quadrupole interaction :
case studies & symmetry

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Analytical examples

Simplest case: I=1 (I=0 and I=1/2 have Q≡0)

Non-zero matrix elements :

$$\langle \pm 1 | H_{qq}^{nuc} | \pm 1 \rangle = \frac{eQV_{zz}}{4}$$
$$\langle \pm 1 | H_{qq}^{nuc} | \mp 1 \rangle = \frac{eQV_{zz}}{4} \eta$$
$$\langle 0 | H_{qq}^{nuc} | 0 \rangle = - \frac{eQV_{zz}}{2}$$

Matrix for 1st order perturbation :

not ordered

$$E_Q = \frac{eQV_{zz}}{4} \begin{array}{c} \boxed{1 \quad 0 \quad -1} \\ \begin{bmatrix} 1 & 0 & \eta \\ 0 & -2 & 0 \\ \eta & 0 & 1 \end{bmatrix} \end{array} \boxed{\begin{array}{c} 1 \\ 0 \\ -1 \end{array}}$$

ordered

$$E_Q = \frac{eQV_{zz}}{4} \begin{array}{c} \boxed{1 \; -1 \; 0} \\ \begin{bmatrix} 1 & \eta & 0 \\ \eta & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \end{array} \boxed{\begin{array}{c} 1 \\ -1 \\ 0 \end{array}}$$

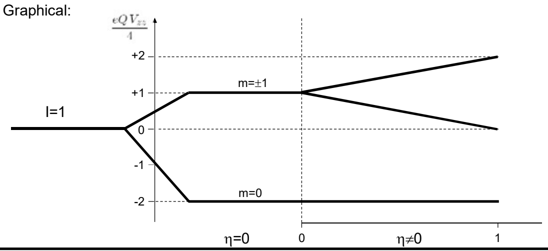
Analytical examples

Simplest case: I=1 (I=0 and I=1/2 have Q≡0)

After diagonalization

$$E_Q = \frac{eQV_{zz}}{4} \begin{bmatrix} 1+\eta & 0 & \\ 0 & 1-\eta & 0 \\ 0 & 0 & -2 \end{bmatrix}$$

Graphical:



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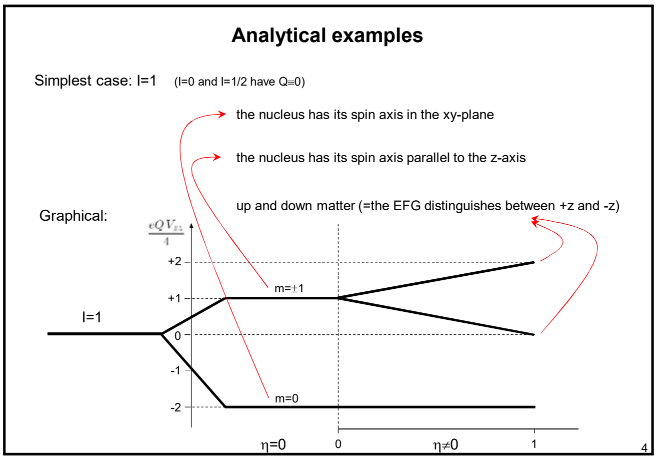


Analytical examples

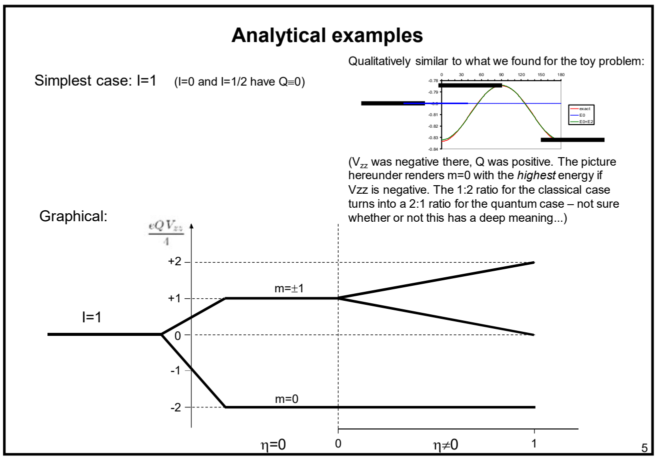
Simplest case: I=1 (I=0 and I=1/2 have Q≡0)

the nucleus has its spin axis in the xy-plane

the nucleus has its spin axis parallel to the z-axis

up and down matter (=the EFG distinguishes between +z and -z)

Graphical:



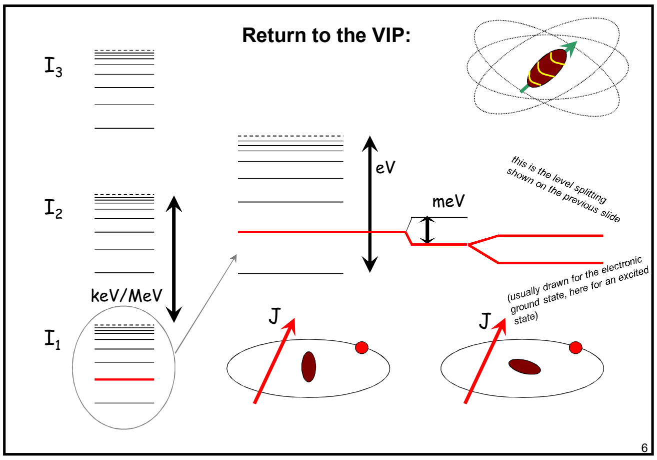
Analytical examples

Simplest case: I=1 (I=0 and I=1/2 have Q≡0)

Qualitatively similar to what we found for the toy problem:

(V_{zz} was negative there, Q was positive. The picture hereunder renders m=0 with the *highest* energy if Vzz is negative. The 1:2 ratio for the classical case turns into a 2:1 ratio for the quantum case – not sure whether or not this has a deep meaning...)

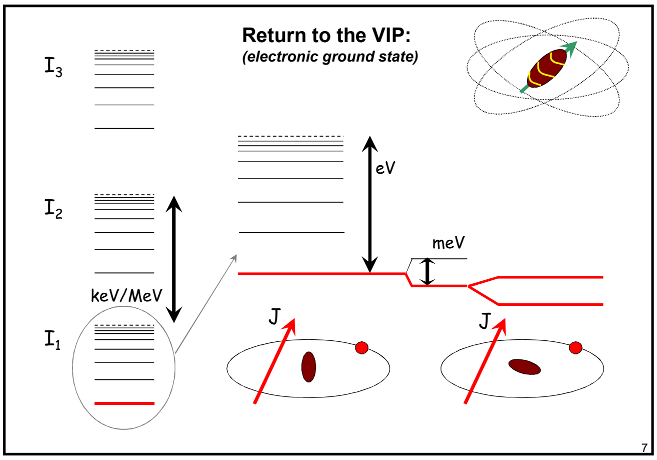
Graphical:



Return to the VIP:

this is the level splitting shown on the previous slide

(usually drawn for the electronic ground state, here for an excited state)



Return to the VIP:

(electronic ground state)

Analytical examples

Next simple case: I=3/2 (I=0 and I=1/2 have Q≡0)

Non-zero matrix elements :

$$< \pm\frac{1}{2} | H_{qq}^{nuc} | \pm\frac{1}{2} > = -3\,\frac{eQV_{zz}}{12}$$
$$< \pm\frac{3}{2} | H_{qq}^{nuc} | \pm\frac{3}{2} > = +3\,\frac{eQV_{zz}}{12}$$
$$< \pm\frac{3}{2} | H_{qq}^{nuc} | \mp\frac{1}{2} > = \sqrt{3}\,\eta\,\frac{eQV_{zz}}{12}$$

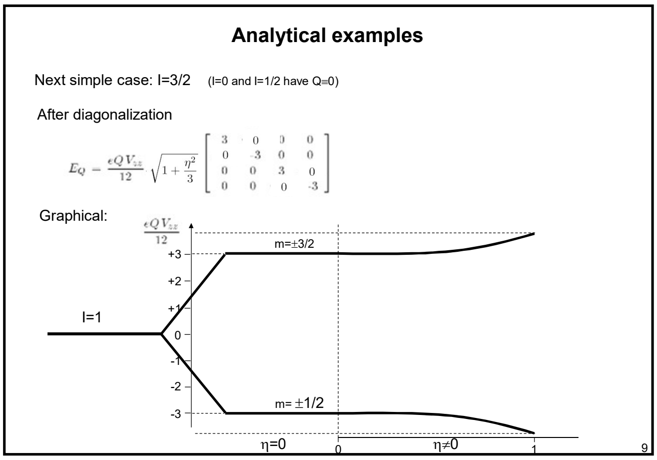
Matrix for 1st order perturbation :

not ordered

$$E_Q = \frac{eQV_{zz}}{12} \begin{array}{cccc|c} +3/2 & +1/2 & -1/2 & -3/2 & \\ \hline 3 & 0 & \sqrt{3}\,\eta & 0 & +3/2 \\ 0 & -3 & 0 & \sqrt{3}\,\eta & +1/2 \\ \sqrt{3}\,\eta & 0 & -3 & 0 & -1/2 \\ 0 & \sqrt{3}\,\eta & 0 & 3 & -3/2 \end{array}$$

ordered

$$E_Q = \frac{eQV_{zz}}{12} \begin{array}{cccc|c} +3/2 & -1/2 & -3/2 & +1/2 & \\ \hline 3 & \sqrt{3}\,\eta & 0 & 0 & +3/2 \\ \sqrt{3}\,\eta & -3 & 0 & 0 & -1/2 \\ 0 & 0 & 3 & \sqrt{3}\,\eta & -3/2 \\ 0 & 0 & \sqrt{3}\,\eta & -3 & +1/2 \end{array}$$



Analytical examples

Next simple case: I=3/2 (I=0 and I=1/2 have Q≡0)

After diagonalization

$$E_Q = \frac{eQV_{zz}}{12}\sqrt{1+\frac{\eta^2}{3}} \begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & -3 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix}$$

Graphical:

General statements

- integer spin
  - η=0
    - ➩ ±m degeneracy
  - η≠0
    - ➩ ±m degeneracy lifted in first order for m=1 (proof p. 107-109)
    - ➩ ±m degeneracy lifted in higher orders for m>1
- half-integer spin
  - η=0
    - ➩ ±m degeneracy
  - η≠0
    - ➩ ±m degeneracy not lifted

o *Graphical illustration: fig. 6.2 (p. 109)*
o *Proof for distinction between integer and half-integer spin: p. 112-114*

General statements

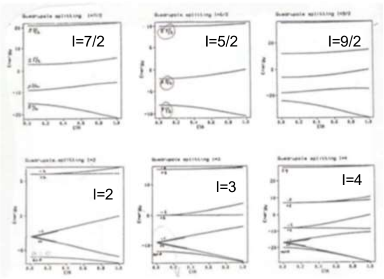


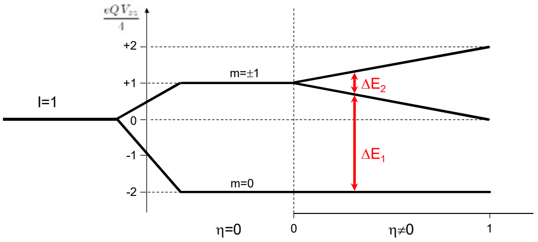
Fig. 6.2. *Quadrupole splittings for half integer (top, 7/2, 5/2, 9/2) and integer (bottom, 2, 3, 4) spins. The vertical energy axis is in units of $eQV_{zz}/I(2I-1)$, while the horizontal axis scans all possible values of the asymmetry parameter η $(0 \rightarrow 1)$.*

(sorry for this low-quality picture – it has an emotional justification)

Experimental consequences

The energy differences ΔE can be measured – see nuclear methods discussed in later lectures.

- if Q is known from nuclear physics: measuring ΔE gives access to V_{zz}
- if V_{zz} is known from ab initio calculations: measuring ΔE gives access to Q



Symmetry properties of the EFG tensor

EFG tensor = 5 numbers, depending on the choice of axis system

Theorem 1

- *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 η=0.*

Proof : p. 116

Theorem 2

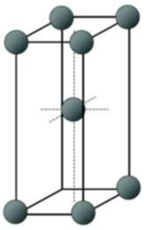
- *If there are two or more 3-fold (or more) rotation axes, then the EFG tensor is zero.*

Proof : p. 117

In solids, the situation of this second theorem appears only in 5 point groups, which are all cubic (23, -43m, m-3, 432 and m-3m).

Symmetry properties of the EFG tensor

Examples:



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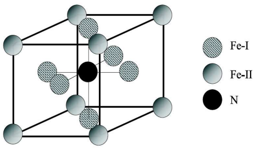

2 Fe-sites in Fe_4N

Reconsider the 2 gravitational examples:
- understand why the EFG is (sometimes) axially symmetric
- discuss the situation where the EFG due to the double ring is zero: can the 2nd theorem be inverted?