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

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

ordered

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

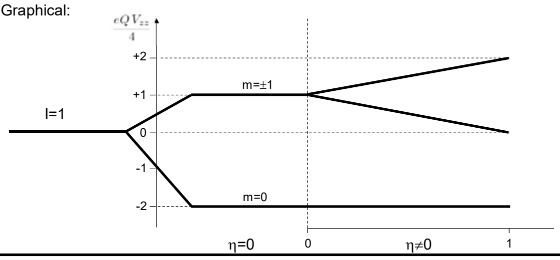
Analytical examples

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

After diagonalization

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

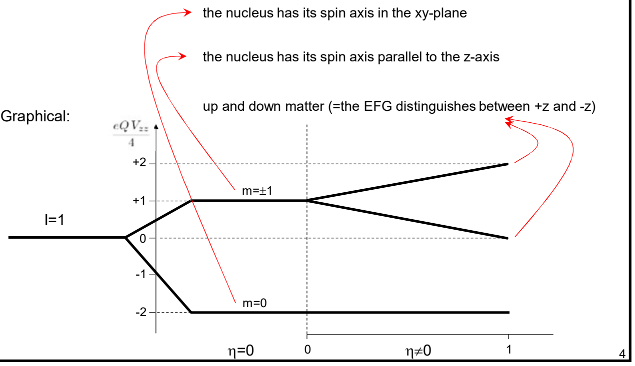
Graphical:



Analytical examples

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

Graphical:


the nucleus has its spin axis in the xy-plane

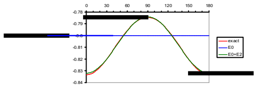
the nucleus has its spin axis parallel to the z-axis

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

Analytical examples

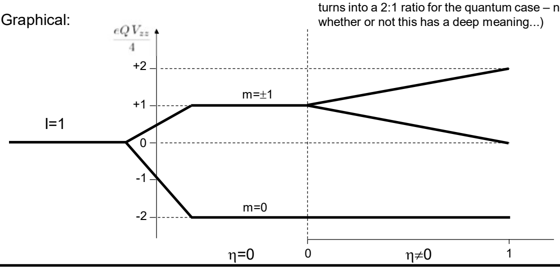
Simplest case: I=1 (I=0 and I=1/2 have Q≡0)

Qualitatively similar to what we found for the toy problem:

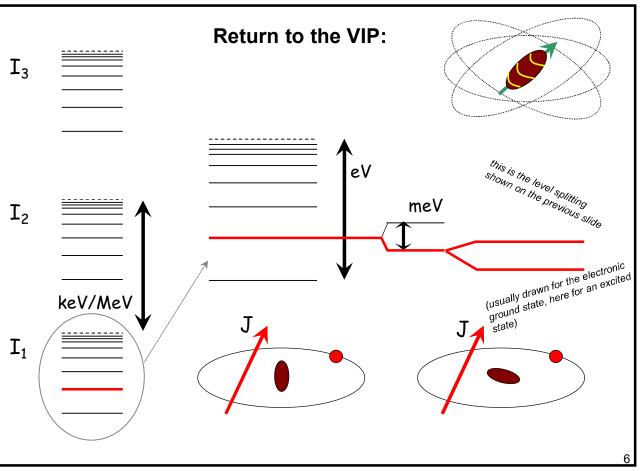


(V_{zz} was negative there, Q was positive. The picture hereunder renders m=0 with the *highest* energy if Vzz is negative. The 1:2 ratio for the classical case turns into a 2:1 ratio for the quantum case – not sure whether or not this has a deep meaning...)

Graphical:



Return to the VIP:

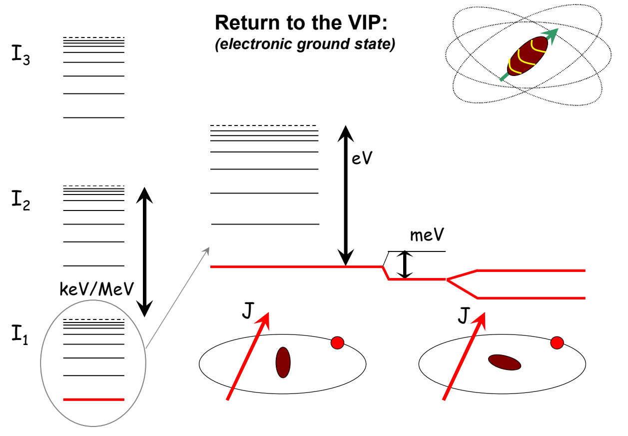


this is the level splitting shown on the previous slide

(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

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

ordered

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

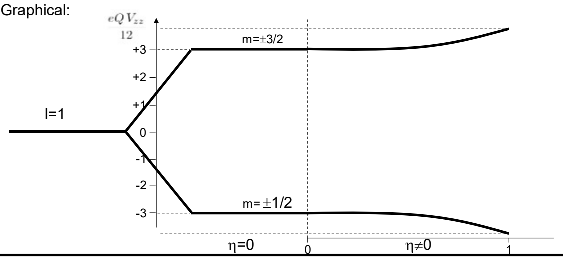
Analytical examples

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

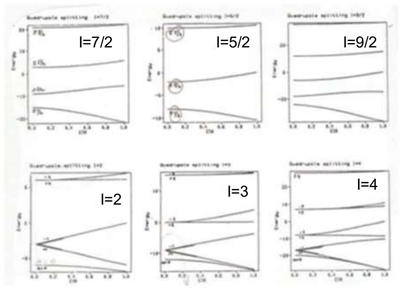


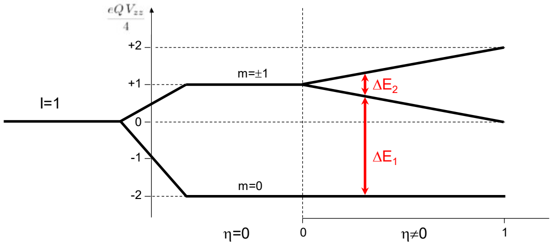
Fig. 6.2. *Quadrupole splittings for half integer (top, 7/2, 5/2, 9/2) and integer (bottom, 2, 3, 4) spins. The vertical energy axis is in units of $eQV_{zz}/I(2I-1)$, while the horizontal axis scans all possible values of the asymmetry parameter η (0 → 1).*

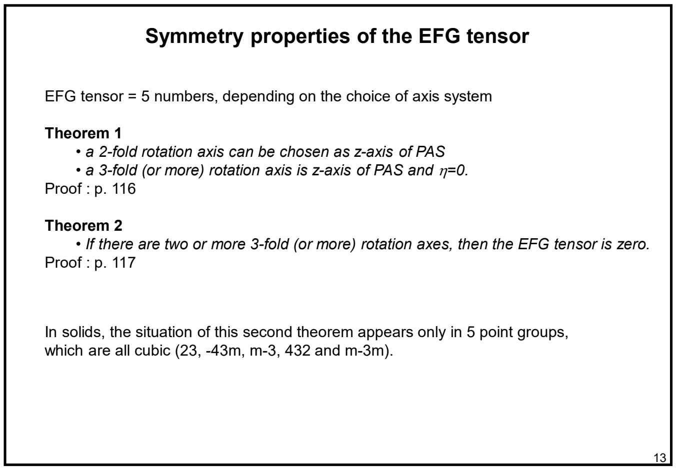
(sorry for this low-quality picture – it has an emotional justification)

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

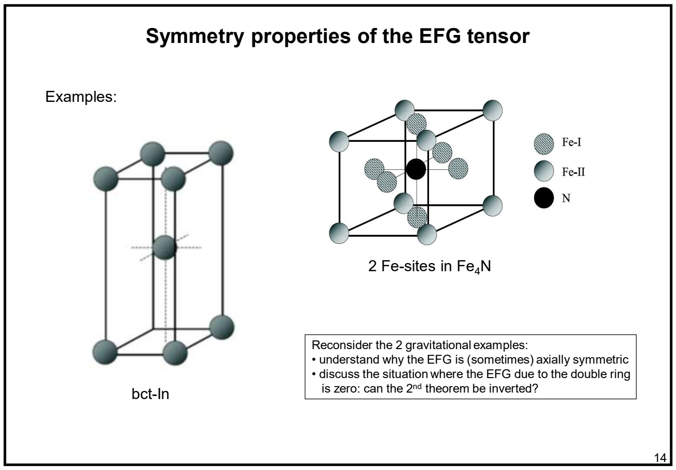
Theorem 1
- *a 2-fold rotation axis can be chosen as z-axis of PAS*
- *a 3-fold (or more) rotation axis is z-axis of PAS and η=0.*

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:

bct-In

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?