \alpha x e^{-\alpha x^2} \right) = 0. \]

Dividing both sides by the constant terms,

\[ x e^{-\alpha x^2} = 0. \]

Since the exponential term is never zero except if \( x \to \infty \), the solution is

\[ x = 0. \]

Thus, the most probable position for the ground state of the harmonic oscillator occurs at \( x = 0 \).

**First Excited State**

The wavefunction for the first excited state of the harmonic oscillator is

\[ \psi_1(x) = 2N_1 \sqrt{\alpha} x e^{-\alpha x^2 / 2}. \]

The probability density for this function is

\[ \psi_1^* (x) \psi_1 (x) = \psi_1^2 (x) = 4 N_1^2 \alpha x^2 e^{-\alpha x^2}. \]
Setting the derivative equal to zero,

\[ \frac{d}{dx} \left\{ \psi_1^*(x) \psi_1 (x) \right\} = 0 \]
\[ 4 N_1^2 \alpha \frac{d}{dx} \left\{ x^2 e^{-\alpha x^2} \right\} = 0 \]
\[ 4 N_1^2 \alpha \left( 2x e^{-\alpha x^2} - 2 \alpha x^3 e^{-\alpha x^2} \right) = 0 \]
\[ 8 N_1^2 \alpha x \left( 1 - \alpha x^2 \right) e^{-\alpha x^2} = 0 \ . \]

Dividing both sides by the constant term \( 8 N_1^2 \alpha \), the equation becomes

\[ x \left( 1 - \alpha x^2 \right) e^{-\alpha x^2} = 0 \ . \]

Since the exponential is never zero unless \( x \to \infty \), the equation can be simplified to

\[ x \left( 1 - \alpha x^2 \right) = 0 \ . \]

This equation has solutions when

\[ x = 0 \quad \text{or} \quad 1 - \alpha x^2 = 0 \ . \]

It is easy to see from a plot of the probability density for the first excited state that the solution \( x = 0 \) corresponds to a node in the wavefunction and therefore a minimum in the probability distribution. The other solution is

\[ 1 - \alpha x^2 = 0 \]
\[ \alpha x^2 = 1 \]
\[ x^2 = \frac{1}{\alpha} \]
\[ x = \pm \frac{1}{\sqrt{\alpha}} \ . \]

Thus, there are two most probable positions for the first excited state of the harmonic oscillator. The most probable positions are \( x = \frac{1}{\sqrt{\alpha}} \) and \( x = -\frac{1}{\sqrt{\alpha}} \).