Science by degrees

Atomic structure and the periodic table

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In this article, we hope to develop an understanding of atomic structure and the periodic table, from the beginning of secondary school/junior-high level, to first/second year undergraduate physics/chemistry, via one fictional conversation. We hope that people at any stage of that journey will find a section that speaks to them. We would love it if it turned out to be useful to teachers, too. It is not a history of discoveries about the atom; it is a conceptual, rather than historical, journey. It might be worth having a periodic table available while reading…!

SIGRID: I've been reading that everything is made of atoms, and that the types of atoms are shown in a diagram called the periodic table. It all seems a bit weird, so I want to know more. I've got a load of books, and I've ordered them by complexity, but I'm not sure I can just teach myself this stuff. Can you help?

SALLY: OK, I'll try. What do you know so far? For example, draw me an atom.

SIGRID: What do you mean, draw you one? It's like a ball. I'd just draw a circle.

SALLY: And what's the Periodic Table?

SIGRID: A list of different substances. But there are only about 100 in it. And I know there are loads more than 100 substances. Sugar, salt, wood, nitroglycerine... They're not in there.

SALLY: The periodic table (try the one from the Royal Society of Chemistry at http://www.rsc.org/periodic-table) only shows elements. Other substances are compounds, or mixtures of elements and/or compounds. A compound is two or more elements chemically combined in fixed proportions.

SIGRID: OK so you've explained compounds in terms of elements, but I don't know what an element is.

SALLY: In an element there's just the one kind of atom.

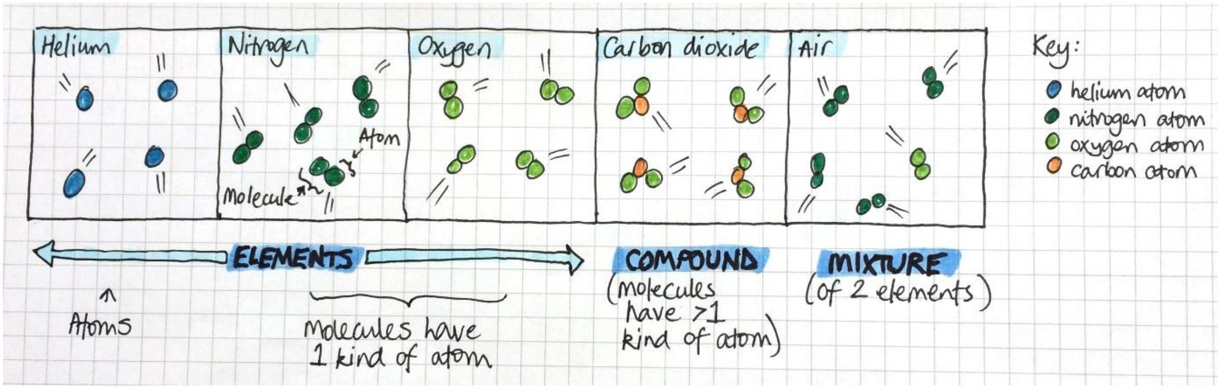
SIGRID: So there are different kinds of atom, one for each element?

SALLY: Yes, and compounds have more than one kind of atom, chemically combined, often into groups of atoms called molecules.

SIGRID: So are you saying that compounds are made of molecules? Because we talk about oxygen molecules and nitrogen molecules. And they're elements – look, I can see them in the Periodic table. Elements numbers 7 and 8.

SALLY: Good point! Molecules can form elements or compounds, just depending on whether the atoms are the same type or not. In fact I often use the word 'particle' to cover both atoms and molecules to get over that problem, unless the difference is important to what I am describing. This is potentially confusing, so why don't you find out about and draw the structures of helium, nitrogen, oxygen, carbon dioxide and air, to explain all these terms.

SIGRID: OK, here goes.



Here's my picture. The first three are in the periodic table because they only have one kind of atom each (and the fact the second and third are grouped into molecules doesn't matter). The fourth one is a compound and the fifth is a mixture, so they are not in the Periodic Table.

SALLY: Exactly. And that's why you won't find sugar, salt and the others in your list in the periodic table. The periodic table is just reserved for elements.

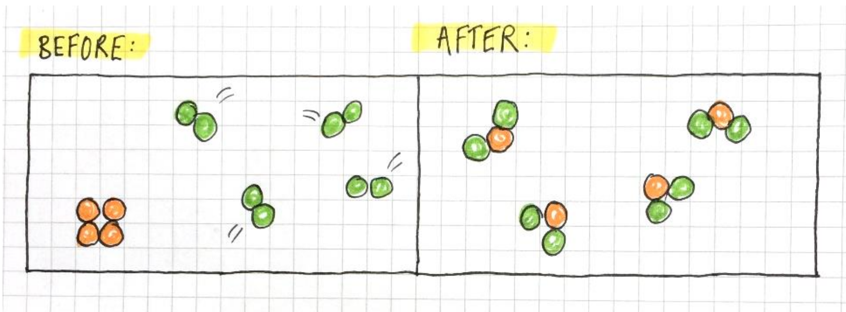
SIGRID: One kind of atom...

SALLY: Yep.

SIGRID: In the pictures of molecules, the atoms are joined together. How does that work?

SALLY: Ah, that's called chemical bonding, and we'll have another conversation after this one to cover that. But we'll need to have this discussion about atomic structure and the periodic table first. For now it's enough to know that chemical reactions involve a rearrangement of atoms, but there are still the same number of atoms, and of the same elements, before and after a chemical reaction.

SIGRID: So if we burn carbon completely in oxygen to make carbon dioxide, a picture might look like this, and there are the same number of dots of each colour before and after.



SALLY: Precisely. That's pretty much how Dalton got his ideas of atoms in the first place. In the reaction you mentioned, 3 g of carbon will always react with 8 g of oxygen to make 11 g of CO_2. Those fixed ratios make perfect sense when you consider that it is all to do with rearranging dots like in your picture.

SIGRID: OK, that all makes sense, but I don't think I can learn about 100 different types of atom.

SALLY: You don't have to.

SIGRID: How come?

SALLY: Can you spell 100 words?

SIGRID: Yeah, of course. Thousands maybe. Don't be silly.

SALLY: And how is that possible?

SIGRID: Well, the words are made of letters and there are only 26 of those.

SALLY: And atoms are made of other things, like words are made of letters. But atoms are much easier. There are only 3 things they are made of instead of 26. They also follow patterns and rules, which will help you work things out when you can't remember them.

SIGRID: What do you mean, 'they are made of other things'. In this book it says that an atom is the smallest part of an element that can exist.

SALLY: Yes – just as molecules are made of atoms, so too atoms are made of other things. Let's cut to the chase and call them protons, neutrons and electrons. What your book is saying is that atoms of, say, lithium, neon, gold and uranium are all different, but a proton in a lithium atom is identical to a proton in a neon atom; an electron in a gold atom is identical to an electron in a uranium atom.

SIGRID: So you don't have a lithium proton and a neon proton.

SALLY: Exactly – protons are protons. What makes a lithium atom different from a neon atom is the *number* of protons, neutrons and electrons in the atom. Specifically the protons actually. What makes lithium lithium is that its atoms have three protons.

SIGRID: Every single one?

SALLY: Every one.

SIGRID: But there must be trillions of atoms of lithium in the universe. They can't all have three protons.

SALLY: They do! Because an atom that doesn't isn't lithium! That's what *makes* it lithium. We could call it 'the-element-with-three-protons-in-its-atoms' but that's not as catchy.

SIGRID: OK, we're arguing about protons, neutrons and electrons, and I don't even know what they are.

SALLY: They are particles that make up atoms.

SIGRID: Hang on, you said that atoms and molecules were both particles. I let that go, but I didn't like it much, because we had particles being made of particles. Now we have particles being made of particles that are made of particles. Why don't you just invent a word that means what it says?!?

SALLY: Fair point. I guess we use the word 'particle' as it suits us. It sort of just means 'a useful bit of matter on whatever scale we are talking about'. So if we are looking at gas pressures, we might talk about atoms and/or molecules as particles, because they are the things whizzing round and doing the stuff that we are interested in.

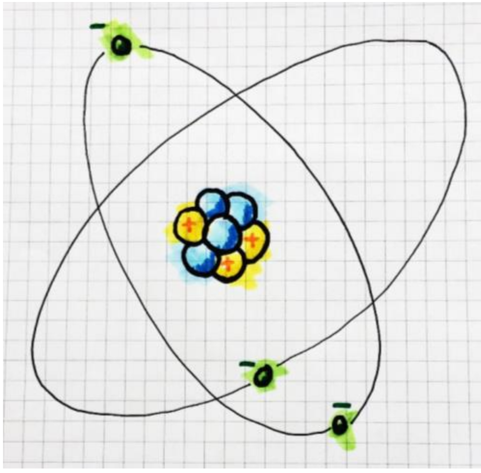
SIGRID: Whereas for our new understanding of the atom, we are looking one layer deeper, so the protons, neutrons and electrons are the 'particles' of interest.

SALLY: Exactly. How it was discovered they even exist, let alone make up atoms, is a huge story for another conversation. You'll just have to accept their existence for now.

SIGRID: Hmm. I suppose.

SALLY: Now, to apply this abstract knowledge of forces to the atom, it would be helpful to have a picture of an atom that's one layer deeper, as you describe it, than the picture of an atom as an indivisible sphere.

SIGRID: Yeah, there's one in this book. The protons and neutrons form a central part, called the nucleus, and the electrons seem to orbit it, like the planets orbit the Sun.



SALLY: Right, and if you asked a member of the public to draw an atom, that's probably what they would give you. We are going to get more sophisticated eventually, but this is a really useful stopping off point. Just bear in mind that this diagram can't be drawn accurately – to make it to scale, with the nucleus that size, you would need a piece of paper the size of a swimming pool to fit the electrons on.

SIGRID: But that means an atom is mainly empty space!

SALLY: Crazy, eh? And since you are made of atoms, you also are mainly empty space!

SIGRID: Now, look - there's also a table in all of the books I have found. It gives the masses and charges of the protons, neutrons and electrons.

	Proton	Neutron	Electron
CHARGE (relative to proton)	+1	0	-1
MASS – approximate (in atomic mass units)	1	1	So close to 0 that we often don't worry about it
MASS – accurate (in atomic mass units)	1.007 28	1.008 66	0.000 55

Does the last picture and the table mean that protons are yellow?

SALLY: NO! A proton is *not* yellow! It's not *any* colour. They are too small to even have a colour because they are way smaller than the wavelength of light. But people like to draw pretty pictures, and in the future some idiots are going to put this conversation on their website, so we are just matching their colour scheme…

SIGRID: And do we worry about the accurate masses?

SALLY: Probably not for this conversation –the proton and neutron masses are so similar that we'll imagine they are the same, and the electron mass is a lot, lot less than either of those. But it would be useful to bear in mind that the electron mass is not exactly zero (if it was, electrons would have to travel at the speed of light), and when you study radioactivity or particle physics, you will need to know the neutron has a mass slightly greater than the proton.

SIGRID: I have to say, the table still doesn't really help me feel like I've got to know these things very well.

SALLY: Really? Let's try something else first. How would you describe how people are different?

SIGRID: Well, there are loads of ways. They have different likes and dislikes. They look different. Some are taller, some shorter. They have different skin colours. Different genders. Some are calm, some irritable. Some kind, some mean.

SALLY: Exactly. People are complicated. Particles aren't. There is a very limited number of ways that protons, neutrons and electrons can be different from one another. For now, mass and charge are going to be the two we concentrate on. But there really aren't all that many more...

SIGRID: And what does differing mass and charge do to how they behave? I mean, I know that the charge of an object tells you how much force it will experience in an electric field, and the mass tells you how much force it will experience in a gravitational field.

SALLY: That's a good comparison! But these things are too tiny for gravity to be important. So what else does the mass tell you?

SIGRID: Oh, how much it is accelerated by a force. Like the attraction and repulsion of charges, I guess.

SALLY: Yes! And these things are overwhelmingly in the grip of exactly those electrical forces.

SIGRID: The neutrons aren't. They can't be. They have no charge.

SALLY: True. They help to glue the nucleus together using something called the strong force, otherwise it would fly apart due to the electrostatic repulsion of the protons.

SIGRID: Because positives repel other positives.

SALLY: Yes, but the strong force is very short range, so the nucleus as a whole interacts with electrons via electrical forces. So going back to the mass/charge thing, what can you tell me now?

SIGRID: The electrons and nucleus will be attracting each other because one is positive and the other negative. And Newton's Third Law tells me that they will attract each other with equal forces. But the effect of those equal forces will be very different. An electron has a tiny mass, so it orbits the comparatively heavy nucleus, rather than the other way round. Just like the planets orbit the Sun, not the other way round.

SALLY: Exactly.

SIGRID: OK. So, it's the protons and neutrons that give the atom almost all its mass. And the protons that tell you which element it is. How do I know how many electrons there are?

SALLY: An atom is electrically neutral.

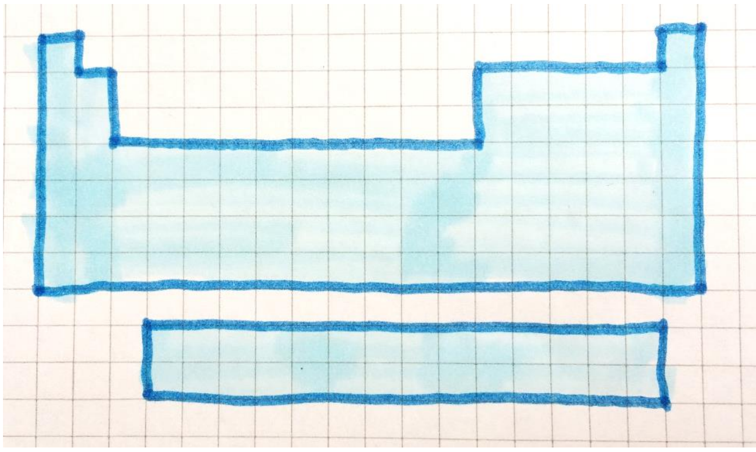
SIGRID: Oh. Protons and electrons have equal and opposite charge, so in an atom the number of electrons and protons must be equal so that the charges cancel out. And what's the point of electrons?

SALLY: Well, where do we start? I mean, whereas protons and neutrons give an atom almost all its *mass*, the electrons give it almost all its *size*. And the number of electrons also pretty much determines all its chemical properties.

SIGRID: So the number of protons determines what element it is, and the number of electrons matches it. The number of electrons determines the chemistry. Seems to me that electrons are more important – why don't *they* determine the element?

SALLY: Because atoms can lose or gain electrons to become ions, and then their number of electrons changes. But the ion is still an ion of the original element, because the protons are securely locked in the nucleus – and their number never changes. Well, unless it's radioactive, but that's a whole different conversation (or go here for a shortcut).

SIGRID: Oh OK, so in this book I have it says that the atomic number of an element, Z, is the number of protons. I guess that's what you've just told me. And I guess this has something to do with why the periodic table is this funny shape and not just a rectangle.

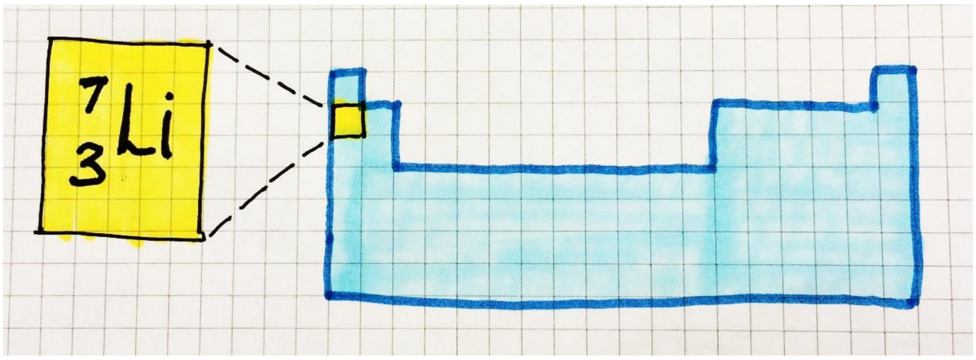


SALLY: Yes – in the periodic table the elements are arranged in order of atomic number (number of protons) from left to right, but the rows are arranged so that related elements are placed into columns.

SIGRID: But when Mendeleev made the periodic table protons, neutrons and electrons hadn't even been discovered yet.

SALLY: True, but there are two ways that elements can be related. One is that they have similar chemical properties. And *that*, Mendeleev *did* know about. To make the periodic table with only these experimental and empirical facts is an amazing achievement. The second way elements can be related is to have similar atomic structures, in terms of the way their electrons are arranged. And in fact they have similar chemical properties *because* their electron arrangements are similar.

SIGRID: OK. Now, in this periodic table, where it describes lithium as ${}^{7}_{3}\mathrm{Li}$, I get that Li is a shortcut for lithium...



SALLY: ...That's right, but they aren't always sensible like 'Li'. For example, 'Au' is gold.

SIGRID: Oh, OK. Well I suppose I'll just have to learn those then. So does lithium have 3 protons and 7 neutrons?

SALLY: No. You might think that. And the 3 is indeed the number of protons. But the 7 means the total of the protons and neutrons in the nucleus.

SIGRID: Which means the total is 7, and 3 of them are protons. So there must be 4 neutrons.

SALLY: Exactly.

SIGRID: But that's more conceptually complicated than just labelling it with the number of neutrons.

SALLY: More conceptually complicated maybe, but more useful. Have another look at your table of protons, neutrons and electrons, and tell me what the protons and neutrons have in common.

SIGRID: Oh, they both have one unit of mass, and together they pretty much account for the mass of atoms.

SALLY: And because normal stuff is made of atoms, they account for the mass of normal stuff. So if carbon is ${}^{12}_{6}C$ and oxygen is ${}^{16}_{8}O$, that means that an oxygen atom has 16 units of mass and a carbon atom has 12 units of mass. That number is called the mass number.

So does that mean that if you weigh oxygen and carbon out in the ratio of masses 16:12, the two lumps will have the same number of atoms?

SALLY: Yes! 16 g of oxygen has the same number of atoms as 12 g of carbon. 32 g of oxygen has twice as many atoms as 12 g of carbon. And that's useful to know if you are trying to burn carbon to make carbon dioxide, because every carbon atom needs 2 oxygen atoms, just like in your drawing earlier.

SIGRID: That means if you have 12 g of carbon, you would need 32 g of oxygen, so that neither element has any left over.

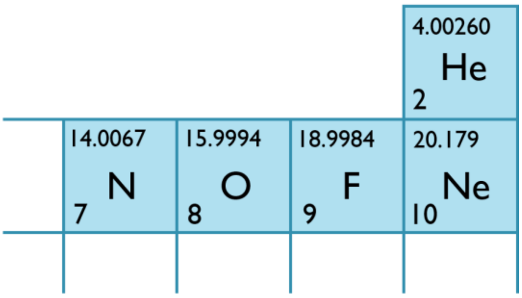
SALLY: Exactly.

SIGRID: And you can just scale it up or down. Because you probably don't have 12 g of carbon. If you had 3 g of carbon, that's one quarter the amount, so you would need 8 g of oxygen because it's one quarter of 32.

SALLY: Your career as a synthetic chemist awaits! So you see why it's more useful to display the top number as the mass number, rather than the number of neutrons.

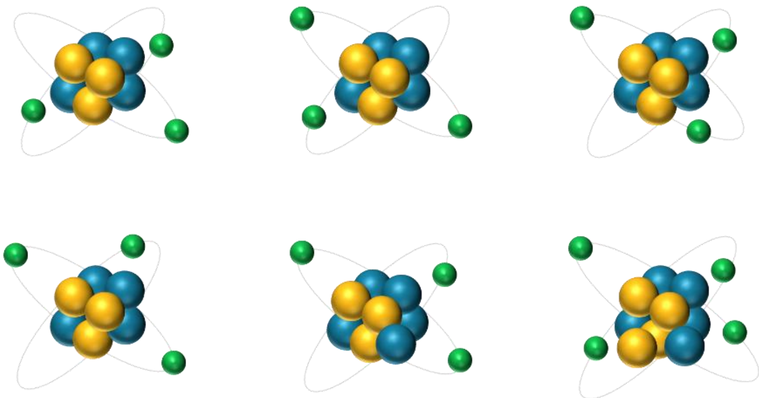
SIGRID: Yeah, it helps you weigh out the right amount of stuff. And we can always find the number of neutrons if we need to from the difference between the two numbers. So in a ${}^{19}_{9}\mathrm{F}$ atom, there are 9 protons, 9 electrons and 19 – 9 = 10 neutrons. So what's going on here? My periodic table gives ${}^{35.5}_{17}\mathrm{Cl}$, but you can't have 18 and a half neutrons. Can you?

SALLY: No, but actually that's the least of your worries. Look at this portion of a more sophisticated periodic table. None of the mass numbers are whole numbers!



SIGRID: Go on then. What's happening?

SALLY: Well, have a look at these pictures of six atoms, and tell me what you see.



SIGRID: OK. Five of them are lithium because they have three protons. And the bottom-right one is beryllium, because it has four protons.

SALLY: Good. Anything else?

SIGRID: One of the lithium atoms is different from the others because it has an extra neutron.

SALLY: Exactly – the one at bottom-centre. Forms of the same element with different numbers of neutrons are called isotopes. They do the same chemistry, because there is basically no difference in what their electrons are doing, but they vary in mass.

SIGRID: And in a ‘lump’ of an element there will be trillions of atoms and you might have more than one form, so that the top number is like an average of the mass numbers of all the atoms in the lump.

SALLY: Exactly. So the mass number describes a specific isotope, for example the ‘4’ for helium in your simpler periodic table. Whereas the ‘4.00260’ in my more sophisticated table describes the mixture of isotopes that actually exists, and is called the relative atomic mass.

SIGRID: Why didn’t my easier periodic table do that?

SALLY: I suppose it was probably trying to simplify things for you. It just picked the most common isotope, worked with that and ignored the others. I admit the chlorine thing is a bit confusing because they have used two isotopes for that, but I guess chlorine’s average is further from a whole number than most of the others, so they felt they had to.

SIGRID: In that case, does chlorine have an equal mixture of two isotopes with mass numbers 35 and 36?

SALLY: Well, that *would* work, but in fact the isotopes in question have mass numbers 35 and 37.

SIGRID: That means there must be more of the 35 than the 37, to make the average 35.5, which is closer to 35 than to 37.

SALLY: Exactly.

SIGRID: And going back to our new, improved periodic table, rather than saying that 32 g of oxygen reacts with 12 g of carbon, we can now say that 15.9994 g x 2 = 31.9988 g of oxygen reacts with 12.0111 g of carbon.

SALLY: Yes!

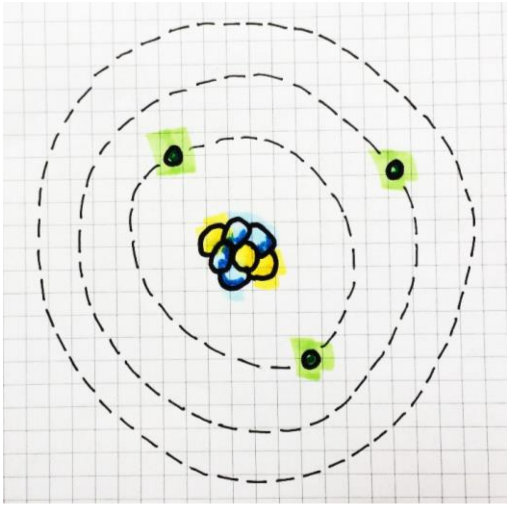
SIGRID: But what’s happening with hydrogen? If it is ^1_1H, then it has 1 proton and no neutrons.

SALLY: That’s right. It’s the simplest atom – just one proton with one electron ‘orbiting’. In the history of atomic theory the hydrogen atom was really important, because it’s often nice to try to solve the simplest example first, and then make adjustments for the harder cases. So in 1913 Niels’ Bohr came up with a theory of the hydrogen atom.

SIGRID: Why did he bother? I mean, don’t we already have a theory – one proton with one electron orbiting it?

SALLY: There was a theoretical problem and a conceptual one. The theoretical problem is that an orbiting electron must be accelerating (because all things moving in circles are changing their direction, hence changing their velocity, hence accelerating). And accelerating charges radiate electromagnetic energy. So electrons should, by right, radiate away their energy and spiral down the plughole of the nucleus, if you like, never to be seen again. Bohr suggested that electrons could only exist in discrete orbits, each at a particular distance from the nucleus. The greater the radius of the orbit, the higher the energy of the electron.

SIGRID: Oh, so that’s why I see pictures of atoms like this.



SALLY: Yes. To move an electron to a higher orbit requires an input of energy, maybe from absorbing a photon of light, or maybe from a collision with another atom.

SIGRID: What's a photon?

SALLY: Light exists in little particle-like packets of energy called photons. The energy of a photon is related to the wavelength of the light. When you read a book, there are countless photons travelling to your eyes (and everywhere else – the direction of your eyes isn't special), and your brain interprets the signal from all those discrete packets of energy as a coherent, continuous picture of the words on the page.

SIGRID: A bit like when you pour sand you get the impression of a single fluid rather than a collection of grains.

SALLY: Yes – quite like that.

SIGRID: What happens to the energy when the atom has absorbed it? Does it stay in the atom somehow?

SALLY: Generally, no. And what I'm about to say is one of the most important lessons of this whole tale... Have you ever heard of Sisyphus?

SIGRID: Yeah, Greek guy. What, *he's* the most important thing?

SALLY: No! He's an analogy for the important thing. I wish I hadn't mentioned him now. Anyway, too late – why is he famous?

SIGRID: Well, unless he's the guy who kept getting his liver eaten...

SALLY: He's not.

SIGRID: ...then he was condemned to push a boulder up a hill forever, and it kept falling back down again. What has this got to do with...? Oh, I see. Boulders spontaneously fall downhill, not uphill. To get a boulder to move uphill you need to put in some energy.

SALLY: And therein lies the message. *Spontaneous processes tend to occur so as to move to a state of lower energy*. The boulder has less potential energy at the bottom than at the top. The electron has less energy in the inner orbit than the outer orbit.

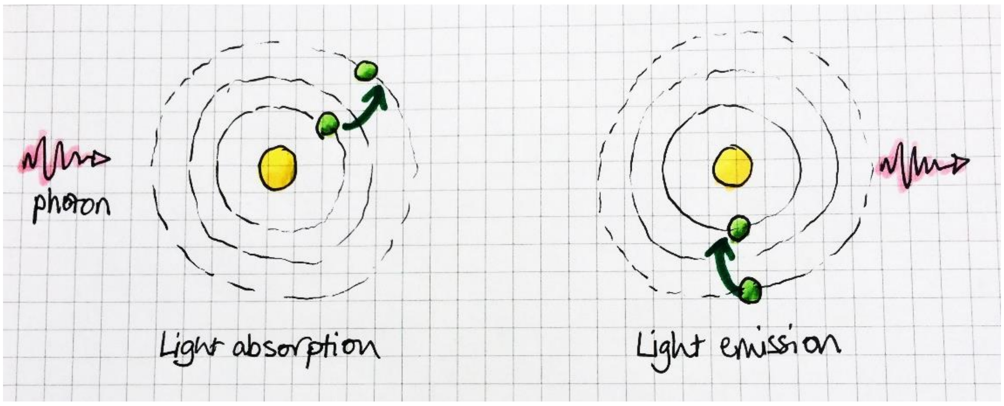
SIGRID: And so the electron spontaneously falls back down into the inner orbit. What happens to the energy?

SALLY: Well, how did we 'excite' the atom? In other words, how did we move the electron 'uphill' to a higher energy level?

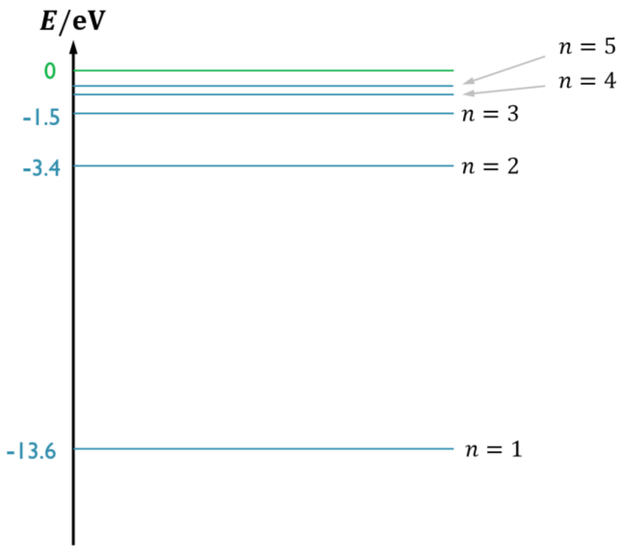
SIGRID: We got the atom to absorb light. Oh, I see, so in reverse, when the electron falls back to a lower energy level, it releases that energy in the form of light.

SALLY: Yes. As a photon with a fixed amount (a 'quantum') of energy equal to the difference in energies between the two orbits. That's your first meeting with the word 'quantum'!

SIGRID: So a hydrogen atom spends its life with the electron in the lowest orbit, unless something makes it jump up, at which point it will jump back down and release a photon of light.



SALLY: We're going to start calling the orbits 'energy levels' now, because the energy of them is the most relevant thing at this stage. We can draw the energy levels of the hydrogen atom as a one-axis graph, like this.



The lowest energy state for the atom is called the ground state (like the ground floor of a building); the others are called excited states. The units on the axis are electronvolts. Don't worry about them – they are just a unit of energy that is conveniently small for processes on this scale.

SIGRID: What's n?

SALLY: n is just a label for the energy level. $n = 1$ means the first (lowest) energy level. $n = 2$ is the second lowest, and so on. n is the first 'quantum number' you have met – it is called the principal quantum number. A quantum number describes the value of a quantity that is constrained to have only certain values. n describes the energy levels of the atom.

SIGRID: What's the biggest number for n?

SALLY: In theory n can be any value up to infinity, but the energy levels get closer and closer together (we have stopped at 5 to stop the picture getting squashed), so that the energy does not increase forever – it has a maximum labelled 0 on the graph. If you give the atom enough energy to get to 0 the electron will not be 'excited' – instead it will leave the atom altogether, and the atom has just been 'ionised'.

SIGRID: Why are the energies negative? I didn't think negative energy was a thing?

SALLY: Don't worry about that. It's just a convention. It's like the contours on a map. We plot the altitudes in metres relative to sea level, and that way we are currently at 250 m and the summit of Everest is 8850 m. The Dead Sea is 430 m below sea level, which we would call an altitude of -430 m. But we *could* call Everest 0, and label the contours to describe places' 'depth' relative to Everest.

SIGRID: Then sea level would be -8850 m and we would be at -8600 m.

SALLY: Yes. And physics would still work. Going from here to the sea would still be a reduction in altitude of 250 m, and a corresponding reduction in gravitational potential energy.

SIGRID: It doesn't much matter where you zero the scale, then, provided it is always *differences* you are interested in.

SALLY: That's a quite profound general truth.

SIGRID: You said that Bohr had experimental evidence that led to him coming up with this theory?

SALLY: Yes – there was quite a bit, but we'll focus on one particular instance. Do you know the meaning of the term 'emission spectrum?'

SIGRID: I know that if you pass white light through a prism it separates all the different wavelengths out and we see it the colours of the rainbow, and we call it a spectrum.

SALLY: An emission spectrum is like that, but without most of the colours. In fact only a few colours are present. You can make one by passing electricity through a gas at low pressure. Here's the emission spectrum for hydrogen.

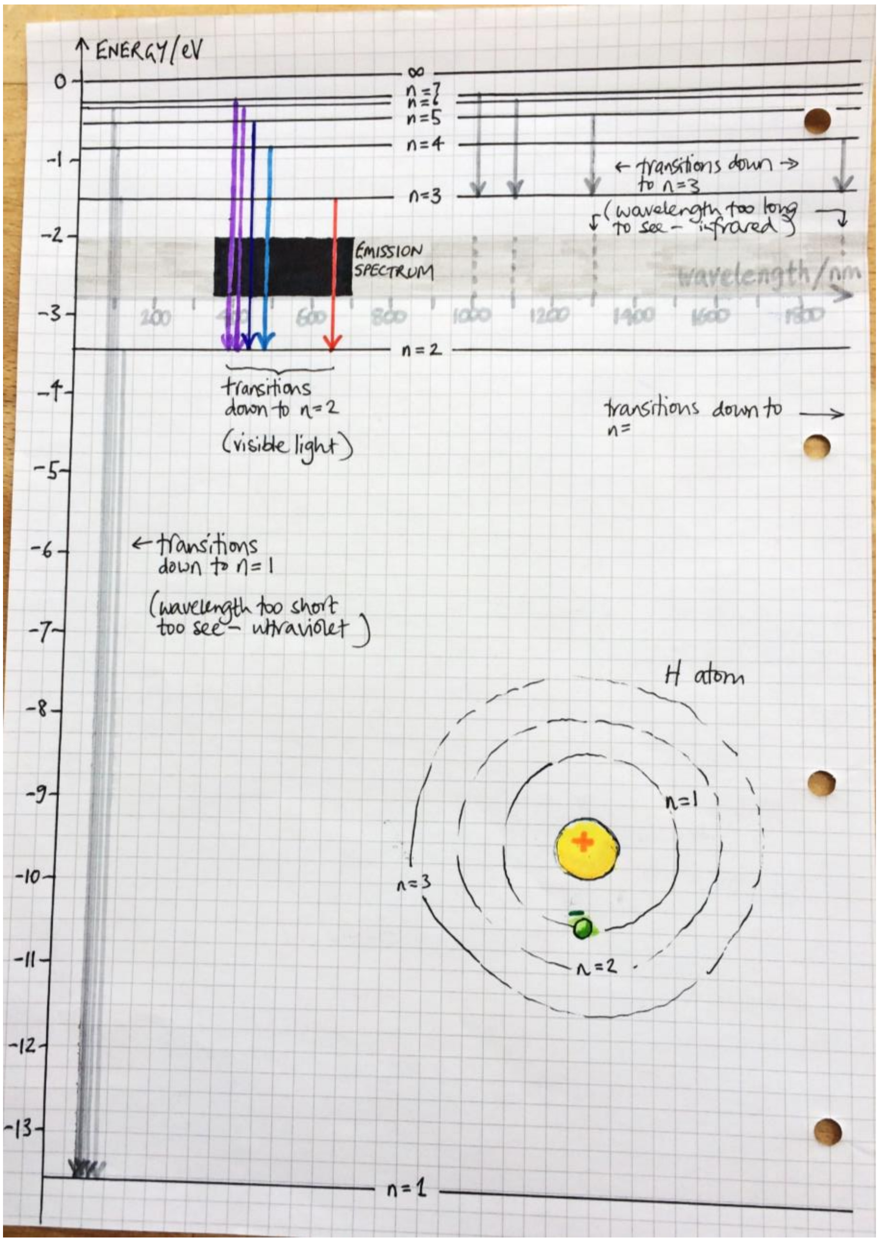
SIGRID: Do other gases have a spectrum like this?

SALLY: Yes, but they tend to be more complicated for reasons you'll understand before the night is through. Why do you think only certain well-defined colours are present?

SIGRID: Well, if the electricity is exciting the hydrogen atoms into an excited state and they spontaneously fall back to lower energy levels, they will give out photons of specific energies – each energy corresponds to light of a specific colour.

SALLY: The emission spectrum is really closely linked to the energy level diagram we saw a few minutes ago. Do you think you could find a way to draw the two combined so the link is really clear? One thing to note is that downwards electron transitions don't have to go directly to $n = 1$. They can 'stop off' at intermediate levels, and return to the ground state in a series of jumps, rather than just one.

SIGRID: I'll have a go. Back in a bit...



SALLY: That's really good. I like the way your transitions are at the appropriate place on the wavelength scale!

SIGRID: Thanks! So If this agrees so well with experiment, is this the endpoint of our learning about atoms.

SALLY: Well, we certainly know quite a bit now about the *hydrogen* atom. But why is hydrogen unique?

SIGRID: It's the simplest. But that doesn't make it unique, because 'simplest' is a relative term. Hmm... Oh! It's the only element with a single electron in its atoms.

SALLY: Yes, all the other elements have more than one. Some have a lot more than one!

SIGRID: But that will be easy. Pick an element.

SALLY: Gold.

SIGRID: Let's see. Gold's atomic number is 79. So an atom of gold has 79 electrons. They'll all just crowd down into the $n = 1$ orbit and behave just like the hydrogen electrons.

SALLY: Ah, it turns out they don't! What does that book tell you about 'electronic configurations'?

SIGRID: Hmm. It says that you can only fit two electrons in the $n = 1$ shell, and 8 in the second ($n = 2$). I assume a 'shell' here is what we have described as an 'energy level'.

SALLY: Yes. What does it say about the third shell?

SIGRID: It says it can take 8 before the $n = 4$ shell starts filling up.

SALLY: OK, hold that thought. Now, does it give any examples?

SIGRID: Yes! It says that the electron configuration of carbon is 2.4.

SALLY: And what do you think that means?

SIGRID: Well, I know a carbon atom has 6 electrons. I suppose it means that it has two electrons in its first shell, and the second shell takes the remaining four.

SALLY: Precisely, so can you work out the electronic configurations of fluorine and potassium? You'll need to look at your periodic table.

SIGRID: OK! Fluorine is element number 9, so its electron configuration will be 2.7. And potassium is number 19. So, going by the rules in this book, it will have 2 in the first shell, 8 and the second, and 8 in the third. That's 18 so far, so the 19^{th} and final electron will start a brand new fourth shell, $n = 4$. So the answer is 2.8.8.1.

SALLY: Good. Now it is really important to realise that what you have described is the ground states of the atoms. Just like our discussion of the hydrogen emission spectrum, if you give the atom enough energy, electrons can jump into higher shells, and you have an excited state.

SIGRID: And the atom will then spontaneously return to the ground state and emit a photon.

SALLY: Right.

SIGRID: So the ground state doesn't mean $n = 1$. Well it did for hydrogen, because it had just the one electron so it can fit in the first shell. But the ground state of potassium, for example, involves electrons in four shells.

SALLY: Right again. So to summarise here's a picture of the top three rows of the periodic table, but with electronic configurations added.

H 1.								He 2.
Li 2.1	Be 2.2	– – – – –	B 2.3	C 2.4	N 2.5	O 2.6	F 2.7	Ne 2.8
Na 2.8.1	Mg 2.8.2	– – – – –	Al 2.8.3	Si 2.8.4	P 2.8.5	S 2.8.6	Cl 2.8.7	Ar 2.8.8

SIGRID: Wow, so elements in the same column have the same number of electrons in the outer shell. Those in the first column have one in the outer shell...

SALLY:...The columns of the periodic table are called groups, so they are called Group 1 elements.

SIGRID: OK, and Group 2 elements have two in the outer shell.

SALLY: What about the final column?

SIGRID: Hmm, that's weird - they don't all have the same number in the outer shell. Helium only has 2, and the others have 8. But they do all have a *full* outer shell, so they still belong together I guess.

SALLY: Well done. I've cheated a bit, and led you to this conclusion by showing only the first three rows. And we'll come back to this later. But at this stage of your atomic education, we can go with that...

SIGRID: Then the periodic table is arranged by chemical properties and by atomic number as we said before, but it's also arranged according to electronic configuration. That's a lot of information in one table!

SALLY: It is pretty amazing. But it's no coincidence, because the atomic number determines the electronic configuration, and that in turn goes a very long way towards determining the chemical properties.

SIGRID: Those elements in the final group with the full outer shell. They are the noble gases aren't they? They hardly take part in chemical reactions at all – I mean argon, for instance, is deliberately used as an inert atmosphere when you want to prevent chemical reactions, generally with oxygen. So how does a 'full outer shell' lead to that kind of behaviour?

SALLY: Good question. We say the noble gases are particularly 'stable', which means they don't react much. The reason for that goes back to energy discussion we had before. The electronic configurations of the noble gases are particularly low energy states.

SIGRID: So when fluorine reacts, what happens to its electronic configuration?

SALLY: Well, one version of fluorine reacting has it gaining an extra electron. The *electronic configuration* then turns into that of neon – it goes from 2.7 to 2.8 – but the *atom* doesn't become a neon atom. It's still fluorine because nothing has happened to the number of protons. That's still 9.

SIGRID: And why *are* the noble gas electronic configurations particularly stable?

SALLY: Well, that's a pretty technical question. At this stage though we can have a quick go at answering it by comparing a noble gas with its neighbouring elements. Pick a noble gas and tell me its electronic configuration.

SIGRID: OK, let's go with our old friend neon. It is element number 10 – so the electronic configuration is 2.8.

SALLY: And now find the two elements either side – elements 9 and 11.

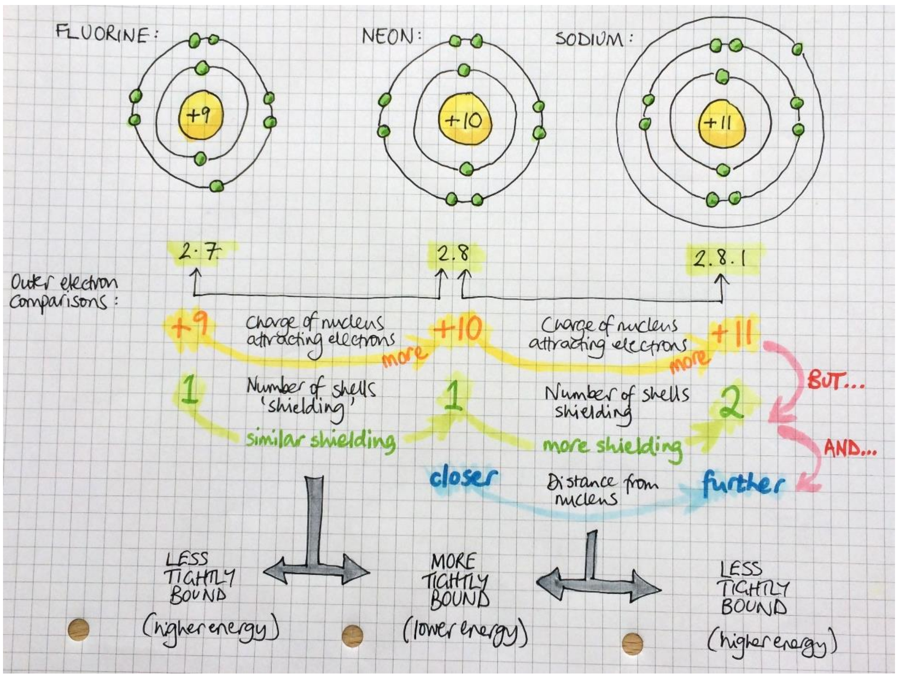
SIGRID: We've met fluorine before – that's element 9, it's 2.7. And element 11 is sodium, so 2.8.1.

SALLY: Now see if you can work out why neon's electronic configuration would be the most stable of the three. It might help to think of it in the terms 'more strongly bound electrons' equals 'lower energy configuration'. You can think of the boulder as being 'more strongly bound' to the earth at the bottom of the valley than the top of the hill. In other words it will take an input of energy to move it back up, whereas it will spontaneously fall down. There's another thing to consider, too. And that is the idea of 'shielding'. Inner electrons can 'shield' the outer electrons from the attraction of the nucleus, making the outer electrons less tightly bound than they would otherwise be.

SIGRID: OK… Well, fluorine's outer electrons are in the same shell as neon's, so there will be roughly the same amount of shielding, but the nucleus of fluorine has less positive charge than that of neon. So fluorine's outer electrons will be less strongly attracted, and less tightly bound, and be in a higher energy state than neon's. In other words an atom of neon will be more chemically stable than an atom of fluorine.

SALLY: Good! A similar argument can be made to explain why it's harder to add an electron to fluorine, as well as remove one, but let's not get sidetracked. And what about comparing neon with sodium?

SIGRID: Well, sodium's outer electron is less tightly bound to the nucleus because it's further from it. And even though there are more protons in the nucleus attracting the outer electron, there is also an extra inner shell to provide shielding from the nucleus. So again, sodium's outer electron will be less tightly bound than neon's, and an atom of neon will be more chemically stable than an atom of sodium. Right, that's a lot to take in. I might need to draw a summary picture of this.



SALLY: Remember we said that spontaneous processes tend to happen so as to minimise energy? Well, you can think of a lot of chemical reactions as happening when atoms move towards the electronic configuration of a noble gas.

SIGRID: I've heard people say that when chemical reactions take place, the elements are 'trying to get a full outer shell'.

SALLY: What they mean is that processes take place that lead to lower energy configurations, and the noble gas electronic configurations, what we are for now calling a 'full outer shell', are such low energy configurations.

SIGRID: Fluorine has 7 electrons in its outer shell (2.7), and so it 'needs one more'. And this is why it can bond by receiving an electron from another atom?

SALLY: Exactly – that's called ionic bonding. So what happens if fluorine bonds with sodium (1 in the outer shell)?

SIGRID: The fluorine atom can take sodium's 'extra one'. But then sodium doesn't have a full outer shell – it has an empty one!

SALLY: Ah, don't worry about that. A sodium atom is 2.8.1 – the third shell is the outer shell. But when it loses that 1, and becomes 2.8, then the second shell becomes the outer shell. Empty shells don't count.

SIGRID: Good, because otherwise we'd have to keep track of all the empty shells all the time.

SALLY: OK, so what happens if fluorine is reacting with an element whose atoms *also* want to gain electrons? Everything involved wants to gain more electrons.

SIGRID: They could share?

SALLY: And that's called covalent bonding. In fact, chemical bonding is more complicated than what we have described, but we'll need to leave that for another conversation.

SIGRID: Yeah, you always say that. Well, let's get back to atomic structure then. I feel like there is a big shock on the way. I mean – you keep showing me the first three rows of the periodic table, and this book I've got just talks about the electronic configuration for the first 20 elements. I'm thinking something weird must happen at element 21.

SALLY: What would you expect to happen?

SIGRID: Well, element 20 (calcium) has electronic configuration 2.8.8.2, and we fill electron shells from the inside outwards, so the 21st element must be 2.8.8.3?

SALLY: And that's a perfectly reasonable thing for you to think, based on what we know. What did that book tell you about the number of electrons that the shells hold?

SIGRID: The first holds two, the second holds 8, the third holds 8 before the fourth starts to fill…

SALLY: That's a clever use of words so that the explanation can be 'contained' at a certain level! Do you see the trick? Nobody has said that the third only holds 8!

SIGRID: Just that once you put 8 in it, then the fourth shell starts to fill. There could still be 'room' in the third shell.

SALLY: There is. $n = 3$ is NOT full with 8 electrons in it. It can take 18.

SIGRID: So the electronic configuration for scandium (number 21) wouldn't be 2.8.8.3 because the 21st electron goes into the third shell. It would be 2.8.9.2.

SALLY: That's right. So see that block of elements from scandium to zinc?

SIGRID: As we go across that row, the third shell is filling up, and they still have two in the outer shell.

SALLY: What's the electronic configuration of zinc then?

SIGRID: 2.8.18.2. And then the third shell really is full, and we go back to adding electrons to the outer ($n = 4$) shell.

SALLY: Find gallium.

SIGRID: Next to zinc.

SALLY: So gallium is in group 3, under boron and aluminium because, like them, it has 3 in the outer shell.

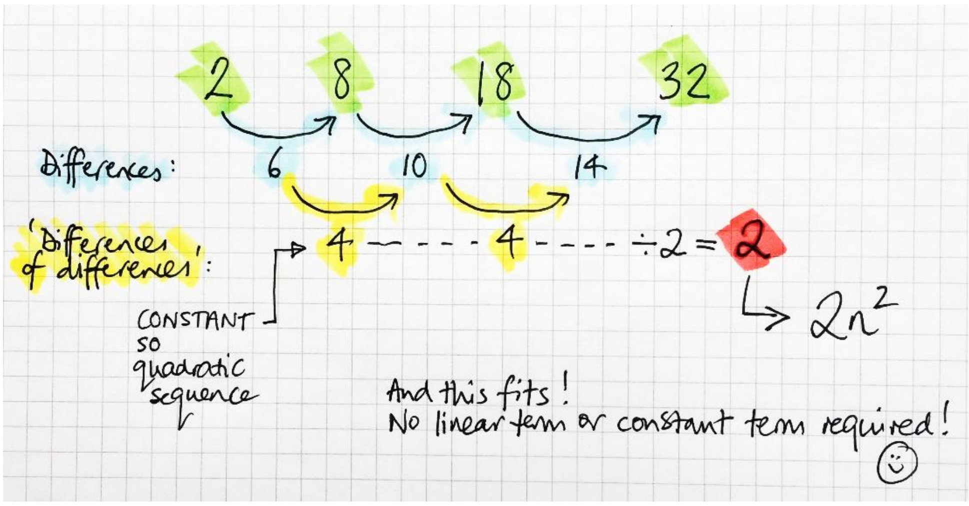
SIGRID: And then all the noble gases will have 8 in the outer shell because even though some of their outer shells can take more than 8, we are actually filling inner shells first.

SALLY: Exactly. That's called the 'octet rule' – 8 in the outer shell is particularly stable, even though it's not necessarily a full outer shell once we get past neon.

SIGRID: How many can the fourth shell take?

SALLY: 32.

SIGRID: There must be a pattern here. I know some maths that might help – don't worry if you can't follow it – this is my area of expertise! Give me a minute, and I'll work it out...



SIGRID: OK, so that means the nth shell can take $2n^2$ electrons.

SALLY: Well done.

SIGRID: How does that work on the periodic table? We had scandium to zinc because we had to fit in an extra 10 elements...

SALLY: …That's right – and that led to the rectangular block that we call the transition metals…

SIGRID: …Yeah, but further down the table, we are going to need to fit in more than 10 extras, because of $2n^2$.

SALLY: Well spotted.

SIGRID: So where do they go?

SALLY: Have you spotted the lanthanides and actinides?

SIGRID: What are they?

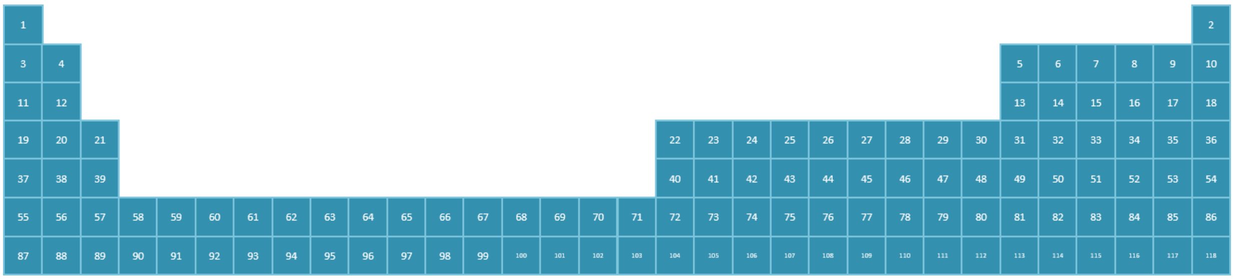
SALLY: All these elements down in a separate block at the bottom of the periodic table.

SIGRID: I've often wondered why they are separate, but to be honest I hardly notice them – I'm always too busy concentrating on the top half of the table! Actually, there's loads of them!

SALLY: Yes, they are comparatively rare, so you tend not to deal with them much in school science. But they really aren't separate in the way they appear! Look – the lanthanides are numbers 57 – 71. They belong between barium and hafnium.

SIGRID: And the actinides are numbers 89 – 103, and so go between radium and rutherfordium. So why don't we draw them there?

SALLY: Well we *could*, but then the periodic table would look like this.



It would be 'more accurate' or 'less misleading' if you like. But it also wouldn't fit on the average page of a book or a website.

SIGRID: That's the only reason for putting them down there? Wow. And you know the next question… *Why* $2n^2$? In other words, *why* can you fit 2 in the first, 8 in the second, 18 in the third, and so on?

SALLY: Well, we can answer that, but it's going to need a whole new approach. Welcome to the world of 'orbitals'. So far we have drawn the atom like a solar system, with electrons in definite orbits around the nucleus, like planets around the Sun. But it's not really like this. Planets have well defined trajectories through space. Electrons not so much.

SIGRID: But they must be orbiting. Bohr said so. And all of our drawings show them orbiting.

SALLY: Have you heard of the Heisenberg Uncertainty Principle?

SIGRID: Heard of it. But no idea what it means.

SALLY: The uncertainty principle says that there are pairs of quantities that we cannot know to arbitrary accuracy.

SIGRID: Because we can't measure them well enough?

SALLY: It's worse than that. Even *in principle* they can't be simultaneously known, even with the best not-yet-invented measurement process imaginable. Two such quantities are momentum p and position x. The uncertainty principle is then written $\Delta p \Delta x \geq \hbar/2$. It means that when you multiply the uncertainty in the two quantities, it can't be less than the right hand side – don't worry about the 'h-bar' – it's just a very small number.

SIGRID: So the better you know one of the quantities, the worse you know the other, because the product of their uncertainties has to fit that rule.

SALLY: That's it.

SIGRID: The 'delta' symbols Δ mean 'uncertainty in', right?

SALLY: Yes, sorry – should have said that. This level of uncertainty is tiny (because h-bar is a very small number) and it makes no difference for macroscopic moving objects like birds, ice hockey players, or planets.

SIGRID: But what's all this got to do with atoms?

SALLY: Atoms are tiny, and on that scale that level of uncertainty *does* make a difference. As far as the electrons are concerned, you can think of x as 'where it is' and p as 'where it's going'. The combination of those two things maps out its trajectory in space.

SIGRID: Then the uncertainty principle is saying that even in principle we can't know an electron's trajectory, and our picture of an atom is wrong?

SALLY: It's a useful picture, and it has got us this far. And in some situations you don't need anything more. But yes – the orbits are a bit misleading.

SIGRID: What's an orbital then, as compared to an orbit? And why is the uncertainty principle involved?

SALLY: Well, if we can't know the electron's path, then its position becomes a matter of probability. An orbital is a region of space with a high probability of containing an electron. Often 95 % is the 'high probability' specified.

SIGRID: OK, but the picture of the atom is just going to look the same as before, but drawn a bit more 3D and with some probabilities on it!

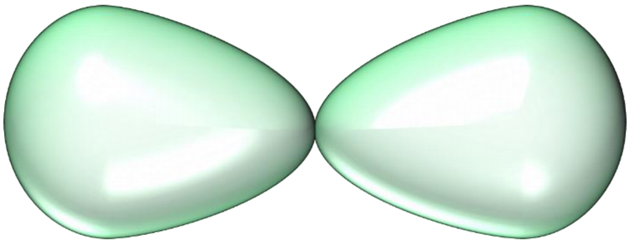
SALLY: And some electrons do behave like that. But not all electrons have spherical orbitals. Spherical orbitals are called 's' orbitals.

SIGRID: 's' for spherical – I like it!

SALLY: Actually, 's' stands for 'sharp', but we are not going to worry about the etymology of the orbital names. Just go with the idea that there are orbitals called s, p, d and f. And they all have different shapes.

SIGRID: For example?

SALLY: Well, what we call the 2p orbital is dumbbell shaped, like this.



SIGRID: But that makes no sense. Every time an electron goes from one lobe of the dumbbell into the other, it will crash into the nucleus.

SALLY: You need to stop thinking of these pictures as the paths of electrons – they are regions where electrons are likely to be.

SIGRID: Hmm, maybe. Although I feel you have tricked me here in a way I can't quite put my finger on.

SALLY: No, really, not this time! It makes literally no sense to consider the trajectory of an electron in an atom – remember the uncertainty principle!

SIGRID: But things do have trajectories! Stuff moves from A to B!

SALLY: Macroscopically, yes. But microscopically, in the world of quantum physics, not so much! Heisenberg's approach was to let the maths do all the work and make the predictions, and not worry too much about what was 'really going on'. Maybe our minds are not cut out for thinking about what is 'really going on' at that scale.

SIGRID: No wonder there's that quote about how 'anyone who says they understand quantum mechanics, hasn't' or something.

SALLY: I know how you feel.

SIGRID: Anyway, how does this help us understand electronic configurations?

SALLY: For this stuff, you'll need to move on to your next book – one level up, as it were.

SIGRID: OK, here we are. Electronic configurations... Let's see – here we are.

- The first shell (corresponding to $n = 1$) can only contain one s-orbital.
- The second shell ($n = 2$) can have one s-orbital and three p-orbitals
- The third shell ($n = 3$) can have one s-orbital, three p-orbitals and five d-orbitals (and the d-orbitals have a more complicated shape than the p-orbitals)
- The fourth shell can have one s-orbital, three p-orbitals, five d-orbitals and seven f-orbitals

And that will do for now…

SALLY: OK – we're getting somewhere. The different types of orbitals are sometimes called '*subshells*' - so for example the $n = 2$ shell has an s subshell, and a p subshell, and within the p subshell are three p-orbitals. And the orbitals, as well as a certain shape, have a certain orientation to each other. I'm not going to get you to draw this – have a look at this one from chemistryonline. https://chemistryonline.guru/orbitals

SIGRID: You said that $n = 1$ can take two electrons, but it only has one orbital. And we know that $n = 2$ can take 8 electrons, whereas it has 4 orbitals – an s and 3 p-orbitals. So does that mean that each orbital can contain two electrons?

SALLY: That's exactly what it means... Did you know that electrons 'spin'?

SIGRID: *What*? Oh, it says that here, but it calls it 'intrinsic angular momentum'.

SALLY: Good! And do you know what angular momentum is?

SIGRID: Yes! Linear momentum is the product of mass and velocity. And angular momentum is an analogous quantity for rotational motion, given by the product of mass, velocity and radius of motion.

SALLY: Exactly! Well, on an atomic scale the angular momentum of electrons consists of two parts. Angular momentum due to its orbit...

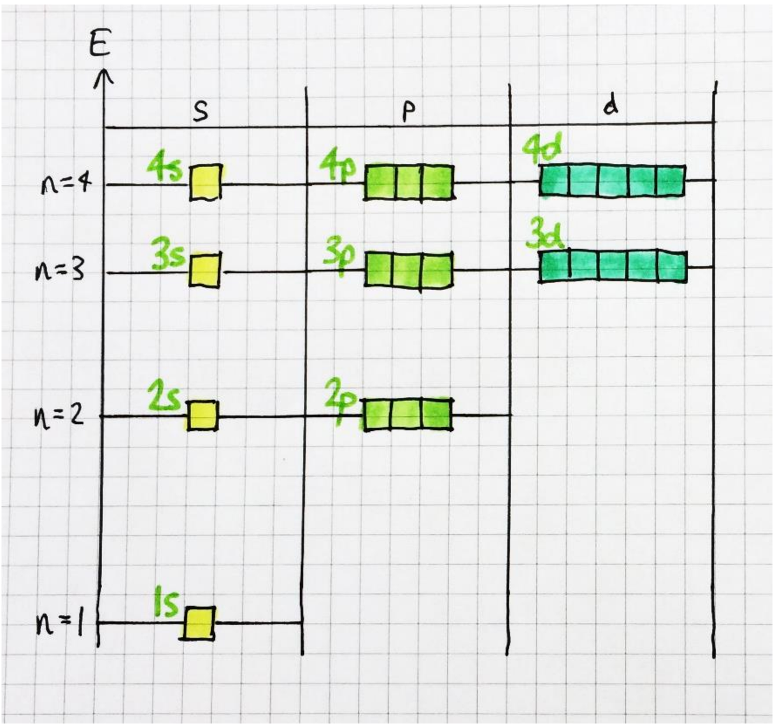
SIGRID: ...I thought we couldn't determine the trajectory of an electron in an atom?

SALLY: We can't – but we can know its orbital angular momentum... And it also has 'intrinsic angular momentum' – angular momentum that is just a property of the electron and doesn't depend on what it is doing. That's what we call 'spin'. All electrons have the same amount of spin and it can be in two orientations, which we call 'up', labelled $\uparrow$, and 'down', labelled $\downarrow$.

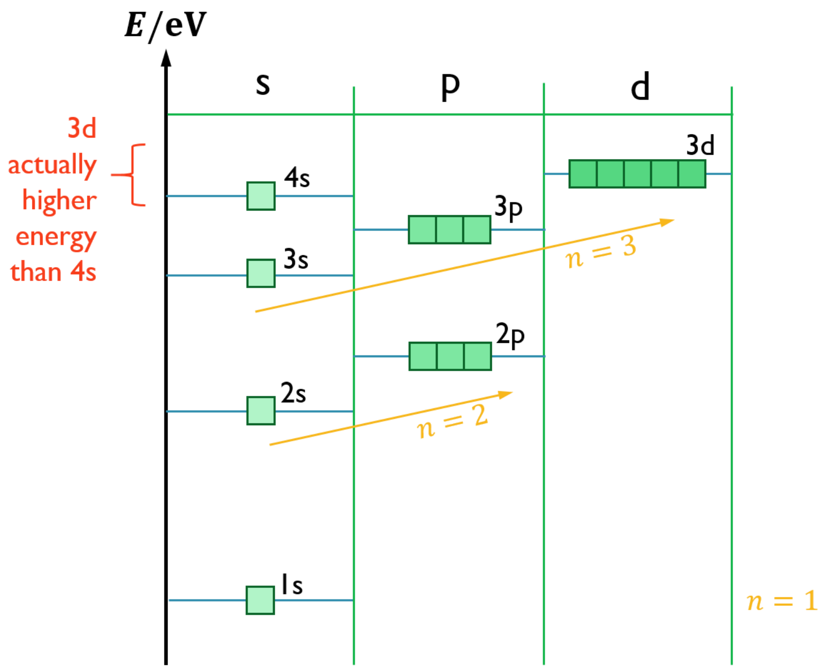
SIGRID: OK, so what has spin got to do with electron configurations?

SALLY: Well, one orbital holds up to two electrons, as you said, but two electrons in the same orbital have to have opposite spins. So to summarise all that new information, go and draw an energy level diagram for $n = 1$ to $n = 4$ with all the orbitals in it.

SIGRID: OK. Here it is...



SALLY: That's a great effort. It's not *quite* right – but there's no reason you should have realised why yet. Look at my version and compare the two…



SIGRID: Hmm. The different types of orbital within a shell have different energies. Why is that? And does it matter?

SALLY: It *really* matters, because it explains why the potassium and calcium start to fill the $n = 4$ shell before the $n = 3$ shell is full, and why the transition metals, actinides and lanthanides have blocks on the periodic table of their own. As for why it happens, there's a three stage explanation. Firstly, remember that 'more attraction from the nucleus' is the same as 'more tightly bound' is the same as 'lower energy' is the same as 'more chemically stable'! Next, p-orbitals are on average further from the nucleus than s-orbitals of the same shell, because of their dumbbell, rather than spherical shape. In turn, d-orbitals are further than p, and f-orbitals are further than d. Finally, electrons that are far from the nucleus are 'shielded' from its attraction by the effect of the electrons closer in.

SIGRID: That must mean that f-orbitals have more shielding than d, which have more shielding than p, which have more shielding than s.

SALLY: Exactly – so what will be the effect on the energy levels?

SIGRID: s electrons are the least shielded and the closest to the nucleus, so they will have lower energy than p electrons. And so on. The order will be s<p<d<f.

SALLY: And that's exactly what is shown the diagram I just showed you.

SIGRID: So because the energy levels for each shell are spread out, and because the energies for each n get closer together as n increases, that means that the energy of the $n = 3$ p-orbitals (called 3p for short) are actually higher than the $n = 4$ s-orbital (called 4s for short). And that's why the $n = 4$ shell starts to fill before the $n = 3$ shell is full. It's the marked bit on the diagram…

SALLY: If we are going to build some atoms, what order should we fill the orbitals?

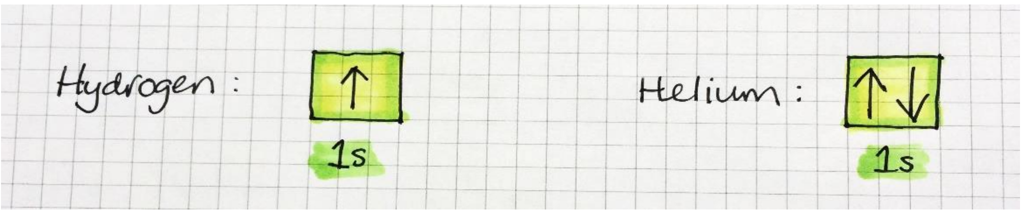
SIGRID: Like this I guess: 1s, 2s, 2p, 3s, 3p, 4s, 3d, etc, by working up the new energy level diagram from bottom to top.

SALLY: Yes, that's right. You know how you built some atoms before, using electronic configurations like 2.8.1 for sodium? Well, why don't you repeat that with your new notation? You'll find you can get further than the first 20 elements.

SIGRID: Ok, well for hydrogen, we obviously put the single electron in the 1s orbital. The '1' signifies the first shell (energy level), the s specifies the orbital within it.

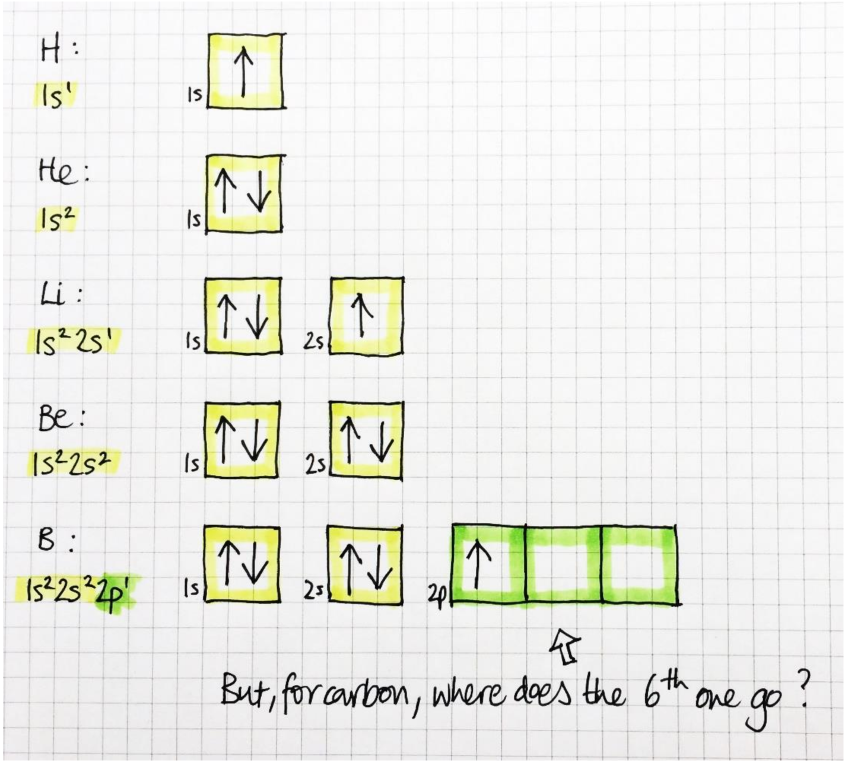
SALLY: Yes, and we label that $1s^1$, where the superscript '1' means '1 electron in this orbital'.

SIGRID: Then hydrogen is $1s^1$ and helium is $1s^2$. We can draw them like this:



SALLY: Good – keep going…

SIGRID: OK, well I've done up to boron (element number 5). Here it is.



But for carbon I need to put another electron in an $n = 2$ orbital, and I don't know whether it makes any difference where it goes. I mean, wherever it goes, I write $1s^2 2s^2 2p^2$, but it affects how I draw the diagram.

SALLY: It does matter! There is something called Hund's rules to help you. Basically, you add an electron to each orbital with spins in the same directions (we say 'parallel spins'), before adding the second electron to any orbital.

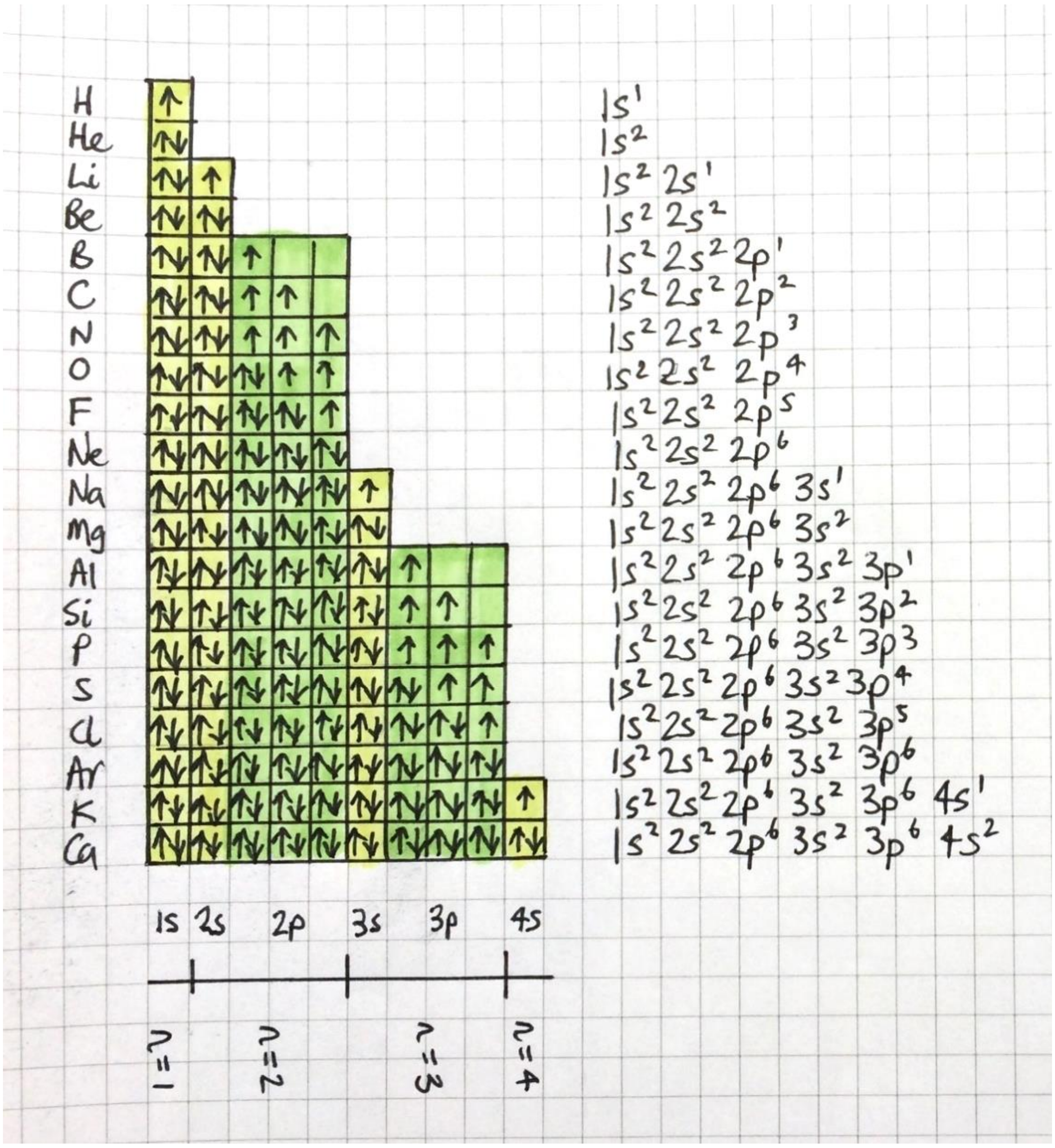
SIGRID: Why does that work?

SALLY: Basically, electrons in the same orbital are on average closer than electrons in different orbitals. That means they have greater mutual repulsion and thus higher energy.

SIGRID: So the lower energy state is the one utilising more orbitals without doubling up.

SALLY: Exactly.

SIGRID: OK, now I know that I can carry on. I'll go up to 20 just to show I can match the previous method. Here you are…

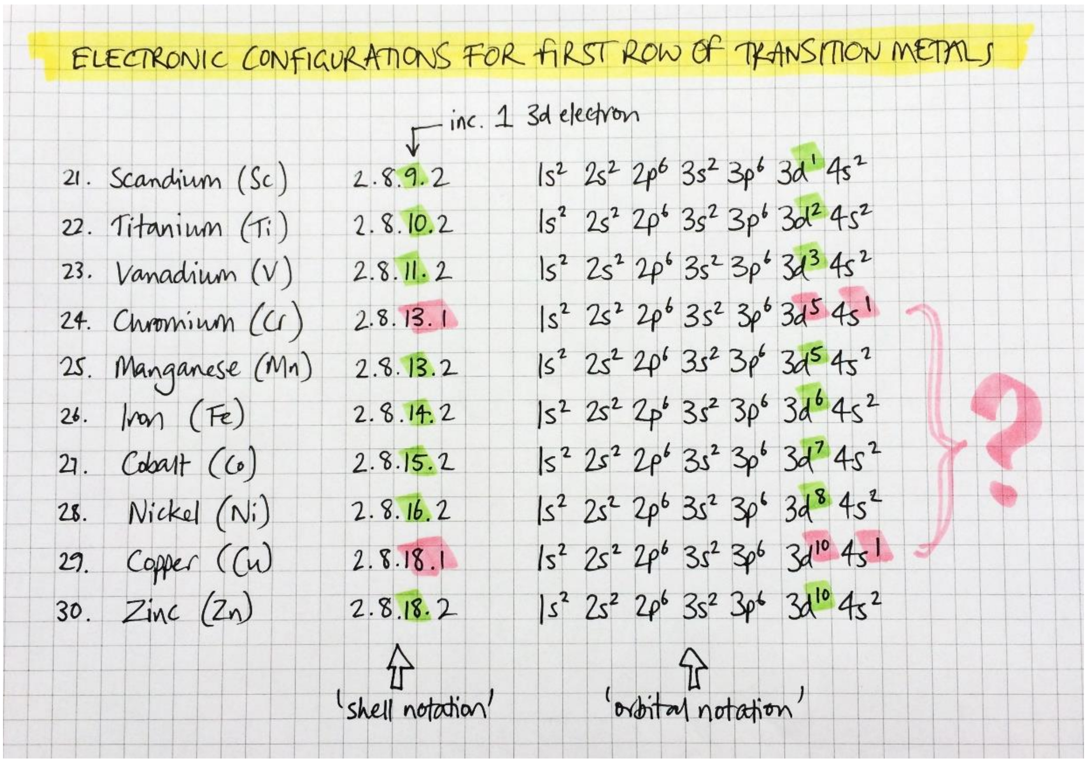


SALLY: Well done. And now look at your list of order of filling, and see what happens to the 21st element.

SIGRID: OK, so the order is 1s 2s 2p 3p 4s 3d, and the first 20 elements get us up to the 4s orbital. Element 21 (scandium) must use the 3d orbital. So when I wrote it before as 2.8.9.2 instead of 2.8.8.3, that 9th electron in the $n = 3$ shell corresponds to the 3d electron in our new notation: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$.

SALLY: And whichever way you write it, when filling shells, that 21st electron is the first we have seen that doesn't go into the outer shell.

SIGRID: So the first row of the transition metals look like this…


ELECTRONIC CONFIGURATIONS FOR FIRST ROW OF TRANSITION METALS

		'shell notation' (inc. 1 3d electron)	'orbital notation'
21.	Scandium (Sc)	2.8.9.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
22.	Titanium (Ti)	2.8.10.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
23.	Vanadium (V)	2.8.11.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
24.	Chromium (Cr)	2.8.13.1	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
25.	Manganese (Mn)	2.8.13.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
26.	Iron (Fe)	2.8.14.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
27.	Cobalt (Co)	2.8.15.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
28.	Nickel (Ni)	2.8.16.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
29.	Copper (Cu)	2.8.18.1	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
30.	Zinc (Zn)	2.8.18.2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

I thought Cr would be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$ and Cu would be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$, but when I cheated, I mean checked my working out against a number of textbooks, I found this table is definitely correct. It seems like Cr and Cu are preferentially half-filling and filling the 3d subshell.

SALLY: That's right. An electron shifts from 4s into 3d to gain extra stability. And remember – by extra stability, we mean 'it's a lower energy state that way'… Can you see why the transition metals are often called the d-block elements?

SIGRID: Yes! Because that whole rectangle of the periodic table are the elements for which the 'most recently' filled orbital is a d-orbital. And the rectangle is 10 elements wide because each shell from $n = 3$ onwards has 5 d-orbitals, each of which can hold 2 electrons.

SALLY: Do you realise you have just explained that 'gap' between beryllium and boron, and between magnesium and aluminium?! It's because lower down the periodic table, you need to fit in the d-block elements. And can you explain the octet rule now?

SIGRID: OK! For the noble gas electronic configurations, the outer shells have fully occupied s and p orbitals. And that accounts for 8 electrons in the outer shell, even if there are unoccupied d and f orbitals in inner shells. And that's the octet rule…

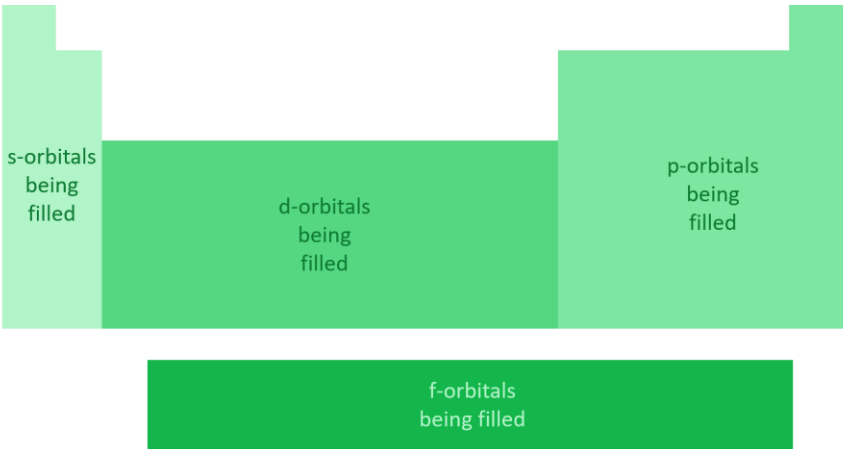
SALLY: And what about the $2n^2$ rule?

SIGRID: That was about how many electrons in total you can fit in each level, or value of n, if you will. Well that hinges on the odd number of orbitals of each type in each shell. $n = 1$ has 1 orbital, $n = 2$ has 1+3 orbitals, $n = 3$ has 1+3+5 orbitals, and so on, and this rule generates the square numbers, n^2. Each orbital holds 2 electrons. So $2n^2$!

SALLY: And what about the lanthanides and actinides?

SIGRID: Well, we said before that $2n^2$ causes us to need to fit more in further down. So just like the rectangle of transition elements that we squeeze in is because of the d orbitals, are the actinides and lanthanides the elements with occupied f-orbitals.

SALLY: That's exactly it. Like this…



SIGRID: Hmmm. That's pretty weird.

SALLY: Try being a nuclear physicist! A similar energy level structure exists for protons and neutrons in nuclei too, but it's much worse there! The energy levels overlap almost straight away, so you don't even get the first 20 behaving themselves, like we did here! At least those first 20 provided you with a step on the road to a better understanding.

SIGRID: Yeah, OK. Maybe I'll stick to atomic physics and chemistry…

SALLY: Just one thing. That energy level diagram that shows the order of filling orbitals? That applies to the ground states of atoms. And basically it's the interactions between electrons with the nucleus and also with the other electrons (including the shielding that we mentioned) that lead s, p, d and f orbitals to have different energies within the same energy level. But hydrogen with 1 electron also has an $n = 3$ state – it's just an excited state, rather than the ground state. And for hydrogen there's no energy difference between, say, the 3s and 3p excited states, because there are no other electrons to affect them. The equivalence of energy in different states is called degeneracy, so we could say that the 3s and 3p states are degenerate in hydrogen, but not, say in chlorine. We'll look at the idea of degeneracy a bit more later on.

SIGRID: OK, so now I've got a more sophisticated idea of what an atom 'looks like' in terms of orbitals, rather than electron orbits. But you've only shifted the point of attack of my question. Before, I asked why the shells can only hold 2, 8 etc electrons, and we explained that in terms of orbitals. But we've just transformed the same question into 'why are there as many orbitals as there are?'

SALLY: Hmm. I was rather hoping you'd be satisfied with what we've done so far, but I can tell you want to know more. So we'll carry on. Just one thing – be wary of 'why?' questions. Quite often, we do end up explaining one thing after another until we get to an idea that just seems to work and we don't know why. You can see Richard Feynman talking about that at https://youtu.be/MO0r930Sn_8

SIGRID: What's the next step? I promise not to be angry if I still have questions after that.

SALLY: Do you remember how the number n came out of Bohr's theory of the hydrogen atom? We called it the 'principal quantum number'? Well, the next step involves a different model of the atom, which uses the 'wavefunction' of the system. That's, if you like, a map in space and time, of the probabilities of finding the electrons in particular places.

SIGRID: Like a mathematical version of the orbitals we have drawn.

SALLY: Exactly, and in fact we know what shape to draw orbitals because people have determined mathematical functions for the wavefunction.

SIGRID: Where does the wavefunction come from?

SALLY: From a thing called the Schrödinger equation, which you can use to tell you the amount of energy an atom has. When you solve this equation, the solution involves n, just like in Bohr's model. But it also involves a second quantum number, which we call l.

SIGRID: And that corresponds to some property of an electron, other than energy?

SALLY: Yes – the orbital angular momentum we talked about earlier.

SIGRID: OK, but how does that help?

SALLY: Well, when you solve the Schrödinger equation, which we won't do here, it turns out that l cannot have just whatever value it likes…

SIGRID: …It is quantised, like n was…

SALLY: Exactly, and in particular units, it too can only have whole number values. But it is also constrained by the value of n. It turns out that the value of l for an electron in an atom can have values 0, 1, 2, etc up to $n - 1$.

SIGRID: One less than n…

SALLY: Exactly.

SIGRID: But how can l be 0? That would mean it has 0 angular momentum and isn't orbiting!

SALLY: I thought we had got away from thinking about electrons in terms of their orbits?

SIGRID: Oh, yeah. Sorry. Anyway, by those rules, for an $n = 1$ electron, l would have to be 0.

SALLY: Keep going.

SIGRID: An $n = 2$ electron could have l values of 0 or 1. An $n = 3$ electron could have l values of 0, 1 or 2. And so on.

SALLY: Do you notice any similarities here with our discussion on orbitals?

SIGRID: I can see that $n = 1$ has only one value of l available, and we know the $n = 1$ shell has only a single s-orbital. So does $l = 0$ correspond to the s-orbital?

SALLY: Yes! n tells you the main energy level, and l tells you the type of orbital.

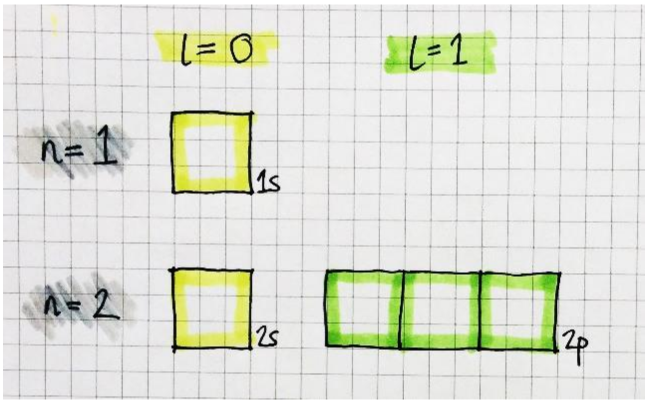
SIGRID: So $l = 1$ represents p, $l = 2$ represents d…

SALLY: … Exactly.

SIGRID: But isn't this just relabelling stuff? I mean is there any deeper understanding to be gained from this?

SALLY: Maybe!

SIGRID: Oh hang on, for $n = 2$, we said that l could be 0 or 1. And $l = 0$ is an s-orbital. But there are 3 p-orbitals. So it would look like this.



SIGRID: But how does $l = 1$ give you three p-orbitals.

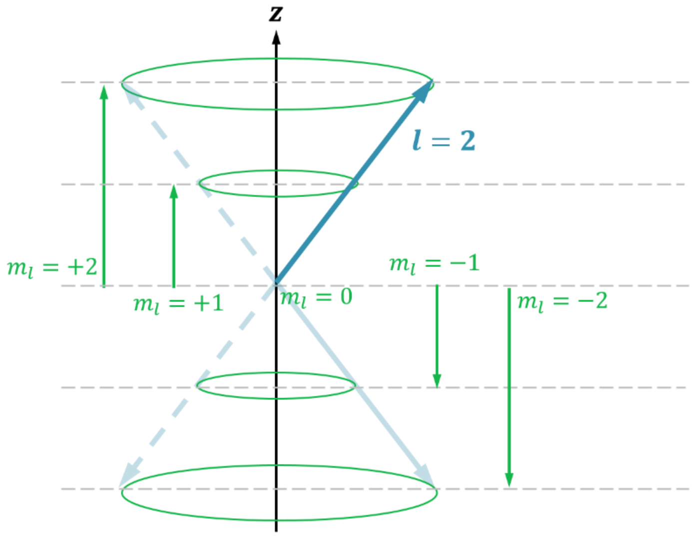
SALLY: Good question, and one that will get us somewhere… Would you believe me if I said there is a third quantum number?! If l represents orbital angular momentum, then m_l is the component of the angular momentum orientated in a particular direction.

SIGRID: Which direction?

SALLY: Sort of *any* direction we choose, but it becomes important in energy terms if there is something like a magnetic field in a particular direction.

SIGRID: So what's the rule this time? So far, we've got that n can be any whole number starting at 1, and l can be any whole number starting at 0 and going up to $n - 1$. What's the rule for m_l?

SALLY: Maybe if you look at this diagram, and if I tell you that m_l is also quantised as a whole number, then you will be able to work it out.



SIGRID: Well, if that picture is to be believed, in the magnetic field the angular momentum in a particular direction can be parallel to the axis of interest, anti-parallel or any whole number in between.

SALLY: So what's the rule?

SIGRID: m_l can range from – l through 0 to $+l$.

SALLY: And now can you see whey there are 3 p-orbitals for a given value of n?

SIGRID: Yes! I know that p orbitals correspond to $l = 1$. And if $l = 1$, then m_l can have values -1, 0 and 1. Three different values! So the three different p-orbitals have the same value of angular momentum ($l = 1$) but different values of m_l.

SALLY: -1, 0 and 1. Exactly – but only for $n = 2$ and above, because for $n = 1$, l can only be 0.

SIGRID: And that explains the five d-orbitals, too. If $l = 2$, then m_l can take values -2, -1, 0, 1 and 2. Five values, five d-orbitals!

SALLY: Which is only possible for $n = 3$ and above.

SIGRID: $l = 3$ gives seven f-orbitals! But only for $n = 4$ and above – I get it!

SALLY: And remember you can fit two electrons into each orbital.

SIGRID: I suppose there's a quantum number for that too?

SALLY: Yes, you've half met it before. It's the spin quantum number, m_s.

SIGRID: You mean the 'intrinsic angular momentum number', since a particle with no size can't really 'spin'.

SALLY: OK! It's good to see you realising that analogies from everyday life sort of break down on the atomic scale. I'm still going to call it 'spin' though!

SIGRID: We called the possible values of spin 'up' and 'down'. So they are sort of opposite each other. Does that mean their quantum numbers are +1 and -1?

SALLY: Good thinking, but no! We aren't free to give spin any value we like – it has to compare correctly to the other type of angular momentum, l and m_l. So actually the possible values of m_s for an electron in an atom are +½ and -½.

SIGRID: Weird.

SALLY: Yeah – that's another conversation again. We'd need to talk about the standard model, fermions and bosons to say more about that. Let's not for now. After all, we've been talking a long time, and it will be a miracle if anyone is still reading.

SIGRID: OK, but we haven't finished yet. We need to talk about how we build atoms in this new language.

SALLY: You're right. OK, here goes… Each electron in an atom has its set of four quantum numbers, n, l, m_l, m_s. And in a given atom, no two electrons can have the same set of four quantum numbers. So 'building atoms' is about allocating quantum numbers to electrons, and minimising their energies.

SIGRID: And the lower the quantum numbers, the lower the energies?

SALLY: At first, yes. But we will find that there are overlaps between $n = 3$ and $n = 4$ and so on, just like when we filled the 4s orbitals before the 3d orbitals. Anyway let's start easy – what would be the ground state of hydrogen in this notation?

SIGRID: Well, we are using the first main energy level (shell). So $n = 1$. Then that forces l to be 0, which in turn forces m_l to be 0, and shall I choose m_s to be +½?

SALLY: Exactly! {1,0,0,+½}. And what's the orbital representation of that?

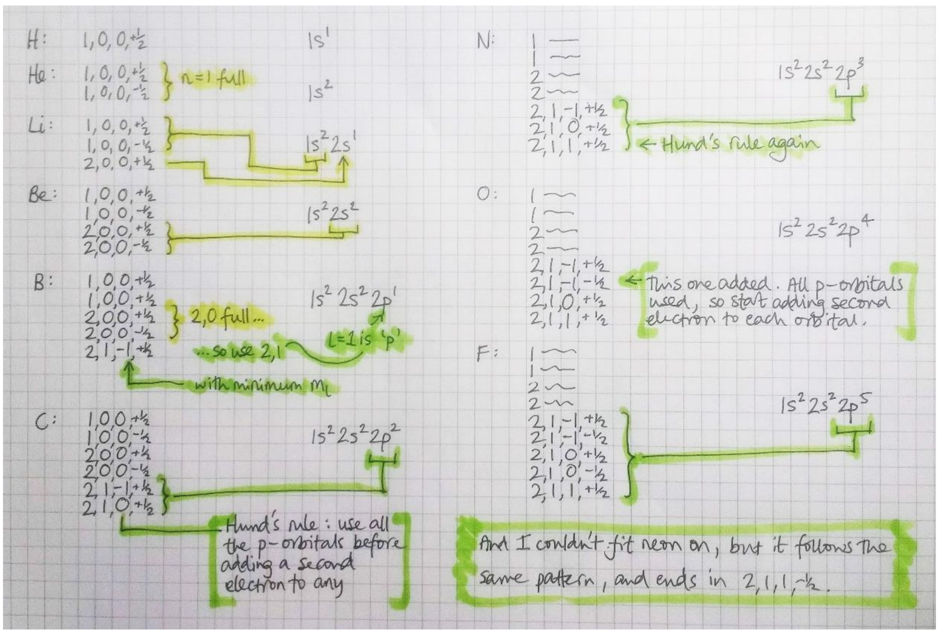
SIGRID: $1s^1$.

SALLY: Good, and why is it important to specify that it is the ground state?

SIGRID: Because an excited state could have any four quantum numbers, but the atom would quickly return to {1,0,0,+½}. Then for the ground state of helium, we can fit the other electron in the 1,0,0 state, so it would have one electron in {1,0,0,+½} and one in the state {1,0,0,-½}. And we could write that in terms of orbitals as $1s^2$.

SALLY: Can you do the same for elements up to number 10? Remember Hund's rule!

SIGRID: Ah, so I use up all the orbitals before adding the second electron to an orbital. Right, here we go…



I like the way both representations show the same thing. But the quantum number version is for each electron, and you need a full list of them, whereas the orbital version summarised the electrons within an atom.

SALLY: And there's a whole other nomenclature which gives the information about spins and angular momenta for the atom as a whole, rather than the individual electrons, but I don't think that would give you any fresh insights. I'm just telling you so that when you see hydrogen written $^2S_{1/2}$ and fluorine $^2P_{3/2}$, you'll know that's what's going on, and you'll have to look it up.

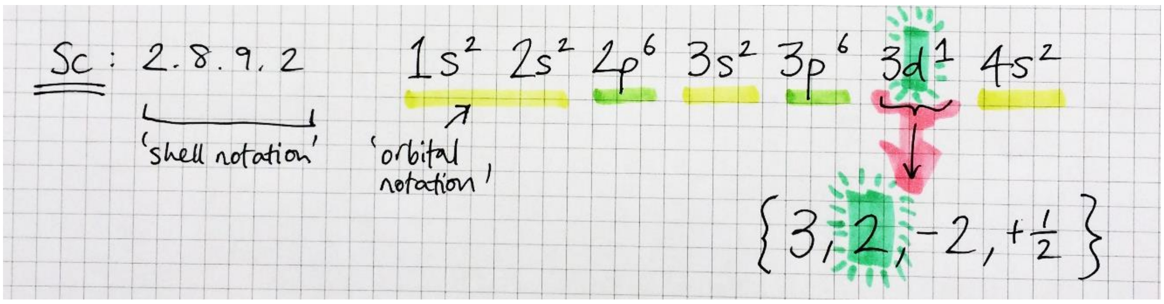
SIGRID: OK!

SALLY: I like the way you have shown in the diagram that an electron in a p-orbital has angular momentum $l = 1$. I wonder whether you could work out a similar thing for scandium?

SIGRID: Oh, because that's the first transition metal, so we are using the d-block. And that must then be the first element with an electron with $l = 2$.

SALLY: Exactly! Go on – work it out!

SIGRID: OK!



SIGRID: I know all this seems to work, but you could still be making it all up. I mean, is there any actual experimental evidence for all this?

SALLY: There is, actually! From measuring the energy needed to rip an electron of an atom for successive elements, you can tell how tightly bound the electrons are from one element to the next. And the pattern gives evidence for the shells (n values) and subshells (l values, or if you prefer, s, p, d and f orbitals).

SIGRID: But here's something that's troubling me. Angular momentum is not the same thing as energy. So why would different orbitals within the same shell (n value) have different energies?

SALLY: Ah, you are right to say that angular momentum is not the same thing as energy. But depending on the circumstance, it can *affect* the energy. Remember we spoke about 'degeneracy'? If l had no effect on energy, then all the orbitals within a shell would be degenerate, and have the same energy.

SIGRID: So what?

SALLY: When we solve the Schrodinger equation, we need to add information about the 'electrical potential'. That's a measure of the electrical potential energy of an electron at any point due to the attraction of the nucleus and repulsion from other electrons, and it is function of the distance, r, from the nucleus.

SIGRID: Again, so what?

SALLY: It turns out that if the electric potential is spherical and inversely proportional to r, then solutions to the Schrodinger equation for the energy, E, do not depend on l. That is, there is l degeneracy, and all orbitals within a shell have the same energy.

SIGRID: When *is* the potential inversely proportional to r?

SALLY: Pretty much only in the hydrogen atom! And we have already discussed the l-degeneracy in the hydrogen atom. If the potential is still spherically symmetric but not inversely proportional to r, and that is true in multi-electron atoms, then different values of l have different energies.

SIGRID: Which is why it matters in what order you fill the orbitals within a shell for multi-electron atoms! So that s-orbitals for a given n fill before the p-orbitals.

SALLY: Precisely! Even then, there is still m_l-degeneracy, so that, say the three p-orbitals within a shell are at the same energy.

SIGRID: Then the energy depends on l, but does not depend on the value of m_l within that sub-shell (orbital type). And is it possible to get rid of the m_l-degeneracy so that m_l does affect the energy?

SALLY: Yes, and then the different p orbitals within a shell will also have different energies. We talk of the degeneracy being 'lifted'. And that happens if the potential is not spherically symmetric. For example, when the system is in an external magnetic field.

SIGRID: And what's so special about a magnetic field?

SALLY: In one sense, nothing, except that it is an easily achievable way to lift the degeneracy! But in another sense, everything! Because electrons and nuclei themselves act like tiny magnets, since they are spinning charges, and moving charges create magnetic fields. Electrons and protons have a 'magnetic moment' which is a measure of how they are affected by a magnetic field. Those m_l arrows that we drew before are a representation of that magnetic moment.

SIGRID: Right, but why is there any limit at all on the number of electrons in a given orbital. Ages ago I thought that the 79 electrons of gold would all live in the first shell. Now I see that they don't but I don't really know *why*. I guess my question is: *why* can't all 79 electrons have the quantum numbers {1,0,0,+½}?

SALLY: This is another one of those times where I'll give you an answer, and you'll just question my answer. But here it is, anyway – electrons are fermions. That means they have spin ½. But having half-integer spin, rather than integer spin, means that they follow a certain type of behaviour, called Fermi-Dirac statistics (rather than Bose-Einstein statistics for integer-spin particles called bosons). Fermions take up space, rather than being able to pile on top of each other. And in an atomic context that leads to the Pauli Exclusion Principle, which says that *no two electrons in an atom can have the same set of four quantum numbers*.

SIGRID: I feel like have learned a lot here. But I still get the impression you haven't told me everything!

SALLY: I suppose. The spectra of atoms other than hydrogen are all more complicated than we would predict from our discussion. Remember we said that electrons act like tiny magnets? Well, the magnetic behaviour due to the *spin* of an electron can interact with its magnetic behaviour due to *orbital* angular momentum, and that complicates things – it's called spin-orbit coupling. Then we have multi-electron atoms, where the magnetic moments of a single electron interact with those of the other electrons. Then there's the effect of the nucleus. The electrons and nucleus orbit a common centre of mass, much like the planets and the Sun (the Sun wobbles too, dues to the influence of the planets), and that complicates things. And the nucleus acts like a tiny magnet too, influencing the electrons.

And that's just for single atoms, where we can concentrate on the interactions between a nucleus and its electrons. They are extra interactions in molecules. Or in crystal lattices of millions of atoms lined up in rows.

But it's good that there's always more to look at another day, right? ☺

- THE END -