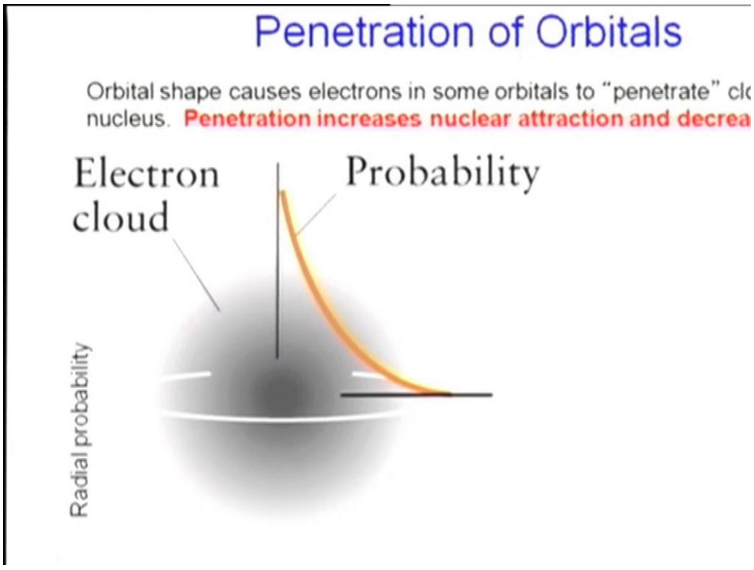
Concepts of Chemistry for Engineering
Professor Debabrata Maiti
Department of Chemistry
Indian Institute of Technology, Bombay
Lecture No. 24
Electronic Configuration of Elements

(Refer Slide Time: 0:13)



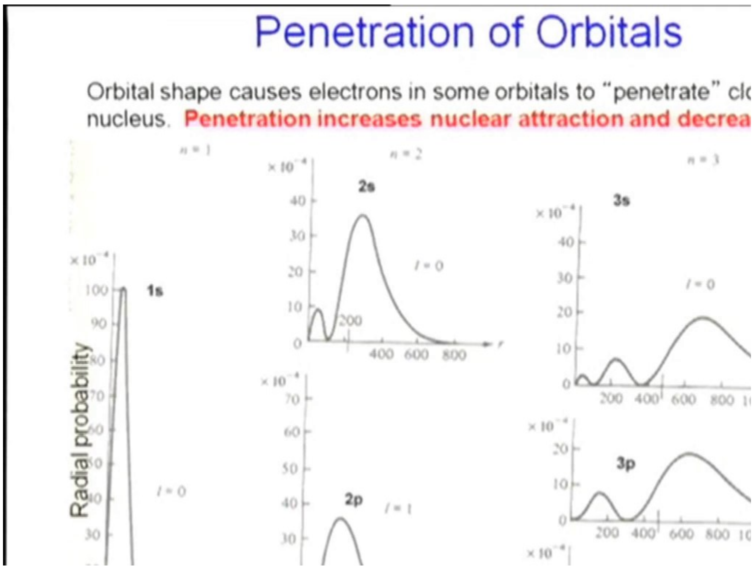
Penetration of Orbitals

Orbital shape causes electrons in some orbitals to "penetrate" cl
nucleus. **Penetration increases nuclear attraction and decrea**

Now, this is something, these electrons how does the electrons are distributed outside the nucleus, or, this probability of finding electron, as you would like to call them can be more clearly be taught in physical chemistry course, here I will give you just a brief idea, may not be exactly, exactly clear idea, but it is something which will give you an idea to go forward.

How are the orbiter's shapes? Of course, we have learned that shapes are different, but then if you want to see that electron distribution, of course, my physical chemistry colleague will perhaps kill me if I try to define like that, but let me do it anyway, you are going to learn better in physical chemistry course.

(Refer Slide Time: 1:08)



Penetration of Orbitals

Orbital shape causes electrons in some orbitals to “penetrate” cl

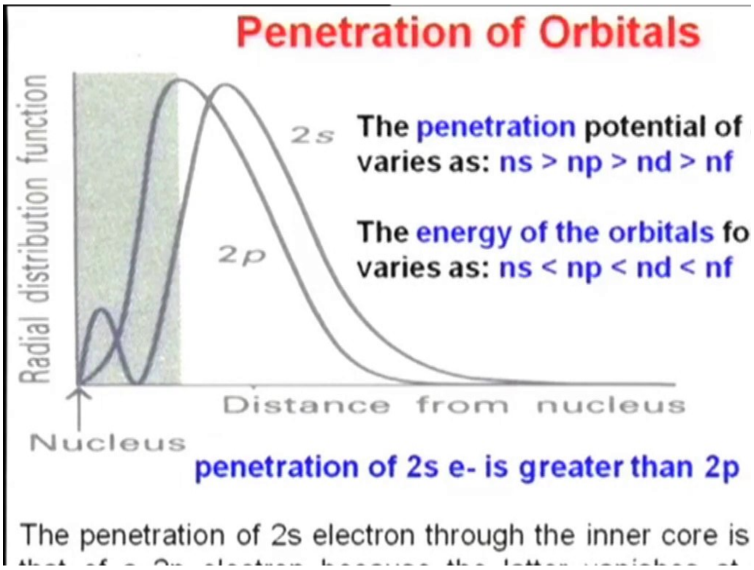
nucleus. Penetration increases nuclear attraction and decrea

So, if this is the 1s electron we are talking about, then 1s electron is distributed with respect to the nucleus, if the nucleus is at the center, we would like to think like that, the probability of finding the 1s electron is going to be like this, so the probability of finding 1s electron towards nucleus is quite high. If you look at 2s electron, probability at finding 2s electron at the nucleus is not that much of course, there is a node at this distance after that, there is a probability of finding this 2s electron is quite high.

If you look at 3s electron it is one more node added and you can see this if you compare 2s versus 2p, you can further see of course, 2s has some component very close to the nucleus over here 2p does not have really that much component very close to the nucleus. So, the penetration is actually meaning that how much these orbitals are contributing towards or how much close they are towards the nucleus.

So, as you can see, 1s is very close to the nucleus, and thereby, the penetration of 1s is going to be the maximum and it can neutralize the positive charge most efficiently. As you can see for the other, for example, 3d, 3d is distributed or the maximum probability of finding 3d electrons are really far from the nucleus. Therefore, the neutralization ability of 3d electrons are going to be kind of list out of all these orbitals shown in here.

(Refer Slide Time: 3:07)



Penetration of Orbitals

The **penetration** potential of varies as: **ns > np > nd > nf**

The **energy of the orbitals** fo varies as: **ns < np < nd < nf**

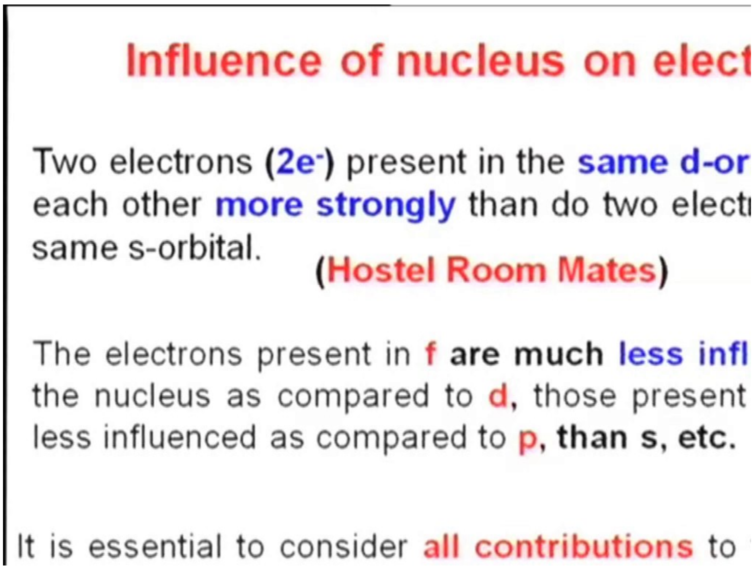
penetration of 2s e- is greater than 2p

The penetration of 2s electron through the inner core is

Now, if you compare it directly 2s versus 2p, you kind of overlap these 2s and 2p electron and then this is what the distribution curve you see, as you can see penetration of 2s electron is greater than 2p electron because you have a very good component of 2s very close towards, towards this nucleus.

So, the penetration that means, that no the positive component is getting neutralized by these electrons at the orbitals, the penetration of the 2s electron through the inner shell or inner core is greater than that of 2p electron, because the latter vanishes at the nucleus. So, the 2p electron vanishes at the nucleus whereas, 2s electron are still there. Therefore, the 2s electrons are less shielded than 2p electrons. 2s electrons are basically penetrating much more compared to 2p electrons.

(Refer Slide Time: 4:21)



Influence of nucleus on elect

Two electrons **($2e^-$)** present in the **same d-or**
each other **more strongly** than do two elect
same s-orbital.
(Hostel Room Mates)

The electrons present in **f are much less infl**
the nucleus as compared to **d**, those present
less influenced as compared to **p, than s, etc.**

It is essential to consider **all contributions** to

Now, another thing you really need to understand very simply is the d electrons repel each other much more compared to p or s electron. How is that, show me? So, it is like involvement. How much involved you are in a particular thing? Well, let me give you an example of your hostel rooms. In your hostel, if you have let us say, 3 people in a room, it is possible or 2 people in a room or 3-4 people, 4 people in a room.

Now, if out of the 4 people, 1 or 2 of them are involved in something, it could be music, it could be studying, it could be sports, it could be anything outside, outside the normal thing you would like to do. So, if they are too much involved, they, it is less likely that they will have much more time to interact with the third or the fourth, roommates. So, if the first and second person in your hostel room are involved in something deeply, they are less likely that they will disturb you.

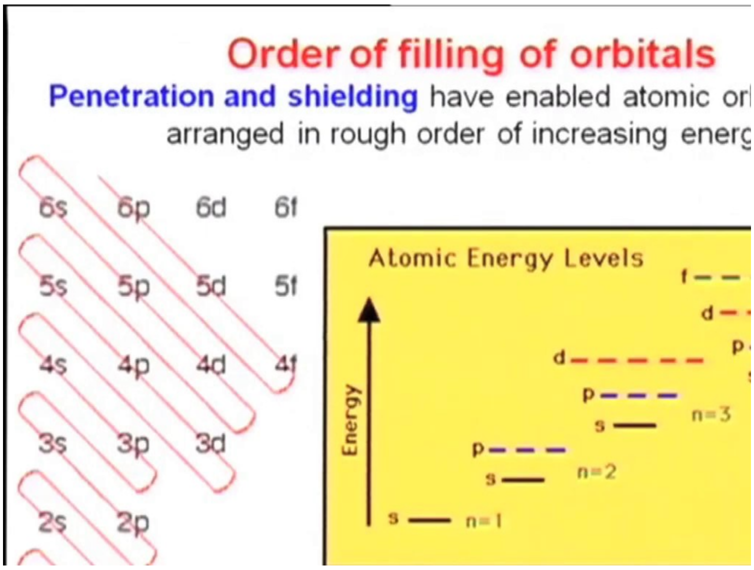
But on the other hand, third, student or third mate, and the fourth one are not being involved in anything that way, so it is more likely that these two guys third and fourth guy will be having more number of fights or more number of disagreement. So, this is what we are trying to see in d electrons. What is happening is d electrons are not really involved with the with that with the nucleus, d electrons are kind of not capable of neutralizing or engaging with the nucleus. And therefore, the d electrons will be repealing each other very strongly, or will have more conflict.

On the other hand, if you look at comparatively, let us say, s electron, they are much more penetrating, they are much more involved with the nucleus. And therefore, the s orbital having two electrons will repel less compared to d orbital having two electron. So, what I am trying to say is two electrons, if it is in d orbitals, those two electrons will repel each other more strongly, compared to two electrons in the s orbital because s orbital is more engaged with the nucleus.

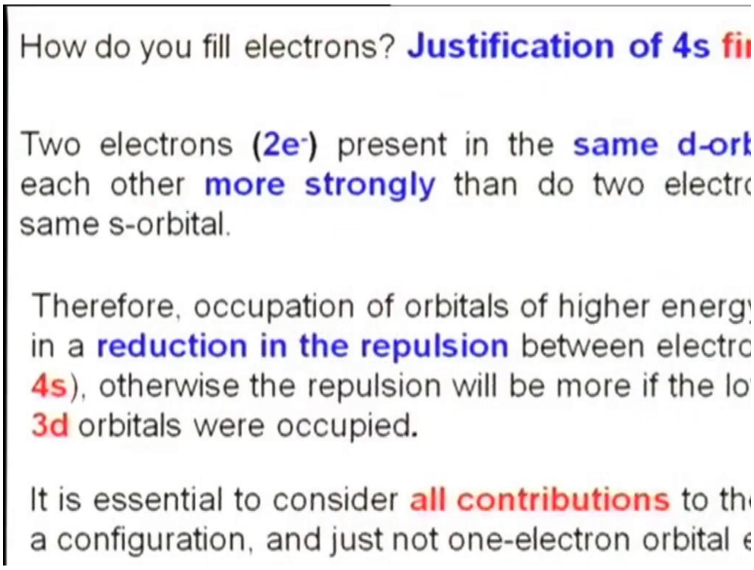
So, two electrons present in the same d orbital, repel each other more strongly than two electrons in the same s orbitals. So, that is what I am trying to say, it is hostel roommate, the electrons present in f are obviously much less influenced by the nucleus as compared to the two electrons. So, electrons in s orbital is much more involved with the nucleus, the p orbital it is a little bit close involve with the nucleus, d orbital electrons are less further less involved, f electrons are even I kind of least involved with the nucleus.

And therefore, the repulsion among the f electrons will be much more, among each other will be much more compared to any two electrons in any other orbitals. So, you find us trying to calculate in a are trying to understand any effect or any effect by these different electrons, you have to you have to essentially think of a bigger picture, you have to you have to think how much penetrating they are, you have to think how, how much repulsion they will be having with each other and so on, we will come to that.

(Refer Slide Time: 8:50)


Order of filling of orbitals

Penetration and shielding have enabled atomic or
arranged in rough order of increasing energ



How do you fill electrons? **Justification of 4s fi**

Two electrons **($2e^-$)** present in the **same d-or**
each other **more strongly** than do two electr
same s-orbital.

Therefore, occupation of orbitals of higher energ
in a **reduction in the repulsion** between electr
4s), otherwise the repulsion will be more if the lo
3d orbitals were occupied.

It is essential to consider **all contributions** to th
a configuration, and just not one-electron orbital

So now, I will discuss order of filling of orbitals, you have studied quite long back I guess, that order of filling should be 1s should we fill out first and then 2s, then 2p, 3s, 3p, not 3d then, then after 3p it should be 4s then 3d. And this is where I think we need to understand a little bit better, why after 3s, 3p gets filled but after 3p not really 3d is getting filled, but 4s is getting filled.

Technically speaking, 4s is having more energy compared to 3d, because the principal shell is of higher number. 3s since it is, the electron in 3s should be more or more stabilized means less energy compared to 3p, so 3s should we fill out first then 3p. After 3p, then it should be 3d then 4s.

But in reality, what we see that 4s is fill out before 3d, of course, first thing we need to understand that 4s and 3d are having very similar energy. If anything, we would like to think that 3d is having lower energy compared to 4s. But for that, we must we must think of something which is which we try to discuss just briefly like 5 minutes back we were discussing, so, the d electrons are less penetrating, d compared to let us say, s electron.

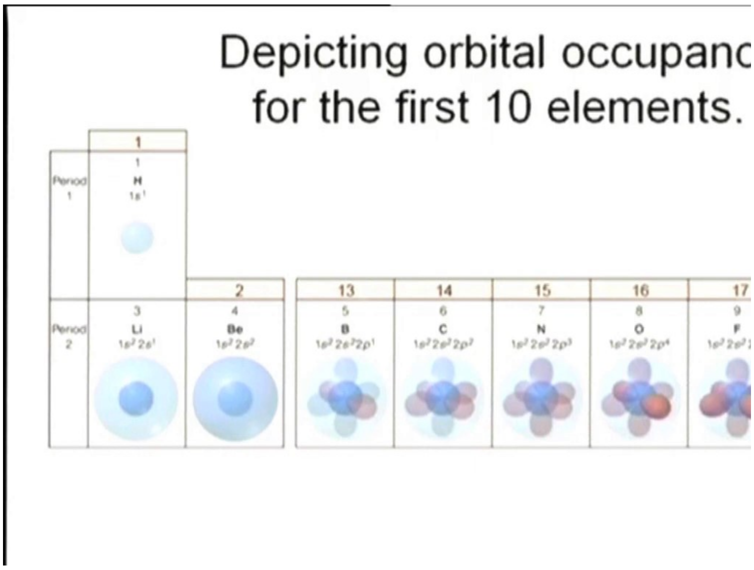
So, compared to 3d electron, 4s electron is going to be more penetrating. And therefore, repulsion of electrons in 4s orbital will be less compared to repulsion in the 3d electron. So, 4s and 3d, first of all, they are having very little difference in energy. Since that repulsion in 4s is going to be much less compared to 3d what will happen that 4s is going to get preferably filled out compared to 3d. So, this is an exception and this is how it can be perhaps explained.

Therefore, occupation of orbitals of higher energy can result in a reduction in the repulsion. So, in this case, if you occupy the electrons in the 4s orbital it is going to repel less consequently, what we see is 4s electron is getting 4s orbital is getting filled out preferentially over the 3d. Once again I think this is kind of becoming a disclaimer, you have to really consider all other contributions.

Not only numerically, we should not be seeing that 1s, 2s, 2p, 3s 3p 3d. Instead, we should be looking at their relative energy and the consequences that is going to have if you fill out these orbitals let us say 4s versus 3d, in this case, once again the repulsion among the electrons determines which one is going to be preferentially filled out.

(Refer Slide Time: 12:56)

Depicting orbital occupanc
for the first 10 elements.



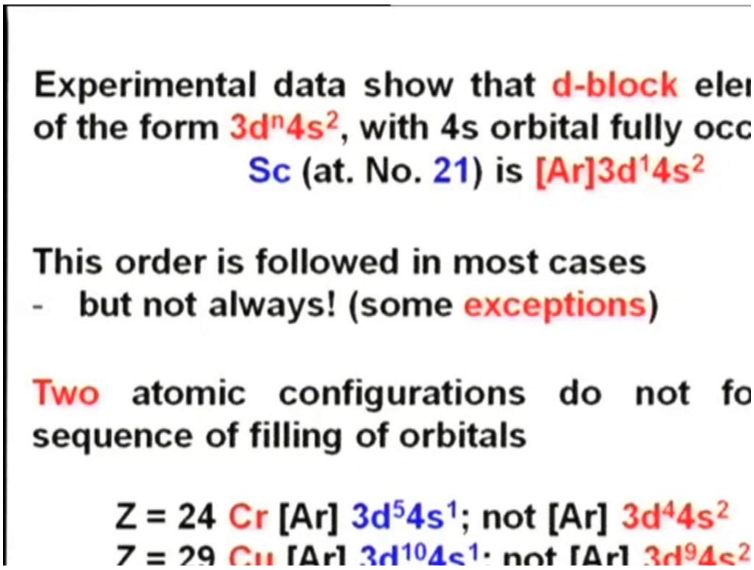
Now, let me show you some other data which I think I like it very much where it is clearly showing how kind of electrons are getting filled out. 1s, you have one electron filled out for hydrogen let us say 1s1, 1s2 two electrons filled out compared to this one, you are seeing that dark curve ball of the same size, 1s electron getting filled out. Now over here for the lithium you have 1s2 and 2s1. So, the 1s orbital is this one, 2s orbital is this one.

So, it is overall, you see the distribution of electrons kind of not so accurate picture once again, but this is something you can visualize, to basically understand, for 1s2 2s2 you will see that 1s of course is very dark, 2s orbital also becoming very dark. If you see the boron that is 1s2, 2s2 and 2p1, now one of the p orbital is getting occupied by electron and then from 2p1 if you see

2p2, 2p electrons are getting occupied, then 2p3, 2p4, you are seeing the p electron clouds are getting more and more deeper.

And therefore the overall if you see neon, that is 1s2, 2s2, 2p6, this should be something like this, this is again, this is an approximate picture, this is just to give you a feeling, how perhaps the electrons are distributed with respect to the nucleus. In reality, this picture perhaps, in reality, this does not exist. I think I have discussed this.

(Refer Slide Time: 14:45)



Experimental data show that d-block ele
of the form $3d^n4s^2$, with 4s orbital fully occ
Sc (at. No. 21) is [Ar]$3d^14s^2$

This order is followed in most cases
- but not always! (some exceptions)

Two atomic configurations do not fo
sequence of filling of orbitals

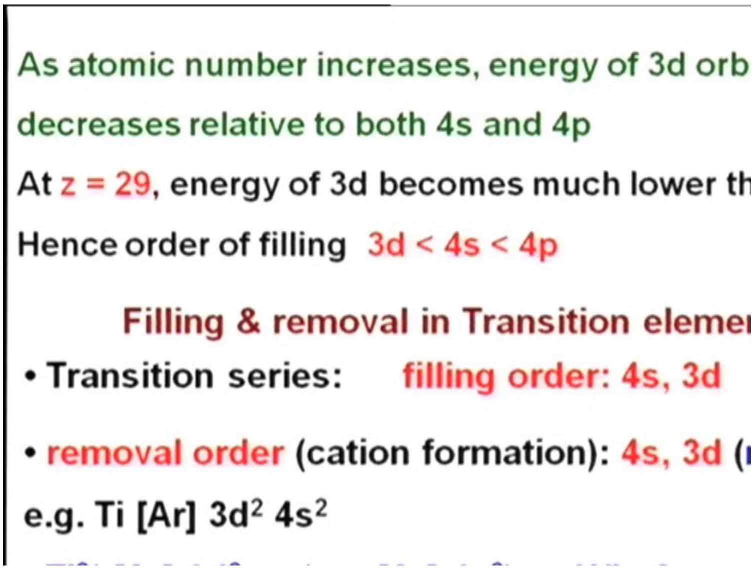
Z = 24 Cr [Ar] $3d^54s^1$; not [Ar] $3d^44s^2$
Z = 29 Cu [Ar] $3d^{10}4s^1$; not [Ar] $3d^94s^2$

Now, of course, what we find that experimental data show that d block elements are of the form 3dn4s2. That means 4s electrons are getting filled out preferentially compared to 3d electron with 4s orbital fully occupied, for example scandium atomic number which is 21 by electronic configuration for scandium would be, this the argon configuration and then 3d14s2. So, it should be 4s filled out first, two of them and then 3d1. If atomic number scandium, titanium let us say, if you have then it would be 3d2 and 4s2 and so on.

This order is followed in almost all cases, that means 4s two electrons will be distributed first or given first and then the remaining electron if any should be going to your 3d electron. Two atomic configuration actually kind of violates this general principle. What are those cases? You might will know that it is chromium and copper. What is happening in these cases? In these cases, it should be, according to what we are discussing, it should be 3d4 4s2 electronic configuration.

Of course, now, this is going to be a half fill, full fill configuration or the zone where you can have 3d5 electronic configuration to gain the further stability, the electronic configuration will become now 3d5, 4s1, not 3d4 4s2. In case of copper, it is a similar situation where according to what we were discussing earlier the electron repulsion in the d orbitals it should be 3d9 and 4s2, but it is not it should it is 3d10 and 4s1, because the d orbital if gets one more electron it becomes 3d10 which is a full filled electron configuration.

(Refer Slide Time: 16:58)



As atomic number increases, energy of 3d orb

decreases relative to both 4s and 4p

At z = 29, energy of 3d becomes much lower th

Hence order of filling 3d < 4s < 4p

Filling & removal in Transition eleme

- Transition series: filling order: 4s, 3d
- removal order (cation formation): 4s, 3d (

e.g. Ti [Ar] $3d^2$ $4s^2$

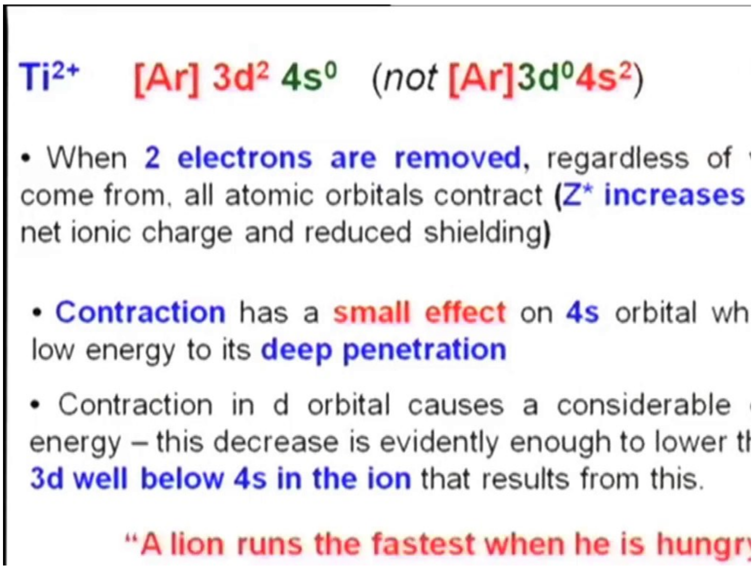
So, the cases where you have half fill or full fill electronic configuration attainment, then you are going to see the deviation from the standard 4s filling first and then 3d electron. As atomic number increases, energy of 3d orbitals decreases relative to both your 4s and 4p. So, we are trying to say that 3d should be having comparable energy with 4s, 4s should be having lower energy compared to 4p that is fine.

Since the d electrons can repel each other strongly compared to 4s electron, this repulsion energy or the destabilization energy preferentially allows 4s electrons to be filled out first, but once d electrons getting filled out more and more, what happens is d orbitals is no longer having a higher energy compared to 4s the energy of d orbital 3d orbital decreases compared to 4s. So, in that case, the filling order should be as expected or normal 3d should be filled out first and then 4s and then 4p.

Now, another thing to understand, see, overall what we tried to say 4s should be filling out first, then 3d, but removal what will be the removal order? So, this is what we now need to understand for transition metal series, your filling order should be 4s and 3d. Removal order should be again 4s and 3d, this is what I think it is a little bit contradictory, I think you would expect since 3d is filling out later on, so the removal time 3d electrons should go first.

But that is not the case, 4s fills out first, 4s gives out first. How is that possible or what is the explanation? Let us say take the examples of titanium. So, it is 3d2 4s2, fine 4s filled out first and then 3d filled out. When titanium 2 plus we are thinking, then it should be according to the filling order 3d orbital electrons should go out, that is not happening. What we are seeing is in reality 4s electron is going out, not the 3d electron. How can you explain this? This is one of the small topics we need to discuss.

(Refer Slide Time: 19:56)



Ti^{2+} $[Ar]\ 3d^2\ 4s^0$ (*not* $[Ar]3d^0 4s^2$)

- When **2 electrons are removed**, regardless of come from, all atomic orbitals contract (**Z* increases** net ionic charge and reduced shielding)
- **Contraction** has a **small effect** on **4s** orbital wh low energy to its **deep penetration**
- Contraction in d orbital causes a considerable energy – this decrease is evidently enough to lower t **3d well below 4s in the ion** that results from this.

"A lion runs the fastest when he is hungr

So, now once again I think you have to see the clear picture before and after electronic electron removal, during filling out what is the consequences we have understood that d electrons repel each other strongly therefore, the electron should not be filled out first, that is the filling time, so, the 4s electron fills out first. 4s electron fills out first because 4s electron is kind of more stabilized compared to the 3d electron.

Now, once you are trying to remove, let us say you have removed two electron titanium 2 plus. Now, you have to see this overall stability, 4s electron is having lower energy or s electron in general is having lower energy mainly due to the fact that it is more penetrating, it is more penetrating, therefore, it is getting more stabilized. Now, when you remove two electron either from 4s irrespective of 4s or 3d, overall what is happening is, your attraction of the nucleus towards the electron is going to be much more, electrons have less.

So, the atomic number remains same, the attraction of nucleus towards the outer sphere electron or towards all the electrons is going to be much more compared to the normal or neutral situation, since the Z star that means effective nuclear charge is going to increase dramatically, this will give the stability, this will reduce the shielding of the electron. So, there will be some sort of contraction, contraction has a small effect in 4s.

Because 4s is already very close to the nucleus, comparatively the stabilization or the contraction will cause the stabilization to 3d are much more compared to your 4s. So, what is happening here is after removing two electrons, the effect of contraction is going to be much more felt at 3d compared to your 4s, because 4s is already lower in energy and the lower energy is the reason why they are going to be, they were filling out first.

Now, during removal, thinks 4s is already kind of neutralized or 4s is already having lower energy, the removal effect is going to be felt much more at that d orbital, so d orbital energy will be much more stabilized and removal of the electrons will be much more easier from the 4s compared to your 3d, 3d energy is going to be stabilized, 3d electrons are going to be stabilized compared, much more compared to 4s. So, the stabilization will lead to the removal of electrons from the 4s not from 3d.

So, that is what we try to summarize in here. Contraction in d orbital causes a considerable decrease in energy. This decrease is evidently enough to lower the energy of 3d well below 4s in the ion that results from this. The removal of electron from 4s will be easier compared to 3d electron.