One and One and One is Three

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1 Unanswered Questions

- 1. The basic building blocks of matter, called elementary particles, must all have zero volume. What, then, prevents them from piling in so closely together that the matter they form does *not* have zero volume?
- 2. Why does the work function kick in so suddenly in the photoelectric effect?
- 3. If the work function is so well defined, how are electrons arranged within a material?
- 4. How does electric current really work?
- 5. What kinds of orbits can electrons have?

2 Volume of Matter

As we learn more and more about the subatomic world, we solve some problems with our models, but introduce others just as quickly. One question which has been lingering since our first lesson can finally be addressed: if matter is made out of pieces with zero volume, then why do any objects have volume? In most public school models, atoms fit together like little billiard balls, so the size of these billiard balls determines how closely the atoms can be packed together. We cannot depend on this logic any more. If atoms are made of objects without volume, why do they align themselves into arrangements which do have volume? In short, how do isolated atoms come together to form the world we live in?

3 Molecule Formation

The simplest combination of two or more atoms is called a molecule. This arrangement has a definite microscopic start and end point, and is the easiest to imagine.

As we know from our previous lesson, electron orbits exist not as circular paths, but as regions in space around a nucleus in which an electron is allowed to exist. As two atoms get close to each other, these regions can overlap and interact with each other. This interaction can form a new region for the electrons to exist in. It is this new region which forms a bond.

An electron is bound to a nucleus in an atom by electrostatic attraction. If it drifts too far, the attraction between the positively charged nucleus and the negatively charged electron wanes, and the electron "falls" back into the "well" the nucleus creates, and the electron remains bound. When picturing one atom existing in isolation, this is easy to see. What happens if two atoms drift close to each other?

Imagine two hydrogen atoms.¹ Imagine that they have drifted close enough together that the distance between them is comparable to the volume of space that is occupied by the regions the electrons and protons exist in anyway. Now consider the shape of the regions that the electrons exist in.

We know from our previous lesson that the shape of the region an electron is likely to be in is defined in part by positively charged particles in the vicinity. Because electrons are attracted to protons, the regions in which they exist become biased, making it more likely to find an electron near any neighbouring protons than in an empty region of space away from the protons.

In the case of our two hydrogen atoms, we have two protons and two electrons. Each electron is attracted to both protons, and repelled by the other electron. With our current model of the atom, we see no particular reason for these atoms to bond together. Yes, a given electron will be attracted to the other nucleus, but it will be equally repelled by the other electron. They need a reason to connect, and some attractive force to hold them together. In other words, our picture of the atom is *still* incomplete.

 $^{^1\}mathrm{Hydrogen}$ is the simplest atom to picture; it has one electron, one proton, and usually zero neutrons.

4 Electricity and Magnetism

Throughout these lessons, the electric and magnetic forces have often been treated as a single entity. They are certainly related, but at this point, the interplay between these two factors needs to be made more clear.

Electrostatic attraction is relatively well known and understood. By the end of grade school, most public school students can tell you that like charges repel and opposite charges attract, and have rubbed balloons on heads and stuck them to walls at least once. This simple model is enough to discuss interactions when nothing is moving. When the electrically charged objects move, we need more.

Hans Christian Oersted was a sloppy enough experimentalist to become the first to discover the connection between electricity and magnetism. Experimentalists are taught to keep their experimental areas clear of anything which is not involved in the current experimental apparatus, simply to ensure that whatever is cluttered around did not impact their results. Oersted did not follow this practice consistently, and left a compass out on a countertop when he went to work on an experiment involving circuits. He noticed that turning on the electric circuit caused his compass needle to move. Closer experimentation revealed that every moving charge, be it part of an electric current or a single particle moving through space, produced a magnetic field. This provides the link we need to turn our atoms into a molecule.

5 Nature's Smallest Bar Magnets

Every electron is a charged particle. Protons and neutrons are both made of quarks,² and those quarks have electric charges.³ Could they produce magnetic fields? Experiment says they do. Every electron, proton and neutron behaves like a tiny bar magnet, and that behaviour makes all the difference in the world.

The bar magnet nature of electrons, protons and neutrons also shapes electron orbits. The interplay between these factors determines the shapes the allowed regions take, and they get quite bizarre. In some cases, they are simple spherical regions. They are nothing like planetary orbits, but they are the next most intuitive step.⁴ It is when we start adding more than one electron

²Section 3.2 of lesson two revealed that these particles have internal structure, and are made of other particles. These particles are called quarks.

³The *total* charge on the neutron is zero, but the charges on the particles it is made of are not zero themselves.

⁴At least, they are as intuitive as anything can be when you are dealing with quantum physics.

that they get strange. They begin to show a preference for forming along the directions of the bar magnets themselves. They form teardrop shapes, donut shapes, ellipsoid shapes, jellybean shapes and more. Because the electrons orbit in alignment with the direction of their bar magnets, the molecules they form also align themselves with their internal bar magnets in many cases. When this happens consistently enough in a material, the atoms form something we see as a magnet in the macroscopic world.

Let us return to our pair of hydrogen atoms. With each particle acting like a bar magnet, the net attractive force on them is *not* zero. That extra little magnetic attraction, although much weaker than either individual electrostatic force, is just enough to nudge the electron orbits together and form a bond. Each electron no longer exists in a single "well" created by the nucleus it was originally bonded to, but now exists in a W-shaped well, in which it can travel between the two nuclei with relative ease. The electrostatic repulsion still keeps the electrons a fair distance away from each other, but that gap is tempered by the magnetic attraction. A bond forms, and the two hydrogen atoms form the simplest molecule in nature. This type of bond is known as a covalent bond.

6 The Pauli Exclusion Principle

Most molecules are far more complicated than the simple hydrogen molecule. With our current picture, a bond formed between two carbon atoms (which have 6 electrons each) is much harder to predict. Is it a single, indistinguishable mishmash of 12 electrons? Do they somehow pair off to form the bonds, instead? If so, why not just pair off with other electrons that are already in the atom? There are a number of ways these particles can arrange themselves with our model. However, the arrangements in reality are actually quite well defined and restrictive. No atom easily forms more than four bonds, and most form fewer than four. Some atoms, for elements known as the noble gases, do not easily form even a single bond. Why is that the case? Why do different atoms have such wildly varying bond forming behaviours?

Wolfgang Pauli proposed a solution, referred to as the Pauli Exclusion Principle, which not only solved all of these problems, but allowed scientists to rearrange the periodic table entirely.⁵ Pauli examined the mathematics describing electron orbits, and proposed an idea that fit experimental data perfectly: what if any given electron orbit could only be occupied by one electron at a

⁵When Dmitri Mendeleev created the first effective periodic table, it was arranged like a checkerboard, with empty spaces in half the squares and rules for moving through the table vertically, horizontally, and along both diagonal directions. The modern table is far more compact and effective, but Mendeleev's was good enough to predict several elements before they were discovered in nature.

time? When you know that electrons have zero volume, this seems an unnecessary feature, as multiple electrons could fit in the same allowed region as long as they didn't outnumber protons in the nucleus to the point that they drive the atom apart. Pauli proposed it out of necessity: at this stage, it needs to be driven into the theoretical model with a sledgehammer to explain experimental observations, but is not yet motivated by a theoretical need. It is required to form the particular types of complex molecules we see, but we do not yet see a need for these particular types of molecules to be favoured over the mishmash options mentioned earlier. This will be explored further in our final lesson next week. For the rest of this lesson, the implications of the idea will be used to answer most of our unanswered questions.

7 Insulators and Covalent Bonds

With the Pauli Exclusion Principle in place, the observed electron bonding options amongst electrically insulating materials makes complete sense. Each atom has certain orbits that electrons are allowed to be in, and once there is an electron in an orbit, that orbit cannot be occupied by another electron. More importantly, these orbits come in groups. The regions in which our electrons are allowed to exist are then restricted to empty orbits. The first group of orbits includes two possibilities for electrons to fill. This is why the first row of the periodic table has only two elements. The next group has eight orbits. This is why the second row of the periodic table has eight elements, and why carbon never easily forms more than four bonds: the atom's six electrons fill the first group (of two) completely, and only fill half of the next eight.⁶ When that carbon atom comes near another carbon atom, the electrons of the two atoms can expand their orbits across both atoms, filling in the same empty orbit for both atoms. Due to the way the magnetic interactions play out, the orbits within a group always come in pairs. This is why two electrons are involved in each such bond: the bonds form across the two unpaired electron orbits. These bonds also have distinct lengths due to the geometry of the orbits; this is why materials formed this way have volume. They do not have volume because their constituent atoms have volume, but because the bonds that hold the atoms together have volume.

There is no reason to restrict this model to two atoms. Electrons can pair off between atoms, and in cases such as carbon (which can create four bonds in pairs like these) they form these bonds with four different atoms if at all

⁶The groups also have subgroups, and the subgroups fill in sequence. This is why so few atoms have more than four bonds at a time; no subgroup holds more than eight electrons. The reason the bond limit is half the number of orbits in a subgroup will be covered in the next section.

⁷These orbits have volume because they, like the orbits around single atoms, are determined in part by the wavelengths of the electrons themselves.

possible.⁸ This is how the molecules of electric insulators form. The atoms are bound together with relative security, but the electrons are bound to the two nuclei whose orbits they complete. The electrons are *not* free to travel throughout the entire material.

8 Insulators and Ionic Bonds

In some materials, bonds are formed without the use of covalent bonds. A covalent bond is, in effect, a way for an atom to "pretend" that it has more electrons than it really has. One of its own electrons starts to spend half of its time near another atom, while one of the other atom's electrons spends half its time near the first atom. This farce might be easy to pull off if the entire group of orbits is only short a few electrons, but what happens when it takes a relatively large number of electrons to fill the orbits? If we look at sodium instead of carbon, we find an atom with its first group of orbits filled to capacity and a single electron in its next group of eight available orbits. Filling seven orbits with "half time" electrons will not be particularly convincing if the atom is trying to pretend all orbits are full. Instead, sodium takes the easy way out: it dumps off the electron entirely.

When the electrons pair off in their orbits, the paired electrons feel a strong magnetic bond. If you put sodium and chlorine in close proximity, you get a violent chemical reaction. This is because the third electron from sodium bonds with the chlorine in its empty orbit so strongly that it is ripped from the sodium entirely. When large quantities of sodium and chlorine are brought together, this process happens on a massive scale. Electrons are violently ejected and recaptured by neighbouring atoms, releasing significant heat energy in the process.⁹

When sodium and chlorine combine in this fashion, we get regular table salt. However, the picture seems incomplete. Salt is solid, and yet the above description does not appear to have any rigid bond connecting two neighbouring atoms. How are the components of salt arranged in a way that gives it volume?

⁸One atom can certainly form up to three bonds with a single neighbour. However, doing so means the bonded electrons get "bunched up" along the geometric line that can be drawn between the two nuclei, and the electrostatic repulsion gets harder and harder to overcome. It takes a lot less energy to form the bonds in four different, widespread directions.

⁹If it takes 15 units of energy to hold an electron in place in its atom, but only 10 units of energy once it has bonded, 5 units of energy will be replaced in the process. These reactions happen naturally, such as combustion, and are referred to as exothermic reactions. Endothermic reactions are when you give energy back to the system and force the bonds to reverse themselves. For example, the extra electron in chlorine has enough energy to break free and get recaptured by a nearby sodium.

If we picture just two atoms making an electron exchange of this type, we would expect them to collapse in on each other. After all, the sodium now has more protons than electrons, making it positively charged, while the chlorine is now negatively charged. They are made of zero volume particles and do not shared a rigid covalent bond, so there is no reason for them to stay apart from one another. Part of the problem is that we are picturing only two atoms, and not a large number of them.

First, picture two sodium atoms and one chlorine atom of each type. If the electrons have already been exchanged, then the sodiums will both be attracted to the chlorine, and vice versa. However, the sodiums will also be repelled by each other. There is only one stable arrangement for the chlorine: the three need to be equally spaced along a line with the chlorine in the middle. While the chlorine is in the middle, it feels no net force, as it is pulled equally in opposite directions. If it starts to drift off of the line in space that the sodiums are on, then the net attraction pulls it back to that line. The sodiums repel each other, but not as strongly as the chlorine attracts them. The chlorine isn't going anywhere, but the sodiums would seem to collapse in on it.

We are one step closer to building solid salt. We now have a chlorine pinned in place. In fact, if we extend this picture in all three dimensions we exist in, we can pin it down even further: if the chlorine is in the middle of a three dimensional cross, then that chlorine is pinned in all directions. The sodiums forming the cross are now much less stable, though: there are now six of them around, all repelling each other. We can counteract that by adding more chlorines behind them along the lines of the cross, and even surrounding them with more chlorines around them in the other two dimensions. We end up with a picture of the true structure of salt: sodiums and chlorines alternate in all three directions, forming a fairly regular pattern. They can jitter back and forth on the spot a bit, but for the most part, they stay where they have been placed. In the real world, it is not a perfect pattern. To start, the particles on the edges are always more weakly bound to the structure than the others, which is one reason salt (and other materials) can break. It is also rare to find 100% pure sodium and chlorine, so we often have other materials in the middle mucking up our crystals. Finally, random motion from heat also comes into play while the crystals form, causing deviations in the crystal that are surrounded by properly made crystals. These deviations can be hard to repair without breaking another part of the crystal structure, due to the tightly packed nature of them. Still, the constant electrostatic tug of wars between neighbouring atoms keeps the atoms bound together closely enough to seem solid, while still far enough apart to form a solid with volume.

9 Conductors

Some materials conduct electricity very well. The electrons within them are free to move throughout the structure, but neither of the pictures we have formed yet can explain this behaviour.

If you will recall, in covalent bonds the electrons are tightly bound to two nuclei, and it is these rigid bonds that hold the material together. The atoms require less energy to hang on to electrons when a group of orbits are either completely filled or completely empty. The covalent bonds typically form in materials which have groups of orbits that are nearly full. Metallic bonds, on the other hand, exist when the groups of orbits in the atoms are nearly empty. ¹⁰

When two metallic atoms get close to one another, they form a bonds much like covalent bonds using electrons from their partially full group of orbits. Things change when a third atom is introduced. With these atoms, it takes less energy to expel electrons than to capture them, and that pattern continues. The bonds joining the first two atoms expand to include the third. As each new atom joins the structure, a new bond forms throughout the entire structure for each electron in the incomplete group of orbits. Eventually, there are so many bonds involved that there are available orbits with only slightly different energies, leaving the electrons to jump from orbit to orbit and move freely through the crystal. They do so constantly, but randomly, so there is no overall current in a typical metal sample. However, when a voltage is applied across the material, then there is a direction in which electrons can flow which leaves them with less energy.

In many ways, electrons behave like fish in a fish tank. Fish have limited mental capacity; in the absence of food and predators, they will naturally spread out, and move virtually at random throughout the fish tank. If you take those same fish and put them in a slow moving stream, also without food or predators, they will still choose their own directions at random, but will drift along with the current. Electric currents move much the same way; the voltage creates an electric current just as gravity causes a water current. The difference is that an electric circuit can be downstream all the way, unlike a water current. The atoms are still bound by bonds with volume, and the material they form will therefore also have volume.

 $^{^{-10}}$ The noble gases do not readily form bonds because their groups of orbits are naturally full.

¹¹Exceptions to this rule for water current were once reported by Rick Marshall, but this claim has been brought into doubt by the facts that he claimed he and his children also found living dinosaurs and hostile, intelligent, reptilian Sleestak in the same location, and that he cannot produce a convincing reason for abandoning his children in such an environment.

9.1 Electrical Resistivity

The picture of electrical resistance covered in most public school systems is the Debye model, named after its developer. In this early model, electrons experienced electrical resistance when they collided with other nuclei as they moved through the material. With nuclei made out of zero volume particles and orbits that cover the entire material, this picture is called into question. Even more damning, when experiments were performed to test the theory, they proved the theory was wrong. ¹² It is still taught because it is a simple model to picture, so students can walk away thinking they understand reality, but that does not make the model correct. As Einstein once said, "things should be made as simple as possible, but *not* simpler."

More advanced calculations indicate that the actual truth is related to the imperfections and defects in the crystal already mentioned. In a perfectly formed solid, electrical resistance is zero. The fewer irregularities there are in a crystal, then the better it conducts. Perfectly formed solids do not exist in nature at any attainable temperature. However, at different temperatures, it is possible that many of these irregularities smooth themselves out as the atoms jitter around more or less, creating a path through the material which avoids the defects. Electrons can then travel that path, as long as there are enough orbits available passing through it for all of the electrons to fit. In superconducting materials, the electrons find ways to partner up and circumvent the Pauli Exclusion Principle¹³ so that they can all take this path, and the measurable resistance to current flow drops to zero.

9.2 Photoelectric Conductors and Semiconductors

Photoelectric materials are a form of semiconductor, meaning they are neither pure conductors nor pure insulators.¹⁴ In these materials, there are multiple types of bonds available.

Most electrons find themselves in low energy covalent bonds when they are in semiconducting materials. It is possible, however, for these particles to move into orbits formed by metallic bonds, if they have enough energy. If enough

¹²There are degrees of wrong. When experiments started proving Newton wrong, it was by a small degree, indicating that Newton's theories needed to be tweaked in some way, but were a useful point to build off of. It was akin to having theory predict that a certain measurement would be between 999,999 and 1,000,001, but experiments measure 1,000,005. The number is not very wrong, but it is outside the acceptable range. The Debye model, on the other hand, is not even close. If Debye theory predicts an experimental value between 999,999 and 1,000,001, then the actual experiment might measure 50.

¹³We will see how this works in the next lesson.

¹⁴In actuality, very few materials are pure in one sense or the other, but these materials fall very close to the middle.

voltage is applied across the material, a weak current flows, as some of these electrons are driven into the metallic bond orbits that conduct well, but not many electrons get there. For photoelectric materials, that energy comes not from a battery or voltage source, but from the incoming light. The electrons in the covalent bonds capture light. The manner in which they do this not only reverses the direction of that particle's bar magnet, ¹⁵ but gives it enough energy to jump up to the higher energy conductive orbits. The gap in energies between the covalent bonds and the conductive bands is the material's work function. This is why we have a well defined work function that allows continuous energies while conducting, as we have been wondering since lesson five.

10 Next Steps

This now explains the major phenomena we see in solids. The last of our unanswered questions will be answered in our final lesson, in which we investigate the phenomenon that gives rise to the bar magnet behaviour of atoms: spin.

 $^{^{15}}$ The bar magnet reversal will be explained in the final lesson.