CH1200 General Chemistry

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Lecture 1

Welcome!

Welcome to your chemistry degree. In this module (CH1200 – "General Chemistry") we are going to cover the foundations you need to be successful going forward. A lot of the content will likely be somewhat familiar from the A level, but we'll cover some new topics and learn to think about some things that you already know in a different way. Today, though, we are going to think about what chemistry is, so we can start to think how to approach studying it.

1.1 Chemistry

Chemistry is the study of molecules and how they look, behave, and interact with each other. These interactions govern everything about the physical world around us, and so understanding them will allow us to understand and manipulate the world around us. Chemistry, and a chemical understanding of the world, has led to countless discoveries that have revolutionised human existence, such as:

- The development of medicines and drugs – revolutionising human health.
- The harnessing of natural energy sources – powering industry and discovery.
- Developments of artificial fertiliser – supporting half of the human population on earth.

And many more besides these. We can argue about whether these developments were all 'good' for humanity and the earth or not –but they are all driven by chemistry, for better or worse, and the solutions to any problems they create, or have created, will inevitably also come from chemistry.

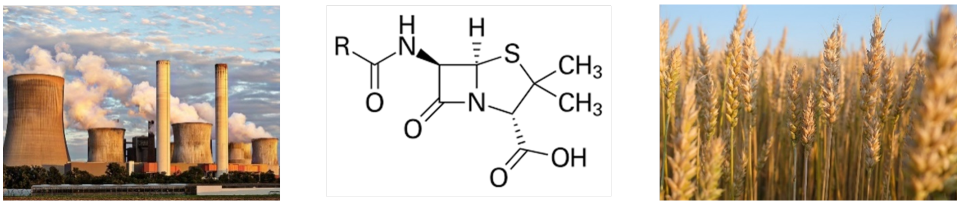


Figure 1.1: From left to right: a coal power station, penicillin, and some dwarf wheat. Chemistry enables all of these things, and will inevitably solve any problems they create!

In this course we'll talk about a few of these in more detail, and with Sandeep you'll learn things like "why the wedged and hashed bonds in the penicillin structure are important" . The first thing I want you to realise, though, is:

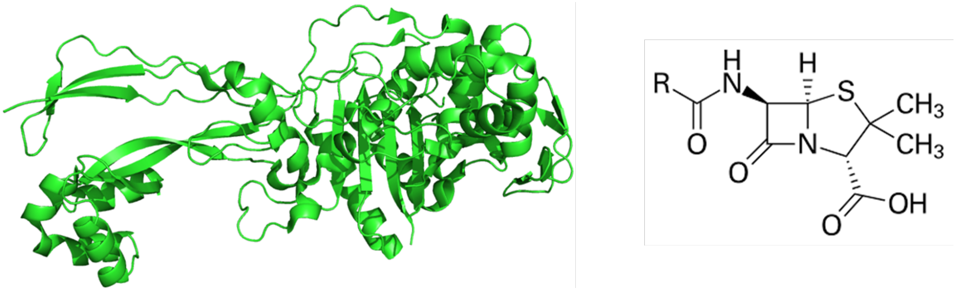


Figure 1.2: A penicillin binding protein (left) and penicillin (right). The penicillin stops this protein performing its usual function in cell reproduction.

The modern world is the way it is because of chemistry and chemists. The solutions to most of the big issues facing humanity are all going to be chemical in nature, and developed by chemists.

We are going to start seeing how to think about chemistry today, to underpin the rest of your time here.

1.2 Thinking about Chemistry

So how do we understand these processes? We said it is all about molecules –so what is a molecule?

> **A molecule is an arrangement of atoms, where the atoms are bound together by chemical bonds.**

So atoms are the fundamental building block of chemistry. Atoms are in turn made of subatomic particles (protons, neutrons, and electrons). We are going to get into atomic structure next time. But before then, let's take a step back and think about the examples of impactful chemistry shown above, to motivate how we're going to think about this subject.

There are basically two key things that drive chemistry: **structure** (of molecules), and **energy**.

1.2.1 Structure: Medicines and Drugs

We had the structure of penicillin, a common antibiotic, shown above. Antibiotics like penicillin work by disrupting the way in which bacterial cells reproduce. The mechanism is something like:

- Bacterial cells reproduce, which is what causes infection and makes people ill. If you can inhibit the reproduction, you stop the immune system being overwhelmed by the bacteria.
- Bacterial cells have a cell wall around them, which is built by a specific protein.
- Penicillin acts to bind to this protein and stop it building cell walls.
- Without cell walls, the bacterial cell doesn't have any 'skin' and so falls apart very easily.

I'll try and draw some pictures of how this actually works, but that's the main idea. The fundamental thing is that the antibiotic interacts with the protein and stops it doing its normal job. The antibiotic and an example of the protein are shown below.

As you can see proteins are massive and look ridiculously complex. Ultimately though, the behaviour often boils down to a single **active site** which performs the main useful chemistry. The penicillin works by binding into this active site and stopping it working (I'll draw a cartoon of this in the lecture).

So, why do we have to use penicillin do this? Why can't any molecule just bind into the active site and stop the protein doing its job? The answer is that the *structure of the penicillin looks like the normal part of the cell that the protein works on*. Effectively this tricks the protein into thinking it's bound to the cell wall, but actually it's bound to the penicillin molecule and the cell wall falls apart. Ultimately:

- **Molecular structure is one the fundamental things that drives chemistry.**
- If we can understand molecular structure, we are well on the way to understanding chemical reactivity and being able to design molecules with specific functions in mind.

Therefore, developing an understanding of:

- Why molecules look the way the way they do (why they have certain structures).
- How we know molecules look that way (how we know they have those structures).

Is going to be a core part of this course, and fundamental to the rest of the degree.

1.2.2 Energy: Power Plants

Also at the start of this lecture, we talked about coal power plants. These exist because burning coal (which is basically carbon) releases a lot of energy:

$$\mathrm{C(s) + O_2(g) \rightarrow CO_2}(g)$$

For one mole of solid carbon (12 grams), this reaction releases 393.5 kJ of **energy**. We're going to talk about what specifically 'energy' means later, but for now know that that's enough energy to charge a typical smartphone about 10 times over.

Energy dictates all kinds of things in chemistry, such as:

- Why molecules adopt a specific structure.
- Why some molecules are stable and others are unstable.
- Why specific chemical reactions occur and some don't occur.
- Why some chemical reactions that do occur are fast and others are slow.
- Why spectroscopy is able to distinguish between molecules with different structures.

And more than this. Throughout your degree, you'll be hearing a lot of phrases like *this is a higher energy state*, or *this molecule is in a lower energy conformation*, or *this reaction has a higher activation energy*. An understanding of energy is fundamental to chemistry, and because energy is a quantitative thing, we need to be OK with looking at and dealing with numbers. To give you a sense of this, let's look at a few energies of some typical chemical things **Remember that when we look at numbers and talk about them in chemistry, they always relate to something physical and real**. We aren't doing maths for the sake of maths.

- Energy of a van der Waals force: $\sim$1 kJ mol^{-1}
- Energy of a hydrogen bond: $\sim$10 kJ mol^{-1}
- Energy of a chemical bond: $\sim$100 kJ mol^{-1}
- Energy holding an electron in an atom: $\sim$1000 kJ mol^{-1}
- Energy holding a nucleus together: $\sim 1 \times 10^9$ kJ mol^{-1}

You can see the typical **orders of magnitude** that the energy of these things have. A chemical bond energy is somewhere around 100 kJ mol^{-1}. A hydrogen bond is normally about 10x weaker, and the energy holding an electron into an atom is about 10x stronger. Van der Waals forces are about 100x weaker than a chemical bond, and energies holding nuclei together are much higher: about 10 million times higher than chemical bond energies.

It's useful to remember these typical values, so that when someone talks about something being "higher energy" or "lower energy" , you know what they're talking about.

Energy is going to be fundamental to how we approach our study of chemistry.

1.3 The Road Ahead

Our plan is to start by thinking about structure, and then moving to reactivity. Roughly:

- The first half of the course will be about structure, and how we determine structures (spectroscopy) – which is driven by energy.
- The second half of the course will be about reactivity – which is driven by structure.

We'll start with thinking about **atomic structure** next time.

Lecture 2

Atomic Structure

We said last time that we're going to approach thinking about chemistry by thinking about **molecular structure**. Given that molecules are made of atoms, the place we have to start here is by thinking about **atomic structure**. The atom is the fundamental building block of chemistry.

Atomic structure is a surprisingly recent discovery. My grandparents grew up in a time where no one had discovered the neutron, for example. The pace of change has been extreme since then!

Lecture 1 Aims

- To understand what we mean by **atomic structure**.
- To understand that we describe electrons using **quantum numbers**, and draw them as **orbitals**.
- To start to understand the **Aufbau principle.**

2.1 Protons, Neutrons, and Electrons

Atoms are made of subatomic particles, and there are three that we care about as chemists:

- The proton, which has a charge of $+1$ elementary charge unit, and is quite heavy.
- The neutron, which has a charge of zero, and is also quite heavy.
- The electron, which has a charge of –1 elementary charge units, and is very light.

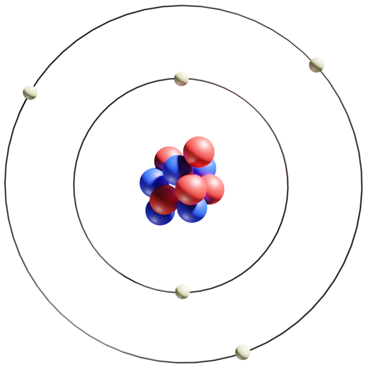
As a rule of thumb, an electron is about 2000 times lighter than a proton or neutron. An **atom** consists of a **nucleus** (containing protons and neutrons) with some **electrons** floating around it. In a **neutral atom** the number of protons and electrons is equal. In an **ion** there is an imbalance –more protons than electrons make a **positive ion (cation)**, and more electrons than protons make a **negative ion (anion)**. Sometimes you can have two atoms that have the same number of protons and electrons (so are atoms of the same element), but have different numbers of neutrons so have different masses. These are called **isotopes**.

But really, the electrons in the atom are the bit that dictate the chemistry, so are the bit we care most about as chemists. The periodic table sorts the elements according to their number of electrons (or equivalently, protons) for this reason.

A picture of an atom like the one below is probably familiar from school. It isn't the worst picture in the world, but there are a few obvious questions:

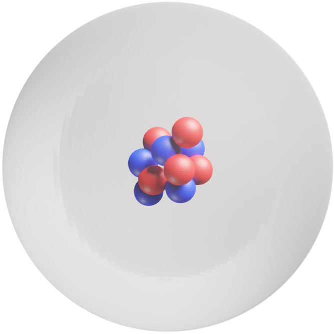
- What are the 'rings' the electrons are orbiting on?
- How many electrons are we allowed to have on each ring?

These are excellent questions.



2.1.1 Atomic Orbitals and Quantisation

Without getting too far into the underlying physics, what we have to understand is that the 'electrons orbiting the nucleus on rings' picture is fundamentally a **classical** picture of atomic structure. In reality, the electrons don't exist on these well-defined rings[1] , and a better way to think of the atom is as being surrounded by diffuse clouds of electrons –like the figure below.



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[1] At least, not in space. You could think of the rings as defining the energy of the electrons, and the picture is a bit more realistic then.

We call these clouds of electrons **orbitals**, and each electron occupies its own orbital. Orbitals interacting with each other are what drive chemistry.

To understand atomic orbitals fully, we really have to understand some quantum mechanics. "Quantum mechanics" sometimes seems to be used as a synonym for "really complicated subject" , but it really isn't. There are basically three things to know:

- Electrons in atoms exist in a **quantum state** defined by some **quantum numbers**. Each quantum state has a well defined energy. The **atomic orbital** is a way of representing this quantum state on paper as a picture.
- There are only a few different quantum states that can exist. This means that the electron can only have certain energies – the energy of the electron cannot vary continuously.
- Two electrons in the same atom cannot be in the same quantum state, due to something called the **exclusion principle**. The exclusion principle is why all the different elements in the periodic table have such diverse and different chemistry.

We'll talk more about what 'quantum state' really means later –- for now just think of it as meaning the 'state' (i.e. the current situation/condition) that the individual electron is in. These are defined by quantum numbers, which are numbers that describe the quantum state, in the same way that words like 'bald', 'beard', and 'wearing glasses' can be used to describe me.

2.1.2 Quantum Numbers and Orbitals

We need four quantum numbers to describe an electron in an atom[2]. They are:

- The **principal quantum number**, n.
    - This determines the *size* and *energy*[3] of the orbital.
    - Takes values of $n = 1, 2, 3, 4, ...$
    - The value of n refers to the **shell** that the electron is in.
- The **angular momentum quantum number**, l.
    - This determines the *shape* of the orbital.
    - Takes values of $l = 0, 1, 2, ...n$.
    - The value of l refers to the **subshell** that the electron is in within a given shell.
- The **magnetic quantum number**, m_l.
    - This determines the *orientation* the orbital.
    - Takes values of $m_l = -l, -l + 1, -l + 2, ..., l - 1, l$ in integer steps.
    - The value of m_l refers to the specific **orbital** the electron is in within a given subshell.
- The **spin quantum number**, m_s
    - This determines the orientation of the electron spin (up or down).
    - Takes values of $m_s = -1/2, 1/2$ for an electron.

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[2] Think of it as one for each of the dimensions of 3D space, and another for the spin.

[3] If our atom only has one electron.

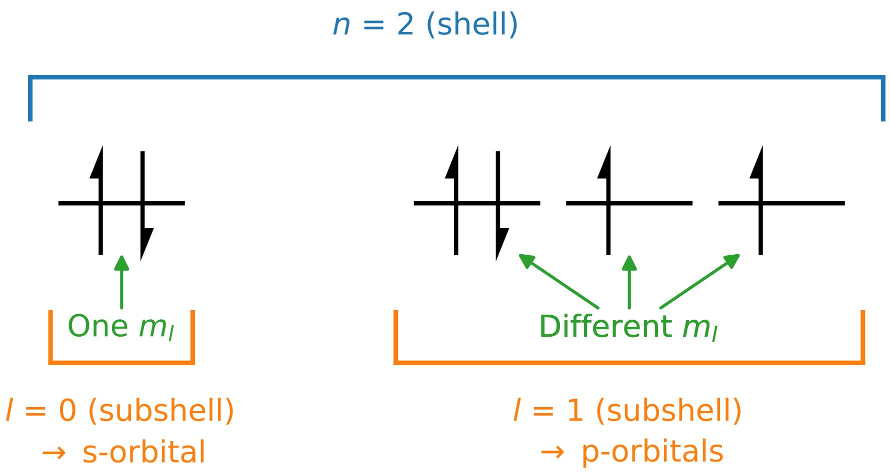

Figure 2.1: How the quantum numbers relate to different shells, subshells and orbitals.

You can completely define the state of an electron in an atom by defining these four numbers. When we describe an electron in an atom, we normally call it something like a "1s" or "2p" electron. The "1" or "2" here refers to the value of n, and the letter refers to the value of l.

The best way to think about electrons in chemistry is to think about them as orbitals[4], we'll see soon that orbital overlap is the best way to think about chemical bonding and reactivity.

2.2 Shapes of Orbitals

Let's look at some orbital shapes, which should hopefully be familiar. The shapes of the orbitals result from the solution of something called the **Schrödinger Equation** –the most important equation in the world. We'll talk about this more next year, but it's useful to know now that the atomic orbitals are wavefunctions of electrons in atoms. and that wavefunction is the mathematical solution to the Schrödinger Equation.

2.2.1 s-orbitals

Some s-orbitals are shown below. These are spherical, and just get bigger as n increases. Internally there is also a change to the shape as there are some **radial nodes** in the orbital. A **node** in an orbital is a place where there is no chance of finding an electron , and has some interesting consequences for chemistry that we'll see later. **What are the quantum numbers of these orbitals?**

2.2.2 p-orbitals

The three p-orbitals in the $n = 2$ level are shown below. There are three of them (you can tell me why). These orbitals are clearly not spherical, and have an **angular node** in the middle of them, separating the (as drawn) red half from the blue half. The red and blue colours represent parts of the orbital that have a different sign or a different phase. This has important consequences for chemical bonding.

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[4] We have a tendency in chemistry to talk about electrons *occupying* orbitals. This is functional but isn't really accurate –the orbital *is* the electron. You can't really have an empty orbital –that just means that there isn't an electron with those quantum numbers yet.

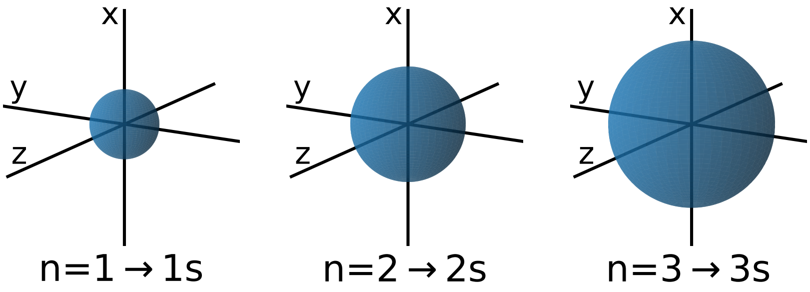

Figure 2.2: The first three s-orbitals - note that the size increases as n increases.

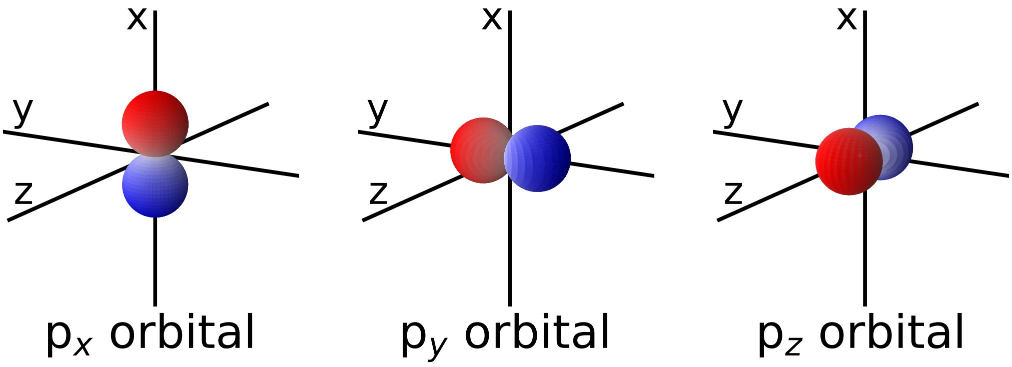

Figure 2.3: The three p-orbitals in the $n = 2$ shell.

2.2.3 d-orbitals

The five d-orbitals in the $n = 3$ level are shown below. These orbitals play an important role in the chemistry of the transition metals, and you need to be able to draw them. Unless you're a more talented artist than me, drawing them in 3D is a pain –what we normally do is draw the 2D projection of the 3D orbital, labelling the axes. We'll do it together in the lecture.

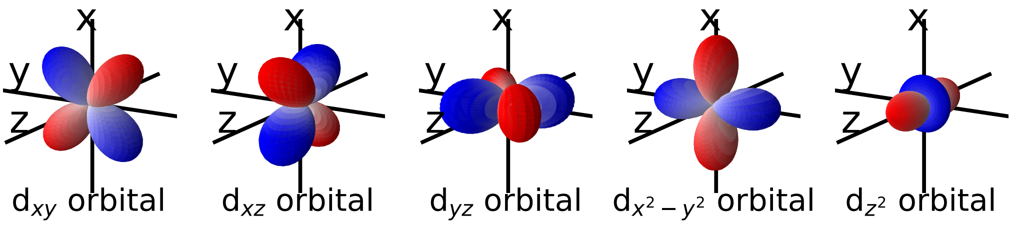

Figure 2.4: The five d-orbitals of the $n = 3$ shell.

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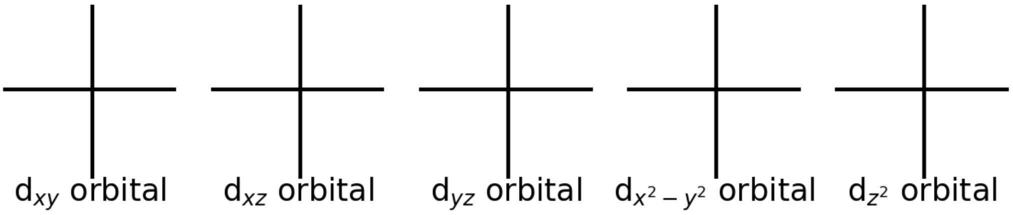
2.2.4 f-orbitals

The seven f-orbitals in the $n = 4$ level are shown below. In most common chemistry these orbitals are relatively infrequently encountered, but if you get into lanthanide and actinide (f-block) chemistry in later life you'll see them a lot. They're here for completeness.



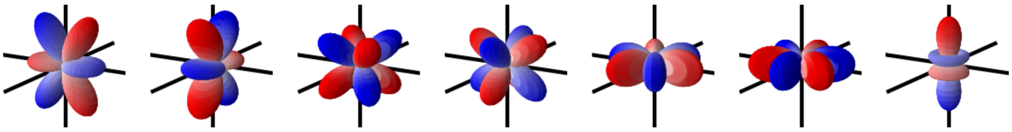


Figure 2.5: The seven different f-orbitals in the $n = 4$ level.

2.3 Many-Electron Atoms

If we look back at our 'electrons orbiting the nucleus' picture from the start of this lecture, we see we have more than one electron in our atom. An obvious question to ask is then *how do multiple electrons arrange themselves into different orbitals*? Or, put another way, *what's the difference between atoms of different elements?* The fundamental rule here is that as you add electrons to an atom, **each new electron will go into the orbital that minimises the overall energy of the atom** This principle can (mostly) be expressed by something called the **Aufbau principle**.

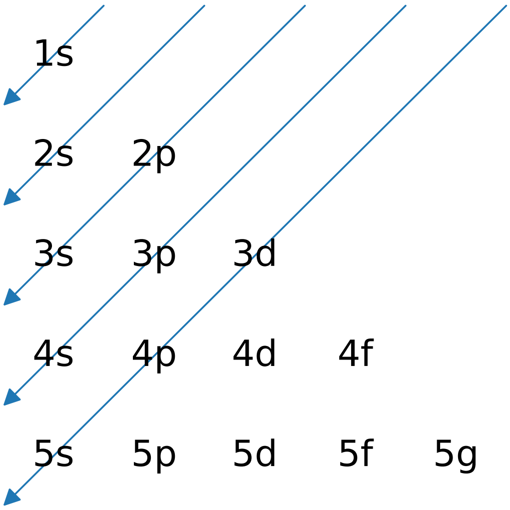


Figure 2.6: Aufbau Principle - write out the orbital names in a grid like this, and then follow the arrows from top to bottom.

In general, atoms and molecules always want to minimise their energy as much as possible – this principle applies to, and drives, all of chemistry, and is worth remembering!

So, if we have an atom (say, carbon), we can look up how many electrons it has (for carbon, 6) on the periodic table. The Aufbau principle can be distilled into a diagram like the one above to show how these six electrons will be put into orbitals. The Pauli exclusion principle says that

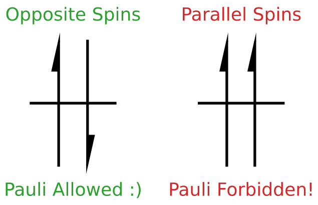


Figure 2.7: The Pauli Principle. Electrons are lower in energy (happier) with opposite spins (left). Having parallel spins (right) violates the Pauli principle, and is forbidden.

each orbital can contain two electrons (spin up and spin down). The Aufbau principle works because 1s electrons are lower in energy than 2s, which are lower in energy than 2p, and so on.

Next time, we're going to talk about this some more, and have a look at the **Periodic Table**.

Lecture 1 Take Home Messages

- Atoms are made of protons, neutrons, and electrons. Electrons and electronic structure dictate all of chemistry.
- Electrons exist in **orbitals**, which are like clouds around the nucleus of an atom.
- Atoms and molecules always want to do the thing that minimises their energy!

Lecture 3

Electron Configurations and The Periodic Table

Lecture 3 Aims

- To see how atomic orbitals get filled, and how electronic configurations are built up.
- To understand Hund's rules and the Pauli principle.
- To start to think about trends in the Periodic table.

Today we're going to think about atomic structure a bit more, do some basic work with **electron configurations** and take a look at the **Periodic Table**.

3.1 Electron Configurations

The arrangement of electrons in an atom or molecule is called the **electron configuration** of the atom or molecule. We saw the **Aufbau Principle** last time that helps us find electron configurations, and we know the golden rule that **each new electron is added the orbital that minimises the energy of the atom**. Remember that electrons will repel each other, so when we have multiple electrons we want to minimise this as much as possible.

That electrons repel each other leads to another rule about available orbitals. If we have a set of p, d, or f orbitals (where there is more than one orbital in the subshell, but they all have the same energy), then electrons will fill each individual orbital singly first, before they start to pair up. You'll get one electron in each of the p_x, p_y, and p_z orbitals before you get two in any orbital. This is called **Hund's Rule of Maximum Multiplicity**, or simply **Hund's Rule**.

This maximises something called the *spin multiplicity*, but the crucial thing is that this is the **lowest energy way to fill the orbitals**, because it minimises the repulsions between the electrons. Remember the golden rule: **orbitals are always filled in a way that minimises the overall energy of the atom or molecule**. This rule **never** gets broken!

3.1.1 Writing Electronic Configurations

We are now in a position to start thinking about how to write an **electronic configuration** (or sometimes just **electron configuration**) for a given species - an atom, or an ion. The electronic configuration helps us to understand the chemistry of the atom/ion.

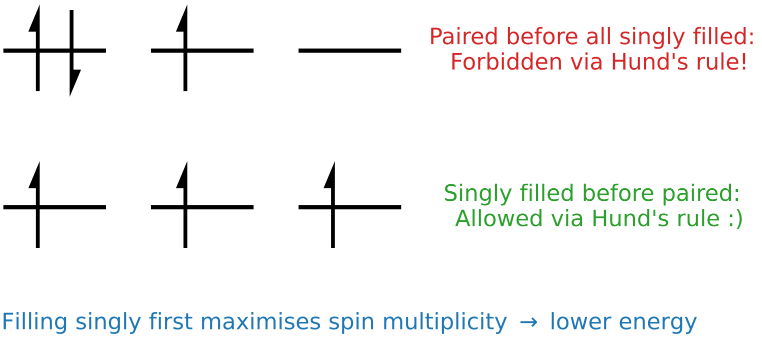


Figure 3.1: Hund's Rule. Unoccupied orbitals are filled singly first, before any electrons are paired.

All we do to write the electronic configuration is to count how many electrons we have, and then put them in orbitals according to all the rules in the past few sections. This is best shown by example, so let's do that.

Example: Electron Configurations

Write electron configurations for the following species:

1. Na (11 electrons in atom)
2. Cl^- (17 electrons in neutral atom, but Cl^- has 18 due to the negative charge)
3. Mg^{2+} (12 electrons in neutral atom, but Mg^{2+} has 10 due to the positive charge)

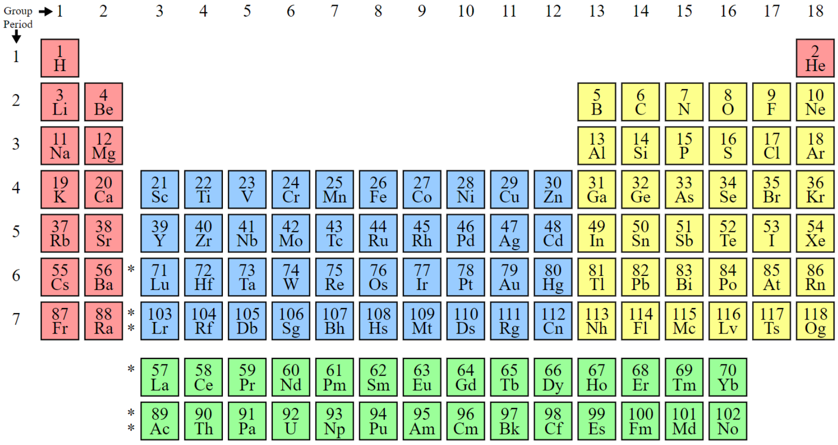
Answers (we will go through method in the lecture)

1. Na $1s^2\ 2s^2\ 2p^6\ 3s^1$
2. Cl^- $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
3. Mg^{2+} $1s^2\ 2s^2\ 2p^6$

Note that when we fill up something like a p-orbital, we don't write it out with two electrons in each individual orbital. Instead we just write the total number of electrons in the shell. We can rationalise some chemistry based on these configurations, which is why they're useful:

- Na is reactive, because it would like to get rid of that single 3s electron and have the a **closed shell** (a shell that is totally full of electrons).
- Cl^- is relatively unreactive relative to atomic Cl, because it has gained an extra electron and so got a closed shell.
- Mg^{2+} is also unreactive relative to atomic Mg, because it has lost two electrons and got a closed shell.

It's generally the case that completely filled shells are especially stable, and the same is true of half filled shells (such as $3d^5$), this leads to a few exceptions to the normal ordering rule (but remember that the rule that the orbitals fill to minimise their energy is **always** true!).



Group → Period ↓	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Figure 3.2: The Periodic Table. Periods go from left to right, groups go from top to bottom.

Exceptions to Ordering Rule

- For Cr, we would expect the outer shell to be 4s^{2}3d^4 from our ordering diagram. In reality it is 4s^{1}3d^5. This is because the half-filled 3d orbital is especially stable.
- For Cu, we would expect the outer shell to be 4s^{2}3d^9. In reality it is 4s^{1}3d^{1}0, because the filled 3d orbital is especially stable.
- For Ag, we expect 5s^{2}3d^9, but find 5s^{1}3d^{1}0 for the same reason as above.

Later in the course you'll find other slight exceptions to the ordering rule shown - remember that all that is happening is that the electrons are filling the orbitals in such a way as to **minimise their energy**. That rule doesn't break!

3.2 The Periodic Table

Hopefully we have all seen the periodic table before. The periodic table is a way of arranging the elements into some kind of systematic order, such that we can identify trends and predict the chemistry of unknown elements based on other elements around them. The periodic table was invented by the Russian chemist Dmitri Mendeleev in 1871 - at this point, people were discovering new elements all the time[1], and so a way to organise and keep track of them was getting pretty necessary. You'll see in the rest of this lecture how it's built up, and why is it useful.

The periodic table is organised into **groups** which go from top to bottom, and into **periods** that go from left to right. The groups are numbered from one to eight - the number refers to how many electrons there are in the outermost shell of the atoms in the group. In group 1 (the 'alkali metals'), there is only one electron in the outermost shell (as we saw with the electronic configuration of sodium above). In group 7 (the 'halogens'), there are seven electrons in the outermost shell. The other groups all have 'english' names too, which you'll learn in due course - but I prefer to just call them by numbers!

The periodic table is also organised into blocks, called the s-, p-, d-, and f-block. These refer to the orbital that the outermost electron on each atom in the block is in. In the s-block, the

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[1] About one every year in the 1800s!

outermost electrons are in s-orbitals. In the p-block, they are in p-orbitals, and so on. In the periodic table above, these are shown in red (s-block), yellow (p-block), blue (d-block), and green (f-block). When you start learning about more advanced inorganic chemistry, you'll learn about d- and f-block chemistry. For now, we're only going to worry about the s- and p-block.

3.2.1 Periodic Trends

One of the main uses of the periodic table is to try and predict the chemistry of an unknown element. This makes use of **trends** in the physical and chemical properties of the elements. You'll see that as you go along periods and down groups, various properties systematically change. Study of this is called **periodicity**, and is what we're going to introduce briefly now. You'll hear **much** more about this in inorganic chemistry...

Let's now look at some properties and analyse their periodic trends.

Atomic Radius

The **atomic radius** of an atom is defined as the distance from the nucleus to the outermost electron[2]. This is pretty difficult to actually measure! As you go down a group, the atomic radius increases because with every step the electrons are an extra 'shell' away from the nucleus (and are more shielded), and so get further away from the nucleus. However, as you go across a period (left to right), you put more electrons into the same shell, and the nuclear charge increases (as there are more protons in the nucleus). The net effect of this is that as you go across a period, the effective nuclear charge increases and the electrons are held more tightly - the atomic radius decreases.

Atomic Radius

Atomic radius is the distance from the nucleus to the outermost electron of an atom.

- Atomic radius **increases** as you go down a group, because with every step you put an extra shell of electrons between the nucleus and valence electron(s).
- Atomic radius **decreases** as you go across a period, because of increased effective nuclear charge that holds electrons more tightly.

But don't take my word for it - the data is in Figure 3.3. The wiki page on the periodic table has it for many other elements too - have a look if you're interested.

Ionisation Energy

Another property we care about is **ionisation energy**. This is the amount of energy it takes to do the following process:

$$\mathrm{A(g)} \longrightarrow \mathrm{A^+(g)} + \mathrm{e^-}$$

That is, the energy to remove an electron from a **gaseous** atom. Strictly, this is the *first* ionisation energy (the second would the energy to ionise $\mathrm{A^+}$ again[3].), but when people say 'ionisation energy' they normally mean the first ionisation energy. You might also see it called **ionisation potential** in some books. We're going to call it IE for the following discussion.

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[2] This is normally called the **valence electron**.

[3] And is predictably normally massively higher than the first ionisation energy

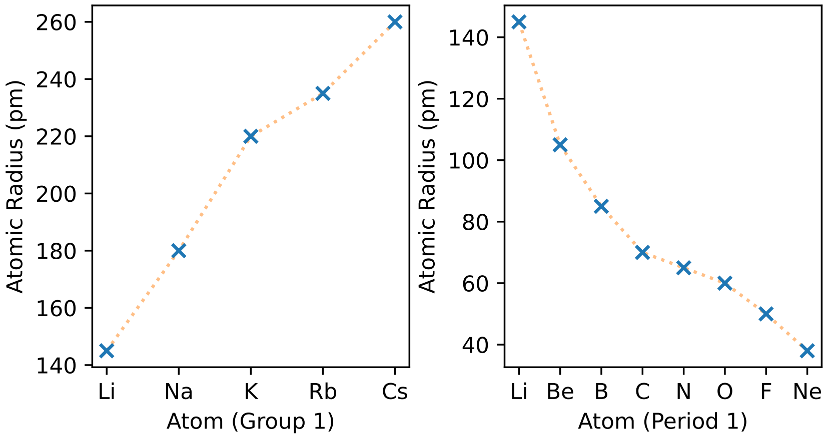

Figure 3.3: Trends in atomic radii down group 1 (left) and across the first period (right).

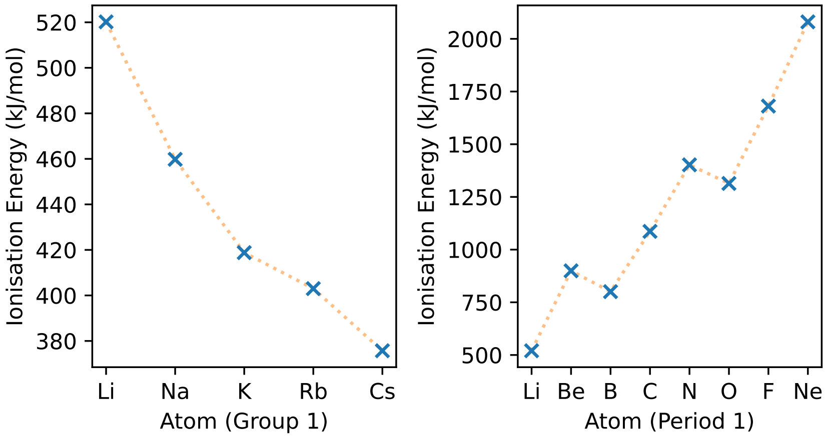

Figure 3.4: Trends in ionisation energy down group 1 (left) and across the first period (right).

You can imagine that if an atom holds onto its electrons tightly then the IE will be high, and if an atom doesn't hold its electrons tightly then the IE is low. So we would expect sort of the inverse trend to what we saw with atomic radii - that going down a group IE will decrease (because electrons are held less tightly), and across a period IE will increase (because the electrons are held more tightly). And this is exactly what is observed!

Figure 3.4 shows that the general trends we predicted are true - IE decreases down a group (as the electrons are more shielded from the nucleus and held less tightly), and tends to increase across a period (as the nuclear charge increases and isn't compensated for entirely by increased shielding). However, you can see in the right hand plot of Figure 3.4 that there are two obvious 'steps' at Boron and Oxygen - they're lower than we'd expect. You can explain this by thinking about the electron configurations, remembering that half-filled shells are especially stable.

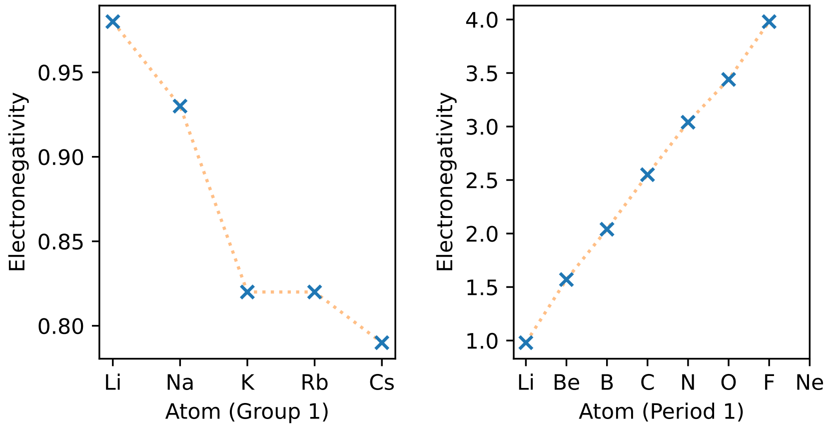

Figure 3.5: Trends in electronegativity down group 1 (left) and across the first period (right). Note there is no data for Neon - can you guess why?

Ionisation Energy

Ionisation energy is the energy required to remove an electron from a gaseous atom (or a mole of gaseous atoms).

- Ionisation energy decreases as you go down a group, as the electrons are held less tightly due to shielding.
- Ionisation increases as you go across a period, due to increased effective nuclear charge. However, there are some discontinuities at boron and oxygen caused by the stability of half-filled shells.

Electronegativity

The final property that we will look at is a thing called **electronegativity**. Electronegativity is a measure of much an atom will attract electrons to itself when it's in a molecule or ion. Electronegativity is really useful because it lets us predict where the **electron density** is concentrated in a molecule - understanding this is basically the entire subject of organic chemistry[4].

If an atom is very electronegative, then it will attract electrons towards it. A very electronegative atom is fluorine - in a molecule like HF (hydrogen fluoride), almost all of the electrons in the bond are pulled towards the fluorine, making the molecule polar.

There's a lot of different definitions of electronegativity, which means the precise values are often different. But this doesn't matter for us, because what matters is the **trends** in the values, and also the **relative differences** between different atoms - and these are the same regardless of definition.

We can see the trends down group 1 and across the first period in Figure 3.5. Electronegativity decreases down groups, but not in a very strong way for group 1 (it is more pronounced for group 7). This is because the extra electron shells between the outer electrons and the nucleus shield the nuclear charge, and cause the atoms to extert less of a 'pull' on other nearby electrons. Across periods, the electronegativity increases - because effective nuclear charge increases (as

---

[4] Don't tell Dr Blackburn I said this.

we have just seen for the other properties!). Fluorine has the highest electronegativity for any element - but note that there is no data point for Neon. Why do you think this is?

Electronegativity

Electronegativity is a measure of how much an atom attracts electrons to itself when bonded in a molecule (or as an ion).

- Electronegativity decreases as you go down a group, as the effective nuclear charge drops due to increased shielding.
- Electronegativity increases as you go across a period, due to increased effective nuclear charge.

Ok. We have covered a lot, and that's enough periodicity for now. Having ended with electronegativity - which is all about bonding in molecules and where electron density lies in chemical bonds - the next obvious question is to ask about chemical bonds. That's where we're going next time, when we start to look at **chemical bonding**. Strap yourselves in.

Lecture 3 Take Home Messages

- Orbitals fill with electrons in the way the keeps their energy as low as it can be. The arrangement of filled orbitals is called an electron configuration.
- Rules like the Aufbau principle, Hund's rule, and the Pauli principle help us to predict electron configurations.
- Elements are arranged in a periodic table, and by understanding the structure of the table (and trends in it), we can start to understand their diverse chemistry.

Lecture 4

Chemical Bonding I

Lecture 4 Aims

- To begin to understand why atoms bond together.
- To understand different types of bonding.
- To understand basic molecular orbital theory.

We have talked so far about atoms, and made a good start at understanding atomic structure with s, p, d, and f orbitals, and how electrons fill the orbitals. Now it is time to talk about what happens when two or more atoms become joined together: **chemical bonding**

In this course we're only going to talk about bonding in the s-block and p-block. We'll leave the transition metals to another time and another person who is more competent than me. Some of the rules of thumb we will learn here only apply to the s- and p-block, but I'll make a point of telling you this when it happens so that you don't think chemistry is a science of exceptions...

4.1 Chemical Bonding

Why do molecules exist as molecules? Why don't atoms just hang around on their own? The fundamental reason is **energy**. It is **energetically favourable** for the atoms to be in the molecule compared to being individual atoms. *Energetically favourable* can mean two things:

1. The molecule has a lower energy than the constituent atoms, so making a molecule reduces the overall energy of the atoms.
2. The molecule has as higher energy than the constituent atoms, but the *energy barrier* to turning the molecule back into atoms means it is hard to do.

These two definitions are known as **thermodynamic stability** and **kinetic stability** respectively. Just remember that the fundamental driving force for chemical bonding is **energy.**

4.1.1 The Chemical Bond

What is a chemical bond? Entire books have been written about this subject, but fundamentally a chemical bond arises when two or more atoms use each others electrons in some way – a collection of atoms can reduce their overall energy by coming together and sharing/exchanging electrons. This means the atoms have to stay close together for mutual benefit - they become **bonded**.

You're probably familiar with three types of chemical bonding from A level:

- **Covalent bonding** – when electrons are shared between the atoms.
- **Ionic bonding** – when the electrons are transferred from one atom to another, making a cation and anion that mutually attract.
- **Metallic bonding** – when the atoms sit in a kind of 'soup' of electrons.

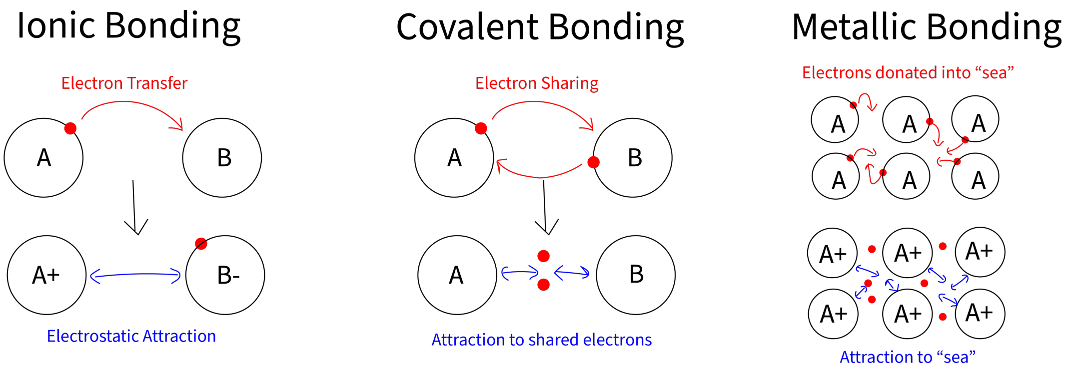

Figure 4.1: Ionic, covalent, and metallic bonding. Beautifully hand-illustrated by me.

The Bonding Triangle

An important point here is that most of the time none of these three types of bonding exist as absolutes. Bonding is always **somewhere on a spectrum between covalent-ionic-metallic**. Some bonds are very covalent (like the bond between the fluorines in F_2), with almost no ionic character. Other bonds are overwhelmingly ionic (like the bond between Na^+ and Cl^- in NaCl), with almost no covalent character. Others lie somewhere in the middle - like the bond between hydrogen and fluorine in HF. This is a covalent bond, but the electrons are very concentrated on the fluorine and not on the hydrogen, so the molecule ends up being **polar**, and the bonding is somewhere between ionic and covalent.

These different types of bonding are well represented on something called the **bonding triangle**.

When you talk about compounds in inorganic chemistry, you may often hear people talk about a bond having a certain percentage of 'ionic character' or 'covalent character'. This is what they are referring to - where it lies on this bonding triangle.

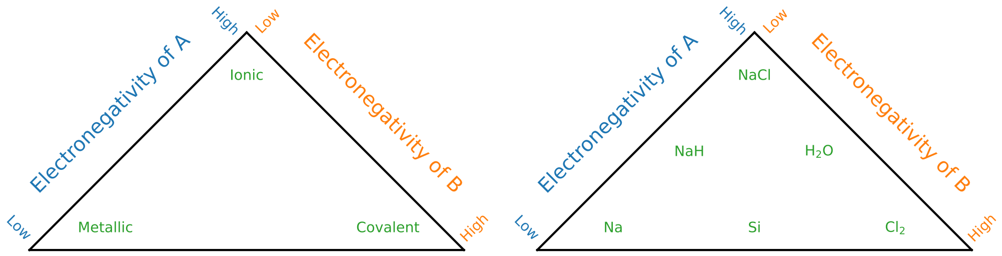

Figure 4.2: The bonding triangle, showing the extremes of ionic, covalent, and metallic behaviour (left). The same triangle with example compounds (right).

When we talk about **molecules** we're talking about covalent bonding. This is the only kind of bonding you get in small molecules. Ionic and metallic bonding require larger networks of atoms - you can't really talk about a 'molecule' of a metal, or salt. They always exist in these extended 3D structures - like crystals. Most often they are solid, but not always. For the rest of this course, we're only going to talk about covalent bonding in small molecules.

4.2 Orbital Overlap and Covalent Bonding

Covalent bonding occurs when atoms share electrons. We know already that electrons sit in orbitals, and that these orbitals are like clouds that extend out beyond the atomic nucleus. When atoms get close enough to form bonds, these orbitals overlap with each other. **Orbital overlap is how covalent bonds form.** You'll see later in this course that understanding orbital overlap, and how electrons travel between orbitals, is fundamental to understanding reactivity and reaction mechanisms.

We said that the electrons in atoms sit in **atomic orbitals**. When we overlap atomic orbitals to form bonds we make new orbitals, and we call these **molecular orbitals**. How this looks is illustrated below for a simple case.

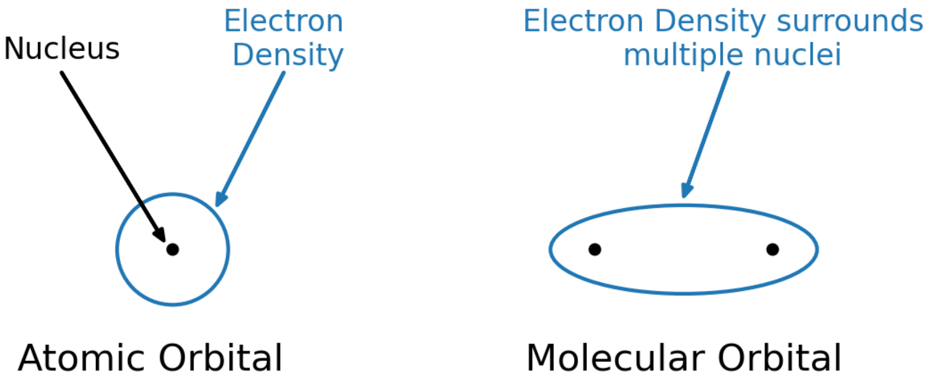

Figure 4.3: Atomic orbitals describe electron density around a single nucleus. Molecular orbitals describe electron density around multiple nuclei.

This kind of picture, where the positively charged nuclei form a framework that is held together by more delocalised electron density, is a good way to think about molecular structure.

4.2.1 Orbital Overlap?

In classic chemistry style, the picture is not quite as simple as the figure above implies. When we overlap atomic orbitals to make molecular orbitals, what we are really doing is *overlapping electron wavefunctions to form new electron wavefunctions*. Let' s not worry about what wavefunction means in deep detail for now, but accept the following:

- All matter has wave-like properties (this is the big thing Albert Einstein is famous for).
- Electrons are matter, and so have wave-like properties. The wavefunction of an electron encapsulates these wave-like properties.

We already said that *'wavefunction of an electron in an atom'* is just another term for *atomic orbital*. So when we overlap atomic orbitals, we're really just overlapping waves that describe the electrons. We'll talk a lot more about waves later in this course, but you might know that waves can **interfere** with each other and can do this **constructively** or **destructively**.

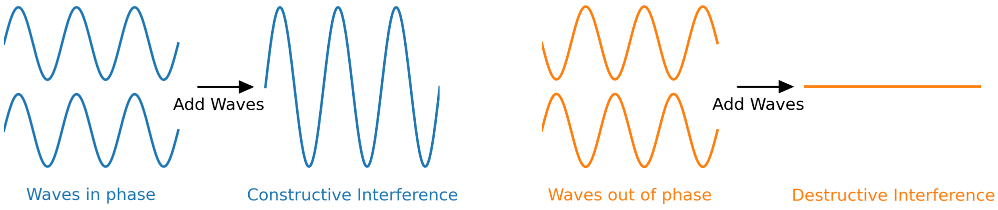

Figure 4.4: Interference of two waves can be constructive (left), or destructive (right).

This exact same principle applies to orbital overlap, and means that atomic orbitals can either overlap constructively or destructively, generally forming a **bonding** or an **anti-bonding** molecular orbital in each case. An example with the overlap of two s-orbitals to form bonding and anti-bonding molecular orbitals is shown below.

We call the molecular orbital you get from overlapping two s-orbitals a σ (sigma) orbital for reasons of symmetry. s- and p-orbitals can also overlap in a variety of ways shown below. Keep these ideas in mind when you come to talk about the structures of bigger molecules with Sandeep later.

4.2.2 Molecular Orbital Diagrams

Not content with just sketching our molecular orbitals, we can also think about the energy they'll have. This is critical for understanding their chemistry and spectroscopy. A nice way to do this is to draw something called a **molecular orbital diagram** or **MO diagram**[1].

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[1] Pedantic people get all stressed about this and insist it's a *'molecular orbital energy level diagram'*, not just a *'molecular orbital diagram'*. These people need to get a grip.

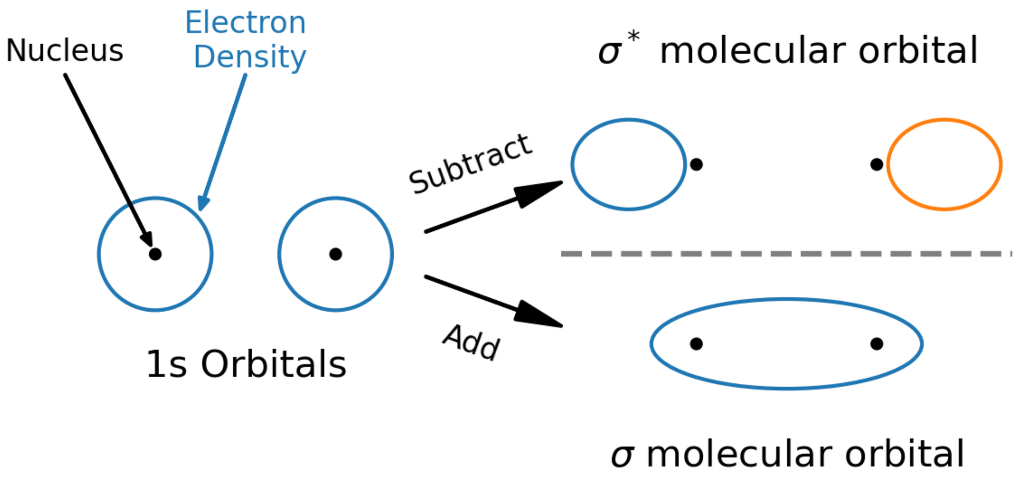


Figure 4.5: Two 1s orbitals combining to produce σ and σ^* molecular orbitals.

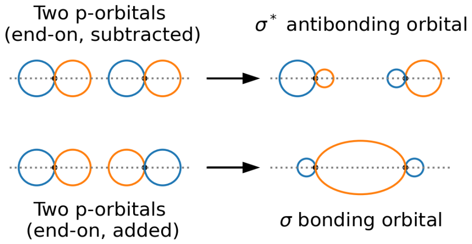


Figure 4.6: End-on overlap of p-orbitals leads to σ and σ^* bonds.

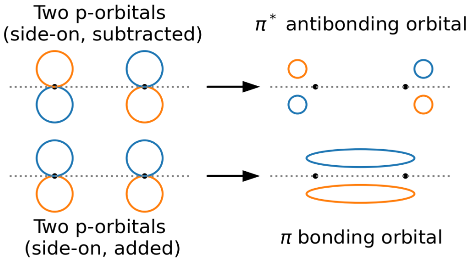


Figure 4.7: Side-on overlap of p-orbitals leads to π and π^* bonds.

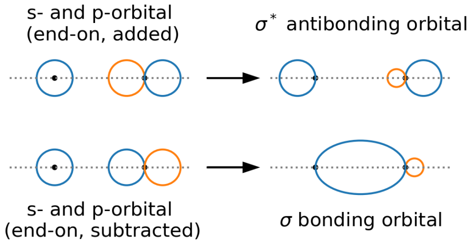


Figure 4.8: End-on overlap of an s-orbital and a p-orbital leads to σ and σ^* bonds.

Drawing MO diagrams for complex molecules requires lots of symmetry and group theoretical arguments (or just the ability to access a computer) –so we’ ll do that later. We’ ll look at a couple of simple MO diagrams to finish today and then some more complex ones together in the problems.

Basically an MO diagram shows the **energies of the atomic and molecular orbitals in the molecule:**

- The molecular orbitals are in the middle of the diagram, and the two constituent sets of atomic orbitals are either side.
- Energy increases from bottom to top –so higher up in the diagram is higher energy.
- Each orbital is shown as a horizontal line, and can hold two electrons.
- Dashed lines sometimes connect the molecular orbitals to the atomic orbitals that made them, but this isn’ t always shown (can get quite cluttered in complex systems).
- The orbitals are labelled by their symmetry (here just s, p, σ, π).

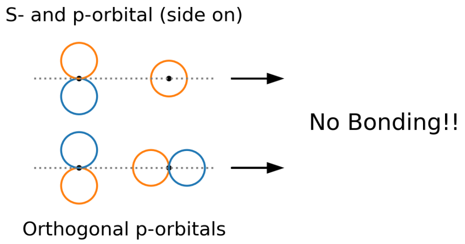


Figure 4.9: Some kinds of overlap cannot lead to bonding!

- When you fill in the electrons, remember:
  - Each orbital holds two electrons.
  - You fill from the lowest energy to the highest energy.
  - When you have more than one orbital of the same energy, you fill the orbitals with single electrons before you pair any electrons up.

We'll construct the MO diagram for H2 together in the lecture –it looks like the below.

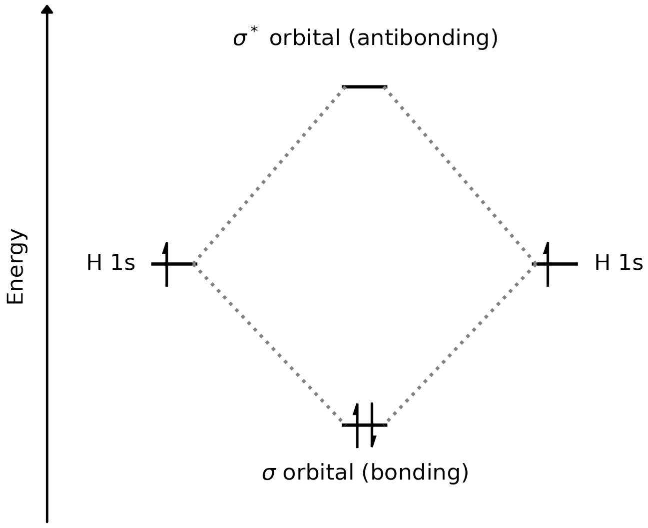


Figure 4.10: Molecular orbital diagram showing formation of H_2 from two hydrogen atoms.

We can use this diagram to rationalise some basic chemistry about things like H2, He, and other massively exciting molecules containing H, He, and with four or less electrons. We'll look at some more exciting things in the problem sheets. Next time, we're going to look at some bigger molecules and see a method you might already know from A level called VSEPR (I don't think they call it that in the A level, for some reason, but the method is in there).

Lecture 4 Take Home Messages

- The ultimate driving force for chemical bonding is **energy**. Atoms bond with other atoms because it is a way to lower their energy and become more stable.
- Chemical bonding can be split into three ‘types’, and molecules lie on a spectrum between these types. This spectrum is called **the bonding triangle**.
- Covalent bonds form by overlap of atomic orbitals to form molecular orbitals.

Lecture 5

Chemical Bonding II

Lecture 5 Aims

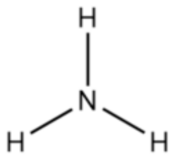
- To understand basic Lewis structures and the octet rule.
- To recap different 3D geometries of molecules.
- To understand how VSEPR theory lets us predict shapes of molecules

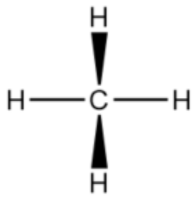
Last time we looked at the fundamentals of chemical bonding –and especially talked about covalent bonding and orbital overlap. You probably also know how to draw simple **Lewis structures** of molecules from your A level, where you overlap valence electrons to give each atom eight electrons.

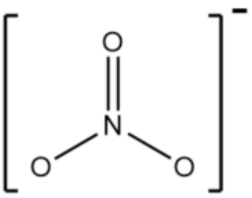
Today we’re going to recap this and go a little further on, and learn a simple way to predict the structure of simple molecules. We are going to talk ,mostly about molecules made of p-block elements, as these are the ones that build up the majority of molecules that make our world! Remember that they’re called p-block elements because their outer electrons lie in p-orbitals.

5.1 Lewis Structures and The Octet Rule

A **Lewis Structure** is a structure like the one below where you draw bonds as straight lines connecting atoms. Each line represents a bonding pair of electrons – two electrons shared between the two atoms.







These sort of Lewis structures are how we draw molecules in proper chemistry. **We don’ t draw things like the diagram of Fluorine below anymore**, as it gets too cluttered.

So we need to know how to draw Lewis structures, like the ones from the earlier figure. The first thing to know is called the **octet rule**, which says that atoms like to have eight electrons in their outer (valence) shell. This is true for atoms in the p-block, because in a p-block atom our outer shell contains an s-orbital and three p-orbitals: a total of four orbitals. Each orbital can

Figure 5.1: A diagram of F2 showing all valence electrons. **We don't draw things like this in proper chemistry!**

hold two electrons = **eight electrons in total**. Of course, the *octet rule* is only really true for the p-block, but p-block elements (like carbon, oxygen, and nitrogen) make up the vast majority of molecules that we encounter in chemistry. The basic rule is that:

> **Atoms like to have a filled outer shell of electrons.**

The reason is energy (again). Think about an atom with a filled outer shell:

- Adding another electron would mean the electron has to go into a new, higher energy orbital – **which is a bad thing energetically.**
- Losing an electron would reduce the attraction between the electrons and nuclei – also a bad thing energetically.

Generally atoms want to react and form molecules so they have no gaps in their outer shells. We call an atom that has a filled outer shell a **closed shell** atom. An atom that doesn't have a filled outer shell is called **open shell**.

- Closed shell atoms have no gaps in their outer shells. They have the same electron configuration as a Noble gas and are unreactive (stable).
- Open shell atoms have gaps in their outer shells. They have space to gain electrons, or extra electrons to lose, and so are more reactive in general (unstable).

I think we can all count to eight, but we'll do some examples of this electron-counting in the problems. Let's accept that we can probably draw a Lewis structure.

The next question is:

> *How do those bonds arrange themselves in 3D space, to produce the actual 3D molecular structure?*

5.2 VSEPR Theory

The question above is one of those chemistry questions where a properly accurate answer is very complex and involves lots of electronic structure calculations, but where there are also useful rules of thumb that make it easy. Remember that the beauty of chemistry is that we sit in this middle ground between 'rigorous detail' and 'useful simple models'. We can and will understand the fundamental reasons why molecules are shaped the way they are. But in the meantime, we will learn some useful rules of thumb that make predicting molecular geometries quick, easy, and pretty accurate (at least for simple molecules)[1].

The simple model for predicting shapes of molecules we are going to learn about is called **Valence Shell Electron Pair Repulsion Theory** or **VSEPR Theory** for short. The fundamental idea of it is quite simple:

VSEPR Theory

Electron pairs (bonding pairs or lone pairs) will arrange themselves in a molecule so that they are as far apart as possible - minimising electron-electron repulsions.

This should make sense – electrons repel each other, so to reduce the energy of the molecule those electrons are going to want to be as far as apart as possible. This model works well for small covalent molecules.

5.2.1 Doing VSEPR Theory

It's easiest to just see some examples of VSEPR to learn how to do it, so that's the plan for the rest of today. I think it's pretty easy (and I'm not even someone who can draw things neatly, so if I can do it you have no excuse) except for a couple of subtleties. The fundamental process is as follows:

1. Decide on the 'central atom' – the one that the electron pairs are arranged around.
2. Count the number of bonds to the central atom as one electron pair each, and the number of lone pairs on the central atom. Treat double and triple bonds as just one electron pair. Add these numbers together to get the total number of electron pairs.
3. From the number of electron pairs, figure out the preferred arrangement to minimise repulsion, and therefore the shape of the molecule.

The only tricky thing here is to know what the preferred arrangements of electron pairs are. We just have to remember these (but it is logical).

5.2.2 Ideal VSEPR Geometries

When we work out a structure using VSEPR, the first thing we do is work out the 'base' structure that the electron pairs will take. Then, we look at if there are any lone pairs, and decide what the 'actual' structure the molecule will have is. Let's look at the possible geometries now.

1 Electron Pair

If there's only one bond then the molecule can only be linear, as there are only two atoms! Like in Cl_2 or H_2 or O_2 (remember in O_2 that we say the double bond is just a single bond for the purposes of VSEPR).

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[1] This is why chemistry is great. If we left it to the physicists they' d still be arguing about the shape of the H_3^+ ion. Instead, we take the simple model and go and synthesise antibiotics and discover how to make solar cells.

Figure 5.2: Linear molecules: chlorine, oxygen, and nitrogen.

Figure 5.3: Linear molecules: beryllium difluoride and carbon dioxide.

Figure 5.4: Trigonal planar molecules: formaldehyde and the nitrate ion.

2 Electron Pairs

If there are two electron pairs, and both are bonding pairs, then the preferred geometry is **linear**, like in BeF_2, or CO_2 (remember again that a double bond counts as a single pair!).

This geometry makes sense - as the bonds are 180° apart around the central atom - as far away as they can be.

If there are two electron pairs, and one is a lone pair (so there is one bond), then the preferred geometry is also linear, just as in the example for one electron pair.

3 Electron Pairs

If there are three electron pairs, and all are bonding pairs, then preferred geometry is **trigonal planar**, like in formaldehyde (H_2CO), or the nitrate ion ($NO_3{}^-$).

If there are three electron pairs and one lone pair (so two bonding pairs), then the preferred geometry is **bent**, like in methylene(CH_2).

4 Electron Pairs

If there are four electron pairs, and all are bonding pairs, then the geometry is **tetrahedral**, like in methane (CH_4), or chloroform ($CHCl_3$).

If there are four electron pairs and one is a lone pair, then the geometry is **trigonal pyramidal**. A classic example of this is ammonia (NH_3).

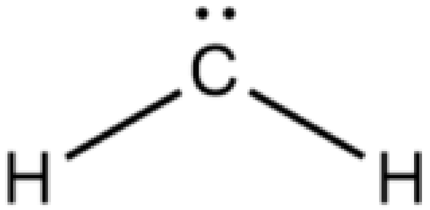

Figure 5.5: Methylene has a bent molecular geometry.

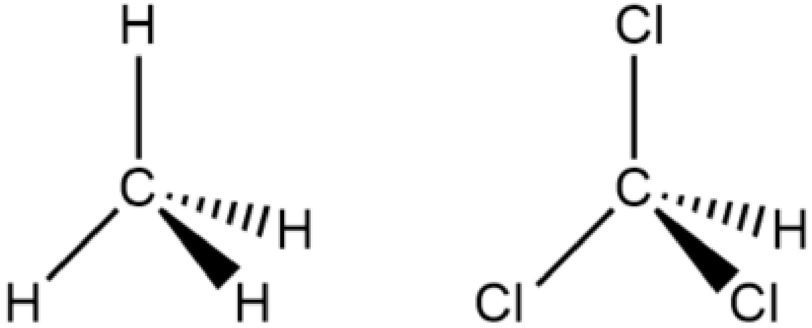

Figure 5.6: Tetrahedral structure: methane and chloroform.

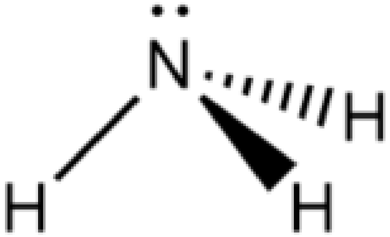

Figure 5.7: Trigonal pyramidal structure: ammonia.

Figure 5.8: Bent structures: water, and sulphur dichloride.

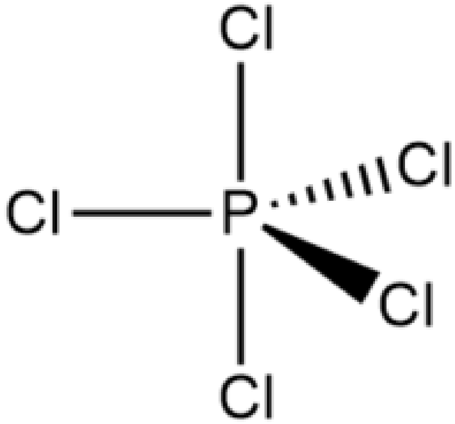

Figure 5.9: Trigonal bipyramidal: phosphorus pentachloride.

If there are four electron pairs and two lone pairs, then the geometry is also called **bent**. An example of this is sulphur dichloride (SCl_2), or water (H_2O).

5 Electron Pairs

By now you probably see the pattern! If we have five electron pairs, and all are bonding, then we call the geometry **trigonal bipyramidal**, as it's like a double-sided triangle based pyramid. An example of a molecule with this structure is PCl_5 - phosphorous pentachloride.

If we have one lone pair, then the geometry is called a **see-saw** geometry. Sulphur tetrafluoride (SF_4) is the classic example:

IF we have two lone pairs, the geometry is called **T-shaped** - the classic example being ClF_3, chlorine trifluoride. It is T-shaped rather than trigonal planar because the lone pairs prefer to be in the equatorial position around the chlorine.

And if we have three lone pairs, the geometry is **linear** again, but with three equatorial lone pairs. An example of a molecule with this geometry is xenon difluoride - XeF_2.

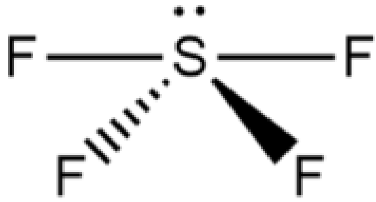

Figure 5.10: See-saw: sulphur tetrafluoride.

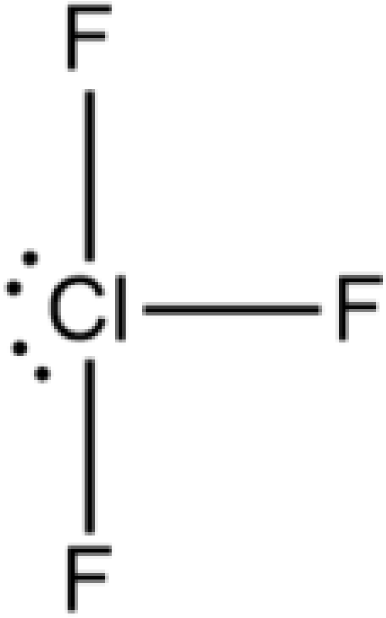

Figure 5.11: T-shaped: chlorine trifluoride

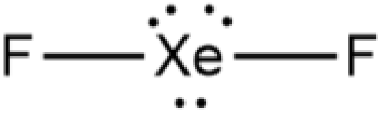

Figure 5.12: Linear: xenon difluoride.

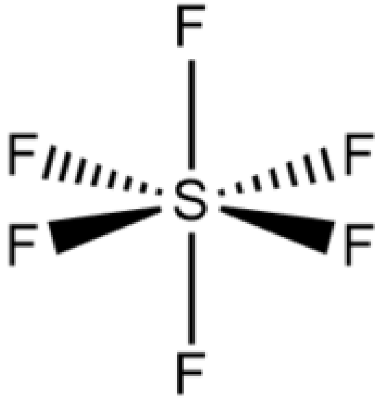

Figure 5.13: Octahedral: sulphur hexafluoride.

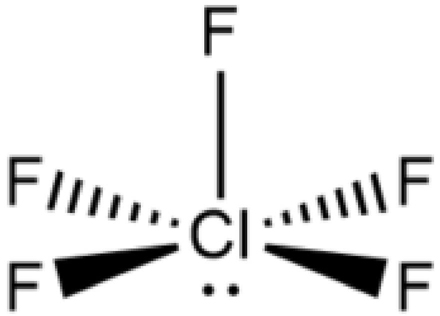

Figure 5.14: Square pyramidal: chlorine pentafluoride.

6 Electron Pairs

Finally, we can have six electron pairs. If they are all bonding pairs, then the geometry is **octahedral**, and this is a common geometry you will see often in inorganic chemistry. Sulphur hexafluoride (SF_6) is the classic example.

If we have one lone pair, then our geometry becomes **square pyramidal**. Chlorine pentafluoride is an example of this (ClF_5).

Finally, if we have two lone pairs, then the geometry is **square planar**. Xenon tetrafluoride is the classic example of this (XeF_4).

That's a lot of geometries covered, and you'll need to know them. Luckily, I think it follows quite a logical order (do you agree?). We're going to spend the rest of the lecture just doing examples of VSEPR theory, but before we do this there is one important thing to note.

Figure 5.15: Square planar: xenon tetrafluoride.

5.2.3 Deviations from VSEPR Geometry

Most of the time, VSEPR theory gives us a good idea of the geometry, and we can work out the bond angles based on the geometry (for example, the bond angle in a tetrahedral molecule is 109.5° - which you can work out mathematically if you like!), because the bonding pairs repel each other equally.

However, lone pairs and bonding pairs do **not** repel equally - a lone pair actually repels a bonding pair more than another bonding pair does. So if we have a molecule like ammonia (base geometry is tetrahedral, but the lone pair means the true geometry is trigonal pyramidal), then the bond angles are actually a bit less than 109.5° - in ammonia they are more like 106.5°. This is because the lone pair 'pushes' the bonding pairs closer together due to its greater repulsion. Water (H_2O) is another example of this - the bond angle is about 104° - much less than VSEPR would predict for the tetrahedral base geometry. Generally speaking, lone pair - lone pair repulsions are greater than lone pair - bonding pair, which are greater than bonding pair - bonding pair.

Here we can also explain why we can regard double and triple bonds as like single bonds in VSEPR. The reason is that the electrons in a π-bond (which is what double and triple bonds are) don't take up much more space than the electrons in a σ-bond alone, so as far as VSEPR is concerned, they repel other things to the same extent.

Deviations from VSEPR

Deviations from VSEPR geometries occur because lone pairs repel more strongly than bonding pairs. In order of decreasing repulsions:

- Lone pair - lone pair (most repulsion)
- Lone pair - bonding pair
- Bonding pair - bonding pair (least repulsion)

Let's do some more examples now (only those present in the lecture will get my glorious drawn answers).

VSEPR Practice

Draw VSEPR structures for the following molecules:

- $POCl_3$
- SO_{42}^-
- IF_4^+
- PF_6^-

That's it for VSEPR, but we have to think now: *what about molecules that aren't small and symmetrical?* We can't easily use VSEPR on a big molecule like the penicillin structure we saw in Lecture 1. In this case, we have other methods to help us understand the structure – and that's what you'll discuss with Sandeep next.

Lecture 5 Take Home Messages

- Atoms like to have a filled outer shell (closed shell). Open shell species tend to be more reactive and unstable.
- Determining molecular structures can be complex, but for simple molecules we can use VSEPR theory.
- The idea behind VSEPR is that the geometry is formed to minimise repulsions between electron pairs (getting electron pairs further apart in space).

Lecture 6

Basic Physics

We are now going to dig a bit deeper into the fundamentals of chemistry. The boundaries of scientific disciplines that you had at school - where chemistry is separate to physics which is separate to biology - are artificial. Science is a spectrum and 'pure chemistry' sits somewhere on that, but it's not a useful distinction. We can't understand chemistry without understanding some physics, in the same way that you can't understand biology without understanding some basic chemistry.

In this lecture, we're going to get everyone up to speed with the basic physics that we will need in the rest of the course. If you've already done A-level physics, this may all be familiar to you, but we will be approaching it in a way that is probably quite different to how you were taught in school. Notably, we're not going to be worried about learning specific equations - it's more important that you understand the concepts than that you remember an equation.

Lecture Aims

- To understand the basics of energy and work.
- To understand the concepts of force and momentum.
- To understand how to calculate velocity, momentum, and kinetic energy.

6.1 Energy

We've said that **energy** is probably the most fundamental of concepts in chemistry. It is the answer to all of the following questions (in one way or another):

1. Why do some molecules exist and some molecules not exist?
2. Why do some reactions 'go' and other reactions don't?
3. Why can I find out the structure of a molecule from an IR/NMR spectrum?

So it is important that we have an understanding of what energy is, and of different kinds of energy. The most useful definition of energy for us as chemists is:

> **Energy is the capacity of something to *do work*.**

Figure 6.1: In a burning candle, chemical energy stored in the wax molecules is converted into thermal energy (heat) and radiant energy (light).

Something with high energy has the capacity to do a lot of *work* - that 'work' could accomplish a lot of things:

- Making an object move around (increasing the objects **kinetic energy**).
- Driving an electrical circuit (pushing electrons around a circuit - **electrical energy**).
- ...And many others!

So we can see that really doing *work* is just transferring energy from one place to another, but we will talk more about this in a bit. This is an important fundamental point: we never *create* or *destroy* energy - we only *transfer* it from one place to another, or into one form from another. For example:

- Boiling a kettle: turning electrical energy into thermal energy.
- Charging a phone: turning electrical energy into chemical energy (stored in the chemicals that make up the battery).
- Burning a candle: turning chemical energy (in the wax molecules) into thermal energy and light (radiant energy).

To give a chemical example, a molecule with **high** energy might be able to undergo some kind of **chemical reaction** to make a new molecule - transferring that energy into chemical energy in the bonds of the new molecule.

The energy of any object (such as a molecule) can be separated into two parts - the **kinetic energy**, and the **potential energy**. The total energy of an object is always the sum of the kinetic and potential energies:

$$\text{Total Energy} = \text{Kinetic Energy} + \text{Potential Energy}$$

We already saw that **kinetic energy** was the energy associated with an object moving around [1]. Kinetic energy is energy that an object has by virtue of its **motion**. We will talk about **potential energy** later on, but can briefly say that it refers to the *potential* for an object to have kinetic energy - a ball balanced on a hill (so it could roll down and gain kinetic energy) is the classic example. Potential energy is the energy an object has by virtue of its **position**.

Energy

- Energy is the capacity of something to do *work*.
- Energy cannot be created or destroyed, just transferred from one place (or form) to another.
- The total energy of an object is the sum of all the **potential** and **kinetic** energy of the object.
- **Kinetic Energy** is the energy an object has due to its **motion**.
- **Potential Energy** is the energy an object has due to its **position**.

When we first defined energy, we said it was the capacity of something to do work. Let's explore what we really mean by **work** now.

6.1.1 Work

When we say **work** in science, we don't mean 'work' in the sense of doing a job[2]. When we say something is *doing work* on an object we are saying that it is *transferring energy to that object via application of a* ***force***[3]. Here are some examples that may illustrate it further:

- **Lifting a heavy weight**: transferring **kinetic energy** to the weight and raising the weights **gravitational potential energy**. The force we apply comes from our muscles, and opposes the gravity that tries to keep the weight on the ground. This kind of work is called **mechanical work**.
- **Turning on a light**: transferring **electrical energy** to **radiant energy**. The force we apply is an **electromotive force**, that pushes the electrons through the electrical circuit and opposes electrostatic forces that keep the electrons still. This kind of work is called **electrical work**.
- **Ionising an atom**: transferring **kinetic energy** to an electron in the atom so it can overcome the **potential energy** holding it near the nucleus and fly off. The force we apply could be an electrostatic force that opposes the other electrostatic force that binds the electron to the nucleus.

In all cases, we **apply a force to something** and end up **transferring energy to it**. That's all there is to it! You can think of a lot of complicated examples but they all just boil down to this in the end. You will learn a lot more about work in thermodynamics next semester.

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[1] And actually, thermal energy and electrical energy are really just other forms of kinetic energy: the random motion of particles (thermal) and the motion of electrons in a circuit (electrical).

[2] There are a lot of words like this with a different meaning in science: potential, work, matter, medium...

[3] There are other ways of transferring energy to an object, such as via *heat*.

Figure 6.2: Here Robert Oberst is doing a lot of work on the atlas stone, lifting it to a higher position (giving it **gravitational potential energy**)

.

Work

- *Doing work* on an object means we are **transferring energy** to that object, via application of some **force**.
- If we do more work, we transfer more energy, and vice versa.
- We could also do **negative work**, where the object gains energy from something else.

We've just defined work in terms of **force** - but what is **force**? Let's look at this next.

6.1.2 Force and Momentum

We said that when we do work on something to raise its energy, we do that by applying a **force**. More specifically, a force is something which is used to **change the motion** of an object - or, using more technical language, to **change the momentum** of an object.

An example of a force would be me throwing a ball. I apply a force to the ball and it starts to move (its **momentum** increases). If I throw the ball harder, I apply more force, and it moves

Figure 6.3: Me and my cousin applying pedalling force to overcome the wind and road friction, so that we moved at a constant speed.

faster (its momentum increases more). If the forces applied to an object are balanced, then the object is stationary or moving at a constant speed. If the forces are unbalanced, then its momentum changes[4]. Some examples of this that might help to illustrate it are:

- **A cyclist going down a hill**: the force from gravity pushing them down the hill is bigger than the force from friction keeping them still. The forces are **unbalanced**, and they accelerate down the hill, increasing momentum.
- **A cyclist coasting along the flat**: the force the pedalling pushing them forward is equal to the friction and drag keeping them still. The forces are **balanced**, and they move at a constant speed (not accelerating or decelerating - constant momentum).

So we can see that applying forces to things makes them move and changes their momentum. So what's momentum? Momentum is just a quantity which tells us about the motion of an object - it's defined as the product of the objects **mass** and **velocity**:

$$\text{Momentum} = \text{Mass} \times \text{Velocity} \tag{6.1}$$

Velocity tells us how fast something is moving, and *mass* tells us how heavy something is. So if a very heavy object is moving very fast, it has a very high momentum. Conversely, if a very heavy object is moving slowly, it might still have more momentum than a very light object moving faster. You can sort of think about momentum as a measure of how hard it would be to stop an object if it was going to hit you:

- **A tennis ball moving slowly**: very easy to stop - **low momentum**.
- **A bullet moving very fast**: very hard to stop - **high momentum**.
- **A car moving very slowly**[5]: pretty easy to stop - **low momentum**
- **A car going at 70mph on a motorway**: very hard to stop - **high momentum**.

---

[4] This is Newton's First Law.

[5] Like you've forgotten to put the handbrake on

So you can see that both the speed (velocity) of the thing moving, as well as how heavy it is, affects the momentum. Momentum rolls both of these factors into one concept, which is part of why it is so useful. You'll hear a lot more about momentum later in the course - especially in quantum mechanics when we start thinking about the motion of atoms and molecules.

We can relate momentum to force quite intuitively. Remember that we said applying a force to something will change its momentum - well, we can actually *define* force like this. We can say that:

$$\text{Force} = \text{Rate of change of Momentum} = \frac{\text{Change in Momentum}}{\text{Change in Time}} \tag{6.2}$$

So if our applied force makes something change its momentum really quickly, then it must have been a pretty big force! Conversely, if the momentum change is very small, or happens very slowly, then the force applied must have been quite small. Think about kicking a football really hard (big force), compared to dribbling the ball with a small kick (small force) - how does the momentum of the football change in each case?

6.2 Calculating Things

By now, we have a pretty decent understanding of energy, work, force, and momentum. The most important thing is to understand these concepts qualitatively - but it will also be useful to be able to calculate them too. It'll be really useful in your degree (and future scientific careers) to be comfortable with all these concepts, so there is also an extra short problem sheet with more examples you can do to practice.

Let's start with calculating momentum. We saw that:

$$\text{Momentum} = \text{Mass} \times \text{Velocity} \tag{6.3}$$

We can now give these things their usual symbols:

$$\text{Momentum} = p = \text{Mass} \times \text{Velocity} = mv \tag{6.4}$$

Or simply:

$$p = mv \tag{6.5}$$

Where p is momentum, m is mass, and v is velocity. We can get the mass just by weighing something, and we know that velocity is given by:

$$\text{Velocity} = v = \frac{\text{Change in Position}}{\text{Change in Time}} = \frac{\Delta x}{\Delta t}$$

Let's take an example:

Example: Calculating Velocity

Q: Usain Bolt runs the 100 m sprint in 9.58 s. What is his velocity?

A: Velocity $= \frac{\text{Change in Position}}{\text{Change in Time}} = \frac{100-0}{9.58-0} = 10.44\,\text{m}\,\text{s}^{-1}$.

And let's go a bit further and calculate his momentum:

Example: Calculating Momentum

Q: Usain Bolt weighs 94 kg. Using the velocity from above, what is his momentum?

A: Momentum $= \text{mass} \times \text{velocity} = 94 \times 10.44 = 981.4\,\text{kg}\,\text{m}\,\text{s}^{-1}$

Note the units - can you see how we worked them out?

Exercise: Usain Bolt Vs Bullet

A typical bullet moves at about $500\,\mathrm{m\,s^{-1}}$. How heavy would the bullet have to be to have the same momentum as Usain Bolt winning the 100m sprint?

Now let's look at force, and keep using Usain Bolt as our test subject:

Example: Calculating Force

Q: Imagine that when Usain Bolt pushes off the starting block, that his momentum increases from zero to the value calculated above in 0.5 s. How much force does he apply to the starting block?

A: Force $= \frac{\text{Change in Momentum}}{\text{Change in Time}} = \frac{981.4-0}{0.5-0} = 1962.8\,\mathrm{kg\,m\,s^{-2}}$

The complicated units for force we've just shown have another name - the **Newton**, or N. So the force Usain Bolt applies is about 2000 N. This is a lot!

Continuing on, we can also calculate work. The *work done* by application of a force is defined as the size of the force multiplied by the distance over which it is applied. If we apply a force over a large distance, we do more work, and vice versa. Imaging pushing a heavy trolley around Aldi - if you push it up and down every aisle, then you will use more energy than you would if you just pushed it straight to the bakery aisle. Equally, if you push the trolley really hard so it moves very fast (applying a lot of force), that takes more energy than pushing it gently (applying a small force).

$$\text{Work Done} = \text{Force} \times \text{Distance} \tag{6.6}$$

Or to give the usual symbols:

$$W = Fd \tag{6.7}$$

Let's do an example:

Example: Calculating Work

Q: You apply a force of 200N to a trolley and move it over a distance of 5 m. How much work did you do on the trolley?

A: Work = Force × Distance $= 200 \times 5 = 1000\,\mathrm{kgm^2/s^2}$

Ok, the units of this look horrible. What on earth is a kilogram metre squared per second squared? Helpfully, previous people in history also thought that this was a stupid unit and so gave it another name: **the Joule**, or J. The Joule is a unit of energy and $1\,\mathrm{J} = 1\,\mathrm{kgm^2/s^2}$. We can see from the equation that if we pushed the trolley for 10 metres, we would do twice as much work - twice the distance, twice the work.

This tells us how to calculate the energy transferred to an object by application of a force (the *work done* on the object). It would also be useful to be able to calculate the energy of something from its momentum (you might have to trust me that this will be useful!). Remember that the energy associated with an objects motion is called its **kinetic energy**. We can calculate **kinetic**

energy as follows (kinetic energy normally gets the symbol T, for some reason):

$$\text{Kinetic Energy} = T = \frac{p^2}{2m} \tag{6.8}$$

So, the kinetic energy of an object with mass m and momentum p, is given by the squared momentum divided by twice the mass. This might seem a bit odd[6], but if we work out the units then we can start to understand it:

$$\text{Kinetic Energy Units} = \frac{(kgms^{-1})^2}{kg} = kgm^2s^{-2} = \text{Joules!} \tag{6.9}$$

The units work out as Joules! How pleasant.

Before we do an example, we can actually write our kinetic energy equation in another form:

$$\text{Kinetic Energy} = T = \frac{p^2}{2m} = \frac{(mv)^2}{2m} = \frac{m^2v^2}{2m} = \frac{1}{2}mv^2 \tag{6.10}$$

This form might be more familiar to you if you did A level physics at school. It's the same equation though - the first equation is more useful if we know the objects momentum, and the second is more useful if we know the velocity. Let's do some examples using Usain Bolt again:

Example: Calculating Kinetic Energy

Q: Usain Bolt weighs 94kg and we calculated his top speed as $10.44\,\mathrm{m\,s^{-1}}$. What is his kinetic energy at this speed?

A: Use the equation in terms of velocity, because we are given that. $T = 0.5 \times 94 \times (10.44)^2 = 5122\,\mathrm{J}$. We could also calculate his momentum from the given data and then work out the energy - try it and confirm you get the same result!

Alright. We are almost done. We have one thing left though, and that's to talk about **potential energy**.

6.3 Potential Energy

We sort of glossed over potential energy before, and just said that its the energy an object has due to its **position**. The example we gave was a ball balanced on top of a hill - that ball has the *potential* to roll down the hill and thus gain a lot of kinetic energy. The force that would cause it to roll down is gravity, so in that case we would say it has **gravitational potential energy**. Another example could be when we stretch an elastic band - as we stretch it, it gains the potential to snap back and gain a lot of kinetic energy. In this case, the elasticity of the band would make it snap back and gain energy, so we say it has **elastic potential energy**.

There are as many types of potential energy as there are forces, and there's no single nice equation for it, like we had for kinetic energy, really[7]. A really good system for understanding potential and kinetic energy is a pendulum - like you get in an old fashioned clock.

As the pendulum swings, the total energy stays constant, but it is constantly converted between kinetic and potential energy. At the edges of the pendulum motion, the pendulum stops moving (briefly!) and has maximum potential energy and zero kinetic energy. It then swings back (due to gravity), and gains kinetic energy. As it swings through the middle position it has maximum

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[6] But you can actually derive it from the work equation from earlier,

[7] Alright, thats not really true. But the equation involves some calculus so we will leave it for later.

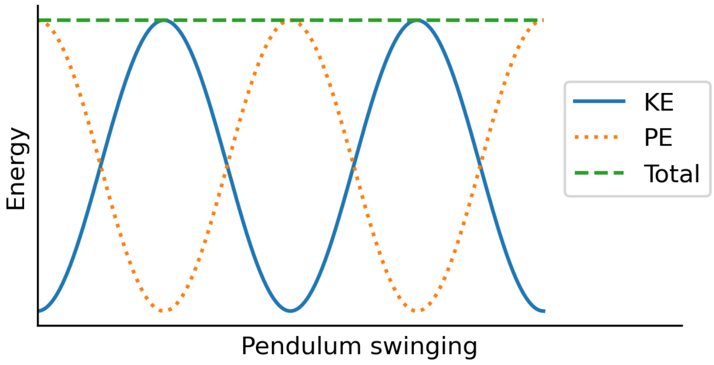

Figure 6.4: Kinetic (blue solid), potential (orange dashed), and total (green dashed) of a pendulum swinging. The pendulum starts stationary, with zero kinetic energy.

kinetic energy and zero potential energy. It then rises to the other side and loses kinetic energy until it stops, and again has maximum potential energy. The total energy is always the same at all points - it just interconverts between kinetic and potential energy. This idea is shown graphically in Figure 6.4, and we will do some more drawings of it in the lecture.

6.3.1 Electrostatic Potential Energy

Ok, we are almost done. There is one kind of potential energy that is really important in chemistry - this is the **potential energy between two charged objects**, or the **electrostatic potential energy**. We know that opposite charges attract and like charges repel - this is because of the electrostatic potential energy. This is relevant in all kinds of chemical situations:

- Understanding the forces between electrons and protons in atoms.
- Understanding the bonding in ionic crystals - like salt.
- Understanding how light interacts with electrons in spectroscopy.

If I had more lectures, we could do all of this justice and I could show you all the breathtaking beauty of it all. But apparently you also have to learn things that aren't physical chemistry[8], and so we don't have that much time. Let's end by seeing the formula for electrostatic potential energy.

If we have two charged particles, we might imagine that the energy of attraction/repulsion between them depends on two things:

- The size of the charges (more charge = more energy).
- The distance between them (further apart = less energy).

Makes intuitive sense, right? Right. And the equation for the electrostatic potential energy (normal symbol, U) is:

$$\text{Electrostatic Potential Energy} = U = k\frac{q_1 q_2}{r} \tag{6.11}$$

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[8] I feel your pain.

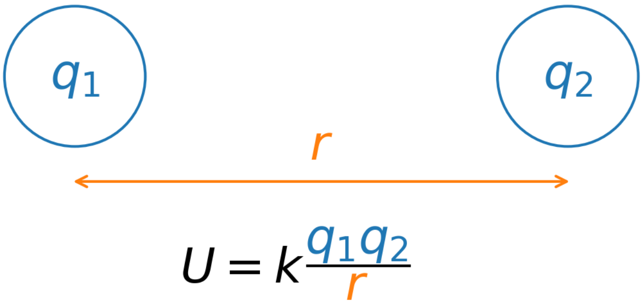

Figure 6.5: Electrostatic force between two charged particles (such as ions) depends on the size of the charges (q_1, q_2) and the distance between them (r).

Where q_1 and q_2 are the **signed** sizes of the charges on each particle (in Coulombs), and r is the distance between them (in metres). The constant k is called *Coulomb's Constant* and has a value of $8.987 \times 10^9\,\mathrm{Nm^2/C^2}$.

Let's end on an example:

Example: Calculating Electrostatic Potential Energy

Q: An electron and a proton are separated by 1 Ångstrom (1×10^{-10} m). What is the electrostatic potential energy of the system?

A: The charge of an electron is -1.6×10^{-19} C, and of a proton is 1.6×10^{-19} C. Plugging values into the formula above, we find that the energy is -2.3×10^{-18} J. Note the negative sign - this is because the force between an electron and proton is attractive, and so when they are close together the energy of the system is lower than it would be if they were far apart.

We have covered an awful lot today! Do not worry if you didn't get it all at once, we will see these concepts over and over again so you'll get used to them over time. Next time we are going to talk a bit more about molecules and quantum mechanics, building on some of the things you have seen in earlier lectures.

Take Home Messages

- Energy is the capacity of something to do work.
- Work is the transfer of energy to or from an object via the application of a force.
- We can calculate things like energy, work, momentum, and force using some relatively simple formulae.

Lecture 7

Waves and Light

Today we will continue talking about some physics - sorry! It's some physics that is very important in chemistry, especially in spectroscopy, and we need to understand it a bit. As ever, let's not worry too much about understanding all the mathematics - I want you to have intuitive pictures in your head of how this all works. This is much more valuable than any equation!

We've talked a bit about waves here and there earlier - I have probably at some point mentioned how light can sometimes be a wave and sometimes be a particle. Last lecture, we talked mostly about mechanics of balls moving and things, you can think of this as the mechanics of **particles** - we talked about momentum and energy and things. Today we will talk about the 'mechanics' of waves.

Lecture Aims

- To understand basic physics of waves.
- To understand some properties of wave behaviour.
- To start to understand the EM spectrum.

7.1 Waves

Waves are everywhere:

- Waves in the sea make summer holidays enjoyable.
- Waves make your radio and WiFi work.
- Light can be thought of as a wave - which is everywhere!

Understanding waves as chemists is really important because of the field of **spectroscopy**. As we will see, **spectroscopy** is just studying the interaction of light waves and matter (molecules, or atoms, or whatever). It all ultimately boils down to a wave causing a molecule to gain energy - so to understand spectroscopy, we have to understand both waves and molecules! Today we will do the first one.

Figure 7.1 shows a drawing of a typical wave. The thing that makes it a 'wave' is that repetitive oscillation - you can see it goes up and down over and over again. We call each of these oscillations a **cycle**. This wave could be a water wave, or it could be a light wave[1]. The first

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[1] The same principles apply to both, which is why waves are awesome!

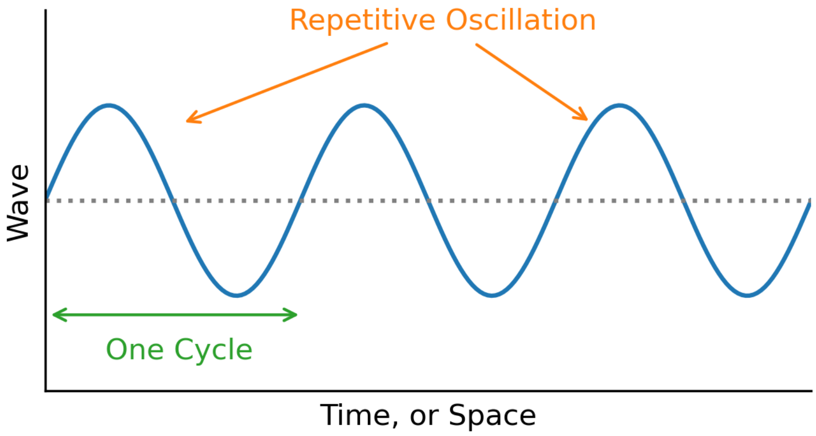

Figure 7.1: A simple wave. Waves can travel in both time and space, and the key hallmark is this repetitive oscillation.

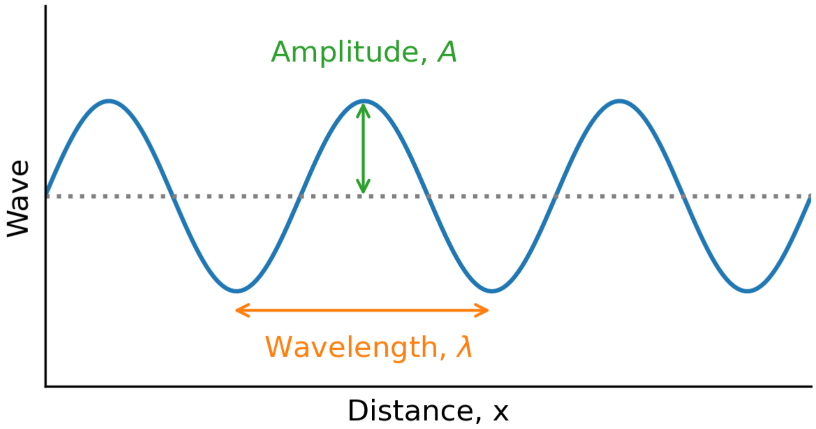

Figure 7.2: A wave travelling in space, along x. The wavelength is the distance travelled in one cycle, and has the symbol λ.

thing we have to get clear in our minds is that the wave is **travelling** - it's moving in **both** time and in space. For a water wave at the beach, you can see that they travel towards the shore (moving in space), but if you picked a certain point on the sea to look, you would see the wave moving as time passes.

How we describe the wave depends on whether we talk about the wave travelling in time or in space, but you'll see that basically it makes no difference and we can relate the two descriptions, so we can just pick whichever is most convenient! Let's look at a wave travelling through space, along the x-axis:

There's a couple of intuitive ways that we can describe the wave that are annotated in Figure 7.2. The first is by a quantity called the **wavelength** - this is the distance the wave travels between two peaks, or two troughs, or just the distance between any two equivalent points on the wave: the distance travelled in **one cycle**. We can also talk about the **amplitude** of the wave - this is the height of a peak of the wave (or the depth of a trough). Another thing you will hear about in chemistry is something called the **wavenumber**. The **wavenumber** is defined as the number of cycles the wave will go through in one metre of travel - it's related to the wavelength as follows:

$$\text{Wavenumber} = \frac{1}{\text{Wavelength}} \tag{7.1}$$

If our wavelength is in metres, then we will calculate a wavenumber in **inverse metres**, m^{-1}. More commonly, we talk about the wavenumber in cm^{-1} - in fact this unit is often just called 'wavenumbers' in spectroscopy.

An obvious question is *'what is the point of introducing wavenumbers?'*. The answer is that a wavenumber is directly proportional to energy - a bigger wavenumber is a bigger energy. This makes talking about energies much easier, where we would like a bigger number to be a bigger energy! A bigger wavelength is actually a **smaller** energy - as we will see later. Let's now think about waves moving in **time**.

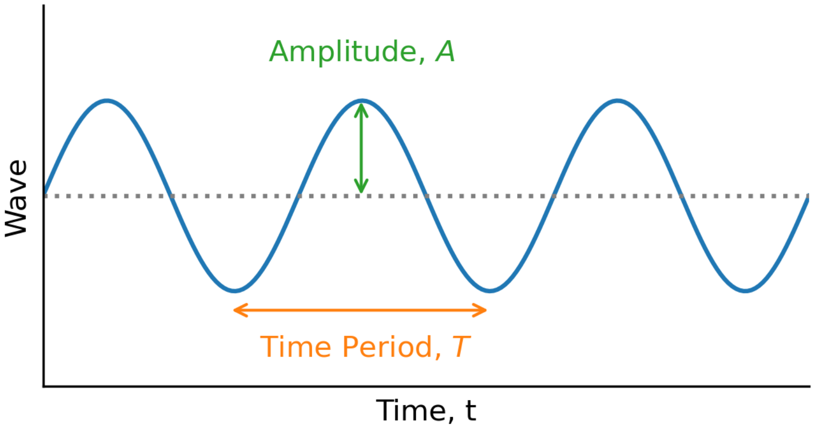

Figure 7.3: A wave travelling in time, along t. The wavelength is the distance travelled in one cycle, and has the symbol T.

We can define waves moving in time in a really similar way to what we did above for waves moving in space, shown in Figure 7.3. Clearly the amplitude has the same definition. We can also define something called the **time period** or **period** of the wave - this is the time between two peaks: the time taken for the wave to complete one cycle. Can you see that this is the same idea as the wavelength, but just defined in terms of time taken rather than distance travelled?

Just as we introduced the wavenumber as the number of cycles the wave will go through per metre of travel, we can introduce something called the **frequency** as the number of cycles the wave will go through in one second. Frequency is related to the time period as follows:

$$\text{Frequency} = \frac{1}{\text{Time Period}} \tag{7.2}$$

If our time period is in seconds, then we calculate the frequency in **inverse seconds**, which actually has it's own name: the **Hertz**. $1\,s^{-1} = 1\,Hz$. I'm not really sure why Hertz gets its own name and cool symbol and wavenumber doesn't, but there we are.

Can you see how in each description (time and space), we define these concepts that are analogous to each other? The table below summarises it:

We also talked about the **amplitude** of the wave, which is the same in both pictures. The final important wave concept is called the **phase** of a wave. The **phase** of a wave tells you which part of the wave cycle you are in. If two waves are **in phase**, that means that their cycles are

Concept	**Time Picture**	**Distance Picture**
One Cycle	Time Period	Wavelength
Cycles Per Unit	Frequency	Wavenumber

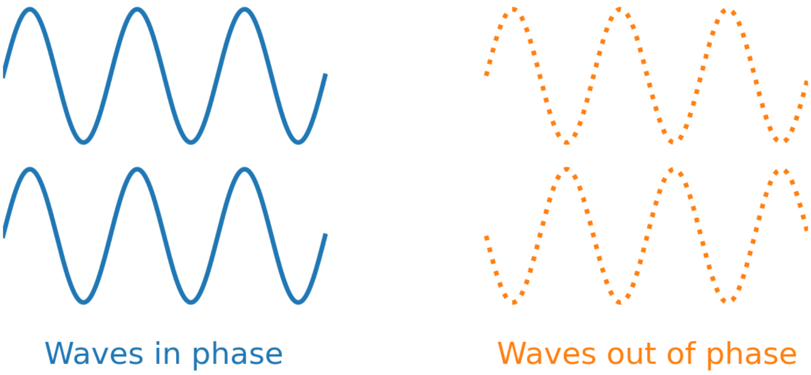

Figure 7.4: Two waves that are in phase (blue solid), and two waves that are out of phase (orange dashed).

aligned - one reaches a peak when the other reaches a peak, and vice versa. Conversely, if they are completely **out of phase**, then one reaches a peak when the other reaches a trough. The concept of phase is illustrated in Figure 7.4.

A good question now is: *'can these two pictures - time and distance - be linked?'*. The answer is **yes.** If we think about how far the wave travels in one cycle (the wavelength), and how long it takes to complete one cycle (the time period), we can work out the **speed** of the wave intuitively (remembering speed is distance divided by time):

$$\text{Wave Speed} = \frac{\text{Wavelength}}{\text{Time Period}} \tag{7.3}$$

Which is often written as:

$$\text{Wave Speed} = \text{Wavelength} \times \text{Frequency} \tag{7.4}$$

As we will see shortly, for a light wave, the wave speed is always[2] constant - this constant is called the **speed of light**, and has the value of $3 \times 10^8\,\mathrm{m\,s^{-1}}$. That's 300 million metres a second. If you ran this fast you could get from the Oadby student halls to George Porter Lecture Theatre A in 10 microseconds (0.01 milliseconds). Light waves are *quick*.

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[2] Alright, in vacuum, but basically in air too.

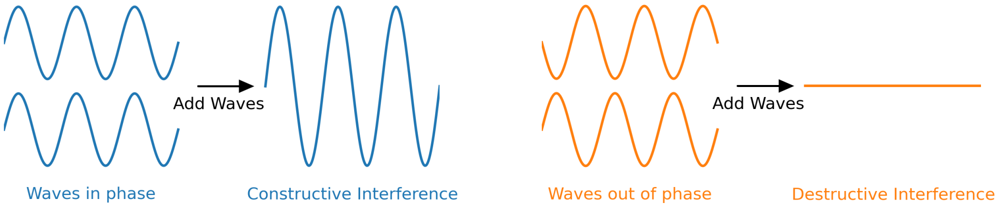

Figure 7.5: Interference of two waves can be constructive (left), or destructive (right).

Waves

- Waves can be equivalently described with both a **time** and **distance** picture.
- In the **time** picture, we talk about the **time period** and **frequency** of the wave. The **frequency** is the inverse of the **time period**.
- In the **distance** picture, we talk about the **wavelength** and **wavenumber** of the wave. The **wavenumber** is the inverse of the **wavelength**.
- The two pictures are related by the **wave speed** - this is a constant for light waves: the **speed of light**.

7.2 Wave Interference

Waves do a lot of cool things, like **diffraction**, **refraction**, **reflection**, and **absorption**, but we don't have time today to talk about all of them. We're going to talk about a concept called **interference**, which underpins all the other important wave behaviour. If you can understand and visualise interference, you're well on the way to becoming a certified wave mechanic™.

When two waves meet, they can **interfere**. This means that the amplitudes of the waves add together to make a new wave. What this new wave looks like depends on the relative **phases** of the two incoming waves - look at Figure 7.5.

You can think of interference as just adding the waves together - and as you can see, if the two waves are perfectly **in phase**, they interfere and create a new wave which has twice the amplitude of the original waves. We call this situation **constructive interference**. Conversely, if they are **out of phase**, the peaks of one wave cancel out the troughs of the other, and we get a wave with zero amplitude as a result. We call this situation **destructive interference**. Interference can happen with water waves which is easy to visualise - see Figure 7.6.

But as chemists, we are mostly going to be interested by light waves - or **electromagnetic waves**.

7.3 Electromagnetic Waves

We have said that we can think of light as a wave - but what kind of wave is it? Light is a form of an **electromagnetic wave**, or **EM wave**. You'll also hear it called **EM Radiation** - this doesn't mean radiation in the 'nuclear meltdown' sense, but means radiation in sense that EM waves radiate out from their sources (like light radiating from a light bulb, or heat radiating from a **radiator**).

It's called **electromagnetic** wave because it consists of both an electric bit (an electric field)

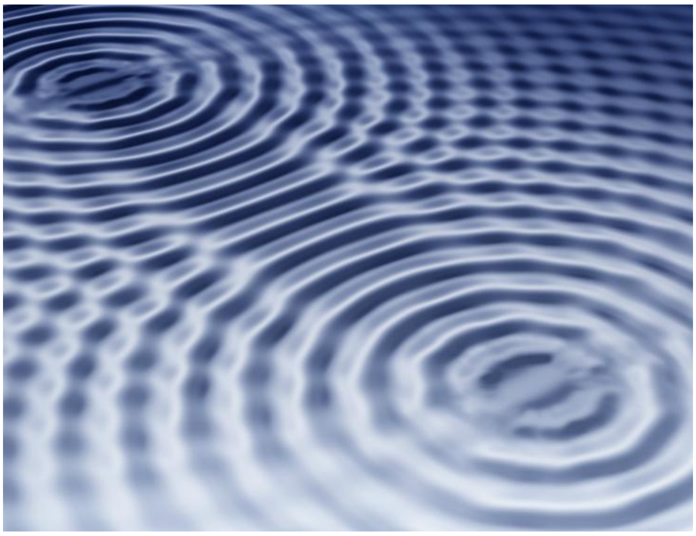

Figure 7.6: When two drops of water hit a surface, they radiate water waves which interfere in the region between the drops.

and a magnetic bit (a magnetic field). However, we don't need to worry about this - as chemists, the **electric** part of the EM wave is what we are going to care about, because this is the part that interacts with the **electrons** in molecules and makes spectroscopy happen. If you think of light as just an **electric field**, that will explain everything you need to understand in chemistry.

It's going to be useful for us to be able to take an EM wave and then work out it's frequency/wavelength/wavenumber/time period. Next time we will also see how we can calculate **photon energy** by reconciling the wave and particle descriptions of light (hype). Remember that for any EM wave travelling in air or a vacuum, the speed of the wave is always the speed of light, $3 \times 10^8\,\mathrm{m\,s^{-1}}$, which conventionally has the symbol c.

Wave Calculations

Calculate the following values:

1. The frequency of a wave with a wavelength of 800 nm.
2. The wavelength of a wave with a wavenumber of $3000\,\mathrm{cm^{-1}}$.
3. The wavelength of a wave with a frequency of 1500 THz.
4. The wavenumber of a wave with a time period of 20 fs.

We will go through the working out in the lecture, but you should find:

1. Frequency = 374.7 THz.
2. Wavelength = 3333.3 nm.
3. Wavelength = 199.9 nm.
4. Wavenumber = $1667.8\,\mathrm{cm^{-1}}$.

Note that I have given these values in their usual units. You could also give wavelength in metres, rather than nanometers (for example). Getting used to converting between these units is **essential**.

7.3.1 The EM Spectrum

We define any EM wave by putting it on a spectrum called the **Electromagnetic Spectrum** (EM spectrum). A spectrum (in science) is what you get if you order something by its energy - conventionally low energy on the left, and high energy on the right[3]. If we order EM waves by their energies, we get a spectrum like that shown in Figure 9.6.

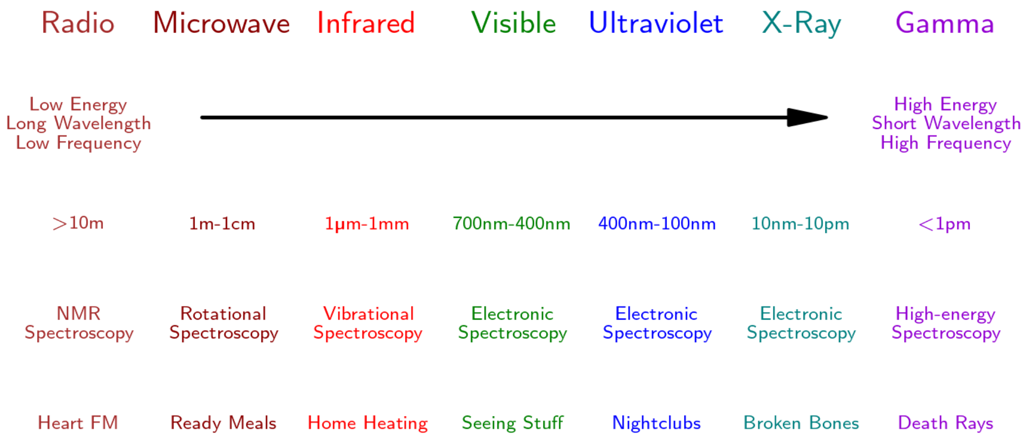

Figure 7.7: The EM spectrum. Wavelengths, chemistry uses, and other uses are shown below each type of wave.

Before we jump into the spectrum, note how all the various wave parameters we talked about before link into this. Low energy is on the left and high energy is on the right, and this means that:

- Low frequency is on the left, and high frequency is on the right.
- Long wavelength is on the left (big numbers), and short wavelength is on the right (small numbers).
- Low wavenumber is on the left, and high wavenumber is on the right.

It's worth going over this a few times to make sure you're happy with it - that short wavelength corresponds to high frequency and high energy (and vice versa).

Looking at the spectrum in Figure 9.6, a lot of things we have heard of but may not have thought of as EM waves are actually EM waves! Radio waves, for example, are a very low energy form of EM wave, and they get used in chemistry in NMR spectroscopy. Moving to higher energies, we have microwaves (familiar from your kitchens), and then infrared (IR) waves. IR waves are what make us feel warm in the sunshine, but aren't visible to our eyes. They're useful in chemistry when we want to do **vibrational spectroscopy**, and you will probably use an IR spectrometer in the teaching lab very soon. Keeping on moving, we then get to the nice and familiar realm of **visible light** - red is low energy and blue is high energy - and going even further we get into the **ultraviolet** (UV) light familiar to nightclub goers or sunbed users. UV and visible light are used in electronic spectroscopy. Further on from there we get into the realm of scary things like X-rays and gamma rays - X-rays are used a lot in chemistry, but gamma rays just blow up anything they touch so aren't as useful.

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[3] Although organic chemists always mess this up when they show NMR spectra.

Different bits of the spectrum correspond to different kinds of spectroscopy, and therefore to different kinds of molecular motion. Later in the degree you'll learn a lot more about some parts of the EM spectrum - but remember fundamentally they are all just EM waves, and all behave like all waves behave.

Next time, we are going to talk about how waves can also be thought of as particles, as we start introducing **quantum mechanics**. I am very excited.

Take Home Messages

- Waves can be described using the concepts of **wavelength**, **frequency**, **wavenumber**, and **time period**.
- When two waves meet, they **interfere** in a way that depends on their **amplitudes** and **relative phases**.
- EM waves are the most important kind for us, and the EM spectrum tells us a lot about the energies of different waves.

Lecture 8

Quantum Mechanics

All of chemistry is ultimately dictated by the **quantum mechanical** nature of matter. We will see that the idea of 'a chemical bond' doesn't really make sense unless we know a bit of quantum mechanics - and quantum mechanics is the basis of all of spectroscopy and a number of other analytical techniques. It's also the only way to understand chemical reactivity as it's most fundamental level.

We don't need to know much at this point though, we just need to know a couple of the key ideas. We will leave most of the mathematical detail for later on in the degree.

Lecture Aims

- To appreciate what quantum mechanics is.
- To begin to understand wave-particle duality and the internal structure of atoms and molecules.
- **To not be scared by the word 'quantum'.**

Before we start, it's useful to define what exactly we mean by **quantum**. The fundamental idea of quantum mechanics is that **energy is quantised** - **quantised** means that it is divisible into individual discrete parts, which are called **quanta**. A good analogy is to imagine a piano vs a violin. On a piano, we can only play specific notes defined by the keys - the notes we can play are quantised. On a violin, we can play any note we like just by moving our finger up and down the fingerboard - the notes are not quantised.

Quantum Mechanics

- The word 'quantised' means 'split up into discrete parts'.
- Energies of atoms and molecules are quantised - a molecule is only allowed to exist with certain well-defined energies.
- 'Quantum mechanics' is the study of this concept.
- Quantum mechanics fundamentally underpins **all** of chemistry, physics, and biology.

Quantum mechanics can seem weird when you first see it, but it's not overly difficult. It's definitely not anything to be scared of, even if people like to use the phrase 'like doing quantum physics' to mean 'really really hard'. These people are silly and obviously don't know anything about it. Quantum mechanics, as far as you need to use it at chemists, is not anything to be scared or worried about.

8.1 Key Quantum Principles

There are two key principles we have to understand: **wave-particle duality**, and **energy quantisation**. The former leads to the latter, as we will see.

8.1.1 Wave-Particle Duality

The idea of **wave-particle duality** is that **every particle can behave like a wave, and vice versa**. This means when we talk about an electron, we can either think of it like a small solid particle, or we can think of it like a diffuse wave (which is what we do when we draw orbitals). Both of these pictures are correct and are **complimentary**.

How does a particle like an electron *'behave like a wave'* though? In the previous lecture, we said that showing **interference** was a key piece of wave-like behaviour. Electron waves interfering with each other is what is happening when atomic orbitals overlap to make molecular orbitals, and you can also make electrons do things like **diffract** through apertures, like light waves do.

8.1.2 de Broglie Wavelengths

Every particle can exhibit these wave-like properties, and it turns out every particle has a characteristic wavelength called the **de Broglie wavelength**. For a particle with a given momentum p, the corresponding de Broglie wavelength λ is:

$$\lambda = \frac{h}{p} \tag{8.1}$$

Where h is the Planck constant. Most particles we can see have such tiny de Broglie wavelengths that we would never be able to see the wave-like properties unless they were travelling ridiculously fast - let's do an example.

de Broglie wavelength of James

Q: James weighs about 78 kg, and is riding his bike through Oadby at $40\,\mathrm{km\,h^{-1}}$ ($11.1\,\mathrm{m\,s^{-1}}$). What is his de Broglie wavelength?

A: First, calculate his momentum: mass × velocity $= 865.8\,\mathrm{kg\,m\,s^{-1}}$. Then, calculate his de Broglie wavelength: $\frac{6.626\times10^{-34}\,\mathrm{J\,s}}{865.8\,\mathrm{kg\,m\,s^{-1}}} = 7.65\times10^{-37}\,\mathrm{m}$. Much too small to see!

8.1.3 Quantised Energy

The final key principle of QM that we will talk about today is that of **quantised energy**. You've probably seen that the spectra of atoms and molecules consist of a few sharp lines, rather than a broad range of colours. This is because the energy states inside the atoms and molecules are **quantised**: only a few energy states are allowed. You've also already seen this idea without realising it when you talked about MO theory - remember how you make individual **energy levels**? The reason these are specific levels is due to the quantisation of energy.

This idea of things only having a few energy states they are allowed to exist in isn't specific to electrons. It actually applies to all kinds of motion on the atomic/molecular scale. You will find out later on that molecular rotation and vibration are also quantised. Energies of atoms and molecules are quantised, and so atoms and molecules can only exist in specific energy states. **This is the basis of spectroscopy.**

The fundamental reason that these kinds of motion are quantised is because the motion is **confined** in some way. A completely free electron can have whatever energy it wants, but an electron that is held in a molecule isn't free any more, and so it is only allowed to have specific energies. You can think of it like driving a car:

- If you can drive the car on a huge infinite square of tarmac, then you can go wherever you like and at whatever speed you like. This car is not quantised.
- If you confine the car to driving on roads with speed limits, then your speed is constrained - and you can only go to certain places. The car has become quantised by the confinement.

We'll see this again shortly when we think about the **particle in a box** - a very simple quantum mechanical system.

Right now, we don't need to go a lot further than this. Next year you will do a bit more of the mathematics behind this[1], and start talking about things like **wavefunctions** and **Hamiltonians** in more depth. We're going to talk about spectroscopy now, which is the fun application of QM in chemistry.

Take Home Messages

- Classical mechanics describes the behaviour of macroscopic objects, where QM describes the behaviour of microscopic objects.
- All particles can exhibit wave-like properties, and the characteristic wavelength of a particle is called the de Broglie wavelength.
- Quantisation of energy is a backbone of QM, and arises when the motion of particles is confined.

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[1] Which is not very complicated maths, certainly easier than a lot of the maths in classical mechanics or thermodynamics.

Lecture 8.5: Particles in Boxes

Today we will encounter the first simple model quantum system: **the particle in a box**. This simple system (literally just a very small ball stuck in a box) illustrates quite a lot of the key principles of quantum mechanics we need to know.

We are going to keep the discussion of this as qualitative as possible, and won't be directly solving the Schrödinger Equation today (this can wait until next year). We can actually learn most of what we need to know by thinking about particles, waves, and energies.

We'll treat this more like an interactive problem session than a lecture. The notes below sketch out the argument but I'll add a lot more detail during the lecture.

Lecture Aims

- To start to understand the particle in a box system.
- To be able to calculate energies of particles in boxes.
- To understand how confinement and particle size affect quantisation.

8.2 The Particle

The particle we will talk about in this lecture is going to be a small particle with a mass of m. This particle could be an electron, or a proton, or anything we like. The particle is going to able to move around in one dimension (along a line and back), and we will call that direction x. We will call the momentum of the particle p. We are going to want to calculate the **kinetic energy** of this particle:

$$T = \frac{p^2}{2m} \tag{8.2}$$

Our particle also has a characteristic wavelength, the de Broglie wavelength, λ_{dB}:

$$\lambda_{\mathrm{dB}} = \frac{h}{p} \tag{8.3}$$

If the momentum of the particle is small enough, then the wavelength of our particle might be big enough that we can see interference effects and things. This will become crucially important later - as it will turn out that the size of our box is going to be similar to the wavelength of our particle. Get ready for weird quantum stuff.

If our particle isn't trapped inside a box, but is free to move wherever it wants along our 1D line, then it can have any momentum and energy it wants to have. At this point, in the absence of a box (or if the box was infinitely big), the particle energy is **unconstrained**. We know from last time that if we constrain it somehow, that the energy will become quantised. We are going to constrain the particle by putting it in a **box**. Let's think about the box now.

8.3 The Box

Our box is one dimensional, which makes life a bit easier. The box will have a length of L, and at each end there is an infinitely big wall that the particle cannot get over.

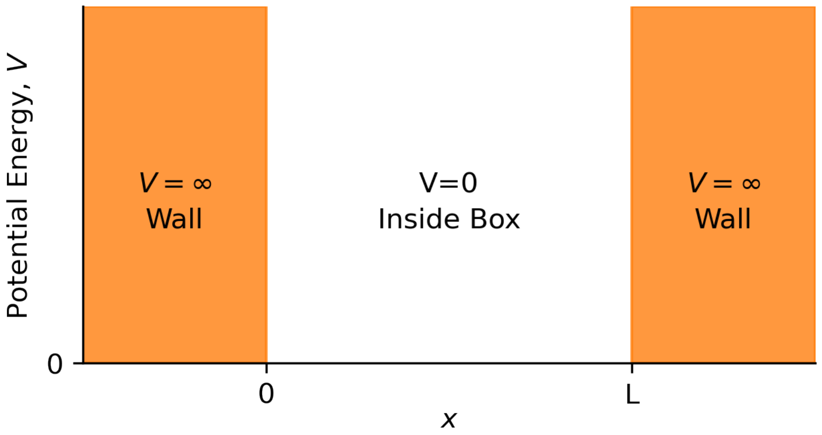

Figure 8.1: The box our particle is trapped in. The two walls are infinitely high, and the box has a length of L.

We can model this box by saying that **inside** the box, the potential energy of the particle is zero. This means that the total energy of the particle is just the same as the kinetic energy - remember:

$$\text{Total Energy} = \text{Kinetic Energy} + \text{Potential Energy}$$

Or, to give the usual symbols:

$$E = T + V$$

Outside of the box, however, the potential energy of the particle is **infinite**. Things can't have infinite energy, so this is just a fancy way of saying that the particle can't be outside the box[2].

Now, we will imagine that the length of our box is quite similar to the de Broglie wavelength of our particle. This is important, as it means we will be able to see the wave-like behaviour of our particle. It also accurately mimics things like electrons trapped in molecules - molecules are pretty small, so the 'box' they provide is also pretty small.

8.4 Wavefunctions

So the particle is in the box, and the box is small so that we can see the wave-like nature of the particle. We can represent the particle as a wave that is **standing** in the box. A **standing wave** is one that looks like those in Figure 8.2.

Note that the waves all go to zero at the edges of the box (i.e. the wave never starts with a peak or trough at the edge of the box), and that there are always a whole number of half-wavelengths in each box - it never does something like the waves in Figure 8.3

This is important, because what we are actually looking at when we look at this wave is something called a **wavefunction** of the particle. **Wavefunctions** are one of the most important things in quantum chemistry, and later on you will learn more about the mathematics behind them. The wavefunction is a mathematical function that contains **all the dynamical information**

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[2] If it could be, it would have infinite energy, and that breaks all kinds of laws.

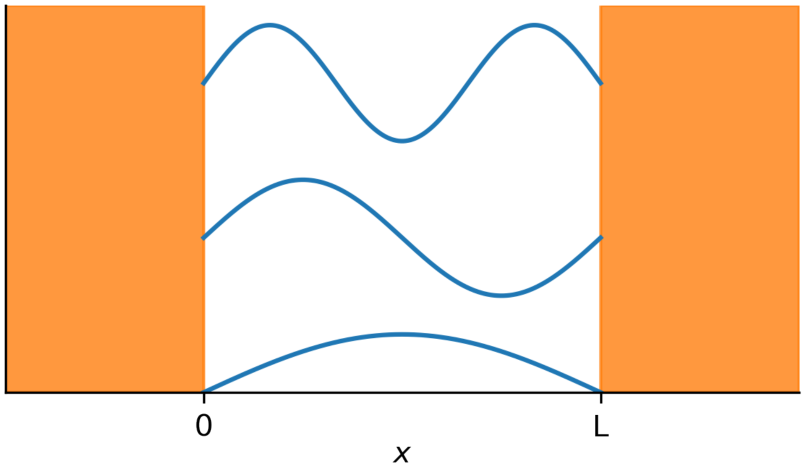

Figure 8.2: Standing waves in a box. The lowest wave has one half-wavelength, the next has two, and the third has three.

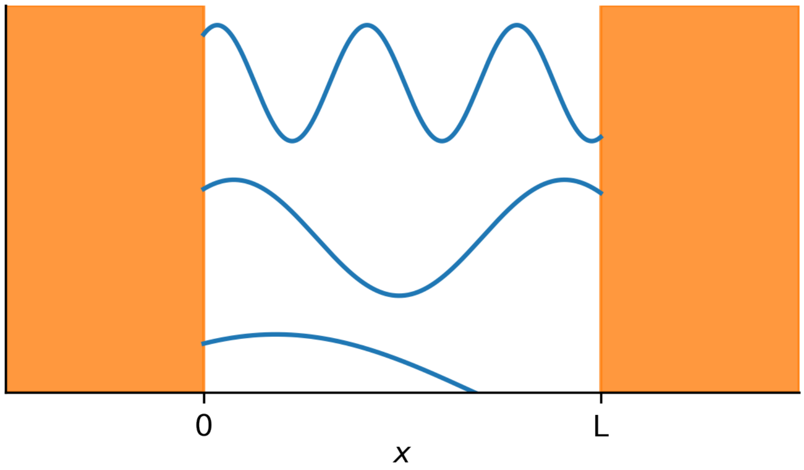

Figure 8.3: Standing waves that are not allowed. There must be a whole number of half-wavelengths, and the wave must go to zero at the edge of the box.

about a particle. By 'dynamical information', we mean information about the motion of the particle. If we know the wavefunction for a particle or system, then we know everything about it! Unfortunately, as you'll learn later, it's really really hard to find good wavefunctions for most things.

The wavefunction is normally given the symbol Ψ. An important property of wavefunctions is that the probability of finding a particle at a certain location is proportional to the **square** of the wavefunction at that location. We can say:

$$P(\text{Location}) \propto \Psi(\text{Location})^2 \tag{8.4}$$

So if we know the wavefunction at a certain place (say, in the middle of our box), then we also know the probability of finding a particle at that place.

We said before that the particle can't be outside of the box, otherwise it would have infinite energy (and that's not allowed). This means that outside the box, the square of the wavefunction has to be zero - and this means that the wavefunction has to be zero outside the box. It turns out that the wavefunction also has to be zero at the **edge** of the box - because the wavefunction has to be **continuous** and so can't jump from non-zero to zero at the edge of the box[3].

Ok, that's a lot of new information. So let's recap:

- The particle is in the box, and can't be outside the box.
- We can represent the particle as a **standing wave** inside the box.
- That standing wave is called the **wavefunction**, Ψ, of the particle.
- The square of the wavefunction (Ψ^2) at a certain point is proportional to the probability of finding the particle at that point.
- Ψ^2 therefore must be zero outside the box (from the first point), so $\Psi = 0$ outside the box.
- $\Psi = 0$ at the edges of the box, to ensure the wavefunction is **continuous**.

So we can draw lots of different waves that will fit into the box, but they all must start and end at zero, which means that there must always be a whole number of half-wavelengths in each box. Some examples were already shown in Figure 8.2. What we want to do now is find out the energy of each of these waves - that's our ultimate goal in a lot of quantum chemistry, finding wavefunctions and their energies.

8.4.1 Particle In a Box Energies

Let's start with what we know:

1. The total energy of the particle in the box is equal to the kinetic energy of the particle.
2. As the particle is exhibiting wave-like behaviour, the energy must also be related to the wavelength of the particle.
3. We know that we can only have certain specific wavelengths in our box - because the wave has to go to zero at the edges of the box.

We are going to end up showing that the energy of the particle in a box is **quantised**. Buckle up.

Let's start with point 1 above. We know that the kinetic energy of the particle, T, is equal to the total energy, E, and given by:

$$T = E = \frac{p^2}{2m} \tag{8.5}$$

We know that the momentum of the particle is related to the de Broglie wavelength:

$$\lambda = \frac{h}{p} \tag{8.6}$$

Which we can rewrite as:

$$p = \frac{h}{\lambda} \tag{8.7}$$

---

[3] The reasons for this are mathematical - come and talk to me later if interested.

We can then insert Equation 8.7 into Equation 8.5:

$$E = \frac{\left(\frac{h}{\lambda}\right)^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{8.8}$$

So now we have an equation for the energy of the particle in terms of the wavelength it has in the box - as we predicted in point 2 above. We now have to think about what wavelengths are allowed in our box. We said that there has to be a whole number of half-wavelengths in the box, and we also know that lower energies correspond to longer wavelengths, so the lowest energy wave we are allowed to have is going to be when $\lambda = 2L$ (one wavelength is two box-lengths). The next lowest energy will be when $\lambda = L$ (one wavelength is one box length), and the next is when $\lambda = \frac{2L}{3}$ (one wavelength is one and a half box lengths). Let's draw the waves for the lowest three energies on separate boxes for clarity:

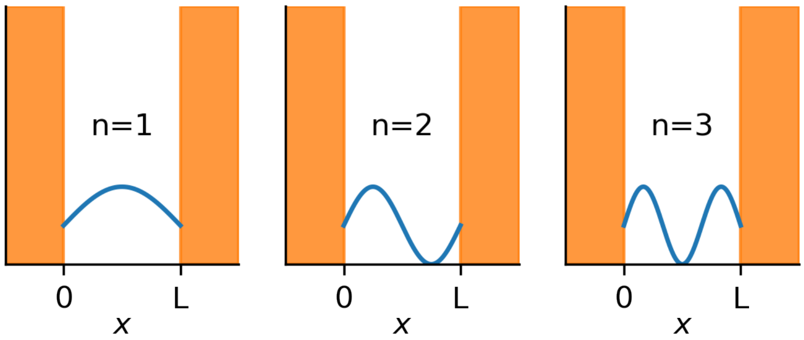

Figure 8.4: The three lowest energy allowed waves, labelled with the quantum number n.

We label each state with a number, n, and say that the lowest energy state has $n = 1$, the next has $n = 2$, and so on. The lowest energy state has $\lambda = 2L$ (left panel of Figure 8.4), and so the energy of this state is then:

$$E = \frac{h^2}{2(2L)^2 m} = \frac{h^2}{8mL^2} \tag{8.9}$$

Ok. Bear with me, and lets calculate the next allowed energy. This is going to be when one whole wavelength is in the box (middle panel of Figure 8.4). In this case, $\lambda = L$, and $n = 2$, and:

$$E = \frac{h^2}{2(L)^2 m} = \frac{h^2}{2mL^2} \tag{8.10}$$

The next one will be when $\lambda = {}^2\!/_3 L$, ($n = 3$):

$$E = \frac{h^2}{\frac{8}{9}mL^2} \tag{8.11}$$

Can you see any pattern here? We didn't introduce that label n for no reason, and we can actually say the energy of the nth state of the particle in our box, E_n, is given by:

$$E_\mathrm{n} = \frac{n^2 h^2}{8mL^2} \tag{8.12}$$

So let's take stock. We have just calculated the energies of the particle in our 1D box - we can see that the energies are **quantised**. We are only allowed to have certain values of the energy, and we labelled these using the number n. This number is called a **quantum number**. The

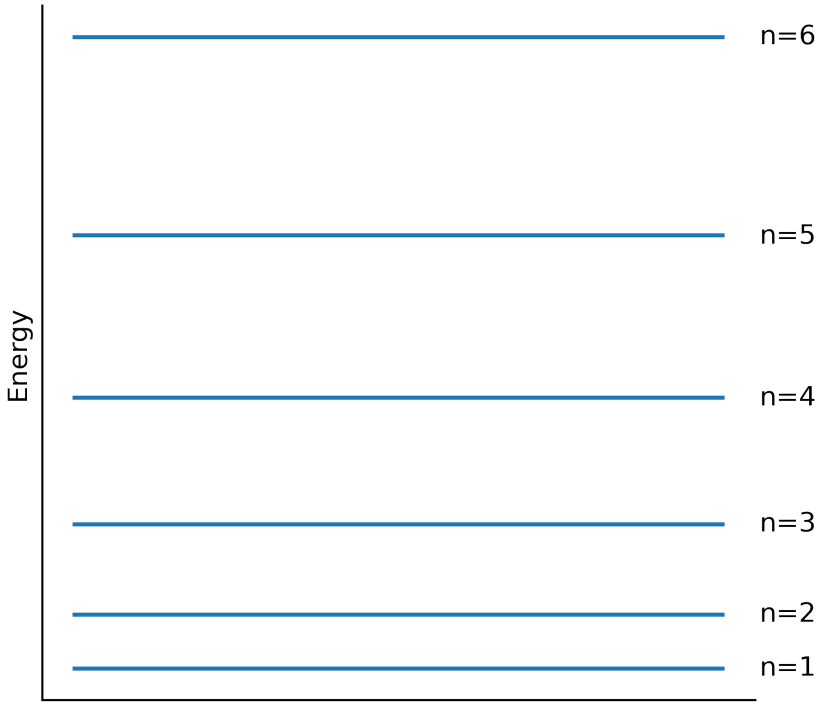

Figure 8.5: Allowed energy levels for our particle in a box. Note that the gap between levels increases as n increases.

value of n can be any integer from 1 up to infinity. The allowed energy levels of our particle in a box are plotted on the diagram below:

We can see that the gap between two levels increases as n increases, and we could actually derive an equation for the gap (ΔE) between two adjacent levels, n_1 and n_2:

$$\Delta E = \frac{h^2}{8mL^2}(n_2^2 - n_1^2) \tag{8.13}$$

This will be useful later when we talk about UV-Vis spectroscopy, but for now - think about how the level spacing changes if we change m and L.

- If we make m larger, then the energy spacing decreases - if m was really big (like for a macroscopic object, say a potato), then ΔE would be so small it's almost zero - then our particle isn't quantised really, as the energy spacing is so small.
- If we make L larger, the same thing happens. If our box was infinitely big, then the spacing of levels would be infinitely small, and our particle isn't quantised.
- Smaller particles, and more confined particles, exhibit **more severe quantisation**.

This should make some intuitive sense (maybe!). If I (a big particle) stand in this lecture hall (a big box), you can't see or experience any of my wave-like behaviour. Conversely, if an electron (a small particle) is trapped in a molecule (a small box), then you **can** see its wave-like behaviour and its energy is quantised. If I had an electron that was in free space (say, floating around outer space), then it is in an infinitely big box and its energy is not quantised - it can be whatever it wants to be.

I think this is a good place to stop, as we've introduced a lot of new and weird things today. Do not panic if you found this hard to follow - make some time to go through the equations again, and do the associated problems, and it will start to click. Quantum mechanics is a bit weird, but once you get used to it it's really nothing to worry about. Next time, we are going to talk about the basics of **spectroscopy** - the most important thing in all of chemistry.

Take Home Messages

- The particle in a box is a simple quantum system that illustrates lots of key phenomena.
- The confinement of the particle to the box makes its energy levels become quantised.
- Smaller particles, and smaller boxes, will make the quantisation more severe, and the quantum mechanical behaviour more pronounced.

Lecture 9

Spectroscopy Fundamentals

Today we are going to talk about **spectroscopy**. Spectroscopy is the study of the interaction of light and matter - for us, matter is just atoms and molecules. Spectroscopy is how we know more or less everything we know about chemistry, and it's a technique used daily (in one form or another) in every field of chemistry. Spectroscopy is really a **quantum mechanical** subject - you can't explain it without understanding that energies are quantised.

We will start by talking about some fundamentals that will apply to all spectroscopy, and then later on we will talk about some specific kinds of spectroscopy that we use often in chemistry. Spectroscopy is a fascinating subject - everything we know about molecules and chemistry ultimately comes from using different kinds of spectroscopy to study them. As a technique, it underpins almost everything else we do in chemistry. Spectroscopy is the magnifying glass we have to look at how atoms and molecules behave, and that is what makes it so exciting - at least, I love it (it's what I do with my time I'm not teaching!) and I hope you will too.

Lecture Aims

- To understand the fundamentals of spectroscopy.
- To understand absorption and emission of light.
- To understand how different parts of the EM spectrum correspond to different kind of molecular motion.

9.1 Spectroscopy

Spectroscopy is based on a quite simple process. The fundamental idea is that you have **two states**[1] in an atom or molecule, and you use some kind of **EM radiation** (light) to cause a **jump**[2]between these two levels. We've met two of these ideas in the last few lectures - we know that atoms and molecules exist in specific quantised energy **states**, and we know that electromagnetic radiation is what light really is (even if the light isn't visible light). The energy of the EM radiation that caused the transition then tells you what the energy spacing between the two levels was, and this links beautifully to all kinds of molecular properties: structure, dynamics, solvation environments... endless things. This is why spectroscopy is fundamentally a **quantum mechanical** phenomenon - it relies on there being these two distinct energy levels in the thing being studied. Figure 9.2 shows the fundamental process.

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[1] Or levels - we can use levels/states interchangeably.

[2] Technical term: transition :)

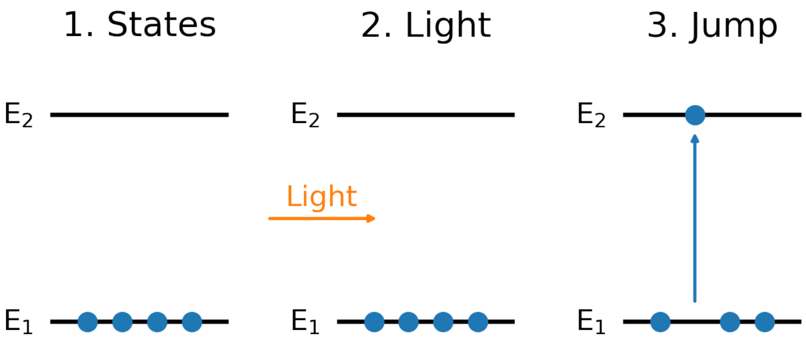

Figure 9.1: Simple picture of spectroscopy: 1. Two states exist in a molecule. 2. Light with the same energy as the gap between the states hits the molecule. 3. The molecule jumps from the lower state to the upper.

We are going to explore this process in this lecture. I'm going to use the terms 'EM Radiation' and 'light' interchangeably, as is common in spectroscopy (because they are ultimately the same thing!).

Spectroscopy comes in a dazzling array of different flavours: *NMR* spectroscopy, *IR* spectroscopy, *microwave* spectroscopy, *X-ray* spectroscopy, *fluorescence* spectroscopy, *UV-Vis* spectroscopy, *Raman* spectroscopy... . and the list goes on and on, and keeps on growing every year. However, all of these ultimately boil down to the same thing:

- You have two energy states in an atom or molecule.
- You use some kind of light to cause the atom or molecule to jump between these states.
- You measure the energy of the light at which that jump happens.

That is it - that is what spectroscopy is. **It is fundamentally all the same process!**

You will find a lot of people (and a lot of textbooks) that talk about the different spectroscopies as if they are all unrelated to each other - IR is totally different to NMR, which is totally different to UV-Vis, etc... **This is not true**. They all have their individual quirks and complexities, but all boil down to the same thing:

1. Two states.
2. Light.
3. Jump.

Once you get that, you realise they all have much more in common than they do different.

If Richard Blackburn would let me, I would happily deliver a 50 lecture course on different kinds of exciting spectroscopy. Unfortunately, he won't let me do that. So we only have the next few lectures. What we are going to do today is go over this fundamental process ('*two states, light, jump*') and show how different kinds of light result in different kinds of spectroscopy, and probe different kinds of molecular motion.

9.2 Two States and Light

As you may be realising, the central idea in spectroscopy is that we have two states in an atom or molecule. These states are just the **quantised energy levels** that we have spoken about in the last few lectures. Let's imagine they are in a molecule for the sake of argument.

The key idea is that when that molecule is exposed some EM radiation (say, visible light), it can **jump** from the lower state to the higher state. You can think of this process as the molecule **absorbing** a photon of the light and thus gaining energy. Crucially, it only does this if the energy of the photon **exactly** matches the energy gap between the lower state and the higher state. If we then record the energy of the photon that caused the absorption, we can find out the energy gap.

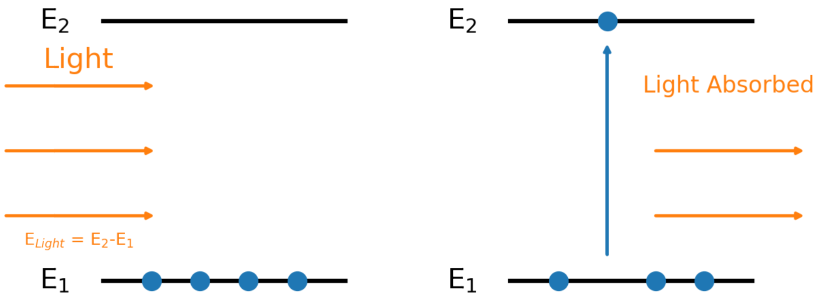

Figure 9.2: When the energy of the incident light (orange) matches the energy gap E_2-E_1, then it can cause a transition and be absorbed in the process. Here three photons go in, but only two come out - absorption.

Why does it help us to know the energy gap between the two states? Well, it turns out that the gaps between energy levels can be easily linked to a **huge** range of molecular properties: bond lengths, bond angles, bond strengths, molecular geometries, and others. Remember what we had for a particle in a box in the last lecture:

$$\Delta E = \frac{h^2}{8mL^2}(n_2^2 - n_1^2) \tag{9.1}$$

If we knew the energy gap (ΔE), and knew the quantum numbers of the states involved (n_1 and n_2), then we could figure out the mass of the particle (if we knew the length of the box), or the length of the box (if we knew the mass of the particle). You'll see loads of examples of this throughout the degree - working out molecular structure from spectra you collect. Just remember it's fundamentally all the same - **you shine EM radiation on something and measure when it's absorbed**[3].

Different kinds of EM radiation from the EM spectrum correspond to different energy gaps. In molecules, there are energy levels associated with all different kinds of molecular motion - you will learn about this in more depth later, but there are energy levels that are associated with molecular **rotation** and **vibration**, and energy levels associated with energy levels of electrons. The spacing between these energy levels is all different, and so we use different parts of the EM spectrum to do spectroscopy on the different levels.

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[3] Or emitted, and there are some other complications. But it's still always two states and radiation.

9.2.1 Jumping

We have our two states, and we have the light that causes our atom/molecule to jump from one state to the other. The technical term for this 'jump' is a **transition**. Transitions happen between two states, and the transition can either be a jump 'up' or a jump 'down'. When an atom/molecule jumps up into a higher energy state after interaction with some light, we call that **absorption**. When it jumps down from a higher energy state to a lower energy state, it has to emit some light (to get rid of the excess energy), and we call this **emission**.

Whether a molecule undergoes absorption or emission depends on the **populations** of the two states. By **population** we mean the number of molecules that are in a certain state. If all the molecules in a sample are in one state then that state is **populated**, and other states are **unpopulated**.

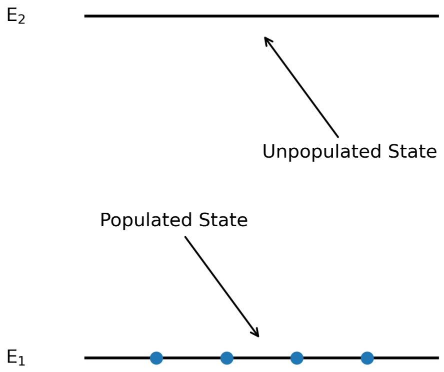

Figure 9.3: State populations, here state E$_1$ is populated, and state E$_2$ is unpopulated. We could only have a transition from E$_1$ to E$_2$ in this situation.

Most of the time, for a transition to happen, it has to be a transition from a more populated state to a less populated state, and we can't have a transition from an unpopulated state for obvious reasons! A good question then, is:

> How do we know which states are populated, and therefore which states we can have transitions from?

The amount of population in a state at a given temperature depends on two things:

1. The **energy** of that state.
2. The **energy available** to the population - this depends on the **temperature**.

Imagine we have some molecules at absolute zero, the lowest temperature possible. The molecules have no energy available to them, and so they all exist in the **lowest energy state** - the **ground state**. If we raise the temperature a bit, the molecules start to gain energy, and so some of them will be able to jump into the state above the ground state using that thermal energy. Let's call this next state the **excited state**. The number of molecules that can do that jump depends on the energy gap between the ground state and the excited state. If the gap is very small, then its quite easy for molecules to make the jump, and a lot of them will be in the excited state. Conversely, if the gap is very large, then only the highest energy molecules will be able to make that jump. This is probably easier to explain with a drawing. Imagine we are putting six particles into two states in different situations - high and low temperature, and high and low energy gaps:

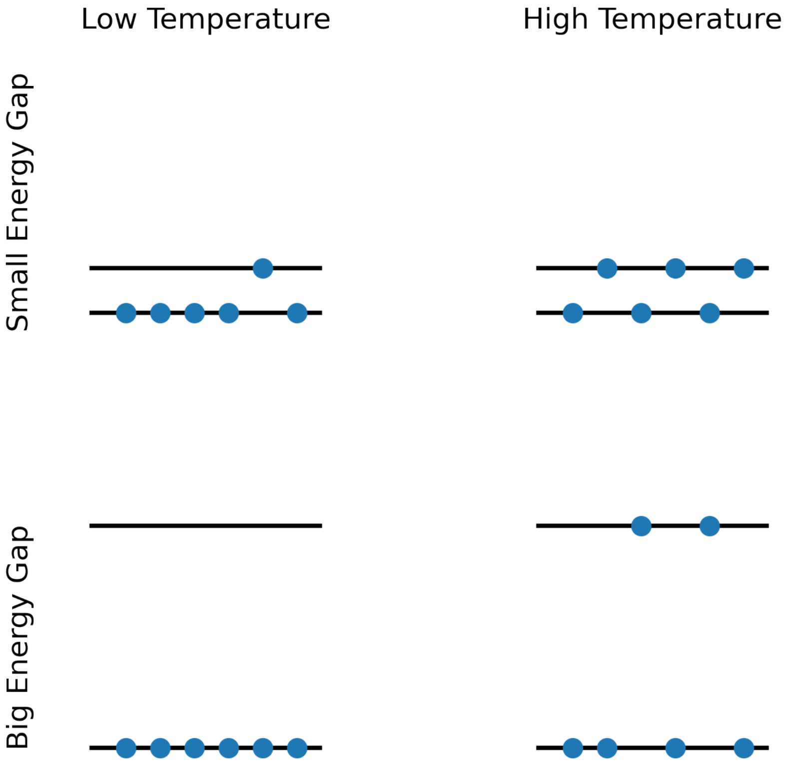

Figure 9.4: State populations at different temperatures and with different energy gaps. High temperatures result in more population in higher energy states, but bigger energy gaps counteract this.

So we can see that:

- A bigger energy gap between the lower and upper state means that we get less population in the upper state, for a given temperature.
- A higher temperature means that we have more energy available, and so more population can get into the upper state.

At absolute zero, every single molecule is in the lowest energy state. Conversely, if we went to infinitely high temperature, then every state is **equally populated**, we can never get a situation where all the population is in the higher state just by heating something up[4].

If we have two states (let's call them 'lower' and 'upper'), then the ratio of the population in the upper state (n_{upper}) to the population in the lower state (n_{lower}) is given by the **Boltzmann Law**:

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \exp\left(-\frac{\text{Energy Gap}}{\text{Available Energy}}\right) = \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{9.2}$$

---

[4] To do this we need to do something more drastic like **optical pumping** - which is how lasers work.

Where $\Delta E = E_{\text{upper}} - E_{\text{lower}}$ is the energy gap (in Joules), k_B is the Boltzmann constant $1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$, and T is the temperature in Kelvin. The quantity k_BT tells you how much thermal energy (in Joules) there is available at a given temperature, T. Let's calculate some example population ratios for some different situations:

Population Ratios

Calculate $\frac{n_{\text{upper}}}{n_{\text{lower}}}$ for:

1. The gap between two electronic states of O_2 (energy gap $= 185\,\mathrm{kJ\,mol^{-1}}$ at room temperature (298 K).
2. The gap between two rotational states of O_2 (energy gap $= 3\,\mathrm{cm^{-1}}$), at room temperature (298 K).

What do the results tell you about the population of the different states?
We will go through the working in the lecture, but you should find:

1. $\frac{n_{\text{upper}}}{n_{\text{lower}}} = 0$. No molecules are in the excited state at room temperature.
2. $\frac{n_{\text{upper}}}{n_{\text{lower}}} = 0.98$. Half of the molecules are in the excited state at room temperature!

So we can see that at room temperature, pretty much every molecule will be in its electronic ground state, but that many rotational states will be populated. As we heat molecules up that changes, and the excited states become more populated. We have to heat things up a lot to get into an electronic excited state, but only a bit to get into a vibrationally excited state.

Our original question was about absorption and emission though - and we can see now that if we have lots of population in higher energy states then we are more likely to see emission, but a lot of the time in spectroscopy we are doing absorption.

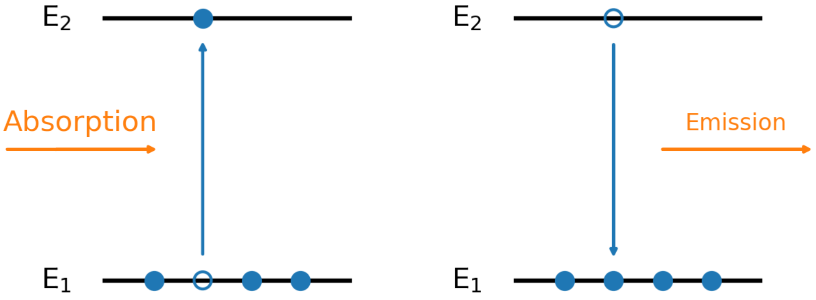

Figure 9.5: Absorption (left) can be thought of as the molecule absorbing a photon and jumping to a higher energy state. Emission (right) can be thought of as the molecule falling to a lower energy state and releasing a photon in the process.

By now, we should be ok with the idea that we have two states, and some light causes population to jump between the two states. **This is literally all spectroscopy is!** The information we get from it depends on the energy gap between the two states and therefore the light we use to cause the jumping. For the rest of the lecture, let's explore some of the different kinds of spectroscopy we use in chemistry.

9.2.2 EM Spectrum and Spectroscopy

Figure 9.6 shows the EM spectrum that we saw a couple of lectures ago. All of these different kinds of EM waves are used for spectroscopy. In the next couple of lectures, we will talk about a couple of them in some more detail, but let's do a brief overview now.

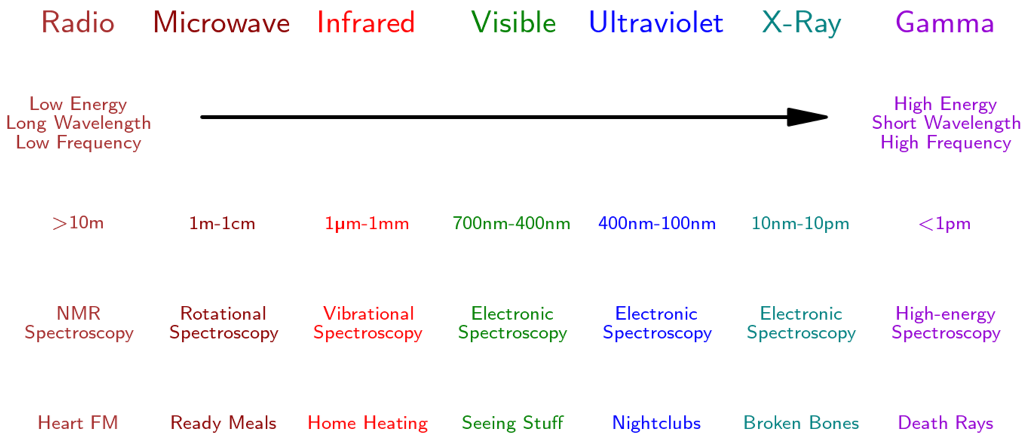

Figure 9.6: The EM spectrum, as seen previously.

Radio Waves: NMR

Radio waves are used to do **NMR spectroscopy**. NMR stands for Nuclear Magnetic Resonance, and it's probably the most widely used kind of spectroscopy today. To do NMR, you put a molecule in a ridiculously strong magnetic field and this makes some energy levels appear that have a very tiny spacing. Radio waves are the lowest energy kind of EM radiation, so we use these for NMR as the energy gap is so small.

NMR is an **exquisite probe of molecular structure**, more sensitive to small changes in structure than any other technique. However, it's inherently quite a **slow** technique, and one where you need a lot of molecules to measure a big signal. It's the go-to technique for synthetic chemists who want to characterise the molecules they make.

Microwaves: Rotational Spectroscopy

Microwaves are used to do **rotational spectroscopy** (or just 'microwave spectroscopy'). This probes **rotational energy levels** - when a molecule absorbs microwaves it will start rotating. The rotations of a molecule are linked to lots of structural parameters - especially bond lengths. Normally you need to do rotational spectroscopy in the gas phase to avoid solvent messing everything up.

Rotational spectroscopy isn't used as much nowadays as it used to be - but it is still king for lots of small molecule spectroscopy. You can also use it (in conjunction with powerful lasers) to control rotation of molecules and use a laser beam to hold them in a certain orientation - imagine tying a molecule up so you can look at it, that's about the picture.

Infrared: Vibrational Spectroscopy

Infrared radiation is used to do **vibrational spectroscopy** (or just 'IR spectroscopy'). This probes **vibrational energy levels** - when a molecule absorbs IR radiation it will start vibrating (this is what makes you feel warm when you stand infront of a radiator). Vibrations of molecules are intrinsically linked to a lot of molecular parameters, and the vibrations of a molecule can be shifted by things like solvation environment - making it a very useful thing for many kinds of chemistry.

IR spectroscopy is very widely used, and especially within physical chemistry. It competes somewhat with NMR[5] - it has nowhere near the structural sensitivity of NMR, but unlike NMR it is a very **fast** technique, and you don't need a lot of molecules to get a big signal. This makes it ideal for studying **dynamics** - how molecules move around and react with each other.

UV-Visible: Electronic Spectroscopy

UV and visible radiation is used to do **electronic spectroscopy** (or just 'UV-Vis spectroscopy'). This probes **electronic energy levels** - when a molecule absorbs UV or visible radiation its electrons can jump between energy states. This can massively change the structure of the molecule, and can even make the molecule break apart[6].

UV-Vis is useful for things that are colourful (as they must absorb some kind of visible light!). It can also tell you about the electronic structure of molecules, but it can often be hard to interpret the spectra compared to IR or NMR spectroscopy. It's often used to initiate **photochemistry** - shoot some light at a molecule and watch it do something.

X-Rays and Gamma Rays: High Energy Spectroscopy

X-rays are used widely in chemistry to study the **core electronic structure** of molecules - this means the electrons that are buried deep near the nucleus, rather than the ones in the outer shells. Gamma rays are so high in energy that they destroy a lot of things they touch, but they are used to study the behaviour of **nuclei**, rather than electrons.

That's a whistlestop tour of different kinds of spectroscopy - we can't do it all in half a lecture! Spectroscopy is amazing, and to me is the most interesting part of chemistry. I hope I've managed to convince you that the central underlying idea is relatively simple, just remember:

1. Two states.
2. Light.
3. Jump.

That's it - all the rest is just technicalities :)

Next time we will start to talk about **atomic spectroscopy** - which is a kind of UV-Vis spectroscopy. I'll bring in a blowtorch and make some things colourful. Be excited.

Take Home Messages

- Spectroscopy is the study of light and matter, and the central idea is that we have two quantised energy levels and EM radiation causes a transition between them.
- We can have absorption and emission spectroscopy, depending on the relative populations of the states involved.
- Different kinds of EM radiation probe different kinds of atomic/molecular motion, and thus provide us with different chemical information.

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[5] Spoiler: I'm an IR guy.

[6] Which is why you get sunburn from UV!

Lecture 10

Spectroscopy II

Last time we talked about the fundamentals of spectroscopy (states, light, jump). Today we are going to talk about some more key concepts that apply to all kinds of spectroscopy.

Lecture Aims

- To understand spontaneous and stimulated emission.
- To understand how to read a generic spectrum, and to understand the idea of selection rules.
- To understand and be able to use the Beer-Lambert law.

10.1 Absorption and Emission Again

Last time we talked about the difference between absorption and emission of light, and mentioned that we can have absorption from a lower energy state to a higher energy state, or emission from a higher energy state to a lower energy state. To get either absorption or emission from a state requires that there is **population** in that state to begin with, and we can calculate the populations of different states at a given temperature using something called the **Boltzmann law**.

Absorption is quite easy to grasp conceptually - a photon of light goes in and makes the molecule jump up to a higher energy state. The photon hitting the molecule causes the absorption to happen. So how does emission happen? What causes emission? There are two ways in which emission can happen: **spontaneous emission** and **stimulated emission**.

Spontaneous emission happens when a molecule (seemingly) randomly emits light and drops from a higher energy state to a lower one. Atoms and molecules tend to want to get to lower energy states, and so when a molecule is in an excited state, there is always a chance that it might spontaneously drop into a lower energy state. The process appears spontaneous because there is no other light coming in to drive the emission - in contrast to the case of **stimulated emission**.

Stimulated emission happens when light hits a molecule and causes it to jump *from a higher state, to a lower state.* You can think of this as like the opposite of absorption - the presence of the light causes a transition from an upper state to a lower state, rather than the other way around. To understand this, you can think of the light wave going in as 'shaking' the molecule so that it drops down from a higher state to a lower state (you can think of absorption in the same way). Stimulated emission is only really efficient if we have **more** molecules in the upper state than the lower state - which is relatively uncommon, but is how things like lasers function.

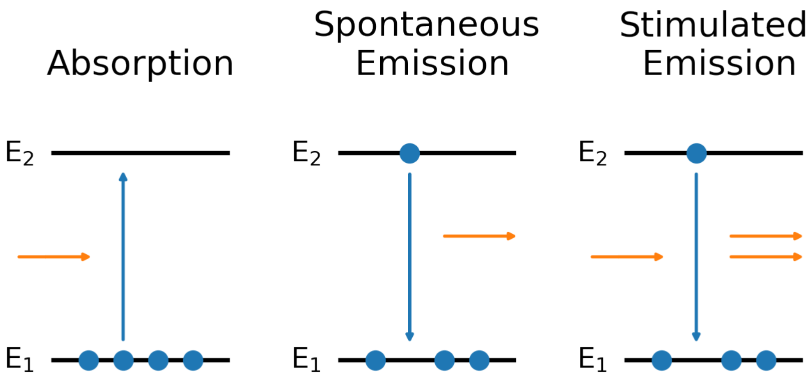

Figure 10.1: Absorption, spontaneous emission, and stimulated emission. These processes are the bulk of how light interacts with molecules.

These three processes - absorption, spontaneous emission, and stimulated emission - describe the key ways in which light can interact with a molecule. Albert Einstein was the one who first had this idea to explain atomic spectra, and mathematically the processes can be described by the **Einstein coefficients**. There are three coefficients - one for each process - and you'll learn about them later. For now, just know that they exist!

Now we have a good handle on what can happen when light hits a molecule. Normally in spectroscopy, we shine light of many different colours (energies) at a molecule and see what happens at each energy. This results in the creation of a **spectrum**. Let's look at that now.

10.2 Reading a Spectrum

We've already seen the **EM spectrum**, and other spectra are fundamentally very similar looking to this. On the x-axis we have energy (or wavelength, or frequency - something we can always relate to energy), and on the y-axis we have intensity, or some other measure of how much light was absorbed or emitted by the molecule.

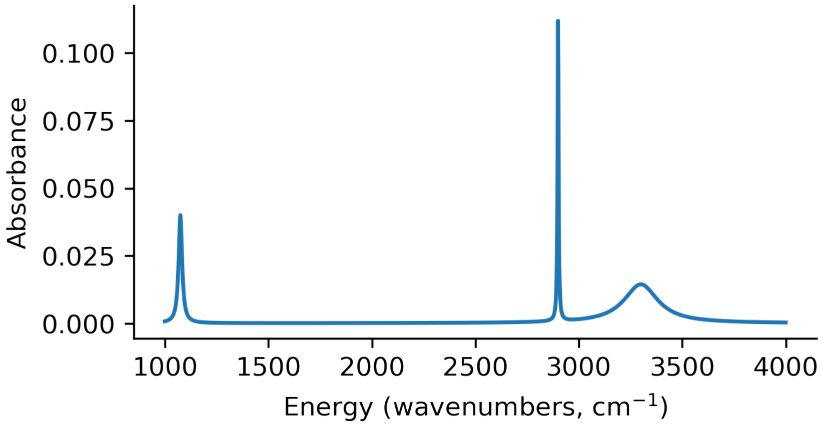

Figure 10.2: An example absorption spectrum. Energy (here given as wavenumbers) is on the x-axis, and absorption on the y-axis.

Let's imagine that we are looking at an absorption spectrum in Figure 10.2. We can clearly see that light is absorbed at three different energies: $\sim$1100 cm^{-1}, $\sim$2900 cm^{-1}, and $\sim$3300 cm^{-1}. We can also see that the two lower energy peaks are quite narrow, and that the higher energy peak is broad. The peaks also all have different heights - you can relate the peak height and width to how much light the molecule has absorbed at a given energy[1]. All spectra are fundamentally the same as the one shown in Figure 10.2, although sometimes you might see them with an inverted y-axis, like this:

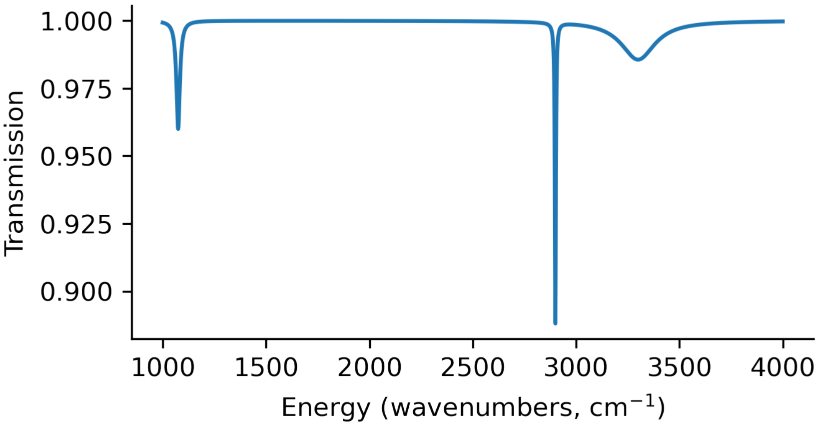

Figure 10.3: The same spectrum as in Figure 10.2, but now shown with transmission rather than absorption.

It's the same idea, just now we see the absorptions as dips rather than peaks, because we are measuring how much light the sample **transmits**. The same information is shown in both Figure 10.3 and Figure 10.2. Most spectra you will see look like Figure 10.2, but in organic chemistry people still like to show their IR spectra by measuring transmission, like in Figure 10.3.

In any spectrum, the x position (energy) of a peak/dip, and the size of the peak/dip on the y-axis tells us about the underlying molecule. Exactly *how* these relate to the underlying molecule depends on the spectroscopy you are doing - and that's the job of researchers that use spectroscopy! For now, I want you to be able to look at any spectrum and understand roughly what it is showing you, but you don't need to be able to relate that to molecular properties yet.

Reading Spectra

- The x-axis of a spectrum tells you **energy** - but often in a unit like wavelength, frequency, or wavenumber, that is directly related to energy.
- The y-axis of a spectrum tells you how strongly the molecules responded to the light. Most often, the y-axis shows absorption, but this isn't always the case.
- The positions of peaks, widths of peaks, and height of peaks in a spectrum can give you exquisitely detailed information about the molecules that were having light shone at them.

10.2.1 Real Spectra: Selection Rules

Let's look at a couple of examples of some real spectra:

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[1] Strictly, the area *under* the peak is what determines how much light was absorbed.

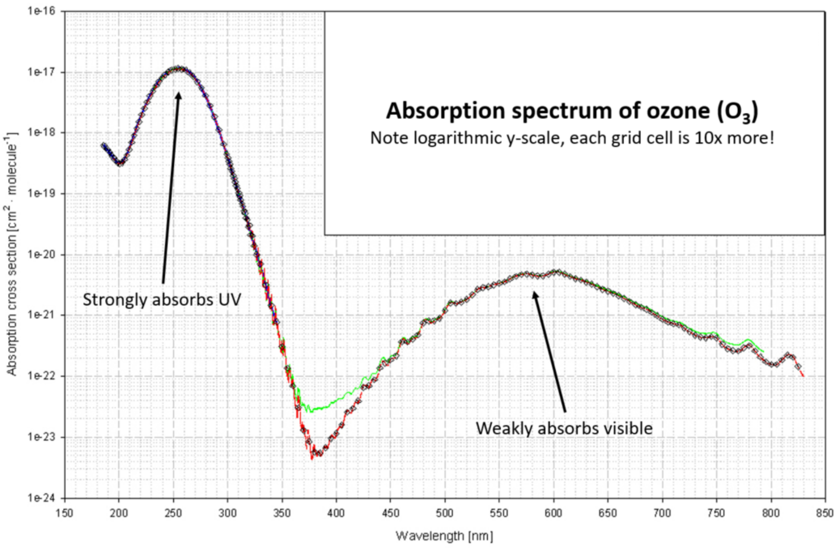

Figure 10.4: The UV-Vis absorption spectrum of Ozone (O_3). You can see big absorption by the UV region, but less absorption by the visible region.

Figure 10.4 shows a UV-Vis absorption spectrum of ozone (O_3). You may have heard of ozone in the context of **the ozone layer** in the atmosphere, which protects us from harmful UV radiation between 200 and 300 nm coming from the sun. Can you see from the spectrum why ozone would protect us from harmful UV radiation? Can you also see why ozone gas is colourless?

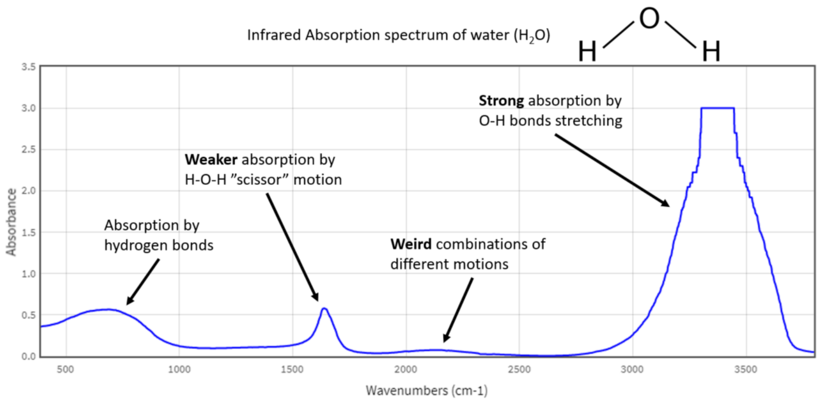

Figure 10.5: The IR absorption spectrum of water (H_2O). You can see big contributions from the absorption by O-H bonds, as well as some other structure. The square top of the big peak is because there was so much absorption the detector saturated.

Figure 10.5 shows an infrared spectrum of everyone's favourite molecule, water. Infrared (IR) spectroscopy works by the IR light causing the molecule to **vibrate**. We see this big peak in our spectrum at about $3300\,\mathrm{cm}^{-1}$, which comes from the stretching of the O-H bonds in water. We also see peaks that come from other vibrations, like the "scissor" bending vibration (imagine pushing the hydrogens closer together and then pulling them apart) at $1600\,\mathrm{cm}^{-1}$, and some other smaller peaks from hydrogen bonding and other exotic things.

At this point, it is going to be useful to discuss something called **selection rules**, which are an important thing in spectroscopy. Our simple picture of states, light, jump is very informative, but not *every* photon can cause a jump between two states, even if the energy of the photon matches the gap between the states perfectly. This is because there are other things to consider, like how easily the photons can ‘grab hold’ of the molecule, or how momentum is conserved when the photon hits the molecule. These other considerations result in something called **spectroscopic selection rules**, or just **selection rules**.

A **selection rule** is a rule we have to obey if we want to see light absorbed by a molecule. In IR spectroscopy, the main selection rule is that **the dipole moment of the molecule must change during a vibration**. In a molecule like O_2, stretching the O=O bond will not change the dipole moment, and so you will never see this vibration in an IR spectrum. However, in a water molecule, changing the length of the O-H bonds by stretching **will** change the dipole moment (I'll do a demo in the lecture if you don't believe me), and so we see these as a big peak in our spectrum.

Selection Rules

- Not every photon can cause a transition between two different states, even if they have the right energy.
- **Selection rules** are rules that determine which transitions (jumps) are allowed to be induced by light for different molecules.
- For IR spectroscopy, the main selection rule is that any vibration that is excited by the IR photon has to cause the dipole moment of the molecule to change.

10.3 Beer Lambert Law

We can see that when we measure a spectrum, different wavelengths of light are absorbed differently by the molecule. It would be useful to be able to predict how much light a particular molecule would absorb at a particular wavelength. Imagine a simple experiment like the one shown below, shining some light through a cuvette containing a solution of some molecule.

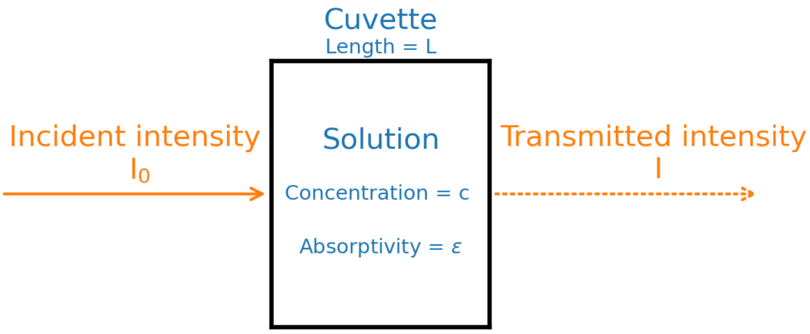

Figure 10.6: Typical absorption spectroscopy experiment - light is shone into a cuvette, and the amount of transmitted light is measured.

How much light do we see at the other end of the cuvette? Or, what is the intensity of the transmitted light, I? We could imagine that the following would all be important when trying to figure this out:

- The amount of light we send in, I_0 - more light in, means we get more light absorbed.

- The concentration of the molecule in solution, c - more concentrated solution means we get more light absorbed.
- The length of our cuvette, L - a longer path means more light gets absorbed.
- The **molar absorptivity** ϵ - some molecules will absorb more light than others.

These parameters combine together to give the following expression for the intensity of transmitted light:

$$I = I_0 \exp(-\epsilon c L) \tag{10.1}$$

This equation is called the **Beer-Lambert Law**, or sometimes just **Beer's Law**. This equation doesn't just come from nowhere, and in fact it is actually quite easy to derive, but it requires a bit of calculus. You can see the derivation on blackboard if you can't wait, but we will do it together next semester in CH1204 anyway.

The Beer-Lambert law can be written as above, if we are interested in the amount of transmitted light. Equally, we can define a new quantity called the **absorbance**, A, and write:

$$A = \ln \frac{I_0}{I} = \epsilon c L \tag{10.2}$$

The absorbance tells us **how much light the sample absorbs**. If the absorbance is high, it absorbs a lot of light, and vice versa. It also makes sense that if our solution is very concentrated (high c), or that our light travels through a lot of solution (high L) that more light gets absorbed. The molar absorptivity (ϵ) is a value specific to a molecule at a certain wavelength which tells you how much light that molecule absorbs - if it is high, then the molecule absorbs more light. Absorbance (A) is dimensionless, and so the SI unit of the molar absorptivity is m^2/mol. Sometimes you will hear ϵ called the **extinction coefficient** or the **absorption coefficient** (probably by me by accident, because I am old school).

Sometimes you will encounter absorbance, and sometimes you will be given intensities. Other times you might encounter something called the **transmittance**, T, which is given by:

$$T = \frac{I}{I_0} \tag{10.3}$$

Thus we can define the absorbance as $A = -\ln T$. Let's practice using these quantities in some examples for the rest of this lecture.

Beer-Lambert Law

1. A 0.002 mol dm^{-3} solution of Rhodamine 6B dye was placed in a cuvette of length 1 mm. Blue light (400 nm) was shone into the cuvette, and the light intensity was reduced to 63% of its original value. What is the molar absorptivity of the dye at 400 nm?
2. The molar absorptivity of benzene is 160 mol^{-1} dm^3 cm^{-1} at 256 nm. What concentration of benzene solution would you need to put into a 1 cm cuvette in order to absorb 10% of the incident 256 nm light?

We will go through the working in the lecture, but you should get:

1. $\epsilon =$2230 mol^{-1} dm^3 cm^{-1}
2. $c =$0.0006 mol dm^{-3}

Complication: On Logarithms

When you look into the Beer-Lambert law you will sometimes see it defined as I have presented, using natural logarithms, and other times you will see it presented using base-10 logarithms, like this:

$$A = \log_{10} \frac{I_0}{I} = \alpha c L \tag{10.4}$$

The difference arises because chemists are rubbish at agreeing on and using standards. If you use the base-10 version, your absorptivity is known as the **decadic absorptivity** and has the symbol α. In the natural logarithm (base e) version, the absorptivity ϵ is sometimes called the **natural absorptivity**.

There's no real difference between the two methods - it's just like choosing to define a circle by its radius or its diameter. I prefer the version with natural logarithms, as it falls more naturally out of the mathematics when you derive it, and it's more in line with other concepts you'll learn later on. However, you might encounter both, so just be aware. Any question I ask you in this course will be using the **natural** logarithm version.

Take Home Messages

- Absorption, spontaneous emission, and stimulated emission, are three important ways in which light can interact with molecules.
- When reading spectra, energy is along the x-axis and how strongly the light interacts with the molecule is on the y-axis. Selection rules play a part in determining which peaks are visible or not.
- The Beer-Lambert law allows us to calculate the absorption of light by a solution.

Lecture 11

Spectroscopy in Practice

Today is our last lecture on spectroscopy :(We will talk about two common kinds of spectroscopy you'll encounter throughout the course (and your life as chemists). These are **UV-Vis** and **IR** spectroscopy. The other 'big' kind of spectroscopy is **NMR** spectroscopy, but we will leave this for another time.

Lecture Aims

- To understand the principles of UV-Vis spectroscopy.
- To understand the principles of IR spectroscopy.
- To start to understand spectrometers.

11.1 UV-Vis Spectroscopy

UV-Vis spectroscopy is a form of **electronic spectroscopy**, where you are looking at transitions of atoms between **electronic states**. If we are looking at spectra of atoms, we call this **atomic spectroscopy**, and you've done this (maybe without realising it) when you learnt about flame tests at A level. If we look at transitions between electronic states in molecules, we call it **electronic spectroscopy**, or **UV-Vis spectroscopy** - because the wavelength of the light involved is in the visible or UV region.

UV-Vis spectroscopy is commonly used in inorganic chemistry to study ligand binding strength, and is also used to monitor reaction progress in organic chemistry. It's also widely used in studying dynamics of molecules, and lots of the chemistry that happens in the atmosphere can be studied using UV-Vis techniques. UV-Vis light causes a lot of **photochemistry**, which is chemistry that's initiated by light. An example you are indirectly familiar with in sunburn - this happens when a DNA molecule gets blasted apart by absorbing a UV photon.

As we said, UV-Vis or electronic spectroscopy is a spectroscopy where the two states we are jumping between are **electronic states**. In an atom, these states are just atomic orbitals. In a molecule, they are **molecular orbitals**. We've talked about molecular orbitals in earlier lectures on MO theory, and let's recap the idea of the HOMO and LUMO:

- **HOMO**: **H**ighest **O**ccupied **M**olecular **O**rbital
- **LUMO**: **L**owest **U**noccupied **M**olecular **O**rbital

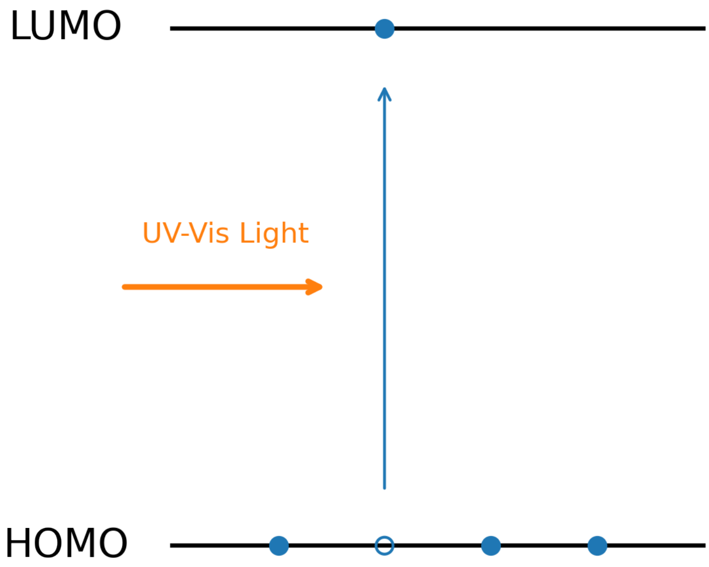

Figure 11.1: UV-Vis spectroscopy: UV-Vis light causes a transition between the HOMO and LUMO of a molecule.

So, if we imagine a molecule with its molecular orbitals (just like an atom with atomic orbitals), then the **highest energy** orbital that has electrons in it is the **HOMO**. The orbital immediately above this in energy is the **LUMO** - the **lowest energy** orbital without electrons in it. In UV-Vis spectroscopy of molecules, most of the time we are using our light to cause a transition between the HOMO and the LUMO. The energy gap determines the wavelength of light that causes the transition, and for most molecules that wavelength is somewhere between 190-900 nm, or about 10000-50 000 cm^{-1} - corresponding to the UV/Visible region of the EM spectrum.

As the energy gap is often in the visible region of the spectrum, we can use this to explain why some compounds look coloured. A molecule like β-carotene has a HOMO-LUMO gap with an energy of about 22 000 cm^{-1}, which corresponds to a wavelength of about 450 nm. This is blue/green light, and so the molecule will absorb any blue/green light that shines on it. This means that the molecule reflects other wavelengths - and thus it looks orange/red to our eyes. You're familiar with this molecule even if you don't realise it - what colour is a carrot?

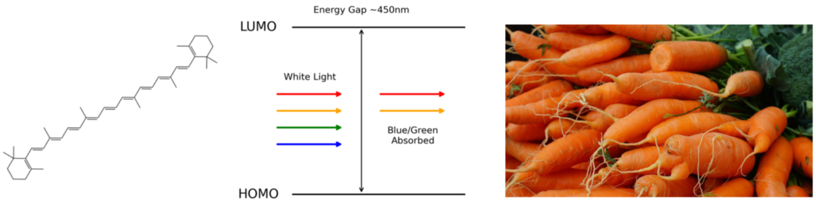

Figure 11.2: β-carotene absorbs blue and green light, reflecting orange and red wavelengths. This makes carrots look orange.

This goes for many other compounds too - chlorophyll is a compound you may have heard of. It absorbs light in the red/orange region of the visible spectrum, and in the blue region. This means that chlorophyll will reflect green light. Chlorophyll is the molecule present in all plants - so can you explain why a leaf looks green?

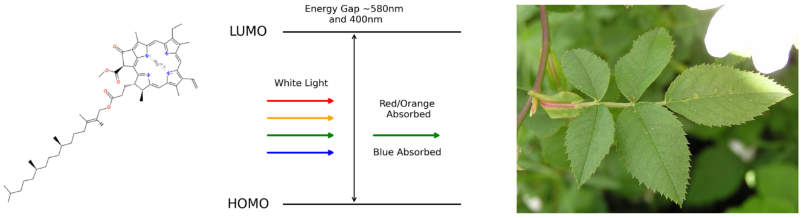

Figure 11.3: Chlorophyll absorbs blue, orange, and red light, reflecting green wavelengths. This makes leaves look green.

Lycopene is a compound that is present in tomatoes and watermelons. What wavelength would you expect it to absorb?

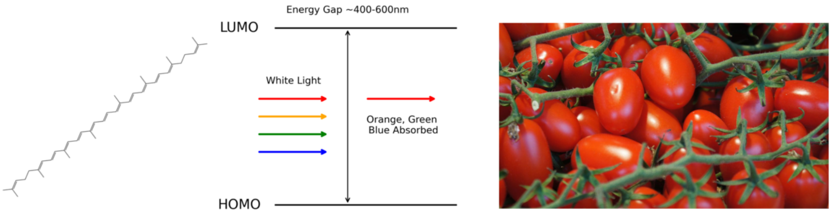

Figure 11.4: Lycopene absorbs blue, green, and orange light, reflecting red wavelengths. This makes tomatoes (and watermelons!) look red.

Another, slightly different, example would be water. Water is a molecule we all rely on to survive. The HOMO-LUMO gap in water is huge - it actually only really absorbs quite deep into the UV region of the EM spectrum, and doesn't absorb any visible light at all. If it doesn't absorb *any* visible light, can you explain why it looks colourless?

UV-Vis is a useful technique and is especially useful for things that are colourful. A common thing to do with it is to calculate the absorptivity (ϵ) of a molecule using the Beer-Lambert law. Let's do an example:

Calculating Absorptivity

A UV-Vis spectrum of a 0.02 mol dm^{-3} solution of Lycopene was measured in a cuvette of length 1 mm. At 650 nm, the intensity of the incident light was 1 W cm^{-2}, and the intensity of the transmitted light was measured to be 0.015 W cm^{-2}.

What is the molar absorptivity of lycopene at 650nm?

We will go through the working in the lecture, but you should find that ϵ =2100 mol^{-1} dm^{3} cm^{-1}.

One complication with UV-Vis is that it can be difficult to determine if our measured 'absorption' is entirely due to absorption, or if there is some contribution from scattered light too (cloudy solutions or solutions containing small particles can scatter, rather than absorb, light). Obviously if our solution scatters light, then we would pick that up as if it was an absorption in our spectrometer. You'll see this in the teaching labs - but its useful to be aware of it.

11.2 IR Spectroscopy

Infrared (IR) spectroscopy uses infrared light with a wavelength of around 2500-10 000 nm, which corresponds to an energy of around 1000-4000 cm^{-1}. This is a much smaller energy spacing than is probed by UV-Vis, so we are no longer probing electronic states with this energy. IR spectroscopy is instead used to probe **molecular vibrations**. Molecules vibrate in a few different ways, the most common types are **stretching** and **bending** vibrations. **Stretching** is where the bond lengths in the molecule change, and **bending** is where bond angles change. Some common vibrations are shown in Figure 11.5.

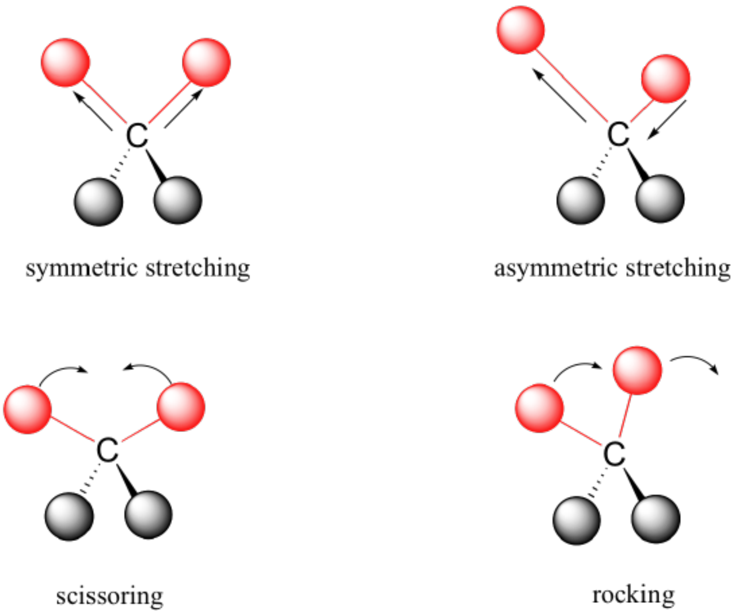

Figure 11.5: Stretching (top row) and bending (bottom row) vibrations in molecules. Figure from chem.libretexts.org

How does this stretching/bending result in the two states that we need for spectroscopy? Well, like any kind of molecular motion, the energies of the different vibrations are **quantised**. The maths behind this gets a bit tricky but you'll see it next year, and for now I'll try and convince you with some hand-wavy arguments. Remember when we saw the standing waves on a vibrating string - and how only some of the vibrational frequencies gave rise to a standing wave? Molecules behave in the same way, and each type of molecular vibration has a **fundamental frequency** that it vibrates at, and when the frequency of the IR light matches this fundamental frequency, the molecule starts to vibrate. So, our two levels are a **vibrational ground state** and a **vibrationally excited state**. You can think of the molecule absorbing the photon and thus starting to vibrate. We call the different vibrations **vibrational modes**, like how we have different **modes** of vibration in our string. Water has a few different vibrational modes with different energies, shown in Figure 11.6.

Different bonds all have different vibrational frequencies, and actually even if we just restrict ourselves to thinking about bond stretches, there are loads of different things we can detect in an IR spectrum. The frequency of a bond stretch can depend a lot on the rest of the molecule that the bond is in, and this is what makes IR such a useful technique. We can also work out

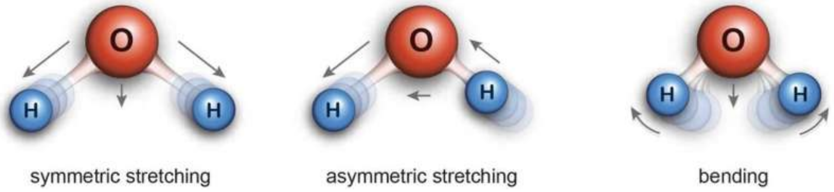

Figure 11.6: Three vibrations in the water molecule. The two stretches have higher frequencies (symmetric 3652 cm^{-1} and asymmetric 3756 cm^{-1}), while the bend has a lower frequency (1595 cm^{-1}). Note that the dipole moment of the molecule will change during all these vibrations. Image credit: Adzio Holtorp, VU Amsterdam.

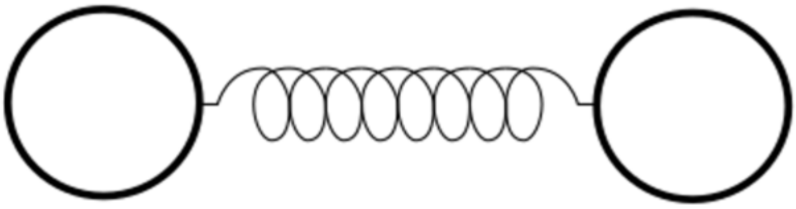

Figure 11.7: Simple model of a chemical bond - two weights at each end of a spring.

how many vibrational modes we expect to see in a given molecule, if N is the number of atoms in the molecule:

- For a linear molecule, there are $3N - 5$ vibrational modes.
- For a non-linear molecule, there are $3N - 6$ vibrational modes.

You can rationalise this result by thinking about something called the **degrees of freedom** in a molecule. We won't go into huge depth now, as you'll cover it again later - but think of a degree of freedom as *a place you can put energy*. An atom has 3 degrees of freedom - one for each dimension it moves in. A molecule containing N atoms therefore has $3N$ degrees of freedom. Three of these are associated with moving the molecule around in space (one for each dimension), and either two (for a linear molecule) or three (for a non-linear molecule) are associated with rotating the molecule in space. All the rest are associated with vibrations. Can you see where the formulae above come from?

How many vibrational modes should we expect for water? Does the result match up with what we saw above?

11.2.1 Vibrational Frequencies

A good way to think about a chemical bond is a spring with two weights at each end to represent the atoms. Imagine pulling it apart, letting it go, and watching it vibrate. If the spring is very weak, or the atoms are very heavy, then it will vibrate quite slowly. Conversely, if the atoms are light, and the spring is very stiff, then it will vibrate faster. A **slow vibration** corresponds to **low vibrational frequency** which corresponds to **low energy**. Conversely, a **fast vibration** corresponds to **high vibrational frequency** which corresponds to **high energy**. The stiffness of the spring corresponds to bond strength (stronger bonds are stiffer springs), so we can say:

- Stronger bonds produce higher vibrational frequencies.
- Lighter atoms produce higher vibrational frequencies.

And vice versa. Lots of different bonds give rise to different IR stretching/bending frequencies - normally a bending vibration has lower frequency than a stretching vibration. You might come across tables of different IR frequencies like the one from Wiki in Figure 11.8.

C=O	aldehyde/ketone	saturated aliph./cyclic 6-membered	1720	
		α,β-unsaturated	1685	
		aromatic ketones	1685	
		cyclic 5-membered	1750	
		cyclic 4-membered	1775	
		aldehydes	1725	influenced by conjugation (as with ketones)
	carboxylic acids/derivates	saturated carboxylic acids	1710	
		unsat./aromatic carb. acids	1680–1690	
		esters and lactones	1735	influenced by conjugation and ring size (as with ketones)
		anhydrides	1760	
			1820	
		acyl halides	1800	
		amides	1650	associated amides
		carboxylates (salts)	1550–1610	
		amino acid zwitterions	1550–1610	
O–H	alcohols, phenols	low concentration	3610–3670	
		high concentration	3200–3400	broad
	carboxylic acids	low concentration	3500–3560	
		high concentration	3000	broad
N–H	primary amines	any	3400–3500	strong
			1560–1640	strong
	secondary amines	any	>3000	weak to medium
	ammonium ions	any	2400–3200	multiple broad peaks
C–O	alcohols	primary	1040–1060	strong, broad
		secondary	~1100	strong
		tertiary	1150–1200	medium
	phenols	any	1200	
	ethers	aliphatic	1120	
		aromatic	1220–1260	
	carboxylic acids	any	1250–1300	
	esters	any	1100–1300	two bands (distinct from ketones, which do not possess a C–O bond)

Figure 11.8: IR frequency table (from Wikipedia). These are useful when assigning IR spectra.

So, we can see that IR and UV-Vis spectroscopy tell us a lot about molecular structure. But how do you practically measure this stuff? What does the spectrometer look like?

11.3 Spectrometer Design

Spectrometers are all a bit different, and there are lots of different designs. However, they all have some features in common:

- A source of light (IR, or UV-Vis, or even Radio waves (NMR)).
- A way of separating the light into different energies.
- A way of detecting the absorbed light.

We won't go into that much detail now, but you'll get used to seeing this (and you'll build a UV-Vis spectrometer out of Lego in the teaching labs next year). Let's look at a typical spectrometer now, in Figure 11.9, so we understand the basic idea.

The first thing we have is some kind of **light source**, which could be a white LED (for UV-Vis) or an infrared glow lamp (for IR). We then direct this light onto our sample, where some of it gets absorbed. The light is then passed through some kind of **dispersive element** that splits

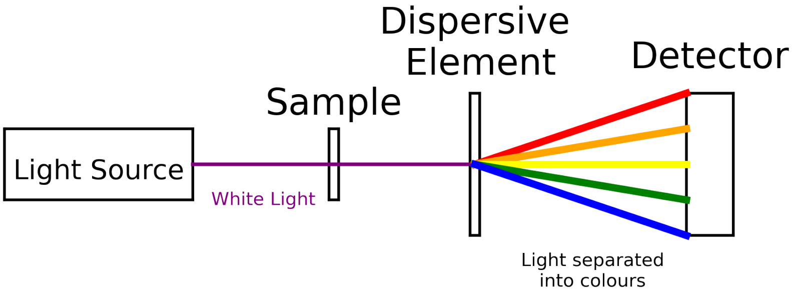

Figure 11.9: A simplified generic spectrometer. Key components are a light source, a place to put a sample, some kind of dispersive element (to split the light into different frequency (energy) components), and a detector.

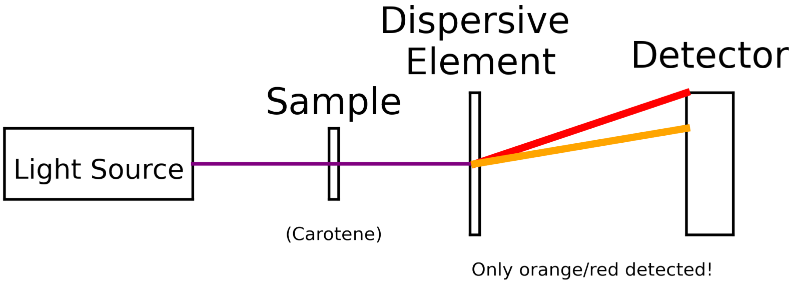

Figure 11.10: Measuring the spectrum of carotene - the yellow, blue, and green parts of the white light are absorbed, leaving only the red and orange parts to be detected.

it up into its different energies (colours) - the light from our source consists of many different colours and we need to separate them out to actually make a useful spectrum. This dispersive element could be something like a prism, or a diffraction grating.

We then direct our dispersed light onto some kind of detector - this could be something that's a lot like a webcam, for UV-Vis. For IR you need a more specialised detector, but the principles are the same[1]. This detector then produces a spectrum. What would happen if we put β-carotene from earlier into this sample holder...

I think it's important that, as inquisitive young scientists, you don't look at things like NMR/IR/UV-Vis spectrometers as incomprehensible black boxes that just spit you out a spectrum. What happens underneath the bonnet of those things is often not very complex, and by understanding it you:

1. Understand its limitations.
2. Might be able to fix it when it breaks.

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[1] Modern IR spectrometers work a bit differently to this, but the principle is similar.

3. Get a better understanding of the data it gives you.

The first point is very important - a disappointingly large amount of chemists probably couldn't tell you how an NMR spectrometer works, even if they use one every day! This ends up with people not realising the limitations of their instrument - and sometimes making big errors in their data analysis as a result.

This marks the end of our time talking about quantum mechanics and spectroscopy (at least for this year). Next time, we will talk about **chemical reactions**. More exciting? Maybe for some :)

Take Home Messages

- UV-Vis spectroscopy probes electronic states of molecules.
- IR spectroscopy probes vibrational states of molecules.
- Spectrometers essentially consist of a box containing a light source, a dispersive element, and a detector.

Lecture 12

Chemical Reactions and Equilibrium

Today we are going to talk about **chemical reactions** for the first time, having spent most of our time up until now talking about the structure/behaviour of single atoms and molecules. *Why chemical reactions happen* is a big question, and an excellent book has been written about it by James Keeler, which I'd recommend reading. A concept that lies at the heart of understanding chemical reactions is the idea of **chemical equilibrium**, which is what we will talk about today.

Lecture Aims

- To understand chemical equilibrium.
- To start to understand equilibrium constants.
- To understand and apply Le Chatelier's Principle.

12.1 Chemical Equilibrium

Let's imagine a chemical reaction. I am a physical chemist, so I don't like to think about actual molecules unless I really have to. Hence we are going to think about the following reaction:

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$$

A, B, C, and D could be anything we want them to be - the discussion we are going to have today doesn't care what the molecules are.

We wrote this reaction with a single arrow ($\longrightarrow$). A single arrow means that this reaction **goes to completion**, in other words, basically all the reactants (A and B) turn into products (C and D). An example would be salt dissolving in water - pretty much all the salt will dissolve. However, note that I said *basically* all the reactants. This is because in reality every chemical reaction exists as an **equilibrium.** There is always some balance between reactants and products, even if the balance is more or less 100% in favour of the products. When the reaction is **complete**, the amounts of the reactants and products no longer change with time, and the reaction is said to be **at equilibrium**.

Some reactions don't go to 100% to products when they are complete, and they are left with a mixture of reactants and products. We represent these reactions with a double-sided equilibrium arrow ($\rightleftharpoons$), like so:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$$

The use of this arrow makes it clear that the reaction ends up with a significant amount of reactant left at equilibrium, so that chemists know not to expect the reaction to produce 100%

product. An example of this would be the equilibrium between an alcohol and its vapour, we can smell the vapour above the liquid, but there is still a lot of liquid, and we have an equilibrium between the two phases.

The point at which the reaction stops and the amounts of reactant and product no longer change with time is called the **position of equilibrium**. Sometimes you also see arrows like $\ce{A <=>> B}$ and $\ce{A <<=> B}$, which mean that the position of equilibrium lies far to one side of the reaction (but not so far that the reaction essentially goes 100% in one direction). Today we will see how we can measure and manipulate the position of equilibrium of chemical reactions.

12.1.1 Dynamic Equilibrium

When we draw that double headed arrow, it implies that there are two reactions occurring, one forward ($\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$) and one reverse ($\mathrm{C} + \mathrm{D} \longrightarrow \mathrm{A} + \mathrm{B}$). This is exactly what is happening - we have these two competing reactions, that each want to push the equilibrium in opposite directions. If the forward reaction is faster than the reverse reaction, then the products are formed faster than they turn back into reactants, and the equilibrium moves towards the products. Conversely, if the reverse reaction is faster than the forward reaction, then the products turn back into reactants faster than the reactants form products, and the equilibrium moves towards the reactants.

When the reaction is at equilibrium, the position of equilibrium doesn't change with time. This means that the **rates of both the forward and reverse reactions must be equal**. This is a key concept in chemical equilibria, and is called the idea of **dynamic equilibrium**. This is shown in Figure 12.1.

Dynamic equilibrium is important because it's not as if the forward and reverse reactions both stop once equilibrium is reached. Both reactions are still going on, just they have equal rates, and so reactants turn into products as fast as products turn back into reactants, so there's no observable change to the position of equilibrium. Think of it like cars driving between two cities, Leicester and Nottingham:

- If more cars leave Leicester for Nottingham each hour than arrive from Nottingham, then there is a net movement of cars leaving Leicester, and the number of cars in Leicester decreases.
- If more cars arrive into Leicester from Nottingham each hour than leave, then there is a net movement of cars into Leicester, and the number of cars in Leicester increases.
- If the same number of cars leave Leicester for Nottingham each hour as arrive to Leicester from Nottingham, then the number of cars in both Leicester and Nottingham stays the same. This is **dynamic equilibrium** - the cars are still moving, but there is no net change.

Once a reaction has reached equilibrium, there is **no more observable change to the concentrations/amounts of products or reactants**. This is a key concept.

Chemical Equilibrium

- All chemical reactions end with some **equilibrium** between the reactants and products.
- **Equilibrium** occurs when the rates of the forward and reverse reactions are equal.
- Equilibrium is **dynamic**, the forward and reverse reactions do not stop at equilibrium!

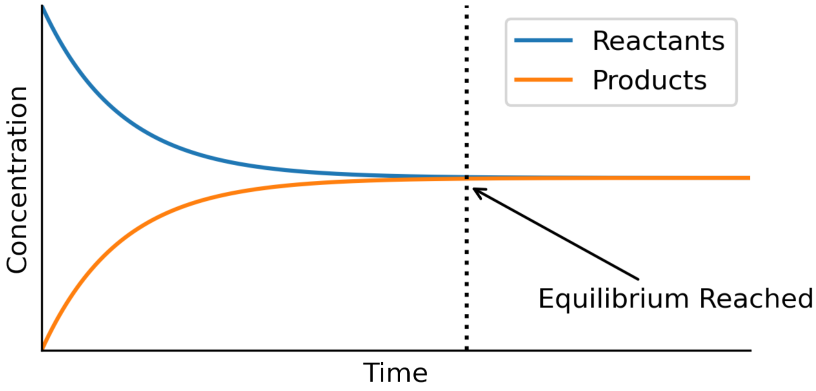

Figure 12.1: How the concentrations of reactants (blue) and products (orange) changes with time Equilibrium is reached at the dashed line, when there is no more observable change to the concentrations of either reactants or products.

12.2 Equilibrium Constants

So, if we can tell when a reaction has reached equilibrium, how do we know **where** the position of equilibrium is? We need a number that we can relate to the position of equilibrium so we can compare between different reactions, right? This number is called the **equilibrium constant**, K. Let's think about what would be a natural way to define the equilibrium constant, starting with our favourite equilibrium reaction:

$$\mathrm{A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D}$$

Where I have added two **rate constants** above and below the arrow that refer to the rates of the forward (k_1) and reverse (k_{-1}) reactions, respectively. As you will learn more thoroughly next semester in CH1203, the **rate** of a chemical reaction is given by:

$$\text{Rate} = k[\text{Reactants}]$$

Where k is the rate constant and the square brackets denote a concentration. We can then define the rates of our forward and reverse reactions:

$$\text{Rate Forward} = k_1[A][B]$$

and:

$$\text{Rate Reverse} = k_{-1}[C][D]$$

At equilibrium, these rates are the same, so we can say that:

$$k_1[A][B] = k_{-1}[C][D]$$

The equilibrium constant, K, is then given by:

$$K = \frac{k_1}{k_{-1}} = \frac{[C][D]}{[A][B]} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

To understand the meaning of the **equilibrium constant**, think about what happens in some differenet cases. For example, it will be a big number if we have more products than reactants, and a small number if we have more reactants than products. If we have an equal number of reactants and products, then it will be 1. The equilibrium constant is **never negative**, and is

dimensionless (it has no units)[1]. We have a final technicality to worry about though - how do we deal with a reaction like this:

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

Where we have stoichiometric coefficients in front of the reactants and products? I'll leave it as an exercise to you to show that for this reaction, K is given by:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

An equilibrium constant is, by definition, calculated on a system **at equilibrium**. We could, however, calculate a similar quantity when the reaction is not at equilibrium. This quantity is called the **reaction quotient**, Q:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \quad \text{When not at equilibrium!}$$

You can use the reaction quotient as a way to track the progress of a reaction, which you'll learn about more later on. When $Q = K$, then the reaction is **at equilibrium**, otherwise it is not, and we can tell in which direction the reaction is going to go by looking at the difference between Q and K - if Q is smaller than K, then the reaction needs to produce more products to increase Q until $Q = K$, and vice versa.

12.2.1 Beyond Solutions

The symbol K refers to a generic equilibrium constant, but sometimes we have reactions that occur in different phases. There are conventions here, and sometimes you will see the equilibrium constant written as K_c for reactions in solution (expressed using concentrations). Other times we will encounter reactions that happen in the gas phase, and then we define it in terms of **partial pressures** of the reactants/products instead of concentrations. The partial pressure of a component is the gas-phase analogue of concentration. In this case, the equilibrium constant is called K_p (p for pressure, innit).

For the reaction:

$$\mathrm{aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)}$$

Where each component A has a partial pressure, p_A, and so on, we define K_p as:

$$K_p = \frac{(\frac{p_C}{p^\circ})^c(\frac{p_D}{p^\circ})^d}{(\frac{p_A}{p^\circ})^a(\frac{p_B}{p^\circ})^b}$$

Where we have also defined the **standard pressure**, p°, which is equal to 1×10^5 Pa (roughly one atmosphere). We have to include this to make sure that our final equilibrium constant, K_p, is dimensionless. **Equilibrium constants must always be dimensionless!**

We can relate K_c and K_p using the ideal gas equation ($pV = nRT$), by noting that concentration, c, is moles divided by volume, and so:

$$c = \frac{n}{V} = \frac{p}{RT}$$

Thus, we can easily relate partial pressure (p) to concentration (c). You can show that the two equilibrium constants are related by:

$$K_p = K_c(RT)^{\Delta n}$$

I will leave the proof of this as an exercise for you.

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[1] Even if you have a reaction like $\mathrm{A + B \longrightarrow C}$, because strictly you express the concentrations as a ratio of a concentration to a standard concentration, each concentration is unitless. In fact, in general, the equilibrium constant is defined as a ratio of *thermodynamic activities* instead of concentrations, but this is a story for later...

12.3 Affecting Equilibrium

Ok, so we know what equilibrium is about. But how do we affect the position of equilibrium? We have a few controls we can play with to do this:

- Changing concentrations of reactants/products (if solutions).
- Changing the pressures of reactants/products (if gases).
- Changing the temperature of the reaction.

Le Chatelier's Principle tells us how the equilibrium will change if we change some of the reaction conditions. The principle states:

> When an external change is made to a system in dynamic equilibrium, the system responds to minimise the effect of the change.

What does this mean?

- If we heat the reaction up, it will try to cool itself down.
- If we increase the concentration of a reactant, it will try and decrease the concentration of that reactant.
- If we increase the pressure of the reaction, it will try to decrease that pressure.

You can think of it as follows. The reaction at equilibrium is like a ball that has rolled into the bottom of a valley. It is happy and stable. You changing some external condition pushed it back up the hill, and the reaction wants to get back to equilibrium by rolling down, so will try and reverse the change you made to it.

The classic example of this is **the Haber process**. We do seem to talk a lot about these weird old men from the 1800s, but most of us are probably alive today thanks to the Haber process, so maybe it's justified in this case. The Haber process (or Haber-Bosch process) is a way to synthesise ammonia (NH_3) that was developed by Fritz Haber - a German chemist. Ammonia is needed to make fertiliser, and food production using fertilisers made using the Haber process accounts for about 2/3 of the world's food production, and supports almost **half** of the population of the earth. Don't let anyone tell you chemistry isn't important! However, Fritz Haber also spent quite a lot of time developing chemical weapons (like the chlorine gas shells used in the first world war), so let's not pretend that he isn't a complex character. The fact remains that he had a very large impact on world history, for good or evil.

The Haber process is:

$$N_2(g) + 3\,H_2(g) \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} 2\,NH_3(g)$$

The forward reaction (making ammonia) is exothermic, so produces heat. The reverse reaction is therefore endothermic, taking in heat. We can also see that the reactant side of the equation has more moles of gas (4) than the product side (2). So let's think about what would happen if we changed the temperature, pressure, and amount of reactant/product.

- Heating up the reaction:

  - Adding heat means under LCP, the reaction wants to cool down, so it will favour the reverse (endothermic) process.
- Cooling the reaction:
  - Under LCP, the reaction wants to heat up, so will favour the forward (exothermic) process.
- Increasing the pressure:
  - Increasing pressure means that the reaction wants to minimise the pressure by LCP, so the forward reaction (producing less moles of gas) is favoured.
- Decreasing the pressure:
  - Decreasing pressure means the reaction wants to increase the pressure, so reverse reaction is favoured.
- Removing reaction products:
  - The reaction wants to minimise this change under LCP, so will create more products.

So we can see that to favour the forward reaction as much as possible, we want:

- Low temperature.
- High pressure.
- To keep removing ammonia as it's formed.

So this is what they do in the Haber process! However, this only tell us about the **thermodynamics** of the reaction (where the equilibrium will eventually get to), but tells us nothing about the **kinetics** of the reaction (how fast it will get to the equilibrium). If you cooled the reaction down so much that the forward reaction was really favoured, it would shift the position of equilibrium, but would mean the reaction goes so slowly that you might never get there! This balance between **thermodynamics** (where you get to) and **kinetics** (how fast you get there) is crucial in chemistry.

On this note, it is worth mentioning **catalysts**. A catalyst is something that makes a reaction go faster (in the Haber process, they use an iron catalyst). However, **a catalyst makes both the forward and reverse reaction go faster, so has no effect on the position of equilibrium**. This is important to remember - catalysts don't affect equilibrium constants!

Next time, we will talk about a classic use of equilibria in chemistry, when talking about **acids and bases**.

Take Home Messages

- Dynamic equilibrium is reached when the rates of forward and reverse reactions are equal.
- Equilibrium constants quantify the position of equilibrium, and are dimensionless.
- Le Chatelier's Principle tells us how we can affect the position of equilibrium by altering reaction conditions.

Lecture 13

Acids and Bases

> There are three types of chemical reactions. Proton transfers; electron transfers; and the rest.

The above quote might be slightly flippant, but illustrates an important point. Most chemical reactions involve either transfer of protons or electrons, and having an understanding of which molecules can donate/accept electrons or protons to other molecules is therefore an important thing to have.

Acids and **bases** are two classes of molecule which can act as proton donors/electron acceptors (acids) or proton acceptors/electron donors (bases). A good understanding of acids and bases is therefore essential for chemists. In this lecture, I'm going to do the intellectual equivalent of throwing a load of stuff at you. The idea is just that you can get exposed to these concepts for a first time, as you'll see them over and over in your degree.

Lecture Aims

- To understand the Brønsted and Lewis definitions of acids and bases.
- To understand pH and pK_a.
- To understand buffer solutions.

13.1 Definitions

Two definitions of acids and bases are commonly used in chemistry[1]. These are the **Brønsted** (or **Brønsted-Lowry**) definition, and the **Lewis** definition.

13.1.1 Lewis Definition

The **Lewis** definition states that:

- **Acids** are **electron pair acceptors**.
- **Bases** are **electron pair donors**.

An example of a Lewis acid is boron trifluoride, BF_3. The central boron atom has an empty orbital that it can accept an electron pair into. An example of a Lewis base is ammonia, NH_3.

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[1] There are others too, but these will do for now.

Ammonia and boron trifluoride would react together as follows:

$$BF_3 + NH_3 \rightleftharpoons H_3N \longrightarrow BF_3$$

Here ammonia is donating an electron pair to boron trifluoride, resulting in the creation of a dative covalent bond. We're not going to talk much more about Lewis acids today, but a lot of the discussion we will have relates to both kinds of acids.

13.1.2 Brønsted Definition

The **Brønsted** definition states that:

- **Acids** are **proton donors**.
- **Bases** are **proton acceptors**.

Remember that a proton is just an H^+ ion. An example of a Brønsted acid is hydrochloric acid (HCl)

$$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

In this equation, HCl is acting as a Brønsted acid (donating a proton), and H_2O is acting as a Brønsted base (accepting a proton). We then define H_3O^+ as the **conjugate acid** of H_2O (i.e. what you get when you add a proton to the base), and Cl^- as the **conjugate base** of HCl (what you get when you remove a proton from the acid). An acid-base reaction is just a **proton transfer reaction** under this definition. Lots of the acids you are very familiar with are Brønsted acids.

Ammonia is an example of a Brønsted base, because it can accept a proton:

$$HCl(aq) + NH_3(aq) \rightleftharpoons {NH_4}^+(aq) + Cl^-(aq)$$

In this equation, ${NH_4}^+$ is the conjugate acid of NH_3. Note that we also said ammonia is a Lewis base - these definitions are not mutually exclusive. In fact, they encompass each other. Lewis theory is a wider definition than Brønsted theory, and all Brønsted acids are Lewis acids, but not all Lewis acids are Brønsted acids (and the same is true for bases).

Water is an interesting case, in that it can act as either an acid or a base. Consider:

$$HF(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Here it is clearly acting as a base - accepting the proton from HF which is acting as an acid. However, what about this:

$$NH_3(g) + H_2O(l) \rightleftharpoons OH^-(aq) + {NH_4}^+(aq)$$

Here it is acting as an acid, donating the proton to NH_3 which is acting as a base. Water is an **amphoteric** molecule, meaning that it can be **either an acid or a base**, depending on what it is reacting with.

It's also important to understand the meaning of **conjugate acid** and **conjugate base** (defined above). What are the conjugate acids and bases in the two reactions above?

Generally speaking, the reaction is always doing something like this:

$$\text{Acid}_1 + \text{Base}_1 \rightleftharpoons \text{Conj Acid of Base}_1 + \text{Conj Base of Acid}_1$$

The reactions are also generally equilibria that don't lie at 100% completion.

Sometimes you will see reactions where it's not immediately obvious what the conjugate acids and bases are, because they are hidden within other compounds. For example:

$$\mathrm{HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)}$$

Here, clearly the acid is HCl and the base is NaOH (sodium hydroxide). The conjugate base of HCl is Cl^- and is tied up in the metal salt NaCl with sodium. Equally, the conjugate acid of NaOH is H_2O - the sodium ion doesn't really take part, and just serves to balance all the charges out (we call it a *spectator ion*, because it just watches and doesn't really do anything else). The key ionic reaction is:

$$\mathrm{H^+ + OH^- \rightleftharpoons H_2O}$$

It's important to be able to identify conjugate acids and conjugate bases. Let's take an example or two.

Conjugate Acids and Bases

Identify the conjugate acid-base pairs for the following reactions:

1. $\mathrm{CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)}$
2. $\mathrm{NH_3(aq) + HF(aq) \rightleftharpoons {NH_4}^+(aq) + F^-(aq)}$
3. $\mathrm{HBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Br^-(aq)}$

We will go through the working in the lecture, but you should find:

1. CN^- acts as base, and HCN is its conjugate acid. H_2O is acting an acid, and OH^- is its conjugate base.
2. NH_3 acts as base, and ${NH_4}^+$ is its conjugate acid. HF is acting an acid, and F^- is its conjugate base.
3. H_2O acts as base, and H_3O^+ is its conjugate acid. HBr is acting an acid, and Br^- is its conjugate base.

13.1.3 pH

You have almost definitely come across the concept of **pH** as a way of measuring acid strength. It measures the concentration of H^+ or H_3O^+ ions in solution, and if we know the concentration we can work out the pH:

$$\mathrm{pH} = -\log_{10}[H_3O^+]$$

Equally, if we know the pH, we can work out the concentration of ions:

$$[H_3O^+] = 10^{-pH}$$

The pH scale is **logarithmic**. If the pH of a solution decreases by 1, then there are 10 times more H^+ ions in that solution. Note also that low pH = high H^+ concentration = more acidic, and vice versa.

A solution with a pH of 7 is **neutral**, and neither acidic or basic. This comes from the concentration of H^+ ions in pure water at 298 K, which is $1 \times 10^{-7}\,\mathrm{mol\,dm^{-3}}$. Can you see why pure water has a pH of 7?

You can also define an equivalent thing for bases called the **pOH**, but nobody really ever bothers doing this. But for completeness:

$$\mathrm{pOH} = -\log_{10}[OH^-]$$

Then we can work out that:

$$[OH^-] = 10^{-pOH}$$

You can convert pH to pOH easily - we'll derive the equation in the lecture (or do it yourself!).

13.2 Strong and Weak

We can further classify acids and bases into **strong** or **weak** acids and bases. When we put an acid into water, it dissociates and makes protons (which make H_3O^+ ions - **hydronium ions**). There's an equilibrium set up between the undissociated acid (HA) and the dissociated acid $H^+ + A^-$:

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}$$

We can quantify how strong an acid is by looking at the **extent of the dissociation**. If an acid dissociates completely, so there's hardly an undissociated acid left, then we say it is a **strong acid**. If it doesn't dissociate much, then we say it is a **weak acid**. Some examples are as follows:

- Strong acids: HCl, H_2SO_4, H_3PO_4
- Weak acids: CH_3COOH, HF, HCOOH

Looking back at the equilibrium we set up, we might wonder if we can use the equilibrium constant of this equilibrium to tell us about acid strength. Let's call that equilibrium constant K_a (a for acid):

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

Where we ignore the pure water, as we said last lecture. This equilibrium constant, K_a is called the **acidity constant**. A large acidity constant implies that our acid dissociates completely and so is a strong acid.

The K_a value varies over a really wide range, like the H_3O^+ concentration before. In that case, we used the **pH** scale to make interpreting it easier. Ever adventurous, chemists came up with a similar scale for K_a called (you guessed it) the **pKa** scale.

$$\mathrm{pK}_a = -\log_{10} K_a$$

pKa is very useful in organic chemistry, and I'm not going to pretend to properly understand like some of those people do. But we can say that:

- Anything with a pKa less than zero is a **strong acid**.
- Anything with a pKa greater than zero is a **weak acid**.

An equivalent scale exists for bases, based on the equilibrium reaction of a base B and water:

$$\mathrm{B} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH^-} + \mathrm{BH}$$

We define something called the K_b (no prizes for guessing why):

$$K_b = \frac{[\mathrm{OH^-}][\mathrm{BH}]}{[\mathrm{B}]}$$

Thus, we can go the whole hog and also define the **pKb**:

$$\mathrm{pK}_b = -\log_{10} K_b$$

Again, low pK_a values are strong bases and vice versa. In my part of this course, I'll only ask you to do simple calculations on pK_a and pK_b - and will leave it to Kal and the organic gang to go further.

13.3 Buffer Solutions

A very common use of acids and bases is in **buffer solutions**. A buffer solution is a solution which resists changes in pH if you add acid or base to it. They're used very widely in chemistry, and especially in biological chemistry where you spend half your life making and degassing buffer solutions so that you can keep your proteins held at the right pH (or whatever they do). Anything biological is generally very sensitive to pH, so using buffer solutions is essential.

A generic buffer solution consists of a weak acid HA mixed with a salt of its conjugate base A^- (or a weak base mixed with a salt of its conjugate acid). Let's use the acidic buffer as an example. The equilibrium we set up is:

$$\mathrm{HA(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{A^-(aq)} + \mathrm{H_3O^+(aq)}$$

Note that we get the A^- from a salt - so we could have acetic acid (weak acid) and sodium acetate (the salt of the conjugate base). In this equilibrium:

- The acid is weak, so remains mostly undissociated.
- All of the A^- ions from the salt.
- The pH is determined by the concentration of H_3O^+.

Let's now think what happens if we add some strong acid or base.

- If we add some strong acid (H_3O^+):
  - The excess of A^- ions from the salt neutralise the added H_3O^+ ions.
  - This prevents the added H_3O^+ from lowering the pH.
- If we add some strong base (OH^-):
  - The H_3O^+ ions already present neutralise the added OH^-.
  - The undissociated HA dissociates to replace the lost H_3O^+, maintaining the pH.

Cool, isn't it? Obviously there is a limit to how well a buffer solution will work - it won't work if you add too much acid or base. The extent to which it can absorb added acid or base is called the **buffering capacity** of the buffer.

We can use an equation called the **Henderson-Hasselbalch Equation** to calculate the pH of buffer solutions:

$$\mathrm{pH} = \mathrm{pKa} + \log\left(\frac{[\text{Conj Base}]}{[\text{Acid}]}\right)$$

You can derive this equation quite easily actually, and we will do it in one of the problem sheets.

Take Home Messages

- We have two definitions of acids and bases: Brønsted, and Lewis.
- We use the quantities pH, pKa, and pKb to quantify the strength of acids and bases.
- Buffer solutions resist changes in pH. We can calculate the pH of a buffer solution using the Henderson-Hasselbalch equation.