Chapter 4: subDoppler spectroscopy (also known as saturated absorption spectroscopy)

Learning goals: By the end of this chapter, you should understand
- subDoppler Spectroscopy
- crossover peaks

4.1 SubDoppler spectroscopy is a really neat trick to do spectroscopy on a vapor cell with hot atoms, but the transmission plot will have features that come from only the atoms that are at zero velocity. Reread that sentence! It is really quite amazing. Suppose the atoms are at 400 K. We know that if we use a single laser beam, we would expect to see a Doppler shaped spectrum from these atoms that is Gaussian in shape. SubDoppler spectroscopy uses two laser beams and the end result is a small Lorentzian feature on top of the Gaussian shape. The small Lorentzian feature comes from only those atoms that have zero speed in the direction of the laser.\(^1\)

This is how we do it. We send in two laser beams from opposite directions. The laser beam moving right has a small amount of power. We call this laser the probe beam. The other laser is moving to the left and has a large amount of power. We will call this laser the pump beam.

Once again, we are going to use our simple two-level atom. If the pump beam wasn’t there, we know the transmission of the probe beam looks like this:

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\(^1\) Remember that if an atom can be moving perpendicular to the laser beam, it will experience no Doppler effect. Only the velocity component in moving towards or away from the laser will contribute.
This plot is calculated using the mass of a Europium-151 atom and a vapor cell at 400 Kelvin. The natural linewidth of the transition in Europium-151 is about 24 MHz, which is much smaller than the Doppler width of 320 MHz.

Now, let’s add in the pump beam. We are going to ask the question, how does the transmission plot of the probe beam change with the addition of the pump beam? Let’s start thinking about it when the laser frequency is at $f_A$, see the above graph. Both the pump and the probe beam come from the same laser so they have the same frequency; they are just moving in opposite directions. We want to ask the question: What atoms interact with each laser beam?

As a reminder, the Doppler shift for an atom moving at velocity $v$ is given by the formula $\Delta f = \frac{v \lambda}{c}$. I find it useful to use numbers, so let’s say that the frequency of the lasers is set to $f_A$ that is 500 MHz below $f_r$. The probe beam is moving to the right. Since the frequency of the laser is below resonance, we know that atom has to be moving to the left (towards the probe beam). That means an atom in the gas would have to be moving at:

$$v_{\parallel} = (500 \times 10^6 \text{Hz}) \left(\frac{3 \times 10^8 \text{ m/s}}{652 \times 10^{12} \text{Hz}}\right) = 230 \frac{\text{m}}{\text{s}} \text{ (to the left)}$$

to absorb light from the probe beam. The pump beam is moving to the left. That means the atoms that absorb light from the pump beam must be moving to the right. The math is the same, but direction is opposite:

$$v_{\parallel} = (500 \times 10^6 \text{Hz}) \left(\frac{3 \times 10^8 \text{ m/s}}{652 \times 10^{12} \text{Hz}}\right) = 230 \frac{\text{m}}{\text{s}} \text{ (to the right)}.$$

Spend a few minutes on the above argument to make sure it all makes sense.

Here is the important take home message: When the frequency of the laser is at $f_A$ and $f_A < f_r$, different atoms interact with the probe beam and the pump beam. Both lasers are losing photons, but they are losing photons to different atoms.

Since we are monitoring the probe beam transmission, when the frequency of the laser is at $f_A$ the pump beam might as well be off. In other words, when the frequency of the laser is at $f_A$, the probe beam transmission is the same whether the pump beam is on or off.

Your turn! The laser frequency is now at frequency $f_B$, which we will assume is 500 MHz higher than $f_r$. What velocity does an atom need to have to absorb light from the probe beam? From the pump beam? Answer is in the footnotes.²

² Probe: $230 \frac{\text{m}}{\text{s}}$ (to the right); Pump: $230 \frac{\text{m}}{\text{s}}$ (to the left); notice the directions are switched from when the laser frequency was $f_A$. 
The conclusion is the same: When the frequency of the laser is at \( f_B \), the probe beam transmission is the same whether the pump beam is on or off.

The trick happens when the laser frequency is at \( f_r \). The Doppler shift is 0, so both the probe and the pump beams interact with \textit{the same} atoms. When the laser frequency is at \( f_A \) or \( f_B \), the pump and the probe lasers interact with different atoms. Now, the two laser beams are going to compete for the same atoms!

To explore this more, let’s do a thought experiment. First, we either block or turn off the pump beam. Now imagine an atom that is just hanging out and not moving. The atom is going to absorb a photon, and the probe beam gives the atom 10 photons (remember the probe beam doesn’t have much power) to pick from. The atom absorbs 1 photon from the 10 possible choices reducing the probe beam transmission. Now we turn the pump beam back on. The pump beam has a lot more power than the probe. Let’s say the pump beam provides an additional 990 photons. The atom is going to randomly pick 1 photon from a possible 1000 photons (10 from the probe and 990 from the pump). Most likely, the atom is going pick a photon from the pump beam. That means the transmission of the probe beam is larger when the pump beam is on compared to when it is off. What is really important is that this only happens for the atoms that are not moving. For any other velocity, the probe beam transmission is exactly the same whether the pump is on or off.

Let’s recap all of this in a table:

<table>
<thead>
<tr>
<th>Frequency of laser</th>
<th>Velocity of atoms needed to absorb from probe beam</th>
<th>Velocity of atoms needed to absorb from pump beam</th>
<th>How does the pump beam change the transmission of the probe?</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_A )</td>
<td>-230 m/s</td>
<td>+230 m/s</td>
<td>It doesn’t</td>
</tr>
<tr>
<td>( f_r )</td>
<td>0 m/s</td>
<td>0 m/s</td>
<td>Transmission increases</td>
</tr>
<tr>
<td>( f_B )</td>
<td>+230 m/s</td>
<td>-230 m/s</td>
<td>It doesn’t</td>
</tr>
</tbody>
</table>

\textbf{Generalized statement:} If the laser frequency is below resonance, the probe beam loses photons to atoms with a negative velocity while the pump beam loses photons to atoms with a positive velocity; the two beams interact with different atoms. If the laser frequency is above resonance, the probe beam loses photons to atoms with a positive velocity while the pump beam loses photons to atoms with a negative velocity; the two beams interact with different atoms. On resonance, the two lasers compete for the same atoms.
Here is the transmission of the probe beam with the pump beam off and with the pump beam on:

If we subtract the two plots, we are left with a Lorentzian feature with a full width half maximum equal to the natural linewidth of the transition. This is the same plot as the absorption plot from the thought experiment that we did in section 3.1, which was an absorption plot for atoms at 0 Kelvin. Neat trick, huh!

### 4.2 Crossovers

SubDoppler spectroscopy is super cool (pun intended). It allows us to get rid of Doppler broadening all together. Now suppose you had 1 ground state and 2 excited states. The two excited states have resonant frequencies $f_{r1}$ and $f_{r2}$. From the above arguments, you might expect transmission plots like:

In the “Pump off” plot, I also plotted the individual Doppler profiles for both transitions (red and blue dashes). If you add these two together you will get the black curve. With the pump beam on, you might (correctly) expect to get Lorentzian features at laser frequencies $f_{r1}$ and $f_{r2}$.

While this is true, you also end up with a Lorentzian feature exactly halfway between $f_{r1}$ and $f_{r2}$. This extra feature is called a crossover peak. This is a physics class, so let’s explore!

I always find it easier to use numbers, so let’s say that $f_{r2} - f_{r1} = 600$ MHz. The feature occurs when the laser frequency is set to 300 MHz above $f_{r1}$ and 300 MHz below $f_{r2}$.

Your turn: Having the laser frequency precisely between $f_{r1}$ and $f_{r2}$, calculate the atom speeds needed to absorb from the pump and the probe beam to excite atoms to either excited state #1 or excited state #2. The answers are in the table below this fabulous xkcd comic:

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*3 The FWHM is actually the power broadened linewidth (see homework 3 question 4)*
Velocity of atoms needed to absorb from probe beam | Velocity of atoms needed to absorb from pump beam
--- | ---
$f_{r1}$ | -138 m/s | +138 m/s
$f_{r2}$ | +138 m/s | -138 m/s

First, notice that the pump and probe beams are exciting different atoms to excited state #1 and excited state #2. Specifically, for an atom to be excited by the probe to excited state #1 it would have to be moving at -138 m/s. An atom would have to be moving at +138 m/s to be excited by the pump beam to excited state #1. Nothing new here.

But now notice that the pump beam is trying to excite atoms moving at -138 m/s to excited state #2 at the same time that the probe beam is trying to excite those same atoms to excited state #1. Those atoms that are moving at -138 m/s get to pick which laser to absorb from! They can absorb from the probe beam and be excited to excited state #1 or absorb from the pump beam and be excited to excited state #2. It is more likely to absorb a photon from the pump beam leaving fewer atoms for the probe to interact with. Even though the two lasers are trying to excite to different states, the pump beam still “steals” atoms from the probe beam meaning the transmission of the probe beam will increase at that frequency. With this new information, the transmission plot of the probe beam is given below. There are two Lorentzian features that correspond to the actual frequencies of the transitions. There is also an additional feature exactly half way between that we call a crossover peak.

I think now is a good time to remind everyone that the amplitudes of the peaks in the above graphs are completely made up. The crossover peak often turns out to be larger than the actual...
transitions. Also, the amplitude for resonance 1 will not be the same as the amplitude for resonance 2.

We can add a third excited state to the mix.\(^4\) Let’s call the resonant frequencies \(f_{r1}, f_{r2},\) and \(f_{r3}.\) We will get 3 crossovers features calculated using the same logic as above. One crossover will be directly between \(f_{r1}\) and \(f_{r2}\) (i.e. \(\frac{f_{r1}+f_{r2}}{2}\)), one between \(f_{r1}\) and \(f_{r3}\) (i.e. \(\frac{f_{r1}+f_{r3}}{2}\)), and one between \(f_{r2}\) and \(f_{r3}\) (i.e. \(\frac{f_{r2}+f_{r3}}{2}\)). In total, subDoppler spectroscopy on an atom with 1 ground state and 3 excited states will have 6 features.

**Important Comment:** If the two transitions are separated such that the Doppler profiles of each transition are separated, you will not have any crossovers because there are no atoms moving with the correct speeds to cause the excitation!!

If the vapor cell was heated to increase the Doppler width, the crossover peak would return.

**Summary:** If there are a) two excited states and one ground state and b) the Doppler profiles for the two individual transitions are overlapping one another, there will be a crossover feature directly between the two transitions.

Using the same logic, there will also be a crossover feature if a) there are two ground states and one excited state and b) the Doppler profiles for the two individual transitions are overlapping one another. This idea will be explored more in section 4.3.

\(^4\) We can’t add more than that for a single ground state due to the rules for exciting atoms; see Homework 2 question 5.
As with many things in experimental science, there are trade-offs to subDoppler spectroscopy. While subDoppler spectroscopy gives us really narrow spectroscopy features, it gives us more features to deal with. Fortunately, we know precisely where those crossovers will be. Here is a plot from a recent paper from my research group that did spectroscopy on a cesium line. The ground state for this spectrum is given by the label \( F = 4.5 \) There are three excited states that we label \( F' = 3, F' = 4, \) and \( F' = 5 \). Here is the transmission of the probe beam after subtracting off the Doppler profile (like the pump on-pump off plot at the top of the page). 

There are 3 labeled peaks are the excited states \( F' = 3, F' = 4, \) and \( F' = 5 \). These are the real transitions. Notice there are additional Lorentzian features directly any two real transitions. Also notice that all of the amplitudes are different. The crossover between \( F' = 4 \) and \( F' = 5 \) is really big while the real transition from the ground state to the \( F' = 3 \) excited state turns out to be really small. The peak directly to the right of \( F' = 4 \) is the crossover between \( F' = 3 \) and \( F' = 5 \). Even if this plot wasn’t labeled, we can still figure out the real transitions vs the crossovers! We just look for the features directly between two other features to find the crossovers. Also, the smallest and largest frequency peaks have to be real transitions; a crossover has to be between two real transitions.

### 4.3 Multiple ground states

We now have the basic building blocks to interpret a spectrum from an atom with as many ground or excited states that we want. Suppose we have an atom with two ground states and 4 excited states. We will label the ground states as \( F = 1 \) and \( F = 2 \) and label the excited states \( F' = 1, F' = 2, \) and \( F' = 3 \). An atom in the \( F = 1 \) ground state can be excited to the \( F' = 1 \) or \( F' = 2 \) excited states. An atom in the \( F = 2 \) ground state can be excited to the \( F' = 1, F' = 2, \) or \( F' = 3 \) excited states. Each of these 5 transitions will have a Doppler profile that has a Doppler width associated with it.

When we do subDoppler spectroscopy, we will see crossovers. Crossovers come from two possible sources. 

- If there are two excited states that are excited from the same ground state and the Doppler profiles from the individual transitions are overlapping, we will have a crossover whose frequency is directly between the two transitions. This is what we argued in Section 4.2.
- If there are two ground states that can be excited to a single excited state and the Doppler profiles from the individual transitions are overlapping, we will have a crossover whose

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5 Don’t worry about the letter designations; we’ll get to those in Chapter 6. However, the transition rules still apply. An \( F = 4 \) ground state can only go to an \( F = 3, 4, \) or 5 excited state.
frequency is directly between the two transitions. The logic (and math) is exactly the same as the previous scenario.

**Summary:** If there are two transitions that a) have the same ground state or have the same excited state and b) have overlapping Doppler profiles, the spectrum will have a crossover directly between the two transitions.

Let’s assume that all 5 transitions have overlapping Doppler Profiles. There will be lots of crossovers. I’m going to list them below, but make sure you think through and understand each bullet point. As always, ask if you have any questions.

- There will be 1 crossover from the fact that an atom in the $F = 1$ ground state can be excited to $F' = 1, F' = 2$ excited states.
- There will be 3 crossovers from the fact that an atom in the $F = 2$ ground state can be excited to $F' = 1, F' = 2$, or $F' = 3$ excited states.
- There will be 1 crossover from the fact that an atom can be excited to the $F' = 1$ excited state from either the $F = 1$ or $F = 2$ ground states.
- There will be 1 crossover from the fact that an atom can be excited to the $F' = 2$ excited state from either the $F = 1$ or $F = 2$ ground states.
- There will be 0 crossovers from the $F' = 3$ excited state because it can only be excited form the $F = 2$ ground state.

So, in this example, our transmission plot will have 11 features for 5 transitions. 5 of those features will be the real transitions, and the remaining 6 are all crossovers.

### 4.4 Europium-151

Here are the ground states and $J=\frac{5}{2}$ excited states of Europium-151:

As a reminder from homework 2, we call the 0 frequencies on the two diagrams the center of gravity of the ground state and center of gravity of the excited state. We will discuss this very important property more in Chapter 6.

The Doppler width for a vapor cell at 400 K is $\sim 350$ MHz. Here is a plot of the probe beam transmission with no pump beam; we just get normal Doppler broadened features:
I plotted the individual transition Doppler profiles in alternating blue-dashed and green-dashed lines. If you add up the blue and green curves, you get the black spectrum. The red lines are the actual transition frequencies.

Here is a table of the transition frequencies with the corresponding ground and excited state:

<table>
<thead>
<tr>
<th>( f ) (MHz)</th>
<th>F (GS)</th>
<th>( F' ) (ES)</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>
<td>1</td>
<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>
<tr>
<td>1068.9 MHz</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1204.9 MHz</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

I want to repeat that summary statement: If there are two transitions that a) have the same ground state or have the same excited state and b) have overlapping Doppler profiles, the spectrum will have a crossover directly between the two transitions.

For example, the transitions at -1008.3 MHz and -908.0 MHz share an excited state \( F' = 5 \) and the Doppler profiles of those two transitions overlap (see graph on previous page). So, there will be a crossover feature at -958.15 MHz.

The transitions at -1008.3 MHz and 364.4 MHz have the same ground state \( F = 4 \) but are separated by 1372.7 MHz. The Doppler profiles for these two transitions are not overlapping, so there wouldn’t be a crossover from these transitions.

Our transmission plot will have a lot of transitions (15 of them) and a lot of crossovers. Some of the features will be distinct while others will be partially on top of each other. The number of crossovers all depends on the temperature of the atoms in the discharge. Our goal is to sort through all of this information and try to extract the ground and excited states energies.

Despite the complexity of our transmission plots, we will, remarkably, only have 5 free parameters that will determine the position of all of the peaks. I think this is amazing. We are going to have like 30 or so spectral features, and the position of all of them are determined by only 5 parameters.
This is because the frequency differences between all 6 ground states are determined by only 2 parameters, which are called the magnetic dipole hyperfine constant and the electric quadrupole hyperfine constant for the ground state. The same with each excited state; the frequency differences are determined by only 2 parameters: the magnetic dipole hyperfine constant and the electric quadrupole hyperfine constant for that state. While the transmission plot will have a ton of spectral features, the frequency position of every feature, including the crossovers, are determined by 4 parameters. In addition, other research groups have already measured the 4 parameters. We are also going to determine those 4 parameters from the frequencies of the peaks, but we will be able to compare those values to the values measured by other groups. We will discuss these parameters more in Chapter 6.

The last parameter is specific to our experimental setup. We will discuss that parameter more in the lab section.
**Homework 4:** Only 2 questions this week, but both are in depth.

1. Here are the energy levels for a transition in rubidium-87:
Source: [https://steck.us/alkalidata/rubidium87numbers.1.6.pdf](https://steck.us/alkalidata/rubidium87numbers.1.6.pdf)

The center of gravity for the ground and excited states are shown on the far left. That means the F=1 ground state has an energy of -4,271.676 MHz and the F=2 ground state has an energy of 2,563.005 MHz. The two ground states are separated by 6,834.682 MHz, which is much larger than the width of the Doppler profile of any transition, which is about 400 MHz at 300 K. This means there will be no crossovers due to two transitions sharing the same excited state. All of the excited states are separated by frequencies smaller than the Doppler width. This means that we will have crossovers from any two transitions that share the same ground state.

The center of gravity frequency is 384,230,484.468 MHz, or ~780.24 nm.
The energies of the excited states with respect to the center of gravity of the excited state are:

<table>
<thead>
<tr>
<th>F</th>
<th>Energy (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-302.1</td>
</tr>
<tr>
<td>1</td>
<td>-229.9</td>
</tr>
<tr>
<td>2</td>
<td>-72.9</td>
</tr>
<tr>
<td>3</td>
<td>+193.7</td>
</tr>
</tbody>
</table>

Here is how we use these numbers: Suppose if we wanted to excite an atom from the $F = 1$ ground state to the $F = 0$ excited state. We would use a laser with frequency: $\frac{v - 302.1}{F} = 0 + 4,271.676 MHz$. If we want to excite an atom from the $F = 1$ ground state to the $F = 0$ excited state, we need set the laser frequency to be 3969.6 MHz larger than $f_{coG}$.

a) Make a “pump on-pump off” plot using the above energy levels assuming atoms are only in the $F = 1$ ground state. Remember to use the excitation rule: $\Delta F = -1, 0, or + 1$. As always, don’t worry about amplitudes. The horizontal axis should be with respect to $f_{coG}$ (see graph below as an example). On your plot, label which features are real transitions and which are crossovers.

b) Make a “pump on-pump off” plot using the above energy levels assuming atoms are only in the $F = 2$ ground state.

c) The plots in part a) and part b) are separated by about 6,830 MHz.

d) In the scenario outlined in part c), why would there be no crossovers due to the two ground states and the $F=0$ excited state?

[Over]
2. Here are the energy level diagrams for the ground and J=5/2 excited state of Europium-151:

With respect to the center of gravity frequency, the real transitions are:

<table>
<thead>
<tr>
<th>$f$ (MHz) − $f_{cog}$</th>
<th>F (GS)</th>
<th>F (ES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1008.3 MHz</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>-908.0 MHz</td>
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<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

a. Assuming the Doppler profiles are wide enough to give crossovers, what are the frequencies of the crossovers for the transitions that share the same $F = 3$ ground state?

b. Assuming the Doppler profiles are wide enough to give crossovers, what are the frequencies of the crossovers for the transitions that share the same $F = 5$ excited state?