Notes for Hyperfine interactions

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Contents

1 Introduction

These notes were written as preparation for the exam of the *hyperfine interactions* course. They were typed while watching the videos of the lectures for a second time, and are therefore very minimalistic, with very poorly constructed sentences. But they reflect the most important content discussed in the lectures, and are therefore still useful when studying the course. I want to point out that a much more detailed summary of the course is made by former student Jeffrey De Rycke, which I have compiled into a single PDF file and can be accessed here. However, his summary is rather long and very detailed and also includes a lot of the equations, while my summary is more to the point and puts the focus towards the main contents of the course and the take-away messages. Moreover, I will also include my notes from watching the feedback webinars, which point out some difficulties about that chapter that many students struggled with. Sometimes I was too lazy to write down all the answers from these webinars and take multiple screenshots, so I just mentioned where it can be found in the video. This is unfortunately only useful for students taking the course this academic year.

2 The Nucleus

We cannot talk about hyperfine interactions without discussing some properties of nuclei that go beyond the point charge. That's what this first chapter will be about.

2.1 Nuclear properties

We will refresh knowledge on nuclei and their properties. Number of proton, neutrons, mass, deformation parameter β (elongated or squeezed), stable or unstable so lifetime, Z, A, spin, parity, energy if excited compared to ground state, how large: mean square radius, magnetic dipole moment, electric quadrupole moment (this contains information about elongated or not)... Two examples are given in the slides.

To get a feeling for the numbers and spread of these quantities, we give a few of them: charge Z: 1 - 100, mass A: 1 - 300, spin: 0 to 10 are typical values but this can be any value, parity: only plus or minus, lifetime: fs to who knows how long (we are still not sure if the proton is really stable), energy: 0 to 1000 MeV, mean square radius: 1 to 6 fm, magnetic dipole moment: 0 to $\pm$ 10 μ_N, electric quadrupole moment: 0 to $\pm$ 5 barn.

2.2 Multipole moments

Our cartoon for the nucleus is a general charge distribution ρ, any shape. It must not be positive at all points, since quarks can be positive and negative, but of course overall sum is positive. Charge distribution itself not necessarily positive everywhere. Do a multipole expansion for this charge distribution: monopole term, point charge: same total charge. Electric dipole, quadrupole: two dipoles combined. The higher moments have a smaller contribution (typically).

How does this work? Details about Laplace expansion, general needed later. Interpretation monopole and quadrupole moments NOTE no dipole contribution (see later why).

Monopole: a scalar, quadrupole: tensor of rank 2 so has 5 components. Can represent it as 3 x 3 traceless symmetric matrix, so only 5 degrees of freedom left. Or as a spherical tensor: behaves as spherical harmonics with ℓ of rank 2, so $2\ell+1$ degrees of freedom, indeed 5. Or a combination of both, a matrix where the entries are these functions.

There is a PDF document where the general equations are given to compute the moments: this was an exercise, so probably need to know these. They are

$$Q = \int \rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\,, \tag{1}$$

$$Q_i = \int r_i \rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\,, \tag{2}$$

$$Q_{ij} = \int (3r_i r_j - r^2\delta_{ij})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\,. \tag{3}$$

So monopole and quadrupole terms for the charge distribution, quadrupole: deviation spherical symmetry. Nucleus has a spin: will spin around its symmetry axis. Iron 57: precession frequency in a classical approximation: they are spinning really fast, so every structure that is breaking the symmetry is washed out: imagine nucleus is a cube, if it spins fast enough you have the behaviour of a cylinder, so we don't need the full quadrupole tensor! We have axial symmetry: Q_{ZZ} is most important, this is the **spectroscopic quadrupole moment** Q so instead of the full tensor, often only cite this number since it's the most important (note, here we assume that z points along the symmetry axis). Due to axial symmetry and tracelessness of the tensor: the Q_{XX} and Q_{YY} components are then both $-Q/2$. So we will work with the charge (monopole), deviation from spherical symmetry along axis of the spin, but multipole expansion tells us only about shape: we don't have the absolute size, is independent, we need the mean square radius which is the 'best approximating sphere' to the nucleus. Size charge, deviation from spherical symmetry. β_2 deformation parameter from the slides is the quadrupole deformation. Octopole term is zero also: will be explained later on.

Trends in the spectroscopic quadrupole moment: Typically growing with size of nucleus:

larger radius, heavier nucleus, more chance to have large quadrupole moment, Q is large if β or a is large (cf slides) and we have a periodic-table like effect: after a while we reach spherical symmetry, then starts over again so oscillation like. For mean square nuclear radius: no more info, but we can consider this as being known.

We considered so far the scalar potential due to a static charge distribution for the nucleus, into its multipole components. But a similar story applies to the vector potential due to a static current distribution: also has a multipole expansion. What is different: the odd terms survive, not the even terms as was the case for the electric multipoles. First non-zero moment is the magnetic dipole moment, second is octupole (tensor rank 3) but this one is very small etc. Complication: now dot products between vectors so mathematically a bit more complicated. Most important: dipole, so the 'bar magnet' idea.

2.3 Nuclear moment tabulation

So in the previous subsection we introduced the *nuclear moments*. They are tabulated in an online databases.

2.4 Why are odd electric moments zero?

Not all nuclear multipole moments are different from zero. But as mentioned before, all odd nuclear electric multipole moments (dipole, octupole,...) are zero, and all even nuclear magnetic multipole moments (monopole, quadrupole,...) are zero as well. We will now see why this is the case.

We have to look at the parity operator in three dimensions: $P(x, y, z) = (-x, -y, -z)$ has two real eigenvalues $\lambda_{\pm} = \pm 1$. Meaning in one dimension: even or odd functions. Recall that integrals over space of a function with odd parity is zero. Also recall the observational fact that nuclear states have a well-defined parity: $+1$ (even), -1 (odd) (the wavefunctions).

What is the dipole moment:

$$Q_x = \int x\rho(\vec{r})\,\mathrm{d}\vec{r}, \tag{4}$$

and similar for y and z. Translate to QM:

$$Q_x = \int \Psi_I^* x \Psi_I\,\mathrm{d}\vec{r} = \langle I|\hat{x}|I\rangle\ . \tag{5}$$

Nuclear wavefunctions have a well-defined parity, preserved under complex conjugation: so the combination in this integral is always even, parity one. The x operator has odd parity, so the integrand has odd parity, and therefore vanishes since it is an integral over a function with odd parity. So direct consequence of well-defined parity properties of nuclear wavefunctions. Also an explanation based on symmetry: not very important.

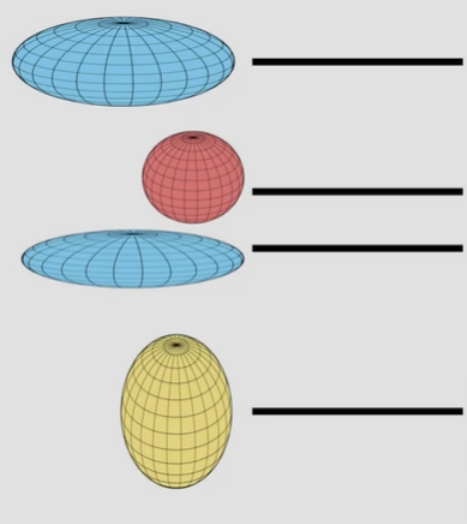

Figure 1: Schematic representation of different deformations of the nucleus at different energy levels.

2.5 Multipole radation

We can interact with nuclei by the radiation they emit or absorb. Just as we describe the shape of the nucleus by multipole components, the properties of the emitted radiation can be described in a multipole framework as well. We will need this to some extent in hyperfinecourse B, on experimental methods based on hyperfine interactions.

We will discuss it for classical and quantum systems, and see why quantum systems need a different treatment. See the video for nice GIFs that illustrate these radiations! Dipole, quadrupole... Quadrupole has smaller amplitude than dipole so we can also do a multipole expansion for the radiation. Is there then a monopole term for radiation? Corresponds to a point charge which carries a time-dependent charge, so *no monopole radiation for EM waves*. But this does exist for e.g. something which changes in size, so sound waves: these do have a monopole expansion.

Now what about quantum systems? An oscillating multipole is not a good model for a decaying nucleus emitting photons as radiation! Why? Two reasons: A dipole (classical) emits energy, so needs power otherwise, if it reaches the ground state then no way to emit radiation: a nucleus is not "powered". Second: all these different energy states have different multipole moments, can be with different deformations! So when we go from level to level, the multipole moments change, so no vibration in any level. So the decay is not associated with oscillating multipole.

Describe the sitatuion quantum mechanically: from $|i\rangle$ to $|f\rangle$. So $\langle i|\hat{H}_{nn}|i\rangle$: H describes interaction between neutrons and protons, the expectation value is then all the multipole moments of nucleus in that level. If there is a decay, we have $\hat{H}_{nn} + \hat{W}$, interaction with

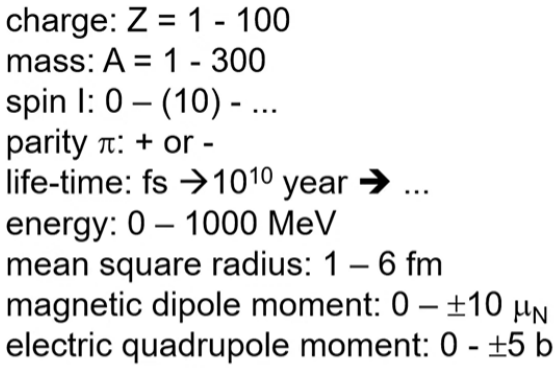

Figure 2: The nuclear properties and range of some values.

the EM field. So we have perturbation theory, compute $\langle f|\hat{W}|i\rangle$. This transition matrix element can be multipole expanded:

$$\langle f|\hat{W}|i\rangle = E_1 + E_2 + E_3 + \cdots + M_1 + M_2 + M_3 + \ldots \tag{6}$$

Nucleus cannot have an electric dipole, but this transition matrix element *can* have a dipole contribution! Again lower ones dominant ones. Nucleus can emit radiation pattern that has the symmetries of an oscillating dipole, but is itself never an oscillating dipole! See Wikipedia page for multipolarity of gamma radiation for more details.

2.6 Feedback webinar

About the properties of the nucleus: repeat the proprties, they are given in a table.

About the units of the quadrupole moment: database give them in barns, but should be coulomb times barn? This is because they are given in electrobarn, so barn is really electronbarn. Sometimes the database give different experimental values.

About the quadrupole: if represented as a matrix, we can choose an axis system where the symmetry axis lies along the z-axis and there are only three relevant non-zero terms on the diagonal. In this case, the larger these diagonal terms are, the more the nuclear shape deviates from spherical symmetry.

Solution to expressing multipole moments exercise: 53:20 in the video. Note that the value of the dipole and higher multipole moments depend on the axis system. Note: for the 2D example, we still need to look at the z-direction, because otherwise we have a 2×2 matrix, and this will not be traceless. 1:00:52.

About the trends of the spectroscopic quadrupole moment. We found $Q \propto \beta$ and $Q \propto a^2$. One trend: heavier nuclei, the larger the Q *can* be (still: some are very small) but no light

nuclei that have large Q. This is the influence by the radius a: heavy nuclei have a large a. On top of that, we have an oscillating pattern. This is related to the nuclear shell model: some closed shells have complete spherical symmetry so $Q = 0$.

3 Framework

Where can you fit hyperfine interactions into the science framework we know? That's what we will examine in this chapter, starting from innocent situations that you can mentally imagine.

3.1 VIP-1

How do hyperfine interactions relate to other interactions you know about in atoms, molecules or solids? After this section, you will understand the relation between hyperfine interactions and other interactions in atoms, and you will understand the origin of their name. We also give the Very Important Picture nr. 1 (VIP-1), which is the graphical summary of hyperfinecourse A.

First: back to basics: the H and He atoms. We made the approximations: non-relativistic, effective electron-electron interactions, infinitely heavy nucleus, point nucleus. We: still non-relativistic etc, but we will drop the point nucleus approximation! Consider also the energy scales that we saw for the H atom. This is exciting electrons inside an atom $\Delta E = 13.6$ eV.

Now let us zoom into the nucleus: itself an object that has a ground state and can be excited: from nuclear physics. Distance between the levels is keV or MeV, so promoting nuclei requires much more energy. If we let the charge distribution of the nucleus and the electrons come together (if they are infinitely far way from each other: we have the ground state), then it settles down in its atomic ground state. So combined picture of different nuclear levels, large separation, and with smaller separation the energy levels of the atomic spectrum.

Now let us look at more details. Take an energy level of the atom. Describe the properties for that atom. Energy of the atom depends on the relative orientation of the angular momentum and spin momentum, L and S. The energy difference between these levels is of order meV. This is the **fine structure**. Most often: every fine-structure level corresponds to a value of J, sum of the angular momenta. An example for sodium is given.

Now let us go to the **hyperfine structure**. If we zoom in to one of the hyperfine levels: these correspond to several levels again, with a separation of μeV: depend on how the nucleus is oriented with respect to the total electron cloud. So we have a definite value

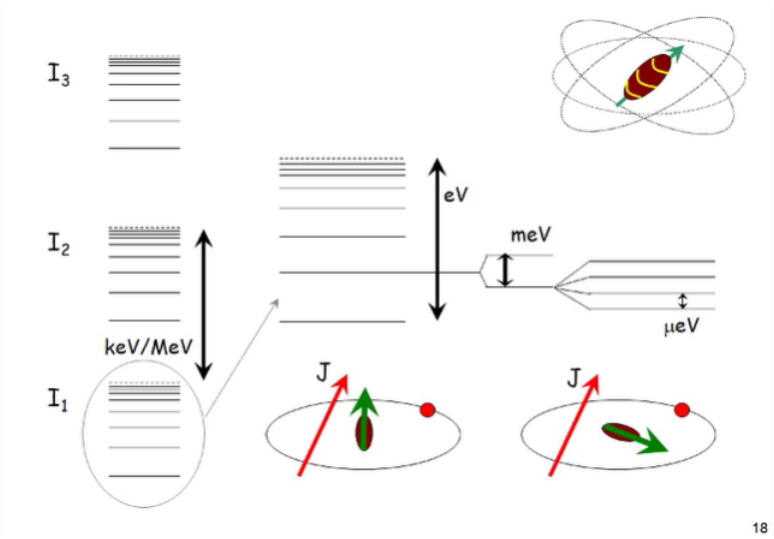

Figure 3: VIP-1: a picture which summarizes the content of hyperfine course A.

of J for the fine-structure energy level, but since this J can have multiple orientations with respect to the nucleus, we can have different energy levels. How is this orientation done if the nucleus is a point? NONE: nucleus has also a nuclear magnetic moment, is a vector so we can say something about the relative orientation of the J vector with this vector. Idea is that the electrons will induce a magnetic field at the nucleus, also a vector, and the dot product between these two is a first hyperfine interaction. Similarly, nucleus has a shape so deformation of nucleus (quadrupole moment) and electron cloud will give an electric field gradient (also a tensor) and the interaction between these two tensors is another hyperfine interaction: dot product between tensors. We have now found all information for VIP-1.

3.2 Gravitational analogue

The key idea behind hyperfine interactions is introduced first in a context that might be more familiar to you than the quantum world of nuclei and electrons: the world of gravitational interaction between massive objects. After this section, we will understand how the gravitational quadrupole moment of a mass distribution affects the gravitational energy of a system of masses and we will see the role and purpose of a multipole expansion.

A situation with only gravity: two mass distributions $\rho_{1,2}$, and assume the center of axis system is in mass distribution 1. We will calculate the gravitational potential energy of m_1 in the field of m_2. So need field of m_2 needed, so we find

$$E = -G \int_1 \int_2 \frac{\rho_1(\mathbf{r}_1)\rho_2(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \tag{7}$$

But how to treat this double integral? Expand this division of distances, this is the **Laplace**

expansion, with spherical harmonics. This expansion has $r_<$ and $r_>$ so a bit complicated, so make an assumption that $r_1 < r_2$ for any pair of such vectors. Then we have a simplification: group terms that depend on m_1 and terms that depend on m_2.

$$E = \sum_{n,q} Q_q^{n\star} V_q^n \,. \tag{8}$$

Q is like a spherical harmonic, depends only on m_1 (full expression given in the slides: not that important), V depends only on m_2.

Let us look at these terms in the summation in more detail. The monopole V and Q terms give a scalar contribution to the monopole energy: Q_0^0 is m_1 (total mass now), and V_0^0 is field as if it were a point mass. So monopole approximation is interaction between two point masses. Dipole term: both Q_q^1 and V_q^1 are vectors (q has three possibilities). Dipole moment Q_q^1: position in space of CoM of mass distribution 1 with respect to origin axis system. If the origin is inside mass distribution, will be zero. The dipole field V_q^1 is also a vector, is the opposite of the gravitational field by m_2 at the origin. The dot product gives then the dipole contribution to the energy. But as mentioned before, contribution is zero since Q_q^1 is zero. The quadrupole term: the quadrupole moment of the mass distribution is a tensor of rank 2, deviation from spherical symmetry. The quadrupole field is also a tensor of rank 2, this is the gradient of the graviational field of the mass distribution 2 at the origin of the axis system. Again, the dot product gives the quadrupole contribution to the energy.

Focus on quadrupole moment: this is a matrix, but in the principle axis system (PAS), and largest component is the z-component and is Q. $Q > 0$ is elongated, $Q < 0$ is squeezed mass distribution. Something similar for the quadrupole field. Both are symmetric and traceless. The meaning is more clear if we use a Taylor expansion (for vectors). This then gives the V_{ij} matrix of second derivatives (also traceless: the trace is proportional, due to Poisson equation, to $\rho_2(\mathbf{0})$, but the origin lies in mass distribution one so this is zero).

Comparing the Taylor and Laplace approach: dot product between matrices gives a matrix again. Quadrupole moment tensor is not really a spherical tensor, since it is not traceless, make it traceless by decomposing intro traceless + a trace. Same for field, so we have sum of spherical tensor and 'something else'. Make the dot product. We have additional terms compared to the Laplace approach, this gives a **monopole shift**, and is proportional to an integral which is like a mean square radius of mass distribution one multiplied with $\rho_2(\mathbf{0})$. If m_2 extends up to the origin (suppose we drop the assumption from above, the more general case), then the Cartesian expansion is more general than the Laplace expansion, leading to a correction term. All of this is summarised in a table. In the table, no overlap means the assumption $r_1 < r_2$ is always valid, for which we did the Laplace expansion. The table summarizes the interpretation of the various terms. For mass 1, we call these the moments, for mass 2, these are called fields, corresponding to the approach of computing the energy of m_1 in the presence of the field of m_2.

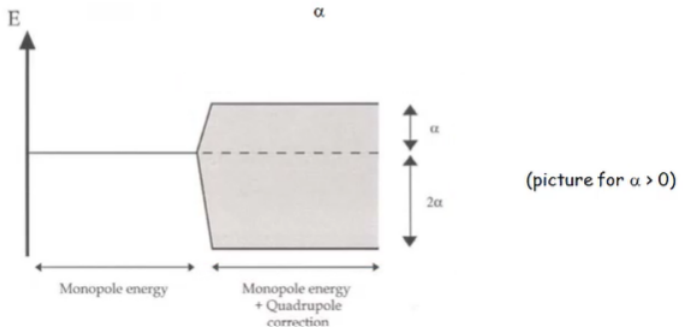

Figure 4: Energy level of the double-ring, with characteristic shape for the level-schemes of quadrupole interactions.

3.3 The double ring

What we learned in the general derivation of the gravitational multipole expansion, can now be applied to this specific example of a a double ring system. We will understand better how the details of the shape of a dumb-bell relative to a double ring system determine the corrections to the baseline value of their gravitational energy.

Mass distribution one is a dumbbell: two point masses with distance ℓ_1 connected by massless rod. CoM of this rod coincides with the origin. This dumbbell is analogue of a nucleus. Mass distribution two are two rings with radius R and distance h apart from each other. Use our Taylor expansion from the previous section to find an approximate solution. This is tedious and not important.

Main result: dipole contribution is zero, next correction is quadrupole term. Note that the quadrupole field is a diagonal matrix, so our axis system is PAS for the double-ring system. Draw the quadrupole correction as a function of angle θ which is the orientation of the dumbbell with respect to the double rings. If $\theta = 0$, then the dumbbell lies parallel to the z-axis, if $\theta = 90\circ$, then lies in the xy-plane. We see that the quadrupole correction is most negative when it is parallel to z axis, most positive when it is along z. So the lowest energy configuration is where the dumbbell is along the z-axis. Note that this still depends on the sign of the prefactor, called α in the slides. We can draw a picture of this situation like an energy diagram. This will be generalised to nucleus and electrons systems, with the important difference that θ can take all values, so everything in the grey area is a valid configuration for the system (since it is classical), while later on we will need quantum mechanics such that only some discrete energy levels, from this grey area, will remain as allowed configurations for the energy spectrum. The shape of this spectrum is, however, characteristic and worth remembering.

3.4 Feedback webinar

About why is spin-orbit coupling a relativistic effect: 1) Lorentz invariant, 2) result of the relativistic Dirac equation 3) spin-orbit interaction is due to electric field of the nucleus when we switch reference frame to one where the electron is at rest: electric field gives rise to a magnetic field (and spin orbit is due to coupling of magnetic field with spin of the electron: electron is like a bar magnet and the nucleus travels around it: a current).

About sodium lamp: around 26:00. Look at $3p_{1/2}$: how is spin of electron oriented with respect to the angular momentum. Term symbols are constructed as ${}^{2S+1}X_J$, this summarizes the information about the entire system! X is the total angular momentum: $L = 0$ for S, $L = 1$ for P, $L = 2$ for D etc. J is from $|L - S|$ to $L + S$ so specifies the relative orientation. So this last value J only difference between the two levels of the sodium lamp. We had 1/2, so opposite since minimal energy.

About the exercise for the monopole and mean square radius: 52:00. Note the definition:

$$\langle r^2 \rangle = \frac{\int r^2 \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r}}{\int \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r}} \,. \tag{9}$$

About the monopole shift in Taylor expansion but not in Laplace expansion: the Taylor expansion was more general, and in this, the quadrupole term actually contained tensors of rank zero, and these give a monopole term. Recall that we had to separate intro traceless + trace, so this is referring to that decomposition giving the new terms.

4 Quantum version

Since the previous chapter, we know the role of hyperfine interactions in an essentially classical framework. In order to carry this over to the world of atoms, molecules and crystals – where quantum physics rules – some more work has to be done. That's the topic of this chapter.

4.1 Perturbation theory

Perturbation theory will come in handy for constructing the equations that describe the hyperfine structure. This part recapitalutes the main concepts, but I won't give them here. In short, what is discussed: non-degenerate case, perturbation does not lift degeneracies, $\Delta E = \langle n|H_1|n\rangle$ with new eigenstates (not given here). For the degenerate case, and H_1 does lift the degeneracy: find an orthonormal basis of degenerate subspace and get matrix in this basis, and diagonalize.

4.2 Quantum multipole expansion

For a quantum system, we cannot make a multipole expansion in the same way as we did for a classical system. The difference is that we will now need perturbation theory in the quantum case, which we discuss below.

First we start with a description of a free nucleus, so no electrons, no interactions. The Hamiltonian gives the kinetic energy and the strong interaction between nucleons: we could find the energy levels $|I\rangle$, separated by keV and MeV (see VIP-1). Now consider the free electrons, we find the states $|\psi_e\rangle$. Third, we try a description of these two but turn off the reaction between protons and electrons. So the energy levels are the sum of the separate eigenvalues, and we have a tensor product for the states and the operators, so complete separation. Now we can switch on the interaction as a perturbation: $\hat{Q} \otimes \hat{V}$. This already hints at what we saw earlier for the gravitational analogue. This interaction term is complicated, so simplify using a multipole expansion: the monopole term of this interaction Hamiltonian: these are the atomic energy levels of eV separation. Or meV if we consider relativistic corrections. If we now consider the higher order multipole terms, which are $\hat{Q}^{(1)} \otimes \hat{V}^{(1)}$ and $\hat{Q}^{(2)} \otimes \hat{V}^{(2)}$, then we find the μeV splitting: the *hyperfine structure*.

We will consider the nuclear properties as known, so its Hamiltonian is 'known' but inferred from experiments. Interaction between nucleus and electron cloud is known: solved in usual quantum mechanics, usual atoms. We can then consider all multipole terms (so not including monopole) as the perturbation, and apply perturbation theory to this. So for the first interaction, we have energy corrections due to the nuclear shape, and given by

$$E_T = E_0 + \left\langle \psi_e^{(0)} \otimes I \middle| \hat{H}_1 \middle| I \otimes \psi_e^{(0)} \right\rangle . \tag{10}$$

with $\hat{H}_1 = \hat{Q}^{(1)} \otimes \hat{V}^{(1)}$. The gravitational problem is fully equivalent to the quantum problem. For example, r_1 is now vector inside the nuclear charge density, r_2 of the electrons, m_1 becomes eZ, m_2 becomes $-eN$. We will again encounter, then, a double integral over the charge distributions which interact, and again there is $1/|\mathbf{r}_e - \mathbf{r}_n|$, and we again have to do a multipole expansion to treat this term.

If we do this with the Laplace expression (where we again assume $r_n < r_e$ holds always, an important assumption to be remembered!), we find some intricate equations, not too important. Like before, we have Q_q^n respectively V_q^n, which are now matrix elements, with I, respectively $\psi_e^{(0)}$ as bra and ket, and the operator depends on the multipole moment under consideration. As before, the Q's only depend on the nucleus while the V's only depend on the electron cloud: **nuclear multipole moments** and **electric multipole fields**.

Focus on the **charge-charge interaction**, so the interaction between nuclear and electron charge distributions: leading term is the quadrupole term since the dipole terms vanish as seen before. The next term is the octupole term vanishes as well, and the other terms are very small: so focus on the quadrupole operator. For the **current-current interaction**:

order	multipole moment / field		first order quasi moment / quasi field		second order quasi moment / quasi field	
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$ $V \propto v(0)$	MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$ $\tilde{V}^{(1)} \propto \Delta v(0)$	$\text{MS}^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$ $\tilde{V}^{(2)} \propto \Delta^2 v(0)$	$\text{MS}^{(2)}$
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$ $V_{ij} \propto \partial_{ij} v(0)$	QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$ $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$	$\text{QS}^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$ $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$	$\text{QS}^{(2)}$
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$ $V_{ijkl} \propto \partial_{ijkl} v(0)$	HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$ $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$	$\text{HDS}^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$ $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$	$\text{HDS}^{(2)}$

Figure 5: Table summarising the interactions we will see and cover. Interactions shown in red are very small.

we generalize the above procedure, but now we don't have scalars but we have vectors, so things come a bit more complicated, but the story is similar to the one above. Like before, we now have **nuclear magnetic multipole moments** and **magnetic multipole fields**. Now the dipole is the leading term. A summary of the above is given in the slides. Note that we had the assumption of 'no overlap': we will see again corrections when this assumption is dropped. These corrections are actually an infinite series, various orders of so-called **multipole shifts**.

4.3 Feedback webinar

About perturbation theory and lifting degeneracies: example: the hydrogen atom. Adding a perturbation like the magnetic field will lift the degeneracy of the energy level. A perturbation that does not lift the degeneracy is the spin-orbit coupling or a gravitational attraction. Or first an electric field (no lift), then a magnetic field (lifts).

About the complications we would run into if we use perturbation theory to study a system with a nucleus of general shape without having made a multipole expansion first: solving the integral, with that Hamiltonian, may not be analytically solvable. The electron-nucleus interaction is too difficult to solve exactly. The expansion will break this down into more simpler expressions.

About when we can truncate multipole expansion etc: it is correct if the multipole expansion converges rather quickly. This depends on the smallness of the ratio r_n^N / r_e^{N+1} with moment N. So if nuclear dimensions are much smaller than the dimensions of the electron cloud, early truncation is valid. When is it valid to stop at first order perturbation theory? When the second order term and higher order do not change the energy much: usually when the unperturbed energy levels are far from each other or when the matrix element of the second order correction Hamiltonian is small. About truncating multipole *and* perturbation? The truncation can be done independently: for example, we can see all the multipole terms as one perturbation. If $r_n \ll r_e$; multipole converges rapidly and

Order	Multipole moment or field	First-order quasimoment or quasifield	Second-order quasimoment or quasifield
$O(0)$	MI: $M \propto r^0 Y_{00}$ $V \propto v(0)$	$\mathrm{MS}^{(1)}$: $\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$ $\tilde{V}^{(1)} \propto \Delta v(0)$	$\mathrm{MS}^{(2)}$: $\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$ $\tilde{V}^{(2)} \propto \Delta^2 v(0)$
$O(2)$	QI: $Q \propto r^2 Y_{20}$ $V_{ij} \propto \partial_{ij} v(0)$	$\mathrm{QS}^{(1)}$: $\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$ $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$	$\mathrm{QS}^{(2)}$: $\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$ $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$
$O(4)$	HDI: $H \propto r^4 Y_{40}$ $V_{ijkl} \propto \partial_{ijkl} v(0)$	$\mathrm{HDS}^{(1)}$: $\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$ $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$	$\mathrm{HDS}^{(2)}$: $\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$ $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$
...	...	...	...

Figure 6: Better resolution and slightly different table, but still nicely summarising all the interactions that we will see.

multipole terms are small so perturbation is small, and the perturbation expansion also converges rapidly. It's the same physical condition.

About thechnical difference between applying a multipole expansion to a classical vs quantum system: For classical: we need the multipole expansion. For quantum: do the multipole expansion, this is at the level of the Hamiltonian, but need to get energies out of this, so we have to apply perturbation theory.

About the table summarising all the interactions: if $r_n < r_e$ is always satisfied: we have all the interactions in the first column, other columns are not important. If it is not fulfilled, then extra contributions from other parts of each row.

5 Electric monopole shift

We're done with the general framework of hyperfine interactions. The next task ahead, is to examine specific manifestations of hyperfine interactions. These are the features that later on will play a role in experimental measurements. In this chapter, we deal with the first one, the electric monopole shift.

5.1 Expression and physics

Here we will meet the first kind of experimentally observable hyperfine effects, which are due to the electric monopole shift. We will understand the physics behind the electric monopole shift and we can put it in relation to the general framework. We will understand how it gives rise to experimentally observable features, namely the isotope shift and isomer shift.

Interaction which we knew already is the one from the upper-left corner, we repeat this for the case of the H atom: see the slides. Here, we will not discuss what happens if we drop the assumption of spherical symmetry (will be done later), but rather we will focus on what happens if we change the assumption from above that $r_n < r_e$ is not always fulfilled. This is going to the right in the above table. This overlap has some influence: the three are given by the second column: the first-order monopole shift, quadrupole shift and hexadecapole shift. The first is well-known, while the second is rather new and the latter is very small and neglected.

So we focus on the first order monopole shift. Looking back at gravitational analogue: we had a monopole shift there too by dropping the same assumption: was proportional to the size of the first distribution, and to $\rho_2(\mathbf{0})$. Translate this to quantum mechanics: what are the relevant operators: for the charge distribution of the electrons, we use a Dirac delta function at the origin: takes out only contribution at the origin. For the mean square radius of the nucleus, this operator is $\hat{r}^2$. Note that we form a matrix element with these operators using the $\psi_e^{(0)}$ or I wavefunctions, respectively. So the monopole shift is proportional to

$$\langle \psi_e \otimes I | \hat{\delta}(\mathbf{r} \otimes \hat{r}^2 | \psi_e \otimes I \rangle \ . \tag{11}$$

Left and right are the unperturbed wavefunctions. Leads to energy corrections. The regular monopole interaction is written $\tilde{Q}$ (monopole moment nucleus) multiplied by what is left, the monopole field. Now with the no-overlap, we get another term: we force it in the same structure by isolating the $\tilde{Q}$, and so we interpret that there is an extra contribution to the potential. The monopole field depends only on the electrons, but this new potential/field, depends on the electron cloud but also on properties of the nucleus! This extra potential disappears if there are no electrons inside the nucleus or when the nucleus is a point, so it has no radius: this is precisely as before in the gravitational analogue where this shift depended on the mean square of the first mass distribution and how much mass of distribution two is inside of the first distribution.

But are there electrons inside the nucleus? For this, we have to examine the wavefunctions, focus on their radial part (we focus on the H atom). It turns out that non-relativistic s-electrons do have a non-zero wave function at $r = 0$, but only these ones! However, in a relativistic picture, then $p_{1/2}$ electrons also enter the nucleus. So only the s electrons and the $p_{1/2}$ electrons will give rise to an electric monopole shift as described above. This monopole shift is always positive, depends on the number of electrons and radius of the nucleus. So this effect is different for different isotopes, and two states (isomers) of the nucleus may also have different radii, so we have an isomer shift. Therefore this splitting depends on the isotope, but also on the nuclear state (isomer).

Now, we turn to the second order monopole shift. This is much smaller, but becomes important for muonic atoms. Why smaller? Depends on r^4 instead of r^2. The muon is 200 times heavier than electron, so brings it much closer to the nucleus, such that the probability to find it inside the nucleus is much larger, and the effect becomes a bit more expressed.

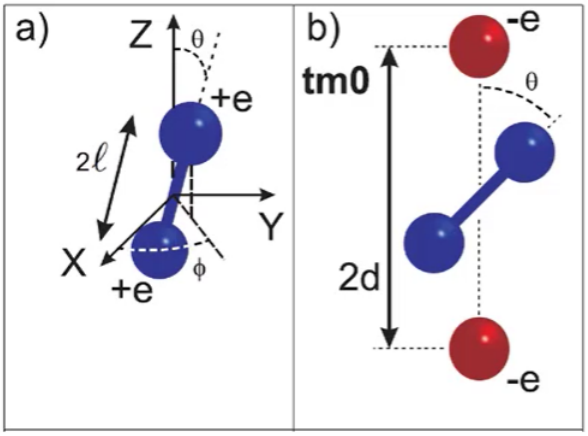

Figure 7: First toy models we encounter.

5.2 Toy model

The essential ideas behind the monopole shift can be captured in a simple toy model. You will understand how the phenomenon that we call 'monopole shift' can arise in simple mechanical systems as well. It is not restricted to atoms or other quantum systems.

Electron charge distributions: two electron point particles. The nuclear charge distribution is simplified to a dumbbell. We plot this expression: we find the orange curve. The energy is lowest when θ is zero or maximal, and energy is maximal if θ is 90 degrees. The dashed line is the monopole contribution, the solid line is the exact solution. The shape of the nucleus, now a dumbbell, gives deviations from this and lowers/raises the energy for some orientations. This toy model is **toy model 0**. We now introduce toy model A. This introduces a small negative charge at the centre of the dumbbell: electrons enter the nuclear volume. The extra contribution is independent of orientation, so there is just an additional constant in the energy. In the graph, toy model A is the dark blue curve, and it is the same but dropped by a constant value. We can use this as the model of an isotope shift: the extra constant just introduced scales as $\propto \ell^{-1}$, with ℓ the distance between the 'protons' of the dumbbell. So if ℓ is different, i.e. a different size, then this shift is different. This is a classical illustration of the isotope shift.

5.3 Feedback webinar

About isotope/isomer, what is the difference? Isotope: same number of protons but different number of neutrons, isomer: different (excited) state of the same nucleus; if lifetime > 1 ns so long-living excited state, then it is an isomer.

About the question asking if MSR becomes infinite, the energy correction becomes infinite

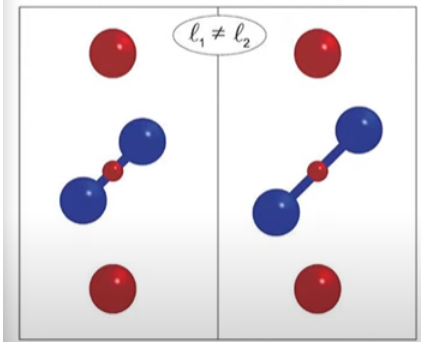

Figure 8: Two different toy models, showing what lies behind the effect of the isomer shift.

as well: this is not correct since the operator for the monopole shift was $\hat{\delta}(r) \otimes \hat{r}^2$, and this is a perturbation operator so has to be small. Moreover, the no-overlap condition is not fulfilled if the nucleus is infinite, so all our assumptions are not valid anymore.

About the overlaps: an example where this becomes most prominent is het muonic atom: smaller orbit so higher charge density at the nucleus. For these, the second order monopole shift is also needed such that we get a decent contribution to the monopole shift: i.e. the correction terms become larger. On the other hand, antihydrogen, with positron instead of electron and antiproton instead of proton.

About monopole shift in toy models: we concluded that the electric monopole shift always give a positive contribution to the energy levels, but in the toy model, there is a negative energy shift, why? This was about the difference between the two models, tmA and tm0, the positive contribution is the first-order perturbation theory while in the toy models we have the exact result. So looking back at the table, the correction in the first row, second column is always positive, but in this case we are looking at the total monopole term so the sum over all corrections in the first row, and the entire summation turns out to be negative. Note that both isotope and isomer shifts relate to the monopole shift.

Added later on: certainly have a look at the PDF discussing the toy models, which is given somewhere on one of the pages of this chapter in the hyperfinecourse website. You'll recognise it by the pictures of the toy models. It is clean and nicely summarises the results.

6 Magnetic hyperfine interaction

Another type of hyperfine interaction is the magnetic hyperfine interaction. We'll examine it in free atoms and in crystals/solids. The actual magnetic hyperfine interaction is always composed from several contributions, each with a different physical origin.

6.1 In free atoms

How does that tiny bar magnet at the nucleus make itself felt? We will examine this first for a single atom, with a nucleus that is more than just a point charge: the nucleus has a magnetic moment. What does this mean for the energy levels of the atom?

We will first review the topic of the coupling of spin and orbital angular momenta. Having understood this, the coupling of the nuclear spin to the total electronic angular momentum is just copy-paste. We will understand how perturbation theory allows to get the energy levels of a free atom with a nuclear spin.

This is the first non-zero term in the multipole expansion for a current distribution for the nucleus interacting with a current distribution of the electron cloud, the dipole term. So we examine the interaction between the magnetic dipole moment with the dipole field, the field by the electron cloud at the position of the nucleus. This requires coupling of angular momenta I and J, so we will first refresh on L-S coupling. The question we ask is *for a given shell, how to a given number of electrons occupy the available orbitals?* Hund's rules: 1) select those states where the total spin angular momentum is maximal, 2) within this set, consider configurations where the total orbital angular momentum is maximum. But note that we have Pauli exclusion principle for electrons. So from the total number of possibilities, only a subset remains as possibilities.

So which of the remaining states is the ground state? If there is no interaction between L and S, these are degenerate. If there *is* an interaction, 3) J minimal if shell is less than half-filled, or J maximal otherwise. So the mutual orientation of L and S becomes important. We have then the Landé interval rule

$$\frac{E_J - E_{J-1}}{E_{J-1} - E_{J-2}} = \frac{J}{J-1}\,. \tag{12}$$

Now, the previous is seen in previous courses. We generalize this for the situation of the nucleus: again two angular momenta: the one for the nucleus I, and the electron cloud with total angular momentum J. Again, if there is no interaction, there are $(2I+1)(2J+1)$ possibilities which have the same energy. The spin I is related to the nuclear magnetic moment, and each J state provides a specific magnetic hyperfine field (dipole field for the current-current case). So again we ask: which mutual orientation of I and J corresponds to the lowest energy? As before, discuss as a new angular momentum F, which takes values between $I+J$ and $|I-J|$. Each F corresponds to a mutual orientation of I and J, and has different m_F values. $I+J$, then they point i, same direction, $|I-J|$ then they point opposite.

What is the quantum meaning of this nuclear magnetic dipole moment? We have to associate a magnetic dipole operator:

$$\hat{\boldsymbol{\mu}}_I = \frac{\mu}{I\hbar}\hat{\boldsymbol{I}}\,. \tag{13}$$

μ is what experiments would measure: we can imagine this is as the magnitude of the dipole moment vector of the nucleus (classical picture). We also have the magnetic hyperfine field operator

$$\hat{\boldsymbol{B}}_J = \frac{B_J}{J\hbar}\hat{\boldsymbol{J}}\,, \tag{14}$$

again B_J is from experiments. The interaction Hamiltonian is then

$$\begin{aligned}\hat{H}_{jj} &= -\hat{\boldsymbol{\mu}}_I \cdot \hat{\boldsymbol{B}}(\mathbf{0}) \\ &= -\frac{\mu B_J}{\hbar^2 IJ}\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{J}}\,.\end{aligned} \tag{15}$$

Now apply a trick: write

$$\hat{\boldsymbol{F}}^2 = (\hat{\boldsymbol{I}}+\hat{\boldsymbol{J}})^2 = \hat{I}^2 + \hat{J}^2 + 2\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{J}}\,. \tag{16}$$

So we find

$$\hat{H}_{jj} = -\frac{\mu B_J}{2\hbar^2 IJ}\left(\hat{F}^2 - \hat{I}^2 - \hat{J}^2\right)\,. \tag{17}$$

Note: I've written this down rather cumbersome, it's best to look at the summary by Jeffrey De Rycke or the slides: these equations may be a bit more important than usually in this course. Now we can apply perturbation theory with this Hamiltonian. The unperturbed states are direct products of I and J states so can be described by states $|F\rangle$. Again, squeeze Hamiltonian between states, note that this is a degenerate case.

The matrix elements are known, since $|F\rangle$ are eigenstates of the I, J, and F operators. So we can completely work out the matrix elements if we have the I and J states and the orientation. No diagonalization is needed (since $|F\rangle$ is eigenvector), and we can read out the eigenvalues. for state $I = 3/2$ and $J = 3/2$. Switch on dipole interaction: turns out that I and J opposite ($F = 0$) then energy is maximal, if they are parallel ($F = 3$) then the energy is minimal. Again we have some sort of Landé interval rule.

$$\frac{E_F - E_{F-1}}{E_{F-1} - E_{F-2}} = \frac{F}{F-1}\,. \tag{18}$$

This formalism is exact *only if* applied to free atoms or free ions, but is a good approximation for atoms in ionic compounds (salts).

6.2 In solids

We turn now to a (crystalline) solid, with nuclei that are more than just point charges: the nuclei have a magnetic moment. How does this change the energy levels of the solid?

We will understand how the crystal symmetry affects the way how we use perturbation theory in a solid. We will have a mental picture for the three major contributions to the

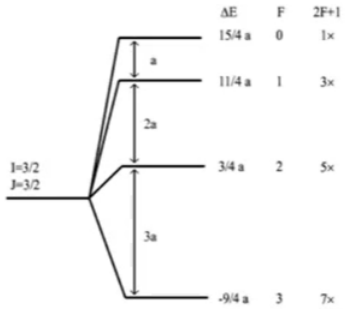

Figure 9: Energy diagram for $I = 3/2$ and $J = 3/2$

magnetic hyperfine field. And we have a first impression about the magnitude of hyperfine fields on native and on impurity nuclei in solids.

Before, total angular momentum F used, only justified in an isotropic space, so clearly this does not hold for a crystal: the rotational invariance is broken. We need to apply a different formalism. The Hamiltonian $\mu\dot{B}$ and perturbation theory are still valid, however. So just need to have the unperturbed wavefunctions, which now cannot be written as F, so they are $|I \otimes \psi_e\rangle$. Let us assume that we know the $|\psi_e\rangle$ wavefunctions (computed numerically). That means we can compute the magnetic field these can produce at the nuclei of the solids, so we know the magnetic hyperfine field: value and orientation. Let us take a PAS for this field, in which this becomes as simple as possible, so one of the axes is parallel to the magnetic hyperfine field. Therefore, we only have to think about the magnitude, and for the dot product, only z component is relevant to us. So we have

$$E_{jj} = -\langle I|\mu\hat{I}_{,z}|I\rangle\, B(\mathbf{0})\,. \tag{19}$$

We cannot just get the wavefunctions, so we have to bring in experimental values to treat this first factor. How is this done? Bring back the above version of the μ operator to do . There, we had the experimental value, which can be used now. The angular momentum operator is now used to get the raising and lowering operators $I_\pm$ and the I_z operator. So we can write

$$\hat{\boldsymbol{\mu}}_{I,x} = \frac{\mu}{2I\hbar}\left(\hat{I}_+ + \hat{I}_-\right) \tag{20}$$

$$\hat{\boldsymbol{\mu}}_{I,y} = \frac{\mu}{2I\hbar}\frac{1}{i}\left(\hat{I}_+ - \hat{I}_-\right) \tag{21}$$

$$\hat{\boldsymbol{\mu}}_{I,z} = \frac{\mu}{I\hbar}\hat{I}_z\,. \tag{22}$$

With these operators, the nuclear states are eigenfunctions of these operators and the eigenvalues depend on quantities which can be experimentally determined. The price we pay is the experimentally determined value μ entering this expression. We ask ourselves: how will the nucleus orient in the presence of the hyperfine field? Which has the lowest energy? Unperturbed, there are m degenerate level and diagonalize this.So the nuclear matrix element

that we need is

$$\langle m_I', I|\hat{\mu}_z|I, m_I\rangle = \frac{\mu}{I} m_I \delta_{m_I', m_I} \,. \tag{23}$$

So there is a Zeeman splitting, with equidistant energy levels. In nuclear physics, we have the g factor:

$$E^{m_I+1} - E^{m_I} = -g_I \mu_N B_{hf} = \hbar\omega_L \,. \tag{24}$$

Let us look at this g factor and its meaning. We find the relation

$$\hat{\boldsymbol{\mu}} = \frac{g\mu_N}{\hbar} \hat{\boldsymbol{I}} \,. \tag{25}$$

We can also define $\gamma = \frac{g\mu_N}{\hbar}$. The sign of g determines the orientation of μ with respect to I: positive for same orientation, negative for opposite orientation. Note that nuclear magnetic moment and spin are two different quantities! Magnetic moment is independent of the spin. The nuclear spin fixes the orientation of the magnetic moment, but says nothing about its value, this is determined by g.

What about the hyperfine field in the solid? Without derivation, this hyperfine field has three terms. Each has a well-defined classical meaning which we will study. How can the electron cloud be responsible for a magnetic field inside the nucleus? There is 1) orbital contribution, 2) spin-dipolar contribution and 3) Fermi contact contribution. These are well explained from earlier. The Fermi contact does not really have a classical analogue, but the idea is that if there is a different amount of spin up than spin down electrons inside the nucleus, then there is an extra magnetic field at the position of the nucleus. Some numbers for bcc iron: orbital around 10 T, dipolar very small, Fermi contact around 45 T. In total, this is (with signs) -35.3 T: every nucleus in bcc iron feels a magnetic field of 35 Tesla!

There are symmetry rules related to crystal structure which decide if some of these contributions will appear or not. There can be cubic symmetry or not (chemical) by replacing neighbour atom. On top of that, look at magnetic vectors: if there was cubic symmetry and the magnetic moments preserve this symmetry, then the cubic symmetry remains. We can prove that the orbital and spin dipolar contributions vanish if there is cubic symmetry. Exactly, if this symmetry is chemical and magnetic. This happened for the dipolar hyperfine field in bcc iron.

The hyperfine field is minus in bcc iron: why? Because this indicates the orientation of the hyperfine field with respect to the spin moment of the atom: if the hyperfine field is negative, they are oriented anti-parallel, while if the field is positive, they are oriented parallel. Another example is Fe_4N: see the exercise we had to make.

We ask ourselves: if we replace one of the atoms in bcc iron by another element X. What is the hyperfine field at the nucleus of X? The answer is given in the slides. The hyperfine fields range from -800 Tesla to 400 Tesla. There is a repeated trend through every period of the periodic table. At the beginning of period, fields are small and negative. Transition metals, typical S shape. Through f elements, get really large then positive and then negative.

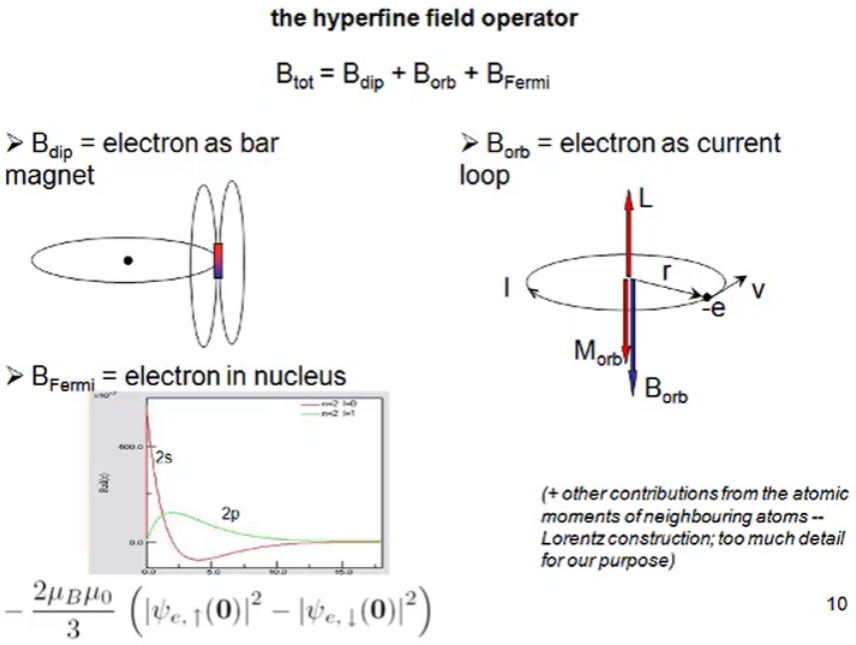

Figure 10: Three contributions to the EFG, with classical analogues.

6.3 Overlap contribution

In the monopole term of the Coulomb interaction between nuclei and electrons, there was an additional effect due to electron penetration in the nucleus (monopole shift). Now, we'll examine what happens to the magnetic dipole term (current-current interaction) when electrons penetrate the nucleus. We will understand similarities (in principle) and differences (in practice) between the impact of electron penetration in the nucleus for the electric monopole term and the magnetic dipole term. We will understand the Bohr-Weisskopf effect, and why it matters for nuclear physics.

Overlap in the current-current interaction? The dipole operator was $\mu \cdot B$. The no-overlap assumption corresponds to the orbital and the spin-dipolar contributions, and the overlap correction was, partly, the Fermi contact contribution. Note that there is a difference with the shift from the charge-charge one: this does not vanish if the nucleus becomes a point! This was the case for the charge-charge interaction, since this was proportional to the mean square radius. Here, there is no size information needed. Another difference is that this field can be the dominant field, as was the case for bcc iron. So it is not really a 'correction' in magnitude. Another contribution from overlap, which is related to the size, is the Bohr-Weiskopf effect.

Imagine two different isotopes of the same element with a different nuclear moment. The spatial distribution of this moment over the nuclear volume is not necesarrily homogeneous. The neutron and proton have nuclear moments (different), they move in the nuclear volume

which generates nuclear moments and so on. So the nuclear moment of the nucleus is dependent on regions in space, so the energy due to the interaction of some magnetic field with the nuclear magnetic moment is an integral

$$E = -\int_{nuc} B_{hf} \cdot \mathrm{d}\mu_I \,. \tag{26}$$

With the two isotopes, these have different magnetic moments too, distributed in space. For the moment, consider them to be naked nuclei. Bring them in an external magnetic field which is homogeneous, such that it goes out of the integral, and then we find

$$\frac{E_1}{E_2} = \frac{\mu_{I,1}}{\mu_{I,2}} \,. \tag{27}$$

So from the energies we measure from the isotopes, the ratio of nuclear magnetic moments can be made. Repeat this, but bring them in the same atom. The electrons will generate a magnetic hyperfine field. This does not guarantee that the hyperfine field will have the same value at all points inside both nuclei: *the field now varies over the nuclear volume*! The field B does not just pop out of the integral. The result is now

$$\frac{E_1}{E_2} = \frac{\mu_{I,1}}{\mu_{I,2}}(1+\Delta) \,. \tag{28}$$

This is known as the **Bohr-Weisskopf effect**. Δ is the hyperfine anomaly, usually a few percent. Note that since this relates to the nuclear volume, this correction depends on the size of the nuclear volume.

6.4 Feedback webinar

Note: now we switch to the current-current interaction, and the first non-zero term is the dipole term, unlike the charge-charge interactions. Visually: imagine the nuclear magnetic moment (vector) and the magnetic hyperfine field (vector) interacting with each other: vectors and therefore a dipole interaction.

About the Hund's rules: they give rise to the fine-structure splitting, at meV level, one step before hyperfine splitting, based on relative orientation L and S, determined by the value of J. This was generalized to I-J coupling. So different J orientations. For each J orientation, then 'add' the nucleus to this picture: it has a spin as well so a nuclear magnetic moment: different orientations with respect to J lift the degeneracy of this energy level: the hyperfine splitting.

About the exercise where we had to compute $\langle 1|\hat{H}_{jj}|1\rangle$: we have

$$\langle F|H_{jj}|F\rangle = -\frac{1}{2}aC \,, \quad a = \frac{\mu B_J}{IJ} \,, \quad C = F(F+1) - I(I+1) - J(J+1) \,. \tag{29}$$

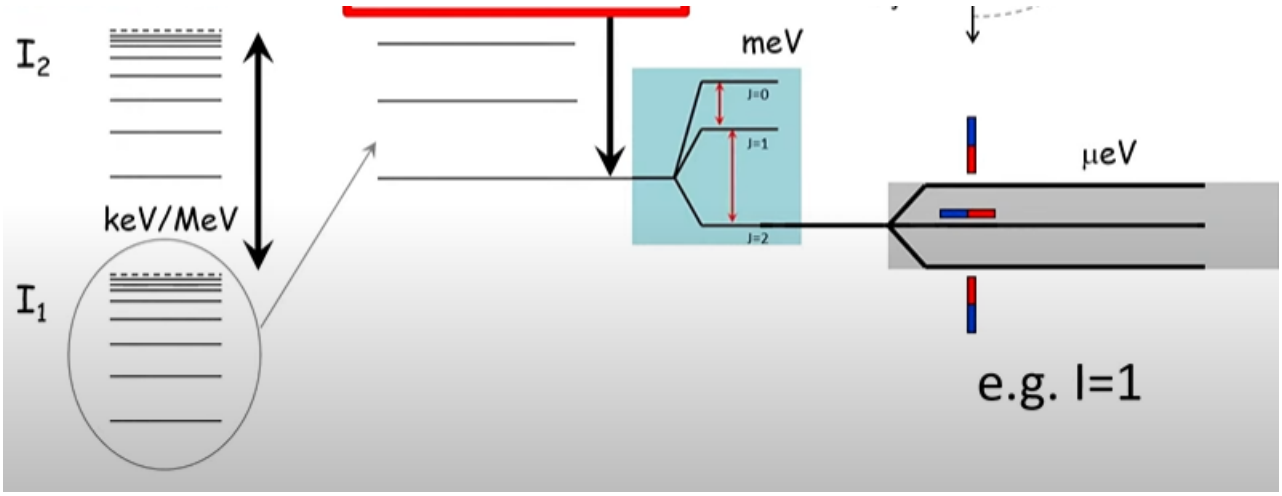

Figure 11: The bar magnet illustration of this hyperfine level splitting.

Note that we can use a for different values of the parameters, **but** $B_1/J_1 = B_2/J_2$. The information of the electron-cloud does not change between isotopes, so we can use the inferred value for B_J/J for the second isotope. So the only unknown in a_2 is μ_2, and a_2 can be measured. We measure two atomic properties, and get a nuclear property!

About calculations in the g-factor: a magnetic moment operator is always related to a spin operator $\hat{\mu}_s \propto \hat{S}$. We also define

$$\mu_B = \frac{e\hbar}{2m_e} \tag{30}$$

$$\mu_N = \frac{e\hbar}{2m_n}\,. \tag{31}$$

Take the z-component of these $\hat{\mu}$ and $\hat{I}$ operators and squeeze between $|m = I\rangle$ operators to find

$$g = \frac{\mu}{\mu_N I}\,. \tag{32}$$

So often, they express $g\mu_n$. At 33:28, the solutions are given for this exercise.

About overlap contribution and the perfectly spherical nucleus exercise: the Fermi contact correction is zero if there are no electrons inside the nucleus. This is not true for the Bohr-Weisskopf effect: this does not depend on whether there are electrons in the nucleus or not. Note that the spherical symmetry does not mean that the magnetic moment of the nucleus is uniform: this was the crux of the Bohr-Weisskopf effect. This effect is sensitive to how the nuclear magnetic moment is distributed over the nuclear volume, so depends on the magnitude of the total moment, but also on the distribution. But in reality: the Bohr-Weisskopf effect is strongly amplified by presence of electrons, so if there are no electrons, the effect is still there, but it is negligible.

7 Electric quadrupole interactions

The third and last category of hyperfine interactions, is the electric quadrupole interaction. Mathematically speaking, this interaction involves tensors of rank 2. This makes it less intuitive than the magnetic hyperfine interaction. We will see, however, several handles to establish the similarity between the electric quadrupole interaction and the magnetic hyperfine interaction.

7.1 From toy model to quantum

By studying the quadrupole term for a toy model, we'll distinguish the essential features of the quadrupole interaction in atoms. And we'll see sharply the major difference between the classical and the quantum case. After having studied this, we will understand how the quadrupole interaction term for a classical electrostatic toy model translates into the quadrupole splitting of the energy levels of a quantum system.

This is the second row of the above table of interactions. Corrections due to the nucleus not having a spherical shape. We discussed toy models 0 and A, so let us return to these to discuss this new interaction. Recall that ℓ is the distance between the dumbbells and d the distance between the point charges: this will be important later on. Make the multipole expansion; we have the nuclear monopole moment (total charge of the nucleus) and the electric one is the monopole field, potential generate by the electron cloud. Multiply them to get the monopole energy. The dipole term vanishes, so the next is the quadrupole term.

What are the relevant nuclear quadrupole quantities? These are tensors of rank 2. In the axis system chosen for the toy models, quadrupole field due to electrons is diagonal, so is a PAS for that quadrupole field, but the quadrupole moment for the nucleus is not diagonal, and also depends on the orientation. The dot product is orientation dependent and also on ℓ^2/d^3, so the contribution depends on this combination. Stopping after the quadrupole term is valid if $\ell \ll d$. In a real situation, 5 times smaller so is justified.

Now, let us bridge towards the real quantum situations. Recall the above picture refer to it and that all energy levels, all orientations, could be taken. This is not possible in quantum mechanics, for example spin 1 then only three orientations, but two are degenerate. Level schemes like this are frequent, typical signature of quadrupole interaction. But we see it is nothing more than the classical picture where we have taken out the energy levels which correspond to the quantum case.

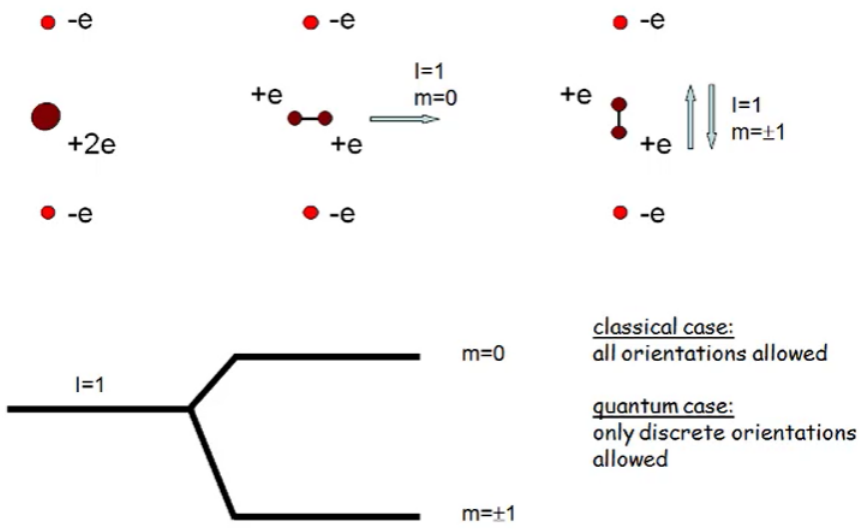

Figure 12: Fork-like diagram corresponding to a quadrupole interaction.

7.2 Quadrupole operator

We (probably) were familiar with the Hamiltonian for the magnetic interaction. We met it many times in your education, in classical physics and in quantum physics. But how does the Hamiltonian of the quadrupole interaction look like? We will now learn how to construct it (in a sketch-like way), starting from the classical expression for the quadrupole interaction.

The Hamiltonian is just copy pasted from the one from the gravitational analogue, we again have the $Q \otimes V$ type of operator. Recall that V^2 is the gradient, so now the **electric-field gradient**. Assume this gradient tensor is known, computed ab initio. We now examine how the nucleus behaves in the presence of such a electric field gradient (EFG). This EFG has to be specified by 5 components as usual. Make as much as possible zero: so all off-diagonal are zero. If we work with the matrix representation, we do not specifiy V_{xx}, V_{yy} and V_{zz} but give V_{zz} and η, which is

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad 0 \leq \eta \leq 1\,. \tag{33}$$

This η is called the **asymmetry parameter**. If we have axial symmetry, then $V_{xx} = V_{yy}$ and η is zero. So EFG with $\eta = 0$ is an axially symmetric field gradient.

Now go to the nucleus: similar to magnetic case, we have to infer experimental information. We will rewrite the nuclear quadrupole moment operator so that we recognise new operators from which we know the eigenvalues of the nuclear wavefunctions. The information about the deformation of the nuclear is provided by the quantity Q, this is the experimental value, the spectroscopical quadrupole moment. This is defined as the deviation from sphere

seen in PAS of the nucleus, since we then had Q along the z-axis by convention (see earlier). Note that this is not necessarily the same PAS as the PAS for the electrons in which we had the diagonal EFG! So again, we pay the price of inferring experimental information, but now we have an operator which we squeeze between I states. After inserting the 5 numbers of the EFG, and transform the 5 numbers of the nuclear operator, we find the perturbing Hamiltonian

$$H = \frac{eQV_{zz}}{4I(2I-1)\hbar^2}\left[(3I_z^2 - I^2) + \frac{\eta}{2}\left(I_+^2 + I_-^2\right)\right] . \tag{34}$$

Now, we go back to the toy-model. This learns some general features: $V_{zz} < 0$ means that z component of the EFG decreases with increasing z. A similar conclusion holds for $V_{yy} > 0$: y component of EFG increases with increasing y. We can get the quadrupole moment for the nucleus. Like before, we can get the deformation of the nucleus from the Q_{zz}: if it is positive, it is a prolate nucleus.

7.3 Case studies & Symmetry

In courses about hyperfine interactions, one often "defines" the hyperfine interaction by an energy level splitting scheme. In this course, this topic has been postponed until now. For a good reason: now we have the background to understand what this level splitting scheme means. Additionally, we'll examine the impact of symmetry on a level scheme. After this, we will understand how the eigenvalues of the quadrupole Hamiltonian lead to an energy level scheme, and we will understand the role of such a level scheme within the framework of interactions (cf. Very Important Picture 1). We will understand how the point symmetry at the site of the nucleus that feels the hyperfine interaction determines particular features of the level splitting scheme.

Consider first the simplest case: $I = 1$. Why is this the simplest? Nuclei with spin zero and spin 1/2 have a vanishing quadrupole moment tensor, so cannot be deformed! This is why $I = 1$ is the simplest one. Therefore, the tensor is a 3×3 matrix and the energy levels are degenerate. The cross terms have a factor η. If we write the projections as 1, -1 and 0, then the matrix is block-diagonal, which makes the diagonalization easier. Note that this is for $V_{zz} > 0$, and that the distance between energy levels depends on η, so depends on (the amount of) axial symmetry. Note that a non-zero η also lifts the degeneracy of the $m = \pm 1$ level. This is because if there is axial symmetry, we cannot distinguish between these two levels, but this becomes possible once axial symmetry is dropped.

Now relate this back to the VIP-1: it is at the far right. Note that there is the confusion to think of these pictures as having a nuclear state which has a hyperfine splitting, but don't look at it this way! This is not really a nuclear state: fine-structure state is a state of the entire system, so including the electrons too! These fine-structure energy levels, when applying the effect of the shape of the nucleus, splits further into energy levels.

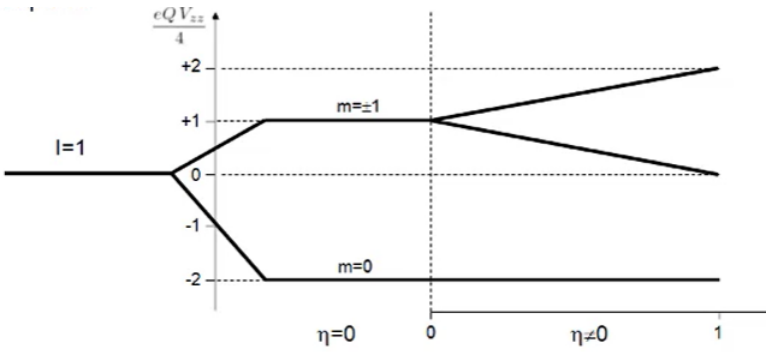

Figure 13: The level scheme for the simple $I = 1$ case.

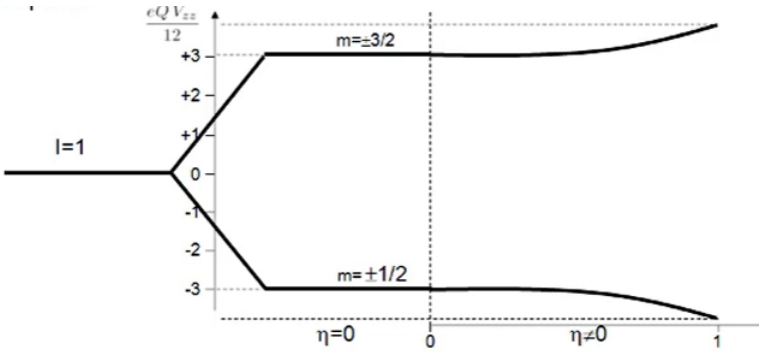

Figure 14: The level scheme for the simple $I = 3/2$ case.

The next example is $I = 3/2$ so the tensors are 4×4 matrices, again order such that we have block-diagonal matrices. These block-diagonal matrices turn out to be identical, means that they have the same eigenvalues so there is at least two-fold degeneracies! This is indeed what happens, moreover, the η parameter does not lift this degeneracy.

These are in fact generally true:

- If we have a nucleus with integer spin and
  - $\eta = 0$: $\pm m$ degeneracy
  - $\eta \neq 0$: $\pm m$ degeneracy lifted in first order for $m = 1$, lifted in higher orders for $m > 1$.
- If we have a nucleus with half-integer spin and
  - $\eta = 0$: $\pm m$ degeneracy
  - $\eta \neq 0$: $\pm m$ degeneracy **not** lifted.

What are the experimental consequences? We know that the energy differences ΔE can

be measured. Suppose for $I = 1$, and if we know Q, we can get V_{zz}. Other way around, if we know V_{zz}, we get Q.

Now what about symmetry properties of EFG tensor? For the EFG tensor, we have to specify 5 numbers. We have some theorems depending on choice of PAS. First theorem: a 2-fold rotation axis can be chosen as z-axis of PAS. A 3-fold (or more) rotation axis is z-axis of PAS and moreover, $\eta = 0$. Second theorem: if there are two or more 3-fold (or more) rotation axes, then the EFG tensor is zero. These are applied to two examples. Good, visual explanation around 20 minutes into this video.

7.4 Miscellaneous topics

We finish the quadrupole interaction topic with a series of small topics which are touched in a descriptive way only. We will get an impression

- about how to calculated electric-field gradients from first principles (the old and the new ways),
- about the effect of temperature on the quadrupole interaction,
- about energy level splitting schemes when a magnetic dipole interaction and an electric quadrupole interaction act simultaneously,
- and about the effect of a finite nucleus on the quadrupole interaction (quadrupole shift).

7.4.1 Ab initio EFG calculations

Point charge model (for solids): approximation that the electron distribution is localized electron charges at positions for the ions. Also an infinite lattice, then this gives V_{zz}^{latt}. So nucleus feels this lattice contribution, but is surrounded by its own electron cloud, can be estimated from free-atom codes. This gives the factor γ_∞. Finally, there is an effect from unfilled orbitals, giving a factor K. So we have

$$V_{zz} = (1 - K)(1 - \gamma_\infty)V_{zz}^{latt}\,. \tag{35}$$

But it turns out that the EFG was dominated by contributions from the region very close to the nucleus: tails of the wave functions, which carry over the influence of bonds with the neighbouring atoms to the nuclear site. So most of the value for the EFG tensor is determined by electrons in a sphere very close around the nucleus, not much as half of a Bohr; this is very different from the point charge model, where it is the infinite lattice determines the EFG, but in reality it is very localised.

7.4.2 Temperature dependence of EFG

Summary from experimental observations

$$V_{zz}(T) = V_{zz}(0)(1 - BT^{\alpha})\,. \tag{36}$$

With spd-electrons, often $\alpha \approx 1.5$. With f-electrons, often $\alpha \approx 1$. Sometimes more complicated behaviour.

Studies suggest the 1.5 exponent is the average of many harmonic modes, and is more accidental than analytical.

7.4.3 Combined electric magnetic interaction

The formalism remains as before: write the combined Hamiltonian, find all matrix elements (degenerate first order perturbation theory), diagonalize the matrix and find the eigenvalues. This can be involved but there are simple situations: 1) if one of the two interactions is much stronger than the other one, consider the weak interaction as a new perturbation (i.e. work in the PAS of the dominant contribution), 2) axial symmetry, and 3) magnetic hyperfine field is aligned with the z-axis of the PAS of the EFG, so the magnetic and electric PAS coincide (can be treated exactly). The result for the case of $I = 1$, axially symmetric EFG with co-linear interaction is given below. But we get the same result if you apply the HFF first, and afterwards the EFG. Note that the only reason we are allowed to use this procedure/approach is because the two axis systems are identical: if the two PAS would not coincide this simple addition is *not* possible. A useful exercise for this is the Fe sites on Fe_4N.

7.4.4 Quadrupole shift

What is the effect of an extended nucleus on the quadrupole interaction? This was studied before for the monopole term for the charge-charge interaction using toy model A, by adding an extra charge at the centre, which gave a new potential which depended on properties of the nucleus and the electrons. With the same picture from before, this corresponds to toy model B (light blue line), where the one point charge inside the dumbbell now becomes itself a new dumbbell. This changes the orientation dependence of the nucleus: no longer just a shift (toy model A) but also changes the curvature of the line. So an anisotropic electron charge inside the nucleus will lead to an additional contribution to the EFG, which will be size-dependent. However, this is a very small effect. Conclusion is: there is an effect when electrons enter the nucleus but *only* if they do so in a non-isotropic way. So s-electrons will not change the quadrupole interaction, but relativistic $p_{1/2}$ electrons will have an effect.

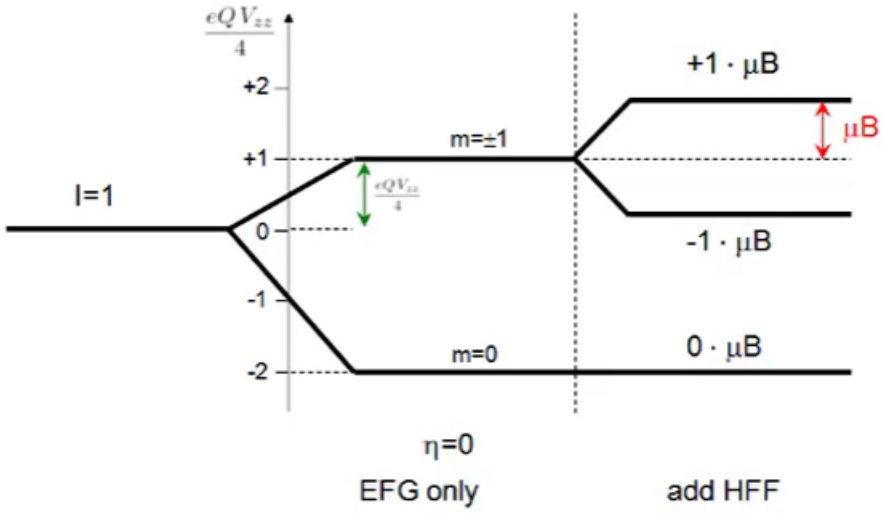

Figure 15: Combining an HFF with an EFG.

7.5 Feedback webinar

We are now at the charge-charge interaction, with the nuclear *quadrupole* moment, and the electric field gradient, which is a charge-charge interaction of two tensors, so a quadrupole term.

About the slide with tm0 and quadrupole interaction (green line) for various values of ℓ/d: recall that in an earlier feedback webinar, it was emphasized that the multipole expansion converges rapidly if $r_n/r_e \ll 1$: in the toy model, this condition is equivalent to $\ell \ll d$. Another feature (a question) about the scale is: the size of the quadrupole term itself becomes smaller if the nucleus becomes smaller with respect to the electron cloud. So smaller correction, and better correction, for decreasing ℓ/d. Also can be seen from the exact solution $E(\theta)$, look at the two maxima $E(90\circ) - E(0\circ)$, and look at expansion in ℓ/d.

About constructing the quadrupole operator, similar to magnetic operator: most importantly: both have that scalar quantities, which have to be determined from experiment, enter the expressions (like μ and Q).

About the EFG tensor in PAS and axial symmetry: it is diagonal, and xx and yy components are equal as well.

About a toy example where the EFG is not axially symmetric: do not change the nucleus! Axial symmetry is a property of the EFG so of the *electron cloud*.

About calculating matrix elements: see the optional video on one of the pages.

About the Fe_4N example: 43:14 in the video. 2 fold rotation axis: 46:35 in the video.

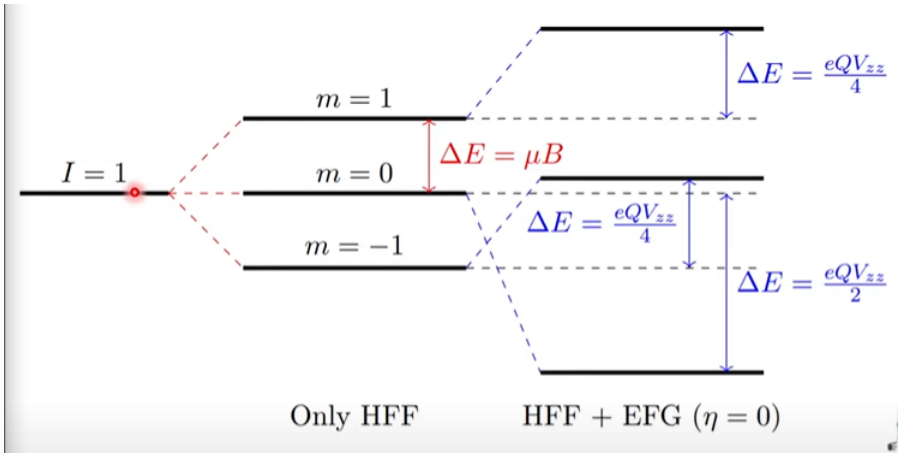

Figure 16: Reverse situation of what we saw in the video: first the HFF and then add the EFG.

Every iron 2 atom has one four-fold rotation axis (has to go through the same nucleus). Iron one has more than one four-fold rotation axes: take axes along the three edges at which this iron atom is: they are all four-fold rotation axes. Full correct answer at 55:50 in the video. A nice example showing the two theorems at 1:01:00.

About the combined HFF and EFG interactions: note, as I've written above as well, that this is only allowed if the PAS of the two coincide. For the magnetic interaction, we have the vector of the hyperfine field which we take to point along the z-axis, but for the EFG, this has probably an independent z-axis for its PAS. We want to solve the Hamiltonian, i.e. diagonalize it, for which we have to choose a specific basis. Hence if the two PAS coincide, these bases coincide, and both are diagonalized at the same time. If they do not coincide, this is not possible.

About the PAS of the magnetic interaction and the PAS of the quadrupole interaction for the three Fe atoms in Fe_4N and whether or not they coincide: this is at 1:09:30 in the video. For the Fe two, these do not coincide.

Note: it may be useful to have a look at VIP-2, since this is a summary of part A again.