webinar 6: the electric quadrupole interaction

(automated transcription)

This is already the sixth webinar of the course, this time about another observable hyperfine property, the electric quadrupole interaction. And there is not really much administration or housekeeping to do this week, just mention that this is the last topic about the physics part of the course, so with the electric quadrupole interaction we will have studied all physical manifestations of hyperfine interactions and from next week on it will be about experimental methods. Several people made the comment that this week was mathematically hard and dark sometimes and I agree with that, this is the module where it becomes most difficult to keep the balance between focusing on the concepts and not on the math, especially because the math of the past week was with tensors of rank 2 and although in the end that is not very different from working with vectors which are tensors of rank 1, we are so much more familiar with vectors that these tensors sometimes confuse us, they feel less familiar and therefore, especially when touching the math only superficially, it can seem dark. So if you are in that case, know that more than the math itself, the concepts remain the important thing, if you succeed to see the reasoning behind the math without getting all the mathematical details, that's totally fine for this course. I hope that if you ever need the math, that by remembering these concepts when you study books where they deal with the math in detail, that the math will be easier because you realize what are the concepts behind. And be sure, from next week on the level of math will be much less again. So from next week onwards we will deal with this list of experimental methods. But today the electric quadrupole interaction, which is a multipole term, namely it's the quadrupole term in the multipole expansion of the charge-charge interaction. Not the current-current interaction that we had last week with the magnetic hyperfine field, no, now we go back to the charge-charge interaction and we look at the first correction that is not due to overlap, that was the monopole shift with overlap, now the first correction that is not due to overlap and that's the quadrupole term. And just as all the other hyperfine interactions, the quadrupole interaction will split the fine structure levels according to some properties that you discovered in this week. We started the week with the toy model and tried to make from the toy model the step to the quantum description. And here we had the toy model again and for the quadrupole term this toy model does not need any modification, no charges inside the nucleus, we can just deal with the simple model. And somebody asked a question about the toy model and I just put the entire question there, I will read with you through it step by step, it's an interesting question but it's a bit involved to ask the question, so let's go through. In the slides about the toy model and the question in that sub-chapter there is concluded that the absolute value of the quadrupole splitting becomes smaller if the nucleus becomes smaller with respect to the electron cloud. Yes, if L becomes smaller than D, the smaller L is, the smaller the quadrupole splitting becomes. So the splitting also gets bigger if the nucleus becomes bigger with respect to the same electron cloud, yes. However in the quantum mechanical formula of the quadrupole splitting the magnitude only depends on Q, so on the spectroscopic quadrupole moment, on the deformation of the nucleus and on Vzz which is the electron property, so I would expect that the magnitude only would become larger with larger deformation and yes that makes sense, larger deformation for the same EFG that would be a larger quadrupole splitting. Therefore does the magnitude of the electric quadrupole moment also becomes larger if the nucleus becomes larger or is this only an effect of the classical approximation? And now, well I had an answer in mind but when reading this question now again with you slowly I start doubting whether my answer is fully correct. Let me tell you what I had in mind as an answer and well I will not tinkle out here and now, if I would come to a second opinion I will tell you next week, that for the fact that the size of this Dumbbell nucleus and the quadrupole moment are related, so if the Dumbbell becomes larger then the mean square radius of the Dumbbell becomes larger obviously but also the quadrupole moment will become larger. For this

particular toy model, for the Dumbbell, they are unavoidable because you have only one degree of freedom. For a more realistic nucleus, for a sphere with some mean square radius, you can deform the sphere, you can make an ellipsoid out of the sphere, you can give it a quadrupole moment while keeping the mean square radius similar, even probably identical. If the sphere expands in some direction you can make it shrink in the other direction and therefore the mean square radius can remain more or less the same but the quadrupole moment definitely grows. So I would say that this strong connection is a consequence of the Dumbbell and that this connection is less strong for realistic nuclei. In any case the quadrupole splitting itself does not depend on the mean square radius, it is not size dependent, it depends only on the deformation, whether that is a deformation for a very large nucleus or a very small nucleus, for the quadrupole term that is irrelevant. For the overlap corrections, which are anyway very small for the quadrupole moment, that can make a difference, but we usually do not bother about that. A confidence question that related to that toy model was, I can explain how to recognize the effect of the quadrupole interaction in the point charge toy model and if you hesitated about that, let me say in one sentence what is that effect? The fact that you have the curvature in this graph. If the deformation of the nucleus would not play a role for the orientation dependence of the total energy, like in the monopole term, then you would have a horizontal line, the energy is independent on the orientation of the nucleus, but due to the interplay between the quadrupole moment of the nucleus and the gradient of the electric field by the electron cloud, due to that interplay, the energy does depend on how they are mutually oriented, and therefore you get this curvature, deviation from a flat line, and that is the signature of a quadrupole interaction. I asked you about these pictures, you saw three times this picture for three different ratios of the nuclear dimension over the electron cloud dimension, L over D, and you see that if we make L over D smaller, there were three examples given here, then the green line which is the quadrupole interaction plus the monopole interaction, and that green line becomes a better and better approximation of the red line, which is the exact solution. For that toy model we can obtain an exact solution, which in general for an atom would not be possible, otherwise we would not have needed the multipole expansion. Now I asked you to inspect the vertical axis of these pictures, and to reason about the question what can you conclude about the size of the quadrupole term itself if the nucleus becomes smaller. Here we have the pictures a bit larger, and let's look at two correct answers. If the nucleus becomes smaller, smaller with respect to the distance to the electron cloud, then the size of the quadrupole term decreases. So not only does the quadrupole term become a better approximation to the exact result, also the size of the quadrupole term decreases, and therefore it is quite obvious that truncation after the quadrupole term becomes more satisfactory, because the multipole expansion converges faster. So one reason indeed why with smaller L over D you have a better approximation of the exact result, is that the correction term becomes in that case smaller and smaller. You have a smaller and smaller perturbation, and nuclear dimensions being much smaller than electron cloud dimensions, that was the convergence criterion for the multipole expansion. So the better you satisfy that criterion, the faster the multipole expansion will converge, and therefore if you always cut after the quadrupole term, the better the approximation at that point will be. In one of the previous years somebody made a very nice statement that I kept here as a memory, the fact that the nucleus is not a point charge becomes less important when the nucleus is smaller. That captures the essence, because the quadrupole moment indicates a deviation from a point charge, but the farther away the electron cloud is from the nucleus, so the smaller the nucleus is with respect to the electron cloud, the less important it is that the nucleus is not a point charge. That we calculated in detail with this toy model. For this toy model we can write the electric field gradient tensor, we can write the quadrupole moment tensor, we can make their tensor dot product to have the quadrupole energy, and so that is how you get that green line, and we also have the exact solution which in this case is actually simpler than making all these quadrupole expressions. The exact solution you can find without having to know anything about the multipole expansion, and so we can examine all the properties of these tensors in this simple toy model. What I have just said that the size of the nucleus, the smaller the

size of the nucleus the smaller the quadrupole interaction is, you can get this exactly from the exact expression for the energy, which you had here on top of the slide, and if you now examine the maximal value for that energy, so when theta is 90 degrees, you reach the maximal value, compared to the minimal value when theta equals 0 or 180, so you calculate the spread, which is the energy at 90 minus the energy at 0, so twice this expression but filled out with different angles, if you would write that one, you would see that that expression too depends on L over D, so the smaller L over D, the smaller the spread of the energies in the quadrupole correction, exactly what we reasoned to be true before. Confidence question, I can explain in which situations stopping after the quadrupole interaction is a good approximation, for the toy model as well as for the actual atom, most of you were confident about that, so the key word is dimensions, if the nuclear dimensions are much smaller than the electron cloud dimensions, then stopping after the quadrupole term will be acceptable. Let me have a look at the chat, no open questions so far, then we continue with the quadrupole operator, the Hamiltonian that describes the quadrupole interaction, and here I asked I can explain the relation between the quadrupole energies in a classical system and the quadrupole levels in an actual quantum system, again most of you feel rather confident, this is the idea that we in the previous week showed explicitly with the magnetic hyperfine interaction, in a classical approach you had this black box, this continuous range of allowed energies, but due to the quantization of orientation in a quantum system, you pick only certain lines within that black box, exactly the same will be true for the quadrupole interaction. Because these mathematical ways to construct the quantum version of the quadrupole, let me say that again, because constructing the quadrupole Hamiltonian is mathematically rather involved, more involved than the magnetic hyperfine interaction, let me go through this reasoning here once again in a slightly different way, and let me explicitly compare the situation for the magnetic case with the quadrupole case. So the energy in the magnetic case classically is minus mu dot B, and when we convert that to a Hamiltonian, to an operator of which the eigenvalues will give these energies, we can recognize the three different ingredients, the magnetic field, the hyperfine field, that appears just as a scalar quantity in the Hamiltonian, the magnetic moment is often expressed as the g-factor, g-factor times the nuclear magneton, that comes directly as a scalar quantity in the expression for the Hamiltonian, and the dot product, which indicates the orientation of mu versus B, that is translated into the operator for the z-component of the angular momentum of the nucleus, because we take the hyperfine field along the z-axis, and we describe the orientation of the magnetic moment with respect to that z-axis, so therefore you need to know the z-component of the nuclear spin, and that is given by that z-operator. So the entire id of the classical expression, the energy is determined by the orientation of mu with respect to B, that entire id can be found in the Hamiltonian expression itself. So this is a direct translation of the classical case to the quantum situation. And exactly the same is possible with the quadrupole interaction, where the energy depends on the orientation of the quadrupole moment tensor with respect to the electric field gradient tensor, and once again we have shown that explicitly in the toy model, where we had the quadrupole moment tensor, where we had the field gradient tensor, and when we make the dot product between these two, which means multiplying each matrix element with each other and summing everything, if you do that you get a scalar property, the energy, for that given orientation, which is the expression we derived for the toy model. But now we want to translate this classical expression to the quantum case, and that is in the end identical to what happens for the magnetic case. The quadrupole moment tensor is reflected by one number, the spectroscopic quadrupole moment. The field gradient tensor that is represented by two numbers, the principal component Vzz and the asymmetry parameter eta, and the dot product, the mutual orientation between the two, that is given by the Iz operator, which appears here squared, and that will have some consequences. And then there are some other operators, the raising and lowering operators, the square of the spin, these appear too, but well, it's not straightforward to point out classical analogues to this. So the analogy is that these three ingredients, Q, V and the dot product, that they are reflected in the Hamiltonian. If you really want to find the form of this Hamiltonian, then you have to construct it from scratch. Another concept that was important was

the principal axis system, also something that for some people raises concerns, and also here I want to draw explicitly the analogy between the magnetic and the electric case, because for the magnetic case we work in a spontaneous way with the principal axis system. We even do not realize often that we use a principal axis system. So let me show you first what is the principal axis system for the magnetic hyperfine interaction. We have some magnetic hyperfine fields, a vector property, and I want to describe that in some axis system, and in general I need for that three numbers, the three components of the magnetic hyperfine field vector in that axis system. But I could make my life easier by choosing a dedicated axis system that makes as many as these components as possible zero, by turning the axis system like this. I take the z-axis parallel to the hyperfine field, and I can do whatever I want for the x and y-axis, because for a vector that doesn't matter. So I have a recipe that guarantees me that I can make two out of the three components of this vector zero. An axis system that makes as many components of the vector zero as possible, that's a principal axis system. So here we have the principal axis system for a magnetic hyperfine interaction, in general for every vector property, for every tensor of rank one. And now you can tell the same story for a tensor of rank two, for the electric field gradient. That can be represented by a three by three matrix, and we can prove mathematically that it is always possible to choose an axis system such that the electric field gradient matrix, three by three matrix, is diagonal. So that it will have as many zeros as possible, six out of the nine numbers will be zero. And if we look at the electric field gradient tensor for the toy model, the electric field gradient that is generated by these two electrons at the center of the axis system, that electric field gradient tensor appears to be diagonal, which means that this xyz axis system that we had used here was already a principal axis system for that field gradient tensor. A task that was related to this is, it has been said in the video that the electric field gradient tensor has axial symmetry in its principal axis system. And that was not written explicitly in the task, but I implicitly meant axial symmetry around the z-axis. Well, tell how you can know this, if you look at this expression, or if you visually look at the picture of the toy model. So what were your answers there? Axial symmetry that is expressed by this eta parameter, and that eta parameter has in its numerator Vxx minus Vyy. So you see that if you have axial symmetry, if whatever happens in the x direction is the same as what happens in the y direction, if Vxx is identical to Vyy, then eta must be zero, or the other way around. If you have axial symmetry, if eta is zero, then Vxx should be equal to Vyy, and that is what you see here. So from this expression, from the field gradient tensor in its principal axis system, by comparing the xx and yy element, you will know whether there is axial symmetry or not. From visual inspection, how can we make this conclusion there? In this answer, they say very correctly that only the electrons matter, some people were confused about that. So this is the field gradient, so it has nothing to do with the nucleus, it is a property of the electron cloud, so also in the toy model we can forget the nucleus and focus only on these two static classical electron charges. And so once you realize that, you see that this is actually symmetric about the z axis, because you can turn these two charges around the z axis, and nothing will change. They are point charges, they lie on the z axis, so if you turn the system by say 90 degrees about the z axis, you will not have noticed that anything changed. If you turn it about 5 degrees or 37 degrees, nothing will ever change. So there is full axial symmetry about the z axis. And then finally I asked you, can you make another toy model, as simple as possible, that leads to an EFG tensor that is not actually symmetric? And I have some suggestions, one of you made this picture, and this cannot be correct, because what is done here is to make a change to the nucleus, and that does not make sense, because the field gradient tensor is a property of the electron cloud. It was actually symmetric for this electron cloud, we want to have another electron cloud that makes it not actually symmetric. Another suggestion that someone gave is, well, replace one of the two charges by a larger or smaller charge. And no, that will not change the axial symmetry, because these two charges will still lie on the z axis, if you rotate about the z axis, nothing will change. You can even displace them along the z axis to make the distances of one charge to the origin different than for the other charge, but still that will not destroy the axial symmetry. Then somebody said, well, if I first look at the following videos with these symmetry properties, then I would say here I can make a cuboid with different lengths for

the three sides, so I will have eight charges that are each on the corners of such a cuboid, there will be no 3-fold rotation axis or 2-fold rotation axis there. Yeah, 2-fold there may be, but no 3-fold, so there will not be axial symmetry. However, this person added, I think that this is more complex than it could be. So yes, we will see more simple examples, but at least this is a correct answer that requires eight point charges. Another answer, here I assume that the z axis is out of the screen, that was not explicitly told, but let's assume that this is the case. So if that is true, then this was a correct answer for five point charges. Then some people gave answers with three point charges, and also these are correct. You know by now about these symmetry properties, so if you would search for 3-fold rotation axis that are anywhere in the system of three electron charges, you will not find them. So therefore, definitely these are correct non-axially symmetric field gradients. A few other examples with three point charges, and I made here the note, somebody said make the distances between the negative charges that were there unequal. That is not needed, because that remains axially symmetric, and on top of that, and that's the only thing that is really needed, add a third charge somewhere in the xy plane, and that's basically the same as what has been done here, and that will indeed be not axially symmetric. The simplest answer that has two point charges, and that is simply moving one of the two electrons away from the z-axis, and now you cannot find a rotation axis that goes through the origin of the axis system, and that is at least a three-fold rotation axis for the electron system. So it can be as simple as this. The simplest toy problem for a non-axially symmetric electric field gradient is one with two point charges that are not on the same axis through the origin where the nucleus sits. A suggestion, not of this year, but of one of the previous years, which is a very interesting one, is somebody who suggests a solution with five point charges, four of them on a square, and with the nucleus in the center of that square, and then the fifth one above the nucleus. And we will see in a few minutes that this still is axially symmetric, so it's not a correct answer, and that you can easily notice that. Let me first go back to the chat. No questions there. Okay. Then let's look at symmetry and a few specific case studies for nuclear spins in electric field gradients. And this was one of the places where the math can become a bit important. So for those of you who were not familiar with evaluating Hamiltonians in m states, I gave this video with an explicit calculation for one case. So in case you skipped over that and you still feel that this can be useful for you, then feel free to look at this again, and then you will see step by step how you can find the values for these matrix elements. Somebody worried about these point groups that were mentioned. At some place you had these point groups with scary names. So this person said I'm not a solid state physicist, so I've never met these point groups. Is this something we are expected to know? No. If you haven't delved into crystallography that deeply before, then you do not need to do it now. And just know that in crystallography, the point symmetries that can give rise to electric field gradients that are zero or actually symmetric, and that these can be classified according to the properties of the point groups. So for a crystallographer, part of this is less magic than for somebody who does not know crystallography. The task here was, well we have made now an explicit calculation for spin one. You put a spin one nucleus in an electric field gradient. What will be the energy levels? And we found that there are two different solutions, two energy levels. Whereas in the classical case, the toy model, there was again this continuous range of energy values, just as for the magnetic hyperfine interaction. So again we see that due to the quantization of orientation, quantization of the direction of the nuclear spin, you pick out a few discrete values from the continuous range, the infinite set of values that is classically allowed. But these classical and quantum pictures, they are not independent from each other. There should always be a way to go from a quantum situation to a classical situation, because the classical situation is somehow the limit of the quantum situation. And in order to think more deeply about this, I asked you what should change in that explicit example that we discussed, in order to get something that is similar to the continuous classical case. And somebody answered, if we want to go from the quantum picture that is quantized to the classical picture that is continuous, we need very small energy steps, such that it becomes almost continuous. So yes, rather than picking out two levels, maybe we would need 1000 levels, and then this would look already much more continuous. Correct, but how could you

realize that? What would be a system that has 1000 energy levels? So that is missing from this answer. And in these two answers, you see what is the real situation that you can use. You need a nucleus with a very high spin. For spin 1, there are two possibilities. For spin 2, there will be three possibilities, and so on. So for spin 1000, you will have about 1000 possibilities, for spin 1 million, and so on. So a classical system has a spin that is very high. That is the essential difference. And then we also looked for, that's then for the topic on symmetry, to the principal axis systems in this very high symmetry unit cell. I like this unit cell because it contains only five inequivalent atoms, but nevertheless there are many different rich situations. So far, we do not look at the magnetic hyperfine interaction, so I will treat it, that was the point of this exercise, we treat this unit cell just as if there was only the quadrupole interaction, and we search for the two inequivalent iron sites, the iron 1 at the corner, and the iron 2 in the face centers, and we do not distinguish between A and B, because that is only related to the magnetic hyperfine field, which we assume not to be there right now. So for these two inequivalent iron sites, iron 1 and iron 2, find as much information as possible about the principal axis system for the electric field gradient. And in order to do so, we need to apply these two symmetry theorems. So if there is a two-fold rotation axis, so an axis that goes through the nucleus, and if you rotate about that axis over 180 degrees, then nothing changes to the electric system. So if you can find such axis, that can always be chosen as the z-axis of a principal axis system. If that rotation axis is three-fold or more, then it is even a z-axis with axial symmetry. And if you have two or more of this three-fold or more-fold rotation axis, then the EFG tensor is zero. Now if you can apply these theorems, and that is what the confidence statement was about, if you can apply these theorems, then you are able to find features of the principal axis system, not necessarily the entire principal axis system, just by visual inspection of a crystal structure. And that is what in this exercise we try to do. And that is related to indeed the similar confidence statement, I can explain how symmetry properties of the environment, so the fact whether or not these rotation axes are present, that is dictated by the environment, by the crystal in which the nucleus sits, I can explain how symmetry properties of the environment simplify the EFG tensor. Also here there was a bit of doubt, but it is maybe more due to the way how the question is asked, maybe not everybody recognised that symmetry properties of the environment, that these are the rotation axes in the crystal structure. Good, I used the word n-fold, or two-fold, three-fold, four-fold rotation axis already a few times, and there were some people who hesitated about the meaning of that word. So let me therefore, for others it will have been obvious, but if you haven't met that concept before, it may not be entirely intuitive. So let me illustrate with a few simple pictures what I mean by these. A two-fold rotation axis for a point, because rotation axis is always related to a given point, and for us it will be the point where the nucleus sits, so the rotation axis at a given point for a given molecule or crystal, that's an axis if you rotate about the prescribed angle, then the crystal will be transformed into itself. Now let's look at this rectangular two-dimensional crystal. I consider a nucleus that sits at the center of this atom, so here is my origin, and I wonder, is there for this point and this lattice a two-fold rotation axis? Two-fold, that means if you rotate twice about that axis, then the crystal will have come to its original position, but also if you rotate once, it will also be undistinguishable from the original crystal. So rotating once for a two-fold axis, 360 degrees divided by two, so if I rotate over 180 degrees for an axis that is perpendicular to the screen and that goes through the origin that I indicate now, then we have a two-fold rotation axis. Is that true? Does that happen? Well, let's rotate our axis, rotate our crystal, and the light gray points, they indicate the original positions, the black points are the rotation over say, well, 15 degrees, then we rotate more and more and more, we have rotated over 90 degrees, clearly this is distinguishable from the original crystal. I see some gray atoms here that are not covered by a black atom, and I see black atoms here under which there is no gray atom, so we have no full coverage yet, I continue rotating, and now I have rotated over 180 degrees, and now we see that every gray point is covered by a black point again. And you might say, oh, I see differences here, but this is because we have a finite example, you have to do this with an infinite lattice, and in an infinite lattice you will see no difference between this situation and the one where we started from. Some lattices have rotation axes that are higher than two-fold, so I have

here another lattice, so not the same as this one here, this one was rectangular, this one is square, and this axis system has a four-fold rotation axis, so if I rotate over 360 divided by 4, that's 90 degrees, if I rotate over 90 degrees, then it will cover itself. So let's do that. Here we have 90 degrees, and okay, the picture is just hand-made, so not perfect, but you get the point that you will have full covering. This is a lattice with a three-fold rotation axis, so we have rotated over 360 divided by 3, so 120 degrees, and we have full covering again. And in crystallography, if you see symmetry pictures of unit cells, then there are different symbols that will indicate this 2, 3, 4 and 6-fold rotation axis. So crystallographic symmetry pictures look like that, and you see immediately, aha, here at this point there is a two-fold rotation axis, and here there is a six-fold one, and here with these triangles there is a three-fold one. So crystallographers have mapped out all these properties for all space groups for us. If you can make use of that, then this will be helpful. So I get back to my theorems, and we have to apply this to this crystal of iron-4-nitrogen to the two different iron sites, and I show a few answers. Green means a correct part of the answer, red a part that is not correct. So let's look at iron-1, so this atom here at the corner. I think the z-axis, which is this axis here, is a four-fold rotation axis, and that's correct. If you try in your mind or on paper to rotate that crystal about this axis, then for instance this atom will be mapped to the face-centered atom in the top of the neighboring unit cell, and this atom will be mapped into this atom, and you will always find a correct mapping. So that z-axis is a four-fold rotation axis, while the x- and y-axis are both a two-fold rotation axis. That's not true. Try to, okay we were looking at this atom, try to look at this x-axis here. There is no difference between the crystal seen from this direction and the crystal seen along this direction. This x- and z-axis are exactly identical. So if the z-axis is a four-fold rotation axis, then the x-axis must be one as well, and similarly for the y-axis. For iron 2, this person says, and let's consider this iron 2 atom, I think the z-axis is a four-fold rotation axis, so the z-axis goes through the iron, through the nitrogen, and to the bottom iron. If we rotate over 90 degrees, then this atom will be mapped into this one, this one will be mapped into this one, the nitrogen and this atom, they will not change, so everything okay. But in this answer they say that also the x-axis will be a four-fold rotation axis. Let's try that. The x-axis goes like this, I rotate over 90 degrees, and look at this nitrogen, it's here, you rotate 90 degrees and it would appear here. And no, there is no nitrogen there. So that's not a four-fold rotation axis. But if you rotate it over 180 degrees, then the nitrogen will be mapped to the nitrogen that is here on top. So a two-fold rotation axis, this x-axis is a two-fold rotation axis, but not a four-fold one. Okay, I will not go through the details of what is wrong here, I think. Yeah, okay, this one just took a different axis that is even not going through the center of the atom we are considering. So this answer here is a correct one, where the person said, well, when I made that answer, I considered also the presence of the magnetic hyperfine field, which at this stage we shouldn't do yet. So this iron 2a and iron 2b will actually be identical. But if you allow for that, then the iron 1 atom has these three four-fold rotation axes, x, y and z are all four-fold rotation axes. There are even some three-fold rotation axes that go through the body diagonal. So the criterion for a zero EFG is more than fulfilled. As soon as you have two of these four-fold axes or two of these three-fold axes, you will have zero EFG. So that's definitely happening at the iron 1 side. At the iron 2 side, we have, if we neglect the magnetic hyperfine field, we have one four-fold rotation axis and two two-fold rotation axes. So we know all axes of the principal axis system. As soon as there is a two-fold rotation axis, it is part of the principal axis system. So we have found the three axes of the principal axis system and the one that is perpendicular to the face, that is a four-fold one, so that will be an axis with axial symmetry. For this iron atom, that four-fold axis will be here, pointing in this direction. And for this one, it will be pointing in this direction. So for all of these iron 2 atoms, we know the principal axis system and we know which is the axis of axial symmetry. If you can apply these ideas to simple unit cells, then you know already in advance a lot about what you can expect for the field gradient. This will be relevant for experiments, because if you do a hyperfine experiment with whatever method on a crystal with this unit cell, then you know iron atoms that are at this position will never feel a field gradient, so you should not expect one. Iron atoms here will always feel an actually symmetric field gradient. So if you would measure in this spectrum iron positions with a

not actually symmetric field gradient, then you know that there must have something happened to the crystal structure, maybe there are defects somewhere, because in the pure crystal structure there is no place for not actually symmetric field gradients. So with this information, knowing this information is very useful to interpret your experimental results. A side note for people who are more familiar with crystallography. In crystallography, one would say that the iron 1 side has point group M3M, or in a different nomenclature OH, and the representative shape for an OH point group is a pure cube, and that's indeed a pure cube is a situation where there cannot be a field gradient. Cubic symmetry kills the field gradient. Whereas iron 2 has point group 4MMM, or a D4H, and there the prototype is what is the English word for this? I always hesitate about that one. It's not a rectangle, that's in 2D, but rather a beam-like shaped, a beam-shaped thing that has a 4-fold rotation axis here along the vertical axis, and 2-fold rotation axis perpendicular to the other faces. So that's the prototype for an actually symmetric field gradient. And crystallographers would look at these symmetry tables, and that's the symmetry picture for that particular unit cell, and you see these square symbols here, the 4-fold axis that are on the corner atoms, and you see the 4-fold axis that is on the face-centered atom here, this 1.5 means this is not at the surface layer, it's half of a lattice constant deeper. You see the 3-fold axis through the corner atoms, so if you can read these crystallography pictures then you can easily find your rotation axis that way. If you cannot do it by reading these pictures then you have to figure it out by yourself by looking at the unit cell, which of course for more complicated unit cells can be a much more difficult game to play. Now I can come back to this suggestion for a not-actually-symmetric set of point charges, and now you will hopefully see why this is actually symmetric, so it's not a correct answer to that previous question, because you can have an axis that goes through the top and through the center of the square where the nucleus was assumed to be, and this axis is a 4-fold rotation axis, so if you rotate about that axis this charge will stay at the same place, and this charge will be mapped to this one, and so on. So there is 4-fold symmetry, and as soon as you have one 4-fold rotation axis there must be actual symmetry of the field gradient, so this was not a correct suggestion for a not-actually-symmetric field gradient. Let me again go through the chat, no questions there. Okay, then we come to the last part, which is some miscellaneous quadrupole topics, there was not really a uniform common line through this topic, it's more a mixed bag of different aspects that can be, that are sometimes mentioned in the quadrupole context. First of all, I said a few words about calculating an electric field gradient tensor from first principles, and you don't need to know how to do that, but the message is important that this property of a crystal, the electric field gradient tensor, you can get this from quantum physics. So without experimental input, somebody gives you a particular crystal, and quantum physics can tell you, well, if a nucleus would sit at this position in the crystal, it will feel this electric field gradient tensor. The same is true with a magnetic hyperfine field, quantum physics can predict you what are the hyperfine fields at every position in a crystal or a molecule, and that too will be very important and helpful when analyzing experiments. If you know in advance which field gradient corresponds to which position in the crystal lattice, then you can find out, you can reason back from your experiment, I see this and this and this field gradient, and I have seven possibilities in my crystal, so that means that only at three out of these seven places the atom for which I measure the field gradient will be present. Another topic we covered was the temperature dependence of the field gradient, so this is a property that does depend on temperature, and that usually will decrease with increasing temperature, and sometimes, especially if you want to use quadrupole measurements in order to determine nuclear properties, nuclear quadrupole moments, well you need to take into account the temperature in the right way, so it's important to be aware of that. There is quite some recent evolution on understanding and predicting this temperature dependence, and I think for the last, I know about some papers that are going to appear, so for next year I should update that section. Then there was something about the combined magnetic and electric hyperfine interaction, because up to now we examined what happens to a nucleus that is in a magnetic hyperfine field, how will that nucleus orient, or we asked the question how does a nucleus orient when it is in an electric field gradient, but you can also have both of them together, how does a nucleus orient if you have it at a

position where there is a magnetic hyperfine field and an electric field gradient, so when you have a combined interaction, that is what that third topic was about. And the two tasks that were given with this section, these were about that third topic. Now that felt difficult for quite some people, several people said that this was the hardest part to do, it feels like I don't have the necessary formula, or that I don't know where to find the relevant info, so let me therefore tell a bit systematically what was meant here, and I can connect that to another question, not asked this year, but in previous years, that illustrates also why this is relevant. So the question here was how do you, a quadrupole interaction lifts the degeneracy in fine structure levels, a magnetic hyperfine interaction also lifts that degeneracy, but how can you recognize which is which, and that you can see if you compare let's say for spin 1, we know what happens if a nucleus is in a crystal and feels a magnetic hyperfine field, you get this Zeeman type of splitting. If you put a spin 1 nucleus in an electric field gradient, if there is axial symmetry there will be this splitting in two levels, if there is no axial symmetry there will be three levels, but almost never equidistant, except for the very special case where you have full, where the eta parameter is 1. So how can you distinguish whether the nucleus feels a magnetic hyperfine field or a field gradient, by looking at how these energy levels are. If they are equidistant then it must be a magnetic hyperfine field, except for this eta 1 possibility, if they are not equidistant it must be a field gradient. And if both of them are possible, if both act together it can be even more complicated. And that is what we examined here, so I showed you one possibility, one situation where a combined interaction is rather straightforward. Because, let's start from the beginning, okay I will go take one step back, what is the difficult thing here? We apply a perturbing Hamiltonian, we had the degenerate situation, the nuclear spin can point in any allowed direction and without hyperfine interaction all of these allowed directions have the same energy, that's at the fine structure level. Now we apply the hyperfine interaction, we get first order perturbation theory for the degenerate case, so we have this matrix with matrix elements, that is in general not diagonal, we have to diagonalize it, which means we search for the principal axis system of that hyperfine interaction, and then we read from the diagonal what are the energy corrections. And if there is just an electric field gradient, that's what you did this week, you find that the plus and minus m levels, that they are shifted upwards by eq vzz over 4, and that the m equals 0 level is shifted downwards by twice this value, so by eq vzz over 2. If there would be only the magnetic hyperfine field, then you would play the same game, you would search for the matrix elements, diagonalize and then you would find the principal axis system. The difficulty with this procedure is how to do that if there are two hyperfine interactions, because then you have a perturbing Hamiltonian that has an electric and a magnetic part, you make the matrix elements and you diagonalize and you find the principal axis system, that's still possible, but that will be a different principal axis system than if either of these two interactions would have been present alone. And there are, it's less intuitive to predict what this principal axis system will be, except for the very easy situation when the two interactions, the quadrupole and the hyperfine interaction, when they both would have the same principal axis system. If that happens, then you can work in that common principal axis system and you will just find the same results as for the interactions alone, but added. And that was what I asked you here, let's assume we are in this very special situation where the two hyperfine interactions alone have a principal axis system that is the same, so then it's additive, and I did this here by first looking at the field gradient and then add the hyperfine field to that, well now do it the other way around and see whether you get the same result. And one of your answers was, okay since we know that the two axis systems are the same, we are technically spoken, we are working with eigenstates that are eigenstates of both Hamiltonians separately, so we can just add and we have this splitting at the magnetic side, we do that first in this exercise and then we add the EFG part to it and we see that this is the same as before. That was said in words, here you see visually what happens, you first apply the hyperfine, magnetic hyperfine interaction, you get this splitting that is mu b, and then you apply the field gradient to that and just as we had before, the m equals one level is shifted upwards by eq vzz over four, the m equals minus one level is also shifted upwards by eq vzz over four, and the m equals zero is shifted downwards by twice that amount. And so the three final

levels you get in this way, they are exactly the same ones as I found when I first applied the electric interaction. And you see this here on this picture visualized, so this is my original picture with applying first the EFG, then the magnetic one, and this is the picture from the previous slide, but mirrored such that you can see that indeed these three final levels exactly coincide with what we had before. But once again this is the very special situation when these two principal axis systems are identical. Here you have one of you who made the explicit calculations, and here another answer with the explicit calculation, so if you hesitate about the mathematics you can reconstruct it from these notes of your colleagues. The second question was an illustration of that, because now we search again for the principal axis system, for the electric case that we already did, but now also for the magnetic case, so if there is the magnetic hyperfine field that for all of these iron atoms is pointing upwards in this picture, what would be the principal axis system of the magnetic hyperfine field, and does it coincide with the principal axis system of the electric field gradient for each of these iron atoms? And this is in text an answer, the magnetic hyperfine field, well okay, I will first make the reasoning and then compare with this answer, because this answer is the conclusion. So the principal axis system for the vector of the magnetic hyperfine field will have its z-axis parallel to that vector, so for this red iron one atom, the magnetic hyperfine field principal axis system will have its z-axis upwards, and x and y perpendicular to that, and it does not matter in which direction, it's a vector, so the x and y principal axis are unspecified. For the iron 2b atom, that z-axis for the hyperfine field will also be pointing upwards. For the iron 2a, it will be pointing upwards, aha, but upwards here means in the face, and upwards here means perpendicular to the face, so although it's both upwards, it's both the z-direction, it's a different direction within the crystal, within the crystal, and that makes the difference with the electric field gradient, so for the iron 1, the electric field gradient was zero, so we can take any axis system as a principal axis system, so we can easily take our principal axis system the same as for the magnetic one, so they both coincide, but that's not difficult because basically there is only the magnetic hyperfine interaction for this atom, there is no field gradient. For this iron 2b, there we had for the quadrupole interaction, the z-axis was the fourfold axis, so in this direction, and this is the same as the z-axis for the magnetic hyperfine field, which was upwards, so here for this iron 2b, the two axis systems do coincide, and this is a situation where you can perfectly apply the reasoning from the previous exercise, so here you can find the energy levels without any complication. But for the iron 2a, the z-axis, the fourfold axis for the quadrupole interaction was perpendicular to the face, and the z-axis for the magnetic hyperfine interaction is here in this vertical direction. So here the two principal axis systems do not coincide, and therefore you have to make a choice, either you take one principal axis system, or the one for the field gradient, or you take the one for the hyperfine interaction, and then you have to calculate the matrix elements of the other interaction in the principal axis system for your first interaction, which means that the expressions for that other interaction will be more complicated, you will in general have a matrix that is not diagonal, and that has to be explicitly diagonalized to find then the new principal axis system that will be neither of the two original ones for the combined interaction. That rapidly becomes involved, we will not do this in practice, but be aware that this is what has to be done. And then the last part in this mixed bag was a few words about the overlap contribution for the quadrupole interaction, the so-called quadrupole shift, which is in our overview diagram this box here, so we have all the multipole terms, in case there is no overlap, we have for every multipole term an overlap correction that itself is an infinite series, we discussed the first order monopole shift, the isotope shift or isomer shift, which can be measured at many places, in a few rare cases, muonic atoms, there is also this second order monopole shift, and now we do the same for the quadrupole interaction, where we have the first order quadrupole shift, which in a toy model is not due to charges inside the nucleus, but to anisotropic charges inside the nucleus. So for the monopole shift we just needed to have a charge in the nucleus, and that implicitly meant an isotropic charge distribution, an isotropic electron charge distribution inside the nucleus. For the quadrupole shift we need an anisotropic electron charge distribution inside the nucleus, and that will give a very small contribution to the quadrupole interaction, a very small correction that is totally negligible,

except if you do very, very high precision molecular spectroscopy, and this was a topic with which we played more than 10 years ago, time is going fast, this was a very nice topic to hunt for, to set up the formalism for this quadrupole shift, and to see in which experimental situations this may have been detectable, and there are a few cases in molecular spectroscopy where people have come close, but as far as I know there has not been an ambiguous detection of the existence of a quadrupole shift yet. It must be there, it is on the limit of being measurable, but somebody has to do that. Okay, with this we reach the end of this webinar, 1 hour 20 minutes, it was a rather long one. I will immediately look at the chat to see if there are further questions there. I know the people from Leuven, they followed with us the physics part, they will now move on in another way, and they will deal with the experimental methods in a different way. The other people, not from Leuven, we will continue in the following weeks just as we had before. There is a question in the chat, will the quadrupole splitting normally be smaller than the magnetic splitting? No, not at all, that depends, in both cases it depends on what is the nuclear property, how large is the nuclear property. If you have a nucleus with a large quadrupole moment, then there is a chance you will have a large quadrupole splitting. If you have a nucleus with a large magnetic moment, you have a chance to have a large magnetic splitting. And it also depends on the electron property. If you put your nucleus at a position in a crystal with a large electric field gradient, you can have a large quadrupole splitting. If you put your nucleus at a position with a large hyperfine field, you will have a large magnetic splitting. And these two features can cooperate or fight against each other. A nucleus with a large quadrupole moment at a position with a large field gradient, then you will have a very strong quadrupole splitting. You can take a nucleus with a small magnetic moment, put it at a place with a small hyperfine field, and you will have a small magnetic splitting, and all other combinations. So you can just have the opposite as well. So no, you cannot say in general whether quadrupole splittings are smaller or larger than magnetic splittings. I will wait another 30 seconds to see if other questions appear. That does not seem to be the case. So then I will say goodbye here. And for those of you to whom it applies, see you next week. Bye bye.