Will Raven

Atomic Physics for Everyone

An Introduction to Atomic Physics, Quantum Mechanics, and Precision Spectroscopy with No College-Level Prerequisites

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Atomic Physics for Everyone: An Introduction to Atomic Physics, Quantum Mechanics, and Precision Spectroscopy with No College-Level Prerequisites

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To the best person in the world
Prof. Maria-Teresa Herd

Acknowledgments

I have many people to thank for helping me write this book. To properly give praise, I need to provide a little background. I joined Smith College in 2013 and quickly became part of the AEMES (Achieving Excellence in Mathematics, Engineering, and Sciences) mentoring team, led by the amazing *Dr. Valerie Joseph*. This program is designed to increase diversity in STEM fields through a variety of initiatives. One of the key insights I gained was that providing students from underrepresented and/or under-resourced backgrounds with early research experiences is one of the best ways to keep them in STEM majors. Over time, the demand for research experiences grew among students. To address both of these needs—fulfilling the increasing demand for research experiences and providing early research opportunities to students from under-resourced backgrounds—I developed, with the encouragement and help of many people, a course-based research program. This program teaches first-year college students (freshmen) atomic physics, giving them time in the lab to conduct real science. The class has no college-level prerequisites; we use no calculus, linear algebra, or assume any background in introductory mechanics. However, we do use algebra and some trigonometry, specifically sines and cosines. The class was included in the Broader Impacts section of a National Science Foundation (NSF) grant that I was fortunate to be awarded: PHY-2110311.

People Who Helped Me Develop the Pedagogy for the Class I had casual conversations about class development with a large number of people, but there are a few who made substantial contributions including *Prof. Maria-Teresa Herd* (Physics, Assumption University), *Prof. Timothy Malacarne* (Sociology and Data Science, Nevada State University), and *Prof. Patricia DiBartolo* (Psychology and Director of the Sherrerd Center for Teaching & Learning, Smith College). The Smith College Office of the Provost and Dean of Faculty, led by *Prof. Michael Thurston* (English Language and Literature, Smith College), were incredibly supportive and provided personnel support to the physics department to free up my time to develop and teach the class.

My original intent was to write this book as free PDFs for my website. It was my NSF program manager *Dr. John D. Gillaspy* (Physics) who first encouraged me to publish the book for broader distribution. But, if my goal was to attract students from under-resourced backgrounds, it didn't make much sense to have them pay

for a book. With additional support from Smith College, we are able to publish this book open access!

People Who Read the Book and Gave Me Lots of Feedback There are two people in particular who read the book multiple times through all the iterations. I owe *Prof. Maria-Teresa Herd* (Physics, Assumption University) and *Prof. Doreen Weinberger* (Physics, Smith College) so, so much. They were so insightful about approach and organization. This short paragraph seems incredibly insufficient for what they have done for me.

I want to thank the numerous people who read a selected chapter (or chapters). They are *Prof. Michael Thurston* (English Language and Literature, Smith College), *Prof. Gary Felder* (Physics, Smith College), and *Prof. Travis Norsen* (Physics, Smith College). And then there are all of the students who took this class with me. They found countless typos and mistakes, and pointed out confusing sections. More importantly, their questions and thoughtful exploration of the world of the super small helped me organize, expand, and enhance the book.

I also want to directly thank a few people who helped me in the classroom. These folks not only helped teach the class but also provided valuable feedback, sometimes in real time. Three of these individuals were learning assistants in the lab sections of the class the first time I taught it. They are *Bárbara Cabrales*, *Molly Herzog*, and *Chitose Maruko*. *Dr. Karl Ahrendsen* (Physics), who was a postdoctoral scholar in my lab, co-taught the class with me during the second iteration. He also gave an incredible amount of feedback to this text.

A Brief Tour of the Book

This book is divided into two parts. The first part, titled **Atom-Light Interactions**, explores spectroscopic techniques used to extract information about atoms. The second part, titled **Digging Deeper: Quantum Mechanics and Beyond**, examines the underlying physics of atomic structure, covering atomic notation, the principles behind it, current scientific understanding, and ongoing mysteries.

Generally, Part I is for learners interested in *how* we acquire knowledge about atoms, while Part II is aimed at those keen on understanding the fundamental physics of atoms. Readers may skip Part I if they are solely interested in the physics of atomic structure, but they should complete Chap. 1 before moving on to Part II.

The text also includes three appendices and a glossary that should serve as valuable references for readers. Appendix A is a periodic table, Appendix B is a long table that contains a lot of useful information about the atoms on the periodic table, and Appendix C lists all of the quantum mechanic rules that need to be satisfied for an electron to transition between two atomic states.

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Part I

Atom-Light Interactions

Introduction to Atoms and Light

1

Abstract

In this chapter, we explore the nature of light and atoms, focusing on their dual nature as both particles and waves. We examine why atoms have discrete energy levels and how only certain frequencies of light can excite electrons within these atoms. Through this exploration, we will understand the relationship between light's frequency, wavelength, and photon energy. We also explore key concepts such as wave interference and the historical experiments that shaped our understanding of quantum mechanics. Most importantly, this chapter emphasizes the scientific method, encouraging continual questioning of ideas, understanding, theories, and results to uncover the fundamental nature of the universe.

Learning Goals

By the end of this chapter, you should be able to understand:

- the basic structure of an atom.
- the concept of wave-particle duality and how it applies to both light and electrons.
- that atoms have discrete energy levels, and we can think about electrons as waves to understand why these energy levels are discrete.
- the historical experiments that led to the development of quantum mechanics, particularly the double-slit experiment.
- the basic principles of spectroscopy and its importance in studying atomic structure.
- that knowing the frequency of a laser, the wavelength of a laser, or the energy of a photon allows you to determine the other two. All three quantities are related by fundamental constants.

W. Raven, *Atomic Physics for Everyone*,
https://doi.org/10.1007/978-3-031-69507-0_1

1.1 What Is Atomic Physics?

Before we discuss **atomic physics**,[1] we should first ask a more fundamental question: What is **physics**? Before you read further, pause and think for a few minutes. If someone was to ask you, "What is physics?", how would you respond? My answer is below the word search:

Word Search!

E	S	H	T	L	E	A	P	Q	Q
I	C	U	I	H	A	H	Z	I	U
S	I	E	U	D	O	S	Z	W	A
P	S	P	L	T	D	N	E	O	N
E	Y	H	O	E	P	E	Z	R	T
C	H	N	A	L	C	U	N	D	U
T	P	T	U	M	O	T	A	S	M
R	K	S	U	O	U	R	R	G	X
U	G	N	M	W	K	O	K	O	E
M	P	R	O	T	O	N	U	Z	N

Word list:
ATOM
LASER
ELECTRON
PROTON
NEUTRON
QUANTUM
PHOTON
PHYSICS
SPECTRUM

Plus two
hidden words

My answer: Physics is a branch of science that tries to understand the universe. We do this through exploring physical concepts and often explain those concepts using the language of mathematics.

All subfields of physics focus on a particular portion of the universe. For example, plasma physicists try to understand ionized gases, which are called plasmas. Atomic physicists[2] try to understand the world of atoms, which I like to refer to as the world of the super small.

Below are a few reminders that are important starting points for this book. If you aren't familiar with one of them, take 5 minutes to read the Wikipedia page on the topics.

---

[1] Words in the glossary are in bold type the first time we use them.

[2] In the last half of the twentieth century, atomic physics combined with molecular physics and optical physics to make what is now known as atomic, molecular, and optical physics. We use the acronym AMO physics.

- Atoms are composed of three types of particles: **protons**, **neutrons**, and **electrons**.
    - Protons and neutrons form the center of the atom, called the nucleus, and electrons orbit around the nucleus.
    - If an atom has an equal number of electrons and protons, the atom has no net charge. We call this a **neutral atom**. If we take an electron away from the atom or give the atom an extra electron, it is now charged. We call this an ion.
- **Molecules** are made from multiple atoms bound together. They can be the same atoms, like a nitrogen molecule consists of two nitrogen atoms, or different atoms, like a water molecule that has two hydrogen atoms and one oxygen atom.
- Atoms can be in the gas phase, liquid phase, or a solid phase.[3,4] Most atomic physicists study atoms in the gas phase to avoid the complexity of liquids and solids. In liquids and solids, atoms are bonded to one another, which makes the system more complicated. Our ideal system is a single atom all by itself away from all outside interactions.
- The periodic table of elements is a common way to view all the elements we know about. A copy of the periodic table can be found in Appendix A.
- Spectroscopists use light to interact with and learn about the world of the super small.

This book is aims to teach **quantum mechanics**, atomic physics, and **spectroscopy** without any advanced math. The most complicated math we use is algebra and some trigonometry (sines and cosines). Spectroscopy is a subfield of atomic physics that tries to learn about an atom through its interaction with light. Spectroscopy can be thought of as both a subfield and a tool. As a subfield, it is using atom-light interactions to try and understand the world of the super small. Additionally, it serves as a tool. The goal of atomic physics is to understand how atoms work, and spectroscopy is just a tool to accomplish this goal. The important thing is that spectroscopists use light to interact with atoms with the end goal of understanding the world of the super small. Scientists in lots of fields use spectroscopy, including atomic physicists, nuclear physicists, chemists, geologists, atmospheric scientists, and astronomers.

Atomic physicists try to reach this goal by starting with a simple system and building up complexity over time. One of our simplest systems is a single electron

---

[3] There are other phases of matter as well, including plasmas and Bose-Einstein condensates (BEC), which were named after the Indian mathematician and physicist Satyendra Nath Bose and the German born physicist Albert Einstein. A BEC is a really amazing state of matter that was first postulated in 1924. It wasn't until 1995 when American physicists Carl Wieman and Eric Cornell used atomic physics techniques to create the world's first BEC from rubidium atoms. Shortly after, German physicist Wolfgang Ketterle made a BEC from sodium atoms. The three atomic physicists won the 2001 Nobel Prize in Physics for this effort.

[4] One of my readers suggested that adding nationalities would add a bit of fun and extra history (I agreed!). Lots of sources list Einstein as 'German born' because he moved to Switzerland in 1895, giving up his German citizenship. In 1901, he became a Swiss citizen.

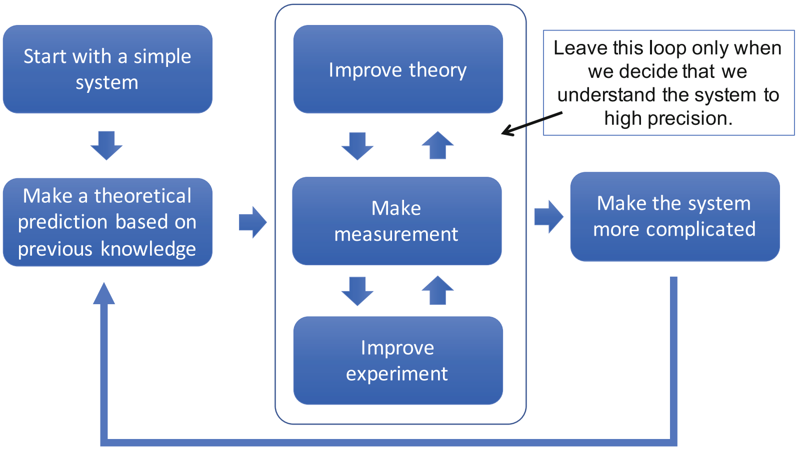

Fig. 1.1 A flowchart for trying to understand something. This is a version of the scientific method showing the interplay between experiment and theory

orbiting a single proton, also known as a hydrogen atom. More complicated systems include helium (2 electrons and 2 protons), lithium (3 electrons and 3 protons), neodymium (60 electrons and 60 protons), europium (63 electrons and 63 protons), and californium (98 electrons and 98 protons). Other fields of physics start with complicated systems and either "build up" or "build down" in complexity. For example, condensed matter physics, which includes subfields like superconductivity, has incredibly complex systems!

Figure 1.1 is a flowchart for how I like to explain how we, as scientists, try to understand something. For atomic physicists, our goal is to try to understand the world of the super small. We start with a simple system, for example the hydrogen atom. Next, we use theory that is based on previous knowledge to make a prediction. If the theory is good, the prediction should be confirmed by experiment. Once experimentalists make their first measurement, they start to improve the experimental setup to measure things better and better. While the experimentalists are improving their setup, the theorists are also improving their models. This process continues over and over and over until we, as a community, conclude that (1) the model is doing a really good job predicting the simple system, and (2) we run out of ways to make the experiment or theory more precise. If, after all that time stuck in that loop, we find that experiment and theory agree, we give out high fives and conclude we understand this simple system. If theory and experiment start to deviate from each other, physicists start to get excited because there is something we don't understand.

Once the atomic physics community is happy with the simple system, we make the system slightly more complex. For example, after we conclude that we understand hydrogen (1 electron, 1 proton, 0 neutrons), we move on to trying to understand deuterium (1 electron, 1 proton, 1 neutron) or helium (2 electrons, 2 protons, 2 neutrons). The most important thing to emphasize here is that if the model/theory is good, it should predict the experimental results before the experimentalists go and measure. If the theorists and experimentalists disagree, either the theorists messed up the math, the experimentalists messed up their experiment, or the theory is simply incomplete or all together wrong. The most exciting time in physics is when this last one happens.

The theoretical framework in atomic physics is quantum mechanics. Quantum mechanics has a more modern and complete version called the **Standard Model of Particle Physics**, the topic of Chap. 11. The Standard Model came about because, while quantum mechanics did a great job describing the world of the super small, it didn't do a perfect job. In other words, quantum mechanics isn't complete (it doesn't describe everything). As we worked through the flowchart, theory and experiment started to disagree as both theorists and experimentalists improved their methods. The Standard Model, which is far more mathematically complicated than Quantum Mechanics, does a much better job, but it is also not complete. For example, the Standard Model doesn't know how to describe lots of things we observe in real life like gravity, dark matter, dark energy, and baryon asymmetry, all of which will be discussed in Chap. 11. Despite these problems, experimental measurements that test the validity of the Standard Model always seem to confirm the Model is accurately describing nature![5] Therefore, we test it over and over again hoping that (1) we find a disagreement between experiment and theory and (2) this discrepancy leads to a more complete model describing the world of the super small.

In this book, we are going to think about atoms in their gaseous form, so we don't have to worry about how two or more atoms interact in a molecule, a liquid, or a solid. If you are reading this book as part of a class, you may also have an experimental portion where you are focusing on a single atom like sodium, cesium, europium, or neodymium. One of the most important things to note right now is that we want to know general properties of the atom of choice. For example, if we want to know the energy separation between two atomic states (more on this below) of a single, isolated atom, we want to know that energy separation in the absence of external interactions. We don't care about these properties in a magnetic field, an electric field, or even a laser field. Imagine a single atom in the middle of outer space, completely in the dark, and far from any other object. We want an experiment that helps us figure out these general properties. If a scientist knows the general properties, they can then calculate or estimate what would happen to that property if the atom was, for example, put in a magnetic field. The important thing is that we provide the general information that can later be used by theorists, other experimentalists, and engineers.

---

[5] To be fair, experiment does not always agree with the Standard Model. For example, the Standard Model says that the universe should be nearly equal amounts of matter and antimatter (this is the baryon asymmetry listed above), which would be bad since then all the matter and antimatter would combine to destroy the universe. In other words, the Standard Model says that the universe shouldn't exist, which disagrees with experiment.

1.2 Conceptually Understanding the Atom

We are not going to discuss the Standard Model right now. We are going to keep things a bit simpler and discuss, conceptually, the atom. Later on in the book, we will add to our conceptual model to make things more complete. So, what does quantum mechanics say about the atom?

To answer that question, let's first think about an electron that is orbiting around a nucleus, as shown in Fig. 1.2. The electron has negative charge and the nucleus has positive charge. According to electromagnetic theory, the electron should radiate away energy. Imagine if you were flying a hand glider and you slowly lost energy. In this scenario you would slowly drift down until you landed on the ground. According to electromagnetic theory, the electron will also lose energy and should orbit closer and closer to the nucleus until it collides with the nucleus. Experiment shows this is not true. In fact, if it were true, we wouldn't be here reading this book because atoms wouldn't exist and thus the universe wouldn't exist,[6] which disagrees with experimental observation.

There were some amazing experiments conducted in the late 1800s and early 1900s that seemed to imply that the electron is *not* like the moon orbiting around the earth. One of my favorite experiments that showed this behavior is called the double-slit experiment. If we assume electrons are like little sticky balls and send them through two small slits in a barrier, as shown in Fig. 1.3, we expect to have two strips of balls stuck to the screen. However, that isn't what is seen experimentally!

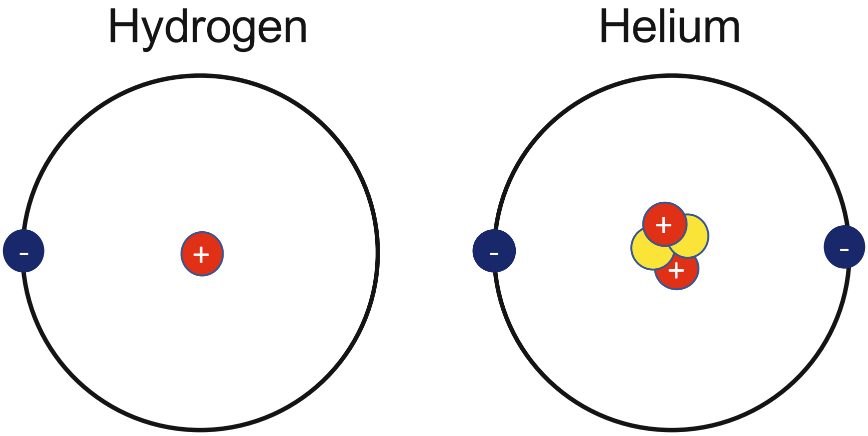

Fig. 1.2 A helpful conceptual, but incorrect, way of thinking about atoms. The model where the electrons orbiting around the nucleus is called the Bohr model, named after Danish physicist Niels Bohr

---

[6] Well, maybe the universe would exist. It would just exist without any matter, which wouldn't be much fun.

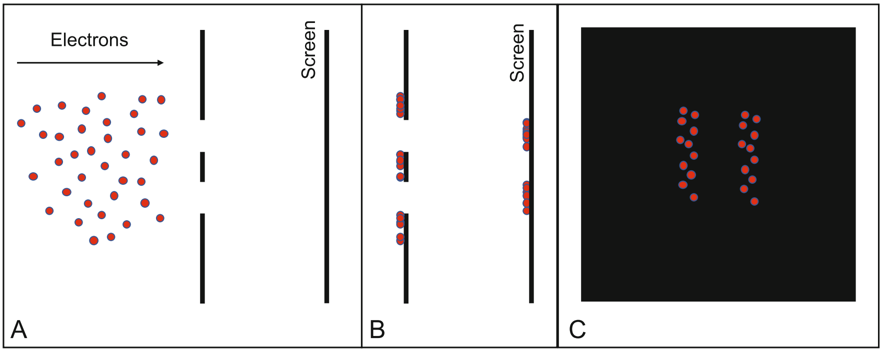

Fig. 1.3 A double-slit experiment where the electrons behave like little sticky balls. In panel A, the electrons are moving towards a barrier that has two small slits in it. Behind the barrier with two small slits is a screen with no holes. In panel B, the electrons have crashed into or passed through the barrier to crash into the screen. Panel C shows a front view of the electrons that passed through the barrier and crashed into the screen

Before we get to the real experimental results, we need to define some important terms and explore the concept of **wave interference**. Below are three important definitions about waves. Figure 1.4 is a visual representation of two of those definitions: wavelength and frequency.

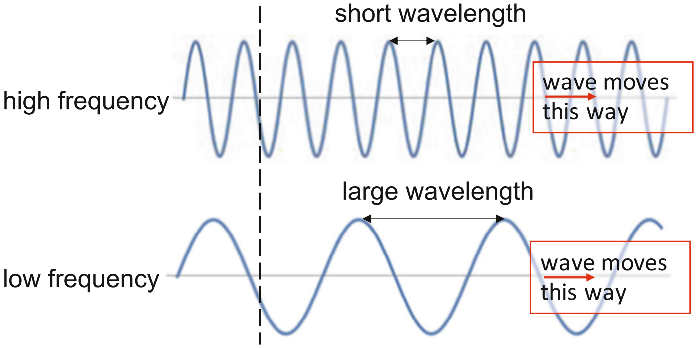

Fig. 1.4 A visual description of wavelength and frequency. Wavelength is the distance between two "like" points on the wave, for example the distance between two adjacent peaks or two adjacent troughs. If the wave is moving towards the right, frequency is how many peaks pass through the dashed line every second. If both waves are moving with the same speed, the upper wave has a higher frequency than the lower wave since more peaks pass the dashed line in 1 second

Definitions

- **Wavelength:** The distance between any two “like” points on a wave, such as two adjacent wave peaks. The variable we use for wavelength is the lowercase Greek letter lambda, λ. Since wavelength is a distance, we use length units such as meter, centimeter, or nanometer.
- **Frequency:** The number of oscillations per second. We use the variable f for frequency. The unit for frequency is 1/seconds, which is called a hertz, named after the German physicist Heinrich Hertz. A hertz is shortened to Hz. Some other units that we use for frequency include a megahertz ($1\ \text{MHz} = 1 \times 10^6\ \text{Hz}$), a gigahertz ($1\ \text{GHz} = 1 \times 10^9\ \text{Hz}$), and a terahertz ($1\ \text{THz} = 1 \times 10^{12}\ \text{Hz}$).
- **Period:** The time it takes for the wave to complete one full oscillation. We use the variable T for period, and the unit is seconds. Frequency and period are related by the formula $T = 1/f$.

Wave Interference Wave interference happens whenever two or more waves overlap. Those waves can be traveling in the same direction, opposite directions, or at an angle with each other. In fact, they don’t even have to look like the waves in Fig. 1.4. They could instead be single pulses like in Fig. 1.5. In this example, the two pulses, represented by the blue and red dashed lines, are on the same rope (the thicker gray line) and traveling in opposite directions. When the pulses overlap, they constructively add to make a larger pulse. The is known as constructive interference.

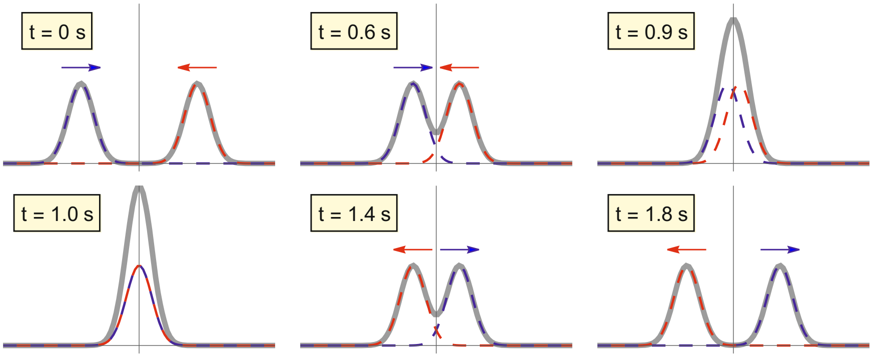

Fig. 1.5 Two pulses that constructively interfere with each other: The thick gray line is what we would actually see. The blue dashed line shows the pulse traveling to the right while the red dashed line shows the pulse traveling to the left. When they pass through one another, they add to create a larger pulse. At $t = 1.0\,\text{s}$, this is 100% constructive interference. At all other times, the pulses are only partially constructively interfering

However, if we have a positive amplitude pulse and a negative amplitude pulse, we will get destructive interference, see Fig. 1.6.

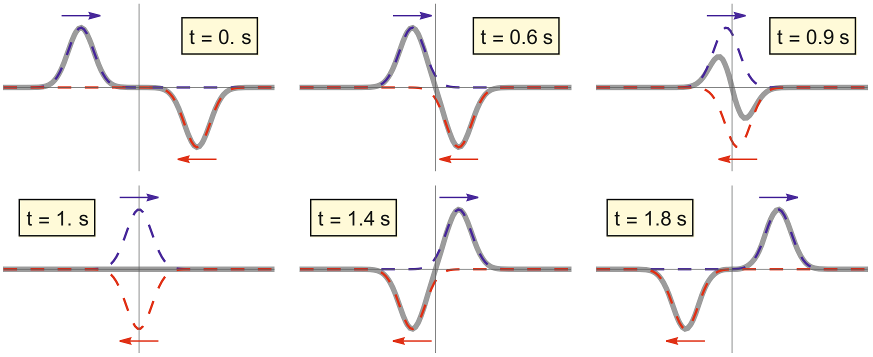

Fig. 1.6 Two pulses that destructively interfere with each other: The thick gray line is what we would actually see. The blue dashed line shows the pulse traveling to the right while the red dashed line shows the pulse traveling to the left. When they pass through one another, they perfectly cancel each other out creating no disturbance on the actual rope for a brief period of time. At $t = 1.0\,\text{s}$, this is 100% destructive interference. At all other times, the pulses are only partially destructively interfering

Try This

Find a piece of thin rope or a slinky and a stopwatch. If you have a friend nearby, have them hold one end of the rope or slinky. If not, tie or connect one end of the rope or slinky to a door knob. Stand a distance apart so that there is a bit of tension on the rope or slinky. Send a pulse down the rope or slinky and watch what happens when the pulse reflects off your friend or the doorknob. Next, start creating a sine wave motion with your hand, see Fig. 1.4. Try to move your arm up and down so that the rope or slinky creates the shapes seen in Fig. 1.7.

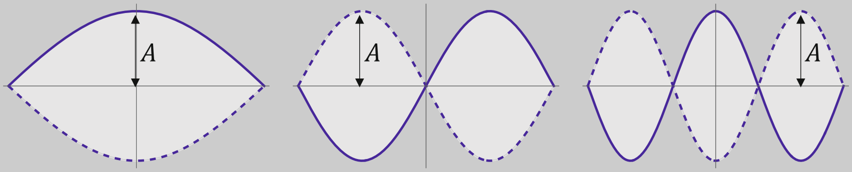

Fig. 1.7 The first three standing waves of a one dimensional rope or slinky. Each standing wave is drawn with the same amplitude A. Interestingly, the frequency of a standing wave is independent of the amplitude of the standing wave

(continued)

You will find that your hand has to move up and down with a very specific frequency to create these shapes, which are called standing waves. When you produce standing waves, the wave that you are creating with your hand is constructively interfering with the reflected wave. No other frequencies produce perfect constructive interference. Using your stopwatch, find the time for ten full oscillations (the time it takes for your hand to move up and down ten times) for each of the first three standing waves. The period of the standing wave is that time divided by 10. If you count twenty full oscillations, you would divide the time by 20 to find the period. Next use the formula $f = 1/T$ to find the frequency needed to produce that standing wave. The frequency of the standing wave with one "loop" (the left picture) is called the fundamental frequency. You should find that the second picture with two loops has twice the fundamental frequency. The third picture with three loops should have a frequency that is three times the fundamental frequency. In general, $f_n = nf_1$, where n is how many loops the standing wave has. Notice that the higher mode standing waves (the waves with more loops) require more shaking energy! This will be important later.

Back to the Double-Slit Experiment Ok, let's run a different experiment. Instead of little, sticky balls, let's send a wave towards the screens, as shown in Fig. 1.8. Panel A shows the wave traveling towards the slits. The vertical lines are supposed to indicate the peaks of the wave. The troughs are halfway between each peak, so you are visualizing the wavelength of the wave. Panel B shows the wave as it passes through the slits. The straight wave turns into two arc waves, one coming from each slit. The arc waves are basically half circles with the center of the circle at the slit. I changed the color of one of the circular waves to better visualize the evolution of each wave. The two circular waves interfere with each other on the screen. Places

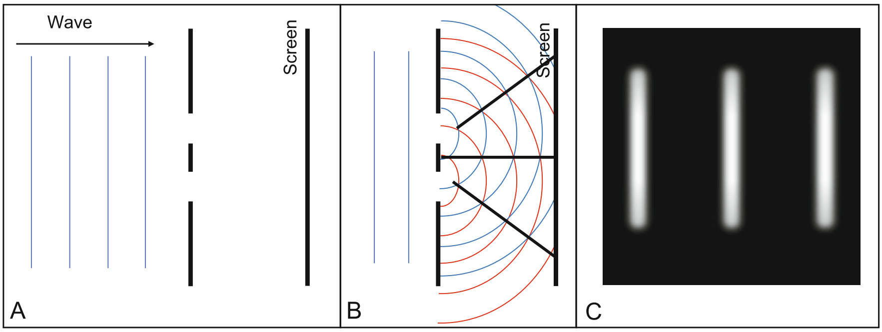

Fig. 1.8 A double-slit experiment using waves

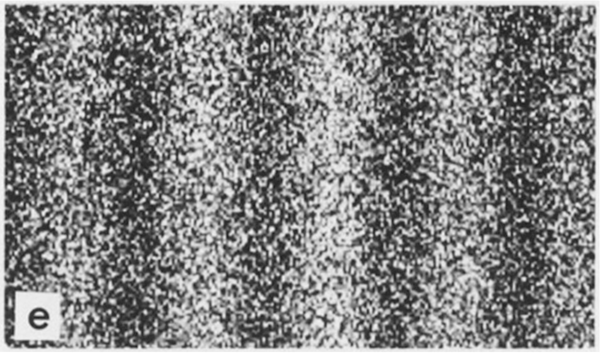

Fig. 1.9 Experimental results of a double-slit experiment with electrons. Image Credit: Dr. Tonomura and Belsazar from Wikimedia Commons CC BY-SA 3.0

where peaks of the waves overlap, indicated by the black lines between the slits and the screen, are where the two circular waves constructively interfere. Half way between the points of constructive interference are points of perfect destructive interference. Panel C shows what we see on the screen. The bright parts are where the two waves constructively interfere. The dark parts are where the two waves destructively interfere. At the very center of the dark parts, the waves are 100% destructively interfering.

Now, let's do the experiment with electrons! Real experimental results can be seen in Fig. 1.9. The electron behaves like a wave! There is actually a lot more to the double-slit experiment, but we aren't going to go into any more detail in this book. You will learn much more about it if you take a Modern Physics class. The really important thing we need to conceptually understand is that the electron has wavelike behavior. This is incredibly important information for us because an electron that is orbiting a nucleus is *not* like the moon orbiting the earth, which is depicted in Fig. 1.2. Experiments show that electrons behave like waves.

► **Important Concept** Electrons in atoms behave like waves, so we need to think about interference effects.

This is a really hard concept to wrap our brains around, but experiments seem to indicate this idea is correct. How does a wave "orbit" around a nucleus? As an analogy, imagine a wave that wraps around upon itself in a circle, see Fig. 1.10. This figure is just a conceptual example since there is no start or end to the wave. But to explore this concept we are going to wrap the electron wave counter-clockwise around the nucleus, and the wave is going to interfere with itself. If the electron wave does not perfectly wrap back around so that two peaks don't overlap perfectly, the electron will destructively interfere with itself. If an electron destructively interferes

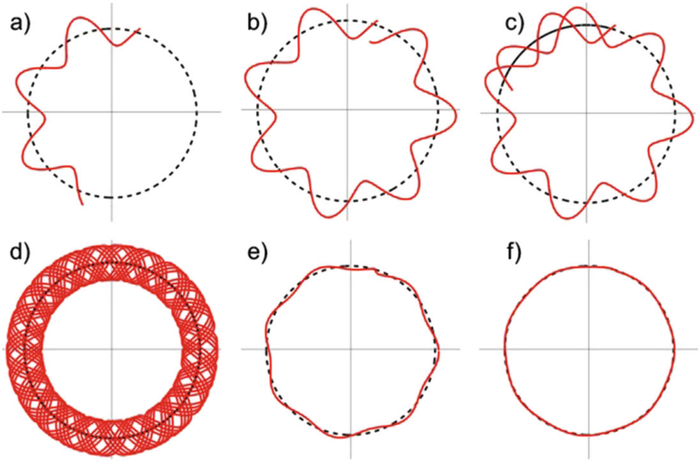

Fig. 1.10 A conceptual exploration of an electron wave orbiting a nucleus that would result in destructive interference. In (**a**), we imagine the electron wave starting at the top of the circle and traveling counter-clockwise. In (**b**), the electron wave has made one full orbit, but notice that the wave does not line up with its starting point. For (**c**), the wave continues and should be interfering with itself, but we aren't going to add the waves together quite yet. In (**d**), the wave continues for 12 orbits. To explore destructive interference, (**e**) shows adding together this wave after 4 full rotations. (**f**) shows destructive interference of this wave after 10 full rotations

with itself, there is no wave! If there is no wave, then there is no electron. Since electrons exist, the electron wave must constructively interfere with itself.

A lot has happened, so let's do a quick recap. We have learned that:

- Electrons have wavelike properties (Fig. 1.9)
- Waves interfere with one another (Figs. 1.5, 1.6, and 1.7)
- A wave can also interfere with itself (Figs. 1.8 and 1.10)
- An electron exists, so it better not destructively interfere itself out of existence.

Pause here and see if you can come up with a conclusion. When you have reached a conclusion, read on. My conclusion is below this fun fact:

Fun Fact

Many musical instruments make noise (hopefully pleasant noise!) because of standing waves. For example, when a guitarist plucks a guitar string, which is fixed at both ends, they are creating many standing waves (see Fig. 1.7) with different amplitudes all at the same time. Each of those standing waves has a frequency that is a multiple of the fundamental frequency. The amplitude of each of those standing waves is what gives the guitar it's distinctive sound. To

(continued)

play a different note, the guitarist changes the length of the string by pressing on the string in a different spot, which in turn changes the fundamental frequency.[a] The same is true for a piano. A piano key strikes a wire that produces standing waves that result in a (hopefully!) pleasant noise. The amplitudes of all the standing waves on a struck piano wire are different than the amplitudes of a guitar string, which is why they sound different.

A note played on a trumpet or saxophone also produces standing waves, but the standing waves are created in the air and are physically manifested as places of high and low air density.

---

[a] They could also pluck a different string that has a different mass density or change the tension on the string. All of these changes will result in a different fundamental frequency.

Conclusion The electron must constructively interfere with itself. This idea is conceptually shown in Fig. 1.11.

An electron can only "orbit" around the nucleus if it satisfies a standing wave condition. Each standing wave has an energy associated with it. Just like how the standing wave on a string with 2 loops has a shorter wavelength and requires more shaking energy than the standing wave with 1 loop, the higher energy "states" of an electron have shorter wavelengths. Thus the allowed energies of the electron are "discrete": they can only have the specific values corresponding to these standing waves.

We call the discrete energies an electron orbiting a nucleus can have "energy levels" or "energy states" and describe them in diagrams like Fig. 1.12. The lowest energy state is called the ground state of the atom, or the ground state for short. States with higher energy are called excited states. These energy level pictures are sometimes called Grotrian diagrams, named after German astronomer and astrophysicist Walter Grotrian. The SI unit for energy is a joule, which is named after

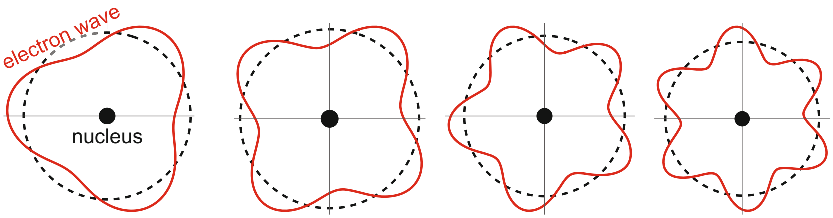

Fig. 1.11 Four conceptual examples of an electron wave orbiting a nucleus that would result in constructive interference. Going from left to right is going from a lower energy state to higher energy states

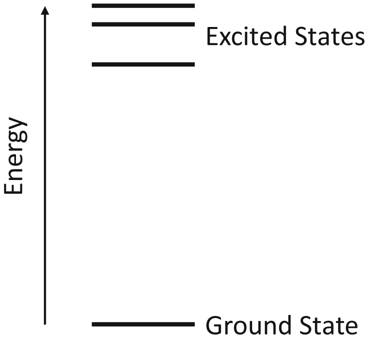

Fig. 1.12 A conceptual picture that shows an atom with a single ground state and three excited states. A real atom has many excited states

the English physicist James Joule. A joule is shortened to J.[7] A joule is shorthand for $\mathrm{kg\,m^2/s^2}$. For reference, the energy of a baseball moving at 50 mph is about 36 joules. The energy of an apple moving at 1 meter/second is about 0.05 joules.

▶ **Important Comment** Atomic physicists and spectroscopists often say that the ground state energy is 0. This is not true! Think about the standing wave on a string with a single loop. This is the standing wave with the smallest amount of shaking energy, but it still has energy! The ground state of an atom also has energy. In experiments, we measure the energy difference between the ground state and excited states. For this purpose, we assign the lowest energy state to be 0 so that everything is measured with respect to that state.

The energy difference between the ground state and the lowest energy excited state in the hydrogen atom is $0.000000000000000001634\,\mathrm{J} = 1.634 \times 10^{-18}\,\mathrm{J}$. That is a small number! A more common unit for energy in atomic physics is the electronvolt (eV). The conversion is $1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$, so the energy of the lowest excited state is 10.2 eV above the energy of the ground state.

One Final Thing The above description of an electron in an atom is a good starting point to understanding how and why atoms behave the way they do. Think about this chapter as making a first pass-through Fig. 1.1. The conceptual idea you just learned is correct. However, the electron wave turns out to be more complicated than the simple picture given above. For one thing, the electron wave is going to be in 3 dimensions. But, more importantly, the actual wave that describes the electron in an atom, which is called a wavefunction, is a bit messier to deal with. All of the concepts like wave interference and energy levels in the atom are still correct, but the presentation of the electron wave has been simplified. You will refine these ideas in future classes such as Modern Physics and Quantum Mechanics.

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[7] Notice the unit 'joule' is not capitalized. In general, a unit named after a person is not capitalized.

A Little Bit Extra

A careful reader might have noticed something odd about Fig. 1.9. While there was clearly a wave interference pattern, this wave interference is composed of tiny bright dots. The electrons are moving through the slits as waves. However, we have experimentally found that when the electron hits the screen, which is often called a measurement, the electron wave "collapses" to a single point. You may have heard the phrases "wavefunction collapse" or "**wave-particle duality**". This is a fancy way of saying that the electron behaves like a wave until something interacts with it before it starts behaving like a particle (i.e. a single point on the screen). The amplitude of the wave interference tells us the *probability* of where the wave collapses back to a point. Thus where the electron wave destructively interferes on the screen produces 0 probability that the particle will be detected at that point. The process of going from a wave to a point is a fascinating and yet unexplained phenomenon! There are many physicists and philosophers who think very hard about how this "collapse" occurs. We will explore more about the probabilistic interpretation of quantum mechanics, which is often called the orthodox or Copenhagen interpretation, in Chap. 6.

1.3 Photons and Spectroscopy

Suppose we want to measure the energy difference between the ground state and any one of the excited states. How do we do it? Answer: Spectroscopy! We shine light onto the atoms and look at what happens to the light. In modern spectroscopy, we use laser light. Light, including laser light, is composed of tiny particles known as **photons**.[8] As an analogy, think about a stream of water. The water looks continuous, but it is actually made up of tiny water molecules. The same thing is true with light. Light is composed of tiny particles we call photons. There is, however, a really important difference between water molecules and photons. The energy of a photon is determined only by the frequency of the light wave. The more the light wave oscillates up and down in one second, the larger the energy of an individual photon that makes up that light wave. The energy of a water molecule, on the other hand, is related to how fast the molecule is moving, rotating, and vibrating. We will explore the connection between the frequency of the light wave and the energy of a photon more in the next section.

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[8] German physicist Max Planck won the 1918 Nobel Prize in physics for discovery of the photon. Albert Einstein won the 1921 Nobel Prize in physics for explaining the photoelectric effect, which determined that a beam of light is made up of a bunch of photons. I may be biased, but Einstein's explanation of the photoelectric effect was the most important discovery of the twentieth century.

▶ **Important Statement** If a photon has the same energy as the energy difference between the ground state and an excited state, the atom will absorb that photon and move an electron to the excited state. If the photon does not have the same energy as that energy difference, the atom will completely ignore the photon. [9]

Thought Experiment Time Imagine you have an electron behaving like a wave orbiting around a nucleus. That electron wave has to constructively interfere with itself, and we can think about that standing wave as having some amount of energy. Let's call this energy E_1. If we wanted to add another loop to the standing wave, we need to add energy to the system. Suppose an electron with 1 more standing wave loop has energy E_2. Remember that the electron needs to be a standing wave, which has a specific energy. If it wasn't, the electron would experience destructive interference. We want to move an electron from the lower energy standing wave to the higher energy standing wave. How much energy do we need to put into the system? The answer is in the footnotes.[10]

This is the basic idea behind spectroscopy. If we want to excite an electron from one energy level, which has some energy, to another energy level, which has a different energy, we need to provide the system with the correct difference in energy.

Restating that in terms of an actual experiment: We send a laser through an optically clear container, called a cell or vapor cell, filled with atoms. We will smoothly scan the energy of the photons over time and monitor the transmission of the laser through the cell. If the energy of the photons does not match the energy difference between the ground state and an excited state, the laser light will pass right through the atoms with no losses. If the energy of the photons matches that energy difference, light will be lost from the laser and the transmission will decrease. Experiments that match the above description are known as absorption spectroscopy experiments. We, as experimentalists, simply monitor the transmission of the laser through an atomic sample as we change the photon energy. When the amount of transmitted light drops, we learn what energy is required to excite the atoms from the ground state to an excited state. Believe it or not, that is, conceptually, all there is to it. In the lab things are a bit more complicated, but this is the basic idea. We will finish up this section with a new definition.

---

[9] This important statement is super important, but it also isn't 100% correct. We are going to start with this statement to get at some important concepts. In the next few chapters, we are going to discuss some more physics and then restate this important statement to something more correct. It's kind of like the flowchart from the beginning of the chapter. We start simple and build up complexity.

[10] We would need to add precisely $E_2 - E_1$ of energy.

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 correctly into a trumpet, a standing wave is excited in the pipe to create a note. The same thing happens with an atom. When you excite an atom with the right energy photon, the electron goes from one standing wave mode to another. Atomic physicists use the word "excitation" and "resonance" interchangeably.

1.4 Math

The speed of light, the wavelength of the laser light, and the frequency of the laser light are all related using the formula:

$$c = f\lambda, \tag{1.1}$$

where $c = 299,792,458\,\text{m/s} \approx 3 \times 10^8\,\text{m/s}$ is a constant of nature known as the speed of light.[11] The energy of a photon is given by the formula:

$$E_{\text{ph}} = hf, \tag{1.2}$$

where h is a constant of nature known as Planck's constant, named after German physicist Max Planck. Planck's constant is a very small number, $h = 6.626 \times 10^{-34}\,\text{Js}$. The units are joules times seconds, where joules is the unit of energy. The most important thing to emphasize here is that we have multiple ways to state the same property of a photon. If I tell you the wavelength of the light, you can immediately calculate the frequency of the light and the energy of the photons that make up that light. Since all three quantities are related by constants, an atomic physicist will claim that wavelength, frequency, and the energy of a photon are all the same thing. An atomic physicist might very well say, "the energy of the photon is 632 THz" and think nothing of it. It takes some practice to use "wrong" units to describe something! Imagine if you asked me my height, and I responded with 150 MHz. For physicists, there is nothing wrong with doing this since we would only be off by a constant of nature.

A common energy unit is inverse centimeters. For example, the statement, "The energy difference between the two states is 12,460 cm^{-1}" is very common. For spectroscopists, this number means the same thing as 2.475×10^{-19} J. Converting

---

[11] This is the speed of light in a vacuum. It is exactly 299, 792, 458 m/s.

between the two numbers requires multiplying by the correct combination of the fundamental constants h and c. This energy unit is explored more in Problem 1.6.

We can now make a new definition:

Definitions

- **Resonance 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 resonance frequency. We use the variable f_r to represent resonance frequency. Since resonance frequency is a frequency, it uses units of Hz, MHz, GHz, or THz.

Common Misconception Power is not the same thing as energy. Power is the *rate* at which energy is exiting the laser. Imagine two laser beams with two different frequencies. The light from laser #1 has a higher frequency than the light from laser #2. We now know that the photons that make up laser #1 have more energy than the photons that make up laser #2. Power is how much energy is exiting the laser per second. If the same number of photons per second are leaving both lasers, laser #1 has a larger power. In math form, the power of a laser is:

$$P = NE_{\mathrm{ph}}, \tag{1.3}$$

where N is how many photons per second that leave the laser and $E_{\mathrm{ph}} = hf$ is the energy of a single photon. The unit for power is a watt, named in honor of Scottish chemist James Watt. A watt is shortened to W and is equivalent to joules per second. Imagine you have a 1 watt laser and a 10 watt laser that have photons with the same energy. The 10 watt laser emits 10 times as many photons per second as a 1 watt laser.

1.5 Extra: Polarization

The frequency of light tells us how many times that light wave oscillates up and down in 1 second. Polarization tells us the direction the light is oscillating. There are three major groupings of light polarization: linear, circular, and elliptical. Linearly polarized light is the most common light we use in spectroscopy, so we aren't going to talk about circularly or elliptically polarized light here. However, there are types of spectroscopy experiments that do use circularly polarized light. If you are curious about them, image search the phrases to find some neat animated gifs showing light with different polarizations moving through space. For now, we will focus on linearly polarized light.

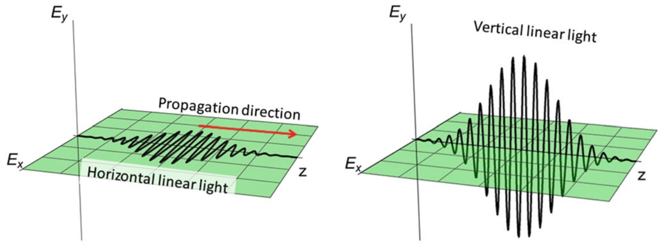

Fig. 1.13 Examples of oscillating electric fields propagating along the z-direction. The left picture shows horizontal linear light while the right picture shows vertical linear light

Linear polarization is light that is oscillating up and down in a single plane. There are two specific types of linearly polarized light: horizontal and vertical. Horizontal light oscillates ... horizontally with respect to some surface, and vertical light oscillates ... vertically to that surface, see Fig. 1.13 Remarkably, we can use these two polarizations to describe any linearly polarized light. For example, suppose the light was oscillating at a 45° angle. We would describe the light as half horizontal and half vertical.

In the lab, there are optical devices called half-waveplates, sometimes written as $\lambda/2$ plate or just $\lambda/2$. A half-waveplate can rotate the linear polarization of light. If you have horizontally polarized light, you can use a half-waveplate to change the polarization so that it is 10% vertical and 90% horizontal, 50% vertical and 50% horizontal, 75% vertical and 25% horizontal, etc. You can even make the light exiting the half-waveplate be completely vertical. That might seem like a neat trick, but the real usefulness comes when we put a second optical device after the halfwave plate called a polarizing beam splitter (PBS), see Fig. 1.14.

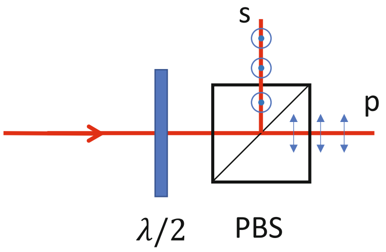

Fig. 1.14 Using a half-waveplate and a polarizing beam splitter, we can create two beams of light. You can rotate the half-waveplate to control the ratio of light in each path. In normal spectroscopy setups, you are looking down on the light and optics from above. In this orientation, p-polarized light is horizontal, indicated by the blue arrows and s-polarized light is vertical, indicated by the dotted circles

By tradition, the light that bounces off the PBS is called s-polarized light while the light that passes through is called p-polarized light.[12] This is because the PBS can technically be in any spatial orientation. For safety reasons, we almost always keep the light in a horizontal plane. In this typical setup, s-polarized light is vertically polarized light while p-polarized light is horizontally polarized light. If you were to rotate the PBS so that the s-polarized light was going straight up (don't do this, it is an eye hazard!!), that s-polarized light is now horizontally polarized while the p-polarized light is now vertically polarized. This is why we use "s" and "p".

In the lab, we use half-waveplates and polarizing beam splitters to split a single laser beam into two beams and also control the power in each of them. If the waveplate is oriented such that the light polarization leaving the waveplate is completely vertical, all of the light would bounce off the PBS. If the polarization of the light leaving the waveplate was at 45°, there would be equal power in both lasers leaving the PBS.

1.6 The Most Important Equation in All of Science

$$\text{questions} + \text{repetition} + \text{critical thinking} = \text{mastery}$$

Don't be afraid to ask questions. Don't be worried about asking for clarification. Don't expect to remember or understand every single concept the first time you read or hear about it. Mastery is not a short journey. Developing critical thinking skills is not a 5 minute activity that you figure out after watching a 3 minute YouTube video. Practice deep learning, keep a growth mindset, and, most importantly, have fun!

Problems

1.1 Go through the chapter and write down all of the fundamental constants (there are two of them). Don't forget units.

1.2 Go through the chapter and write down each equation. For each equation, write a brief description about what the equation means.

---

[12] Fun fact: the "s" stands for the German word "senkrecht", which translates to perpendicular; the "p" stands for the German word "parallel", which translates to parallel (that isn't a misprint, the German word for parallel is parallel). I like to use "s" for skip and "p" for pass-through.

1.3 (A Different Way to Find the Energy of a Photon)

(a) Using two formulas from Problem 1.2, derive a formula for the energy of a photon in terms of only fundamental constants and wavelength.
(b) Check to make sure the units are correct. Physicists always check units. Always. Hint: $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2/s^2}$

1.4

(a) What is the energy of a photon that is in a laser that has a frequency of 647.8 THz (647.8×10^{12} Hz)? Express your answer in both joules (J) and electronvolts (eV). Your final answer should have 4 significant figures.
(b) What is the wavelength of the light in nanometers?

1.5 (Assessments) Physicists are trained to assess everything. It is what makes us special ☺.

Assess the formula you found in Problem 1.3(a) by re-finding the energy of a photon using the numbers from Problem 1.4(b). If you get the same answer as Problem 1.4(a), we have built confidence that the formula you derived is correct.

1.6 In atomic physics, energy is often measured in the units of cm^{-1}. The method of calculating energy in these units is to first find the wavelength of the laser in centimeters, and then take the inverse. In equation form, this is

$$E\left(\mathrm{cm}^{-1}\right) = \frac{1}{\lambda(\mathrm{cm})}. \tag{1.4}$$

Note that in the above formula, the units to use for each symbol are included in parentheses; the formula does not say "λ multiplied by cm", but rather "make sure wavelength has units of cm before plugging into the formula."

Using $\lambda = 852.347$ nm, find the energy in units of inverse centimeters. Your answer should have 6 significant figures.

1.7 The equation in Problem 1.6 can be confusing. Energy has units of joules and not inverse length! Why are atomic physicists comfortable with using energy in this weird unit? There are multiple correct answers here.

1.8 It isn't only atomic physicists who use energy in weird units. Astronomers, nuclear physicists, and a good number of chemists also use energy in inverse centimeters. Some chemists and condensed matter physicists prefer to use electronvolts (eV). Virtually no one uses the SI unit (joules)! Any thoughts why?

2

“Natural Light”

Abstract

In this chapter, we explore how light from sources such as the sun or a lamp can be dispersed into its spectral components. We discuss various dispersive elements, including gratings and prisms, and the phenomena of refraction and diffraction that allow these elements to spatially separate light. The chapter explores blackbody radiation and the historical significance of the ultraviolet catastrophe. Additionally, we introduce the concepts of absorption and emission lines, which provide insights into atomic and molecular energy levels.

Learning Goals

By the end of this chapter, you should be able to understand:

- the concept of spectral components and how white light is composed of various wavelengths of light.
- the function and importance of dispersive elements like prisms and gratings in spectroscopy.
- the difference between refraction and diffraction.
- blackbody radiation and the ultraviolet catastrophe.
- the principles of emission and absorption lines in spectroscopy and their significance in understanding atomic structure.
- the Stefan-Boltzmann law and Wien’s displacement law in the context of blackbody radiation, and how to determine temperature from the blackbody spectrum.
- how light collected from the sun gave us our first evidence of atomic energy levels.

W. Raven, *Atomic Physics for Everyone*,
https://doi.org/10.1007/978-3-031-69507-0_2

2.1 Breaking Light into a Spectrum

Definitions

- **Spectral component:** "White" light is made up of many different wavelengths of light. Even light from the sun, which looks yellow, is made up of many different wavelengths of light. A single wavelength of light that makes up a broader spectrum of light is called a spectral component.
- **Dispersive element:** Anything that spatially separates light into its spectral components.
- **Spectrometer:** Any tool that allows us to separate out and measure the amount of each spectral component.
- **Refraction:** the redirection of a wave as it passes from one medium to another medium (like air to water).
- **Diffraction:** when waves bend around the corners of an obstacle.

A spectrometer only needs two items: a dispersive element and a screen. A dispersive element is anything that takes light and spatially separates it into its spectral components. A common dispersive element is a prism, as shown in Fig. 2.1, which works due to refraction. If you send white light into a dispersive prism, you will see a rainbow exiting because each spectral component refracts at a different angle. For a prism, the smaller the wavelength of light, the larger the refraction angle. So, blue light ($\lambda_b = 400$–$490\,\text{nm}$) refracts at a larger angle than red light ($\lambda_r = 620$–$750\,\text{nm}$). If you calibrate the prism so that you know at what angle each

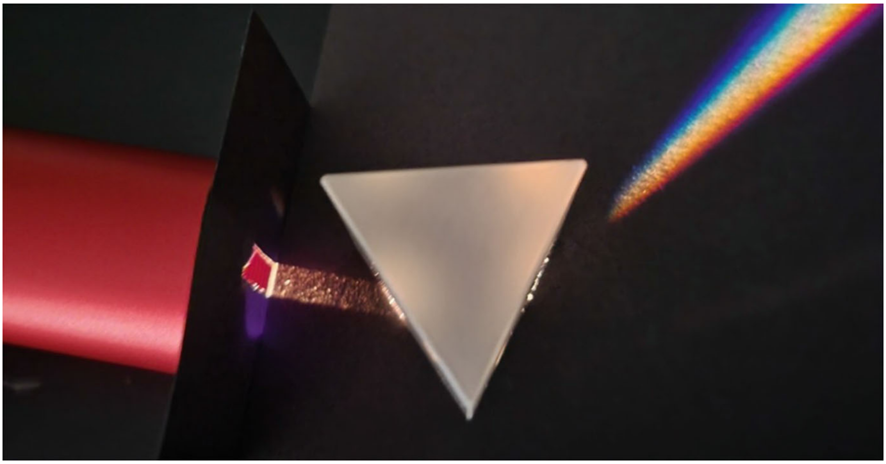

Fig. 2.1 A dispersive prism takes white light, which enters the prism from the left, and makes a rainbow. Each wavelength is refracted at a different angle. The white light source I used to make this picture is a tungsten lamp

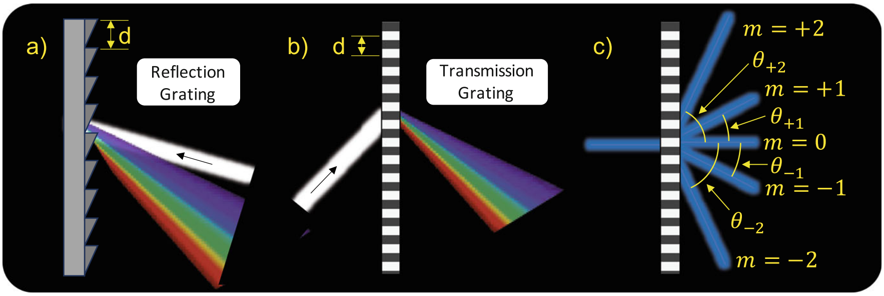

Fig. 2.2 (**a**) An example of white light, which is composed of many spectral components, reflecting off a reflection grating. For illustrative purposes, d, which is usually very small, is greatly enlarged. We also only show one order to keep the example a little cleaner. (**b**) An example of white light diffracting through a transmission grating. Again, d is greatly enlarged and we only show one order. (**c**) An example of blue light with $\lambda = 455\,\text{nm}$ hitting perpendicular to the transmission grating and being diffracted. In this example, we show all diffraction orders. The angles of diffraction are calculated using Eq. 2.1

wavelength refracts, you can send in an unknown wavelength, measure the angle of refraction, and use math to determine the wavelength of the light. You can also send in light from, for example, a hydrogen lamp and see what wavelengths or spectral components are in that light. Knowing how each wavelength refracts allows you to determine what wavelengths make up the hydrogen lamp spectrum.

In spectroscopy, the most common dispersive element is an optical grating, which works due to diffraction. Optical gratings commonly come in two types: transmission and reflection, see Fig. 2.2. Either way, the optical grating is a dispersive element that will spatially separate light into its spectral components because each spectral component diffracts at a different angle.

To create the diffraction, both types of gratings have small structures separated by a distance d. A reflection grating has a bunch of small tilted mirrors called rulings while a transmission grating has a bunch of small slits. The only physical criterion for a grating is that $d > \lambda$. The size of d in Fig. 2.2 has been greatly enlarged for visual purposes. While d must be larger than λ, in practice we also make sure that d is typically less than about 5λ to ensure suitable diffraction angles.

We will start with the equations that describe how spectral components are diffracted through a transmission grating; we will find that each spectral component can be diffracted at multiple, but well defined, angles. The math behind the next equation is a little complicated, but the end result is really what we care about. Let's start by keeping things simple and assume the incoming light is perpendicular to the grating, see Fig. 2.2c. The light diffracts through the grating according to the equation:

$$d \sin \theta_m = m\lambda \tag{2.1}$$

$$\text{for incident light perpendicular to a transmission grating}$$

In this equation, d is the distance between the slits, m is an integer known as the diffraction order (the fact that a spectral component diffracts at multiple but well defined angles is mathematically represented by m), λ is the wavelength of a spectral component of the light, and θ_m is the angle of diffraction for order m. m can be a negative integer, zero, or a positive integer. If you know d and m, you can then measure θ_m and use that to calculate λ.

Example A transmission grating has $d = 1\ \mu$m. There are three laser pointers: a blue laser pointer with $\lambda_b = 450$ nm, a green laser pointer with $\lambda_g = 532$ nm, and a red laser pointer with $\lambda_r = 650$ nm. All three lasers hit the grating perpendicular. What angles do the three lasers diffract for $m = +1, 0, -1$, and $+2$?

First, we use the diffraction equation to solve for θ_m: $\theta_m = \sin^{-1}(m\lambda/d)$, where $\sin^{-1}$ is the inverse sine function. For $m = 0$, we plug in numbers to find $\theta_{0,b} = 0°$, $\theta_{0,g} = 0°$, $\theta_{0,r} = 0°$. So, let's not use the $m = 0$ diffraction order since we can't learn anything here!

For $m = +1$, we plug in numbers to find $\theta_{+1,b} = 26.7°$, $\theta_{+1,g} = 32.1°$, $\theta_{+1,r} = 40.5°$. That is a pretty big difference! Your light only needs to travel a short distance to separate out the three colors.

Quick Math Aside

Let's put the screen 10 cm from the grating. On the screen is a ruler that will serve as our z-axis. If the grating wasn't in place, all spectral components would hit the screen at the same place. Let's call this spot $z = 0$ cm. With the grating in place and the white light hitting the grating perpendicular, the blue light, which diffracts at 26.7°, hits the screen at $z = (10\text{ cm})\tan 26.7° = 5.04$ cm while the green light hits the screen $z = 6.28$ cm. You could also skip the angle calculation and use the formula:

$$z = \pm\frac{L}{\sqrt{(\frac{d}{m\lambda})^2 - 1}} \tag{2.2}$$

for incident light perpendicular to a transmission grating,

where L is the distance between the diffraction grating and the screen. z is positive for positive m and negative for negative m. You have the opportunity to derive this formula in problem 2.4. Notice that the diffraction order in the denominator is squared, so the sign of m only determines the sign of z.

For $m = -1$, we plug in numbers to find $\theta_{-1,b} = -26.7°$, $\theta_{-1,g} = -32.1°$, $\theta_{-1,r} = -40.5°$.

For $m = +2$, we find something interesting when we plug numbers into a calculator: $\theta_{+2,b} = 64.2°, \theta_{+2,g} = (90 - 20.4i)°, \theta_{+2,r} = (90 - 43.3i))°$. Blue light diffracts at 64.2°, but the other two have weird looking answers that came out of my calculator. These numbers are called complex numbers. Complex numbers are a huge topic in both math and physics, but what it means for us is that green and red light cannot diffract into the $m = +2$ order. Experimentally, we would see blue light diffracted at 64.2°, but we would not see second order diffraction for red light and green light. They just wouldn't be there. In general, whenever you calculate a number that is supposed to represent something physical and you get a complex number, that means this is something you cannot measure or it doesn't exist.

From this example, we would want to design our spectrometer to use either $m = +1$ or $m = -1$ because all spectral components diffract with a real, measurable angle (i.e. not a complex number). In the end, it doesn't matter which diffraction order we pick. As long as we know the angle at which a spectral component diffracts, we can use that information to determine the wavelength of an unknown spectral component.

A reflection grating does a similar job as a transmission grating, but the equation looks slightly different:

$$\begin{gathered} d \sin \theta_m = -m\lambda \\ \text{for incident light perpendicular to a reflection grating} \end{gathered} \tag{2.3}$$

All that is different is the minus sign on the righthand side. Finally, let's suppose the incoming light isn't perpendicular to the grating but hits the grating at an angle θ_i with respect to the perpendicular (in optics, the perpendicular is called the "normal"), see Fig. 2.2b. The formula describing the diffraction of a spectral component is:

$$\begin{gathered} d(\sin \theta_m - \sin \theta_i) = \pm m\lambda \\ (\text{use } +m \text{ for transmission and } -m \text{ for reflection}) \end{gathered} \tag{2.4}$$

While this formula is more complicated, it is important to note that the concept is far more important than the formula. The concept is simply this:

Take Home Message

If you know how your dispersive optic bends (diffracts or refracts) different wavelengths of light, you can use that information to determine the wavelength of an unknown spectral component from any light source.

Fun History

- The first known exploration of a diffraction grating was by the Scottish mathematician and astronomer James Gregory in the mid 1600s. He observed the diffraction of sunlight caused by light passing through a bird feather. The individual feathers acted like the small slits of a transmission grating. The German physicist Joseph von Fraunhofer made the first diffraction grating in 1814. He discovered something amazing, which is the topic of the next section.
- Diffracting light from a light bulb whose gas is a particular element like hydrogen, nitrogen, or oxygen is the topic of Sect. 2.3. Classical physics had no way of explaining the observed spectral components, and this mystery was one of the puzzling experiments that led to quantum mechanics.

2.2 Blackbody Radiation

I pointed a commercial spectrometer at the sky, see Fig. 2.3. Collecting this data was spectroscopy! A few important notes before we continue:

- This spectrometer has a dispersive element that was pre-calibrated, so the angle the light hits the detector is automatically converted to a wavelength.
- Spectrometers are not uniformly sensitive. This means that the detector you are using might be more sensitive to red light than blue light. Graphs like Fig. 2.3 are useful for identifying the wavelengths present in the light, but unless the detector has been calibrated to correct for wavelength sensitivity, the shape may

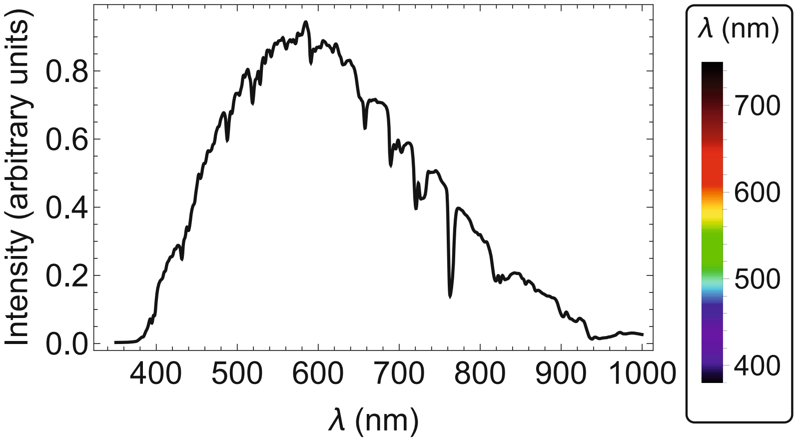

Fig. 2.3 The spectral components of light from the sun after it passes through the atmosphere

be incorrect. In fact, the real spectrum of the sky goes to far longer wavelengths, but this spectrometer is not sensitive to light at those frequencies.

- When this type of spectrum was first taken in the 1800s, those dips were a mystery, and physicists love a good mystery. Whenever a physicist is presented with data, the first thing they ask themselves is, “Why does the data look the way it does?” If we understand the concepts, we should be able to produce a mathematical model to describe (and predict) the data.
- For this data, there are, at least, two things that need to be thought through. The first is the overall shape. The second is, what are those dips?

Historically, it was a fun journey to figure out the overall shape. Physics known in the 1800s predicted a far different shape. In fact, when challenged with describing the overall shape, physics failed hard. When physicists tried to predict the spectrum in Fig. 2.3, the model was close for large wavelengths but very, very wrong for small wavelengths. Starting at the larger wavelengths and moving to shorter wavelengths, the math says the spectrum should get larger and larger and larger instead of turning around and getting smaller, which would require infinite energy. The dramatic result of the math is this: the universe doesn’t exist. Whenever the model says the universe doesn’t exist, there is something we don’t understand.[1] This result is now known as the “ultraviolet catastrophe.” It is a dramatic name, but the predictions from the mathematical model were also dramatic. We clearly needed a better model!

A Short Aside

Imagine you had a room with perfectly reflecting, parallel walls. Only light with particular wavelengths that create standing waves (perfect constructive interference like in Fig. 1.7) can exist in this room. Even though only certain wavelengths are allowed in the room, there are still an infinite number of them (you can always add one more loop to the standing wave). According to classical thermodynamics, a well tested and very successful theory, each standing wave has the same amount of energy. If you learned about heat capacity in high school chemistry, this classical thermodynamics model predicted an infinite heat capacity. Yikes!

According to the model, since each mode has the same energy, Fig. 2.3 should keep going up and up at small wavelengths. As a practical example, this mathematical model says that if you stood in a closed room and lit a match, the entire room and everything in it would burst into flames due to the infinite energy density at short wavelengths. Ultraviolet catastrophe indeed!

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[1] I feel like this might be the understatement of the millennium.

In 1901, after a lot of thought and model development, German physicist Max Planck eventually figured out that if light was composed of photons, then there would be way fewer higher-energy photons than lower-energy ones, which solved the problem. In 1905, German born physicist Albert Einstein built upon this idea with the photoelectric effect. The mathematical result of this new model predicted the shape in Fig. 2.3, which is modeled by the complicated formula:

$$M(\lambda, T) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}, \tag{2.5}$$

where $h = 6.626 \times 10^{-34}$ Js is Planck's constant, c is the speed of light, $k_B = 1.38 \times 10^{-23}$ J/K is a constant known as Boltzmann's constant,[2] and T is the temperature of the object. For temperature, we use the unit kelvin, which is named after British mathematician, physicist, and engineer Lord William Thomson. The unit for Boltzmann's constant is joule/kelvin. Using this model to fit the data from the spectrometer, we can measure the temperature of the surface of the sun to be about 5800 kelvin. We call $M(\lambda, T)$ "spectral radiant exitance", and it tells us how much radiant energy per second is leaving the object per unit area per unit wavelength.[3] The units for $M(\lambda, T)$ are $\mathrm{W/m^3}$. I should note that this equation is for a "perfect" blackbody, which doesn't exist in real life. Not having a perfect blackbody is equivalent to saying there is no such thing as a room with perfectly parallel and reflective walls. However, it still does a pretty good job with modeling the spectrum emitted by objects.

It isn't just the sun that emits a blackbody spectrum. A hot pan on the stove does, you do, and I do as well. The amount of light that is emitted as well as the peak wavelength of the blackbody spectrum only depends upon the temperature of the object. Remarkably, everything else in this model is either a constant or wavelength, which is our horizontal axis. Figure 2.4 shows a few different plots of the spectral radiant exitance for different temperatures. For objects near 5000 K, like the sun, they emit light that is visible to our human eye. For cooler objects, like us, the maximum spectral radiant exitance occurs more near 10,000 nm, which is 10 μm. There are special cameras that can see this wavelength of light. You may have seen thermal imaging or watched the Predator movies. I did not include the vertical scale in this plot because the numbers are big and hard to interpret without really digging into the spectral radiant exitance formula. But hotter objects do emit more light. The maximum spectral radiant exitance for a 6000 K object is about 3 million times larger than for a 310 K object.

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[2] Boltzmann's constant was named by Max Planck in honor of the Austrian physicist and philosopher Ludwig Boltzmann.

[3] The units are, admittedly, confusing! As a rough interpretation, you can think of these units as telling you how much light is being emitted from a blackbody at a given wavelength. If you look at Fig. 2.3, there is more light being emitted at 500 nm than 700 nm, so the spectral radiant exitance is larger at 500 nm. This is what we mean by "per unit wavelength."

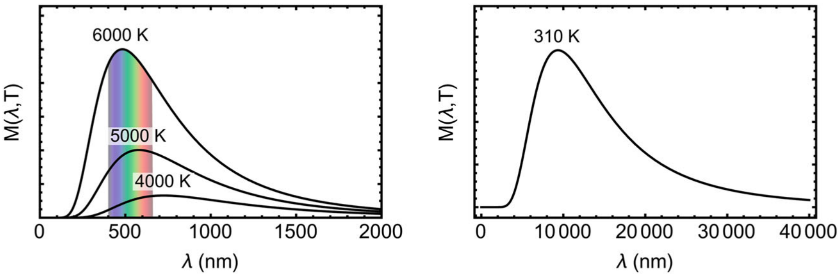

Fig. 2.4 Left: Blackbody spectrum for very hot objects. The surface of the sun is 5800 K. Right: Your blackbody spectrum, assuming you are human (310 K is about 98 F). Notice the horizontal axis is a very different scale

The Stefan–Boltzmann Law and Wien's Displacement Law Imagine you have a blackbody with surface area A. Besides the spectrum of the blackbody, you can also measure the total power emitted by the object. The total power emitted is proportional to the area under a spectral radiant exitance graph. After some math (calculus), the total power emitted by a blackbody:

$$\begin{gathered} P = \sigma \epsilon A T^4, \\ \sigma = \tfrac{2\pi^5}{15} \tfrac{k_B^4}{c^2 h^3} = 5.67 \times 10^{-8} \ \tfrac{W}{m^2 K^4} \end{gathered} \tag{2.6}$$

where σ is a constant known as the Stefan–Boltzmann constant,[4] ϵ is the emissivity, and A is the surface area of the object. Emissivity is a number between 0 and 1 indicating how closely the object behaves like a blackbody. If it is a perfect blackbody, $\epsilon = 1$. For a sphere, like the sun, the surface area is $4\pi R^2$, where R is the radius of the sphere. The emissivity of the sun is about 0.99, so it is nearly a blackbody.

Several years before Max Planck solved the ultraviolet catastrophe, German physicist Wilhelm Wien experimentally noticed that the wavelength of the maximum spectral radiant exitance graph, see Fig. 2.4, was inversely proportional to temperature. He discovered that a blackbody with a temperature of 6000 K had a maximum around $\lambda_{\text{peak}} = 484\,\text{nm}$, 5000 K had a maximum around 580 nm, 4000 K around 725 nm, etc. After studying the trend between temperature and peak wavelength, he determined:

$$\lambda_{\text{peak}} = \frac{b}{T}, \tag{2.7}$$

---

[4] Named after the Carinthian Slovene physicist, mathematician, and poet Josef Stefan, who empirically found the relationship, and Austrian physicist and philosopher Ludwig Boltzmann, who derived the equation.

where $b = 2.898 \times 10^6$ nm K. This formula was later derived from the spectral radiant exitance formula. If you have the calculus background to find the maximum of a function and want to derive this formula, you should know that, unfortunately, the resulting equation is a transcendental equation and thus does not have an analytical solution. However, you can find a numerical solution.

What About Those Dips? Let’s return to the experimental data we took for the spectrum of the sky, see Fig. 2.3. Blackbody radiation explains the overall shape, but what about the dips? What do you think is making those dips? The answer is below the fun little puzzle in Fig. 2.5.

Fig. 2.5 A fun little puzzle to separate the question from the answer

	+	12	+		31
+	■	+	■	−	
8	−		+		2
−	■	−	■	+	
	+	1	−	2	-2
8		28		11	

There are two sources of the dips: atoms and molecules in our atmosphere and the sun itself. For example, the dip near 750 nm is due to oxygen molecules in the atmosphere. There are photons coming from the sun that have the perfect energy to excite oxygen molecules. Because oxygen molecules absorb only photons with the perfect energy, some light is lost at very specific wavelengths before it reaches our spectrometer.

The second source for the dips is the sun itself. While the sun emits blackbody radiation, that light passes through gas at the surface of the sun. That gas absorbs light just like atoms and molecules in our atmosphere. If we wanted just the composition of the sun, we should collect this data from space!

This leads to one method of performing spectroscopy with a spectrometer. You take a light source, which can be a blackbody, a flashlight, or really any light source you want, and send it into your spectrometer. Record this spectrum. Next, place an atomic sample between the light source and the spectrometer and record this spectrum. Comparing the two spectra tells you which wavelengths got absorbed. Each wavelength that is lost from the light due to absorption is the same wavelength needed to excite the atom from one energy level to another. So measuring these absorption dips gives you information about the energy levels of the atoms.

2.3 Discharge Lamps

Another method of spectroscopy using a spectrometer is to point the spectrometer at a lamp filled with an element. Figure 2.6 shows the spectrum of a helium discharge lamp collected using a commercial spectrometer. The spectrum is not continuous like that of a blackbody. Instead, we observe individual spikes at very specific wavelengths. And, we already know the source of these spikes! Atoms have energy levels, and the atoms will only absorb and emit at specific wavelengths. Filling a lamp with a specific element, or the combination of a few elements, and collecting the emitted light with a spectrometer was the most common form of spectroscopy before the invention of the laser. After the spectrum was collected, physicists had to be very clever to back out the energy levels from all of those lines.

Whether you use a white light source and look for lost photons or you collect light from a discharge lamp, you gain the same information, which is the wavelengths of light needed to have an atom go from one energy level to another.

In the lab, spectrometers are still really useful tools, but they are not great for certain applications. Below are a few pros and cons to using spectrometers for spectroscopy.

Pros:

- You get lots of data all at once.
- You get lots of data very quickly.

Cons:

- The resolution is limited. You need to get different wavelengths far enough apart to distinguish between them. For example, let’s see how far apart 450.334 nm is

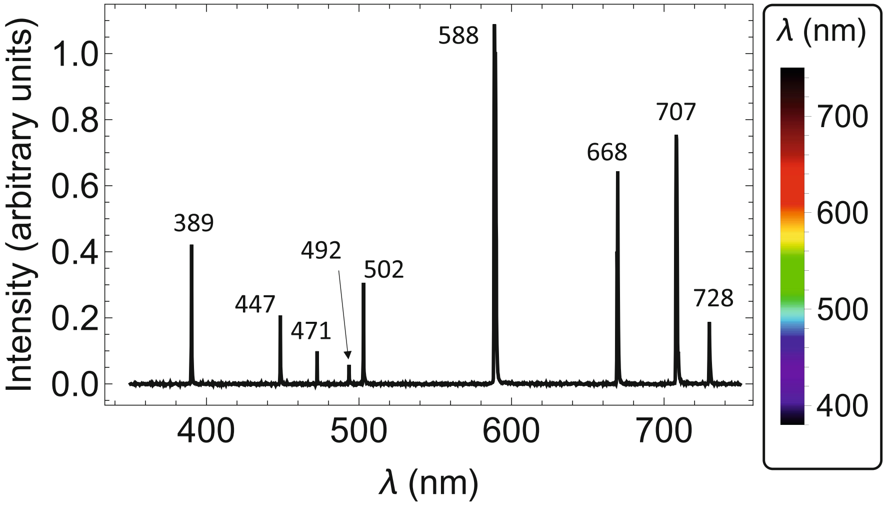

Fig. 2.6 Spectrum collected from a helium discharge lamp collected using a spectrometer with an accuracy of 0.5 nm

from 450.335 nm using Eq. 2.2 with $L = 10\,\text{cm}$, $m = +1$, and $d = 1000\,\text{nm}$:

$$z(\lambda) = \pm\frac{L}{\sqrt{(\frac{d}{m\lambda})^2-1}}$$
$$z(450.335\,\text{nm}) - z(450.334\,\text{nm}) = 140\,\text{nm}.$$

That is small! A possible solution is to make a bigger spectrometer, but then you will have to worry about thermal drifts, how well you can uniformly space the grating slits, and how well you can measure d. In short, it becomes really hard if you want really high resolution.

- The data can be hard to interpret. Getting all the data at once means you are getting all transitions from your atom or molecule all at once. A spectroscopist has to figure out what line comes from what transition (pair of energy levels), which is not an easy task!

For high precision spectroscopy, most spectroscopy groups use a laser to study a single transition instead of collecting light from many transitions at once. As we will find in Chap. 4, having atoms moving around (i.e., a hot gas) is a bad thing if we want to measure something like the energy difference between two energy states to really high precision. Clever physicists developed a neat technique to still use hot atoms to measure properties to high precision, which is the topic of Chap. 5, but we need multiple lasers to do so.

Problems

2.1 Go through the chapter and write down all of the new fundamental constants. Don't forget units.

2.2 Go through the chapter and write down each equation. For each equation, write a brief description about what the equation means.

2.3 What is the frequency difference between light that has a wavelength of 450.334 nm and light that has a wavelength of 450.335 nm? Express your answer in MHz. Your final answer should have 6 significant figures.

2.4 Derive Eq. 2.2. Start by drawing a triangle.

2.5 When introducing gratings we stated, "The only physical criterion for a grating is that $d > \lambda$." Looking at Eq. 2.2, what would happen if $d < \lambda$?

2.6 Figure 2.6 shows the spectrum of a helium discharge lamp collected using a spectrometer. Below is a table of helium energy levels. Pick any three spectral lines from the Figure (except for the feature at 389 nm) and determine which transition produced each line. The lower level for each transition is listed in the third column.

For example, the feature at 389 nm is due to an electron transitioning from level 8 to level 2:

$$\begin{gathered}185,564.6\,\text{cm}^{-1} - 159,856.0\,\text{cm}^{-1} = 25708.6\,\text{cm}^{-1} \\ \rightarrow \lambda = \frac{1}{25708.6\,\text{cm}^{-1}} = 0.0000388975\,\text{cm} = 388.975\,\text{nm}\end{gathered}$$

Level #	Energy (cm^{-1})	Lines with this lower level
1	0	
2	159,856.0	389 nm
3	166,277.4	502 nm
4	169,086.8	447, 471, and 707 nm
5	171,134.9	492 and 728 nm
6	183,236.8	
7	184,864.8	
8	185,564.6	
9	186,209.4	
10	190,298.1	
11	191,446.5	

2.7 You want to design your own spectrometer to measure light collected from a lamp. You need to collect data for light with wavelengths between 1000 and 3000 nm. You have a number of different gratings that you can pick from, each with a different d. What are a few examples of a bad choice for d? What is an example of a good choice for d?

2.8 (Solar Power)

The sun has a surface temperature of 5772 K with a radius of $r_s = 696,340$ km. The surface area of the sun is $A = 4\pi r_s^2$. The emissivity of the sun is about 0.99.

(a) Find the total power output of the sun.

(b) The light from the sun spreads out radially in all directions. A small fraction of that light hits the earth. The earth is $d = 1.496 \times 10^8$ km from the sun. Assuming the earth is a solid disk with radius $r_e = 6371$ km, what fraction of the total power leaving the sun hits the earth?
Hint: We first want to find the ratio of the area of the earth disk (πr_e^2) to the surface area of a sphere with the radius equal to the earth-sun distance: $\frac{\pi r_e^2}{4\pi d^2}$ That ratio tells us fraction of light emitted from the sun that hits the earth.

(c) For solar energy, we care about how much power per area is hitting the solar panel. Power per area is called intensity. Find how much power from the sun is hitting a 1 square meter area of land. This is the intensity of sunlight on the earth.

(d) You have a 10 cm by 10 cm solar panel. Determine the power of sunlight hitting that solar panel.

(e) Your solar panel is 20% efficient at converting sunlight into usable electric power. What is the power output of your solar panel? Is it enough to power a 10 watt LED light bulb?

(f) A refrigerator needs 200 watts of power to run. What area solar panel do you need to run the refrigerator? If the solar panel was a square, what are the dimensions of that square?

2.9 (Numerical Problem)

(a) Figure 2.7 is an amazing figure made by Robert A. Rohde. It shows the spectrum from the sun collected using an amplitude corrected spectrometer. The vertical axis is the spectral irradiance.[5] Included in the graph is a good approximation of what the sun would emit if it were a perfect blackbody. Using your favorite graphing program, estimate the temperature of the surface of the sun by plotting the spectral radiant exitance. Don't worry about the vertical scale. What you are most concerned about is getting the spectral radiant exitance to be a maximum around 500 nm.

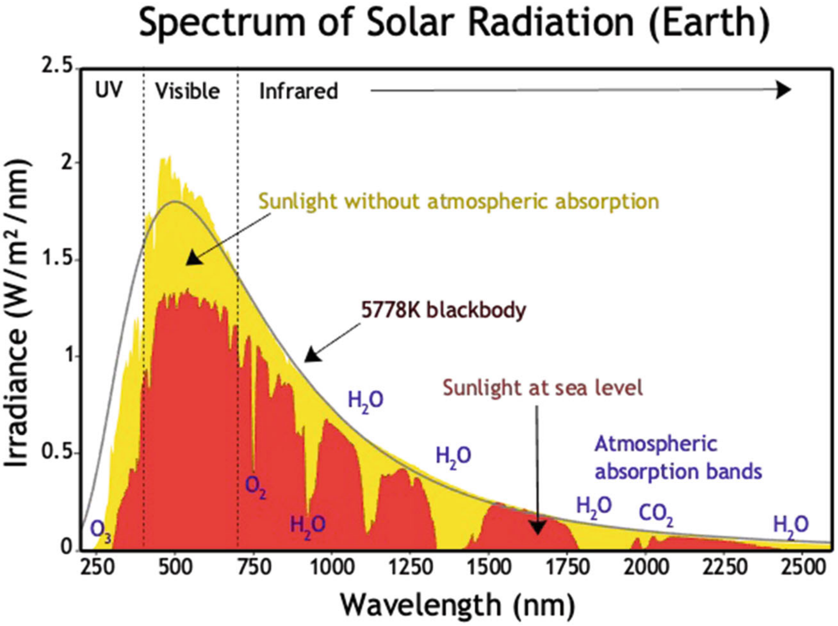

Fig. 2.7 The spectrum from the sun both before the light enters the atmosphere (yellow) and at the surface of the earth (red). A perfect blackbody spectrum is shown by the black curve. Image Credit: Robert A. Rohde, CC BY-SA 3.0 via Wikimedia Commons

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[5] Spectral radiant exitance is the radiant flux *emitted* by a surface per unit area per unit wavelength. Spectral irradiance is the radiant flux *received* by a surface per unit area per unit wavelength. You can think of spectral radiant exitance as what leaves the sun and spectral irradiance as what hits the earth.

(b) Use Wien's displacement law to assess your answer. (In other words, does Wien's displacement law confirm the peak of your graph in part (a)?)

2.10 (Advanced Problem)

(a) Using your favorite numerical program, numerically find and plot the wavelength of maximum spectral wavelength (λ_{peak}) for temperatures between 3000 and 6000 K in steps of 100 K.[6]

(b) Fit your data to b/T to find b. Be sure to use the speed of light accurate to, at least, 5 digits.

2.11 (Advanced Math Problem) Requires calculus.

(a) Find the transcendental equation that you would need to numerically solve to find Wien's displacement law.

(b) Convert the spectral radiant exitance from a function of wavelength to a function of frequency. To do this, you need to use the formula. $M_\lambda(\lambda, T)d\lambda = -M_f(f, T)df$, which guarantees that the same amount of total energy is in a spectral interval $d\lambda$ as in the corresponding interval df. The minus sign is because decreasing wavelength increases frequency.

(c) Find the spectral radiant exitance as a function of wavenumber (inverse wavelength).

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[6] In python, you can use the code scipy.optimize.fmin from the scipy library. The code only finds the minimum, so you would multiply the spectral radiant exitance formula by -1 first. In Mathematica, the function is FindMaximum.

Atoms at Rest

3

Abstract

In this chapter, we consider the factors that lead to complexity in atomic lines. We will learn that all spectral lines have a fundamental (natural) width and exist as a spread of frequencies rather than a single frequency. The width of atomic lines can also be affected by external factors such as pressure and laser power. This will be related to what we observe when probing an atom with a laser. In addition, we will learn about how this fundamental width is related to the lifetime of a state, how many photons per second an atom can absorb from a laser, and the two major types of experimental plots known as absorption plots and transmission plots.

Learning Goals

By the end of this chapter, you should be able to understand:

- the relationship between the natural linewidth of a transition and the lifetime of a state.
- absorption plots and transmission plots.
- the scattering rate and its influence on the absorption and transmission plot.
- the saturation intensity of a transition.
- the saturation parameter.
- power broadening.

W. Raven, *Atomic Physics for Everyone*,
https://doi.org/10.1007/978-3-031-69507-0_3

3.1 A Thought Experiment

An important statement and two definitions from Chap. 1:

▶ **Important Statement** If a photon has the same energy as the energy difference between the ground state and an excited state, the atom will absorb that photon and move an electron to the excited state. If the photon does not have the same energy as that energy difference, the atom will ignore the photon completely.

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. Atomic physicists use the word "excitation" and "resonance" interchangeably.
- **Resonance 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 resonance frequency. We use the variable f_r for resonance frequency. Since resonance frequency is a frequency, it uses units of Hz, MHz, GHz, or THz.

Imagine we have a bunch of atoms in a vapor cell, which is a sealed glass tube containing only the atoms we are interested in. We are going to make a few assumptions:

- The atoms are in their gaseous form.
- All of the atoms are frozen in place. In other words, the speed of every atom is 0 m/s (at rest).
- None of the atoms are interacting with anything, including each other. This means that all the atoms are neutral (each atom has an equal number of electrons and protons)
- Every atom has only 2 energy states. The state with lower energy is called the ground state. The state with higher energy is called the excited state. This simplified atom has a very descriptive label: the two-level atom.

Now, we do spectroscopy. We start by sending a laser through the vapor cell and detecting how much light makes it through, see Fig. 3.1. At the beginning of the thought experiment, the photons in the laser do not have enough energy to excite the atoms from the ground state to the excited state. In other words, the frequency of the laser is lower than the resonance frequency. As such, we don't expect the

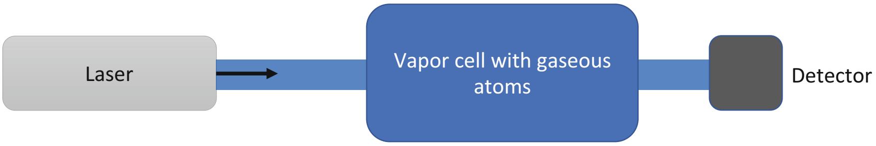

Fig. 3.1 The experimental setup for the thought experiment

atoms to absorb photons from the laser beam. Next, we will smoothly increase the frequency of the laser until the photons in the laser beam have more energy than the energy difference between the ground and excited states. In going from too small to too big, the laser frequency will, at some point, be just right so that the photons have the right amount of energy to excite the atom, which we call resonance. In the lab, smoothly changing the laser frequency over time is referred to as "scanning the laser."

A transmission plot is a plot of the fraction of photons that make it through the vapor cell as a function of laser frequency. The question is, what does our transmission plot look like for this thought experiment? Based on what we've learned so far, a completely reasonable guess would be that the atoms completely ignore the photons unless the photons have the perfect energy to excite the atom from the ground state to the excited state. So, you might guess that our transmission plot looks like the sharp dip in Fig. 3.2. The plot has a single, sharp dip that occurs at the resonance frequency. If the laser has any other frequency the photons do not have the correct energy to excite the atom. However, this is not quite right. A more realistic transmission plot can be seen in Fig. 3.3a. The transmission plot does indeed have a dip at the resonance frequency, but the dip has a width. This width is

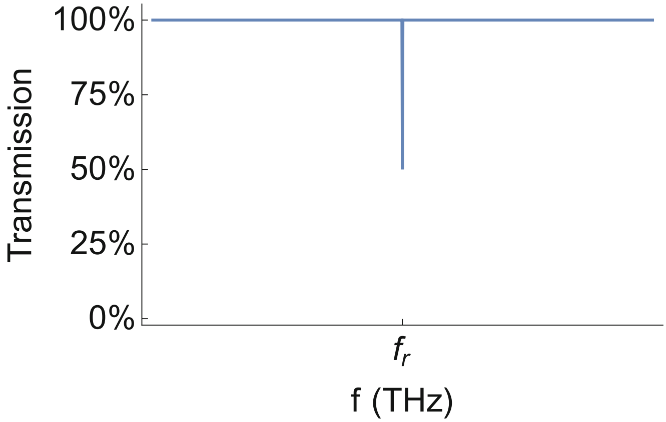

Fig. 3.2 A completely reasonable, but incorrect, guess for the transmission plot. For a transmission plot, 100% means that no photons are absorbed by the atoms, 50% means that half of the photons are absorbed, and 0% means that all of the photons are absorbed by the atoms

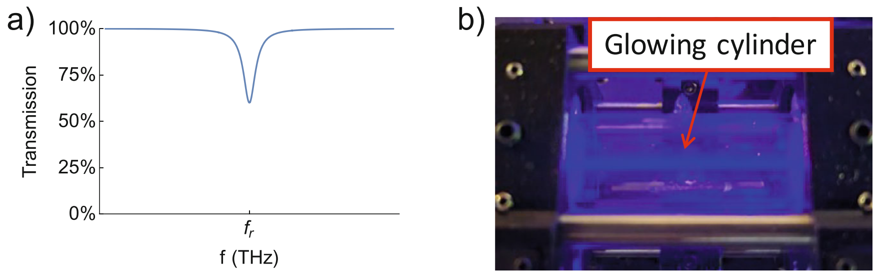

Fig. 3.3 (**a**) A more accurate transmission plot for the thought experiment. (**b**) A picture of a laser beam whose frequency matches a resonance frequency near 459 nm (blue light) passing through a vapor cell of cesium atoms. As we scan the laser frequency from below the resonance frequency to above the resonance frequency, we visually see no glowing cylinder, followed by a glowing cylinder (resonance), followed by no glowing cylinder. On resonance, the transmission decreases as shown in (**a**) because the atoms take photons from the laser and re-emit them in all directions, and almost none of these re-emitted photons continue along their original path to the detector. Note that the transmission plot in (**a**) is a theory plot assuming that the atoms are at rest. In the vapor cell the atoms are not frozen in place. Chapter 4 will explore a transmission plot for atoms moving around

called the **natural linewidth** of the transition and is represented by the lowercase Greek letter gamma, γ. The natural linewidth is a frequency, so it has units of hertz. Spectroscopists often just say "linewidth" instead of "natural linewidth." In an experiment, we would see our atoms start to glow as the laser frequency passes through resonance, see Fig. 3.3b.

Often times spectroscopists would rather look at an absorption plot instead of a transmission plot, see Fig. 3.4. An absorption plot is the fraction of photons lost as a function of laser frequency. It looks very similar to a transmission plot, but it has a bump instead of a dip. Both an absorption plot and a transmission plot tell us the same information: atoms absorb (and re-emit) photons from the laser around the resonance frequency. If you add absorption to transmission, you should get 100% for all laser frequencies.

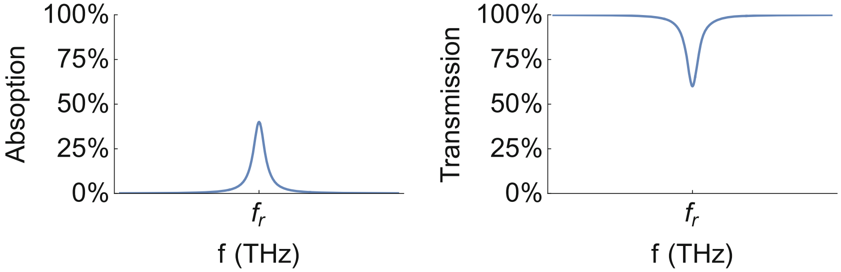

Fig. 3.4 An illustrative example of an absorption plot (left) and a transmission plot (right). If you add these two plots together, you would get 100% for all laser frequencies

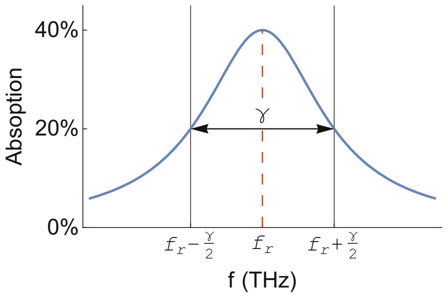

Fig. 3.5 A zoom in of a spectral feature. The natural linewidth is the full width half maximum of this feature

The natural linewidth is the full width at half the maximum (FWHM) of the absorption bump, see Fig. 3.5. It is a property of the transition that we cannot change. As an analogy, think about the charge or mass of an electron. The charge of the electron is simply the charge of the electron, which is 1.602×10^{-19} coulombs. The mass of the electron is simply the mass of the electron, which is 9.11×10^{-31} kg. These are intrinsic properties of the electron that we cannot change. The natural linewidth of a transition is inherent for that transition, and we cannot change it.

The shape of the bump (or dip in the transmission plot) is often referred to as a **spectral feature** or spectral profile. For completeness, the width of the spectral feature we measure in the lab is always larger than the natural linewidth because of various “broadening” mechanisms. One of these broadening mechanisms is laser power, which we will discuss in Sect. 3.5. If the laser power was the only broadening mechanism, we would find that as the laser power gets smaller and smaller, the width gets narrower and narrower until it reaches the natural linewidth. The natural linewidth is the *minimum* possible FWHM of a spectral feature.

The mathematical shape of the spectral feature is a Lorentzian function. In the absence of any broadening mechanism, the mathematical form is:

$$L(f) = \frac{A}{1 + \frac{4(f - f_r)^2}{\gamma^2}}, \tag{3.1}$$

where γ is the natural linewidth[1] and A is the maximum absorption, which describes the amount of laser light lost when traveling 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, which is also 100%). You may be familiar with a similarly shaped Gaussian function. A Lorentzian function looks very similar, but it is slightly different in shape.

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[1] This is for the low power limit. In Sect. 3.5, we will refine this formula slightly to include power broadening. I just want to start basic to get the concepts first.

Math Assessment

Equation 3.1 is the mathematical shape of a spectral feature. According to Fig. 3.5 (and the definition of natural linewidth), the absorption at $f = f_r \pm \gamma/2$ should be half as large as the absorption when $f = f_r$. So, let's check to make sure the formula matches that statement. To do this, we will first plug in $f = f_r$ into Eq. 3.1 to make sure that $L(f_r) = A$:

$$\begin{aligned} L(f_r) &= \frac{A}{1+\frac{4(f_r-f_r)^2}{\gamma^2}} \\ &= \frac{A}{1+\frac{0}{\gamma^2}} = A \end{aligned}$$

Next, we will plug in $f = f_r \pm \gamma/2$ to see if $L\,(f_r \pm \gamma/2) = A/2$. If you are more comfortable doing this twice, once for $f = f_r + \gamma/2$ and once for $f = f_r - \gamma/2$, please do so!

$$\begin{aligned} L(f_r \pm \gamma/2) &= \frac{A}{1+\frac{4(f_r\pm\gamma/2-f_r)^2}{\gamma^2}} \\ &= \frac{A}{1+\frac{4(\pm\gamma/2)^2}{\gamma^2}} = \frac{A}{1+\frac{4(\gamma^2/4)}{\gamma^2}} = \frac{A}{1+\frac{\gamma^2}{\gamma^2}} = \frac{A}{1+1} \\ &= \frac{A}{2} \end{aligned}$$

Yay!

Important Spectroscopists being spectroscopists call the spectral feature many different things. Other common descriptions of the spectral feature include the Lorentzian profile, the absorption profile, the absorption lineshape, the spectral profile, the spectral lineshape, or the Doppler-free spectrum. The description "Doppler-free spectrum" will make more sense after Chap. 5. Some atomic physicists use the descriptor "Lorentzian function", but that should be avoided because that phrase is a mathematical definition 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 used to describe lots of different physical phenomena like an oscillating spring or a swinging pendulum. The same thing is true 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 the term spectral feature or spectral profile.

Definitions

- **Transmission plot:** A plot of the percentage or fraction of photons that passes through a vapor cell as a function of laser frequency.
- **Absorption plot:** A plot of the percentage or fraction of photons lost from a laser after it passes through a vapor cell as a function of laser frequency. A dip in a transmission plot is seen as a bump in the absorption plot.
- **Natural linewidth:** The minimum possible full width at half maximum (FWHM) of a spectral feature. The natural linewidth is a property of a transition, with each transition in an atom having a unique natural linewidth.

One Last Thing We can now update that important statement from Chap. 1, which is also at the top of this section.

> ► **Important Statement** A photon has a probability of being absorbed by an atom depending upon the photon's energy. It is most likely to be absorbed if the photon's energy exactly matches the energy difference between the ground and excited state, but there is a non-zero probability of absorption off resonance.
>
> Specifically, in the absence of any broadening mechanism (like laser power), if the photon's energy is off by $\frac{h\gamma}{2}$ from that resonance energy, the photon is half as likely to be absorbed compared to a photon that has the energy equal to the energy difference between the ground and excited states.

3.2 The Natural Linewidth in Angular Units

Many formulas that spectroscopists and atomic physicists use contain variables with angular units. This is more of a mathematical convenience, but since they are used so often, I wanted to introduce them as a topic. Suppose we had a simple sine wave that described an oscillation in time with frequency f and amplitude A. We would write that as:

$$A \sin(2\pi f t) \tag{3.2}$$

The presence of 2π in the argument of the sine function stems from the inherent periodicity of a sine wave, which repeats itself every 2π radians. Consequently, each time the argument of the sine function increases by 2π, the waveform completes one full cycle. Thus, the frequency denotes the rate at which the sine wave repeats within a time span of one second. This periodicity of 2π is where the "angular" part comes in. Instead of always writing $2\pi f$, we simplify things by using angular frequency,

$\omega = 2\pi f$. That curly-looking symbol is the lowercase Greek letter omega. That same sine wave using angular frequency units is:

$$A \sin(\omega t). \tag{3.3}$$

In the lab, we measure frequency, but, mathematically, we often use angular frequency. The natural linewidth is a frequency, but it is often written in formulas using angular frequency units. In this book, we will use capital gamma, Γ, for the natural width in angular frequency units and lowercase gamma, γ, for normal frequency units. The relationship between the two is:

$$\Gamma = 2\pi\gamma. \tag{3.4}$$

I want to emphasize that frequency, and not angular frequency, is the unit that we work with in the lab. To help us keep these two parameters separate, we use the unit radians/second $\left(\frac{\text{rad}}{\text{s}}\right)$ for angular frequency and inverse seconds $\left(\frac{1}{\text{s}}\right)$ or hertz (Hz) for frequency. If you are given the information that $\Gamma = 10.5 \times 10^6\ \frac{\text{rad}}{\text{s}}$, then we calculate $\gamma = \frac{10.5\times10^6\ \text{rad/s}}{2\pi} = 1.67 \times 10^6\ \frac{1}{\text{s}} = 1.67\,\text{MHz}$ for use in the lab. If we want to change the frequency of a laser by one linewidth, we change the frequency by 1.67 MHz, not 10.5 MHz. Again, to avoid confusion, we don't use the unit MHz for the angular frequency. Instead, we make sure to use rad/s: $10.5 \times 10^6\ \frac{\text{rad}}{\text{s}}$.

Reduced Planck's Constant In the explanation of the photoelectric effect, Einstein discovered that a photon has an energy $E_{\text{ph}} = hf$. If we wanted to write this equation using angular units, we would get $E_{\text{ph}} = h\frac{\omega}{2\pi}$. Physicists absorb that extra 2π into h and call that new constant the "reduced Planck's constant": $\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34}\,\text{Js}$. Notice that the variable for the reduced Planck's constant resembles a lowercase h with a horizontal line drawn across its stem. We call this constant "h-bar". We now have two completely equivalent ways of writing the energy of a photon:

$$\begin{aligned} E_{\text{ph}} &= hf \text{ (frequency units)} \\ E_{\text{ph}} &= \hbar\omega \text{ (angular frequency units)} \end{aligned} \tag{3.5}$$

It doesn't matter what equation you use, you will always calculate the same energy.

Any function expressed in frequency units can be written in angular frequency units. For example, the Lorentzian function from Eq. 3.1 using angular frequency units is:

$$L(\omega) = \frac{A}{1 + \frac{4(\omega-\omega_r)^2}{\Gamma^2}}, \tag{3.6}$$

where $\omega_r = 2\pi f_r$ is the angular resonance frequency.

3.3 The Natural Linewidth and the Lifetime of the Excited State

The natural linewidth is, remarkably, related to the lifetime of the excited state. To understand the lifetime of an atomic state, first imagine that all of the atoms from the above thought experiment 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 at a random time. Spectroscopists 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 while others take their time. Statistically, each atom has a probability of decaying out of the excited state that will look like Fig. 3.6. At $t = 0$, all 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 in Fig. 3.6, about 63% of the atoms have decayed back to the ground state in 6.25 ns, and about 80% of the atoms have decayed back to the ground state in 10 ns. The mathematical form of the decay curve is:

$$e^{-t/\tau}, \tag{3.7}$$

where τ (this is the Greek letter lowercase tau) is called the lifetime of the excited state. This function is called an exponential decay. Like the natural linewidth of a transition, τ has a unique value for every transition in an atom. The lifetime of the excited state used for the decay in the graph is $\tau = 6.25$ ns, which means that after 6.25 ns about 63% of the atoms have decayed. There is nothing special about 63%; it is just what physicists decided to define as the lifetime. Mathematically it is a nice definition because when $t = \tau$, the fraction of atoms that have not decayed is $e^{-1} = 0.368$, or 36.8%. After two lifetimes (2×6.25 ns $= 12.5$ ns), about 86.5% of the atoms have decayed leaving $e^{-2} = 0.135$, or 13.5%, of the atoms in the excited state.

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

$$\tau = \frac{1}{\Gamma} = \frac{1}{2\pi\gamma}. \tag{3.8}$$

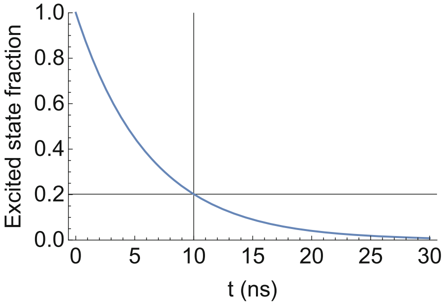

Fig. 3.6 The excited state fraction as a function of time for an excited state that has a lifetime of 6.25 ns

As you can imagine, atomic physicists and spectroscopists often use the angular frequency form of natural linewidth when thinking about lifetime.[2] These two quantities are inversely related to each other. This means:

- If the lifetime is small, the natural linewidth is large. This means that excited states with a small lifetime have absorption and transmission plot spectral features that are relatively wide.
- If the lifetime is large, the natural linewidth is small. This means that excited states with a large lifetime have absorption and transmission plot spectral features that are relatively narrow.

3.4 The Scattering Rate and Saturation

Definitions

- **Waist of a laser:** The half width of the intensity plot where the intensity is 13.5% of the maximum intensity, see Fig. 3.7. We use the variable w to represent waist.
- **Intensity:** The intensity of a laser beam is the power of the laser divided by the cross sectional area of the laser beam, denoted as $I = P/A$.

If you shine a laser on the wall, you will see something that appears to be a circle. However, it isn't actually a circle. If we plotted the intensity of the laser, it would look like Fig. 3.7a. The waist of a laser beam is defined in Fig. 3.7b. It is a bit

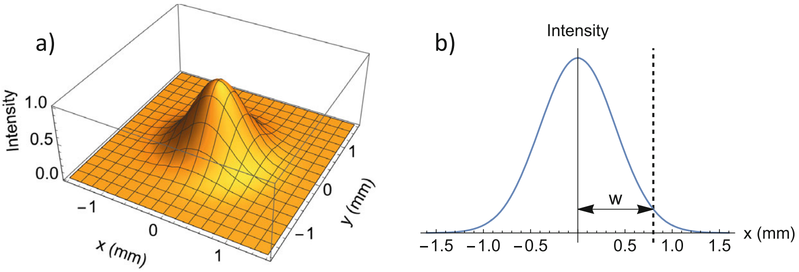

Fig. 3.7 (**a**) The intensity of a laser beam on the wall. (**b**) The intensity along any one of the axes. The waist is the half width of the intensity plot when the intensity is 13.5% of the maximum intensity

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[2] A careful reader might notice the units for lifetime look like $\frac{\mathrm{s}}{\mathrm{rad}}$. You can think of radians as simply a placeholder to remind us to use radians (2π) instead of degrees (360°) in our math when calculating frequency. We do not keep the radian unit for lifetime. That unit for lifetime is seconds (or µs or ns).

confusing since most people think of the waist of a laser as the diameter, but it is more similar to a radius. The intensity profile is described by a Gaussian function.[3] The area of a laser beam is:

$$A = \frac{1}{2}\pi w^2 \tag{3.9}$$

This is, of course, for a perfect laser beam. In real life, the intensity profile is not a perfect Gaussian function and the waist in the x direction and y directions could be different. In the latter case, the cross sectional area of a laser is $\frac{1}{2}\pi w_x w_y$.

Guiding Question: We are interested in the following question: Given a laser and a particular transition in an element, how many photons per second will that atom absorb (and re-emit)? This value is known as the **scattering rate**. Take a few moments to think about this question before continuing.

Intensity Versus Power In the lab, we measure laser power. However, we actually care about laser intensity. Why? (This is a homework problem as well).

How many photons an atom scatters depends upon a few different ideas: (1) how far the laser frequency is from the resonance frequency *relative to* the natural linewidth, (2) how long an atom spends in an excited state, and (3) how a transition reacts to photons from a laser whose frequency matches the resonance frequency. Let's unpack all of these ideas.

(1) We now know that the shape of the absorption bump has the mathematical form of a Lorenztian function. For spectroscopists, the natural linewidth really matters. Suppose an atom has a natural linewidth of $\gamma = 100\,\text{MHz}$ and the laser is 25 MHz below the resonance frequency, see the left spectral profile in Fig. 3.8. For this transition, the atom will "scatter" (i.e., absorb and re-emit) many photons from the laser. The right spectral profile in Fig. 3.8 corresponds to a transition that has a natural linewidth of $\gamma = 1\,\text{MHz}$. For this narrower transition, the atom will not scatter many photons at all even though the laser frequency is still set to 25 MHz below the resonance frequency.

To quantify how far the laser frequency is from the resonance frequency, we define a new parameter called **detuning**. Detuning, which is represented by the lowercase Greek letter delta δ in normal frequency units and capital delta $\Delta = 2\pi\delta$ for angular frequency units, gives us this information. Mathematically, detuning is $\delta = f - f_r$, where f is the frequency of the laser. Notice that if $f < f_r$, then $\delta < 0$. In the lab, we call this "red detuning," which will

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[3] A Gaussian function is very similar to a Lorentzian but it is slightly different. We will explore Gaussian functions more in Chap. 4.4.

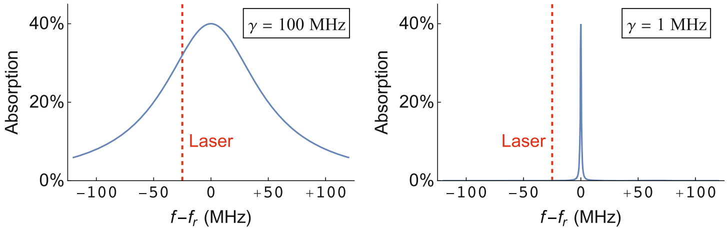

Fig. 3.8 Two examples for how light from a laser interacts with two different transitions. The left transition has a large natural linewidth while the right transition has a small natural linewidth. The laser frequency (red dashed line) is 25 MHz below the resonance frequency for both transitions

make more sense after we discuss the Doppler effect in Chap. 4. Likewise, if $f > f_r$, then $\delta > 0$, which we call "blue detuning." In our thought experiment, the atoms will absorb the largest number of photons when $\delta = 0$ (the laser frequency exactly matches the resonance frequency). In the absence of power broadening (i.e., when the laser power is kept low), the atoms will absorb half as many photons when $\delta = \gamma/2$ or $\delta = -\gamma/2$ compared to when $\delta = 0$.

As discussed above and displayed in Fig. 3.8, detuning is important, but so is the natural linewidth. What we really want to know is how far the laser frequency is from the resonance frequency *relative to* the natural linewidth. For example, if we set the laser frequency such that $\delta = -\gamma/2$, the laser will lose half as many photons compared to when $\delta = 0$. This is true for any transition. The quantity that matters for the scattering rate is the *ratio* of detuning to natural linewidth. So, we expect δ/γ to show up in the relevant scattering rate equation.

(2) The scattering rate tells us how many photons are absorbed (and re-emitted) by an atom. From point (1), we know that detuning matters. The average time an atom spends in the excited state also matters. If an atom, on average, spends only 1 ns in the excited state, it decays very quickly, freeing itself up to be excited again. Contrast that with an atom that spends, on average, 2 seconds in the excited state. That atom will have a very small scattering rate. From Eq. 3.8, we know that the average lifetime is related to the natural linewidth. A large natural linewidth means a short lifetime. Therefore, a large natural linewidth results in a large scattering rate.

(3) Let's consider two transitions with different resonance frequencies. Transition #1 has a resonance frequency f_{r1} and transition #2 has a resonance frequency f_{r2}. We will assume that $f_{r1} > f_{r2}$ and that both transitions have the same natural linewidth. We also have two lasers with the same intensity. The frequency of laser #1 is set to f_{r1} and is sent through a vapor cell with atoms that have transition #1. The frequency of laser #2 is set to f_{r2} and is sent through a vapor cell with atoms that have transition #2. In other words, the only difference between the two experiments is that transitions have different

resonance frequencies. Will both transitions scatter (i.e., absorb and re-emit) the same number of photons per second, or will the scattering rates be different?

Surprisingly, the answer is that the scattering rates are different for the two transitions! The reason is that the cross section (or "size") of the photons is different for the two transitions. Roughly, the cross section of a photon is λ^2. If a transition has a smaller resonance frequency, the laser light has a longer wavelength and photons with a bigger cross section. That means the photons in the laser are "big" and more likely to "hit" the atom and cause the transition. If a photon has a small cross section (high frequency, short wavelength), it is less likely to hit the atom and cause the transition. For the example above, the photons from the laser with $f = f_{r1}$ have a smaller cross section than the photons from the laser with $f = f_{r2}$. If we want the same number of scattered photons from the two transitions, the atom with f_{r1} needs to be exposed to more photons than the transition with f_{r2}. In other words, to achieve the same scattering rate for the two transitions, the transition with f_{r1} requires a higher intensity than the transition with f_{r2}.

Summary

(1) Detuning *relative to* the natural linewidth matters. $\delta = 0$ should have the largest scattering rate.
(2) The natural linewidth (or lifetime of an excited state) matters. Large γ should have a large scattering rate.
(3) Photon cross section matters. A large frequency, or short wavelength, has a smaller scattering rate.

To quantify points (2) and (3), we introduce a parameter known as the **saturation intensity** I_s. The saturation intensity contains all the information about a particular transition that helps us understand how easily an atom interacts with photons in a laser beam whose frequency matches the resonance frequency of a transition (we will quantify this statement soon). Suppose we send a laser beam whose frequency matches the resonance frequency for some transition through a sample of atoms. If an atom absorbs a photon, it will spend some amount of time in the excited state before decaying back to the ground state, where it is free to absorb another photon. The saturation intensity is the laser intensity for an on-resonance laser ($f = f_r$) such that 25% of the atoms are in the excited state at any given time. A transition with a small saturation intensity means that we only need a small laser intensity to have 25% of the atoms in the excited state. A transition with a large saturation intensity means we need a large laser intensity to make that happen.

The ratio of the intensity of light to the saturation intensity is called the **saturation parameter** $s = I/I_s$. We like to use s because, like δ/γ, it means the same thing for every transition. Saying $s = 1$ means that we set the laser intensity equal to the saturation intensity. Some transitions might have a high saturation intensity, like a transition in the beryllium atom that has $I_s = 885\,\mathrm{mW/cm^2}$, while other transitions have a low saturation intensity, like a transition in the cesium atom that has $I_s = 0.40\,\mathrm{mW/cm^2}$. For that transition in the beryllium atom, we would need 885 mW of power for a laser with cross sectional area $A = 1\,\mathrm{cm}^2$ to have $s = 1$, which means 25% of the atoms are in the excited state. 885 mW is a lot of laser power! For the transition in the cesium atom, we only need 0.40 mW of power to have 25% of atoms in the excited state. The formula for the saturation intensity is:[4]

$$I_s = \frac{2\pi^2}{3}\frac{hc\gamma}{\lambda^3}. \tag{3.10}$$

Notice that the saturation intensity is proportional to γ. This is point (2). Also notice that there is a λ^3 in the denominator. One of those λ terms is grouped with hc in the numerator; hc/λ represents the energy of the on-resonance photon. The remaining λ^2 comes from the cross section of a photon. The saturation intensity is a property of a transition! It is whatever it is, and it cannot be changed.

Assessing the Scattering Rate Formula Before We Even Write It Down
Before we write down the formula that models the scatter rate, decide if δ/γ should be in the numerator or the denominator? In other words, would $\delta/\gamma = 100$ result in more or less photons scattered compared to $\delta/\gamma = 0$? What about the saturation parameter s? Should that parameter be in the numerator or denominator?

The scattering rate, which is derived using quantum mechanics, is how many photons per second an atom will absorb (and re-emit). The scattering rate, $r_\Gamma(\Delta, s)$ using angular frequency variables and $r_\gamma(\delta, s)$ using normal frequency variables, is:

$$\begin{aligned} r_\Gamma(\Delta, s) &= \tfrac{\Gamma}{2}\tfrac{s}{1+s+4(\frac{\Delta}{\Gamma})^2} \\ r_\gamma(\delta, s) &= \pi\gamma\tfrac{s}{1+s+4(\frac{\delta}{\gamma})^2}. \end{aligned} \tag{3.11}$$

The equation using normal frequency units is more practical, but you will rarely see that formula written anywhere. Almost every atomic physics textbook will use the scattering rate formula that uses angular frequency variables. Notice that the ratio δ/γ is in the denominator. If that number gets big, the scattering rate decreases. The saturation parameter is in the numerator *and* the denominator, which you might not have guessed. It makes sense for it to be in the numerator because if I increased the

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[4] For completeness, this is the formula for doing spectroscopy with linearly polarized laser light. Experiments with circular polarized light have a slightly different formula.

laser intensity there are more photons for the atom to interact with making it more likely to absorb and emit a photon. But what about the extra s in the denominator?

The first thing to notice is that if the saturation parameter is small, than $1+s \approx 1$, and s would only be in the numerator. The extra s in the denominator 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 $\tau = 1/(2\pi\gamma)$ in the excited state. If the atom is already in the excited state, it can't absorb a photon. If all the atoms were in the excited state, there are no atoms left in the ground state to absorb any photons.

This is important, so let's explore it a little more. Suppose an atom always spends a time $\tau = 10\,\text{ns}$ in the excited state before decaying back to the ground state.[5] In the most extreme case of super high laser intensity, 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 $\frac{1\,\text{photon}}{10\,\text{ns}} = \frac{1\,\text{photon}}{10\times10^{-9}\,\text{s}} = 10^8$ photons every second. Without the s in the denominator, the scattering rate would increase without bound as the power increases. However, with the s in the denominator, the on-resonance scattering rate will "saturate" at $\pi\gamma$.[6]

Summary of Formulas

$$
\begin{aligned}
&r_\gamma(\delta, s) = \pi\gamma \frac{s}{1+s+\frac{4\delta^2}{\gamma^2}} \\
&I = P/A \\
&A = \tfrac{1}{2}\pi w^2 \text{ (for a laser beam)} \\
&s = \frac{I}{I_s} \\
&\delta = f - f_r \\
&I_s = \frac{2\pi^2}{3}\frac{hc\gamma}{\lambda^3}
\end{aligned}
\tag{3.12}
$$

One Final Thing: The fraction of atoms in an excited state was one of the key concepts we used to explore the scattering rate. So, it is no surprise that scattering rate also tells us what fraction of atoms are in the excited state. The fraction of atoms in the excited state is $r_\Gamma(\Delta, s)/\Gamma$ (use the angular frequency formulas for calculating the excited state fraction).

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[5] Remember that an atom actually decays probabilistically with a characteristic time τ. This is just a thought experiment to understand the concept of saturation.

[6] A careful reader might notice the maximum scattering rate is only half as big as our thought experiment predicted. The idea of the thought experiment is correct, but we are ignoring an effect known as coherent state transfer, which includes stimulated absorption and stimulated emission. This is a massive, complicated topic, and one that is beyond the scope of this book. 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 do a quick assessment. If $s = 1$ (or $I = I_s$) and $\Delta = 0$, the excited state fraction should be 25%:

$$\frac{r_\Gamma(0,1)}{\Gamma} = \frac{1}{2}\frac{1}{1+1+\frac{4(0)^2}{\Gamma^2}} = \frac{1}{4} = 0.25$$

3.5 Power Broadening

The scattering rate tells us how many photons per second an atom takes from the laser. A large scattering rate must correspond to a larger amplitude spectral feature in an absorption plot. In fact, atoms scattering photons is the only way to produce a spectral feature. If that is the case, shouldn't the scattering rate be a Lorentzian function (Eq. 3.1) like our spectral features? It looks close, but there is that extra s in the denominator of the scattering rate that is not in Eq. 3.1. While it might not look like it, the scattering rate is a Lorentzian function. We just need to do a little algebra to convert the scattering rate into a new form. The algebraic step is to factor out $1 + s$ from the denominator:

$$r_\gamma(\delta, s) = \pi\gamma\frac{s}{1+s+\frac{4\delta^2}{\gamma^2}} = \left(\frac{\pi\gamma}{1+s}\right)\frac{s}{1+\frac{4\delta^2}{\gamma^2(1+s)}}. \tag{3.13}$$

We are going to define a new parameter $\gamma_s = \gamma\sqrt{1+s}$, known as the power broadened linewidth. With this definition, we can write $\frac{4\delta^2}{\gamma^2(1+s)}$ as $\frac{4\delta^2}{\gamma_s^2}$. To help us assess this formula, we will also switch the positions of s and $\pi\gamma$ in the numerator. With those changes, we have:

$$r_\gamma(\delta, s) = \left(\frac{s}{1+s}\right)\frac{\pi\gamma}{1+\frac{4\delta^2}{\gamma_s^2}}. \tag{3.14}$$

This is now a Lorentzian function with amplitude $\frac{s}{1+s}\pi\gamma$ and FWHM of $\gamma_s = \gamma\sqrt{1+s}$. As we increase the saturation parameter s (i.e., increase the laser intensity), the FWHM of the scattering rate becomes larger by a factor of $\sqrt{1+s}$. Therefore, the width of a spectral feature increases by the same amount. Also notice that when $s \to 0$, the FWHM reaches its minimum value of the natural linewidth.

Next, let's analyse the amplitude. As the saturation parameter gets larger and larger, $1+s \approx s$, so $\frac{s}{1+s} \to 1$. The amplitude saturates! As the laser power increases, the amplitude approaches the maximum scattering rate of $\pi\gamma$. However, the FWHM never saturates; it continues to broaden, as shown in Fig. 3.9.

Finally, let's put some numbers in to start getting comfortable with real scattering rate numbers. For the example in Fig. 3.9, I used the natural linewidth for a transition in the cesium atom near 852 nm. The natural linewdith is about $\gamma = 5.22$ MHz. The on-resonance ($\delta = 0$) scattering rate is 8.2 million photons absorbed (and re-emitted) per second for $s = 1$; 14.9 million photons per second for $s = 10$;

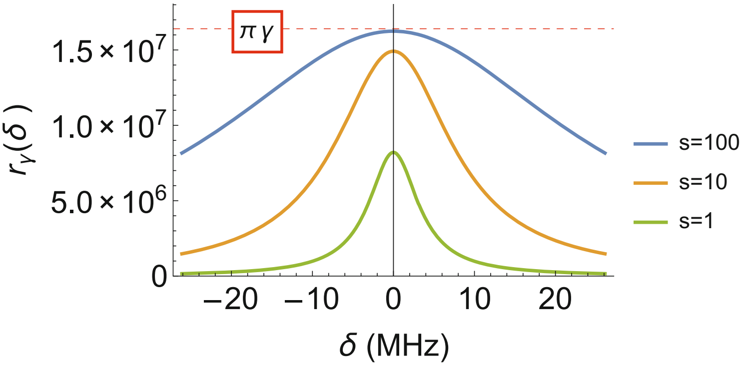

Fig. 3.9 The scattering rate for a transition with $\gamma = 5.22\,\text{MHz}$ as a function of detuning for different saturation parameters. The red dashed line is the maximum possible scattering rate

16.2 million photons per second $s = 100$. For a typical transition, scattering hundreds of thousands to millions of photons per second is not unusual. Notice that when s is small, the scattering rate at $\delta = -20\,\text{MHz}$ is almost 0; mathematically, it is about 270,000 photons/sec for $s = 1$. However, the scattering rate for $s = 100$ remains quite sizable.

For completeness, there are other factors that can broaden the width of a transition including temperature (this is the topic of Chap. 4) and pressure. We do not cover pressure broadening, also known as collisional broadening, in this book.

3.6 Example

A lot has happened in this chapter, but two of the important concepts are that (1) the scattering rate tells us how many photons per second an atom absorbs (and emits) from the laser and (2) the cumulative effect of all the atoms taking photons results in the absorption profile. Let's solidify these concepts with an example. Throughout this example, we will also introduce some commonly used language in atomic physics. A lot of the language will be explored in more detail as we work our way through this book.

A particular type of barium atom[7] called barium-135 has one ground state and three closely spaced excited states, see Fig. 3.10. The spacing between the excited states is called hyperfine splitting, which will be explored in detail in Chap. 9. The reason there are three excited hyperfine states is because the nucleus has angular momentum, a concept we will begin exploring in Chap. 7. If the nucleus did not

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[7] All barium atoms have 56 protons in the nucleus. Neutron number can vary from about 58–97! We call a particular barium atom, for example an atom with 56 protons and 79 neutrons, an isotope of barium. Isotopes are explored in Chap. 10.

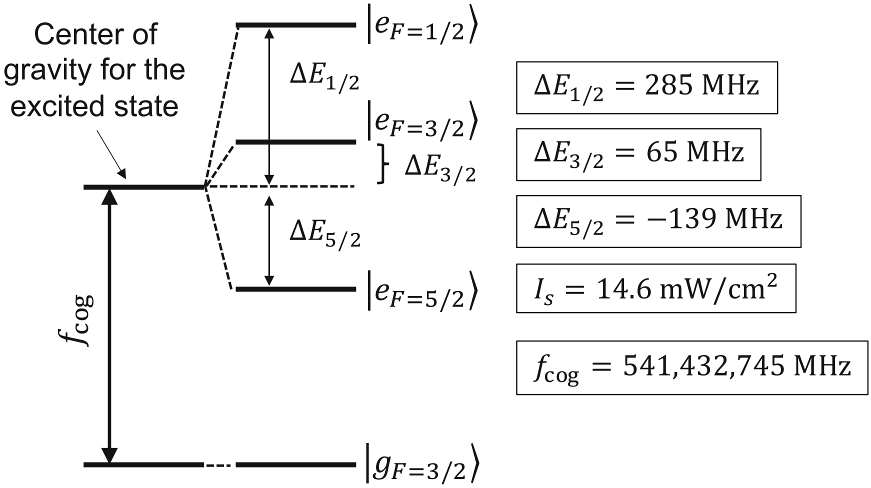

Fig. 3.10 A simplified Grotrian diagram for a transition in the atom known as barium-135. The energy spacings are not to scale. The energy spacings between the excited hyperfine levels are calculated from the results of Baird et al.[1]. The center of gravity frequency is extracted using numbers from both Baird et al. [1] and Karlsson et al. [2]. The uncertainty in the center of gravity frequency is about 30 MHz. [2] While that isn't a terrible uncertainty, modern day spectroscopic methods can do better!

have angular momentum, there would be only one excited state.[8] Again, we will learn the physics behind hyperfine splitting starting in Chap. 7. Before we do an example, we need a few more definitions.

Definitions

- **Center of gravity:** The energy of a state if the nucleus had no angular momentum.
- **Hyperfine splitting:** When the nucleus has angular momentum, the single energy level at the center of gravity splits into multiple energy states. Each of these states is going to shift in energy a small amount compared to the center of gravity energy.
- **Bra-ket notation:** Atomic physicists sometimes use "bra-ket" notation when working with states in an atom. A "ket" is a way to represent a particular state and it looks like this: |put state label here⟩. A "bra", which is not used in this book but you will use it a lot if you take quantum mechanics, looks like this: ⟨put state label here|. Bra-ket notation is also referred to as Dirac notation, named after the English mathematical and theoretical physicist Paul Dirac.

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[8] There are atoms with ground state hyperfine splitting; barium-135 is just not one of those atoms.

Note
Some learners may use only Part 1 of this book. I wanted to introduce you to bra-ket notation so that you have seen it at least once before you take quantum mechanics. We are going to use it in this example and in Problem 3.9, but it will not be used again until Part 2. You are, of course, welcome to use bra-ket notation if you want, but it is not necessary. You may also see bra-ket notation if you take a linear algebra class.

As seen in Fig. 3.10, we are going to label the ground state $\left|g_{F=3/2}\right\rangle$ and the three excited states $\left|e_{F=1/2}\right\rangle$, $\left|e_{F=3/2}\right\rangle$, and $\left|e_{F=5/2}\right\rangle$. F is called a quantum number, and it is always a positive integer, a half integer, or zero; quantum numbers are explored starting in Chap. 6. For now, these quantum numbers are just being used to label our states. Notice there is a center of gravity frequency, f_{cog}, that tells us the energy difference between the center of gravity for the two states. This tells us that our transitions are all around 541.4 THz, or 553.7 nm. Each hyperfine level is shifted from their center of gravity state by a small amount. I want to emphasize that if a nucleus has angular momentum, the center of gravity states do not exist in real life! The hyperfine states are the actual states. However, we can learn a lot of physics by determining how the hyperfine levels shift from the center of gravity, which is explored in Chaps. 9 and 10.

With that nice long intro, let's get into the actual example. We have four states: one ground state and three excited states. We are going to assume that our atoms are all at rest and send a laser beam through the sample, see Fig. 3.1. All of the atoms will start in the ground state $\left|g_{F=1/2}\right\rangle$. An electron can be excited to a higher energy level as long as the following rule, derived from quantum mechanics, is satisfied: A transition can change F by -1, 0, or 1. *Memorize this rule!* For completeness, there is one exception to this rule. If the ground state has $F = 0$, that electron cannot be excited to an $F = 0$ excited state.[9]

The Rule

$$\Delta F = -1,\ 0,\ +1 \qquad (3.15)$$

$$F = 0 \not\rightarrow F = 0$$

In this example, an electron in the barium ground state can be excited to any of the excited states. However, if there were an excited state with quantum number $F = 7/2$, an electron in the ground state could not be excited to this state because $\Delta F = 2$.

The natural linewidth of all three transitions is about $\gamma = 19\,\text{MHz}$ with a saturation intensity of $I_s = 14.6\,\text{mW/cm}^2$. Let's set our laser intensity to $I =$

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[9] We only need this rule for the moment. A full list of the rules that need to be satisfied for an electron to transition between two atomic states is given in Appendix C.

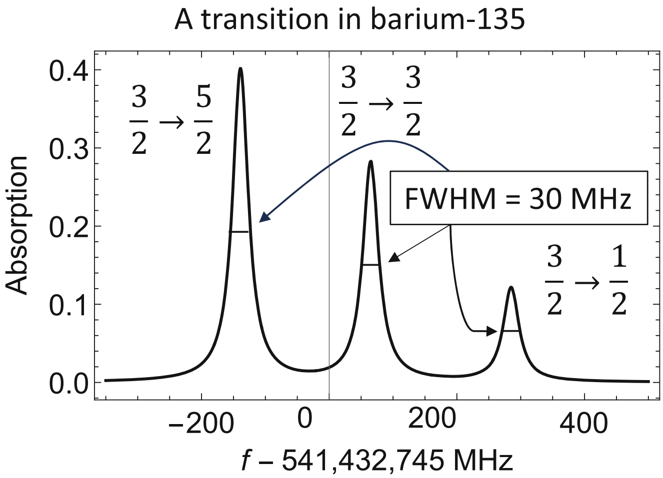

Fig. 3.11 A simulated absorption plot for a transition in barium-135. In this example, we are assuming that all the atoms are at rest and the experimental setup is shown in Fig. 3.1. The horizontal axis is the laser frequency with respect to the center of gravity frequency

21.9 mW/cm^2, corresponding to a saturation parameter of $s = 1.5$, and predict an absorption plot. In this example, we are interested in the frequency of each spectral feature, so we are, for now, going to ignore the amplitudes of the spectral features. We will discuss how to calculate the amplitudes in Chap. 9.5.

First, we calculate the resonance frequency for each transition:

$$\begin{aligned}
\left|g_{F=3/2}\right\rangle \to \left|e_{F=1/2}\right\rangle :\ f_r &= f_{\text{cog}} - 139\,\text{MHz} = 541{,}432{,}865\,\text{MHz} \\
\left|g_{F=3/2}\right\rangle \to \left|e_{F=3/2}\right\rangle :\ f_r &= f_{\text{cog}} + \ \ 65\,\text{MHz} = 541{,}433{,}069\,\text{MHz} \\
\left|g_{F=3/2}\right\rangle \to \left|e_{F=5/2}\right\rangle :\ f_r &= f_{\text{cog}} + 285\,\text{MHz} = 541{,}433{,}289\,\text{MHz}
\end{aligned}$$

These are the center frequencies of each spectral feature, and each feature has a Lorentzian lineshape with a width of $\gamma\sqrt{1+s} = (19\,\text{MHz})\sqrt{1+1.5} = 30\,\text{MHz}$. Figure 3.11 shows the simulated results. The horizontal axis represents the laser frequency relative to the center of gravity frequency, $f_{\text{cog}} = 541{,}432{,}745\,\text{MHz}$.

Problems

3.1 Go through the chapter and write down all the new fundamental constants. Don't forget units.

3.2 For each of the formulas in Eqs. 3.12 and 3.15, write a brief description of what each equation means.

3.3 In the lab, we measure laser power. However, we actually care about laser intensity. Why?

3.4 This problem explores the scattering rate, Eq. 3.11.

(a) What is the on-resonance ($\delta = 0$) scattering rate?
(b) At what laser detuning would the scattering rate be half of the on-resonance scattering rate?
(c) Show that in the low power limit (i.e., the limit where s is very small), the answer for part (b) is $\delta = \pm\gamma/2$.
(d) In the low power limit, what would δ be such that an atom absorbs 1/100 as many photons compared to the on-resonance case?

3.5 A transition in the Europium atom has a natural linewidth of $\gamma = 25.5\,\text{MHz}$. The wavelength of light at the resonance frequency is $\lambda = 466.188\,\text{nm}$. Calculate the saturation intensity in units of mW/cm^2 and mW/mm^2.
Hint: 1 W=1 J/s

3.6

(a) For the transition in Problem 3.5, calculate the on resonance scattering rate ($\delta = 0$) for a saturation parameter of 0.1, 1, 5, 10, and 100.
(b) Find the excited state fraction for each of the above saturation parameters.

3.7 Show that the maximum excited state fraction is 50%.

3.8 If a laser beam has a waist of $w = 1\,\text{mm}$, what power should we set the laser in order to get saturation parameters of 0.1, 1, 5, 10, and 100? Assume the saturation intensity is $I_s = 1.2\,\text{mW/mm}^2$.

3.9 (Graphing Problem) Plot the scattering rate versus detuning for a transition with $\gamma = 10\,\text{MHz}$ for different saturation parameters of 0.1, 1, 5, 10, and 100.

3.10 (Rubidium-80 Spectroscopy)

Rubidium-80 is an atom with 37 protons (all isotopes of rubidium have 37 protons) and 43 neutrons. It is an unstable atom that undergoes radioactive decay to krypton-80. Radioactive decay is discussed in Chap. 10. For this problem, we want to predict an absorption plot assuming all the atoms are at rest.

The transition we are interested in is shown in Fig. 3.12. There are two ground state hyperfine levels labeled $\left|g_{F=1/2}\right\rangle$ and $\left|g_{F=3/2}\right\rangle$. The excited state has three hyperfine levels labeled $\left|e_{F=1/2}\right\rangle$, $\left|e_{F=3/2}\right\rangle$, and $\left|e_{F=5/2}\right\rangle$. The natural linewidth of this transition is $\gamma = 5\,\text{MHz}$ and we set the laser intensity such that $s = 3$.

(a) Using the rule shown in Eq. 3.15, find the resonance frequency for all possible transitions (there are five of them).

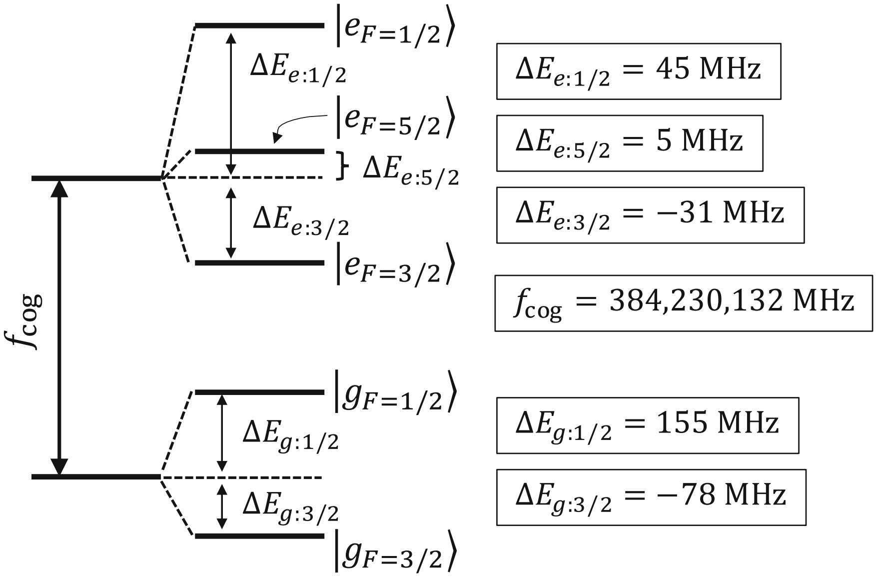

Fig. 3.12 A simplified Grotrian diagram for a transition in the atom known as rubidium-80. The energy spacings are not to scale. The energy spacings are taken from the work of Thibault et al. [3]

(b) What is the width of each spectral feature?
(c) Make an absorption plot with respect to the center of gravity frequency; see Fig. 3.11 for an example. Make all the amplitudes the same. There is a formula to calculate the relative amplitudes, but we won't talk about that until Chap. 9.

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Atoms in Motion

4

Abstract

In this chapter, we explore how motion can affect the perceived frequency of waves, with significant implications for spectroscopy. We cover the broadening and shifting of atomic line frequencies due to atomic movement and investigate the roles of velocity and temperature in these phenomena. Key topics include the Doppler effect, Doppler broadening, the Maxwell-Boltzmann velocity distribution, and the Equipartition Theorem. Additionally, the chapter discusses the application of the Doppler effect in astronomy.

Learning Goals

By the end of this chapter, you should be able to understand:

- the Doppler effect.
- Doppler broadening and how temperature affects the spectral features in absorption and transmission plots.
- the Maxwell-Boltzmann velocity distribution.
- how the temperature of a vapor cell is related to the average speed of an atom in that cell.
- the application of the Doppler effect in astronomy.

4.1 The Doppler Effect

The Doppler effect is likely a phenomenon you have encountered before. When an ambulance, police car, or racecar travels past you, the sound you hear changes pitch. This happens because the motion of the vehicle compresses or extends the

W. Raven, *Atomic Physics for Everyone*,
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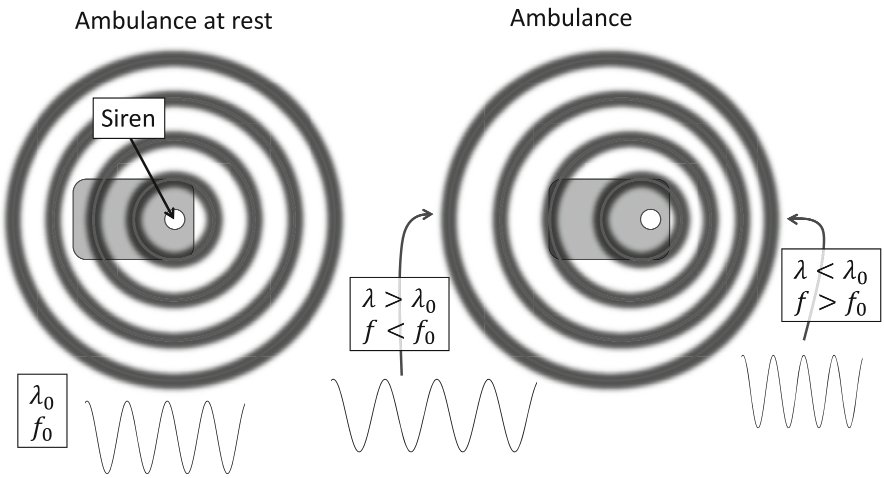


Fig. 4.1 Left: An ambulance at rest emitting a sound wave from its siren. The wavelength λ_0 and frequency f_0 of the sound wave is the same in all directions. Right: Now the ambulance is moving to the right. The sound wave in front of the ambulance is compressed, which means the perceived wavelength is smaller and the perceived frequency is larger (higher pitch). The sound wave behind the ambulance is expanded, which means the perceived wavelength is larger and the perceived frequency is smaller (lower pitch)

sound waves. Figure 4.1 shows the sound waves emitted by a stationary ambulance (left) and a moving ambulance (right). Let's focus on the stationary ambulance. Imagine that you are standing in front of or behind the ambulance. The wavelength of the sound wave that hits your ear is the same for both scenarios, so you would hear the same pitch independent of where you are standing. Now, imagine the ambulance is moving. If you were standing in front of the ambulance (OK, maybe a bit to the side …we don't want you to get hit, even in a thought experiment), the wavelength of the sound wave that reaches your ear is shorter compared to the stationary ambulance. If you were standing behind the moving ambulance, the wavelength is longer compared to the stationary ambulance. The formula that relates the frequency (pitch) that you hear to the wavelength should look really familiar. It is $v_s = f\lambda$, where v_s is the speed of sound in air (replace v_s with c and you have Eq. 1.1 from p. 19). The apparent shift in frequency due to an object moving is known as the Doppler effect, named after Austrian physicist and mathematician Christian Doppler. It is a very important concept in spectroscopy.

The Doppler effect occurs for any type of wave. Whether it is a sound wave, a light wave, or a water wave created by a duck swimming in a pond, the relative motion of the object with respect to the observer will change the wavelength, and thus the frequency of the wave. The EMT driving the ambulance hears no change in pitch because they are stationary with respect to the siren. If you yelled positive encouragement at the ambulance as it passed, the driver would hear your pitch change as they passed by you. Likewise, you don't hear your pitch change as the ambulance passes by you. What is important here is that the Doppler effect is something experienced by the observer because the source of the wave is moving with respect to them.

Definition

- **Doppler effect:** An increase or decrease in the frequency of sound, light, or other waves as the source and observer move toward or away from each other.

4.2 Laser Frequency From an Atom's Perspective

What does this have to do with spectroscopy? In Chap. 3, we made an important statement after analyzing Eq. 3.1 on p. 45. It is so important we will repeat it here:

▶ **Important Statement:** A photon has a probability of being absorbed by an atom depending upon the photon's energy. It is most likely to be absorbed if the photon's energy exactly matches the energy difference between the ground and excited state, but there is a non-zero probability of absorption off resonance.

Specifically, in the absence of any broadening mechanism (like laser power), if the photon's energy is off by $\frac{h\gamma}{2}$ from that resonance energy, the photon is half as likely to be absorbed compared to a photon that has the energy that equals the energy difference between the ground and excited states.

Important Reminder

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

Imagine a laser beam traveling to the right, as shown in Fig. 4.2. Also imagine there are three atoms: atom 2 is traveling to the left, atom 1 is stationary, and atom 3 is traveling to the right. For this thought experiment, we will assume the speeds of atom 2 and atom 3 are the same, just in opposite directions.

In this experiment, the atom is the observer because it is interacting with the laser light and not producing it. To understand the Doppler effect, it is important to recognize that each atom perceives itself as stationary. Atom 2 would claim that

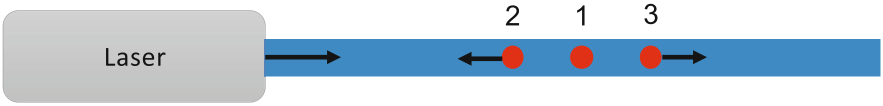
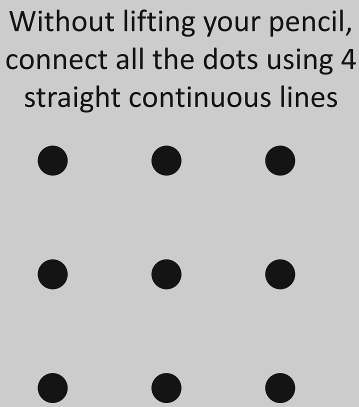


Fig. 4.2 A simple experimental to explore how motion of atoms impacts the interactions between the atoms and laser light

atom 1 is moving to the right and that 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. Because of the Doppler effect, atoms 2 and 3 will disagree. To make this idea a little clearer, let’s say that the laser frequency is 652.0000×10^{12} Hz = 652.0000 THz (terahertz) and that this is the resonance frequency for the atom. Both the scientists and atom 1 will agree that the laser frequency is 652.0000 THz; atom 1 will absorb photons from the laser beam. However, atom 2 and atom 3 will disagree with this claim since atom 2 is moving towards the laser and atom 3 is moving away from the laser.

Two Minute Question
Will atom 2 perceive the laser is higher in frequency or lower in frequency than what we and atom 1 perceive? Decide on an answer before reading on.


Without lifting your pencil,
connect all the dots using 4
straight continuous lines

Answer Atom 2 is moving towards the laser source, so it will perceive the laser frequency as higher than it actually is. Atom 2 will only absorb a photon from the laser if it thinks the laser frequency matches the resonance frequency. Therefore, we, in the observing frame, need to set the laser frequency *smaller* than the resonance frequency (652.0000 THz) so that the actual laser frequency plus the frequency shift due to the Doppler effect results in the resonance frequency in the frame of atom 2. In equation form, this is represented as:

$$f_{\text{atom2}} = f_L + \Delta f_D, \tag{4.1}$$

where f_{atom2} is the laser frequency according to atom 2, f_L is the actual laser frequency (i.e. the frequency measured in the laboratory/stationary frame), and Δf_D is perceived shift in frequency due to the Doppler effect. In this example, $\Delta f_D > 0$ for atom 2, so if we want $f_{\text{atom2}} = f_r$, then we need to set the laser frequency smaller than the resonance frequency such that $f_r = f_L + \Delta f_D$.

Likewise, 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 resonance frequency for atom 3 to absorb a photon.

Understanding the Doppler effect is really important in spectroscopy. Inside a gaseous sample of atoms some atoms are moving towards the laser, some are moving away, and some are not moving towards or away from the laser. As we, in the laboratory/stationary frame, change the frequency of the laser from below the resonance frequency to above the resonance frequency, we will find that atom 2 will absorb light at a different frequency than atom 1 or atom 3. Each atom will claim it is absorbing light at precisely the frequency needed to excite it from the ground state to the excited state, and each atom 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 traveling towards the laser beam, it will see a higher frequency than what we, as scientists in the laboratory/stationary frame, measure.

An Important Correction I simplified the above description by just a little bit. An atom moves in three dimensions, but only the component of the atom's velocity in the direction toward or away from the laser beam contributes 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.

We represent that velocity component with the parameter $v_{\parallel}$. It is defined to be positive if the atom is traveling away the laser and negative if traveling towards from the laser.

Definitions

- **Doppler shift:** The shift in the frequency of a laser seen by an atom due to the Doppler effect.
- $v_\parallel$: The velocity component of an atom in the direction of the laser beam. $v_\parallel$ is negative if the atom is traveling towards the laser and positive if it is traveling away from the laser.

The frequency of laser light as seen by the atom is given by the formula:

$$f_{\text{atom}} = f_L\left(1 - \frac{v_\parallel}{c}\right) \tag{4.2}$$

where f_{atom} is the frequency of the laser as seen by the atom, f_L is the frequency of the laser measured in the lab (rest) frame, and $v_\parallel$ is the velocity component in the direction of (parallel to) the laser beam. Using $c = f_L\lambda$, the right-hand side of Eq. 4.2 can be written as:

$$f_{\text{atom}} = f_L - \frac{v_\parallel}{\lambda}, \tag{4.3}$$

where λ is the wavelength of light measured in the laboratory frame.

Important
$v_\parallel$ is a weird variable in that the sign of $v_\parallel$ depends on whether the atom is moving towards ($v_\parallel < 0$) or away ($v_\parallel > 0$) from the laser. Messing up the sign of $v_\parallel$ is a very common mistake when using this formula. When in doubt, just remember that an atom moving towards the laser beam sees a higher frequency.

Comparing Eqs. 4.1 and 4.3, we find the formula for the Doppler shift:[1]

$$\Delta f_D = -\frac{v_\parallel}{\lambda}. \tag{4.4}$$

---

[1] The full formula is $\Delta f_D = -\frac{v}{\lambda}\cos\theta$, where v is the speed of the atom and θ is the angle between the laser and the velocity of the atom ($\theta = 0$ for an atom moving in the same direction as the laser and $180^\circ = \pi$ rad for an atom moving in the opposite direction). The component of the velocity in the direction of the laser is $v_\parallel = v\cos\theta$. If you have worked with vectors before, you might recognize these as vector components.

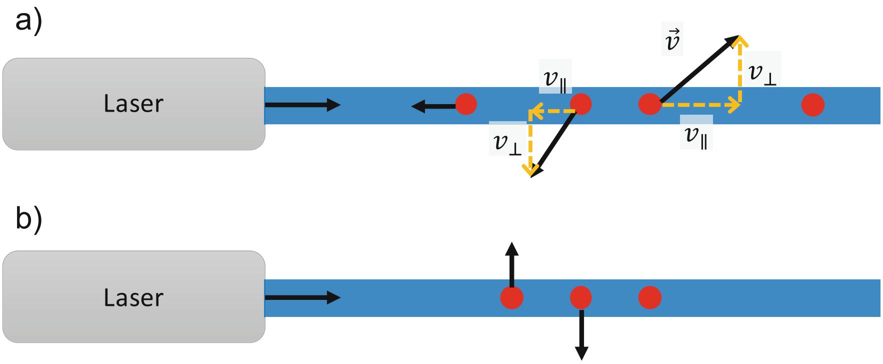


Fig. 4.3 (**a**) Only the component of velocity in the direction of the laser beams results in a Doppler shift. The first two atoms have different velocities, but the same component in the direction of the laser, $v_{\parallel}$. As such, they will experience the same Doppler shift. The third atom has a velocity component in the opposite direction, so it will have a different Doppler shift. The last atom is completely stationary. (**b**) All three of these atoms have no velocity component in the direction of the laser, so they all have zero Doppler shift

A Bit More About Velocity Components The velocity component in the direction of the laser beam is an important, but sometimes confusing, idea when you first encounter it. So, let's spend a bit more time thinking this idea through using Fig. 4.3. In Fig. 4.3a, the first atom's velocity is pointing directly towards the laser, so $v_{\parallel} < 0$. For this atom, there is no perpendicular component to the atom, $v_{\perp} = 0$. If the laser was traveling towards the left, $v_{\parallel} > 0$ for this atom because the sign of $v_{\parallel}$ only depends upon if the atom is moving towards or away from the laser beam.

The second atom has both a perpendicular component and a parallel component. Only the parallel component causes the Doppler shift, and the parallel component tells us the atom is moving towards the laser source, so $v_{\parallel} < 0$. Notice the parallel component for the two first two atoms are the same size and pointing in the same direction. Therefore, they will have the same Doppler shift.

The third atom has a perpendicular component, which we don't care about, and a parallel component pointing away from the laser, so $v_{\parallel} > 0$. 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: $v_{\parallel} = 0$ and $v_{\perp} = 0$. Figure 4.3b shows three examples of atoms with $v_{\parallel} = 0$. Each of these atoms will absorb photons when $f_L = f_r$.

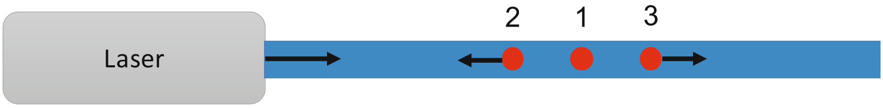
Important
In high precision spectroscopy, we want to extract information from atoms that have $v_{\parallel} = 0$. The rest of the atoms in our sample make our spectrum

(continued)

less precise. How the Doppler shift changes an absorption plot is going to be explored in the rest of this chapter. Chapter 5 introduces a clever experimental trick known as saturated absorption spectroscopy. This technique allows us to remove the issues brought about from the Doppler shifts that we are about to discuss.

4.3 How the Velocity of an Atom Affects the Spectral Feature

Let's go back to a simplified picture where we have 3 atoms.



Atom 1 is at rest, atom 2 is traveling towards the laser at speed v, and atom 3 is moving away from the laser at the same speed as atom 2. For this thought experiment, each atom that experiences a Doppler shift will have $|\Delta f_D| = 150\,\text{MHz}$.

What do the transmission and absorption plots look like? Spend a few moments thinking about it, make a prediction, and then read on! Hint: There are only 3 atoms, so the fraction of light lost is very, very small.

The answer is shown in Fig. 4.4. There are three spectral features. Each spectral feature is identical except for a horizontal offset determined by the Doppler shift formula. Since atom 2 is traveling towards the laser beam, it perceives a higher laser frequency compared to what we measure in the lab. Therefore, atom 2 will absorb photons when the laser frequency is below the resonance frequency. The spectral feature from atom 2 is at $\delta = -150\,\text{MHz}$. Likewise, atom 3 is traveling away from the laser, so it is seeing a lower laser frequency compared to what we measure in the lab. Therefore, atom 3 will absorb photons when the laser frequency is above

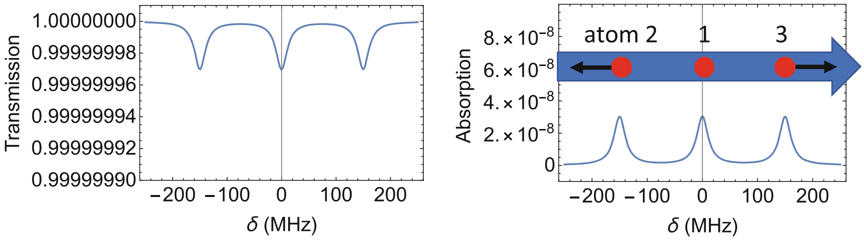


Fig. 4.4 A simulated transmission plot (left) and absorption plot (right) for the three atoms

Table 4.1 A table summarizing the Doppler shifts for the 3 atoms

	Atom 2	Atom 1	Atom 3
Motion	Towards laser	Stationary	Away from laser
The atom sees	Higher frequency light	Actual laser frequency	Lower frequency light
Resonance happens	At lower frequency	At actual frequency	At higher frequency

the resonance frequency. The spectral feature for atom 3 is at $\delta = +150\,\text{MHz}$. This important information is summarized in Table 4.1.

In a real vapor cell, atoms are moving with all sorts of different velocities. Unlike energy levels in an atom, velocity is a continuous variable. In the next two sections, we are going to discuss the distributions of velocities inside a real vapor cell (Sect. 4.4) and use that information to develop what the transmission and absorption plots look like for a vapor cell of atoms at a given temperature (Sect. 4.5).

4.4 The Maxwell-Boltzmann Velocity Distribution

Within a gaseous cloud of atoms, there is a distribution of velocities. This distribution depends on the temperature and mass of the atoms. The distribution of velocities in the direction of the laser beam, which is known as the Maxwell-Boltzmann velocity distribution,[2] is shown by the blue line in Fig. 4.5. The Maxwell-Boltzmann velocity distribution often uses the function $f(v)$ to represent the distribution of velocities. This is not the f we use for frequency. A good rule of thumb is that if it is a function, like $f(v)$, the "f" is probably referring to a distribution. If the "f" is all by itself in a formula, it is probably referring to a frequency.

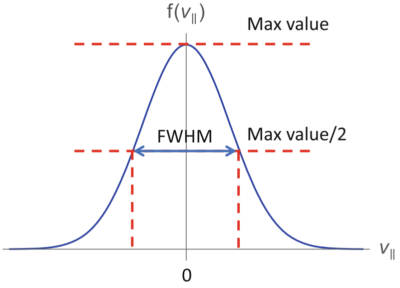


Fig. 4.5 A cloud of gaseous atoms will have a distribution of velocities given by this graph. This distribution, which is derived from thermodynamics, is known as the Maxwell-Boltzmann velocity distribution

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[2] Named after the Scottish mathematician James Clerk Maxwell and the Austrian physicist Ludwig Boltzmann.

The full width at half maximum of a Maxwell-Boltzmann velocity distribution, which is a velocity with units m/s, is:

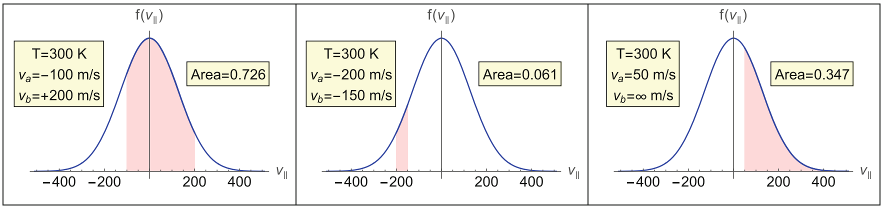
$$\Delta v_{\mathrm{FWHM}} = 2.355\sqrt{\frac{k_B T}{m}}, \tag{4.5}$$

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, 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, and thus the larger the average speed of the atoms in the gas. The mass of an atom is in the denominator, so atoms with larger masses have smaller average speeds compared to an equally hot gas of smaller mass atoms.

How to Use Distributions This section isn't really needed to understand the velocity distribution. However, distributions are incredibly important in many areas of science, so I wanted to spend a bit of time talking about how we use them. The velocity distribution represents the fraction of atoms that fall within a particular velocity range. Since an atom must have some velocity, the total area under the curve in Fig. 4.5 is 1. This is equivalent to saying that each atom must have some velocity between $+\infty$ and $-\infty$.

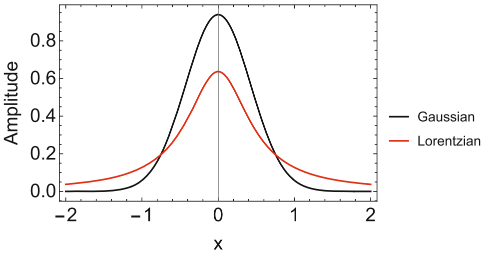
To use a distribution, you ask questions like, "What fraction of atoms have a positive parallel velocity component?", "What fraction of atoms have a parallel velocity component between -2 and 10 m/s?", or more generally, "What fraction of atoms have a parallel velocity component between v_a and v_b?", where v_a and v_b are any velocities we choose.

The answer is the area under the distribution between v_a and v_b. If we want to know the total number of atoms from the sample that have velocity components between those two values, we multiply that fraction by the total number of atoms in the sample. For example, here are three plots with different choices of v_a and v_b:



Suppose we have 5000 atoms in our sample. As shown in the first plot, there are $5000 \times 0.726 = 3630$ atoms with parallel velocity components between $v_a = -100$ m/s and $v_b = +200$ m/s. As shown in the second plot, there are $5000 \times 0.061 = 305$ atoms with parallel velocity components between $v_a = -200$ m/s and $v_b = -150$ m/s, and in the third plot there are $5000 \times 0.347 = 1735$ atoms with parallel velocity components larger than 50 m/s.

Fig. 4.6 A comparison between a Gaussian function and a Lorentzian function. Each function has an area under the curve of 1 and a FWHM of 1



Important Reminder
Due to the Doppler effect, atoms with different velocities will absorb photons at different laser frequencies.

The mathematical function that describes the shape of the Maxwell-Boltzmann velocity distribution is a Gaussian function given by:[3]

$$f_{v_\parallel} = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m v_\parallel^2}{2k_B T}} \tag{4.6}$$

A Gaussian looks similar to the Lorentzian function that models the shape of a spectral feature, but the two functions are different. Figure 4.6 shows a plot of both a Gaussian function and a Lorentzian function with the same area and FWHM. Notice the Lorentzian has larger "tails" and is more spread out compared to the Gaussian function. Both functions are very common in physics and math.

Extra Math for Those Who Have Taken Statistics In statistics, Gaussian functions are written as $e^{-\frac{v^2}{2\sigma^2}}$, where σ is called the standard deviation. For the Maxwell-Boltzmann velocity distribution, the standard deviation is $\sqrt{\frac{k_B T}{m}}$. The FWHM of a Gaussian function defined using the standard deviation is:

$$\Delta v_{\mathrm{FWHM}} = 2\sqrt{2\ln(2)}\sigma \approx 2.355\sigma = 2.355\sqrt{\frac{k_B T}{m}} \tag{4.7}$$

---

[3] This is a distribution for 1 dimension since we are only interested in the velocity component for a single direction. In the future, you might encounter a Maxwell-Boltzmann velocity distribution that has a power of 3/2 instead of 1/2 on the expression in front of the Gaussian function. That would be a velocity distribution for all components of velocity, not just the parallel component.

4.5 Transmission and Absorption Plots for Atoms at a Non-Zero Temperature

Definitions

- **Doppler broadening:** The widening of a spectral feature due to a vapor cell having a given temperature.
- **Doppler profile:** The name given to a spectral feature that is broadened because of temperature.
- **Doppler width:** The FWHM of a Doppler profile.

In Sects. 4.2 and 4.3, we explored a transmission plot with only three atoms with different velocities. What if we had one hundred thousand atoms? Figure 4.7 shows

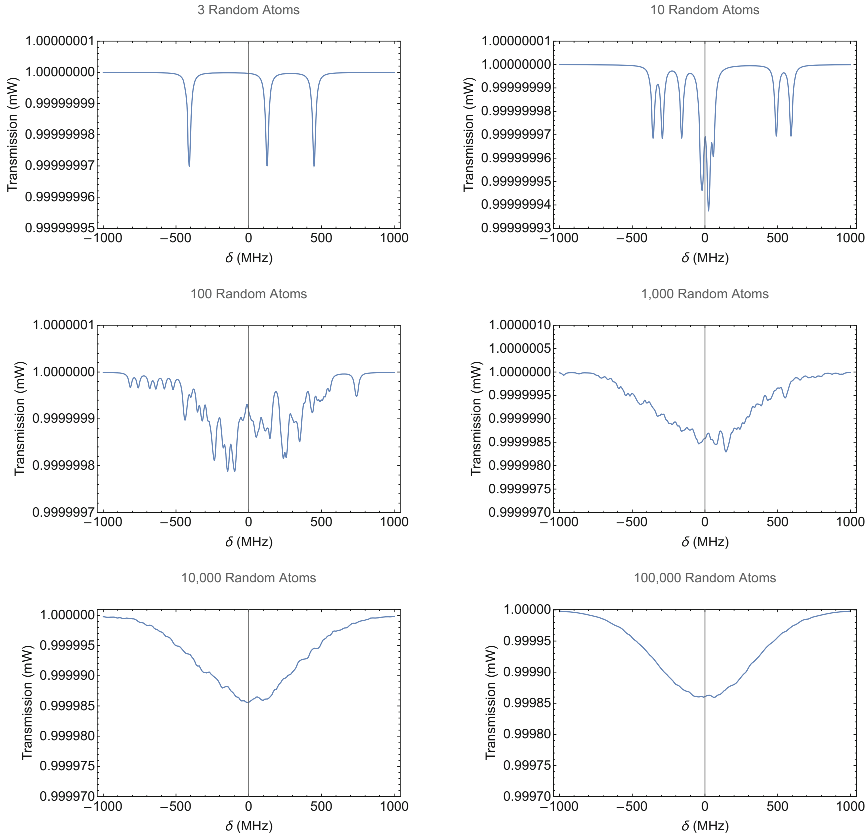


Fig. 4.7 Building a Doppler profile from individual atoms

the results for a simulation of transmission plots as we add more and more atoms to a vapor cell. For this simulation, I assumed that we had a two-level atom with a mass of $m = 2.33 \times 10^{-26}\,\mathrm{kg}$ (this is the mass of a nitrogen atom), a vapor cell temperature of $T = 400\,\mathrm{K}$, an excitation wavelength of $\lambda = 940\,\mathrm{nm}$ ($f \approx 319\,\mathrm{THz}$), and a natural linewidth of $\gamma = 5\,\mathrm{MHz}$. I randomly picked a velocity component using the Maxwell-Boltzmann velocity distribution for each atom I add to the cell.

Note that each transmission plot has a different vertical scale. Individually, a single atom isn't going to absorb a large fraction of a laser's photons. However, the more atoms you have interacting with the light, the more spectral features you have piling up on each other. Ultimately, you get a transmission plot that looks like it has a single feature.

This feature, which is called a **Doppler profile**, is much wider than a spectral feature from a single atom and is pretty close to the same shape as $1 - Af(v_{\|})$, where A is some constant and $f(v_{\|})$ is the Maxwell-Boltzmann velocity distribution. Notice the center of the Doppler profile is still at the resonance frequency $\delta = 0$.

The width of a Doppler profile can be found from FWHM of the Maxwell-Boltzmann velocity distribution, which is a velocity. We can convert this velocity to a frequency using the Doppler shift formula. The FWHM of a spectral feature broadened by temperature, which is called the Doppler width, is given by the formula:

$$\Delta f_{\mathrm{FWHM}} = \frac{2.355}{\lambda}\sqrt{\frac{k_B T}{m}} \tag{4.8}$$

where Δf_{FWHM} is the Doppler width, which has frequency units.

4.6 The Equipartition Theorem

There is a neat theorem from thermodynamics known as the Equipartition Theorem. Before discussing the Equipartition Theorem, we need to understand **kinetic energy**. Kinetic energy is the energy of movement. Any object with mass m and speed v has kinetic energy:

$$K = \frac{1}{2}mv^2. \tag{4.9}$$

Since kinetic energy is a type of energy, the unit is a joule. 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 the gas would be:

$$\frac{1}{3}\left(\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \frac{1}{2}mv_3^2\right). \tag{4.10}$$

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

$$\frac{1}{N}\left(\frac{1}{2}mv_1^2+\frac{1}{2}mv_2^2+...+\frac{1}{2}mv_N^2\right)=\frac{1}{2}m\left(\frac{v_1^2+v_2^2+...+v_N^2}{N}\right). \tag{4.11}$$

That last term that is in parentheses is called the average squared speed. We denote this last term as $\langle v^2\rangle$. In fact, whenever you see the mathematical expression between two angle brackets, $\langle\ \rangle$, 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 v_{rms}, which you may have learned about in high school Chemistry. Putting this all together, we find that the average kinetic energy of all the atoms in the gas is:

$$\langle K\rangle=\frac{1}{2}m\langle v^2\rangle. \tag{4.12}$$

Reading the Above Equation For a gas composed of atoms with the same mass, the average kinetic energy of the atoms is proportional to the average squared speed.

The Equipartition Theorem tells us that the energy of a gas is equally distributed among all "degrees of freedom." Degrees of freedom indicate the number of ways an atom or molecule can move. Atoms have three degrees of freedom because they can move in three dimensions. Molecules have more degrees of freedom because they can rotate and vibrate, so a molecule has more ways to distribute its energy than an atom. The Equipartition Theorem tells us that each degree of freedom has $\frac{1}{2}k_BT$ of energy. In this book, we are only working with atoms, but, in the future, if you work with molecules, the following formulas will be slightly different.

Imagine you have a vapor cell of atoms at some temperature T. The average kinetic energy of the atoms in the gas is:[4]

$$\frac{1}{2}m\langle v^2\rangle=\frac{3}{2}k_BT. \tag{4.13}$$

The 3 on the right hand side represents the three degrees of freedom of an atom $\left(\frac{1}{2}k_BT\text{ for each degree of freedom}\right)$. This formula is very useful because it directly relates the temperature of a sample of atoms to a characteristic speed of the atoms, specifically $\langle v^2\rangle$.

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[4] You can derive this formula from the Maxwell-Boltzmann velocity distribution, but you will need to use calculus.

4.7 Application to Astronomy: Light from the Stars

In our experiment, both we, the scientists, and the laser light source are stationary while the atoms, which act like the observers of the laser light, are moving. The same principles of the Doppler effect apply whether the light source is moving and the observer is stationary, the light source is stationary and the observer is moving, or if both are moving. All that matters is whether the source and observer are moving towards each other or away from each other.

The Doppler effect is a powerful tool in astronomy. Suppose we are using a telescope to collect light from a distant star that is mostly composed of hydrogen gas. That star is emitting light with frequencies corresponding to the difference of the hydrogen energy levels. We now know that if the star is moving towards us, the frequency of light leaving that star will look to us to have a higher frequency than what we would observe if we just had a hydrogen light bulb in our lab. In astronomy, this phenomenon is called blue-shifted light because the light has a higher frequency than we would expect if we measured the spectrum of hydrogen here on earth. If the star is moving away from us, which is far more common in astronomy, the frequency of light that is emitted from the star looks to be lower frequency compared to what we would measure from a source here on earth. This is called red-shifted light.

In summary, if the star is moving towards us, we will see a spectrum that is shifted to higher frequencies compared to what we measure in the lab (blue-shifted; $v < 0$), and we will see a shift to lower frequencies if the star was moving away from us (red-shifted; $v > 0$).

The Doppler effect allows us to calculate the speed of that galaxy. The Doppler formula for a star moving towards (or away) from the earth has a slightly different form than Eq. 4.3:

$$\begin{aligned} f_{\text{obs}} &= \tfrac{f_{\text{em}}}{1+z} \\ z &= \tfrac{v}{c}, \end{aligned} \tag{4.14}$$

where f_{obs} is the Doppler shifted frequency measured on earth, f_{em} is the frequency of the light emitted from the star, and v is the speed of the star or galaxy in the direction of earth. Astronomers also use the parameter $z = \frac{v}{c}$ to describe blue-shift light ($z < 0 \rightarrow v < 0$; the star is moving towards the earth) and red-shifted light ($z > 0 \rightarrow v > 0$; the star is moving away the earth). You will have the opportunity to derive this formula in Problem 4.7.

Finally, astronomers like to use wavelength instead of frequency. Writing Eq. 4.14 using wavelength and solving for z gives:

$$\begin{gathered} z = \tfrac{\lambda_{\text{obs}}}{\lambda_{\text{em}}} - 1, \\ \text{the formula astronomers use} \end{gathered} \tag{4.15}$$

Problems

4.1 For each of the following equations, write a brief description of what each equation means.

(a) Equation 4.3
(b) Equation 4.8
(c) Equation 4.13

4.2 Assess Eq. 4.8. The purpose of any assessment is to increase or decrease our confidence in something. Assessments are challenging because we inherently want our calculations to be correct! To combat this bias for assessing a formula, I find it is easiest to write down all the parameters on the right hand side and then try to forget the formula all together. Then you ask yourself the question, "If I increased T, then the Doppler width should get ______ because ______." You need to decide if "larger" or "smaller" goes into the first blank and explain, using a physics reason, why that should happen in the second blank. Next, repeat that process for every parameter. After I think through each parameter, I go check the formula to make sure my statements match the formula.

If your statement does not match your formula, then either your formula is wrong or your reasoning is wrong. Either way, you now have an opportunity to learn something! But, more importantly, you will understand an equation more after you assess it.

4.3 An atom at rest is excited from the ground state to an excited state by a photon from a laser with frequency $f = 315.11254\,\text{THz}$.

(a) Suppose the laser is positioned to send photons to the right, and an atom is moving towards the laser with a velocity component of $v_{\parallel} = -200\,\text{m/s}$ (the minus sign indicates the atom is moving towards from the laser), see atom 2 from Fig. 4.2 on p. 68. What frequency should the laser be for this atom to absorb a photon?
(b) Now the laser is pointed to send photons to the left, so now the atom is moving away from the laser source. What frequency should the laser be for this atom to absorb a photon?

4.4 Explain qualitatively how the motion of an atom affects the energy (frequency) of a photon it will absorb compared to an atom at rest. Specifically, describe the difference in photon energy required for an atom moving towards the light source versus an atom moving away from the light source.

4.5 A vapor cell has strontium-84 atoms. A strontium-84 atom has 38 protons and 46 neutrons (notice $38 + 46 = 84$). The mass of a strontium-84 atom is $1.393 \times 10^{-25}\,\text{kg}$.

(a) If the temperature of the vapor cell is 350 K, what is the full width at half maximum of the Maxwell-Boltzmann velocity distribution?

(b) There is a transition from the ground state to an excited state at 650.5032 THz. There are no other energy levels nearby, so you can treat this transition as a two-level atom. What is the Doppler width for this spectral feature? Give your answer in MHz.

(c) Sketch the transmission plot of a laser beam as it passes through a vapor cell held at 350 K. You can pick any amplitude you want for the Doppler feature. Hint: You should be using your answer from part b) in this sketch.

4.6 Starting with Eq. 4.14, derive Eq. 4.15.

4.7 (The Full Doppler Shift Formula: Moving Observers and Sources) In non-relativistic physics, the formula for the Doppler shift for a light wave is:

$$f_{\text{obs}} = \left(\frac{c \pm v_{\text{obs}}}{c \mp v_{\text{em}}} \right) f_{\text{em}}, \tag{4.16}$$

where f_{obs} is the frequency measured by the observer and f_{em} is the frequency emitted by the source. v_{obs} is the speed of the observer relative to some background and is always a positive number (it is a speed). It is added to c in the numerator if the observer is moving towards the source and subtracted if the observer is moving away from the source. v_{em} is the speed of the source with respect to that same background and is also always a positive number (it is a speed). It is added to c in the denominator if the source is moving away from the observer and subtracted if the source is moving towards the observer.

(a) Come up with 4 different scenarios for the 4 different sign combinations. For example, what is a scenario where the observer is moving away from the source and the source is moving towards the observer? In this scenario, you would use the formula:

$$f_{\text{obs}} = \left(\frac{c - v_{\text{obs}}}{c - v_{\text{em}}} \right) f_{\text{em}}, \tag{4.17}$$

(b) Check to make sure this formula agrees with Eq. 4.2.

(c) Check to make sure this formula agrees with Eq. 4.14.

4.8 Figure 4.8 is a picture of the spectrum from a distant galaxy that you can download from the Sky Server database.[5] The Sky Server ID for this galaxy is

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[5] Image and data is from the Sloan Digital Sky Survey. Funding for the Sloan Digital Sky Survey (SDSS) has been provided by the Alfred P. Sloan Foundation, the Participating Institutions, the National Aeronautics and Space Administration, the National Science Foundation, the U.S.

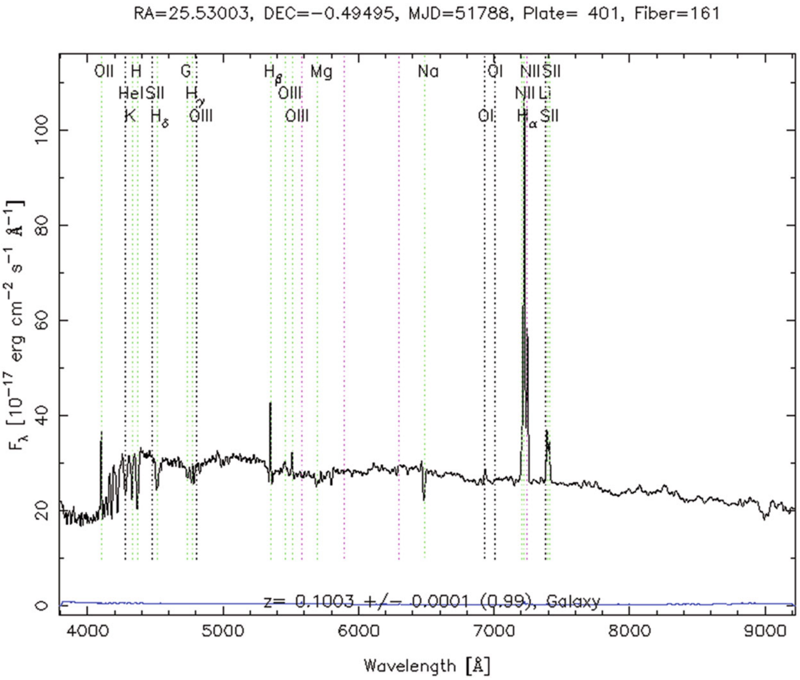

Fig. 4.8 Light collected on earth from galaxy 582102012537667624

Table 4.2 Rest wavelengths of Hydrogen–Balmer series

Name	Wavelength (angstroms)
H_α (H-alpha)	6562.8
H_β (H-beta)	4861.3
H_γ (H-gamma)	4340.5
H_δ (H-delta)	4101.7

582102012537667624. The galaxy is emitting a number of photons from different elements including hydrogen, oxygen, and magnesium. We are going to focus on the hydrogen lines. On earth, we measure those hydrogen lines to have wavelengths that are given in Table 4.2.

Department of Energy, the Japanese Monbukagakusho, and the Max Planck Society. The SDSS Web site is http://www.sdss.org/.

The SDSS is managed by the Astrophysical Research Consortium (ARC) for the Participating Institutions. The Participating Institutions are The University of Chicago, Fermilab, the Institute for Advanced Study, the Japan Participation Group, The Johns Hopkins University, Los Alamos National Laboratory, the Max-Planck-Institute for Astronomy (MPIA), the Max-Planck-Institute for Astrophysics (MPA), New Mexico State University, University of Pittsburgh, Princeton University, the United States Naval Observatory, and the University of Washington.

Use the data graphed in Fig. 4.8 to estimate the wavelengths of those lines that astronomers measured here on earth and find the speed of galaxy 582102012537667624 relative to the earth.

Saturated Absorption Spectroscopy

5

Abstract

In this chapter, we explore the clever spectroscopy technique known as saturated absorption spectroscopy. This technique is used to remove Doppler profiles from spectroscopic signals. We will learn how saturated absorption spectroscopy works, including the roles of probe and pump beams, and the resulting spectral features. Additionally, we will examine the artifacts, specifically crossover features (V, Λ, and X crossovers), that may appear due to this technique and understand the conditions under which they occur. Practical examples using various atoms, advanced techniques for achieving crossover-free spectroscopy, and potential issues are also discussed.

Learning Goals

By the end of this chapter, you should be able to understand:

- saturated absorption spectroscopy: How we use two counterpropagating lasers to produce a spectrum that looks like the atoms are at 0 Kelvin.
- crossover features: Artifacts of saturated absorption spectroscopy.
- the conditions under which different types of crossover features (V, Λ, X) appear and how to identify them in a spectrum.

5.1 Saturated Absorption Spectroscopy

Saturated absorption spectroscopy is a really neat spectroscopy trick used on a vapor cell with hot atoms that creates a transmission plot with only spectral features from the atoms that are moving perpendicular to the laser ($v_{\parallel} = 0$). Reread that

W. Raven, *Atomic Physics for Everyone*,
https://doi.org/10.1007/978-3-031-69507-0_5

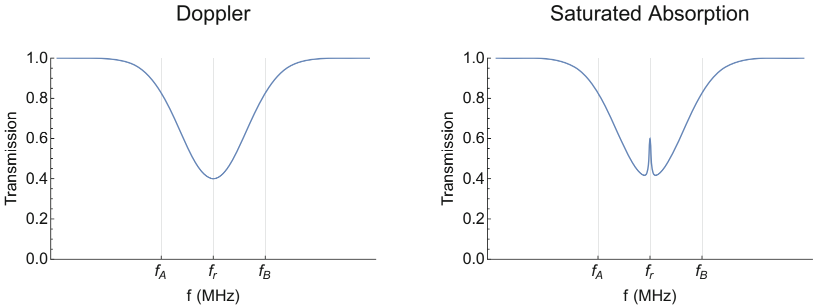

Fig. 5.1 An illustrative example showing the transmission plots for a two-level atom. On the left is the Doppler profile we learned about in Chap. 4. On the right is the transmission plot for a saturated absorption setup

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 broadened spectrum from these atoms that is Gaussian in shape. Saturated absorption spectroscopy uses two laser beams, resulting in a small Lorentzian feature on top of the Gaussian shape, as shown in Fig. 5.1. The small Lorentzian feature comes only from those atoms that have zero speed in the direction of the laser.[1]

This is how we do it: we send two laser beams into a vapor cell from opposite directions, see Fig. 5.2. The laser beam that starts on the left and moves to the right has a small amount of power. We call this laser the **probe beam**. In saturated absorption spectroscopy, we measure the transmission of the probe beam. The other laser starts on the right and is moving to the left and has a large amount of power. We will call this laser the **pump beam**. In most experimental setups, the probe beam and the pump beam originate from the same laser. The laser can be split into two paths using, for example, a λ/2 plate and a polarizing beam splitter, see Sect. 1.5. One would adjust the orientation of the λ/2 plate so that the probe beam has less power than the pump beam.

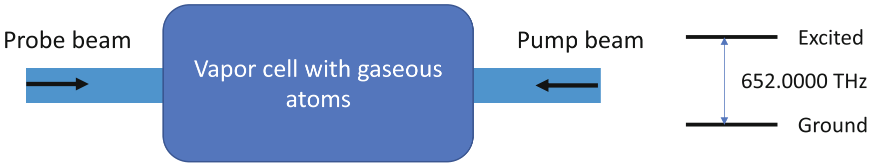

Fig. 5.2 Saturated absorption spectroscopy needs two laser beams: a probe beam and a pump beam. Not pictured is the photodiode with which we monitor the transmission of the probe beam

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[1] Remember that an atom can be moving perpendicular to the laser beam, and it will experience no Doppler effect. Only the velocity component parallel (towards or away) with the laser will contribute to a Doppler shift.

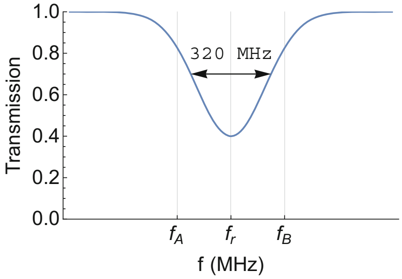

Fig. 5.3 An example of a Doppler profile simulated using parameters for a transition in europium-156 atoms with a temperature of 400 Kelvin

To explore how this technique works, we will use our simple two-level atom. If the pump beam were not present, we know the transmission of the probe beam looks like Fig. 5.3. This plot is calculated using the mass of a europium-156 atom and a vapor cell at 400 Kelvin. The natural linewidth of the transition is about 25 MHz, which is much smaller than the Doppler width of 320 MHz.

Now, let's add in the pump beam. Our ultimate goal is to determine how the transmission plot of the probe beam changes with the addition of the pump beam. Let's start by thinking about the transmission of a laser through the vapor cell when the laser frequency is at f_A, see Fig. 5.1. Since both the pump and the probe beam come from the same laser, they have the same frequency. The only difference is that they are moving in opposite directions. We want to ask the question: Which atoms interact with each laser beam?

As a reminder, the Doppler shift for an atom moving with velocity component $v_{\|}$ is given by the formula:

$$\Delta f_D = -\frac{v_{\|}}{\lambda} = -\frac{v_{\|}}{c} f_L \rightarrow |v_{\|}| = \Delta f_D \frac{c}{f_L} \tag{5.1}$$

where $v_{\|}$ is negative if the atom is moving towards the laser source and positive if it is moving away.

I find it useful to use numbers, so let's say that the frequency of the laser is set to f_A, and f_A is 200 MHz below $f_r = 652.0000$ THz. Since we have two laser beams moving in different directions, we are going to use the magnitude of $v_{\|}$ and the descriptors "to the left" and "to the right" for the following discussion.

Let's start with the probe beam, which is moving to the right. Since the frequency of the laser is below resonance, we know that atoms which interact with the probe beam have to be moving to the left with a specific $v_{\|}$ so that, according to those atoms, the Doppler effect shifts the laser frequency into resonance. That means the atoms would have to be moving at:

$$v_{\|} = (200 \times 10^6\,\text{Hz}) \frac{3 \times 10^8\,\text{m/s}}{652 \times 10^{12}\,\text{Hz}} = 92\,\frac{\text{m}}{\text{s}} \text{ to the left} \tag{5.2}$$

to absorb light from the probe beam.

Now let's think about the pump beam, which 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 the direction of movement is opposite:

$$v_{\parallel} = (200 \times 10^6\,\text{Hz}) \frac{3 \times 10^8\,\text{m/s}}{652 \times 10^{12}\,\text{Hz}} = 92\,\frac{\text{m}}{\text{s}} \text{ to the right.} \tag{5.3}$$

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, ***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, the probe beam transmission is the same whether the pump beam is on or off. Again, this is a very important concept so make sure it makes sense before moving on.

Your turn! The laser frequency is now at frequency f_B, which we will assume is 200 MHz higher than $f_r = 652.0000$ THz. What velocity does an atom need to have to absorb light from the probe beam? From the pump beam? The answers are in the footnotes.[2]

The conclusion for when $f_L = f_B$ is the same as when $f_L = f_A$: 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 the ***same*** atoms. When the laser frequency is at f_A or f_B (or any frequency except f_r), the pump and the probe lasers interact with ***different*** atoms. When the laser frequency is at f_r, the two laser beams 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 so that there is only a probe beam. The probe beam frequency is set to the resonance frequency, and we'll assume it hits a single atom at rest. Let's say the probe beam has 10 photons that pass by the atom for every lifetime of the excited state. From those 10 photons, the atom absorbs 1 photon reducing the probe beam transmission to 9 photons; this is a 10% reduction in probe beam transmission. Now we turn the pump beam back on. The pump beam has more power than the probe beam. Let's say the pump beam provides an additional 990 photons. The atom will 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. Since all 10 photons make it through, the transmission of the probe beam is larger when the pump beam is on. Every once in a while, the atom will randomly absorb from the probe beam, decreasing its transmission percentage. However, the transmission of the probe beam is, on average, larger when the pump beam is present. If we increase the number of atoms in the vapor cell, each atom with $v_{\parallel} = 0$ will randomly absorb from either the pump beam or the probe beam.

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[2] Probe: 92 m/s (to the right); Pump: 92 m/s (to the left); notice the directions are switched from when the laser frequency was f_A.

The conclusion is: *When the laser frequency matches the resonance frequency, the transmission of the probe beam is larger when the pump beam is present.*

What is really important is that this only happens for the atoms that have $v_{\parallel} = 0$. For any other velocity, the probe beam transmission is exactly the same whether the pump beam is on or off. Let's recap all of this in a table. To make things easier, we are going to define "moving to the left" (towards the probe beam) as negative and "moving to the right" as positive.

f_L	Velocity of atoms needed to absorb from probe beam.	Velocity of atoms needed to absorb from pump beam.	How does the pump beam change the transmission of the probe?
f_A	−92 m/s	+92 m/s	It doesn't
f_r	0 m/s	0 m/s	Transmission increases
f_B	+92 m/s	−92 m/s	It doesn't

Summary

If the laser frequency is not on resonance, the probe beam and pump beam are interacting with different atoms. In other words, the probe beam is losing photons to different atoms than the pump beam. On resonance, the two lasers compete for the same atoms, which results in less photons being absorbed from the probe beam.

A simulation of the transmission of the probe beam with the pump beam off (left plot) and with the pump beam on (middle) is shown in Fig. 5.4. If we subtract the two plots (right), we are left with a spectral feature with a full width half maximum equal to the natural linewidth of the transition.[3] This is the same plot as the absorption plot from the thought experiment that we did in Sect. 3.1, which was an absorption plot

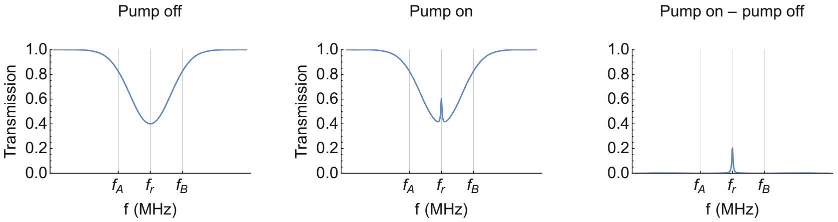

Fig. 5.4 The transmission plots of the probe beam for a 2 level atom with just a probe beam (left), the probe beam and a pump beam (middle), and the difference between the two transmission plots (right)

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[3] Assuming that the width is not broadened from some other effect like power broadening.

for atoms at 0 Kelvin. We call this plot a **saturated absorption plot**. Neat trick, huh!

5.2 Crossovers

Saturated absorption spectroscopy is super cool.[4] It allows us to use hot gas and still produce spectral features as if all of the atoms were frozen in place (absolute zero or 0 K). However, there is a trade off if there are multiple ground or excited states, and that trade-off is additional fake spectral features in our spectrum called crossovers. There are three types of crossovers: V crossovers, Λ crossovers (the Greek letter capital lambda, so we call them "Lambda crossovers"), and X crossovers. The reason for the names should be clear as you examine the energy level diagrams for each in Fig. 5.5. I want to point out that the labels, $F = 4$, $F = 5$, etc. have meaning that we explore in Chaps. 7 and 8. Even though we haven't connected those labels to physics yet, I wanted to remind you about "The Rule" from Eq. 3.15:

$$\begin{gathered}\text{The Rule}\\ \Delta F = -1,\ 0,\ +1 \\ F = 0 \not\rightarrow F = 0\end{gathered} \tag{5.4}$$

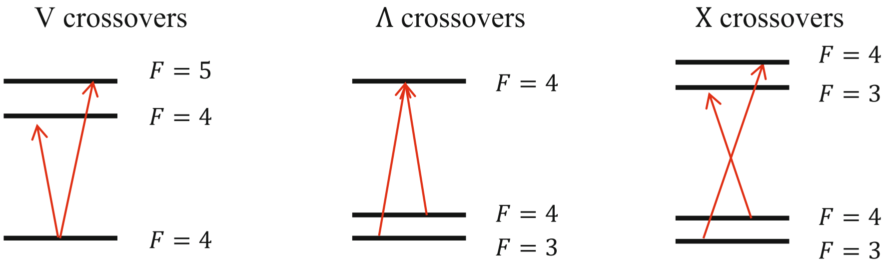

Fig. 5.5 The three types of crossovers. A V crossover is due to the probe beam and pump beam exciting atoms from the same ground state to two different excited states. For a V crossover, the pump beam "steals" atoms from the probe beam. A Λ crossover is due to the probe beam and pump beam exciting atoms from the two different ground states to the same excited state. A X crossover is due to the probe beam and pump beam exciting atoms from two different ground states to two different excited states. For both Λ and X crossovers, the pump beam "gives" atoms to the probe beam

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[4] Yay puns!

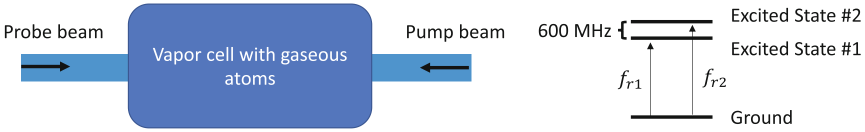


Fig. 5.6 The experimental setup and energy levels to think about V crossovers

5.2.1 *V* Crossovers

Suppose you have an atom with one ground state that can be excited to two different excited states, as shown in Fig. 5.6. The two excited states have resonance frequencies f_{r1} and f_{r2}. Using the arguments explored in Sect. 5.1, you might expect transmission plots shown in Fig. 5.7. 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}.

That prediction is close, but not quite correct. If you do the experiment, you will find that you have an additional Lorentzian shaped spectral feature exactly halfway between f_{r1} and f_{r2}. This extra feature is called a *V* crossover. Let's explore why this happens with an example. 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}. We are also going to define an atom moving right as positive velocity and an atom moving left as negative velocity.

Your turn: Having the laser frequency precisely between f_{r1} and f_{r2}, calculate the velocity that an atom would need in order to absorb from the pump beam to excited state #1, from the probe beam to excited state #1, from the pump beam to excited state #2, and from the probe beam to excited state #2. Use $\lambda = 500$ nm for the math. Make sure you have an answer before moving on. Here is a crossword puzzle to separate the question and answer.

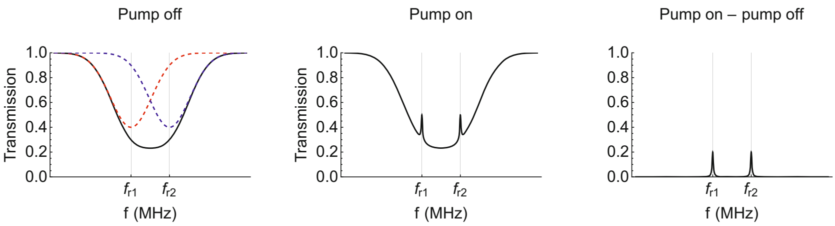
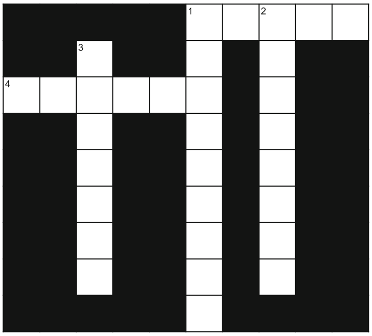


Fig. 5.7 A very reasonable, but incorrect guess for a saturated absorption spectrum for an atom with one ground state and two excited states



Across:

1 An experimental device that provides photons

4 A particle of light

Down:

1 Inversely proportional to the lifetime of a state

2 ____ feature

3 $\frac{v_{\parallel}}{c} f_L$ is the formula for the ____ shift

	Velocity of atoms needed to absorb from probe beam.	Velocity of atoms needed to absorb from pump beam.
Excited state #1	+150 m/s	−150 m/s
Excited state #2	−150 m/s	+150 m/s

First, notice that the pump and probe beams are exciting different atoms to excited state #1. The two beams are also exciting different atoms to excited state #2. Specifically, for an atom to be excited by the probe to excited state #1 it would have to be moving away from the probe beam at +150 m/s. An atom would have to be moving away from the pump beam at −150 m/s to be excited by the pump beam to excited state #1. The pump beam and probe beam are interacting with different atoms; nothing new here.

Now notice that the pump beam is trying to excite atoms moving at +150 m/s to excited state #2 while the probe beam is trying to excite those same atoms to excited state #1. Those atoms that are moving at +150 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. The atom 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. Similarly, the atoms moving at −150 m/s also get to pick between the pump and the probe beam. Therefore, there will be an additional spectra feature that comes from two velocities of atoms (+150 m/s and −150 m/s) when the frequency of the laser is precisely between f_{r1} and f_{r2}. With this new information, the transmission plot of the probe beam has three spectral features: two that correspond to the actual frequencies of the transitions and a third exactly halfway between that we call a crossover peak, see Fig. 5.8.

The two real transitions come from atoms that have no velocity components in the direction of the laser beams. The crossover peak comes from atoms that are moving. I think now is a good time to remind everyone that the amplitudes of the peaks in the above graphs are completely made up. Because there are two sets of

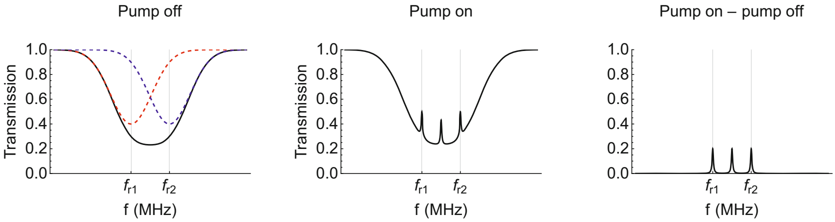


Fig. 5.8 A more accurate simulation of a saturated absorption spectrum with one ground state and two excited states. The amplitudes of the spectral features are made up; in a real experiment, all three features will have different amplitudes

atoms contributing to the crossover peak ($v = +150\,\text{m/s}$ and $v = -150\,\text{m/s}$), 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.

▶ **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 crossover feature, see Fig. 5.9.

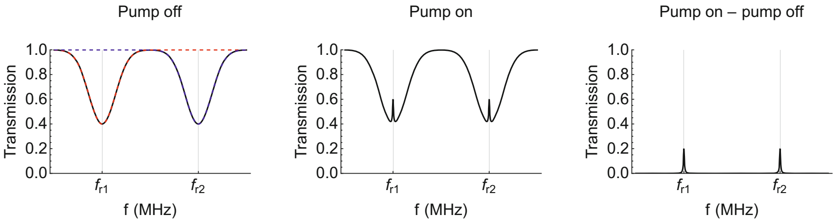


Fig. 5.9 A simulation of a saturated absorption spectrum with one ground state and two excited states, but the two excited states are separated by a large energy. There are no atoms with the correct velocity to create the V crossover. The amplitudes of the spectral features are made up; in a real experiment, the features will have different amplitudes

If the vapor cell was heated to increase the Doppler width, the crossover peak would return, see Fig. 5.10.

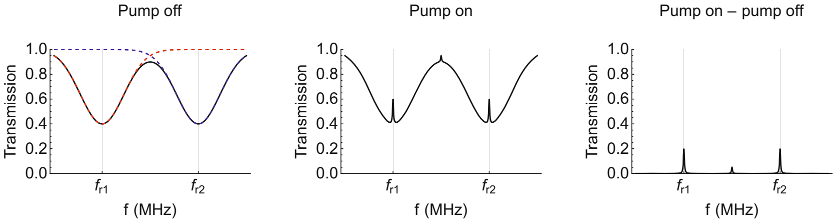


Fig. 5.10 Now the vapor cell is heated so there are a few atoms with the correct velocity needed to create a V crossover

Summary

If there are (1) two excited states and one ground state and (2) the Doppler profiles for the two individual transitions are overlapping one another, there will be a V crossover directly between the two transitions.

The speed of atoms needed to create a crossover feature can be derived from the formula for the Doppler shift. The speed needed is:

$$|v_{\parallel}| = \lambda \frac{|f_{r1} - f_{r2}|}{2}. \tag{5.5}$$

If there aren't any atoms in the vapor cell with that speed, there won't be a crossover feature. As with many things in experimental science, there are trade-offs to saturated absorption spectroscopy. While saturated absorption spectroscopy gives us really narrow spectroscopy features, it gives us more features to deal with. Fortunately, we know precisely where those crossovers will be.

We can add a third excited state to the system.[5] 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., $(f_{r1}+f_{r2})/2$), one between f_{r1} and f_{r3} (i.e., $(f_{r1}+f_{r3})/2$), and one between f_{r2} and f_{r3} (i.e., $(f_{r2}+f_{r3})/2$). In total, saturated absorption spectroscopy on an atom with one ground state and three excited states will have 6 spectral features: 3 real features and 3 crossovers.

5.2.2 Λ Crossovers and X Crossovers

Λ crossovers and X crossovers, see Fig. 5.5, both occur when the pump beam excites an atom with a particular velocity, such that, upon decay to a different ground state, that atom has the correct velocity to be excited by the probe beam. As a reminder, V crossovers occur because an atom gets to pick between absorbing a photon from the pump beam and the probe beam. When an atom picks the pump beam over the probe beam, the transmission of the probe beam increases resulting in a bump on the transmission or absorption plot. Λ crossovers and X crossovers both occur because the pump beam puts more atoms in the probe beam's path. As such, the transmission of the probe beam decreases resulting in a dip on the transmission or absorption plot. Like V crossovers, this feature occurs when the laser frequency is precisely between the two resonance frequencies:

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[5] We can't add more than that for a single ground state due to "The Rule".

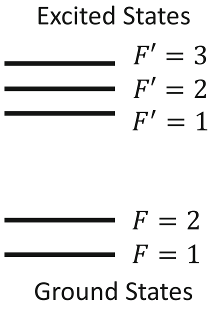

Fig. 5.11 An atom with two ground states and three excited states

$$f_{\text{cross}} = \frac{f_{r1} + f_{r2}}{2} \tag{5.6}$$

As before, the vapor cell needs atoms with a speed

$$|v_{\|}| = \lambda \frac{|f_{r1} - f_{r2}|}{2}. \tag{5.7}$$

to create these features.

There is one important difference for X crossovers. For V crossovers and Λ crossovers, the pump and the probe beam are interchangeable. Consider an atom that has two ground states and three exited states, see Fig. 5.11. We pick the ground states to have labels $F = 1$ and $F = 2$ and the excited states to have labels $F' = 1$, $F' = 2$, and $F' = 3$.[6] As a reminder, "The Rule" is that an atom can be excited as long as $\Delta F = 1$, 0, or -1 with the exception $F = 0 \not\rightarrow F = 0$. Suppose we have a Λ crossover that comes from the two transitions $F = 1 \rightarrow F' = 2$ and $F = 2 \rightarrow F' = 2$. To add numbers, let's say the vapor cell needs atoms with speed $v_{\|} = +35$ m/s or -35 m/s to produce this crossover. It doesn't matter if the pump beam is exciting the first transition or the second. If the pump beam is exciting the first transition, it is "pumping" atoms with $v_{\|} = +35$ m/s from the $F = 1$ ground state to the $F = 2$ ground state via the $F' = 2$ excited state. The probe beam is then exciting those extra atoms on the $F = 2 \rightarrow F' = 2$ transition. If the pump beam is exciting the second transition, it is "pumping" atoms with $v_{\|} = -35$ m/s from the $F = 2$ ground state into the $F = 1$ ground state via the $F' = 2$ excited state. The probe beam is then exciting those extra atoms on the $F = 1 \rightarrow F' = 2$ transition. The important thing to notice here is that the excited state of both transitions can decay into either ground state. We say that there are two "velocity classes" of atoms that are contributing to that crossover feature: $+35$ m/s and -35 m/s.

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[6] I added primes to the excited states to help us distinguish between the ground states and the excited states.

For X crossovers, there are some situations where the two transitions cannot be interchanged. Consider the two transitions: $F = 1 \rightarrow F' = 2$ and $F = 2 \rightarrow F' = 3$. If the pump beam is exciting the first transition, it is "pumping" atoms with, say, $v_{\parallel} = +25\,\text{m/s}$ from the $F = 1$ ground state into the $F = 2$ ground state via the $F' = 2$ excited state. The probe beam is then exciting those extra atoms on the $F = 2 \rightarrow F' = 3$ transition. However, if the pump beam is exciting the second transition, which would be the atoms with $v_{\parallel} = -25\,\text{m/s}$, $F' = 3$ cannot decay into the $F = 1$ ground state. So, the probe beam transmission, which is exciting atoms on the $F = 1 \rightarrow F' = 2$ transition, is not changed. This crossover only has one "velocity class" that contributes to the crossover, so it tends to be smaller than a crossover with two velocity classes.

We now have the basic building blocks to interpret a spectrum from an atom with as many ground and excited states that we want. If our atom has energy levels as shown in Fig. 5.11, we will have multiple real transitions and multiple crossovers. For the real transitions, 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 five transitions will have a Doppler profile that has a Doppler width associated with it.

A saturated absorption plot will have those five spectral features as well as crossovers. For a crossover to occur, the vapor cell has to have atoms with the velocity needed to create that crossover. To conclude this section, let's recap the three types of crossovers and list the possible crossovers for the atom with the energy states shown in Fig. 5.11:

(1) V crossovers: 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. Using Fig. 5.11 as an example, V crossovers occur due to interference between:

Transition #1	Transition #2
$F \rightarrow F'$	$F \rightarrow F'$
$1 \rightarrow 1$	$1 \rightarrow 2$
$2 \rightarrow 1$	$2 \rightarrow 2$
$2 \rightarrow 2$	$2 \rightarrow 3$
$2 \rightarrow 1$	$2 \rightarrow 3$

For this example, there are 4 possible V crossovers.

(2) Λ crossovers: 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 frequency is directly between

the two transitions. Using Fig. 5.11 as an example, Λ crossovers occur due to interference between:

Transition #1	Transition #2
$F \to F'$	$F \to F'$
$1 \to 1$	$2 \to 1$
$1 \to 2$	$2 \to 2$

For this example, there are 2 possible Λ crossovers.

(3) X crossovers: If the pump beam can excite an atom that decays into the ground state for the probe beam and the Doppler profiles from the individual transitions are overlapping, we will have a crossover whose frequency is directly between the two transitions. X crossovers do not share any states. Using Fig. 5.11 as an example, X crossovers occur due to interference between:

Pump	Probe	Notes
$F \to F'$	$F \to F'$	
$1 \to 1$	$2 \to 2$	Interchangeable; two velocity classes
$1 \to 1$	$2 \to 3$	Not interchangeable; one velocity class
$1 \to 2$	$2 \to 1$	Interchangeable; two velocity classes
$1 \to 2$	$2 \to 3$	Not interchangeable; one velocity class

For this example, there are 4 possible X crossovers.

So, in this example, our transmission plot will have up to 15 spectral features. Five of those features will be the real transitions, and the remaining 10 are all crossovers. Again, whether or not those crossovers produce spectral features depend upon there being the correct velocity class of atoms in the sample to produce those features.

5.3 Example with Cesium-133

Cesium-133, which has 55 protons and 78 neutrons, is one of the most studied atoms on the periodic table. Figure 5.12 shows a simplified energy level diagram for a transition that uses 455.6 nm light. The lower state, which has the label 6s $^2S_{1/2}$ (don't worry about what that means right now, we will talk about the physical meaning behind the labeling starting in Chap. 7), has two closely spaced ground states with labels $F = 3$ and $F = 4$ (we will give meaning to these labels in Chaps. 8 and 9). The separation of these two states is just over 9 GHz. In energy units, that would be $hf = (6.626 \times 10^{-34}\,\text{Js})(9.192 \times 10^9\,\text{Hz}) = 6.091 \times 10^{-24}\,\text{J} = 38\,\mu\text{eV}$.

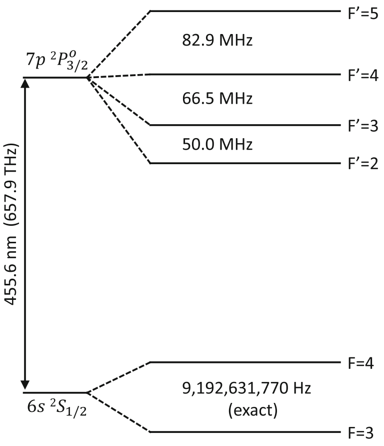

Fig. 5.12 A simplified energy level diagram for the transitions in cesium-133 near 455.6 nm

Fun Fact
This energy separation is how we define 1 second! Imagine you had a pendulum that made exactly 9,192,631,770 oscillations in 1 second. Replace that pendulum with a cesium atom and you have the official definition of a second.

The excited state studied here has four levels. These four levels are far closer together than the two ground state levels. To easily see all of the levels in the figure, the energy spacing scale is different for the ground state and excited state; the energy separation of the two ground states is over 100 times bigger than the excited state separations. Below are 4 questions to work through. Answer the first two questions together before answering the second two questions.

Question #1 What speed does an atom have to have to create a Λ crossover between the two ground states and the $F' = 3$ excited state?

Question #2 Using Eq. 4.5, what temperature would the cesium vapor cell be such that the FWHM of the Maxwell Boltzmann distribution was half of the velocity for Question #1? The mass of cesium-133 is $m = 2.207 \times 10^{-25}$ kg. The answers are below this fun anagram puzzle.

#1: $|v_{\parallel}| = \lambda \frac{|f_{r1} - f_{r2}|}{2} = (455.6 \times 10^{-9}\,\text{m}) \frac{9{,}192{,}631{,}770\,\text{Hz}}{2} = 2094\,\text{m/s} \rightarrow \frac{|v_{\parallel}|}{2} =$ 1047 m/s.

#2: $v_{\text{FWHM}} = 2.355\sqrt{\frac{k_B T}{m}} \rightarrow T = \left(\frac{v_{\text{FWHM}}}{2.355}\right)^2 \frac{m}{k_B} = \left(\frac{1047\,\text{m/s}}{2.355}\right)^2 \frac{2.207 \times 10^{-25}\,\text{kg}}{1.38 \times 10^{-23}\,\text{J/K}} =$ 3161 K.

Anagram Fun
Rearrange the letters in "cesium" to make a new 6 letter word.
How many 5 letter words can you create from the word "cesium"? (I found one, but an online anagram solver found two!)
How many 4 letter words can you create from the word "cesium"?

This is really hot! For reference, room temperature is about 300 K. In short, we don't have to worry about Λ crossovers (or X crossovers).

Question #3 But what about V crossovers? What velocity does an atom have to have to create a V crossover between the $F = 4$ ground state and the $F' = 4$ and $F' = 5$ excited states?

Question #4 Assuming room temperature, $T = 300\,\text{K}$, find the FWHM of the Maxwell Boltzmann distribution. What do you conclude? The answers are in the footnotes.[7]

For V crossovers, $|v_{\|}|$ is well within the full width half maximum of the Maxwell-Boltzmann velocity distribution. So, we are definitely going to have V crossovers. However, the $|v_{\|}|$ needed for Λ crossovers and X crossovers is well outside the distribution, so we won't see any Λ crossovers or X crossovers. Figure 5.13 is a saturated absorption plot between the $F = 4$ ground state and the $F' = 3$, $F' = 4$, and $F' = 5$ excited states. The three labeled peaks are the real transitions. Notice there are additional Lorentzian features exactly halfway between

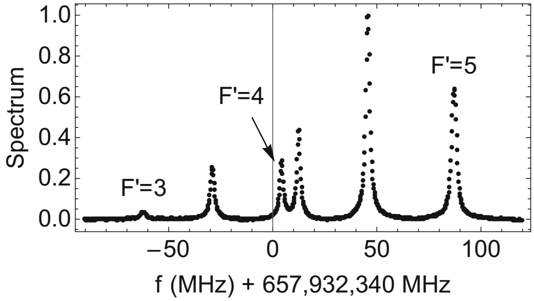

Fig. 5.13 Experimental data taken by my research group showing a saturated absorption plot from the $F = 4$ ground state of cesium-133 to the $F' = 3$, $F' = 4$, and $F' = 5$ excited states, see reference [1]. There are six spectral features. Three of them are real transitions and three are V crossovers

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[7] #3: $|v_{\|}| = \lambda \frac{|f_{r1}-f_{r2}|}{2} = (455.6 \times 10^{-9}\,\text{m})\,\frac{8.29\times10^{6}\,\text{Hz}}{2} = 18.9\,\text{m/s}$.
#4: $v_{\text{FWHM}} = 2.355\sqrt{\frac{k_B T}{m}} = 2.355\sqrt{\frac{(1.38\times10^{-23}\,\text{J/K})(300\,\text{K})}{2.207\times10^{-25}\,\text{kg}}} = 322\,\text{m/s}$. There are definitely atoms in the vapor cell to make this crossover!

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 $F = 4$ 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 V crossover between $F' = 3$ and $F' = 5$. Even if this plot wasn't labeled, we can still figure out which features are the real transitions and which are the crossovers. We just look for the features directly between two other features to find the crossovers. Also, the peaks at the smallest and largest frequency values have to be real transitions; a crossover has to be between two real transitions.

5.4 Oxygen-16: A Spectrum Missing a Crossover

A lot of laser spectroscopy is done from the ground state to an excited state. However, laser spectroscopy can also be performed between two excited states. Figure 5.14a shows a simplified Grotrian diagram for a transition in neutral atomic oxygen-16 (8 protons and 8 neutrons). The lower state, which we give the label $J = 2$, can be excited to three different excited states, which we give the labels $J' = 1$, $J' = 2$, and $J' = 3$. Like in the previous examples, just consider these labels for now. The Rule for these transitions are the same as before, we just replace F with J: $\Delta J = -1, 0,$ or $+1$ with the exception that $J = 0 \not\to J' = 0$.[8] We will explore what the labels actually mean in Chaps. 7, 8, and 9. Oxygen, in its natural form, is a molecule composed of two oxygen atoms. A discharge (basically think

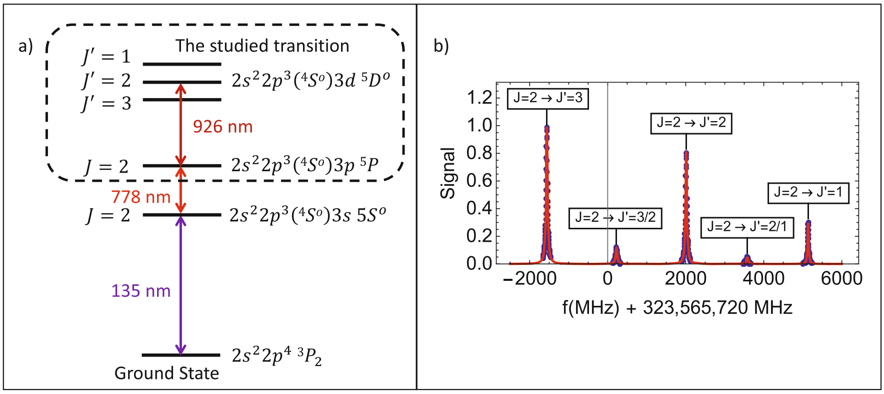

Fig. 5.14 (**a**) A simplified energy level diagram for a spectroscopic study in atomic oxygen-16 near 926 nm. The spectrum is taken between two excited states, which I call the lower state and the upper state. (**b**) Experimental data of a saturated absorption spectroscopy spectrum from the $J = 2$ lower state of oxygen-16 to the $J' = 1$, $J' = 2$, and $J' = 3$ upper states. There are only five spectral features because the vapor cell wasn't hot enough for the V crossover created by the $J = 2 \to J' = 1$ and $J = 2 \to J' = 3$ transitions; the Doppler profiles for these two transitions did not overlap

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[8] A full list of the rules that need to be satisfied for an electron to transition between two atomic states is given in Appendix C.

about a "neon tube" filled with oxygen molecules) can be used to both dissociate the molecule into neutral atomic oxygen as well as excite the electrons into a variety of excited states. Most of the atoms are not in the $J = 2$ lower state, but there are enough for us to do spectroscopy. It should be noted that the $J = 2$ lower state also has a lifetime of about 27 ns, so the discharge needs to continually repopulate the lower state for us to do spectroscopy. Discharges are also typically hotter than room temperature.

Next, take a look at Fig. 5.14b. There is a very visible V crossover created by the large $J = 2 \rightarrow J' = 3$ (real) transition and medium sized $J = 2 \rightarrow J' = 2$ (real) transition. Those transitions are about 3500 MHz apart, but the Doppler profiles of these individual transitions are large enough to create a crossover. This crossover is labeled as $J = 2 \rightarrow J' = 3/2$.[9] The V crossover with the label $J = 2 \rightarrow J' = 2/1$ is created by the medium $J = 2 \rightarrow J' = 2$ and the small $J = 2 \rightarrow J' = 1$ transitions. It is also quite visible, although not as big as the $J = 2 \rightarrow J' = 3/2$ V crossover. Those two transitions are about 3200 MHz apart. We did not see a V crossover created by the $J = 2 \rightarrow J' = 3$ and $J = 2 \rightarrow J' = 1$ transitions, which would have the label $J = 2 \rightarrow J' = 3/1$. Those two transitions are about 6500 MHz apart. Because they are so far apart, the individual Doppler profiles don't overlap resulting in no crossover feature.

5.5 Example with Europium-151

Let's explore a more complex example using europium-151. Consider a transition from the ground state to an excited state that we are going to call the $J' = 5/2$ excited state. Because of nuclear spin, both the ground state and excited state have 6 closely spaced hyperfine levels, see Fig. 5.15. As a reminder, if the nucleus had no angular momentum, there would be a single energy level called the center of gravity that would be located at 0 for both energy level diagrams. The frequency difference between the center of gravity of the excited state and that of the ground state is called the center of gravity frequency. Due to the closely spaced levels, there are a lot of possible transitions and a lot of possible crossovers.

Figure 5.16 is a simulation of a transmission plot with just a probe beam (no pump beam) for a vapor cell with a temperature of 400 K. I plotted the individual transition Doppler broadened spectral features with blue-dashed lines. If you add up the blue curves, you get the black curve. The red vertical lines are the transition frequencies. Because of the temperature of the vapor cell, the individual transitions cannot be resolved. So, this is a good candidate for saturated absorption spectroscopy. The saturated absorption plot will have many transitions (15 of them) and many crossovers (up to 62 of them!). Unfortunately, many of these

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[9] Just to be clear, that 3/2 is not the fraction equivalent to 1.5. It is meant to convey "a V crossover where the two excited states are $J' = 3$ and $J' = 2$."

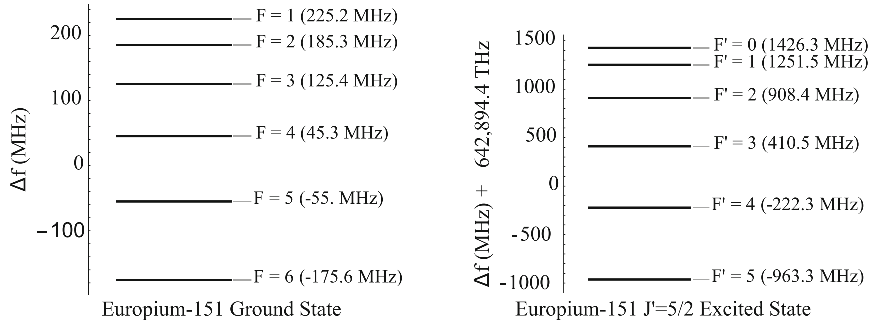

Fig. 5.15 Left: The 6 hyperfine energy levels for the ground state of europium-151. The 6 hyperfine energy levels for a particular excited state that is about 642.9 THz (466.3 nm) above the ground state. The numbers listed for Δf are with respect to the center of gravity

spectral features overlap with each other. Figure 5.17 shows experimental results for a saturated absorption plot collected by my research group on this transition in europium-151. Look how complicated the spectrum is! Although it is a complicated plot, there are spectral features that we can try to attribute to each transition or crossover. Our job, as experimentalists, is to extract as much information as we can from these plots.

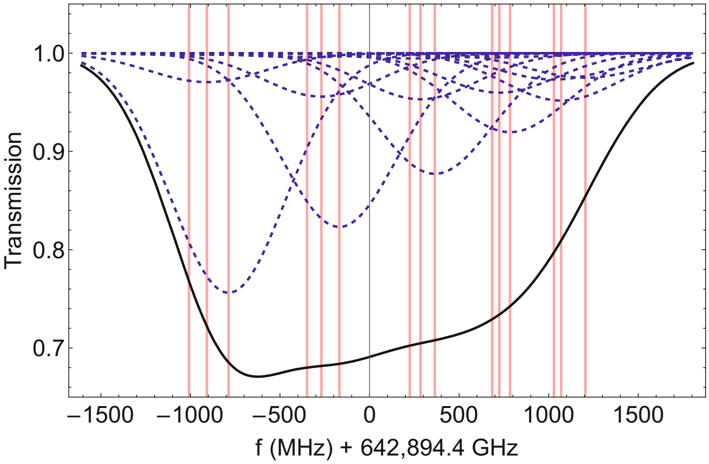

Fig. 5.16 A simulation of a transmission plot with a probe beam (no pump beam) traveling through a vapor cell of europium-151 atoms held at 400 K. There are 15 transitions in total. The Doppler profile for each transition is shown in blue-dashed lines. Some of the amplitudes are quite small and not really visible by eye in this plot. The sum of all the individual Doppler profiles is the black curve, which is what we would measure in the lab. The red vertical lines indicate the center of each transition. As you can see, no single spectral feature can be resolved

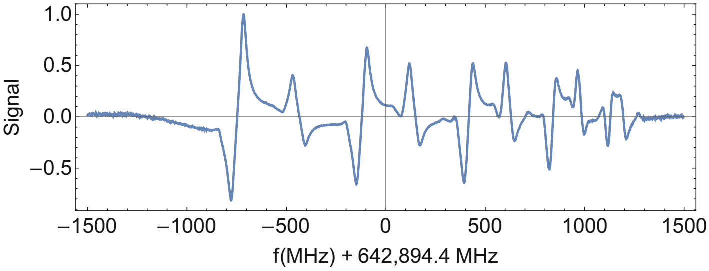

Fig. 5.17 Experimental results of performing saturated absorption spectroscopy on europium-151 atoms, see reference [2]. There are 15 real spectral features and up to 62 crossover features for a total of 77 possible spectral features!

5.6 Extra: Crossover-Free Spectroscopy

Crossovers can be problematic because they introduce additional features into the spectrum. Many times, those crossover features overlap each other or overlap the features from real transitions. So, it isn't too surprising that spectroscopists developed methods of getting sub-Doppler features without crossovers. The simplest idea is to use an atomic beam, see Fig. 5.18.

An atomic beam is created by taking a sample, placing it in a vacuum-compatible oven,[10] and heating the oven. The oven has a small hole to allow the atoms to escape. After the oven, metal pieces called collimators are typically used to block any atoms diverging at large angles. The ideal spectroscopy experiment would have an atomic

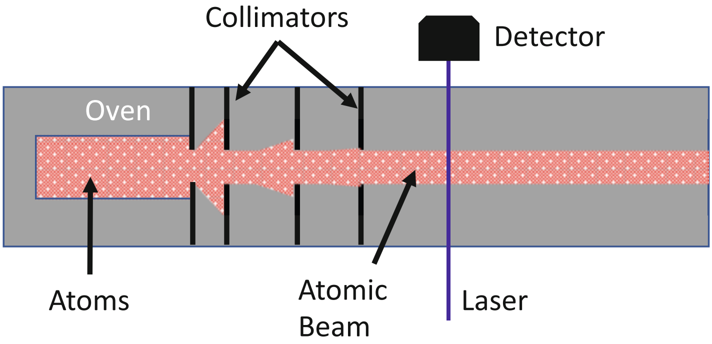

Fig. 5.18 A sketch of how experimentalists use an oven and collimators to make a collimated atomic beam. Since the atoms are not moving vertically, if we sent a laser perpendicular to the atomic beam, then $v_\parallel = 0$

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[10] Assuming the atoms are a solid at room temperature. For gaseous molecules, the oven is replaced with a discharge to dissociate the molecules into atoms.

beam with zero divergence, resulting in a column of atoms exiting the oven. In practice, there will always be some divergence of the atomic beam.

The laser beam intersects perpendicular to the atomic beam. In this experimental design, there are no atoms moving towards or away from the laser so there are no Doppler shifts and there are no crossovers. This type of setup does have a few drawbacks. The first is that you really need to make sure the laser is perpendicular to the atomic beam. If there is a small angle, there will be no atoms moving perpendicular to the laser. And, you can't really tell if there is a non-zero angle either. You still have atoms absorbing from the laser, but they will all be absorbing at the Doppler shifted frequency. So, the spectrum looks the same, but the resonant frequency is off. A common technique to address this issue is to perform saturated absorption spectroscopy on the atomic beam. The other issue you have to deal with is that the atomic beam is never perfectly collimated. Often times, the atomic beam will be diverging more in one direction than the other. That will cause an asymmetry in the spectral signal, even when using saturated absorption spectroscopy.

Another clever method for doing spectroscopy is to have two laser beams that are traveling in the same direction, see Fig. 5.19. Unlike typical saturated absorption spectroscopy, the two laser beams have independent frequency control. In saturated absorption spectroscopy, the pump and probe beams come from the same laser, so changing the frequency of the laser changes the frequency of both the pump and the probe beams. In this setup, the frequency of laser #1 is going to be fixed to a transition, and the frequency of laser #2 is scanned. The transmission of laser #1 is what we monitor. Laser #2 also has more laser power (a higher saturation parameter).

One obstacle for this experimental setup is that you need two lasers, which can be expensive. The other is that laser #1 has to be at the resonance frequency for one of the transitions. If the frequency of laser #1 does not perfectly match a resonant frequency, the frequency scale of your spectrum will be off.

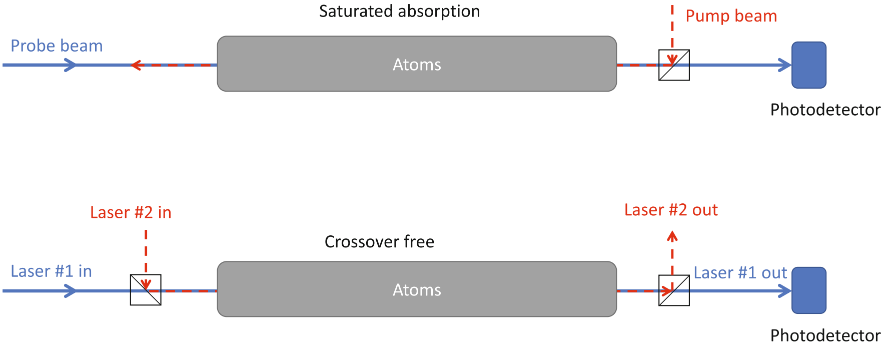

Fig. 5.19 A comparison between a saturated absorption spectroscopy experimental setup and a crossover-free setup. The crossover-free setup requires two separate lasers

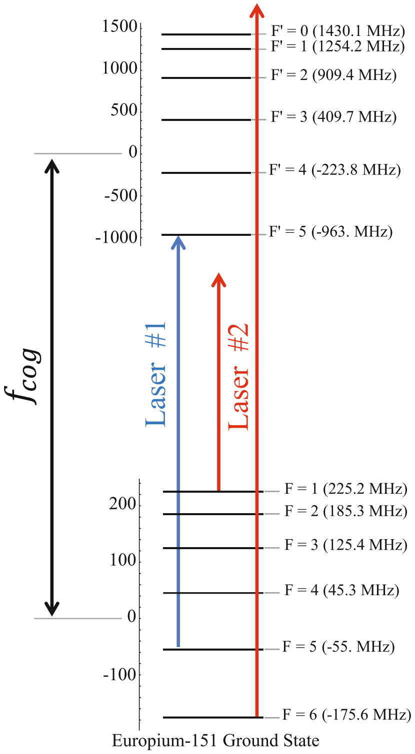

Fig. 5.20 A Grotrian diagram to explore crossover-free spectroscopy. Laser #1 has a frequency that exactly matches the $F = 5 \rightarrow F' = 5$ transition frequency. The frequency of Laser #2 is smoothly scanned from a frequency that is too small to excite any resonant transition to too large

To better understand how the two-laser spectroscopy set up works, consider the following problem on producing a crossover-free spectrum that looks like a spectrum at 0 Kelvin. Figure 5.20 shows a Grotrian diagram for a transition in europium-151. Laser #1 has a frequency that is fixed to the $F = 5 \rightarrow F' = 5$ transition. Laser #2 is going to scan from a frequency below the $F = 1 \rightarrow F' = 5$ transition to above the $F = 6 \rightarrow F' = 0$ transition. Note that neither of these transitions are allowed. I'm just giving an f_{min} and an f_{max} for our frequency scan. For these transitions, the wavelength of light is around $\lambda = 466$ nm. We will monitor the transmission of Laser #1 as a function of frequency for Laser #2.

(a) Considering only the atoms moving with $v_{\parallel} = 0$, explain why scanning the frequency of Laser #2 across the $F = 5 \rightarrow F' = 5$ transition results in a 0 Kelvin spectral feature on the transmission plot for Laser #1. Will you also get a spectral feature when Laser #2 scans across the $F = 5 \rightarrow F' = 4$ transition?
(b) When Laser #2 scans through the $F = 6 \rightarrow F' = 5$ transition, Laser #2 will excite atoms with $v_{\parallel} = 0$ from the $F = 6$ ground state to the $F' = 5$ excited state. Even though Laser #1 is not resonant with that transition, there will be a spectral feature at that frequency on the transmission plot. Why?

(c) Now consider atoms that are moving at a speed $v_{\parallel} \approx 344$ m/s towards Laser #1 (and also towards Laser #2). The atoms are moving with the perfect speed to be excited by Laser #1 on the $F = 5 \rightarrow F' = 4$ transition. Laser #2 now has its frequency scanned. How do these atoms affect the transmission plot for Laser #1?
(d) Next, consider atoms that are moving at a speed $v_{\parallel} \approx 56$ m/s towards Laser #1 (and also towards Laser #2). These atoms are moving with the perfect speed to be excited by Laser #1 on the $F = 6 \rightarrow F' = 5$ transition. How do these atoms affect the transmission plot as the frequency of Laser #2 is scanned?
(e) After considering parts (a) through (d), how many features will our transmission plot have?

Problems

5.1 For each of the following equations, write a brief description of what each equation means.

(a) Equation 5.6
(b) Equation 5.7

5.2 To create a particular crossover, a vapor cell needs atoms that have a speed given by Eq. 5.7. Derive this formula using the Doppler shift equation.

5.3 Consider a transition in an atom with three hyperfine ground states and two hyperfine excited states. The ground states have labels $F = 2$, $F = 3$ and $F = 4$ and the excited states have labels $F' = 3$ and $F' = 4$.

(a) List all of the possible transitions.
(b) List all possible V crossovers.
(c) List all possible Λ crossovers.
(d) List all possible X crossovers.
(e) Optional: Write a computer program to calculate all possible transitions and crossovers for the europium-151 transition studied in Sect. 5.5.

5.4 Figure 5.21 shows energy levels for a transition in rubidium-87. The center of gravity for the ground and excited states are shown on the far left. The ground state labeled $F = 1$ has an energy of −4271.676 MHz with respect to the center of gravity and the ground state labeled $F = 2$ has an energy of +2563.005 MHz with respect to the center of gravity. The two ground states are separated by 6834.682 MHz, which is much larger than the width of the Doppler profile for these transitions, which is about 510 MHz, at 300 K. This means there will be no Λ or X crossovers. However, all of the excited states are separated by frequencies smaller than the Doppler width, which means the saturated absorption spectrum will have V crossovers. The natural linewidth for this transition is 6 MHz.

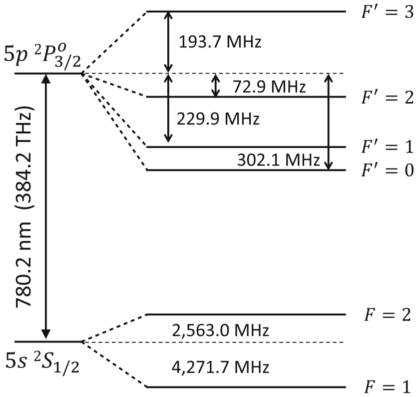

Fig. 5.21 A Grotrian diagram for a transition in rubidium-87

(a) Make a saturated absorption plot using the above energy levels assuming atoms are only in the $F = 1$ ground state. Remember to use The Rule: $\Delta F = -1, 0,$ or $+1$ with the exception $F = 0 \not\to F' = 0$. As always, don't worry about the amplitudes of the spectral features. The horizontal axis should be with respect to center of gravity of the excited state. On your plot, label which features are real transitions and which are crossovers.

(b) Make a saturated absorption plot assuming atoms are only in the $F = 2$ ground state.

(c) The plots in part (a) and part (b) are separated by about 6830 MHz, see Fig. 5.22. The 0 on the horizontal axis in Fig. 5.22 is with respect to center of gravity frequency. Let's assume the rubidium atoms are really hot. So hot that the Doppler profiles from the two ground states are overlapping, which means we will have more crossovers. Where on the above graph would the crossover be due to the two transitions $F = 1 \to F' = 1$ and $F = 2 \to F' = 1$?

(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?

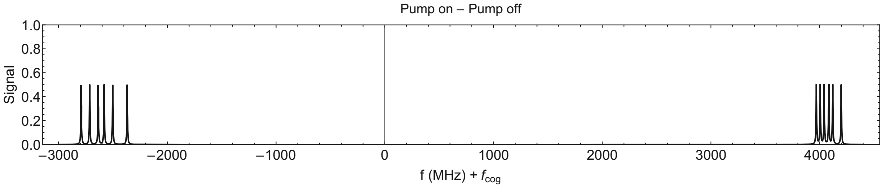

Fig. 5.22 A simulation of a saturated absorption plot (i.e., a pump on - pump off plot) scanning across all possible transitions. The 0 on the horizontal axis is the center of gravity frequency 384.2 THz. The amplitudes for the spectral features are all set to be the same. In a real experiment, the amplitudes will all be different

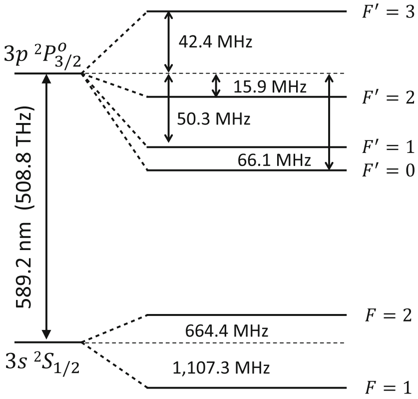

Fig. 5.23 A Grotrian diagram for a transition in sodium-23

5.5 A transition in sodium-23 has a Grotrian diagram that is very similar to the transition studied in Problem 5.4 for rubidium-87. The Grotrian diagram for the sodium transitions studied in this problem are shown in Fig. 5.23: The difference is that the energy levels are much closer together. The natural linewidth for this transition is 10 MHz.

(a) Make a saturated absorption plot assuming atoms are only in the $F = 1$ ground state. Assume we have some power broadening so that the width of the spectral features is 12 MHz. As always, don't worry about the amplitude of the spectral features.
(b) Reflect on your spectrum.
(c) Now assume you collected the spectrum but you used a crossover-free experimental setup. What does your spectrum look like now?

5.6 Answer the questions in Sect. 5.6.

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Part II

Digging Deeper: Quantum Mechanics and Beyond

Quantum Mechanics vs. Classical Physics

6

Abstract

In this chapter, we explore the differences between quantum mechanics and classical physics, focusing on three main ideas: compatible and incompatible observables, states of an observable, and the superposition of states. By examining these concepts, you will gain insight into how measurements impact quantum mechanical systems and the ideas behind the uncertainty principle.

Learning Goals

By the end of this chapter, you should be able to understand:

- the importance of discrete energy states in quantum mechanics.
- compatible and incompatible observables.
- basis sets.
- superposition of states.

I'm often asked some variation of the question, "What is the difference between quantum mechanics and classical physics?" This is a great question! After teaching quantum mechanics many times and having numerous conversations with other atomic and nuclear physicists, I believe the best way to introduce the difference to new learners is to first understand two concepts: states and superposition. By grasping these two ideas, we can begin to explore why quantum mechanics is essential for explaining the world of the super small.

W. Raven, *Atomic Physics for Everyone*,
https://doi.org/10.1007/978-3-031-69507-0_6

A note from Will: Many concepts discussed in this chapter are based on the orthodox or Copenhagen interpretation of Quantum Mechanics. Although it is the most popular interpretation, other interpretations exist, such as the many-worlds interpretation, de Broglie-Bohm pilot wave theory, and various collapse theories including Ghirardi-Rimini-Weber (GRW) theory and Continuous Spontaneous Localization (CSL). This remains an active area of exploration for many physicists and philosophers.

In addition, there are a few places where I simplify things a bit to make sure we focus on the main concepts. Finding the balance between 100% correct and still keeping things accessible was a challenge. For example, there are places where I will write a sum of functions where it should technically be an integral, but since calculus is not required for this book, I purposefully chose to leave them as sums to help us explore the concepts. For equations that should be integrals, I include a footnote to indicate that. For those who have not taken calculus, the ideas we discuss are still correct! We are just going to simplify the math a bit.

The other concept I simplify a bit is concerning compatible observables and sharing states. However, after discussions with my physics pedagogy friends, I decided to keep that language instead of exploring the delicate topic of projections and subspaces. For the advanced readers, keep this in mind. For new learners to quantum mechanics, this chapter is for you! If in the future you decide to learn more advanced quantum mechanics (and I hope you do!), please come back to this chapter to explore the subtleties of "commutation" and "subspaces."

6.1 What Is a State?

Definitions

- **Momentum:** A property of an object that is moving. For a classical object like a baseball, the formula for momentum is $p = mv$, where p is the object's momentum, m is the object's mass, and v is the object's velocity. An object's momentum will change if something acts on the object from the outside. The larger an object's momentum, the harder it is to stop. The unit of momentum is $\mathrm{kg} \cdot \mathrm{m/s}$.
- **Observable:** Something we can measure experimentally. Observables include, but are not limited to, energy, position, momentum, and angular momentum (angular momentum is the topic of Chaps. 7 and 8).

Physical systems, such as atoms, can exist in various conditions. They can be excited or relaxed, located in different places, moving or at rest, and so on. We describe these different conditions as “states,” and use a mathematical “state function” to specify the exact state of a system at a given time.

As we talked about and explored in Part 1 of this book, atoms have *discrete* energy states.

Two minute question: What does that mean?

Here is my answer: If we measure the energy of a quantum mechanical system, we will always find the system to have one value from a set of specific energies. The whole purpose of Part 1 of this book was how we experimentally find the energy between two of these discrete energy states. An electron in an atom can have energy E_1, E_2, E_3, etc. We will never find the electron with any other energy. We represent these discrete energy states in energy level diagrams throughout Part 1 of this book. Figure 6.1 is a copy of Fig. 5.12 as a helpful reminder. This is so important that I want to say it again: An electron in an atom can have energy E_1, E_2, E_3, etc. We will ***never*** measure the energy to be somewhere between E_1 and E_2.

Everything we can measure, which we call an observable, is represented by a state. The state of an observable is described by a mathematical function. Examples of things we can measure include energy, position, and momentum. As such, there are energy states, position states, and momentum states. Every energy we can measure is associated with some energy state. For example, suppose a system is in an energy state described by the state function ψ_1. If we measure the energy of that system, we will find the system has energy E_1. We will never measure any other value for energy. Often those states are discrete (like the energy of an electron in an atom) and sometimes they are continuous (like the position of an electron hanging

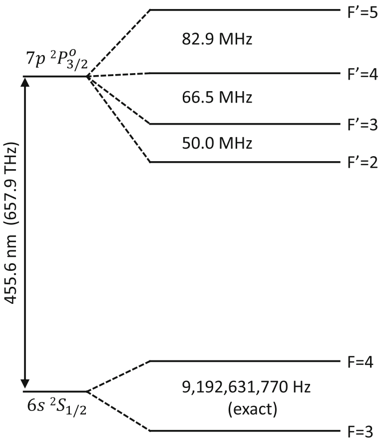

Fig. 6.1 A simplified energy level diagram for the transitions in cesium-133 near 455.6 nm

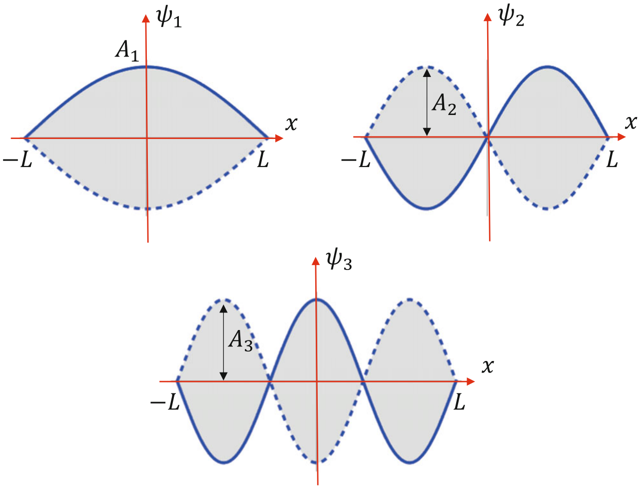

Fig. 6.2 The first three standing waves of a one dimensional rope or slinky. For this example, the rope is fixed at $x = -L$ and $x = +L$

out by itself in free space). *If we measure an observable, the quantum mechanical system will be in a state corresponding to that observable after the measurement.*

To help explore the idea of energy states, we will use a classical analogy that will serve as a helpful visualization tool. Imagine a string fixed at both ends, vibrating to create different standing waves, see Fig. 6.2. These are the same standing waves we discussed in Chap. 1 as a means of illustrating wave interference.

Now, let's shift our perspective from the classical realm to the quantum mechanical domain. If we were to treat this system quantum mechanically and measure its energy, we'd find discrete energy levels. These energy levels correspond to specific configurations of the standing wave—for instance, one loop, two loops, three loops, and so on as shown in Fig. 6.2. Unlike in the classical scenario where the wave can have any arbitrary energy, in the quantum realm, the energy is constrained to certain discrete values.

To formalize this, we use mathematical expressions known as wavefunctions,[1] denoted by the lowercase Greek letter psi (ψ). Each wavefunction, labeled as ψ_n, corresponds to a particular energy level, which will have energy E_n. The wavefunction encapsulates the behavior and properties of the system at that energy level. In quantum mechanics, the equation we use to calculate the wavefunctions and energies is called the **Schrödinger equation**. The Schrödinger equation is a partial differential equation and solving it for a system provides not just the spatial form of the wavefunction, but also how they evolve in time. If you take a quantum

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[1] In quantum mechanics, we prefer the phrase wavefunction over state function.

mechanics class, you will spend a good amount of time solving the Schrödinger equation for different physical scenarios.

Returning to our example of the vibrating quantum mechanical string, we can now describe the wavefunctions for specific energy states. The wavefunction ψ_1 corresponds to the state with one loop of energy, denoted by E_1. Its functional form, see Fig. 6.2, is described by $\psi_1 = A_1 \cos\left(\frac{\pi x}{2L}\right)$, where A_1 represents the amplitude and $2L$ denotes the length of the string. Similarly, ψ_2 represents the state with two loops and has a functional form of $\psi_2 = A_2 \sin\left(\frac{\pi x}{L}\right)$.

Summary So Far

If a quantum mechanical system has a particular energy, we say the system is in an energy state. Mathematically, that energy state is described by the wavefunction ψ_n. If a quantum mechanical system is in an energy state described by the wavefunction ψ_n and we measure its energy, we will measure the system's energy to be E_n. We will never measure anything else.

For the example in this section, n represents how many loops of energy the system has, so ψ_3 is the third picture in Fig. 6.2. In bra-ket notation, see Sect. 3.6, we would write either $|\psi_n\rangle$ or $|n\rangle$. There are other quantities (obersvables) that we can measure, and each thing we measure can change the shape of the wavefunction. Figure 6.3 shows an example of three position states. If we measure the position of a quantum mechanical particle, we would find the particle somewhere between the start and end of the string. Mathematically, we label those position states ψ with a subscript, like ψ_x. Notice that the position wavefunction is zero everywhere

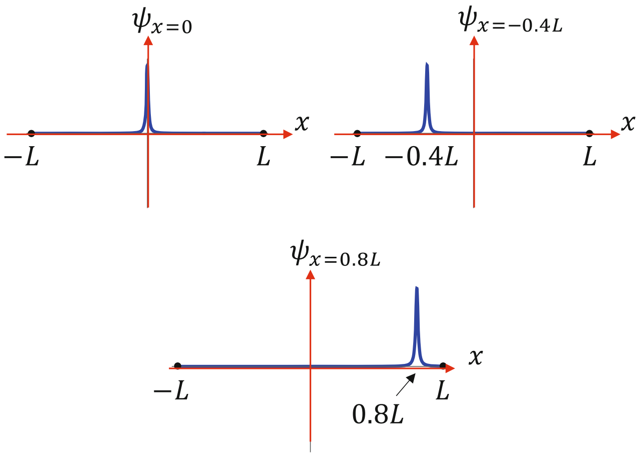

Fig. 6.3 Examples of 3 different position states. Each position state has a specific position associated with it

except for where the particle was measured. For the first example, the particle was measured to have a position at $x = 0$. For the second example, the particle was measured to have a position at $x = -0.4\,L$.

Super Important
For this quantum mechanical system, the energy states ***are not*** position states. They look completely different.

If we measure the energy of a quantum mechanical system, the system will be in an energy state, for example one of the energy states shown in Fig. 6.2. If we measure the position of a quantum mechanical system, the system will be in a position state, for example one of the position states shown in Fig. 6.3. *These are not the same states!!*

That last sentence is super important. If I told you a quantum mechanical system had energy E_3, that statement comes with the understanding that our system is in an energy state (ψ_3 or $|3\rangle$) that has energy E_3.[2] If the system was in the energy state ψ_3 and I were to ask, "Where exactly is the quantum mechanical particle?", we wouldn't be able to answer that question. The wavefunction, see the graph with 3 loops in Fig. 6.2, is spread out over the entire range from $x = -L$ to $x = +L$ and this is *not* a position state, see Fig. 6.3. While we can't state precisely where the particle is, we can, as we will see in Sect. 6.3, answer the question, "What are the probabilities of finding the particle in various locations?"

Likewise, if I told you a quantum mechanical particle was at a position $x = 0.1\,\text{nm}$, that statement comes with the understanding that our system is in a position state with a location at $x = 0.1\,\text{nm}$. If I were to ask, "What is the energy of the quantum mechanical particle?", we wouldn't be able to answer that question exactly because the system is not in an energy state. Like with the example given above where we know the energy but not the exact position, we will be able to answer the question, "If the particle is in the position state $\psi_{x=0.1\,\text{nm}}$, what are the probabilities of finding the particle with a particular energy?"

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[2] As we work through the next few chapters, we will add more parameters to describe the state. Eventually, the state will look something like $|n\ \ell\ s\ j\ m_j\rangle$. The 3 in this example is the n.

Stepping Back

Take a look at one of the energy states shown in Fig. 6.2 and ask the question, "Where is the particle?" The best you can answer is, "The wavefunction is spread out from $x = -L$ to $x = L$. It is not at any single location." The energy has a single value, but the exact position is unknown.

Far less intuitive is if we repeated this thought experiment with position states. Take a look at one of the position states shown in Fig. 6.3 and ask the question, "What is the energy of the particle?" Our intuition tells us there is an answer to this question. However, in quantum mechanics, a particle only has a specific energy if it is in an energy state. A position state is ***not*** an energy state. The best you can answer is, "The energy is spread out. It does not have a single value."

Take as much time as you need to try and understand that last paragraph. That last paragraph is very counterintuitive to our everyday experience. In classical physics, if a car is traveling down the road, I can tell you its position and energy. In quantum mechanics, we cannot know both. If the energy is well defined, it is in an energy state. If the position is well defined, it is in a position state.

There are two really important things to take away from this section:

- If we measure the energy of a quantum mechanical system, that system will be in an energy state with a specific energy. If we measure the position of a quantum mechanical system, that system will be in a position state with a specific position.
- Energy states and position states are not the same. They look completely different. If we measure the energy of a system, the system will now be in an energy state and the position of the particle is spread out. Similarly, if we measure the position of a system, the system will now be in an position state and the energy of the particle is spread out.

6.2 Compatible vs. Incompatible Observables and the Uncertainty Principle

Definitions

- **Incompatible observables:** If two observables cannot be precisely measured at the same time, they are called incompatible. Measuring one observable changes the system, making subsequent measurements of the other observable unpredictable.
- **Compatible observables:** If two observables can be precisely measured at the same time, they are called compatible. Measuring one observable does not change the system in a way that affects the measurement of the other observable. Remeasuring either observable will return the same value as initially measured.

We have learned that for quantum mechanical systems, energy and position are ***incompatible observables***. If the system is in a position state, it is not in an energy state and vice versa. *If we measure the position of the system, it is now in a position state. Since that is not an energy state, we cannot predict the exact outcome when we measure the system's energy.*

If there are two observables that share the same set of states, we say that they are ***compatible observables***. For the system in Sect. 6.1, there are, unfortunately, no compatible observables, but we will be able to explore compatible observables using systems in Chap. 7. So, for now, let's just suppose there is some other observable that is compatible with energy. Let's call that observable A, described by the wavefunction $\psi_{A,n}$ with possible measured values A_n. If we measure the energy of a quantum mechanical system, the quantum mechanical system will now be in an energy state. Let's say we measured the energy of the system to be E_3, which is the third picture with three loops in Fig. 6.2. Now we measure A and obtain A_3. If we went back and measured energy, we will find that the system is still in the state with three loops with energy E_3. Next, we measure A. If energy and observable A are compatible, we will measure A_3. This is because two compatible observables share a set of states. In other words, if the energy state has the wavefunction with three loops (ψ_3), and we measure A, we will find $A = A_3$ and that the wavefunction is unchanged. It still has three loops.

The Uncertainty Principle Part 1

The compatibility or incompatibility of two observables is summarized by the uncertainty principle. If two observables are compatible, they share a set of states. We can measure both observables repeatedly and obtain consistent values. If the two observables are incompatible, they do not share a set of states. Measuring one observable disrupts the outcome of the measurement of the other.

As you see, states are extremely important in quantum mechanics. Every observable has a set of associated states. Each energy state corresponds to a specific energy. If we measure the system's energy, it will be in one of those states with the associated energy. Similarly, measuring position, momentum, or any other observable places the system in one of the states for that observable. Some observables share a set of states (they are compatible, and subsequent measurements do not alter the previous values), while others have different states (they are incompatible, and knowing one means we don't know the other).

6.3 Superposition of States

Definitions

- **Superposition:** A concept in math and physics that says a function can be constructed as the sum of two or more other functions.
- **Basis set:** All of the states for a particular observable for a particular system. All of the possible energy states (for example, 1 loop, 2 loops, 3 loops, 4 loops, etc. for the vibrating quantum mechanical string shown in Fig. 6.2) make up the energy basis set for that system. Similarly, all possible position states (Fig. 6.3 shows a few position states for the vibrating quantum mechanical string) make up the position basis set.

Another really important concept to understand is superposition. Let's explore superposition through an example. Suppose we measure the position of a quantum mechanical system and find it in the position state shown in the top right picture of Fig. 6.3. Although this is not an energy state, we can still infer some information about the system's energy. The concept of superposition will allow us to determine *the probability* that, upon measuring energy, the system will have one loop, two loops, three loops, etc.

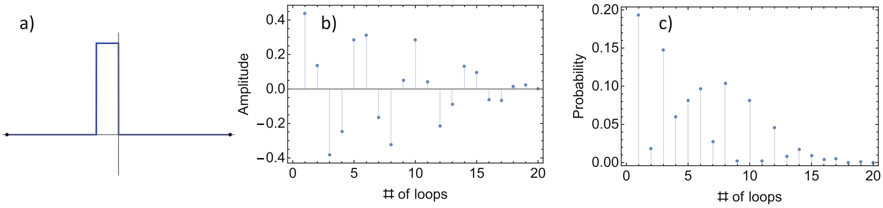

Fig. 6.4 (**a**) The state for our thought experiment. (**b**) The amplitude of each energy state needed to construct the state. (**c**) The probability that, upon measurement of energy, we find the system in a particular energy state

What we will do is "build" a position state by cleverly adding together all of the energy states. Using more mathematical language, we will construct a position state from a superposition of states from the energy basis set. Although this sounds strange–since energy states have loops and the position state we are interested in is a spike–we can, remarkably, build a spike from loops!

To help understand this concept, let's do a thought experiment where we put the system into a state that isn't a position state, but is mathematically simpler, in order to explore the concept of superposition. At the end of this section, I will show graphs to build the position state seen in the top right of Fig. 6.3 from the energy basis set. The example state we will use to explore superposition is shown in Fig. 6.4a.

Mathematically, the energy states (those shown in Fig. 6.2 plus all the other possible energy states) can be added together to construct the desired state. More formally, we say that a state can be constructed as a superposition of the energy basis set:

$$\psi = A_1\psi_1 + A_2\psi_2 + A_3\psi_3 + \ldots = \sum_{i=1}^{\infty} A_i\psi_i \tag{6.1}$$

where A_i is the amplitude of ψ_i that is mathematically determined to reconstruct the desired state ψ. The set of all states ψ_i is called the energy basis set. This equation represents the concept of superposition. We are constructing a specific state from a superposition of states from the energy basis set. The math required to calculate the amplitudes A_i is complicated and requires integrals, so I am just going to show you the results of the math in Fig. 6.4b. In practical terms, we start with the energy state with 1 loop (left picture in Fig. 6.2) and set the amplitude to 0.44. Next, we take the energy state with 2 loops (middle picture in Fig. 6.2), set the amplitude to 0.14, and add it to the energy state with 1 loop that had an amplitude of 0.44. We then take the energy state with 3 loops, set the amplitude to −0.38, and add it to the first two energy states. This process repeats, and the more energy states we include, the closer we get to the actual state. This is illustrated in Fig. 6.5. Adding the first two energy states together (top row) with the appropriate amplitude doesn't resemble the desired state, but after adding the first 30 energy states (third row), the resultant graph starts to look like the desired state. A superposition of the first

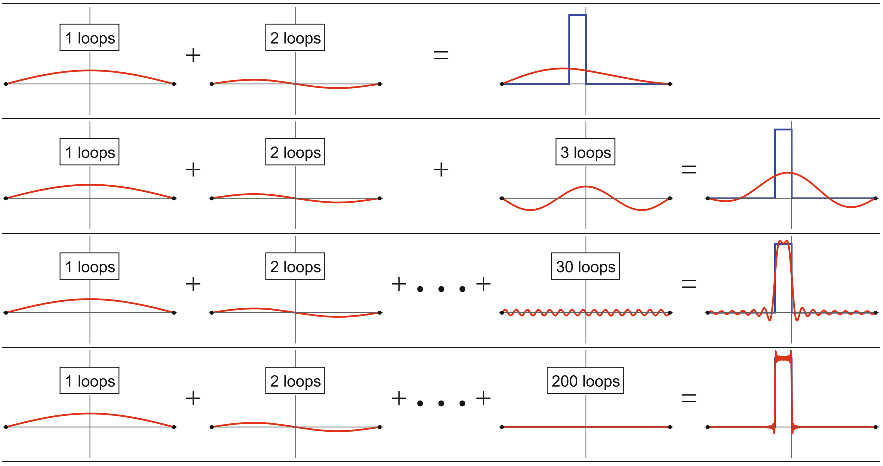

Fig. 6.5 An illustrative example of adding more and more energy states together to build the desired state. The amplitude of the energy state with 1 loop is 0.44, the amplitude of the energy state with 2 loops is 0.14, 3 loops has an amplitude of −0.38, etc. For the bottom row, the energy state with 200 loops looks flat to our eye, but it has a very small amplitude of 0.019

200 energy states (bottom row) results in a close reconstruction. Remarkably, loops can construct this state! Even more astonishingly, you can create any state you want (as long as it is a well-defined single-valued function) from the energy basis set. In other words, you can construct any state from a superposition of energy states.

Since we can construct a state out of energy states, we say that the state is a superposition of states from the energy basis set. Similarly, we could construct an energy state from a superposition of states from the position basis set. All we need is some mathematical method to determine the amplitudes of each of the position states so that when we add them all together we get the desired energy state.

In quantum mechanics, this is a very general idea. We can always construct a single state from any basis set using a superposition of states from another basis set. For example, we can construct a momentum state from a superposition of states from the position basis set, a position state from a superposition of states from the momentum basis set, a momentum state from a superposition of states from the energy basis set, and so on. This is a neat math trick, but is it useful? *It is perhaps the most useful math trick in all of quantum mechanics.*

Suppose we are in the state given by Fig. 6.4a. Now we want to measure the energy of the system. The amplitudes given in Fig. 6.4b can be used to calculate the probability that, upon measurement of energy, we will find the system in a particular energy state. All we need to do is square that amplitude. For example, the amplitude of the first energy state (1 loop) is 0.44. The probability that, upon measurement of energy, we find the system with one loop of energy is $0.44^2 = 0.19$, or 19%. The amplitude of the third energy state (3 loops) is −0.38. The probability that, upon measurement of energy, we find the system with 3 loops of energy is $(-0.38)^2 =$

0.15, or 15%. The probabilities are given in Fig. 6.4c. This rule is universal. If the system is in a particular energy state and we want to measure position, there is an associated probability for where we would find that quantum mechanical particle. Those probabilities are found by first writing the energy state as a superposition of all the position states from the position basis set with the correct amplitudes. Squaring those amplitudes[3] will tell you the probability that, upon measurement of position, a quantum mechanical particle will be found at a particular position.[4]

The above discussion is for two incompatible observables. The two incompatible observables have distinct basis sets, one for each observable. Measuring one of the observables puts the system in a single state from that observable's basis set. However, that single state can be constructed from a superposition of states from the other basis set. But, what if we had two compatible observables? Let's recap some of the important concepts:

- If the two observables are compatible, they share a basis set.
- If we measure one observable, the system is now in a state of that observable.
- If the two observables are compatible, measuring one observable does not change the system in a way that affects the measurement of the other observable.

Interestingly, we can use superposition to answer this question. Suppose energy and our made up observable A are compatible observables. We measure the energy of the system and find the system has energy E_3. The system is now in the energy state ψ_3, which is also the same as $\psi_{A,3}$. Let's write that energy state as a superposition of states from the basis set for observable A:

$$\psi_3 = 0 * \psi_{A,1} + 0 * \psi_{A,2} + 1 * \psi_{A,3} + 0 * \psi_{A,4} + \ldots \tag{6.2}$$

For the system we are exploring, building the energy state from a superposition of A states is really easy! ψ_3 and $\psi_{A,3}$ are literally the same sate. The probability that, upon measurement of A, we find the system with A_1 (the value associated with $\psi_{A,1}$) is 0%. The probability that, upon measurement of A, we find the system with value A_3 (the value associated with $\psi_{A,3}$) is 100%. The system is already in that state! Constructing the energy state from the A basis set is easy because there is one state from the A basis set that perfectly matches the energy state.

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[3] For completeness, the amplitudes could be complex numbers, which is something beyond the scope of this book. In the future, if you see an amplitude that is complex, you calculate the modulus squared of the amplitude.

[4] For completeness (again ☺), position and momentum are, mathematically, a bit harder to deal with since their measured values are continuous and not discrete like energy. The idea we explored is the same, but instead of the summation in Eq. 6.1 we would have an integral. As such, we would state something like, "There is a 25% probability we would find the particle between $x = 0.100$ nm and $x = 0.102$ nm". This is a minor detail, but one I wanted to include a footnote for those who have taken some more advanced math.