

Week 2

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2.1 Lecture 3: Time, Frequency, and Fourier Transforms

1/10:

- Frequency- and time-domain spectroscopy.
 - Two ways of extracting the same information.
 1. Absorption spectrum (frequency domain).
 - Vary frequency of driving field or disperse white light after passing through the sample and look at each frequency component.
 - Measure the power absorbed for different frequencies.
 - Tells us the resonance frequency, how strongly the light interacts with the matter, and damping times or relaxation processes.
 2. Pulsed excitation (time domain).
 - Apply a pulsed driving force.
 - Measure resultant periodic oscillation and relaxation.
 - This is the basis for modern NMR and FTIR instruments.
 - Both represent the time-dependent behavior of a molecule.
- A powerful reason to use the time domain is the formal relationship between time and frequency data, the **Fourier transform**.
- **Fourier transform:** A formal relationship between the time domain and the frequency domain.
 - Underlying idea: Any function can be expressed as a sum of sines and cosines, i.e.,

$$F(t) = \sum_{n=1}^{\infty} [a_n \cos(n\bar{\omega}t) + b_n \sin(n\bar{\omega}t)]$$

- In practice, sample N points over a period T .
 - The values of time at which we sample are $t = n\delta t$ for $n = 1, \dots, m$.
 - Numerical analysis: Expand in harmonics of base frequency, i.e., we let $\bar{\omega} = \pi/T$ be 1/2 cycle of T . The harmonics are $n\bar{\omega}$ for $n = 1$ to N . We thus have as many harmonics as we do data points.
 - Then we plot the expansion coefficients vs. the frequency, and that is the spectrum in the series of expansion coefficients.
 - There's more to it than this, but this is the basic concept.
 - Also, this is only a discrete data set.
- **Fourier analysis:** Determining the coefficients a_n, b_n .

- Fourier transform relations.

- For continuous functions, we use Fourier transform integrals.

- Note that although both of the following integrals are sine transforms, there also exist cosine and complex $e^{-i\omega t}$ transforms.

- Sine and cosine transforms are used for real data; the complex form is more general.

- To convert to the time domain $S(t)$, we write

$$S(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \tilde{S}(\omega) \sin \omega t d\omega$$

- To convert to the frequency domain $\tilde{S}(\omega)$, we write

$$\tilde{S}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} S(t) \sin \omega t dt$$

- Example: Damped harmonic oscillator.

$$S(t) \propto e^{-\gamma t} \sin \omega_0 t \quad \Longleftrightarrow \quad \tilde{S}(\omega) \propto \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2}$$

- Parameters in the time and frequency domains.

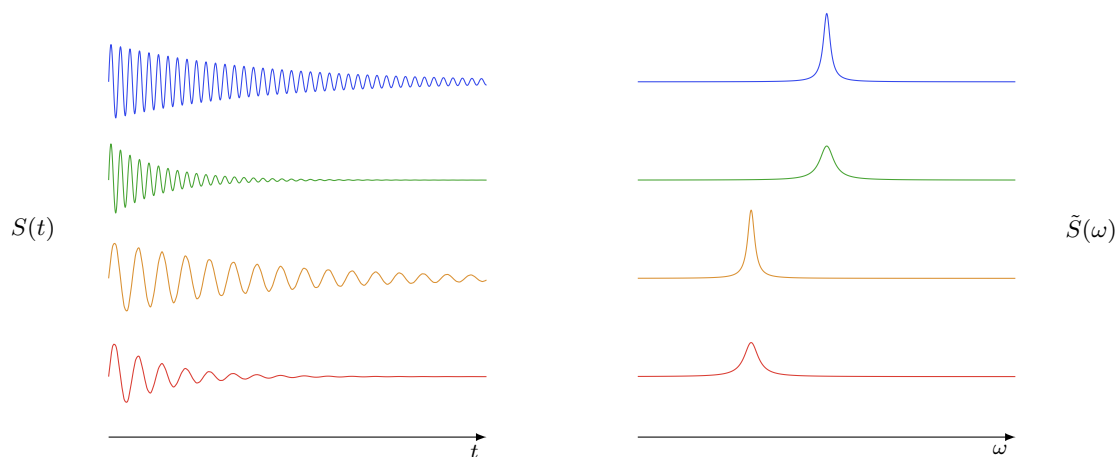


Figure 2.1: Parameters in the time and frequency domains.

| Parameter | Time Domain $S(t)$ | Frequency Domain $\tilde{S}(\omega)$ |
|------------------|--------------------|--------------------------------------|
| Large ω_0 | Fast oscillations | High frequency |
| Small ω_0 | Slow oscillations | Low frequency |
| Large γ | Fast decay | Broad linewidth |
| Small γ | Slow decay | Narrow linewidth |

Table 2.1: Parameters in the time and frequency domains.

- The area under the lines remains constant.
- Notice how the lower-frequency waves (orange and red) have frequency spikes shifted down.
- Broader Lorentzian implies more different types of frequencies are present implies destructive interference takes hold more quickly implies quicker decay.

- F.T. Example: Two resonances.
 - Consider a superposition of two oscillating decaying functions

$$C(t) = e^{-\gamma t} \sin(\omega_1 t) + e^{-\gamma t} \sin(\omega_2 t)$$
 - This implies two resonances in the spectrum.
 - In particular, they manifest as two beat frequencies, one of which is the average frequency, and the other of which is the difference.
 - The average frequency determines the regular vibrations; the difference is the bounding function.
- History of science during the French revolution.
 - Lavoisier and Fourier were both strongly influenced by their time (the French revolution).
 - Lavoisier was an elite tax collector, and was sentenced to be executed. When he asked the judge for mercy, the judge said, “the Republic has no need for scientists.”
 - Fourier got into trouble with Robespierre even though he was a revolutionary, but Robespierre’s regime was overthrown a day before his scheduled execution. Thus, we get Fourier transforms!
- Fourier transform infrared spectrometer.
 - Michelson Interferometer.
 - Named after UChicago’s first physics chair, also the first American to be awarded the Nobel prize in physics.
 - How it works: Intensity changes with pathlength-induced interference.
 - Incoming monochromatic waves get half reflected, half transmitted, allowing for phase separation.
 - Mathematically,

$$\Delta L = \frac{1}{\nu} = \frac{c}{\nu} \qquad \Delta t = \frac{\Delta L}{c}$$
 - Thus, if our light source is emitting monochromatic light (as it should be), the intensity of the light impinging on the sample changes with the pathlength.
 - In particular, if $\Delta L = n\lambda$, there is no change in intensity, but other forms see destructive interference to varying extents.
 - A Fourier transform then takes the monochromatic wave to a Fourier transform spectrum.
 - The frequency resolution for the spectrometer is given by the scan distance is $\Delta \nu = \pi/L_{\text{tot}}$.
 - Frequency resolution given by the scan surface.
 - For higher resolution, you need to scan farther??
 - We use an FTIR lamp (tungsten filament; broad bandwidth).
 - Broad bandwidth is the opposite of monochromatic; thus, it is difficult to obtain repeated peaks, and a Fourier transform yields substantial intensities over a range of frequencies, as expected.
- Measuring an FTIR spectrum.
 - Take reference and sample scans (yielding I_0 and I data) with that broadband bulb.
 - Then take an interferogram with and without the sample.
 - Then take an experimental spectrum, which is leveled and calculated from the previous work using $T = I/I_0$ and $A = -\log T$.
 - What is experimental and what is mathematical manipulations here??

- Wrap up.
 - A spectrum originates in the time-dependent behavior of molecules driven by electromagnetic radiation.
 - It is possible to perform experiments as a function of frequency or time.
 - There are practical differences, but they encode the same information.
 - These are related by a Fourier transform.
 - Fourier transform IR spectroscopy uses interferometry to relate changing optical pathlength to optical frequency.
 - More on this??