

Fourier transforms of molecular vibrations ©

Part I: An Introduction to the Harmonic Oscillator and Fourier Transforms

W. Tandy Grubbs, Department of Chemistry, Unit 8271, Stetson University,
DeLand, FL 32720 (william.grubbs@stetson.edu)

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Goals: The primary goals of this document, and the accompanying documents, are to gain a familiarity with standard models that describe the classical vibrations of a chemical bond and to explore the relationship between the time and frequency representations of vibrational motion. The 'equation-of-motion' associated with each model is a differential equation which is solved using a numerical method called the Runge-Kutta method. This produces the bond displacement as a function of time. In each case, the frequency spectrum of the vibration is obtained by carrying out a Fourier Transform.

Prerequisites: These Mathcad documents are designed to support the quantum mechanics-spectroscopy portion of a Junior-Senior level physical chemistry class. Students should have had at least one year of calculus and physics. It will be helpful if students have some knowledge of c (the vibration of two masses connected by a Hooke's law spring). The equations describing a classical harmonic oscillator can be found in several standard physical chemistry texts [1,2]. While not necessary, it will also be helpful if students are familiar with *Fourier transform* techniques (also described in several physical chemistry texts [3,4]). This document is one of a set of three, the others being

Performance Objectives for Document 1:

After completing this document, you should

- 1) be able to model a bond vibration as a harmonic oscillator by setting up a differential equation of motion, and then solve the equation by using Mathcad's Runge-Kutta numerical algorithm;
- 2) be able to calculate the frequency spectrum of this vibration by performing a Fourier transform of the bond displacement data;
- 3) observe peak distortions in the frequency spectrum that are caused by Fourier transform truncation error.

Harmonic Oscillator Equation of Motion.

Vibrational motion is often approximated using the harmonic oscillator model. Consider two masses (m_1 and m_2) connected by a spring of force constant k . The restoring force of the spring is $F = -k x$. For a chemical bond, k represents the stiffness of the bond and x represents the displacement of the bond length from its equilibrium value ($x = r - r_e$).

Given below are parameters that will allow us to simulate harmonic vibrations in molecular chlorine, Cl_2 (various spring constants for diatomic bonds are available in a number of standard physical chemistry texts: see, for example, reference 5).

$$k := 322.7$$

Spring constant in Newtons/meter.

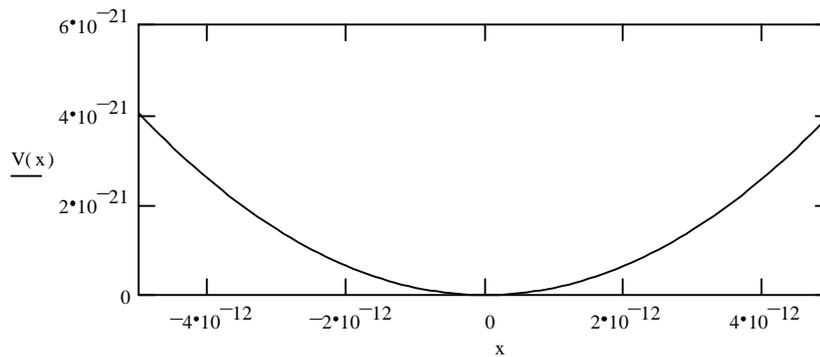
$$x := -5.0 \cdot 10^{-12}, -4.9 \cdot 10^{-12} .. 5.0 \cdot 10^{-12}$$

Range of bond displacements in meters, in increments of 0.1 picometers.

$$V(x) := \frac{1}{2} \cdot k \cdot x^2$$

Potential energy of a harmonic oscillator in Joules.

Graph 1.1: Harmonic potential energy



Exercise 1.1: The spring constant for N_2 is $k = 2293.8 \text{ N/m}$. Repeat graph 1 for N_2 . Compare the harmonic potential energy curves for Cl_2 and N_2 by plotting them together. Calculate how far the Cl_2 bond has to stretch to have a potential energy equal to that of N_2 when $x = 2 \times 10^{-12} \text{ m}$?

Now that we know the potential energy as a function of bond displacement, we can setup the equation-of-motion that will describe the bond displacement as a function of time. The equation-of-motion for a harmonic oscillator is obtained by substituting the force $F = -kx$ into Newton's Second law $F = \mu \frac{d^2x}{dt^2}$, where μ is the reduced mass of the diatomic [$\mu = m_1 m_2 / (m_1 + m_2)$].

$$\frac{d^2}{dt^2} x + \frac{k}{\mu} x = 0 \quad \text{Equation of motion.}$$

$$\mu := 2.903 \cdot 10^{-26} \quad \text{Reduced mass of } Cl_2 \text{ in kilograms.}$$

While an analytical solution is available for this second order differential equation, we will instead solve the expression for a given set of initial conditions using a fourth order Runge-Kutta (RK) numerical method [6]. It is important to become familiar with the RK method at this point in the exercise because it will be used throughout these documents to obtain solutions to differential equations that have no exact analytical solution. Using the Mathcad formalism, the second order differential equation given above is defined as a vector, with the first element describing the first derivative of x with respect to time (the velocity) and the second element describing the second derivative of x with respect to time.

Differential equation

$$D(t, x) := \begin{bmatrix} x_1 \\ -\frac{k}{\mu} \cdot x_0 \end{bmatrix}$$

First derivative: x_1 represents the velocity at each point
<----- in time, which is unknown in our model.

<----- Second derivative: described by the equation-of-motion,
where x_0 represents the position at each point in time.

$$x := \begin{pmatrix} 5 \cdot 10^{-12} \\ 0 \end{pmatrix}$$

One must specify the initial conditions when solving a differential equation. This statement defines the initial position to be $x_0 = 5 \times 10^{-12}$ meters (a typical bond displacement for diatomic chlorine) and the initial velocity to be $x_1 = 0$ meters/second for time $t=0$.

Question: Why was the initial velocity chosen to be zero?

$$t_{\max} := 5 \cdot 10^{-12}$$

The maximum time to which the equation of motion will be evaluated in **seconds**.

$$\text{frequency} := \frac{1}{2 \cdot \pi} \cdot \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$

We must specify the total number of points over which the numerical solution will be evaluated when solving a differential equation with Mathcad's Runge-Kutta algorithm. The total number of points must be large enough to resolve each period of the vibration over the full time range (**tmax**). To accomplish this, one can take the frequency of the oscillator (calculated to the left) and multiply it by **40 tmax**. In this fashion, the total number of points will be great enough to allow 40 points per oscillation.

$$\text{points} := \text{floor}(40 \cdot t_{\max} \cdot \text{frequency})$$

This expression calculates the total number of points as described above, rounded down to the nearest integer value. (Look up the **floor** function in your Mathcad manual.)

The Runge-Kutta algorithm is carried out by invoking Mathcad's *rkfixed* routine. The expression given below solves the equation of motion (**D**) subject to the parameters specified above. **x** is the vector containing the initial values. **0** and **tmax** define the time interval over which a solution will be approximated. The time, position, and velocity of the oscillator are stored in a 3 column matrix (**Z**) with a number of rows equal to **points**. (Note that [**points - 1**] defines the number of points beyond the initial point.)

$$Z := \text{rkfixed}(x, 0, tmax, \text{points} - 1, D)$$

$$\text{time} := Z^{<0>}$$

$$\text{position} := Z^{<1>}$$

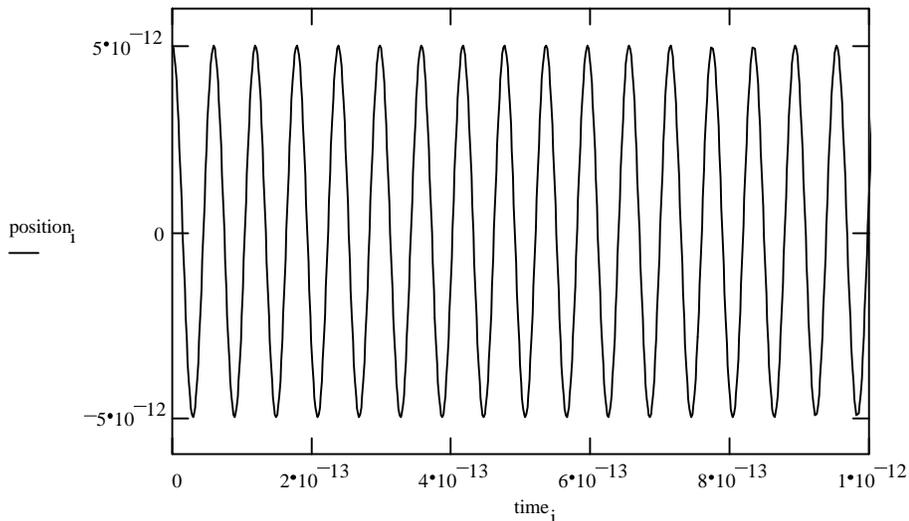
$$\text{velocity} := Z^{<2>}$$

These statements separate the 3 column Z matrix into time, position, and velocity vectors.

$$i := 0.. \text{points} - 1$$

Index numbers to accompany the three vectors given above. Note how *i* starts at zero.

Graph 1.2: A portion of the position vector, showing the amplitude of the vibration as a function of time.



Exercise 1.2:

$$KE_i := \frac{\mu}{2} \cdot (\text{velocity}_i)^2$$

The statement to the left gives the kinetic energy (KE_i) of the oscillator at each time increment. Write the equation for calculating the potential energy (PE_i) at the same time increments. Graph KE_i and PE_i on the same plot from zero to 2x10⁻¹³ s. Is the total energy of the system conserved at all times? Explain.

Calculating the Frequency Spectrum of a Vibration (Fourier Transforms)

Vibrational spectroscopies, like IR and Raman spectroscopy, are used to measure the frequencies of bond vibrations in molecules. Can we simulate a vibrational spectrum from the bond oscillation data? In other words, can we calculate the *frequency-dependent* vibrational spectrum of Cl₂ from the *time-dependent* bond oscillation data contained in the vector **position**? The answer is yes.

Time and frequency dependent functions are related through a mathematical transformation called a Fourier transform [2,3,7]. Mathcad has several built-in functions for performing Fourier transforms. We will use the *cfft* routine which is capable of performing a fast Fourier transform of both real and complex data and allows the input array to be of any size. (While the more common *fft* routine is computationally more efficient than the *cfft* routine, the *fft* routine is limited to input arrays with 2ⁿ elements).

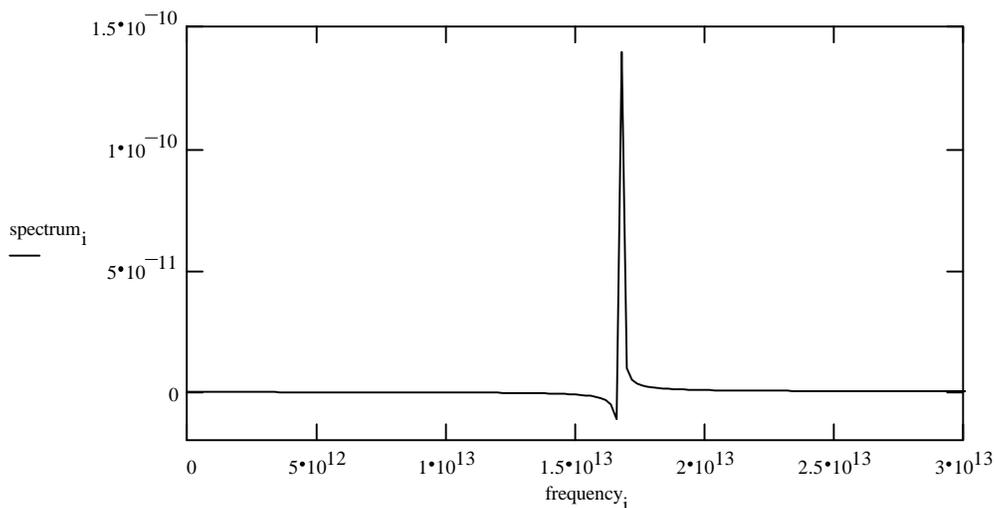
$$\text{spectrum} := \text{Re}(\text{cfft}(\text{position}))$$

The statement *cfft(position)* performs a Fourier transform of the vector **position**. Since the elements of the Fourier transform are complex numbers, we extract the real part of the complex elements, using the statement *Re(cfft(position))*, and store the results in the vector **spectrum**.

$$\text{frequency}_i := \frac{i}{\text{tmax}}$$

This statement defines the frequency associated with each element of the vector **spectrum**. We next plot spectrum -vs- frequency in Graph 1.3.

Graph 1.3: Frequency Spectrum of the Cl₂ Vibration



$$\nu := \frac{1}{2 \cdot \pi} \cdot \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$

$$\nu = 1.678 \cdot 10^{13}$$

The harmonic frequency is related to the spring constant (k) and the reduced mass (μ) through the expression given to the left.

Note: the peak in the above spectrum is centered at ν .

In principle, a Fourier transform of harmonic motion yields an infinitely sharp peak located at the harmonic frequency. The distorted (asymmetric) shape of the peak seen in the spectrum above is an artifact of the transformation process that occurs because we only sampled the oscillation from **0** to **tmax**. In other words, the spectrum is distorted because we *truncated* the input array at **tmax**. An infinitely precise determination of the harmonic frequency would require a Fourier transformation of the temporal data from **0** to *infinite* time.

General Exercises (part 1): (see warnings below before beginning exercises)

- 1) Vibrational spectra are normally plotted as a function of wavenumber (cm^{-1}). Generate a vector of wavenumbers (wavenumbers_i) from the vector of frequencies (frequency_i) and replot Graph 1.3 as a function of wavenumber.
- 2) The truncation error associated with a Fourier transform, and the subsequent spectral distortion, is dependent on the overall time range of the temporal input array (t_{max}). Vary t_{max} from 10^{-12} to 10^{-10} seconds. Account for the changes observed in the vibrational spectrum.
- 3) The bond vibration in diatomic nitrogen, $^{14}\text{N}_2$, gives rise to a peak in the frequency spectrum at 2358.1 cm^{-1} . Calculate the reduced mass (μ) and the spring constant (k) for this molecule and repeat Graphs 1.1-1.3.

Warnings:

- (a) You may have to redefine the axis limits of the graphs when parameters are changed.
- (b) The amount of computational time that is required to solve the equation of motion and to compute the Fourier transform is directly related to **t_{max}** . Therefore, you should not pick any arbitrary value of **t_{max}** . Values of **t_{max}** should be selected that are large enough to reduce the truncation error, yet small enough to minimize the computation time.

References:

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