

magnetic hyperfine interaction in free atoms

(automatic transcription)

In this session we will examine the first non-zero term in the multipole expansion for a current distribution of the nucleus interacting with the current distribution of the electron cloud. This first non-zero term is the dipole term, so we will examine the interaction between the nuclear dipole moment with the dipole field by the electron cloud, and that is the magnetic field that the electron cloud generates at the position of the nucleus. We will do this first for the case of free atoms, the magnetic hyperfine interaction in free atoms. And you will realize that most of the mathematical formalism that we need for this you have seen already in a different context. When you have discussed coupling of angular momenta, more specifically L-S coupling, then you have done something that is nearly identical to what we need here. Here we will need something we will call L-J coupling. So what will we do? We will first go back to L-S coupling, summarize what you have learned about that in previous courses and then immediately apply it to L-J coupling. Where did you meet before the coupling of L and S angular momenta? It was when you were constructing term symbols for atoms, symbols that characterize the state of an atom. Let's look at one specific example, the carbon atom, where we have two 1s electrons, two 2s electrons, both form closed shells, and then two p electrons in a shell that is not completely filled. And for the carbon atom you then wonder how can we distribute these two p electrons over all available states in that shell. There are quite a number of possibilities, you can put the first p electron in one of the three available p orbitals, p_x , p_y , p_z , or m equals minus 1, m equals 0, m equals plus 1, and that with either spin. So six possibilities. The same can be done for the second p electron, again six possibilities, so 36 possibilities to put these two p electrons. Which of these 36 ones is the one that has the lowest energy? Which one is the ground state that will appear in nature? That was the kind of question you tried to solve. And you have seen rules for that, Hund's rules, which is a kind of algorithm to select the ground state from these 36 possible states. What do the Hund's rules tell us for the carbon atom? The first Hund's rule tells us we have to select those states where the total spin angular momentum is maximal. How do you find the total spin angular momentum? You sum the m_s values and take the absolute value out of that. So we have two electrons with spin 1.5, m_s is 1.5, how can we get a maximal value? By having twice the same size of m_s , and then we will have a total spin of 1. So we should only consider states where s equals 1. Second Hund's rule tells us for all of the states that survive after the first Hund's rule, take the one where the total orbital angular momentum L is maximal. You find the total orbital angular momentum by summing the m_l values and take the absolute value out of that. According to our first Hund's rule, the spin of our two electrons is identical, which means they cannot be in the same orbital any longer. So we have to put them in two different orbitals, so two different m_l values, and the absolute value of the sum of these two m_l values should be as large as possible, so the only way how we can realize that is by putting one electron in an orbital with m_l equals plus 1, and the other in an orbital with m_l equals 0, or minus 1 and 0. That gives a sum that is 1, so L equals 1, second Hund's rule. How many of our original 36 states do we still have left after these first two Hund's rules? There are two ways in which you can count that. You can say, well, I have s equals 1, L equals 1. How many possibilities correspond to s equals 1? $2s$ plus 1, 3. And the same for L equals 1, 3 possibilities. So 3 times 3, 9 possibilities to realize s equals 1 and L equals 1 out of the 36 original possibilities where we started from. Another way to count the same is to look at the total angular momentum J ,

which can be 2, 1 or 0. A vector with J equals 2 has 5 different orientations, 5 different z -components. A vector with J equals 1 has 3 different orientations, and one with J equals 0 has 1 possible orientation. So that's 5 plus 3 plus 1, 9 different possibilities out of 36. The same as we found by our first way of counting. The question is now, which of these 9 states is the actual ground state? And that is where the coupling of angular momentum, the interaction between the L vector and the s vector appears. If there is no interaction between L and s , we cannot decide. All of these 9 states have the same energy, they are degenerate. If there is an interaction, and that interaction will be spin-orbit coupling, spin s , orbit L , if there is an interaction, then a third Hund's rule pops up that will allow to select the states with the lowest energy. And that third Hund's rule was, if your shell is less than half-filled, then the ground state is the one with minimal J , if your shell is more than half-filled, the ground state is the one with maximal J . In the situation of the carbon atom, we had 2 out of 6 electrons, our shell is less than half-filled, so it's the situation with minimal J that has the lowest energy. And that is illustrated here on this diagram. So at the left of the diagram, there is no interaction between L and s , all 9 states are degenerate, at the right we have switched on spin-orbit coupling, Hund's third rule, then the J equals 0 situation is the one with the lowest energy. The values that you see here on this diagram are not taken arbitrarily, so these values are calculated, and you probably learned how to calculate them, we will repeat that calculation when we will talk about i - J coupling in a few slides from now. You see this situation illustrated on this picture that comes from an actual atom. So we have here 3 levels that correspond to 3 states, $3P_2$, $3P_1$, $3P_0$, so that means states with L equals 1, that's what the P indicates, s equals 1, that's what the 3 indicates, and 3 different values of J , 2, 1 or 0, and the small energy differences between them were the fine structure of this atom. If you compute the actual values of these 3 levels, the energies that correspond to these 3 levels, then you will notice some regularities, and one of these regularities you called the Linde interval rule, that states that the ratio between the separation between the J equals 2 and J equals 1 level, and the separation between the J equals 1 and J equals 0 level, this ratio equals J over J minus 1, so in this case 2 over 1, 2. So the long arrow here is twice as long as the shorter arrow. And that does not hold only for the case J equals 2, 1 and 0, that holds for any value of J , Linde's interval rule.

Everything I told so far is something you more or less have seen in previous courses. Let's now translate that to the hyperfine interaction in a free atom, because also here we have 2 angular momenta that will be coupled, that will interact with each other. We have the spin angular momentum of the nucleus, I , which has $2I + 1$ possible orientations, the different orientations, quantized orientations of the nucleus, and there is the electron cloud that has a total angular momentum J , the one we just constructed for the electron cloud of a free atom in the previous slides, and this one can have $2J + 1$ possible orientations in space. We wonder now, what is the mutual orientation of I and J that corresponds to the lowest energy of the atom. If there is no interaction at all between I and J , then all these states will have the same energy. If there is an interaction, one or a few will have a lower energy than others. Well, we know there is an interaction, that is what we constructed in the dipole term of the current-current interaction. The I angular momentum is related to the nuclear magnetic moment, a dipole moment, and that will interact with a property of the electron cloud, the hyperfine field, the magnetic field, due to the electron cloud at the position of where the dipole moment is, at the position of the nucleus. So all $2I + 1$ times $2J + 1$ possible orientations of nucleus and electron cloud will be split up and a particular orientation will correspond to the ground state. The overall situation, so the orientation of the nucleus and the orientation of the magnetic field due to the electron cloud, that we can describe by 1

angular momentum. That is exactly what coupling of angular momenta expresses. You have 1 angular momentum, say L , and the other angular momentum, say S , you examine mutual orientations and you express that by a new total angular momentum J . Here we have 1 angular momentum I , another angular momentum J , we examine their mutual orientation and we express that by a new angular momentum F . And quantum mechanics tells us that the possible values of F are restricted to values that appear in this list here, starting from I plus J to the absolute value of I minus J . Every different value of F corresponds to a different mutual orientation of I and J . The largest value of F , I plus J , is a situation where I and J are oriented parallel to each other and are pointing in the same direction, if you express it classically. While the lowest possible value of F , corresponding to I minus J , is one where the nuclear spin and the electron magnetic field are pointing opposite to each other. Let us express that a bit more quantitatively. What is the quantum meaning of a nuclear magnetic dipole moment? Well, we have to associate a magnetic dipole operator to this, and quantum mechanics tells us that this particular expression here is the dipole operator that corresponds to the dipole moment. So you take the spin operator I , and you have some constants in front of it. This I here is the value of the spin, \hbar obviously has its normal meaning, and this μ here is what experiment would measure as the magnetic dipole moment of the nucleus. You can imagine it classically as the magnitude of the dipole moment vector of the nucleus. In a very similar way, you can construct an operator that would give you the magnetic field at the position of the nucleus generated by an electron cloud with total angular momentum J . So that would be the J operator multiplied by a vector that contains the value of the angular momentum quantum number J , \hbar , and the length of the magnetic hyperfine field vector, or what would be experimentally measured as the magnetic hyperfine field B_J . With these two operators, we can construct the dipole term in the current-current Hamiltonian, and that would be this minus μ times B . But now we have the explicit expressions for these two operators, so we can fill them out, and we find something that depends on a dot product between I and J . When you discussed LS coupling, you would have found something here that depends on a dot product between L and S , that would be your spin-orbit Hamiltonian. So now it is our magnetic hyperfine field Hamiltonian. And in order to go from this expression to the next one, we apply a clever trick that you also have used when discussing spin-orbit coupling. You introduce the new angular momentum that combines the previous two, I and J , which is our F . This F squared is identical to I plus J squared. You work out the product, and you see here a way to express I dot J in terms of F squared, I squared, and J squared, which is what is written here in the last line. Now we come to the point where we can use perturbation theory. We have now a perturbing Hamiltonian, our μ dot B . We know the states of the unperturbed system, the system where there is no interaction between I and J . The unperturbed system can be described as direct product states between I and J , but can also be described equivalently by the total F . So these F are states of the unperturbed system. What this perturbation theory tells us, we have to make matrix elements of the perturbing Hamiltonian in the states of the unperturbed system. And because we had a degenerate situation here, we have to write this matrix of matrix elements. So we take the perturbing Hamiltonian, squeeze it between the F equals 0 states, F equals 1, F equals 0, and so on, we make for this particular example, where F can range from 0 to 3, we make this 4 by 4 matrix. Do we know what are the values of these matrix elements? Yes, because these states F , they are eigenstates of the F squared operator, but also eigenstates of the I squared operator, and eigenstates of the J squared operator. So we know what is the effect of F squared operating on F , it's F times F plus 1 times \hbar squared, and the same for I squared and J squared. So we can completely work out these

matrix elements, and if we know the states I and J , and if we know how they are oriented with respect to each other, leading to one particular value of F , then we can fill out all the numbers, and we have the value of this matrix element. If we do this for all matrix elements in our example of 4 by 4 matrix, we get this one here, we find a matrix that is already diagonal, so no need to do an explicit diagonalization step, we can read out the values of the different levels from the diagonal. And that is what is done in this particular example. So for a state I equals 3 halves and J equals 3 halves, if there is no interaction between the nuclear dipole moment and the magnetic hyperfine field, then all these states are degenerate. If we switch on the magnetic dipole interaction, then the energy of the system will depend on the mutual orientation between I and J . So in this case here, it turns out that if I and J are opposite to each other, which means F equals 0, then the energy is maximal. When I and J are parallel to each other, I equals 3, then the energy of the system is minimal. With the expressions on the previous slide, you can also work out this ratio here, the energy difference between the state with a value F and a value F minus 1, compared to the energy difference of the state with F minus 1 and F minus 2, and that ratio is identical to F over F minus 1, which is the Landé interval rule, but now for IJ instead of for LS . And this is an exact formalism when you apply it to really free atoms. It's an approximation, a qualitative picture, if you would apply it to atoms that appear in ionic compounds, in salts. And there the picture of a free atom-like electron shell that can be characterized by a total angular momentum J is still qualitatively valid, and therefore also the splitting into these different hyperfine levels will be qualitatively valid.