the magnetic hyperfine interaction in solids

(automated transcription)

We now turn to the situation of a magnetic hyperfine interaction in a solid, not in a free atom. And that situation is indeed somewhat different. In the free atom we use the formalism of a total angular momentum F, and mathematically that formalism is justified only if you work in an isotropic space, so you have an isotropic vacuum, obviously isotropic, and there you put the free atom, so the object under study is embedded in an isotropic space. In a solid that is different, you have a crystal structure, so the atom which you examine is embedded in a crystal structure that is not isotropic anymore, and that means that the concept of a total angular momentum J for an atom is lost, you cannot characterize the behavior of electrons in a solid in terms of such a total angular momentum J. So we have to do something different. Our Hamiltonian, minus mu dot B, still remains valid, that's the first term in our current current multipole expansion. Perturbation theory still remains valid, so if we evaluate the perturbing Hamiltonian in the states of the unperturbed system, we still get a valid answer. Let's try to do that, so I write here my perturbing Hamiltonian, mu dot B, and now I take the states of the unperturbed system, which are direct products between a nuclear state, I, and a crystal state for the solid, psi E. Let's assume we can somehow know this psi E for the solid, there are methods in computational chemistry and computational solid state physics to determine the ground state wave function of a solid where all nuclei are point nuclei. That means that we also can compute what would be the magnetic field that these solids produce at the positions of the nuclei in these solids. So in principle we can compute how this magnetic hyperfine field inside a solid at the different positions could be, we know its value, we know its orientation. Let us now take a principle axis system for that magnetic hyperfine field vector. So an axis system in which the magnetic hyperfine field vector becomes as simple as possible with as many zero components as possible, that would be an axis system where one of the axes is parallel to the magnetic hyperfine field. In such an axis system, only the magnitude of the magnetic hyperfine field survives, and in the dot product, only the term where that magnitude is the z-component survives, so that will be multiplied by the term where we have as operator the z-component of the magnetic dipole moment operator of the nucleus. If we would know the nuclear wave functions, then we could compute from theoretical nuclear physics the value of this nuclear magnetic moment here in the same way as we just have, at least in principle, computed the magnetic hyperfine field from computational chemistry. Unfortunately nuclear physics is not yet at that level that we can straightforwardly do this. So somehow we have to bring in experimental information to make this term treatable. How will that be done? Well, we have seen before this version of the magnetic dipole moment operator, where we have already incorporated the length of the magnetic dipole moment vector, and by the length we understood the experimental value for the length. So we have already written this operator in a form of another operator, the angular momentum operator, multiplied by a factor that contains experimental information. And this angular momentum operator, well, we have to know its x, y and z-component, which is not directly straightforward. The z-component, that's an operator, iz, that is familiar. We know how it behaves when we apply it to angular momentum eigenstates, but for the x and y that was not so obvious, and that we can circumvent by writing x and y in terms of the raising and lowering operators, i plus and i minus. So the result you see here at the bottom, we can rewrite the x, y and z-component of the nuclear magnetic moment operator in terms of the z-component of the spin of the nucleus, in

the raising and lowering operators. I describe it here in a rather general way, where we then really have the x, y and z-components of this nuclear magnetic moment operator, but we saw on the previous slide that for the hyperfine interaction in a solid, we only need the z-component. Nevertheless, I do it here in this general way, because when we see next time the quadrupole interaction for the charge-charge interaction, we will have a very similar reasoning with tensors of rank 2, and it's nice to inspect the symmetry between our vector reasoning here, and the reasoning with tensors of rank 2 that will come later. And there this x and y-component will matter. So what have we done? We have written the z-component of the nuclear magnetic moment operator in terms of the z-component of the angular momentum of the nucleus, an operator of which we know the eigenfunctions and eigenvalues. The price is that we have introduced an experimental quantity for the length of the total magnetic dipole moment of the nucleus. But if we pay that price, we have now all knowledge we need to get numerical values for these matrix elements. That means we can now fully apply our first-order perturbation theory. What are the states of the unperturbed system? These are only states that are related to the behavior of the nucleus. We have solved already the solid state part, we assume that we do know what is the magnetic hyperfine field in value and in orientation. The only question we ask ourselves right now is how will the nucleus orient given the presence of that magnetic hyperfine field. So that means which of the m levels of the nucleus will be the lowest energy orientation. So in our first-order perturbation theory, the set of unperturbed states are simply the m levels of the nuclear spin, and we have to make matrix elements of the z-component of the nuclear magnetic moment with these unperturbed states. If this would be for a nucleus with spin 5.5, that would be a 6 by 6 matrix, and we can right away write down the matrix elements. From which we see that this is a diagonal matrix, again no explicit diagonalization needed anymore, we can read out the eigenvalues for the perturbed system directly from the diagonal of the matrix. And what you get is a familiar picture, a Zeeman type of splitting, an equidistant splitting between the different m levels. If there would be no interaction between the nucleus and the magnetic hyperfine field, the system would be an energy given by this line. If you switch on the interaction with the hyperfine field, the energy will split up in these six different values. So far we have worked with the value mu of the nuclear magnetic moment. In nuclear physics that is sometimes described in a slightly different way by the so-called g-factor, g or g-index i. The meaning of this g-factor is shown on this slide. We had already before an expression for the relation between the nuclear dipole moment mu and the nuclear spin. That relation can also be written in terms of the g-factor g here, can also be written in terms of the gyromagnetic ratio and all these expressions are related to each other. These are three different ways to relate the nuclear magnetic moment and the nuclear spin with each other. The sign of the g-factor has a physical meaning. If the sign is positive, it means the nuclear magnetic moment and the nuclear spin have the same orientation. If the sign is negative, then they have a different orientation, opposite orientation. Mind that nuclear magnetic moment and nuclear spin are two different quantities. If you fix the nuclear spin, if you say this is a nucleus with spin 5 halves, then that doesn't tell you anything about the magnetic moment. That magnetic moment can still be positive or negative, that depends on the g-factor. The nuclear spin fixes the orientation of the magnetic moment, but doesn't say anything about its value. Up to now we have been a bit silent about this magnetic hyperfine field in the solids. I simply said we assume that we can calculate it and I didn't tell you how. Well, even now we will not make the full derivation, I just show you as a given fact without derivation how the operator looks like that gives you the magnetic hyperfine field in the solids. Why do I show it if we don't derive it? Well, there are three terms in this operator and each of

these terms has a well defined classical meaning. So we will examine what is the classical meaning of the different contributions to the magnetic hyperfine field. How can the electron cloud in a solid be responsible for a magnetic field at the position of the nucleus? We will see that there is an orbital contribution to this, which corresponds to the first term in this expression, there is a spin-dipolar contribution, the second term, and a Fermi contact contribution, the third term. On this slide the classical origin of these three contributions is discussed. So how does the spin of an electron gives rise to a magnetic field at the position of the nucleus? Well, the spin of an electron means that we compare the electron to a bar magnet, to a classical bar magnet, and this bar magnet, even if it would be at rest in space, generates a field around itself, a field that can reach up to the position of the nucleus. That is the spin-dipolar contribution to the hyperfine field. If we forget about the spin of the electron, just consider its charge, then this will give rise to a magnetic field as well, because that charge is orbiting around the nucleus, so you have a ring current here, and also in classical physics, a ring current generates a magnetic field, a magnetic field that is present also in the center of the ring where the nucleus is. The third contribution is a little bit harder to relate to classical physics. It is a classical effect, but it's not so easy to generate a classical system that shows this contribution. It is the Fermi contact contribution, and at this point we will just show mathematically how large it is, where it comes from. It is a magnetic field at the position of the nucleus that is due to the presence of electrons inside the nucleus. So I flash again here the radial part of the wavefunctions of 2s and 2p electrons, where you see that 2s electrons enter the nucleus. If there is a different amount of spin-up electrons inside the nucleus, then the number of spin-down electrons, so if this difference here is different from zero, then there will be an extra magnetic field at the position of the nucleus. That is this Fermi contact hyperfine field. Contact because it is generated by electrons that enter inside the nucleus. Let's put some numbers on this. If you would make the quantum calculations for a solid as BCC iron, then you would find that the orbital contribution to the hyperfine field is slightly below 10 Tesla, the dipolar contribution is very small, and the Fermi contact contribution, well there is a large contribution by the combined 1s, 2s and 3s core electrons, and a smaller contribution by the 4s valence electrons. If you sum all of these, then you get a total hyperfine field of minus 35.3 Tesla, which is huge, it's interesting to ponder the size of this number. Every nucleus in BCC iron feels a magnetic field of minus 35.3 Tesla, which is a non-trivial field if you would try to generate this in a lab. In order to know the value of that field, you have to do quantum chemical calculations, but you don't need to do these if you are just interested in knowing whether that field will be there or not. There are symmetry rules, symmetry rules related to the crystal structure, that will allow to decide whether or not some contributions to the magnetic hyperfine field are present or not. Let us evaluate a few symmetry situations that can arise. First there is something what I will call chemical symmetry. The nucleus marked by X here, that's the nucleus of interest, we will wonder will there be a hyperfine field at the nucleus of this atom or not. And we will distinguish between a situation where the environment of this nucleus has cubic symmetry, here in this 2D cartoon it's square symmetry, or whether there is no cubic symmetry. So if you replace one of the neighboring atoms by a different element, there will be no cubic symmetry anymore. That's chemical symmetry, and on top of that you can also consider magnetic symmetry. Let's take the situation here with cubic symmetry, as far as the neighbors are concerned. If this would be a ferromagnet, then presence of these magnetic moments breaks the cubic symmetry, the vertical direction in this picture is now preferred over the horizontal direction. If there wasn't already chemical cubic symmetry, then the presence of these magnetic moments will not do anything special. If there

was already cubic symmetry and you put your magnetic moments in such a way that they preserve that symmetry, then the cubic symmetry is still there. Why is it interesting to consider the presence of cubic symmetry, either chemical cubic symmetry or cubic symmetry that also takes magnetism into account? That is because you can prove that the orbital and spin-dipolar contributions to the hyperfine field will vanish if there is cubic symmetry. If that cubic symmetry is chemical cubic symmetry plus magnetic cubic symmetry, then these two contributions will exactly vanish. If there is only chemical cubic symmetry but no magnetic cubic symmetry, then they will almost vanish. And that is what happens in the case of BCC iron, so it's a body-centered cubic crystal, there is cubic symmetry chemically, but it's a ferromagnet, so you have this preferred direction in space, so from a magnetic point of view there is no cubic symmetry, and that is why your orbital and dipolar contributions are not exactly zero and rather small. You cannot know at this point whether 10 Tesla is really a small orbital contribution or not, but if you would calculate the orbital hyperfine field in a free iron atom, you would have a value that is much larger than this 10 Tesla. Let me use this occasion also to point to the meaning of the sign of the hyperfine field. You saw here that this hyperfine field in BCC iron is minus 35 Tesla, so what is the meaning of this minus 35 Tesla? The sign of the hyperfine field indicates how the hyperfine field is oriented with respect to the spin moment of the atom. If the hyperfine field is negative, then the hyperfine field is oriented anti-parallel to the spin moment of the atom, if it is positive, it's oriented parallel. This is just another example for a slightly more complicated crystal structure, it's the material iron-4-nitrogen, you have an FCC type of cube formed by iron atoms, and in the center of that cube there is a nitrogen atom. If you inspect the chemical symmetry, then the atoms that are here at the corners of the cube and that are labeled iron-1 in red, they have cubic chemical symmetry. The iron-2 atoms which are at the face centers have non-cubic chemical symmetry. Iron-4-nitrogen is a ferromagnet, so there is a magnetic moment along the vertical axis here that will break the symmetry, so even the iron-1 atoms will be at a non-cubic position if magnetism is considered. The presence of this magnetic moment will even further split the symmetry of the iron-2 atoms, because there will now be situations here in orange where the magnetic moment will be parallel to the 4-fold symmetry axis, and situations in green where the iron magnetic moment will be perpendicular to the 4-fold symmetry axis. So in general in this crystal structure there is not a single iron atom that has really cubic symmetry, and that is reflected in the numbers you see here at the bottom. You have a Fermi contact contribution that is not related to symmetry at all, and orbital and dipolar contributions that are non-zero. Before you continue, it is interesting to look at this particular question here. So I have told you the hyperfine field in BCC iron is minus 35 Tesla. Every iron nucleus in BCC iron feels a magnetic field of minus 35 Tesla. Let us now consider an infinite matrix of BCC iron, and replace one of the atoms by another element of the periodic table. So you make a substitutional impurity in BCC iron. And now you look at the nucleus of that impurity atom. What would be the magnetic field that is present at that impurity nucleus? Is it the same as for the iron nucleus, so minus 35 Tesla? Would it be not exactly the same, but only slightly different? Or would it be totally different? Think about this before you go to the next slide, so you may pause the video at this point for a while. Okay, let's look at the answer, and the answer is given in this graph here, which shows you on the horizontal axis all elements of the periodic table, hydrogen at the left and something as uranium at the right, and on the vertical axis you see the hyperfine field for each of these elements as an impurity in BCC iron. Mind the scale, it goes from plus 400 Tesla to minus 800 Tesla, and that shows you these hyperfine fields can be very very different from the minus 35 Tesla for pure BCC iron. This is a precious picture, because it takes a lot of

experimental work to measure these hyperfine fields. Many of these points, many of these data points were the result of one entire PhD, and all of these 100 data points together, well, they easily represent some 50 years of experimental work. It's not really the goal of this course to understand why the picture looks the way it looks, I just point you to some regularities. You will see that whenever you are at the beginning of a period in the periodic table, your hyperfine fields will be rather small and negative. If you go through the transition metals, 3D, 4D, 5D, you will see a typical S shape, and if you go through the F elements, the lanthanides, your hyperfine fields can get really large, first positive, then negative. There are good physical, chemical arguments that explain why this is the case, but that is not the purpose of this course.