quadrupole operator

www. hyperfinecourse .org

1

Content

dipole (last week)

- Coupling of angular momenta (recapitulation)
- I-J coupling: dipole interaction in a free atom
- magnetic hyperfine interaction in solids
  - operator
  - symmetry
  - case-studies
- An extended nucleus

quadrupole (now)

- electric quadrupole interaction in solids
  - operator
  - symmetry
  - case-studies
- An extended nucleus

2

2

Quadrupole interaction

Apply first order perturbation:

$$E_{qq} = -\left\langle \psi_e^{(0)} \otimes I \right| \frac{e^2 NZ}{5\epsilon_0} \left(\frac{1}{r_e^3} Y^2(\theta_e, \phi_e) \right) \cdot \left(r_n^2 Y^2(\theta_n, \phi_n) \right) \left| I \otimes \psi_e^{(0)} \right\rangle$$

Can be separated because we do not consider charge-charge overlap:

$$E_{qq}^{(2)} = \langle I | {}_s\hat{Q}_{sh}^{(2)} | I \rangle \cdot \underbrace{\left\langle \psi_e^{(0)} \right| {}_s\hat{V}_{sh}^{(2)} \left| \psi_e^{(0)} \right\rangle}$$

(short-hand for the matrix of the degenerate case of first order perturbation theory, with for every matrix element a sum of 5 terms)

- electric-field gradient at r=0, due to electrons
- tensor of rank 2 ➔ 5 numbers
- can be computed by ab initio code
  ➔we consider these 5 numbers as known
- these 5 numbers depend on the choice of axis system (compare to a vector)

in general axis system:

$$\left\langle \psi_e^{(0)} \right| \hat{V}_0^2 \left| \psi_e^{(0)} \right\rangle = \frac{1}{2} V_{zz}$$

$$\left\langle \psi_e^{(0)} \right| \hat{V}_{\pm 1}^2 \left| \psi_e^{(0)} \right\rangle = \mp \frac{1}{\sqrt{6}} (V_{xz} \pm V_{yz})$$

$$\left\langle \psi_e^{(0)} \right| \hat{V}_{\pm 2}^2 \left| \psi_e^{(0)} \right\rangle = \frac{1}{2\sqrt{6}} (V_{xx} - V_{yy} \pm iV_{xy})$$

5 numbers

6-1=5 numbers (traceless)

3

3

Quadrupole interaction

Apply first order perturbation:

$$E_{qq} = -\left\langle \psi_e^{(0)} \otimes I \right| \frac{e^2 NZ}{5\epsilon_0} \left(\frac{1}{r_e^3} Y^2(\theta_e, \phi_e) \right) \cdot \left(r_n^2 Y^2(\theta_n, \phi_n) \right) \left| I \otimes \psi_e^{(0)} \right\rangle$$

Can be separated because we do not consider charge-charge overlap:

$$E_{qq}^{(2)} = \langle I | {}_s\hat{Q}_{sh}^{(2)} | I \rangle \cdot \underbrace{\left\langle \psi_e^{(0)} \right| {}_s\hat{V}_{sh}^{(2)} \left| \psi_e^{(0)} \right\rangle}$$

(short-hand for the matrix of the degenerate case of first order perturbation theory, with for every matrix element a sum of 5 terms)

- electric-field gradient at r=0, due to electrons
- tensor of rank 2 ➔ 5 numbers
- can be computed by ab initio code
  ➔we consider these 5 numbers as known
- these 5 numbers depend on the choice of axis system (compare to a vector)
- there are axis systems where some of these 5 numbers vanish: *Principal Axis System* (PAS)
- symmetry properties often reveal the PAS
- we will work in the PAS of the EFG, to limit the number of terms in the dot product (cfr. choice of Z-axis in magnetic case)

in PAS :

$$\left\langle \psi_e^{(0)} \right| \hat{V}_0^2 \left| \psi_e^{(0)} \right\rangle = \frac{1}{2} V_{zz}$$

$$\left\langle \psi_e^{(0)} \right| \hat{V}_{\pm 1}^2 \left| \psi_e^{(0)} \right\rangle = 0$$

$$\left\langle \psi_e^{(0)} \right| \hat{V}_{\pm 2}^2 \left| \psi_e^{(0)} \right\rangle = \frac{1}{2\sqrt{6}} \eta V_{zz}$$

5 numbers

2 numbers + 3 Euler angles

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad , \quad 0 \le \eta \le 1$$

4

4

Quadrupole interaction

Apply first order perturbation:

$$E_{qq} = -\left\langle \psi_e^{(0)} \otimes I \right| \frac{e^2 NZ}{5\epsilon_0} \left(\frac{1}{r_e^3} Y^2(\theta_e, \phi_e) \right) \cdot \left(r_n^2 Y^2(\theta_n, \phi_n) \right) \left| I \otimes \psi_e^{(0)} \right\rangle$$

Can be separated because we do not consider charge-charge overlap:

$$E_{qq}^{(2)} = \underbrace{\langle I | {}_s\hat{Q}_{sh}^{(2)} | I \rangle}_{} \cdot \left\langle \psi_e^{(0)} \right| {}_s\hat{V}_{sh}^{(2)} \left| \psi_e^{(0)} \right\rangle$$

(short-hand for the matrix of the degenerate case of first order perturbation theory, with for every matrix element a sum of 5 terms)

- electric quadrupole moment operator of the nucleus
- tensor of rank 2 ➔ 5 operators
- nuclear theory cannot provide its eigenvalues ab initio
  ➔ a clever trick and experimental info are needed
  - o determine experimentally the single number Q in an axis system fixed to the I-axis of the nucleus (for now assume this can be done)
  - o write the Q-operators in terms of operators of which we know the eigenvalues (p. 99-101)
  - o note that we applied the same strategy for the nuclear magnetic moment operator

$$\hat{Q}_q^2 = \sqrt{\frac{4\pi}{5}} \frac{eQ}{I(2I-1)\hbar^2} \hat{I}^2 Y_q^2(\hat{\boldsymbol{I}})$$

with

$$I^2 Y_0^2(\boldsymbol{I}) = \frac{1}{2} \sqrt{\frac{5}{4\pi}} \left(3I_z^2 - I^2\right)$$

$$I^2 Y_{\pm 1}^2 = \mp \sqrt{\frac{15}{8\pi}} \frac{1}{2} \left(I_z I_\pm + I_\pm I_z\right)$$

$$I^2 Y_{\pm 2}^2 = \frac{1}{4} \sqrt{\frac{15}{2\pi}} I_\pm^2$$

5

5

Quadrupole interaction

Apply first order perturbation:

$$E_{qq} = -\left\langle \psi_e^{(0)} \otimes I \right| \frac{e^2 NZ}{5\epsilon_0} \left(\frac{1}{r_e^3} Y^2(\theta_e, \phi_e) \right) \cdot \left(r_n^2 Y^2(\theta_n, \phi_n) \right) \left| I \otimes \psi_e^{(0)} \right\rangle$$

Can be separated because we do not consider charge-charge overlap:

$$E_{qq}^{(2)} = \underbrace{\langle I | {}_s\hat{Q}_{sh}^{(2)} | I \rangle}_{} \cdot \left\langle \psi_e^{(0)} \right| {}_s\hat{V}_{sh}^{(2)} \left| \psi_e^{(0)} \right\rangle$$

(short-hand for the matrix of the degenerate case of first order perturbation theory, with for every matrix element a sum of 5 terms)

- electric quadrupole moment operator of the nucleus
- tensor of rank 2 ➔ 5 operators
- nuclear theory cannot provide its eigenvalues ab initio
  ➔ a clever trick and experimental info are needed
  - o determine experimentally the single number Q in an axis system fixed to the I-axis of the nucleus (for now assume this can be done)
  - o write the Q-operators in terms of operators of which we know the eigenvalues (p. 99-101)
  - o note that we applied the same strategy for the nuclear magnetic moment operator
  - o all matrix elements needed for the degenerate case of 1st order perturbation theory can be written:

$$\langle I, m_I' | \hat{Q}_0^2 | I, m_I \rangle = \frac{1}{2} \frac{eQ}{I(2I-1)} \left(3m^2 - I(I+1)\right) \delta_{m_I', m_I} \tag{6.26}$$

$$\langle I, m_I' | \hat{Q}_{\pm 1}^2 | I, m_I \rangle = \mp \frac{1}{2} \sqrt{\frac{3}{2}} \frac{eQ}{I(2I-1)} \sqrt{I(I+1) - m_I(m_I \pm 1)} (2m_I \pm 1) \delta_{m_I', m_I \pm 1} \tag{6.27}$$

$$\langle I, m_I' | \hat{Q}_{\pm 2}^2 | I, m_I \rangle = \frac{1}{2} \sqrt{\frac{3}{2}} \frac{eQ}{I(2I-1)} \sqrt{(I(I+1) - m_I(m_I \pm 1))(I(I+1) - (m_I \pm 1)(m_I \pm 2))} \delta_{m_I', m_I \pm 2} \tag{6.28}$$

6

6

Quadrupole interaction

After
- inserting the "5" numbers for the field gradient and
- transforming the 5 nuclear operators to a form with known eigenvalues,

we end up with this perturbing hamiltonian:

$$H_{qq}^{nuc} = \frac{eQV_{zz}}{4I(2I-1)\hbar^2}\left[(3I_z^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2)\right]$$

of which all matrix elements in the degenerate |I,m>-levels have to be evaluated (=degenerate case of 1st order perturbation).

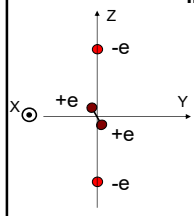
number, known from experimental nuclear physics

numbers, computable by ab initio (solid state/molecular) methods

7

7

Illustration for the toy problem:



Electric-field gradient tensor:

$$V^{(2)} = \frac{-e}{4\pi\epsilon_0}\frac{1}{3d^3}\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}$$

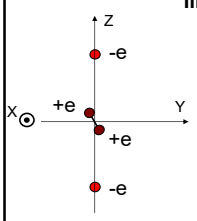
- is already diagonal. The chosen axis system is a PAS.
- V_{zz} is negative: at (0,0), E_z decreases with z
- V_{yy} is positive: at (0,0), E_y increases with y

For this simple case, you might verify this.

8

8

Illustration for the toy problem:



nuclear quadrupole moment tensor:

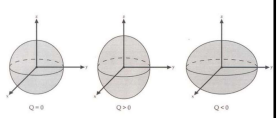
$$Q^{(2)} = 2e\ell^2\begin{bmatrix} -1 & 0 & 0 \\ 0 & 3\sin^2\theta - 1 & -\sin\theta\cos\theta \\ 0 & -\sin\theta\cos\theta & 3\cos^2\theta - 1 \end{bmatrix}$$

The intrinsic properties of the nucleus are seen if you examine this tensor in an axis system that is consistent with the symmetry of the nucleus (Z // dumb-bell axis = direction of spin I)

$$Q^{(2)} = 2e\ell^2\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}$$

Q_{zz} is positive: prolate nucleus

You can consider the quadrupole moment tensor for any orientation as the result of this 'intrinsic' quadrupole moment tensor, followed by a rotation. This is the idea behind the nuclear operator transformation on one of the previous slides: take the intrinsic shape given by Q_{zz}=Q (why are Q_{xx} and Q_{yy} fully determined by this?), and a rotation (given by the z-component of I in the given axis system).



spherical ***prolate*** ***oblate***

9

9

Quadrupole interaction vs. magnetic dipole interaction

➔ Look back at the chapter on the magnetic dipole interaction, and try to recognize all the steps on the previous slides in that derivation as well.
Every step made for the quadrupole interaction has an exact match for the magnetic dipole interaction (but with vectors rather than with tensors of rank 2).
In contrast to what we will see in the next few slides for the quadrupole interaction, the level splitting due to the magnetic interaction in solids is equidistant.

10

10