Chapter 3: Building up to subDoppler spectroscopy (also known as saturated absorption spectroscopy)

Learning goals: By the end of this chapter, you should understand
- the Equipartition Theorem
- the relationship between the natural linewidth of an atom and the lifetime of a state
- the scattering rate
- saturation

3.1 Spectroscopy at 0 Kelvin

There is a neat theorem from thermodynamics known as the Equipartition Theorem.¹ This theorem relates the temperature of a gas to the average kinetic energy of all of the atoms in that gas. You may have not heard of kinetic energy before, so, briefly, you can think of kinetic energy as the energy of movement. Any object with mass \( m \) and speed \( v \) has kinetic energy:

\[
K = \frac{1}{2}mv^2
\]

Since kinetic energy is a type of energy, the unit is Joules. Imagine you have 3 atoms in your gas. We will assume that all the atoms have the same mass, but different speeds. The average kinetic energy of the atoms in your gas would be:

\[
\frac{1}{3}\left( \frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \frac{1}{2}mv_3^2 \right)
\]

If we had \( N \) atoms in our gas, all with the same mass, the average kinetic energy would be:

\[
\frac{1}{N}\left( \frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \cdots + \frac{1}{2}mv_N^2 \right) = \frac{1}{2}m\left( \frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N} \right)
\]

That last term in parentheses we call the average speed squared.² We write that last term as \( \langle v^2 \rangle \). In fact, whenever you see the mathematical expression between two angle brackets, \( \langle \ldots \rangle \), you are being asked to take the average of that property. \( \sqrt{\langle v^2 \rangle} \) has a special name which is called the root mean squared speed; you may have learned about this in high school Chemistry. Putting this all together, we find that the average kinetic energy is:

\[
\langle K \rangle = \frac{1}{2}m\langle v^2 \rangle
\]

Reading the above equation: Given a gas made up of atoms with the same mass, the average kinetic energy of the atoms is found by \( \frac{1}{2}m\langle v^2 \rangle \), where \( m \) is the mass of an atom and \( \langle v^2 \rangle \) is the average speed squared.

The Equipartition Theorem tells us that gas moving around in 3 dimensions has a temperature given by the equation:

² This can be read two different waves. This means square the speeds first and then take the average, not average the speeds and then square.
\[
\frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle \rightarrow T = \frac{1}{3} k_B \langle v^2 \rangle.
\]

Likewise, if you had the temperature of a gas, you can find the root mean square velocity:
\[
\frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle \rightarrow \langle v^2 \rangle = \frac{3 k_B T}{m} \rightarrow \\
\sqrt{\langle v^2 \rangle} = v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}}.
\]

**An important comment:** When we studied the Doppler effect, our focus was on \( v_\parallel \). The \( v \) in the equipartition theorem is the full velocity, not the parallel or perpendicular component.

The above equation is only for gaseous atoms moving in 3 dimensions. Molecules use a slightly different equation. The full Equipartition Theorem says that each degree of freedom contributes \( \frac{1}{2} k_B T \) of energy. It is a bit complicated for this class, but you can learn more about degrees of freedom on the Googles.\(^3\) For us, we will just use the above formula as a way to relate the speeds of the atoms to the temperature of the gas.

Ok, let’s do another thought experiment. We start with our trusty two-level atom, which has a single ground state and a single excited state. The atoms in our vapor cell are still a gas, but all of the atoms are frozen in place. In other words, the speed of every atom is 0 m/s. The Equipartition Theorem tells us that the temperature of the gas is also 0 Kelvin. This is actually how we define absolute zero: 0 Kelvin is when all atoms stop moving. You can’t get any colder than this.

Now, we do our spectroscopy. What does our transmission plot look like?

The first thing to note is that there is no Doppler broadening. All of the atoms will absorb photons from the laser at the precise frequency needed to excite them. From the information you currently have, you might guess that our transmission plot looks like a spike.

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But there is more to learn 😊! ⁴

There is a minimum width that a spectroscopic feature will have in a transmission plot. This minimum width is called the natural linewidth of the atom which is described by the lowercase Greek letter gamma, \( \gamma \). The natural linewidth is a frequency so it has units of Hertz. ⁵ Spectroscopists will often just say “linewidth” instead of “natural linewidth.”

Let’s make both an absorption plot and a transmission plot for our two-level atoms that are at 0 Kelvin. It will look like this:

The shape of the absorption profile is called a Lorentzian function, and it has the mathematical form of:

\[
L(f) = A \frac{\gamma^2/4}{(f - f_r)^2 + \gamma^2/4},
\]

where \( \gamma \) is the natural linewidth. ⁶ The natural linewidth is also the full width half maximum of the Lorentzian function. \( A \) is the absorption coefficient that describes the fraction of laser light lost when travelling through an atomic sample when the laser light is perfectly on resonance. \( A \) is a number between 0 (no light absorbed) and 1 (all light absorbed). The graph of a Lorentzian function looks very similar to a Gaussian, but they are slightly different in shape.

**Important:** Spectroscopists will almost always call the Lorentzian function the absorption profile, the absorption lineshape, Doppler-free spectra, or the spectral feature. The Lorentzian function is more a description of that function itself. As an analogy, think about how many times you have used a sine wave or a cosine wave in math. These are mathematical functions that are

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⁴ A common method of teaching, which is what I’m using in this class, is to build up complexity. To simplify things when learned about Doppler broadening, we ignored the transmission plot for really cold gasses. Now we are adding this part in. As the semester progresses, we will continue to add more and more information to our model to make it more and more complete.

⁵ If you look in other books, you may see slightly different formulas than what we write in this book. The reason is because most atomic physics formulas use angular frequency units, which are less intuitive than normal frequency units. To keep things simple, all of the variables in this book are defined using normal frequency. Formulas you may find elsewhere might be using angular frequency units. The only difference will be a factor of \( 2\pi \). For example, on the next page we will define lifetime as \( \tau = \frac{1}{\Gamma} \). Many books will define lifetime as \( \tau = \frac{1}{\Gamma} \) where \( \Gamma \) is the linewidth in angular frequency units. Angular frequency vs frequency is only important when applying numbers to formulas; the concepts are the same. Everything in this book is explained and written using frequency units. I just wanted to give a warning if you supplement with other readings. When in doubt, come chat 😊

⁶ This is for the “low intensity” limit. As we work through the chapter, we will refine this formula slightly. I just want to start basic to get the concepts understood first.
used to describe lots of different mathematical and physical phenomena. The same thing with the Lorentzian function. There are other physical phenomena described by a Lorentzian function, so we instead use more specific language. For the rest of the book, we will use absorption profile or Doppler-free spectra.

3.2 The natural linewidth

The natural linewidth is actually related to the lifetime of an excited state. To understand the lifetime of an atomic state, first imagine that all of our atoms are in the excited state. Next, we turn off the laser beam. As time progresses, the atoms will each emit a photon to go back to the ground state. Spectroscopists will often use the word “decay” when talking about an atom emitting a photon to go back to the ground state. This is a random process. So, some atoms decay back to the ground state quickly, some take their time. Statistically, each atom has a probability of decaying back to the ground state that will look like the graph to the left. At $t = 0$, all of the atoms are in the excited state. As time marches on, atoms start to decay and the excited state fraction gets smaller. For the graph to the left, after about 10 ns, 80% of the atoms have decayed back to the ground state. The mathematical form of the decay curve is:

$$e^{-t/\tau},$$

where $\tau$ (this is the Greek letter lowercase tau) is called the lifetime of the state. This function is called an exponential decay. The lifetime of the state for this graph is $\tau = 6.25$ ns.

Amazingly, the natural linewidth and the lifetime are related to each other! The formula relating the two quantities is:

$$\tau = \frac{1}{2\pi\gamma}.$$

These two quantities are inversely related to each other. That means:

- If the lifetime is small, the natural linewidth is large. This means the absorption and transmission plots will have a spectral feature that is relatively wide.
- If the lifetime is large, the natural linewidth is small. This means the absorption and transmission plots will have a spectral feature that is relatively narrow.
3.3 The scattering rate and saturation.

Let’s start with the absorption and transmission plots from above.

In chapter 1, we made an important statement.

**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.

We are going to refine this statement to something a little more correct. The above statement assumes that the spectral feature has zero width, which we now know is untrue. Even if the laser frequency is slightly below $f_r$, an atom that is not moving has a probability of absorbing a photon from the laser. The probability is smaller than if the laser was perfectly on resonance, but there is still a sizeable probability.

To the left is a zoom in on the absorption profile. There is technically a probability that the atom will absorb a photon with any energy, but that probability decreases the further the laser frequency is from $f_r$. So, for spectroscopists, the linewidth really matters. Suppose an atom has a natural linewidth of 100 MHz and the laser is 25 MHz below the resonant frequency. That atom will still absorb quite a few photons because the frequency of the laser is still nicely inside the spectral feature. However, if the atom has a natural linewidth of 1 MHz, it will not absorb many photons at all.

We are now going to define a new parameter called detuning. This parameter will help us refine that important statement above. Detuning, which is represented by the Greek lowercase delta ($\delta$), is how far from resonance the laser frequency is.\(^7\) Mathematically, detuning is $\delta = f - f_r$, where $f$ is the frequency of the laser. Notice that if $f < f_r$, then $\delta < 0$. Likewise, if $f > f_r$, then $\delta > 0$. In our thought experiments, the atoms will absorb the largest number of photons when $\delta = 0$ (the laser frequency exactly matches the excitation frequency). The atoms will absorb half as many photons when $\delta = \frac{\gamma}{2}$ or $\delta = -\frac{\gamma}{2}$.

\(^7\) A lot of learners will confuse the two Greek letters delta ($\delta$) and gamma ($\gamma$). They look very similar and both have units of frequency. But they mean very different things.
From these ideas, we can define a scattering rate. The scattering rate is how many photons per second an atom will absorb (and re-emit). The scattering rate, \( r_\gamma \), is:

\[
r_\gamma(\delta) = \frac{\pi \gamma s}{1 + s + \frac{4\delta^2}{\gamma^2}}
\]

where \( s \) is called the saturation parameter. We will explore the saturation parameter in a homework problem, but here is the definition:

\[
s = \frac{I}{I_0}; \quad I = \frac{P}{A}; \quad I_0 = \frac{4\pi^3 h c \gamma}{3\lambda^3},
\]

where \( I = P/A \) is the intensity of the laser light measured in Watts/meter\(^2\), \( P \) is the power of the laser light measured in Watts, \( A \) is the cross-sectional area of the laser beam measured in meter\(^2\), and \( I_0 \) is a parameter of the atom known as the saturation intensity that has units of Watts/meter\(^2\). Notice the saturation intensity is a constant for a transition in the atom. However, the saturation parameter is something we control by changing the power or the size of the laser.

The scattering rate looks a lot like the absorption profile!

\[
r_\gamma(\delta) = \frac{\pi \gamma s}{1 + s + \frac{4\delta^2}{\gamma^2}} \quad L(f) = A \frac{\gamma^2/4}{(f - f_r)^2 + \gamma^2/4}
\]

Let’s do some algebra on the absorption profile. The first thing I notice is that \((f - f_r)^2 = \delta^2\).

\[
L(\delta) = A \frac{\gamma^2/4}{\delta^2 + \gamma^2/4}
\]

Next let’s factor out \( \gamma^2/4 \) from the denominator:

Here is the scattering rate and the absorption profile in its new form:

\[
r_\gamma(\delta) = \frac{\pi \gamma s}{1 + s + \frac{4\delta^2}{\gamma^2}} \quad L(\delta) = A \frac{1}{1 + \frac{4\delta^2}{\gamma^2}}
\]

Take a few moments to compare these two formulas.

Here is what I noticed:

1. They are both functions of detuning.
2. The denominators are almost the same.
3. The numerators are quite different.

Let’s talk about each one.

1. Both functions are maximum when \( \delta = 0 \). The functional form is also very similar, which leads us to point 2.
2. Back when we first wrote the Lorentzian function, I had a footnote saying this was the low intensity limit. If the intensity is really small, \( s \ll 1 \) and \( 1 + s \approx 1 \). So, in the low intensity limit, the scattering rate matches that Lorentzian function. But this is a physics class! Let’s talk about where the extra \( s \) in the denominator of the scattering rate comes from.

The extra \( s \) comes from the fact an atom will always spend some amount of time in the excited state. If we got rid of the \( s \) in the denominator, the number of photons scattered
per second (i.e. the scattering rate) is linear with laser power. That means if we increase the laser power by some factor, we increase the scattering rate by the same factor. However, the atom spends, on average, time $\tau$ in the excited state. The scattering rate must saturate at some point!

This is important, so let’s explore it a little more. Let’s pretend the atom always spends a time $\tau = 10$ ns in the excited state before decaying back to the ground state.\(^8\) In the most extreme case, an atom would be immediately re-excited back to the excited state before having to wait another 10 ns to decay. In this most extreme case, the atom can only absorb 1 photon every 10 ns. That means, at most, an atom can absorb \(\frac{1 \text{ photon}}{10 \text{ ns}} = 10^8 \frac{\text{photons}}{s}\).

Without the $s$ in the denominator, the scattering rate increases without any bounds as the power increases. However, with the $s$ in the denominator, the scattering rate will max out at $\pi \gamma = \frac{1}{2\tau}$ (homework problem #3) due to the logic above.\(^9\)

3. Now let’s talk about the numerators. While the functions look similar, they mean very different things. The absorption profile describes what fraction of laser light is absorbed by the atoms as a function of laser frequency. The numerator, $A$, is a number between 0 and 1 that describes the fraction of the laser light that is absorbed when the laser is perfectly on resonance. If, on resonance, 13% of the power is lost as the laser travels through the atoms, then $A = 0.13$.

The scattering rate describes how many photons each atom scatters in 1 second. The scattering rate is specific to an atom, while the absorption profile comes from all of the atoms. We can actually convert the scattering rate into the Lorentzian function. To do that, we just need to know how many atoms are in the path of the laser. The more atoms to absorb light, the more laser photons are lost from the laser, and the larger the absorption coefficient. Each atom will scatter a certain number of photons. If we add up all of the photons that are lost, we can figure out the absorption coefficient.

**Extra math:** The rest of this chapter is not required, but I wanted to include it for folks who want to see the math to convert the scattering rate to the absorption profile. It is also a bit advanced, so don’t worry if it is confusing. If it is confusing, and you want to step through the logic with me, please stop by 😊

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\(^8\) Remember that an atom actually decays probabilistically with a characteristic time $\tau$. This is just a thought experiment to understand saturation.

\(^9\) A careful reader will notice the maximum scattering rate is twice as small as our thought experiment predicted. The idea of the thought experiment is correct, but we are ignoring an effect known as coherent state transfer. This is a massive, complicated topic and one that is beyond the scope of this class. In fact, most quantum mechanics classes don’t get to this idea until the very end of the semester, if they get to it at all. Including this extra physics reduces the maximum scattering rate by a factor of 2.
Let’s return to our thought experiment. As a reminder, we are using our trusty two-level atom, and we assume all of the atoms are frozen in place (0 Kelvin). We will also assume that the laser power is small so that we are in the low intensity limit, $s \ll 1$.

Each atom in the vapor cell will absorb $r_\gamma(\delta)$ photons/second. Let’s say the laser hits $N_a$ atoms as it travels through the vapor cell. The total number of photons absorb per second by all atoms is just

$$N_a r_\gamma(\delta) = \frac{N_a \pi \gamma s}{1 + \frac{4\delta^2}{\gamma^2}} \text{ (low intensity limit)}$$

To get the fraction of photons lost, we have to divide by how many photons/second are coming out of our laser beam. Before we continue, we need to convert power of a laser to photons/second. Conceptually, the power of a laser is how many photons per second are coming out of the laser times the energy of each photon: $P = N_{ph} E_{ph}$, where $N_{ph}$ is how many photons per second coming out of the laser and $E_{ph} = hf$. Solving for $N_{ph}$, we get $N_{ph} = \frac{P}{hf}$. And we are almost done! Next, we divide the total number of photons absorbed per second by the number of photons leaving the laser each second:

$$\frac{N_a r_\gamma(\delta)}{N_{ph}} = \frac{N_a r_\gamma(\delta)}{P} \frac{P}{hf} = \frac{hf}{P} N_a r_\gamma(\delta) = \frac{\left(\frac{hf}{P}\right) N_a \pi \gamma s}{1 + \frac{4\delta^2}{\gamma^2}}$$

That is our absorption profile. The absorption coefficient is the numerator of this expression:

$$A = \left(\frac{hf}{P}\right) N_a \pi \gamma s$$

This is fraction of light absorbed by the atoms.
Homework 3:

<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>
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<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>
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<td>meters/second</td>
<td>m/s</td>
</tr>
<tr>
<td>Planck’s Constant</td>
<td>h</td>
<td>Joules seconds</td>
<td>J s</td>
</tr>
<tr>
<td>Boltzmann Constant</td>
<td>k_B</td>
<td>Joules/Kelvin</td>
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<tr>
<td>Doppler shift</td>
<td>Δf</td>
<td>Hertz (1/second)</td>
<td>Hz (1/s)</td>
</tr>
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<td>kg</td>
</tr>
<tr>
<td>Temperature</td>
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<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>

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

\[
\Delta f_D = \frac{2.355}{\lambda} \sqrt{\frac{k_B T}{m}} = \frac{2.355}{c} \sqrt{\frac{k_B T}{m}} f \quad \frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle \quad \tau = \frac{1}{2 \pi \gamma}
\]

1. Below is a table that shows the natural linewidth and wavelength for the three Europium transitions we are studying. Calculate the saturation intensity in units of mW/cm^2 and mW/mm^2 for your group’s transition.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>λ (nm)</th>
<th>γ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J=5/2</td>
<td>466.188</td>
<td>25.5</td>
</tr>
<tr>
<td>J=7/2</td>
<td>462.722</td>
<td>24.4</td>
</tr>
<tr>
<td>J=9/2</td>
<td>459.403</td>
<td>23.1</td>
</tr>
</tbody>
</table>

2. For your transition, calculate the on resonance scattering rate (δ = 0) for a saturation parameter of 0.1, 1, 5, 10, and 100.

3. The saturation parameter has the equation \( s = \frac{I}{I_s} = \frac{P/A}{I_s} \). You found the saturation intensity for your transition in question 1. The area of a laser beam is given by the equation \( A = \frac{1}{2} \pi w^2 \), where \( w \) is the radius of your laser beam.\(^{10}\) If the laser beam radius is \( w = 1 \) mm, what power should we set the laser beam at to get a saturation parameter of 0.1, 1, 5, 10, and 100?

4. Power Broadening: The scattering rate without the extra \( s \) in the denominator is a Lorentzian function. The FWHM of the function is the natural linewidth. Interestingly, the scattering rate with the extra \( s \) in the denominator is still a Lorentzian function, but with a different FWHM. Use algebra to manipulate the denominator of the scattering rate to get it into the form of a Lorentzian function.

Ans:

\[
r_\gamma(\delta) = \frac{\pi \gamma s}{1 + (\frac{\gamma \delta}{\gamma'})^2}, \quad \gamma' = \gamma \sqrt{1 + s}
\]

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\(^{10}\) It is actually called the waist of the laser. Most folks think of waist as a diameter, but it is actually the radius.
5. Re-read question 5 from chapter 2 and then do this problem.
Europium-151 has 6 “ground” states and 6 “excited” states.
Here are the energy level diagrams for the ground state and the $J = \frac{5}{2}$ excited state of Europium-151:

As a reminder, the vertical scale for the excited state levels are no centered around 0. The 0 on that diagram is actually 642,892.3 MHz, but that doesn’t fit well on the chart.

a. Suppose all of the atoms are in the $F = 3$ ground state. Sketch a transmission plot for a laser travelling through a vapor cell that is at 0 Kelvin. Label your plot well! There should be 3 Lorentzian shapes. Don’t worry about the amplitude of the absorption. There is no easy rule to find amplitudes. The natural linewidth of this state is 23 MHz. In other words, all 3 of your Lorentzian shapes should have a full width half maximum of 23 MHz.

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:

Notice that all the lines are resolved!