Using Mathematical Software To Introduce Fourier Transforms in Physical Chemistry To Develop Improved Understanding of Their Applications in Analytical Chemistry

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S *Supporting Information*

ABSTRACT: This manuscript presents an exercise that utilizes mathematical software to explore Fourier transforms in the context of model quantum mechanical systems, thus providing a deeper mathematical understanding of relevant information often introduced and treated as a "black-box" in analytical chemistry courses. The exercise is given to undergraduate students in their third year during physical chemistry, thus providing a theoretical foundation for the subsequent introduction of such material in analytical instrumentation courses. With the reinforcement of familiar concepts such as the Heisenberg Uncertainty Principle, classical correspondence, and linear combinations in the context of both position and momentum space for a particle in a box, a better understanding of the mathematical implications of the Fourier transform is fostered. Subsequent analysis of a time-dependent function constructed via a linear combination and its transformation to the frequency domain provides a practical example relating to the Fourier processes applied in analytical spectroscopy. The final portion of the exercise returns to the position/momentum conjugate pair and explores how the construction of a narrow wavepacket via a sum of cosines illustrates the Uncertainty Principle once the probability density functions of each coordinate are analyzed. This exercise has been shown to not only reinforce fundamental concepts necessary for a true appreciation of quantum mechanics, but also help demystify the Fourier transform process for students taking analytical chemistry.

KEYWORDS: *Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, Computer-Based Learning, Fourier Transform Techniques*

■ INTRODUCTION

One of the main functions of physical chemistry in the overall progression of the undergraduate student is to provide a mathematical basis for ideas and subjects that are found in other chemistry subdisciplines. The underlying physics is introduced, and details that can only be expressed in the context of a math-based course are more fully explored. Concepts from thermodynamics, kinetics, and quantum mechanics can be introduced in general chemistry, but physical chemistry is where these topics can be expounded in rigorous detail. Upper-division classes such as inorganic, analytical, and advanced organic chemistry rely on physical chemistry to build a deeper understanding of spectroscopy, group theory, and bonding theories in hopes of producing students with a more well-rounded view of the theoretical foundations of the field as a whole. The activity presented in this article fits the established paradigm, and with the help of computational software packages, provides a mathematical understanding of the Fourier transform (FT) to students in physical chemistry, establishing a foundation for better comprehension of the practical applications which are introduced in analytical and instrumentation courses.[1−3] The FT plays a key role to chemists of all disciplines,[4] and has prompted several educational exercises

designed to elucidate understanding for students.[5−12] Our goal in this particular exercise is to combine previously reported work with a novel investigation of the Heisenberg Uncertainty principle involving a linear combination of cosine functions. This activity provides an integrated approach toward teaching the subject by coordinating and emphasizing a direct link between disciplines, becoming a useful tool to educators in this area.

The FT, on its most fundamental level, is a mathematical technique that relates information between two conjugate domains. A general form of the FT relating frequency, ω, and time, t, is[13,14]

$$H(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} h(t)\, e^{i\omega t}\, dt \tag{1}$$

where $h(t)$ is a general function dependent on time, $i = (-1)^{1/2}$, and $H(\omega)$ is the resulting function in the frequency domain. Spectroscopic instrumentation often utilizes this technique, extracting frequency information from time dependent data. Useful examples covered in instrumentation courses include multiplex techniques applied to infrared spectroscopy, nuclear
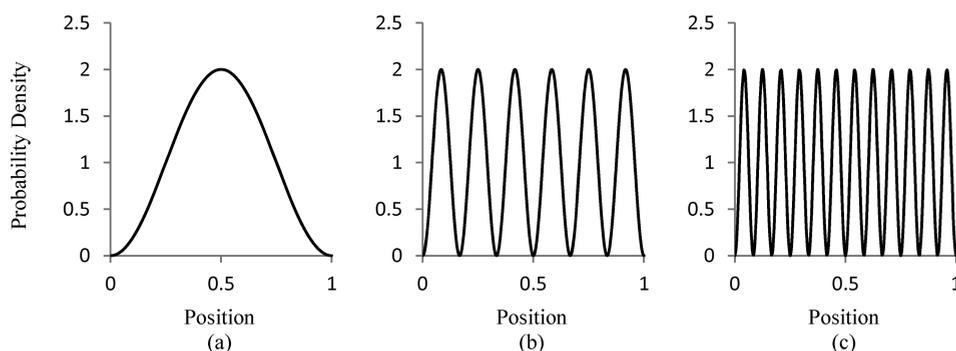
Figure 1. Particle in a box probability distributions in position space for $L = 1$ and (a) $n = 1$, (b) $n = 6$, and (c) $n = 12$.
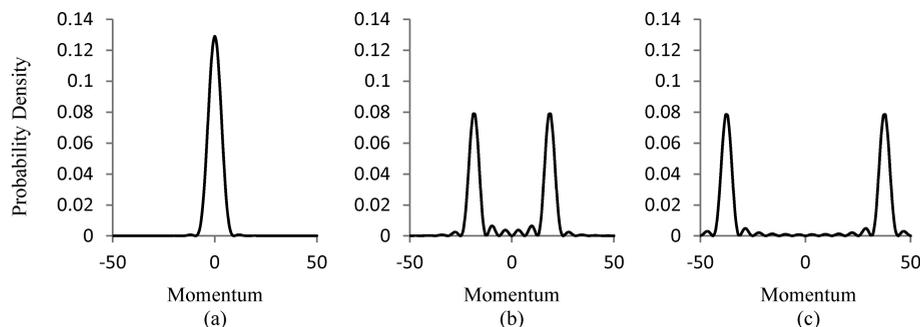

Figure 2. Particle in a box probability distributions in momentum space for (a) $n = 1$, (b) $n = 6$, and (c) $n = 12$.

magnetic resonance spectroscopy and mass spectrometry.[1] As a further example, in inorganic chemistry the FT is used to extract structural information from X-ray diffraction data.[15]

Just as time and frequency can be related via the FT, position and momentum can also be related. For example, a position dependent wave function can be transformed into one that is dependent on momentum.[16,17] Physical chemistry students, who have a basic knowledge of concepts such as wave functions, linear combinations, the Born interpretation, classical correspondence, and the Uncertainty Principle, have all the necessary tools that allow for a true mathematical and conceptual understanding of the FT and the physical information one can glean from its application. Exploring (and thus reinforcing) the aforementioned concepts in the realm of position *and* momentum dependent wave fuctions provides the perfect proving ground to establish a deep understanding of the impacts of the FT, and in turn, allows for the FT to no longer be treated as a "black-box" in other advanced courses.

We have chosen to use Mathcad as the mathematical software package for evaluation of the FT (when applicable) and for the graphical representation of resulting data because it is the platform used in the balance of the physical chemistry curriculum at our university. However, the exercise is presented in a general format, allowing for its easy translation to other commonly used mathematical programs such as Mathematica, MATLAB, Maple and even Excel.

Provided in the Supporting Information is a general laboratory procedure that can be employed by instructors who wish to use this approach; also supplied is an example Mathcad document that explicitly shows all of the important mathematical exercises described in the text below and their accompanying graphs.

■ EXERCISE DETAILS

The exercise begins with students producing familiar plots of the position probability density functions associated with standard one-dimensional particle-in-a-box solutions. The wave functions themselves have the form[18,19]

$$\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \tag{2}$$

where L is the length of the box and n is the quantum number ranging from 1 through ∞. It should be noted that, on the basis of the definition of the potential energy associated with this system, the given wave functions are valid inside the box, defined as the region $0 \leq x \leq L$, while outside the box in the regions $-\infty \leq x < 0$ and $L < x \leq \infty$, the wave function is zero. By increasing n incrementally, the traditional indication of classical correspondence is shown by a more even distribution of probability, $|\psi(x)|^2$ across all regions of the box, as demonstrated in Figure 1.

Next, students are asked to plot the analytical expression associated with the momentum probability density of this system.[16,17] Through analytical integration, or the use of a symbolic integrator, the FT of the position wave function yields a momentum (p) wave function of the form

$$\psi(p) = \frac{1}{\sqrt{2\pi}} \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) e^{-ipx} \, dx$$

$$= \frac{n\pi L}{\sqrt{2\pi}} \left(\frac{2}{L}\right)^{1/2} \left(\frac{e^{-ipL} \cos(n\pi) - 1}{L^2 p^2 - n^2 \pi^2}\right) \tag{3}$$

The reader should note that the Fourier transform integral shown in eq 3 has been performed with $\hbar$ set to unity to retain generality but avoid complications associated with units. Plots of the momentum probability function, $|\psi(p)|^2$, for this system are less common, but classical correspondence is shown in the

same manner as before; as the quantum number is increased, the probability distribution of momentum approaches the expected, intuitive result of two possible values of momentum for a fixed energy, equal in magnitude but opposite in sign. Figure 2 indicates this trend, showing the formation of two distinct peaks that shift to higher values of momenta with the increase in n.

This result establishes the general use of the FT, as students can readily see position information transformed into momentum information, while also noting that the expected results associated with correspondence are shown in momentum space as well as position space. It should be noted, however, that quantum effects are still prevalent in each of the plots shown in Figure 2. The peaks themselves are not delta functions, implying some distribution of momenta exists around each classical result. Moreover, one can see the existence of peaks positioned between the classical results, indicating the probability (albeit smaller) of nonclassical momentum states which contribute to the overall momentum distribution.

The next step in the exercise asks students to produce, on their own, an explanation of how the Heisenberg Uncertainty Principle can be indicated by use of the given functions.[20,21] After being prompted to increase the length of the box for a fixed n, students get a stark visual picture of the position probability stretching over a larger region of the x-axis, and how a simultaneous narrowing of the momentum probability accompanies such a change, as demonstrated in Figure 3.

Again, this result speaks to the utility of this exercise as a tool not only to introduce ideas related to the FT, but to also pictorially reinforce concepts that are intrinsic to every undergraduate physical chemistry course dealing with quantum mechanics.
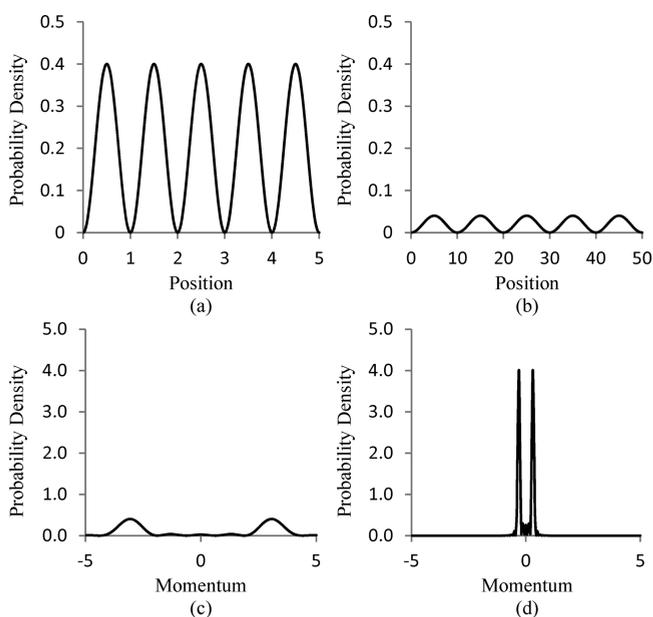
From here, the exercise switches to a standard method of introducing a Fourier analysis in the context of the relationship between the time and frequency domains as might be utilized in analytical spectroscopy. Through the use of a linear combination, a square wave (represented below as $h(t)$) can be synthesized from a set of time dependent sine functions (each possessing a different frequency) via the equation[2,22]

$$h(t) = \sum_{j}^{j\text{max}} \left(\frac{4}{(2j-1)\pi} \right) \sin\left(\frac{(4j-2)\pi t}{T} \right) \tag{4}$$

where j is the index for each term in the series, j_{max} is the number of terms in the sum, t is time and T is the period. Note again that as the index j changes, the sine term associated with said index has a higher frequency than all preceding terms before it. Convergence in the context of linear combinations is then tested by adding more and more terms to the sum within eq 4. Typical results of such a convergence test are given in Figure 4.
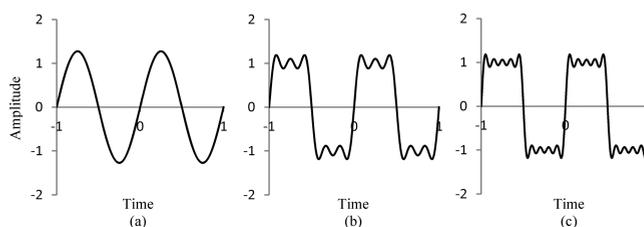

Figure 4. Summing of sine waves to synthesize a square wave. Each wave is constructed with (a) one term, (b) 3 terms, and (c) 5 terms.

The FT of eq 4 takes the time dependent information found in the terms of the sum and converts these data to the frequency domain via eq 1 where $H(\omega)$ is now the resulting spectrum in terms of frequency. To perform the prescribed analysis, a different method of integration is utilized in the document: the intrinsic Fast Fourier Transform (FFT) subroutine,[5] which is a convenient tool to numerically perform the required mathematics. Students investigate the necessary input for the FFT via the numerical software package's help file and then produce a discretized function (necessary for the application of the FFT subroutine) along with the resulting frequency spectrum, as is shown in Figure 5.

Because this process requires discretization of the function, and thus introduces the need for a sampling frequency, it also allows for the exploration of the Nyquist theorem, which defines the required digital sampling frequency to fully preserve all high frequency information in a spectrum of interest.[1,5] As

Figure 3. A comparison of the position space and momentum space probability distributions of quantum state $n = 5$ for boxes of different length: (a) position distribution with $L = 5$; (b) position distribution with $L = 50$; (c) momentum distribution with $L = 5$; (d) momentum distribution with $L = 50$. Note that (c) results from a FT of the wave function in (a), and (d) results from the FT of the wave function in (b).
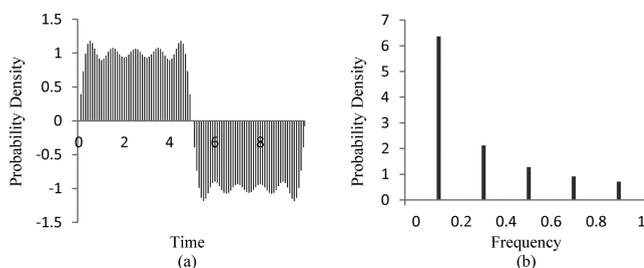

Figure 5. Input and output functions resulting from the application of the FFT: (a) input discretized square wave consisting of 5 sine terms of varying frequencies, and (b) output spectrum with peaks at each of the five frequencies used in the square wave synthesis.
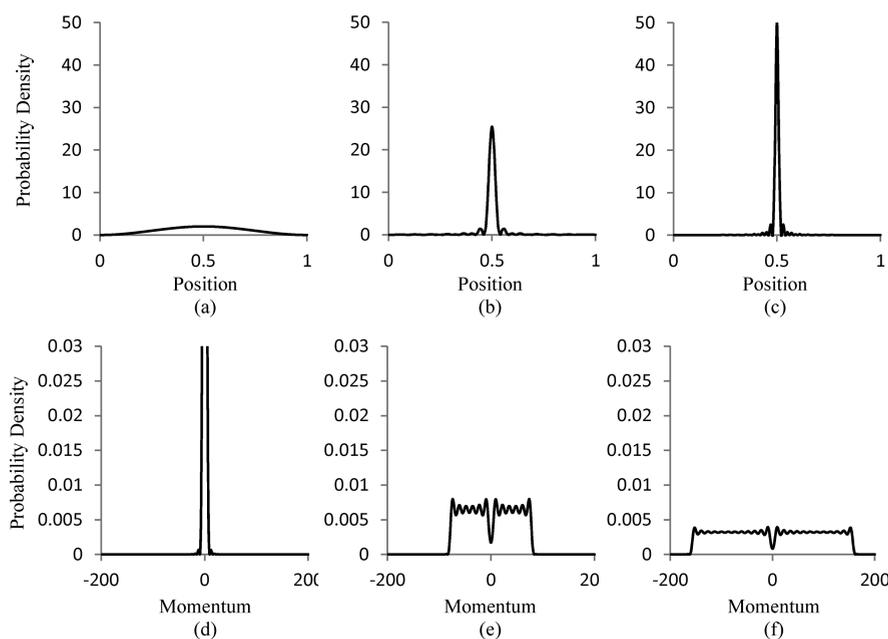
Figure 6. Demonstration of the Heisenberg Uncertainty Principle through the use of the FT of a linear combination of cosine functions built up in the center of a box with length $L = 1$. Plots a–c are in position space with (a) 1, (b) 25, and (c) 50 terms used in the sum constructing the wavepacket. Plots d–f are in momentum space with (d) 1, (e) 25, and (f) 50 terms in the linear combination.

an additional exercise, students are prompted to change the sampling frequency and produce plots that show loss of high frequency information if the Nyquist theorem is not properly applied to this system (i.e., lower frequency of discretization results in a loss of spectral information, as shown by disappearance of high frequency peaks in the frequency domain spectrum). Not only does this approach give a practical, albeit simple, explanation of how FT instrumentation interprets time dependent data, but from the standpoint of integration techniques, it introduces discussion of analytical versus numerical solutions, which is again a common point of emphasis in physical chemistry courses.

Finally, ideas relating to the Heisenberg Uncertainty Principle and linear combinations are investigated in the culminating portion of the exercise. Through the use of a wavepacket construction in the position domain and the subsequent FT of this wavepacket into momentum space, visual verification of the Uncertainty Principle is established. A box is once again defined as the region $0 \leq x \leq L$. A linear combination of cosine functions is centered at the midpoint of the box using

$$\psi(x) = \frac{1}{N} \sum_{j=1}^{N} \cos\left(j\pi\left(\frac{x - \frac{L}{2}}{L}\right)\right)$$

(5)

where N is an adjustable parameter representing the total number of terms in the linear combination. Again, integration (over the limits of the box) can be carried out via a symbolic integrator, or one can work out the analytical solution by hand. The result of such integration is

$$\psi(p) = \frac{1}{\sqrt{2\pi}} \frac{1}{N} \sum_{j=1}^{N} \int_{0}^{L} \cos\left(j\pi\left(\frac{x - \frac{L}{2}}{L}\right)\right) e^{-ipx} \, dx$$

$$= \frac{1}{N\sqrt{2\pi}} \sum_{j=1}^{N} \left(\frac{L}{L^2 p^2 - j^2 \pi^2}\right)$$

$$\times \left[\left(j\pi \, \sin\left(\frac{-\pi j}{2}\right) + iLp \, \cos\left(\frac{-\pi j}{2}\right)\right) e^{-ipL}\right.$$

$$\left. - \left(j\pi \, \sin\left(\frac{\pi j}{2}\right) + iLp \, \cos\left(\frac{\pi j}{2}\right)\right)\right]$$

(6)

Figure 6 shows typical student output, as taking the limit of increasing N and plotting the position and momentum probabilities readily shows the impact that the Heisenberg Uncertainty Principle has on these Fourier related variables.

As N increases, the interference occurring in the linear combination of cosine terms yields an increasingly more localized wavepacket, narrowing the position probability and thus increasing the certainty associated with this region of space. Simultaneously, the momentum probability function widens, encompassing more and more possible momenta and thus increasing uncertainty. Like the FT analysis associated with the linear combination of time dependent sine terms, the thoughtful student will notice that each cosine term in eq 5 can be viewed as possessing a different momentum. Thus, the addition of an increasing number of higher momentum terms to the linear combination yields a function distributed over a wider range in momentum space.

■ DISCUSSION

This exercise was enacted in the first of a two-part physical chemistry course sequence that covers quantum mechanics and chemical kinetics. The software-dependent portion was done during a 3 h lab session, with questions and problems done

post-lab. It was given during the beginning third of the course, after the general tenets of quantum mechanics had been established, and the particle in a box introduced. Students who performed this exercise were either enrolled in analytical chemistry concurrently with physical chemistry, or would take analytical chemistry in a year's time. Students were thus exposed to the mathematical aspects that are the focus of the FT before they were introduced to the practical applications emphasized in their analytical chemistry course. The topic was initiated from a mathematical standpoint, and then to maximize reinforcement, covered shortly thereafter in the analytical instrumentation course. The greatest benefit was achieved by the students taking the courses concurrently, as the short turnaround resulted in these students reporting a deeper understanding of the material and a better appreciation for the FT process as utilized in analytical chemistry.

The instructor of the analytical chemistry course introduced the FT using the time to frequency portion of the document itself as an interactive tool. The square wave synthesis was reintroduced, the transform was briefly explained as a mathematical tool, and finally, it was demonstrated how loss of high frequency information can result from improper application of the Nyquist theorem. Utilization of the document in this manner provided students with a familiarity that helped solidify the concept of the transform as a whole, not seeing it only as a mathematical tool but having an appreciation for the details behind its real-world application to analytical spectroscopy. As an interesting aside, it can be noted that the relationship in multiplex spectroscopy between total mirror displacement and resolution matches the trend observed when the length of the box is increased leading to a narrower distribution of momentum (see Figure 3).[1]

Feedback provided from the physical chemistry students focused on the visual nature of the document. Being able to graphically visualize the effects that the prescribed parameter changes had on the plots of position and momentum probability functions helped solidify concepts such as correspondence, linear combinations, and the Uncertainty Principle. Moreover, students who successfully completed the analytical integration of the position wave functions into momentum space reported that, while such calculations were lengthy and challenging, they provided a useful setting to practice mathematical and integration techniques that are necessary for other quantum mechanical calculations. Specifically, the Euler identity, Born Interpretation, and proper application of boundary conditions were all crucial concepts necessary for the completion and analysis of the exercise.

ASSOCIATED CONTENT

Supporting Information

The supplement contains the described exercise in the form of two separate Mathcad documents. Sample problems, exercises and questions in the form of a general lab handout are included as a separate file. The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00493.

> Exercise in the form of a Mathcad document (ZIP)
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> Exercise in the form of a second Mathcad document (ZIP)
>
> General lab handout with sample problems, exercises, and questions (PDF), DOCX

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Notes

The authors declare no competing financial interest.

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