

Femtochemistry©

by

Mark D. Ellison
Department of Chemistry
Wittenberg University
Springfield, OH 45501

mellison@wittenberg.edu

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Introduction: In this document, you will study the application of a simple solution to the time-dependent Schrödinger equation in the context of understanding the research of Ahmed Zewail, the winner of the 1999 Nobel Prize in chemistry. First, you will review the harmonic oscillator for molecular vibration. Next, you will see how the use of ultrafast lasers to excite molecules leads to a superposition of quantum states. This superposition has time-dependent properties, which you will explore. After completing this document, you will be able to describe the effect of the laser pulse duration on the excited state and correlate that to the implications for studying chemical reactions at the femtosecond scale.

Goal: To introduce the students to the time-dependent Schrödinger equation

Prerequisites:

1. Basic skills with MathCad including defining constants and functions, graphing functions, and integrating.
2. Familiarity with the harmonic oscillator model.
3. Understanding of the concepts of normalization and the wave function as a probability distribution.
4. Read the article "Freezing Atoms in Motion: Principles of Femtochemistry and Demonstration by Laser Stroboscopy by J. S. Baskin and A. H. Zewail, *J. Chem. Ed.*, vol. 78(6), June 2001, pp. 737-51. Discuss the article with instructor and classmates.

Performance Objectives:

1. Plot the harmonic oscillator wavefunction and probability distribution for several energy levels. Describe these and calculate the average displacement and the variance in the displacement.
2. Model the laser pulse. Determine its center frequency, wavelength, and its energy distribution.
3. Determine which energy level(s) will be populated after absorption of the laser light and the relative populations.
4. Define the probability distribution and graph it. Describe the distribution at different times.
5. Calculate the average displacement and the variance at different times.
6. Explore the effect of pulse length on the probability distribution.
7. Correlate the probability distribution to the ability to study chemical reactions at the femtosecond time scale.

Introduction

This MathCad document is designed to introduce students to the time-dependent Schrodinger Equation. It does so by exploring the work of recent Nobel Prize winner Ahmed Zewail. Zewail has written an excellent description of his work in the *Journal of Chemical Education*, vol. 78 (6), pp. 737-751. Using a femtosecond laser, scientists in Zewail's laboratory prepare reactant molecules in excited vibrational states, as shown in the figure on page 8. The fast laser pulse has a fairly broad energy distribution. This leads to excitation to a range of excited states. The superposition of states so formed has time-dependent behavior, and MathCad can be used to examine this behavior.

The notes for the instructor are given in this size font in maroon. Questions and tasks for the students to complete are in **bold** throughout the document. Answers to most questions are given in this document. I recommend that the instructor use the accompanying student document that provides neither the answers (obviously!) nor the equations for answering most questions. The students should know where to start. Nevertheless, some instructor assistance will be necessary, particularly with the product of the sums, some graphs, and the animations.

The students first review the harmonic oscillator model for molecular vibration. This should reinforce what they already know and keep it fresh in their minds for the exercise. It also allows them to refresh their knowledge of MathCad commands. In this part of the exercise the students plot the wavefunction for several vibrational states. They also plot the square of the wavefunction and are asked to describe the physical meaning of the wavefunction and the square of the wavefunction. Finally, the students check whether the wavefunction is normalized and calculate the average displacement (from the equilibrium bond length), the root mean square displacement, and the standard deviation of the displacement. They then compare these values to the equilibrium bond length.

Next, the students model the energy distribution of the laser pulse. Given a pulse length (time), the students use the uncertainty relation between energy and time to determine the energy uncertainty. The laser pulse is assumed to have a Gaussian distribution of energy, so the energy uncertainty is taken to be the standard deviation of the distribution. They then plot the laser pulse energy distribution.

The laser is assumed to be tuned to the proper wavelength so that the maximum intensity will excite the molecules from $v = 0$ in the ground state to $v = 18$ of an excited electronic state. (This assumption is somewhat arbitrary and is made primarily for consistency with Zewail's article.) A graph provided by the instructor shows the vibrational levels near $v = 18$ and, on the same scale, the energy distribution of the laser pulse with the maximum centered at $v = 18$. The students quickly realize that the laser pulse will not excite only to $v = 18$ but also to nearby levels. They determine which excited levels will be significantly populated by calculating the laser intensity at a laser energy that corresponds to a transition to a given level. If that intensity divided by the peak intensity is greater than 0.050, the level is significantly populated. All other levels are disregarded. The wavefunction, then, is a weighted sum over all significantly populated levels. The weighting constants are the intensity ratios.

One more concept needs to be included. The transition being studied in this document is a *vibronic* transition, so the probability of the transition from the ground state to the excited state will also depend on the overlap of the vibrational wavefunctions of the ground and excited states. The square of this overlap is called the *Franck-Condon factor*. In this document, enough background is given so that the students can calculate the Franck-Condon factors for the possible transitions given the laser energy spread. For a more detailed treatment of Franck-Condon factors, please see:

“Introduction to Frank-Condon Factors: FrankCondonBackground.mcd.” T.J. Zielinski, G.M. Shalhoub, *J. Chem. Educ.* 75, 1191 (1998).

“The Frank-Condon Factors FrankCondonComputation.mcd.” T.J. Zielinski, G.M. Shalhoub, *J. Chem. Educ.* 75, 1192 (1998).

The probability distribution is then written as the complex conjugate of the wavefunction times itself. The wavefunction is a product of a spatial part, which is the same as a harmonic oscillator wavefunction, and a temporal part, which is a simple exponential involving the energy of a given state times the time. The probability distribution, then, is the product of two sums. When like terms are multiplied, the temporal part becomes unity. (i.e., The time dependence vanishes.) However, for the cross terms, this does not happen, and the wavefunction does depend on time. That is, the wavefunction will evolve as time elapses. This can be seen in the graph the students create; the motion of the wavepacket can be animated. The wavefunction itself is not graphed because it has an imaginary part.

The probability distribution is checked to ensure that it is normalized. The way the program handles integration causes the normalization integral to give a result of zero if the limits are larger in magnitude than about 10^{-9} . This is not a problem if the limits of integration are consistently set to completely encompass the function. For the conditions used in the calculations given, the functions are essentially zero at x values greater than 10^{-10} . Thus, that is the suggested integration limit. The spread of the wavepacket is examined at several different times, both graphically and numerically. This standard deviation is compared to the harmonic oscillator model. Also, the standard deviation is determined for the wavepacket at several different times. The importance of these results is emphasized in a question that links these quantities to Zewail's experiments.

The exercise is repeated for a longer laser pulse. The results for short and long laser pulses are compared, and a connection is made to better spatial resolution. Finally, several wrap-up questions summarize the important aspects of this exercise.

Units are not used in this document because, although MathCad handles units well for the most part, it does not allow them to be included in the argument of some functions, such as trigonometric functions and exponentials. For example, if the variable x has units, then MathCad will not evaluate or graph $\sin(x)$. However, it would evaluate $\sin(x/\text{UnitsOf}(x))$. However, given the length of many of the equations in this document, I believe it would be too cumbersome to divide by $\text{UnitsOf}(x)$ in all necessary places. Thus, I have opted not to include units. This is unfortunate, because all instructors rightly emphasize to their students the importance of including units. Perhaps a future version of MathCad will have a less cumbersome means of handling units in arguments of functions.

First, define the constants

You will need Planck's constant, the speed of light, the force constant of iodine, the reduced mass (in kg/molecule), and \hbar . Also write formulas (look in your textbook) for the fundamental vibrational frequency, ν , α , and the normalization constant for the harmonic oscillator wavefunctions.

$$h := 6.6260755 \cdot 10^{-34} \quad c := 299792458$$

$$\hbar := \frac{h}{2\pi}$$

Calculate the reduced mass (in kg) of an I_2 molecule.

$$\mu := \frac{126.91 \cdot 126.91}{2 \cdot 126.91} \cdot 1.6605402 \cdot 10^{-27} \quad \mu = 1.0537 \times 10^{-25}$$

The vibrational frequency of the excited state is 128 cm^{-1} . Convert this value to units of Hz.

$$\nu := 128 \cdot 100 \cdot c \quad \nu = 3.8373 \times 10^{12}$$

Now use the vibrational frequency to calculate the force constant.

$$k := (2 \cdot \pi \cdot \nu)^2 \cdot \mu$$
$$k = 61.2543$$

Define α .

$$\alpha := \sqrt{\frac{k \cdot \mu}{\hbar^2}}$$

Instructor's Notes

The constants shown here are for molecular iodine. Constants for other molecules would work with minimal effect on the results. Only the extent of the graphs (particularly the limits on the x-axis) would be affected.

The energy of the excited state is given by the electronic energy, $3.10712 \times 10^{-19} \text{ J}$, plus the energy of the vibrational state.

Define the energy of the excited state. Use $E(\nu)$ as the variable to represent the energy of a given vibrational state.

$$E(\nu) := 3.10712 \cdot 10^{-19} + \left(\nu + \frac{1}{2} \right) \cdot h \cdot \nu$$

Define the normalization constant for the vibrational wavefunction. Use $N(\nu)$ as the variable.

$$N(\nu) := \frac{1}{\sqrt{2^{\nu} \cdot \nu!}} \cdot \left(\frac{\alpha}{\pi} \right)^{\frac{1}{4}}$$

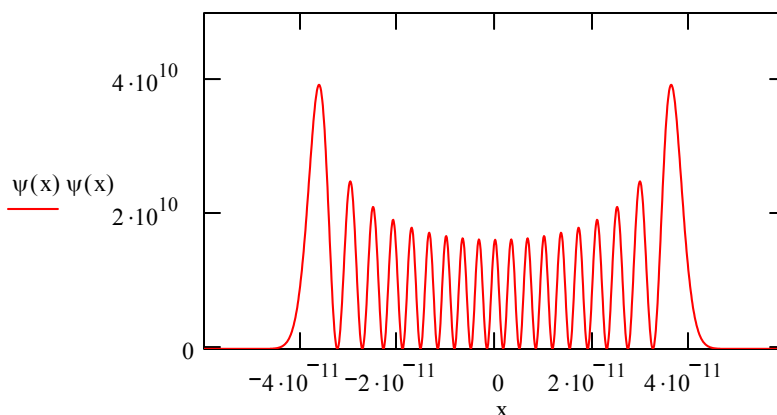
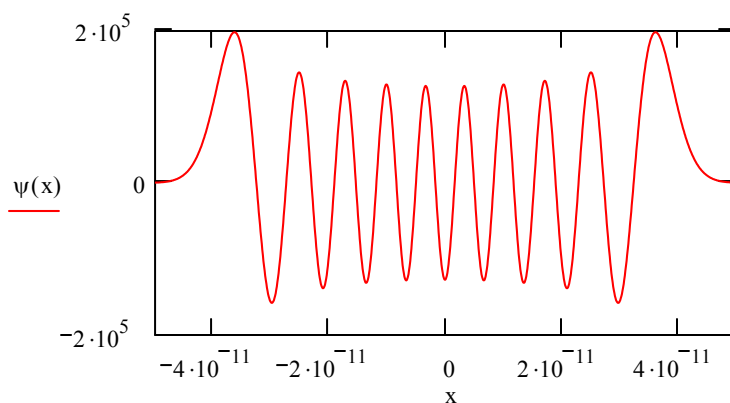
Review of the Harmonic Oscillator

Define the harmonic oscillator wavefunction. You first need to define the vibrational quantum number, v , to some value, such as zero or a positive integer.

$$v := 18$$

$$\psi(x) := N(v) \cdot \text{Her}[\nu, (\sqrt{\alpha} \cdot x)] \cdot \exp\left(\frac{-\alpha \cdot x^2}{2}\right)$$

Display the Wavefunction (ψ) and the Probability Distribution (ψ^2) on separate graphs.



Use the wavefunction to obtain graphs of $v=0$, $v=1$, and $v=2$. How do your graphs compare to those given in your textbook? Describe the probability distribution for these three levels. Finally, make the plots for $v=18$. For all of these levels, does the wavefunction and/or probability distribution change with time?

Make sure you set $v=18$ for the following exercises.

Now let's check to see if the wavefunctions are normalized. It's always important to have normalized wavefunctions, especially if you are going to use them in further calculations, such as the average displacement. Look in your textbook and refresh your memory as to how you determine whether a wavefunction is normalized and how to calculate the average displacement of the bond in a harmonic oscillator.

In doing the following integrals, use limits that are no bigger than 1×10^{-10} . Note that these limits extend beyond the range of the wavefunctions we are using.

Is the wavefunction normalized?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} \psi(x) \cdot \psi(x) dx = 1$$

What is the average displacement?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} \psi(x) \cdot x \cdot \psi(x) dx = 0$$

An important measure of a distribution is the variance, which is a measure of the spread of the distribution about its average value. The variance is defined as $\langle (x - \langle x \rangle)^2 \rangle$ and is also equal to $\langle x^2 \rangle - \langle x \rangle^2$. You will determine the variance of several quantities by finding the mean square displacement ($\langle x^2 \rangle$) and subtracting from it the square of the average displacement ($\langle x \rangle^2$). The average displacement is zero for all levels of a harmonic oscillator. The variance gives us an idea as to how far from the equilibrium bond length the bond is stretched.

The square root of the variance is the standard deviation. Heisenberg formulated the uncertainty principle in terms of the standard deviations, so it is useful to determine the standard deviation of the displacement for vibrational wavefunctions.

What is the mean square displacement (variance)?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} \psi(x) \cdot x^2 \cdot \psi(x) dx = 8.3272 \times 10^{-22}$$

Now take the square root of the variance (mean square displacement in this case) to get the standard deviation (akin to uncertainty).

$$\sqrt{8.3272 \times 10^{-22} - 0} = 2.8857 \times 10^{-11}$$

What is the equilibrium bond length? How does the standard deviation of the displacement compare to the equilibrium bond length?

Instructor's Note: The equilibrium bond length is 2.663×10^{-10} m.

Model the Pump Laser Pulse

Some of the lasers in the Zewail lab have a 100-femtosecond pulse length. This gives them an inherent spread in energy. You can easily calculate this energy spread using the uncertainty relation between energy and time, $\Delta E \cdot \Delta t \geq h$

The energy spread of the pulse is important because, if more light is emitted at a wavelength (energy) that matches the difference between the ground state and an excited state, there is a higher probability that a molecule will be excited to that excited state. On the other hand, if little light is emitted that matches the energy difference between the ground state and another excited state, the probability is low that a molecule will be excited to that upper state.

Given that the pulse length (Δt) is 100 fs, what is the minimum energy spread of this pulse? Define this minimum energy spread to be ΔE as shown here.

$$\frac{h}{100 \cdot 10^{-15}} = 6.6261 \times 10^{-21}$$

$$\Delta E := 6.6261 \times 10^{-21}$$

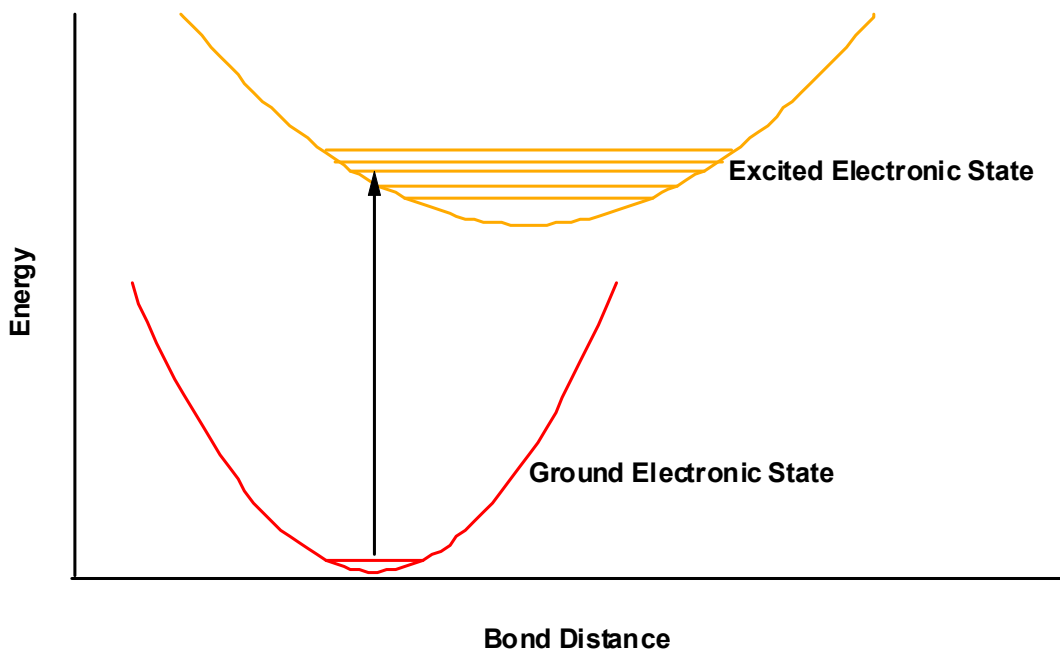
This is the minimum energy spread of a 100-fs pulse.

In the experiments, the laser is tuned so that the peak of the energy spread matches the energy difference between $v = 0$ in the ground state and $v = 18$ in the excited state (this is a typical condition in Zewail's experiments). The energy of the ground state is 4.2623×10^{21} J, so the laser energy is given by:

$$E(18) - 4.2623 \cdot 10^{-21} = 3.5349 \times 10^{-19}$$

The energy of the ground state is obtained by using the fundamental vibrational frequency of iodine's ground state, 214.57 cm^{-1} . One converts this to Hertz by multiplying by the speed of light. The energy is obtained by multiplying the resulting number of Hertz by $1/2 \cdot h$.

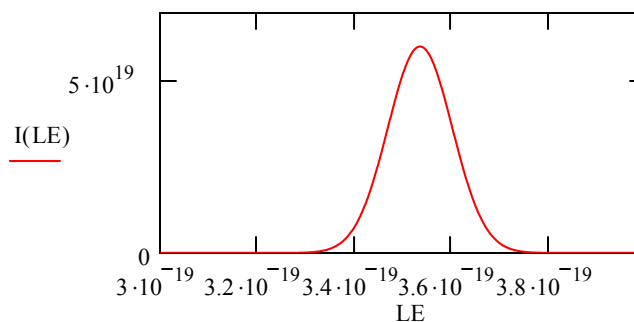
Of course, the laser emits light of other energies, too. This is just the energy (wavelength) at which the laser emits the most light. The intensity of light of this energy is the greatest for this laser pulse. See the following figure.



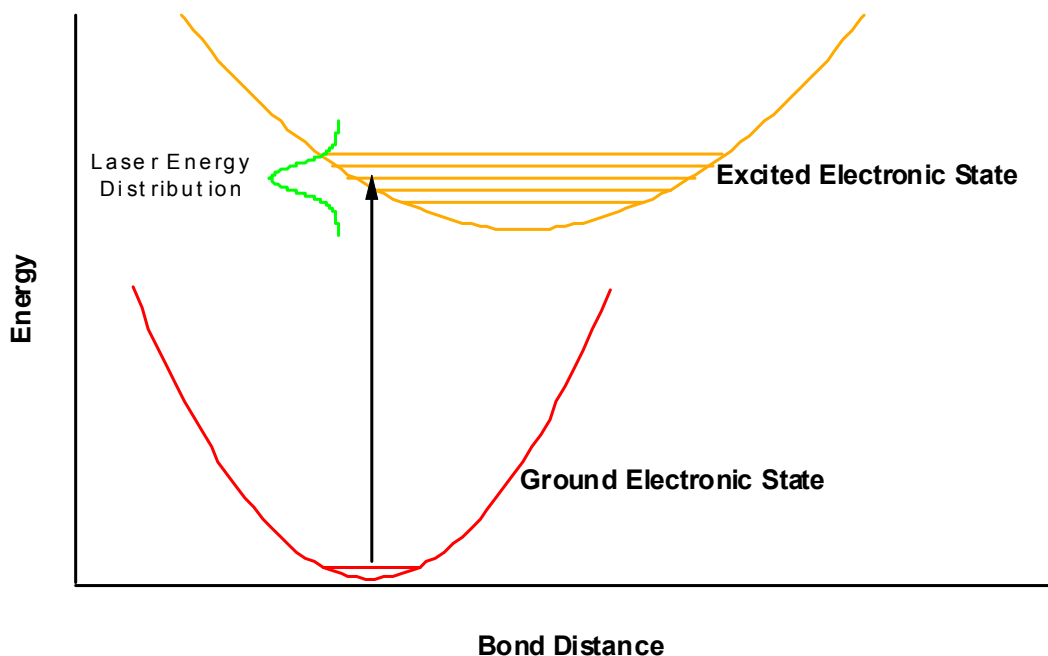
Let's plot the intensity of the laser pulse as a function of energy. The variable I will represent the intensity, and the variable LE will represent the laser energy. (We use LE because we already used E for the vibrational energy levels.) The laser emits light as a Gaussian distribution of energies. The peak is the energy value calculated directly above, and the width of the Gaussian distribution is the ΔE that we calculated at the beginning of this section.

$$I(LE) := \frac{1}{\sqrt{2\pi \cdot (\Delta E)^2}} \cdot \exp \left[\frac{-(LE - 3.5349 \times 10^{-19})^2}{2 \cdot (\Delta E)^2} \right]$$

Graph I vs LE



This plot is useful for visualizing the fact that the laser emits more light at some energies than others. As discussed above, if the intensity of the light that matches the difference between the ground state and an excited state is near the peak of the graph, there is a high probability that a molecule will be excited to that excited state. On the other hand, for those excited states whose energy difference is on the wings of the curve, the probability is low that a molecule will be excited to that upper state. Below is a figure that shows the laser energy distribution relative to the vibrational states of the molecule. Clearly, the energy spread is large enough to excite to several different vibrational states. You can use these ideas to determine the relative probability of reaching a particular excited state.



The light is most intense at the peak, which corresponds to an excitation to $v = 18$ in the excited state. Because the intensity at this energy is the highest, the probability of exciting to $v = 18$ is the greatest. We will work with relative probabilities, so we note:

$$\frac{I(3.5349 \times 10^{-19})}{I(3.5349 \times 10^{-19})} = 1 \quad \text{The relative probability of exciting to } v = 18 \text{ is } 1.$$

The expression for E for any harmonic oscillator quantum state was given by the equation near the bottom of page 4.

What is the relative probability of exciting to $v = 17$ in the excited state? Well, it is lower than the probability of exciting to $v = 18$. We can determine the relative probability by:

$$\text{Relative probability of exciting to state } v = \frac{\text{prob}(v)}{\text{prob}(18)}$$

$$\frac{I(E(17) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.929 \quad \text{The probability is also quite high to excite to } v = 17.$$

The probability will decrease as the intensity of the laser light that matches the energy difference between ground and excited states gets lower. We will consider only those states that have at least a 5% relative chance of being excited; that is, those states whose ratio is greater than 0.050.

Calculate the ratios for values of v near $v = 18$ and find the v states that will be excited.

$$\frac{I(E(16) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.7448$$

$$\frac{I(E(22) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.308$$

$$\frac{I(E(14) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.3078$$

$$\frac{I(E(24) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.0706$$

$$\frac{I(E(12) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.0706$$

$$\frac{I(E(25) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.0271$$

$$\frac{I(E(11) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.0271$$

Which levels will be populated? How do you know?

(ANS $v = 12-24$ will be populated.)

These ratios are called weighting constants because they determine the relative probability of exciting to a particular vibrational state. They can easily be defined like this:

$$w(v) := \frac{I(E(v) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})}$$

w is used for the weighting constant because c is the speed of light, and k is the force constant.

Determine the Franck-Condon Factors

In Zewail's experiments, the iodine molecules are excited from $v = 0$ in the ground electronic state to one of several possible vibrational levels in the excited electronic state. This type of transition, in which the molecule changes vibrational and electronic state, is called a *vibronic* transition. Remember that the harmonic oscillator selection rule is $\Delta v = \pm 1$, but this is for a transition that does not change electronic state. For a vibronic transition, Δv can be any integer, so the vibrational energy quantum can change by more than one. This is why, in our experiment, the molecule can go from $v = 0$ in the ground state to $v = 18$ (or so) in the excited state. However, the probabilities of transitions to the various upper states are not the same.

The probability of a transition between vibrational levels in a vibronic transition depends on the overlap of the vibrational wavefunctions. This is based on the *Franck-Condon Principle*, which states that the electron jump in a molecule takes place much more rapidly than the nuclear motion, so the nuclei have essentially the same position and velocity before and after the jump. Thus, on the diagram of potential energy curves for the molecule above, the transition between electronic states is indicated by a vertical line (any slope to the line would mean that the nuclei move during the transition). The probability of a transition is related to the overlap of vibrational wavefunctions in the lower and upper states.

Knowing that the lower vibrational state is $v = 0$, the ground state vibrational wavefunction is given by a harmonic oscillator expression. The numbers in the following equation are the correct values for the ground state. The values you defined above are for the excited state.

$$\text{GSHO}(r) := 336193 \cdot e^{-\left[\frac{(4.0133) \cdot 10^{22} \cdot (r - 2.666 \cdot 10^{-10})^2}{2} \right]}$$

This is the harmonic oscillator expression for the ground state. The constant out front is the normalization constant. The values in the exponential are α and the equilibrium bond length for the ground state.

The excited state vibrational wavefunction is:

$$\psi(v, r) := N(v) \cdot \left[\text{Her}\left[v, \left[\sqrt{\alpha} \cdot (r - 3.016 \cdot 10^{-10}) \right] \right] \right] \cdot \exp\left[\frac{-\alpha \cdot (r - 3.016 \cdot 10^{-10})^2}{2} \right]$$

The overlap of the vibrational wavefunctions is found by evaluating the integral:

$$v := 0..50$$

$$F_v := \int_{-1 \cdot 10^{-9}}^{1 \cdot 10^{-9}} \text{GSHO}(r) \cdot \left[N(v) \cdot \left[\text{Her}\left[v, \left[\sqrt{\alpha} \cdot (r - 3.016 \cdot 10^{-10}) \right] \right] \right] \right] \cdot \exp\left[\frac{-\alpha \cdot (r - 3.016 \cdot 10^{-10})^2}{2} \right] dr$$

(It helps MathCad calculate **much** faster in later exercises if we have the Franck-Condon factors as an array of pre-calculated values. That is why v is defined as a range value, and the Franck-Condon factors are F_v .)

The probability of the transition is called the Franck-Condon factor and is proportional to the square of the integral, $(F_v)^2$.

What are the Franck-Condon factors for all of the vibrational transitions that will be considered?

$$(F_{12})^2 = 5.8308 \times 10^{-9}$$

$$(F_{19})^2 = 7.2451 \times 10^{-8}$$

$$(F_{13})^2 = 1.1906 \times 10^{-7}$$

$$(F_{20})^2 = 4.3384 \times 10^{-9}$$

$$(F_{14})^2 = 4.7265 \times 10^{-8}$$

$$(F_{21})^2 = 1.2183 \times 10^{-7}$$

$$(F_{15})^2 = 2.4483 \times 10^{-8}$$

$$(F_{22})^2 = 6.2893 \times 10^{-8}$$

$$(F_{16})^2 = 1.1208 \times 10^{-7}$$

$$(F_{23})^2 = 6.3039 \times 10^{-10}$$

$$(F_{17})^2 = 1.1326 \times 10^{-8}$$

$$(F_{24})^2 = 1.6254 \times 10^{-10}$$

$$(F_{18})^2 = 5.8477 \times 10^{-8}$$

Write the probability distribution for this superposition. This will take the form

$P(x,t) = N(\sum w F \psi(x) e^{-i\omega t})(\sum w F \psi(x) e^{i\omega t})$, where N is a normalization constant, w is the laser intensity weighting constant, F is the Franck-Condon factor, $\psi(x)$ is the harmonic oscillator wavefunction, and

ω is $\frac{E \cdot t}{\hbar}$. \sum indicates a sum over the vibrational states determined above.

Discuss with your instructor what N could be.

First define the Excited State of the Harmonic Oscillator in the form $\psi(x)e^{i\omega t}$.

$$\text{ESHO}(v, x, t) := N(v) \cdot \text{Herf}\left[v, (\sqrt{\alpha} \cdot x)\right] \cdot \exp\left(\frac{-\alpha \cdot x^2}{2}\right) \cdot \exp\left(\frac{-i \cdot E(v) \cdot t \cdot 10^{-15}}{\text{hbar}}\right)$$

Use ESHO to create a compact probability function.

$$P(x, t) := \frac{1}{\sum_{v=12}^{24} \left[w(v) \cdot (F_v)^2 \right]^2} \left[\sum_{v=12}^{24} w(v) \cdot (F_v)^2 \cdot \text{ESHO}(v, x, t) \cdot \sum_{v=12}^{24} w(v) \cdot (F_v)^2 \cdot \text{ESHO}(v, x, t) \right]$$

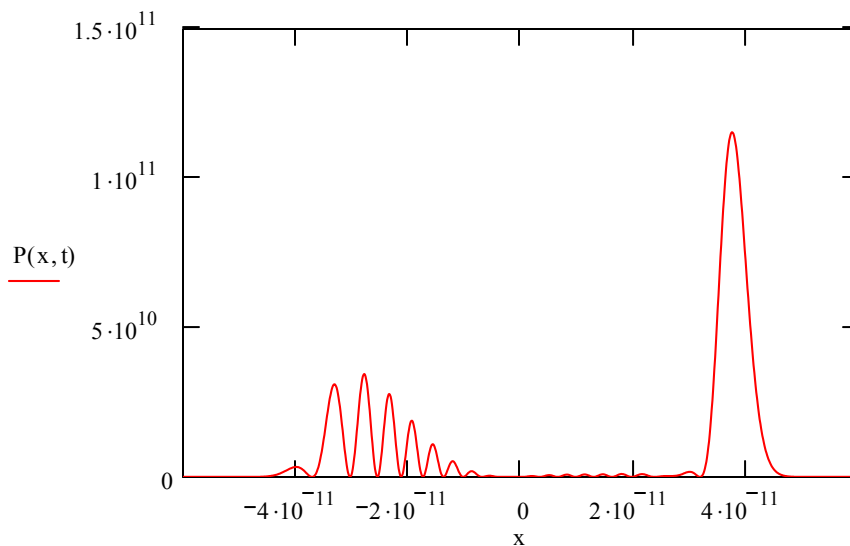
Instructor's Notes: The term at the beginning of the above equation is necessary to normalize the probability distribution. The students might have difficulty understanding this concept, so the instructor must make some effort to help them grasp this idea.

FRAME can be used as the variable for time so that the time evolution of the probability distribution can be animated using MathCad's built-in animation capability. The probability distribution can be viewed at any specific time by entering a specific value for FRAME.

Graph the probability distribution at $t = 0$.

$t := 0$

With states $v = 12 - 24$ populated, it takes about 130 fs to complete a half cycle.



Describe the probability distribution at $t=0$ fs. Is it broad or narrow? How does it compare to the probability distribution for $v=18$ of the harmonic oscillator? According to the graph, what is the likelihood of finding the bond at its equilibrium length at $t=0$?

Now let's look at the probability distribution at other times. Describe the probability distributions at $t=65$ fs and at $t=130$ fs. Are they broad or narrow? How do they compare to the probability distribution for $v=18$ of the harmonic oscillator?

Animate the probability distribution. Ask your instructor for assistance if needed. (This could take up to one hour, so it might be best to do it last.)

Is the probability distribution normalized?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} P(x, 0) dx = 1$$

Due to rounding errors, the answer might not be exactly 1. Also, if the limits of integration are much larger than this, MathCad 2000 gives an answer of zero. It is best to use integration limits that encompass the entire function but are not bigger than 10^{-10} .

The probability of finding the system between x and $x+dx$ at a time t is $P(x,t) dx$. Here, dx is taken to be 1 pm.

What is the probability of finding the bond length at the equilibrium value at $t = 0$? Remember that the probability of finding the bond length between x and $x + dx$ at any time t is $P(x,t) dx$. Take $dx = 1$ pm.

$$P(0,0) \cdot 10^{-12} = 6.6616 \times 10^{-6}$$

Is the probability distribution normalized at other values of t ? Pick two values of t beside zero and make sure the wavefunction is normalized at those times.

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} P(x, 65) dx = 1 \qquad \int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} P(x, 130) dx = 1$$

Several other values of t can be tried; they yield similar results.

What are the average displacement and the mean square displacement at t = 0 fs?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x \cdot P(x, 0) dx = 1.2728 \times 10^{-11} \qquad \int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x^2 \cdot P(x, 0) dx = 1.1507 \times 10^{-21}$$

How do these values compare with those for v = 18 of the harmonic oscillator?

What is the standard deviation of the displacement at t = 0?

$$\sqrt{1.1507 \times 10^{-21} - (1.2728 \times 10^{-11})^2} = 3.1444 \times 10^{-11}$$

What are the average displacement and the mean-square displacement at t = 65 fs?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x \cdot P(x, 65) dx = 5.811 \times 10^{-14} \qquad \int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x^2 \cdot P(x, 65) dx = 3.6749 \times 10^{-22}$$

What is the standard deviation of the displacement at t = 65 fs?

$$\sqrt{3.6749 \times 10^{-22} - (5.811 \times 10^{-14})^2} = 1.917 \times 10^{-11}$$

Is the system more or less localized at t = 65 fs than t = 0?

Some of the experiments performed in Zewail's laboratory are designed to study the reactions of molecules that are very likely to have their bond stretched, and some are designed to study the reactions of molecules that are very likely to have their bonds compressed. Once the experimenters excite the molecules to this superposition, how long should they delay their probe laser to study each of these cases? Use the numerical and graphical results to explain your answers.

The students can now explore the effect of using a longer laser pulse. 350 fs is chosen here because, for molecular iodine, a pulse much longer than that will excite only to one or two excited states. A superposition of one state is identical to the harmonic oscillator, and a superposition of two states varies only slightly with time.

What if the pump laser pulse is longer? 350 fs

What is the energy spread of a 350-fs pulse? Define this to be ΔE .

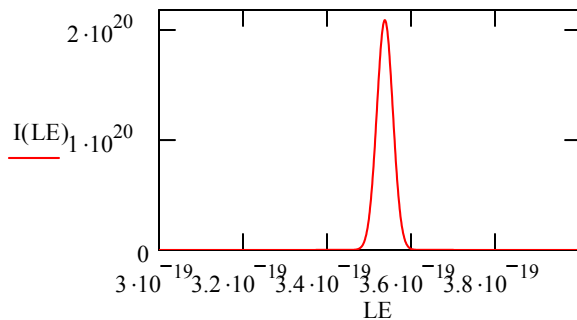
$$\frac{h}{350 \cdot 10^{-15}} = 1.8932 \times 10^{-21} \quad \Delta E := 1.8932 \cdot 10^{-21} \quad \text{This is the energy spread of a 350-fs pulse.}$$

$$E(18) - 4.2623 \cdot 10^{-21} = 3.5349 \times 10^{-19} \quad \text{The laser is tuned so that the center frequency will excite from } \nu = 0 \text{ to } \nu = 18.$$

Again, the laser will emit a distribution of energies that is well-described by a Gaussian function.

$$I(\text{LE}) := \frac{1}{\sqrt{2\pi \cdot (\Delta E)^2}} \cdot \exp\left[\frac{-(\text{LE} - 3.5349 \times 10^{-19})^2}{2 \cdot (\Delta E)^2} \right]$$

Graph I vs LE.



As before, the probability of exciting to a particular state will depend on the intensity of emitted light that matches the energy difference between the final and initial states.

Determine which vibrational states will be significantly populated by the laser pulse.

$$\frac{I(E(18) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 1$$

$$\frac{I(E(19) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.4062$$

$$\frac{I(E(17) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.4055$$

$$\frac{I(E(20) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.0272$$

$$\frac{I(E(16) - 4.2623 \cdot 10^{-21})}{I(3.5349 \times 10^{-19})} = 0.0271$$

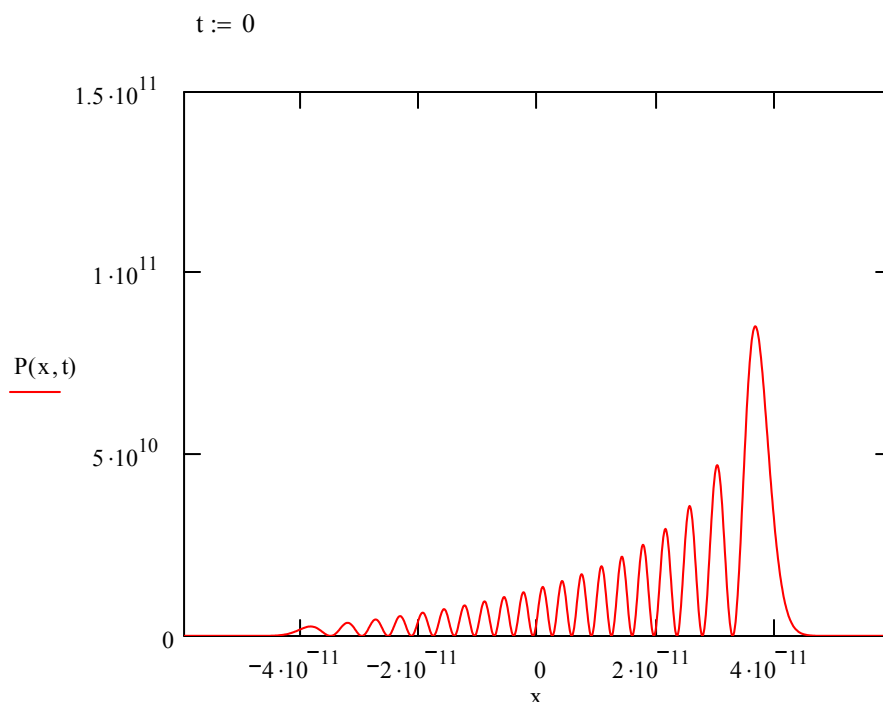
ANS $v = 17-19$ will be populated

The Franck-Condon factors depend only on the final and initial states, not on the laser pulse length. Thus, you can use the same Franck-Condon factors that you used with the 100-fs pulse.

Write the probability distribution for this superposition.

$$P(x, t) := \frac{1}{\sum_{v=17}^{19} [w(v) \cdot (F_v)^2]^2} \left[\sum_{v=17}^{19} w(v) \cdot (F_v)^2 \cdot \text{ESHO}(v, x, t) \cdot \sum_{v=17}^{19} w(v) \cdot (F_v)^2 \cdot \text{ESHO}(v, x, t) \right]$$

Graph the probability distribution.



Describe the probability distribution at $t=0$ fs. Is it broad or narrow? How does it compare to the probability distribution for $v=18$ of the harmonic oscillator? According to the graph, what is the likelihood of finding the bond at its equilibrium length at $t=0$?

Describe the probability distributions at $t=65$ fs and at $t=130$ fs. Are they broad or narrow? How do they compare to the probability distribution for $v=18$ of the harmonic oscillator?

Animate the probability distribution (ask your instructor for assistance if needed).

Is the probability distribution normalized?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} P(x, 0) dx = 1$$

What is the probability of finding the bond length at the equilibrium value at $t = 0$ fs?

$$P(0, 0) \cdot 10^{-12} = 6.8896 \times 10^{-3}$$

What are the average displacement and the mean square displacement at t = 0 fs?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x \cdot P(x, 0) dx = 2.0772 \times 10^{-11} \qquad \int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x^2 \cdot P(x, 0) dx = 7.4826 \times 10^{-22}$$

What is the standard deviation of the displacement at t = 0?

$$\sqrt{8.6484 \times 10^{-22} - (2.0772 \times 10^{-11})^2} = 2.0817 \times 10^{-11}$$

What are the average displacement and the mean square displacement at t = 65 fs?

$$\int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x \cdot P(x, 65) dx = 6.4064 \times 10^{-14} \qquad \int_{-1 \cdot 10^{-10}}^{1 \cdot 10^{-10}} x^2 \cdot P(x, 65) dx = 5.9702 \times 10^{-22}$$

What is the standard deviation of the displacement at t = 65 fs?

$$\sqrt{5.9702 \times 10^{-22} - (6.4064 \times 10^{-14})^2} = 2.4434 \times 10^{-11}$$

Is the system more or less localized at t = 65 fs than t = 0?

Which delay times would be optimal for studying the reactions of molecules with stretched bonds and compressed bonds? Use the numerical and graphical results to explain your answers.

Summary Questions

1. Which pulse length gives better spatial resolution?
2. What do the graphs represent? Do they show the compression and lengthening of a single molecule's bond? Why or why not?
3. Describe two ways in which the superposition probability distribution is different from that of the harmonic oscillator.