magnetic hyperfine interaction in solids

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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

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

nuclear wave function

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computable by point-nucleus DFT codes

nuclear wave function

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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.

$$\hat{\boldsymbol{\mu}}_{Ix} = \frac{\mu}{2I\hbar}\left(\hat{I}_+ + \hat{I}_-\right)$$
$$\hat{\boldsymbol{\mu}}_{Iy} = \frac{\mu}{2I\hbar}\,\frac{1}{i}\left(\hat{I}_+ - \hat{I}_-\right)$$
$$\hat{\boldsymbol{\mu}}_{Iz} = \frac{\mu}{I\hbar}\,\hat{I}_z$$

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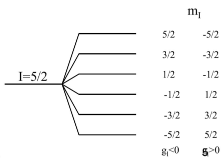
magnetic hyperfine interactions in solids

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).

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



Equidistant:

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

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

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

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

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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:

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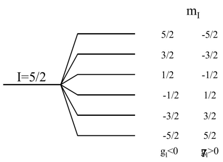
(i.e. we circumvent the lack of nuclear physics theoretical knowledge by using experimental input).

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

computable



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

magnetic hyperfine interactions in solids
the hyperfine field operator

Without derivation:

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

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magnetic hyperfine interactions in solids
the hyperfine field operator

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- orbital contribution
- spin dipolar contribution
- Fermi contact contribution

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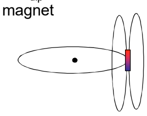
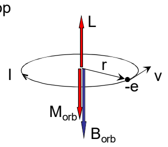
magnetic hyperfine interactions in solids
the hyperfine field operator

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

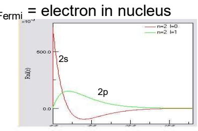
- B_{dip} = electron as bar magnet



- B_{orb} = electron as current loop



- B_{Fermi} = electron in nucleus



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

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

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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

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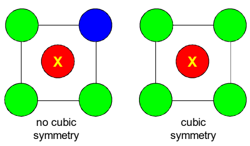
magnetic hyperfine interactions in solids
symmetry properties

chemical



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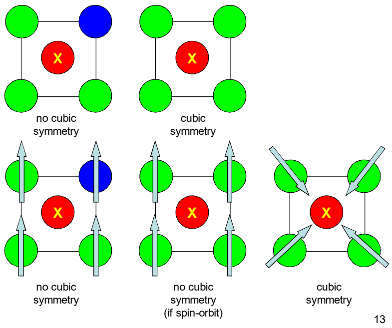
magnetic hyperfine interactions in solids

symmetry properties

chemical

chemical + magnetic



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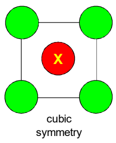
magnetic hyperfine interactions in solids

symmetry properties

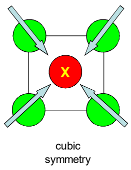
chemical



orbital and spin dipolar contributions vanish for cubic symmetry

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

chemical + magnetic



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magnetic hyperfine interactions in solids

case studies

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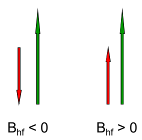
What does the sign mean:

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



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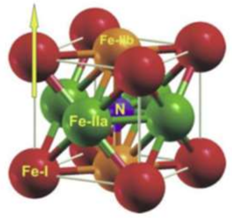
magnetic hyperfine interactions in solids

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

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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

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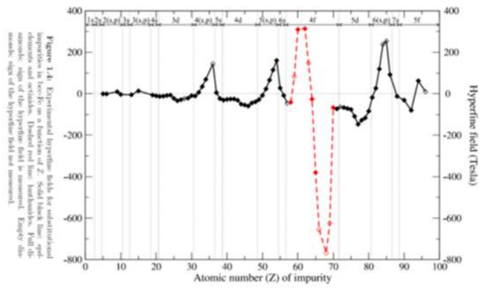
magnetic hyperfine interactions in solids

case studies

isolated substitutional impurities in bcc-Fe



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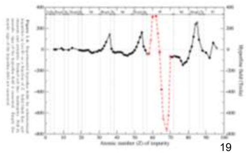
magnetic hyperfine interactions in solids
case studies

- 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)



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