## webinar 7: laser spectroscopy

(automated transcription)

With this feedback webinar we leave the physics of hyperfine interactions behind us and we move on into the territory of the experimental methods. But as usual first some housekeeping information. So as this is a course that is synchronized with the spring teaching term at Flemish universities we have an Easter break and that means that in the next two weeks there will be no feedback webinars. The next feedback webinar will be on the 17th of April and by that time there will be daylight saving time in Europe so that means that in terms of UTC the time of the webinar will have changed. Nothing changes for the people living in Europe, it remains 8.30 local time but if you follow this from a different time zone then mind that change. I guess I will be traveling on the 17th of April so probably that feedback webinar will not be live, I'm not sure yet, depending on the traveling time maybe I can do it before I leave but if I would not be able to do it live then I will record it the evening before and it will still be streamed as a recorded live stream and then put on the course site afterwards. Specifically for the students from Flemish universities and not the University of Leuven I have been informed by one of you that the exam has been scheduled by the faculty on Monday May 27th. I didn't check this yet in the agenda I can see but I assume that this is correct information so that means that let's fix the exam that day. If you have any problem with this, overlap with another exam then please let me know by email as soon as possible but I hope that we can have one exam session for everybody on that day. That exam is an on-campus exam but open book, open internet and the type of questions that will be asked, well I discussed that in the introduction webinar so if you don't have, if you don't remember this clearly please go back to the introduction webinar. Of course if there are any questions related to the practical organization of the exam let me know. So much for the housekeeping. Then as I told in the very beginning we have finished now part one of the course about the physics of hyperfine interactions and in the transition module, the module that connects the two parts of the course, there is a summarizing video about part one so this is a good opportunity, I noticed some people watched it by now, if you didn't do so, it's good after you have studied, digested the content of the first part to watch that summarizing video to check your understanding, there you hear the main messages of the first part summarized in 25 minutes or so. After the physics of hyperfine interactions we start with the second part about experimental methods, experimental methods that make use of hyperfine interactions. And the first part there is something that is not connected to one experimental method but something that is related to all experimental methods, that's the transition from our very important picture number one to the very important picture number two. Picture one summarizes the first part of the course, picture two summarizes the second part of the course. The very important picture number one was this one and I show it here in the version for the quadrupole interaction but you have a similar picture for the hyperfine interaction, for the magnetic hyperfine interaction and for the monopole shift. The point here is that in order to go from picture number one to picture number two we will now draw all the fine structure levels here at the left hand side. It is as if you collapse the fine structure part of the picture onto the left hand side. Every line that is drawn at the left hand side is now a fine structure level of the system under consideration and on top of the fine structure levels then the hyperfine splittings will be shown. So that is what this very important picture number two tells us, every line here is a fine structure level and the fine structure levels are hyperfine splits. The picture that is given here is as an illustration for a nuclear spin one half in the nuclear ground state, a nuclear spin three halves in the first excited state of the nucleus and on the side of the electron cloud we show a magnetic hyperfine field only. That's as a way of illustration, you could make the same picture for an electric field gradient or for a combined interaction, that does not matter. What this picture tries to bring across is that you can classify the different hyperfine methods in terms of the energy of the transitions that are involved. So you can have transitions in the frequency range of radio waves, in the

frequency range of microwaves up to visible light and in the frequency range of gamma rays and with each of these three ranges there is a different class of methods associated. And I asked you several questions about this, questions that should help to make sure that we understand this picture in the right way. The first question was, on this cartoon you see that in this block the splitting by the magnetic hyperfine field, and it's written here that this picture is specifically for a magnetic hyperfine field, that in the magnetic, the splitting induced by the magnetic hyperfine field is twofold, I have two separate lines here, I have two separate lines here. Is that a cartoon? Could I have drawn anything there? Do I need the same number of lines in this level or in this level or can they be different? That's behind that question. So why do I draw here two lines? And a correct answer would be, well this cartoon is made for a nuclear spin 1.5, that means the spin of this nucleus can be pointing in the positive C direction or in the negative C direction, two different orientations, just two, exactly two, and therefore we have two lines. The hyperfine interaction shows the energy difference due to the different orientations of the nucleus in a given hyperfine field, so if the nucleus can have two different orientations I have here two different lines. I show here one specific answer that one of you gave that is interesting because it's a correct answer but it's slightly less general than the best possible answer. So the reasoning goes as follows, because you have here a nuclear spin of 1.5, the only possible values of the total angular momentum F would be J plus 1.5 and J minus 1.5, so two possible values of F and therefore two lines. That's completely correct but this is a reasoning that is only valid for a free atom because that total angular momentum F is only correctly defined for a free atom. So therefore with this answer you cannot discuss the situation of crystals. I would say there is no need to stick to that total angular momentum F, you can answer the question just by considering the angular momentum of the nucleus. If there are two possible orientations of the nuclear angular momentum then we must have two lines. Then another aspect of this cartoon, the amount of splitting here in this level is different from this level. Why is that? Is this just a cartoon, I could have drawn anything or is there a reason behind? And I show here one answer that is not correct, somebody told, electrons in this upper level they are in higher energy levels, that means that typically they will be farther away from the nucleus and therefore the shape of the nucleus will matter less. That is in general true, but as long as you stay within a typical atomic electron cloud then the shape of the nucleus will be similarly important. It will make a difference if you are say 5 atomic radii away from the nucleus, but the orbitals, the excited orbitals of an atom, they are still much closer to the nucleus than 5 radii away. So this effect will not play a role. Another answer that is not correct, the amount of splitting relies on the level of the electronic state, lower levels have a much smaller distance of splitting, so lower levels here the splitting is less than higher levels. That statement here just pretends that this is the case without explaining why this is the case and the claim is not correct, it is not like this that lower levels can have a smaller splitting, I could have drawn the cartoon the other way around with a larger splitting in the lower level, smaller splitting in the upper level. What is a correct answer? Because the electron configuration is different, these are different fine structure levels, so we have two different electron configurations here, so the electron configuration is different and therefore also the hyperfine field by that electron configuration is different. Not higher, not lower, we cannot know that in general, just different. So it would have been misleading if I would have drawn here the same splitting for both levels, that could be the case, but in general the splitting is just different. So summarized, different electronic configuration means different hyperfine field. Next question, if we now go to a different nuclear state, then suddenly the splitting of these same levels is fourfold, why is that? One answer that is partially correct, I think there are more possible orientations, so four orientations rather than two, but I do not know why this is the case for excited nuclei. Excited nuclei, that's not the point here, why can there be two orientations here? Because we had spin 1 half, the excited nucleus happens to have in this example spin 3 halves and therefore four different orientations, but it could have been a spin 7 halves or a spin 1, everything is possible, it could have been even a spin 0, so with no degeneracy in orientations. So the fact that we have four lines is a consequence of the fact that in the example we took here a spin 3 halves. Now that we understand why the cartoon is as it is, let's

see what happens with the different types of transitions and I asked you, can you describe what happens physically when the system jumps between two hyperfine levels that belong to the same fine structure level. So we know that this is a splitting in the order of magnitude of microelectron volts, so in the electromagnetic spectrum that corresponds to radio waves. So our system absorbs a photon of that frequency range and as a result the system goes from the lower state to the upper state. What is different between the system in the lower state and the system in the upper state? That is the question. I start with an answer that is not correct, the reasoning goes like this, when the system absorbs a radiofrequent photon, the atom transitions to a higher energy state, in this transition the electron and the nuclear spin of the atom changes, leading to a different total angular momentum and energy level of the system. But that is not the case, if I look at these two hyperfine levels, they belong to the same fine structure state, so the same configuration of electrons, so there is no way that the angular momentum of the electron cloud would change and this level belongs to the same nuclear ground state with spin 1.5, so there is no way why the nuclear spin would change. So this answer cannot be correct. What is correct is that the nucleus will rotate compared to the electron cloud, the nuclear spin will not change, the magnetic hyperfine field generated by the electron cloud will not change, but the orientation of the nuclear spin with respect to the hyperfine field, that will change. And because one of these orientations is the lowest energy orientation, the other orientations will have a higher energy. You use the energy of the photon to rotate the nucleus with respect to the electron cloud. And of course, in order to rotate the nucleus, you need a nucleus that is not a point, you cannot rotate a point, but our nucleus, here in this example, has a vector property, the nuclear magnetic moment, related to the nuclear spin, and that vector can rotate with respect to the vector of the magnetic hyperfine field. And if it would be about field gradients, the tensor of the nuclear quadrupole moment can rotate with respect to the tensor of the electric field gradient. Another way of putting the same is, this transition will change the relative orientation between the magnetic hyperfine field and the nuclear magnetic moment. And yet another way to summarize it, the hyperfine field remains the same, because we stay in the same fine structure level, the nuclear magnetic moment remains the same, we stay in the same nuclear ground state, and what changes is the mutual orientation between these two. Next step, what happens physically when our system jumps between two hyperfine levels that belong to different fine structure states, for the same nucleus? These are now transitions of the order of magnitude of electron volts, so microwaves to visible light. An answer that is not correct is, I think there is not really a difference between such a transition and a type one transition. Oh yes, there is, and we will see here why. We have now different fine structure levels, so different electron cloud configurations, and therefore the hyperfine field can be different, that's why these splittings here were different. When our system absorbs this photon and goes to this state, then suddenly the nucleus feels a different hyperfine field. And now the nucleus can change, another way to formulate this, we change the electron configuration, and we can have a difference, I have here two different arrows, green arrows and red arrows. If we look at the green arrow, then, well let's start with this one here, my system is in the ground state, the nucleus is oriented in such a way with respect to the hyperfine field that the energy of the system is lowest, the system absorbs this microwave photon and goes to this state, where the electron cloud has been excited, the hyperfine field has become different, and the nucleus keeps the lowest energy orientation. That's this green arrow, in this green arrow the nucleus starts from the least favourable orientation and keeps that least favourable orientation in the upper state. For the red arrows we start from the most favourable orientation and we go to least favourable orientation, and the other way around for this other red arrow. So we can have, all of these four transitions have in common that the value of the hyperfine field changes, but for two of the transitions the relative orientation between nucleus and hyperfine field will not change, for the other two transitions the relative orientations will change. So summarized in a systematic way, the value of the hyperfine field changes, the nuclear magnetic moment does not change, remains the same, and the mutual orientation between these two may or may not change. Third step, what happens physically if the system jumps between two hyperfine levels that belong to the same or

different electronic states, for different nuclear states. So now we jump to an excited state of the nucleus. An answer that is partially correct, the nucleus is spinning faster. Is that the case? Yes, in this example this is the case, because the nuclear angular momentum increases and that means classically that you have something that is spinning faster. So that part of the statement is correct. And then the reasoning goes, a nucleus that is spinning faster has a stronger magnetic moment and a more exaggerated deformation. That is not correct. A nucleus with a different angular momentum will have a different magnetic moment and a different quadrupole moment, but not necessarily larger or stronger. It can be that you excite a nucleus, that it goes to a higher spin and that the magnetic moment becomes lower. There is no direct connection between the value of the magnetic moment and the spin. Remember the g-factor, the g-factor expresses that relationship and the g-factor is something that you need to know for every state. You cannot have a general rule that tells you this is the nuclear spin, so therefore the g-factor will be this and you know the magnetic moment. No, it has to be measured case by case or in nuclear theory predicted case by case. So a more correct statement would be the protons or neutrons of the nucleus get excited, one particle excitation, many particle excitation, all are possible, there is some excitation of the nucleus, therefore the nuclear properties change and part of that energy can be used to change also the electron cloud. So this green arrow here, the electron cloud is not changed, we go from the lower block of hyperfine levels, so from this fine structure to this fine structure level. So in the red dashed arrow we stick to the same fine structure level, so the electron cloud is not changed. In this transition the electron cloud is changed and we move from this fine structure level to this fine structure level but with a nucleus that is excited, so this fine structure level. In all of these cases the relative orientation may or may not change, if you stay always in the lowest possible orientation, in the mutual orientation with the lowest possible energy that is possible but you can also change the relative orientation. Another way of formulating it, the nuclear state will change, the electron state will change or can change, must not but no, let me say that again, the electron state is allowed to change but does not change mandatorily and their mutual orientation can also change but can also remain the same. In the systematic summary, the value of the hyperfine field may or may not change, the value of the nuclear magnetic moment will definitely change because you go to a different nuclear state and the mutual orientation between these two may or may not change. I want to use this picture also to highlight a misconception that often happens, it's something I told in the very beginning but it's useful to come back to it now, try to formulate for yourself what are these energy levels here, the energy levels in the cartoon. If you watch this video not live, you may press the pause button here and make up your mind if you have to tell in general what does such an energy level mean, it's the energy level of ... so what is on the three dots, what is the missing word, these levels here at the right hand side, these are the energy levels of what? If you remember when we constructed our very important picture number 1, I said these are the energy levels of an entire system, one atom or one crystal but where we also take the nuclear information into account, if you forget all these upper states here and we just look at a lower block, these would be the energy levels of an atom with the nucleus always being in the ground state. Why do I repeat that? Because in the previous weeks we saw pictures like this which are just blown up versions of a part of the cartoon, so this is a fine structure level, this could be for instance this level, this is a fine structure level and by the hyperfine interaction here, a quadrupole interaction it's split in these two levels and we mark that fine structure level by the nuclear spin. This part of the information, here it's for a spin 1.5, this part of the information is given next to the fine structure level and you need to know that because thanks to that information you know in which levels the hyperfine interaction will split this. But this is misunderstood by many people by the fact that we mention here the nuclear spin, people tend to think that this is a nuclear energy level and that the hyperfine interaction splits the nuclear energy level, which doesn't make sense because hyperfine interaction is about mutual orientation, so if you have just a nuclear energy level, how can you specify different orientations? So no, this is an energy level of the entire system, electron cloud and nucleus together, spin 1 system, for that system you have a total energy, which is this line and because my nucleus has three different orientations by this nuclear

spin 1, depending on how these orientations are, here in an electric field gradient, the entire system can lower or increase its energy. So once again, regardless of the fact that there is a nuclear spin given here, these are energy levels of a total system, not of a nucleus. So we spent quite a bit of time to zooming in on details of that very important picture number 2, which highlights that it really is very important and this picture will now be our road map through the rest of the course for all the different experimental hyperfine methods. Let me have a look at the chat whether there is anything there, no, feel free to post questions in the chat if there is something you want to know or ask. Good, with this we move to laser spectroscopy, ah ok, no, there was one question first, yeah, that's a question that was not specifically asked this year, but I kept it here because it can be useful, I already told it in the beginning, sometimes people wonder why is only a magnetic hyperfine interaction shown in this very important picture, this is just a choice for convenience, I could have done this with a quadrupole interaction, I could have even done this with a combined interaction, but just choose an easy one, a magnetic hyperfine interaction, then at least there is no degeneracy in M states and we can clearly count the allowed orientations, that's an advantage of using the magnetic hyperfine interaction. One of the confidence questions, I can give the three types of transitions between hyperfine levels and I understand what qualitatively happens to the system when it undergoes one of these transitions, well we have discussed this at length, so if you have the correct physical pictures in mind of what happens with the three different transitions then you can be confident about this statement. Now we are ready to tackle the first experimental method and that was laser spectroscopy, and laser spectroscopy is a type 2 method, so you have a laser that sends microwaves up to visible light onto a system, it absorbs this, it changes the electron cloud and based on that you will detect something that is related to hyperfine interactions, so that module was about how can laser spectroscopy do that. A confident statement was I can explain why laser spectroscopy is a type 2 hyperfine method, so if you can tell it absorbs a photon with an energy that is sufficient to modify the electron cloud, but it does not modify the nuclear state, then you can confidently answer that you can explain this. In order to understand laser spectroscopy we took one paper, just rather randomly a paper that discusses laser spectroscopy measurements on free lanthanum atoms, and we also introduced a database by NIST about atomic spectra information, that was particularly useful here, and with that database and with a table that was in the paper I made this cartoon, so I select here a particular transition in this list, and this is a transition between an energy level 4F that I could find in the NIST database, and an energy level 2F here, with 4F and 2F I did not specify everything yet, these are multiplet symbols, we introduced them before, you probably know them from other courses. The upper index here refers to the spin in the electron cloud, the letter refers to the orbital angular momentum of the electron cloud, and the number here at the right hand side that would appear as a lower index, that is the J, that is the relative orientation between the spin angular momentum and the orbital angular momentum. So the actual transition that we are discussing, so these are fine structure levels, it's a transition from this fine structure level, which is 4F 7 halves, to this fine structure level, which is 2F 7 halves, so this is a real life version of the cartoon in the very important picture number 2. We have the fine structure levels and we observe transitions between these fine structure levels. This is a measurement, so you shine with a laser on your lanthanum atoms, you tune the laser such that you have this energy here, and you excite these 4F 7 halves levels to 2F 7 halves levels. By telling that in this way, you would be tempted to think, then I would see in a frequency spectrum one peak, so you change the frequency of the laser, if the frequency does not match this transition, then nothing will change, nothing will be absorbed, when you hit the transition, then the photons will be absorbed, and when the energy of the photons is even higher, then they will not be absorbed anymore, so a kind of one peak. But the experimental spectrum in the paper shows that there are many peaks. Why is that? Some of your answers. We look here at fine structure levels, and that does not yet include the hyperfine information Between these two fine structure levels, there are many different hyperfine transitions possible. Or told in other words, the horizontal scale, the horizontal axis in this picture is in GHz, which is a relatively small energy change, so these are not the transitions between fine structure

splittings, these are the transitions between hyperfine levels. That's formulated in words, let's formulate this graphically, so you see in the caption of the picture it was mentioned that this is the hyperfine spectrum, and what does that mean on the picture? I have my electron cloud in a 4f7.5 state, but I have a nucleus with some nuclear spin, which one? Let me count, 1, 2, 3, 4, 5, 6, 7, 8, so 2i plus 1 possible orientations is 8, now I have to do some math out of the hat, 2i plus 1 is 8, so 2i is 8 minus 1 is 7, so i is 7 divided by 2, this is a spin 7.5 nucleus, so i is 7.5. So we have 8 possible orientations of this nucleus with respect to the electric field gradient and magnetic hyperfine field that is created by this particular electron cloud. And in the upper state we still have our nucleus with spin 7.5, so 8 possible orientations, but now a different electric field gradient and different magnetic hyperfine field because we have a different electron cloud, and we can have transitions between any of these levels and any of these levels, well not any, there are transition rules that forbid some of the transitions while others are not forbidden, but that is not something we go into. And the scale, so this is a micro-EV splitting, these are hyperfine levels, while this is a fine structure splitting, so milli-EV, you can see this on the axis here, the axis is in EV, it's a bit more than milli-EV, so this picture is not to scale, this is a much smaller splitting than the splitting you see here, it's just drawn in such a way that you can easily see the transitions. So every time you have an allowed transition like this red one, which goes, it's marked in the picture 7 to 7, that's one that goes from the F, the total angular momentum that now includes the nuclear spin, so i and j combine to F, it goes from F equals 7 to F equals 7 for the upper state, so this red arrow is a 7 to 7 transition. This green arrow is 4 to 5 is marked in the picture, so it goes from an F equals 4 to an F equals 5 level. And therefore all allowed transitions are labelled here in the picture and you could draw arrows here that correspond to these transitions. Remember that we can fully characterize these splittings because we have seen the formalism for the hyperfine interaction in free atoms, here assuming that it's just a magnetic hyperfine interaction, so we can draw the energy differences, the energy lowering of these hyperfine levels with respect to the fine structure level or the energy increase for these levels with respect to the fine structure level, we can calculate all that and it will depend on the hyperfine structure constant A, lowercase a, here indexed 1 because it's for this level and we will have another hyperfine structure constant A2 for this level. So for one level we have the entire formalism to do this, so these numbers here is something you could calculate yourself with the information of the module on the magnetic hyperfine interaction for free atoms. Sometimes this lowercase a is also written as uppercase A, that's different conventions. Here on this slide I highlight visually the lower fine structure level and the upper fine structure level in red and the spread of the hyperfine states in blue and I do this to make the connection to the very important picture number 2, so the equivalent situation on the cartoon would be a lower and an upper state with different widths of hyperfine interaction and a transition that connects these two, a transition of type 2. So this is laser spectroscopy and you can apply the same on this optional video from a conference where somebody reports results on laser spectroscopy and the first few minutes of that talk were a summary of laser spectroscopy and you saw for the system that was studied there this same reasoning. So once you understand that concept you can easily recognize this in all papers and all talks about laser spectroscopy. In order to familiarize yourself further with this I gave you one other paper where laser spectroscopy is used, a paper by Forrest and co-workers from 10 years ago, we had this table 1, it's for ruthenium, here you have that table in a somewhat larger font and what I asked you to do here was to draw some energy levels and transitions for ruthenium based on the information you find in the NIST atomic spectra database and in that paper and the confidence statement is I can use the NIST atomic spectra database to draw the energy levels of a free atom up to the fine structure level. So let's see how that went, what can be a hurdle is to find out which information do I have to put in the interface at the website for the NIST atomic spectra database. So you can choose your units, I work most spontaneously in EVs but depending on your background that can be different so you have different units that you can use. We do this for the ruthenium atom because that is the one that is mentioned in that paper and then we have to choose do we do this for a neutral ruthenium atom or for an ion and here it can be a bit confusing so if you look at the help pages then the

neutral atom is either with a capital I or with a zero or even with a lowercase i so you have three allowed values to indicate that this is a neutral atom. So if I put ruthenium capital I then I do the neutral ruthenium atom and then I get things like this so you have the occupied orbitals, the term symbol, upper and lower index and sorry upper index and letter and the lower index the J is given here and here you have the energy values of each of these J values or more explicitly said you have the energy values of the levels that correspond to these five different J values for this state of S and L. And with that you can make pictures so you can draw this state it's the 5F state with J values from 1 to 5 so from 1 to 5 the state 1 has the highest energy so this picture here you see is not entirely correct if you put the zero here that should be the J5 that's more correct here so the zero corresponds to J5 and J2, J4, J3, J2 so all of them have higher energies. This state so you have to pick one transition so here from the 5F to for instance this 5G state which is here so just as we did before you can have the transition from fine structure level to fine structure level and I show here a few more of your screenshots or submitted papers where you see possible allowed transitions. This one here is one where also for one case the fine structure levels are drawn that's a picture from a previous year so from a 5F with J equals 5 as the lower one to for instance a 3P with J equals 2 as the lower one and you take here a J equals 2, a J equals 2 with the different hyperfine levels. So just to illustrate that with these tools with that database and with your knowledge about the magnetic hyperfine interaction you can construct the diagrams that are relevant for a particular paper. The last part we will do today is this confidence statement now that we know laser spectroscopy I can explain how laser spectroscopy can be used to measure nuclear magnetic moments and or nuclear quadrupole moments. So we have a method that excites the electron cloud of an atom but we can use it to measure nuclear information and remember we had that reasoning some time ago by measuring the difference in hyperfine levels we can know something about the nucleus and well that is something you can realize from this picture. I identified for instance this 7,7 peak with a transition between 2 hyperfine levels and I did the reasoning for a magnetic hyperfine interaction and that depended on the hyperfine structure constant of the lower state, lower case a1 or in this terminology upper case a and that would be then upper case a1 and so it depends on the hyperfine structure constant for the lower level and the one of the upper level a2. If you have all these different peaks you have enough information to reconstruct what was a1 what was a2 especially if you know for instance the, ok that is sufficient and if you know a1 or a2 and you know the corresponding nuclear spin and the corresponding atomic angular momentum you can reconstruct from that what is the value of the magnetic moment of the nucleus by measuring two different isotopes and so on. The same reasoning can be done for the quadrupole interaction where the constant that matters is now the nuclear quadrupole coupling constant. I will show in the next slide how we called it before but in laser spectroscopy it is often called b or if they are both present then you will have a combined interaction and these peaks will be shifted and shuffled a bit but still you have enough information to deduce this a and b from them. And that is what was done in this picture, in this paper. So they determine the a values and a well here with upper case and we know that it has lower case these were our hyperfine structure constants and they also determine b values capital b's the nuclear quadrupole coupling constant and we wrote it more explicitly as eq vzz over h. So always the same reasoning the nuclear property times the electron property as a scalar number so here the nuclear property times the electron property as a scalar number. If you can determine this capital a and capital b then depending on what you know, if you know the atomic or solid state information then you can determine the nuclear information and the other way around. That is something that will be true for all of these experimental methods. Okay so I've reached the end of this webinar, once more the reminder the next two weeks there will be no webinars due to the Easter break at Flemish universities, in three weeks from now we will have the next webinar on Maesbauer spectroscopy so April 17th. If there are questions about the current module then I stay online for one minute more to see if you have specific questions so you can put them in the chat. I also noticed that there were some questions in the Zulip channel so I've answered the questions that have been raised there this morning. No questions, fine, so see you back on April 17th, bye bye.