19: Molecules and Bonding

19.1 Inter-Atomic Bonds

Once we have successfully described individual atoms and their behavior, the next thing to ask our theory is about how atoms interact with one another. It would have been hard to expect much from the Bohr model of the atom when asked these questions, because it was clear from its inability to answer many questions about the atom itself that it was incomplete. But since we can answer almost anything we want to know about atom with Schrödinger’s equation (given a big enough computer) then it stands to reason that solving for two atoms in close proximity would be doable as well.

This turns out to be true, tho actually solving the systems certainly gets trickier. The central question at hand becomes: do two atoms form a bond, and what properties result from that bonding or lack thereof?

19.1.1 Covalent

If we bring two atoms close together, there are a few competing effects. First, the electrons around each nucleus (and the nuclei themselves tho this doesn't really matter) will repel. This presents an initial barrier to bonding. However, the electrons of each atom are attracted to both nuclei. This attraction is what allows bonds to happen. However, figuring out which effect dominates requires us to consider some details.

For the sake of argument, lets consider the hydrogen molecule, $H_2$. $H_2$ is symmetrical and composed of the simplest atoms so it is very simple and special, but the ideas we learn from it will apply very generally.

If two hydrogen are brought near each other, their electrons can either be pointing in the same direction or opposite directions. You may think that they can be pointed in any direction with respect to each other, because that seems obviously true, but quantum mechanics doesn’t allow this. When you ask “is electron 1 spinning parallel to electron 2?” the answer is either “yes”
or “no, they are anti-parallel”. There is, unlike for rotating baseballs, never an instance where the two spins are at an angle of 37° or even 90°. This is the same property that causes the EPR experiment to give hoaky results: if I ask, along a specific direction, whether an electron is pointing up or down, I will get a definite answer. One way to ask if an electron is pointing up or down is to bring another electron close by such that they interact. We aren’t getting into the addition of angular momentum, but the upshot of this property is that angular momentum for these 2 electrons either adds or cancels, with nothing in between. \( S = \frac{1}{2} + \frac{1}{2} = 1 \) or \( S = \frac{1}{2} - \frac{1}{2} = 0 \).

We think of electrons (and particles in general) as being specific objects. This is this electron, this is that one, there’s another over there, etc. But electrons are in fact completely indistinguishable. The electron in two atoms are distinct only to the extent that they have spatially distinct wavefunctions. This means that if the wavefunctions (and their probability densities) start to overlap, the two electrons lose their distinguishability. When this happens, Pauli’s exclusion principle kicks in: they cannot have the same quantum numbers. This means that if the electrons from each hydrogen atom have the same spin (are pointing in the same direction) then they must necessarily be spatially separated. If, however, they have opposite spins then the two can go wherever they want. The exclusion principle can effect a repulsive force in practice, and that is what we are seeing. This makes more sense if we state the principle in terms of the wavefunction. With some simplification, Pauli’s exclusion principle becomes

*Electrons with the same quantum numbers will interfere destructively*

Pauli’s Exclusion Principle

If this is the case, then the wavefunctions for the two electrons will cancel one another out between the hydrogen atoms. This then results in the wavefunctions being spatially separated, and a repulsion rather than attraction between the atoms. A bond requires an attraction at some point.

If we instead consider the case in which the electrons are aligned in opposite directions (\( S = 0 \)) the electrons are able to interfere constructing
and go wherever they otherwise want to. We have seen before how, left to roam freely, a collection of positive and negative electrical charges will arrange themselves in a line of alternating positive and negative charges, or possibly in a grid with the same property. This same tendency comes up here. We have 2 positively charged nuclei (just protons at the moment, and 2 electrons floating around them. The combined electron distribution will thus try and put about an electron’s worth of negative charge between the two atoms. In this scenario both electrons are essentially part of both atoms, and have the same quantum numbers for each. A more accurate statement at this stage becomes that both electrons are part of a single system, the \( \text{H}_2 \) molecule. This system is just like that of a hydrogen atom, except with two nuclei. As such, it can be solved with a more complicated potential in Schrödinger’s equation. A new set of accepted states (rather than the states of the hydrogen atom) can be calculated, with wavefunctions and energy values for the electrons.

But how do we know if this is a bond, or a temporary rearrangement of electrons as the two atoms bounce off of one another? In general, nature prefers things to be in the lowest possible energy state. If a system is not in such a state, it will undergo whatever process is available to put itself in the lowest energy state. Sometimes this may take longer than others, but that’s the preferred state. So, in order to know of we have achieved a chemical bond between the two hydrogen atoms, we need to know if the molecule would have a lower energy than the two hydrogen atoms in the ground state (1S). To get a definite answer to this question, one would need to solve the Schrödinger equation (that’s what we have it for, after all), but we can make some good arguments to see that, in this case at least, a bond will in fact form.

Each of two hydrogen atoms alone forms a potential well for an electron. Near to the nucleus, the potential drops rapidly \( \left( \frac{1}{r} \right) \) while far away it asymptotically approaches 0 (assuming we have defined it to be 0 at infinity). If we consider an electron to be in the potential well of both nuclei, then its potential energy is the sum of its potential energy in each potential well. If we draw the summed potential wells, we find a that in between the two
nuclei is lower than out at an equal distance to either side. In particular, we see that if we bring the nuclei closer together, the potential between them becomes smaller, meaning that the electron will pull them closer. Of course, our picture is very incomplete. To start with, we have ignore the repulsion of the nuclei, so our picture suggests that the electron would suck them together all the way, which makes no sense. Nonetheless, at long distances this perspective is valid, and so while it breaks down eventually, the central point that the electron being in both potentials at once draws the atoms together remains valid. We will look at potential energy in a slightly different way later.

While we have argued that the electrons will be drawn between the nuclei to some degree, our arguments make no statement about the specific probability distribution of the electrons. Solving Schrödinger’s equation would give us essentially the result in Figure 40-2 of your text.

19.1.2 Ionic

Covalent bonds are generally described as being caused by the sharing of electrons between atoms, and the description above shows why. The electrostatic system creating a bond in a covalent bond is essentially (+) (−) (+). In an ionic bond, one of the atoms in a molecule will (for reasons we’ll get into shortly) exert a stronger pull on one of its partner’s electrons than its partner itself does. The probability distribution of that electron will then essentially shift to the atom with the stronger attraction, creating two charged atoms (ions) in close proximity. This is an even simpler example of electrostatics (assuming we accept the theft of the electron by one atom) than covalent bonds. We are left with a positive and negative charge (+) (−) attracting each other. It is clear in this case that the two will form some bond, tho the details again need Schrödinger’s equation to work out.

The interesting part of ionic bonds isn’t the bond itself, but rather how one atom can steal electrons from the other. We are assuming here that both atoms are neutral to start with, such that the total charge of the molecule
is still 0. So what gives? The answer lies in the shapes of the other electron orbitals of an atom. The simple hydrogen atom doesn’t give us enough to explain this process, so we refer instead to the simple example of table salt, NaCl or Sodium Chloride. Both Sodium and Chloride are large enough (11 and 17 respectively) to have multiple layers of electron shells ($n > 1$). Chemical bonding generally deals with the sharing or stealing of the outermost layers of an atom. This is because of Gauss’s Law. Assume for a moment that all electrons exist in spherically symmetrical orbitals. If we then draw a spherical Gaussian surface at the outermost orbital, the charge enclosed will be much less than the total charge of the atom. The inner electrons are canceling out the nucleus from the perspective of Gauss’s law. We call this “shielding” because the outer layers are shielded from the influence of the nucleus by the inner layers. This translates into a weaker bond between the outer electrons and the nucleus which makes them free to participate in chemical bonding.

In the case of NaCl, the inner 10 electrons of sodium have a total distribution which is essentially symmetrical (the each orbital is not). This means they shield 10 protons worth of charge and the outer electron feels a single proton charge. However, the Chlorine has an asymmetrical distribution of its inner 16 electrons. As a result different locations around the outside of the atom (unoccupied orbitals a stolen electron from sodium might occupy) will “see” a different proportion of the nuclear charge (our simple interpretation of Gauss’s Law falls apart with the asymmetrical electron distribution). For one open chlorine orbital, the electron will feel 5 protons, as there are only 12 electrons shielding the nucleus here.

The difference between seeing 1 or 5 protons is very significant, so the chlorine is able to strip the outermost electron from the sodium. Precise calculations of the shapes of electron orbitals for each type of atom allow us to predict the electronegativity of each atom. This is a numerical measure of how strongly a particular element attracts electrons. In a bond between two atoms, the one with the higher electronegativity will become negative as it steals an electron.

The difference in electronegativity of sodium and chlorine is unusually
large, and so it forms a particularly “ionic” bond. Usually, one atomic cannot fully steal an electron from its partner, and some mixture of ionic and covalent bonds forms.

### 19.1.3 The real world: a mixture

The idea of a bond which is partially covalent and partially ionic is fairly natural. Start with a picture of an even covalent bond like that of $H_2$, but now imagine that the electron likes one of the atoms a little more than the other. This will just cause a slight shift in the probability distribution of the electron until the charge imbalance is large enough to counter the greater attraction of the atom with a larger electronegativity.

Purely ionic bonds tend not to just form single easily identified molecules, because an ion is an ion, so a positively charged Sodium can easily be surrounded by a couple of negatively charged chlorine. We can then add more sodium around that, then chlorine, and so on. Where do you draw the line and say “this is one molecule, that’s a new one?” You can’t, and we talk more about this when we discuss crystalline solids.

Covalent bonds, on the other hand, give a very clear demarcation line (well, they can. Atoms capable of forming multiple covalent bonds are common and can be arranged much like the ionic bonds, but a covalent bond has the capability of locking up its constituents entirely such that they don’t bond with other atoms). Partially ionic bonds are more like covalent bonds in this sense, but it always depends on where along the spectrum from covalent to ionic the bond sits. A partially ionic bond forms a polar molecule such as water. A polar molecule is tightly bound via a covalent sharing of an electron, but has a dipole moment because of the uneven electronegativity of its component atoms. This dipole moment gives rise to an intra-molecular force which is the weaker analog to the repeated strong ionic bonds found in a salt crystal.

### 19.1.4 Potential Energy perspective

We can learn a lot about the bonding process, beyond just whether two atoms can form a bond, by looking at the potential energy of a potential molecule.
In some sense the definition of a bound state is that the constituents (our atoms) stay within some distance of one another due to some sort of mutual interaction. In the case of chemical bonding (and most everything else) this can be represented by writing the potential energy of the collection of constituents as a function of their separation. This is complicated to draw on papers for more than 2 constituents, so we stick with 2, but the idea is general.

Plotting potential energy $U$ vs. atomic separation $r$ shows us where the atoms attract, repel, and remain relaxed. The bound states exist around local minima in the potential energy.

Remember when I mentioned earlier that nature prefers being in the lowest allowed energy state. That remains true here, and is in fact the main reason why these diagrams are useful to look at. At any given moment, our system will exist in a state with some value of $r$ (within some uncertainty due to Heisenberg). If we locate that value of $r$ on our potential energy plot, we can tell what forces the system will feel by checking in which direction potential energy decreases. The system will want to “move” in the direction of decreasing potential energy, just like a ball rolling down a hill, and so this is the direction the combined forces of the system will push in. For instance, if in the hydrogen molecule at a given instant $r < r_0$, we can see that potential increases to the right (larger $r$). This means a force will push the nuclei towards larger $r$, or push them apart through a repulsive force. If, on the other hand, $r > r_0$, the opposite will happen and the nuclei will be pulled together through an attractive force. The details of the shape of this curve depend on the atoms involved, and is ultimately the result of adding up all of the potentials of the electrostatic pairs in the system.

There can be different general shapes for the potential, as well.

Very often, the repulsion of the outer electron shells will dominate over any attractive forces for larger distances, and yet if the atoms are forced close enough a bond can form. When this occurs we say that an activation energy
is needed to form a bond. This just means that we have to put some energy into the system to get a bond to form, even tho in the end more energy is released than absorbed since the bound energy is less than the unbound energy. This barrier is why you need to heat flammable material up to get it to burn, but that it will keep going once started. Once you’ve provided enough energy to get those first few reactions going, they release even more energy, which activates a few more, which produce even more energy, and rapidly the effect spreads and self-perpetuates in a chain reaction. To some degree the flammability of a substance is determined by how much energy is released by the forming of a bond relative to the activation energy needed to start a new one. If you barely generate enough energy to activate another reaction, it is hard to do more than smolder.

It is also possible to have metastable bonds. A metastable bond actually has a higher potential energy than the unbound system, but there is an activation energy barrier that the system needs to overcome somehow in order to release the stored energy. This is the concept behind energy-storing molecules like ATP and glucose.

The most obvious way for a molecule of this sort to break up from a physical perspective is for it to be knocked around by something energetic enough to kick it apart past the activation peak. Another option would be tunneling, which is generally going to be extremely rare. Luckily, catalysts can interact with the molecule in various ways that can modify the molecular structure and thus potential shape without binding to the molecule. This, for the right catalyst, can lower the barrier holding the molecule together, making it easier and more likely for the molecule to break apart and release its energy.

19.2 Wan der Waals Bonding

A Wan der Waals force is an attraction between dipole molecules. This represents a sort of 3rd layer of electrostatic binding. First electrons are
bound tightly to nuclei. Next, atoms are bound fairly strongly together by, essentially, imbalances in the electron-nucleus binding of the individual atoms. Now, even weaker bonds are formed between these molecules and these bonds are again the result of imbalances in the previous binding. Van der Waals forces can be thought of the residues of interatomic forces, which are themselves the residue of subatomic electrostatic forces. As such, they are much weaker than the other forces.

These forces are very important, partially for the very fact that they are weak. Hydrogen, being small, forms some of the strongest van der waals bonds (hydrogen bonds) and forms the basis for holding together some large composite molecules like proteins. If we constructed enormous molecules like DNA based on covalent and ionic bonds, they would be so well held together that they couldn’t come apart, charge, interact, and come back together. None of the metabolic processes that depend on the morphing and activity of large molecules would work without a form of weak bonding.

19.3 Solids

There are two kinds of “solids”, amorphous solids (glasses) and crystalline solids. Debate rages over what in the world is going on with amorphous solids, whether we should really call them solids, how exactly they work, etc., even to this day. We are instead going to focus on crystalline solids. The study of solids (even the relatively simple crystalline ones) and liquids is in generally very complex, but there are some useful, well known results that let us understand some important features of materials.

19.3.1 Molecular Bonds

First of all, solids have to be held together somehow. Frequently this is through repeating covalent or ionic bonds NaCl mentioned earlier is an example of this, while carbon is capable for forming many types of crystal, such as diamond, due to its capacity for multiple simultaneous covalent bonds. These crystals are like huge molecules with a repeating structure, but each individual bond is just like the ones we’ve already discussed.
19.3.2 Metallic Bonds

Metallic bonds are a completely different beast, however. In metallic bonds, the atomic nuclei settle into place (more or less, everything vibrates) while their outermost electron shells all meld together. This is like one huge covalent bond between billions of atoms at once, all equally sharing a common supply of electrons. On average, a metal atom will be surrounded by enough electrons to keep it neutral, but individual electrons aren’t at all associated with individual atoms. In fact, there aren’t orbitals of any sort, the outer orbitals become a sort of intermediate state between free particles, which can have any energy and travel anywhere, and bound electrons which can only have a few set values of energy.

More on that in a second, but first I want to mention the relation of free electrons to metallic appearance. We’ve touched on the idea the we perceive color based on the emission and absorption of different wavelengths of light from different types of material a number of times. However, some materials don’t seem so selective. Metals, in particular, seem quite shiny and will reflect (especially if polished) any collection of colors. This is because in normal materials the electrons can only respond to and emit very specific wavelengths because they only have a few energy levels available to them. Electrons in a metal can vibrate with pretty much any frequency when driven by a field, so they do. The result is the shiny reflective appearance we associate with metals. This is actually the same feature which makes them good antenna’s, but at a different frequency range.

19.3.3 Band Theory of Solids

The details are of course involved, but the final structure of allowed electron energies in a metal is fairly simple. A single metal atom will have a set of allowed energies like any other. Interatomic interactions amongst many such atoms will split all of those energy levels, with more splits the more atoms are present. At some point it starts to make more sense to thing of continuous bands of allowed energies, separated by gaps of disallowed energies. Electrons are then able to have a wide variety of energies, but not
all.

Just like an atom can have either full or partial full or empty energy levels, a metal can have either full or partially full energy bands. The occupation of these bands and the size of the gaps determine most of a metal’s properties.

If the highest energy band is only partially full, it allows the electrons in it to absorb small amounts of energy very easily, which can get them moving around and flowing; such metals are good conductors. If the highest occupied energy band is completely full, then in order to move freely electrons must jump across the gap to the next higher band. This requires much more energy than if there is free space in the current band, so such materials don’t allow current to flow easily.

If the highest occupied band is full, but the next band happens to be extremely close (separated by a small gap) we call the material a semiconductor. The behavior of these materials is special because it is fairly easy to get current flowing in them, but since it isn’t entirely automatic conditions can be manipulated to produce either conductive or insulating behavior on a changing basis. This property is critical for many applications, most notably transistors and the integrated circuits of computer chips.