Electron Paramagnetic Resonance: the free atom case

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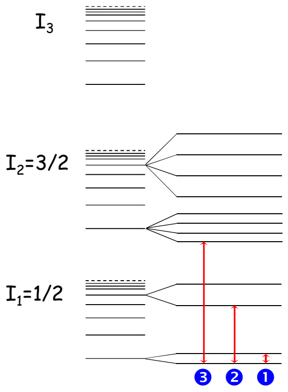
Classification of nuclear methods

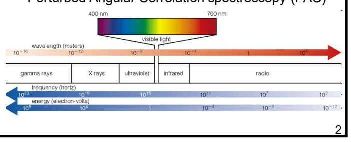


These 3 energy scales distinguish
3 different classes of experimental methods:

1
- Nuclear Magnetic Resonance (NMR)
- Nuclear Quadrupole Resonance (NQR)

2
- laser spectroscopy
- Electron Paramagnetic Resonance (EPR)

3
- Low-Temperature Nuclear Orientation (LTNO)
- NMR on Oriented Nuclei (NMR/ON)
- forward scattering of synchrotron radiation
- Mössbauer Spectrocopy (MS)
- Conversion Electron Mössbauer Spectrocopy (CEMS)
- Perturbed Angular Correlation spectroscopy (PAC)

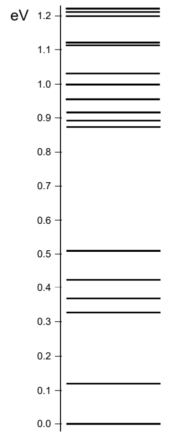


2

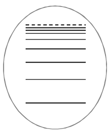
no hyperfine interaction

3

Atomic energies for La : bare values



This is a real-life example of our cartoon :



(up to the fine structure, does not yet include hyperfine structure !)

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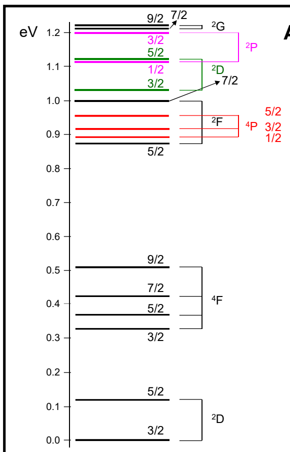
Atomic energies for La : interpreted



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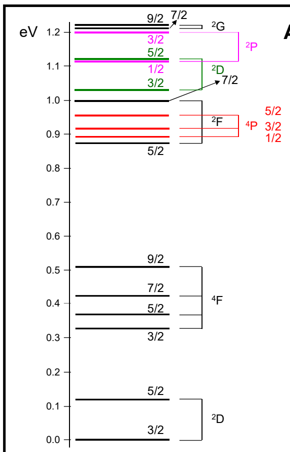
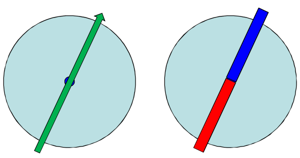
Atomic energies for La : interpreted





The atom has an angular momentum J=3/2 in its ground state.

A magnetic dipole moment ('bar magnet') must be associated with this angular momentum :

$$\vec{\mu}_J = g_J \frac{\mu_B}{\hbar} \vec{J}$$

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Apply an external magnetic field

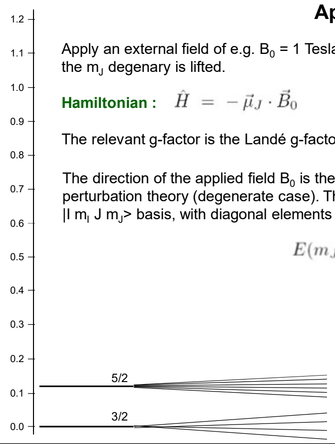
Apply an external field of e.g. B_0 = 1 Tesla : the m_J degenary is lifted.

Hamiltonian : $\hat{H} = -\vec{\mu}_J \cdot \vec{B}_0$

The relevant g-factor is the Landé g-factor.

The direction of the applied field B_0 is the quantization axis (Z). Use first order perturbation theory (degenerate case). The matrix is already diagonal in the $|I\, m_I\, J\, m_J>$ basis, with diagonal elements being:

$$\begin{aligned} E(m_J) &= -\langle m_J | \hat{\mu}_{J_z} | m_J \rangle \, B_0 \\ &= -g_J \frac{\mu_B}{\hbar} B_0 \, \langle m_J | \hat{J}_z | m_J \rangle \\ &= -g_J \, \mu_B \, B_0 \, m_J \end{aligned}$$



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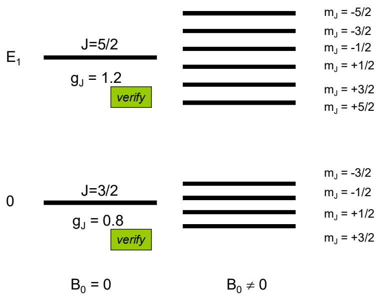
2. EPR for free ions (no hyperfine interaction)



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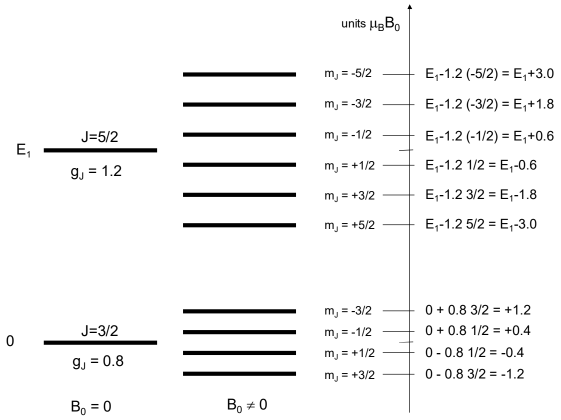

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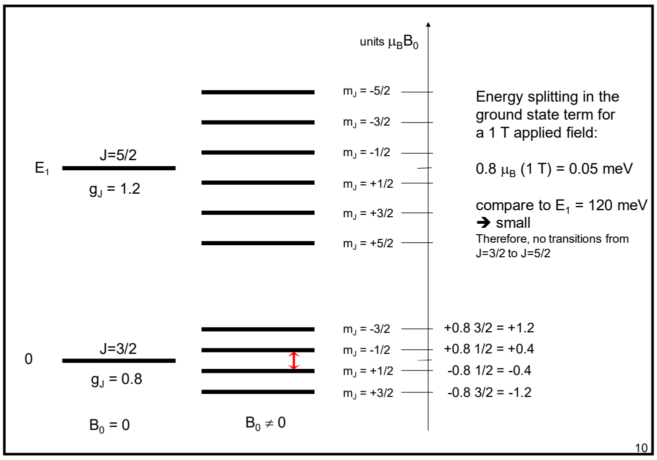
units $\mu_B B_0$
m_J = -5/2
m_J = -3/2
m_J = -1/2
m_J = +1/2
m_J = +3/2
m_J = +5/2
E_1
J=5/2
g_J = 1.2
Energy splitting in the ground state term for a 1 T applied field:
0.8 μ_B (1 T) = 0.05 meV
compare to E_1 = 120 meV → small
Therefore, no transitions from J=3/2 to J=5/2
0
J=3/2
g_J = 0.8
m_J = -3/2
m_J = -1/2
m_J = +1/2
m_J = +3/2
+0.8 3/2 = +1.2
+0.8 1/2 = +0.4
-0.8 1/2 = -0.4
-0.8 3/2 = -1.2
B_0 = 0
$B_0 \neq 0$
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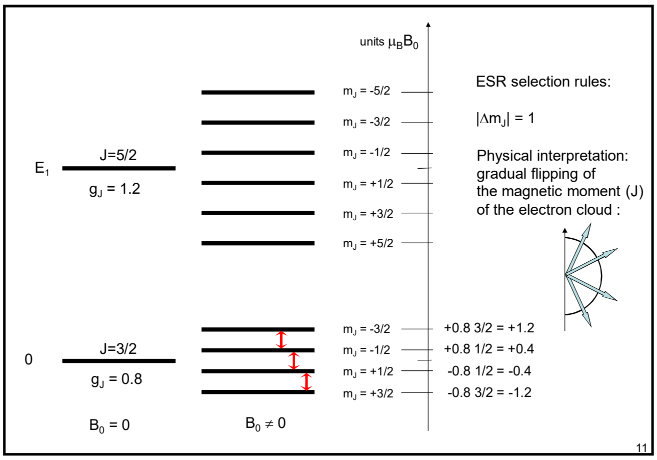
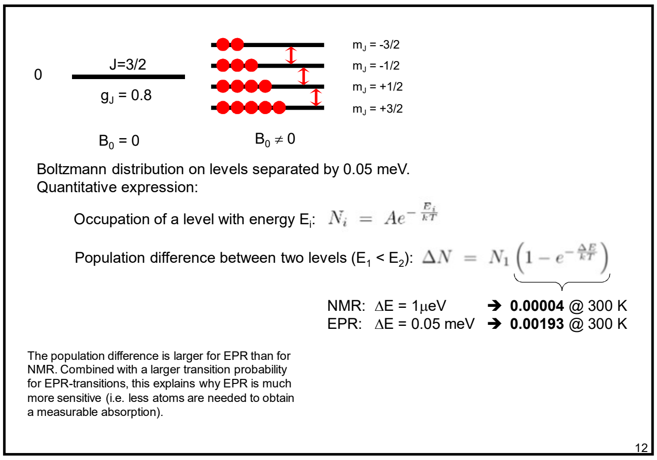

units $\mu_B B_0$
m_J = -5/2
m_J = -3/2
m_J = -1/2
m_J = +1/2
m_J = +3/2
m_J = +5/2
E_1
J=5/2
g_J = 1.2
ESR selection rules:
$|\Delta m_J| = 1$
Physical interpretation: gradual flipping of the magnetic moment (J) of the electron cloud :
0
J=3/2
g_J = 0.8
m_J = -3/2
m_J = -1/2
m_J = +1/2
m_J = +3/2
+0.8 3/2 = +1.2
+0.8 1/2 = +0.4
-0.8 1/2 = -0.4
-0.8 3/2 = -1.2
B_0 = 0
$B_0 \neq 0$
11


0
J=3/2
g_J = 0.8
m_J = -3/2
m_J = -1/2
m_J = +1/2
m_J = +3/2
B_0 = 0
$B_0 \neq 0$
Boltzmann distribution on levels separated by 0.05 meV.
Quantitative expression:
Occupation of a level with energy E_i: $N_i = Ae^{-\frac{E_i}{kT}}$
Population difference between two levels ($E_1 < E_2$): $\Delta N = N_1 \left(1 - e^{-\frac{\Delta E}{kT}}\right)$
NMR: ΔE = 1μeV → **0.00004** @ 300 K
EPR: ΔE = 0.05 meV → **0.00193** @ 300 K
The population difference is larger for EPR than for NMR. Combined with a larger transition probability for EPR-transitions, this explains why EPR is much more sensitive (i.e. less atoms are needed to obtain a measurable absorption).
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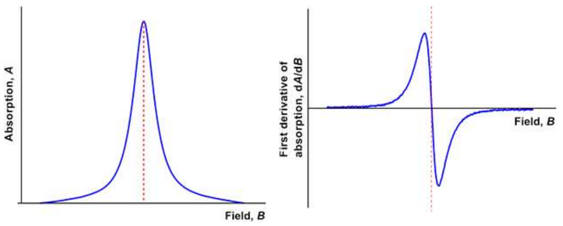

EPR = use microwaves to rotate the (total) magnetic moment of an electron system interacting with a point nucleus (μ=Q=0), subject to an external magnetic field.

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with hyperfine interaction

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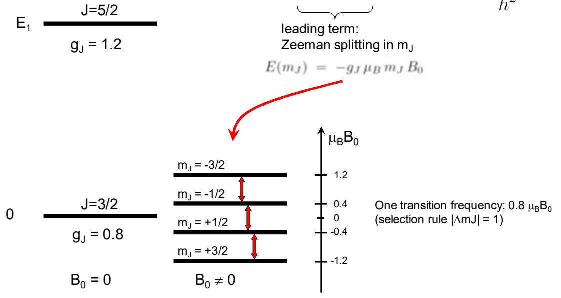
Hamiltonian:

$$\hat{H} = \underbrace{-\vec{\mu}_J \cdot \vec{B}_0}_{} - \vec{\mu}_I \cdot \vec{B}_0 + \frac{A}{\hbar^2}\vec{I} \cdot \vec{J}$$

leading term:
Zeeman splitting in m_J

$$E(m_J) = -g_J\,\mu_B\,m_J\,B_0$$



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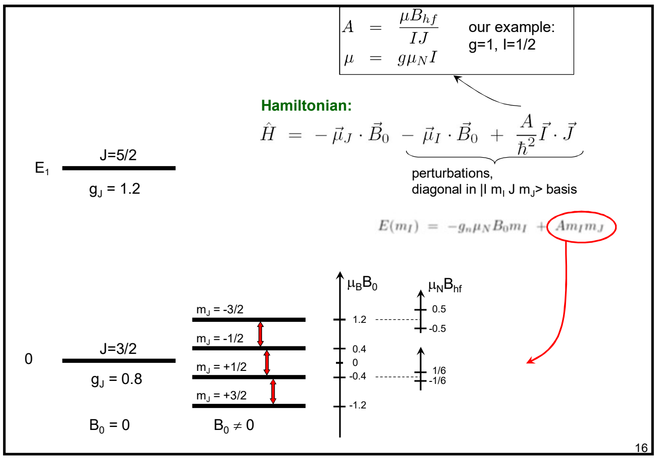
$A = \frac{\mu B_{hf}}{IJ}$
$\mu = g\mu_N I$
our example:
g=1, I=1/2
Hamiltonian:
$\hat{H} = -\vec{\mu}_J \cdot \vec{B}_0 - \vec{\mu}_I \cdot \vec{B}_0 + \frac{A}{\hbar^2}\vec{I}\cdot\vec{J}$
perturbations,
diagonal in |I m$_I$ J m$_J$> basis
$E(m_I) = -g_n\mu_N B_0 m_I + A m_I m_J$
E$_1$
J=5/2
g$_J$ = 1.2
0
J=3/2
g$_J$ = 0.8
B$_0$ = 0
B$_0$ ≠ 0
m$_J$ = -3/2
m$_J$ = -1/2
m$_J$ = +1/2
m$_J$ = +3/2
μ$_B$B$_0$
1.2
0.4
0
-0.4
-1.2
μ$_N$B$_{hf}$
0.5
-0.5
1/6
-1/6
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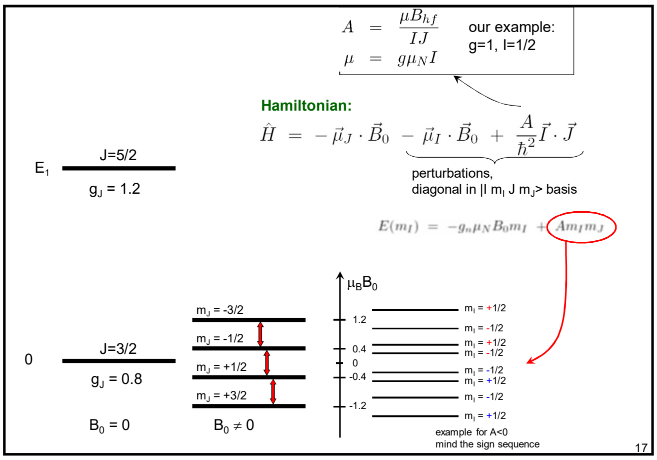
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perturbations,
diagonal in |I m$_I$ J m$_J$> basis
$E(m_I) = -g_n\mu_N B_0 m_I + A m_I m_J$
E$_1$
J=5/2
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0
J=3/2
g$_J$ = 0.8
B$_0$ = 0
B$_0$ ≠ 0
m$_J$ = -3/2
m$_J$ = -1/2
m$_J$ = +1/2
m$_J$ = +3/2
μ$_B$B$_0$
1.2
0.4
0
-0.4
-1.2
m$_I$ = +1/2
m$_I$ = -1/2
m$_I$ = +1/2
m$_I$ = -1/2
m$_I$ = -1/2
m$_I$ = +1/2
m$_I$ = -1/2
m$_I$ = +1/2
example for A<0
mind the sign sequence
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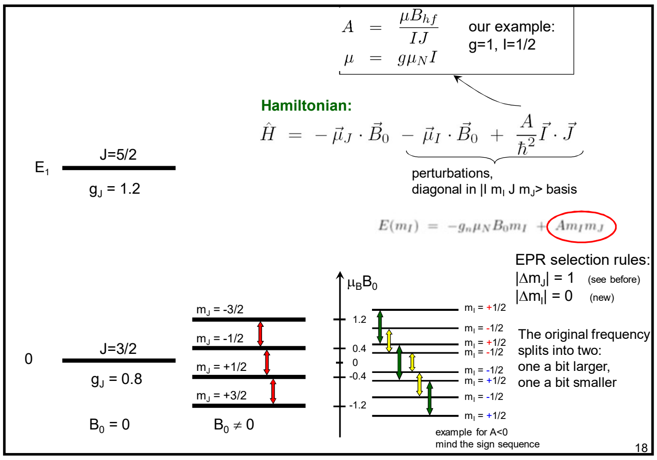

$A = \frac{\mu B_{hf}}{IJ}$
$\mu = g\mu_N I$
our example:
g=1, I=1/2
Hamiltonian:
$\hat{H} = -\vec{\mu}_J \cdot \vec{B}_0 - \vec{\mu}_I \cdot \vec{B}_0 + \frac{A}{\hbar^2}\vec{I}\cdot\vec{J}$
perturbations,
diagonal in |I m$_I$ J m$_J$> basis
$E(m_I) = -g_n\mu_N B_0 m_I + A m_I m_J$
EPR selection rules:
|Δm$_J$| = 1 (see before)
|Δm$_I$| = 0 (new)
The original frequency
splits into two:
one a bit larger,
one a bit smaller
E$_1$
J=5/2
g$_J$ = 1.2
0
J=3/2
g$_J$ = 0.8
B$_0$ = 0
B$_0$ ≠ 0
m$_J$ = -3/2
m$_J$ = -1/2
m$_J$ = +1/2
m$_J$ = +3/2
μ$_B$B$_0$
1.2
0.4
0
-0.4
-1.2
m$_I$ = +1/2
m$_I$ = -1/2
m$_I$ = +1/2
m$_I$ = -1/2
m$_I$ = -1/2
m$_I$ = +1/2
m$_I$ = -1/2
m$_I$ = +1/2
example for A<0
mind the sign sequence
18

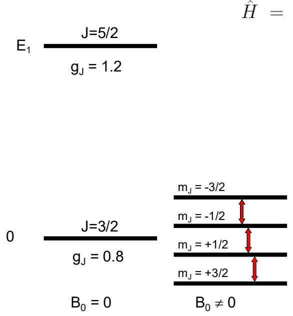
Hamiltonian:

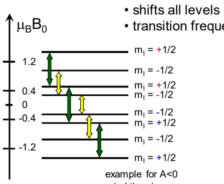
$$\hat{H} = -\vec{\mu}_J \cdot \vec{B}_0 \underbrace{- \vec{\mu}_I \cdot \vec{B}_0 + \frac{A}{\hbar^2}\vec{I} \cdot \vec{J}}$$

perturbations,
diagonal in |I m_I J m_J> basis

$$E(m_I) = -g_n \mu_N B_0 m_I + A m_I m_J$$

- often 10 times smaller
- shifts all levels
- transition frequencies unaltered





example for A<0
mind the sign sequence

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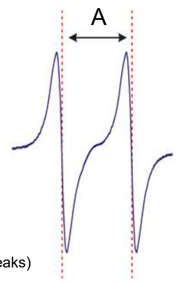
EPR = use microwaves to rotate the (total) magnetic moment of an electron system interacting with a real nucleus (here I=1/2).



The experimental graph tells you
- the hyperfine coupling constant (distance between peaks)
- the nuclear spin (number of peaks)

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