Concepts of Chemistry for Engineering
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Lecture No. 23
Concept of Effective Nuclear Charge

Hello everyone, I am Debabrata Maiti, I am the instructor for this course CH105. Welcome to the class, my contact address is Department of Chemistry, IIT Bombay. You can also reach me by email, that is dmaiti at iitb dot ac dot in. Once again, it is d maiti dmaiti at the rate iitb dot ac dot in. My office phone number is 02225767155 and my cell phone number is 09820907155. Please feel free to contact me whenever you need.

So, this course is mainly on inorganic chemistry. I assume that all of you have had some sort of introduction in inorganic chemistry, basic introduction, I will not take you through, I will mainly focus on the contact or content of this course.

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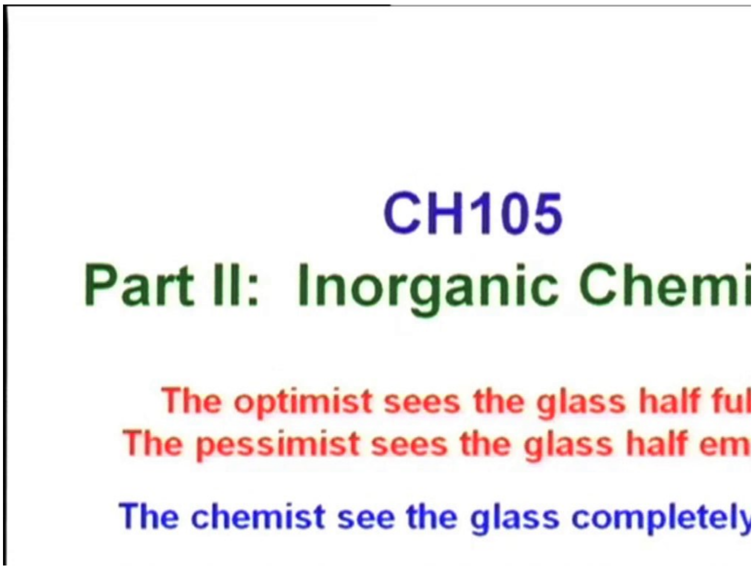

Well, let us start with some simple understanding. It says, optimist sees the glass half full, the pessimist sees the glass half empty. But the chemist which we think, hopefully better of all of them, chemist sees the glass completely full, of course half in liquid state half in vapor.

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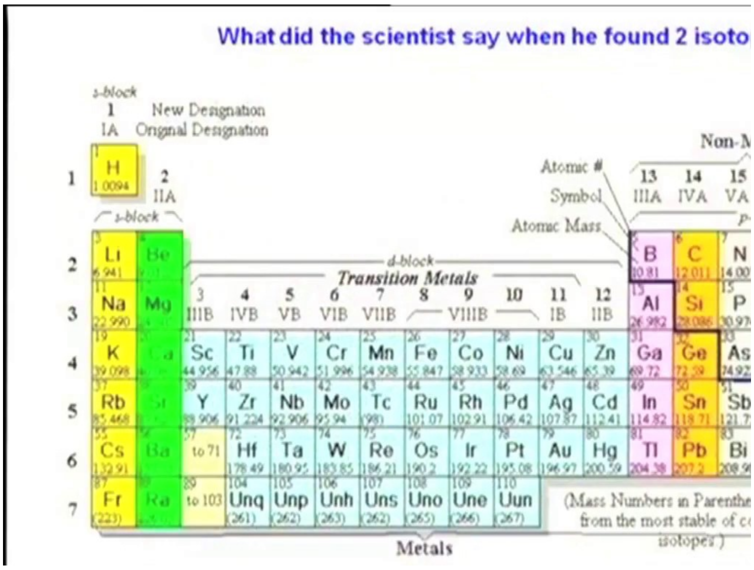

With this note, I will briefly go into the periodic table. Periodic table is something all of you have come across. It is the gathering of all the elements that we have seen so far. It is an ever evolving process. For example, steel after 105 elements, which we are thinking for quite long that is the maximum number, there could be a lot of other elements which are recently developed or recently discovered.

Not only that, the list does not really stop over here, it is as I said ever increasing and thereby their accommodation in the periodic table has to be also be there. Based on their atomic number and their properties as these atoms are organized in a particular fashion, I will come back to that later.

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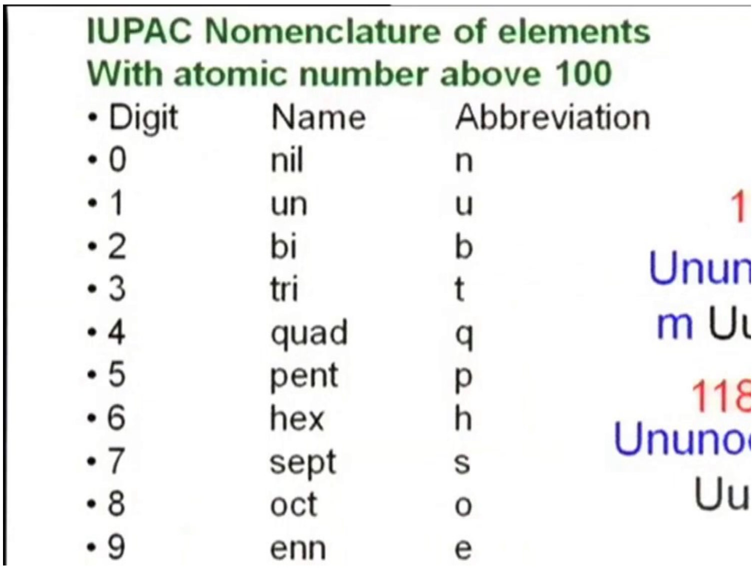

First, let us look at that, try to look at the nomenclature of the unknown entities, unknown atoms. So, a lot of other, lot of new elements are getting discovered if something like 114 atomic number containing element is discovered what will be the nomenclature? The nomenclature for the earlier elements are already done. So, we do not have to worry about their nomenclature like hydrogen, helium, lithium, beryllium, these carbon, nitrogen, so on, but if a new element which is having atomic number let us say more than 100; 105, 100, so on is discovered what would be the way to nomenclature them in terms of IUPAC.

The simple rule here is given as you can see 0 should be pronounced or should be stated as nil. 1 should be un, 2 should be bi and so on up to 8 should be oct, 9 should be enn. So for example, if some element is having atomic number 114, then it should be named as Ununquadium. It would be Uuq. So, this ium should be at the end of it. Anyway, un is 1 as I said, for 1 you should use un; second 1 will be another un, un un; quad for 4 we have quad and it ends with ium.

So, the name for 114 element number 114, atomic number 114 should be Ununquadium. If it is 118, I am sure you can name it by now. So, it would be Ununoctium, 1 1 that is un un, 8 that is octium, Ununoctium. Well, this is a small homework for you, the money which had recently been discovered, although money has been discovered long back, let us assume that money has been recently discovered to be not yet identified super heavy element.

Let us say money is an element, heavy element what should be its IUPAC nomenclature. Simply the IUPAC nomenclature you can say it is Unobtainium. Money, the proposed name for this should be unobtainium.

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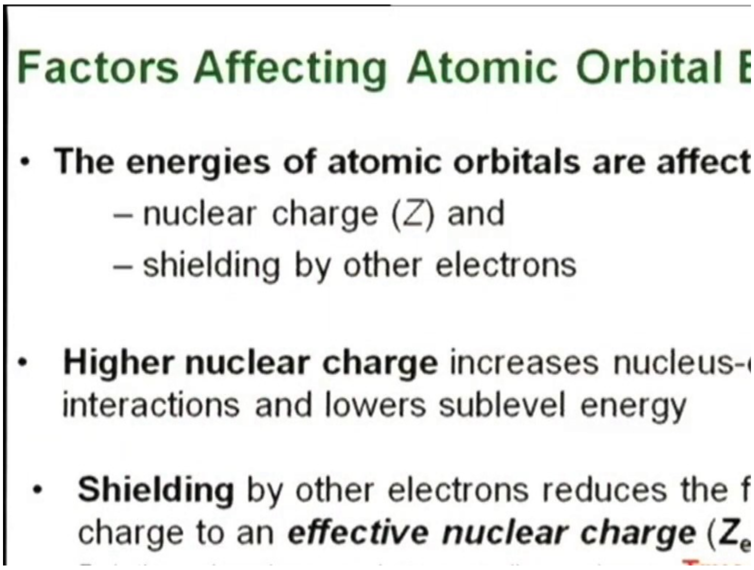

Let us move on, the factors that affects the atomic orbital energies, that is something we need to quite understand before we try to understand the periodic table. Of course, principal quantum number wise if you look at 1s should be having lower energy than 2s than 3s and then 4s and so on. 2p should be having lower energy than 3p, 4p, 5p, but still there are a few factors we need to really understand quite detail, quite simply.

So, atomic orbitals energies are affected mainly by few factors. One is nuclear charge. What is the charge at the nucleus? That is very simple, you can determine that is the atomic number let us say and shielding by other electron, this is what we need to simply understand how it can affect the atomic orbital energy.

So, in an ideal world, what we see is number of protons and number of electrons are equal, it is equal in any atoms, if you see number of protons and number of electrons are equal, but still you see that different electrons let us say outer sphere electrons for different atoms will be filling or will have different filling. Why is that? That is mainly due to the fact that that electrons, that the inner electrons are affecting the outer electrons indirectly.

Let me try to give you an example. So, if you have atomic number, let us say 3, that is lithium. Lithium is having 3 electrons and 3 protons of course. Now, for the third electron that means that the outer sphere electron, the most outside electron will have 2 electrons that is inside. Now, these two electrons, which are inner orbital electrons, will try to neutralize the nucleus charge because, it is a positive charge and negative charge should be neutralizing, in an ideal world 3 proton and 3 electron should be kind of cancelling each other.

But in reality, that does not happen, because, that is because of the fact which we are going to discuss now. Let us say another one having, atomic number 5. So 5 proton and 5 electron and once again they should neutralize the outer one, 1s2, 2s2 and 2p1 that is the p 1 electron will be having total 4 inner electrons, 1s2 and 2s2. So, these 4 electrons will be trying to neutralize the positive charge at the nucleus.

So, thereby, the fifth electron for this atomic number of elements having atomic number 5, should have 4 electrons trying to neutralize the 5 positive charge. So, the way atomic number 3 containing element or atomic number 5 containing element will face the nuclear positive charge is going to be different. Let us look at, we will come back to that again. So, higher nuclear charge increases nucleus electron interaction and lowers the sublevel energy that is quite understandable.

If you have a higher nuclear charge at the nucleus, that will try to attract the electron close to it. Nucleus electron interaction will be higher and thereby their sublevel energy will be minimized. Now, since the atomic orbitals so called s, p, d and so on can have different orientation, can neutralize the nucleus charge to different extent, we are going to see the extent to which the nucleus is attracting the outer sphere electron that is also going to be varied.

For example, if some electrons are penetrating too much that means are able to neutralize the nuclear charge more effectively, then the neutralization will be much more felt and therefore, the attraction between the nucleus and the outer sphere electron will be less. So, s electron being more penetrating that means, s electron can be neutralizing the positive charge at the nucleus more effectively and thereby the penetration power gives more neutralization of the positive charge and in turn what happens I mean you will have very little attraction between the nucleus and the outer sphere electron.

So, the shielding, this neutralization of this positive charge by the inner sphere electrons are called shielding, it is just like a battlefield. If you are, the kings are protected by the different layers of soldiers. Now, the soldiers which are at the outmost zone will be facing the heat they are the one who are fighting, they are the outer sphere electrons comparable to outer sphere electron.

Now, if these inner sphere electrons or the soldier in the inner sphere zone or soldiers which are close to the king can protect can neutralize or can protect the nucleus very effectively. Therefore, the king will not have much attraction towards the outer sphere those soldiers or electrons. So, it is this is the shielding is basically, you try to protect something from, you try to protect the outer sphere electrons from the nucleus, that is what is shielding, you have nucleus which is attracting the outer sphere electron, now, this attraction can be minimized by this inner sphere electron based on their penetration power, based on their neutralization power.

So, this is something equivalent to what I would like to call it true love, what is that? It is something like when everything settles down how much attraction still left for between this outer sphere electron and the nucleus. So, there are a lot of factors, one of those factors is inner sphere electron, inner sphere electron try to neutralize the positive charge, after this neutralization how much attraction still left at the outer sphere electron. So, this is what is called a Z effective or the effective nuclear charge Z star. That is something very important.

And I would like to call very simply, just firmly, it is a true love. So, what we tried to discuss so far is simply it really matters that inner electron really matters a lot, if you want to talk about the outer sphere electrons. Outer sphere electron, although they are not directly attached with the inner sphere electron but inner sphere electrons are the one who are going to take care of the outer sphere electron. If inner sphere electrons are very much penetrating, then the attraction between your nucleus and the outer sphere electron is going to be very little, so we will come back to that.

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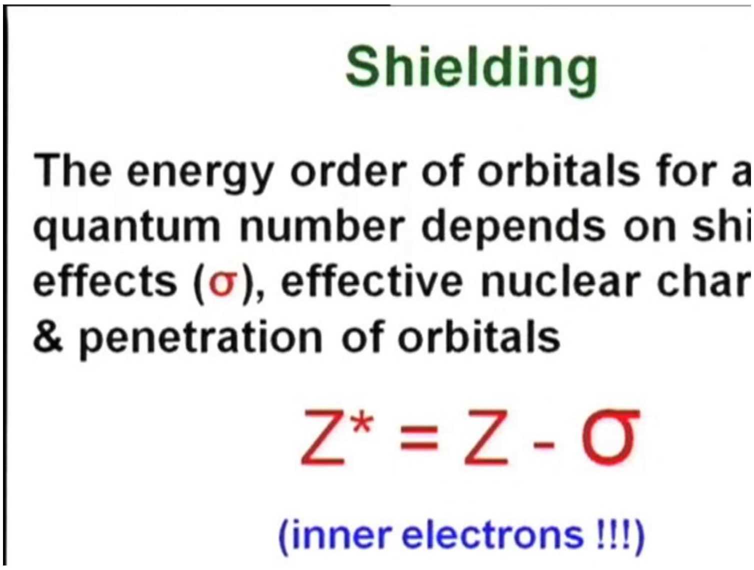

So, what is effective nuclear charge then Z star? Effective nuclear charge Z star is your total atomic number whatever it is, let us say 5, atomic number 5, that is hydrogen helium, lithium, beryllium and boron 5, 5 minus that shielding total those 4 electrons let us say if we are talking about the fifth electrons, so the 4 electron how much shielding that is having, that is going to be the effective nuclear charge or Z star for the fifth electron. So the inner electrons, that is the one which matters most.

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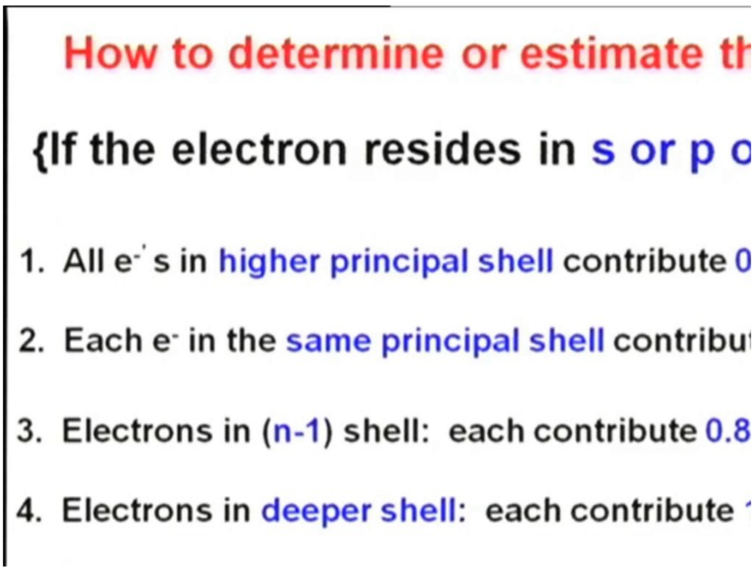

Now, how to calculate the Z star, we should have a clear idea, it is more than basic understanding how Z star is getting affected by different orbitals, we should have some sort of clear understanding how to calculate the Z star. Of course, it is not possible to calculate exactly, but some sort of theory perhaps can be, can be summarized or can be brought to estimate the Z star.

So, there are no uniform ways available to determine Z star, we can have Z star calculation, let us say you can follow the procedure I am trying to discuss over here. Actually, if you look at different books, they might will be discussing different ways to calculate the Z star, but let us follow the procedure what we are trying to discuss over here, it is the procedure I think it is also in this textbook which is going to be very standard textbook for you is Shriver Atkins this inorganic chemistry book.

If the electrons that means the outside electron or the whatever electrons you are interested in, if that electron is s or p orbital, then you can calculate that Z star as follows; all electrons in higher principal shell, let us say you have 1s2 2s2 2p1 electronic configuration, you want to calculate the Z star for 2s electron, you of course, you can calculate the Z star for 2p electrons just for example, you want to calculate the Z star for 2s electron, 2s second electron.

So, the fourth electron you would like to calculate the Z star for. So, therefore, the 2p electron so any electron, let us say in this case you would like to calculate the Z star for 1s electron not 2s electron. 1s electron means, so you have total electronic configuration 1s2 2s2 2p1, you want to calculate that Z star for 1s electron. That means the outer sphere electron that is 2s and 2p, you do not have to worry about, you just have to worry about the electrons in the same orbital or that of the lower atomic number. So, lower principle number, n minus 1 principal shell.

Now, all electrons in higher principal shell contribute 0 to sigma. So, electrons that is outside you do not have to worry about that, each electron in the same principal shell should contribute 0.35, I will come with an example very soon. Electrons in the n minus 1 shell should contribute 0.85, electrons in deeper shell that means, n minus 2, n minus 3 and n minus 4 and so on should contribute 1 to sigma.

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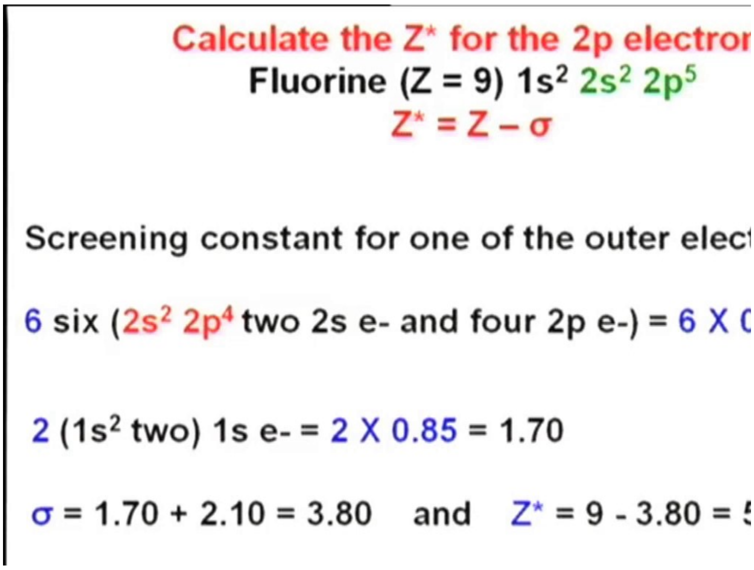

Let me show you one example then it should be clearer. So, for fluorine for example, you want to calculate the Z star for the fifth electron. So, it is 1s2, 2s2, 2p5, this p5, fifth electron you want to calculate the Z star for. So, the formula you have to follow in simply Z star equals Z minus shielding this sigma. So, the screening constant for one of the outer electron 2p remains constant for one of the outer electron 2p, that means, this p fifth electron is…

So, the same quantum number is 2s and 2p. So, the fifth electron you are considering, so you should not be calculating the fifth electron, so you should take 2p4 electronic configuration because you are trying to calculate the Z star of the fifth electron, so overall in the principal shell 2, you have 2s2 and 2p4, total 4 plus 2, 6 electron. 2s2 2p4 that means 2 2s electron and 4 2p electron should contribute 0.35 is, this is the same principal shell as that of the one we are interested in, so 6 time 0.35 that is 2.1.

Now, one below, below the principal shell n minus 1 should contribute 0.85, so it should be 0.85 times 2, because 1ss orbital has two electrons. So, 0.85 times 2, it should be 1.7. So, the sigma or the shielding constant should be the combination of all these effects, so 1.7 for two electrons plus 2.1 for the 2s and 2p electron overall sigma is going to be 3.8 as you can see and the Z star should be equal to 9, that is the atomic number of the fluorine, 9 minus this sigma which is 3.8 that is 5.2.

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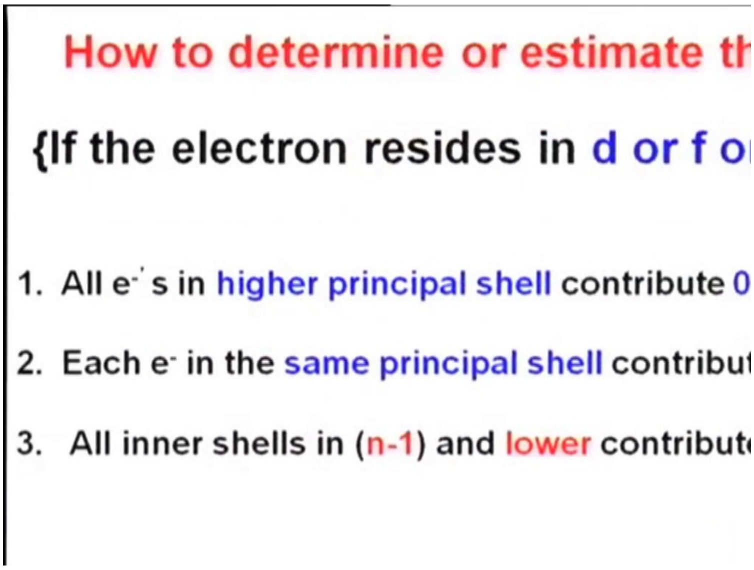

Now, once again that rule is very simple just to remind you anything outer sphere outside the zone we are interested in should contribute to 0. If for example, in if you are interested in 1s electron then 2s and 2p electrons they should not contribute anything. Since we are interested in fifth electron, so, all the electrons below this should be considered anything above it if there is anything above it should not be of any interest for calculating the shielding constant.

After that you should see that same principal shell quantum number, principal shells that is 2s and 2p and each of these electrons should contribute 0.35, anything less, 1 less that is n minus 1 should contribute 0.85. If there was more electrons below this, in this case, it is not possible, then that should have contributed to 1, that means, effectively it will be neutralizing all of the positive charge that is over there.

What essentially we are talking about? We are trying to tell you that for each electron we add technically we are also increasing one proton at the nucleus, this proton and electron should be neutralizing each other, but in reality they do not neutralize each other. To what extent this electron, that is negative charge is neutralizing the positive charge that is what we are trying to calculate.

If it is the electron which is little bit outside or the electrons we are interested in the same shell those electrons are there, then they should not be neutralizing the nucleus charge completely, the one which is deeply buried or inner sphere electron will be neutralizing the positive charge of the nucleus effectively. If it is n minus 1 shell electron, they will be neutralizing the positive charge of the nucleus little more effectively compared to the outer sphere, if it is n minus 2, they or n minus 3, essentially they should be neutralizing, one electron should be neutralizing one positive charge. So, that is what they are contributing 1 to the sigma.

So, this calculation or this mode of calculation whatever we have discussed here right now is valid for the electrons if we are calculating for p and s orbitals. Now, if we are interested in discussing the effective nuclear charge Z star for d orbitals or f orbitals, why they are different? Of course, their penetration, their shapes are different and their ability to neutralize that nuclear charge is completely different and actually very less.

So, therefore, the calculation varies a little bit over here. For example, first thing remains same, anything, any electron outside that electron which we are interested in, should contribute 0, they should not be affecting in the calculation. Each electron in the same principal shell as before for the s and p shell should contribute 0.35 to sigma. All inner shell; n minus 1, n minus 2 and so on should contribute 1.0.

Previously you have seen n minus 1 shell is contributing 0.85, but in these cases it should be contributing 1 not 0.85. So, all the inner shell electrons, n minus 1, n minus 2, n minus 3, n minus 4, whatever possible should contribute 1.0.

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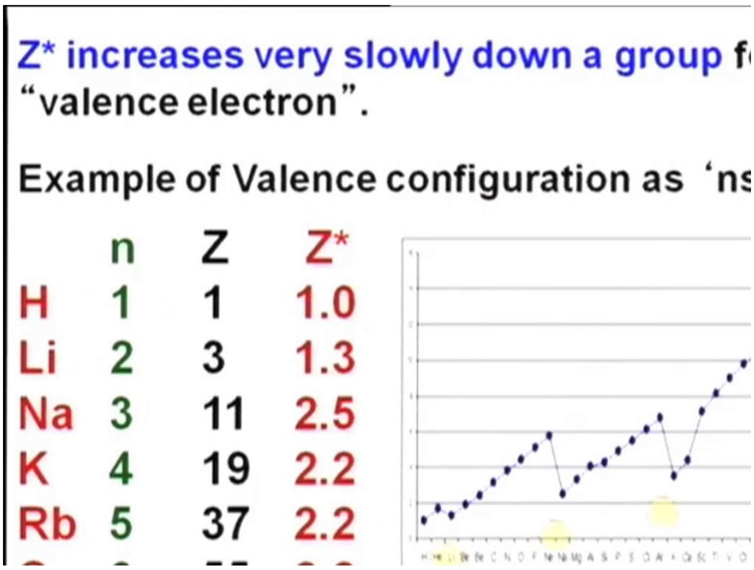

So, it is actually calculation is very simple, you can take a look at any standard textbook as we mentioned Shriver Atkins perhaps would be a good idea. So, here is some effective nuclear charge that we are looking at for the outermost electron. For example, hydrogen; hydrogen's effective nuclear charge should be 1. If you go down the periodic table; hydrogen, lithium, sodium, potassium, rubidium, cesium, you see there is very little increase if any or very little value for the Z star.

So, what essentially happening here is every time you are going from top to bottom you are increasing a new shell as we are saying, the since the shell number is increasing, inner shell can effectively neutralize the positive charge inner shell electrons can effectively neutralize the positive charge and thereby overall what you are seeing the Z star remain almost constant, as specifically if you can see potassium, rubidium, cesium they remain constant.

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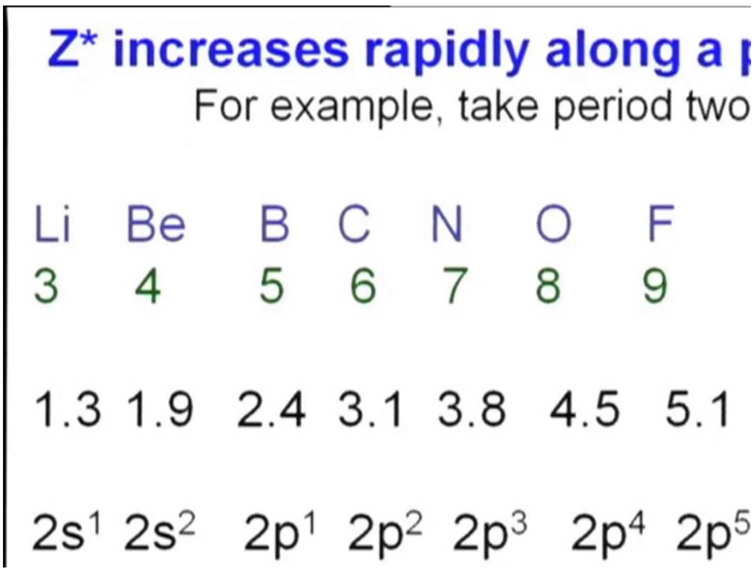

Now, if you look at periodic table carefully and try to work from left to right, if you are working from left to right, let us say for the series for lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon. What is happening here, your atomic number increases 3, 4, 5, 6, 7, 8, 9, 10, of course. Now, quite interestingly, your effective nuclear charge is also increasing dramatically. What that does mean?

Simply that does mean that, the electrons each case electrons are increasing and each case your atomic number is also increasing, the electrons cannot neutralize the nuclear charge effectively.

It is the same principal shell, where electrons are entering, since the same principal shell electrons cannot neutralize that nucleus charge effectively, what essentially we are seeing is the contribution instead of 1 neutralizing one electron by one proton, electron is only contributing 0.35 towards the neutralization of the positive charge and therefore, effective nuclear charge is gradually increasing.

So, if you look at the attraction of the nucleus for lithium towards the outer shell or outer electron, let us say x, whatever it is, if you go down the period, if you work from left to right, you will see the nucleus will be trying to attract the outer electron very effectively, that will in turn will have an effect in your size, size of the atoms technically speaking, if your nuclear charges increasing or effective nuclear charge is increasing, so effectively nucleus will pull in that electrons towards it. So, your size will be decreasing from left to right. So, we will come back to that again.

So, what we have seen in the periodic table, I think you have already learned about it. So, if you are working from top to bottom in a periodic table, top to bottom, your principal shell increases. So, 1s, 2s, 3s, 3p, 4s and then 5s and so on, your effective, so the principal shells increases. Since the inner electron can neutralize the nuclear charge effectively in these cases, so, 1s2, 2s2, 3s2, 4s2, 5s, since this inner electron can neutralize the positive charge effectively, thus increase in this atomics, atomics, this shell or this principal shell will result in increasing size.

From top to bottom size should increase and in the periodic table if you work from left to right, then what will happen, electrons are getting into the same shell one by one, exactly in the same shell, let us say in this case 2p. So, the electronic configuration over here is 1s2, 2s1, then 2s2 then 2p1, 2p2, 2p4, 2p5, 2p6.

So, it is the same principal shell the electrons are getting incorporated and therefore the neutralization of these electrons, neutralization of the positive charge by these electrons are not going to be too much. And since the Z star therefore is going to be increased, they will try to pull in the outer sphere electron and the size will get smaller and smaller. So, the Z star will try to squeeze in kind of the size, the size will decrease dramatically.