Chapter 2: Doppler spectroscopy

Learning goals: By the end of this chapter, you should understand
- the Doppler Effect
- how the Doppler Effect changes a spectroscopic signal

2.1 The Doppler Effect

The Doppler Effect is likely a phenomenon you have encountered before. When an ambulance, police car, or race car travels past you, the sound you hear changes pitch. This is because the sound waves being emitted by the source travel at the speed of sound, but the car is also moving, which compresses or extends the sound wave. The image below\(^1\) shows the sound waves being emitted by a stationary car and the sound waves being emitted by a moving car. Let’s focus on the stationary car. Imagine standing in front of the car or behind the car. The wavelength of the sound wave that hits your ear is the same, so you would hear the same pitch. Now imagine the car is moving. If you were standing in front of the car (ok, maybe a bit to the side … we don’t want you to get hit even in this thought experiment), the wavelength of the sound wave that hits your ear is shorter compared to the nonmoving car.

If you were standing behind the car, the wavelength is longer compared to the nonmoving car. The formula that relates the frequency (pitch) that you hear and wavelength should look really familiar. It is \(v_s = f\lambda\), where \(v_s\) is the speed of sound in air. The apparent shift in frequency due to an object moving is called the Doppler Effect. It is a very important concept in spectroscopy.

The wiki page for the Doppler Effect has a neat animated gif: [https://en.wikipedia.org/wiki/Doppler_effect](https://en.wikipedia.org/wiki/Doppler_effect)
YouTube video: [https://www.youtube.com/watch?v=h4OnB.YrbCjY](https://www.youtube.com/watch?v=h4OnB.YrbCjY)

The Doppler Effect is a phenomenon for any type of wave. Until I watched the above video, I never thought of a duck making waves in a pond as an example of the Doppler Effect, but it makes sense. Whether it is a sound wave, a light wave, or a water wave, the relative motion of the object with respect to the observer will change the wavelength, and thus the frequency of the wave.

Two-minute thought question: When the car passes you, you hear the engine (or horn) change pitch. What does the person in the car hear? Make sure you settle on an answer before you continue.

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\(^1\) Image Source: [https://flypaper.soundfly.com/discover/what-is-the-doppler-effect/](https://flypaper.soundfly.com/discover/what-is-the-doppler-effect/)
The person in the car hears no change in pitch because they are stationary with respect to the thing that is making the noise (the engine or horn of the car). If you yelled at the car as it passed, the driver would hear your pitch change as they passed, but not their own. Likewise, you don’t hear your pitch change as the driver passes you. What is important here is that the Doppler Effect is something experienced by the observer.

2.2 Connecting the Doppler Effect to spectroscopy

So, what does this have to do with spectroscopy? From Chapter 1.3, we made an important statement. It is so important we will repeat it here:

**Important statement:** If a photon of light has the exact energy as the energy difference between the ground state and an excited state, the atom will absorb that photon and move to an excited state. If the photon of light does not have the exact energy as that energy difference, the atom will ignore the photon completely.

**Important reminder:** Frequency, energy, and wavelength are all the same quantity. Each of these parameters is related to the other parameters only by constants.

**Definitions:**
Resonance: When an atom gets excited by a photon from one state to another, we say the atom “goes through resonance.” This is similar to playing the trumpet. When you blow into a trumpet, you excite a standing wave in the pipe to create a note. The same thing happens with an atom. When you excite an atom, the electron goes from one standing wave mode to another. So, atomic physicists use the word “excitation” and “resonance” interchangeably.
Resonant frequency: When the frequency of the laser is just right to excite the atom from the ground state to an excited state, we call that the resonant frequency. We use the variable $f_r$ for resonant frequency.

Imagine a laser beam is travelling to the right. Also imagine there are three atoms: One travelling to the left, one that is stationary, and one that is travelling to the right. For this thought experiment, we will assume the speeds of the moving atoms are the same, just in opposite directions.

I labelled the three atoms as 1, 2, and 3. Atom 1 is not moving, atom 2 is moving to the left, and atom 3 is moving to the right. In this experiment, the atom is the observer. Atom 2 doesn’t think it is moving. Atom 2 would claim that atom 1 is moving to the right and atom 3 is moving twice as fast as we (as the scientists looking from the outside) would say atom 3 is moving. Both atom 1 and us, as the observing scientists, will agree on the frequency of the laser. To add numbers, let’s say that the laser frequency is $652.0000 \times 10^{12} \text{ Hz} = 652.0000 \text{ THz}$ (terahertz). Both the scientists and atom 1 will agree that the laser frequency is $652.0000 \text{ THz}$. But atom 2 and atom 3 will disagree. Atom 2 is moving towards the laser and atom 3 is moving away from the laser.
Two-minute thought question: Will atom 2 claim the laser is higher in frequency or lower in frequency than what we and atom 1 claim? Be sure to have an answer before reading on.

I like to put fun stuff to separate questions and answers. On November 7, 1940, the Tacoma Narrow Bridge in Washington state was experiencing sustained winds at ~40 mph. These winds created excited the bridge through a mechanical resonance that resulted in a standing wave on the bridge. This resonance caused the bridge to collapse. Check out the wiki page for some dramatic video: https://en.wikipedia.org/wiki/Tacoma_Narrows_Bridge_(1940)

Answer: Atom 2 is moving towards the laser source, so it will claim the frequency of the laser is higher than it actually is. If we want atom 2 to absorb laser light, we need to set the laser frequency smaller than the resonant frequency. If the actual laser frequency, which is lower than the resonant frequency, plus the frequency shift due to the Doppler effect results in the resonant frequency in the frame of atom 2, atom 2 will absorb light. Atom 3 is moving away from the laser source, so it will claim the laser frequency is lower. As a result, the actual laser frequency will have to be higher than the resonant frequency for atom 3 to absorb light.

Why does this matter? Inside a gaseous sample of atoms, some atoms are moving towards the laser, some are moving away, and some aren’t moving towards or away from the laser.

As we, in the laboratory/stationary frame, change the frequency of the laser from below the resonant frequency to above the resonant frequency, we will find that atom 2 will absorb light at a different frequency than atom 1 or atom 3. Atom 2 will claim it is absorbing light at precisely the frequency needed to excite from the ground state to the excited state, and atom 2 is correct! Atom 2 “sees” a higher frequency than the actual frequency of the laser. When atom 2 “sees” the correct frequency, it will absorb light. For us in the laboratory frame, the laser frequency is too low. This can be confusing, so here is a summary:

- From atom 2’s reference frame, the frequency of the laser is just right to excite atom 2 from the ground state to the excited state.
- From the laboratory reference frame, the frequency of the laser is too low.
- The Doppler Effect tells us that because atom 2 is travelling towards the laser beam, it will see a higher frequency that what we, as scientists in the laboratory/stationary frame, measure.

An important correction: I simplified the above description by just a little bit. Importantly, only the component of the atom’s velocity in the direction towards or away from the laser beam will contribute to the Doppler Effect. An atom that isn’t moving toward or away from a laser can still be moving; it is just moving perpendicular to the laser. A more correct statement is: Inside a gaseous sample of atoms, some atoms have a velocity component pointing towards the laser, some atoms have a velocity component that is pointing away from the laser, and some atoms have no velocity components pointing towards or away from the laser. Below is an example of three atoms each with a velocity component along the laser axis:
**Definition:** Doppler shift: The shift in frequency seen by an atom due to the Doppler effect. The Doppler shift is given by the formula \( \Delta f_D = \frac{v_\parallel}{\lambda} \), where \( v_\parallel \) is the velocity component in the direction of (parallel to) the laser beam.

Let’s shoot the laser directly down the positive x-axis. The first atom’s velocity is pointing directly towards the laser in the negative x-direction. For this atom, there is no perpendicular component to the atom, \( v_\perp = 0 \).\(^2\) The parallel component of the velocity is negative, \( v_\parallel < 0 \). The second atom has a negative perpendicular component and a negative parallel component, \( v_\perp < 0 \) and \( v_\parallel < 0 \). Only the parallel component causes the Doppler shift. Notice the first and second atom have the same parallel velocity component. The parallel component for the two atoms is the same size and pointing in the same direction. Therefore, they will have the same Doppler shift. The third atom has a positive perpendicular component and a positive parallel component, \( v_\perp > 0 \) and \( v_\parallel > 0 \). Again, only the parallel component is used to calculate the Doppler shift. This atom will absorb photons with a different laser frequency than atoms 1 and 2. The last atom is not moving at all. It has no perpendicular or parallel component, \( v_\perp = 0 \) and \( v_\parallel = 0 \). The laser frequency to excite this atom is the actual answer we want to measure. We will talk about how we extract information from only that fourth atom in the next few chapters. For now, notice that as we scan the frequency of the laser from a lower frequency to a higher frequency, atom 1 and atom 2 absorb photons first, atom 4 is next, and atom 3 is last.

Here are three atoms that experience no Doppler shift:

None of these atoms have a parallel velocity component, so all three of these atoms will be excited from the ground state to an excited state at the same laser frequency. Again, this is the actual laser frequency we want to measure.

As mentioned in the definition of Doppler shift, the frequency shift seen by an atom is \( \Delta f_D = \frac{v_\parallel}{\lambda} \), where \( v_\parallel \) is the velocity component in the direction of (parallel to) the laser beam. If the atom is travelling towards the laser beam, then \( v_\parallel < 0 \). That atom will absorb light at a lower frequency.

\(^2\) If you have worked with vectors before, you can also write this as \( v_y = 0 \). I like to use parallel and perpendicular because it is independent of how we picked the axes.
than the resonant frequency (this is called RedShift). If the atom is travelling away the laser beam, then \( v_\parallel > 0 \). That atom will absorb light at a higher frequency than the resonant frequency (this is called BlueShift).

Inside a gaseous cloud of atoms, there is a distribution of velocities. This distribution depends upon the temperature of the atoms. The hotter the atoms, the higher the average speed. The distribution of velocities in the direction of the laser beam\(^3\) is shown by the blue line in the figure to the left. The shape is known as the Maxwell-Boltzmann velocity distribution. The Maxwell-Boltzmann distribution often use the function \( f(\nu) \), which is unfortunate because we also use \( f \) for frequency. A good rule of thumb is that if it is a function, like \( f(\nu) \), the \( f \) is probably referring to a distribution. If the \( f \) is all by itself in a formula, it is probably referring to the frequency of the laser.

**Definition:** Full width half maximum (FWHM): The full width half maximum of a distribution is the width of the distribution at half of its maximum value.

The full width half maximum of a Maxwell-Boltzmann velocity distribution, which is a velocity, is 
\[
\text{FWHM} = 2.355 \sqrt{\frac{k_B T}{m}}
\]
where \( k_B = 1.38 \times 10^{-23} \text{J/K} \) is a constant known as the Boltzmann constant (the unit is Joule/Kelvin), \( T \) is the temperature of the gas (the unit is Kelvin), and \( m \) is the mass of an atom in the gas (the unit is kilogram). The hotter the gas, the wider the velocity distribution. That also means that the hotter the gas, the more atoms are moving with larger speeds. Since the FWHM is a velocity, the units are m/s.

**How to use distributions:** This distribution can be thought of as how many atoms fall within a particular velocity range. The first thing I want to point out is the total area under the distribution is equal to 1. To use a distribution, you ask questions like, “How many atoms have a positive parallel velocity component?”, “How many atoms have a parallel velocity component between -2 m/s and 10 m/s?”, or more generally, “How many atoms have a parallel velocity component between \( v_a \) and \( v_b \)?”, where \( v_a \) and \( v_b \) are any velocities we choose.

The answer to that question is the area under the distribution between \( v_a \) and \( v_b \) times the total number of atoms. For example, here are three plots with different choices of \( v_a \) and \( v_b \):

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\(^3\) We are not worried about any velocity components that are perpendicular to the laser beam since those velocity components don’t contribute to the Doppler Effect.
Suppose we have 5000 atoms. As shown in the first plot, there are \(5000 \times 0.726 = 3630\) atoms with parallel velocity components between \(-100\) m/s and \(+200\) m/s. As shown in the second plot, there are \(5000 \times 0.061 = 305\) atoms with parallel velocity components between \(-200\) m/s and \(-150\) m/s, and in the third plot there are \(5000 \times 0.347 = 1735\) atoms with parallel velocity components larger than \(50\) m/s. The atoms at each velocity in the above distribution will absorb a photon with a different laser frequency.

The shape of the Maxwell-Boltzmann distribution is called a Gaussian function. The mathematical shape is given by:

\[
f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}}
\]

Check out the Mathematica file named “Maxwell.nb” to explore this function more. This program will also be useful for your homework.

**Extra math for those who have taken statistics:** If you have taken a probability or statistics course, you may have seen this before. In statistics, Gaussian functions are written as \(e^{-\frac{v^2}{2\sigma^2}}\), where \(\sigma\) is the standard deviation. In the case of the Maxwell-Boltzmann velocity distribution, the standard deviation is \(\sqrt{\frac{k_B T}{m}}\). The full width half maximum of a Gaussian function defined using the standard deviation is:

\[
\text{FWHM} = 2\sqrt{2\ln(2)\sigma} \approx 2.355 \sqrt{\frac{k_B T}{m}}.
\]

**Thought experiment time:** Suppose we had a nice simple atom with a single excited state.

We are going to run two thought experiments. The first thought experiment is going to have a sample of gaseous atoms that are cold (low temperature). The second thought experiment will have hot atoms.

Each experiment has two steps:

1. First, we are going send a laser beam through the sample of gaseous atoms. After passing through the sample, the laser is going to hit a detector that measures how much power is in the laser. The idea is that if no atoms are excited, all of the laser power hits the detector. If atoms absorb light, less power will hit the detector.
2. Next, we scan the frequency of the laser from below resonance, which means the frequency of the laser is too small to excite any atoms, to above resonance, which means the frequency of the laser is too big to excite any atoms.

What does the detector signal look like as a function of laser frequency for the cold sample? What does the detector signal look like as a function of laser frequency for the hot sample?

I don’t like to put answers immediately below the questions, so here is another comic to fill up space 😊


Answer:

A few things to notice:
Hot is wider than cold because, for the hot gas, there are more atoms with larger speeds. A large speed means a larger Doppler shift.
Cold is deeper than hot because we have the same number of atoms in each experiment. The total number of photons lost is the same for both though experiments. In other words, the lost area is the same!\(^4\)

**Definitions:**
Doppler broadening: the hotter the gas, the wider the spectral feature. When a spectral feature is wider because of temperature, we say that the spectrum is Doppler broadened.

\(^4\) For some reason, when I look at this plot the areas don’t look the same. I did the math to calculate the areas, and they do match. Apparently, I’m just really bad at visually estimating areas!
Doppler width: The FWHM of the Maxwell distribution is a velocity. We can convert this to a frequency using the Doppler shift formula. The FWHM of a spectral feature that is broadened because of temperature is given by the formula $\Delta f_D = \frac{2.355}{\lambda} \sqrt{\frac{k_B T}{m}}$. We call $\Delta f_D$ the Doppler width.

Transmission Plot: A plot of transmitted laser power as a function of laser frequency. If the laser frequency happens to match a resonant frequency, the power of the laser beam will decrease in the transmission plot. The image on the previous page are two transmission plots, one for a cold vapor cell and one for a hot vapor cell.

Absorption Plot: We often think about transmission plots in spectroscopy. This makes sense because it is what we are going to measure in the lab. Absorption plots can also be useful to think about. The absorption plot tells us how much laser light is absorbed by the atoms as a function of frequency. The transmission plot tells us how much laser light is transmitted through as a function of frequency. The absorption plot plus the transmission plot equals 1. Try drawing the absorption plot for the above graph.
Homework 2:
Starting this homework, the last problem will be an exploration problem. They take a little longer to do, but you will really get to explore some fun physics.

<table>
<thead>
<tr>
<th>Variable</th>
<th>SI Unit</th>
<th>SI Unit abbr.</th>
<th>Value if a constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>( \lambda )</td>
<td>meters</td>
<td>m</td>
</tr>
<tr>
<td>Frequency</td>
<td>( f )</td>
<td>Hertz (1/second)</td>
<td>Hz (1/s)</td>
</tr>
<tr>
<td>Speed of Light</td>
<td>( c )</td>
<td>meters/second</td>
<td>m/s ( \approx 3 \times 10^8 ) m/s</td>
</tr>
<tr>
<td>Planck’s Constant</td>
<td>( h )</td>
<td>Joules seconds</td>
<td>J s ( 6.626 \times 10^{-34} ) Js</td>
</tr>
<tr>
<td>Boltzmann Constant</td>
<td>( k_B )</td>
<td>Joules/Kelvin</td>
<td>J/K ( 1.38 \times 10^{-23} ) J/K</td>
</tr>
<tr>
<td>Doppler shift</td>
<td>( \Delta f )</td>
<td>Hertz (1/second)</td>
<td>Hz (1/s)</td>
</tr>
<tr>
<td>Mass</td>
<td>( m )</td>
<td>kilogram</td>
<td>kg</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T )</td>
<td>Kelvin</td>
<td>K</td>
</tr>
<tr>
<td>Resonant frequency</td>
<td>( f_r )</td>
<td>Hertz</td>
<td>Hz</td>
</tr>
</tbody>
</table>

\[
c = f \lambda, \quad E_{ph} = hf, \quad \Delta f = \frac{v_{\parallel}}{\lambda}, \quad \text{FWHM} = 2.355 \sqrt{\frac{k_B T}{m}}
\]

\[
\Delta f_D = \frac{2.355}{\lambda} \sqrt{\frac{k_B T}{m}} = \frac{2.355}{c} \sqrt{\frac{k_B T}{m} f}
\]

1. An atom at rest is excited from the ground state to an excited state by a photon from a laser with frequency \( f = 652.000000 \) THz. Suppose the laser beam is moving to the right and atom is moving towards the laser beam with a velocity component of \( v_{\parallel} = -200 \) m/s (the minus sign indicates the atom is moving towards the left). What frequency should the laser be for this atom to absorb a photon?

2. Now the laser beam is moving to the left. Using the same numbers as question 1, what frequency should the laser be for this atom to absorb a photon?

3. Assess your answer to question 2 by assuming the laser is moving to the right, but the atom is moving away from the laser beam. Make a general statement about direction of the laser and direction of the moving atom.

4. A vapor cell has Europium-153 atoms. A Europium-153 atom has 63 protons and 90 neutrons (notice 63+90=153). The mass of a Europium-153 atom is \( 2.539 \times 10^{-25} \) kg. Assume that the Europium-153 atom has a single ground state and a single excited state.5
   a. If the temperature of the vapor cell is 400 K, what is the full width half maximum of the Maxwell-Boltzmann velocity distribution?
   b. What is the Doppler width?
   c. Suppose an atom that is not moving absorbs photons from a laser with \( f = 652.000000 \) THz. Sketch the transmission plot of a laser beam as it passes through a vapor cell. Remember we are assuming the Europium atom has a single ground state and a single excited state. We will explore a real Europium atom in the next question. You can pick any amplitude you want for the spectral feature. Hint: You should be using your answer from part b) in this sketch.

5 This is not true! The Europium atom has a more complicated energy level structure! More on this in question 5.
5. Europium-151 actually has 6 “ground” states. While, technically, one of these ground states has the lowest energy, they are all really close together so we call them all ground states. The physical reason for this is that the nucleus of Europium-151 has angular momentum, something we call nuclear spin. We won’t talk much about nuclear spin until chapter 6 so, for now, we will just use the fact that Europium-151 has 6 ground states separated from each other by a small frequency (energy).

Each experimental group is doing spectroscopy from these ground states to a different excited state. Because the nucleus has spin, the excited state is also split into 6 closely spaced levels. Again, we will explore this more in Chapter 6. I do want to note that if the europium atom had no nuclear spin, there would be only 1 ground state and 1 excited state. The nucleus having spin makes our experiment a bit more complicated, but we can actually learn a lot about the nucleus from the effects it has on the energy levels.

Anyway, here is an energy level diagram for the ground state of Europium-151:

![Energy Level Diagram for Europium-151 Ground State](attachment:Europium-151_Ground_State_Diagram.png)

Notice the vertical scale is in MHz. The F=6 state (we will talk about what these labels mean in chapter 6. If Europium had no nuclear spin, the single ground state would be at 0. I recognize these numbers are coming out of nowhere, but trust me in that they will make sense once we get through chapter 6. For now, just assume them to be true.

Here is an energy level diagram for the $J = \frac{5}{2}$ excited state of Europium-151:

![Energy Level Diagram for Europium-151 J=5/2 Excited State](attachment:Europium-151_J=5/2_Exited_State_Diagram.png)

Again, the vertical scale is in MHz. This vertical scale is with respect to the excited state. The “0” on the above graph isn’t really 0. It is really a big number, 642,892.3 MHz, but that doesn’t fit well on the chart.

Ok, now we are going to predict a transmission plot (frequency vs laser power loss). There is one rule that you have to memorize for spectroscopy. We are not going to prove it, but this rule comes from the mathematics behind quantum mechanics.

“A photon can change $F$ by -1, 0, or 1.”

In other words, an excitation follows the rule: $\Delta F = -1, 0, \text{ or } +1$. Memorize this!!

What this means is the following: Suppose an electron is in the $F = 3$ ground state. Exciting this electron with a photon can only move it to the $F = 2 \ (\Delta F = -1)$ excited state, the $F =$
3 ($\Delta F = 0$) excited state, or the $F = 4$ ($\Delta F = 1$) excited state. The electron cannot be excited to $F = 5$ ($\Delta F = 2$) or to $F = 1$ ($\Delta F = -2$).

a. Suppose the atoms are all in the $F = 3$ ground state. Sketch a transmission plot for a laser travelling through a vapor cell that is at 10 Kelvin. Label your plot well! There should be 3 Gaussian shapes. Don’t worry about the amplitudes of the absorption. There is no easy rule to find amplitudes. Be sure to indicate the center frequencies as well as the FWHM of each shape. If you’d like, send me an email once you are done, and I’ll email you the answer.

Hint: to calculate the FWHM of the shapes, you first need to find $\Delta f_D$.

b. Challenge problem! Even if you don’t do this problem, read on!

Suppose you have electrons in all 6 ground states. Sketch the transmission plot.

Answer:

The red lines are the resonant frequencies for each possible transmission. Notice you can resolve almost all of the transitions! There are two transitions near 700 MHz and two just above 1000 MHz that are merged together, but the rest are resolved.

They are given by the numbers:

<table>
<thead>
<tr>
<th>$f$(MHz) − 642,892.3 MHz</th>
<th>F (ground state)</th>
<th>F (excited state)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1008.3 MHz</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>-908.0 MHz</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>-787.4 MHz</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>-349.2 MHz</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>-269.1 MHz</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>-168.8 MHz</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>224.4 MHz</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>284.3 MHz</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>364.4 MHz</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>684.1 MHz</td>
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<td>2</td>
</tr>
<tr>
<td>724.1 MHz</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>784.0 MHz</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>1029.0 MHz</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
c. Challenge problem 2: What would the graph look like if the vapor cell is a more realistic temperature, say 400 K?

Answer:

The lines are not resolved! So clearly, the colder the better.

The next two chapters are going to cover a neat trick for how to get a transmission plot that looks like atoms at 0 Kelvin!!