

A Chemical Progression

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Chapter 0

Notes to Our Test Reader

0.1 What We'd Like You to Do

Thanks a lot for agreeing to test read this chapter! (Sorry that we are giving you the impersonal version of this page. Don't worry, we do like you.) Note that we are interested in your comments on everything, ranging from content to grammar. However, the real thing that we are looking for is your thoughts on the style: is the narration at the right level of formality? Are the problems interesting? Too trivial? Do you find yourself being intrigued, or where do you find yourself being put off? How is the pace? Any parts that are too hard? The other parts are easy enough to fix later, but the style and ideas are pretty much the core of the book. That being said, feel free to nitpick about anything you want.

We'd appreciate if you can read in as much detail as possible, trying to work the problems as if you were actually a student reading the text. The more detailed feedback, the better. Also, if you could let us know about how much time you spent working on the chapter (for our reference), that would be great.

Finally, we'd appreciate answers to the following questions, relative to other chemistry texts you have read. If you have not read a chemistry text, just rate it against what you think the average high school chemistry text is like. Please express your answers as real numbers in the interval $[-1, 1]$ (so -0.204 would be acceptable, but 15 would not).

1. How interesting was what you read?	-1 (completely boring) 0 (neutral) 1 (amazingly cool)
2. How informative was what you read? This includes learning how to reason chemically.	-1 (there was information in this chapter?) 0 (learned a bit (or would have learned, had I not known it all)) 1 (wow, I learned (or would have learned) so much!)
3. How was the pace?	-1 (the tortoise, hare, and slug are all dancing on the finish line) 0 (just right!) 1 (was that the Concorde you passed back there?)
4. Would you recommend this over your other text?	-1 (no way) 0 (they are pretty much equivalent, in my opinion) 1 (your textbook rocks!)

0.2 How to Give Us Your Feedback

Any way that works for you. Our preferred method is via in-text comments (which are cleverly concealed under the pseudonym “Notes,” for reasons unfathomable), which you can make using Adobe Reader 7.0 or higher. (If it tells you that you don’t have permission to comment, we made a mistake and sent you the wrong copy; just let us know.)

0.3 Style of This Book

Confused by what’s up with our style? See <http://achemicalprogression.googlepages.com>.

0.4 Topics in our Problems and Solutions

0.4.1 The Problems

You’ll notice that the problems we include are usually not cut-and-dried problems with a definite answer like “5.” Rather, they tend to be open-ended tests of qualitative reasoning. This is because this is what chemistry really is at this level, and this book seeks to help students build a powerful chemical intuition. That being said, please let us know if you find that a question is too vague or have any other complaints!

All problems in a section are intended to build off of one another. The book as a whole will have a similar structure; each chapter building off the previous ones.

0.4.2 Symbols to Denote Problems

Here are the symbols you may see at the beginning of a problem. We might add more later if we think of any.

(To Think About) Problem is interesting but may be too difficult/ill-defined for student to answer alone. Will provide solutions to these.

(Open-Ended Exploration) Problem has many possible results; our answer is just one of many. Generally included to allow the student to do an amount of creative work; perhaps designing a theory or notation.

(*) Problem is difficult, but reasonably so.

0.4.3 The Solutions

Every in-text problem has its own solution. The end of chapter problems (in the Further Explorations section) will have solutions in the Solutions Manual (which has not yet been written). Exercises will also be solved there. We denote the end of a solution with a small box on the right side, as is standard with math texts.

0.5 Background Info for What You Are About to Read

You'll notice that the document begins with Chapter 2. That's because we have not yet written anything that comes before it. The following topics will be covered in Chapter 1:

1. The basic form of chemical reactions
2. Energy and its meaning
3. Meaning of matter and mass
4. Elements and compounds
5. Dimensional analysis and significant figures

The chapter you are about to read is currently planned to be Chapter 5 in our final book. Thus it assumes a working knowledge of the previous chapters.

- Chapter 1 (“Intro to Chemistry”) will deal with dimensional analysis, fundamentals of chemistry, and the basics of matter and energy (we haven't written it yet).
- Chapter 2 (“Discovering the Atom”) deals with the history and general structure of the atom, including subatomic particles (however, it does not cover electron configurations).
- Chapter 3 (“Quantum Mechanics”) presents a qualitative description of quantum mechanics.
- Chapter 4 (“Atomic Structure”) deals with the electronic structure of the atom. Covers ideas such as electron configuration and periodic trends.

We've been pretty careful to make sure that we assume no prior knowledge of chemistry or physics. We haven't yet decided how much math we're going to assume.

Thanks once again, and we look forward to your honest feedback. Feel free to tear us apart!

Greg and Will

Chapter 2

Discovering the Atom

In chemistry, we want to understand the properties of different kinds of matter and figure out how those properties are related to one another. Since science is a description of the real world, we usually start by looking at reality and then using our results to build theories. If the theories that we make are worth their salt, we can use them to make predictions, which can then be tested against reality. The experiments we perform then often lead to the observation of new phenomena, which starts the whole cycle over again.

So we see that theories are often layered upon one another. A new theory generally does not spring out of nowhere; it builds upon some existing foundation (or replaces a faulty one). Of course, there must be some lowest level foundation upon which everything else rests. In chemistry this is the theory of the underlying structure of matter, at the **microscopic**, or most small-scale, basic level. This should make sense; once we know what matter really looks like on that level, we can build up until we reach the **macroscopic** world, or the one we see around us. We will see that on all levels, the theories we develop will be powerful enough to make predictions, allowing us to solve a wide range of problems.

In this chapter, we are going to discover some components of the underlying theory of chemistry. We'll see that while our intuition works well at first, as we delve deeper some very weird things start to happen. Ultimately, we'll need to put our intuition aside in favor of a formal theory, which will be the subject of Chapter 3 (sorry for spoiling the plot!). In any case, our goal for this chapter is summarized in the following "Big Question."

The Big Question: Chapter 2

What is the underlying structure of matter, at its most basic level?

2.1 History

Problems

In our modern society, most people have at least a vague notion of how to answer Big Question 2. Indeed, ask someone on the street, and you will probably get an answer along

the lines of “Everything is built out of atoms, which are like tiny building blocks.” This might even seem obvious to you. But ask someone from the 1700s, and he will tell you that the very idea of an atom is preposterous. Indeed, the theory of the atom gained popularity only relatively recently in history, as we will see.

That being said, you might find it surprising that we have records of speculations about the atom dating from around 600 B.C.E. in India. And furthermore, the Greeks came up with their own ideas about atoms around 450 B.C.E.. For a quick warmup, let’s consider the following thought experiment.

THOUGHT EXPERIMENT 2.1.1: ZENO’S PARADOX

In ancient Greece, Zeno of Alexandria published a number of paradoxes that he was unable to resolve. One of them, relevant to our story of the atom, is posed in this thought experiment. Imagine yourself standing in a room; there is a door in front of you. Now, try to walk out the door. Before you can do this, note that you must first get halfway from where you stand to the door. But before you can perform this feat, you must first get halfway to that point. And before that, you must make it halfway to this halfway point. As you’ll see, we can continue this argument indefinitely, and thus you must complete an infinite number of moves before you can move in the first place! Since you can never get started, you can never move anywhere, and all motion is an illusion.

PROBLEM 2.1 (SOLUTION ON PAGE 10)

(Open-Ended Exploration) The ancient Greeks could not come up with a mathematical resolution to this paradox (although today we do have one). However, the Greeks did come up with another resolution, one that predicted the existence of some smallest unit of distance. Can you guess what this resolution is? (Hint: It has something to do with the atom.)

EXPERIMENT 2.1.2: LAWS OF DEFINITE AND MULTIPLE PROPORTIONS

The following experiment is a combination of the work of the French chemist Joseph-Louis Proust and the English schoolteacher John Dalton, both of whom were looking into the nature of matter around 1800. Dalton is generally credited with discovering the first evidence that the atom exists.

In this experiment, we consider quantitatively how elements combine. Specifically, we measure the relative masses of the elements making up various similar compounds. (In practice we can do this by decomposing the relevant compounds and simply measuring the masses of the resulting elements.) When we do this, we find that a given compound always has the same ratio of masses of constituent elements, regardless of where the compound came from. Below, we have tabulated some of our results among similar compounds.

- | | | |
|----|----------------------|---|
| 1. | Water | 8 g of oxygen for every 1 g of hydrogen. |
| | Hydrogen peroxide | 16 g of oxygen for every 1 g of hydrogen. |
| 2. | Nitrous oxide | 8 g of oxygen for every 7 g of nitrogen. |
| | Nitric oxide | 16 g of oxygen for every 7 g of nitrogen. |
| | Dinitrogen pentoxide | 20 g of oxygen for every 7 g of nitrogen. |
| 3. | Carbon monoxide | 4 g of oxygen for every 3 g of carbon. |
| | Carbon dioxide | 8 g of oxygen for every 3 g of carbon. |

PROBLEM 2.2 (SOLUTION ON PAGE 10)

Proust showed that different samples of the same compound have the same ratio of constituent elements, an observation he called the **Law of Definite Proportions**. The rest of Experiment 2.1.2 is due to Dalton. Using his results, he came up with the **Law of Multiple Proportions**, which is just a generalization of the results we have tabulated. Formally, it states that when we have two elements that combine with each other in different mass ratios, dividing one of these ratios by another will always yield a fraction with numerator and denominator both small whole numbers. (You should check that this law indeed applies to the data above.)

How does the Law of Multiple Proportions provide evidence for the existence of indivisible, fundamental building blocks of matter? You may assume that these building blocks have the following properties: they must combine with each other in fixed patterns, they are preserved in chemical reactions, and elements are made out of only one kind of building block with fixed mass.

PROBLEM 2.3 (SOLUTION ON PAGE 11)

So all substances are made of these building blocks, which are today known as **atoms**. In terms of atoms, what is a compound? What is a chemical reaction?

EXPERIMENT 2.1.3: CATHODE RAYS

This experiment is based off the work of the British physicist J. J. Thomson in 1897. Thomson explored the phenomenon of cathode rays, and he was able to show the existence of a subatomic particle, called an electron. Thus Thomson is considered to be the discoverer of the electron.

In this experiment, we need to use an electrical field. This is just something that acts to push or pull objects with a property called charge, which can be either positive or negative. In chemistry we generally write charges as a whole number, without any explicit units (we'll look at the implicit units on charge later in this chapter). This charge is additive, so if we have an object made out of two pieces each with a +1 charge, the **net**, or total, charge of that object would be +2. An object with a **net charge**, or total charge, of zero is not affected by an electric field.

A strong electric field is put between two **electrodes**, or metal surfaces. Some sort of beam, which is termed a **cathode ray**, is then emitted from one of the electrodes towards the other. We find that cathode rays are bent towards positive electrical charges and away from negative electrical charges.

However, when we put a sample of the metal composing these electrodes in a weak electric field, there is no visible effect or tendency for motion.

PROBLEM 2.4 (SOLUTION ON PAGE 12)

Since light is not affected by electrical forces, cathode rays must be made of particles. Could they be atoms of the metal electrode or maybe clusters of these atoms? If not, where did these particles come from?

PROBLEM 2.5 (SOLUTION ON PAGE 12)

What implications does this have for the indivisibility of atoms?

Solutions and Discussion (2.1)

THOUGHT EXPERIMENT 2.1.1: ZENO'S PARADOX

PROBLEM 2.1

(Open-Ended Exploration) The ancient Greeks could not come up with a mathematical resolution to this paradox (although today we do have one). However, the Greeks did come up with another resolution, one that predicted the existence of some smallest unit of distance. Can you guess what this resolution is? (Hint: It has something to do with the atom)

SOLUTION

Examine the assumptions implicit in our thought experiment. If you notice, the paradox only works if we can keep cutting distance down into smaller and smaller chunks. The Greek's resolution was that perhaps space cannot be infinitely divided, and there is a smallest, fundamental unit of distance. \square

This resolution was thought up by another ancient Greek philosopher, named Democritus. By extension, he predicted that all matter should be made up of indivisible units, or as he called them, "atomos" (meaning "uncuttable" in Greek). Thus, the existence of what we today call atoms was theoretically predicted thousands of years before there was any experimental evidence regarding them. Although Democritus's resolution wasn't necessarily true, since the paradox can be resolved mathematically, his idea still had merit. For the first time, people began thinking about what it would mean if there were a smallest, fundamental unit of matter.

For the next two thousand years, atomic theory sat essentially untouched. The atom might have seemed like a cool idea, but there was not yet any experimental evidence that it existed. But then in the 1800s, everything changed, due to the results of the following experiment.

EXPERIMENT 2.1.2: LAWS OF DEFINITE AND MULTIPLE PROPORTIONS

PROBLEM 2.2

How does the Law of Multiple Proportions provide evidence for the existence of indivisible, fundamental building blocks of matter? You may assume that these building blocks have the following properties: they must combine with each other in fixed patterns, they are preserved in chemical reactions, and elements are made out of only one kind of building block with fixed mass.

SOLUTION

In this problem, we want to show how an experimental result implies a theory. We can do this by showing that the theory predicts the result, and that in the absence of the theory the result is either unclear or false.

Consider two elements A and B that have reacted to form a compound. We notice that the Law of Multiple Proportions is really just saying that, in a compound with a given amount of A , we can only have certain amounts of B . In particular, these amounts should all be related by a simple ratio of whole numbers.

If we could cut matter down indefinitely, there certainly wouldn't be an apparent reason for this to be true. Why would nature care if we were to start off with a compound with $\frac{\text{Mass}(A)}{\text{Mass}(B)} = \frac{8}{1}$ and then try to make one with $\frac{\text{Mass}(A)}{\text{Mass}(B)} = \frac{8\sqrt{2}}{1}$? If there is no scale at which we cannot keep cutting a material without its losing its identity, we would think that we could have any of a continuum of ratios of masses of A to B , contrary to observation.

However, if matter can only be cut down until we reach an indivisible unit (characteristic of the element we are cutting) and, just as importantly, these units must combine with others in a regular way, the story is quite different. First of all, note that we get the Law of Definite Proportions for free, without doing any work (incidentally, we also get conservation of mass)! Now suppose that all units of A have a mass of a and those of B have a mass of b .

Consider some compound of A, B where $\frac{\text{Units}(A)}{\text{Units}(B)} = \frac{x}{y}$. Then we see that $\frac{\text{Mass}(A)}{\text{Mass}(B)} = \frac{ax}{by}$. Once we have this compound, we can reasonably construct a similar compound with, say, double the number of units of A , and hence twice the mass of A (we just stick an extra unit of A wherever there already is one). This results in a new mass ratio of $\frac{\text{Mass}(A)}{\text{Mass}(B)} = \frac{2ax}{by}$. Basically, we can add ax a couple times in the numerator and by a couple times in the denominator, ending up with something of the form $\frac{(\text{small whole number})}{(\text{small whole number})} \cdot \frac{ax}{bx}$, just as the Law of Multiple Proportions says.

However, there is certainly no way we can hope to end up with anything like a mass ratio of $\frac{\sqrt{2}ax}{by}$! Similarly, complicated mass ratios should be difficult, if even possible, to obtain.

Thus we have shown that the Law of Multiple Proportions implies the existence of some fundamental units of matter. Note the similarity to Democritus's argument here: we realized that if we could cut matter into arbitrarily small packets, we would end up with a result that is contrary to what we observe. \square

PROBLEM 2.3

So all substances are made of these building blocks, which are today known as atoms. In terms of atoms, what is a compound? What is a chemical reaction?

SOLUTION

First, think about what we already know. A given compound is built out of a definite combination of atoms, which are built up in a fixed pattern (why must the pattern be fixed? If it weren't, we could slice a compound into macroscopic pieces with differing ratios of atoms.). Thus a compound is simply some arrangement of atoms, which possibly interact with one another in some as-yet mysterious way.

Now what do we know about reactions? The atoms of a substance are themselves conserved in chemical reactions. So after a chemical reaction, we must end up with all of the atoms that we started with. This means that at an atomic level, the only method that we have of altering our reacting substances is by changing the positions of atoms.

Thus we have shown that a chemical reaction is just a rearrangement of atoms in some manner. Perhaps one reaction randomly mixes a bunch of atoms. Or maybe their linkage with one another has changed. In any case, we now know what a chemical reaction actually is, which gives us a great deal of predictive power. \square

With the discovery of the Law of Multiple Proportions, science at last had experimental evidence that substances are composed of some sort of basic building units, or atoms. Indeed,

at this point, Dalton was sure that he had proved the existence of an indivisible, smallest unit of matter. Unfortunately for him, he was not quite correct—while he had shown that macroscopic matter is built of atoms, he overlooked the possibility that atoms could consist of smaller particles still.

Box 2.1. Technical Note

As it turns out, the Law of Multiple Proportions by itself wasn't enough to convince everyone. In the 1900s, spectroscopy (a subject which we will explore later) provided the final evidence that indeed matter is made out of atoms.

EXPERIMENT 2.1.3: CATHODE RAYS

So now we know that everything in the macroscopic world is made up of atoms, which are packets of matter that we can use to build all the matter we see around us. At this point in our exploration, however, we really don't know much more about the atom. Is it truly indivisible, as we might like to think (and its name seems to imply)? If not, what can we break it down into? To answer these questions, we must turn to experiment.

PROBLEM 2.4

Since light is not affected by electrical forces, cathode rays must be made of particles. Could they be atoms of the metal electrode or maybe clusters of these atoms? If not, where did these particles come from?

SOLUTION

Our metal as a whole is not pushed or pulled by an electrical field. Thus it has a net charge of zero, since anything with a charge is affected by an electrical field. Since our substance is built out of many atoms, its net charge is just the sum of the charges on our atoms. But these atoms are all the same kind, meaning that they all must have a net of zero charge as well. Thus cathode rays aren't atoms of our substance, and they also aren't clusters of these atoms.

However, these particles certainly didn't appear out of nowhere, since this would violate conservation of mass. Thus, we are forced to conclude that cathode rays must have come from inside of the electrode's atoms. \square

PROBLEM 2.5

What implications does this have for the indivisibility of atoms?

SOLUTION

We have realized that cathode ray particles must have come from inside the sample's atoms. Thus the atom is divisible after all! \square

As we can see from Experiment 2.1.3, contrary to the Greeks' and Dalton's beliefs, the atom is itself divisible. We have already shown it contains at least two different types of particles. Other experiments prove that there are precisely three kinds of particles in an atom. These three types of **subatomic particles**, or those particles which make up atoms, are called electrons, protons, and neutrons. Note that when we refer to an atom, unless otherwise specified we mean one that has a net charge of 0.

2.2 Subatomic Particles

Problems

Now, you should be wondering, what are the properties of these subatomic particles? We can think about the subatomic particles as being incredibly tiny spheres. As it turns out, protons and neutrons can be further divided into sub-subatomic particles called **quarks**, but we currently think that electrons truly cannot be cut further. Quarks are crazy little objects that are always bound in protons and neutrons; we can never observe them on their own. Although further details of the subdivision of protons and neutrons are fascinating, they are not relevant to our discussion.

We explore other properties of subatomic particles in the following problems.

PROBLEM 2.6 (SOLUTION ON PAGE 16)

Electrically speaking, protons have a +1 charge, neutrons have charge of 0, and electrons have a -1 charge (this is why we can write charge without units; it is impossible to have a fractional charge on a normal particle). Note that the signs of these charges are arbitrary and do not have physical meaning; all that matters is that protons have a charge opposite to electrons. Given this information, what particle composes cathode rays?

PROBLEM 2.7 (SOLUTION ON PAGE 16)

We'll find that we often have to deal with extremely large numbers of objects. This is because individual atoms have such small masses relative to macroscopic objects, meaning in any reasonably-sized sample there are huge numbers of atoms. To make things easier on ourselves, we'll define a new unit that just means "a lot of things." The unit that chemists use is called a **mole**, and there are $6.0221 \cdot 10^{23}$ objects in a mole of that object, just as there are 12 objects in a dozen and 144 objects in a gross. As a conversion factor, we write $N_A = 6.0221 \cdot 10^{23} \text{ mol}^{-1}$ (why don't we include a unit of "objects"?), where N_A stands for **Avogadro's Number** after the chemist who first came up with the idea. Note that we can leave off the "e" at the end of "mole" as shorthand.

An amu is defined as $\frac{1}{[N_A]}$ g, where $[N_A] = 6.0221 \cdot 10^{23}$ denotes the value of Avogadro's number without units. **Protons** and **neutrons** have approximately equal masses close to 1.00 amu (atomic mass unit). More precisely, a proton weighs 1.0073 amu while a neutron weighs 1.0086 amu. **Electrons** have a mass of 0.00054858 amu (about 1/2000 amu), making their mass negligible for most purposes.

Find the mass, in grams, of 2.0 moles of protons. Going the other direction, if a mole of atoms of type X weighs x g, how many amu does a single atom of type X weigh?

After you have completed this problem, you should realize why the mole and atomic mass unit are such convenient units.

PROBLEM 2.8 (SOLUTION ON PAGE 17)

At the microscopic level, so far as we know there are four kinds of forces in our universe. We have listed them in order of increasing strength, when the particles they act between are very close.

The first, **gravity** acts to attract all particles with mass. It is considered a **long-range force** because it falls off relatively slowly with distance, decreasing only as the second power

of distance. The more mass two objects have, the more gravitational force there is between them. This force is thus significant between hugely massive bodies such as planets, but for our purposes, on the atomic level it is wholly negligible.

The second, the **electromagnetic force**, acts between pairs of particles with some (for our purposes) magical property called **charge**. As we have seen, the particles electrons and protons have charge. Charge can be either positive or negative. Like charges repel and opposite charges attract one another. The electromagnetic force falls off as the square of distance, and thus is also termed a long-range force.

The third, the **weak interaction**, acts to attract quarks together, even those bound in separate subatomic particles. This force is responsible for radioactivity. It falls off rapidly with distance, making it a **short-range force**.

The fourth and final force in our universe is the **strong interaction**, which also acts between pairs of quarks. It is extremely powerful at short ranges but falls off rapidly with distance; it is also a short-range force. However, at *very* short ranges it suddenly turns repulsive.

Given this information, find the forces that act between all possible pairs of subatomic particles (that is, electron, neutrons, and protons).

Box 2.2. Technical Note

To be precise, we should note that the weak interaction and electromagnetic forces are really just different aspects of the same thing. However, they are only unified at very high energies, and so we can disregard this.

Box 2.3. Delving Deeper

For those interested, the equation for the amount of gravitational force between two particles is

$$F_{\text{grav}} = \frac{Gm_1m_2}{r^2}$$

and the equation for the amount of electrical force is

$$F_{\text{elec}} = \frac{k|q_1||q_2|}{r^2},$$

where m_1, q_1 are the mass and charge on the first particle, m_2, q_2 are the mass and charge on the second particle, r is the distance between the particles, $G = 6.67 \cdot 10^{-11} \frac{\text{N}\cdot\text{m}^2}{\text{kg}^2}$, and $k = 8.98 \cdot 10^9 \frac{\text{N}\cdot\text{m}^2}{\text{C}^2}$ (the unit ‘‘C’’ stands for ‘‘coulombs’’; an electron has a charge of $1.6022 \cdot 10^{-19}$ C).

Just by looking at the values of G and k , you can imagine how much more powerful the electromagnetic force is than the gravitational force. To make things even worse for gravity, particles like electrons and protons have much smaller masses than charges.

PROBLEM 2.9 (SOLUTION ON PAGE 17)

Assume that two atoms must always be a reasonable distance away from one another, such

that short-range forces are negligible. What effect do the neutrons of an atom have on its interaction with other atoms?

PROBLEM 2.10 (SOLUTION ON PAGE 18)

Since atoms themselves have an internal structure, we see that we can have many different varieties of atoms. Furthermore, any given chunk of matter can contain a number of these different types of atoms. But at this point, such a chunk of matter is too complex for us to examine. We are thus motivated to examine substances composed of only single types of atoms; from these basic building blocks we can later work our way up to more complex compounds. (If you haven't noticed, this theme of starting from the simple and using it to work up to the complex is a general strategy we will see again and again in chemistry.)

Using the result of Problem 2.9, we see that we should define our basic substance, or **element**, as a collection of one or more atoms, all of which have the same number of protons. The number of protons in an element's atoms is called that element's **atomic number** and commonly denoted by Z .

However, there is a problem here—we have already defined the term “element”! Show that this new definition of an element is equivalent to the one that we came up with in Chapter 0.

PROBLEM 2.11 (SOLUTION ON PAGE 18)

To this day, we have either observed or created 117 different elements. The ordered arrangement of all these known elements is called the **periodic table**, which you can find on the inside cover of this book (unless we come up with a more creative location for it). On the modern periodic table, elements are arranged in order of increasing atomic number; the whole number by each element's name is that element's atomic number.

Just as atoms can have differing numbers of protons, they can have varying numbers of electrons. Of course, there is only one number of electron with which the atom is **neutral**, or has a net charge of 0 (why?). Now, an atom with an overall net charge is called an **ion**. Positively charged ions are called **cations**, and negatively charged ions are called **anions**.

A certain atom is ionized to a net charge of -1 . It is then found to have a total of 36 electrons. The original atom was an atom of which element?

Box 2.4. Fun Fact

The organization of elements on periodic the table has a number of very nice characteristics. For example, elements in the same column, or **group**, have similar physical and chemical properties, a phenomenon called **periodic law**. This is not a coincidence, as we will see when we explore atomic structure in Chapter 4.

Box 2.5. Notation

As you should notice on the periodic table, to each element is associated a one- to three-letter symbol. To refer to that element in chemical equations, we write its symbol rather than its name (this is a nice shorthand notation). In ordinary text we can write either one.

PROBLEM 2.12 (SOLUTION ON PAGE 18)

Not all atoms of an element have the same mass (why not?). The average mass of a given element's atoms as occurs in nature is the **atomic mass** of that element, denoted by M , and is the decimal number shown by that element on the periodic table. The atomic mass on the table is expressed in amu, or equivalently, grams per mole (you should have shown this equivalence in Problem 2.7).

How many neutrons does the average chlorine atom have? Express your answer to the nearest tenth. (Hint: You'll need to refer to the periodic table.)

Solutions and Discussion (2.2)

PROBLEM 2.6

Electrically speaking, protons have a +1 charge, neutrons have charge of 0, and electrons have a -1 charge (this is why we can write charge without units; it is impossible to have a fractional charge on a normal particle). Note that the signs of these charges are arbitrary and do not have physical meaning; all that matters is that protons have a charge opposite to electrons. Given this information, what particle composes cathode rays?

SOLUTION

Recall that cathode rays are deflected towards positive charges and away from negative charges. Thus they are negatively charged. This means that cathode rays must be composed of electrons. □

PROBLEM 2.7

An amu is defined as $\frac{1}{[N_A]}$ g, where $[N_A] = 6.0221 \cdot 10^{23}$ is the value of Avogadro's number (without units). Find the mass, in grams, of 2.0 moles of protons. Going the other direction, if a mole of atoms of type X weighs x g, how many amu does a single atom of type X weigh?

SOLUTION

When you see a problem that involves unit conversions, you should be ready to go for your dimensional analysis skills. That is all we do here.

Goal: Find the mass, in grams, of 2.0 moles of protons.

First, we start with our given 2.0 moles of protons. We want to end up with the mass of this many protons, so we will have to use a factor that gives us the mass of protons, which you should see is just $\frac{1.0 \text{ amu}}{\text{proton}}$. In order to make everything match, we also need to get our moles of protons into plain old protons and then amu into grams. The calculation is shown below.

$$2.0 \text{ mol protons} \cdot \frac{[N_A] \text{ protons}}{\text{mol protons}} \cdot \frac{1.0 \text{ amu}}{\text{proton}} \cdot \frac{1 \text{ g}}{[N_A] \text{ amu}} = 2.0 \text{ g}.$$

We could also reason through this problem qualitatively: we see that 2.0 moles of protons has a mass of 2.0 moles worth of atomic mass units. But a gram is just a mole of atomic mass units, and so we again arrive at a total mass of 2.0 grams.

Goal: If a mole of atoms of type X weighs x g, how many amu does a single atom of type X weigh?

This is again just a dimensional analysis problem. As before, we have two possible approaches. Formally, we can set up the following series of conversions (make sure you see the reasoning behind each step):

$$x \frac{\text{g}}{\text{mol}} \cdot \frac{[N_A] \text{ amu}}{\text{g}} \cdot \frac{1 \text{ mol}}{[N_A] \text{ atoms}} = x \frac{\text{amu}}{\text{atom}} = x \text{ amu},$$

where the final equality follows from the fact that atoms are dimensionless. Alternatively, we could again reason that a gram is a mole's worth of amu, and so a single atom of X must weigh x amu. \square

From this problem, we see that to convert from the molecular level to the macroscopic level, we don't have to do very much calculational work. Thus, for example, we see that atomic masses on the periodic table really have two meanings—they represent both the mass (in grams) of a mole of atoms and the mass (in amu) of a single atom.

PROBLEM 2.8

Find the forces that act between all possible pairs of subatomic particles (that is, electron, neutrons, and protons).

SOLUTION

We know that gravity attracts any two particles with mass, and the weak and strong interactions act to bind together protons and neutrons. Of course, for any practical purpose gravity is negligible on the scale of two particles, but it still acts. The same holds for the interactions between a proton and neutron that are relatively far apart. The electromagnetic force acts between charged particles. Thus, we obtain the following.

Particle	Force
Electrons and protons	Gravity, electromagnetic force.
Neutrons and protons	Gravity, weak interaction, strong interaction.
Electrons and neutrons	Gravity.
Two electrons	Gravity, electromagnetic force.
Two neutrons	Gravity, weak interaction, strong interaction.
Two protons	Gravity, electromagnetic force, weak interaction, strong interaction.

\square

PROBLEM 2.9

Assume that two atoms must always be a reasonable distance away from one another, such that short-range forces are negligible. What effect do the neutrons of an atom have on its interaction with other atoms?

SOLUTION

Because neutrons have no charge, the only long-range force available to them is gravity. But this exerts negligible force on other subatomic particles, so neutrons don't have any real bearing on an atom's interactions with other atoms. As far as other atoms are concerned, neutrons are just dead weight. Thus we see that the reactivity of an atom depends only on its number of protons and electrons. \square

PROBLEM 2.10

Using the result of Problem 2.9, we see that we should define our basic substance, or **element**, as a collection of one or more atoms, all of which have the same number of protons. The number of protons in an element's atoms is called that element's **atomic number** and commonly denoted by Z .

However, there is a problem here—we have already defined the term “element”! Show that this new definition of an element is equivalent to the one that we came up with in Chapter 0.

SOLUTION

Recall that in Chapter 0 we defined an element as a substance that cannot be broken down further by chemical means. Consider something that is an element according to our new definition. If we try to break it down, all the atoms in our product must still have the same atomic number as the original element. Thus we can only decompose an element into the same element, and our new definition implies the old one.

Now if we have something that is an element according to our old definition, it cannot be broken down by chemical means. All of its atoms must therefore have an identical chemical reactivity. But as we have seen, this means that they have the same number of protons. This completes the problem. \square

PROBLEM 2.12

How many neutrons does the average chlorine atom have? Express your answer to the nearest tenth. (Hint: You'll need to refer to the periodic table.)

SOLUTION

First of all, how can two atoms of the same element have different masses? This occurs when the two atoms have differing numbers of neutrons. Ah ha! So now we have qualitatively found the connection between mass and number of neutrons. This qualitative knowledge should guide our quantitative approach.

According to the periodic table, the average chlorine atom weighs 35.45 amu, while every chlorine atom has (exactly) 17 protons, by definition. We start with more significant figures than we strictly need because it is easier to drop significant figures later than pick them up. Thus the average chlorine atom has a mass of $(35.45 \text{ amu} - 17 \text{ protons} \cdot 1.007 \frac{\text{amu}}{\text{proton}} - 17 \text{ electrons} \cdot 0.0005486 \frac{\text{amu}}{\text{electron}}) = 18.32 \text{ amu}$ due to neutrons. (Note that if we had neglected the mass of electrons here, we would have been off in the hundredth's spot. Since we already have more significant figures than we need, ignoring the electrons would not make a difference. In general, we can just leave out the mass of electrons in such calculations.)

We complete the problem with some dimensional analysis: $18.32 \text{ amu} \cdot \frac{1 \text{ neutron}}{1.009 \text{ amu}} = 18.16 \text{ neutrons}$. (You should check to make sure that we kept the proper number of significant figures.) Rounding to the nearest tenth, we our final answer is 18.2 neutrons. Notice that we don't need to have an integral result here, since we are just looking at the average number of neutrons in chlorine. However, if we had wanted the number of neutrons in one *particular* atom, then our result would have to be an integer. \square

PROBLEM 2.11

A certain atom is ionized to a net charge of -1 . It is then found to have a total of 36 electrons. The original atom was an atom of which element?

SOLUTION

Since the atom has a net charge of -1 , it has one too many electrons. So when it was neutral, it had 35 electrons. Thus it must also have 35 protons, meaning this atom has $Z = 35$. Looking on the periodic table, we see that our mystery element is bromine.

Box 2.6. Notation

To denote a specific ion, the standard notation is just to write the symbol of the atom it comes from with a superscript of charge. Usually we write the size of the charge followed by the sign in superscripts, so for example as $2+$ rather than your usual $+2$. The same applies to ions made from different types of atoms “bonded” together, which we’ll explore in Chapter 5. So for example, we can write the sulfur anion with a -2 charge as S^{2-} , or the nitrate ion with -1 charge as NO_3^- . In this problem, the relevant ion was thus Br^- .

□

Box 2.7. Historical Note

In the 1860s, chemists knew about the existence of elements but not about atomic number. The Russian chemist Dmitri Mendeleev found that when he arranged the known elements in a table in order of atomic mass, the columns contained elements of similar chemical and physical properties. This was a very shocking result, and no one really knew why it should be true.

However, there were some discrepancies on his table. In order to rectify them, Mendeleev left some spaces on his table. He thus predicted the existence of other elements that had not yet been observed. Thus, even before the periodic table was well understood, it was a useful theoretical tool.

There was also a problem with some elements that seemed to be in the wrong order. There was nothing that Mendeleev could do in this case, given what was known at the time. But with the discovery of atomic number and the subsequent ordering of elements according to this number, the anomalies in the table have all been worked out.

Exercises for Section 2.2**EXERCISE 2.2.1**

Recall that $N_A = 6.0221 \cdot 10^{23} \text{ mol}^{-1}$. This is a pretty huge number, so gigantic that it’s hard to even think about. So let’s try to get a better handle on it. Suppose that we took 1. mole of lemurs and packed them into a sphere. What would the radius of this sphere be, in kilometers? Suppose that a lemur has a volume of 1. liter.

EXERCISE 2.2.2

What non-negligible forces act between two neutral atoms?

EXERCISE 2.2.3

- (a) How many moles of Na atoms are in 15.5 g of sodium?
- (b) How many carbon atoms are there in 10.0 g of carbon?
- (c) How much does a single gold atom weigh, in grams?

2.3 Snapshot of the Atom

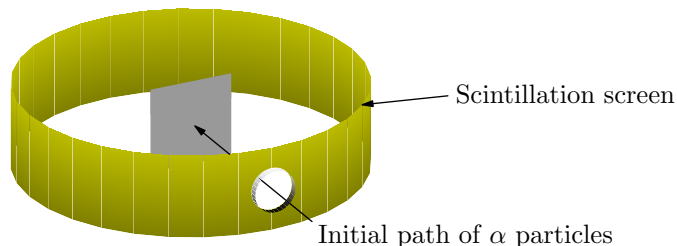
Problems

Since atoms are made out of smaller particles, they must have some internal structure. Just what is that structure? The modern picture of the atom has its origin based in experiment, and so we must delve into reality to answer this question.

EXPERIMENT 2.3.1: GOLD FOIL

This experiment, commonly attributed to Ernest Rutherford, was performed by his students Hans Geiger and Ernest Marsden in 1908. Also, although it is usually called the “gold foil” experiment, it was originally performed with platinum foil.

Radon gas is radioactive and emits alpha (α) particles (a topic which we will explore in depth in Chapter ??). These particles are massive (meaning they have mass, not that the mass is large) and have a +2 charge. When they are ejected from this element, they have a very large kinetic energy. We place a cylindrical screen around a thin piece of gold foil—only a few atoms thick—and cut a small hole in the screen, as shown below. The screen is covered with a zinc sulfide coating, which produces **scintillations**, or flashes of light, where the alpha particles hit it. We can then record the location of these scintillations.



We now place a sample of radon in front of the hole. In this way, alpha particles first hit the gold foil and then are detected by the cylindrical screen.

When we perform this experiment, we observe that most alpha particles continue through the foil undisturbed and strike the screen directly behind the foil. However, a small number of them are knocked far askew—some even ricochet back towards the source!

PROBLEM 2.13 (SOLUTION ON PAGE 21)

When the results of the gold foil experiment were first obtained, they were very surprising. As Ernest Rutherford said, “It was almost as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it had come back and hit you.” What information does this experiment tell us about the structure of the gold atoms? (Hint: Are the subatomic particles distributed uniformly throughout the atom?)

PROBLEM 2.14 (SOLUTION ON PAGE 22)

As we traverse the periodic table from top to bottom, more and more protons are added to the relevant elements. What do you expect will happen to the ratio of neutrons to protons in the relevant elements? Looking at the periodic table, is your prediction consistent with fact? (Hint: Elements need to have stable nuclei that will not fly apart.)

PROBLEM 2.15 (SOLUTION ON PAGE 22)

Looking back on our results from Problem 2.13, notice that our picture of the atom is still missing one crucial ingredient. In particular, we haven’t yet figured out where the electrons are located. Is it possible that they are located in the same place as the neutrons and protons?

Solutions and Discussion (2.3)

EXPERIMENT 2.3.1: GOLD FOIL

PROBLEM 2.13

When the results of the gold foil experiment were first obtained, they were very surprising. As Ernest Rutherford said, “It was almost as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it had come back and hit you.” What information does this experiment tell us about the structure of the gold atoms? (Hint: Are the subatomic particles distributed uniformly throughout the atom?)

SOLUTION

Immediately, we can tell that the structure of the gold foil is far from **homogeneous**, that is, the same no matter where you look. Since most of the alpha particles continue through unimpeded, we know that most of the gold foil (and hence the gold atoms) is empty space with a very small net electric field.

However, since the alpha particles were deflected with low probability, there must be some small region of highly concentrated charge. What is the sign of this charge? Well, some of these particles were knocked back towards the emitter. Thus this region repels the positively charged α particles, and the charge of this region is positive.

Putting this together, we can see that the protons of an atom must all be crammed in some small volume, but the electrons are not found there. The neutrons should also be found in this volume, bound to the protons via the strong interaction. If they were not located there, then there would be no force holding the neutrons in an atom, since neutrons are not affected by the electromagnetic force. \square

When Rutherford first performed the above experiment, he had hypothesized that the subatomic particles were distributed evenly throughout the substance. However, as we have seen this is impossible, and we can only make sense of the results of the gold foil experiment if we assume that the protons and neutrons of a given atom are all concentrated in a small volume. This region is called the **nucleus** (from the Latin word meaning “nut”) of the atom. Thus, protons and neutrons are collectively dubbed **nucleons**.

PROBLEM 2.14

As we traverse the periodic table from top to bottom, more and more protons are added to the relevant elements. What do you expect will happen to the ratio of neutrons to protons in the relevant elements? Looking at the periodic table, is your prediction consistent with fact? (Hint: Elements need to have stable nuclei that will not fly apart.)

SOLUTION

Let’s think about the forces holding the nucleus together. The nucleus exists as a delicate balance between opposing forces: a repulsion due to all proton-proton pairs interacting via the electromagnetic force and an attraction among all proton-proton, proton-neutron, and neutron-neutron pairs due to the strong nuclear interaction. Recall that although the strong interaction is much more powerful than the electromagnetic force at close ranges, its strength rapidly falls off with distance. Hence, the attractive force due to the strong interaction between two nucleons is weak when they are on opposite ends of the nucleus, although the electromagnetic force operates quite well at this distance.

Suppose we take a nucleus with n protons and add a new one. Well, protons can effectively only attract one another by the strong interaction if they are adjacent in the nucleus, and for larger values of n a smaller and smaller proportion of protons are in contact with one another. However, they all repulse each other strongly by the electromagnetic force. Thus the repulsion among protons stacks up more quickly than does any added attraction.

Since neutrons only provide attractions, for higher values of n we will need more and more neutrons per proton in order to keep things stable. Looking at the periodic table, we see that our prediction generally holds true in reality. \square

PROBLEM 2.15

Looking back on our results from Problem 2.13, notice that our picture of the atom is still missing one crucial ingredient. In particular, we haven’t yet figured out where the electrons are located. Is it possible that they are located in the same place as the neutrons and protons?

SOLUTION

At first glance, we might think that the electrons should be found in the nucleus, since they are attracted to it by the electromagnetic force. However, from the gold foil experiment we know that the nucleus is a region of intense positive charge. Furthermore, recall that we saw in Experiment 2.1.3 it is easy to strip electrons from an atom. Thus, we have to conclude that electrons are not found in the nucleus.

However, they are attracted to the nucleus. What stops them from plummeting down into it? The only possibility is that the electrons must orbit the nucleus in some fashion, in a way analogous to planets orbiting the sun (although, as we’ll see in Chapter 4, the details of these orbits are quite different from those of the planets’!). \square

At last, we have gained enough of an understanding of the atom to define it formally in terms of subatomic particles. An **atom** is an object with a stable nucleus composed of protons and neutrons, around which orbit electrons. In most contexts, atoms are taken to be neutral, as distinct from an ion, although this is not always the case. In this book, when the distinction is important we will be sure to point it out.

Box 2.8. Historical Note

The idea that electrons must orbit the nucleus was first formalized by Niels Bohr in 1913, when he came up with the aptly named **Bohr model** of the atom. According to Bohr, electrons move in circular orbits of fixed radius around the nucleus. However, it didn't take long for people to find that this model gave good predictions only for single-electron systems, such as H. Thus, a new picture of these orbits was necessary.

The modern picture of electronic structure, which agrees completely with all experiments tried to this day, is built on top of yet another theory. This later theory is called **quantum mechanics** (indeed, quantum's success as a theory is due in large part to this agreement). Probably unsurprisingly, the atomic model derived from quantum mechanics is called the **quantum mechanical** model of the atom.

We'll take a brief interlude here, and then delve into quantum mechanics in the following chapter.

Exercises for Section 2.3

EXERCISE 2.3.1

From our discussion in this section, we might think that we can add neutrons to nuclei with impunity. However, at very short ranges, the strong interaction suddenly turns repulsive (that is, it likes to keep nucleons at a fixed distance from one another, not too close and not too far). Given this information, is it possible to put too many neutrons in a nucleus? Why might a nucleus with too many neutrons be more stable if it split apart? (Hint: Maximizing attractions is equivalent to minimizing energy (why?).)

2.4 Further Explorations

PROBLEM 2.16

Due to Dr. Doug Osheroff

Suppose that all the electrons in your body suddenly changed their masses to ten times their current amount. What would happen to the volume of your body? (Hint: Think about the Bohr model of the atom.)

PROBLEM 2.17

Recall Albert Einstein's famous equation $E = mc^2$, where E is energy, m is mass, and

$c = 2.99 \cdot 10^8 \frac{\text{m}}{\text{s}}$ is the speed of light. Qualitatively, this equation states that mass is just another form of energy.

The masses of protons and neutrons we cited in the chapter are only accurate when the neutrons and protons are free, that is, when they are not bound in a nucleus. Should the mass of a bound nucleon be more or less than that of a free nucleon of the same type?

PROBLEM 2.18

In the Middle Ages, a number of people, known as alchemists, tried to achieve **transmutation**, or the changing of one element into another. In particular, they wanted to convert common substances, such as tin or lead, to gold. What does atomic theory say about the possibility of accomplishing transmutation by means of chemical reactions? (Hint: In a chemical reaction, can a nucleus be altered?)

PROBLEM 2.19

We saw in Experiment 2.1.2 that all substances are ultimately made up of atoms. The modern conception of an atom was first put forth as a theory by Dalton as his **atomic hypothesis**. This hypothesis had four parts:

1. All atoms of a given element are identical.
2. Atoms of different elements have different masses.
3. A compound is a specific combination of different types of atoms.
4. In chemical reactions atoms change their arrangements without being created or destroyed.

Since Dalton's day we have come to better understand what is actually going on at the atomic level. Which parts of Dalton's hypothesis are true? Which are not?

PROBLEM 2.20

The electromagnetic and gravitational forces both decrease at the same rate, as the square of the distance between the relevant particles. Among electrons or protons, the force due to the electromagnetic force is thus always much larger than that due to gravity. Why then are the motions of the planets around the sun controlled by gravity rather than its stronger cousin, the electromagnetic force?

PROBLEM 2.21

The radius of a nucleon is around 1 fm (femtometer, $1 \cdot 10^{-15}$ meters), and the volume of a nucleus is roughly proportional to the number of nucleons. The radius of a hydrogen atom is given by the **Bohr radius** of $a_0 = .53 \overset{\circ}{\text{A}}$ (angstrom, 10^{-10} meters) (other atoms typically have radii within an order of magnitude or two of this). Find the percentage of space in a hydrogen atom that is occupied by the nucleus.

PROBLEM 2.22

The density of iron at room temperature is $7.86 \text{ g} \cdot \text{cm}^{-3}$, while its atomic radius is 140 pm (picometer, $1 \cdot 10^{-12}$ meters). Assuming that iron atoms do not overlap with one another (which is not true but will give us a decent approximation) find what percent of the volume of iron is "empty space" (that is, not taken up by atoms).

Chapter 3

Quantum Mechanics

Around the turn of the 1900s, physicists thought they understood the workings of the world. The physics set down in Newton's day seemed to have the potential to predict everything; the only task left was to work out the remaining consequences of Newton's laws. However, a number of experiments yielded results that were completely inconsistent with both intuition and Newtonian mechanics. Some of these experiments dealt with very large systems, on the scale of galaxies; these experiments prompted Einstein to develop his theories of special and general relativity. (While the details of these experiments are interesting, they are outside of our current exploration.)

On the other hand, some experiments dealt with the behavior of very small systems, on the scale of atoms or smaller. As we will see, these experiments showed that the world of the very small is not bound by Newton's laws. A new set of rules, called **quantum mechanics**, had to be developed to describe this world. With the development of these modern theories, Newtonian mechanics became known as **classical mechanics**.

Throughout this chapter, we will be trying to answer the following Big Question, as we make the transition from classical mechanics to modern quantum physics.

The Big Question: Chapter 3

What are the laws that govern very small systems?

3.1 Classical Mechanics: Particles and Waves

Problems

In order to talk about the inconsistencies in small systems, first we need to understand the two kinds of objects that classical mechanics deals with: particles and waves. A **particle** is just some solid piece of matter. It is located at some definite location in space. On the other hand, a **wave** is an oscillation in a medium. Examples include ocean waves (water oscillating up and down) and sound (air oscillating back and forth). Waves have the shape of the sine function's graph.

PROBLEM 3.1 (SOLUTION ON PAGE 26)

The distance between crests of a wave (points of maximum height) is called that wave's **wavelength**, commonly denoted λ (the Greek letter lambda), and the number of cycles that pass a given point in a given period of time is called that wave's frequency, denoted ν (the Greek letter nu—don't confuse it with v !). Find the velocity of a wave with wavelength λ and frequency ν .

PROBLEM 3.2 (SOLUTION ON PAGE 26)

You should already be familiar with what happens when two particles collide (think about two pool balls). But what happens when two waves collide with one another? In particular, consider two overlapping waves, and say that for each (planar) position x , the height of one wave alone would be $H_1(x)$ and the height of the other wave alone would be $H_2(x)$. What is the height of the **superposed**, or combined, wave at x ?

Solutions and Discussion (3.1)

PROBLEM 3.1

The distance between crests of a wave (points of maximum height) is called that wave's **wavelength**, commonly denoted λ (the Greek letter lambda), and the number of cycles that pass a given point in a given period of time is called that wave's frequency, denoted ν (the Greek letter nu—don't confuse it with v !). Find the velocity of a wave with wavelength λ and frequency ν .

SOLUTION

Suppose for the moment that ν is in hertz, which you should recall from Chapter 0 is just cycles per second. Every second, for each cycle that passes a given point, the wave travels a distance of λ . Hence the total distance traveled is just $\lambda(\nu \cdot 1 \text{ second})$. Thus the velocity of the wave is $v = \frac{\text{distance}}{\text{time}} = \frac{\lambda(\nu \cdot 1 \text{ second})}{1 \text{ second}}$, or simply

$$v = \lambda\nu.$$

You should verify that dimensional analysis shows that this expression is reasonable (what is the dimension of a cycle?). □

PROBLEM 3.2

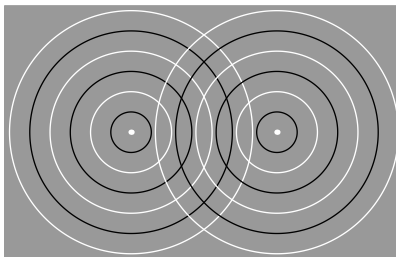
You should already be familiar with what happens when two particles collide (think about two pool balls). But what happens when two waves collide with one another? In particular, consider two overlapping waves, and say that for each (planar) position x , the height of one wave alone would be $H_1(x)$ and the height of the other wave alone would be $H_2(x)$. What is the height of the **superposed**, or combined, wave at x ?

SOLUTION

In order to get a better conceptual handle on this problem, let's translate into a more concrete example. Think about simultaneously dropping two pebbles in a pond, a few centimeters

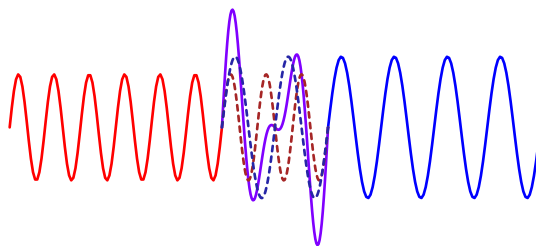
apart. They will each generate waves traveling outwards from where they land. What happens when the two waves reach each other? First let's make things simpler. Consider a plane that cuts through the two waves in a natural way, giving us a cross-section of the two waves. Then we can draw a picture like that shown below:

We can draw the following picture, where black represents places where the waves are at their maximum and white represents where they are at their minimum.



For the moment, let's pretend the right wave is not present, so the left wave is alone. Then at each position x , the height of our medium is just $H_1(x)$. Now add on the second wave. What will happen? Well, we can think about a wave as something that takes a fluid from a certain height and disturbs it according to its height function. Thus, at each position x we raise up an additional $H_2(x)$ (this includes "raising up" a negative distance). Thus we see that the height of the resulting wave at x should be $H_1(x) + H_2(x)$.

Alternatively, we could have approached this problem by drawing a simpler, one-dimensional diagram. We can just pay attention to the cross section of the waves and think about what happens when these cross sections overlap. For example, we draw the following, where the dotted lines are where the relevant wave would be without the other's interfering:



Looking back, perhaps such a diagram is simpler than our original two-dimensional plot. However, making this new one requires us to have some intuition about how overlapping waves combine, which is precisely what we need to figure out. In any case, we see as a general rule how helpful it is to be flexible in switching between different modes of thought (here, between one, two, and three dimensions). \square

We see that overlapping waves fundamentally affect one another, an effect called **interference**. This property of waves will become very important to us later in the chapter.

Exercises for Section 3.1

EXERCISE 3.1.1

Find the frequency of a wave with wavelength 2.51 m and speed $20.0 \frac{\text{m}}{\text{s}}$.

EXERCISE 3.1.2

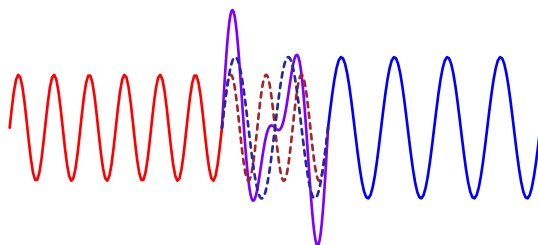
The maximum height of a wave is called its **amplitude**. Consider two waves, one of amplitude x and the other of amplitude y . What is the maximum possible amplitude of the wave resulting from these waves overlapping? What is the minimal possible amplitude?

EXERCISE 3.1.3

The places where a wave is at its maximum height are called **peaks** (a synonym for “crests”), and those where it is at its minimum are called **troughs**. When two waves overlap such that their peaks coincide, there is said to be **constructive interference**. If they overlap such that the peaks of one wave occur where the other wave has troughs, there is said to be **destructive interference**. Which type of interference results in a net wave of larger amplitude?

EXERCISE 3.1.4

In the first diagram of this section, reproduced below, where do the peaks occur? Where do the troughs occur?



3.2 Light

Problems

Now for most objects we observe in the world around us, it seems relatively easy to say whether they are particles or waves. A baseball clearly behaves like a particle (being made up of many sub-particles), while sound is a wave. But what about light? Is it a particle or a wave?

In 1864 the Scottish physicist James Clerk Maxwell theoretically derived that light is a wave consisting of oscillating electric and magnetic fields, traveling at a speed of $c = 2.99 \cdot 10^8 \frac{\text{m}}{\text{s}}$ (he did not arrive at this exact number, due to the experimental data available to him at the time). Thus light is sometimes called **electromagnetic radiation**. In a sense, since light does not travel on any physical medium—electromagnetic fields are conceptual rather than physical objects—it is pure energy: pretty cool, huh? At the time of Maxwell’s discovery, it seemed that the story of light was complete, but we’ll see shortly that there is much more to be said.

Box 3.1. Fun Fact

The letter c (the same c from Einstein's famous equation $E = mc^2$) is short for *celeritas*, which is Latin for “swiftness.”

Box 3.2. Kinds of Light

Light is commonly characterized by specifying its wavelength. The various other regions of the **electromagnetic spectrum** are given their own names. Note that the regions are not very well-defined, as the division of the spectrum is really just a human way of organization and has no physical significance. All types of light are generated in outer space, although on earth we usually only encounter low-energy electromagnetic waves (we'll explore why in the upcoming text)—this is quite fortunate, or else life as we know it would have no chance of survival. We have ordered the following in order of decreasing energy. (XYZ: may add a graphic at some point.)

Gamma ray These rays are emitted only from very high energy processes, such as the nuclear fusion reaction that generates the sun's light. Thankfully, these rays are blocked by the Earth's atmosphere, as they are very damaging to living tissue. Gamma rays can also accompany the radioactive decay of certain elements. They are usually defined as having $\lambda < 0.01$ nm.

X-ray These should be familiar to you as being used to see through objects that are opaque in the visible region, ranging from luggage to human beings. These are somewhat damaging to living tissue and are blocked by the Earth's atmosphere. They have wavelength between 0.01 nm and 20 nm.

Ultraviolet Most ultraviolet light is blocked by our atmosphere. However, a certain amount of it still gets through. Ultraviolet light can damage living tissue; it is responsible for sunburns. The wavelength of this electromagnetic radiation is generally taken to be from 20 nm to 400 nm.

Visible The light that we see. It ranges from a wavelength of about 400 nm (violet) to 700 nm (red). White light is made up of all colors of visible light. Lucky for us, visible light is not at all harmful to living tissue.

Infrared We feel these rays as heat. Night-vision goggles use infrared radiation to build a picture of the world. This radiation is too low in energy to be harmful to tissue. Its wavelength ranges from 700 nm to 1 mm.

Microwave As you might have guessed from the name, these rays are used in microwave ovens. Water absorbs light in this region, making microwaves a good way to give energy to your food (thus heating it up). These waves are also too low in energy to directly damage living tissue; their wavelengths are between 1 mm and 1 m.

Radio Very low energy radiation that is commonly used to transmit information. A radio, unsurprisingly, receives radio waves. These waves are not harmful, and have any wavelength longer than 1 m.

THOUGHT EXPERIMENT 3.2.1: ULTRAVIOLET CATASTROPHE

This thought experiment was first pointed out in 1905 by two independent groups of physicists. The first consisted of Einstein and the second was composed of Lord Rayleigh and Sir James Jeans.

Consider the phenomenon of **black body radiation**. A **black body** is just an object that radiates light at all frequencies but does not prefer any one particular frequency over another. Think about a stovetop—when it is warm, it radiates light in the infrared region, and when it is very hot it glows red. The fact that a black body does not prefer any frequency does not mean that it emits in all regions equally; rather, a black body emits many wavelengths but one maximally, with the maximum wavelength depending only on temperature.

Now, here's where the cool part comes in. Classical physics can be used to derive a law called the Rayleigh-Jeans Law, which shows that at a given temperature, the intensity of light emitted from a black body is inversely proportional to λ^4 . So as $\lambda \rightarrow 0$, the intensity of emitted light goes to infinity. In all, we find that a black body should be emitting enough light in the ultraviolet, X-ray, and gamma regions to completely destroy all life in the vicinity, an effect called the **ultraviolet catastrophe**. The Rayleigh-Jeans Law agreed well with experiment at high wavelengths but differed sharply at low wavelengths. (XYZ: might put in a graph)

PROBLEM 3.3 (SOLUTION ON PAGE 33)

(To Think About) Light of a given frequency is emitted from a black body by atoms oscillating at that same frequency (since atoms have charged particles in them, this oscillation makes oscillating electrical and magnetic fields). The Rayleigh-Jeans Law is derived by looking at the oscillation of atoms and assuming that, at a given frequency, these oscillations can have any amount of energy. Can you think of a clean way to modify our theory to avoid the ultraviolet catastrophe?

EXPERIMENT 3.2.2: PHOTOELECTRIC EFFECT

In 1887, the German physicist and mathematician Heinrich Rudolf Hertz (you guessed it, the man for whom the hertz is named) observed this effect experimentally. However, the theory behind the effect remained a mystery until Albert Einstein published an explanation in the year 1905.

When high frequency light is shined on a sample of metal, electrons are ejected from its surface. When we try this experiment with a number of different types of metals and different frequencies of light, we find that electrons are ejected precisely when the frequency of light is above a certain threshold value, characteristic of the specific metal under consideration. Also, the kinetic energy of the ejected electron varies linearly with the frequency of the incident light. Finally, electrons are ejected immediately, regardless of the **intensity**, or brightness, of the incident light. This phenomenon as a whole is called the **photoelectric effect**.

PROBLEM 3.4 (SOLUTION ON PAGE 34)

According to this experiment, which has a higher energy: light with a high frequency or light with a low frequency? How did you derive this?

PROBLEM 3.5 (SOLUTION ON PAGE 34)

Albert Einstein noticed that the photoelectric effect could be explained if you assumed that light consisted of discrete particles, which he called **photons**. Qualitatively, how does this assumption explain the photoelectric effect?

PROBLEM 3.6 (SOLUTION ON PAGE 34)

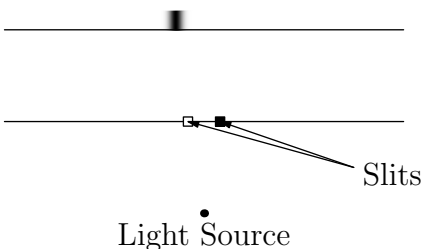
(*) Suppose that all the energy of a photon absorbed by the metal first goes towards ejecting an electron and then increasing the electron's kinetic energy (that is, none is dissipated as heat). Suppose also that as $\nu \rightarrow 0$, the energy of a photon goes to 0. Finally, let the minimum amount of energy required to eject an electron from the metal be Φ , also known as the **work function** of that metal. Quantitatively, how should the energy of a photon vary with frequency?

EXPERIMENT 3.2.3: DOUBLE-SLIT EXPERIMENT

This experiment is based off of one performed in 1801 by the English scientist Thomas Young. The results of this experiment are quite surprising, so hold onto your seat!

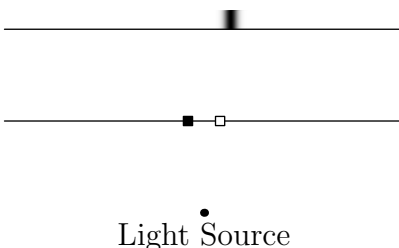
We take an opaque barrier and cut two narrow vertical slits in it. Behind the barrier we place a photosensitive screen. We cover the right slit and shine a beam of light at the barrier. The distribution of light on the back screen is as you might expect and is shown below. (Note we have represented an open slit as an unfilled box and a closed slit as a filled box.)

Light Distribution on Photosensitive Screen



Next, we cover the left slit and obtain the following distribution of light on the back screen.

Light Distribution on Photosensitive Screen



Such a distribution is called a **probability distribution** since it gives the probability of finding intensity of light in any given position.

PROBLEM 3.7 (SOLUTION ON PAGE 35)

Let the probability distribution of light in the first case be $P_1(x)$ and in the second case be $P_2(x)$, where x is some arbitrary position parameter. If light were composed of particles, what should the function for the probability distribution of light be when both slits are uncovered? What should the distribution diagram look like?

PROBLEM 3.8 (SOLUTION ON PAGE 36)

How does your answer to the previous exercise change if light were a wave? Note that you will only be able to answer this question qualitatively.

PROBLEM 3.9 (SOLUTION ON PAGE 37)

When we uncover both slits, we obtain the following distribution of light on the back screen. Do the results of this experiment lend credence to light's being a wave or a particle?

Light Distribution on Photosensitive Screen



Light Source

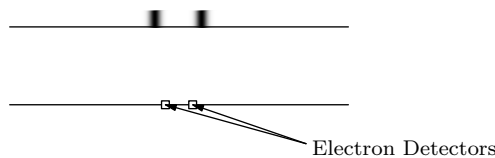
PROBLEM 3.10 (SOLUTION ON PAGE 37)

Of course, there is one issue here: maybe the pattern obtained only looks like it does because the photons hit one another after going through the slits. We can also perform this experiment with single photons of light. That is, rather than sending a full beam of light through the slits, we send one photon at a time. When we do this, over many trials the same pattern is obtained on the back screen. Does this seem to imply a photon is a particle or a wave?

PROBLEM 3.11 (SOLUTION ON PAGE 37)

(To Think About) However, we know that photons have some properties of particles. We can try to be clever and place photon detectors at one or both of the slits. In this way, we can see which slit the photon went through (or see if it somehow went through both!). When we perform this experiment with single photons, the detectors worked fine. We found that each photon went through only one slit, but the interference pattern vanished to be replaced by the distribution of light shown.

Light Distribution on Photosensitive Screen



Light Source

Take a moment to think about what is going on here. How could simply observing a system affect the probability distribution on the back screen?

Solutions and Discussion (3.2)

Historically, just when everyone thought they understood light, people found that there was a problem with their ideas. This was shown by the following thought experiment.

THOUGHT EXPERIMENT 3.2.1: ULTRAVIOLET CATASTROPHE

PROBLEM 3.3

(To Think About) Light of a given frequency is emitted from a black body by atoms oscillating at that same frequency (since atoms have charged particles in them, this oscillation makes oscillating electrical and magnetic fields). The Rayleigh-Jeans Law is derived by looking at the oscillation of atoms and assuming that, at a given frequency, these oscillations can have any amount of energy. Can you think of a clean way to modify our theory to avoid the ultraviolet catastrophe?

SOLUTION

Since the Rayleigh-Jeans Law gives inaccurate predictions, there must be a flaw in its derivation or the theory behind its derivation. If we instead assume that at a given frequency, the energy of oscillation of atoms is limited to a set of values, then the Rayleigh-Jeans Law is no longer valid. Now the question becomes, in what way should the oscillation of atoms be limited?

Well, first of all we could assume that there is only some allowable interval of energy for this oscillation. However, in this case there is no real apparent reason that this should be true, and what happens when we try to add some energy to an atom at the upper end of this interval? So we must do the next best thing and assume that there are discrete possibilities for this energy. That is, from any given energy oscillation we can't change by an arbitrarily small amount, destroying our continuum of different oscillatory energies. Note that since there is no arbitrary upper bound for energy of an atom, we don't run into the issues we did previously.

For what reason could the possible oscillations of an atom at a given wavelength be discrete? Well, note that if this is true, then light energy of a given frequency must be transferred in discrete packets rather than being able to be cut into arbitrarily small pieces. So we can justify our assumption if light cannot be infinitely divided. \square

The ultraviolet catastrophe essentially is just a modern-day version of Zeno's paradoxes. Just like Zeno ran into problems (so he thought, anyway) when he tried cutting distance into arbitrarily small pieces, it shows that if we could cut energy into arbitrarily small packets, then we would have (actual) problems. These packets of light are called **quanta** (singular quantum). The word "quantum" is Latin for "how much," and the fact that energy is quantized is extremely relevant to our exploration of chemistry.

Box 3.3. Historical Note

Interestingly enough, the idea that light must come in discrete packets did not originate with the ultraviolet catastrophe. Indeed, although you'll commonly see otherwise, the ultraviolet catastrophe was historically not a motivation for quantum mechanics! In 1900, in order to get his theory of thermodynamics to work, Max Planck had to assume that light is emitted in quanta (he coined this term). On the other hand, the ultraviolet catastrophe wasn't published until 1905, and even then it did not make any real ripples. It is only now, in retrospect, that we see the true significance of this result.

EXPERIMENT 3.2.2: PHOTOELECTRIC EFFECT

When it was proposed, Planck's idea was revolutionary, but there was not yet enough evidence to support it. The needed evidence came from another source, which we explore in this experiment.

PROBLEM 3.4

According to this experiment, which has a higher energy: light with a high frequency or light with a low frequency? How did you derive this?

SOLUTION

Since the kinetic energy of the ejected electrons increases with the frequency of light, and their kinetic energy must come from this light, light with a high frequency must have higher energy. Note that this fact is consistent with our claim in Box 3.2. \square

PROBLEM 3.5

Albert Einstein noticed that the photoelectric effect could be explained if you assumed that light consisted of discrete particles, which he called **photons**. Qualitatively, how does this assumption explain the photoelectric effect?

SOLUTION

Under Einstein's assumption, a beam of light consists of a bunch of particles. When one of these photons strikes an electron, what should happen? Well, just like one pool ball striking another, the electron should be knocked out of the atom, provided the photon had enough energy. Since this collision depends only on a single photon hitting a single electron, we see that the electron should be ejected immediately independent of the light's intensity.

Interestingly enough, in this picture of light, the intensity of light is proportional to the number of photons present. \square

Note that Einstein's photons are just quanta of light! So indeed the photoelectric effect provides evidence for Planck's quanta.

PROBLEM 3.6

(*) Suppose that all the energy of a photon absorbed by the metal first goes towards ejecting an electron and then increasing the electron's kinetic energy (that is, none is dissipated as

heat). Suppose also that as $\nu \rightarrow 0$, the energy of a photon goes to 0. Finally, let the minimum amount of energy required to eject an electron from the metal be Φ , also known as the **work function** of that metal. Quantitatively, how should the energy of a photon vary with frequency?

SOLUTION

We know that the energy of an ejected photon varies linearly with ν , the frequency of the incident light. We can thus write that

$$E_{\text{ejected electron}} = h\nu + C,$$

where h and C are some arbitrary constants. Also, we know that, by conservation of energy,

$$E_{\text{ejected electron}} + \Phi = E_{\text{photon}}.$$

Through substitution, we have

$$E_{\text{photon}} = h\nu + C + \Phi.$$

But ν is the only variable on the right side of this equation, and as $\nu \rightarrow 0$, $E_{\text{photon}} \rightarrow C + \Phi$. But we were given that as $\nu \rightarrow 0$, $E_{\text{photon}} \rightarrow 0$. Hence $C = -\Phi$ and we have

$$E_{\text{photon}} = h\nu.$$

This relation is completely general; it works for all types of light. The constant h is called **Planck's constant** and has a value of $6.6261 \cdot 10^{-34}$ J · s. \square

From Experiment 3.2.2, we see that light has properties of a particle! But we had said before that light was a wave. If this is not confusing, you are missing something. Perhaps Maxwell was wrong after all, and the fact that his theory worked was due to pure chance? Let's try another experiment and see if it can help us straighten things out.

Box 3.4. Quote

In the words of the Nobel Prize-winning physicist Richard Feynman, "If you think you understand quantum mechanics, you don't understand quantum mechanics."

EXPERIMENT 3.2.3: DOUBLE-SLIT EXPERIMENT

PROBLEM 3.7

Let the probability distribution of light in the first case be $P_1(x)$ and in the second case be $P_2(x)$, where x is some arbitrary position parameter. If light were composed of particles, what should the function for the probability distribution of light be when both slits are uncovered? What should the distribution diagram look like?

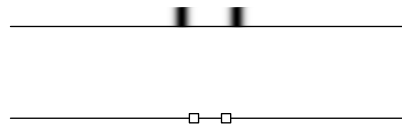
SOLUTION

Suppose that light is a particle. When we have both slits uncovered and shoot a particle of light at the slits, it must go through the left or the right slit. It does each of these with $\frac{1}{2}$ probability. Afterwards, its probability distribution on the back screen is just $P_1(x)$ or $P_2(x)$, depending on which slit it went through. Thus, the total function for the probability distribution of light when both slits are uncovered should be

$$\frac{1}{2}P_1(x) + \frac{1}{2}P_2(x).$$

To draw the appropriate diagram, we just have to take the two given diagram and superimpose them (why?). We thus obtain the following.

Light Distribution on Photosensitive Screen



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Light Source

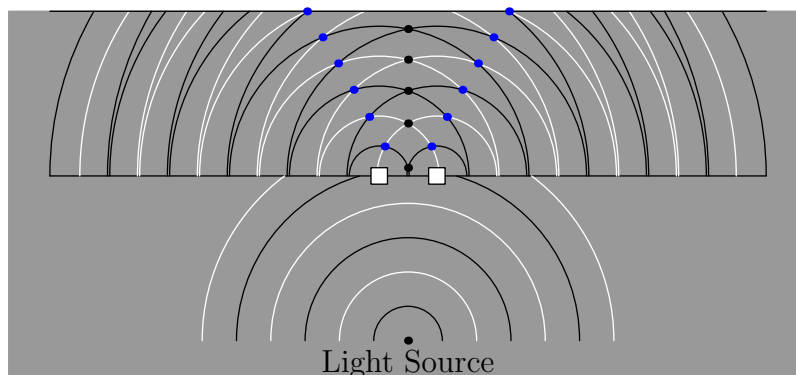
□

PROBLEM 3.8

How does your answer to the previous exercise change if light were a wave? Note that you will only be able to answer this question qualitatively.

SOLUTION

If light is a wave, then everything is changed. A wave does not have to go through one slit or the other; it can go through both at the same time! We can sketch the following diagram. Here, the black lines are where the wave is at a peak and the white lines are where it is in a trough. The blue dots are where the waves interfere destructively (a height of zero) and the black dots are where they interfere constructively.

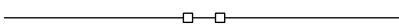


This gives us a rough picture of our probability distribution. Note we obtain alternating regions of high amplitude and zero amplitude. Thus, our probability distribution should consist of alternating regions of high probability and low probability. \square

PROBLEM 3.9

When we uncover both slits, we obtain the following distribution of light on the back screen. Do the results of this experiment lend credence to light's being a wave or a particle?

Light Distribution on Photosensitive Screen



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Light Source

SOLUTION

Since the results line up with what we expect from a wave and contradict the behavior of a particle, we see that this experiment implies light is a wave. \square

PROBLEM 3.10

Of course, there is one issue here: maybe the pattern obtained only looks like it does because the photons hit one another after going through the slits. We can also perform this experiment with single photons of light. That is, rather than sending a full beam of light through the slits, we send one photon at a time. When we do this, over many trials the same pattern is obtained on the back screen. Does this seem to imply a photon is a particle or a wave?

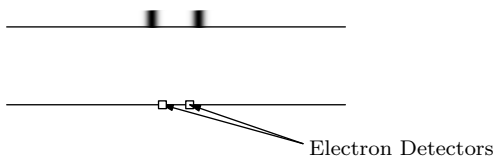
SOLUTION

We saw in our experiment that photons are able to self-interfere. However, if a photon just went through one slit, then no interference pattern would be obtained. Thus we must conclude that a single photon must go through both slits, and hence photons are waves. \square

PROBLEM 3.11

(To Think About) However, we know that photons have some properties of particles. We can try to be clever and place photon detectors at one or both of the slits. In this way, we can see which slit the photon went through (or see if it somehow went through both!). When we perform this experiment with single photons, the detectors worked fine. We found that each photon went through only one slit, but the interference pattern vanished to be replaced by the distribution of light shown.

Light Distribution on Photosensitive Screen



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Light Source

Take a moment to think about what is going on here. How could simply observing a system affect the probability distribution on the back screen?

SOLUTION

Consider what we already know. The probability distribution was characteristic of a wave when we did not know which slit the photon went through, and it was characteristic of a particle when we did. The only difference in experimental setup between these two cases was that we detected the photon as it went through the slits. Thus the very act of measuring altered the system.

This should make sense on some level to you. To measure a system, we have to interact with it somehow. Thus in addition to getting information from the system, we must pass information to it. No matter how careful we try to be in interacting with a system, it will thus always “know” that we are measuring it. This gives it the opportunity to respond in some way. \square

In sum, light is indeed both a particle and a wave! Its wave nature dominates when we are not observing it. However, when we try to determine where light is, it behaves like a particle. So our observation fundamentally changed the system, an idea that we will explore in more depth later.

Exercises for Section 3.2**EXERCISE 3.2.1**

We said in Box 3.2 that types of light are commonly characterized by specifying their wavelengths. Is there any reason they couldn't instead be characterized by specifying their frequencies?

EXERCISE 3.2.2

Night-vision goggles work by sensing infrared light and electronically representing it as visible. Why couldn't night-vision goggles instead be designed to use ultraviolet light?

EXERCISE 3.2.3

How much more energy does a photon of violet light (wavelength 400 nm) have than a photon of red light (wavelength 700 nm)? Express your answer in J.

EXERCISE 3.2.4

A certain atom is vibrating at a frequency of $1.5 \cdot 10^{15}$ Hz. Find the minimal energy it can be vibrating with.

3.3 Wave-Particle Duality**Problems**

The results of the double-slit experiment are extraordinarily important. They are completely counterintuitive, and are classically impossible. This should lead us to be suspicious of a lot of what we think we know at this point. For example, we said that electrons are particles. But how do we know they are not also waves?

EXPERIMENT 3.3.1: ELECTRON DOUBLE SLIT

The double slit experiment was first performed with something other than light in 1961, when researcher Claus Jönsson performed it with electrons. (However, it was not done with single electrons until 1974.)

We can repeat Experiment 3.2.3 with single electrons instead of photons. The same interference pattern is obtained. Again, when we place detectors at the slits, the interference pattern vanishes.

PROBLEM 3.12 (SOLUTION ON PAGE 40)

Well, what does this mean for our idea that electrons are just particles?

PROBLEM 3.13 (SOLUTION ON PAGE 40)

As you might suspect, these experiments show that we need to rethink our naive notions of the world. First of all, we need to formulate new principles. The first principle we need is that of **wave-particle duality**. Wave-particle duality is the idea that there is no such thing as what we classically think of as a “particle” or a “wave”, but rather all matter (as well as light) has characteristics of both. Now, if this is true, then matter should have a wavelength.

The **momentum** of a particle, usually denoted p , is defined as mv (where m is the particle’s mass and v is its velocity). Find a relation between the momentum and wavelength λ of a photon. (Note you will need to use Einstein’s equation $E = mc^2$ that relates the mass and energy of any object.) By extension, we will suppose that this same relation holds for all matter.

PROBLEM 3.14 (SOLUTION ON PAGE 40)

When we look at the world around us, it certainly doesn’t look like objects have a wavelength. Why is this? What is, for example, the wavelength in meters of a 5.00 g object traveling at 2.00 m/s?

PROBLEM 3.15 (SOLUTION ON PAGE 41)

According to the relation we derived in Problem 3.13, as $v \rightarrow 0$ at fixed mass, $\lambda \rightarrow \infty$. Why don’t we see a wavelength for objects that are at rest? (XYZ: this problem may be moved to a later chapter)

PROBLEM 3.16 (SOLUTION ON PAGE 41)

(To Think About) Wave-particle duality allows us to understand a great deal of the double-slit experiment, but not all of it. One issue that the double-slit experiment raises is that of the meaning of position. What ramifications does Experiment 3.3.1 have for talking about the position of an electron, as long as we are not detecting it?

EXPERIMENT 3.3.1: ELECTRON DOUBLE SLIT

PROBLEM 3.12

Well, what does this mean for our idea that electrons are just particles?

SOLUTION

It completely annihilates that idea. We already know that these experimental results can be obtained only by objects with wave-like properties. \square

Box 3.5. Historical Note

Historically, this experiment was not the first to show that electrons are wavelike. In 1929, two independent groups performed a different sort of diffraction experiment, verifying the De Broglie hypothesis (and incidentally garnering a Nobel prize).

PROBLEM 3.13

The **momentum** of a particle, usually denoted p , is defined as mv (where m is the particle's mass and v is its velocity). Find a relation between the momentum and wavelength λ of a photon. (Note you will need to use Einstein's equation $E = mc^2$ that relates the mass and energy of any object.) By extension, we will suppose that this same relation holds for all matter.

SOLUTION

Consider a photon of wavelength λ and frequency ν . We know that $E = h\nu$. Since we derived in Problem 3.1 that $c = \lambda\nu$, we see that $\nu = \frac{c}{\lambda}$. Also, we can obtain the following:

$$\begin{aligned} E &= mc^2 = h\nu \\ &= \frac{hc}{\lambda}, \end{aligned}$$

which after rearrangement yields $\lambda = \frac{h}{mc} = \frac{h}{p}$, where $p = mc$ is the momentum of our photon. Generalizing, we see that for any particle,

$$\lambda = \frac{h}{p} = \frac{h}{mv}.$$

This equation is known as the **De Broglie relation** and was first put forth by the French physicist Louis De Broglie in 1924. \square

PROBLEM 3.14

When we look at the world around us, it certainly doesn't look like objects have a wavelength. Why is this? What is, for example, the wavelength in meters of a 5.00 g object traveling at 2.00 m/s?

SOLUTION

The wavelength of an object is given by the De Broglie relation. We just need to plug and play. Make sure to keep track of units!

$$\begin{aligned}
 \lambda &= \frac{h}{m \cdot v} \\
 &= \frac{6.63 \cdot 10^{-34} \text{ J} \cdot \text{s}}{5.00 \text{ g} \cdot 2.00 \frac{\text{m}}{\text{s}}} \\
 &= \frac{6.63 \cdot 10^{-34}}{5.00 \cdot 2.00} \text{ J} \cdot \text{s} \cdot \frac{\text{s}}{\text{m}} \cdot \text{g}^{-1} \\
 &= 6.63 \cdot 10^{-35} \frac{\text{J} \cdot \text{s}^2}{\text{m} \cdot \text{g}} \cdot \frac{1 \text{ kg} \cdot \text{m}^2}{\text{s}^2} \cdot \frac{1000 \text{ g}}{\text{kg}} \\
 &= 6.63 \cdot 10^{-32} \text{ m}.
 \end{aligned}$$

Thus the wavelength of such an object is incredibly tiny, much too tiny for us to detect. Indeed, it should be clear that any macroscopic object we see moving at a reasonable speed will thus also have an undetectably small wavelength. The objects around us look like they have no wavelength because that wavelength is incredibly small. \square

PROBLEM 3.15

According to the relation we derived in Problem 3.13, as $v \rightarrow 0$ at fixed mass, $\lambda \rightarrow \infty$. Why don't we see a wavelength for objects that are at rest?

SOLUTION

Well, if an object were ever perfectly at rest, then by our relation, we would indeed have an infinite wavelength. At this point you should be suspicious: we certainly don't ever observe things with infinite wavelength. So there must be something wrong with our theory. First of all, we might be tempted to reject the De Broglie hypothesis, but there are no real grounds for doing so. Are we operating under any hidden assumptions?

Examining the exercise for a second time, you should see that we first need to obtain an object perfectly at rest (or at least with an incredibly small velocity). Do such objects exist? Well, let's suppose we have such an object. Now think about its atoms—they must all also be perfectly still. But this will happen only at 0 K, which is an impossible temperature to obtain. Thus we do not see wavelengths for objects at rest because objects are never really still; their atoms are always vibrating back and forth. \square

PROBLEM 3.16

(To Think About) Wave-particle duality allows us to understand a great deal of the double-slit experiment, but not all of it. One issue that the double-slit experiment raises is that of the meaning of position. What ramifications does Experiment 3.3.1 have for talking about the position of an electron, as long as we are not detecting it?

SOLUTION

When we were not detecting the electron, it was able to go through both slits at once. Thus we see that it does not have a well-defined position at a single point in space. It makes no

sense to talk about “the” position of an electron, since it is present over a spread of space, just like any wave.

Of course, when we observe the electron, we always see it at a single point in space. Thus when we detect an electron we can force it to choose one point in space to be located in. (We will explore the details of this “choice” in the Section 3.4.) \square

On the whole, we have shown that objects behave like waves when we are not looking at them and particles when we are.

Exercises for Section 3.3

EXERCISE 3.3.1

Find the mass in grams of a particle with velocity $63.2 \frac{\text{m}}{\text{s}}$ and wavelength $3.50 \cdot 10^{-35} \text{ m}$.

EXERCISE 3.3.2

The average atom of neon gas at 300.K has a velocity of $609 \frac{\text{m}}{\text{s}}$. Find the De Broglie wavelength of this average atom. Is the magnitude of this wavelength consistent with our claim that for common objects the De Broglie wavelength is too small to be seen in the macroscopic world?

3.4 Wave functions and Superposition

Problems

We can think of any wave as just something that has a value (which we can think of as its height) at each point in space. For example, with ocean waves, our space is only two dimensional, and the wave height is how physically high the water rises above the relevant point. On the other hand, for sound waves, our space is three dimensional, and this height is how intense the sound is at a given point. An electron wave is like a sound wave in that it has a value at every point in three-dimensional space.

The function giving this value is called a **wave function**, which we usually denote by Ψ (the Greek letter psi). A wave function can be either positive, negative, or zero. However, when we observe an electron (perhaps by using a detector), we force it to be in only one well-defined spot. The wave function is also useful here; according to the **Born** interpretation of quantum mechanics the probability of an electron’s being observed at a point in space is proportional to Ψ^2 at that point.

Box 3.6. Technical Note

Our description of the Born interpretation is not completely accurate, because the probability of being found at any one point is actually 0. Really, the Born interpretation is that the probability of an electron’s being found in a small volume of space is proportional to the value of Ψ^2 over that volume. To do this quantitatively, one needs to turn to calculus.

PROBLEM 3.17 (SOLUTION ON PAGE 44)

The points where Ψ passes through 0 are called **nodes** of the wave function (that is, points where $\Psi = 0$ and changes sign). What is the significance of these points?

PROBLEM 3.18 (SOLUTION ON PAGE 44)

Suppose that x and y are two points in space such that $\Psi(x) = -\Psi(y)$. What can we say about the probability of observing an electron at x as opposed to y ?

PROBLEM 3.19 (SOLUTION ON PAGE 45)

The principle that allows us to understand an electron's wave function is called **superposition**. In general, this principle lets us keep track of what's going on in a system when it is not being observed. Superposition is the idea that when a quantum system is not under observation, its wave function is the sum of the wave functions of all possible things that the system could be doing when we look at it. As a consequence, when a system has multiple possible things it can do, it does them all! So when we shoot an electron at the slits in Experiment 3.3.1, the overall wave function of the electron is given by the sum of the wave function of the electron while going through the left-hand slit and the wave function of the electron going through the right hand slit, giving rise to the observed interference. Superposition is closely related to wave-particle duality and gives us a more precise description of what is happening.

When a system in superposition is observed (maybe by taking some measurement), the system randomly chooses one of the possible states, and all of the others vanish. Indeed, in a sense they have never existed, although they may have affected the system through interference. This process is called the **reduction of quantum states**. Although the result is random in that it cannot be predicted ahead of time, not all states are equally likely to be chosen; they are weighted by their respective probabilities, as determined by their respective wave functions.

Previously, we saw empirically that an electron does not have a well-defined position, so long as it is not under observation. How does superposition theoretically give us this same result?

PROBLEM 3.20 (SOLUTION ON PAGE 45)

Since quantum mechanics states that the universe is, at the quantum level, random, does that mean that we can never predict anything with certainty? (Hint: What happens when we consider systems with lots and lots of random elements?)

PROBLEM 3.21 (SOLUTION ON PAGE 45)

How does superposition explain why our interference pattern vanished after placing photon detectors at the slits in Experiment 3.2.3?

PROBLEM 3.22 (SOLUTION ON PAGE 46)

When we measure some variable of a system, the variable goes from some indefinite superposition of values to a measurable result. However, we usually just measure an approximate value for a variable, meaning that the superposition is just squashed rather than being completely gone. Now if we want to measure more than one variable at a time, we can run into trouble. We can show that every observable variable of a system has a counterpart variable, called its **complement**, that becomes more indistinct as it becomes more definite. So as one

variable is measured to greater and greater certainty, its complement less and less known, or has a greater **uncertainty**.

This law is known as the **Heisenberg Uncertainty Principle**, and can be expressed quantitatively as

$$\Delta v \Delta v' \geq \frac{h}{4\pi},$$

where h is Planck's constant (which we saw earlier), Δv is the uncertainty on variable v , and $\Delta v'$ is the uncertainty on its complement v' . (More precisely, these deltas are the standard deviations—a concept from statistics—on the relevant quantities.)

- (a) Suppose that we know a variable v completely. Then what must be the uncertainty on its complement v' ?
- (b) The complement of position is momentum. Explain this fact in terms of the De Broglie relation and wave-particle duality.

THOUGHT EXPERIMENT 3.4.1: SCHRÖDINGER'S CAT

Erwin Schrödinger, the inventor of the quantum wave function, published this thought experiment in 1935 in an attempt to point out the absurdity of quantum mechanics. However, at this date scientists are completely comfortable with the result of this experiment. In any case, don't try this at home, kids!

Consider building an apparatus consisting of a vial of cyanide (a poison) and a radioactive element (one with an unstable nucleus) such that if the element decays (that is, its nucleus splits apart), the vial of cyanide is broken. Each minute, the compound decays with probability 50%. Now place the apparatus, along with a live cat, into a sealed box. If the vial is broken, the cat will die.

PROBLEM 3.23 (SOLUTION ON PAGE 47)

The cat is undeniably a macroscopic object. The decay of a radioactive element is undeniably quantum, and so it is affected by superposition. While the box is closed, do the statements “the cat is alive” or “the cat is dead” have any meaning? What about when the box is opened and we observe the system?

Solutions and Discussion (3.4)

PROBLEM 3.17

The points where Ψ passes through 0 are called **nodes** of the wave function (that is, points where $\Psi = 0$ and changes sign). What is the significance of these points?

SOLUTION

At a node, $\Psi^2 = 0$, and so there is a probability of 0 that the electron will be found there. Hence nodes are places where it is impossible for the electron to be located. \square

PROBLEM 3.18

Suppose that x and y are two points in space such that $\Psi(x) = -\Psi(y)$. What can we say about the probability of observing an electron at x as opposed to y ?

SOLUTION

The probability of observing an electron at a given point is proportional to Ψ^2 at that point. Since $\Psi(x)^2 = \Psi(y)^2$, the probability of finding an electron at x is the same as finding it at y . \square

PROBLEM 3.19

Previously, we saw empirically that an electron does not have a well-defined position, so long as it is not under observation. How does superposition theoretically give us this same result?

SOLUTION

Consider a quantum system consisting of an electron not under observation. There are many possible states that it could be in; in particular, it could be located in a number of different locations. By superposition, we know that the electron actually exists at all of these locations at once, and thus does not have a single well-defined position. \square

Box 3.7. Technical Note

Now, there are a few issues with superposition, as we've outlined it, the main one of which is the *measurement problem*. In particular, just what defines an observation? What gives an observer the power to force a quantum system to adopt a single state? However, these issues are more philosophical than chemical in nature and so we do not explore them. For our purposes, an observation is just a measurement we take of a system.

PROBLEM 3.20

Since quantum mechanics states that the universe is, at the quantum level, random, does that mean that we can never predict anything with certainty? (Hint: What happens when we consider systems with lots and lots of random elements?)

SOLUTION

Although we cannot predict the outcome of a single event with certainty, we can find the probability of each possible outcome. Thus, as we repeat that same event more and more times, the set of outcomes will align precisely with the probabilities, since that is precisely what it means to be a probability.

Hence we can predict average outcomes with very good certainty. So for example think about a system of just one electron with known wave function. We can't be certain what the electron will be doing for any given observation. But if we instead take a macroscopic system of trillions and quadrillions of electrons, we can be very certain about what is going on. \square

PROBLEM 3.21

How does superposition explain why our interference pattern vanished after placing photon detectors at the slits in Experiment 3.2.3?

SOLUTION

Before we placed the photon detectors, the only observation in the system was when the photon struck the photosensitive plate. Hence before this observation, the photons were in a superposition of states and were able to go through both slits, since there was a nonzero probability of going through one or the other.

However, after adding the photon detectors, we collapsed the superposition of states at the slits. This meant that the photon could only go through one slit or the other, but not both. Once through whichever slit it chose, the photon was again in a superposition, but it had already missed its opportunity to self-interfere. \square

Box 3.8. Quote

Well superposition is all well and good to explain how things happen, but just what exactly is happening with superposition? In the words of physicist Allen Adams, “Superposition means that we don’t know what . . . is going on.” As with much of quantum mechanics, superposition is something that gives the right results and makes sense mathematically, although we really don’t know the philosophical *why* behind it.

PROBLEM 3.22

- (a) Suppose that we know a variable v completely. Then what must be the uncertainty on its complement v' ?
- (b) The complement of position is momentum. Explain this fact in terms of the De Broglie relation and wave-particle duality.

SOLUTION

Goal: Suppose that we know a variable v completely. Then what must be the uncertainty on its complement v' ?

If we know v completely, then there is no uncertainty to its value. Thus $\Delta v = 0$. But if this is true, it seems that automatically $\Delta v \cdot \Delta v' = 0$, which is not larger than $\frac{h}{4\pi}$. So is this a problem? Actually, it would be, if we hadn’t let a hidden assumption get the better of us. Note that $\Delta v'$ doesn’t have to be a finite number. If we have an infinite uncertainty on v' (that is, we have absolutely no idea what its value could be; it is completely in superposition), then our problem vanishes. (In this case, the left hand side of Heisenberg’s Uncertainty Principle becomes $0 \cdot \infty$, which is indeterminate in value.) So, by process of elimination we must have that $\Delta v'$ is infinite.

Goal: The complement of position is momentum. Explain this fact in terms of the De Broglie relation and wave-particle duality.

Recall that the De Broglie relation gives us a relation between the momentum and wavelength of a particle. So as we measure momentum with more and more precision, we are also measuring wavelength with more and more precision. This means we are forcing our particle to behave more wavelike. But position is completely meaningless for a wave, and the net effect is that measuring momentum forces position to become more indefinite. Reversing this logic, we see that measuring position forces momentum to become more uncertain. Hence indeed position and momentum are complements. \square

Box 3.9. Fun Fact

You will sometimes see the Heisenberg Uncertainty Principle stated as the idea that as we measure a system, our instruments inevitably tamper with it and so we can never measure it precisely. This interpretation is mainly a historical artifact. It took quite some time for the idea of superposition to be widely adopted. Today we know that the fact that we cannot know a variable and its complement is not because of our measurement skills but rather because these quantities are in a superposition and are not well-defined.

We know at this point that superposition affects the quantum world. But does it have any ramifications for the macroscopic one? As we saw with the wavelength of macroscopic objects, it is entirely conceivable that the effects of superposition have no real effect on the scale of which we live.

THOUGHT EXPERIMENT 3.4.1: SCHRÖDINGER'S CAT**PROBLEM 3.23**

The cat is undeniably a macroscopic object. The decay of a radioactive element is undeniably quantum, and so it is affected by superposition. While the box is closed, do the statements “the cat is alive” or “the cat is dead” have any meaning? What about when the box is opened and we observe the system?

SOLUTION

At any given time, the element has a nonzero probability of being in a decayed state and a nonzero probability of not having decayed. Thus while it is not under observation, it is in a superposition of having decayed and not decayed.

Thus everything that the element's decay affects must be in a superposition as well. In particular, for the state where the element has not decayed, the vial is unbroken, while for the state where it has, the vial has broken. Thus the vial is in a superposition as well. Applying the same reasoning, we see that the cat is also in a superposition of states. Hence, without observing the system the cat is neither dead nor alive; rather, it is in a superposition of the states corresponding to each. It makes no sense to ask the question “Is the cat dead or alive?” because the state of the cat is a mixture of both!

Once the box is opened and the system is observed, the quantum states are reduced. This means that the element chooses whether or not it is decayed, according to the appropriate probability. This then determines whether or not the vial is broken and whether or not the cat is dead. So we do not see the superposition; instead, we see the cat as either dead or alive, as is normal in our experience. \square

Thus indeed macroscopic objects can be in superposition.

Exercises for Section 3.4

EXERCISE 3.4.1

(To Think About) Albert Einstein never accepted quantum mechanics at face value. This is encapsulated in his famous quote, “God does not play dice with the universe.” Take a moment to think about the consequences of quantum mechanics. Do you have any thoughts on the philosophical issues quantum implies?

EXERCISE 3.4.2

Find the minimal uncertainty in the position of an atom of helium if its velocity has uncertainty of $10.0 \frac{\text{m}}{\text{s}}$.

EXERCISE 3.4.3

It is entirely possible that suddenly all the atoms in book will suddenly be located a meter in the air above you. Why don't we observe this happening? Are there any circumstances under which this actually does happen, whether or not you notice it? (Hint: Think about superposition.)

EXERCISE 3.4.4

Using superposition, explain how spontaneous transitions can occur in systems between observations. For example, if we look away from an unstable nucleus, the next time we look it could have decayed.

3.5 Further Explorations

PROBLEM 3.24

Consider placing a particle inside of a box with thin, strong walls. Now scrunch the walls tighter and tighter, constricting the space available for the particle. If we have a device for measuring momentum inside of the box as well, then it looks like we can defeat the uncertainty principle, since we already know position and can measure momentum simultaneously! Where is the flaw in our plan?

PROBLEM 3.25

What should be the effect of continuously observing a certain unstable quantum system? (Hint: For example, suppose we keep an unstable nucleus under observation. Will it be able to decay?)

PROBLEM 3.26

In this problem we assume that all atoms we consider are atoms of a black body.

- (a) A vibrating atom must have at least enough energy to emit one photon of the appropriate frequency. Find the minimum amount of energy, in joules per mole, an atom needs to have in order to vibrate at a frequency of ν .
- (b) We know that the possible energies of a vibrating atom are quantized, but we don't know any details of this quantization. Let's try to find the second minimal amount of energy needed to vibrate at a frequency of ν . If we emit a photon from this vibration,

how much energy must be left? Therefore, how much energy do we need to have in the first place?

- (c) Generalize your answer to (b) to find all possible energies of an atom vibrating with frequency ν .

PROBLEM 3.27

(To Think About) Throughout the previous two chapters, we've seen that quantization is a common theme in the real world. Matter is quantized; it can only be traded in discrete packets (that is, atoms). Energy is quantized; we cannot divide a photon. Although we didn't discuss it, distance is also sort of quantized—on a very small scale (called the **Planck scale**), our concept of physics breaks down. As an interesting question to ponder, what would the consequences be of time's being quantized?

Chapter 4

Atomic Structure

We spent the previous two chapters building a picture of world at a very microscopic level, operating largely through experimentation. At this point we have essentially asked enough of the world and are ready to start building up our theory. In this chapter, we will look at how the atom is put together. Particularly, we will be looking at how electrons are organized around the nucleus. In a nutshell, we will be trying to answer the following question.

The Big Question: Chapter 4

What is the structure of the atom, and how does this structure determine an atom's properties?

4.1 Atomic Orbitals

Problems

PROBLEM 4.1 (SOLUTION ON PAGE 53)

In the Bohr model of the atom (which we mentioned in Chapter 2), electrons moved around the nucleus in circular orbits of fixed radius. What fatal holes does quantum mechanics poke in the Bohr model of the atom?

PROBLEM 4.2 (SOLUTION ON PAGE 53)

By our results from Problem 4.1, we need to modify Bohr's model to obey quantum mechanics. Instead of orbits, we'll say that our electrons are found in **orbitals**, or **atomic orbitals**, which are three-dimensional regions of space where the electrons that occupy them are very likely to be found (by convention, the cutoff for "very likely" is generally taken to be 90%). How does quantum mechanics predict that there should only be discrete levels of wave functions that will fit around a nucleus, rather than a continuous spectrum?

Box 4.1. Background Information

The electrons in a given orbital are described by the same wave function, which we can thus think about as the wave function of the orbital. (It is possible to actually compute this function and do calculations with it. We will not concern ourselves with such calculations, however. While these calculations are interesting in their own right, we can build our picture of the atom just as well qualitatively.)

Our qualitative description of a given orbital depends on four **quantum numbers** to completely specify the type of orbital and the state of the electron occupying it, if any. These numbers specify the various properties of the orbital by grouping them into categories of shared characteristics. We can think about orbitals as existing whether or not there is actually an electron in them, just as a bucket can exist whether or not it is filled with water.

PROBLEM 4.3 (SOLUTION ON PAGE 53)

The first category that orbitals are grouped according to is **energy level**, or **shell** (this term comes from the fact that these levels are discretely layered upon one another), and is given by the **principle quantum number** n . By the “energy of an orbital,” we really mean the electrical potential energy, with respect to the nucleus, of an electron within that orbital. Orbitals in the same shell have energies that are close to one another. So while different orbitals in a certain energy level can have different energies, they tend to be closer to in energy to one another than to an orbital in any other energy level.

The allowed values of n are the positive integers $1, 2, 3, \dots$. Energy level $n = 1$ has the lowest energy orbitals (so that means an electron in these orbitals would have the lowest potential energy), $n = 2$ is higher, and so forth.

Suppose that orbital A has $n = 1$ and orbital B is in the third energy level. All else being equal, which of these two orbitals takes up a larger volume? How do you know this?

PROBLEM 4.4 (SOLUTION ON PAGE 54)

Within the n th energy level are a number of different possible orbital shapes, or possible **subshells**. Each orbital shape is assigned a number $l = 0, 1, \dots, n - 1$, where l is called the **angular quantum number**. The **angular momentum** of an electron, or its tendency to be thrown away from the nucleus, is specified by this number (just think about an electron as a ball on a string being spun around your head). Two orbitals with the same value of l but different n have the same overall shape, although they have different volumes.

The number l also equals the number of **angular nodes** (often just called nodes) or surfaces through the nucleus where the orbital’s wave function changes sign (i.e. passes through 0).

How many differently-shaped orbitals are there in the n th energy level?

PROBLEM 4.5 (SOLUTION ON PAGE 55)

The third quantum number specifies the spatial orientation of an orbital. While l specifies the overall shape of an orbital, the third quantum number specifies the specific orbital we are talking about. It is given the symbol m_l (read “ m sub l ”) and is called the **magnetic quantum number**. The possible values of m_l are $-l, -(l - 1), \dots, 0, \dots, l - 1, l$.

How many orbitals are there in the n th energy level?

PROBLEM 4.6 (SOLUTION ON PAGE 55)

The fourth and final quantum number describes not an aspect of an orbital but rather a property of an electron in that orbital. Electrons have a property called **spin**; we can think of electrons as little billiard balls “spinning” on their axes in either the counterclockwise or clockwise direction, which gives rise to two possibilities for spin. (Note that electrons don’t *really* spin on their axis—spin is in reality some mysterious quantum mechanical property—but pretending otherwise gives us a convenient visualization.) Our fourth number, the **spin quantum number**, has a value of $m_s = -\frac{1}{2}, +\frac{1}{2}$ (read “ m sub s ”) and determines the spin of the relevant electron.

Is it possible to have an electron with the following (ordered) set of quantum numbers: $(n, l, m_l, m_s) = (4, 6, -3, \frac{3}{2})$?

Solutions and Discussion (4.1)

PROBLEM 4.1

In the Bohr model of the atom (which we mentioned in Chapter 2), electrons moved around the nucleus in circular orbits of fixed radius. What fatal holes does quantum mechanics poke in the Bohr model of the atom?

SOLUTION

In Bohr’s model of the atom, electrons move in definite orbits around the nucleus, just as planets move around the sun. However, quantum mechanics implies that electrons cannot be pinned to such a limited range of positions, especially with a fixed momentum. Rather, we need more uncertainty in the orbit, both in terms of position and momentum, in order for the Heisenberg Uncertainty Principle to be satisfied. □

PROBLEM 4.2

By our results from Problem 4.1, we need to modify Bohr’s model to obey quantum mechanics. Instead of orbits, we’ll say that our electrons are found in **orbitals**, or **atomic orbitals**, which are three-dimensional regions of space where the electrons that occupy them are very likely to be found (by convention, the cutoff for “very likely” is generally taken to be 90%). How does quantum mechanics predict that there should only be discrete levels of wave functions that will fit around a nucleus, rather than a continuous spectrum?

SOLUTION

From quantum mechanics, we know that energy is quantized. It comes in small indivisible packets. Since an electron has a certain potential energy depending on its orbital’s position relative to the nucleus, it follows that there must be discrete allowable wave functions.

Note also that if an electron is to, in some sense, orbit a nucleus, if we travel in a circle around the nucleus, the value of the wave function must be the same when we finish as it was when we started. This constraint is binding. Just like an organ pipe can only have certain notes played on it, a nucleus can only have certain wave functions fit around it. □

PROBLEM 4.3

Suppose that orbital A has $n = 1$ and orbital B is in the third energy level. All else being equal, which of these two orbitals takes up a larger volume? How do you know this?

SOLUTION

Orbital B has $n = 3$, and thus is higher in energy than Orbital A . An orbital has a high energy when an electron in it is at a high potential energy. Since electrons are attracted to the nucleus, potential energy must increase with distance from the nucleus (since if we let the electron go, it would fall towards the nucleus and could do work). Thus we see that B must keep the electron farther from the nucleus and hence takes up more volume than orbital A does. \square

PROBLEM 4.4

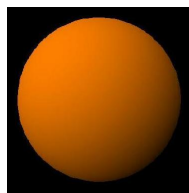
How many differently-shaped orbitals are there in the n th energy level?

SOLUTION

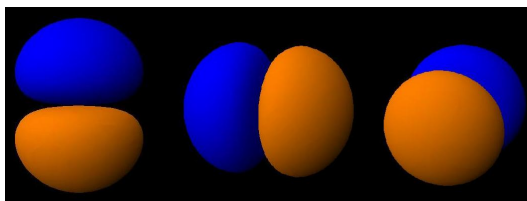
The shape of an orbital is determined by the angular quantum number l . We know that $l = 0, 1, \dots, n - 1$. Hence there is a total of $(n - 1) - 0 + 1 = n$ differently shaped orbitals (or equivalently, subshells). \square

Box 4.2. Types of Orbitals

The simplest orbital shape has $l = 0$. Such orbitals are called **s-orbitals**. They are spherically shaped and have no nodes passing through the nucleus. They are unique in both of these aspects; all other orbitals have nodal surfaces passing through the nucleus. Below we have included a picture of an s orbital. (Our convention is that blue represents a positive value of the wave function and orange a negative value.)



Next comes $l = 1$, the **p-orbitals**. These are shaped like dumbbells and have a nodal plane passing through the nucleus. The p -orbitals in a given energy level are all perpendicular to one another, as shown below. Note how having a nodal plane through the nucleus affects the shape of a p orbital. (XYZ: will try to get a better diagram at some point.)



Also, orbitals with $l = 2$ are called ***d*-orbitals** and have complicated shapes, which we will explore later. *d*-orbitals have two nodal surfaces passing through the nucleus. Last among the orbitals we will talk about are those with $l = 3$, or ***f*-orbitals**, which are very complicated and have equally complicated nodal surfaces. In principle, it is possible to have higher l values, and such orbitals would be labeled g, h, i, \dots , but such orbitals would be too high in energy and never arise in practice. On the whole, the two orbital types s and p are the ones we will be seeing the most of.

Now, you're probably wondering what the letters denoting the various orbitals mean. Really, in modern times they are just convention. They were originally chosen to describe the spectral lines associated with each orbital type—sharp, principal, diffuse, and fundamental. (We'll explore spectral lines in the Further Explorations section of this chapter.)

Below is a summary of the information we have presented about the various values of angular momentum.

Types of Orbitals

l	Type of orbital	Shape	Number per energy level	Nodes through nucleus
$l = 0$	s	Spherical	1	None
$l = 1$	p	Dumbbell-like: mutually perpendicular	3	1 (a plane)
$l = 2$	d	Ugly—will talk about later	5	2
$l = 3$	f	Very ugly	7	3
$l \geq 4$	g, h, i, \dots	Ditto—and never used anyway	$2l + 1$	l

PROBLEM 4.5

How many orbitals are there in the n th energy level?

SOLUTION

For each value of l , we know that m_l ranges from $-l$ to l . Thus there are $l - (-l) + 1 = 2l + 1$ orbitals. But l ranges from 0 to $n - 1$. So the total number of orbitals in the n th energy level is

$$(2 \cdot 0 + 1) + (2 \cdot 1 + 1) + \dots + (2 \cdot (n - 1) + 1) = 1 + 3 + \dots + 2n - 1 = n^2.$$

□

PROBLEM 4.6

Is it possible to have an electron with the following (ordered) set of quantum numbers: $(n, l, m_l, m_s) = (4, 6, -3, \frac{3}{2})$?

SOLUTION

It is certainly true that n can equal 4. But then $l \leq n - 1$, so $l = 6$ is not allowed. Thus an electron cannot have this ordered quadruple of quantum numbers.

Furthermore, an electron cannot have spin $\frac{3}{2}$; the only allowed spins are $\pm\frac{1}{2}$.

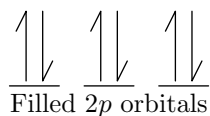
□

Box 4.3. Notation

We can represent an orbital and its electrons in several ways. First of all, we can simply list the relevant quantum numbers as we did in the previous problem (that is, (n, l, m_l, m_s)).

However, a much more common notation is as follows (indeed, this one is going to be assumed as basic knowledge for, well, basically the rest of your life, so you should get comfortable with it). First, to specify an orbital as a whole, we first writing the value of n and then the letter corresponding to l . If we like, we can then tack on a superscript of the number of electrons in that orbital. So for example, a p orbital with $n = 2$ could be written $2p$. Alternatively, an orbital in the third energy level with $l = 2$ and containing one electron could be denoted as $3d^1$.

There is also a schematical representation of orbitals. Here, we can write orbitals as horizontal lines and their electrons as vertical arrows, where arrows pointing up have $m_s = +\frac{1}{2}$ and arrows pointing down have $m_s = -\frac{1}{2}$; we have drawn an example below.



In summary, the first three quantum numbers specify properties of an orbital while the fourth specifies the spin of an electron it contains. When doing quantitative calculations, this organization of data is helpful. When doing things qualitatively, this organization of data becomes *crucial*. Using this model, we gain the power to predict an immense range of phenomena.

Exercises for Section 4.1**EXERCISE 4.1.1**

What is the lowest energy level that contains f orbitals?

EXERCISE 4.1.2

Use quantum mechanics to explain why electrons do not simply fall into the nucleus and stay there.

4.2 Orbital Filling**Problems**

PROBLEM 4.7 (SOLUTION ON PAGE 58)

In quantum mechanics, the **Pauli Exclusion Principle** states that no two electrons can be in exactly the same state. What does this imply about two electrons in the same atom having the same set of quantum numbers?

PROBLEM 4.8 (SOLUTION ON PAGE 59)

What is the maximum number of electrons that can occupy a given orbital?

PROBLEM 4.9 (SOLUTION ON PAGE 59)

Electrons with spins of the same sign are said to have **parallel spins**, and electrons with spins of opposite sign are said to have **antiparallel spins**. Given two electrons occupying the same orbital, what can we say about their spins: should they be parallel or antiparallel?

PROBLEM 4.10 (SOLUTION ON PAGE 59)

Consider an atom (not necessarily neutral) with n electrons. The **building-up principle**, or the **Aufbau Principle**, states that we can find the lowest-energy state of this atom inductively: take the lowest-energy state of the same atom with $n - 1$ electrons, and then put the remaining electron in the least-energy orbital available. (This rule has only a few exceptions, which we will explore later.) Said another way, electrons enter the orbitals of lowest energy first and then work their way up.

Now, orbitals with the same energy are said to be **degenerate**. In this problem we explore the case where the orbital with least energy is degenerate, meaning there is more than one orbital with this same energy.

The $2p$ orbitals of a given atom are degenerate. (To distinguish the individual orbitals we will arbitrarily label them $2p_x, 2p_y, 2p_z$, as is convention). Now consider filling an atom's orbitals using the building-up principle. Suppose that our first electron to enter the $2p$ orbitals entered the $2p_x$ orbital. The next electron then seems to have a choice: it can enter the $2p_x$ orbital or one of the (equivalent) $2p_y$ or $2p_z$ orbitals. Which option will the electron choose?

PROBLEM 4.11 (SOLUTION ON PAGE 59)

In the previous problem, there is a subtle energetic effect in action that you probably did not take into account. Electrons with parallel spins have a slightly lower total energy than electrons with antiparallel spins. Does this effect reinforce your answer to Problem 4.10 or counteract it?

PROBLEM 4.12 (SOLUTION ON PAGE 60)

An electron is said to be **paired** if it shares its orbital with a second electron. If it is the only electron in its orbital, it is said to be **unpaired**. Given two unpaired electrons in the same atom, what can we say regarding whether their spins are parallel or antiparallel? (Note the distinction between this problem and Problem 4.9.)

PROBLEM 4.13 (SOLUTION ON PAGE 60)

We are still missing one key piece of information. Namely, we know we need to fill orbitals in order of their energies, but what is the ordering of energies among orbitals? There is no really straightforward way to derive this qualitatively, but the overall energy of an orbital is

determined by $n + l$; the lower this value the lower the orbital's energy. If two orbitals have the same value of $n + l$, the one with the smaller n is lower in energy, as you might expect.

Find the highest-energy occupied subshell of an atom (not necessarily neutral) with 17 electrons. Does your answer depend on the identity of the atom?

Box 4.4. Notation

There is a standard notation for representing electron configurations. It is of the form

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 \dots,$$

where we group together electrons into subshells. Here, the superscripts represent the number of electrons in each subshell. Sometimes subshells that are not completely filled are written in expanded form to emphasize where the various electrons are; for example, $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$.

In writing electron configurations, why do we write the $3d$ orbital before the $4s$ if the $3d$ is higher in energy? While this statement is true for an empty $3d$ orbital, once it contains electrons its energy is lowered. This same statement holds true for higher nd and $(n + 1)s$ orbitals. This is a somewhat confusing statement, but blame quantum mechanics, not us!

PROBLEM 4.14 (SOLUTION ON PAGE 61)

A certain ion has charge -2 and electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. Write the formula of this ion.

Solutions and Discussion (4.2)

So now we know how to specify orbitals and the electrons they contain. But given an element with a certain number of electrons, how do we know which orbitals are occupied and how many electrons are in each? Or equivalently, how can we find the states of all the electrons in a given atom? The formal term for the list of occupied orbitals in an atom, together with how many electrons are in each, is the **electron configuration** of that atom.

We can solve this problem in general if the atom is in its **ground state**, or has the lowest potential energy possible, and exists as individual atoms (generally meaning that the element must be in the gas phase), since right now that is all our picture of orbitals can handle. If, however, our atom is not in its ground state, there are many possible electron configurations and more information is needed. Also, starting in Chapter 5, we will explore what happens when atoms group together.

Now before going on, why is it important to know the electron configuration of an atom? Remember that electrons control the reactivity of an atom. So if we know what the electrons of a certain atom are doing, then we can figure out what the atom as a whole will do.

PROBLEM 4.7

In quantum mechanics, the **Pauli Exclusion Principle** states that no two electrons can be in exactly the same state. What does this imply about two electrons in the same atom having the same set of quantum numbers?

SOLUTION

The state of an electron in an atom is completely determined by its quantum numbers. Thus the Pauli Exclusion Principle just means that no two electrons can have the same set of four quantum numbers. \square

PROBLEM 4.8

What is the maximum number of electrons that can occupy a given orbital?

SOLUTION

Consider two electrons in the same orbital. Since n , l , and m_l specify the orbital, we see that these electrons must have the same value for n , l , and m_l . But the state of an electron is specified by (n, l, m_l, m_s) , and hence for electrons in the same orbital to be in different states, they must have different m_s s. There are two possible values for m_s (namely $+\frac{1}{2}$ and $-\frac{1}{2}$), and so at most two electrons can occupy a given orbital. \square

PROBLEM 4.9

Electrons with spins of the same sign are said to have **parallel spins**, and electrons with spins of opposite sign are said to have **antiparallel spins**. Given two electrons occupying the same orbital, what can we say about their spins: should they be parallel or antiparallel?

SOLUTION

We derived in the previous problem that electrons in the same orbital must have different values for m_s . Thus one will have spin $+\frac{1}{2}$ and the other spin $-\frac{1}{2}$. We conclude that electrons in the same orbital have antiparallel spins. \square

PROBLEM 4.10

The $2p$ orbitals of a given atom are degenerate. (To distinguish the individual orbitals we will arbitrarily label them $2p_x, 2p_y, 2p_z$, as is convention). Now consider filling an atom's orbitals using the building-up principle. Suppose that our first electron to enter the $2p$ orbitals entered the $2p_x$ orbital. The next electron then seems to have a choice: it can enter the $2p_x$ orbital or one of the (equivalent) $2p_y$ or $2p_z$ orbitals. Which option will the electron choose?

SOLUTION

By the Aufbau principle, we know that the electron will enter the orbital that gives it the least potential energy. As far as the electron is concerned, what is the difference between the $2p_x$ and $2p_y$ orbitals? Since their shape and distance from the nucleus is the same, these are not factors in the electron's decision. However, the $2p_x$ already has an electron in it, and the $2p_y$ does not.

But as always, electrons repel each other. Thus if we put our next electron in the $2p_x$ orbital, it will be forced into close vicinity with the electron already there, resulting in an increase in potential energy. This does not happen with the $2p_y$ orbital. Hence, the electron will enter a vacant orbital before entering a half-filled one. In our specific case, it will enter one of the $2p_y$ or $2p_z$ orbitals. \square

PROBLEM 4.11

In the previous problem, there is a subtle energetic effect in action that you probably did not take into account. Electrons with parallel spins have a slightly lower total energy than electrons with antiparallel spins. Does this effect reinforce your answer to Problem 4.10 or counteract it?

SOLUTION

We showed in the previous problem that the electron will enter one of the vacant $2p_y$ or $2p_z$ orbitals rather than the half-filled $2p_x$ orbital, due to electromagnetic repulsion between electrons in the same orbital. Now suppose that both electrons were in the $2p_x$ orbital. We derived earlier that they must have antiparallel spins, which we are told results in an increase in energy. When the electrons are in different $2p$ orbitals, their spins may be parallel, and hence the system can have a lower total energy.

This effect therefore reinforces our answer; the energetics also favor having electrons in separate degenerate orbitals. \square

PROBLEM 4.12

An electron is said to be **paired** if it shares its orbital with a second electron. If it is the only electron in its orbital, it is said to be **unpaired**. Given two unpaired electrons in the same atom, what can we say regarding whether their spins are parallel or antiparallel? (Note the distinction between this problem and Problem 4.9.)

SOLUTION

We know that electrons have slightly lower energy when their spins are parallel. Two unpaired electrons are in different orbitals, and hence their spins do not have to be antiparallel. Thus, their spins will probably be parallel, unless there is a force acting to make their spins antiparallel. \square

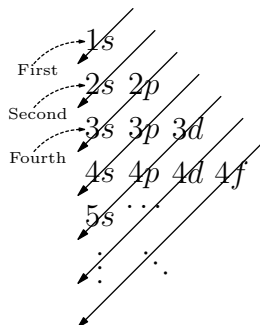
At this point, we have deduced **Hund's Rule**, the third and final principle of orbital filling. Hund's Rule states that if an electron has a choice among several equal-energy orbitals, it will enter a vacant orbital over a half-filled one. Furthermore, the spins of the unpaired electrons in a given atom will all be parallel.

PROBLEM 4.13

Find the highest-energy occupied subshell of an atom (not necessarily neutral) with 17 electrons. Does your answer depend on the identity of the atom?

SOLUTION

As presented, the information about the ordering of orbital energies is not overly easy to apply, since we need to keep track of so much data in order to use it. So let's convert it into a more compact graphical form. If we put orbitals into a table according to their n value in one direction and l value in the other, then we see that the orbitals on the diagonals of the table will have the same value of $n + l$. So we can construct the following diagram to give us the ordering of orbital energies. (Each row represents an energy level and contains all of the subshells in that level. If we draw lines from the top left corner on down as shown, the orbitals are hit in order of their energy.)

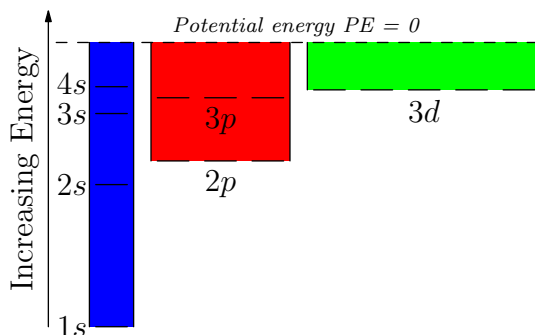


Hence we find that orbital energies obey the following: $1s < 2s < 2p < 3s < 3p < 4s < 3d < \dots$. Note that, contrary to what you might expect, $3d$ is *higher* in energy than is $4s$, and consequently $4s$ is filled first.

Now, can just list out orbitals and build them up until we reach 17 electrons. So we start with $1s^2 2s^2 2p^6$, which is ten electrons so far. We can add in the $3s^2$ orbital, leaving 5 electrons unaccounted for. The $3p$ orbitals are next to be filled, and we can fit these electrons in them as $3p_x^2 3p_y^2 3p_z^1$ (or simply $3p^5$). Hence the highest-energy occupied subshell is the $3p$ subshell.

Note we can also solve this problem by simply reasoning about the number of electrons in each energy level and subshell. Clearly the first energy level of this atom is filled, requiring only 2 electrons. The second energy level is also filled, requiring 8 electrons. Now, the third energy level requires 8 electrons before the $4s$ orbital starts filling, so we know that the highest-energy occupied subshell is in the third energy level. Two electrons fit into the $3s$ orbital, and the remaining 5 can be safely accommodated into the $3p$ orbitals. \square

We can also represent the ordering of orbital energies using an **orbital energy diagram**, such as the one shown below.



Recall that when two objects with a force acting between them have been pulled infinitely far apart, we usually set their potential energy as 0. Thus, the lower the energy of an orbital, the more negative its energy. This is demonstrated by our choice of shading in the above diagram.

PROBLEM 4.14

A certain ion has charge -2 and electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. Write the formula of this ion.

SOLUTION

There are a total of 18 electrons in this ion. Since right now our ion has a -2 charge, if we remove two electrons, it will become neutral. Hence we are looking for an element that is neutral with 16 electrons, or just one that has 16 protons. The element with atomic number 16 is sulfur. This means that the original ion was S^{2-} . \square

Exercises for Section 4.2

EXERCISE 4.2.1

What orbital is filled right after the $4d$ orbital?

EXERCISE 4.2.2

How many electrons in a given atom can have $n = 3$ and $l = 2$?

EXERCISE 4.2.3

Find the formula of an ion with a charge of $+1$ and electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.

EXERCISE 4.2.4

Find the electron configuration of a gaseous ion with 26 electrons.

EXERCISE 4.2.5

Since orbitals are given by a wave function, we can think about them as probability densities as well. These wave functions trail off continuously; there is no distance from the nucleus beyond which the value of a given orbital's wave function is always zero. So an electron can be found arbitrarily far from the nucleus. Given this, why do we still always observe electrons around their respective atoms, rather than in random distant locations?

4.3 Electron Configuration and the Periodic Table

Problems

PROBLEM 4.15 (SOLUTION ON PAGE 64)

Let's consider the **groups**, or columns, of the periodic table. Recall that the groups were originally established because elements in the same group have similar physical and chemical properties. But what is the electron configuration of Li? Na? K? Rb? What about O, S, Se, and Te? Do you notice any pattern? Does this pattern work in general? Why or why not? (Hint: Pay attention to the highest energy level)

PROBLEM 4.16 (SOLUTION ON PAGE 64)

How many elements are in the first **period**, or row, of the periodic table? The second? The third? In terms of orbitals, to what does the number of elements in each row correspond?

PROBLEM 4.17 (SOLUTION ON PAGE 65)

The **core electrons** of an element are those below filling the energy levels below the valence shell; **valence electrons** are those in the valence shell. (Note that the distinction between valence and core electrons is blurred in the case of d -orbitals). Consider the core electron configuration of Na. What element has that as its overall electron configuration? In general, the core electron configuration of a given element will be the same as the electron configuration of an element in what group of the periodic table?

Box 4.5. Blocks of the Table

The periodic table is separated into several blocks, each labeled according to whatever type of subshell is being filled, or has just been filled, in the elements in that group. The groups of the table are given numbers, starting from 1 on the left up to 18 on the right. (Note that hydrogen, although commonly written as though in Group 1, is not considered an element of any group.) The **s-block** consists of Groups 1 and 2, the **d-block** consists of Groups 3-12, and the **p-block** consists of Groups 13-18. The **main group** is the union of the s and p blocks.

Now look at the two blocks of the table that are set off by themselves. The first, from La to Lu, is called the **lanthanides** (or **lanthanide series**), and corresponds to filling the $4f$ -orbitals. The second, the **actinides** (or **actinide series**), goes from Ac to Lr and corresponds to $5f$ -orbital filling. Together, the lanthanides and actinides constitute the **f -blocks** of the periodic table.

We generally find metals on the left of the table and nonmetals on the right. Here is a listing of the names of the various groups of the table:

- The elements in Group 1 are called the **alkali metals**
- Those in Group 2 are called the **alkaline earth metals**
- The members of the d -block are known as the **transition metals**
- The elements B, Si, Ge, As, Sb, Te, and Po are called the **semimetals** or **metalloids**, as they have properties of both metals and nonmetals. If you look at their location on the table, they made a kind of staircase shape, often called a stepped line.
- The Group 17 elements are called the **halogens**.
- The Group 18 elements are called the **noble gases**.

PROBLEM 4.18 (SOLUTION ON PAGE 66)

Most of the time ground-state electron configurations line up where we would expect, following the building-up principle to the letter. However, there are a few exceptions. Remember that the $3d$ orbital changes its relative ordering with the $4s$ after an electron is added. Also, a fully-filled subshell gains a degree of stability, as does a half-filled one, albeit to a lesser extent. This secondary effect is enough to provide for a deviation in the electron configuration of a few d -block elements.

In the fourth period, only Cr and Cu are exceptions to the Aufbau Principle. Predict the electron configurations of each.

Solutions and Discussion (4.3)

PROBLEM 4.15

Let's consider the **groups**, or columns, of the periodic table. Recall that the groups were originally established because elements in the same group has similar physical and chemical properties. But what is the electron configuration of Li? Na? K? Rb? What about O, S, Se, and Te? Do you notice any pattern? Does this pattern work in general? Why or why not? (Hint: Pay attention to the highest energy level)

SOLUTION

We proceed by applying the rules for electron filling.

Element	Number of Electrons	Electron Configuration
Lithium	3	$1s^2 2s^1$
Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Potassium	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	37	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$

Note that in all cases, the electron configuration of the highest energy level is the same (just ns^1).

For O, S, Se, and Te, proceeding in the same manner, we obtain the following

Element	Number of Electrons	Electron Configuration
Oxygen	8	$1s^2 2s^2 2p^4$
Sulfur	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Selenium	34	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
Tellurium	52	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^4$

The exact same trend is obtained: the electron configuration of the highest energy level is identical, just $ns^2 np^4$.

Thus our general trend is that all elements in a group have the same highest energy level electron configuration. Does this hold in general? Well, since all the Group 1 elements have the same electron configuration in their highest level, adding one electron all Group 2 elements must satisfy our trend as well. Repeating our reasoning, we see that indeed all groups have the relevant property. \square

PROBLEM 4.16

How many elements are in the first **period**, or row, of the periodic table? The second? The third? In terms of orbitals, to what does the number of elements in each row correspond?

SOLUTION

There are 2 elements in the first period, 8 elements in the second period, and 18 in the third. The number of elements in each row equals twice the number of orbitals in each energy level, or simply the number of electrons in each energy level. \square

As you should have deduced from Problems 4.15 and 4.16, the periodic table is, at its heart, a manifestation of electron configurations. The n th period corresponds to filling the n th energy level, and thus all elements in a given period have the same energy level of their **valence shells**, or outermost layer of electrons.

Moving down a group, all elements have the same valence configuration, although their valence configurations belong to different energy levels. For example, the Group 17 elements (F, Cl, Br, etc.) all have a valence configuration of ns^2np^5 .

PROBLEM 4.17

The **core electrons** of an element are those below filling the energy levels below the valence shell; **valence electrons** are those in the valence shell. (Note that the distinction between valence and core electrons is blurred in the case of d -orbitals). Consider the core electron configuration of Na. What element has that as its overall electron configuration? In general, the core electron configuration of a given element will be the same as the electron configuration of an element in what group of the periodic table?

SOLUTION

Sodium has 11 valence electrons. Thus its electron configuration is $1s^22s^22p^63s^1$. Its valence configuration is $3s^1$, meaning sodium's core configuration is $1s^22s^22p^6$, which is the configuration of Ne.

In general, if we strip away the valence shell of an element in the n th period, we move to the end of the $(n - 1)$ st period. Thus we will always end up in Group 18, meaning we end up with the electron configuration of a noble gas. \square

Box 4.6. Notation

Most of the time, for a given element all that we care about is its valence shell, since the core electrons tend to remain fixed (why?). Furthermore, valence electrons are responsible for the chemical reactivity of elements, since they are the only objects that an atom is able to mess with to try to lower its energy (besides nuclear decay, which we will discuss in Chapter ??). Thus, we need a more compact notation for our electron configurations, one where we can compress the core electrons.

Based on Problem 4.17, we can invent a general notation that is compact enough for our purposes, yet still clearly conveys the necessary information. Instead of writing the core electron configuration, we can just write [Noble gas], where this "Noble gas" is the element with the same electron configuration as the core.

Take for example Ca from the fourth row of the periodic table. It has a valence configuration of $4s^2$, and its core electrons look exactly like those of Ar. Thus we write that Ca's electron configuration is $[\text{Ar}]4s^2$. Now for something like Mn, we must write $[\text{Ar}]3d^54s^2$; even though the $3d$ orbitals belong to the third energy level, they are not part of Ar's electron configuration.

PROBLEM 4.18

Most of the time ground-state electron configurations line up where we would expect, following the building-up principle to the letter. However, there are a few exceptions. Remember that the $3d$ orbital changes its relative ordering with the $4s$ after an electron is added. Also, a fully-filled subshell gains a degree of stability, as does a half-filled one, albeit to a lesser extent. This secondary effect is enough to provide for a deviation in the electron configuration of a few d -block elements.

In the fourth period, only Cr and Cu are exceptions to the Aufbau Principle. Predict the electron configurations of each.

SOLUTION

According to the Aufbau Principle, Cr should have an electron configuration of $[\text{Ar}]3d^44s^2$. However, we know that chromium does not follow the building-up principle to the letter. In order to half-fill its $3d$ orbitals, Cr must move an electron from another orbital into the $3d$. Now, from which orbital should this electron be moved? Since we seek to minimize total energy, it must come from the highest-energy orbital available, or the $4s$ orbital. Hence Cr's electron configuration is $[\text{Ar}]3d^54s^1$.

Similarly, we see that the electron configuration of copper must be $[\text{Ar}]3d^{10}4s^1$. \square

Exercises for Section 4.3

EXERCISE 4.3.1

(To Think About) Based on our discussion to this point, what characteristic of an element seems to be most important for determining its physical and chemical properties?

EXERCISE 4.3.2

What is the electron configuration of Se?

EXERCISE 4.3.3

How many unpaired electrons are there in a gas-phase chromium atom in the ground state?

EXERCISE 4.3.4

Why is hydrogen not considered a part of any group?

EXERCISE 4.3.5

Let's examine the periodic table with a bit more specificity. Notice that the first row of the table has two elements, which corresponds to filling the first energy level with electrons (remember, each new element has one more electron than the previous one does). The second row has eight elements, which corresponds to filling the second energy level. In particular, for the first two (Li and Be) we are putting our new electrons into the $2s$ orbital and for B through Ne we put them into the $2p$ orbitals. Something strange happens with the third row though. For Na and Mg we fill the $3s$ orbital. For Al through Ar we fill the $3p$ orbital. But when do we fill the $3d$ orbital?

4.4 Some Cool Effects

Problems

PROBLEM 4.19 (SOLUTION ON PAGE 68)

The valence electrons in an atom are layered upon shells of core electrons. While the valence electrons are attracted by the highly positively-charged nucleus, they are also repelled by these inner electrons, and so they experience less of an attractive force than you might otherwise expect. The valence electrons are thus effectively blocked from much of the nucleus's charge, and they are said to be **shielded**. The amount of positive charge that a valence electrons "sees," as measured by the magnitude of the force exerted on it, is referred to as the **effective nuclear charge** and is often denoted Z_{eff} .

In a given valence shell, as the value of l increases, does the amount of shielding increase or decrease?

PROBLEM 4.20 (SOLUTION ON PAGE 68)

An electron is said to be **penetrating** if it can, with relatively high probability, dig through the lower shells of electrons. In other words, a penetrating electron has a high chance of being found near the nucleus. Order the following subshells in terms of having the most highly penetrating electrons, assuming n is fixed: ns , np , nd , nf .

Box 4.7. Background Information

In the following problems, we'll be working with **periodic trends**, or how certain properties change as we move across or down the main group of the periodic table. Note that we are only dealing with the main group right now. The transition metals become more tricky to make predictions about.

PROBLEM 4.21 (SOLUTION ON PAGE 69)

The **atomic radius** of an element is what you might expect, namely the radius of an atom of that element. Actually, it is not easy to rigorously define this quantity, since an electron in an atom could theoretically be found arbitrarily far away from the nucleus. We can think of the atomic radius qualitatively as the distance from the nucleus to the boundary surface of the outermost occupied orbital (that is, the distance beyond which electron density becomes negligible). In practice, chemists define this term empirically as half the distance between neighboring nuclei in a sample of the element.

Predict, generally, what happens to atomic radius as we move from the left of the periodic table to the right, excepting the noble gases. Also predict what happens to atomic radius as we move from top to bottom.

PROBLEM 4.22 (SOLUTION ON PAGE 69)

The **electronegativity** of an atom is its ability to pull electrons towards it in compounds. Predict (again, generally) what happens to electronegativity as we move from the left of the periodic table to the right, excepting the noble gases. Similarly, what should happen as we move from top to bottom?

PROBLEM 4.23 (SOLUTION ON PAGE 70)

When we form an ion, we essentially either push an electron onto an atom or pull an electron off of one. The **ionization energy** of a species is the amount of energy needed to pull an electron off it. The **first ionization energy** is the amount of energy needed to rip only one electron off of that species (just a more specific name for “ionization energy”). The **second ionization energy** is the amount of energy needed to rip a second electron off after the first has already been removed. By convention, the sign of ionization energy is positive if energy is required to remove an electron.

Can an element have a negative ionization energy? Also, predict how ionization energy varies as we move from right to left across a period. What exceptions should there be to this general rule? (Hint: Don’t forget to take into account the special stability of a half- or fully-filled orbital!) Predict in general what should happen to ionization energy as we move from top to bottom along a group.

PROBLEM 4.24 (SOLUTION ON PAGE 71)

Many of the later-period p -block elements form two different ions, one of which is two units lower in charge than expected for that group number. For example, the only ion that aluminum forms is Al^{3+} , while its **congener** (fellow group member) indium forms both In^{3+} and In^+ . This observation is called the **inert pair effect**. Explain this effect using orbitals. (Hint: Think about penetration.)

Solutions and Discussion (4.4)

PROBLEM 4.19

In a given valence shell, as the value of l increases, does the amount of shielding increase or decrease?

SOLUTION

Recall that l specifies the angular momentum of an orbital, and this momentum tends to fling the electron from the nucleus. Alternatively, we can think about the nodes present in each type of orbital. An s electron ($l = 0$) has a nonzero probability of being found all the way at the nucleus, while p ($l = 1$) electrons have a nodal plane that cuts through the nucleus.

According to both ways of thinking, we see that s electrons have much less opportunity to experience shielding than do p electrons, since they can get closer to the nucleus and are less apt to be thrown away. Extending our reasoning further, we realize that shielding increases with l (and thus Z_{eff} decreases). \square

PROBLEM 4.20

An electron is said to be **penetrating** if it can, with relatively high probability, dig through the lower shells of electrons. In other words, a penetrating electron has a high chance of being found near the nucleus. Order the following subshells in terms of having the most highly penetrating electrons, assuming n is fixed: ns , np , nd , nf .

SOLUTION

Clearly the penetration of an electron is higher if it has a higher probability of being found close to the nucleus. Think about nodes through the nucleus, as we did in the previous problem. Since s electrons are the only ones without a node through the nucleus, we see that they are most penetrating. But because the number of nodes through the nucleus increases with l , we see that p comes next, followed by d and then f . So therefore, in terms of penetration $s > p > d > f$. \square

Now we really get to have fun. Until now, we largely worked to build a model that could *explain* the phenomena we observed. Now at long last we get to use our knowledge to make definite *predictions* about the elements. This is really one of the great things about chemistry: we get to apply our general knowledge to predict how specific substances must behave.

PROBLEM 4.21

Predict, generally, what happens to atomic radius as we move from the left of the periodic table to the right, excepting the noble gases. Also predict what happens to atomic radius as we move from top to bottom.

SOLUTION

We proceed by applying our knowledge of atomic-level structure.

- Movement from left to right: As we move from left to right across a given period on the periodic table, we add one more proton to the nucleus and one more electron to the valence shell. What implications does this have for atomic radius? Let's think about the effective nuclear charge. Although an electron has the same charge as a proton, it cannot block the entire charge of that proton. This is because the valence electrons are all about the same distance away from the nucleus, and so they cannot align well enough to act as efficient shields for one another. Since Z_{eff} is higher, electrons will experience a higher attractive force, which will make the atomic radius *decrease*.
- Movement from top to bottom: As we move from the top to bottom of a given group on the table, we add a full shell of electrons and an appropriate number of protons. Suddenly, the valence electrons are in a new energy level. This will *increase* the atomic radius greatly, since higher energy levels are at a greater distance from the nucleus.

\square

Box 4.8. Fun Fact

For anything besides a noble gas, empirically measuring atomic radius is pretty straightforward. However, for a noble gas, which does not form any sort of compound with itself (we'll see why this is in Chapter 5), we take the atomic radius to be the same as the **van der Waals radius**, or half the distance between adjacent nuclei in a solidified sample of the gas. Since these atoms are not bonded together, they are much farther apart, and the atomic radii of noble gases are much larger than we would expect.

PROBLEM 4.22

The **electronegativity** of an atom is its ability to pull electrons towards it in compounds. Predict (again, generally) what happens to electronegativity as we move from the left of the periodic table to the right, excepting the noble gases. Similarly, what should happen as we move from top to bottom?

SOLUTION

As you might imagine, something with a high effective nuclear charge should have a high electronegativity. But as we've already realized, Z_{eff} increases as we move from left to right across a period. What about as we go down a group? Since we add a new shell of electrons each time, the core electrons grow better and better at shielding, which leads to a decrease in effective nuclear charge. The most electronegative of all elements is F, followed by O, Cl, and then N.

- Movement from left to right: Electronegativity increases.
- Movement from top to bottom: Electronegativity decreases.

□

PROBLEM 4.23

Can an element have a negative ionization energy? Also, predict how ionization energy varies as we move from right to left across a period. What exceptions should there be to this general rule? (Hint: Don't forget to take into account the special stability of a half- or fully-filled orbital!) Predict in general what should happen to ionization energy as we move from top to bottom along a group.

SOLUTION

Consider removing an electron from an element A. We can represent this chemical process as the equation $A \longrightarrow A^+ + e^-$. But notice that we have separated a positive and negative charge, something that always requires energy. Hence the ionization energy of an element is always positive (what about the second ionization energy?).

- Movement from left to right: So how do we expect ionization energies to vary across the periodic table? As before, the value of Z_{eff} clearly plays a role. The higher its value, the higher the ionization energy. But there is a second, more subtle effect here as well. Remember that filling or half-filling a subshell lends an extra degree of stability. Thus, it should be easier than expected to remove an electron if doing so will result in a subshell becoming completely or half filled. It should also be harder to remove an electron from an atom that already has a half-filled or full subshell. Thus, in general ionization energy should *increase* across a period, except it should *decrease* from Group 2 to Group 13 and Group 15 to 16.
- Movement from top to bottom: Here we don't have to worry about orbital filling. Why not? Since all elements in a given group have the same valence configuration, they each gain about the same stabilization, if any, from the above effect of half- or completely-filling orbitals, and hence there is no net effect. Since the only other relevant property is effective nuclear charge, we see that ionization energy must *decrease* down a group.

□

PROBLEM 4.24

Many of the later-period p -block elements form two different ions, one of which is two units lower in charge than expected for that group number. For example, the only ion that aluminum forms is Al^{3+} , while its **congener** (fellow group member) indium forms both In^{3+} and In^+ . This observation is called the **inert pair effect**. Explain this effect using orbitals. (Hint: Think about penetration.)

SOLUTION

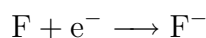
We are told that these ions differ in charge by two units. Thus, sometimes the relevant elements hold some pair of electrons. You should recognize that the subshell that holds two electrons is the s subshell. This should lead you to suspect that the inert pair effect has something to do with the ns orbital of these late p -block elements.

Now, we know that s electrons are highly penetrating and are thus poorly shielded. This allows them to experience more of the nucleus's attractive force, and we see that s orbitals with high n are relatively low in energy. So ions can sometimes form without losing the "inert" pair of electrons in the valence s orbital. □

Exercises for Section 4.4

EXERCISE 4.4.1

At the other end of the spectrum from ionization energy is electron affinity. The **electron affinity** of a species is the amount of energy *released* when an electron is added to that species. For example, the electron affinity of F is $+328 \text{ kJ} \cdot \text{mol}^{-1}$, meaning that sticking an electron onto a mole of F atoms releases 328 kJ of energy. Said another way, the reaction



releases 328 kJ per mole. What can we say about the sign of the electron affinity of an anion (if you recall from Chapter 2, this is a negatively charged ion)? What about for a cation (a positively charged ion)?

Also, predict, generally, how electron affinity varies from left to right across a period, as well as any exceptions to this general trend. Predict how electron affinity varies down a group.

EXERCISE 4.4.2

We know that atomic radius decreases as we go down a group and increases across a group. The magnitudes of these effects are comparable, and main group elements that are diagonal from one another (that is, from one you can go down and to the right to get to the next) often have similar atomic radii. A similar statement can be made for ionization energy. Hence, diagonal elements such as Li and Mg, Be and Al often have similar chemical properties. This idea of **diagonal relationships** allows us to predict similarities in reactivity between diagonal elements. (Diagonal relationships also help account for the stepped line of the metalloids.)

Why is there no diagonal relationship between neon and potassium?

EXERCISE 4.4.3

Which pair of the following elements has the smallest difference in first ionization energies?

Be, B, Na, Al

4.5 Further Explorations

PROBLEM 4.25

In the text of this chapter, we examined atoms only in their ground state. However, if an electron is given the appropriate amount of energy, it is able to jump from a lower orbital to a higher one, a process called an **electron transition**. At this point, the atom and electron are both said to be in an **excited state**, since they have more potential energy than in the ground state. Note that an electron in an excited state can make a spontaneous transition to a lower energy orbital.

- (a) Find which of the following transitions requires the largest input of energy. For the latter two, we have represented orbitals in the form (n, l, m_l) .

$$1s \rightarrow 2p, 2s \rightarrow 2p, (2, 0, 0) \rightarrow (3, 1, -1), (5, 0, 0) \rightarrow (2, 1, 1)$$

- (b) Suppose that an electron is excited from a $3p$ orbital to a $4d$ orbital; this excited state then decays via the following transition pathway: $4d \rightarrow 4s \rightarrow 3p$. Is there a net consumption or release of energy?

PROBLEM 4.26

We know that light is pure energy. But we also know that many substances absorb light. When we shine light on a substance which absorbs this light, by conservation of energy, this energy must then be transferred to the substance in some manner.

- (a) Consider shining a beam of light on an element, which the element then absorbs. Consider further the role of a single photon of this light. It is able to affect only charged particles, since it is essentially just a fluctuation in an electromagnetic field. Given this information, where should the energy of this photon go after it is absorbed? (Hint: what methods of potential energy storage are available to an atom?)
- (b) We shine a beam of white light, consisting of all visible wavelengths, on a sample of an element. We can determine which wavelengths the element absorbs, or its visible **absorption spectrum**, by recording the wavelengths of light that pass through the element. Using your answer from part (a), predict the form of the absorbed regions—should they be discrete bars or continuous areas?
- (c) We can also look at the **emission spectrum** of an element, or the wavelengths of light that are emitted from an excited sample of that element. Should a given element absorb and emit at the same or different wavelengths?

- (d) The absorption and emission spectra of each element are unique to that element. Thus these can serve as a sort of atomic “fingerprint.” Absorption and emission spectra are the subject of the field **spectrophotometry**, where they are put to work providing us with all sorts of information. But wait a minute—since all elements have the same sets of atomic orbitals, how can they have differing spectra?

PROBLEM 4.27

Electron spin largely determines the magnetic properties of an element or a compound. A substance is **paramagnetic** if it has any unpaired electrons; otherwise, it is **diamagnetic**. (There is a third type of magnetism, called **ferromagnetism**, but since it is an emergent property of a substance, we will not explore it here.) A paramagnetic substance is weakly drawn into an external magnetic field, while a diamagnetic substance is weakly repelled. Arrange the elements N, Mg, Cl, and Cr in order of decreasing attraction into a magnetic field.

PROBLEM 4.28

(XYZ: based off of 2001: 47 of Chem Olympiad)

Predict which of the following metals requires the shortest wavelength of light to exhibit the photoelectric effect and which has the lowest work function:

Na, Mg, K, Ca.

PROBLEM 4.29

What is the most electronegative element on the periodic table? Which is the most **electropositive** (that is, least electronegative)?

PROBLEM 4.30

In problem 4.21, we derived how atomic radius generally varies as we traverse the periodic table. If we look at empirical data, we find that our predictions work pretty well in practice. However, towards the bottom of the table we start to find some strange deviations. For example, the atomic radius of Zr is 160 pm, while the atomic radius of its **cogener** (fellow group member) Hf is 156 pm. Similarly, the atomic radius of silver is 144 pm while that of gold is also 144 pm.

The smaller-than-expected atomic radii of the 6th period transition metals is an effect called the **lanthanide contraction**.

- (a) Provide an atomic-level explanation for the lanthanide contraction. Why is this effect so called?
- (b) Predict the location of a similar contraction elsewhere in the table.
- (c) Do you expect this second contraction to be more or less pronounced than the lanthanide contraction? Why?

PROBLEM 4.31

Which of the elements in the second period has the highest third ionization energy? Which has the lowest?

PROBLEM 4.32

We saw before that l determines the number of angular nodes. However, the total number of nodes is determined by n ; there are $n - 1$ nodes in all subshells of a given energy shell. Nodal surfaces that are not angular (that is, they don't pass through the nucleus) are called **radial nodes**. Find the number of radial nodes in a $6d$ orbital.

Chapter 5

Making Molecules

We have spent a great deal of time in the past couple chapters building a picture of individual atoms. In this chapter, we'll use our knowledge of the structure of single atoms to understand how and why atoms combine with each other to build compounds.

Throughout this entire chapter, it is important to keep in mind the main theme of atomic behavior—atoms always seek the lowest possible energy. We have already looked at how energy is minimized within an isolated atom. But when lots of atoms are present together, as is normally the case, they will try to interact in a way such that their total energy is minimized. In this chapter, we will look at how main group elements tend to combine with one another.

The Big Question: Chapter 5

How do individual atoms combine with others?

5.1 The Octet Rule

Problems

PROBLEM 5.1 (SOLUTION ON PAGE 76)

Recall that atoms gain a degree of stability from having a fully-filled subshell. Having a fully-filled energy shell gives atoms even more stability. The **octet rule** is an empirical rule that states that neutral atoms tend to acquire or lose electrons in order to have a full valence shell. It works very well for Group 1 and 2 metals and the definite nonmetals such as O and the halogens. Note that we need only to have full *s* and *p* orbitals; the *d* and *f* orbitals are excessively high in energy to contribute to this special stability.

How many electrons are there in the valence shell of a species after it gains or loses electrons to satisfy the octet rule?

PROBLEM 5.2 (SOLUTION ON PAGE 76)

Main group elements react with others in order to fulfill the octet rule. Use the octet rule to predict which group of the periodic table should contain very unreactive elements.

PROBLEM 5.3 (SOLUTION ON PAGE 77)

In general, do main group elements on the left of the periodic table form cations (positively-charged ions) or anions (negatively-charged ions)? How about elements on the right?

Solutions and Discussion (5.1)

In order to answer our Big Question, we start out by looking at how individual atoms can gain stability.

PROBLEM 5.1

Recall that atoms gain a degree of stability from having a fully-filled subshell. Having a fully-filled energy shell gives atoms even more stability. The **octet rule** is an empirical rule that states that neutral atoms tend to acquire or lose electrons in order to have a full valence shell. It works very well for Group 1 and 2 metals and the definite nonmetals such as O and the halogens. Note that we need only to have full s and p orbitals; the d and f orbitals are too high in energy to contribute to this special stability.

How many electrons are there in the valence shell of a species after it gains or loses electrons to satisfy the octet rule?

SOLUTION

Consider an atom that fulfills the octet rule. Suppose it has full valence s and p orbitals. In the valence shell there are one s and three p orbitals, and each orbital holds two electrons. Thus there are a total of 8 electrons in the atom's valence shell.

Alternatively, we could be in an atom that does not have any p valence orbitals. In this case we have only a lone s orbital in our valence shell, leading to a total of 2 electrons.

Thus a species satisfying the octet rule has 2 electrons in its valence shell if that shell has $n = 1$ and 8 electrons otherwise. (Note that the word "octet" means "group of eight" in Latin.) \square

PROBLEM 5.2

Main group elements react with others in order to fulfill the octet rule. Use the octet rule to predict which group of the periodic table should contain very unreactive elements.

SOLUTION

The octet rule states that main group elements want to have a full valence shell, as such an electron configuration is very low in energy. But the elements in Group 18, called the noble gases, already have full valence shells. Thus, we expect that the noble gases should be very inert. \square

Box 5.1. Fun Fact

However, even the noble gases are not *completely* inert. In 1961, a Canadian chemistry professor named Neil Bartlett realized that he had accidentally made a compound of xenon, fluorine, and platinum some years back. In 1962 he proved his hypothesis experimentally.

Today, chemists have synthesized many other kinds of xenon compounds. Krypton and argon have also been shown to form stable compounds with fluorine. Under extreme conditions (of temperature and pressure), it's possible to force neon and helium to form compounds; however, no known compounds of these elements are stable under normal conditions.

PROBLEM 5.3

In general, do main group elements on the left of the periodic table form cations (positively-charged ions) or anions (negatively-charged ions)? How about elements on the right?

SOLUTION

Main group elements want to satisfy the octet rule; in order to accomplish this they must either lose all of their valence electrons or fill their current valence shells. Elements on the left of the table have only a few electrons in their valence shells, making it much easier to shuck these electrons than to fill the entire shell. Thus, elements found on the left of the periodic table should tend to form positively-charged ions, or cations.

In contrast, elements on the right of the table already have valence shells that are almost full, meaning it takes much less energy to fill their shells than to discard all their valence electrons. So these elements should form negatively-charged ions, or anions. \square

Recall that elements on the left side of the table are metals while those on the right are generally nonmetals. Thus we see that metals like to be positively charged and nonmetals like to be negatively charged. Also, notice that any atom (besides hydrogen), after gaining or losing electrons to satisfy the octet rule, will have an electron configuration identical that of a noble gas. So a species that has achieved its octet configuration is said to have a **noble gas configuration**.

Box 5.2. What Happens with Everything Else?

The semimetals (B, Si, Ge, As, Sb, Te, Po; those on the stepped line) do not really bother with the octet rule; if anything they tend to lose their p electrons during ion formation. Elements to their left in the p -block, such as Ga or Sn, generally have **variable valence**, or can form several types of ions. Sometimes they behave like you would expect with the octet rule, while sometimes they lose only their p electrons (recall the inert pair effect from Chapter 4). Note however that Al only forms Al^{3+} , as the octet rule predicts.

On the other hand, most transition metals like to shed their highest-energy s electrons, so many of them have a +2 charge on their ions. Many of them also form more than one stable ion.

At this point, we can understand the basic motivations for two elements combining with one another. In particular, when elements combine in the right way, they can satisfy the octet rule. In the next section, we will examine this idea in a bit more detail.

Exercises for Section 5.1

EXERCISE 5.1.1

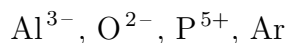
We have already seen that transition metals can form more than one ion (for example, copper forms both Cu^+ and Cu^{2+} ions). How many different types of ions do you expect a Group 1, Group 2, or nonmetal atom to form?

EXERCISE 5.1.2

Find the charge of the most stable ion formed by the alkaline earth metals (elements in Group 2). Do the same for the halogens (elements in Group 17).

EXERCISE 5.1.3

Which of the following have a noble gas configuration? Which would you expect to be stable in nature?



EXERCISE 5.1.4

When hydrogen fulfills the octet rule, it generally does this by losing its lone valence electron rather than gaining a new one, resulting in the formation of H^+ . In contrast, which elements have 2 electrons in their valence shells upon fulfilling the octet rule?

5.2 Bonding

Problems

When we have two main-group, non-noble gas elements A and B that react with one another, there are three general cases we need to consider. We'll examine these cases and some of their consequences in the following sequence of problems.

PROBLEM 5.4 (SOLUTION ON PAGE 79)

(*) (First case) Suppose that we take element A from the left of the periodic table and element B from the right. Using the octet rule, predict how these two elements will react with one another. What state of matter (solid, liquid, or gas) will the product be under normal conditions? (Hint: Ions will form. In what general way will these ions structure themselves?)

Box 5.3. Notation

There's a huge variety of compounds out there, and we often want to talk about this one or that one in ordinary conversation. Thus chemists have made a whole set of naming conventions for compounds to make communication easier. Depending on the level of detail needed and the type of compound, different naming rules can be used. In this book, we'll explore the rules for different types of compounds as they come up.

Let's start with the most basic, general name of a compound. We can denote any compound by writing the formulas of the elements making up that compound; such a name is called that compound's **chemical formula**. We write subscripts to show the number of each type of atom in one unit of whatever compound we're looking at, almost always expressed as a whole number; leaving off a subscript means there's really an implicit one. For example, we denote magnesium fluoride as MgF_2 , meaning that there are two atoms of fluorine for every (one) atom of magnesium. However, such a molecular formula often doesn't hold all of the information we might like to convey, as we will see for the first time in Section 5.4.

PROBLEM 5.5 (SOLUTION ON PAGE 80)

Determine the product of the reaction $\text{Ca(s)} + \text{Cl}_2(\text{g}) \longrightarrow ?$. Assume that Cl_2 behaves just like two separate atoms of Cl (we'll explore what Cl_2 actually is later in this chapter).

PROBLEM 5.6 (SOLUTION ON PAGE 81)

The **ionic radius** of an element is defined as that element's radius when it is in an ionic solid, as measured by looking at the average distance between neighbors in the various ionic compounds that it makes. What main-group elements (besides the noble gases) have ionic radii larger than their atomic radii? Which ones have ionic radii smaller than their atomic radii? (Hint: On the atomic level, the radius is determined by how far out electrons can go. When are electrons more attracted to the nucleus? When are they driven further out?)

PROBLEM 5.7 (SOLUTION ON PAGE 81)

(Second case) Now consider the case where A and B both come from the left side of the periodic table (note we are not necessarily assuming that A and B are different elements here). Can A and B trade electrons with one another such that both satisfy the octet rule?

PROBLEM 5.8 (SOLUTION ON PAGE 81)

(Third case) Suppose that the orbitals of an atom stay the same regardless of whether the atom is isolated or present with other atoms. Consider the case where A and B are both nonmetals. Then how can A and B react with one another to satisfy the octet rule? (Hint: Electrons can be shared between different atoms)

PROBLEM 5.9 (SOLUTION ON PAGE 82)

On the atomic level, describe the form in which a sample of fluorine should exist. Does your reasoning extend to the rest of the halogens? What about to hydrogen?

Solutions and Discussion (5.2)

PROBLEM 5.4

(*) (First case) Suppose that we take element A from the left of the periodic table and element B from the right. Using the octet rule, predict how these two elements will react with one another. What state of matter (solid, liquid, or gas) will the product be under normal conditions? (Hint: Ions will form. In what general way will these ions structure themselves?)

SOLUTION

We know that elements on the left side of the periodic table tend to lose electrons to form cations. On the other hand, those on the right tend to gain electrons to form anions. Thus we see there is an easy way for A and B to both achieve their goals: they can simply trade electrons. Thus they will react with one another to form ions such that A will end up with a positive charge and B will end up with a negative charge.

But what happens now? We have all these positive ions and negative ions sitting around. There are some very strong electromagnetic forces in action here. So nature will try to find the lowest-energy arrangement, which occurs when attractions are maximized (since doing so releases energy). Let's think about what this arrangement should look like. Consider picking up a single ion of A . Since it is positively charged, a number of ions of B will jump up and surround it. But all of these B ions are negatively charged, so around these B ions, we'll end up with a bunch of A s. So our outermost layer now contains unshielded positive charges, and clearly this process will repeat. Ultimately, we see that we'll end up with some regular 3-dimensional arrangement of ions.

But this structure will not be very flexible. In order to maintain it, the ions must be locked into their positions. (If they were to slide past one another, then suddenly rather than having adjacent A s and B s, we would have adjacent A - A pairs and B - B pairs, which would require a very large input of energy.) But recall from Chapter 0 that this is precisely the description of a solid. Thus we must end up with a solid \square

A solid made out of ions is called an **ionic compound**. As we saw, the ions in such a solid are held together only by electrostatic attractions; this method of binding together ions is called an **ionic bond**.

Box 5.4. Notation

To name an ionic compound (in words, rather than by formula), first take the name of the cation and then the name of the anion. By convention, a main group element in cation form keeps its name unchanged, while one in anion form has its ending changed to *-ide*. So for example, the formula NaCl represents the compound sodium chloride and AlBr_3 represents aluminum bromide.

Transition metals have variable valence (that is, they form more than one type of stable ion) and hence we need to name them more carefully. One way is to write the name followed by its charge (as a Roman numeral) in parentheses, without spaces. For example, Fe_2O_3 is named as iron(III) oxide, and CuCl is copper(I) chloride.

An older, less general naming convention you'll sometimes see—which works only for elements that form two different kinds of ions—is to take the Latin name of the relevant element and stick *-ous* after it to denote the form of lower charge and *-ic* after it to denote the form of higher charge. So under this convention, Fe^{2+} becomes ferrous and Fe^{3+} becomes ferric, making FeBr_2 ferrous bromide and FeBr_3 ferric bromide. In order to keep things simple and consistent, we will not use this notation further in this book.

PROBLEM 5.5

Determine the product of the reaction $\text{Ca(s)} + \text{Cl}_2\text{(g)} \longrightarrow ?$. Assume that Cl_2 behaves just like two separate atoms of Cl (we'll explore what Cl_2 actually is later in this chapter).

SOLUTION

In order to satisfy the octet rule, each atom of Ca will lose 2 electrons to form Ca^{2+} while each atom of Cl will gain 1 electron to form Cl^- . Thus given one atom of Ca, we need to have two atoms of Cl. Our final product will be $\text{CaCl}_2\text{(s)}$. (Quick question, what is the name of this compound? Answer: calcium chloride.) \square

PROBLEM 5.6

The **ionic radius** of an element is defined as that element's radius when it is in an ionic solid, as measured by looking at the average distance between neighbors in the various ionic compounds that it makes. What main-group elements (besides the noble gases) have ionic radii larger than their atomic radii? Which ones have ionic radii smaller than their atomic radii? (Hint: On the atomic level, the radius is determined by how far out electrons can go. When are electrons more attracted to the nucleus? When are they driven further out?)

SOLUTION

When we form an ion, our resulting species must be either positively or negatively charged. Consider forming a cation by removing electrons, as we do in Groups 1 and 2. Then we have decreased the electron-electron repulsions, increasing Z_{eff} , and thus the remaining electrons are more strongly attracted to the nucleus. On the whole, this decreases the ionic radius relative to the atomic one.

Now if we form an ion by adding electrons, as at the right of the table, we have added electrons to the valence shell. These repel each other and decrease the effective nuclear charge, which allows electrons to float away from the nucleus. This results in an increase in radius. In sum: anions are big, cations are small. \square

PROBLEM 5.7

(Second case) Now consider the case where A and B both come from the left side of the periodic table (note we are not necessarily assuming that A and B are different elements here). Can A and B trade electrons with one another such that both satisfy the octet rule?

SOLUTION

Both A and B need to lose electrons to satisfy the octet rule, since they are both metals. Thus they cannot both satisfy the octet rule by reacting with one another.

We might be tempted to try pulling electrons from atoms of A and pushing 6 or 7 of them at a time onto atoms of B , completing B 's valence shell and emptying A 's. However, this process would require lots and lots of energy, which you should be able to see from the magnitude of the charge we would be building. \square

We'll see in Chapter ?? that, although A and B cannot satisfy the octet rule if both are from the left of the periodic table, they can combine with each other in a way that lowers their total energy. This is quite fortunate because otherwise metals would not be solids but rather gaseous collections of individual atoms!

PROBLEM 5.8

(Third case) Suppose that the orbitals of an atom stay the same regardless of whether the atom is isolated or present with other atoms. Consider the case where A and B are both nonmetals. Then how can A and B react with one another to satisfy the octet rule? (Hint: Electrons can be shared between different atoms)

SOLUTION

If we try to repeat the strategy we used in Problem 5.4 and have A and B form discrete ions, we clearly run into trouble. If one atom flat-out gains electrons, another other must flat-out lose them.

However, what if instead of giving up electrons we just share them? Since nonmetal atoms just need to supplement their valence shells with a few electrons, we won't need too many sharings in order to accomplish this. Now, of course, the question is how this sharing can actually be accomplished. By assumption, during this sharing the original atomic orbitals remain unchanged. But since electrons simultaneously belong to two different atoms, we see that the relevant orbitals of the atoms must overlap with one another. \square

The force holding together atoms in Problem 5.8 is called a **covalent bond**. Usually, the shared electrons come in pairs, one from each of the atoms they are shared between (using reasoning about orbitals, think about why this should be true). The theory that states bonds are formed by the overlapping of atomic orbitals is called the **valence bond model**, and we will be exploring it in more detail in the upcoming text.

Discrete groups of atoms that are covalently bonded together are called **molecules**. Most compounds that we deal with in everyday life are molecules. Note that different molecules can be put together in different ways; the way in which a given molecule is put together is called that molecule's **structure**. If a molecule is very simple in that everything is bonded to one atom, this main atom is called the **central atom**.

Box 5.5. Fun Fact

You might be wondering if electrons can ever be shared between three or more atoms. Actually, they can, although this occurs only in special compounds. For example, some compounds of boron [B, element that is found in the ores borax and ulexite] can attach themselves to an existing covalent bond, forming a **three-center two-electron bond**. (We'll look at why this happens in Chapter ??.) However, make sure to keep in mind that while it is rare to have a given electron pair shared among three atoms, it is common to have a given atom bonded to multiple other atoms—for example, consider ammonia [NH_3 , a toxic gas; household ammonia is actually a solution of ammonia and water], which has a nitrogen bonded to three hydrogens.

PROBLEM 5.9

On the atomic level, describe the form in which a sample of fluorine should exist. Does your reasoning extend to the rest of the halogens? What about to hydrogen?

SOLUTION

Fluorine is found at the right of the periodic table. We thus know from Problem 5.8 that fluorine will combine with itself, forming a covalent bond. Recall that an atom of fluorine has seven valence electrons, meaning that it has a filled $2s$ orbital, two filled $2p$ orbitals, and one half-filled $2p$ orbital. Thus, it can share (and needs to share) exactly one electron with another fluorine atom. This can be accomplished by overlapping the half-filled $2p$ orbital in each fluorine atom, meaning each atom contributes one electron to the shared pair, or bond.

In total, we expect that fluorine should have its atoms exist in pairs, where each pair is covalently bonded together. Since our reasoning depended only on the valence configuration of fluorine, we see that the rest of the halogens should also exist in this form. A molecule that is made out of two atoms is called a **diatomic molecule**, and hence we see that the halogens all form diatomic molecules.

Finally, note that our reasoning also extends to hydrogen. Hydrogen's electron configuration is simply $1s^1$, meaning that it possesses a half-filled orbital and needs only one electron to complete its valence shell. Thus it should exist in the same form, namely as H_2 . \square

The fact that hydrogen exists as H_2 is interesting because when hydrogen forms ions, it behaves like a metal and forms H^+ . (Note that, since most hydrogen nuclei have no neutrons, H^+ is generally just a single, bare proton!) In general, however, hydrogen forms covalent compounds.

Box 5.6. Notation

A molecule's chemical formula is often written to try to indicate its structure, and so different kinds of molecules can have their formulas written in different ways. For simple molecules, usually (but not always) the central atom is written first. For example, in the molecule SO_3 , sulfur is the central atom.

As to naming in words, here we'll consider simple binary molecules (made out of only two kinds of atoms). In this case, we name the compound by writing (Greek number prefix)first atom (number prefix)second atom, where this number prefix (di-, tri-, tetra-, penta-, etc.) indicates the subscript, if greater than 1, of each atom in the molecule. Also the second atom's ending is changed to *-ide*. Using this system, we can name NO_2 as nitrogen dioxide or P_2O_5 as diphosphorous pentoxide.

Exercises for Section 5.2

EXERCISE 5.2.1

In a sample of potassium chloride, which component ion (potassium or chloride) takes up the most total volume?

EXERCISE 5.2.2

Predict which of the following metals has the smallest ionic radius.

Na, Mg, K, Ca.

EXERCISE 5.2.3

Write the molecular formula of barium chloride. Do the same for copper(I) oxide.

EXERCISE 5.2.4

Predict the type of bonding (ionic, covalent, or neither) present in the following species:



5.3 Hybridization

Problems

(XYZ: this entire section needs more pictures. we haven't yet found a good orbital-drawing client; let us know if you have any suggestions)

PROBLEM 5.10 (SOLUTION ON PAGE 85)

Using the valence bond model, predict the shape of a methane molecule, CH_4 . (Hint: All of the bonds in this molecule are covalent. What determines the alignment of atoms in a covalent bond?)

PROBLEM 5.11 (SOLUTION ON PAGE 85)

Experimental studies have determined that in methane, all hydrogens are equivalent (that is, the molecule looks the same from each hydrogen's point of view). Geometrically, this means that they must point towards the corner of a tetrahedron, and that the $\text{H}-\text{C}-\text{H}$ bond angle is about 109.5° . Since this is contrary to the predictions of our theory, we must have made an inaccurate assumption somewhere. What is this assumption?

PROBLEM 5.12 (SOLUTION ON PAGE 86)

We can refine our valence bond model by adding a more sophisticated component called **orbital hybridization**. Here, we suppose that when one atom combines with another, the valence orbitals on a given atom can first average with each other to form a number of identical orbitals. So for example, in methane, the carbon s and three p valence orbitals would combine to form four identical orbitals (which we call an **sp^3 hybrid** orbital, read "s p three") that are 25% like an s orbital and 75% like a p orbital. (XYZ: show a picture)

How must the sp^3 orbitals be oriented relative to one another? How does this hybridization result in a net of lower energy relative to the structure we derived in Problem 5.10?

PROBLEM 5.13 (SOLUTION ON PAGE 86)

Now let's consider the elemental form of something besides the halogens. Experiments show that gaseous oxygen exists as O_2 . How can we describe the bonding in oxygen in terms of the orbital hybridization model? Assume that hybridized orbitals orient themselves symmetrically. (Hint: Not all orbitals have to be hybridized; however, orbitals hybridize whenever they can.)

PROBLEM 5.14 (SOLUTION ON PAGE 87)

In a molecule, predict whether **lone pairs**, or unshared pairs of electrons, are found in hybridized or unhybridized orbitals.

PROBLEM 5.15 (SOLUTION ON PAGE 87)

The **formal charge** on an atom in a molecule is the effective net charge on that atom, assuming that the electrons in any given bond are shared exactly evenly between the two relevant atoms. (This assumption is an overexaggeration of covalent bonding, but it gives us a useful framework for understanding molecules.) Find the formal charge on an atom that has v valence electrons when neutral if it has b covalent bonds and l lone pairs.

Solutions and Discussion (5.3)

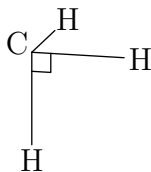
PROBLEM 5.10

Using the valence bond model, predict the shape of a methane molecule, CH_4 . (Hint: All of the bonds in this molecule are covalent. What determines the alignment of atoms in a covalent bond?)

SOLUTION

We know that hydrogen forms only one covalent bond, while carbon forms four. Thus, the four hydrogens must all be bonded to the carbon atom. Hence, we can think about carbon as the central atom in methane.

Now, recall that we showed bonds result from the overlapping of atomic orbitals. In this case, the overlapping orbitals must be the hydrogen $1s$ with either the carbon $2s$ or one of the carbon's $2p$ orbitals. But the $2p$ orbitals are mutually perpendicular, so we should expect that the hydrogens bonded to them should form a shape such as that shown below.



Now, the hydrogen bonded to carbon's $2s$ orbital is free to go anywhere, since this orbital is spherical. But since the electron clouds of adjacent hydrogen atoms repel one another, we would expect this hydrogen to be located as far away from the other three hydrogens as possible. In particular, it should end up pointing directly away from the plane containing the three hydrogens. □

PROBLEM 5.11

Experimental studies have determined that in methane, all hydrogens are equivalent (that is, the molecule looks the same from each hydrogen's point of view). Geometrically, this means that they must point towards the corner of a tetrahedron, and that the $\text{H}-\text{C}-\text{H}$ bond angle is about 109.5° . Since this is contrary to the predictions of our theory, we must have made an inaccurate assumption somewhere. What is this assumption?

SOLUTION

Examining our assumptions, we see that the most questionable one is that atomic orbitals retain their form when atoms are bonded in molecules. If we get rid of this assumption, then our theory no longer yields the inaccurate prediction from Problem 5.10. \square

PROBLEM 5.12

We can refine our valence bond model by adding a more sophisticated component called **orbital hybridization**. Here, we suppose that when one atom combines with another, the valence orbitals on a given atom can first average with each other to form a number of identical orbitals. So for example, in methane, the carbon s and three p valence orbitals would combine to form four identical orbitals (which we call an **sp^3 hybrid** orbital, read “ s p three”) that are 25% like an s orbital and 75% like a p orbital.

How must the sp^3 orbitals be oriented relative to one another? How does this hybridization result in a net of lower energy relative to the structure we derived in Problem 5.10?

SOLUTION

We know that in methane the hydrogen atoms are oriented as the vertices of a regular tetrahedron. Since the $1s$ orbital of the hydrogen atoms must overlap with the relevant sp^3 orbital on carbon, we see that the sp^3 orbitals are also oriented towards the corners of a regular tetrahedron.

Note that we have maximized the distance between all pairs of orbitals. Since orbitals contain electrons, which repel each other, increasing the distance between orbitals lowers energy. Furthermore, we have maximized the distance between adjacent atoms not bonded to one another, whose electron clouds repel one another. On the other hand, our structure in Problem 5.10 has the valence orbitals and adjacent atoms much more closely squashed together, forcing the electrons to be closer together and thus raising energy. \square

The relative orientations of hybrid orbitals come from their symmetry. It happens that this symmetry results in the minimal total amount of repulsion among the electrons in these orbitals because we allow these orbitals to be as far apart as possible.

Box 5.7. Fun Fact

The study of the repulsions due to crowding of electron clouds is called **sterics**. The phenomenon itself is hence called **steric hindrance**.

PROBLEM 5.13

Now let's consider the elemental form of something besides the halogens. Experiments show that gaseous oxygen exists as O_2 . How can we describe the bonding in oxygen in terms of the orbital hybridization model? Assume that hybridized orbitals orient themselves symmetrically. (Hint: Not all orbitals have to be hybridized; however, orbitals hybridize whenever they can.)

SOLUTION

Recall that oxygen has six valence electrons. Thus each oxygen must share two electrons with its partner, leading to the formation of two covalent bonds between the atoms. This is different from what we saw before; previously there was at most one bond between any two atoms.

What happens if we try to apply the same hybridization scheme as before, and say that oxygen is sp^3 hybridized? We can certainly form one bond easily enough, but the remaining orbitals are all oriented the wrong way to overlap and form our second bond. Thus, we cannot be sp^3 hybridized. So let's try the next-best thing: leave one p orbital unhybridized and combine the s and two p valence orbitals into three identical orbitals, which we'll by analogy call **sp^2 orbitals**.

By symmetry, we see that the three sp^2 orbitals must all lie in the same plane and point towards the vertices of an equilateral triangle. Furthermore, the remaining unhybridized p orbital will be perpendicular to the plane containing the sp^2 s. Now how can we form two bonds with such an arrangement of orbitals? Clearly, it is easy for one of the sp^2 orbitals to overlap with one on the other atom. However, the remaining two are oriented the wrong way to form another bond. Hence, the second bond must come from the side-by-side overlap of unhybridized p orbitals. (XYZ: will add an image) \square

We saw in the previous problem that there are essentially two different ways that orbitals can overlap to form a bond. First of all, they can overlap head-on (as the sp^2 orbitals do); such bonds are called **σ bonds** (the Greek letter sigma). Alternatively, parallel unhybridized p orbitals can indirectly overlap; such a bond is termed a **π bond** (the Greek letter pi). These names come about because the relevant bonds look sort of like the letters (if you really squint).

Also, we have seen that a covalent bond can involve more than one shared pair of electrons. Such a bond is called a **multiple bond**. If two pairs are shared in a given multiple bond, we call it a **double bond**; if there are three shared pairs, it is a **triple bond**.

PROBLEM 5.14

In a molecule, predict whether **lone pairs**, or unshared pairs of electrons, are found in hybridized or unhybridized orbitals.

SOLUTION

We saw that energy in a molecule is lowered by putting electrons into a hybridized orbital. Electrons are found in unhybridized orbitals only when the bond geometry forces them to do so. But lone pairs are by definition not part of any bond, and so they should be found in hybridized orbitals. \square

PROBLEM 5.15

The **formal charge** on an atom in a molecule is the effective net charge on that atom, assuming that the electrons in any given bond are shared exactly evenly between the two relevant atoms. (This assumption is an overexaggeration of covalent bonding, but it gives us a useful framework for understanding molecules.) Find the formal charge on an atom that has v valence electrons when neutral if it has b covalent bonds and l lone pairs.

SOLUTION

Each of the atom's b bonds contains two electrons. However, these electrons are only present at this atom half of the time, leading to a total effective charge of $-b$ due to bonds. Each lone pair also contains two electrons, but these electrons are always present on our relevant atom, leading to an effective charge of $-2l$ due to lone pairs. Finally, this atom has a charge of $+v$ without any valence electrons because it has a **valence** of v (or is neutral with v valence electrons). Since charges are additive, the atom's formal charge is $v - b - 2l$. \square

Problem 5.15 gives us a convenient way of calculating formal charge. In the next section, we'll see that there is a much quicker, less formulaic way of calculating formal charge.

Exercises for Section 5.3

EXERCISE 5.3.1

What percent s -character does an sp^2 orbital have?

EXERCISE 5.3.2

Describe the hybridization of atoms in water, H_2O .

EXERCISE 5.3.3

Experiment shows that elemental nitrogen [N_2 , the main component of our atmosphere] exists in diatomic form. Describe the bonding in the nitrogen molecule. What are the shapes of the hybridized orbitals on each nitrogen atom?

EXERCISE 5.3.4

Within the same multiple bond, which is stronger: a σ bond or π bond?

EXERCISE 5.3.5

The **order** of a bond is the number of shared electron pairs that form it. So for example, a double bond has order two. What is the highest order bond that can be formed using only s and p orbitals?

EXERCISE 5.3.6

Consider a certain polyatomic ion with a charge of n . What is the sum of the formal charges on the atoms that compose this ion?

5.4 Lewis Structures

Problems

In this section, we will explore a simple notation that will allow us to easily solve a wide range of problems. For now, we'll be focusing mainly on its use in figuring out the connectivities and bonding of molecules. In Chapter ??, we'll extend it to include more information, such as bond angles.

PROBLEM 5.16 (SOLUTION ON PAGE 89)

(Open-Ended Exploration) Often, just writing a molecule as a collection of atomic symbols doesn't convey sufficient information about the structure of a molecule. For example, there are multiple possible molecules that have the formula C_4H_{10} . And furthermore, even when structures are unambiguous, writing them as strings of symbols doesn't help us very much in picturing a molecule. Thus, we need a better notation, one that is unambiguous and that we can easily extract information from.

Try experimenting and see if you can come up with a new notation. It needs to clearly specify the relevant molecule's connectivity. Preferably, it should also help us easily visualize the structure of a molecule. That being said, it might also be nice if the notation is easy to generate, but that's up to you! (Note that your notation doesn't have to fit nicely into a line of text.)

PROBLEM 5.17 (SOLUTION ON PAGE 91)

Using your notation, draw the structures of the following molecules: water [H_2O , commonly used to dissolve ionic compounds], ethane [C_2H_6 , a colorless, odorless gas mainly used to generate the chemical ethylene]. Include the molecules' connectivities and draw all lone pairs.

PROBLEM 5.18 (SOLUTION ON PAGE 92)

Now use your notation to find the structures of sulfur dioxide [SO_2 , a gas produced as a waste product from some industrial processes and can then react in the atmosphere to become a component of acid rain] (in accordance with our naming conventions, S is the central atom of this molecule) and nitric acid [HNO_3 , a strong acid, colorless when pure, although it can yellow with age due to the formation of nitrogen oxides] (note that all oxygens in this molecule are connected to the nitrogen). Include connectivity, lone pairs, and formal charges, if any.

PROBLEM 5.19 (SOLUTION ON PAGE 94)

If your notation is powerful enough, it should help you solve the following problem: on what atom of the ammonium cation [NH_4^+ , a weak acid that comes from reacting ammonia with an acid] does the positive charge reside?

PROBLEM 5.20 (SOLUTION ON PAGE 94)

Find the formal charge on the carbon atom in cyanide [CN^- , cyanide is a highly toxic anion; the poisonous gas hydrogen cyanide—HCN—is used in gas chamber executions, and the ionic solid potassium cyanide—KCN—is a notorious poison]. Your notation should also be of use here.

Solutions and Discussion (5.4)

PROBLEM 5.16

(Open-Ended Exploration) Often, just writing a molecule as a collection of atomic symbols doesn't convey sufficient information about the structure of a molecule. For example, there are multiple possible molecules that have the formula C_4H_{10} . And furthermore, even when

structures are unambiguous, writing them as strings of symbols doesn't help us very much in picturing a molecule. Thus, we need a better notation, one that is unambiguous and that we can easily extract information from.

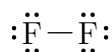
Try experimenting and see if you can come up with a new notation. It needs to clearly specify the relevant molecule's connectivity. Preferably, it should also help us easily visualize the structure of a molecule. That being said, it might also be nice if the notation is easy to generate, but that's up to you! (Note that your notation doesn't have to fit nicely into a line of text.)

SOLUTION

Let's think about what information we want in such a notation. We need to know the **connectivity** of our molecule; that is, exactly which atoms are bonded to which other atoms. We also need to be able to indicate the order of our bonds. Finally, we should be able to stick in unshared valence electrons and have the flexibility to add in formal charges if we want. On the whole, we need to have something that is a two-dimensional snapshot of a three-dimensional molecule (which is certainly better than the one-dimensional sketch we've been using up until now).

To represent the various atoms in our molecule, we can just write their chemical symbols, as before (although we should spread them out some). Perhaps the most obvious way of representing bonds is just marking them as lines between connected atoms and having multiple lines for multiple bonds. This gives us both connectivity and bond order immediately. Intuitively, we can then represent unshared electrons as dots. Finally, we can just write formal charges directly above the relevant atoms, if we want to emphasize that information.

The representation we have just described is called a **Lewis structure**, or a **Lewis dot structure**, the invention of the American chemist G. N. Lewis in 1902. As an example, we can draw the structure of F_2 as



or that of oxygen as



We'll get more practice with Lewis structures in the following problems. □

Compare the notation you came up with to Lewis structures. Note how Lewis's notation elegantly captures the desired information about the structure of a molecule. Although they are very simple, these structures are a valuable tool for understanding a wide range of molecules.

Box 5.8. Delving Deeper

Note that at this point in the text, we won't need to completely specify the actual three-dimensional structure of a molecule. With complicated molecules, however, knowing this structure becomes key to understanding the molecule's reactivity, as different structures often lead to different modes of reaction (even if they have the same connectivity). When necessary,

a Lewis structure can be drawn to emphasize the three-dimensional arrangement of atoms in a molecule. One such way is shown in the following two pictures of chlorofluorobromomethane (read as “chloro-fluoro-bromo-methane”), although there are other drawing styles that can be more useful depending on context.



By convention, bold bonds are coming out of the page towards you and dashed bonds are into the page away from you. As you can check, the two molecules are actually different! (Although the two look very similar—indeed, they are mirror images—you can’t rotate one in space to superimpose it on the other, just as you can’t use rotations to align your left hand with your right hand. In general, a molecule that can’t be superimposed on its mirror image is called **chiral**, a subject we will explore in Chapter ??.)

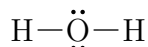
PROBLEM 5.17

Using your notation, draw the structures of the following molecules: water [H_2O , commonly used to dissolve ionic compounds], ethane [C_2H_6 , a colorless, odorless gas mainly used to generate the chemical ethylene]. Include the molecules’ connectivities and draw all lone pairs.

SOLUTION

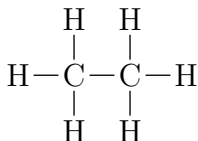
We’ll work through this problem using Lewis structures. Note in each case that generating the structure is not difficult, but the result is very helpful in picturing the relevant molecule. *Goal: Lewis structure of water.*

Recall the formula of water is H_2O . Since water is neutral, there are a total of $6 + 1 + 1 = 8$ valence electrons floating around, and hence four electron pairs. We know that the hydrogens are bonded to the oxygen using single bonds, since hydrogen can form at most one bond. The two remaining pairs must then be lone pairs on the oxygen atom. We hence obtain the following structure:



Goal: Lewis structure of ethane.

Looking at the periodic table, each carbon contributes four valence electrons and each hydrogen contributes one, so there are a total of 12 valence electrons, leading to 6 electron pairs. Since hydrogen can form only one bond, all of the hydrogens must be directly bonded to the carbons. Thus the carbons must also be bonded to one another; so we can write down “C–C,” as this **moiety**, or part of a molecule, definitely appears in ethane. Finally, since carbon can have at most 4 bonds, we see that there must be three hydrogens on each carbon, and hence our completed Lewis structure is



□

Note that in the previous problem, we thought about the electrons as being grouped into pairs. While this is not always the case, generally molecules with unpaired electrons tend to be less stable (think about why in terms of orbitals). We'll explore this topic in more detail in Chapter ???. Also, note that given the connectivity of the molecule, it was fairly easy to determine where the electrons should be.

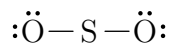
PROBLEM 5.18

Now use your notation to find the structures of sulfur dioxide [SO_2 , a gas produced as a waste product from some industrial processes and can then react in the atmosphere to become a component of acid rain] (in accordance with our naming conventions, S is the central atom of this molecule) and nitric acid [HNO_3 , a strong acid, colorless when pure, although it can yellow with age due to the formation of nitrogen oxides] (note that all oxygens in this molecule are connected to the nitrogen). Include connectivity, lone pairs, and formal charges, if any.

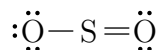
SOLUTION

Goal: Lewis structure of sulfur dioxide.

Both sulfur and oxygen have six valence electrons when neutral, so there are a total of 18 valence electrons on this molecule, or 9 pairs. We know that the connectivity of the sulfur dioxide atom is "O-S-O"; thus we can start by drawing only this bare σ structure, or arrangement of σ bonds. Now we have six electron pairs left to place. We can try to complete the octets on the oxygens by adding the appropriate number of electron pairs, arriving at the following

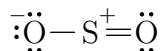


However, notice that in this structure S does not have a complete octet. But if one of the oxygen lone pairs moves to form a double bond with sulfur, then every species satisfies the octet rule; we have drawn this structure below.



Thus this latter structure is more stable than the one above it, and so it is the best representation of the molecule. (Now, one interesting question is how nature chooses which oxygen should be double bonded to the sulfur. We'll come back to this issue in Chapter ???.)

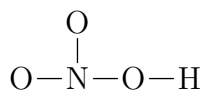
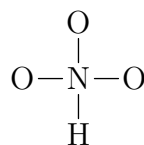
Now, let's check formal charges. Since each bonding pair on a given atom effectively counts as only one electron, the doubly-bonded oxygen effectively has 6 electrons (and hence a formal charge of 0), the singly-bonded oxygen has 7 electrons (hence formal charge of -1), and the sulfur has 5 electrons (hence formal charge of $+1$). Putting this all together, our final Lewis structure is the one drawn below.

**Box 5.9. Tip**

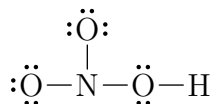
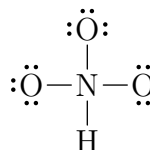
To determine the formal charge on a certain atom, you can just count the number of lone electrons and bonds and subtract this quantity from the atom's valence.

Goal: Lewis structure of nitric acid.

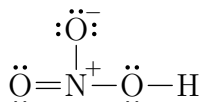
Again, we count electrons. We find a total of $1 + 5 + 3 \cdot 6 = 24$ valence electrons, meaning there are 12 electron pairs. First, let's determine the connectivity of this molecule because there are many atoms to deal with. We know that the oxygens are all directly attached to the nitrogen atom. So we have two choices for the hydrogen: either it can be on the nitrogen as well, or it can be attached to one of the oxygens. At this point, we can't definitively say which one is correct; thus we sketch the σ structure in either case.

Possibility 1*Possibility 2*

Now we fill in valence electrons; we have 8 pairs remaining. In each possibility, we go ahead and attempt to complete the octets for the oxygens. After all pairs are placed, we arrive at the following diagram.

Possibility 1*Possibility 2*

In Possibility 1, we can move one of oxygen lone pairs to form a double bond with nitrogen (we'll see in Chapter ?? that we shouldn't use the oxygen bonded to hydrogen). However, in Possibility 2, N already has a complete octet and so one oxygen must remain with an incomplete valence shell. Since from the first possibility we can build a structure in which every species has a complete octet, we see that possibility 1 gives the correct connectivity (or σ structure) for nitric acid. After drawing the appropriate π bond and calculating formal charges, we obtain the final structure shown.



□

Box 5.10. Tidbit

In general, species with an O–O single bond are very unstable due to the weakness of this bond. Such compounds are called **peroxides** and are quite reactive. At this level, you'll very rarely see a structure with an O–O single bond, so try to avoid drawing this moiety in a Lewis structure.

From the above, you should see the usefulness of Lewis structures in determining hybridization and bonding. Lewis structures also give us the ability to predict other features of molecules, as we will see in the following problems.

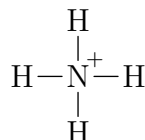
PROBLEM 5.19

If your notation is powerful enough, it should help you solve the following problem: on what atom of the ammonium cation $[\text{NH}_4^+]$, a weak acid that comes from reacting ammonia with an acid] does the positive charge reside?

SOLUTION

In the model we have developed to this point, the amount of charge localized on an atom is that atom's formal charge. We have seen that Lewis structures allow us to quickly determine formal charges. Therefore, we need to construct the Lewis structure of NH_4^+ .

Note that our task is quite simple, as each hydrogen can have only one bond, and they are therefore all bonded to the nitrogen. Since nitrogen contributes 5 electrons, each of the four hydrogens contributes 1, and we are in total short 1 electron from being neutral, we have a total of $5 + 3 \cdot 4 - 1 = 8$ electrons. Thus we obtain the following structure (you can check that there are the proper number of electrons).



There is a formal charge of +1 on the nitrogen since it has four bonds and valence of five. Thus we expect the positive charge to be located on the nitrogen atom. \square

PROBLEM 5.20

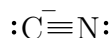
Find the formal charge on the carbon atom in cyanide $[\text{CN}^-]$, cyanide is a highly toxic anion; the poisonous gas hydrogen cyanide—HCN—is used in gas chamber executions, and the ionic solid potassium cyanide—KCN—is a notorious poison]. Your notation should also be of use here.

SOLUTION

First of all, the connectivity of this ion is clear; we must have a σ bond between C and N. So we can write down “C–N” immediately. Now we have $4 + 5 + 1 = 10$ electrons on this anion in total (4 from carbon, 5 from nitrogen, and 1 for the extra negative charge), and thus we have 4 remaining pairs to place. Your intuition should tell you that we're going to end up with a multiple bonding between C and N, since C needs 4 bonds to be neutral while N needs three bonds and a lone pair. But let's proceed naively. Temporarily put the lone pairs wherever you want, such as we have shown.



But in this case, both C and N have incomplete octets. Thus they need to donate electrons to one another. Moving electrons as appropriate, we end up with the structure shown below. We see that carbon has a negative one formal charge since it has three bonds and a lone pair but a valence of four.



Thus the negative formal charge resides on the carbon. (However, as we'll see how to predict later, the negative charge on this anion isn't at all localized on the carbon. Indeed, this charge is denser on the nitrogen than on the carbon! For now, you can take it for granted that the assumption of equal sharing of electrons does not hold for cyanide.) \square

Box 5.11. Notation

In our exploration of Lewis structures, we saw that groups of atoms which are covalently bonded together can themselves form an ion, called a **polyatomic ion**. Thus, we see that we can have covalent and ionic bonding within a single compound. In this case our naming conventions for ionic compounds still apply—the name is the cation followed by the anion. Also, when a single polyatomic ion should have a subscript, we put it in parentheses, such as $\text{Al}(\text{NO}_3)_3$ (aluminum nitrate). Since the names of many polyatomic ions are both common and somewhat arbitrary, it is a good idea to learn them at some point. However, throughout this text we will always couple the name with the structure because our focus is on learning concepts rather than memorizing names.

Exercises for Section 5.4

EXERCISE 5.4.1

Find the number of bonding pairs and lone pairs on the central atom in a molecule of sulfur dichloride [SCl_2 , used in organic chemistry to add sulfur to carbon compounds].

EXERCISE 5.4.2

Find the number of σ and π bonds in a molecule of ethene [C_2H_4 , a gas that is used in a huge range of applications. Although it has officially been called “ethene” since 1892, its common name “ethylene” is still used by many chemists around the world]. As before, your notation should be able to help you solve this problem.

5.5 Further Explorations

PROBLEM 5.21

Between atoms A and B , we can denote a single bond as $A-B$, a double bond as $A=B$, and

a triple bond as $A\equiv B$. Order the following bonds in terms of increasing length: $C-C$, $C=C$, $C\equiv C$. (Hint: Think about **interatomic attractions**, or attractions between atoms.)

PROBLEM 5.22

Note that in our method of drawing Lewis structures in this chapter, we just placed electrons on arbitrary atoms and then moved them to where they needed to go. In general, a more accurate model is to think of starting with a collection of neutral atoms and then combining them together (this can get complicated to conceptualize in practice, because sometimes electrons have been removed or migrate). A covalent bond is said to be **coordinate** if both of its electrons came from the same atom, using the model we have just described. Which of the following species possess a coordinate covalent bond: ammonium $[\text{NH}_4^+]$, sulfur dichloride $[\text{SCl}_2]$, carbon monoxide $[\text{CO}]$, a colorless, odorless toxic gas found in car exhaust and cigarette smoke]?

PROBLEM 5.23

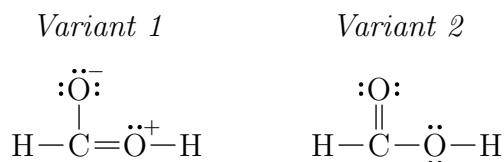
In general, what effect does increasing the magnitude of the charge on a cation have on that cation's radius? What effect does increasing the magnitude of the charge on an anion have on that anion's radius?

PROBLEM 5.24

Suppose that an oxygen atom in a molecule satisfies the octet rule. If it has a formal charge of 0, how many bonds does it have? Repeat this problem with nitrogen, carbon, and the halogens.

PROBLEM 5.25

Consider the following two Lewis structures of methanoic acid $[\text{CO}_2\text{H}]$, found in the venom of bee and ant stings. Its common name is formic acid]. Which one is a more stable structure? (In the next chapter, we'll examine which one is actually the "true" structure of methanoic acid.)



PROBLEM 5.26

Which type of bond requires more energy to break: a σ or a π bond?