



9. Quick! We Need a Better Model!

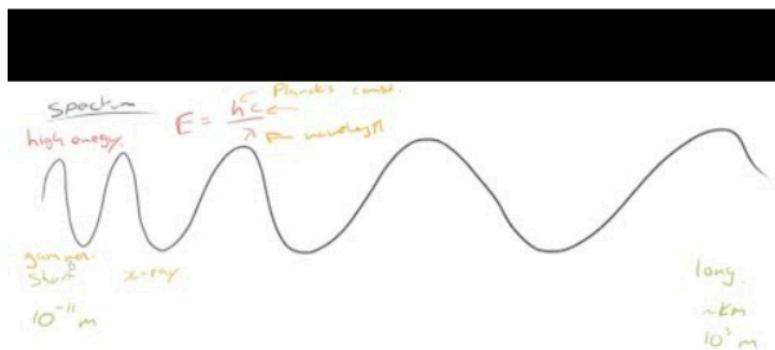
Learning Objectives

1. Describe the requirements for optical transparency in terms of scattering events
2. Recognize that neither crystallinity nor glassy microstructure are requirements for optical transparency
3. Explain the electromagnetic spectrum in terms of photon energy and photon wavelength
4. Convert energy from J to eV
5. Use the Bohr model of the atom to explain absorption and emission of energy accompanying transitions in electron energy levels
6. Identify the shortcomings of the Bohr model, specifically the need for four quantum numbers to fully describe the energy level of an electron
7. Provide intuitive descriptions of each of the four quantum numbers
8. Determine the electron configuration of a neutral atom or charged ion
9. Identify the allowable values for each of the quantum numbers
10. Apply the principle of octet stability to explain covalent, ionic and metallic (sea-of-electrons) bonding
11. Differentiate between the mechanism of formation of each of the primary bonds and provide examples of several properties that can be explained by each
12. Conclude that crystals form in ordered solids according to a decrease in energy
13. Demonstrate how the allowable energy states in an isolated atom separate into many closely spaced states in the formation of a solid leading to a band structure
14. Apply the band theory of solids to explain the classification of materials as metals, insulators, and semiconductors
15. Given a semiconductor material and a dopant, determine if a p-type or n-type semiconductor is created
16. Given the electron and hole mobilities and concentrations, calculate the conductivity of a semiconductor
17. Justify the optical transparency or opacity of a material in terms of its band structure and the energy of the incident photons
18. Explain the general principle of solid ionic conductivity
19. Explain the tetrahedral symmetry found in diamond, silicon or methane in terms of the sp³ hybridized bonding
20. Describe the diamond cubic crystal structure, and the tetrahedral interstitial site



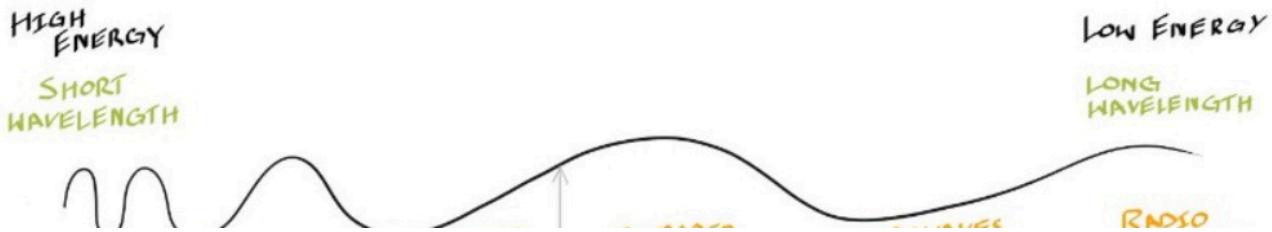
What's Light Got To Do With It?

In the previous section I told you that we'd need to be sure to understand light before we can understand optical transparency properly. You'll recall that with PMMA we were able to have a transparent polymer because PMMA is 100 % amorphous and this ensured that there was no boundaries between crystalline regions and amorphous regions that would scatter the light. We could say that optical transparency requires the absence of *scattering* events. However, we also discussed glassy metals that are fully amorphous but opaque. Even a single crystal metal, such as a silicon semiconductor, or a nickel-based single crystal jet turbine blade are both opaque, so neither being fully amorphous, not fully crystalline ensures optical transparency. Why is this, you ask? Well, it all has to do with how the material absorbs light energy, which is why we need to spend a little while discussing what light is.



[Link to this video on U of T servers.](#)

Visible light is only a very tiny portion of a massive spectrum of radiation that includes radio waves, microwaves, infrared radiation, ultraviolet radiation, x-rays, and even gamma rays. Our eyes can only see a tiny portion of this spectrum, the so-called *electromagnetic spectrum*. You can't see (with your eyes) the radiation that carries the signal to a radio, nor can you see the radiation that is used for a diagnostic x-ray, as you might get at a hospital or a dentist. However, the x-ray film in older x-ray machines or x-ray detectors in modern machines can "see" x-ray radiation. All of this amazing radiation is part of the broader electromagnetic spectrum and is illustrated in Figure 1.



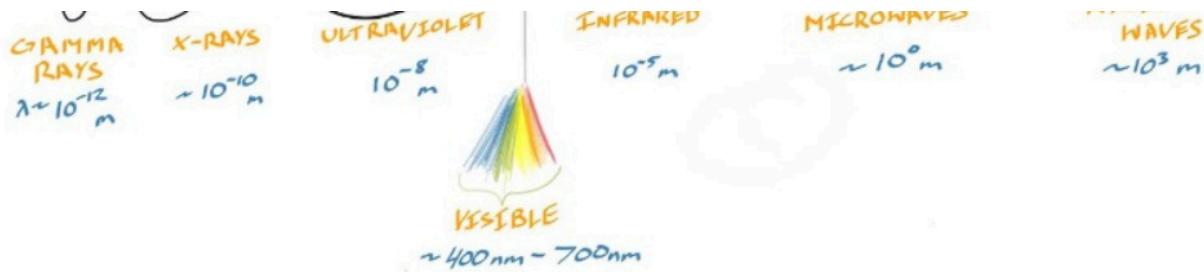


Figure 1. The electromagnetic spectrum. Visible light is only a tiny little bit of the spectrum.

Another feature of electromagnetic radiation is that the energy within the electromagnetic spectrum exists as chunks of energy, or photons. That is, it is more like filling a glass with ice-cubes than it is filling a glass with water. In this analogy, the water is more-or-less continuous while the ice cubes only exist in individual units. When things exist only as individual, non-divisible units we say that they are *quantized*. So, energy in the electromagnetic spectrum is quantized, and it turns out that the amount of energy in each so-called *quanta* or *photon* is inversely proportional to the wavelength of the radiation. Therefore, we say that radio waves are less energetic and ultraviolet waves, x-rays and gamma rays are more energetic. As humans we worry more about exposure to higher energy radiation than low energy radiation. This is why we wear sunscreen and try not to get too many x-rays each year. The value of energy in a quanta of radiation can be calculated from Equation 1.

$$E = \frac{hc}{\lambda} \quad (1)$$

where h is the Planck constant equal to $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$, c is the speed of light in a vacuum equal to $3 \times 10^8 \frac{\text{m}}{\text{s}}$ and λ is the wavelength of the light in $\frac{\text{m}}{\text{s}}$.

People dealing with energy around this scale tend to get tired of saying, "aitch-cee-over-lambda," over and over again, so frequently you'll see equation 1 written as

$$E = h\nu \quad (2)$$

where ν is the frequency of the light, in Hertz ($1 \text{ Hz} = \frac{1}{\text{s}}$). Neat, right? See how that works? $\nu = \frac{c}{\lambda} [= \frac{\text{m}}{\text{s}} = \frac{1}{\text{s}}]$, and frequency is inversely proportional to wavelength.

 9.1.1
Review

Mark as: [None ▾](#)

Which of the following items would you expect to be optically transparent? A. B. C. D.

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a	Non-porous, polycrystalline, silicon dioxide
b	Non-porous, single crystal, silicon dioxide
c	Porous, polycrystalline, silicon dioxide

d Porous, single crystal, silicon dioxide



9.2.1
Review

Mark as: [None ▾](#)

A single crystal of diamond is optically transparent, so would a single crystal of aluminum also be transparent?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a Yes

b No



9.2.2
Review

Mark as: [None ▾](#)

Polymethylmethacrylate is completely amorphous, so would an amorphous sample of a metal also be transparent?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a Yes

b No



9.3.1
Review

Mark as: [None ▾](#)

Which of the following correctly orders these types of electromagnetic radiation from lower energy to higher energy?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a Radio waves, infrared, ultraviolet, microwaves, x-ray, gamma ray

b Radio waves, microwaves, infrared, ultraviolet, x-ray, gamma ray

c Infrared, microwaves, ultraviolet, gamma ray

d Gamma ray, infrared, x-ray, ultraviolet

 9.3.2
Review

Mark as: [None ▾](#)

Which of the following photons has the highest energy?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a A photon with a wavelength of 700 nm

b A 3 eV photon

c A photon having a wavelength of 1.54 Å

d An ultraviolet photon

Einstein's Nobel Prize

Prof. Jun Nogamiⁱ

Albert Einstein won the 1921 Nobel Prize in Physics "for his services to Theoretical Physics, and

especially for his discovery of the law of the photoelectric effect". The first part of the citation is very vague, but it most probably refers to his work on special relativity. His ground breaking paper on Special Relativity was published in 1905, but it was regarded as still too controversial at the time of the award.

In writing the second part of the citation, the committee went for a sure thing. The photoelectric effect is seen in experiments that measure electron emission from a surface that results from energy deposited by incoming light. In a classical picture, light energy should accumulate in the atoms of a material until electrons bound to these atoms can be emitted. However, experiments showed that electron emission was a function of the frequency of the light, and that below a certain critical value, there was no light emission regardless of the intensity of the incident light. Above that threshold value, the maximum kinetic energy of the emitted electrons was a linear function of the frequency.

Einstein explained this in terms of the quantization of light into photons of energy $E=h\nu$, where if the photon energy was below a certain value called the work function, the material will not emit electrons. The work function can be thought of as the energy barrier that has to be surmounted in order for electrons to escape the material.

Of course light can behave both as a stream of particles as well as a wave, and it turns out this is true of electrons as well, but that is something that is beyond the scope of this sidebar.

Accelerating an Electron

When dealing with energies from the electromagnetic spectrum the units of joules are sometimes a little cumbersome. For example, a typical red laser pointer has a wavelength of **650 nm**, which is convenient enough, however, let's calculate the energy of a quanta of red light, in joules.

$$E = \frac{h \cdot c}{\lambda}$$
$$\frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \cdot 3 \times 10^8 \frac{\text{m}}{\text{s}}}{650 \times 10^{-9} \text{ m}}$$
$$= 3.06 \times 10^{-19} \text{ J}$$

Which is correct, but the *order of magnitude* is irritating and a little tedious for our human brains to process, and our mouths to speak and our fingers to type when we are dealing with numbers around this order of magnitude a lot.

When we are talking about **small amounts of energy**ⁱ, like those relevant in the discussion of a single atom, a more convenient unit of energy is the electron volt.

Here, as it turns out, we are dealing with energy levels that you might find if you took an electron, which is a charged particle (units of Coulombs), and accelerated it through a volt (units of $\frac{\text{J}}{\text{C}}$) of

potential. The electrical charge on an electron is known as the *fundamental charge* and is equal to $1.602 \times 10^{-19} C$. So, an electron accelerated through one volt would have one *electron volt of energy*, written 1 eV.

$$1 \text{ eV} = E_{(1 \text{ e}^- \text{ through } 1 \text{ V})} = 1.602 \times 10^{-19} \text{ C} \cdot 1 \frac{\text{J}}{\text{C}} = 1.602 \times 10^{-19} \text{ J}$$

In these units, it is also convenient to use Planck's constant in the form:

$$h = 4.136 \times 10^{-15} \text{ eV} \cdot \text{s}$$

For example, the photon energy for red light, in eV is

$$E_{(\text{Red Photon})} = \frac{3.06 \times 10^{-19} \text{ J}}{1.602 \times 10^{-19} \frac{\text{J}}{\text{eV}}} = 1.91 \text{ eV}$$

Now that rolls off the tongue nicely doesn't it? And look how easily I can type it: 1.91 eV. Try saying it. Isn't that convenient? If you're a hipster, you could even round it up and say, "red light is about 2 eV."



9.4.1
Review

Mark as: None ▾

Which of the following is the correct conversion of 5 J into eV?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 8.0×10⁻¹⁹ eV

b 3.1×10¹⁹ eV

c 8.0×10¹⁹ eV

d 3.1×10⁻¹⁹ eV



8.4.2
Review

Mark as: None ▾

Which of the following is the correct conversion of 1 eV into J into eV?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 1.6×10¹⁹ J

b 6.2×10^{18} J

c 1.6×10^{-19} J

d 6.2×10^{-18} J

The Atom

I believe that we have previously determined that you believe in the existence of atoms, so that's a good thing. In fact, in the previous section we even discussed the electron and the charge that it carries and discussed the concept of the quantization of energy, so we are actually well on our way to understanding the basic structure of the atom. The basic structure of the atom is illustrated in Figure 2.

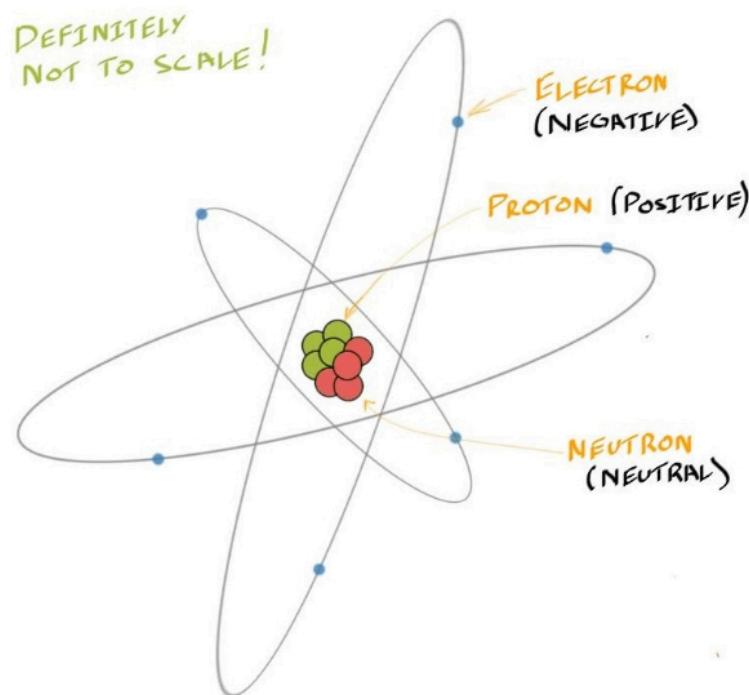
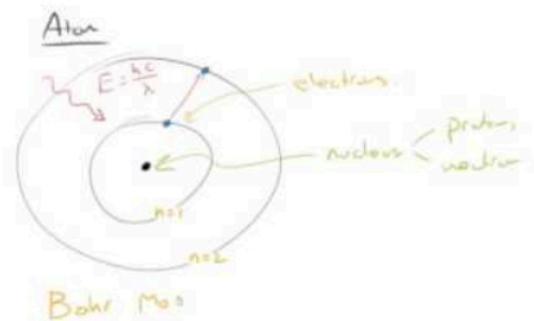


Figure 2. The basic structure of an atom. A central nucleus contains protons and neutrons and the vast majority of the mass. Protons carry positive charge and orbiting electrons carry negative charge.

A central nucleus contains positively charged particles called protons. The nucleus also contains particles having no charge, known logically as neutrons. The mass of a proton is roughly the same as

the mass of a neutron and is equal to $1.67 \times 10^{-27} \text{ kg}$. Orbiting around the nucleus are negatively charged particles called electrons. The mass of the electron is $9.1 \times 10^{-31} \text{ kg}$ making each of protons and neutrons roughly 1800 times more massive than electrons. It's safe to say that most of the mass of an atom comes from the nucleus. The number of protons in a nucleus is a hugely important number. This is what determines what element an atom is and is called the *atomic number*. We frequently use the capital letter Z for atomic number. Differing numbers of neutrons in an atom give us so-called *isotopes* of an element. For example, you may have heard of carbon-14, also written ^{14}C , that can be used to determine the age of some organic archaeological specimens. ^{14}C is an isotope of carbon that contains extra neutrons. Carbon always contains 6 protons, because, as we said, that's what makes it carbon. Five protons and it would be boron. Seven protons and it would be nitrogen, but I digress. Most naturally occurring carbon contains 6 neutrons in its nucleus and we would call it ^{12}C or carbon-12, however ^{14}C contains eight neutrons, or 14 particles in its nucleus. The amount of carbon-14 in the atmosphere is generally constant over time, however ^{14}C is unstable and decays at a known rate over time so by observing the amount of ^{14}C in an organic specimen we can approximate its age. So interesting!

The Bohr Model of the Atom



[Link to this video on U of T servers.](#)

By now we've got a fairly good sense for the basic structure of the atom. Let's look at things in a little more detail. Through history there were a few different models of the atom, each being usurped by the next, improved model when new experiments poked holes in the previous model. The first model that made a significant stride in explaining quantitatively, the experimental results of the time was the Bohr model, named after Niels Bohr. Even though the Bohr model can't explain all of the experimental data that we have now, it is a pretty significant model and is actually still quite useful in some discussions, so we're going to start with it. The essential features of the Bohr model are a central nucleus with

orbiting electrons, electrons orbit at fixed distances from the nucleus, and electrons may jump to higher orbits if they absorb a quanta of energy exactly equal to the difference in energy between the two orbits and similarly release a quanta of energy if the electron drops back down to a lower orbit.

There are a number of problems with the Bohr model, one of which is that it only allows calculations of atoms with one electron. That is, hydrogen H, a helium ion H^+ , or a doubly ionized lithium ion Li^{+2} , etc. There are other problems with it as well, much of it related to not being able to predict line splitting experiments, where closely spaced energy levels were revealed within the orbits further away from the nucleus than the first orbit.



9.5

Review

Mark as: None ▾

In an experiment, a high energy beam of electrons is used to eject (ionize) a core electron from an atom of iron. A picosecond later, another electron drops down in energy to fill the vacancy left by the ejected electron. When this second electron drops down in energy what energy change occurs for this atom?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a There is no change in the energy of the atom
- b A quanta of energy is absorbed
- c Several different amounts of energy are absorbed
- d A quanta of energy is released



9.6

Review

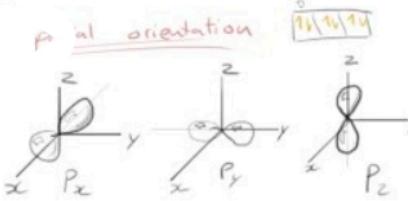
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Which of the following would NOT be considered a shortcoming of the Bohr model of the atom?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a Electron energy levels exist in shells and sub-shells
- b Electron energy levels may be described with a spin quantum number
- c Electrons may follow non-spherical orbitals
- d Electron energy levels are quantized

The Quantum-Mechanical Model of the Atom

- 1) Principal Q.N. $n = 1, 2, 3, 4, \dots$ size
- 2) Angular momentum Q.N. $\ell = 0, 1, 2, \dots (n-1)$ shape
 $\Rightarrow \ell = 0 \Leftrightarrow s$  $\ell = 1 \Leftrightarrow p$ 
- 3) Magnetic Q.N.
 $-\ell \leq m_\ell \leq \ell$
 $\Rightarrow \ell = 1 \Leftrightarrow p$ 

[Link to this video on U of T servers.](#)

So, how do we address these problems with the Bohr model? Our current best model takes a bit of quantum mechanics and a bit of classical mechanics together to explain the atom: thus the name, *quantum-mechanical model*, or sometimes, the *wave-mechanical model*. In this model, to fully describe the energy state of an electron, we must use four quantum numbers (recall that Bohr only had one). In the interests of expediency and in discussing what we need to here, let's get right into these four quantum numbers.

The Principal Quantum Number n

You are already familiar with the principal quantum number from the Bohr model. The principal quantum number describes the **size** of the electron orbit. It can have any integer value beginning at 1 and increasing from there. Sometimes you'll see the principal quantum number described with letters instead of numbers. The letters are always upper case and start at K and move along the alphabet from there so the *K shell* is $n = 1$, the *L shell* is $n = 2$, the *M shell* is $n = 3$, and so on.

The Angular Momentum or Azimuthal Quantum Number ℓ

The angular momentum quantum number (also sometimes referred to as the azimuthal quantum

number) describes the **shape** of the electron orbital. The angular momentum quantum number can have any value ranging from zero to one less than the principal quantum number, that is $\ell = 0, 1, 2, \dots n - 1$. Frequently, the angular momentum quantum number is referred to using lower case letters. There is very little intuitive meaning to the letters so it is likely best to just take a deep breath and memorize these. Angular momentum quantum number $\ell = 0$ is the *s sub-shell*, $\ell = 1$ is the *p sub-shell*, $\ell = 2$ is the *d sub-shell*, and $\ell = 3$ is the *f sub-shell*. There is very little need to go beyond that, so we'll stop there.

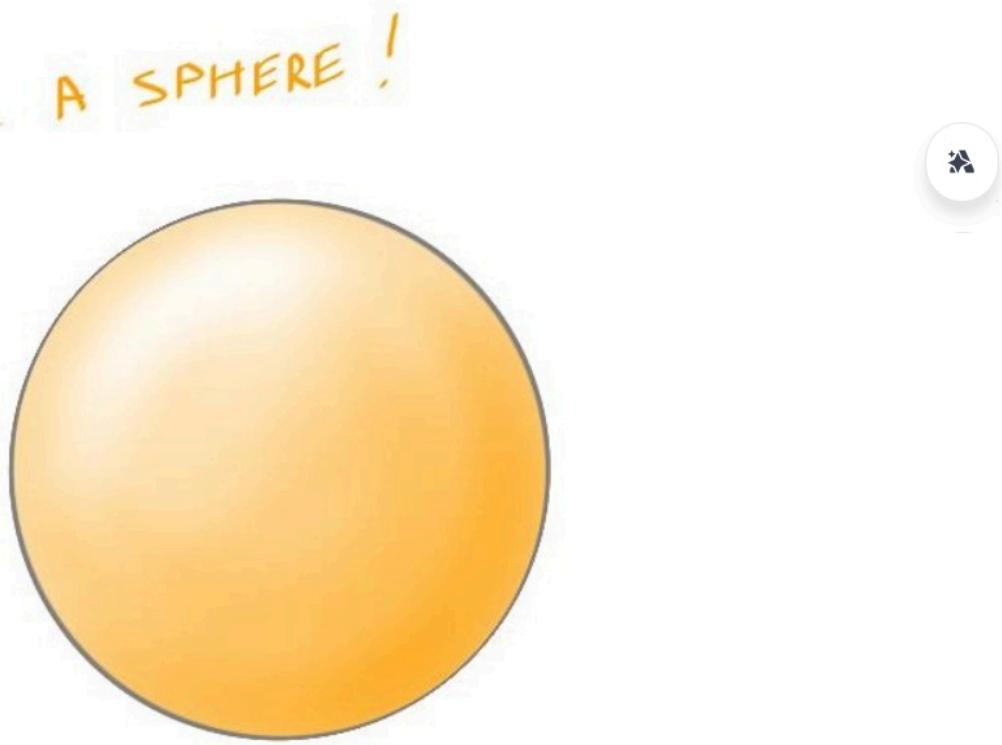


Figure 3. The *s* sub-shell is spherical. I thought about re-using a sphere that I drew for an atom earlier, but I thought that would be a little cheeky.

The *s* sub-shell has a spherical shape, as shown in Figure 3.

I always liked the fact that *sphere* starts with an *s*, although the letter *s* isn't used for this reason. It actually has to do with the way that lines appeared in early spectroscopy experiments: sharp, principal, diffuse, and fundamental. Of course, this little nugget of history isn't particularly relevant, at least for our discussion, but I find it helps to know so that your brain doesn't dwell on it.

The *p* sub-shell has two lobes and is frequently described as being shaped like a dumbbell, as shown in Figure 4. Of course, if I went to the gym to do some arm curls and picked up a dumbbell that looked like that I'd be pretty surprised, but I suppose there's no better object to draw a comparison to so we're stuck describing the *p* sub-shell as being dumbbell shaped.

"DUMBBELL"

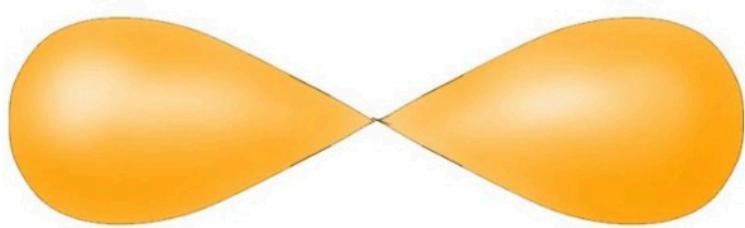


Figure 4. The *p* sub-shell has two elongated tear-drop shaped lobes. This shape is often called a dumbbell shape. I tried my best to shade the lobes to make them look three-dimensional, but I'm not sure how well that came across.

For most of the materials that we are concerned with, the outermost parts of the atom consist of either s or p subshells, and these are the ones involved in bonding. The f subshells are localized around the nucleus and so are not involved in bonding and remain "atomic like" even in solid materials. For these reasons we won't discuss the shapes of the d or f subshells.

The Magnetic Quantum Number m_l

The magnetic quantum number describes how many different ways each subshell can be **orientated**.

Each of the unique orientations is called an *orbital*. The possible number of orientations or orbitals within a given subshell are given by the magnetic quantum number. These are twice the angular momentum quantum number plus one and are written as integers ranging from the negative to the positive value of ℓ , or

$$-\ell \leq m_l \leq \ell$$



For example, for the *p* subshell, or $\ell = 1$, there are three orbitals and the magnetic quantum number could be -1, 0, or 1. Within each of these orbitals, or any orbital for that fact, there may be a maximum of two electrons. These electrons are distinguished from one another by the spin quantum number.

The Spin Quantum Number m_s

The spin quantum number doesn't really describe anything intuitive. It can be thought to describe the electron spinning on an axis one way or the other, but electrons don't actually spin, so that's potentially misleading. The spin quantum number reflects the slightly different energy level for two electrons within a specific orbital. The values of the spin quantum number are either positive or negative one half, or

$$m_s = \pm \frac{1}{2}$$



The principal quantum number most closely describes which of the following features of the electron probability distribution?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The size

b The spin

c The spatial orientation

d The shape

 9.7.2
Review

Mark as: [None ▾](#)

The angular momentum quantum number most closely describes which of the following features of the electron probability distribution?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The spin

b The shape

c The size

d The spatial orientation

 9.7.3
Review

Mark as: [None ▾](#)

The magnetic quantum number most closely describes which of the following features of the electron probability distribution?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The shape

b The spatial orientation

c The size

d The spin



9.7.4

Review

Mark as: **None** ▾

The spin quantum number most closely describes which of the following features of the electron probability distribution?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The colour

b The smell

c The size

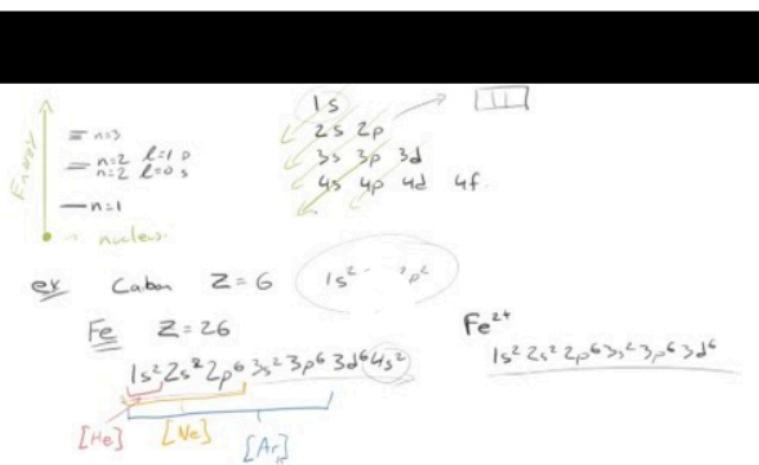
d The spin

Putting All of This Into Action

There is an entire rich history of how these electron behaviours were discovered and how these quantum numbers were first characterized. There is also a great deal more detail that could be explored around each quantum number. However, for our purposes, to bring us to atomic bonding, we should have just about enough information at this point. What's missing is knowledge of how these quantum numbers are used to describe the energy levels of electrons in isolated atoms (as

opposed to the energy states in molecules or solids). We'll also need to talk about how the individual energy levels stack up against each other.

The Relative Magnitudes of Electron Energy Levels



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If you've never studied this topic you would likely make the very reasonable assumption at this point that the electron shell closest to the nucleus, having the highest value of **energy**ⁱ would be the shell with a principal quantum number of one, or $n = 1$. This is correct. You may then reasonably assume that the energy levels would decrease in magnitude, and move further away from the nucleus according to only the principal quantum number, that is, $n = 1, 2, 3, 4, 5$ and so on. This is what we would expect from the Bohr model. However, things are actually a little more interesting than that and we find that some of the subshells within different shells actually overlap one another. This is frequently summarized, and memorized, using a simple sketch, shown in Figure 5.

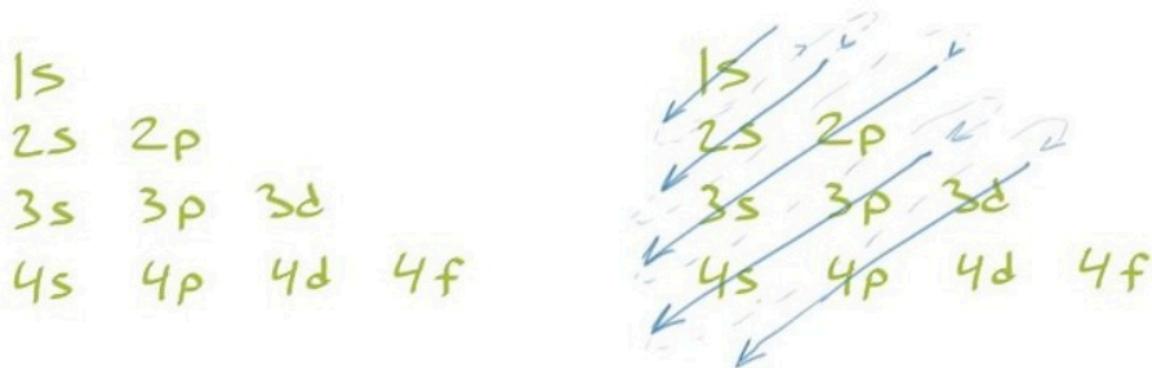


Figure 5. A common sketch used to describe and memorize the general rule for the relative energy levels of subshells. The shells and subshells are first drawn out using numbers for the principal quantum number and letters (s, p, d, f) for the angular momentum quantum number. Leftwards and downwards arrows are then drawn through these subshell labels, showing the order of filling of electrons into isolated atoms.

Referring to Figure 5 you'll see that everything proceeds logically, according to increasing values of the principal quantum number until we reach 4s. The 4s subshell seems to have jumped the queue and began filling before the 3d subshell. This is true and in just a moment I'll show you the elements where this occurs. But first, let's look at an example for a smaller, lighter element.

The Electron Configuration of Carbon

Our old friend carbon, as you can confirm from the periodic table, has an atomic number of 6. This means there are six protons in the nucleus of an atom of carbon. So, for us to build a neutral atom of carbon we will need to place six electrons into shells and subshells around the nucleus. Let's refer again to Figure 5 to help us. The arrow goes through 1s first. Since we know there is only one orientation (one orbital) within the s subshell we can only put two electrons into the 1s subshell. The notation that is typically used is $1s^2$, showing that 1s contains two electrons. Again referring to Figure 5 we see that the arrows next go through 2s. Now, even though this is now the second shell, or principal quantum number equal to two, what matters here is that we are filling a s subshell and that will only hold two electrons, so we write $2s^2$. At this point we have filled four electrons around the nucleus and we need to add two more. Figure 5 shows us that we will fill into 2p next. Again, since there are only 2 electrons we write $2p^2$. The full electron configuration for an isolated atom of neutral carbon is then

$$1s^2 2s^2 2p^2.$$

Sometimes another shorthand is used and we can use the electron configurations of the inert gases, enclosed in square brackets, to abbreviate electron configurations. We could write, for carbon, $[He]2s^2 2p^2$, since the electron configuration for helium is $1s^2$. Of course, for carbon this is hardly a time saver, but for bigger elements it becomes handy.

When 4s is Closer Than 3d

Let's figure out when 4s will fill before 3d. Figure 5 shows that 4s begins to fill after 3p is filled. This means that we have filled 1s, 2s, 2p, 3s, and 3p. Let's tally up those electrons so that we can hone in on which element to look at. The electron configurations immediately before 4s fills is

$$1s^2 2s^2 2p^6 3s^2 3p^6,$$

which means that we have 18 electrons. Atomic number 18 is argon, so adding one more proton gives us potassium and a neutral atom of K will have 19 electrons and this electron configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1.$$

We see that the 4s subshell is populated even though the n=3 shell is not full; 3d is empty. Adding another proton gives us Z = 20, or calcium and the electronic configuration for calcium is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2,$$

exactly as Figure 5 tells us. Okay, you may think this is a little tedious but I am getting to a little surprise. Bear with me here and permit me to add two more protons to bring us to $z = 22$, or titanium, which unsurprisingly has this electron configuration, or does it...

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2?$$

Well, I'm being a tad provocative here. About what, you ask? About the order that I wrote the electron configuration with 4s before 3d. Yes, it may look a little odd to have 3 before 4, but the conversation is more interesting than that. You see, our rule-of-thumb only really takes us as far as calcium. Once we get to scandium and higher, with enough electrons to populate into the 3d shell, according to Figure 5, there is a shift in energy levels and 4s is actually filled after 3d. The reason I took us to titanium is because it illustrates this nicely. When titanium exists as an ion, it is commonly observed to exist as Ti^{2+} and has this electron configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$$

showing that the 4s electrons were ionized and were therefore further from the nucleus. For this reason, it is really better to write the electron configuration in order of increasing principal quantum number, so titanium would be

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$$

or, written in the abbreviated form

$$[Ar] 3d^2 4s^2$$

A Few Exceptions

It is worthwhile at this point to mention a couple of exceptions to the electron configurations we have discussed so far. These both involve the 3d subshell in either a half filled or completely filled state. It turns out that having the 3d subshell half filled (5 electrons) or completely filled (10 electrons) is slightly lower energy than you would otherwise expect. This leads to unexpected electron configurations for chromium and copper. Let's take a quick look at vanadium with atomic number of 23, which is one less proton than chromium. Vanadium has this electronic configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2.$$

Moving up one element to chromium would mean adding one more electron and so we would expect chromium to have electron configuration of $[Ar] 3d^4 4s^2$, however, it is slightly energetically favorable for one of the 4s electrons to move to 3d in order for 3d to achieve a half filled state. This gives

chromium the otherwise unexpected electron configuration of

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1.$$

Similarly, copper sees a 4s electron move to create a completely filled 3d subshell and has this electronic configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1.$$



9.8.1
Review

Mark as: None ▾

Which of the following is the correct electronic configuration for a neutral atom of scandium Sc, in its ground (unexcited) state?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 1s² 2s² 2p⁶ 3s² 3p⁶ 3d³

b 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹ 4s²

c 1s² 2s² 2p⁶ 3s² 3p⁶ 3d² 4s¹

d 1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 4p¹



9.8.2
Review

Mark as: None ▾

Which of the following would you expect to be the most stable charge on an ion of strontium Sr?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 1+

b 1-

c 2+

d 2-



9.8.3
Review



No Correct Answer

Mark as: None ▾

What is the electronic structure of Zn²⁺?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹

b 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s²

c 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹ 4s¹

d 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰



9.8.4
Review

Mark as: None ▾

Which of the following is the correct electronic configuration for an ion of Ge⁴⁺?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶

b 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰

c 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁶ 4s² 4p²

d 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p²



9.9.1
Review

Mark as: None ▾

Which of the following cases are possible quantum numbers for 3d electrons in Fe?

- (a) $n=3, l=2, m_l=-2, m_s=-1/2$
- (b) $n=2, l=1, m_l=-1, m_s=+1/2$
- (c) $n=3, l=2, m_l=0, m_s=+1/2$
- (d) $n=4, l=2, m_l=+1, m_s=-1/2$
- (e) $n=3, l=2, m_l=-1, m_s=+1/2$
- (f) $n=1, l=0, m_l=0, m_s=+1/2$
- (g) $n=3, l=1, m_l=-1, m_s=-1/2$

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a a,c,e,g

b b,d,e

c c,g

d a,c,e



Octet Stability



[Link to this video on U of T servers.](#)

This is a great time to start discussing the foundation for bonding. We've used the inert gas abbreviation a few times in writing out electron configurations and you may have noticed something special about the inert gas configurations. Here they are in order

He $1s^2$

Ne $1s^2 2s^2 2p^6$

Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

Kr $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6$

That “something special” about the inert gases, in fact what makes them inert or unreactive, is that their electron configurations are very stable. This stable configuration involves eight electrons in their outermost shell^①. Sometimes the so-called *octet rule* is written as

$ns^2 np^6$

Atomic Bonding



[Link to this video on U of T servers.](#)

Let's maintain our learning momentum here and jump right off of octet stability and get into bonding. We can do this quite smoothly actually since the basis for the primary bonds is achieving a stable octet. The three primary bond types are ionic, covalent, and metallic, and we will soon see that each of these allows the participating atoms to achieve a stable octet.

Ionic Bonding

Ionic bonding involves a *transfer* of electrons followed by a subsequent charge attraction between oppositely charged ions. Let's start with a classic example, sodium chloride (NaCl).

The atomic number of chlorine is 17 and so the electronic configuration of chlorine is

$$1s^2 2s^2 2p^6 3s^2 3p^5,$$

or only one electron away from having the electron configuration of argon. If only chlorine could pick up an electron it would become a negatively charged ion, or anion, Cl^{-1} , with electron configuration $3s^2 3p^6$. But where, or where is chlorine to get an electron? The old electrical engineering joke goes, "where do electrons come from? Batteries." So funny. But seriously, the electron needs to come from another atom. Enter sodium.

The atomic number of sodium is 11 and so the electronic configuration for sodium is

$$1s^2 2s^2 2p^6 3s^1,$$

or

$$[\text{Ne}] 3s^1.$$

Written in the abbreviated form it is quite obvious that sodium has one electron more than Ne, or one electron in excess of octet stability. This means that if sodium could get rid of one electron it could achieve octet stability and would become a positively charged ion, or cation, Na^+ . Now, sodium can't just go around dropping an electron anywhere it likes. Isn't this just a perfect *meet-cute*? Sodium can transfer an electron to chlorine and they both achieve octet stability. Now comes the ionic bond. There is a coulombic, or charge attraction between these oppositely charged ions. Figure 6 shows a schematic cross-section through a crystal of NaCl^{\circledR} .

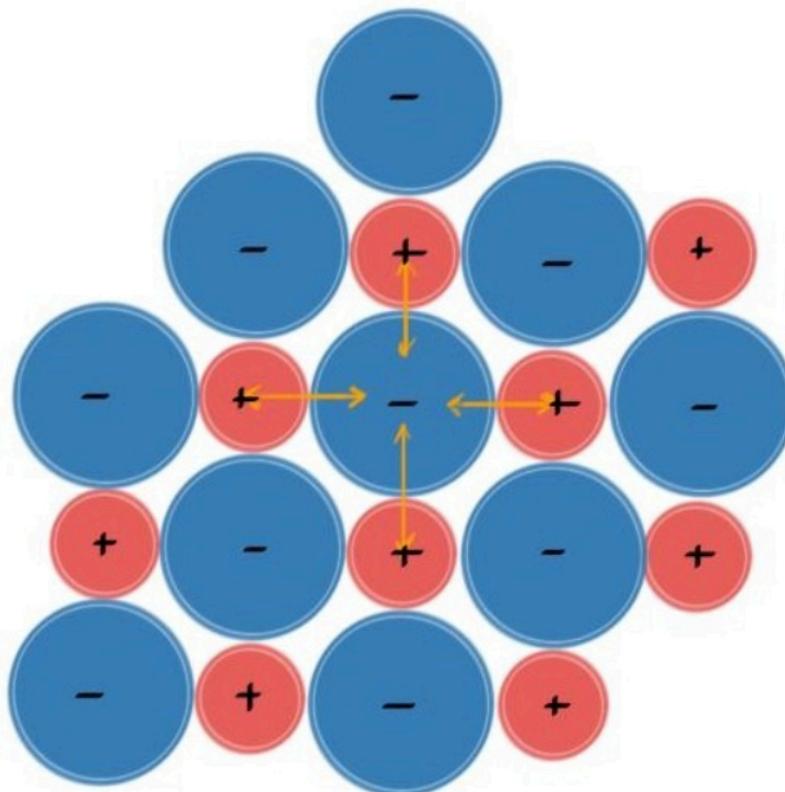


Figure 6. A cartoon slice through a crystal of NaCl. The charge attractions between the nearest neighbour oppositely charged ions have been schematically illustrated.

An important feature of ionic bonds is that the charge attraction is general, between all oppositely charged ions. Furthermore, the charge on an ion is not depleted by its participation in an ionic bond. For this reason, ionic bonding is said to be *non-directional*.

It is worth noting here that we can explain the fact that ionic solids do not conduct electricity by noting the stability of these ions, with all their electrons strongly bound to their respective nuclei. This means that there are no free

Covalent Bonding

Covalent bonding involves the sharing of electrons. In fact, the name tells us this is the case: there is a sharing of the valence electrons, or a co-valency. Covalent bonding is found in molecules and a great place to start is with a simple molecule, methane CH_4 . As we already know, carbon has atomic number of 6 and an electron configuration of

$$1s^2 2s^2 2p^2$$

which is four electrons away from the next stable octet, the electron configuration of neon. Hydrogen on the other hand has atomic number of one and an electron configuration of

$$1s^1$$

which is only one electron away from the electron configuration of helium. So, if carbon can obtain four valence electrons and hydrogen can obtain one, then each of them will have a stable electron configuration. It makes sense then, that the formula for methane is one carbon to four hydrogens, CH_4 . This is shown, along with the valence electrons, in Figure 7.

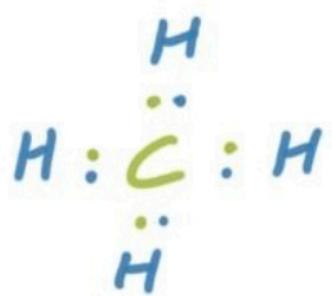


Figure 7. A cartoon depiction of the electron sharing in methane. This type of sketch with valence electrons illustrated as dots is known formally as a Lewis electron dot diagram.

Covalent molecules are frequently drawn with a short straight line representing each pair of shared

electrons and I've illustrated that in Figure 8. We also saw this, although we hadn't formally discussed it yet, when we discussed polymers.

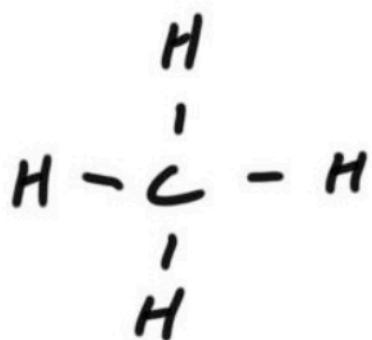


Figure 8. A cartoon depiction of the bonding in methane. Commonly, to simplify things, each pair of shared electrons is drawn as a single line.

One important way that the covalent bond differs from the ionic bond is that the covalent bond only occurs between specific atoms. That is, in methane, the carbon atom is bonded only to each of the four hydrogens and not to any other atoms. Any other interactions are *secondary* and are much weaker, and not covalent. Those would be the secondary (intermolecular) bonds that we discussed in the polymer section. Because covalent bonds occur between specific atoms we refer to them as *directional* bonds.

Covalent bonding can also occur between like atoms. For example, gas phase hydrogen exists as the molecule H_2 with two atoms sharing each of their single valence electrons in a single covalent bond. This sharing of electrons is the defining characteristic of the covalent bond and what distinguishes it from the ionic bond, where there is an electron transfer between the atoms involved in the bond.

Metallic Bonding

There are two main models used to describe metallic bonding: the sea-of-electrons model, and the band theory of solids. We will cover the sea-of-electrons model first. In the sea-of-electrons model the valence electrons are not bound to a specific nucleus, but are instead thought to be free to move around while the nuclei are bound into their lattice positions, as we have already learned about when we covered crystalline solids. The valence electrons form the *sea-of-electrons* while the core electrons plus the nucleus form what is sometimes called the *ion core*, as illustrated in Figure 9.

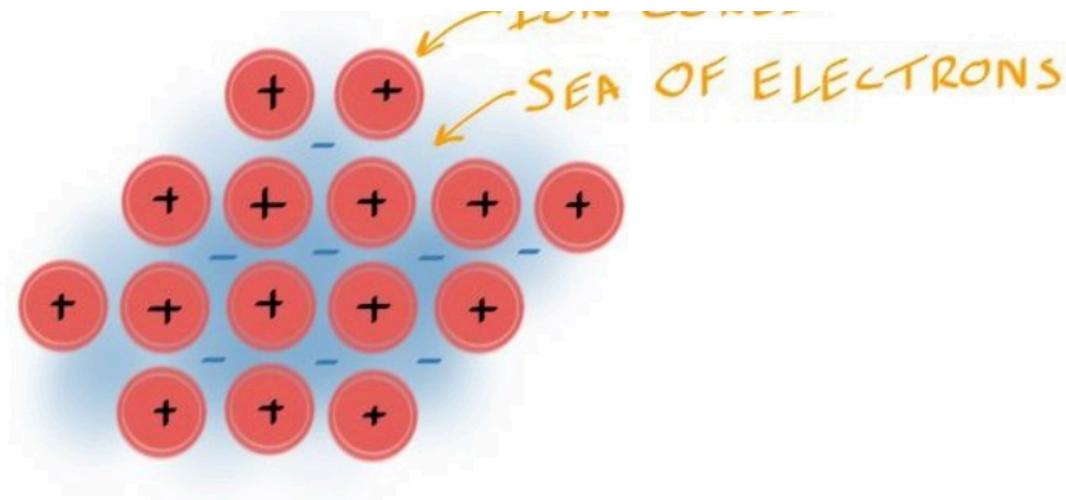


Figure 9. A cartoon depiction of a slice through a metal showing the sea-of-electrons bonding together the ion cores in a lattice.

9.10.1
Review

Mark as: [None ▾](#)

How many covalent bonds would you expect oxygen to form in a molecule, typically?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 2

b 1

c 3

d 4

9.11.1
Review

Mark as: [None ▾](#)

The covalent bond is formed by which of the following?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a A transfer of electrons

b A collection of delocalized electrons holding together the ion cores

c Two electrons sharing exactly the same set of quantum numbers

- d A sharing of electrons



9.11.2

Review

Mark as: [None ▾](#)

The ionic bond is formed by which of the following?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a A transfer of electrons
- b A collection of delocalized electrons holding together the ion cores
- c Two electrons sharing exactly the same set of quantum numbers
- d A sharing of electrons



9.11.3

Review

Mark as: [None ▾](#)

The metallic bond is formed by which of the following?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a A sharing of electrons between two specific nuclei
- b A transfer of electrons
- c Two electrons sharing exactly the same set of quantum numbers
- d A collection of delocalized electrons holding together the ion cores

Explaining Some Properties

With the electrons in the sea-of-electrons model being free to move past the ion cores (or so-called *delocalized*) it is fairly clear how these electrons can readily conduct electricity in metals. What's more, our understanding of covalent bonding, with electrons shared between atoms specific atoms and not free to conduct helps to explain the electrically insulating property of polymers.

The sea-of-electrons model can also help to explain the ductility of most metals. If a sufficiently high stress is applied to a metallic crystal, eventually one plane of atoms will move past another, as we discussed in the section on plastic deformation and dislocations. There is an energy requirement to move the planes, however, it is generally possible for the planes to move past one another since they are always held together by the sea of negatively charged electrons. Figure 10 depicts theoretical plastic deformation in both a metal and a ceramic.

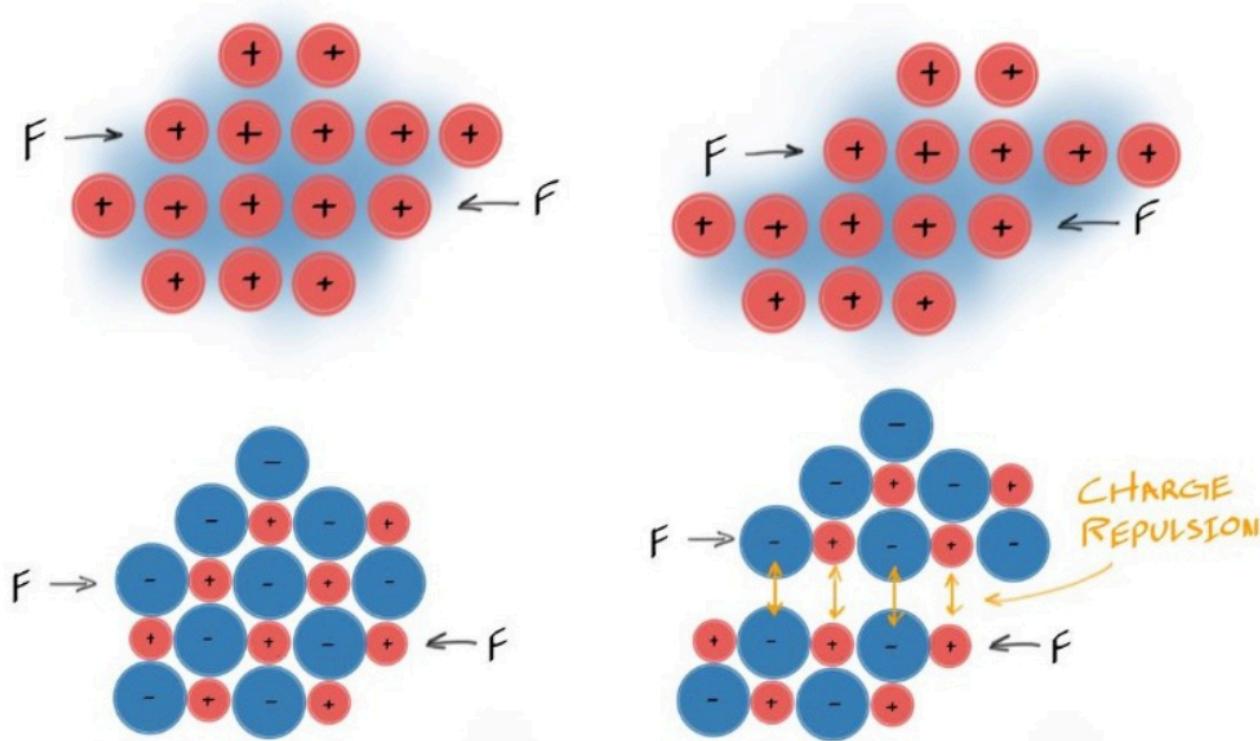


Figure 10. A cartoon depiction of plastic deformation occurring in a metal and in a ceramic. In a metal, the ion cores are always held together by the sea of negatively charged electrons, while in the ceramic like charges must come closer to each other. This raises the stress required to deform a ceramic higher than the strength of the ceramic and we get fracture before deformation.\

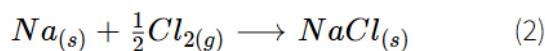
In a ceramic, for one plane to move past another we would need to have similarly charged ions pass

through an intermediate position in which they come closer to one another. This significantly raises the stress required to move a plane of atoms in a ceramic and typically leads to fracture before deformation.

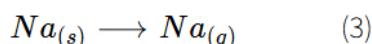
Of course, with polymers we have already seen how the strong covalent bonds are not generally broken during plastic deformation, but rather the weaker secondary interactions are overcome as molecules slide past one another. When we consider the electrical properties of polymers we can quite easily explain their electrically insulating properties due to the lack of any free electrons; all of the valence electrons are tightly bound in the strong covalent bonds.

Why Does Salt Form a Crystal Anyway?

So, we have avoided a question that you may have actually had quite a while ago when we first covered the crystalline structure of solids. That question may have been something along the lines of, "okay, I know that NaCl forms an ordered solid, but why? What is the reason that it forms this structure?" That is, in fact, a great question, and one that we'll begin to answer here. What would make us feel comfortable with salt forming a crystal at room temperature? That is, I wouldn't be comfortable with my water bottle suddenly flying up from the ground where I dropped it and landing on my desk. While it would be highly entertaining, I wouldn't be comfortable with a bird poo suddenly coming off of my shoulder and flying back up to the offending bird. Frequently the reason given that these things don't occur is that they are not energetically favourable, which is just a fancy way of saying that things tend to proceed from higher energy to lower energy. So, let's consider the formation of solid crystalline salt from gas phase chlorine and solid sodium:

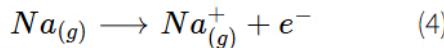


There's actually quite a lot going on in Equation 2 so it might be useful to break this equation down into a few smaller steps. It turns out that we can do this safely, and correctly, and we'll discuss why later in the course. First, let's see what we can do with that solid elemental sodium. We could break it down into a single gas phase atom. There are other logical ways we could proceed, but a nice little isolated gas phase atom seems to me like a good step.

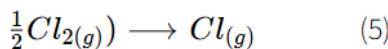


Now, we said that we wanted to look at the energy changes here to confirm that this was energetically favourable. We actually need to be really careful about how we account for these energy changes and we'll need to discuss this in more detail later. For now, I'll tell you that the a solid going directly to a gas, without melting first is called sublimation and the so-called *sublimation enthalpy* for sodium is $\Delta H_{\text{sublimation}} = 109 \frac{\text{kJ}}{\text{mol}}$. A quick word on the sign convention here is worthwhile. Positive values mean that we need to put energy into our system for the reaction to proceed from left to right. That is, it takes energy to melt and then boil sodium. Not too surprising. What's next? Well, we know that salt

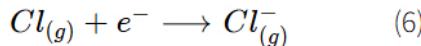
It takes energy to melt and then boil sodium. Not too surprising. What's next? Well, we know that salt has ionic bonds, so let's make that nice little gas phase sodium atom into an ion.



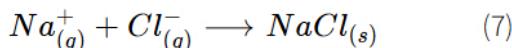
The *ionization energy* is $IE_{Na} = 497 \frac{kJ}{mol}$ and again, you'll notice that it is positive. Not looking so good for my comfort with sodium chloride existing as a crystalline solid. Maybe we'll have more luck with chlorine. Chlorine is already in the gas phase, but is present as a diatomic molecule. Irritating. Let's make it into a single gas phase atom as we did for sodium.



This is the breaking of a chlorine-chlorine bond and we can call this *bond dissociation*, and the bond dissociation energy for chlorine is $BDE_{Cl_2} = 121 \frac{kJ}{mol}$. That didn't seem to help us out in terms of energy. We're still putting energy in. Hmm. Thinking back to our discussion of electron configuration we recall that chlorine only needed one electron to obtain a stable octet, so perhaps the formation of a chlorine anion will be a particularly energetic step.



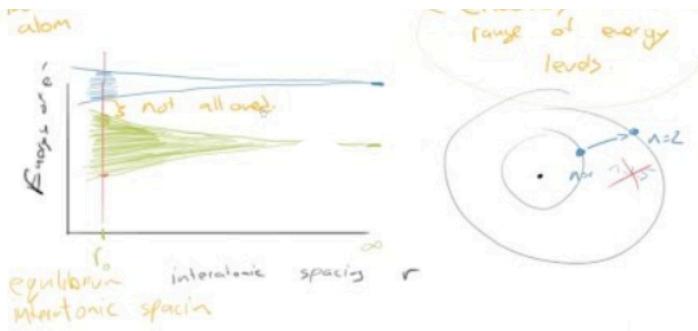
This step was the chlorine acquiring an electron and so the *electron affinity* is $EA_{Cl} = -364 \frac{kJ}{mol}$. You'll notice that this energy carries a negative sign; finally, something that gives us some energy. What about the final step, forming the ionic crystal?



And the so-called *crystallization energy* $E_{\text{crystallization}} = -777 \frac{kJ}{mol}$. Wow, that step put out a lot of energy! If we add each of these energy terms up we see that the total energy change for the formation of NaCl in Equation 2 is $-414 \frac{kJ}{mol}$. The fact that this reaction produces some heat makes me a little more comfortable. At least, until I think about what might happen if we considered this at higher temperatures. I happen to know that salt can be melted, so our preceding energy discussion seems to have some problems. Similarly, I know that frozen water absorbs energy and melts all on its own at room temperature. So, there is clearly more to discuss here, and we will get into all of this a little later in the course. For now, we can just say that it is energetically favourable for salt to form a crystal at room temperature. What's more, our energy analysis has shown us that the crystal formation step itself is particularly important.

Bonding in Solids - The Band Theory





[Link to this video on U of T servers.](#)

Alright. We actually started this chapter with me promising to teach you about how light interacts with solids. We're on the doorstep of this discussion! We've covered electronic configuration in an isolated atom, but now we need to consider what happens to all those electron energy levels when a massive collection of atoms comes together, as they do in a solid.

You see, when atoms begin to get atomically close to one another, the electrons in each atom run the risk of having the same energy levels. This is called degeneracy and doesn't happen. Instead, as the atoms approach one another, the energy levels begin to spread out slightly so that, for a given electron energy level in an isolated atom, there are two corresponding energy levels when two atoms are close to one another, three for three atoms, four for four atoms, and so on. This is illustrated in Figure 11. At the same time, the difference in energy between these levels becomes smaller as the number of atoms increases.

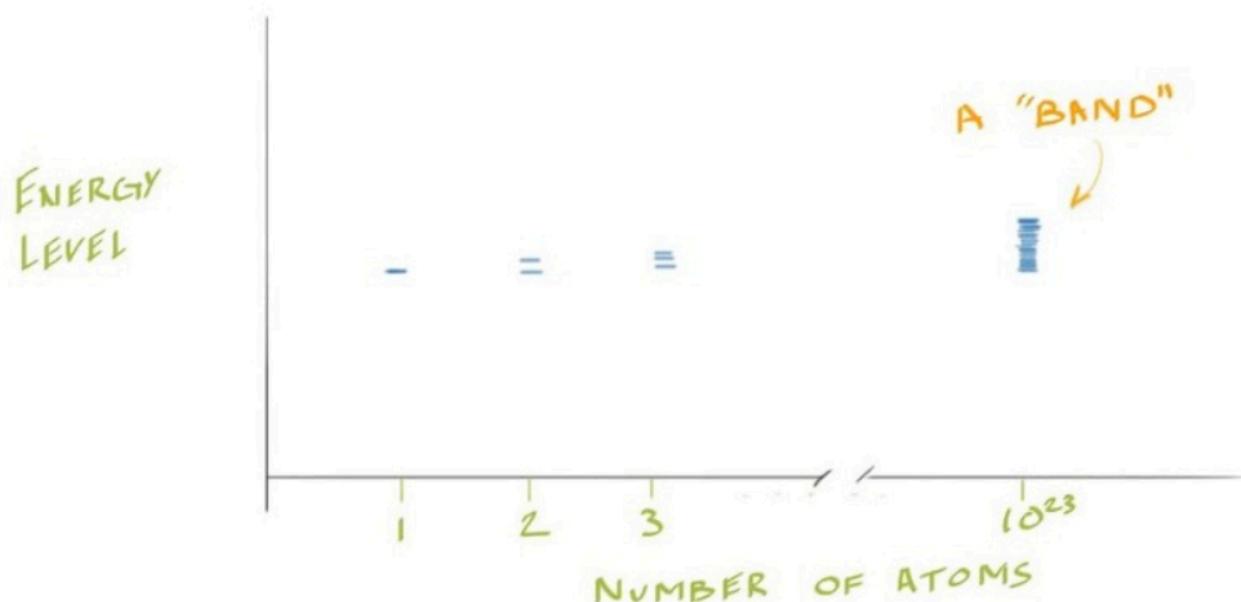


Figure 11. A schematic depiction of a particular energy level in an isolated atom, two atoms, three atoms, and so on up to a massive collection of atoms, as in a solid. The number of energy levels in a solid, for a corresponding single energy level in an isolated atom, is equal to the number of atoms, so that when we have a solid there are so many closely spaced energy levels as to

isolated atom, is equal to the number of atoms, so that when we have a solid there are so many closely spaced energy levels as to be essentially continuous. We call this a band.

So, this is actually really pretty cool because now we have the possibility for electrons to be promoted up to energy levels that are essentially continuous. Remember in an isolated atom how an electron would need to be given enough energy to make a quantum leap from, say, $n = 1$ to $n = 2$? An atom couldn't jump to $n = 1.5$, for instance. Well now, in a solid, there are so many energy levels that might be available, under the right circumstances. Let's look at a few of these circumstances.



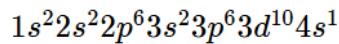
Bonding in Metals Like Copper



[Link to this video on U of T servers.](#)



Everything goes back to electronic structure, right? I mean, electronic structure dictates how materials behave. So, let's start with the electronic structure of an isolated atom of copper. Copper has atomic number 29, so we need to fit in 29 electrons. By my calculations, keeping in mind the shift of one electron to make a full 3d that gives Cu an electron structure of



When a massive collection of copper atoms come together in a solid, the $4s$ energy levels spread out into a band, but notice that only half of these states will be filled. That is, $4s$ can accept two electrons, one spin up and one spin down. Each of these states has a corresponding level in the band structure, even though only half are filled. The so-called band structure for copper is shown in Figure 12.



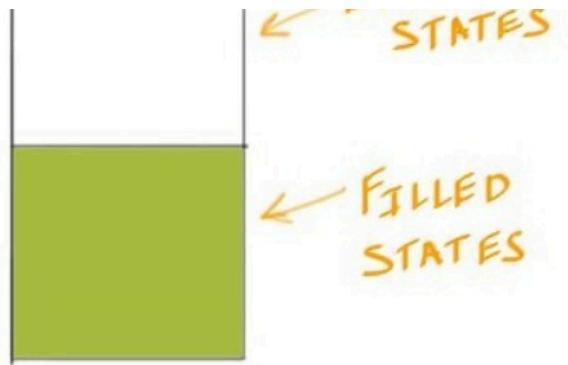
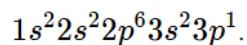


Figure 12. The band structure for copper.

This means that it is very easy to promote an electron up within the band structure into one of the empty states.

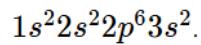
Another metal that is a very good conductor is aluminum. Let's check out the band structure of aluminum. Aluminum has atomic number of 13, so we need to add 13 electrons to build a neutral atom of aluminum. This gives us an electron configuration for neutral Al of



Similarly to the situation that we had with copper, we have a partially-filled band, this time from the energy levels from the 3p electrons.

Bonding in Metals Like Magnesium

Since we know that metals should be decent electrical conductors, let's take a look at another metal, magnesium. Interestingly, you'll note that Mg has one less proton than Al, meaning that the atomic number for Mg is 12 and its electron configuration is



Whoa! I can hear you saying it now, "magnesium should be a conductor, why does it have a filled band structure?" Great question. Well, it turns out that even though the 3s band is filled, the energy levels for the 3p states actually spread out enough that they overlap with the 3s levels. Just because the 3p levels are empty doesn't mean that they are not available. It's similar to an empty seat in theatre.

Even though nobody is sitting in the seat, the seat is still there and available for someone to sit in. As a result of the overlapping 3s and 3p levels, the band structure for magnesium is typically drawn as is shown in Figure 13.



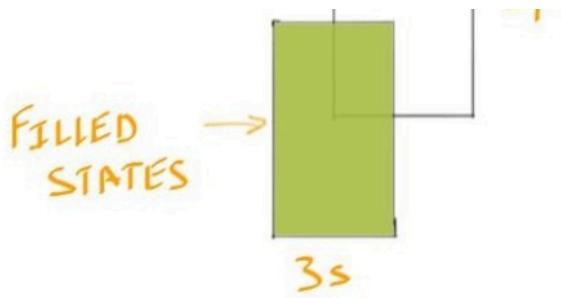


Figure 13. The band structure for magnesium.

We can see that the unfilled states from the 3p levels provide available energy levels for electrons to be easily promoted into, from the 3s levels. Because of the overlap between the 3s and the 3p states, Mg still behaves like a metal.

Bonding in Ceramics and Polymers

Now, let's see if we can apply our new model, the Band Theory, that is, to explain another result that we are already familiar with: that ceramics and polymers are electrically insulating. Recall that ceramics tend to be held together by ionic bonds and ionic bonds involve electrons being transferred from one atom to another. Remember also that this electron transfer happened so that each atom could achieve a filled valence shell. Since the valence shell is filled there are not electron energy states immediately adjacent to filled states. Also, these electrons are tightly bound to the nucleus, so there are no free electrons. The same is true for polymers, except that the bonding is covalent. Of course, in covalent bonds the valence electrons are shared between two atoms and are bound tightly to them. Both of these types of materials are insulators. The band structure for a typical insulator is shown in Figure 14.

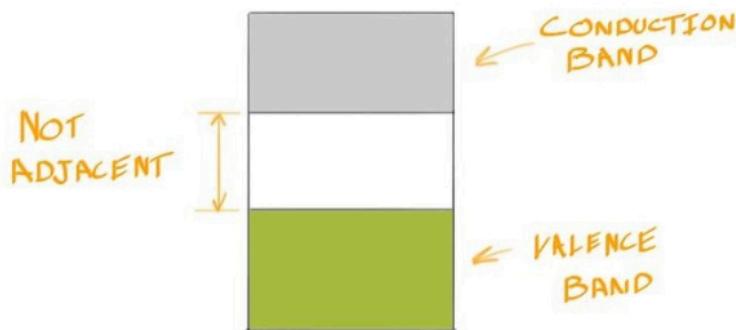


Figure 14. The band structure for an insulator, showing the valence and conduction bands with a large gap between them

You'll notice from Figure 14 that there is a large gap between the valence band and the so-called *conduction band*. You can think of this gap as being analogous to the forbidden energy levels between shells in the electron configuration of an isolated atom. Recall that we said the energy levels in an atom were quantized and, for example, an electron could not exist at N=1.5. In the band structure, since this is a gap between bands, we refer to it as, surprise, surprise, the *band gap*. The band structure for an insulator, with the band gap identified this time, is shown in Figure 15.

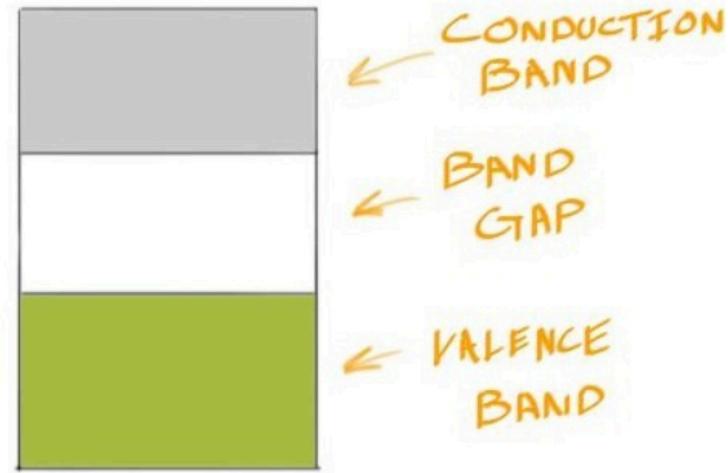


Figure 15. The band structure for an insulator, with the band gap identified as well as the valence and conduction bands.

In order for electrical conduction to occur in an insulator, an electron would have to be given enough energy to cross the band gap. In such a case we say that it is promoted into the conduction band, where it is free to move. The valence band states arise from the valence electrons on the outermost parts of the atoms in the solid, which is why we call it the valence band.

Bonding in Semiconductors

Some materials, namely the semiconductors, have a band gap that isn't as large as in an insulator. This is important because it means that we can control the flow of electrons in these materials. This is the basis for solar photovoltaics, LED lighting, and all of our modern electronics. Clearly, semiconductors are hugely important to society, however, we won't discuss their application here. What we want to discuss here is basic nature of the band structure of a semiconductor. As I mentioned, the band gap in semiconductors isn't too big. There isn't a formal or fundamental size of the band gap that distinguishes semiconductors from insulators, but about 4 eV is generally a good number. If a material has a band gap that is larger than 4 eV, we can consider it to be an insulator, and if the band gap is less than 4 eV (but isn't zero) we can consider the material to be a semiconductor. This means that, in many cases, thermal energy or photons of visible light can promote electrons across the band gap in semiconductors.

Defining Conductors, Insulators, and Semiconductors

Armed with our new understanding of the band structure of solids we are ready to put it all together and summarize the band structure for conductors, insulators, and semiconductors. I have sketched out the band diagrams in Figure 16.

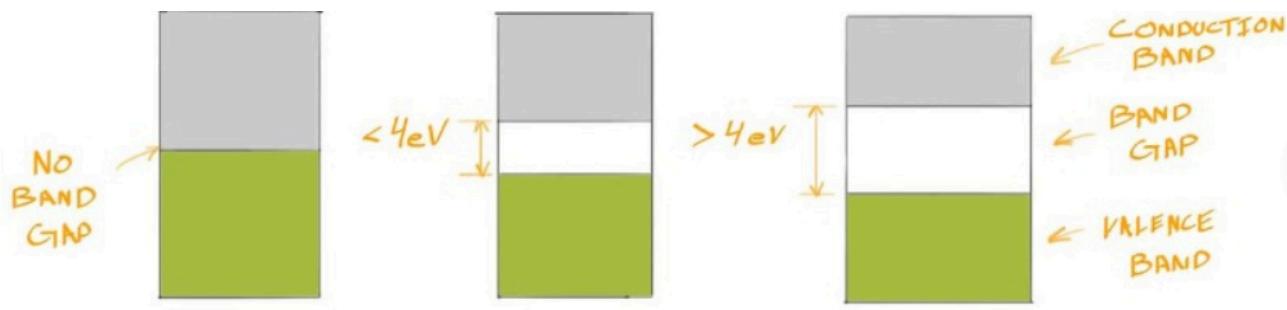


Figure 16. The band structures of conductors, insulators and semiconductors. For our purposes, we'll consider the dividing line between semiconductors and insulators to be 4 eV.

So, we have conductors with no band gap, insulators with a band gap larger than 4 eV and semiconductors in between with band gaps between 0 eV and 4 eV. It is worth noting that you may come across people and textbooks that draw the line at different values, for example at 2 eV. That's fine. Roll with it. The important thing is that you understand that semiconductors are intermediate between conductors and insulators and that conductors have no band gap.

9.12.1
Review Mark as: None ▾

The permissible energy level is to the Bohr model of the atom what the _____ is to the Band Theory of Solids

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The conduction band

b The valence band

c The band gap

d The nearly continuous set of permissible energy levels in a solid

9.13.1
Review Mark as: None ▾

A conductor can be described as having which of the following relationships between the valence and conduction bands?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a No gap between the valence and conduction bands

b A large gap between the valence and conduction bands

c A moderate gap between the valence and conduction bands

d Conductors don't have valence bands



9.13.2

Review

Mark as: [None ▾](#)

An insulator can be described as having which of the following relationships between the valence and conduction bands?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a A large gap between the valence and conduction bands

b A moderate gap between the valence and conduction bands

c No gap between the valence and conduction bands

d Insulators don't have valence bands



9.13.3

Review

Mark as: [None ▾](#)

A semiconductor can be described as having which of the following relationships between the valence and conduction bands?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a A large gap between the valence and conduction bands

b Conductors don't have valence bands

c No gap between the valence and conduction bands

- d A moderate gap between the valence and conduction bands

And Finally, Back to Light Again

I seem to recall a long time ago (read: the start of this chapter) we were talking about light. At this point we know that visible light is composed of photons having photon energies between 2-3 eV. We're ready now to consider what might happen when a photon in this range interacts with the band structures of various solid materials. The short story is that if the material has a high band gap (greater than 3 eV) the photons will pass through and the material, barring any internal diffraction events, will be optically transparent. Window glass, composed mostly of SiO_2 , which forms a three dimensional network of covalent bonds will have a high band gap and is optically transparent. As an interesting side note, for windows in buildings, in order to improve the energy efficiency of the building we want to reduce the solar heating that can occur within the building from sunlight passing through the windows and heating the interior of the building. This is costly and inefficient since air conditioning is very energy intensive and expensive (it is hard to fight entropy, but we'll talk more about that later). To reduce some of this solar gain in buildings modern windows can be coated with a thin metallic layer. If the layer is thin enough it transmits much of the visible light, but, since it has no band gap, absorbs some of the photons, especially in the ultraviolet region of the spectrum. This brings us nicely to the interaction of light with metals. As we just mentioned, the visible photons will have no trouble promoting electrons, since there is no band gap in a metal. As a result, metals are opaque. What's more, the electron promotions are temporary and when the electrons drop back down to their lower energy states they re-emit the photons. As a result, metals are shiny.



9.14.1

Review

Mark as: [None ▾](#)

Which of the following are requirements for optical transparency?

- (a) High band gap
- (b) Low band gap
- (c) Internal scattering events
- (d) Absence of internal scattering events

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a b, c

- b b, d

c a, c

d a, d



The Structure of Silicon

Shortly, we'll get into the electrical behaviour of semiconductors, but it will help us to first look at the structure of silicon, the most important semiconductor material. As we've done many times by now, let's consider the electronic configuration first. Silicon has atomic number 14, meaning that it will have 14 electrons and an electron configuration of

$$1s^2 2s^2 2p^6 3s^2 3p^2$$

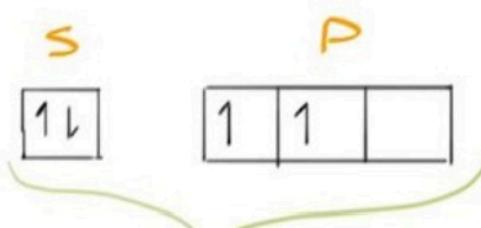
Now, you'll notice that there are 4 valence electrons, in **3s** and **3p**. These are the electrons that will participate in bonding. This actually seems to introduce a problem for us since we can experimentally determine the bond length in silicon and we know that each silicon has four identical bonds. So, the problem is that we have four electrons at two different energy levels that need to form four identical bonds. If we are limited to only the energy levels given by our electronic configuration for an isolated atom we can't do it. Our model is limited. It can't explain bonding in silicon.



sp₃ Hybridization

So, what often happens when a model fails? Someone proposes a fix, or an update to the model. It's almost like a software update, in that it's an incremental patch to address a specific failing.

(Occasionally, of course, an entirely new model comes along, that describes things under specific conditions that the previous model fails at; like quantum mechanics and classical mechanics.) So, the fix that was proposed here was this: let's just take the one **s** orbital and the **3p** orbitals and blend them together to form four equivalent energy levels, as shown in Figure 17.



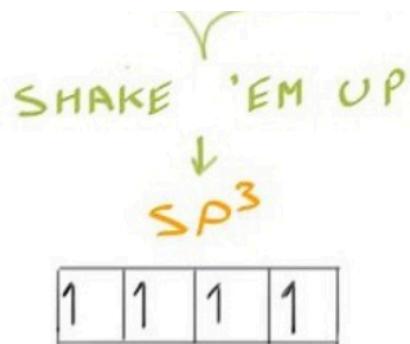


Figure 17. The formation of sp^3 hybridized orbitals, as in silicon.

When we take a little bit of one thing and a little bit of another, for example, a car that has both an internal combustion engine as well as electric motors, we often call the result a hybrid. Similarly, here we call these new orbitals hybrid orbitals, and since we blended one *s* with 3 *p* orbitals we call the resulting orbitals *sp*³ *hybridized orbitals*.

Diamond Cubic



[Link to this video on U of T servers.](#)

Now that we have four equivalent orbitals we can start to consider how they are oriented in space. Since they are all equivalent, it wouldn't make sense for, say, three of them to be clumped close to one another and one bond to be all alone. No, each will be spaced and an equal spacing from the others. This is achieved by adopting a so-called *tetrahedral* configuration. We can consider this in familiar terms by comparing it to other interstitial sites. We previously saw the octahedral interstitial site, which you'll recall had a coordination number of 6. The tetrahedral interstitial site has a coordination number of 4. Note, however, that the name comes from the solid geometry that is formed, and not from the coordination number. It just so happens that for the tetrahedral site the coordination number matches the number of faces on the solid geometry formed by this site. I find that one of the best ways to picture the tetrahedral interstitial site is at the centre of a cube, as shown in Figure 18.

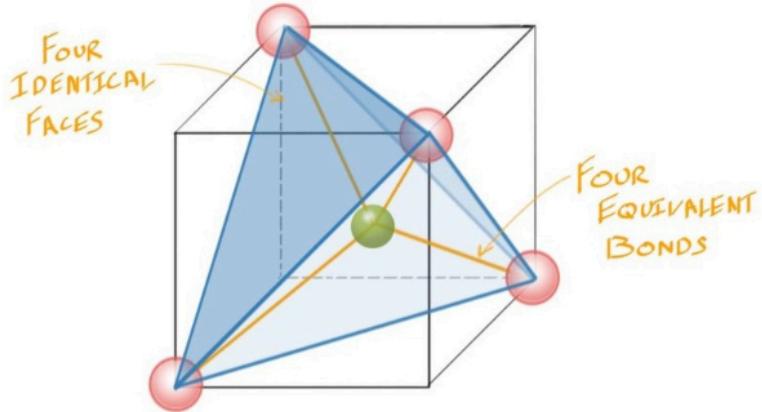


Figure 18. The tetrahedral interstitial site at the centre of a cube. Note that the coordination number is also 4, in addition to the number of faces on the solid formed by this site, however the name comes from the solid geometry, not the coordination number.

From Figure 19 we can see this beautiful little piece of tetrahedral symmetry, but it is difficult to see how these fit together into three dimensions. In fact, to represent this properly we need to go a little larger. This is what we call the *diamond cubic* crystal structure, so named, because it is also the crystal structure for pure carbon in its diamond phase, or allotrope. The structure of diamond cubic is shown in Figure 20.

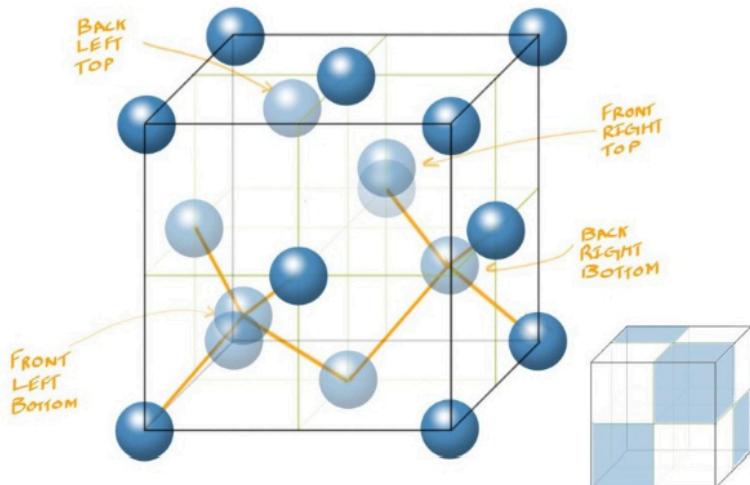


Figure 19. The structure of diamond cubic. This structure can be thought of as an FCC lattice of atoms with the same atoms occupying half of the available tetrahedral interstitial sites, in alternating positions. The alternating positions are illustrated with the shaded "sub-cube" faces in the second cube.

I find it is easiest to understand the diamond cubic crystal structure by first thinking of an FCC lattice of atoms. This is a good place to start because you are already a bit of an expert on FCC, from our discussion of metallic crystal structures and also from rock salt. In fact, with rock salt you'll recall that we placed cations into the octahedral interstitial sites. Well, with diamond cubic we will place atoms into the tetrahedral interstitial sites. The only think that we need to be careful of here is that we can't fill each of the eight available tetrahedral interstitial sites. If we did this, we'd have too many bonds on each atom. Instead, we fill only half of the sites, and we place them as far apart from each other as

possible, giving us the alternating arrangement shown with the shaded cubes in Figure 19.



9.16.1
Review

Mark as: None ▾

The valence electron configuration for carbon is $2s^2 2p^2$ meaning that two of the four bonds from each carbon atom in diamond are actually at a slightly different level than the other two bonds?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a True

b False



9.17.1
Review

Mark as: None ▾

How many atoms are present within a single unit cell of the diamond cubic crystal structure?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 14

b 18

c 6

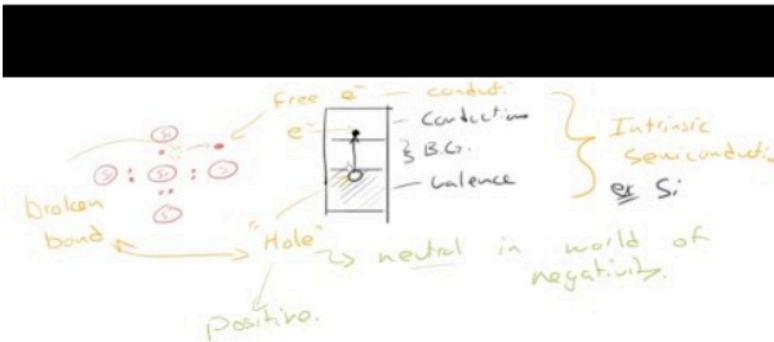
d 8

Semiconductors

It is important for us to be able to control the electrical conductivity of semiconductors. As with

controlling the mechanical behaviour of metals by controlling defect populations (imperfections) we will introduce impurities into semiconductors to change their electrical conductivity. First, let's be sure that we understand the electrical conductivity of a pure semiconductor material, like silicon.

Intrinsic Semiconductors



[Link to this video on U of T servers.](#)

We'll start here with a lattice of silicon atoms, each having four equivalent covalent sp^3 bonds, as we've previously discussed. For simplicity's sake, we will often just sketch this in a two-dimensional cartoon depiction, as shown in Figure 20.

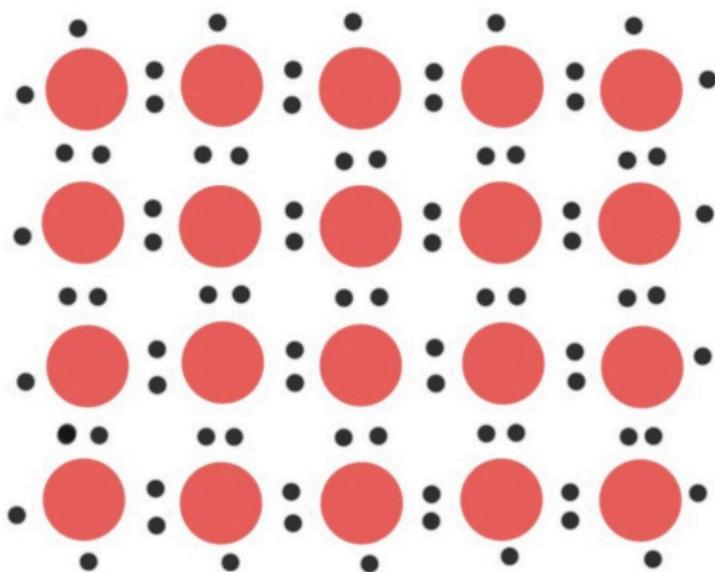


Figure 20. A cartoon depiction of the bonding in crystalline silicon, with no electrons promoted to the conduction band; or, all electrons involved in bonds, as would be the case at absolute zero temperature. Each silicon has four equivalent bonds, each represented in a flattened manner, in the plane of the page.

At a very low temperature, say absolute zero, to be specific, all of the electrons would be bound to the atoms that are sharing them in each covalent bond. That is what is depicted in Figure 21. Now consider what happens when the temperature is raised, or a voltage is applied and we get some promoted electrons. When an electron is promoted into the conduction band, it leaves behind a broken bond. This broken bond is really a neutral charge, amongst an array of negative charges. When everything else is negative, something neutral looks positive and so we often refer to this missing electron as being a positive "thing". Since it is a missing electron, it looks a little bit like a hole in the structure, as shown in Figure 21, and so we call it a *hole*.

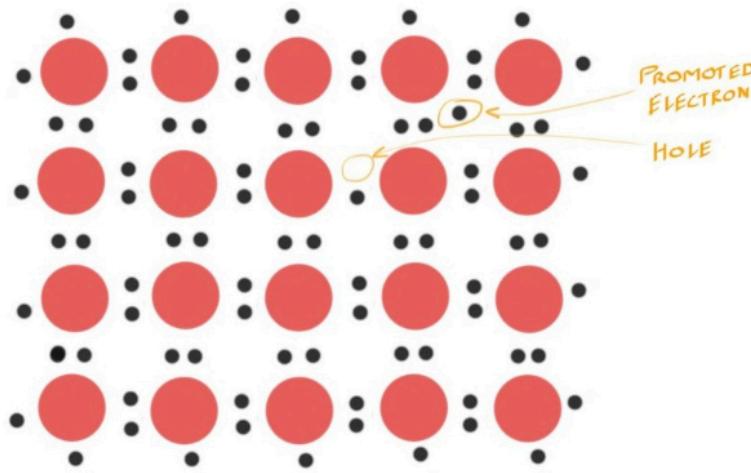


Figure 21. A cartoon depiction of the bonding in crystalline silicon with an electron promoted into the conduction band, leaving behind a broken bond, or a so-called **hole**.

You will likely have observed that if a hole is created for every promoted electron, these features are created in pairs. This type of semiconductor is called *intrinsic* semiconductor, since everything that is available to conduct electricity comes from the semiconductor itself, not from anything that we add to it. Intrinsic semiconductors are not especially useful in practice, since we almost always add impurities to control the conductivity, but I think it will be helpful to cover this first. Since both the electron and the hole can be thought of as charged particles, it is possible for both of them to conduct electricity, just in opposite directions. To calculate the conductivity, σ , of an intrinsic semiconductor we would need to know the concentration of electrons promoted to the conduction band, which we could call n , since electrons carry a negative charge. We could express the concentration in $\frac{\text{no.of electrons}}{\text{m}^3}$. We would also need to know the concentration of holes in the valence band, which we could call p , since holes are effectively positive. We would also need to know the mobility of the holes and the electrons. We typically use the lower case Greek letter μ to describe the mobility, so we have μ_n and μ_p for the electron mobility and the hole mobility, respectively. The mobility is expressed in $\frac{\text{m}^2}{\text{Vs}}$. Of course, we know that the charge, q on the electrons and holes has the magnitude of the fundamental charge, $1.602 \times 10^{-19}\text{C}$. Finally, then, the conductivity for an intrinsic semiconductor is

$$\sigma = nq\mu_n + pq\mu_p \quad (8)$$

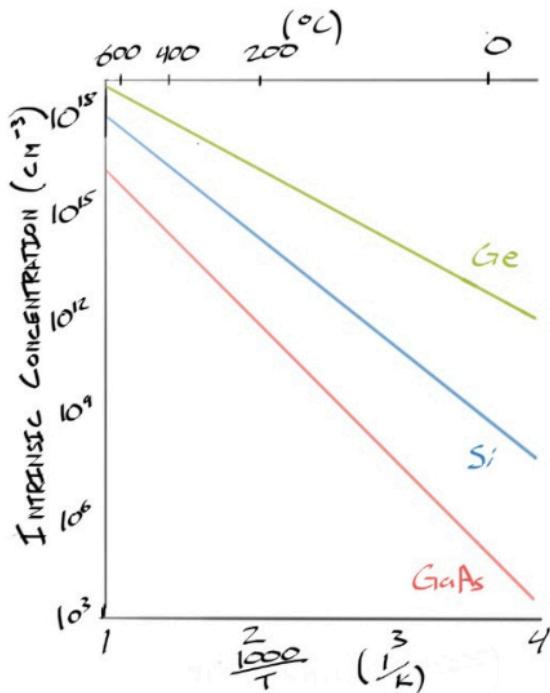
Of course, since one hole is created for every promoted electron, we know that $n = p$ and we can write

$$\sigma = nq(\mu_n + \mu_p) \quad (9)$$

Getting Excited

Professor Jun Nogami

Let's take a bit of a closer look at the ways we can excite an electron across the band gap. Thermal excitation has already been mentioned, and in fact, if you look at the electrical conductivity of silicon as a function of temperature it looks like this.



Intrinsic carrier concentration plotted against reciprocal temperature for Si, Ge, and GaAs.

The conductivity plotted versus $1/T$ follows an Arrhenius dependence, like any kinetic phenomenon, and the slope is a function of the band gap of the semiconductor

$$\sigma = e^{\frac{-E_g}{2kT}}$$

The band gaps for Si and Ge are 1.1 eV and 0.6 eV respectively.

The other way that we can excite electrons across the bandgap is by absorbing photon energy. The band gap of Si is 1.1 eV, which means that it will absorb light with photon energies greater than this amount. Visible light ranges in the wavelength from 400 – 700 nm, which in photon energy terms is 3.1 – 1.8 eV, which means that Si absorbs all wavelengths of visible light. If you have seen a solar cell, you can see that

it is not optically transparent.

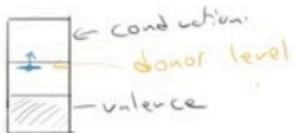
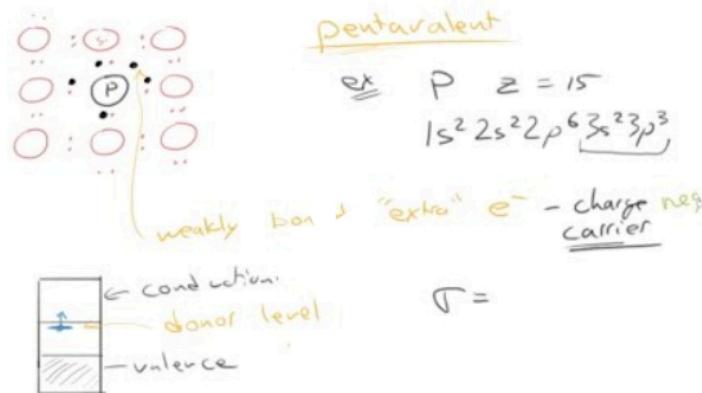
However, in absorbing a photon of visible light, it excites an electron hole pair, and if you put an electric field across the silicon, the electrons can be detected as a current. This can lead to two applications, depending on how the silicon is put into a device structure. You can build either a Si based photo detector, or you can convert the incident light into an electrical current, as in a solar cell.

Note that the band gap of diamond is 5.47 eV, which means that it does not absorb visible light, i.e. it is transparent.

Extrinsic Semiconductors

As I mentioned, intrinsic semiconductors are not especially practical; instead we typically add impurities (called *dopants*) to semiconductors to carefully control their conductivity. When we add even a very small amount of dopant to a semiconductor, the conductivity introduced by the dopant overpowers any of the intrinsic conduction and so we call these *extrinsic* semiconductors. There are two ways that we can dope a semiconductor, essentially with either extra electrons, or with extra holes. If we add extra electrons, since electrons are **negative**, we call it a *n-type* semiconductor. If we add holes, which we think of as being **positive** we call it a *p-type* semiconductor.

Extrinsic n-Type Semiconductors



$$T =$$

[Link to this video on U of T servers.](#)

Alright, we want to add extra electrons, but how do we do that? The classic electrical engineering joke goes something like, "where do electrons come from? A battery!" So funny! But really, it doesn't work like that. We can't just have a bottle of electrons and pour them into our semiconductor. Instead, we need to add impurity atoms (point defects) that bring along with them some extra electrons.

Assuming that we are considering a silicon semiconductor, and knowing that silicon has 4 valence

electrons ($3s^23p^2$) we need only look to atoms to the right of silicon in the periodic table to find atoms that will carry along extra electrons. For example, let's look at doping silicon with phosphorous, P. Phosphorous has atomic number 15 and so has the following electron configuration

$$1s^22s^22p^63s^23p^3.$$

Clearly, P has 5 valence electrons and so when added as a point defect in a silicon lattice there will be one extra electron kicking around when four covalent bonds have been formed with the neighbouring silicon atoms, as shown in Figure 22.

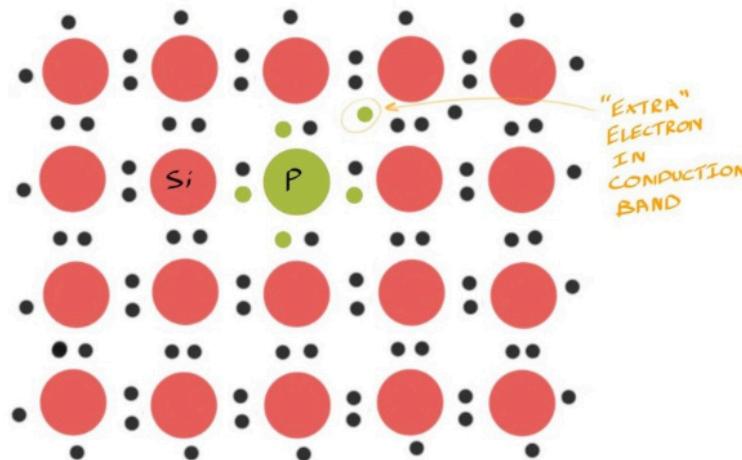


Figure 22. A cartoon depiction of the bonding in crystalline silicon with a phosphorous dopant atom. I've color coded the electrons for conceptual clarity, but remember that all of the electrons are actually equivalent. That is, a silicon electron is the same as a phosphorous electron.

The extra electron from phosphorous is only weakly bound and can be easily promoted, and made available for conduction. That is, only a small amount of energy is required to get this extra electron, *donated* by the dopant, into the conduction band. For this reason, a n-type semiconductor is said to have a *donor* energy level within the band gap, close to the bottom of the conduction band, as illustrated in Figure 23.

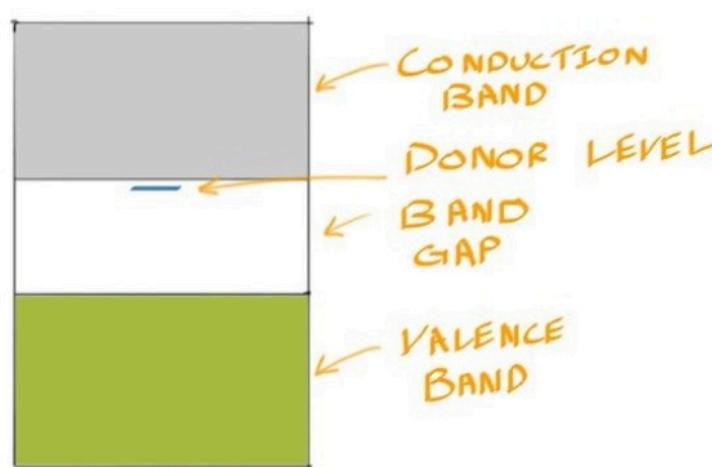
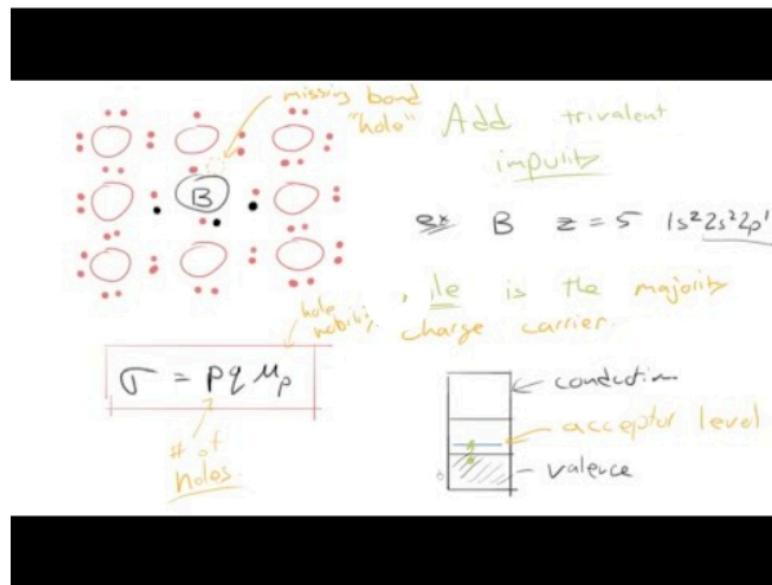


Figure 23. The band diagram for a n-type semiconductor, showing the donor level within the band gap, close to the bottom of the conduction band. Only a small amount of energy is required to free up that electron and get it conducting.

Since the dopant atoms contribute so many more *charge carriers* to the semiconductor than are created through intrinsic promotion we can neglect the intrinsic semiconduction and calculate the conductivity of a n-type semiconductor with only the electron concentration and mobility:

$$\sigma_{n\text{-type}} = nq\mu_n \quad (10)$$

Extrinsic p-Type Semiconductors



[Link to this video on U of T servers.](#)

Where do holes come from? Group 13! So funny. I just made that up. But really, it's true. If we dope with elements to the left of silicon there will be less than 4 valence electrons and there will be broken bonds, or holes introduced. For example, if we dope silicon with boron, the boron will only bring along 3 valence electrons, $2s^2 2p^1$. This means that there will be one broken bond, or hole for every dopant atom , as shown in Figure 24.

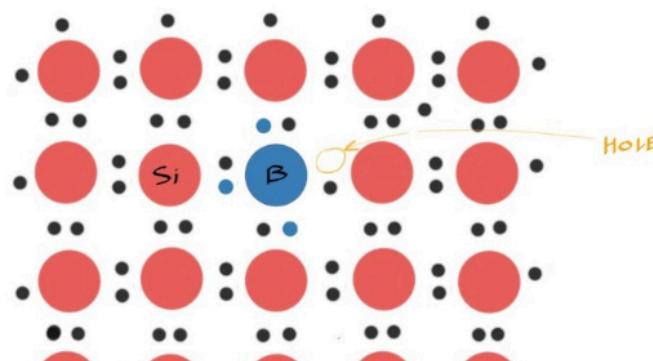




Figure 24. A cartoon depiction of the bonding in crystalline silicon with a boron dopant atom, creating a hole.

Since the hole is now a place that an electron can be promoted into, we describe the energy level from the hole as an *acceptor* level and this acceptor level is located within the band gap, close to the top of the valence band, as shown in Figure 25.

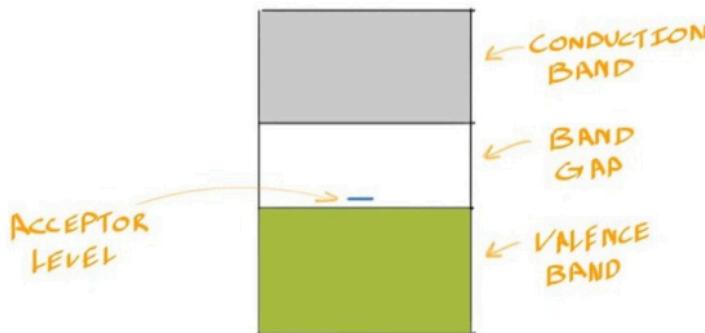


Figure 25. The band diagram for a p-type semiconductor, showing the acceptor level within the band gap, close to the top of the valence band. Only a small amount of energy is required to promote an electron up into that level.

And the conductivity of a p-type semiconductor can be calculated assuming that only the holes are charge carriers, neglecting any intrinsic conduction.

$$\sigma_{p\text{-}type} = pq\mu_p \quad (11)$$

Solid Ionic Conductivity

A quick note at this point is probably worthwhile. Generally, when we think and speak of conductivity within solid materials we consider the movement of electrons, and in the case of semiconductors, also the movement of "holes." However, it is possible for electrical conductivity to occur via the movement of ions within an ionic solid. We won't explore this phenomenon further here, but I don't want you to be surprised if you encounter it down the road.



9.15.1
Review

Mark as: None ▾

Electrical conduction in a solid may only occur through the movement of electrons and holes?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a False

b True

All images and videos are created by the author.

