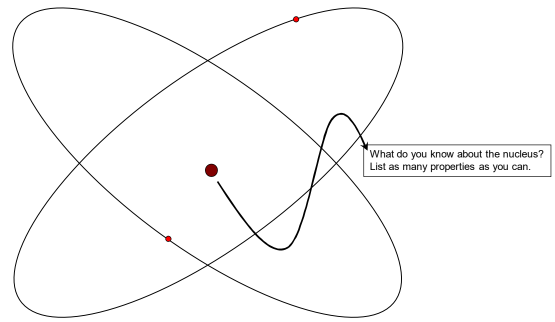
nuclear properties

www. hyperfinecourse .org

1

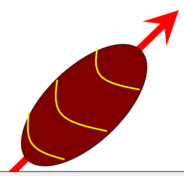
Phenomenological description of a nucleus



2

2

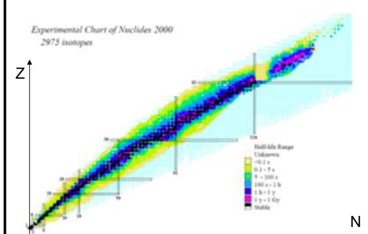
Phenomenological description of a nucleus



spoiler prevention

3

Spread in nuclear properties



spoiler prevention

4

nuclear electric multipole moments

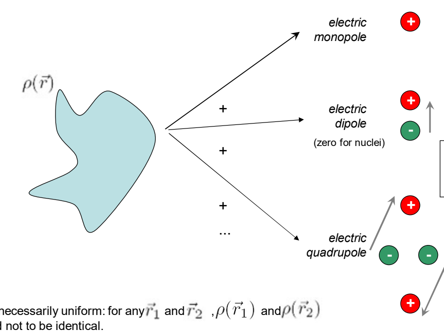
www. hyperfinecourse .org

1

electric nuclear multipole moments

A charge distribution of a general shape...

... can be written as a sum of multipole contributions :



Exercise: convince yourself that a dipole has no monopole moment, and that a quadrupole has no monopole and dipole moments.

Not necessarily uniform: for any $\vec{r}_1$ and $\vec{r}_2$, $\rho(\vec{r}_1)$ and $\rho(\vec{r}_2)$ need not to be identical.

2

2

electric nuclear multipole moments

Derivation in cartesian form : see pdf-pages

Derivation in spherical form :
- general formula:
- far-field case: see pdf-pages

$$\frac{1}{|r_2 - r_1|} = 4\pi \sum_{n,q} \frac{r_<^n}{r_>^{n+1}} \frac{1}{2n+1} Y_q^{n*}(\theta_1, \phi_1) Y_q^n(\theta_2, \phi_2)$$

Interpretation of monopole and quadrupole moments.

Different ways of representing the 5 degrees of freedom of the quadrupole moment tensor:
- As traceless and symmetric 3x3 matrix

$$\begin{bmatrix} Q_{xx} & Q_{xy} & Q_{xz} \\ Q_{xy} & Q_{yy} & Q_{yz} \\ Q_{xz} & Q_{yz} & Q_{zz} \end{bmatrix} \qquad Q_{xx} + Q_{yy} + Q_{zz} = 0$$

- As 5 components of a spherical tensor of rank 2

$$Q_m^\ell = eZ \sqrt{\frac{4\pi}{2\ell+1}} \langle I | r^\ell Y_m^\ell | I \rangle \qquad (\ell = 2)$$

- As a **combination of both**

$$Q_{ij} = \begin{bmatrix} Q_2^2 - \frac{1}{\sqrt{3}} Q_0^2 & Q_{-2}^2 & Q_1^2 \\ Q_{-2}^2 & -Q_2^2 - \frac{1}{\sqrt{3}} Q_0^2 & Q_{-1}^2 \\ Q_1^2 & Q_{-1}^2 & \frac{2}{\sqrt{3}} Q_0^2 \end{bmatrix}$$

Recommended reading: appendix on tensors.

3

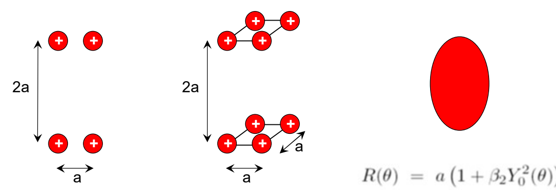
3

electric nuclear multipole moments

Exercise :

Apply the general equations to calculate the monopole, dipole and quadrupole moments of

this point charge configuration (2D) : and this one (3D) : and this one (3D) :



$$R(\theta) = a\left(1 + \beta_2 Y_0^2(\theta)\right)$$

(e.g. $\beta_2 = 0.2$)

4

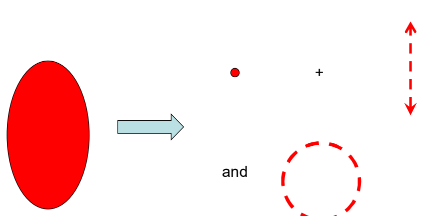
4

approximate shape of a nucleus: average radius and quadrupole deformation

The nucleus spins fast about its I-axis ➔ in axis system with z // I we have axial symmetry

$$\begin{bmatrix} -\frac{Q}{2} & 0 & 0 \\ 0 & -\frac{Q}{2} & 0 \\ 0 & 0 & Q \end{bmatrix}$$

The spectroscopic quadrupole moment Q (a scalar) says it all.



$$R(\theta) = a\left(1 + \beta_2 Y_0^2(\theta) + \beta_4 Y_0^4(\theta) + \ldots\right)$$

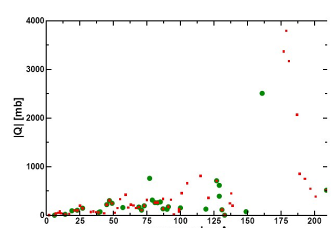
5

5

Trends in the (spectroscopic) quadrupole moment

$$eQ \simeq 3\sqrt{\frac{4\pi}{5}} \frac{eZ}{2\pi} \beta a^2$$

Q is large if:
- β is large (strongly deformed nuclei)
- a is large (heavy nuclei)



- oscillating behaviour due to nuclear shell structure
- increasing trend due to a-dependence

6

6

Trends in the mean square nuclear radius

Extensive experimental tabulation by I. Angeli (2004)

global summary of trend: $\sqrt{\langle r^2 \rangle} = 1.153\, A^{0.294}\ \text{fm}$

(just a snippet) *I. Angeli / Atomic Data and Nuclear Data Tables 87 (2004) 185–206* 197

Table 1 (*continued*)

Z	El	A	R (fm)	$\Delta_{tot}R$ (fm)	$\Delta_{rel}R$ (fm)
		112	4.5950	.0020	
		113	4.6006	.0020	.00002
		114	4.6137	.0019	
		115	4.6170	.0054	.0049
		116	4.6284	.0021	.00002
		118	4.6316	.0037	.0024
		120	4.6379	.0059	.0045
49	In	104	4.5168	.0119	.0016
		105	4.5298	.0105	.0015
		106	4.5364	.0096	.0013
		107	4.5487	.0082	.0011
		108	4.5566	.0071	.0005
		109	4.5684	.0061	.0008
		110	4.5742	.0056	.0009
		111	4.5859	.0043	.0005
		112	4.5911	.0039	.0007
		113	4.6018	.0025	.00003
		114	4.6066	.0027	.0002
		115	4.6169	.0024	

Table 1 (*continued*)

Z	El	A	R (fm)	$\Delta_{tot}R$ (fm)	$\Delta_{rel}R$ (fm)
		126	4.7703	.0048	.0007
		128	4.7755	.0048	.0004
		129	4.7762	.0047	.0001
		130	4.7832	.0046	.0003
		131	4.7812	.0046	.0001
		132	4.7866	.0047	.0002
		134	4.7921	.0047	.0001
		136	4.7991	.0047	
		137	4.8143	.0048	.0003
		138	4.8359	.0054	.0003
		139	4.8511	.0060	.0006
		140	4.8694	.0067	.0002
		141	4.8845	.0075	.0004
		142	4.9016	.0086	.0009
		143	4.9137	.0092	.0004
		144	4.9300	.0102	.0005
		146	4.9575	.0119	.0005
55	Cs	118	4.7834	.0092	.0002
		119	4.7898	.0090	.0006

7

7

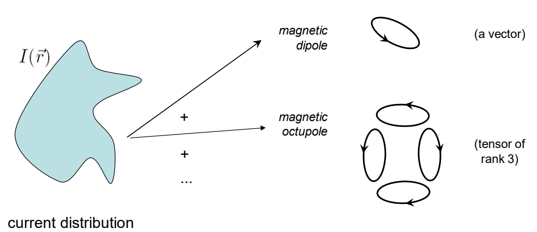
magnetic nuclear multipole moments

- What we discussed so far is the scalar potential due to a static charge distribution, developed into multipole components.
- A similar story applies to the vector potential due to a static current distribution, which can be developed into multipole components as well (mathematically a bit more involved).
- The parity of these magnetic nuclear multipole moments is different: odd terms survive.
- The first non-zero term is the magnetic dipole moment (a vector).
- The second non-zero is the magnetic octupole moment (a tensor of rank 3).

8

8

magnetic nuclear multipole moments



9

9

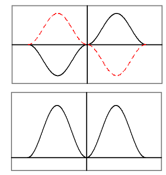
why are odd electric moments zero ?

www. hyperfinecourse .org

1

Why are odd electric nuclear multipole moments zero ?

- Definition of the parity operator in 3D :
  change the sign of all three dimensions: x→-x, y→-y, z→-z, hence r→-r
- Real eigenvalues: +1 or -1
- Meaning of parity in one dimension (x→-x):



P f(x) = f(-x) = -1 f(x) odd

P f(x) = f(-x) = +1 f(x) even

- Integrals over all space for a function with odd parity are zero.
- Observational fact: nuclear states have a well-defined parity (i.e. +1 or even, or -1 or odd)

2

2

Why are odd electric nuclear multipole moments zero ?

classical dipole moment: $Q_x = \int x\rho(\vec{r})\,d\vec{r}$ (x-component of dipole moment vector only, as example)

translate to quantum mechanics: $Q_x = \int \Psi_I^*(\vec{r})\,x\,\Psi_I\,d\vec{r} = \langle I|\,\hat{x}\,|I\rangle$

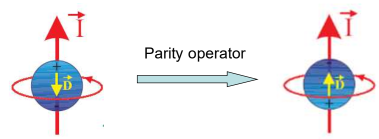
Parity of ρ is always even (product of two states with the same parity).
Parity of the x-operator is odd.
The parity of the integrand is odd → the dipole moment expectation value is zero.

3

3

Why are odd electric nuclear multipole moments zero ?

Symmetry explanation:



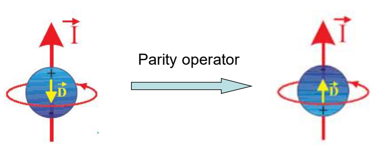
Imagine nuclei would have an electric dipole moment.
The parity operator leaves the spin unaffected.
The parity operator flips the dipole moment.
The orientation of the dipole moment w.r.t. the spin is changed.
→ this does not agree with parity being a good quantum number for nuclei
→ the electric dipole moment must be zero.

4

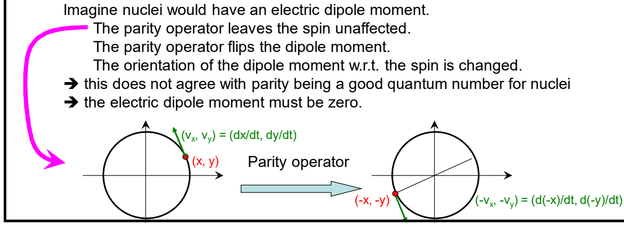
4

Why are odd electric nuclear multipole moments zero ?

Symmetry explanation:



Imagine nuclei would have an electric dipole moment.
The parity operator leaves the spin unaffected.
The parity operator flips the dipole moment.
The orientation of the dipole moment w.r.t. the spin is changed.
→ this does not agree with parity being a good quantum number for nuclei
→ the electric dipole moment must be zero.



5

5

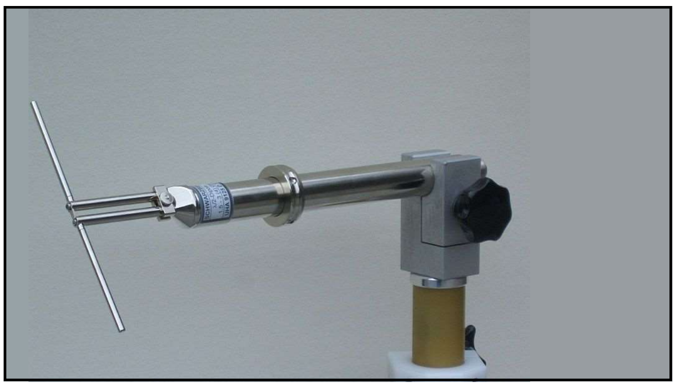
multipole radiation

www. hyperfinecourse .org

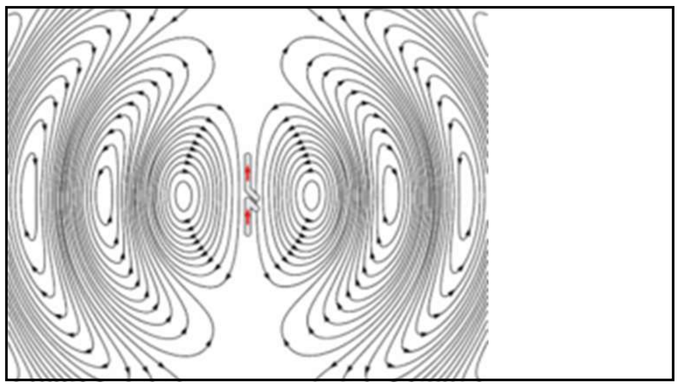
1

multipole radiation
for **CLASSICAL** systems

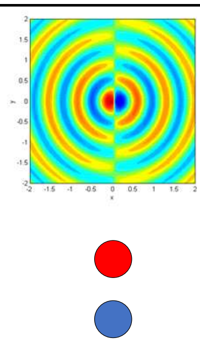
2



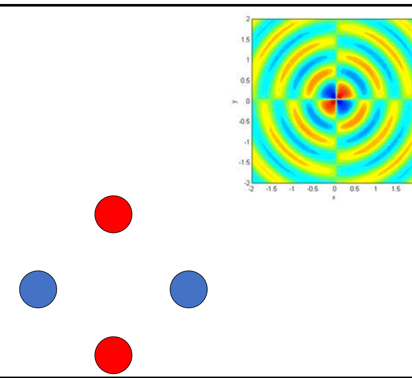
3



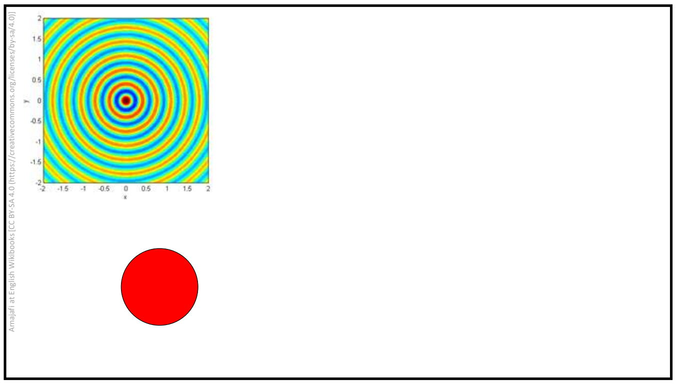
4



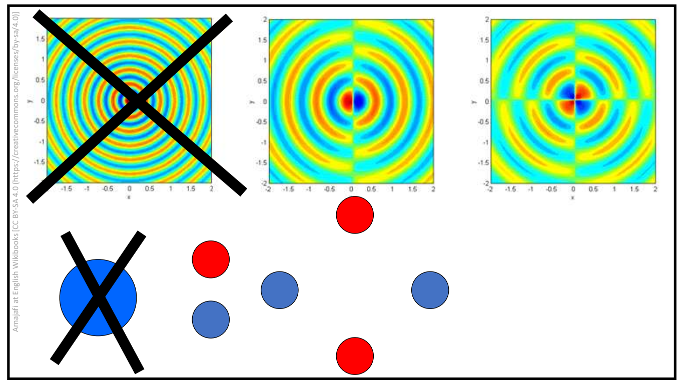
5



6



7



8

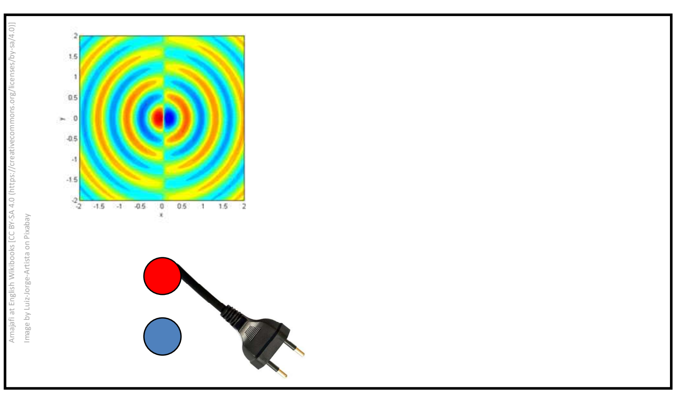
multipole radiation

for **QUANTUM** systems

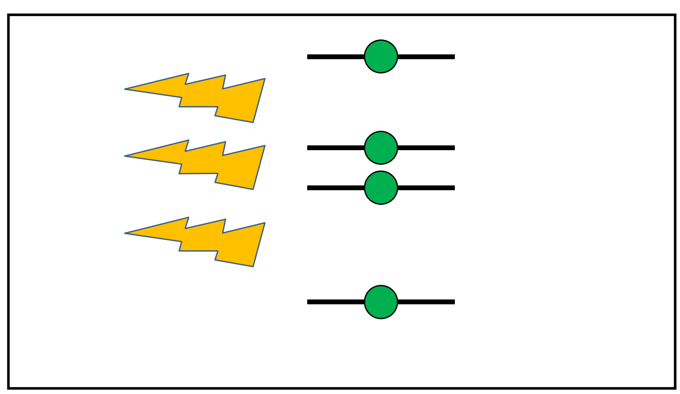
9

Why is an oscillating multipole not a good model for a decaying nucleus emitting radiation?

10



11

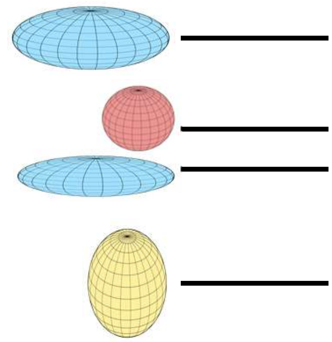


12

Why is an oscillating multipole not a good model for a decaying nucleus emitting radiation?

1. a nucleus is not "powered"

13



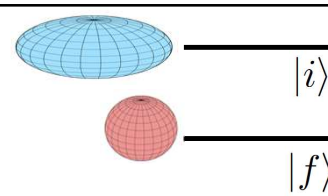
14

Why is an oscillating multipole not a good model for a decaying nucleus emitting radiation?

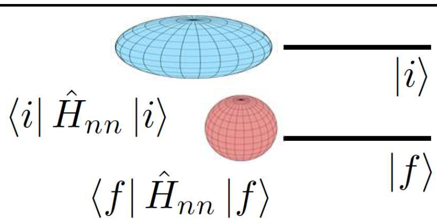
1. a nucleus is not "powered"

2. a nucleus decays from one multipole moment to another, it is not an oscillating multipole moment.

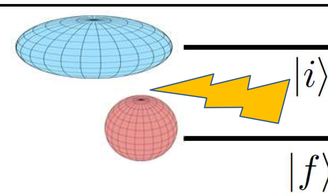
15



16

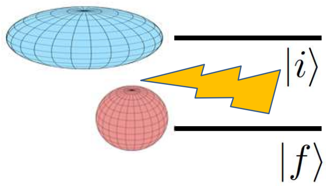


17



$$\hat{H}_{nn} + \hat{W}$$

18



$$\langle f|\,\hat{W}\,|i\rangle$$

$$\hat{H}_{nn} \; + \; \hat{W}$$

19

$$\langle f|\,\hat{W}\,|i\rangle$$

= E1 + E2 + E3 + …

electric multipole radiation

+ M1 + M2 + M3 + …

magnetic multipole radiation

https://en.wikipedia.org/wiki/Multipolarity_of_gamma_radiation

20

VIP - 1

www. hyperfinecourse .org

1

back to basics: the H- or He-atoms

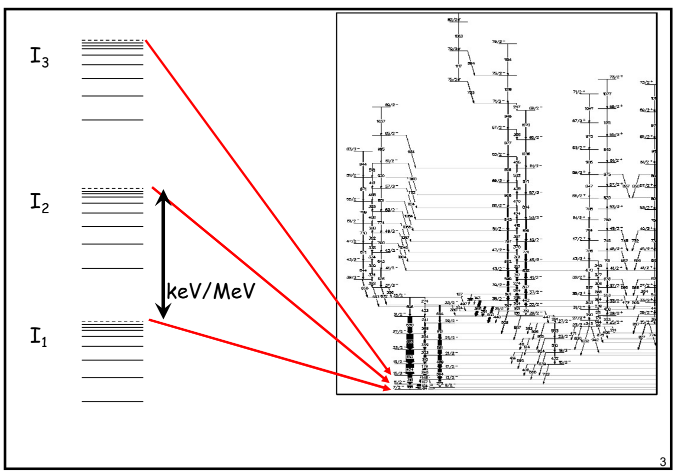
When you studied H or He in your first courses on quantum physics, you made the following approximations :

- **non-relativistic**
- **effective electron-electron interactions (He, not H)**
- **infinitely heavy nucleus**
- **point nucleus**

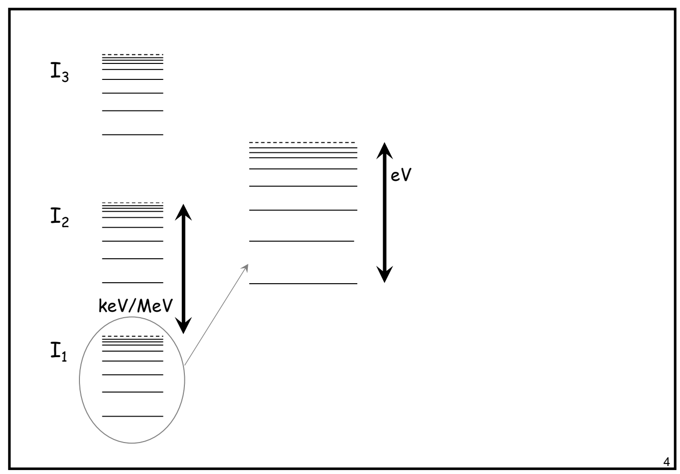
this course:
examine and exploit the new features that appear once the approximation of a point charge nucleus has been abandonned.

2

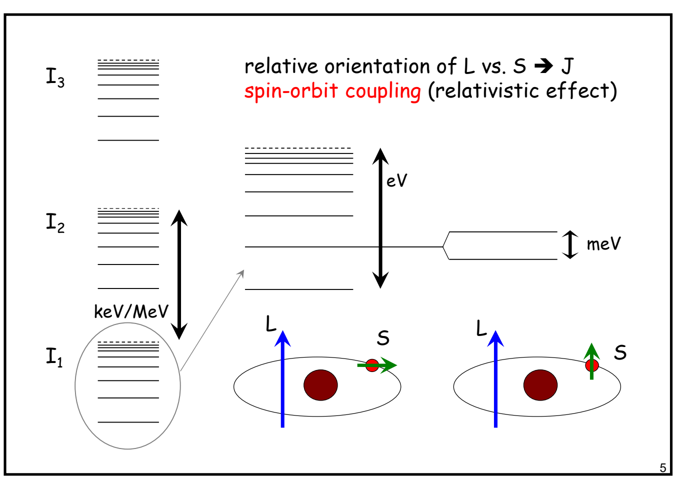
2



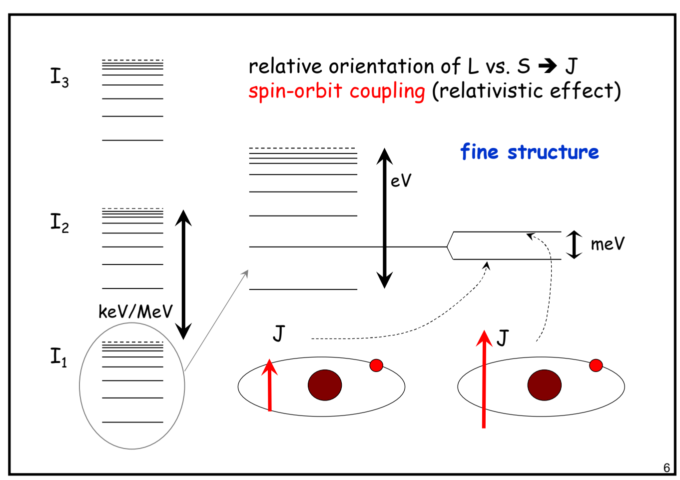
3



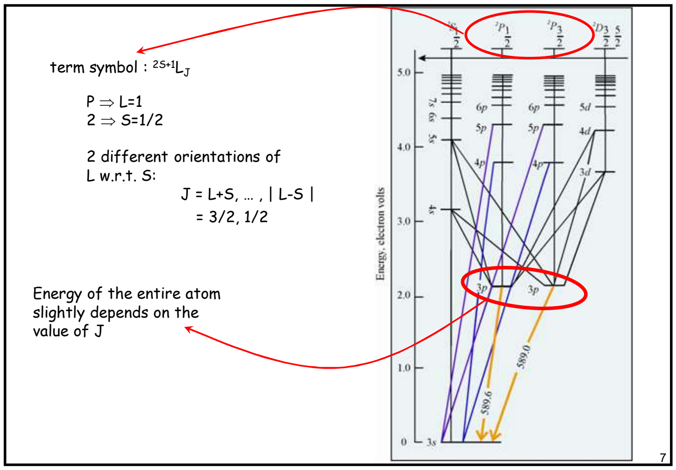
4



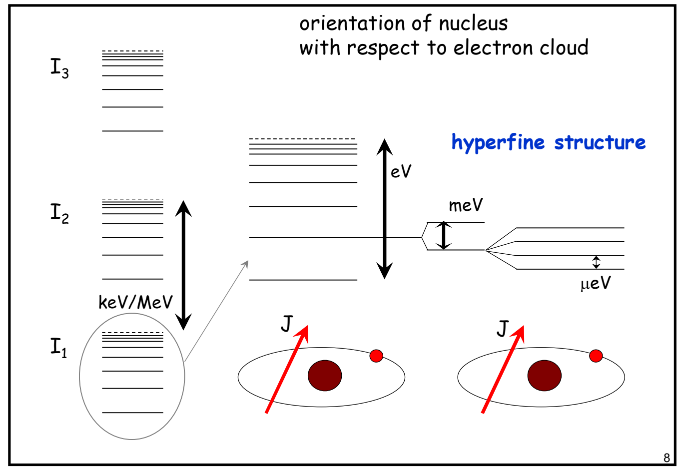
5



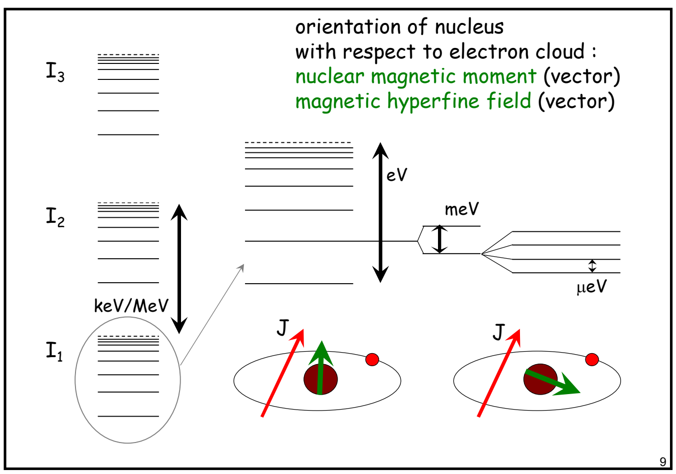
6



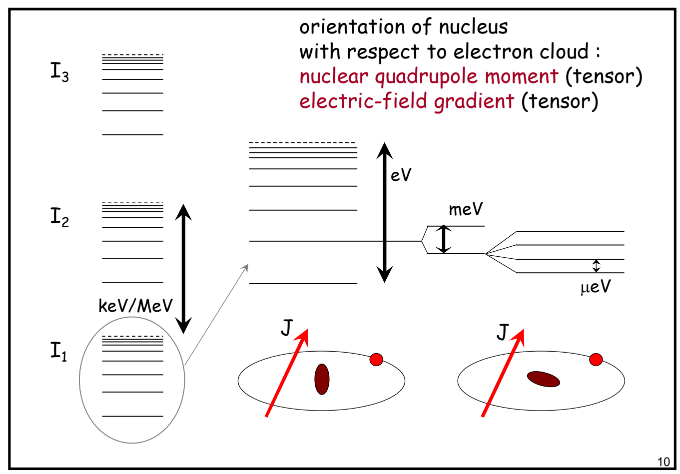
7



8



9



10

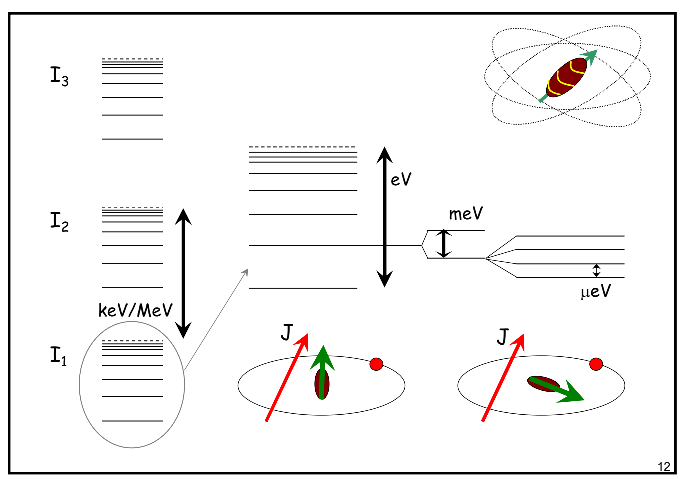
Attention !

There will be 2 VIPs(*) in this course, and on the following slide you have the first one.

(*) Very Important Pictures

11

11



12

gravitational analogue

www. hyperfinecourse .org

1

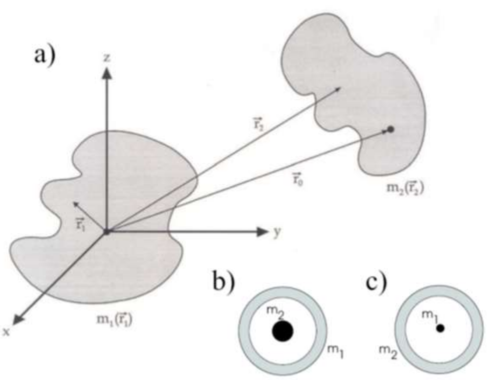


Fig. 2.1. *Three situations of two mass distributions interacting by gravitation.*

2

2

Gravitational potential energy of this system =

- gravitational potential energy of m_2 in the field of m_1

or

- **gravitational potential energy of m_1 in the field of m_2**

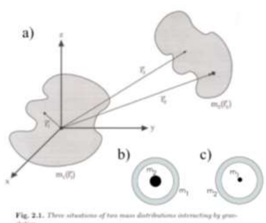
$$E_{pot} = \int_1 \rho_1(\boldsymbol{r}_1)\, V_2(\boldsymbol{r}_1)\, d\boldsymbol{r}_1$$

Potential field of m_2 at position r_1 :

$$V_2(\boldsymbol{r}_1) = -G \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{|\boldsymbol{r}_2 - \boldsymbol{r}_1|}\, d\boldsymbol{r}_2$$

And hence :

$$E_{pot} = -G \int_1 \int_2 \frac{\rho_1(\boldsymbol{r}_1)\rho_2(\boldsymbol{r}_2)}{|\boldsymbol{r}_2 - \boldsymbol{r}_1|}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2$$



3

3

How to treat the double integral? ➔ Laplace expansion

$$\frac{1}{|\boldsymbol{r}_2 - \boldsymbol{r}_1|} = 4\pi \sum_{n,q} \frac{r_<^n}{r_>^{n+1}} \frac{1}{2n+1} Y_q^{n*}(\theta_1, \phi_1) Y_q^n(\theta_2, \phi_2)$$

$$r_< = min\,(r_1, r_2)$$

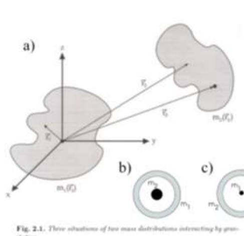
$$r_> = max\,(r_1, r_2)$$

$$E_{pot} = -4\pi\, G \int_1 \int_2 \rho_1(\boldsymbol{r}_1)\rho_2(\boldsymbol{r}_2) \left(\sum_{n,q} \frac{r_<^n}{r_>^{n+1}} \frac{1}{2n+1} Y_q^{n*}(\theta_1, \phi_1) Y_q^n(\theta_2, \phi_2) \right) d\boldsymbol{r}_1\, d\boldsymbol{r}_2$$

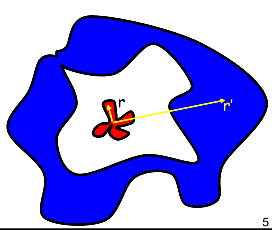
4

4

Assumption: the mass distributions are such that any r_1 is smaller than any r_2



Imagine an example where this is not fulfilled…



5

5

Condition: consider only cases for which any r_1 is smaller than any r_2

Consequence: $r_< = r_1$
$r_> = r_2$

$$E_{pot} = -4\pi\, G \int_1 \int_2 \rho_1(\boldsymbol{r}_1)\rho_2(\boldsymbol{r}_2) \left(\sum_{n,q} \frac{r_<^n}{r_>^{n+1}} \frac{1}{2n+1} Y_q^{n*}(\theta_1, \phi_1) Y_q^n(\theta_2, \phi_2) \right) d\boldsymbol{r}_1\, d\boldsymbol{r}_2$$

$$E_{pot} = \sum_{n,q} Q_q^{n*} V_q^n$$

$$Q_q^n = \sqrt{\frac{4\pi}{2n+1}} \int_1 \rho_1(\boldsymbol{r}_1)\, r_1^n\, Y_q^n(\theta_1, \phi_1)\, d\boldsymbol{r}_1$$

$$V_q^n = -G \sqrt{\frac{4\pi}{2n+1}} \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{r_2^{n+1}}\, Y_q^n(\theta_2, \phi_2)\, d\boldsymbol{r}_2$$

6

6

Discussion :

monopole term

monopole moment $Q_0^0 = m_1$ scalar

monopole field $V_0^0 = -G \int \frac{\rho_2(\boldsymbol{r}_2)}{|\boldsymbol{r}_2|}\, d\boldsymbol{r}_2$ scalar

monopole energy $E_{pot}^{(0)} = Q_0^{0*} V_0^0$ dot product ➔ scalar

7

7

Discussion :

dipole term

dipole moment $Q_q^1 = \sqrt{\frac{4\pi}{3}} \int_1 \rho_1(\boldsymbol{r}_1)\, r_1\, Y_q^1(\theta_1, \phi_1)\, d\boldsymbol{r}_1$ vector

dipole field $V_q^1 = -G \sqrt{\frac{4\pi}{3}} \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{r_2^2}\, Y_q^1(\theta_2, \phi_2)\, d\boldsymbol{r}_2$ vector

dipole energy $E_{pot}^{(1)} = \sum_{q=-1,0,1} Q_q^{1*} V_q^1$ dot product ➔ scalar

8

8

interpretation of the dipole moment of m_1:

$$Q_x = \frac{\sqrt{2}}{2}\left(Q_{-1}^1 - Q_{+1}^1\right)$$
$$= \int_1 \rho_1(\boldsymbol{r}_1)\, r_1\, \sin\theta \cos\phi\, d\boldsymbol{r}_1$$
$$= \int_1 \rho_1(\boldsymbol{r}_1)\, x_1\, d\boldsymbol{r}_1$$
$$Q_y = \int_1 \rho_1(\boldsymbol{r}_1)\, y_1\, d\boldsymbol{r}_1$$
$$Q_z = \int_1 \rho_1(\boldsymbol{r}_1)\, z_1\, d\boldsymbol{r}_1$$

position vector of center of mass of m_1

interpretation of the dipole field by m_2:

$$V_x = -G \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{|r_2|^3}\, x_2\, d\boldsymbol{r}_2$$
$$V_y = -G \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{|r_2|^3}\, y_2\, d\boldsymbol{r}_2$$
$$V_z = -G \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{|r_2|^3}\, z_2\, d\boldsymbol{r}_2$$

opposite of the gravitational field by m_2 at the origin

9

9

Discussion :

quadrupole term

quadrupole moment $Q_q^2 = \sqrt{\frac{4\pi}{5}} \int_1 \rho_1(\boldsymbol{r}_1)\, r_1^2\, Y_q^2(\theta_1, \phi_1)\, d\boldsymbol{r}_1$ tensor

quadrupole field $V_q^2 = -G \sqrt{\frac{4\pi}{5}} \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{r_2^3}\, Y_q^2(\theta_2, \phi_2)\, d\boldsymbol{r}_2$ tensor

quadrupole energy $E_{pot}^{(2)} = \sum_{q=-2,\dots,2} Q_q^{2*} V_q^2$ dot product ➔ scalar

10

10

quadrupole moment :

$${}_cQ_{sh}^{(2)} = \int_1 \rho_1(\boldsymbol{r}_1) \begin{bmatrix} 3x_1^2 - r_1^2 & 3x_1y_1 & 3x_1z_1 \\ 3x_1y_1 & 3y_1^2 - r_1^2 & 3y_1z_1 \\ 3x_1z_1 & 3y_1z_1 & 3z_1^2 - r_1^2 \end{bmatrix} d\boldsymbol{r}_1$$

- symmetric
- trace-less (show)

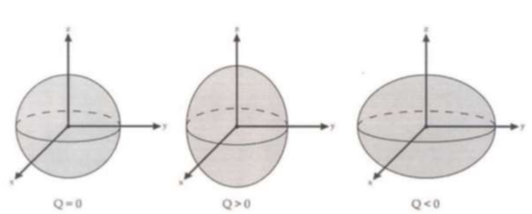


Fig. 2.2. *A spherical, prolate and oblate mass distribution (with respect to the z-axis).*

11

11

quadrupole field :

$${}_cV_{sh}^{(2)} = -G \int_2 \frac{\rho_2(\boldsymbol{r}_2)}{|\boldsymbol{r}_2|^5} \begin{bmatrix} 3x_2^2 - r_2^2 & 3x_2y_2 & 3x_2z_2 \\ 3x_2y_2 & 3y_2^2 - r_2^2 & 3y_2z_2 \\ 3x_2z_2 & 3y_2z_2 & 3z_2^2 - r_2^2 \end{bmatrix} d\boldsymbol{r}_2$$

- symmetric
- trace-less (show)

$$V_{ij} = \begin{bmatrix} \frac{\partial^2 V_2(\vec{0})}{\partial x_2^2} & \frac{\partial^2 V_2(\vec{0})}{\partial y_2 \partial x_2} & \frac{\partial^2 V_2(\vec{0})}{\partial z_2 \partial x_2} \\ \frac{\partial^2 V_2(\vec{0})}{\partial x_2 \partial y_2} & \frac{\partial^2 V_2(\vec{0})}{\partial y_2^2} & \frac{\partial^2 V_2(\vec{0})}{\partial z_2 \partial y_2} \\ \frac{\partial^2 V_2(\vec{0})}{\partial x_2 \partial z_2} & \frac{\partial^2 f(\vec{0})}{\partial y_2 \partial z_2} & \frac{\partial^2 V_2(\vec{0})}{\partial z_2^2} \end{bmatrix}$$

The meaning of this tensor is more clear when deriving it using a cartesian Taylor expansion:

➔ (gravitational) field gradient tensor

Traceless?

$$\Delta V_2(\mathbf{0}) = \frac{\partial^2 V_2(\mathbf{0})}{\partial x^2} + \frac{\partial^2 V_2(\mathbf{0})}{\partial y^2} + \frac{\partial^2 V_2(\mathbf{0})}{\partial z^2} = 4\pi\, G\, \rho_2(\mathbf{0})$$

Poisson equation

12

12

Taylor expansion of a scalar function defined on a vector domain:

Consider a function

$$f(\boldsymbol{r}) = \int \frac{g(\boldsymbol{r}_v)}{|\boldsymbol{r}_v - \boldsymbol{r}|}\, d\boldsymbol{r}_v \qquad \text{(B.1)}$$

The integral runs over that part of space where $g(\boldsymbol{r}_v)$ is not zero, which might be a finite or infinite region. If g is a charge or mass distribution, f gives the electric or gravitational potential in a point $\boldsymbol{r}$ (apart from an appropriate factor). That point can be either inside or outside the non-zero region of g (Fig. B-1***). If it lies inside, the denominator in the integral becomes zero and we have to care about the convergence of the integral. The latter is determined by the properties of g. We assume that we know the value of f and of all its derivatives *at the origin* **0**. What we want to know is the value of f at points $\boldsymbol{r} = (x, y, z)$ that are not far away from **0**. This means we need a Taylor expansion of $f(\boldsymbol{r})$ around **0**. The general form of a Taylor expansion around **0** for a function with vectors as argument, is:

$$f(\boldsymbol{0} + \boldsymbol{r}) = \sum_{j=0}^{\infty} \left[\frac{1}{j!} (\boldsymbol{r} \cdot \boldsymbol{\nabla}_{\boldsymbol{r}'})^j \, f(\boldsymbol{r}') \right]_{\boldsymbol{r}'=\boldsymbol{0}} \qquad \text{(B.2)}$$

dot product between scalars, vectors, tensors,...

13

13

- monopole and dipole terms from Taylor expansion are identical to the Laplace expansion
- difference in the quadrupole term:

$$E_{pot}^{(2)} = \frac{1}{2} \begin{bmatrix} \int \rho_1(\boldsymbol{r}_1) x_1^2\, d\boldsymbol{r}_1 & \int \rho_1(\boldsymbol{r}_1) x_1 y_1\, d\boldsymbol{r}_1 & \int \rho_1(\boldsymbol{r}_1) x_1 z_1\, d\boldsymbol{r}_1 \\ \int \rho_1(\boldsymbol{r}_1) y_1 x_1\, d\boldsymbol{r}_1 & \int \rho_1(\boldsymbol{r}_1) y_1^2\, d\boldsymbol{r}_1 & \int \rho_1(\boldsymbol{r}_1) y_1 z_1\, d\boldsymbol{r}_1 \\ \int \rho_1(\boldsymbol{r}_1) z_1 x_1\, d\boldsymbol{r}_1 & \int \rho_1(\boldsymbol{r}_1) z_1 y_1\, d\boldsymbol{r}_1 & \int \rho_1(\boldsymbol{r}_1) z_1^2\, d\boldsymbol{r}_1 \end{bmatrix} \cdot \begin{bmatrix} \frac{\partial^2 V_2(\vec{0})}{\partial x_2^2} & \frac{\partial^2 V_2(\vec{0})}{\partial y_2 \partial x_2} & \frac{\partial^2 V_2(\vec{0})}{\partial z_2 \partial x_2} \\ \frac{\partial^2 V_2(\vec{0})}{\partial x_2 \partial y_2} & \frac{\partial^2 V_2(\vec{0})}{\partial y_2^2} & \frac{\partial^2 V_2(\vec{0})}{\partial z_2 \partial y_2} \\ \frac{\partial^2 V_2(\vec{0})}{\partial x_2 \partial z_2} & \frac{\partial^2 f(\vec{0})}{\partial y_2 \partial z_2} & \frac{\partial^2 V_2(\vec{0})}{\partial z_2^2} \end{bmatrix}$$

$${}_cK^{(2)} = \frac{1}{3} \begin{bmatrix} \{3x_1^2\} - \{r_1^2\} & \{3x_1 y_1\} & \{3x_1 z_1\} \\ \{3y_1 x_1\} & \{3y_1^2\} - \{r_1^2\} & \{3y_1 z_1\} \\ \{3z_1 x_1\} & \{3z_1 y_1\} & \{3z_1^2\} - \{r_1^2\} \end{bmatrix} + \frac{1}{3} \begin{bmatrix} \{r_1^2\} & 0 & 0 \\ 0 & \{r_1^2\} & 0 \\ 0 & 0 & \{r_1^2\} \end{bmatrix} \qquad (2.58)$$

$${}_cW^{(2)} = \begin{bmatrix} \frac{\partial^2 V_2(\boldsymbol{0})}{\partial x_1^2} - \frac{\Delta V_2(\boldsymbol{0})}{3} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial y_1 \partial x_1} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial z_1 \partial x_1} \\ \frac{\partial^2 V_2(\boldsymbol{0})}{\partial x_1 \partial y_1} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial y_1^2} - \frac{\Delta V_2(\boldsymbol{0})}{3} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial z_1 \partial y_1} \\ \frac{\partial^2 V_2(\boldsymbol{0})}{\partial x_1 \partial z_1} & \frac{\partial^2 f(\boldsymbol{0})}{\partial y_1 \partial z_1} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial z_1^2} - \frac{\Delta V_2(\boldsymbol{0})}{3} \end{bmatrix} + \begin{bmatrix} \frac{\Delta V_2(\boldsymbol{0})}{3} & 0 & 0 \\ 0 & \frac{\Delta V_2(\boldsymbol{0})}{3} & 0 \\ 0 & 0 & \frac{\Delta V_2(\boldsymbol{0})}{3} \end{bmatrix} \qquad (2.59)$$

14

14

$$E_{pot}^{(2)} = \frac{1}{6} \begin{bmatrix} \{3x_1^2\} - \{r_1^2\} & \{3x_1 y_1\} & \{3x_1 z_1\} \\ \{3y_1 x_1\} & \{3y_1^2\} - \{r_1^2\} & \{3y_1 z_1\} \\ \{3z_1 x_1\} & \{3z_1 y_1\} & \{3z_1^2\} - \{r_1^2\} \end{bmatrix} \cdot \begin{bmatrix} \frac{\partial^2 V_2(\boldsymbol{0})}{\partial x_1^2} - \frac{\Delta V_2(\boldsymbol{0})}{3} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial y_1 \partial x_1} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial z_1 \partial x_1} \\ \frac{\partial^2 V_2(\boldsymbol{0})}{\partial x_1 \partial y_1} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial y_1^2} - \frac{\Delta V_2(\boldsymbol{0})}{3} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial z_1 \partial y_1} \\ \frac{\partial^2 V_2(\boldsymbol{0})}{\partial x_1 \partial z_1} & \frac{\partial^2 f(\boldsymbol{0})}{\partial y_1 \partial z_1} & \frac{\partial^2 V_2(\boldsymbol{0})}{\partial z_1^2} - \frac{\Delta V_2(\boldsymbol{0})}{3} \end{bmatrix} + \frac{1}{6} \begin{bmatrix} \{r_1^2\} & 0 & 0 \\ 0 & \{r_1^2\} & 0 \\ 0 & 0 & \{r_1^2\} \end{bmatrix} \cdot \begin{bmatrix} \frac{\Delta V_2(\boldsymbol{0})}{3} & 0 & 0 \\ 0 & \frac{\Delta V_2(\boldsymbol{0})}{3} & 0 \\ 0 & 0 & \frac{\Delta V_2(\boldsymbol{0})}{3} \end{bmatrix}$$

monopole shift :

$$\frac{1}{6}\, {}_cQ_{sz}^{(0)} \cdot {}_cV_{sz}^{(0)} = \frac{1}{6} \Delta V_2(\boldsymbol{0}) \langle r_1^2 \rangle = \frac{4\pi G}{6} \rho_2(\boldsymbol{0}) \int \rho_1(\boldsymbol{r}_1)\, r_1^2\, d\boldsymbol{r}_1$$

only if m_2 extends up to the origin !
(i.e. impossible if always $r_1 < r_2$ ➔ this was a more general derivation)

15

15

no overlap	monopole term	dipole term	quadrupole term
m_1	mass of m_1	position vector center of mass of m_1	quadrupole moment of m_1
m_2	potential by m_2 at origin	opposite of field by m_2 at origin	gradient of gravitional field by m_2 at origin
with overlap			
	correction depending on the size of m_1 and the mass contribution of m_2 at the origin		

16

16

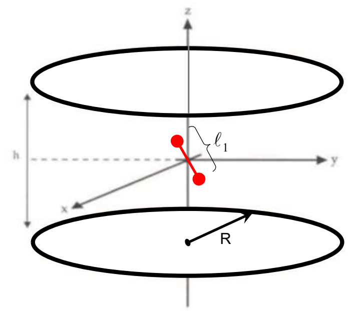
the double ring

www. hyperfinecourse .org

1

Example: a dumb-bell and a double ring.

total mass of dumbbell: m_1
total mass of double ring: m_2



$$\frac{r_1}{r_2} \ll 1 \quad \Rightarrow \quad \frac{l_1}{2} \ll \sqrt{\frac{h^2}{4} + R^2}$$

2

2

monopole energy :

$$E_{pot}^{(0)} = V_{sh}^{(0)} \cdot Q_{sh}^{(0)} = -\frac{G m_1 m_2}{\sqrt{\frac{h^2}{4} + R^2}}$$

quadrupole moment tensor of dumbbell:

$$_cQ_{sh}^{(2)} = \frac{3 m_1 l_1^2}{4} \begin{bmatrix} \sin^2\theta\cos^2\phi - \frac{1}{3} & \sin^2\theta\sin\phi\cos\phi & \sin\theta\cos\theta\cos\phi \\ \sin^2\theta\sin\phi\cos\phi & \sin^2\theta\sin^2\phi - \frac{1}{3} & \sin\theta\cos\theta\sin\phi \\ \sin\theta\cos\theta\cos\phi & \sin\theta\cos\theta\sin\phi & \cos^2\theta - \frac{1}{3} \end{bmatrix}$$

quadrupole field due to double ring:

$$_cV_{sh}^{(2)} = -\frac{G m_2 (h^2 - 2R^2)}{8R(R^2 + \frac{h^2}{4})^{\frac{5}{2}}} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}$$

(diagonal! ➔ PAS)

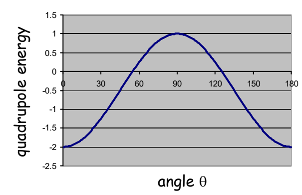
3

3

quadrupole energy :

(dot product between tensors = term by term multiplication, no matrix multiplication)

$$\frac{1}{6} Q_{sh}^{(2)} \cdot V_{sh}^{(2)} = -\underbrace{\frac{3 G m_1 m_2 l_1^2 (h^2 - 2R^2)}{32R(R^2 + \frac{h^2}{4})^{\frac{5}{2}}}}_{\alpha} (2\cos^2\theta - \sin^2\theta)$$



(picture made for α=1)

4

4

quadrupole energy :

(dot product between tensors = term by term multiplication, no matrix multiplication)

$$\frac{1}{6} Q_{sh}^{(2)} \cdot V_{sh}^{(2)} = -\underbrace{\frac{3 G m_1 m_2 l_1^2 (h^2 - 2R^2)}{32R(R^2 + \frac{h^2}{4})^{\frac{5}{2}}}}_{\alpha} (2\cos^2\theta - \sin^2\theta)$$

α > 0   α = 0   α < 0

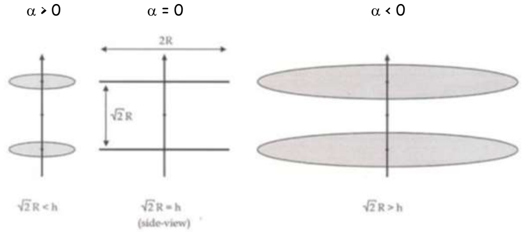


Fig. 2.6. *The three distinct classes of double-ring systems.*

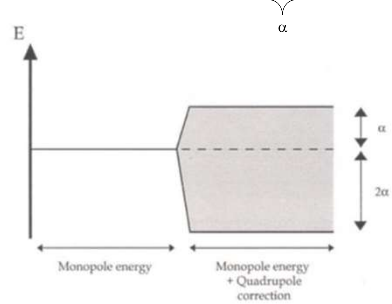
5

5

quadrupole energy :

(dot product between tensors = term by term multiplication, no matrix multiplication)

$$\frac{1}{6} Q_{sh}^{(2)} \cdot V_{sh}^{(2)} = -\underbrace{\frac{3 G m_1 m_2 l_1^2 (h^2 - 2R^2)}{32R(R^2 + \frac{h^2}{4})^{\frac{5}{2}}}}_{\alpha} (2\cos^2\theta - \sin^2\theta)$$



(picture for α > 0)

6

6

perturbation theory

www. hyperfinecourse .org

recapitulation: perturbation theory

Assuming we know eigenvalues and eigenfunctions of a hamiltonian H_0:

$$H_0 \,|\, n_0 > = E_n^0 \,|\, n_0 >$$

what are the eigenvalues and eigenfunctions of a hamiltonian H that has the form

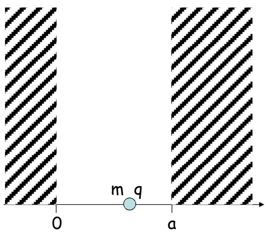
$$H \;=\; H_0 + \epsilon\, H_1 + \epsilon^2\, H_2 + \ldots$$

where ε is a small number (<< 1) ?

(Note: H_2 can be zero).

2

Example 1: charged particle in an infinitely deep potential well

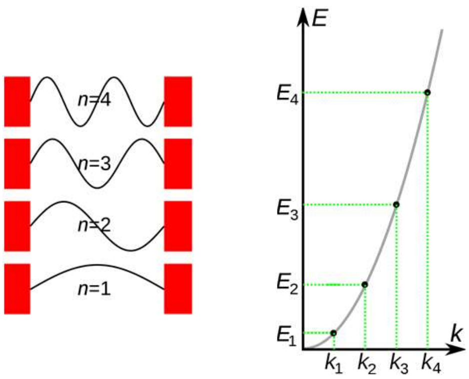


$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$E_{0,N} = \frac{\hbar^2\pi^2}{2ma^2}N^2 \qquad (N = 1, 2, 3, \ldots)$$

$$\Psi_{0,N}(x) = \sqrt{\frac{2}{a}}\,\sin\frac{N\pi x}{a}$$

3



(pictures taken from Wikipedia)

4

perturbation: constant electric field

electric field : $\vec{E}(x) = K\vec{e}_x$

potential energy: $V(x) = -qKx$

perturbing operator: $\hat{H}_1 = -qK\hat{x}$

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_1 \\ &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - qKx\end{aligned}$$

form of hamiltonian $\propto \frac{d^2}{dx^2} + \underbrace{\frac{2qmK}{\hbar^2}}_{\text{small if the electric field is not too strong}} x$

5

recapitulation: perturbation theory

Solution up to first order in ε :

1) non-degenerate case

For eigenvalues that are non-degenerate (i.e. H_1 does not lift any degeneracy), the new eigenvalues and eigenfunctions are given by:

$$\Delta E_n^1 = <n_0|\ H_1|n_0>$$

$$\Rightarrow \quad E_{\tilde{n}} = E_n^0 + \epsilon \Delta E_n^1$$

$$|\tilde{n}_1> = \sum_{m \neq n} \frac{<m_0|\ H_1|n_0>}{E_n^0 - E_m^0} |m_0>$$

$$\Rightarrow \quad |\tilde{n}> = |n_0> + \epsilon |n_1>$$

6

recapitulation: perturbation theory

Application to example 1:

$$\begin{aligned}\Delta E_N^1 &= \langle \Psi_{0,N} | \hat{H}_1 | \Psi_{0,N} \rangle \\ &= -\frac{2qK}{a} \int x \sin^2 \frac{N\pi x}{a}\, dx \\ &= -\frac{qKa}{2}\end{aligned}$$

Downward shift of all levels, independent of N.

Exercise: find the wave functions and probability density.

7

recapitulation: perturbation theory

Solution up to first order in ε :

2) l-fold degenerate case

For eigenvalues that are degenerate (i.e. H_1 does lift a degeneracy), the new eigenvalues and eigenfunctions are found by this procedure:

➔ orthonormalize
Find an orthonormal basis $|n_0^i>$ for the l-dimensional subspace

➔ diagonalize
The l energy corrections are found as the l eigenvalues of this matrix:

$$\begin{bmatrix} <n_0^1|\,\epsilon H_1|\,n_0^1> & <n_0^1|\,\epsilon H_1|\,n_0^2> & \cdots & <n_0^1|\,\epsilon H_1|\,n_0^\ell> \\ <n_0^2|\,\epsilon H_1|\,n_0^1> & <n_0^2|\,\epsilon H_1|\,n_0^2> & \cdots & <n_0^2|\,\epsilon H_1|\,n_0^\ell> \\ \vdots & \vdots & \ddots & \vdots \\ <n_0^\ell|\,\epsilon H_1|\,n_0^1> & <n_0^\ell|\,\epsilon H_1|\,n_0^2> & \cdots & <n_0^\ell|\,\epsilon H_1|\,n_0^\ell> \end{bmatrix}$$

The new eigenstates are the eigenvectors of this matrix.

8

recapitulation: perturbation theory

Example 2: free electron under an applied magnetic field

without field, up and down spin are degenerate: $\Psi_\uparrow \quad \Psi_\downarrow$

$$\begin{aligned}\hat{H}_0 &= \hat{1\!\!1} \\ \hat{H}_1 &= -\hat{\vec{\mu}} \cdot \vec{B} \\ &= -\left(\frac{-2\mu_B \hat{\vec{S}}}{\hbar}\right) \cdot \vec{B}\end{aligned}$$

$$\begin{bmatrix} \langle \Psi_\uparrow | \hat{S}_z | \Psi_\uparrow \rangle & \langle \Psi_\uparrow | \hat{S}_z | \Psi_\downarrow \rangle \\ \langle \Psi_\downarrow | \hat{S}_z | \Psi_\uparrow \rangle & \langle \Psi_\downarrow | \hat{S}_z | \Psi_\downarrow \rangle \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\hbar & 0 \\ 0 & -\frac{1}{2}\hbar \end{bmatrix}$$

This is already diagonal.

9

recapitulation: perturbation theory

A derivation and more examples can be found at

http://en.wikipedia.org/wiki/Perturbation_theory_(quantum_mechanics)

(section 2.1, 2.2 and 5)

stefaan.cottenier@ugent.be

quantum multipole expansion

www. hyperfinecourse .org

- We did discuss the multipole expansion for a classical system
- We did discuss the perturbation theory method

➔ We will now discuss the multipole expansion for a quantum system. We will conclude it is identical to the classical case, except for the role of perturbation theory.

2

multipole expansion in quantum physics

1) Description of a free nucleus

$$\hat{H}_n = \hat{T}_n + \hat{U}_{nn}$$

$$\hat{H}_n \left| I \right\rangle = E_I \left| I \right\rangle$$

separated by keV/MeV

3

multipole expansion in quantum physics

2) Description of a free electron cloud

$$\hat{H}_e = \hat{T}_e + \hat{U}_{ee}$$

$$\hat{H}_e \, |\psi_e\rangle = E_\psi \, |\psi_e\rangle$$

unbound

4

multipole expansion in quantum physics

3) Description of nucleus that is NOT interacting with an electron cloud

$$\left(\hat{H}_n \otimes \mathbb{1} + \mathbb{1} \otimes \hat{H}_e\right) |I \otimes \psi_e\rangle = (E_I + E_\psi) \, |I \otimes \psi_e\rangle$$

(somewhat artificial, this is combining the two independent systems in one mathematical picture)

5

multipole expansion in quantum physics

4) Description of a nucleus that is interacting with an electron cloud

Hamiltonian: $\hat{H}_n \otimes \mathbb{1} + \mathbb{1} \otimes \hat{H}_e + \hat{Q} \otimes \hat{V}$

It is the interaction term that makes life difficult. We can make a multipole expansion:

$$\hat{Q} \otimes \hat{V} = \hat{Q}^{(0)} \otimes \hat{V}^{(0)} + \hat{Q}^{(1)} \otimes \hat{V}^{(1)} + \hat{Q}^{(2)} \otimes \hat{V}^{(2)} + \ldots$$

This leads to a hierarchy in energy scales (➔ perturbation theory will be convenient !) :

$\hat{T}_n \otimes \mathbb{1} + \hat{U}_{nn} \otimes \mathbb{1}$	$T_n + U_{nn}$	$keV - MeV$	*nuclear energy levels*
$\mathbb{1} \otimes \hat{T}_e + \mathbb{1} \otimes \hat{U}_{ee} + \hat{Q}^{(0)} \otimes \hat{V}^{(0)}$	$T_e + U_{ee} + E_{ne}^{(0)}$	$eV \ (meV)$	*atomic energy levels*
$\hat{Q}^{(1)} \otimes \hat{V}^{(1)} + \hat{Q}^{(2)} \otimes \hat{V}^{(2)}$	$E_{ne}^{(1)} + E_{ne}^{(2)}$	μeV	*hyperfine structure*

6

stefaan.cottenier@ugent.be

multipole expansion in quantum physics

In the multipole-expanded formal hamiltonian, we will treat all nuclear properties as phenomenological parameters that are known (Z, I, Q, μ, <r^2>,...)

The electronic properties will be kept as operators, and will have to be solved for.

$$\underbrace{\underbrace{\hat{H}_n \otimes \mathbb{1}}_{\text{known}} + \underbrace{\mathbb{1} \otimes \hat{H}_e + \hat{Q}^{(0)} \otimes \hat{V}^{(0)}}_{\text{the usual electron problem}}}_{\text{known}} + \underbrace{\hat{Q}^{(1)} \otimes \hat{V}^{(1)} +}_{\hat{H}_1}$$

known — the usual electron problem (you solved the hydrogen atom this way)

known

$\hat{H}_1$ small correction

multipole expansion in quantum physics

Solution of the usual problem:

$$E_0 = \left\langle \psi_e^{(0)} \otimes I \middle| \hat{H}_0 \middle| I \otimes \psi_e^{(0)} \right\rangle$$

this wave function can be considered as known
(found by ab initio calculations for atoms, molecules or solids)

$$E_{tot} \approx E_0 + \left\langle \psi_e^{(0)} \otimes I \middle| \hat{H}_1 \middle| I \otimes \psi_e^{(0)} \right\rangle$$

known known known known

energy corrections due to nuclear shape are computable ! (first order perturbation)

multipole expansion in quantum physics
(charge-charge interaction)

⇨ The gravitational problem is fully equivalent to the quantum problem, except for the need to use perturbation theory.

Translation for the charge-charge interaction:

$$<\psi_n|\,\psi_n> = <I|\,I> = 1 = \int_n \psi_n^*(\boldsymbol{r}_n)\psi_n(\boldsymbol{r}_n)\,d\boldsymbol{r}_n = \frac{1}{Ze}\int_n \rho_n(\boldsymbol{r}_n)\,d\boldsymbol{r}_n$$

$$<\psi_e|\,\psi_e> = 1 = \int_e \psi_e^*(\boldsymbol{r}_e)\psi_e(\boldsymbol{r}_e)\,d\boldsymbol{r}_e = -\frac{1}{Ne}\int_e \rho_e(\boldsymbol{r}_e)\,d\boldsymbol{r}_e$$

$G \leftrightarrow \frac{-1}{4\pi\epsilon_0}$

$\boldsymbol{r}_1 \leftrightarrow \boldsymbol{r}_n$

$\boldsymbol{r}_2 \leftrightarrow \boldsymbol{r}_e$

$m_1 \leftrightarrow eZ$

$m_2 \leftrightarrow -eN$

⇨

$$E_{pot}^{qq} = \frac{1}{4\pi\epsilon_0}\int_n\int_e \frac{\rho_n(\boldsymbol{r}_n)\rho_e(\boldsymbol{r}_e)}{|\boldsymbol{r}_e - \boldsymbol{r}_n|}\,d\boldsymbol{r}_n\,d\boldsymbol{r}_e = -\frac{e^2NZ}{4\pi\epsilon_0}\,\langle\psi_e \otimes I|\,\frac{1}{|\boldsymbol{r}_e - \boldsymbol{r}_n|}\,|I \otimes \psi_e\rangle$$

multipole expansion

stefaan.cottenier@ugent.be

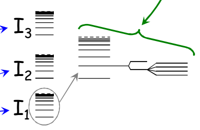
multipole expansion in quantum physics
(charge-charge interaction)

multipole expansion of the hamiltonian :

$$\hat{H}_{ne}^{qq} = -\frac{e^2 NZ}{\epsilon_0}\left(\sum_{n=0}^{\infty}\frac{r_n^n}{r_e^{n+1}}\frac{1}{2n+1}Y^n(\theta_n,\phi_n)\cdot Y^n(\theta_e,\phi_e)\right)$$

we assume here that electrons do not penetrate into the nucleus

$$E_{tot}^{qq} = \langle\psi_e\otimes I|\underbrace{\hat{T}_n+\hat{U}_{nn}}+\underbrace{\hat{T}_e+\hat{U}_{ee}+\hat{H}_{ne}^{qq}}|I\otimes\psi_e\rangle$$
$$= (E_I + E_{el})\,|I\otimes\psi_e\rangle$$



10

multipole expansion in quantum physics
(charge-charge interaction)

$$E_{el} = \langle\psi_e\otimes I|\underbrace{\hat{T}_e+\hat{U}_{ee}-\frac{e^2NZ}{4\pi\epsilon_0 r_e}}_{\hat{H}_0}|I\otimes\psi_e\rangle \;+$$
$$\langle\psi_e\otimes I|\underbrace{-\frac{e^2NZ}{\epsilon_0}\left(\sum_{n=1}^{\infty}\frac{r_n^n}{r_e^{n+1}}\frac{1}{2n+1}Y^n(\theta_n,\phi_n)\cdot Y^n(\theta_e,\phi_e)\right)}_{\hat{H}_{1\to\infty}}|I\otimes\psi_e\rangle$$

$$Q_q^n = eZ\sqrt{\frac{4\pi}{2n+1}}\,\langle I|\,r_1^n Y_q^n(\theta_n,\phi_n)\,|I\rangle$$

nuclear multipole moments
(lousely computable in ab initio nuclear physics theory – we take it as a (experimentally) given object)

$$V_q^n = -\frac{eN}{\sqrt{4\pi\epsilon_0}}\sqrt{\frac{1}{2n+1}}\left\langle\psi_e^{(0)}\middle|\frac{1}{r_e^{n+1}}Y_q^n(\theta_e,\phi_e)\middle|\psi_e^{(0)}\right\rangle$$

electric multipole fields
(reasonably well computable in ab initio "electron" theory [=atoms, molecules, solids])

11

multipole expansion in quantum physics
(charge-charge interaction)

$$H \approx \hat{T}_n+\hat{U}_{nn}+\underbrace{\hat{T}_e+\hat{U}_{ee}-\frac{e^2NZ}{4\pi\epsilon_0 r_e}}_{\hat{H}_0}+\underbrace{\frac{-e^2NZ}{5\epsilon_0}\left(\frac{r_n^2}{r_e^3}Y^2(\theta_e,\phi_e)\cdot Y^2(\theta_n,\phi_n)\right)}_{\hat{H}_1}$$

- odd terms vanish
- truncate after quadrupole term

$$E_{tot} \approx E_0 + \left\langle\psi_e^{(0)}\otimes I\middle|\hat{H}_1\middle|I\otimes\psi_e^{(0)}\right\rangle$$

known — known — known — known

known

12

multipole expansion in quantum physics
(current-current interaction)

Vector potential due to a given current distribution: $\boldsymbol{A}(\boldsymbol{r}) = \frac{\mu_0}{4\pi} \int \frac{\boldsymbol{j}(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} \, d\boldsymbol{r}'$

Energy for the interaction between two current distributions :

$$E^{jj}_{pot} = \int_n \boldsymbol{j}_n(\boldsymbol{r}_n) \cdot \boldsymbol{A}_e(\boldsymbol{r}_n) \, d\boldsymbol{r}_n = \frac{\mu_0}{4\pi} \int_n \int_e \frac{\boldsymbol{j}_n(\boldsymbol{r}_n) \cdot \boldsymbol{j}_e(\boldsymbol{r}_e)}{|\boldsymbol{r}_e - \boldsymbol{r}_n|} \, d\boldsymbol{r}_n \, d\boldsymbol{r}_e$$

Multipole expansion (different mathematics due to vector quantities) :

$$\hat{H}_{jj} = \sum_{n=0}^{\infty} \frac{B^{(n)} \cdot M^{(n)}}{2n+1}$$

- nuclear magnetic multipole moments
- magnetic multipole fields

Even terms vanish – dipole term is the leading one :

dipole hamiltonian: $-\hat{\boldsymbol{\mu}}_I \cdot \hat{\boldsymbol{B}}(\boldsymbol{0})$

13

multipole expansion in quantum physics
(summary / overview)

We want to have the energy corrections due to H_1, with and without overlap :

$$\hat{H} \approx \underbrace{\hat{T}_n + \hat{U}_{nn} + \hat{T}_e + \hat{U}_{ee} - \frac{e^2 N Z}{4\pi\epsilon_0 \, r_e}}_{\hat{H}_0} + \underbrace{\frac{-e^2 N Z}{5\epsilon_0}\left(\frac{r_n^2}{r_e^3} Y^2(\theta_e, \phi_e) \cdot Y^2(\theta_n, \phi_n)\right) - \hat{\boldsymbol{\mu}}_I \cdot \hat{\boldsymbol{B}}(\boldsymbol{0})}_{\hat{H}_1}$$

14

multipole expansion in quantum physics
(summary / overview)

Fig. 3.1	monopole	dipole	quadrupole	octupole
charge-charge (no overlap)	"normal" electronic structure [a] Q V(0)		electric-field gradient [b] $Q^{(2)} \cdot V^{(2)}(0)$	
charge-charge (overlap)	isotope shift isomer shift [d] $Q\{\langle r^2\rangle \rho_e(0)\}$		(too small) [e]	
current-current (no overlap)		orbital field spin dipolar field $\vec{\mu}_I \cdot \vec{B}_{el}$		(too small)
current-current (overlap)		Fermi contact field $\vec{\mu}_I \cdot \vec{B}_{el}$ Bohr-Weisskopf		(too small)

Fig. 3.1. *A schematic overview of all contributions to electric (charge-charge) and magnetic (current-current) hyperfine fields, ordered according to their multipole order, and split into shape-dependent and size-dependent contribution. Contributions that do not exist are barred, contributions that are too small to be relevant are indicated. When a dashed line is present in a box, the contribution above the line does not vanish for a point nucleus, while the contribution below the line does. Explaining this scheme is the task of chapters 4 to 7.*

(the letters in square brackets refer to the next page).

15

multipole expansion in quantum physics

(summary / overview)

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $MS^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $MS^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$ } $QS^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$ } $QS^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$ } $HDS^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$ } $HDS^{(2)}$	…
…	…	…	…	…

Table 1. Systematic overview of nuclear multipole and quasi multipole moments and electronic multipole and quasi multipole fields that appear in the multipole expansion of for two interacting (and overlapping) classical charge distributions. The first column gives the regular multipole expansion for point nuclei: the monopole interaction (labeled by [a]) which provides the unperturbed hamiltonian in a quantum frame-work. This is perturbed by [b] the quadrupole and [c] the hexadecapole interaction. The next columns give the quasi multipole moments/fields for every multipole interaction, denoted by a tilde. They provide first order corrections (shifts) to the multipole interactions of the first column, due to the extendedness of the nucleus. The box labeled [d] gives rise to the isomer/isotope shift, while the box labeled by [e] is the main topic of the present paper. Colored (gray) text is by extrapolation only, and is not systematically derived in this paper. The objects in each line are spherical tensors of a given rank (rank 0 for line 1, rank 2 for line 2, rank 4 for line 3, …).

- multipole interaction
- first order multipole shift
- second order multipole shift
- ...

16

summary

The quantum case is as the classical (gravitation) case,
apart from perturbation theory.

We have a roadmap of the kind of interactions we have to study.

17

monopole shift

www. hyperfinecourse .org

overview for the charge-charge case

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $\mathrm{MS}^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $\mathrm{MS}^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$ } $\mathrm{QS}^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$ } $\mathrm{QS}^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$ } $\mathrm{HDS}^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$ } $\mathrm{HDS}^{(2)}$	…
…	…	…	…	…

Table 1. Systematic overview of nuclear multipole and quasi multipole moments and electronic multipole and quasi multipole fields that appear in the multipole expansion of for two interacting (and overlapping) classical charge distributions. The first column gives the regular multipole expansion for point nuclei: the monopole interaction (labeled by [a]) which provides the unperturbed hamiltonian in a quantum frame-work. This is perturbed by [b] the quadrupole and [c] the hexadecapole interaction. The next columns give the quasi multipole moments/fields for every multipole interaction, denoted by a tilde. They provide first order corrections (shifts) to the multipole interactions of the first column, due to the extendedness of the nucleus. The box labeled [d] gives rise to the isomer/isotope shift, while the box labeled by [e] is the main topic of the present paper. Colored (gray) text is by extrapolation only, and is not systematically derived in this paper. The objects in each line are spherical tensors of a given rank (rank 0 for line 1, rank 2 for line 2, rank 4 for line 3, …).

- multipole interaction
- first order multipole shift
- second order multipole shift
- …

overview for the charge-charge case

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $\mathrm{MS}^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $\mathrm{MS}^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$ } $\mathrm{QS}^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$ } $\mathrm{QS}^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$ } $\mathrm{HDS}^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$ } $\mathrm{HDS}^{(2)}$	…
…	…	…	…	…

This is what one usually does.

Example for a single atom (if Z=1 : hydrogen) :

$$\begin{aligned} Q_{00} &= \frac{\sqrt{4\pi}}{\sqrt{4\pi}} \int \rho_n(\vec{r})\, d\vec{r} \\ &= eZ \\ V_{00} &= \frac{1}{4\pi\epsilon_0} \frac{\sqrt{4\pi}}{\sqrt{4\pi}} \int \frac{\rho_e(\vec{r})}{r}\, d\vec{r} \\ &= \frac{-e}{4\pi\epsilon_0} \langle \Psi_e | \frac{1}{r} | \Psi_e \rangle \end{aligned}$$

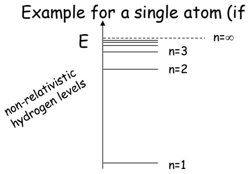
$$\begin{aligned} E_0^{(0)} &= Q_{00} V_{00} \\ &= \frac{-e^2 Z}{4\pi\epsilon_0} \langle \Psi_e | \frac{1}{r} | \Psi_e \rangle \end{aligned}$$

overview for the charge-charge case

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	...
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $\mathrm{MS}^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $\mathrm{MS}^{(2)}$	...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$ } $\mathrm{QS}^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$ } $\mathrm{QS}^{(2)}$	...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$ } $\mathrm{HDS}^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$ } $\mathrm{HDS}^{(2)}$	...
...	...	...	...	...

This is what one usually does.

Example for a single atom (if Z=1 : hydrogen) :



$$E_0^{(0)} = Q_{00} V_{00} = \frac{-e^2 Z}{4\pi\epsilon_0} \langle \Psi_e | \frac{1}{r} | \Psi_e \rangle$$

overview for the charge-charge case

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	...
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $\mathrm{MS}^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $\mathrm{MS}^{(2)}$	...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$ } $\mathrm{QS}^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$ } $\mathrm{QS}^{(2)}$	...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$ } $\mathrm{HDS}^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$ } $\mathrm{HDS}^{(2)}$	...
...	...	...	...	...

Corrections due to the shape of the nucleus (quadrupole moment, hexadecapole moment,....) in the case without overlap

overview for the charge-charge case

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	...
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $\mathrm{MS}^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $\mathrm{MS}^{(2)}$	...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$ } $\mathrm{QS}^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$ } $\mathrm{QS}^{(2)}$	...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$ } $\mathrm{HDS}^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$ } $\mathrm{HDS}^{(2)}$	...
...	...	...	...	...

The influence of overlap:

- first order monopole shift (well-known)
- first order quadrupole shift (recent advancement)
- first order hexadecapole shift (extremely small)

overview for the charge-charge case

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $MS^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $MS^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij}\Delta v(0)$ } $QS^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ } $QS^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl}\Delta v(0)$ } $HDS^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl}\Delta^2 v(0)$ } $HDS^{(2)}$	…
…	…	…	…	…

The influence of overlap:

- second order monopole shift (known but exotic)
- (the rest is too small)

first-order monopole shift

monopole term, no overlap :

$$E^{qq\,(0)}_{sh} = E_I + \left\langle \psi_e^{(0)} \otimes I \middle| \hat{T}_e + \hat{U}_{ee} - \frac{e^2 N Z}{4\pi\epsilon_0 r_e} \middle| I \otimes \psi_e^{(0)} \right\rangle$$

$$= \underbrace{E_I + E_e + E_{ee}}_{E_\alpha} - \frac{e^2 N Z}{4\pi\epsilon_0} \langle I | I \rangle \underbrace{\left\langle \psi_e^{(0)} \middle| \frac{1}{r_e} \middle| \psi_e^{(0)} \right\rangle}_{\langle \frac{1}{r_e} \rangle}$$

$$= E_\alpha - \frac{e^2 N Z}{4\pi\epsilon_0} \left\langle \frac{1}{r_e} \right\rangle$$

first-order monopole shift

monopole term, with overlap :

Look back at the gravitational result :

monopole shift : $\frac{1}{6}\,{}_cQ^{(0)}_{sz} \cdot {}_cV^{(0)}_{sz} = \frac{1}{6}\Delta V_2(\mathbf{0})\,\langle r_1^2 \rangle$

$$= \frac{4\pi G}{6}\rho_2(\mathbf{0}) \int \rho_1(r_1)\, r_1^2\, dr_1$$

only if m_2 extends up to the origin !

Translate this to operators/expectation values for the quantum case:

monopole shift $\propto \langle \Psi_e \otimes I |\; \hat{\delta}(\vec{r}) \otimes \hat{r}^{\,2} \;| \Psi_e \otimes I \rangle$

small perturbation operator

unperturbed wave function

first-order monopole shift

Final result :

$$E_{qq}^{(0)} = E_\alpha - \frac{e^2 N Z}{4\pi\epsilon_0}\left\langle \frac{1}{r_e} \right\rangle - \frac{eZ}{6\epsilon_0}\,\rho_e(\mathbf{0})\,\langle r_n^2 \rangle$$

or

$$E_{qq}^{(0)} = E_\alpha + \tilde{Q}\left\{-\frac{eN}{4\pi\epsilon_0}\left\langle \frac{1}{r_e} \right\rangle\right\} + \tilde{Q}\left\{-\frac{1}{6\epsilon_0}\,\rho_e(\mathbf{0})\,\langle r_n^2 \rangle\right\}$$

monopole moment = eZ

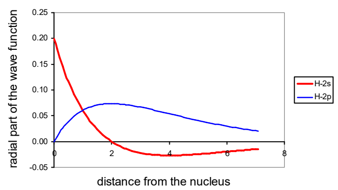
monopole field = potential at the nucleus, depends on integral property of electrons.

Extra potential at the nucleus, depends on point property of electrons and integral property of nucleus.

Vanishes if :
- the nucleus is a point, or
- the electrons do not enter the nucleus

do electrons enter the nucleus ?

Go back to the H-atoms and check the equations on http://winter.group.shef.ac.uk/orbitron/
(take any orbital at the left, then choose the tab 'equations' on top).

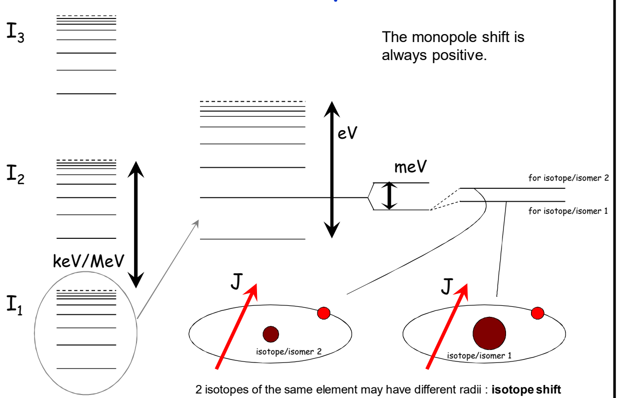


Estimate the order of magnitude of the monopole shift energy (use the non-relativistic equation for H-atom s wave functions, and the nuclear radius trend seen in the first lecture.

- non-relativistic s-electrons do have a non-zero wave-function at r=0.
- the same holds for relativistic $p_{1/2}$ electrons

the electric monopole shift

The monopole shift is always positive.

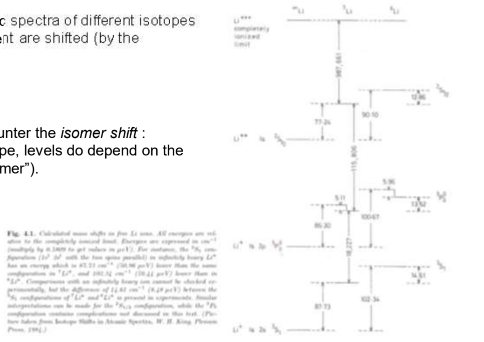


2 isotopes of the same element may have different radii : **isotope shift**
2 states (isomers) of the same nucleus may have different radii : **isomer shift**

experimental consequence: isotope shift

What:
levels in the atomic spectra of different isotopes of the same element are shifted (by the monopole shift).

We will later encounter the *isomer shift* :
for the same isotope, levels do depend on the nuclear state ("isomer").



(shifts in this picture are due to the mass of the isotope -- see lecture 2 – as well as to the isotope shift)

overview for the charge-charge case

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $\mathrm{MS}^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $\mathrm{MS}^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$ } $\mathrm{QS}^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$ } $\mathrm{QS}^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$ } $\mathrm{HDS}^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$ } $\mathrm{HDS}^{(2)}$	…
…	…	…	…	…

The influence of overlap:

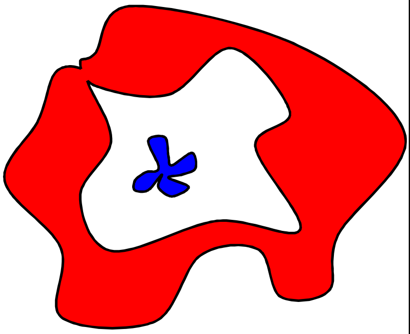
- second order monopole shift (known but exotic)

➔ much smaller (4th power of the nuclear radius)
➔ nevertheless relevant for exotic cases: muonic atoms
(atoms where one of the electrons is replaced by a much heavier muon ➔ closer to the nucleus, more overlap)

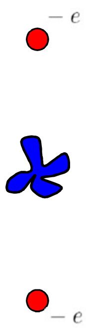
http://en.wikipedia.org/wiki/Exotic_atom#Muonic_atoms

a toy model for the monopole shift

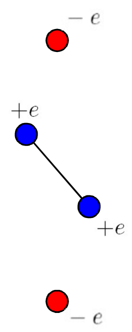
www. hyperfinecourse .org



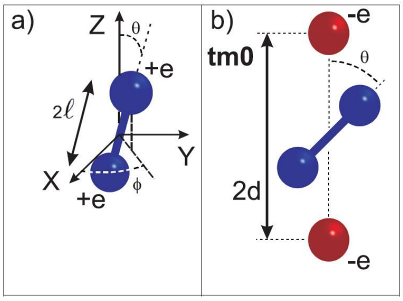
2



3

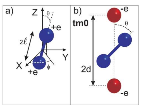


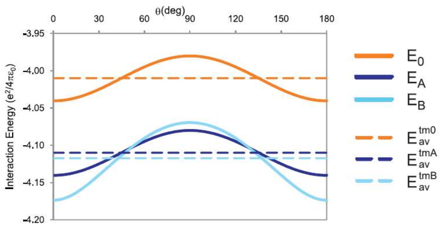
Exactly solvable classical toy model : no electrons in nucleus



$$E_0(\theta) = -2C\left(\frac{1}{\sqrt{\ell^2\sin^2\theta+(d-\ell\cos\theta)^2}}+\frac{1}{\sqrt{\ell^2\sin^2\theta+(d+\ell\cos\theta)^2}}\right) \qquad C=e^2/(4\pi\varepsilon_0)$$

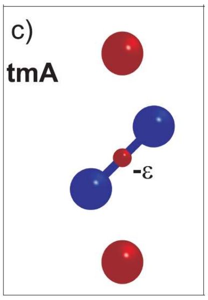
Exactly solvable classical toy model : no electrons in nucleus

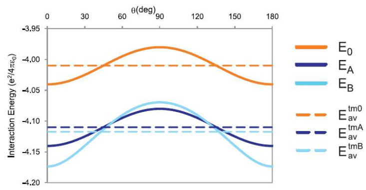




$$E_0(\theta) = -2C\left(\frac{1}{\sqrt{\ell^2\sin^2\theta+(d-\ell\cos\theta)^2}}+\frac{1}{\sqrt{\ell^2\sin^2\theta+(d+\ell\cos\theta)^2}}\right) \qquad C=e^2/(4\pi\varepsilon_0)$$

Exactly solvable classical toy model : with electrons in nucleus

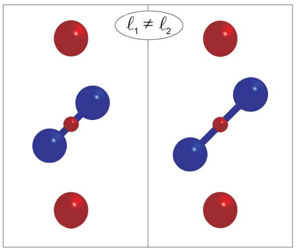




$$E_A(\theta) = E_0(\theta) + \underbrace{\frac{-2\varepsilon C}{e\ell}}_{E_{corA}}$$

7

Exactly solvable classical toy model : isotope shift



$$E_A(\theta) = E_0(\theta) + \underbrace{\frac{-2\varepsilon C}{e\ell}}_{E_{corA}}$$

8

magnetic hyperfine interaction

in free atoms

www. hyperfinecourse .org

1

magnetic hyperfine interaction in free atoms

or

coupling of angular momenta : from L-S to I-J

stefaan.cottenier@ugent.be

2

coupling of angular momenta: L-S

We'll remind first what you saw in earlier courses on the coupling of orbital and spin angular momenta in an atom:

The problem: "**For a given shell (n,l), how do a given number of electrons occupy the available orbitals?**"

Example: C (n=2, l=1), 2 p-electrons

There are 6 different orbitals (m_l=-1,0,+1 and this for either spin), hence 6x6=36 possibilities to put these 2 electrons. Which of those 36 possibilities has the lowest energy (and will therefore be found as the ground state in Nature)?

Hund's rules provide you with an algorithm to find this ground state
(no mathematical justification – these rules were originally derived from experimental trends)

3

3

coupling of angular momenta: L-S

1st Hund's rule

Only configurations where the total S is maximal should be considered further.

S is found as the absolute value of the sum of all m_S values

Our example: only states with S=1 (twice m_S=+1/2 or twice m_S=-1/2) should be considered further.

2nd Hund's rule

Within the previous set, only configurations where the total L is maximal should be considered further.

L is found as the absolute value of the sum of all m_L values

Our example: states with S=1 cannot contain 2 electrons in the same m_L orbital. Hence, the maximal L is L=1 (two electrons in m_L=+1,0, or in m_L=-1,0)

4

4

coupling of angular momenta: L-S

How many of our 36 states are left if we restrict ourselves to S=1 and L=1?

Two ways to count:

First way :

S=1 can have three different orientations (2S+1=3; m_S=-1,0,+1)
L=1 can have three different orientations (2L+1=3; m_L=-1,0,+1)

➔ 3x3=9 out of 36

Second way:

Angular momenta coupling rules: S=1 and L=1 can couple to J=L+S,..,|L-S| = 2,1,0
Each J-value has 2J+1 orientations: 5, 3, 1

➔ 5+3+1=9 out of 36

5

5

coupling of angular momenta: L-S

Which of the remaining (9) states is the ground state?

- If there is no interaction between L and S, all these states are degenerate.
- If there is interaction (spin-orbit coupling), some will have a lower energy than others

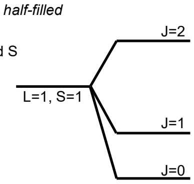
3rd Hund's rule

Of the remaining states, those with the lowest energy are the ones with

- *J minimal if the shell is less than half-filled*
- *J maximal if the shell is more than half-filled*

Physical picture: mutual orientation of L and S

Example: 2 electrons in a p-shell is less than half-filled
➔ J=0 has the lowest energy.



6

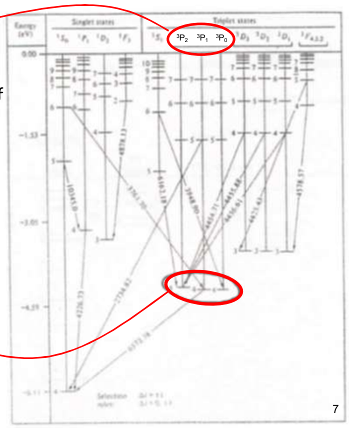
6

P ⇒ L=1
3 ⇒ S=1

3 different orientations of L w.r.t. S:

J = 2, 1, 0

Energy of the entire atom slightly depends on the value of J



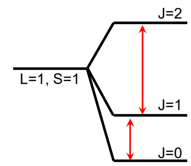
7

7

coupling of angular momenta: L-S

Landé's interval rule:

$$\frac{E_J - E_{J-1}}{E_{J-1} - E_{J-2}} = \frac{J}{J-1}$$



8

8

coupling of angular momenta: I-J

A nucleus with spin I has 2I+1 possible orientations.
An electron cloud with total angular momentum J has 2J+1 possible orientations.

If there is no interaction between I and J, all these (2I+1)x(2J+1) possibilities have the same energy.

I is related to the nuclear magnetic moment (dipole moment for the current-current case)
Each J state provides a specific magnetic hyperfine field (dipole field for the current-current case)

➔ I and J do interact
➔ which mutual orientation of I and J corresponds to the lowest energy?

We will discuss this in terms of a new total angular momentum F:

$$F = I+J,\, I+J-1,\, \ldots,\, |I-J|$$

Each value of F corresponds to a different mutual orientation of I and J.
For a given F, different values of m_F correspond to a rotation of the atom as a whole (mutual orientation is unaffected).

9

9

coupling of angular momenta: I-J

nuclear magnetic moment operator

$$\hat{\boldsymbol{\mu}}_I = \frac{\mu}{I\hbar}\hat{\boldsymbol{I}}$$

experimentally known – the 'size' of the nuclear magnetic moment (scalar).

Magnetic hyperfine field operator:

$$\hat{\boldsymbol{B}}_J = \frac{B_J}{J\hbar}\hat{\boldsymbol{J}}$$

Let us consider this for the time being as known (experimentally or computable).

The perturbing hamiltonian H_1:

$$\begin{aligned}\hat{H}_{jj} &= -\hat{\boldsymbol{\mu}}_I \cdot \boldsymbol{B}(\boldsymbol{0}) \\ &= -\frac{\mu B_J}{\hbar^2 IJ}\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{J}} \\ &= -\frac{\mu B_J}{2\hbar^2 IJ}\left(\hat{F}^2 - \hat{I}^2 - \hat{J}^2\right)\end{aligned}$$

Use $\hat{\boldsymbol{F}}^2 = \hat{F}^2 = (\hat{\boldsymbol{I}}+\hat{\boldsymbol{J}})^2 = \hat{I}^2 + \hat{J}^2 + 2\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{J}}$

10

coupling of angular momenta: I-J

Apply perturbation theory

The states of the unperturbed system are the |F> (direct product of |I> and |J>)

The perturbing hamiltonian is likely to lift degeneracies
➔ perturbation theory for the degenrate case

Fortunately the |F> states are orthonormal already (property of angular momentum eigenstates)

$$\begin{bmatrix} \langle 0|\hat{H}_{jj}|0\rangle & \langle 1|\hat{H}_{jj}|0\rangle & \langle 2|\hat{H}_{jj}|0\rangle & \langle 3|\hat{H}_{jj}|0\rangle \\ \langle 0|\hat{H}_{jj}|1\rangle & \langle 1|\hat{H}_{jj}|1\rangle & \langle 2|\hat{H}_{jj}|1\rangle & \langle 3|\hat{H}_{jj}|1\rangle \\ \langle 0|\hat{H}_{jj}|2\rangle & \langle 1|\hat{H}_{jj}|2\rangle & \langle 2|\hat{H}_{jj}|2\rangle & \langle 3|\hat{H}_{jj}|2\rangle \\ \langle 0|\hat{H}_{jj}|3\rangle & \langle 1|\hat{H}_{jj}|3\rangle & \langle 2|\hat{H}_{jj}|3\rangle & \langle 3|\hat{H}_{jj}|3\rangle \end{bmatrix}$$

11

11

coupling of angular momenta: I-J

Only diagonal matrix elements will survive:

$$\begin{aligned}<F|\hat{H}_{jj}|F> &= -\frac{\mu B_J}{2\hbar^2 IJ} <F|\hat{F}^2 - \hat{I}^2 - \hat{J}^2|F> \\ &= -\frac{\mu B_J}{2\hbar^2 IJ}\hbar^2 \underbrace{(F(F+1) - I(I+1) - J(J+1))}_{C} \\ &= -\frac{1}{2}aC\end{aligned}$$

Hence, no diagonalization needed, the matrix is already diagonal and the eigenvalues (=energy corrections) can be read right away :

$$-\frac{1}{2}a\begin{bmatrix} C_{00} & 0 & 0 & 0 \\ 0 & C_{11} & 0 & 0 \\ 0 & 0 & C_{22} & 0 \\ 0 & 0 & 0 & C_{33} \end{bmatrix}$$

12

12

coupling of angular momenta: I-J

Energy difference between two subsequent transitions (cfr. Landé interval rule):

$$\frac{E_F - E_{F-1}}{E_{F-1} - E_{F-2}} = \frac{F(F+1) - (F-1)F}{(F-1)F - (F-2)(F-1)} = \frac{F}{F-1}$$

Level scheme :

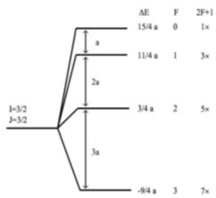


Fig. 5.1. *Magnetic hyperfine splitting for an atom with nuclear spin $I = 3/2$ and electronic spin $J = 3/2$. The energy of the total system depends on how I and J are oriented with respect to each other, which is given by the new total spin F. The picture uses a correct scale. The right column gives the degeneracy of each level. The hyperfine variant of the Landé interval rule is illustrated as well.*

13

13

coupling of angular momenta: I-J

This formalism applies to

- free atoms or free ions *[rigorously]*
- atoms in ionic compounds (salts) *[qualitatively]*

14

14

magnetic hyperfine interaction in solids

www. hyperfinecourse .org

1

magnetic hyperfine interactions in solids

The presence of a crystal lattice in a solid breaks the rotational invariance of space – which is required to get to the concept of |F> etc.

➔ different formalism needed.

The magnetic hyperfine field will have a fixed direction in space (not yet determined/specified which direction). Take the z-axis of your axis system along this direction.
(This means we work in a PAS for the dipole interaction – see later.)

Perturbation theory:

wave function for the point nucleus solid

$$E_{jj} = -\langle I|\,\hat{\boldsymbol{\mu}}_I\,|I\rangle \cdot \left\langle \psi_e^{(0)} \middle| \hat{\boldsymbol{B}}\,(\boldsymbol{0}) \middle| \Psi_e^{(0)} \right\rangle$$
$$= -\langle I|\,\hat{\boldsymbol{\mu}}_I\,|I\rangle \cdot \boldsymbol{B}(\boldsymbol{0})$$
$$= -\langle I|\,\hat{\mu}_{I,z}\,|I\rangle\; B(\boldsymbol{0})$$

nuclear wave function

2

2

magnetic hyperfine interactions in solids

The presence of a crystal lattice in a solid breaks the rotational invariance of space – which is required to get to the concept of |F> etc.

➔ different formalism needed.

The magnetic hyperfine field will have a fixed direction in space (not yet determined/specified which direction). Take the z-axis of your axis system along this direction.
(This means we work in a PAS for the dipole interaction – see later.)

Perturbation theory:

wave function for the point nucleus solid

$$E_{jj} = -\langle I|\,\hat{\boldsymbol{\mu}}_I\,|I\rangle \cdot \left\langle \psi_e^{(0)} \middle| \hat{\boldsymbol{B}}\,(\boldsymbol{0}) \middle| \Psi_e^{(0)} \right\rangle$$
$$= -\langle I|\,\hat{\boldsymbol{\mu}}_I\,|I\rangle \cdot \boldsymbol{B}(\boldsymbol{0})$$
$$= -\langle I|\,\hat{\mu}_{I,z}\,|I\rangle\; B(\boldsymbol{0})$$

computable by point-nucleus DFT codes

nuclear wave function

3

3

magnetic hyperfine interactions in solids

We don't know explicit expression for the nuclear wave functions – how to overcome ?

$$\hat{\boldsymbol{\mu}}_I = \frac{\mu}{I\,\hbar}\,\hat{\boldsymbol{I}}$$

$$\hat{\boldsymbol{I}} = \hat{I}_x\boldsymbol{e}_x + \hat{I}_y\boldsymbol{e}_y + \hat{I}_z\boldsymbol{e}_z$$

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y \qquad \hat{I}_+\,|I,\,m_I\rangle = \sqrt{I(I+1)\,-\,m_I(m_I+1)}\,\hbar\,|I,\,m_I+1\rangle$$

$$\hat{I}_- = \hat{I}_x - i\hat{I}_y \qquad \hat{I}_-\,|I,\,m_I\rangle = \sqrt{I(I+1)\,-\,m_I(m_I-1)}\,\hbar\,|I,\,m_I-1\rangle$$

Rewrite the magnetic moment operator as a sum of operators for which the nuclear states are eigenfunctions – the eigenvalues depend on quantities that can be experimentally determined.

$$\hat{\boldsymbol{\mu}}_{I_x} = \frac{\mu}{2I\hbar}\left(\hat{I}_+ + \hat{I}_-\right)$$
$$\hat{\boldsymbol{\mu}}_{I_y} = \frac{\mu}{2I\hbar}\,\frac{1}{i}\left(\hat{I}_+ - \hat{I}_-\right)$$
$$\hat{\boldsymbol{\mu}}_{I_z} = \frac{\mu}{I\hbar}\,\hat{I}_z$$

4

4

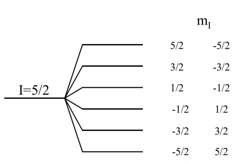
magnetic hyperfine interactions in solids

In this way, we can express the nuclear matrix element that we need in terms of the experimentally accessible quantities μ and I:

$$\langle m_I',\,I|\,\hat{\mu}_z\,|I,\,m_I\rangle = \frac{\mu}{I}\,m_I\,\delta_{m_I',m_I}$$

(i.e. we circumvent the lack of nuclear physics theoretical knowledge by using experimental input).

$$E_{jj}^{m_I} = -\frac{\mu\,m_I}{I}\,B_{hf}$$



Equidistant:

$$E_{hf}^{m_I+1} - E_{hf}^{m_I} = -\,g_I\,\mu_N\,B_{hf} = \hbar\,\omega_L$$

5

Intermezzo: physical meaning of g_I

Two vector properties of the nucleus: I and μ

(μ is related to interaction with magnetic fields, I plays a role in the weak interaction)

They are related to each other by g_I: $\hat{\boldsymbol{\mu}} = \frac{g\,\mu_N}{\hbar}\,\hat{\boldsymbol{I}}$

The sign of g_I determines the orientation of μ w.r.t. I

Gyromagnetic ratio:
$$\hat{\boldsymbol{\mu}} = \gamma\,\hat{\boldsymbol{I}}$$
$$\gamma = \frac{g\,\mu_N}{\hbar}$$

6

6

magnetic hyperfine interactions in solids

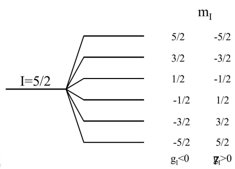
In this way, we can express the nuclear matrix element that we need in terms of the experimentally accessible quantities μ and I:

$$\langle m_I', I |\, \hat{\mu}_z \,| I, m_I \rangle = \frac{\mu}{I}\, m_I \,\delta_{m_I', m_I}$$

(i.e. we circumvent the lack of nuclear physics theoretical knowledge by using experimental input).

$$E_{jj}^{m_I} = -\frac{\mu\, m_I}{I} B_{hf}$$

computable



Equidistant:

$$E_{hf}^{m_I+1} - E_{hf}^{m_I} = -\, g_I\, \mu_N\, B_{hf} = \hbar\,\omega_L$$

7

magnetic hyperfine interactions in solids
the hyperfine field operator

Without derivation:

$$\boldsymbol{B}(\boldsymbol{0}) = -\frac{\mu_B \mu_0}{2\pi\hbar} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{L}_i}{r^3} \middle| \psi_e^{(0)} \right\rangle + \frac{\mu_B \mu_0}{4\pi} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{\sigma} - 3\,(\boldsymbol{\sigma}\cdot\boldsymbol{e}_r)\,\boldsymbol{e}_r}{r^3} \middle| \psi_e^{(0)} \right\rangle + -\frac{2\mu_B \mu_0}{3} \left\langle \psi_e^{(0)} \middle| \boldsymbol{\sigma}\,\delta(\boldsymbol{r}) \middle| \psi_e^{(0)} \right\rangle$$

8

magnetic hyperfine interactions in solids
the hyperfine field operator

Without derivation:

$$\boldsymbol{B}(\boldsymbol{0}) = -\frac{\mu_B \mu_0}{2\pi\hbar} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{L}_i}{r^3} \middle| \psi_e^{(0)} \right\rangle + \frac{\mu_B \mu_0}{4\pi} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{\sigma} - 3\,(\boldsymbol{\sigma}\cdot\boldsymbol{e}_r)\,\boldsymbol{e}_r}{r^3} \middle| \psi_e^{(0)} \right\rangle + -\frac{2\mu_B \mu_0}{3} \left\langle \psi_e^{(0)} \middle| \boldsymbol{\sigma}\,\delta(\boldsymbol{r}) \middle| \psi_e^{(0)} \right\rangle$$

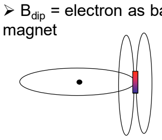
- orbital contribution
- spin dipolar contribution
- Fermi contact contribution

9

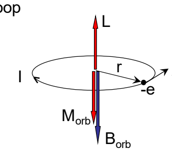
magnetic hyperfine interactions in solids
the hyperfine field operator

$B_{tot} = B_{dip} + B_{orb} + B_{Fermi}$

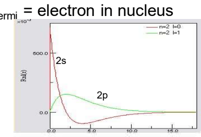
- B_{dip} = electron as bar magnet



- B_{orb} = electron as current loop



- B_{Fermi} = electron in nucleus



$$-\frac{2\mu_B \mu_0}{3} \left(|\psi_{e,\uparrow}(\boldsymbol{0})|^2 - |\psi_{e,\downarrow}(\boldsymbol{0})|^2 \right)$$

(+ other contributions from the atomic moments of neighbouring atoms -- Lorentz construction; too much detail for our purpose)

10

magnetic hyperfine interactions in solids
case studies

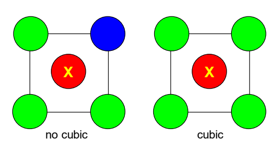
bcc-Fe

orbital hyperfine field:	9.6	T
dipolar hyperfine field:	-0.03	T
Fermi contact hyperfine field:		
1s+2s+3s (core):	-41.2	T
4s (valence):	-3.7	T
Sum:	**-35.3**	T

11

magnetic hyperfine interactions in solids
symmetry properties

chemical

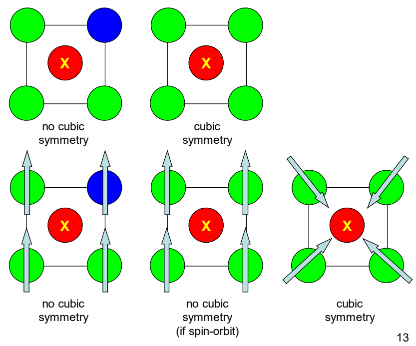


12

magnetic hyperfine interactions in solids
symmetry properties

chemical

chemical + magnetic



13

13

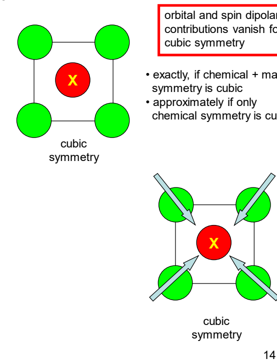
magnetic hyperfine interactions in solids
symmetry properties

chemical

chemical + magnetic

orbital and spin dipolar contributions vanish for cubic symmetry

- exactly, if chemical + magnetic symmetry is cubic
- approximately if only chemical symmetry is cubic



14

14

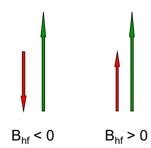
magnetic hyperfine interactions in solids
case studies

bcc-Fe

orbital hyperfine field:	9.6 T
dipolar hyperfine field:	-0.03 T
Fermi contact hyperfine field:	
1s+2s+3s (core):	-41.2 T
4s (valence):	-3.7 T
Sum:	**-35.3** T

What does the sign mean:

Orientation of the hyperfine field (vector) with respect to the spin moment (vector) of the atom



15

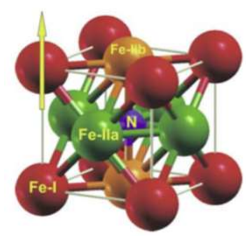
15

magnetic hyperfine interactions in solids
case studies

Fe_4N

chemical lattice:
Fe-I (cubic)
Fe-II (non-cubic)

magnetic lattice:
Fe-I (non-cubic)
Fe-IIa (non-cubic)
Fe-IIb (non-cubic)



Fermi contact hff			orbital hff			dipolar hff		
Fe-I	Fe-IIa	Fe-IIb	Fe-I	Fe-IIa	Fe-IIb	Fe-I	Fe-IIa	Fe-IIb
−29.7	−21.0	−21.1	3.7	0.4	2.7	0.0	3.0	−6.3

16

16

The hyperfine field on a Fe-nucleus in bcc Fe is -35.3 T.

Consider one atom of whatever element X as substitutional impurity in a bcc Fe matrix. What is the hyperfine field at the nucleus of X?

A) the same as for a Fe nucleus

B) slightly different from the value for a Fe nucleus

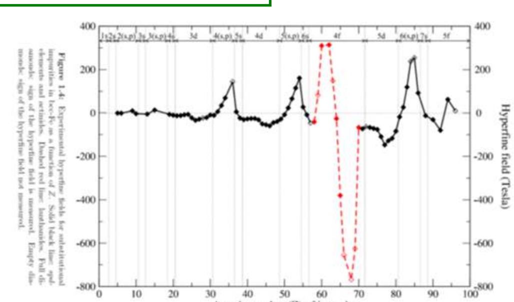
C) totally different

17

17

magnetic hyperfine interactions in solids
case studies

isolated substitutional impurities in bcc-Fe



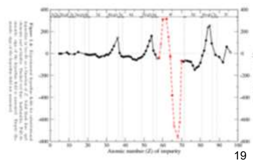
18

18

magnetic hyperfine interactions in solids
case studies

- 50 years of experimental work
- a repeated trend through every period of the periodic table
  - small and negative for s-groups
  - S-shape for d-block
  - rising from small and negative to large and positive in p-block
  - huge fields with positive/negative transition for f-block

➔ all this can be understood (not really the goal of this course)



19

19

overlap contribution
(magnetic hyperfine interaction)

www. hyperfinecourse .org

1

overlap in the charge-charge interaction

What did we have for the charge-charge interaction:

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	...
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $MS^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $MS^{(2)}$	...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij}\Delta v(0)$ } $QS^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ } $QS^{(2)}$	...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl}\Delta v(0)$ } $HDS^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl}\Delta^2 v(0)$ } $HDS^{(2)}$	...
...	...	...	...	...

0^{th} order contribution for a point nucleus

2

2

overlap in the charge-charge interaction

What did we have for the charge-charge interaction:

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	...
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } $MS^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } $MS^{(2)}$	...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij}\Delta v(0)$ } $QS^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ } $QS^{(2)}$	...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl}\Delta v(0)$ } $HDS^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl}\Delta^2 v(0)$ } $HDS^{(2)}$	...
...	...	...	...	...

first order correction to 0^{th} order for overlap (or 'extended nucleus')

$$-\frac{eZ}{6\epsilon_0}\,\rho_e(\mathbf{0})\,\langle r_n^2\rangle$$

➔ vanishes if the nucleus is a point...
➔ ...even if the charge density at r=0 is not zero
➔ correction is small w.r.t. regular monopole term.

3

3

overlap in the current-current interaction

Translate this to the leading term of the current-current interaction

	dipole contribution	first order correction due to overlap
O(1)	$-\hat{\boldsymbol{\mu}}_I \cdot \hat{\boldsymbol{B}}(\mathbf{0})$	
	• orbital • spin	• Fermi contact contribution $-\frac{2\mu_B\mu_0}{3}\left(\lvert\psi_{e,\uparrow}(\mathbf{0})\rvert^2 - \lvert\psi_{e,\downarrow}(\mathbf{0})\rvert^2\right)$ ➔ does not vanish if nucleus becomes a point • field related to Bohr-Weisskopf effect

overlap ⇔ extended nucleus !

'correction' is often dominant w.r.t. regular dipole term (see bcc-Fe)

4

Bohr-Weisskopf effect

Two different isotopes of the same element have a different nuclear moment. The spatial distribution of this moment over the nuclear volume need not to be homogeneous:

$$E_{mag} = -\int_{nuc} \boldsymbol{B}_{hf} \cdot d\boldsymbol{\mu}_I$$

1) Bring the two naked nuclei in an externally applied B and measure the magnetic interaction energy. B is constant over the nuclear volume and goes out of the integral:

$$\frac{E_1}{E_2} = \frac{\boldsymbol{\mu}_{I1}}{\boldsymbol{\mu}_{I2}}$$

2) Bring both nuclei in the same hyperfine field. This varies over the nuclear volume and interacts with the (differently) distributed magnetic moments. B does not get out the integral, which leads to:

$$\frac{E_1}{E_2} = \frac{\boldsymbol{\mu}_{I1}}{\boldsymbol{\mu}_{I2}}\,(1+\Delta)$$

➔ Bohr-Weisskopf effect

hyperfine anomaly (up to 2%)

5

5

from toy model to quantum physics

www. hyperfinecourse .org

1

Overview for the charge-charge case

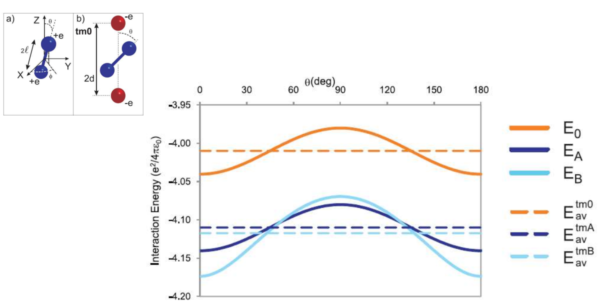
order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	...
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } MS$^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } MS$^{(2)}$	...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij}\Delta v(0)$ } QS$^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ } QS$^{(2)}$	...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl}\Delta v(0)$ } HDS$^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl}\Delta^2 v(0)$ } HDS$^{(2)}$	...
...	...	...	...	...

Corrections due to the shape
of the nucleus (quadrupole moment)
in the case without overlap

2

2

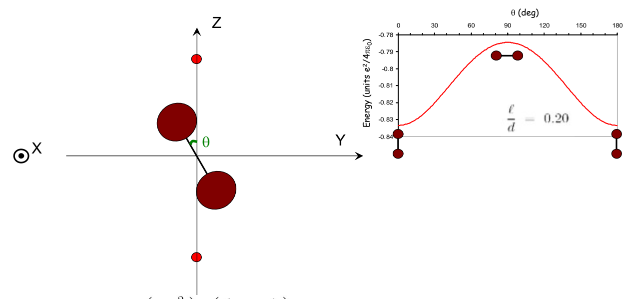
Exactly solvable classical toy model : no electrons in nucleus



$$E_0(\theta) = -2C\left(\frac{1}{\sqrt{\ell^2\sin^2\theta + (d-\ell\cos\theta)^2}} + \frac{1}{\sqrt{\ell^2\sin^2\theta + (d+\ell\cos\theta)^2}}\right) \qquad C = e^2/(4\pi\varepsilon_0)$$

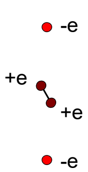
3

3



$$E(\theta) = 2\left(\frac{-e^2}{4\pi\epsilon_0}\right)\left(\frac{1}{r_a} + \frac{1}{r_b}\right)$$
$$= 2\left(\frac{-e^2}{4\pi\epsilon_0}\right)\left(\frac{1}{\sqrt{\ell^2\sin^2\theta + (d-\ell\cos\theta)^2}} + \frac{1}{\sqrt{\ell^2\sin^2\theta + (d+\ell\cos\theta)^2}}\right)$$

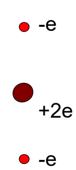
4



	l=0	l=1	l=2
nucleus	charge	dipole moment	quadrupole moment
electrons	electric potential	electric field	electric-field gradient (EFG)
	(scalar)	(vector)	(rank 2 tensor)

5

5

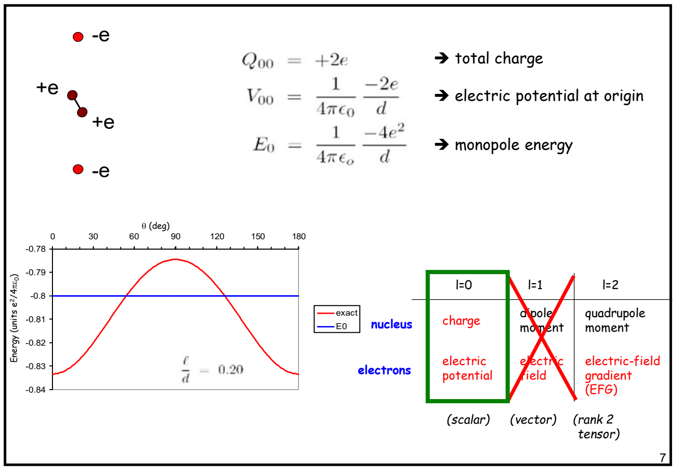


$$Q_{00} = +2e$$ → total charge
$$V_{00} = \frac{1}{4\pi\epsilon_0}\frac{-2e}{d}$$ → electric potential at origin
$$E_0 = \frac{1}{4\pi\epsilon_o}\frac{-4e^2}{d}$$ → monopole energy

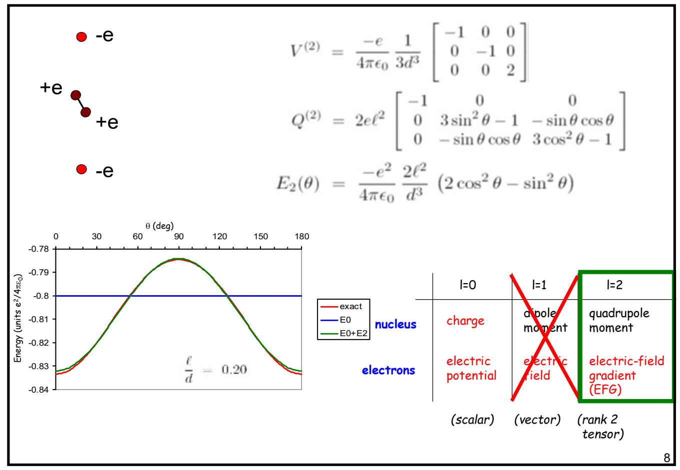
	l=0	l=1	l=2
nucleus	charge	dipole moment	quadrupole moment
electrons	electric potential	electric field	electric-field gradient (EFG)
	(scalar)	(vector)	(rank 2 tensor)

6

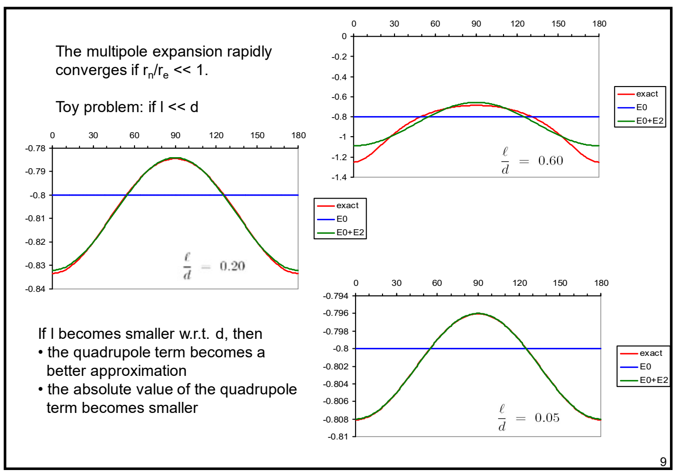
6


-e
+e
+e
-e
Q00 = +2e → total charge
V00 = (1/4πε0)(−2e/d) → electric potential at origin
E0 = (1/4πε0)(−4e²/d) → monopole energy
θ (deg)
Energy (units e²/4πε0)
exact
E0
ℓ/d = 0.20
nucleus
electrons
l=0
l=1
l=2
charge
dipole moment
quadrupole moment
electric potential
electric field
electric-field gradient (EFG)
(scalar)
(vector)
(rank 2 tensor)
7

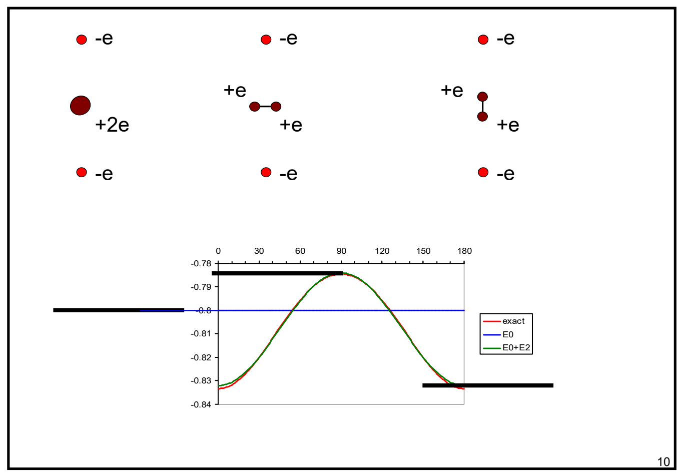
7


-e
+e
+e
-e
V(2) = (−e/4πε0)(1/3d³) [−1 0 0; 0 −1 0; 0 0 2]
Q(2) = 2eℓ² [−1 0 0; 0 3sin²θ−1 −sinθcosθ; 0 −sinθcosθ 3cos²θ−1]
E2(θ) = (−e²/4πε0)(2ℓ²/d³)(2cos²θ − sin²θ)
θ (deg)
Energy (units e²/4πε0)
exact
E0
E0+E2
ℓ/d = 0.20
nucleus
electrons
l=0
l=1
l=2
charge
dipole moment
quadrupole moment
electric potential
electric field
electric-field gradient (EFG)
(scalar)
(vector)
(rank 2 tensor)
8

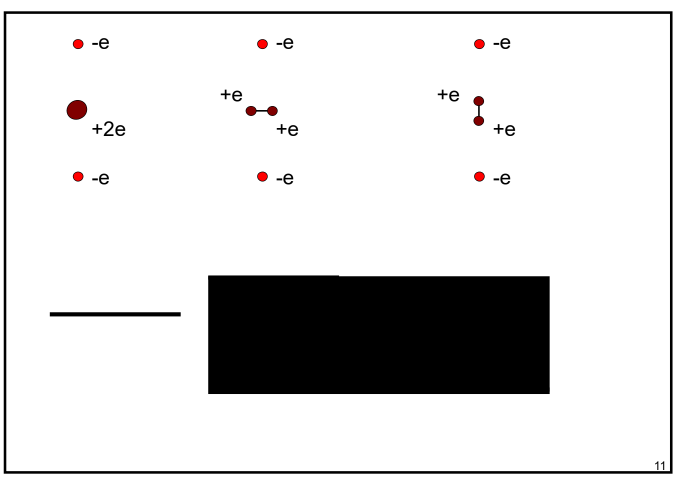
8


The multipole expansion rapidly converges if rn/re << 1.
Toy problem: if l << d
ℓ/d = 0.20
ℓ/d = 0.60
ℓ/d = 0.05
exact
E0
E0+E2
If l becomes smaller w.r.t. d, then
• the quadrupole term becomes a better approximation
• the absolute value of the quadrupole term becomes smaller
9

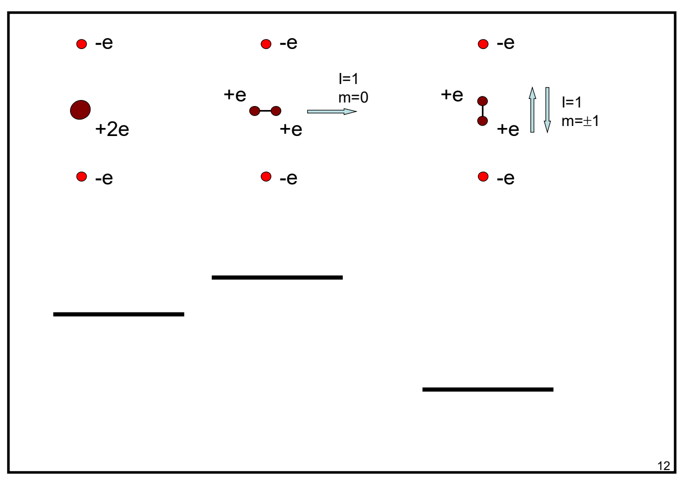
9


-e
+2e
-e
-e
+e
+e
-e
-e
+e
+e
-e
exact
E0
E0+E2
10

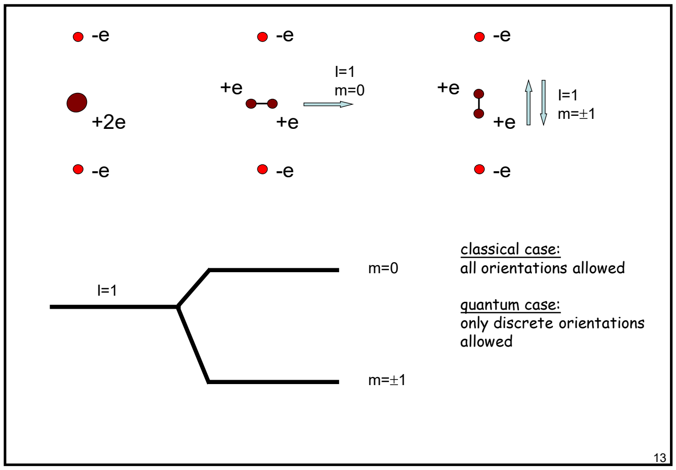
10


-e
+2e
-e
-e
+e
+e
-e
-e
+e
+e
-e
11

11


-e
+2e
-e
-e
+e
+e
-e
l=1
m=0
-e
+e
+e
-e
l=1
m=±1
12

12


-e
+2e
-e
-e
+e
+e
-e
l=1
m=0
-e
+e
+e
-e
l=1
m=±1
l=1
m=0
m=±1
classical case:
all orientations allowed
quantum case:
only discrete orientations allowed
13

13

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:

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

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

in general axis system:

$$\left\langle \psi_e^{(0)} \middle| \hat{V}_0^2 \middle| \psi_e^{(0)} \right\rangle = \frac{1}{2} V_{zz}$$
$$\left\langle \psi_e^{(0)} \middle| \hat{V}_{\pm 1}^2 \middle| \psi_e^{(0)} \right\rangle = \mp \frac{1}{\sqrt{6}} (V_{xz} \pm V_{yz})$$
$$\left\langle \psi_e^{(0)} \middle| \hat{V}_{\pm 2}^2 \middle| \psi_e^{(0)} \right\rangle = \frac{1}{2\sqrt{6}} (V_{xx} - V_{yy} \pm i V_{xy})$$

5 numbers

6-1=5 numbers (traceless)

- 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)

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:

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

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

in PAS :

$$\left\langle \psi_e^{(0)} \middle| \hat{V}_0^2 \middle| \psi_e^{(0)} \right\rangle = \frac{1}{2} V_{zz}$$
$$\left\langle \psi_e^{(0)} \middle| \hat{V}_{\pm 1}^2 \middle| \psi_e^{(0)} \right\rangle = 0$$
$$\left\langle \psi_e^{(0)} \middle| \hat{V}_{\pm 2}^2 \middle| \psi_e^{(0)} \right\rangle = \frac{1}{2\sqrt{6}} \eta V_{zz}$$

5 numbers

2 numbers + 3 Euler angles

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

- 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)

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:

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

(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

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

with

$$I^2\, Y_0^2(I) = \frac{1}{2}\sqrt{\frac{5}{4\pi}}\,(3I_z^2 - I^2)$$
$$I^2\, Y_{\pm 1}^2 = \mp\sqrt{\frac{15}{8\pi}}\,\frac{1}{2}\,(I_z I_\pm + I_\pm I_z)$$
$$I^2\, Y_{\pm 2}^2 = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\, I_\pm^2$$

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:

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

(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:

$$< I, m_I' | Q_0^2 | I, m_I > = \frac{1}{2} \frac{eQ}{I(2I-1)} \left(3m^2 - I(I+1)\right) \delta_{m_I, m_I'} \quad (6.26)$$

$$< I, m_I' | Q_{\pm 1}^2 | I, m_I > = \mp \frac{1}{2} \sqrt{\frac{3}{2}} \frac{eQ}{I(2I-1)} \sqrt{I(I+1) - m_I(m_I \pm 1)}\,(2m_I \pm 1)\, \delta_{m_I', m_I \pm 1} \quad (6.27)$$

$$< I, m_I' | Q_{\pm 2}^2 | I, m_I > = \frac{1}{2} \sqrt{\frac{3}{2}} \frac{eQ}{I(2I-1)} \sqrt{(I(I+1) - m_I(m_I \pm 1))(I(I+1) - (m_I \pm 1)(m_I \pm 2))}\, \delta_{m_I', m_I \pm 2} \quad (6.28)$$

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:

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

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

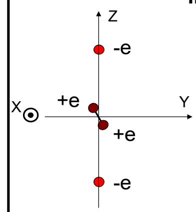
number, known from experimental nuclear physics

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

7

7

Illustration for the toy problem:



Electric-field gradient tensor:

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

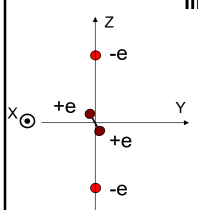
- is already diagonal. The chosen axis system is a PAS.
- V_{zz} is negative: at (0,0), E_z decreases with z
- V_{yy} is positive: at (0,0), E_y increases with y

For this simple case, you might verify this.

8

8

Illustration for the toy problem:



nuclear quadrupole moment tensor:

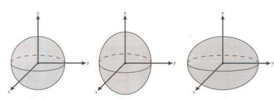
$$Q^{(2)} = 2e\ell^2\begin{bmatrix} -1 & 0 & 0 \\ 0 & 3\sin^2\theta - 1 & -\sin\theta\cos\theta \\ 0 & -\sin\theta\cos\theta & 3\cos^2\theta - 1 \end{bmatrix}$$

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

quadrupole interaction :
case studies & symmetry

www. hyperfinecourse .org

1

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

1 0 -1

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

ordered

1 -1 0

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

2

2

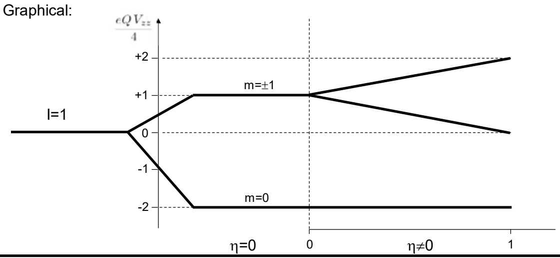
Analytical examples

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:



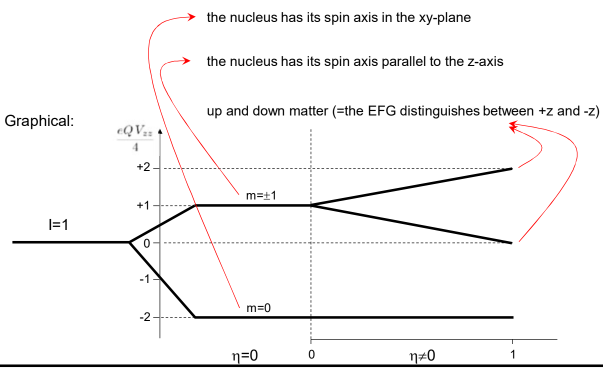
3

3

Analytical examples

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

Graphical:



4

4

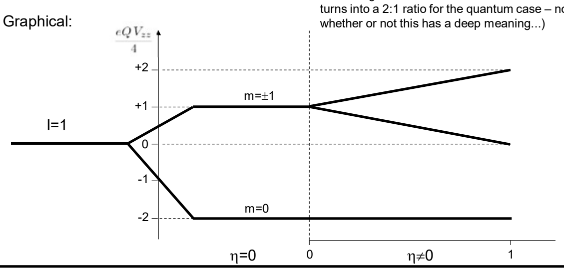
Analytical examples

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...)

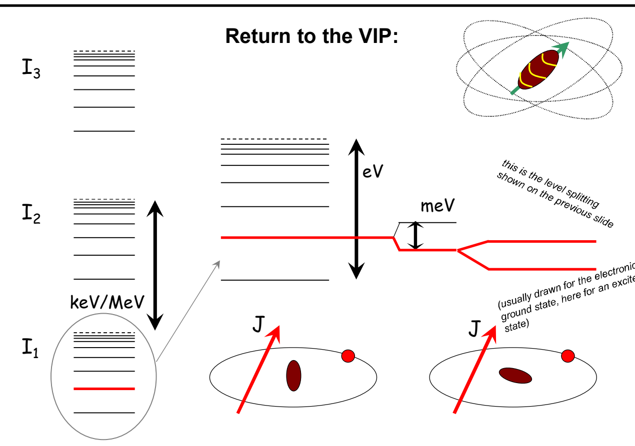
Graphical:



5

5

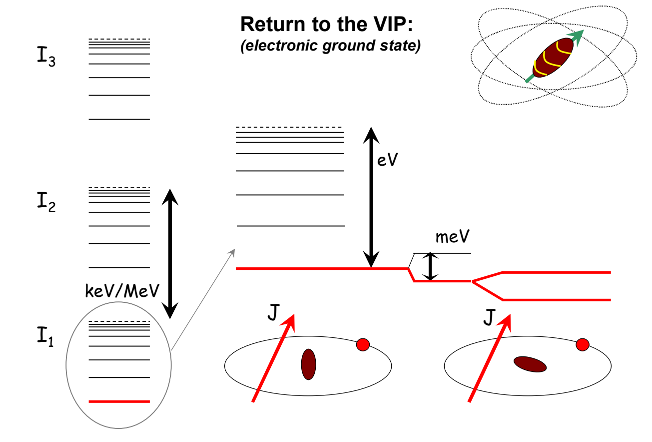
Return to the VIP:



6

6

Return to the VIP:
(electronic ground state)



7

7

Analytical examples

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

Non-zero matrix elements :

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

Matrix for 1st order perturbation :

not ordered

+3/2 +1/2 -1/2 -3/2

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

ordered

+3/2 -1/2 -3/2 +1/2

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

8

8

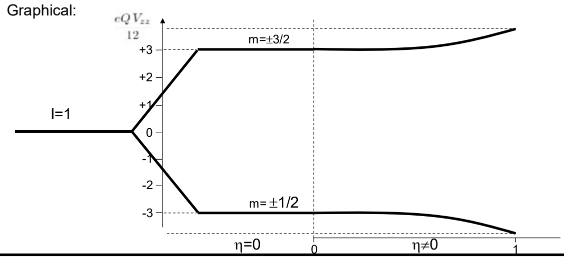
Analytical examples

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:



9

9

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*

10

10

General statements

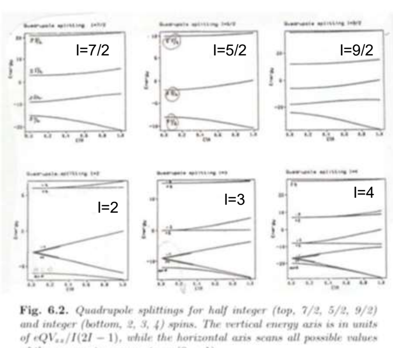


Fig. 6.2. *Quadrupole splittings for half integer (top, 7/2, 5/2, 9/2) and integer (bottom, 2, 3, 4) spins. The vertical energy axis is in units of $eQV_{zz}/I(2I-1)$, while the horizontal axis scans all possible values of the asymmetry parameter η (0 → 1).*

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

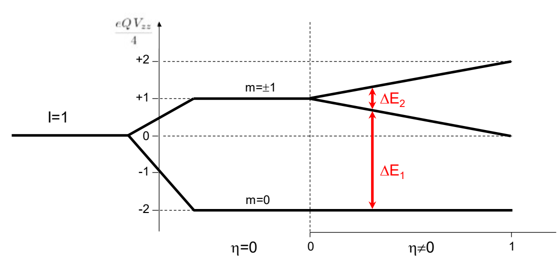
11

11

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



12

12

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

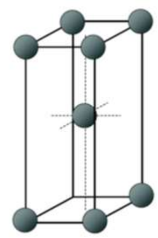
In solids, the situation of this second theorem appears only in 5 point groups, which are all cubic (23, -43m, m-3, 432 and m-3m).

13

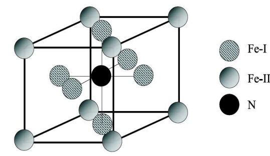
13

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?

14

14

quadrupole interaction :
miscellaneous topics

www. hyperfinecourse .org

1

ab initio calculation of the EFG tensor

- Calculating the EFG tensor for a real solid requires good knowledge of its electron density.
- This was too complicated to calculate for a long time.
- Therefore, a dramatic approximation was frequently used: the point charge model
  - replace the continuous electron density by positive point charges at the atomic sites
  - calculate the EFG tensor due to this set of classical charges
  - the (initially spherical) charge distribution of the atom at r=0 gets deformed by this external EFG. This provides an additional EFG, proportional to the external one. The proportionality factor (Sternheimer antishielding factor) can be estimated from ab initio calculations on free ions
  - an extra proportionality due to an EFG by unfilled orbitals of the atom at r=0 is present as well

$$V_{zz} = (1-K)\,(1-\gamma_\infty)\,V_{zz}^{latt}$$

- Very crude, but there was nothing better and many people strongly believed in this for decades. However, it doesn't really give much insight.

2

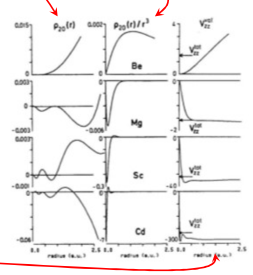
2

ab initio calculation of the EFG tensor

Once ab initio calculations became available, it turned out that the EFG was dominated by contributions from the region very close to the nucleus: tails of the wave functions, which carry over the influence of bonds with the neighbouring atoms to the nuclear site.

related to the second derivative of the density

$1/r^3$ strongly amplifies the region close to the nucleus



the EFG is an integrated property, but the region close to the nucleus contributes most.

Fig. 6.7. *Illustrating which regions in space contribute to V_{zz}. First column: the function $\rho_c(r)$ from the integrand in equation 6.101 (without $1/r^3$). Second column: similarly, but with the factor $1/r^3$. Third column: this function integrated up to r, which is equation 6.101. The arrows indicate the full calculated V_{zz}, including the "lattice contribution" from distant atoms.*

P. Blaha et al., Phys. Rev. B 37 (1988) 2792

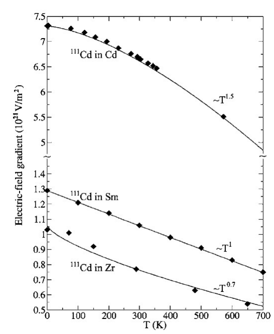
3

3

Temperature dependence of the EFG tensor

Summary of experimental observations:

$V_{zz}(T) = V_{zz}(0)(1-BT^{\alpha})$



with spd-electrons, very often $\alpha \approx 1.5$

with f-electrons, very often $\alpha \approx 1.0$

sometimes more complicate behaviour appears

4

4

Temperature dependence of the EFG tensor

Long-standing question : is there an analytical argument for the α=1.5 ?

ab initio study of thermally induced vibrations for Cd in hcp-Cd (supercell with 24 atoms) : the order of magnitude is recovered.

Prohibitively long calculations on cells with 2000 atoms would be needed to get good numerical accuracy

➔ this strongly suggests the 1.5 exponent is the average of many harmonic modes, and is more accidental than analytical.

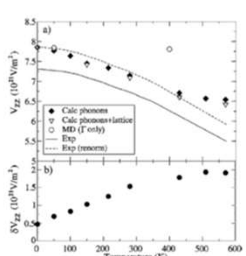


FIG. 6. (a) Calculated values of electric-field gradient for hcp-Cd as a function of temperature: for a fixed lattice constant (diamonds) and for the lattice constant corresponding to that temperature (triangles), compared with experiment. MD results at 50 K and 400 K (circles) are rescaled so that the 50 K result matches the experimental value. (b) The standard deviation of the 9×24 =216 V_{zz} values as a function of temperature.

D. Torumba et al., Phys. Rev. B 74 (2006) 144304

5

5

Combined magnetic/electric interaction

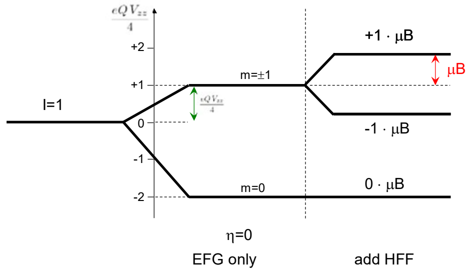
- The formalism remains the same as before
  - write the combined hamiltonian
  - find all matrix elements (degenerate 1st order perturbation)
  - diagonalize the matrix to find eigenvalues
- The general case can be technically involved, but important simpler situations exist:
  - if one of the two interactions is much stronger than the other one, consider the weak interaction as a new perturbation (i.e. you work in the PAS of the dominant interaction)
  - in all cases, expressions are simpler for an axially symmetric EFG
  - the case where the magnetic hyperfine field is aligned with the z-axis of the PAS of the EFG (i.e. the magnetic and electric PAS coincide) can be treated exactly.

6

6

Combined magnetic/electric interaction

Example for I=1, axially symmetric EFG, colinear interaction (no further approximation needed):



Show yourself that in this case you get exactly the same result if you apply the HFF first, and afterwards the EFG

7

7

Combined magnetic/electric interaction

Discuss the relative orientation of the PAS of the magnetic and electric interaction for all Fe sites.

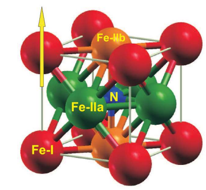


Figure 1 Unit cell of ferromagnetic γ'-Fe_4N, with 3 inequivalent Fe-sites. Fe-I has a larger moment than Fe-IIa and Fe-IIb. Without magnetism, Fe-IIa and Fe-IIb are equivalent. The preferential direction of the magnetic moments (arrow) makes them inequivalent: for Fe-IIa, the fourfold rotation axis perperdicular to the local face of the cube is perpendicular to the moment, for Fe-IIb it is parallel to the moment.

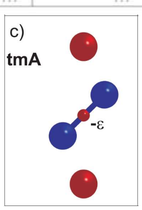
8

8

An extended nucleus

What did we have for the monopole term of the charge-charge interaction:

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } MS$^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } MS$^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2Y_{20}$, $V_{ij} \propto \partial_{ij}v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij}\Delta v(0)$ } QS$^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ } QS$^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4Y_{40}$, $V_{ijkl} \propto \partial_{ijkl}v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl}\Delta v(0)$ } HDS$^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl}\Delta^2 v(0)$ } HDS$^{(2)}$	…
…	…	…	…	…



An extra potential at the nucleus, that depends on nuclear properties and on a point property of the electron system

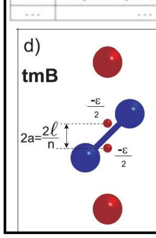
9

9

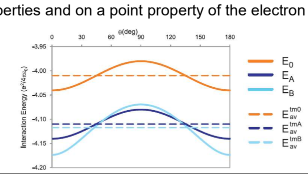
An extended nucleus

Analogous effect for the quadrupole term:

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } MS$^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } MS$^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2Y_{20}$, $V_{ij} \propto \partial_{ij}v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij}\Delta v(0)$ } QS$^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ } QS$^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4Y_{40}$, $V_{ijkl} \propto \partial_{ijkl}v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl}\Delta v(0)$ } HDS$^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl}\Delta^2 v(0)$ } HDS$^{(2)}$	…
…	…	…	…	…



An extra EFG at the nucleus, that depends on nuclear properties and on a point property of the electron system



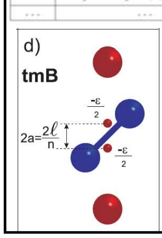
10

10

An extended nucleus

Analogous effect for the quadrupole term:

order	multipole moment / field	first order quasi moment / quasi field	second order quasi moment / quasi field	…
$\mathcal{O}(0)$	$M \propto r^0Y_{00}$, $V \propto v(0)$ } MI [a]	$\tilde{M}^{(1)} \propto \{r^2Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } MS$^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } MS$^{(2)}$	…
$\mathcal{O}(2)$	$Q \propto r^2Y_{20}$, $V_{ij} \propto \partial_{ij}v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4Y_{20}\}$, $\tilde{V}^{(1)}_{ij} \propto \partial_{ij}\Delta v(0)$ } QS$^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6Y_{20}\}$, $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ } QS$^{(2)}$	…
$\mathcal{O}(4)$	$H \propto r^4Y_{40}$, $V_{ijkl} \propto \partial_{ijkl}v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6Y_{40}\}$, $\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl}\Delta v(0)$ } HDS$^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8Y_{40}\}$, $\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl}\Delta^2 v(0)$ } HDS$^{(2)}$	…
…	…	…	…	…



An extra EFG at the nucleus, that depends on nuclear properties and on a point property of the electron system

Very small !

K. Koch et al. Phys. Rev. A 81 (2010) 032507
http://dx.doi.org/10.1103/PhysRevA.81.032507
K. Rose and SC, Phys. Chem. Chem. Phys. 14 (2012) 11308
http://dx.doi.org/10.1039/c2cp40740j

11

11