Electron Paramagnetic Resonance: the free atom case

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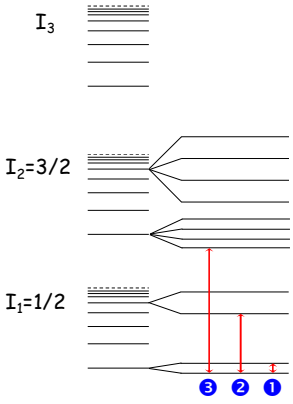
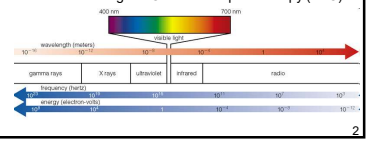
Classification of nuclear methods



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)



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no hyperfine interaction

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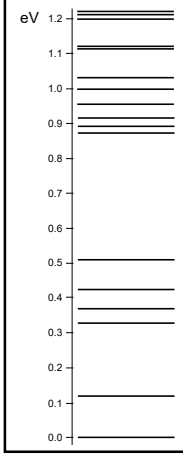
Atomic energies for La : bare values



This is a real-life example of our cartoon :

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

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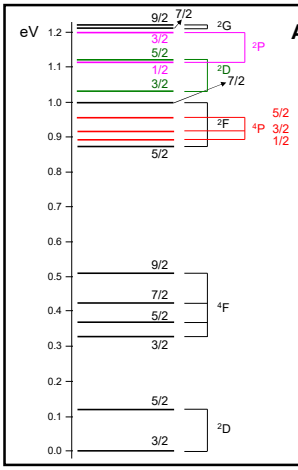
Atomic energies for La : interpreted



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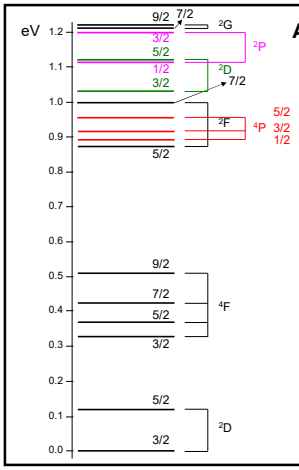
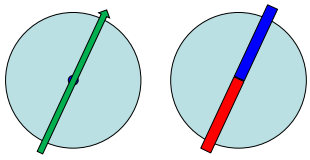
Atomic energies for La : interpreted





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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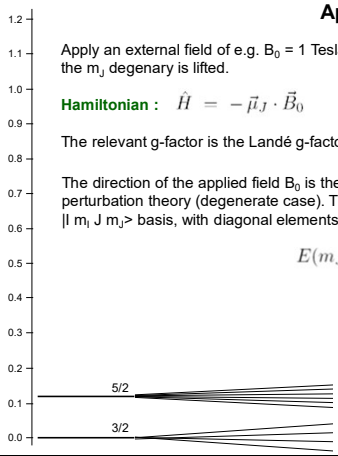
Apply an external magnetic field



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 $|I\ m_I\ J\ m_J\rangle$ basis, with diagonal elements being:

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

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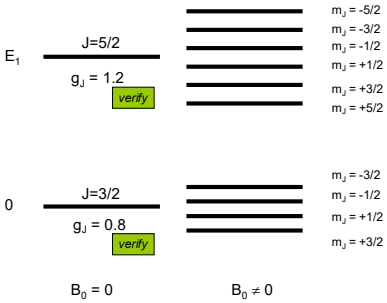
2. EPR for free ions (no hyperfine interaction)



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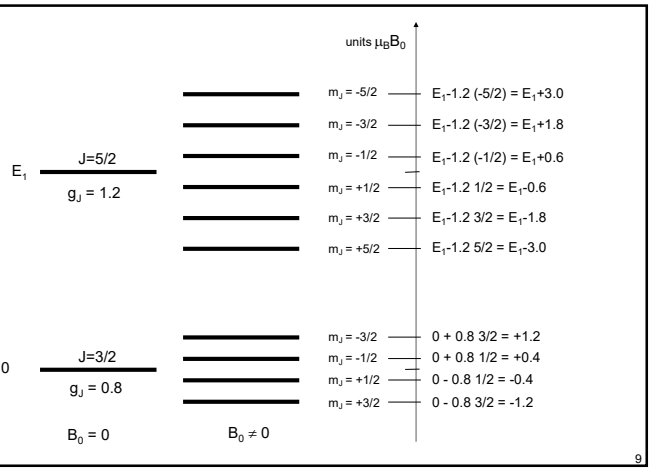

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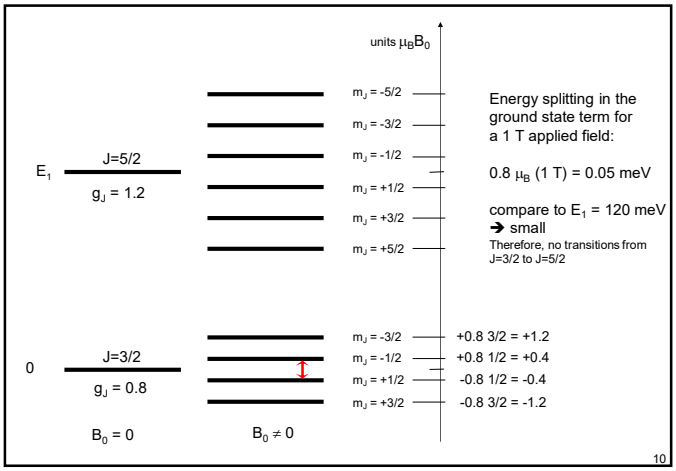

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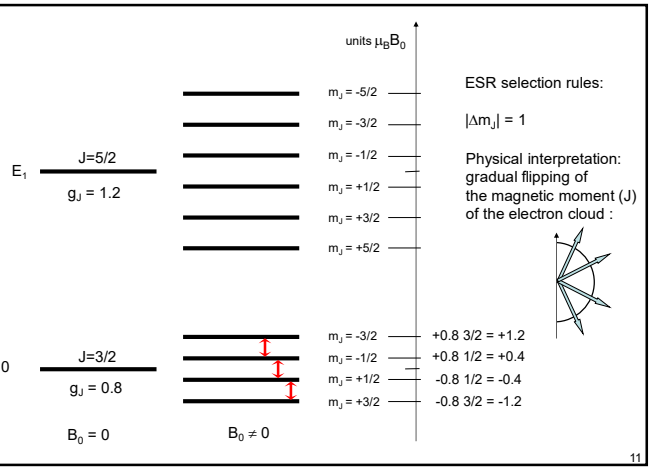

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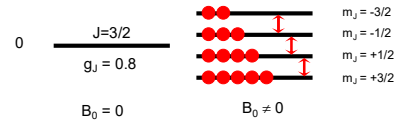

Boltzmann distribution on levels separated by 0.05 meV.
Quantitative expression:

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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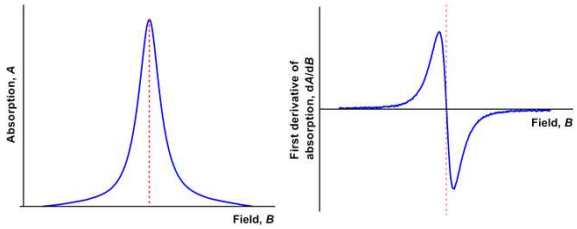

EPR = use microwaves to rotate the (total) magnetic moment of an electron system interacting with a point nucleus (μ=Q=0), subject to an external magnetic field.

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with hyperfine interaction

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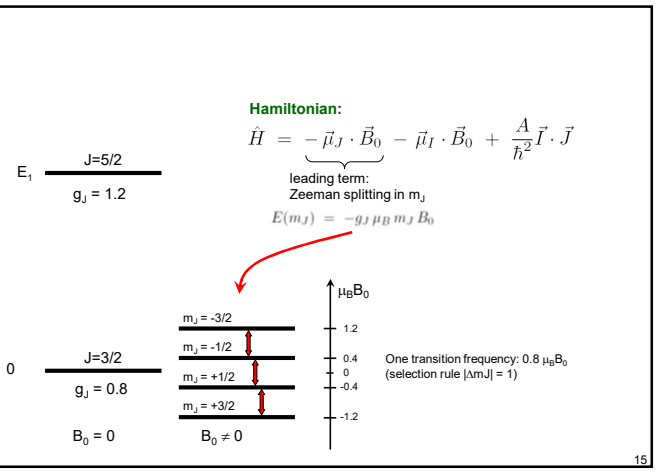

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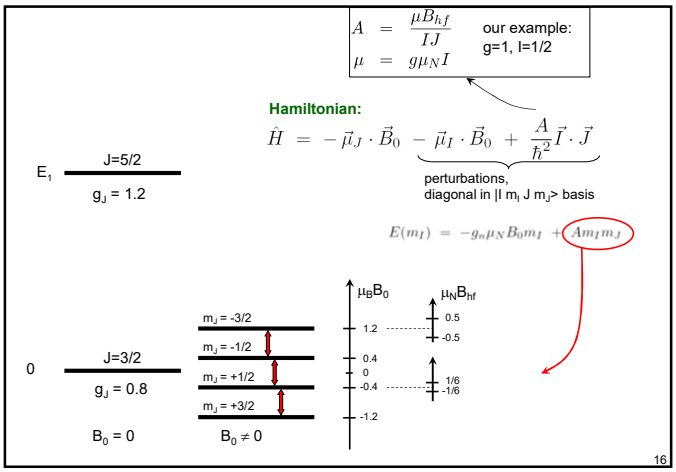

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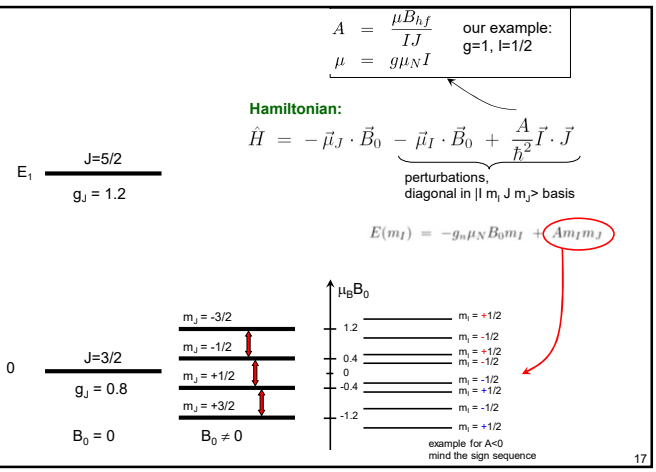

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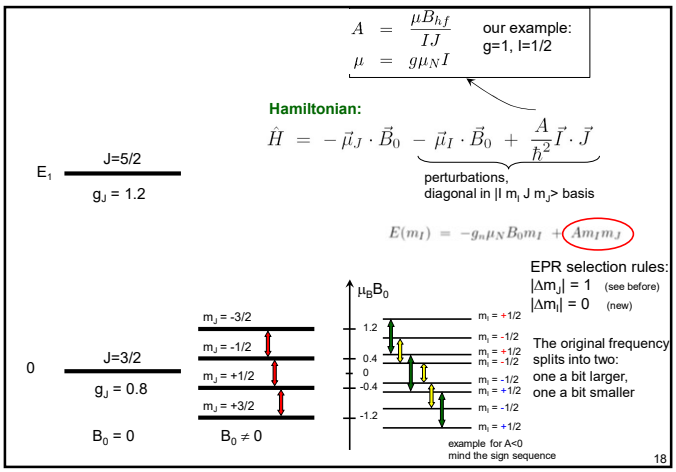

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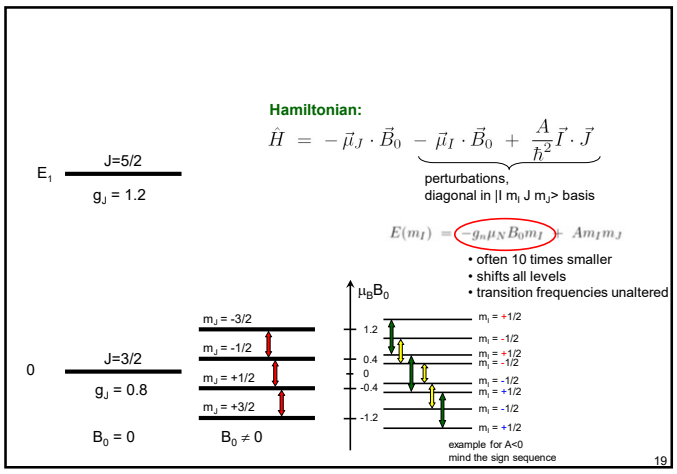

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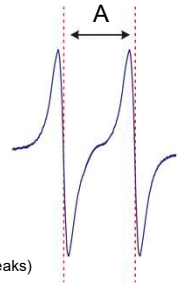
EPR = use microwaves to rotate the (total) magnetic moment of an electron system interacting with a real nucleus (here I=1/2).



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

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