





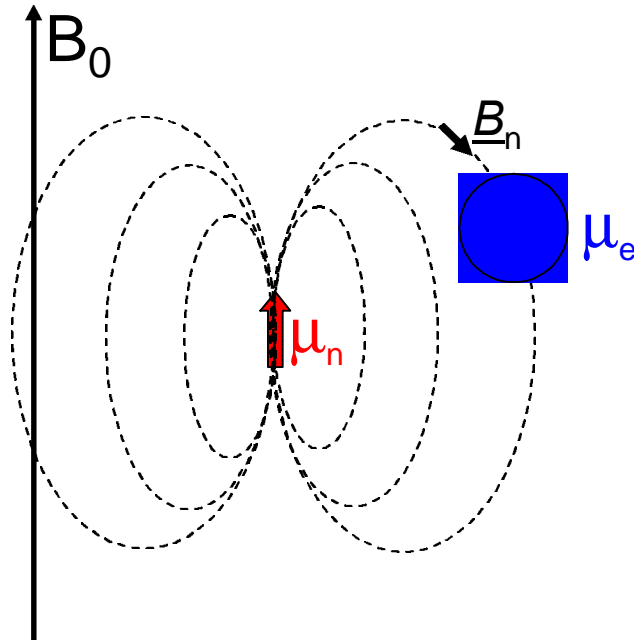
Hyperfine interaction

The notion hyperfine interaction (hfi) comes from atomic physics, where it is used for the interaction of the electronic magnetic moment with the nuclear magnetic moment.

In magnetic resonance this interaction is encountered frequently and is responsible for a number of important aspects of ESR and NMR spectra:

-  In high resolution ESR spectroscopy of e.g. radicals in solution the hyperfine interaction leads to resolved hyperfine splitting of the ESR.
-  If the hyperfine interaction is larger than other unresolved contributions to the ESR line width, the hyperfine splitting is resolved in the ESR of localised centres in the solid state.
-  Unresolved hyperfine interactions with many coupled nuclei are often a major contribution to the ESR line widths in solid state ESR.
-  If the electronic spin is exchanged rapidly due to the exchange interaction or the motion of conduction electrons, the NMR is shifted by the averaged hyperfine interaction of the electrons. This is the **Knight shift** of the NMR.

The hyperfine interaction can be visualized as the motion of the electron in the magnetic dipole field of the nucleus. The nuclear magnetic moment leads to a magnetic field $\underline{B}_n(\underline{r})$, which is called the nuclear field. The electronic magnetic moment interacts with this nuclear field $\underline{B}_n(\underline{r})$.



The interaction energy is: $A = -\underline{\mu}_e \cdot \underline{B}_n(\underline{r})$

There are two contributions:

1. The wave function $\psi(\underline{r})$ of the electron does not vanish at the nuclear position (s-states in atomic terminology). $\psi(0) \neq 0$.

$$A_s = \frac{m_0}{4p} \cdot \frac{8p}{3} \cdot (g_n \cdot \underline{m}_K) \cdot (g_e \cdot \underline{m}_B) \cdot |\psi(0)|^2$$

This is the Fermi-contact interaction.

2. The wave function of the electron has an angular dependence and vanishes at the nuclear position: $\psi(0) \rightarrow 0$ (e.g. a p-function).

$$A_p = \frac{m_0}{4p} \cdot \frac{2}{5} \cdot (g_n \cdot \underline{m}_K) \cdot (g_e \cdot \underline{m}_B) \cdot \left\langle \frac{1}{r^3} \right\rangle \langle 3\cos^2\theta - 1 \rangle$$

Averaging over the electronic wave function

If both contributions are present:

$$A = A_s + A_p \cdot (3\cos^2\theta - 1)$$

θ is the angle between the magnetic field B_0 and the p-function lobe.

In gases and liquids, only the isotropic part A_s is observable, since the rapid reorientation of the atoms or molecules averages the anisotropic contributions to zero.

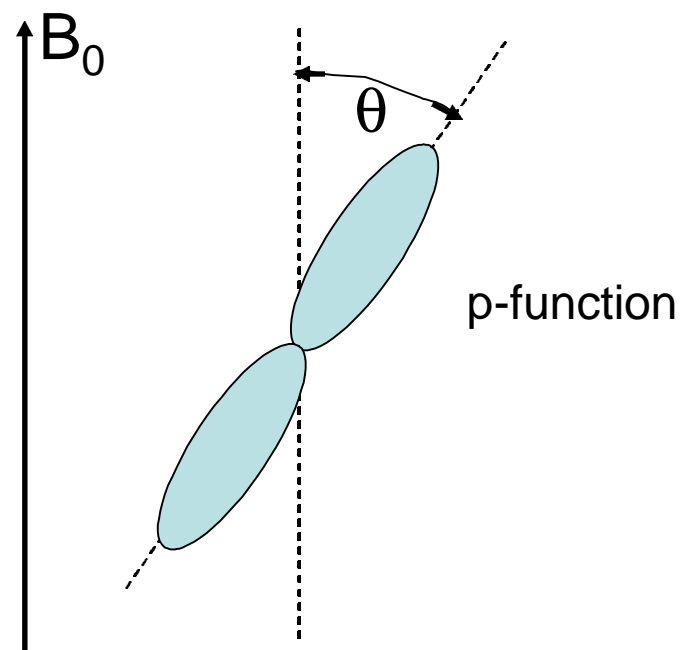
In the solid state, the site symmetry of the nuclear position is important:

For cubic site symmetry, only A_s is retained.

In the general case: the interaction is a 2nd rank tensor, the hyperfine tensor.

$$A^2 = A_{XX}^2 \cdot \sin^2\theta \cdot \cos^2\Phi + A_{YY}^2 \cdot \sin^2\theta \cdot \sin^2\Phi + A_{ZZ}^2 \cdot \cos^2\theta$$

θ and Φ are the angles between the coordinate system axes and the tensor principle axes X, Y, Z.



In general situations, an electronic spin \underline{S} and a nuclear spin \underline{I} are coupled by an interaction

$$\hat{H}_{\text{hfi}} = \underline{\hat{I}} \cdot \underline{\hat{A}} \cdot \underline{\hat{S}}$$

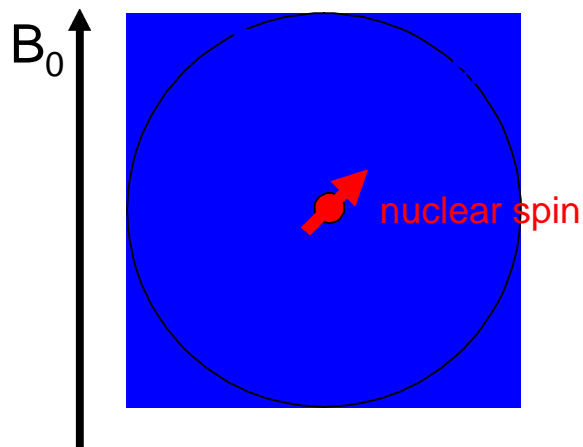
The second rank tensor A is called the hyperfine tensor and it can be described by its three principal axes values A_{XX} , A_{YY} , A_{ZZ} along the principal axis system $\hat{X}, \hat{Y}, \hat{Z}$.

In many situations, the hyperfine interaction is a scalar, independent of the spin direction. This case is e.g. the Fermi contact interaction between s-like electrons at the nuclear site.

In this situation, the hfi leads to a scalar interaction term: $\hat{H}_{\text{hfi}} = a \cdot \underline{\hat{I}} \cdot \underline{\hat{S}} = h \cdot A \cdot \underline{\hat{I}} \cdot \underline{\hat{S}}$

The hfi coupling constant $a = h \cdot A$ is often given in frequency units: e.g. $A = 65 \text{ MHz}$.

It is interesting to note at that point, that our fundamental definition and the experimental realisation of the time unit second is realised by the hyperfine interaction of the s-electron in ^{133}Cs with the nuclear magnetic moment of the Cs $I=7/2$ nucleus.



The Hamiltonian of an electronic spin $\underline{\hat{S}}$ and a nuclear spin $\underline{\hat{I}}$ in a magnetic field \underline{B}_0 along the z-direction:

$$\hat{H} = g_e \cdot \underline{\mathbf{m}}_B \cdot B_0 \cdot \hat{S}_z - g_n \cdot \underline{\mathbf{m}}_K \cdot B_0 \cdot \hat{I}_z + h \cdot A \cdot \underline{\hat{I}} \cdot \underline{\hat{S}}$$

This Hamiltonian is solved by diagonalisation, leading to the energy eigenvalues and the eigenstates. As the base states for the quantum mechanical treatment, we take product states between the electron spin states $|S, m_S\rangle$ and the nuclear spin states $|I, m_I\rangle$

$$|\mathbf{y}\rangle = |S, m_S\rangle \cdot |I, m_I\rangle \quad m_S = -S, -S+1, \dots, S-1, S \quad m_I = -I, -I+1, \dots, I-1, I$$

There are $(2S+1) \cdot (2I+1)$ base states.

In order to avoid a too clumsy notation, one usually omits the S, I in the base states and

writes: $|\mathbf{y}\rangle = |m_S m_I\rangle = |m_S\rangle \cdot |m_I\rangle$

For the case $S = 1/2, I = 1/2$, we have 4 base states:

$$|1\rangle = \left| +\frac{1}{2} +\frac{1}{2} \right\rangle \quad |2\rangle = \left| +\frac{1}{2} -\frac{1}{2} \right\rangle \quad |3\rangle = \left| -\frac{1}{2} +\frac{1}{2} \right\rangle \quad |4\rangle = \left| -\frac{1}{2} -\frac{1}{2} \right\rangle$$

The operators S_z and I_z are diagonal in the base states.

$$\begin{aligned} \hat{S}_z |1\rangle &= \hat{S}_z \left| +\frac{1}{2} +\frac{1}{2} \right\rangle = \frac{1}{2} \cdot \left| +\frac{1}{2} +\frac{1}{2} \right\rangle = \frac{1}{2} \cdot |1\rangle & \hat{S}_z |2\rangle &= +\frac{1}{2} \cdot |2\rangle & \hat{S}_z |3\rangle &= -\frac{1}{2} \cdot |3\rangle & \hat{S}_z |4\rangle &= -\frac{1}{2} \cdot |4\rangle \\ \hat{I}_z |1\rangle &= +\frac{1}{2} \cdot |1\rangle & \hat{I}_z |2\rangle &= -\frac{1}{2} \cdot |2\rangle & \hat{I}_z |3\rangle &= +\frac{1}{2} \cdot |3\rangle & \hat{I}_z |4\rangle &= -\frac{1}{2} \cdot |4\rangle \end{aligned}$$

$$\hat{H}_{\text{hfi}} = h \cdot A \cdot \hat{\underline{I}} \cdot \hat{\underline{S}} = h \cdot A \cdot (\hat{I}_x \cdot \hat{S}_x + \hat{I}_y \cdot \hat{S}_y + \hat{I}_z \cdot \hat{S}_z)$$

$$\hat{H}_{\text{hfi}} = h \cdot A \cdot \left(\hat{I}_z \cdot \hat{S}_z + \frac{1}{2} \cdot (\hat{I}_+ \cdot \hat{S}_- + \hat{I}_- \cdot \hat{S}_+) \right)$$

$\hat{S}_+ 3\rangle = 1\rangle$	$\hat{S}_+ 4\rangle = 2\rangle$	$\hat{S}_- 1\rangle = 3\rangle$	$\hat{S}_- 2\rangle = 4\rangle$
$\hat{I}_+ 2\rangle = 1\rangle$	$\hat{I}_+ 4\rangle = 3\rangle$	$\hat{I}_- 1\rangle = 2\rangle$	$\hat{I}_- 3\rangle = 4\rangle$

S operates on the electronic spin only leaving the nuclear spin state unaffected. Similarly I only operates on the nuclear spin.

$$\hat{I}_+ \hat{S}_- |2\rangle = \hat{I}_+ |4\rangle = |3\rangle \quad \hat{I}_- \hat{S}_+ |3\rangle = \hat{I}_- |1\rangle = |2\rangle$$

$$\hat{H}_{\text{hfi}} = h \cdot A \cdot \left(\hat{I}_z \cdot \hat{S}_z + \frac{1}{2} \cdot (\hat{I}_+ \cdot \hat{S}_- + \hat{I}_- \cdot \hat{S}_+) \right)$$

Is diagonal with matrix elements $\pm hA/4$

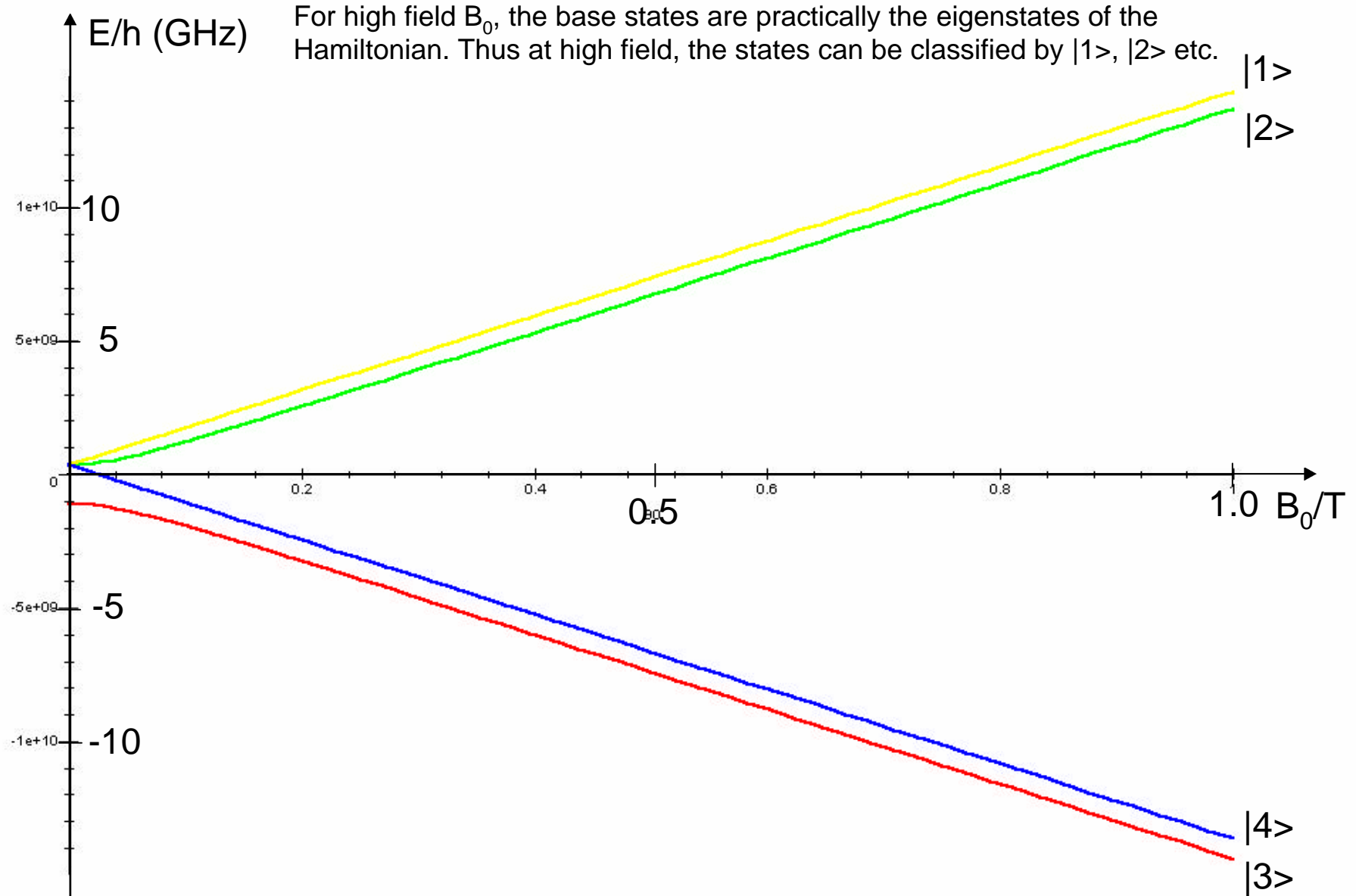
Couples the states $|2\rangle$ and $|3\rangle$ with matrix elements $hA/2$

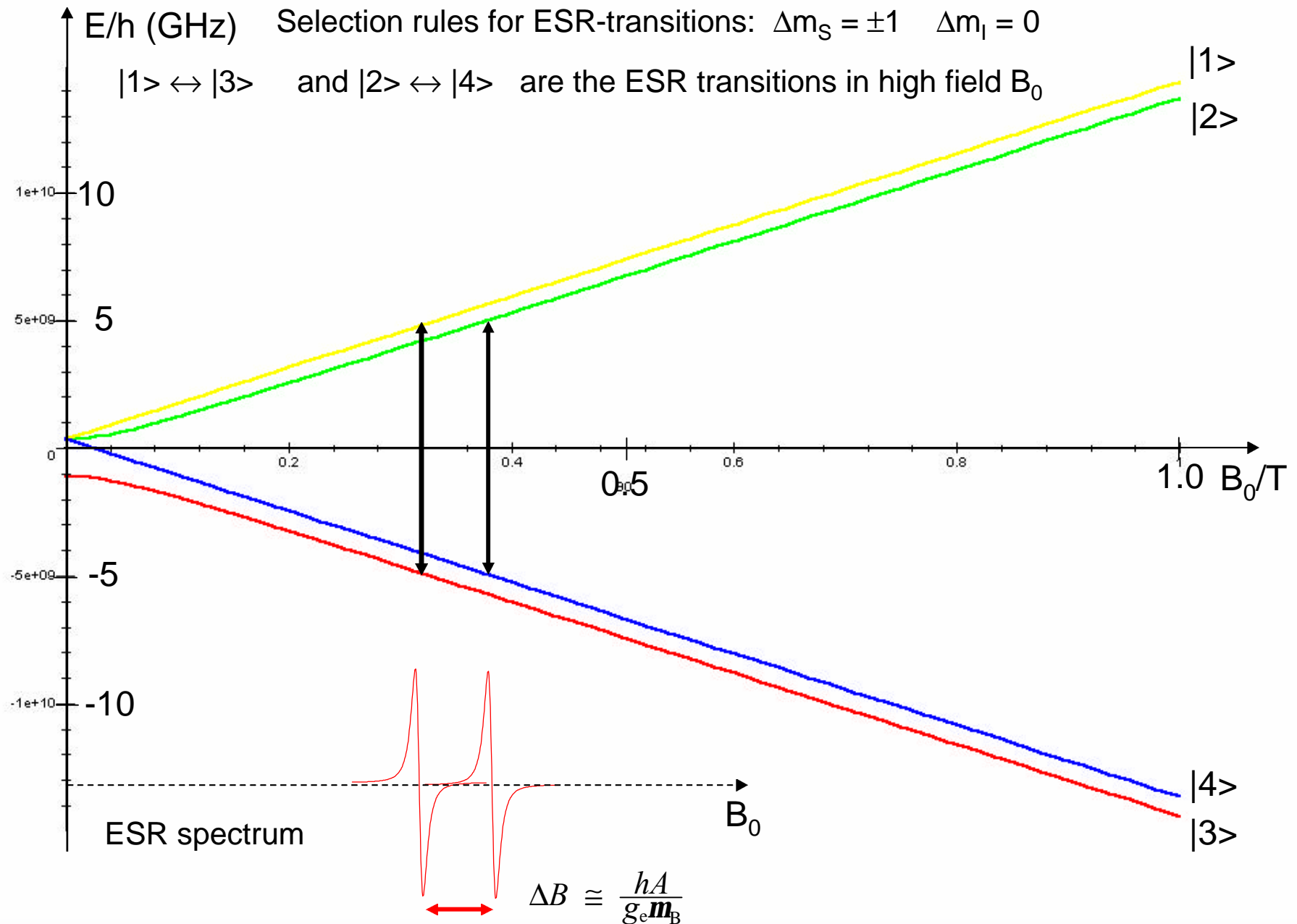
Note: For quantum mechanical calculations with spins, it is generally very practical to express the operators S_x, S_y, I_x, I_y in terms of the shift operators S_+, S_-, I_+, I_- . The matrix elements of these operators are easy to evaluate: S_+ shifts a state $|m_s\rangle$ to $|m_s+1\rangle$, unless $|m_s\rangle$ is the highest state. S_- shifts $|m_s\rangle$ to $|m_s-1\rangle$, unless $|m_s\rangle$ is the lowest state.

Matrix elements of the
Hamilton operator

$$H = g_e \mathbf{m}_B \cdot B_0 \hat{S}_z - g_n \mathbf{m}_K \cdot B_0 \hat{I}_z + h A \hat{I} \cdot \hat{S}$$

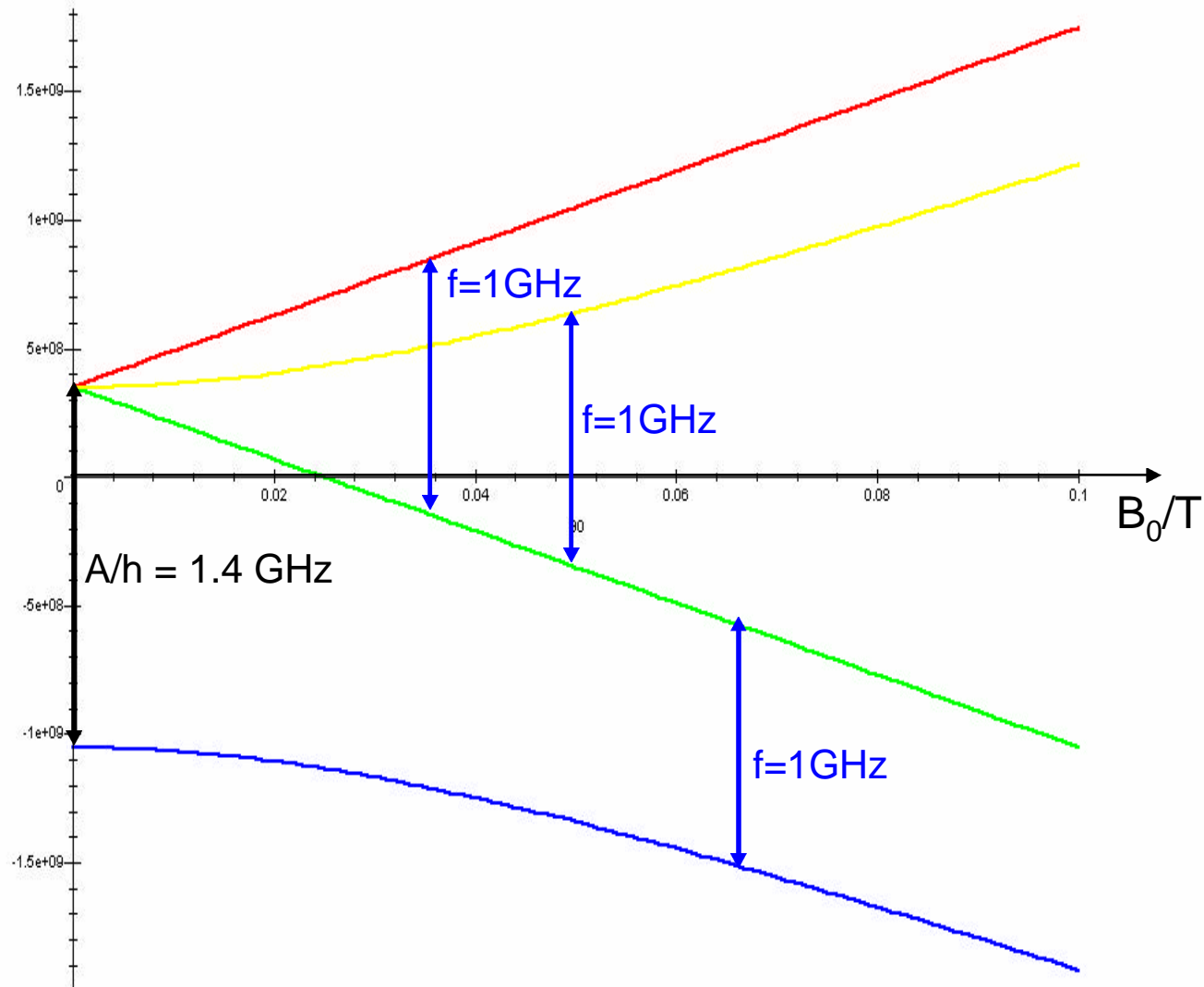
$$\begin{array}{l}
 |1\rangle = \left| +\frac{1}{2} +\frac{1}{2} \right\rangle \quad |2\rangle = \left| +\frac{1}{2} -\frac{1}{2} \right\rangle \quad |3\rangle = \left| -\frac{1}{2} +\frac{1}{2} \right\rangle \quad |4\rangle = \left| -\frac{1}{2} -\frac{1}{2} \right\rangle \\
 \left\langle 1 \right| = \left\langle +\frac{1}{2} +\frac{1}{2} \right| \quad \left\langle 2 \right| = \left\langle +\frac{1}{2} -\frac{1}{2} \right| \quad \left\langle 3 \right| = \left\langle -\frac{1}{2} +\frac{1}{2} \right| \quad \left\langle 4 \right| = \left\langle -\frac{1}{2} -\frac{1}{2} \right|
 \end{array}
 \begin{pmatrix}
 \frac{1}{2} g_e \mathbf{m}_B \cdot B_0 & 0 & 0 & 0 \\
 -\frac{1}{2} g_n \mathbf{m}_K \cdot B_0 + \frac{hA}{4} & 0 & 0 & 0 \\
 0 & +\frac{1}{2} g_e \mathbf{m}_B \cdot B_0 & \frac{hA}{2} & 0 \\
 0 & +\frac{1}{2} g_n \mathbf{m}_K \cdot B_0 - \frac{hA}{4} & \frac{hA}{2} & 0 \\
 0 & \frac{hA}{2} & -\frac{1}{2} g_e \mathbf{m}_B \cdot B_0 & 0 \\
 0 & 0 & -\frac{1}{2} g_n \mathbf{m}_K \cdot B_0 - \frac{hA}{4} & 0 \\
 0 & 0 & 0 & -\frac{1}{2} g_e \mathbf{m}_B \cdot B_0 \\
 0 & 0 & 0 & +\frac{1}{2} g_n \mathbf{m}_K \cdot B_0 + \frac{hA}{4}
 \end{pmatrix}$$





In low field B_0 , the eigenstates clearly are no longer the base states.

As the states are now a mixture of the 4 base states, there can be in principle 6 magnetic resonance transitions. However, it depends on the frequency $\Delta E = h \cdot f$, which are observed.



Transitions which apparently do not obey the selection rules $\Delta m_S = \pm 1$, $\Delta m_I = 0$, are called

‘forbidden’ transitions.

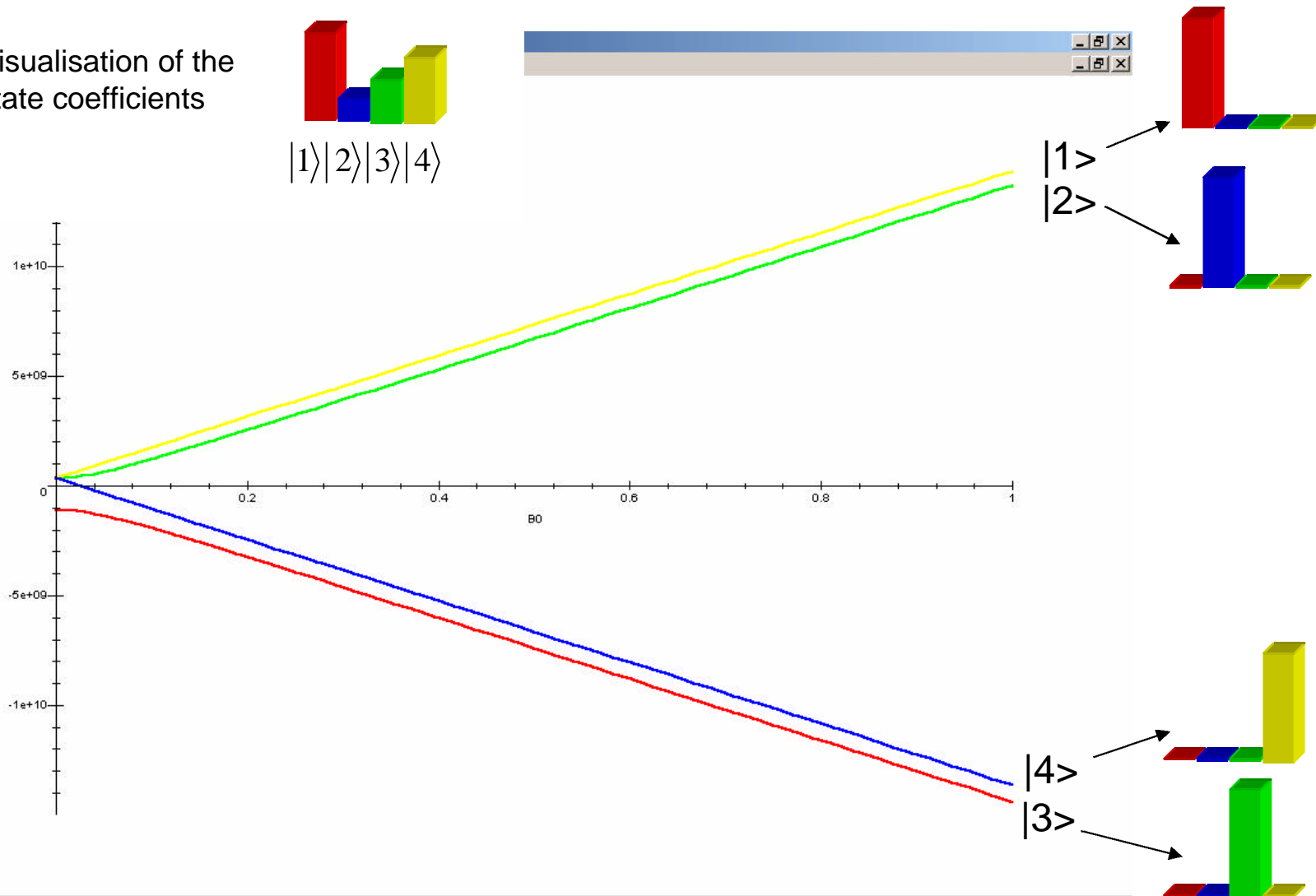
However, there is nothing forbidden with these transitions. The states coupled by these transitions are mixtures of the base states, and the magnetic dipole transitions can occur with the correct selection rules.

What are the states in the limit of $B_0 \rightarrow \infty$ and $B_0 = 0$?

The limit of very large B_0 is: the base states $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$ are the eigenstates.

States $|2\rangle$ and $|3\rangle$ have the S and I spin anti-parallel, thus they are lower in energy through the hyperfine interaction.

Visualisation of the
state coefficients



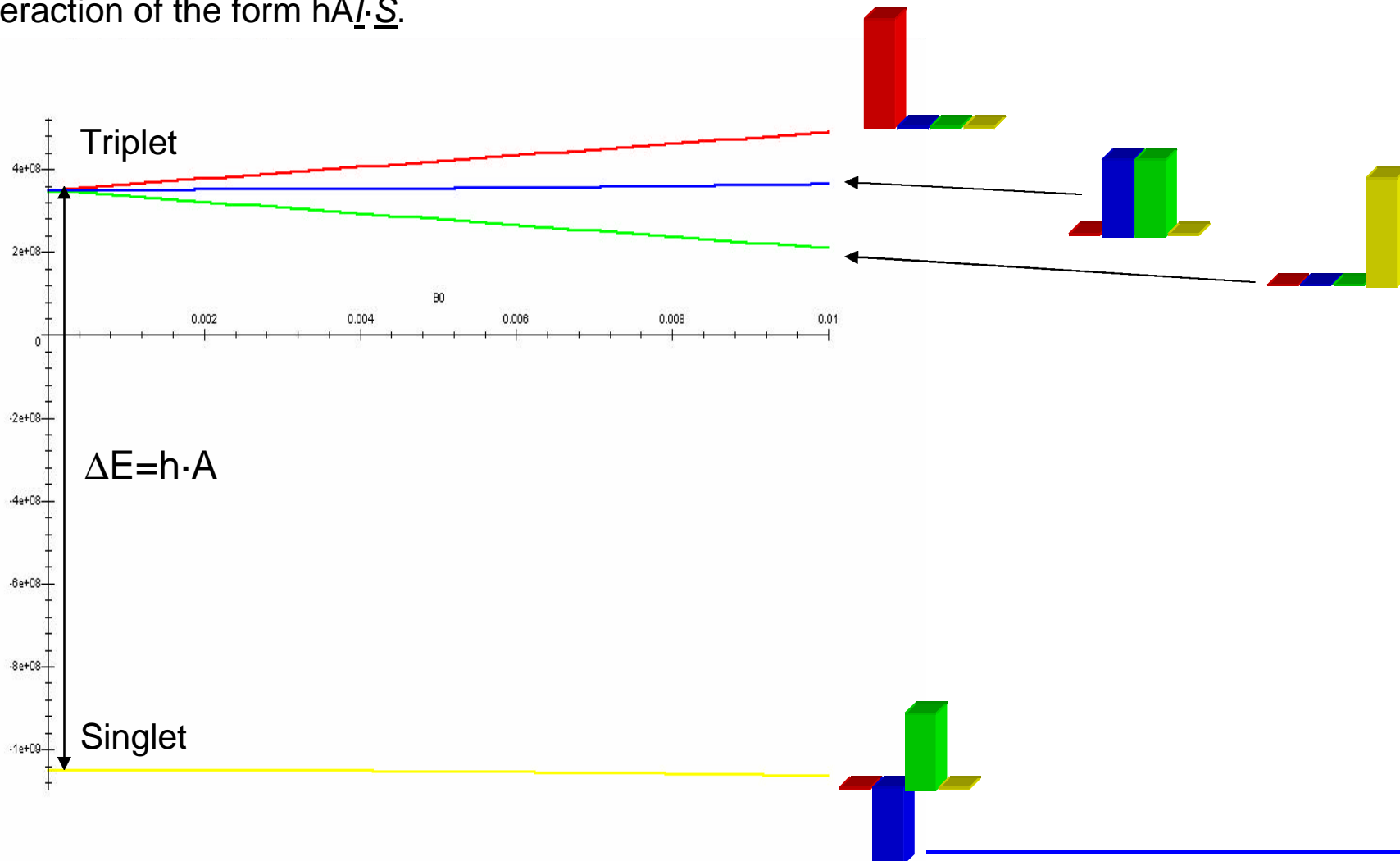
For $B_0 = 0$, the solutions are: a singlet with total spin 0

a triplet with total spin 1

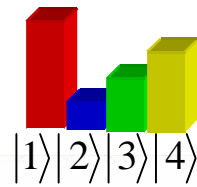
$$\frac{1}{\sqrt{2}} \cdot \left(\left| +\frac{1}{2} -\frac{1}{2} \right\rangle - \left| -\frac{1}{2} +\frac{1}{2} \right\rangle \right)$$

$$\left| +\frac{1}{2} +\frac{1}{2} \right\rangle, \frac{1}{\sqrt{2}} \cdot \left(\left| +\frac{1}{2} -\frac{1}{2} \right\rangle + \left| -\frac{1}{2} +\frac{1}{2} \right\rangle \right), \left| -\frac{1}{2} -\frac{1}{2} \right\rangle$$

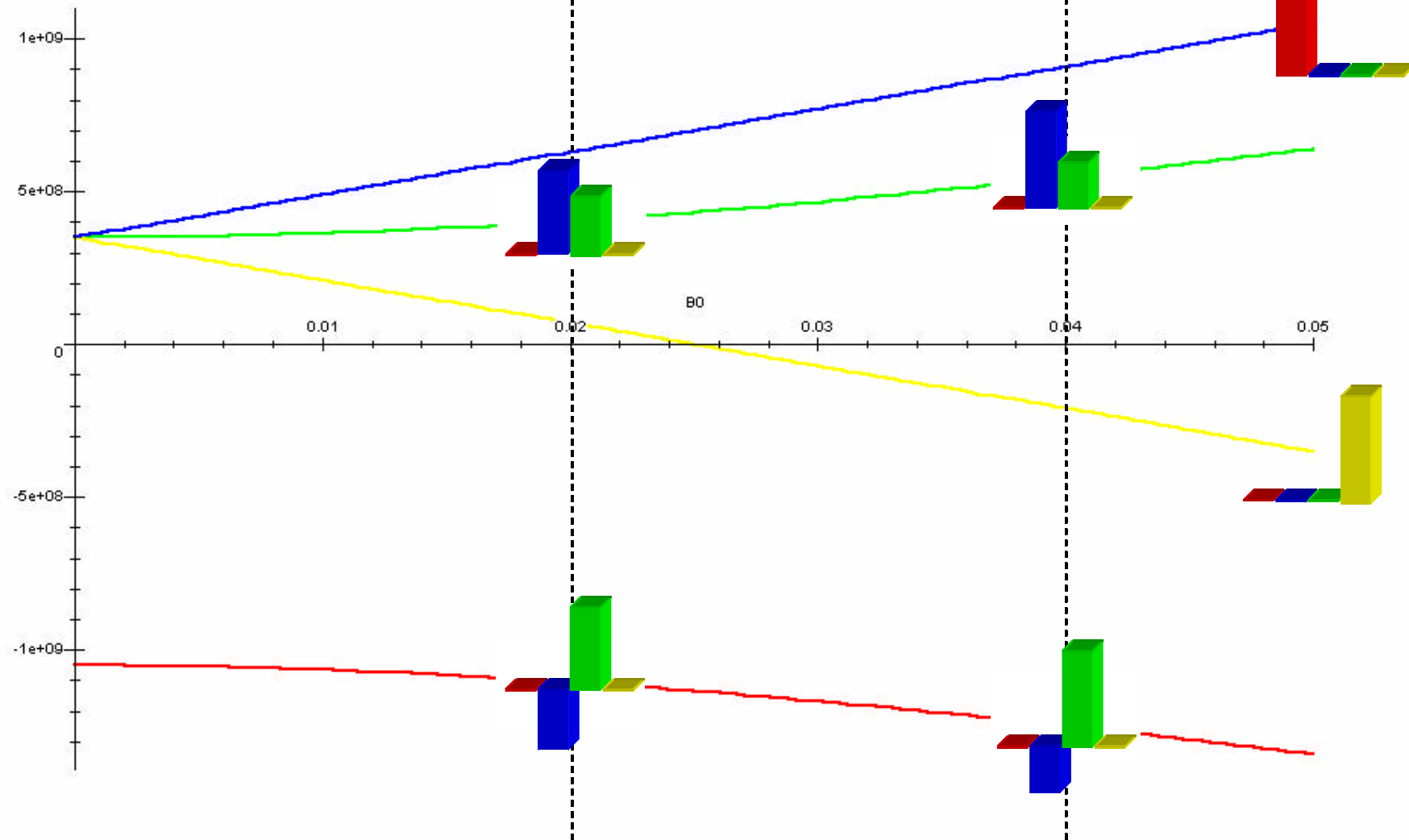
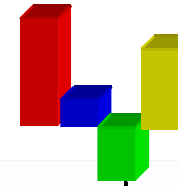
These are very general properties of two spins coupled by an interaction of the form $\hbar A \underline{I} \cdot \underline{S}$.



Visualisation of the
coefficients of the states:



Negative coefficients
are drawn downwards



The following operators are frequently found in calculations of spin systems:

$$\hat{J}^2, \hat{J}_z, \hat{J}_x, \hat{J}_y, \hat{J}_+, \hat{J}_-$$

The operator symbol J stands for any angular momentum operator like $\underline{L}, \underline{S}, \underline{I}, \underline{J} = \underline{L} + \underline{S}, \underline{F} = \underline{J} + \underline{I}$ etc.

The quantum states are written as:

$|Jm_J\rangle$ J is the spin number, m_J the projection of the spin onto the quantisation axis, usually taken as the z-axis.

Fundamental relations for the operators and the states are:

$$\hat{J}^2 |Jm_J\rangle = J \cdot (J + 1) |Jm_J\rangle \quad \text{Diagonal with eigenvalue } J(J+1)$$

$$\hat{J}_z |Jm_J\rangle = m_J |Jm_J\rangle \quad \text{Diagonal with eigenvalue } m_J$$

$$\hat{J}_+ |Jm_J\rangle = \sqrt{J \cdot (J + 1) - m_J \cdot (m_J + 1)} \cdot |Jm_J + 1\rangle \quad \text{"Shifts" one state up.}$$

$$\hat{J}_- |Jm_J\rangle = \sqrt{J \cdot (J + 1) - m_J \cdot (m_J - 1)} \cdot |Jm_J - 1\rangle \quad \text{"Shifts" one state down.}$$

$$\begin{aligned} \hat{J}_+ &= \hat{J}_x + i\hat{J}_y & \hat{J}_x &= \frac{1}{2}(\hat{J}_+ + \hat{J}_-) & \hat{J}_y &= \frac{-i}{2}(\hat{J}_+ - \hat{J}_-) \\ \hat{J}_- &= \hat{J}_x - i\hat{J}_y \end{aligned}$$

Whereas the diagonal operators can easily be calculated, matrix element tables for the operators J_+ and J_- are very convenient for practical quantum mechanical calculations.

J_+, J_-	$ -1/2\rangle$	$ +1/2\rangle$
$\langle -1/2 $	0	1
$\langle +1/2 $	1	0

J_+, J_-	$ -1\rangle$	$ 0\rangle$	$ +1\rangle$
$\langle -1 $	0	$\sqrt{2}$	0
$\langle 0 $	$\sqrt{2}$	0	$\sqrt{2}$
$\langle +1 $	0	$\sqrt{2}$	0

J_+, J_-	$ -3/2\rangle$	$ -1/2\rangle$	$ +1/2\rangle$	$ +3/2\rangle$
$\langle -3/2 $	0	$\sqrt{3}$	0	0
$\langle -1/2 $	$\sqrt{3}$	0	$\sqrt{4}$	0
$\langle +1/2 $	0	$\sqrt{4}$	0	$\sqrt{3}$
$\langle +3/2 $	0	0	$\sqrt{3}$	0

J_+, J_-	$ -5/2\rangle$	$ -3/2\rangle$	$ -1/2\rangle$	$ +1/2\rangle$	$ +3/2\rangle$	$ +5/2\rangle$
$\langle -5/2 $	0	$\sqrt{5}$	0	0	0	0
$\langle -3/2 $	$\sqrt{5}$	0	$\sqrt{8}$	0	0	0
$\langle -1/2 $	0	$\sqrt{8}$	0	$\sqrt{9}$	0	0
$\langle +1/2 $	0	0	$\sqrt{9}$	0	$\sqrt{8}$	0
$\langle +3/2 $	0	0	0	$\sqrt{8}$	0	$\sqrt{5}$
$\langle +5/2 $	0	0	0	0	$\sqrt{5}$	0

J_+, J_-	$ -2\rangle$	$ -1\rangle$	$ 0\rangle$	$ +1\rangle$	$ +2\rangle$
$\langle -2 $	0	$\sqrt{4}$	0	0	0
$\langle -1 $	$\sqrt{4}$	0	$\sqrt{6}$	0	0
$\langle 0 $	0	$\sqrt{6}$	0	$\sqrt{6}$	0
$\langle +1 $	0	0	$\sqrt{6}$	0	$\sqrt{4}$
$\langle +2 $	0	0	0	$\sqrt{4}$	0

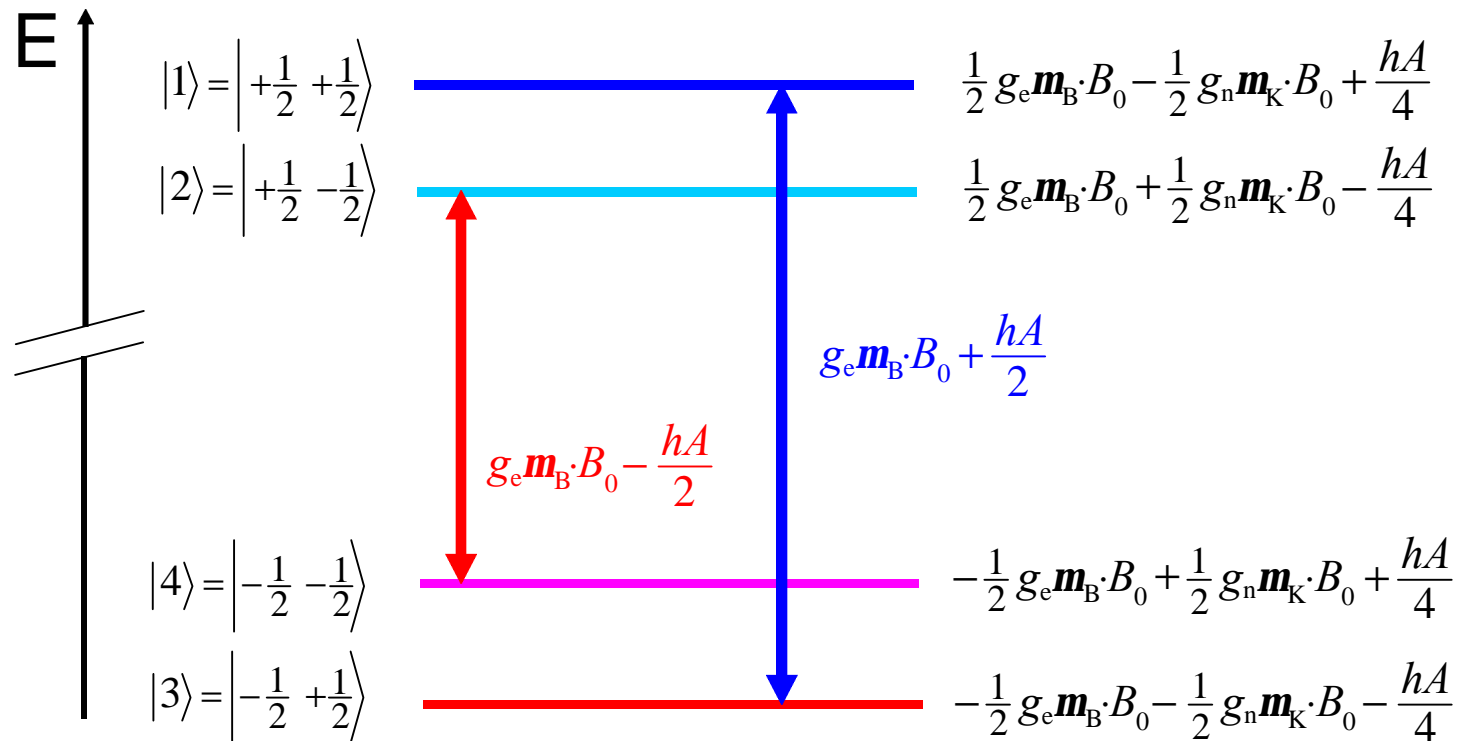
J_+, J_-	$ -3\rangle$	$ -2\rangle$	$ -1\rangle$	$ 0\rangle$	$ +1\rangle$	$ +2\rangle$	$ +3\rangle$	
$\langle -3 $	0	$\sqrt{6}$	0	0	0	0	0	J=3
$\langle -2 $	$\sqrt{6}$	0	$\sqrt{10}$	0	0	0	0	
$\langle -1 $	0	$\sqrt{10}$	0	$\sqrt{12}$	0	0	0	
$\langle 0 $	0	0	$\sqrt{12}$	0	$\sqrt{12}$	0	0	
$\langle +1 $	0	0	0	$\sqrt{12}$	0	$\sqrt{10}$	0	
$\langle +2 $	0	0	0	0	$\sqrt{10}$	0	$\sqrt{6}$	
$\langle +3 $	0	0	0	0	0	$\sqrt{6}$	0	

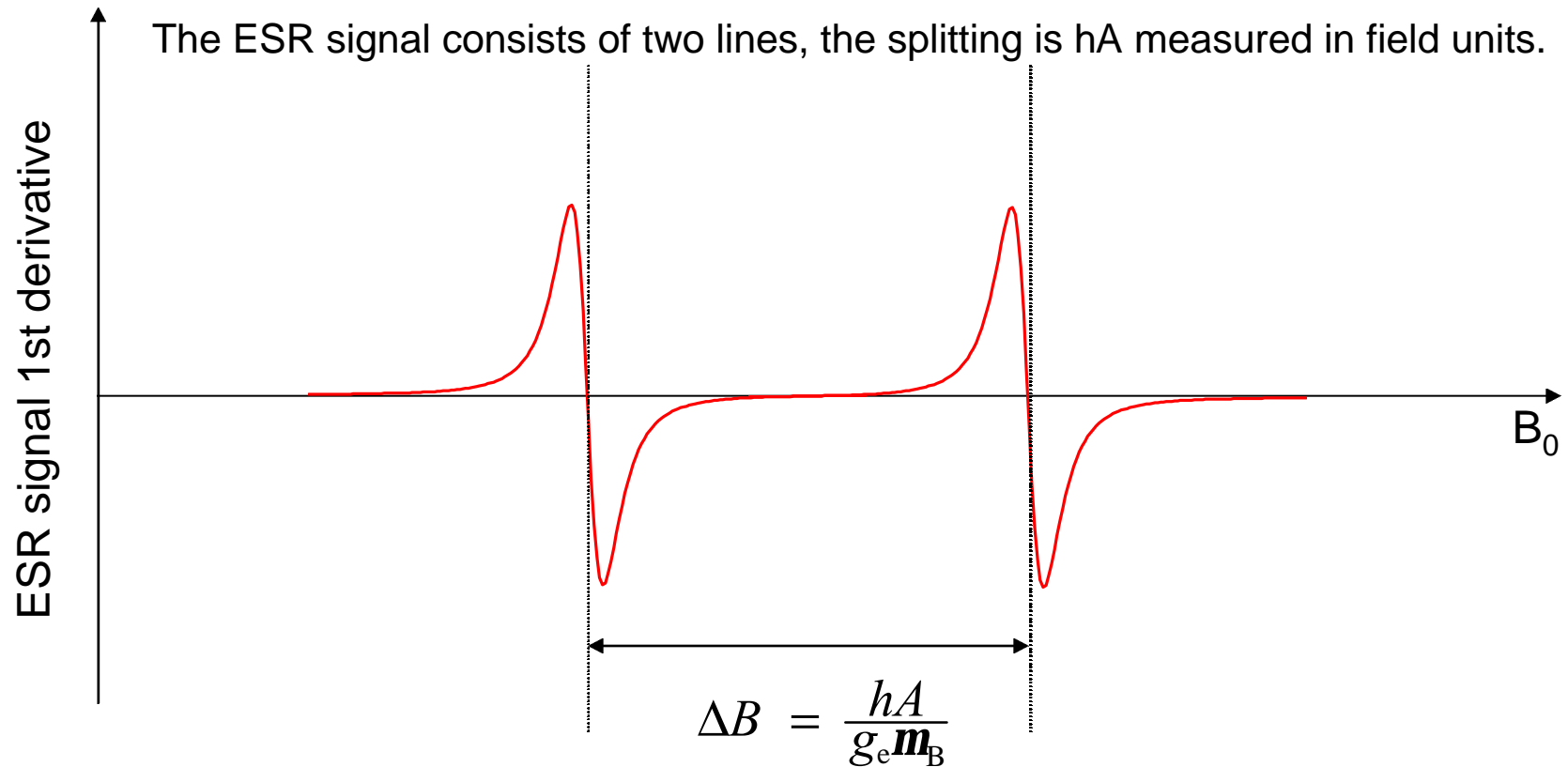
	J_+, J_-	$ -7/2\rangle$	$ -5/2\rangle$	$ -3/2\rangle$	$ -1/2\rangle$	$ +1/2\rangle$	$ +3/2\rangle$	$ +5/2\rangle$	$ +7/2\rangle$
J=7/2	$\langle -7/2 $	0	$\sqrt{7}$	0	0	0	0	0	0
	$\langle -5/2 $	$\sqrt{7}$	0	$\sqrt{12}$	0	0	0	0	0
	$\langle -3/2 $	0	$\sqrt{12}$	0	$\sqrt{15}$	0	0	0	0
	$\langle -1/2 $	0	0	$\sqrt{15}$	0	$\sqrt{16}$	0	0	0
	$\langle +1/2 $	0	0	0	$\sqrt{16}$	0	$\sqrt{15}$	0	0
	$\langle +3/2 $	0	0	0	0	$\sqrt{15}$	0	$\sqrt{12}$	0
	$\langle +5/2 $	0	0	0	0	0	$\sqrt{12}$	0	$\sqrt{7}$
	$\langle +7/2 $	0	0	0	0	0	0	$\sqrt{7}$	0

Hyperfine interaction in high field B_0 : if the electron Zeeman energy $g_e \mu_B B_0$ is large compared to the hyperfine interaction, then the analysis is relatively simple:

The electronic spin is quantized along the axis z of the magnetic field B_0 . The electronic field B_e acting on the nuclei is either in the same direction as or opposed to B_0 , and the nuclear spin is quantized along z as well. The hyperfine interaction is thus $\pm hA/4$, depending on parallel or anti-parallel spins.

In mathematical terms this means, that only the diagonal matrix elements of the operators have to be taken into account. The eigenstates are the base states $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$.



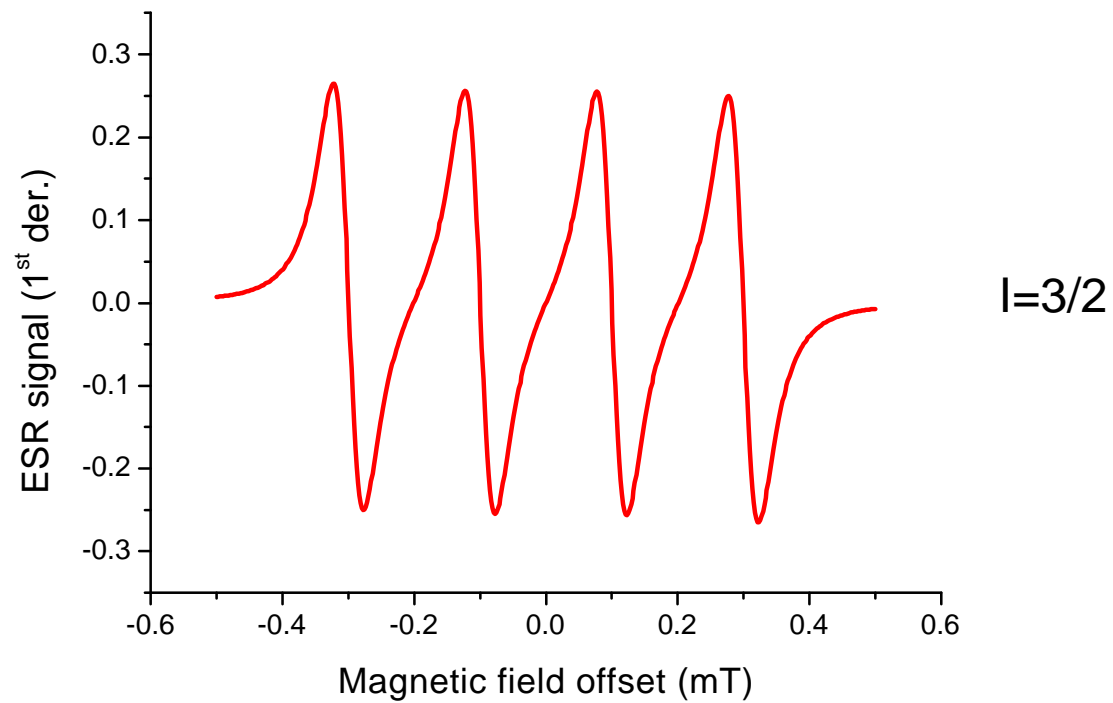


Note: the nuclear Zeeman energy plays no role in high fields, since the nuclear spin is not “flipped” in an ESR transition.

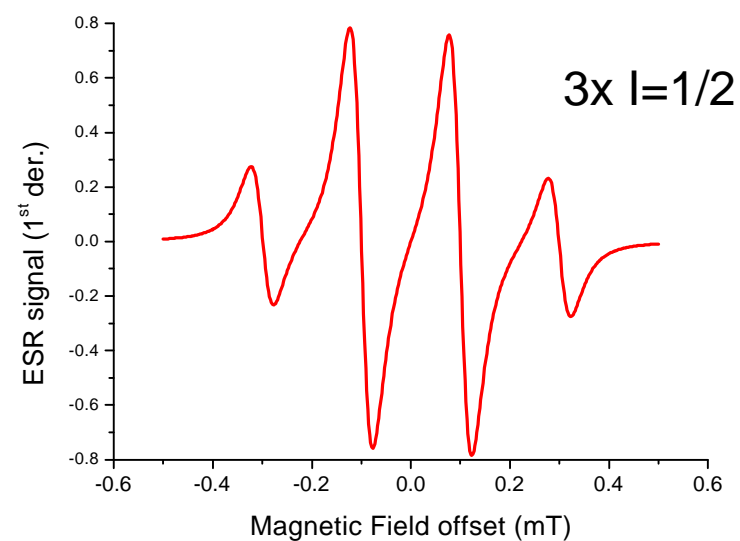
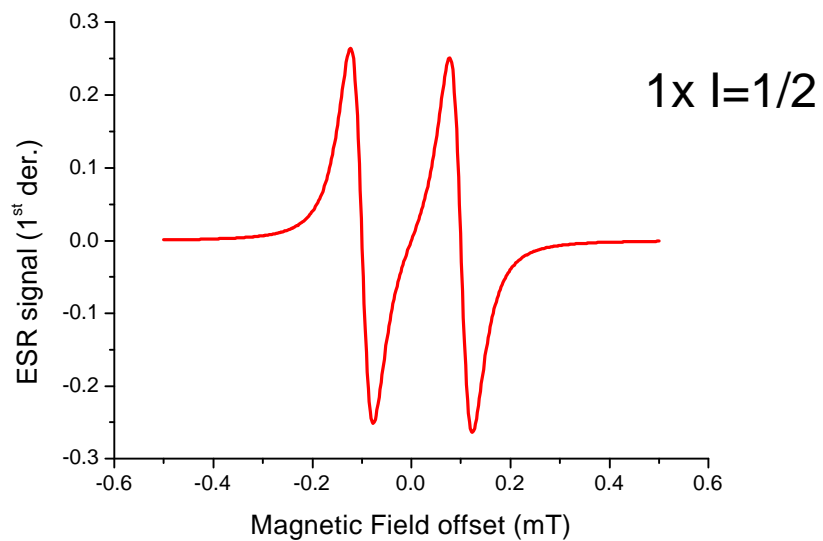
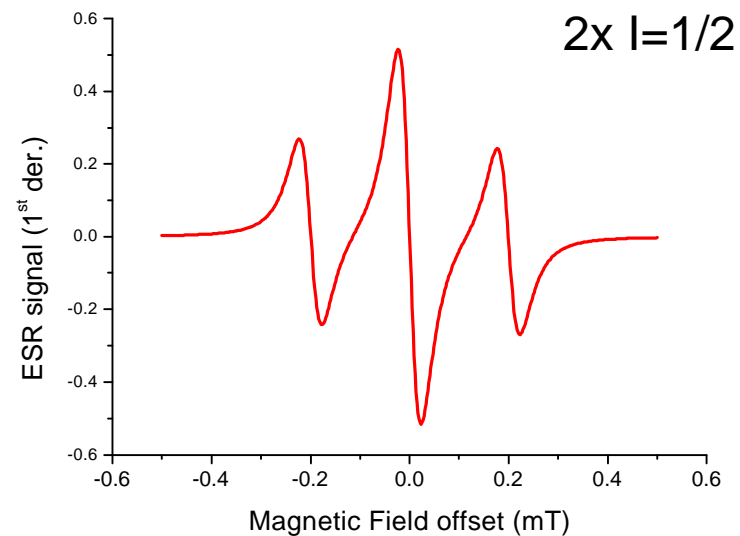
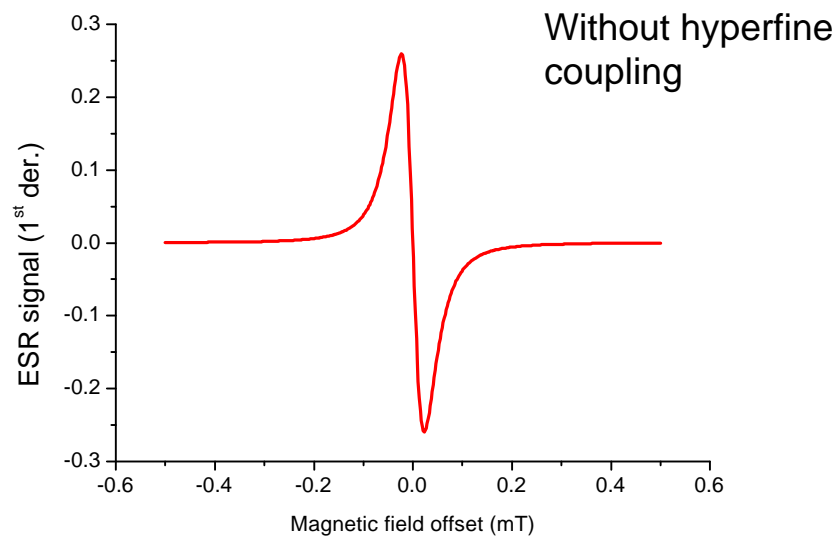
If the hyperfine interaction is resolved in the ESR-spectrum, it can be directly read of the spectrum.

Unfortunately, the hyperfine interaction is often small and not resolved, and very often there is hyperfine coupling to many nuclei, making the ESR spectrum fairly complicated.

Coupling with **one** nuclear spin I : $2 \cdot I + 1$ equidistant lines of practically equal intensity



Hyperfine interaction with a number of equivalent nuclei.



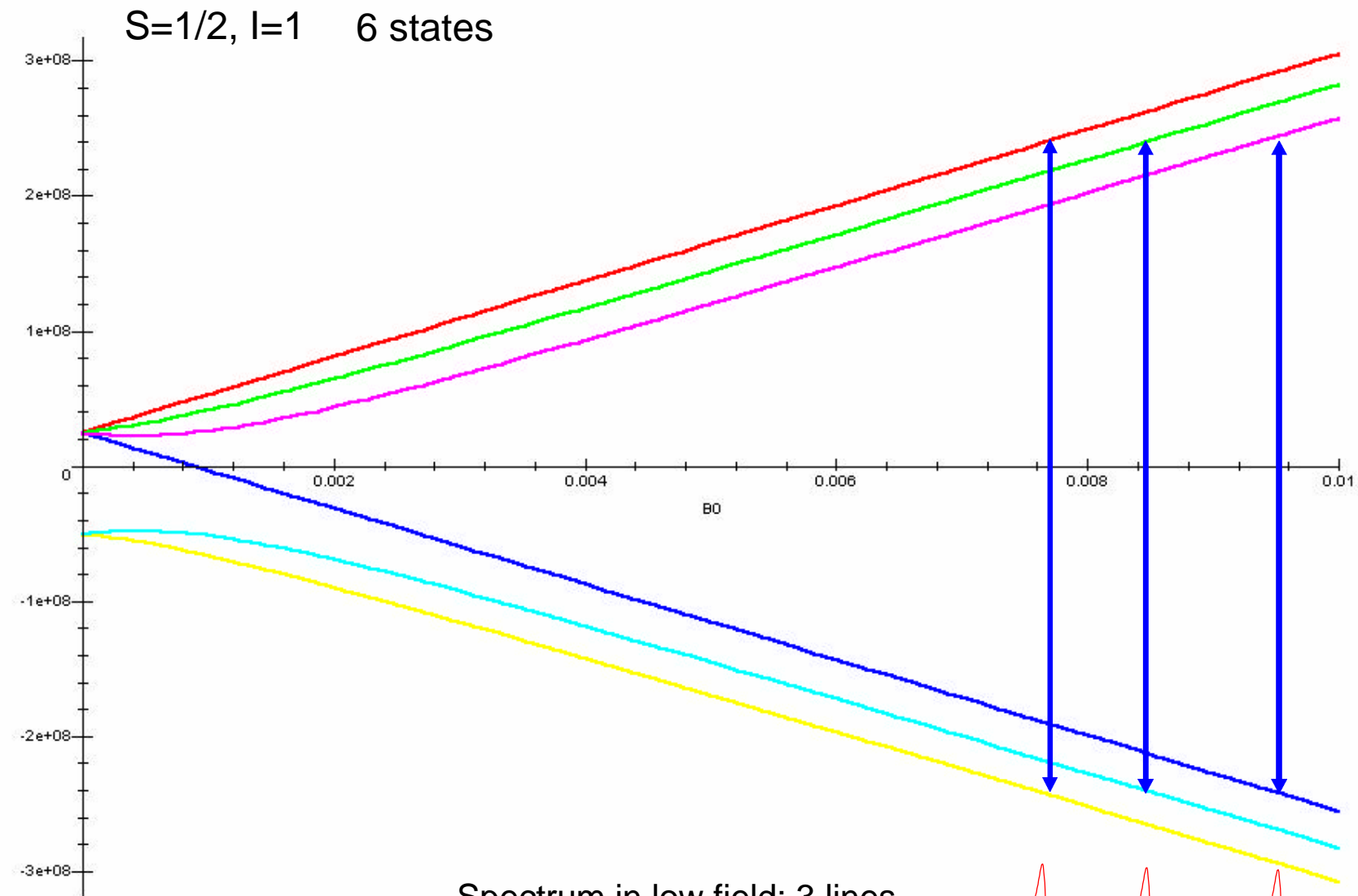
The hyperfine structure is only resolved in the ESR spectra if $A > \text{line width}$.

atom	I	$h \cdot A_s / (g_e \cdot m_B)$	A_s
^1H	1/2	50.8 mT	1422 MHz
^{13}C	1/2	111.0 mT	3.108 GHz
^{19}F	1/2	1720.0 mT	48.16 GHz
^{29}Si	1/2	121.8 mT	3.41 GHz
^{35}Cl	3/2	166.5 mT	4.66 GHz

Selected atomic values for the hyperfine interaction

Calculated values for the complete periodic table:

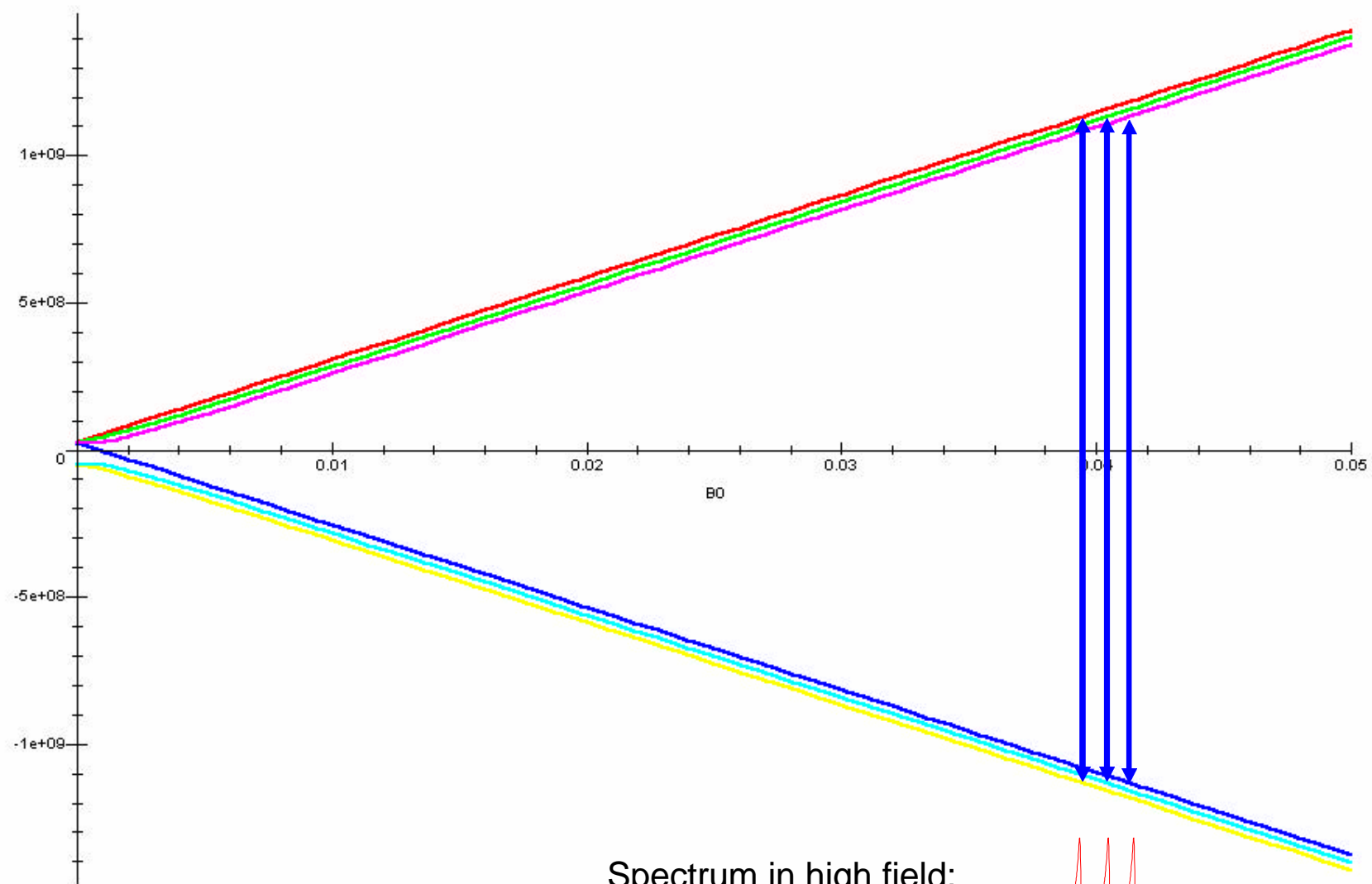
J.R. Morton , K.F. Preston , Journal of Magnetic Resonance **30**, 577 (1978)



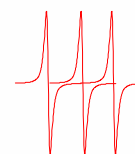
Spectrum in low field: 3 lines

Not quite equidistant

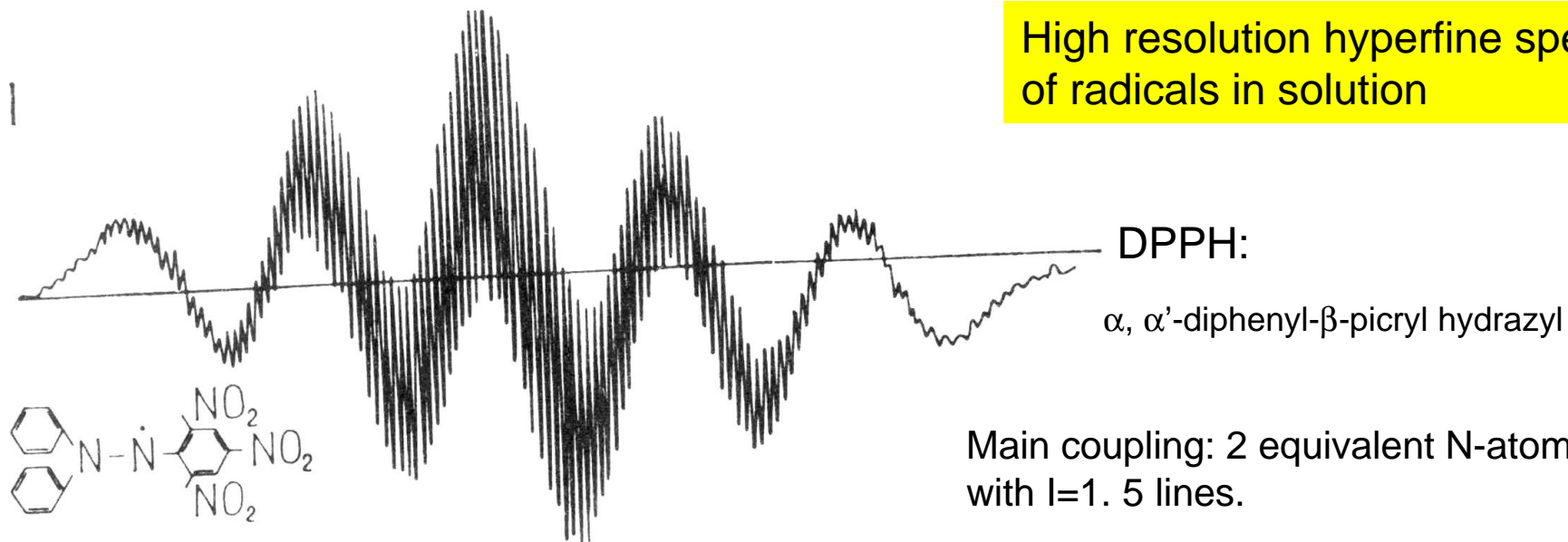




Spectrum in high field:
3 equidistant lines.



High resolution hyperfine spectra of radicals in solution



Main coupling: 2 equivalent N-atoms with $I=1$. 5 lines.

Small couplings: to the protons.

