Joint Research Centre

Neutrons and Magnetic Excitations

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Inelastic neutron scattering offers the ability to measure directly the interactions of magnetic moments with other magnetic moments and with the local environment.
A variety of problems can be investigated in a variety of systems:

- Single ion excitations
- crystal field measurements
- Clusters of spins
- One dimensional spin chains
- Two dimensional square lattices
- Three dimensional system

The neutron has a small dipole moment that causes it to scatter from inhomogeneous internal fields produced by electrons

The magnetic scattering cross section is similar in magnitude to the nuclear cross section

Elastic magnetic scattering probes static magnetic structure

Inelastic magnetic scattering probes spin dynamics

Polarized neutrons can distinguish magnetic and nuclear scattering and specific spin components

The neutron as a magnetic probe

The n^0 has a magnetic moment, due to some substructure of charged particles.

$$\overset{z}{m} = - g\, m_N\, \grave{s} \qquad g = 1.913, \quad m_N = \frac{-e}{2\, m_p}$$

A crude estimate (non-relativistic quarks, no quarks-gluons interaction):

n^0 = ddu, with quarks in s states (no angular momentum)

The magnetic moment of a quark in a s state is due to its spin:

$$\overset{z}{m}_Q = \frac{-e_Q}{2\, m_Q}\, \overset{''}{\bar{S}}_Q \quad \vdash Q = u,\ d;\ e_u = +2\,\hat{e}3,\ e_d = -1\,\hat{e}3,\ m_u > m_d = 350\ \mathrm{MeV}L$$

The spins of the three quarks add up to give the n^0 spin s = 1/2.

Racah algebra gives:

$$\mu_n = \frac{4}{3}\mu_{up} - \frac{1}{3}\mu_{down}$$

In good agreement with exp.

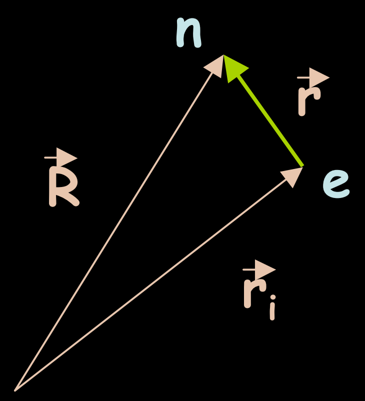
$$\frac{m_e}{m_N} = 960$$

A dipole in a magnetic field has potential energy

$$V(\mathbf{r}) = -\boldsymbol{\mu} \cdot \mathbf{B}(\mathbf{r}) = -\gamma\, \mu_N\, \hat{\sigma} \cdot \mathbf{B}(\mathbf{r})$$

The magnetic field that scatters the neutrons is due to currents and magnetic dipole moments of electrons.
For a single electron in $\mathbf{r}_i$, the field acting on a n^0 in $\mathbf{R} = \mathbf{r}_i + \mathbf{r}$ is:

$$\mathbf{B}_e(\mathbf{r}) = \frac{\mu_0}{4\pi} \nabla \times \frac{-g\, \mu_B\, \mathbf{s}_e \times \mathbf{r}}{r^3} - \frac{\mu_0}{4\pi} \frac{\mu_B}{\hbar} \left(\mathbf{p}_e \times \frac{\mathbf{r}}{r^3} + \frac{\mathbf{r}}{r^3} \times \mathbf{p}_e \right)$$



The total field **B**(**r**,t) in a sample of condensed matter is the sum of the fields generated by all the electrons and depends on the wavefunction of the system .

The matrix element defining the scattering amplitude is

$$|\langle \mathbf{k}', s', \lambda' | -\boldsymbol{\mu}\cdot\mathbf{B}(\mathbf{r}) | \mathbf{k}, s, \lambda\rangle| =$$

$$\mu_0 \, |\langle s' | \boldsymbol{\mu} | s\rangle \cdot \langle \lambda' | \mathbf{M}_\perp(\mathbf{q}) | \lambda\rangle|$$

where

$$-\mu_0 \mathbf{M}_\perp(\mathbf{q}) = \int \mathbf{B}(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{r}$$

The magnetic scattering of neutrons will therefore depends only on the transverse component of the magnetisation.

Ex. #1. Why?

Then, the pdcs for scattering of n^0 in the $|\uparrow>$ spin state into the spin state $<s'|$ at T = 0 is:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{s'} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left| \langle \lambda' | \mathbf{M}_\perp(\mathbf{q}) | 0\rangle \cdot \langle s' | \hat{\sigma} | \uparrow\rangle \right|^2 \delta(E_{\lambda'} - E_0 - \hbar\omega)$$

Ex. #2. Extend to non-zero temperatures

Recalling the matrix elements of the Pauli spin operators

$$\begin{pmatrix} \langle\uparrow|\hat{\sigma}_{\mathbf{x}}|\uparrow\rangle & \langle\uparrow|\hat{\sigma}_{\mathbf{x}}|\downarrow\rangle \\ \langle\downarrow|\hat{\sigma}_{\mathbf{x}}|\uparrow\rangle & \langle\downarrow|\hat{\sigma}_{\mathbf{x}}|\downarrow\rangle \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \langle\uparrow|\hat{\sigma}_{\mathbf{y}}|\uparrow\rangle & \langle\uparrow|\hat{\sigma}_{\mathbf{y}}|\downarrow\rangle \\ \langle\downarrow|\hat{\sigma}_{\mathbf{y}}|\uparrow\rangle & \langle\downarrow|\hat{\sigma}_{\mathbf{y}}|\downarrow\rangle \end{pmatrix} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\begin{pmatrix} \langle\uparrow|\hat{\sigma}_{\mathbf{z}}|\uparrow\rangle & \langle\uparrow|\hat{\sigma}_{\mathbf{z}}|\downarrow\rangle \\ \langle\downarrow|\hat{\sigma}_{\mathbf{z}}|\uparrow\rangle & \langle\downarrow|\hat{\sigma}_{\mathbf{z}}|\downarrow\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

one has (initial spin state $|\uparrow\rangle$):

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\uparrow} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left|\langle\lambda'|M_{\perp\mathbf{z}}(\mathbf{q})|0\rangle\right|^2 \delta(E_{\lambda'} - E_{\lambda} - \hbar\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\downarrow} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left|\langle\lambda'|M_{\perp\mathbf{x}}(\mathbf{q})|0\rangle + i\langle\lambda'|M_{\perp\mathbf{y}}(\mathbf{q})|0\rangle\right|^2 \delta(E_{\lambda'} - E_{\lambda} - \hbar\omega)$$

So, NSF scattering probes the components of $\mathbf{M}_{\perp}$ along the quantization axis of the n^0 spin, whilst SF scattering probes the components of $\mathbf{M}_{\perp}$ perpendicular to z.

Ex. #3. Work out the pdcs for $\downarrow\rightarrow\downarrow$ and $\downarrow\rightarrow\uparrow$ scattering

If the beam is unpolarised we have:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\downarrow} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left| \langle \lambda' \,|\, \mathbf{M}_\perp(\mathbf{q}) \,|\, 0 \rangle \right|^2 \delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

a) The spatial part of the matrix elements can be written in terms of $\mathbf{s}_\perp$, the electron spin component transverse to the momentum transfer $\mathbf{q}$.

$$\mathbf{M}_\perp(\mathbf{q}) = -2\mu_B \sum_n e^{i\mathbf{q}\cdot\mathbf{r}_n} \mathbf{s}_{\perp n}$$

b) Using the Fourier representation of the δ function, the pdcs at non-zero T can be written as a spin-spin time correlation function

$$\langle \mathbf{S}_\perp \cdot \mathbf{S}_\perp \rangle (\mathbf{q}, \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'} - \mathbf{r}_n)} \int_0^\infty e^{-i\omega t'} dt' \sum_\lambda p(E_\lambda) \langle \lambda \,|\, \mathbf{s}_{\perp n}(0) \cdot \mathbf{s}_{\perp n'}(t) \,|\, \lambda \rangle$$

For neutrons with initial spin state $|\uparrow\rangle$:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\uparrow} = A(\mathbf{q})\langle \mathbf{S}_{\perp}\cdot\hat{z}\ \mathbf{S}_{\perp}\cdot\hat{z}\rangle(\mathbf{q},\ \omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\downarrow} = A(\mathbf{q})[\langle(\mathbf{S}_{\perp})_{\perp}\cdot(\mathbf{S}_{\perp})_{\perp}\rangle(\mathbf{q},\ \omega) + i\langle(\mathbf{S}_{\perp}\times\mathbf{S}_{\perp})\cdot\hat{\mathbf{z}}\rangle(\mathbf{q},\ \omega)]$$

$(\mathbf{S}_{\perp})_{\perp}$ is the component of the spin perpendicular to $\mathbf{q}$ and $\mathbf{z}$.

NSF→ correlations of the $\mathbf{S}_{\perp}$ component || to the initial dir. of polarization

SF→ correlations of the $\mathbf{S}_{\perp}$ component ⊥ to the initial dir. of polarization

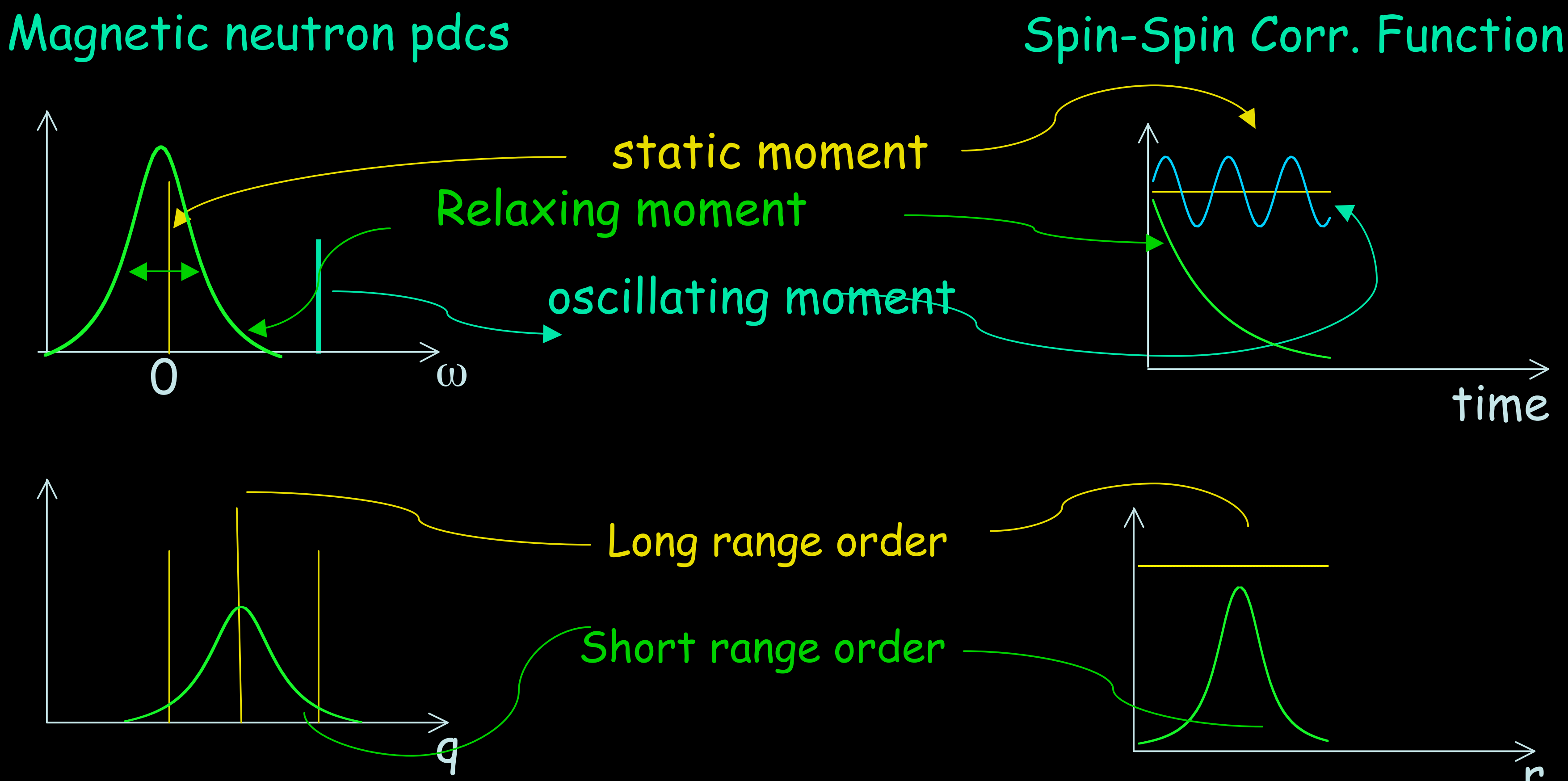
$$A(\mathbf{q}) = \frac{k_f}{k_i}\frac{(\gamma r_0)^2}{2\pi\hbar}|F(\mathbf{q})|^2\exp(-2W(\mathbf{q})) \qquad \gamma r_0 = 0.54\times10^{-12}\ \mathrm{cm}$$

Spin density spread out: scattering decreases at high *q*

$$F(\mathbf{q}) = \int s(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})\,d\mathbf{r}$$

The scalar function $s(\mathbf{r})$ is the density of unpaired e^- divided by their number

$\langle S_n^{\alpha}(0) S_{n'}^{\beta}(t) \rangle$ is the thermal average of the time dependent spin operator and corresponds to the van Hove correlation function: The probability of finding a spin $S_{n'}$ at site n' and at time t when the spin at position n is S_n at t=0



Γ : quasielastic broadening
κ : intrinsic linewidth

τ : lifetime
ξ : correlation length

$\Gamma = 1/\tau$
$\kappa = 1/\xi$

For unpolarised neutrons

$$\frac{d^2\sigma}{d\Omega dE'} = A(\mathbf{q})\langle \mathbf{S}_\perp \cdot \mathbf{S}_\perp \rangle(\mathbf{q}, \omega)$$

or

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \, |F(\mathbf{q})|^2 \, \exp(-2W(\mathbf{q})) \sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) S^{\alpha\beta}(\mathbf{q}, \omega)$$

$(\alpha, \beta = x, y, z)$

Ex. #4. Derive the above result.

$$S^{\alpha\beta}(\mathbf{q}, \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \int_0^\infty e^{-i\omega t'} dt' \sum_\lambda p(E_\lambda)\langle\lambda | s^\alpha{}_n(0)\, s^\beta{}_n(t) | \lambda\rangle$$

or, in terms of matrix elements:

$$S^{\alpha\beta}(\mathbf{q}, \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda | \mathbf{s}^\alpha{}_{n'} | \lambda'\rangle\langle\lambda' | \mathbf{s}^\beta{}_n | \lambda\rangle \delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

Inelastic Magnetic Scattering:

Squared form factor

DW factor

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \, |F(\mathbf{q})|^2 \, \exp(-2W(\mathbf{q}))$$

$$\sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) S^{\alpha\beta}(\mathbf{q}, \omega)$$

geometrical factor

Spin correlation function

For ions with unquenched orbital moment and for $q \rightarrow 0$

$$s_n^\alpha \longrightarrow \frac{1}{2} g J_n^\alpha \qquad \text{with} \quad g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)},$$

J_n^α being an effective angular momentum operator

For a wide class of systems $S^{\alpha\beta}$ satisfies useful sum-rules

Detailed balance

$$S^{\alpha\beta}(\mathbf{q},\ \omega) = \exp(\hbar\omega / k_B T)\ S^{\alpha\beta}(-\mathbf{q},\ -\omega)$$

Total moment

$$\frac{\hbar}{\int d\mathbf{q}} \sum_{\alpha} \int S^{\alpha\alpha}(\mathbf{q},\ \omega)\, d\mathbf{q}\, d\omega = S(S+1)$$

First moment sum-rule

$$\hbar^2 \int S(\mathbf{q},\ \omega)\, \omega\, d\omega = -\frac{1}{3N} \sum_{n,n'} J_{nn'} \langle \mathbf{s}_n \cdot \mathbf{s}_{n'} \rangle \left(1 - \cos \mathbf{q} \cdot (\mathbf{r}_{n'} - \mathbf{r}_n)\right)$$

The scattering function $S^{\alpha\beta}(q, \omega)$ is related to the generalized susceptibility $\chi^{\alpha\beta}$ by the fluctuation-dissipation theorem:

$$S^{\alpha\beta}(\mathbf{q}, \omega) = \frac{N\hbar}{\pi} \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \mathrm{Im}\chi^{\alpha\beta}(\mathbf{q}, \omega)$$

$\chi^{\alpha\beta}$ determines the response of the system to the magnetic field established by the neutron:

$$M^{\alpha}(\mathbf{q}, \omega) = \chi^{\alpha\beta}(\mathbf{q}, \omega) H^{\beta}(\mathbf{q}, \omega)$$

We convert inelastic scattering data to $\chi^{\alpha\beta}$ to
- Compare with bulk susceptibility data
- Analyse the temperature dependence of the response
- Compare with theories

Note that:

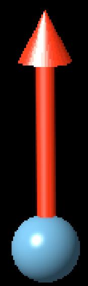
$$\chi(\mathbf{q}, 0) = \frac{1}{2\pi i} \int d\omega \frac{\mathrm{Im}\chi^{\alpha\beta}(\mathbf{q}, \omega)}{\omega}$$

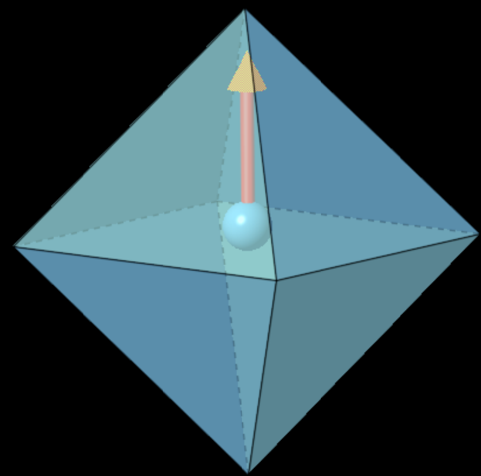
Single-ion Crystal Field Excitations

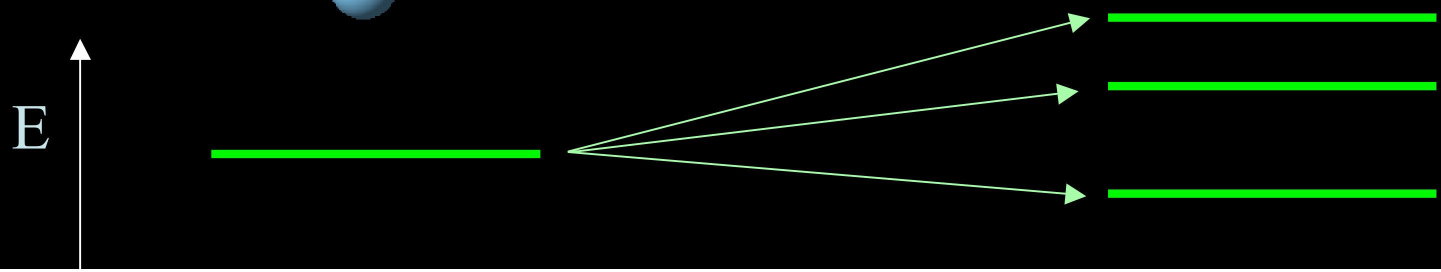
Weak coupling between magnetic ions: the excitation energies are independent from the scattering vector q. We have to deal with a single-ion problem.

Local charge symmetry lifts partially or totally the (2J+1)-fold degeneracy of the ground state multiplet

Isolated magnetic ion: complete rotational symmetry. The total angular momentum J is a good quantum number







The surrounding ions produce an electric field (CF) to which the charges of the central ions adjusts.

CF weak (4f, 5f): smaller than the spin-orbit interaction. Each multiplet J can be considered as isolated. The eigenstates are linear combinations of the 2J+1 free--ion eigenstates $|LSJM_J>$,

$$|\Gamma_n> = \sum_{M=-J}^{J} a_n(M) \, |JM_J>$$

The label Γ refers to the Bethe notation for the IR of the group of rotations.

CF intermediate (3d): if it is stronger than the spin-orbit interaction but weaker than the intra-atomic Coulomb electron-electron interaction. J is no more a good quantum number. The CF effects must be considered on the $|LSM_LM_S>$ states, then the SO corrections must be applied. L and S are good quantum numbers.

CF strong (4d, 5d): comparable to the intra-atomic Coulomb interaction. The CF modifies the state of each single electron. L is not a good quantum number.

The potential in a point $\mathbf{r}$ due to a charge distribution is

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' =$$

$$= \sum_{km} r^k Y_{km}(\hat{\mathbf{r}}) \frac{4\pi}{2k+1} \int_r^\infty \rho(\mathbf{r}') \left(\frac{1}{r'}\right)^{k+1} Y_{km}(\hat{\mathbf{r}}') d\hat{\mathbf{r}}' +$$

$$+ \sum_{km} \left(\frac{1}{r}\right)^{k+1} Y_{km}(\hat{\mathbf{r}}) \frac{4\pi}{2k+1} \int_0^r \rho(\mathbf{r}') (r')^k Y^*_{km}(\hat{\mathbf{r}}') d\hat{\mathbf{r}}'$$

With the following definitions,

$$A_{km} = \frac{4\pi}{2k+1} \int_{r_0}^\infty \rho(\mathbf{r}') \left(\frac{1}{r'}\right)^{k+1} Y_{km}(\hat{\mathbf{r}}') d\hat{\mathbf{r}}'$$

$$A'_{km} = \frac{4\pi}{2k+1} \int_0^{r_0} \rho(\mathbf{r}') (r')^k Y^*_{km}(\hat{\mathbf{r}}') d\hat{\mathbf{r}}'$$

$$B'_{km} = \sqrt{\frac{2k+1}{4\pi}} \left(r^k A_{km} + r^{-(k+1)} A'_{km} \right) \qquad C^k_m(\hat{\mathbf{r}}) = \sqrt{\frac{4\pi}{2k+1}} Y_{km}(\hat{\mathbf{r}})$$

One has:

$$V(\mathbf{r}) = \sum_{k=0,2,4,6} \sum_{m=-k}^{+k} B'_{km}(r)\, C_m^k(\hat{\mathbf{r}})$$

$$V(\mathbf{r}) = \sum_{k=0,2,4,6} \sum_{m=0}^{+k} B''_{km}(r)\left[C_m^k(\hat{\mathbf{r}}) + C_{-m}^k(\hat{\mathbf{r}})\right]$$

$C_m^k(\hat{\mathbf{r}})$ are the Racah tensor operators.

The potential energy of the Z valence electrons of a magnetic ions is:

$$W = -|e| \sum_{i=1}^{Z} V(\mathbf{r}_i)$$

To calculate eigenstates and eigenfunctions in the CF, the matrix elements of the CF potential operator must be evaluated in the basis of the free ion states.

Stevens method of operator equivalents

It consists in the application of the Wigner-Eckart theorem to the calculation of matrix elements of the operator which results from the expansion of W in spherical harmonics.

$\hat{T}_{km} = r^k Y_{km}(\hat{r})$ is an irreducible tensor operator

$$\langle jm | \hat{T}_{kn} | jm' \rangle = \frac{1}{\sqrt{2j+1}} \langle jm' kn | jm \rangle \langle j \| \hat{T}_k \| j \rangle$$

Clebsch-Gordan coefficient containing the directional properties

Scalar matrix element associated to the dynamics of the system

$$\langle jm | \hat{O}_k^n (\hat{J}_z, \hat{J}_\pm) | jm' \rangle = \frac{1}{\sqrt{2j+1}} \langle jm' kn | jm \rangle \langle j \| \hat{O}_k \| j \rangle$$

$$\langle jm | \hat{T}_{kn} | jm' \rangle = \frac{\langle j \| \hat{T}_k \| j \rangle}{\langle j \| \hat{O}_k \| j \rangle} \langle jm | \hat{O}_k^n (\hat{J}_z, \hat{J}_\pm) | jm' \rangle$$

$$\langle jm | \hat{T}_{kn} | jm' \rangle = \alpha(k, j) \langle jm | \hat{O}_k^n (\hat{J}_z, \hat{J}_\pm) | jm' \rangle$$

1) write W as a linear combination of homogeneous polynomial with proper symmetry.
2) Substitutes the one-electron coordinate operators (x_i,y_i,z_i) by the corresponding components of J (beware of non-commuting properties). For instance.

$$\sum_{i=1}\left(3z_i^2-r_i^2\right)\rightarrow\alpha_J\langle r^2\rangle\left(3J_z^2-J(J+1)\right)\equiv\alpha_J\langle r^2\rangle\hat{O}_2^0$$

$$\sum_{i=1}\left(x_i^2-y_i^2\right)\rightarrow\alpha_J\langle r^2\rangle\left(J_x^2-J_y^2\right)\equiv\alpha_J\langle r^2\rangle\hat{O}_2^2$$

$$\sum_{i=1}\left(x_i^4-6x_i^2y_i^2+y_i^4\right)\rightarrow\beta_J\langle r^4\rangle\frac{1}{2}\left(J_+^4+J_-^4\right)\equiv\beta_J\langle r^4\rangle\hat{O}_4^4$$

$$\sum_{i=1}\left(x_i^6-15x_i^4y_i^2+15x_i^2y_i^4-y_i^6\right)\rightarrow\gamma_J\langle r^6\rangle\frac{1}{2}\left(J_+^6+J_-^6\right)\equiv\gamma_J\langle r^6\rangle\hat{O}_6^6$$

z is a crystal axis. The constants α_J (2nd order) β_J (4th order) and γ_J (6th order) depends on Z, L, S and J, but not on M_J. Then

$$H^{CF}=\sum_{k=0}^{\min(2\ell,2j)}\sum_{m=0}^{k}B_k^n\hat{O}_k^n$$

with k even and m equal to a multiple of the order of rotational symmetry around z

$$J = 1, 3/2 \quad k = 0 \quad 2$$

$$J = 2, 5/2 \quad k = 0 \quad 2 \quad 4$$

$$J = 3, 7/2 \quad k = 0 \quad 2 \quad 4 \quad 6$$

Examples of Stevens Operator Equivalents

$$\hat{O}_2^0 = 3 S_z^2 - S(S+1)$$

$$\hat{O}_2^1 = \frac{1}{4}[S_z(S_+ + S_-) + (S_+ + S_-)S_z]$$

$$\hat{O}_2^2 = \frac{1}{2}[S_+^2 + S_-^2]$$

$$\hat{O}_4^0 = 35 S_z^4 - [30 S(S+1) - 25] S_z^2 - 6 S(S+1) + 3 S^2 (S+1)^2$$

$$\hat{O}_4^1 = \frac{1}{4}\{[7 S_z^2 - 3 S(S+1) - 1] S_z (S_+ + S_-) + (S_+ + S_-) S_z [7 S_z^2 - 3 S(S+1) - 1]\}$$

$$\hat{O}_4^2 = \frac{1}{4}\{[7 S_z^2 - S(S+1) - 5](S_+^2 + S_-^2) + (S_+^2 + S_-^2)[7 S_z^2 - S(S+1) - 5]\}$$

$$\hat{O}_4^3 = \frac{1}{4}[S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3) S_z]$$

$$\hat{O}_4^4 = \frac{1}{2}(S_+^4 + S_-^4)$$

Cubic symmetry, quantization axis along the 4-fold axis

$$H_c^{CF} = B_4 \left(\hat{O}_4^0 + 5\,\hat{O}_4^4\right) + B_6 \left(\hat{O}_6^0 - 21\,\hat{O}_6^4\right)$$

Tetragonal symmetry (D_{4h})

$$H_t^{CF} = B_2^0\,\hat{O}_2^0 + B_4^0\,\hat{O}_4^0 + B_4^4\,\hat{O}_4^4 + B_6^0\,\hat{O}_6^0 + B_6^4\,\hat{O}_6^4$$

Trigonal symmetry (D_{3d}), up to fourth order

$$H_{tr}^{CF} = B_2^0\,\hat{O}_2^0 + B_4^0\,\hat{O}_4^0 - \frac{2}{3}\,B_4 \left(\hat{O}_4^0 + 20\sqrt{2}\,\hat{O}_4^3\right)$$

Example 1 $$H^{CF} = D\left(J_z^2 - \frac{1}{3} J(J+1)\right) + \frac{1}{2} E\left({J_+}^2 + {J_-}^2\right)$$

Matrix elements in the |JM> basis

$$\langle M' | J_z^2 | M\rangle = M^2 \delta_{M'M}$$
$$\langle M' | J_+^2 | M\rangle = \sqrt{(J-M)(J-M-1)(J+M+1)(J+M+2)}\, \delta_{M'M+2}$$
$$\langle M' | J_-^2 | M\rangle = \sqrt{(J+M)(J+M-1)(J-M+1)(J-M+2)}\, \delta_{M'M-2}$$

$$\langle JM' | H^{CF} | JM\rangle =$$
$$D\left(\langle M' | J_z^2 | M\rangle - \frac{1}{3} J(J+1)\delta_{M'M}\right) + \frac{E}{2}\langle M' | J_+^2 | M\rangle + \frac{E}{2}\langle M' | J_-^2 | M\rangle$$

Secular equation

$$\det\left(\langle JM' | H^{CF} | JM\rangle - \varepsilon\delta_{M'M}\right) = 0$$

J = 3/2

$$H^{CF} = \begin{pmatrix} D & 0 & \sqrt{3}\,E & 0 \\ 0 & -D & 0 & \sqrt{3}\,E \\ \sqrt{3}\,E & 0 & -D & 0 \\ 0 & \sqrt{3}\,E & 0 & D \end{pmatrix}$$

Eigenvalues

$$\left\{0, 0, 2\sqrt{D^2 + 3\,E^2}, 2\sqrt{D^2 + 3\,E^2}\right\}$$

Eigenvectors

$$a_1 \mid -3/2 > + a_2 \mid -1/2 > + a_3 \mid 1/2 > + a_4 \mid 3/2 >$$

$$-\frac{D + \sqrt{D^2 + 3\,E^2}}{\sqrt{3}\,E} \mid -1/2 > + \mid 3/2 > \qquad \frac{-D + \sqrt{D^2 + 3\,E^2}}{\sqrt{3}\,E} \mid -1/2 > + \mid 3/2 >$$

$$-\frac{-D + \sqrt{D^2 + 3\,E^2}}{\sqrt{3}\,E} \mid -3/2 > + \mid 1/2 > \qquad \frac{D + \sqrt{D^2 + 3\,E^2}}{\sqrt{3}\,E} \mid -3/2 > + \mid 1/2 >$$

INS cross-section for CF excitations

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \, |F(\mathbf{q})|^2 \, \exp(-2W(\mathbf{q})) \sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) S^{\alpha\beta}(\mathbf{q},\omega)$$

$$S^{\alpha\beta}(\mathbf{q},\omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda|\mathbf{s}^\alpha{}_{n'}|\lambda'\rangle\langle\lambda'|\mathbf{s}^\beta{}_n|\lambda\rangle\,\delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

Single ion excitations: n'=n.   N identical ion

$$S^{\alpha\beta}(\mathbf{q},\omega) = N \sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda|\mathbf{s}^\alpha|\lambda'\rangle\langle\lambda'|\mathbf{s}^\beta|\lambda\rangle\,\delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

Average in **q**-space for a polycrystal sample:

$$\frac{1}{4\pi}\int_{4\pi}\sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) S^{\alpha\beta}(\mathbf{q},\omega)\, d\Omega = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\sum_\alpha\left(1 - \frac{q_\alpha^2}{q^2}\right) S^{\alpha\alpha}\sin\theta\, d\theta\, d\phi = \frac{2}{3}\sum_\alpha S^{\alpha\alpha}$$

So that

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|\, F(\mathbf{q}) \,|^2 \exp(-2W(\mathbf{q})) \times$$

$$\times \frac{2}{3} N \sum_{\lambda,\lambda'} \sum_{\alpha} p(E_\lambda) |\langle \lambda | s^\alpha | \lambda' \rangle|^2 \delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

with

$$\sum_\alpha |\langle \lambda | s^\alpha | \lambda' \rangle|^2 = |\langle \lambda | s^z | \lambda' \rangle|^2 + \frac{1}{2}\left(|\langle \lambda | s_+ | \lambda' \rangle|^2 + |\langle \lambda | s_- | \lambda' \rangle|^2\right)$$

Ex. #5: prove the above relation

Esempio. $S = 5$

$D=3B_2^0 = -25\ \mu eV$, $B_4^0 = 9\times10^{-4}\ \mu eV$, $B_4^4 = 7\times10^{-4}\ \mu eV$

$$S_+|m,S\rangle = \hbar\sqrt{(S-m)(S+m+1)}|m+1,S\rangle$$

$$S_-|m,S\rangle = \hbar\sqrt{(S-m+1)(S+m)}|m-1,S\rangle$$

$$S_z|m,S\rangle = \hbar m|m,S\rangle$$

$$S^2|m,S\rangle = \hbar^2 S(S+1)|m,S\rangle$$

$$\langle m',S|D\left(S_z^2-\frac{1}{3}S(S+1)\right)|m,S\rangle = D\left(m^2-\frac{1}{3}S(S+1)\right)\delta_{m',m}$$

$$\langle m',S|B_4^0\hat{O}_4^0|m,S\rangle = B_4^0\left[35m^4-(30S(S+1)-25)m^2-6S(S+1)+3S^2(S+1)^2\right]\delta_{m',m}$$

$$\langle m',S|B_4^4\hat{O}_4^4|m,S\rangle =$$

$$\frac{B_4^4}{2}\left(\sqrt{\prod_{i=0}^{3}(S-m-i)\prod_{i=1}^{4}(S+m+i)}\,\delta_{m+4,m}+\sqrt{\prod_{i=1}^{4}(S-m+i)\prod_{i=0}^{3}(S+m-i)}\,\delta_{m-4,m}\right)$$

$M = -5, -4, -3 \ldots\ldots 4, 5$

$$\langle M'|H^{CF}|M\rangle = \begin{pmatrix}
-\frac{93183}{250} & 0 & 0 & 0 & 3.484 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\frac{38067}{250} & 0 & 0 & 0 & 3.851 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{5683}{250} & 0 & 0 & 0 & 4.080 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{74811}{500} & 0 & 0 & 0 & 4.158 & 0 & 0 & 0 \\
3.484 & 0 & 0 & 0 & \frac{28314}{125} & 0 & 0 & 0 & 4.080 & 0 & 0 \\
0 & 3.851 & 0 & 0 & 0 & \frac{63067}{250} & 0 & 0 & 0 & 3.851 & 0 \\
0 & 0 & 4.080 & 0 & 0 & 0 & \frac{28314}{125} & 0 & 0 & 0 & 3.484 \\
0 & 0 & 0 & 4.158 & 0 & 0 & 0 & \frac{74811}{500} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 4.080 & 0 & 0 & 0 & \frac{5683}{250} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 3.851 & 0 & 0 & 0 & -\frac{38067}{250} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 3.484 & 0 & 0 & 0 & -\frac{93183}{250}
\end{pmatrix}$$

Diagonalization of the matrix gives eigenvalues and eigenvectors

ENERGY (μeV)	Eigenfunctions
0	$\vert\lambda_{0-}> \ = 1.0\ \vert 5,-5>$
0	$\vert\lambda_{0+}> \ = 1.0\ \vert 5,5>$
220.45	$\vert\lambda_{1}> \ = \sqrt{2}\ \vert 5,4> + \sqrt{2}\ \vert 5,-4>$
220.46	$\vert\lambda_{2}> \ = \sqrt{2}\ \vert 5,4> - \sqrt{2}\ \vert 5,-4>$
395.45	$\vert\lambda_{3}> \ = -1.0\ \vert 5,3>$
395.45	$\vert\lambda_{4}> \ = 1.0\ \vert 5,-3>$
522.0	$\vert\lambda_{5}> \ = -\sqrt{2}\ \vert 5,-2> + \sqrt{2}\ \vert 5,2>$
522.63	$\vert\lambda_{6}> \ = -\sqrt{2}\ \vert 5,-2> - \sqrt{2}\ \vert 5,2>$
500.22	$\vert\lambda_{7}> \ = -1.0\ \vert 5,-1>$
500.22	$\vert\lambda_{8}> \ = -1.0\ \vert 5,1>$
624.98	$\vert\lambda_{9}> \ = -1.0\ \vert 5,0>$

Transition probability from the ground state doublet to the 1st excited level

$$|\langle\lambda_1|S_\perp|\lambda_{0+}\rangle|^2 + |\langle\lambda_1|S_\perp|\lambda_{0-}\rangle|^2 = \frac{1}{2}\left(|\langle 5,4|S_-|5,5\rangle|^2 + |\langle 5,-4|S_+|5,-5\rangle|^2\right) = 10$$

Intermultiplet transitions in f-electron systems

We assume that a nf^m configuration is well separated in energy from other configurations: interactions within the *nf shell are dominant*. The appropriate base states are Slater determinants, with elements

$$\psi_{n\ell m_\ell m_s}(\mathbf{r}) = \frac{1}{r} R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi)\, \chi_{m_\ell s}$$

In spherical symmetry these states are degenerate. The intra-atomic Coulomb repulsion remove the degeneracy.

As the Coulomb repulsion is diagonal in the basis $|\gamma SLM_L M_S>$, the

nf^m configuration splits into Russell-Saunders terms ^{2S+1}L, which are $(2S+1)(2L+1)$ times degenerate.

The energy of the terms is given by linear combinations of Slater integrals

$F^{(k)}$ $(k = 0, 2, 4, 6)$

$$F^{(k)} = e^2 \int_0^\infty dr_i \int_0^\infty dr_j \, \frac{r_<^k}{r_>^{k+1}} \left(R_{nf}(r_i) R_{nf}(r_j)\right)^2$$

Example: $4f^2$

$F_2 = F^{(2)}/225;\ F_4 = F^{(4)}/1089;\ F_6 = 25F^{(6)}/184041$

$E(^3H) = F_0 - 25F_2 - 51F_4 - 13F_6$

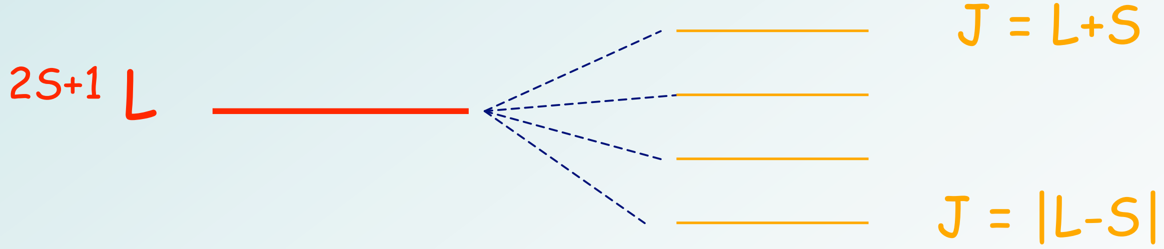
$E(^3F) = F_0 - 10F_2 - 33F_4 - 286F_6$

$E(^1G) = F_0 - 30F_2 + 97F_4 + 78F_6$

Spin-orbit interaction (diagonal in J, small compared to Coulomb):

$$H_{SO} = \sum_i \xi_i(r)\, \boldsymbol{\ell}_i \cdot \mathbf{s}_i = \zeta\, \mathbf{L}\cdot\mathbf{S}$$

where ζ is a radial integral of $\xi(r)$. The SO interaction lifts the degeneracy of the ^{2S+1}L terms, and leads to the formation of J multiplets



L and S are not good quantum numbers; if the SO is strong, levels with the same J but different L and S are mixed: IC

Example $^3H \rightarrow {}^3H_4,\ {}^3H_5,\ {}^3H_6$

The degeneration of J multiplets is partially removed by the CF.
If the CF is strong, J-mixing effects may be important.

In summary: the structure of f multiplets is determined by the 3 Slater integrals, describing the intra.f Coulomb interaction, and by the spin-orbit parameter. These parameters are known with high accuracy for free ions.
INS experiments of intermultiplet transitions allow determining their value also in:

- Metallic systems with unstable magnetic moments
- Intermediate valence systems
- Heavy s (strong hybridization of f electrons with conduction band)
- Systems with delocalised f electrons (actinides).

Inter-terms or Coulomb transitions: $\Delta L \neq 0$; information on Coulomb repulsion between f electrons; probe intra-atomic correlations and depend on Coulomb between *f* electrons. Influenced by the environment.

Intra-term or spin-orbit transitions: L and S do not change, their relative orientation does. $\Delta L = 0$, $\Delta S = 0$, $\Delta J = \pm 1, \pm 2$…. Probing spin-orbit interactions.

INS cross-section for J', J transitions and energy gap Δ.
(Lovesey, Balcar)

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} r_0^2 G(\mathbf{Q}, J, J')d(\hbar\omega - \Delta)$$

$$G(Q, J, J') = \sum_{k'} \frac{3}{k'+1}\left[A(k'-1,k') + B(k'-1,k')\right]^2 +$$

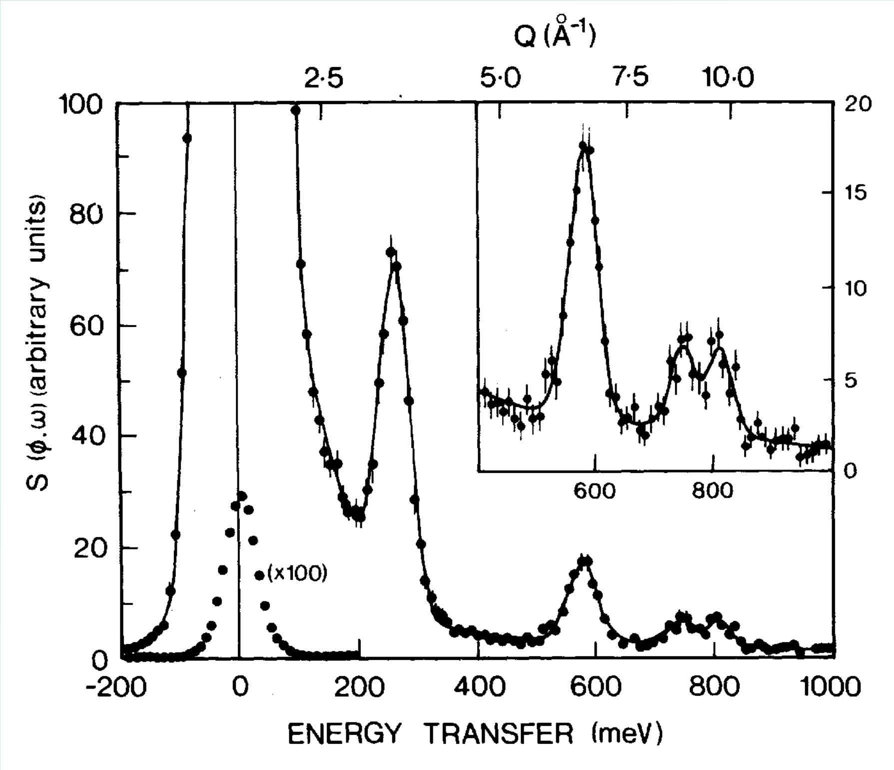
$$\sum_k \frac{3}{2k+1}\left[B(k,k)\right]^2 \qquad (k = 2, 4, 6 \quad k' = 1, 3, 5, 7)$$

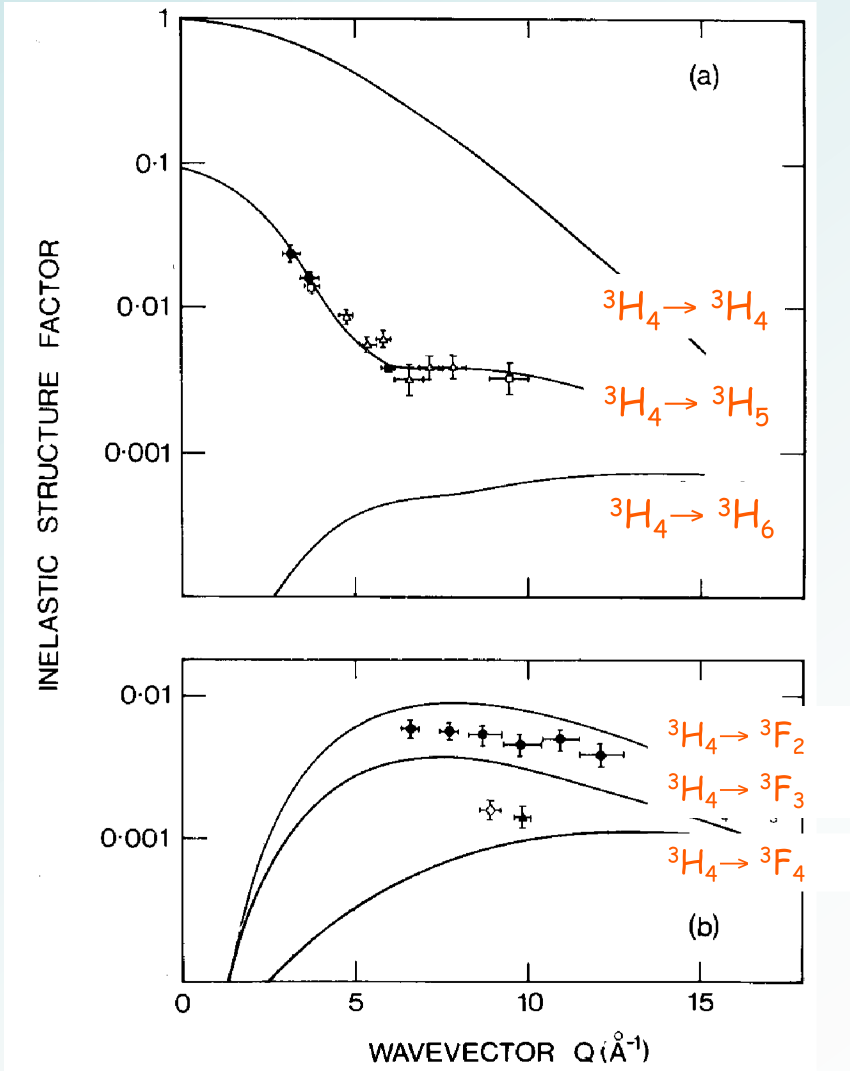
The quantities A(k, k') e B(k, k') are determined by radial integrals

$$\langle j_k(Q)\rangle = \int_0^\infty j_k(QR)\, r^2 R_f^2(r)$$

Coulomb Transitions in Pr metal. A.D. Taylor et al., PRL, 61, 1309 (1988)

Ground state: $^3H_4$ (f^2)





Transition		E (meV)
$^3H_4$	$^3H_5$	261
$^3H_4$	$^3H_6$	529
$^3H_4$	$^3F_2$	578
$^3H_4$	$^3F_3$	751
$^3H_4$	$^3F_4$	809

F_2 = 36.0 meV
F_4 = 5.69 meV
F_6 = 0.55 meV
ζ = 92.2 meV

The Slater integral F_2 is reduced to 90% of the value observed in free ions: The Coulomb repulsion in the metal is reduced by electrostatic screening

Exchange-coupled spins

Dinuclear systems

$$H_{ex} = \vec{S}_A \cdot \overline{D} \cdot \vec{S}_B$$

$$D_{ij} = \frac{1}{3}\,(D_{xx} + D_{yy} + D_{zz})\,\delta_{ij} + \frac{1}{2}\,(D_{ij} - D_{ji}) + \left(\frac{1}{2}\,(D_{ij} + D_{ji}) - \frac{1}{3}\,(D_{xx} + D_{yy} + D_{zz})\,\delta_{ij}\right)$$

$$J = -\frac{1}{3}\,(D_{xx} + D_{yy} + D_{zz})$$

$$d_{ij} = -d_{ji} = \frac{1}{2}\,(D_{ij} - D_{ji})$$

$$\vec{d} = (d_{yz},\, d_{zx},\, d_{xy})$$

$$D^0_{ij} = D^0_{ji} = \frac{1}{2}\,(D_{ij} + D_{ji}) + J$$

$$H_{ex} = -J\,\vec{S}_A \cdot \vec{S}_B + \vec{d} \cdot \left(\vec{S}_A \wedge \vec{S}_B\right) + \vec{S}_A \cdot \overline{D}^0 \cdot \vec{S}_B$$

$$-J\,\vec{S}_A \cdot \vec{S}_B = \text{ isotropic exchange}$$

$$\vec{d} \cdot \left(\vec{S}_A \wedge \vec{S}_B\right) = \text{ antisymmetric exchange}$$

$$\vec{S}_A \cdot \overline{D}^0 \cdot \vec{S}_B = \text{ asymmetric exchange}$$

Polynuclear clusters. Isotropic exchange

$$H_{Ex} = -\sum_{h=i}^{N}\sum_{k<h}^{N} J_{hk}\, S_h \cdot S_k$$

With N centres of spin S there are $(2S+1)^N$ energy levels

- If the isotropic exchange dominates the $(2S+1)^N$ states can be grouped as S_{tot}
- The magnetic anisotropy can be handled as a perturbation of the low lying S_{tot} states

Matrix elements are linear combinations of pair – interaction matrices :

$$< I \mid H^{iso} \mid J > = \sum_{h=1}^{N} \sum_{k>h}^{N} c_{hk} < I \mid \vec{S}_h \cdot \vec{S}_k \mid J >$$

with coefficients c_{hk} determined by exchange integrals $J_{hk.}$

Uncoupled basis states :

$$\mid I > = \mid S_1\, M_1 > \mid S_2\, M_3 > \cdots \mid S_N\, M_N >$$

A base with dimension $n = \prod_{1=1}^{N} (2\, S_i + 1)$ is obtained

$$\vec{S}_h \cdot \vec{S}_k = S_{hx} S_{kx} + S_{hy} S_{ky} + S_{hz} S_{kz} =$$

$$= \frac{1}{2} (S_{h+} S_{k-} + S_{h-} S_{k+}) + S_{hz} S_{kz}$$

The matrix elements are immediately obtained from the eigenvalues equations:

$$S_{h+} | S_h M_h \succ = \sqrt{(S_h + M_h + 1)(S_h - M_h)} \, | S_h M_h + 1 \succ$$

$$S_{h-} | S_h M_h \succ = \sqrt{(S_h - M_h + 1)(S_h + M_h)} \, | S_h M_h - 1 \succ$$

$$S_{hz} | S_h M_h \succ = M_h | S_h M_h \succ$$

Then:

☹ $S_{h+}\, S_{k-}\, |\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ =$

$$= \sqrt{(S_h + M_h + 1)\,(S_h - M_h)}\;\sqrt{(S_k - M_k + 1)\,(S_k + M_k)} \times$$

$$\left|\, S_1\, M_1 \cdots S_h\, M_h + 1 \quad S_k\, M_k - 1 \cdots S_N\, M_N \succ\right.$$

☹ $S_{h-}\, S_{k+} \left|\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ = \right.$

$$= \sqrt{(S_h - M_h + 1)\,(S_h + M_h)}\;\sqrt{(S_k + M_k + 1)\,(S_k - M_k)} \times$$

$$\left|\, S_1\, M_1 \cdots S_h\, M_h - 1 \cdots S_k\, M_k + 1 \cdots S_N\, M_N \succ\right.$$

☹ $S_{hz}\, S_{kz} \left|\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ = \right.$

$$M_h\, M_k \,|\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ$$

Diagonal Elements :

$$\langle \cdots S_h\, M_h' \cdots S_k\, M_k' \cdots |\, S_{hz}\, S_{kz}\, |\, \cdots S_h\, M_h \cdots S_k\, M_k \cdots \rangle = M_h\, M_k\, \delta_{M_h' M_h}\, \delta_{M_k' M_k}$$

Non – Diagonal Elements :

$$\langle \cdots S_h\, M_h' \cdots S_k\, M_k' \cdots |\, S_{h+}\, S_{k-}\, |\, \cdots S_h\, M_h \cdots S_k\, M_k \cdots \rangle =$$
$$\sqrt{(S_h + M_h + 1)\,(S_h - M_h)}\,\sqrt{(S_k - M_k + 1)\,(S_k + M_k)} \times \delta_{M_h'\, M_h+1}\, \delta_{M_k'\, M_k-1}$$

$$\langle \cdots S_h\, M_h' \cdots S_k\, M_k' \cdots |\, S_{h-}\, S_{k+}\, |\, \cdots S_h\, M_h \cdots S_k\, M_k \cdots \rangle =$$
$$\sqrt{(S_h - M_h + 1)\,(S_h + M_h)}\,\sqrt{(S_k + M_k + 1)\,(S_k - M_k)} \times \delta_{M_h'\, M_h-1}\, \delta_{M_k'\, M_k+1}$$

The same result can be obtained using compound spherical tensors to build the scalar product:

$$\vec{S}_h \cdot \vec{S}_k = -\hat{S}_{h\,1,+1}\,\hat{S}_{k\,1,-1} + \hat{S}_{h\,1,0}\,\hat{S}_{k\,1,0} - \hat{S}_{h\,1,-1}\,\hat{S}_{k\,1,+1}$$

$$\begin{aligned}
&\langle \cdots S_h\, M_h^{'} \quad S_k\, M_k^{'} \cdots \,|\, \vec{S}_h \cdot \vec{S}_k \,|\, \cdots S_h\, M_h \quad S_k\, M_k \cdots \rangle = \\
&= - \langle S_h\, M_h^{'} \,|\, \hat{S}_{h\,1,+1} \,|\, S_h\, M_h \rangle \langle S_k\, M_k^{'} \,|\, \hat{S}_{k\,1,-1} \,|\, S_k\, M_k \rangle + \\
&\qquad + \langle S_h\, M_h^{'} \,|\, \hat{S}_{h\,1,0} \,|\, S_h\, M_h \rangle \langle S_k\, M_k^{'} \,|\, \hat{S}_{k\,1,0} \,|\, S_k\, M_k \rangle - \\
&\qquad - \langle S_h\, M_h^{'} \,|\, \hat{S}_{h\,1,-1} \,|\, S_h\, M_h \rangle \langle S_k\, M_k^{'} \,|\, \hat{S}_{k\,1,+1} \,|\, S_k\, M_k \rangle
\end{aligned}$$

using the Wigner – Eckart theorem

$$\prec \cdots S_h\, M_h^{'} \quad S_k\, M_k^{'} \cdots \left| \vec{S}_h \cdot \vec{S}_k \right| \cdots S_h\, M_h \quad S_k\, M_k \cdots \succ =$$

$$-\left[(-1)^{S_h - M'_h} \begin{pmatrix} S_h & 1 & S_h \\ -M_h^{'} & +1 & M_h \end{pmatrix} \langle S_h \| \vec{S}_h \| S_h \rangle\right]\left[(-1)^{S_k - M'_k} \begin{pmatrix} S_k & 1 & S_k \\ -M_k^{'} & -1 & M_k \end{pmatrix} \langle S_k \| \vec{S}_k \| S_k \rangle\right] +$$

$$+\left[(-1)^{S_h - M'_h} \begin{pmatrix} S_h & 1 & S_h \\ -M_h^{'} & 0 & M_h \end{pmatrix} \langle S_h \| \vec{S}_h \| S_h \rangle\right]\left[(-1)^{S_k - M'_k} \begin{pmatrix} S_k & 1 & S_k \\ -M_k^{'} & 0 & M_k \end{pmatrix} \langle S_k \| \vec{S}_k \| S_k \rangle\right] -$$

$$-\left[(-1)^{S_h - M'_h} \begin{pmatrix} S_h & 1 & S_h \\ -M_h^{'} & -1 & M_h \end{pmatrix} \langle S_h \| \vec{S}_h \| S_h \rangle\right]\left[(-1)^{S_k - M'_k} \begin{pmatrix} S_k & 1 & S_k \\ -M_k^{'} & +1 & M_k \end{pmatrix} \langle S_k \| \vec{S}_k \| S_k \rangle\right]$$

Use of the formulae for 3 j – symbols, recalling that $\langle J \| \vec{J} \| J \rangle = \sqrt{J(J+1)}$, gives

$$\prec \cdots S_h\, M_h^{'} \quad S_k\, M_k^{'} \cdots \left| \vec{S}_h \cdot \vec{S}_k \right| \cdots S_h\, M_h \quad S_k\, M_k \cdots \succ =$$

$$= M_h\, M_k\, \delta_{M_h^{'}\, M_h}\, \delta_{M_k^{'}\, M_k} +$$

$$+ \frac{1}{2} \sqrt{(S_h + M_h + 1)(S_h - M_h)} \sqrt{(S_k - M_k + 1)(S_k + M_k)} \times \delta_{M_h^{'}\, M_h+1}\, \delta_{M_k^{'}\, M_k-1} +$$

$$+ \frac{1}{2} \sqrt{(S_h - M_h + 1)(S_h + M_h)} \sqrt{(S_k + M_k + 1)(S_k - M_k)} \times \delta_{M_h^{'}\, M_h-1}\, \delta_{M_k^{'}\, M_k+1}$$

Homonuclear dimer

Allowed spin states : $| S_A - S_B | \leqslant S \leqslant S_A + S_B$

$$S^2 = \left(\vec{S}_A + \vec{S}_B\right)^2 = S_A^2 + S_B^2 + 2\,\vec{S}_A \cdot \vec{S}_B$$

$$H_{ex} = -\frac{1}{2}\,J\left(S^2 - S_A^2 - S_B^2\right)$$

Matrix Elements :

$$\langle S'\,M' \mid H_{ex} \mid SM\rangle = -\frac{1}{2}\,J[S\,(S+1) - S_A\,(S_A+1) - S_B\,(S_B+1)]\,\delta_{S'\,S}\ \ \delta_{M'M}$$

After translation by a constant, the eigenvalues are

$$\varepsilon_S = -\frac{1}{2}\,J\,S\,(S+1) \qquad\qquad 0 \le S \le 2S_A$$

Example $S_A = S_B = 1/2$

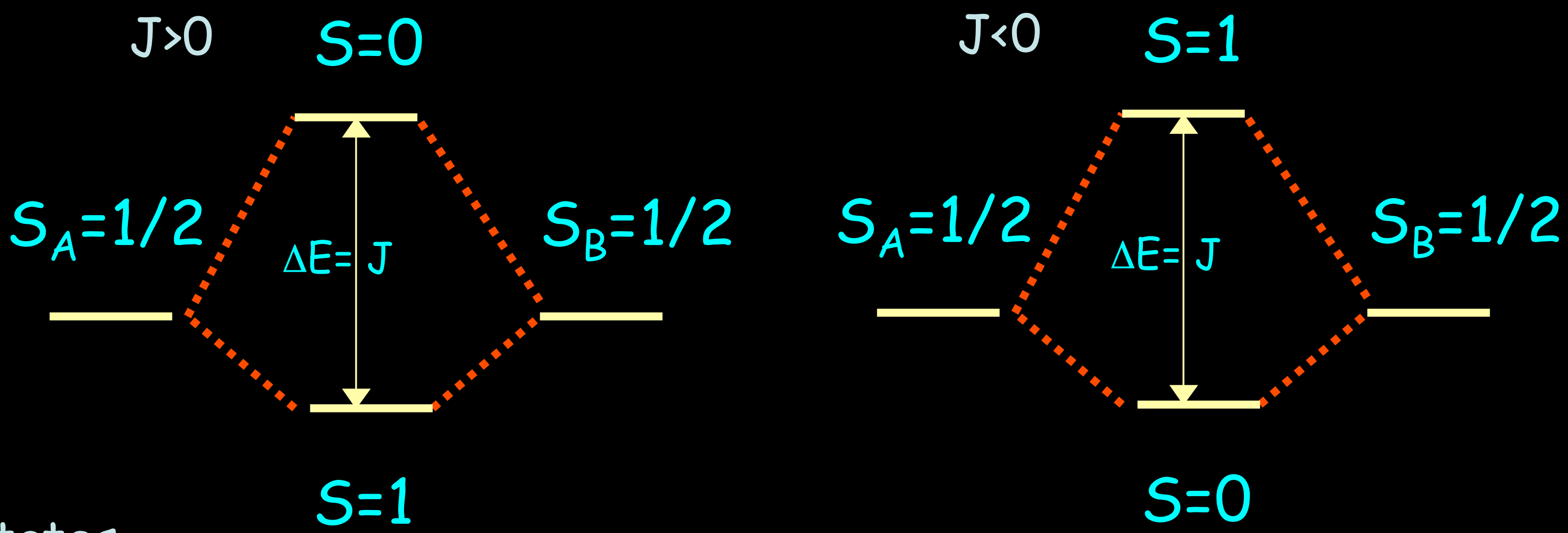
Basis states
$$|\, m_A\, m_B > \; = \begin{pmatrix} |-\frac{1}{2}> \\ |\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |-\frac{1}{2}> \\ |\frac{1}{2}> \end{pmatrix} = \begin{pmatrix} |-\frac{1}{2}>|-\frac{1}{2}> \\ |-\frac{1}{2}>|\frac{1}{2}> \\ |\frac{1}{2}>|-\frac{1}{2}> \\ |\frac{1}{2}>|\frac{1}{2}> \end{pmatrix}$$

Matrix elements

$$\langle m'_A\, m'_B \,|\, \mathbf{S}_A \cdot \mathbf{S}_B \,|\, m_A\, m_B \rangle = m_A\, m_B\, \delta_{m'_A m_A}\, \delta_{m'_B m_B} +$$
$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}+m_A+1\right)\left(\frac{1}{2}-m_A\right)}\sqrt{\left(\frac{1}{2}-m_B+1\right)\left(\frac{1}{2}+m_B\right)}\,\delta_{m'_A\, m_A+1}\,\delta_{m'_B\, m_B-1} +$$
$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}-m_A+1\right)\left(\frac{1}{2}+m_A\right)}\sqrt{\left(\frac{1}{2}+m_B+1\right)\left(\frac{1}{2}-m_B\right)}\,\delta_{m'_A\, m_A-1}\,\delta_{m'_B\, m_B+1}$$

	$\|-\frac{1}{2}>\|-\frac{1}{2}>$	$\|-\frac{1}{2}>\|\frac{1}{2}>$	$\|\frac{1}{2}>\|-\frac{1}{2}>$	$\|\frac{1}{2}>\|\frac{1}{2}>$
$<-\frac{1}{2}\|<-\frac{1}{2}\|$	$\frac{J}{4}$	0	0	0
$<-\frac{1}{2}\|<\frac{1}{2}\|$	0	$-\frac{J}{4}$	$\frac{J}{2}$	0
$<\frac{1}{2}\|<-\frac{1}{2}\|$	0	$\frac{J}{2}$	$-\frac{J}{4}$	0
$<\frac{1}{2}\|<\frac{1}{2}\|$	0	0	0	$\frac{J}{4}$

Eigenvalues $0, -J, -J, -J$



Eigenstates

$$|0,0> = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}>\right|-\frac{1}{2}> - \left|-\frac{1}{2}>\right|\frac{1}{2}>\right)$$

$$|1,\ 1> = \left|\frac{1}{2}>\right|\frac{1}{2}>$$

$$|1,0> = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}>\right|-\frac{1}{2}> + \left|-\frac{1}{2}>\right|\frac{1}{2}>\right)$$

$$|1,\ -1> = \left|-\frac{1}{2}>\right|-\frac{1}{2}>$$

A magnetic field along the z – axis introduces the Zeeman term

$$H^{Z} = g_{z}\,\mu_{B}\,B S_{z}$$

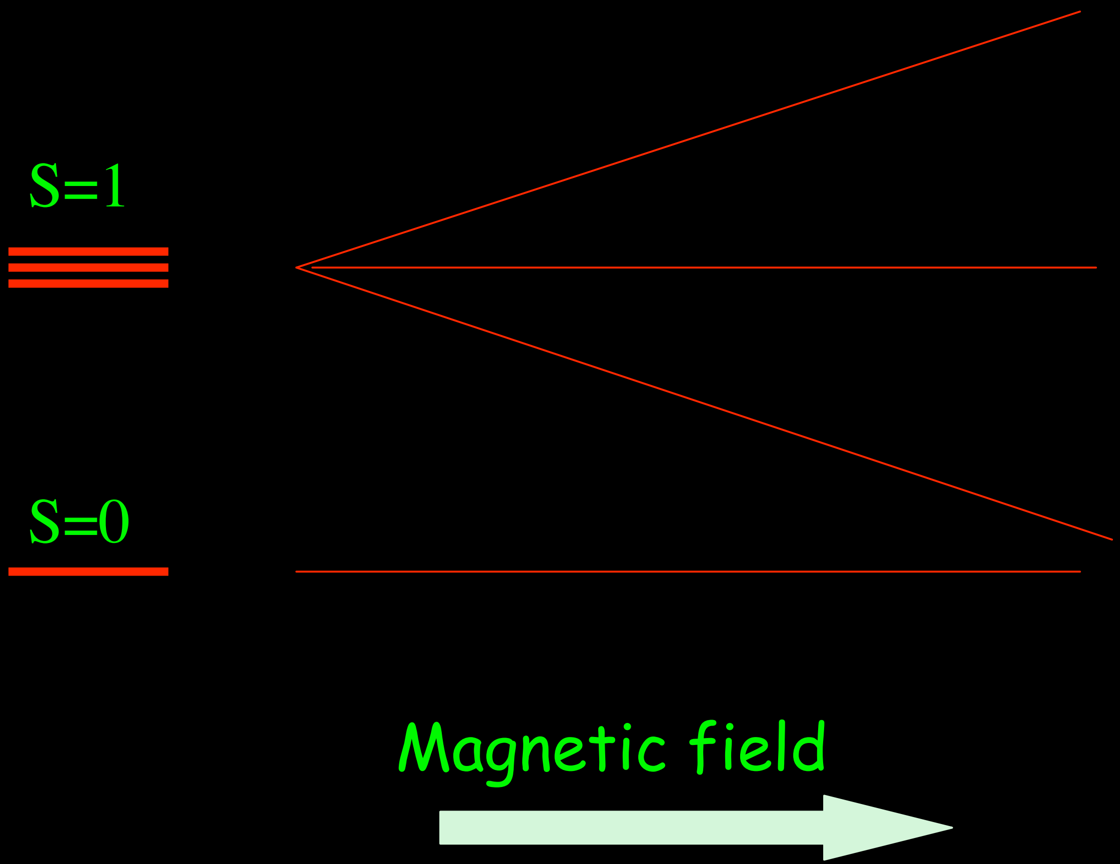
The total hamiltonian matrix is still diagonal, with eigenvalues

$$\varepsilon_{S}(B) = -\frac{1}{2}\,J\,S(S+1) + g_{z}\,\mu_{B}\,B M_{S} \qquad (M_{S} = -S, \;\ldots, \; S)$$

Example: $S_A = S_B = 1/2$

$\varepsilon_0 = 0$

$\varepsilon_1 = -J$



Etero – dinuclear spins.

Same eigenvalues as for omonuclear systems if $B = 0$:

$$\varepsilon_S = -\frac{1}{2} J\, S\,(S+1)$$

The situation changes when $B \neq 0$.

$\overline{g}_A,\ \overline{g}_B\ =$ local $\overline{g}$ tensors

$$H^{ex+Z} = -J\,\vec{S}_A\cdot\vec{S}_B + \mu_B\,\vec{B}\cdot\overline{g}_A\cdot\vec{S}_A\cdot + \mu_B\,\vec{B}\cdot\overline{g}_B\cdot\vec{S}_B$$

The matrix elements

$$H_{ij}^{ex+Z} = \langle i \,|\, H^{ex+Z} \,|\, j \rangle$$

are expressed in the basis of the $(2\,S_A + 1)\,(2\,S_B + 1)$ uncoupled spin states

$$|\, i \succ \;=\; |\, S_A\, M_A \succ |\, S_B\, M_B \succ$$

Alternatively, one can use the basis set of the coupled spin states

$$|\,I\,\succ \;=\; \left|\,S\,M\,\succ\right.$$

$$H^{ex+Z} = -\frac{J}{2}\left(\vec{S}^{2} - \vec{S}_A^{2} - \vec{S}_B^{2}\right) + \mu_B\,\vec{B}\cdot\overline{g}_S\cdot\vec{S}$$

with matrix elements

$$H_{IJ}^{ex+Z} = \langle I\,|\,H^{ex+Z}\,|\,J\rangle$$

The molecular g – tensor $\overline{g}_S$ is a linear combination of the local g – tensors :

$$\overline{g}_S = \frac{1}{2}(\overline{g}_A + \overline{g}_B) + \frac{S_A(S_A+1) - S_B(S_B+1)}{S(S+1)}\frac{1}{2}(\overline{g}_A - \overline{g}_B)$$

i.e.

$$\overline{g}_S = C_A\,\overline{g}_A + (1 - C_A)\,\overline{g}_B$$

with

$$C_A = \frac{S(S+1) + S_A(S_A+1) - S_B(S_B+1)}{2S(S+1)}$$

The Zeeman matrix is NO more diagonal:

$$\langle S\, M \,|\, H^Z \,|\, S'\, M \rangle \neq 0$$

making use of the irreducible tensor operator technique,

one obtains

$$\langle S_A\, S_B,\, S-1\;\; M \,|\, H^Z \,|\, S_A\, S_B,\, S\;\; M\rangle =$$

$$= (\bar{g}_A - \bar{g}_B)\, \mu_B\, B_z \langle S_A\, S_B,\, S-1\;\; M \,|\, S_{Az} \,|\, S_A\, S_B,\, S\;\; M\rangle =$$

$$= -(\bar{g}_A - \bar{g}_B)\, \mu_B\, B_z \sqrt{\frac{[S^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - S^2]\,(S^2 - M^2)}{4\, S^2\, (4\, S^2 - 1)}}$$

$$\langle S_A\, S_B,\, S+1\;\; M \,|\, H^Z \,|\, S_A\, S_B,\, S\;\; M\rangle =$$

$$= -(\bar{g}_A - \bar{g}_B)\, \mu_B\, B_z \sqrt{\frac{[(S+1)^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - (S+1)^2][(S+1)^2 - M^2]}{4\,(S+1)^2[4\,(S+1)^2 - 1]}}$$

Example: $A = Cu^{II}$ $(S_A = 1/2)$ $B = Ni^{II}$ $(S_B = 1)$

$$\Delta = \frac{g_{Cu} - g_{Ni}}{3} \qquad g_{1/2} = \frac{4\,g_{Ni} - g_{Cu}}{3} \qquad g_{3/2} = \frac{2\,g_{Ni} - g_{Cu}}{3}$$

$$\begin{array}{cccccc} |\frac{1}{2}\ -\frac{1}{2}> & |\frac{1}{2}\ \frac{1}{2}> & |\frac{3}{2}\ -\frac{3}{2}> & |\frac{3}{2}\ -\frac{1}{2}> & |\frac{3}{2}\ \frac{1}{2}> & |\frac{3}{2}\ \frac{3}{2}> \end{array}$$

$$H^{ex+Z} = \begin{pmatrix} -\frac{g_{1/2}}{2}\mu_B B & 0 & 0 & -\Delta\sqrt{2}\,\mu_B B & 0 & 0 \\ 0 & \frac{g_{1/2}}{2}\mu_B B & 0 & 0 & -\Delta\sqrt{2}\,\mu_B B & 0 \\ 0 & 0 & -\frac{3}{2}J - \frac{3\,g_{3/2}}{2}\mu_B B & 0 & 0 & 0 \\ -\Delta\sqrt{2}\,\mu_B B & 0 & 0 & -\frac{3}{2}J - \frac{g_{3/2}}{2}\mu_B B & 0 & 0 \\ 0 & -\Delta\sqrt{2}\,\mu_B B & 0 & 0 & -\frac{3}{2}J + \frac{g_{3/2}}{2}\mu_B B & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{3}{2}J + \frac{3\,g_{3/2}}{2}\mu_B B \end{pmatrix}$$

Eigenvalues

$$
\Big\{-\frac{3\,J}{2}-\frac{3}{2}\,B\,g_{\frac{3}{2}}\,\mu_B,\ -\frac{3\,J}{2}+\frac{3}{2}\,B\,g_{\frac{3}{2}}\,\mu_B,
$$

$$
\frac{1}{8}\left(-6\,J+2\,B\,g_{\frac{1}{2}}\,\mu_B+2\,B\,g_{\frac{3}{2}}\,\mu_B-\sqrt{\left(6\,J-2\,B\,g_{\frac{1}{2}}\,\mu_B-2\,B\,g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(-3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)}\right),
$$

$$
\frac{1}{8}\left(-6\,J+2\,B\,g_{\frac{1}{2}}\,\mu_B+2\,B\,g_{\frac{3}{2}}\,\mu_B+\sqrt{\left(6\,J-2\,B\,g_{\frac{1}{2}}\,\mu_B-2\,B\,g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(-3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)}\right),
$$

$$
\frac{1}{8}\left(-6\,J-2\,B\,g_{\frac{1}{2}}\,\mu_B-2\,B\,g_{\frac{3}{2}}\,\mu_B-\sqrt{\left(6\,J+2\,B\,g_{\frac{1}{2}}\,\mu_B+2\,B\,g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)}\right),
$$

$$
\frac{1}{8}\left(-6\,J-2\,B\,g_{\frac{1}{2}}\,\mu_B-2\,B\,g_{\frac{3}{2}}\,\mu_B+\sqrt{\left(6\,J+2\,B\,g_{\frac{1}{2}}\,\mu_B+2\,B\,g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)}\right)\Big\}
$$

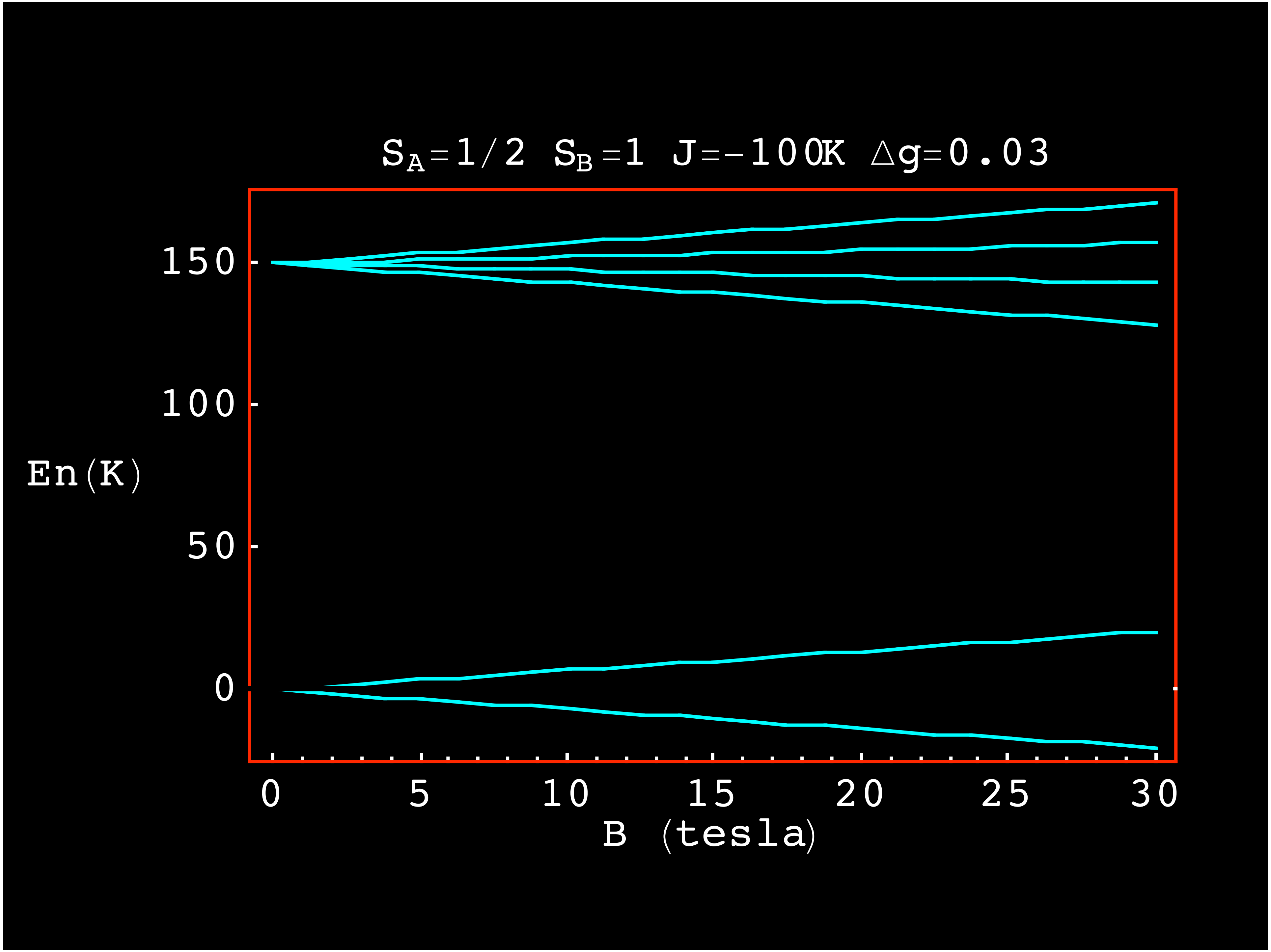
Eigenvectors

$$
\{\{0,0,0,0,0,1\},\{0,0,1,0,0,0\},\{0,\frac{1}{8\sqrt{2}\,B\,\Delta\,\mu_B}\left(-6\,J-2\,B g_{\frac{1}{2}}\,\mu_B+2\,B g_{\frac{3}{2}}\,\mu_B+\sqrt{\left(\left(6\,J-2\,B g_{\frac{1}{2}}\,\mu_B-2\,B g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(-3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)\right)}\right),
$$

$$
0,0,1,0\},\{0,\frac{1}{8\sqrt{2}\,B\,\Delta\,\mu_B}\left(-6\,J-2\,B g_{\frac{1}{2}}\,\mu_B+2\,B g_{\frac{3}{2}}\,\mu_B-\sqrt{\left(\left(6\,J-2\,B g_{\frac{1}{2}}\,\mu_B-2\,B g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(-3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)\right)}\right),0,0,1,0\},
$$

$$
\{-\frac{1}{8\sqrt{2}\,B\,\Delta\,\mu_B}\left(6\,J-2\,B g_{\frac{1}{2}}\,\mu_B+2\,B g_{\frac{3}{2}}\,\mu_B-\sqrt{\left(\left(6\,J+2\,B g_{\frac{1}{2}}\,\mu_B+2\,B g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)\right)}\right),0,0,1,0,0\},
$$

$$
\{-\frac{1}{8\sqrt{2}\,B\,\Delta\,\mu_B}\left(6\,J-2\,B g_{\frac{1}{2}}\,\mu_B+2\,B g_{\frac{3}{2}}\,\mu_B+\sqrt{\left(\left(6\,J+2\,B g_{\frac{1}{2}}\,\mu_B+2\,B g_{\frac{3}{2}}\,\mu_B\right)^2-16\left(3\,B\,J\,g_{\frac{1}{2}}\,\mu_B-8\,B^2\,\Delta^2\,\mu_B^2+B^2\,g_{\frac{1}{2}}\,g_{\frac{3}{2}}\,\mu_B^2\right)\right)}\right),0,0,1,0,0\}\}
$$


$S_A = 1/2$ $S_B = 1$ $J = -100K$ $\Delta g = 0.03$
150
100
En(K)
50
0
0
5
10
15
20
25
30
B (tesla)

The INS pdcs for a dimer

$$S^{\alpha\beta}(\mathbf{q},\ \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda\,|\,s^{\alpha}{}_{n'}\,|\,\lambda'\rangle\langle\lambda'\,|\,s^{\beta}{}_{n}\,|\,\lambda\rangle$$

$S_A = S_B = 1/2$

$|\lambda\rangle = |0\ 0\rangle,\ |1\,{-1}\rangle,\ |1\ 0\rangle,\ |1\ 1\rangle$

$$S^{\alpha\beta}{}_{0\to1} = \sum_{M}\Bigg(\sum_{n=A,B} p(E_0)\Big(\langle 00\,|\,s^{\alpha}{}_{n}\,|\,1\,M\rangle\langle 1\,M\,|\,s^{\beta}{}_{n}\,|\,00\rangle + $$

$$+e^{i\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)}\langle 00\,|\,s^{\alpha}{}_{B}\,|\,1\,M\rangle\langle 1\,M\,|\,s^{\beta}{}_{A}\,|\,00\rangle +$$

$$+\,e^{-i\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)}\langle 00\,|\,s^{\alpha}{}_{A}\,|\,1\,M\rangle\langle 1\,M\,|\,s^{\beta}{}_{B}\,|\,00\rangle\Big)\Bigg)$$

$$|0,0> = \frac{1}{\sqrt{2}}\left(|\frac{1}{2}>|-\frac{1}{2}> - |-\frac{1}{2}>|\frac{1}{2}>\right)$$

$$|1,\ 1> = |\frac{1}{2}>|\frac{1}{2}>$$

$$|1,0> = \frac{1}{\sqrt{2}}\left(|\frac{1}{2}>|-\frac{1}{2}> + |-\frac{1}{2}>|\frac{1}{2}>\right)$$

$$|1,\ -1> = |-\frac{1}{2}>|-\frac{1}{2}>$$

Matrix elements

$$<1-1|\,s_A^x\,|00> = \frac{1}{2} < -\frac{1}{2}\ -\frac{1}{2}\left|(s_A^+ + s_A^-)\,\frac{1}{\sqrt{2}}\left(|\frac{1}{2}\ -\frac{1}{2}> - |-\frac{1}{2}\ \frac{1}{2}>\right)\right. = \frac{1}{2\sqrt{2}}$$

$$<1\,1|\,s_B^y\,|00> = \frac{-i}{2} < \frac{1}{2}\ \frac{1}{2}\left|(s_B^+ - s_B^-)\,\frac{1}{\sqrt{2}}\left(|\frac{1}{2}\ -\frac{1}{2}> - |-\frac{1}{2}\ \frac{1}{2}>\right)\right. = \frac{-i}{2\sqrt{2}}$$

Etc.

$$< 1\ -1 \,|\, s_A^x \,|\, 00 > = \frac{1}{2\sqrt{2}} \qquad < 1\,0 \,|\, s_A^x \,|\, 00 > = 0 \qquad < 1\,1 \,|\, s_A^x \,|\, 00 > = \frac{-1}{2\sqrt{2}}$$

$$< 1\ -1 \,|\, s_A^y \,|\, 00 > = \frac{i}{2\sqrt{2}} \qquad < 1\,0 \,|\, s_A^y \,|\, 00 > = 0 \qquad < 1\,1 \,|\, s_A^y \,|\, 00 > = \frac{i}{2\sqrt{2}}$$

$$< 1\ -1 \,|\, s_A^z \,|\, 00 > = 0 \qquad < 1\,0 \,|\, s_A^z \,|\, 00 > = \frac{1}{2} \qquad < 1\,1 \,|\, s_A^z \,|\, 00 > = 0$$

$$< 1\ -1 \,|\, s_B^x \,|\, 00 > = \frac{-1}{2\sqrt{2}} \qquad < 1\,0 \,|\, s_B^x \,|\, 00 > = 0 \qquad < 1\,1 \,|\, s_B^x \,|\, 00 > = \frac{1}{2\sqrt{2}}$$

$$< 1\ -1 \,|\, s_B^y \,|\, 00 > = \frac{-i}{2\sqrt{2}} \qquad < 1\,0 \,|\, s_B^y \,|\, 00 > = 0 \qquad < 1\,1 \,|\, s_B^y \,|\, 00 > = \frac{-i}{2\sqrt{2}}$$

$$< 1\ -1 \,|\, s_B^z \,|\, 00 > = 0 \qquad < 1\,0 \,|\, s_B^z \,|\, 00 > = -\frac{1}{2} \qquad < 1\,1 \,|\, s_B^z \,|\, 00 > = 0$$

Ex. Work out the above matrix elements

Substituting the above matrix elements into the pdcs, one has
(only the xx, yy and zz terms survive)

$$S^{xx}{}_{0\to1} = S^{yy}{}_{0\to1} = S^{zz}{}_{0\to1} = \frac{1}{2}[1 - \cos \mathbf{q}\cdot(\mathbf{r}_A - \mathbf{r}_B)]$$

And finally

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{0\to1} = A(q)\sum_\alpha\left(1 - \frac{q_\alpha q_\alpha}{q^2}\right)(S^{\alpha\alpha})_{0\to1}\,\delta(-J - \hbar\omega) =$$

$$= A(q)[1 - \cos \mathbf{q}\cdot(\mathbf{r}_A - \mathbf{r}_B)]\,\delta(-J - \hbar\omega)$$

Note that there is no scattering 0-1 if $\mathbf{q}$ is parallel to the axis of the dimer.
For a polycrystalline sample

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{0\to1} = A(q)\frac{1}{4\pi}\int_{4\pi}[1 - \cos \mathbf{q}\cdot(\mathbf{r}_A - \mathbf{r}_B)]\,d\Omega = A(q)\left(1 - \frac{\sin(q|\mathbf{r}_A - \mathbf{r}_B|)}{q|\mathbf{r}_A - \mathbf{r}_B|}\right)$$

For a dimer with general spin values:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{S\to S'} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|\, F(\mathbf{q}) \,|^2 \exp(-2W(\mathbf{q}))\;\; p_S \sum_{\alpha}\left(1-\frac{q_\alpha^2}{q^2}\right)\times$$

$$\times\frac{2}{3}(2S+1)(2S'+1)S_A(S_A+1)(2S_A+1)\left(\begin{Bmatrix} S' & S & 1 \\ S_A & S_A & S_A \end{Bmatrix}\right)^2 \times$$

$$\times\left[1+(-1)^{S'-S}\cos\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)\right]\delta(E_{S'}-E_S-\hbar\omega)$$

Or, for a polycrystal:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{S\to S'} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|\, F(\mathbf{q}) \,|^2 \exp(-2W(\mathbf{q}))\;\; p_S \times$$

$$\times\frac{4}{3}(2S+1)(2S'+1)S_A(S_A+1)(2S_A+1)\left(\begin{Bmatrix} S' & S & 1 \\ S_A & S_A & S_A \end{Bmatrix}\right)^2 \times$$

$$\times\left[1+(-1)^{S'-S}\frac{\sin q\,|\mathbf{r}_A-\mathbf{r}_B|}{q\,|\mathbf{r}_A-\mathbf{r}_B|}\right]\delta(E_{S'}-E_S-\hbar\omega)$$

Trimers

Example. $S_1 = S_2 = S_3 = 1/2$ $\quad (8\times 8)$ matrix

Basis states :

$$|S_A M_A S_B M_B S_C M_C\rangle = \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} =$$

$$= \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \end{pmatrix} =$$

$$= \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \end{pmatrix}$$

$$H_{12} = -J_{12}\, S_1 \cdot S_2$$

$$\langle m'_1\, m'_2\, m'_3 | S_1 \cdot S_2 | m_1\, m_2\, m_3 \rangle = m_1\, m_2\, \delta_{m'_1 m_1}\, \delta_{m'_2 m_2}\, \delta_{m'_3 m_3} +$$

$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}+m_1+1\right)\left(\frac{1}{2}-m_1\right)}\sqrt{\left(\frac{1}{2}-m_2+1\right)\left(\frac{1}{2}+m_2\right)}\,\delta_{m'_1\, m_1+1}\,\delta_{m'_2\, m_2-1}\,\delta_{m'_3 m_3} +$$

$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}-m_1+1\right)\left(\frac{1}{2}+m_1\right)}\sqrt{\left(\frac{1}{2}+m_2+1\right)\left(\frac{1}{2}-m_2\right)}\,\delta_{m'_1\, m_1-1}\,\delta_{m'_2\, m_2+1}\,\delta_{m'_3 m_3}$$

$$H_{12} = -J_{12}\begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & -\frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & -\frac{1}{4} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

$$H_{13} = -J_{13}\, S_1 \cdot S_3$$

$$H_{13} = -J_{13} \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & 0 & 0 & -\frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{4} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

$$H_{23} = -J_{23}\,\mathbf{S}_2 \cdot \mathbf{S}_3$$

$$H_{23} = -J_{23} \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{4} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{4} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

General triangle : $J_{12} \neq J_{13} \neq J_{23}$

$$H = \begin{pmatrix}
\frac{J_{12}}{4}+\frac{J_{13}}{4}+\frac{J_{23}}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{J_{12}}{4}-\frac{J_{13}}{4}-\frac{J_{23}}{4} & \frac{J_{23}}{2} & 0 & \frac{J_{13}}{2} & 0 & 0 & 0 \\
0 & \frac{J_{23}}{2} & -\frac{J_{12}}{4}+\frac{J_{13}}{4}-\frac{J_{23}}{4} & 0 & \frac{J_{12}}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{J_{12}}{4}-\frac{J_{13}}{4}+\frac{J_{23}}{4} & 0 & \frac{J_{12}}{2} & \frac{J_{13}}{2} & 0 \\
0 & \frac{J_{13}}{2} & \frac{J_{12}}{2} & 0 & -\frac{J_{12}}{4}-\frac{J_{13}}{4}+\frac{J_{23}}{4} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{J_{12}}{2} & 0 & -\frac{J_{12}}{4}+\frac{J_{13}}{4}-\frac{J_{23}}{4} & \frac{J_{23}}{2} & 0 \\
0 & 0 & 0 & \frac{J_{13}}{2} & 0 & \frac{J_{23}}{2} & \frac{J_{12}}{4}-\frac{J_{13}}{4}-\frac{J_{23}}{4} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{J_{12}}{4}+\frac{J_{13}}{4}+\frac{J_{23}}{4}
\end{pmatrix}$$

With the following definitions

$$J = \frac{1}{3}(J_{12}+J_{13}+J_{23})$$

$$\Delta = \sqrt{J_{12}^2+J_{13}^2+J_{23}^2-J_{12}J_{23}-J_{13}J_{23}-J_{12}J_{13}}$$

$$a = J_{13}^2 - J_{12}J_{23} + J_{13}\Delta$$

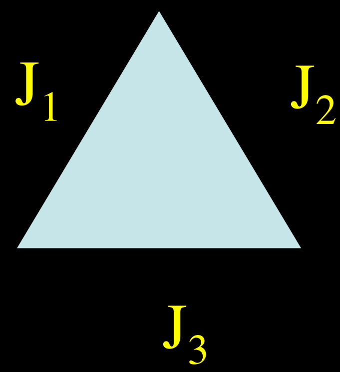
$$c = J_{AB}^2 - J_{13}J_{23} + J_{12}\Delta$$

$$b = J_{23}^2 - J_{12}J_{13} + J_{23}\Delta$$

$$A = J_{AC}^2 - J_{12}J_{23} - J_{13}\Delta$$

$$B = J_{12}^2 - J_{13}J_{23} - J_{12}\Delta$$

$$C = J_{BC}^2 - J_{12}J_{13} - J_{23}\Delta$$



Eigenvalues and eigenvectors are:

$$E(\lambda_0)=\frac{3J}{4}$$

$$\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>$$

$$\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>$$

$$\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>+\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>+\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>$$

$$\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>+\left|-\frac{1}{2}\right>\left|+\frac{1}{2}\right>\left|-\frac{1}{2}\right>+\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>$$

$$E(\lambda_1)=-\left(\frac{3J}{4}+\frac{1}{2}\Delta\right)$$

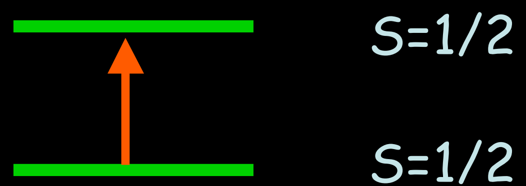
$$-\frac{a+c}{a}\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>+\frac{c}{a}\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>+\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>$$

$$-\frac{a+b}{a}\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>+\frac{b}{a}\left|-\frac{1}{2}\right>\left|+\frac{1}{2}\right>\left|-\frac{1}{2}\right>+\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>$$

$$E(\lambda_2)=-\left(\frac{3J}{4}-\frac{1}{2}\Delta\right)$$

$$-\frac{A+B}{A}\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>+\frac{B}{A}\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>+\left|\frac{1}{2}\right>\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>$$

$$-\frac{A+C}{A}\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|\frac{1}{2}\right>+\frac{C}{A}\left|-\frac{1}{2}\right>\left|+\frac{1}{2}\right>\left|-\frac{1}{2}\right>+\left|\frac{1}{2}\right>\left|-\frac{1}{2}\right>\left|-\frac{1}{2}\right>$$

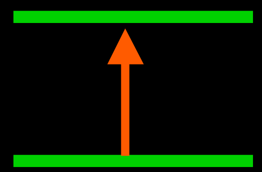


$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda_1\rightarrow\lambda_2} = \frac{k_f}{k_i}(\gamma r_0)^2\,|F(\mathbf{q})|^2\exp(-2W(\mathbf{q}))\;p(\lambda_0)\times$$

$$\times\frac{2}{3}\Big[1+\frac{(J_{12}-J_{23})(J_{13}-J_{12})}{\Delta^2}\,\frac{\sin(qR_{12})}{qR_{12}}+$$

$$+\frac{(J_{12}-J_{23})(J_{23}-J_{13})}{\Delta^2}\,\frac{\sin(qR_{23})}{qR_{23}}+$$

$$+\frac{(J_{12}-J_{13})(J_{13}-J_{23})}{\Delta^2}\,\frac{\sin(qR_{13})}{qR_{13}}\Big]\delta(\hbar\omega+E(\lambda_1)-E(\lambda_2))$$



S=1/2 a

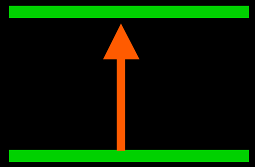
S=3/2

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda_0\to\lambda_1} = \frac{k_f}{k_i}(\gamma r_0)^2\,|F(\mathbf{q})|^2 \exp(-2W(\mathbf{q}))\;p_{(\lambda_0)}\times$$

$$\times\frac{2}{3}\Bigg[2+\left(\frac{-a(a+b)}{a^2+b^2+ab}+\frac{-bc}{b^2+c^2-bc}\right)\frac{\sin(qR_{12})}{qR_{12}}+$$

$$+\left(\frac{ab}{a^2+b^2+ab}+\frac{b(c-b)}{b^2+c^2-bc}\right)\frac{\sin(qR_{13})}{qR_{13}}+$$

$$+\left(\frac{-b(a+b)}{a^2+b^2+ab}+\frac{-c(c-b)}{b^2+c^2-bc}\right)\frac{\sin(qR_{23})}{qR_{23}}\Bigg]\delta(\hbar\omega+E(\lambda_0)-E(\lambda_1))$$



S=1/2 b

S=3/2

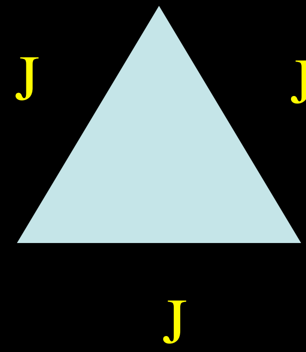
$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda_0\to\lambda_2} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|F(\mathbf{q})|^2 \exp(-2W(\mathbf{q}))\;\; p_{(\lambda_0)} \times$$

$$\times\frac{2}{3}\Bigg[2+\left(\frac{-A(A+B)}{A^2+B^2+AB}+\frac{-BC}{B^2+C^2-BC}\right)\frac{\sin(qR_{12})}{qR_{12}}+$$

$$+\left(\frac{AB}{A^2+B^2+AB}+\frac{-BC}{B^2+C^2-BC}\right)\frac{\sin(qR_{13})}{qR_{13}}+$$

$$+\left(\frac{-B(A+B)}{A^2+B^2+AB}+\frac{-c(c-b)}{B^2+C^2-BC}\right)\frac{\sin(qR_{23})}{qR_{23}}\Bigg]\delta(\hbar\omega+E(\lambda_0)-E(\lambda_2))$$

Equilateral triangle: $J_{12} = J_{13} = J_{23} = J$

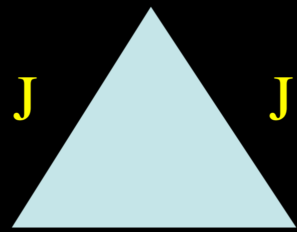


$$H = \begin{pmatrix} -\frac{3J}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{J}{4} & -\frac{J}{2} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & -\frac{J}{2} & \frac{J}{4} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{J}{4} & 0 & -\frac{J}{2} & -\frac{J}{2} & 0 \\ 0 & -\frac{J}{2} & -\frac{J}{2} & 0 & \frac{J}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & \frac{J}{4} & -\frac{J}{2} & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & -\frac{J}{2} & \frac{J}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{3J}{4} \end{pmatrix}$$

Eigenvalues : $\left\{-\frac{3J}{4}, -\frac{3J}{4}, -\frac{3J}{4}, -\frac{3J}{4}, \frac{3J}{4}, \frac{3J}{4}, \frac{3J}{4}, \frac{3J}{4}\right\}$

Two degenerate doublets S = 1/2 and one quartet S=3/2

Isosceles triangle: $J_{12} = J_{13} \quad J_{23} = J'$

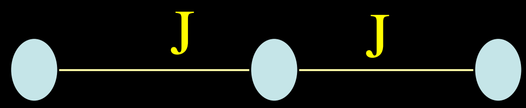


$$H = \begin{pmatrix} -\frac{J}{2}-\frac{J'}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{J'}{4} & -\frac{J}{2} & 0 & -\frac{J'}{2} & 0 & 0 & 0 \\ 0 & -\frac{J}{2} & \frac{J}{2}-\frac{J'}{4} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{J'}{4} & 0 & -\frac{J}{2} & -\frac{J'}{2} & 0 \\ 0 & -\frac{J'}{2} & -\frac{J}{2} & 0 & \frac{J'}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & \frac{J}{2}-\frac{J'}{4} & -\frac{J}{2} & 0 \\ 0 & 0 & 0 & -\frac{J'}{2} & 0 & -\frac{J}{2} & \frac{J'}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{J}{2}-\frac{J'}{4} \end{pmatrix}$$

Eigenvalues : $\left\{\frac{1}{4}(4J-J'), \frac{1}{4}(4J-J'), -\frac{J}{2}-\frac{J'}{4}, -\frac{J}{2}-\frac{J'}{4}, -\frac{J}{2}-\frac{J'}{4}, -\frac{J}{2}-\frac{J'}{4}, \frac{3J'}{4}, \frac{3J'}{4}\right\}$

$S = 1/2, S = 3/2, S = 1/2$

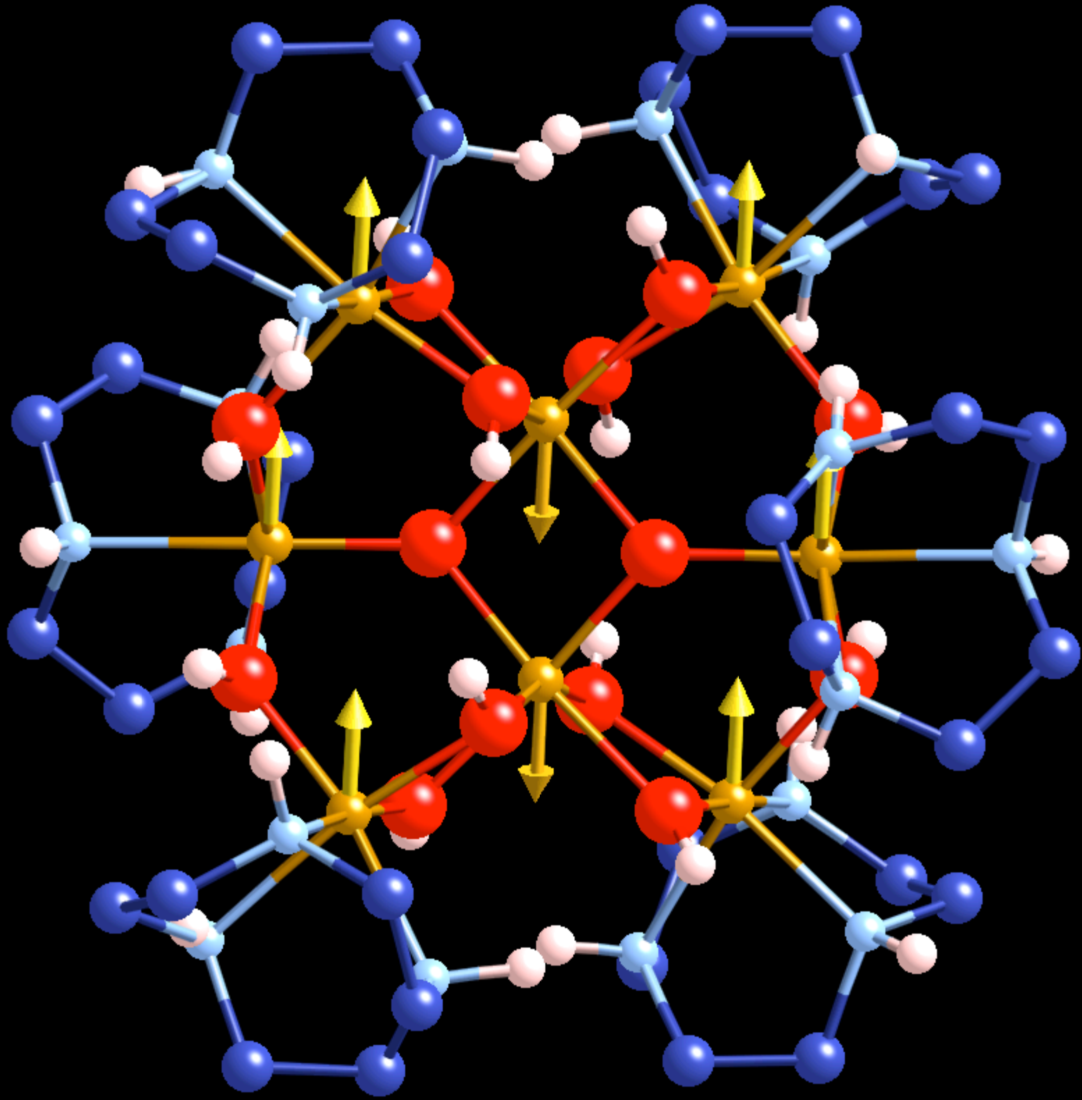
Linear Chain $1-2-3$

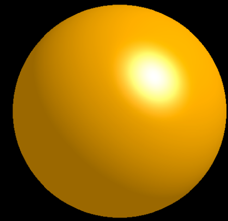


$$H=-J\left(H_{12}+H_{23}\right)=\begin{pmatrix} -\frac{J}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{J}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{J}{2} & \frac{J}{2} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{J}{2} & 0 & 0 \\ 0 & 0 & -\frac{J}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & \frac{J}{2} & -\frac{J}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{J}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{J}{2} \end{pmatrix}$$

$$\text{Eigenvalues}: \left\{0,0,-\frac{J}{2},-\frac{J}{2},-\frac{J}{2},-\frac{J}{2},J,J\right\}$$

$[Fe_8O_2(OH)_{12}(tacn)_6]Br_8\ 9H_2O$

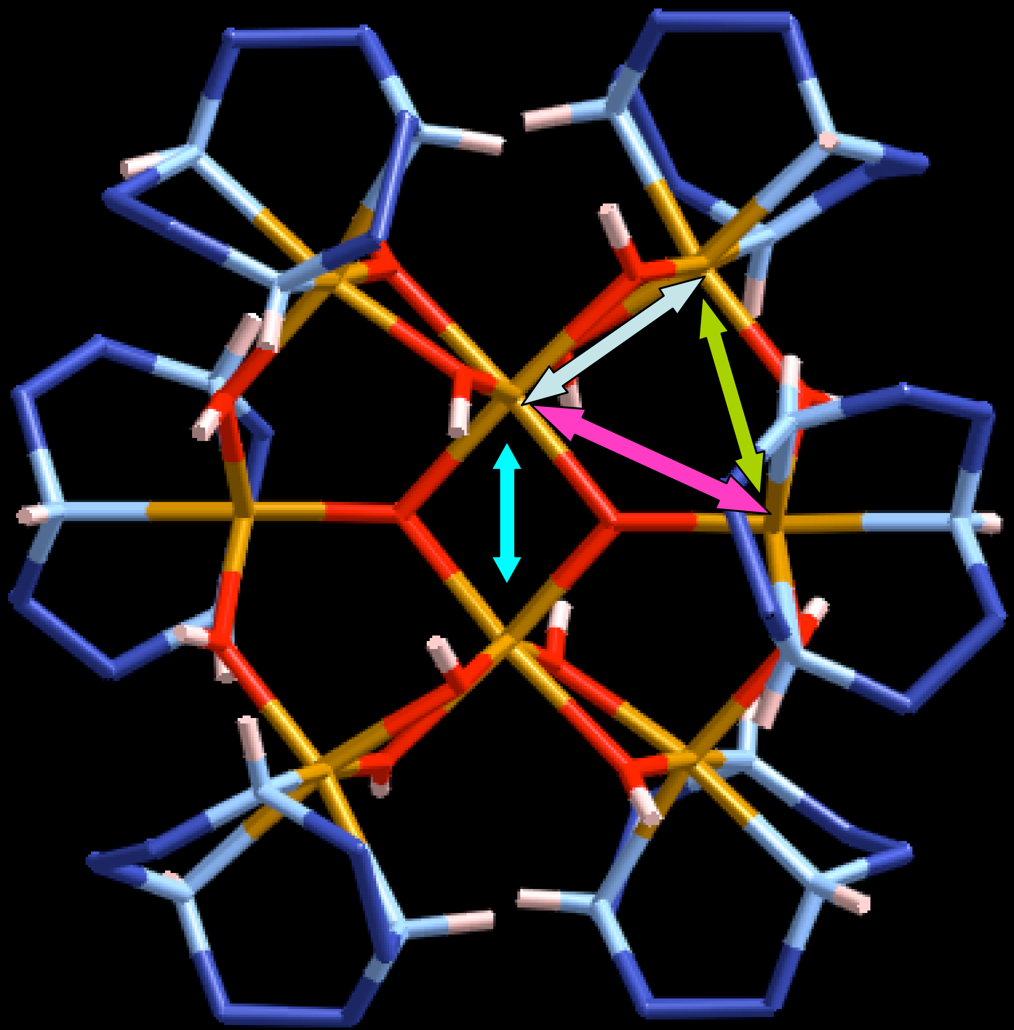


Fe^{3+} 

$s = 5/2$

$S = 10$

Exchange Interactions in Fe_8



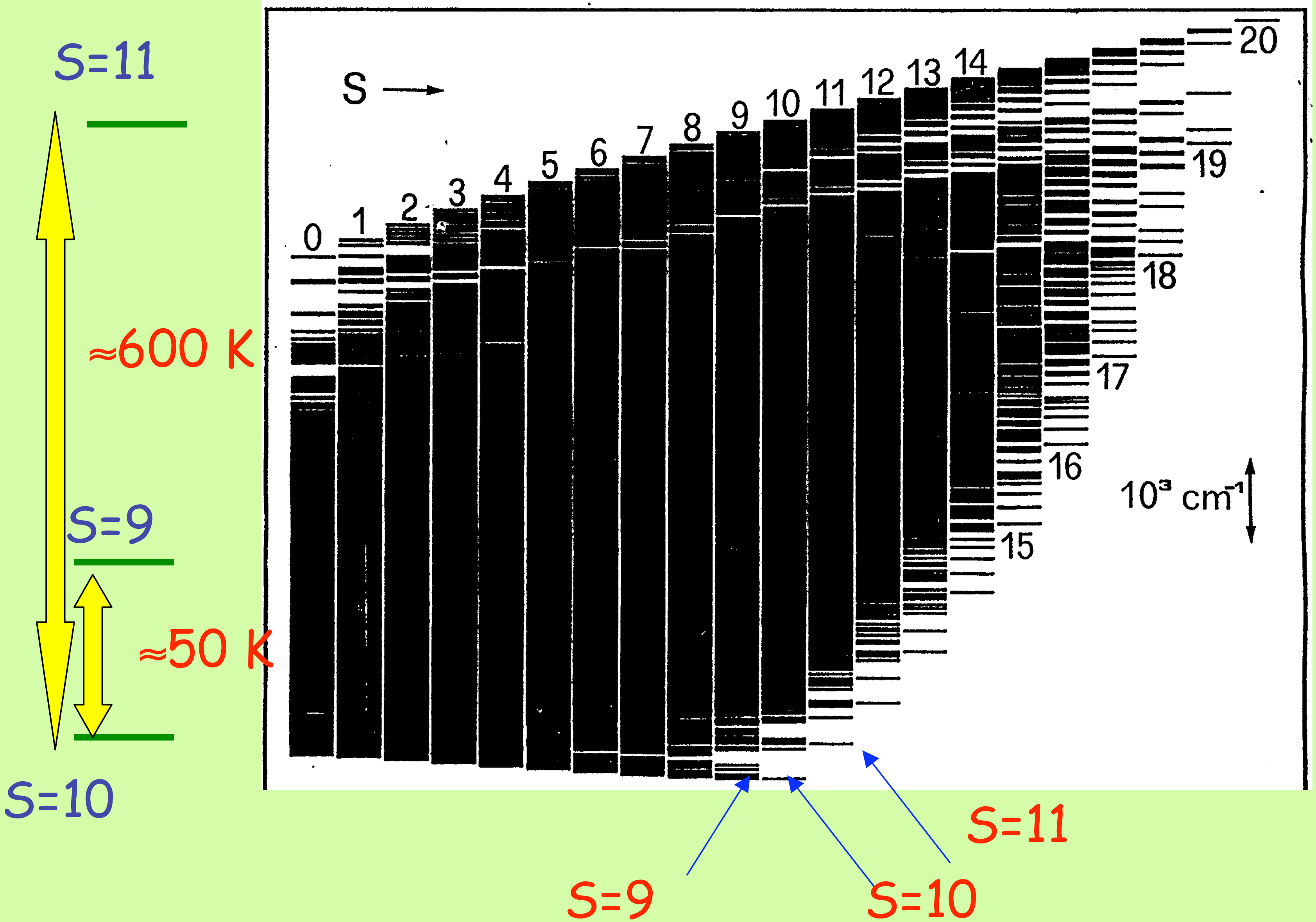
$J_1 = 25\ cm^{-1}$

$J_2 = 140\ cm^{-1}$

$J_3 = 18\ cm^{-1}$

$J_4 = 41\ cm^{-1}$

Energy levels in Fe_8



In the general case:

The Hamiltonian

$$H = \sum_{i<j} J_{ij}\,\hat{S}_i \cdot \hat{S}_j + \sum_i \hat{S}_i \cdot \overline{D_i} \cdot \hat{S}_i + \sum_{i<j} \hat{S}_i \cdot \overline{D_{ij}} \cdot \hat{S}_j + \mu_B \sum_i g_i\,\vec{B} \cdot \hat{S}_i$$

Isotropic exchange   local ZFS   Dipole-dipole interaction   Zeeman term

$$\hat{S}_i \cdot \overline{D_i} \cdot \hat{S}_i = D_i\left(S_{iz}^2 - \frac{1}{3} S_i\,(S_i + 1)\right) + E_i\left(S_{ix}^2 - S_{iy}^2\right)$$

$$D = \frac{1}{2}\,(2\,\overline{D}_{zz} - \overline{D}_{xx} - \overline{D}_{yy}) \qquad E = \frac{1}{2}\,(\overline{D}_{xx} - \overline{D}_{yy})$$

The cluster spin states are linear combinations of basis states:

$$| S_1\, S_2\, (\tilde{S}_2)\, S_3\, (\tilde{S}_3) \cdots S_{N-1}\, (\tilde{S}_N)\, S_N,\ SM > \; = \; | (\tilde{S}),\ SM >$$

coupling scheme

i.e.

$$| \nu > \; = \sum_{(\tilde{S}), SM} | (\tilde{S}),\ SM > \; < (\tilde{S}),\ SM | \nu > \; =$$

$$= \sum_{(\tilde{S}), SM} | (\tilde{S}),\ SM > \; < (\tilde{S}),\ SM | \nu >$$

The coefficients $< (\tilde{S}),\ SM | \nu >$ are the solutions of the eigenvalues problem for the Hamiltonian H

The spin operators can be expressed in terms of ITOs components with k=1 and q = 0, ±1

$$s_x(i) = \frac{s^1_{-1}(i) - s^1_1(i)}{\sqrt{2}}$$

$$s_y(i) = i\,\frac{s^1_{-1}(i) + s^1_1(i)}{\sqrt{2}}$$

$$s_z(i) = s^1_0(i)$$

With matrix elements:

$$\langle SM | \hat{s}^1_q(i) | S'M' \rangle = \frac{1}{\sqrt{2S'+1}} \begin{pmatrix} S' & 1 & S \\ M' & q & M \end{pmatrix} \langle S \| \hat{s}^1(i) \| S' \rangle$$

Pdcs for a polycrystalline sample

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \frac{k_f}{k_i}(\gamma r_0)^2 \exp(-2W(\mathbf{q})) \sum_{nm} \frac{e^{-\frac{E_n}{k_B T}}}{Z} I_{nm}\,\delta(\hbar\omega + E_n - E_m)$$

$$I_{nm} = \sum_{i,j} F_i^*(q)\,F_j(q) \times \left\{ \frac{2}{3}\left[j_0(qR_{ij}) + C_0^2\, j_2(qR_{ij})\right] \tilde{s}_{z_i}\tilde{s}_{z_j} + \right.$$

$$+\frac{2}{3}\left[j_0(qR_{ij}) - \frac{1}{2}C_0^2\, j_2(qR_{ij})\right]\left(\tilde{s}_{x_i}\tilde{s}_{x_j} + \tilde{s}_{y_i}\tilde{s}_{y_j}\right) +$$

$$+\frac{1}{2} j_2(qR_{ij})\left[C_2^2\left(\tilde{s}_{x_i}\tilde{s}_{x_j} - \tilde{s}_{y_i}\tilde{s}_{y_j}\right) + C_{-2}^2\left(\tilde{s}_{x_i}\tilde{s}_{y_j} + \tilde{s}_{y_i}\tilde{s}_{x_j}\right)\right] +$$

$$\left. + j_2(qR_{ij})\left[C_1^2\left(\tilde{s}_{z_i}\tilde{s}_{x_j} + \tilde{s}_{x_i}\tilde{s}_{z_j}\right) + C_{-1}^2\left(\tilde{s}_{z_i}\tilde{s}_{y_j} + \tilde{s}_{y_i}\tilde{s}_{z_j}\right)\right]\right\}$$

$$\tilde{s}_{\alpha_i}\tilde{s}_{\gamma_j} = \langle n|s_{\alpha_i}|m\rangle\langle m|s_{\gamma_j}|n\rangle \qquad (\alpha,\ \gamma = x,\ y,\ z)$$

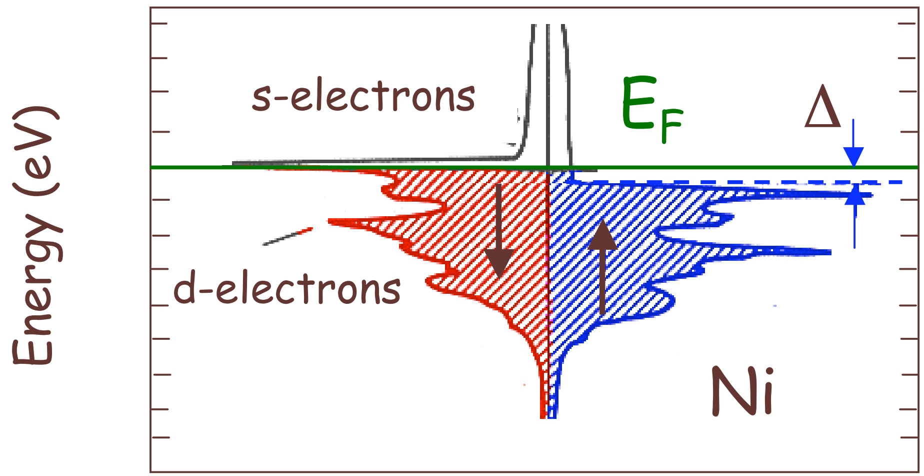
$$C_0^2 = \frac{1}{2}\left[3\left(\frac{R_{ijz}}{R_{ij}}\right)^2 - 1\right] \quad C_2^2 = \frac{R_{ijx}{}^2 - R_{ijy}{}^2}{R_{ij}{}^2} \quad C_{-2}^2 = \frac{R_{ijx} R_{ijz}}{R_{ij}{}^2} \quad C_1^2 = 2\frac{R_{ijx} R_{ijy}}{R_{ij}{}^2} \quad C_{-1}^2 = \frac{R_{ijy} R_{ijz}}{R_{ij}{}^2}$$

Onde di spin

Interazione di scambio: un cambiamento di verso dello spin di un elettrone richiede una energia finita.

In un sistema itinerante, un processo di spin-flip richiede un'energia minima: gap di Stoner

È la differenza tra l'energia più alta della sotto-banda maggioritaria ed il livello di Fermi.



Stati eccitati nei quali uno spin è rovesciato soltanto in media sull'intero cristallo: eccitazione collettiva dell'intero sistema di spin. L'energia di tale eccitazione è < Δ, dipende da $\mathbf{q}$ e può anche tendere a zero: onde di spin

Hamiltoniana di scambio:

$$H = -\sum_i \sum_\delta J_{i\delta} \vec{S}_i \cdot \vec{S}_{i+\delta} =$$

$$-\sum_i \sum_\delta J_{i\delta} \left[S_i^z S_{i+\delta}^z + \frac{1}{2}\left(S_i^+ S_{i+\delta}^- + S_i^- S_{i+\delta}^+ \right) \right]$$

In termini delle matrici di Pauli si ha

$$S^z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad S^x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S^y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$S^+ = S^x + iS^y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad S^- = S^x - iS^y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Se $|\alpha\rangle$ e $|\beta\rangle$ sono gli autostati di S^z

$$\begin{cases} S^z|\alpha\rangle = \frac{1}{2}|\alpha\rangle \\ S^z|\beta\rangle = -\frac{1}{2}|\beta\rangle \end{cases} \qquad \begin{cases} |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{cases} \qquad \begin{cases} S^+|\alpha\rangle = 0 \\ S^+|\beta\rangle = |\alpha\rangle \end{cases} \qquad \begin{cases} S^-|\beta\rangle = 0 \\ S^-|\alpha\rangle = |\beta\rangle \end{cases}$$

J > 0 ⇒ accoppiamento ferromagnetico:
nello stato fondamentale gli spin sono allineati ed equiorientati:

$$|0\rangle = \prod_i |\alpha\rangle_i$$

$$\begin{cases} S_i^z S_{i+\delta}^z |0\rangle = \frac{1}{4}|0\rangle \\ S_i^+ S_{i+\delta}^- |0\rangle = 0 \\ S_i^- S_{i+\delta}^+ |0\rangle = 0 \end{cases}$$

$$H|0\rangle = -\sum_i \sum_\delta J_{i\delta} \left[S_i^z S_{i+\delta}^z + \frac{1}{2}\left(S_i^+ S_{i+\delta}^- + S_i^- S_{i+\delta}^+ \right) \right] |0\rangle = -\frac{1}{4}\upsilon J N |0\rangle$$

N = numero di ioni, v = numero di primi vicini dello ione i-esimo

Dunque, |0> è un autostato di H con autovalore

$$E_0 - \frac{1}{4}\upsilon J N$$

Spin dell'atomo j rovesciato: stato eccitato

$$\left|\downarrow_j\right\rangle = S_j^-\left|0\right\rangle = S_j^-\prod_n\left|\alpha\right\rangle_n$$

ma $\left|\downarrow_j\right\rangle$ *non* è un autostato di H!

Infatti, gli operatori $S_j^+S_{j+\delta}^-$ che appaiono in H trasferiscono lo spin rovesciato dall'atomo j all'atomo j+δ: uno stato diverso!

Per ottenere un autostato di H dobbiamo considerare una combinazione lineare dei possibili stati $\left|\downarrow_j\right\rangle$

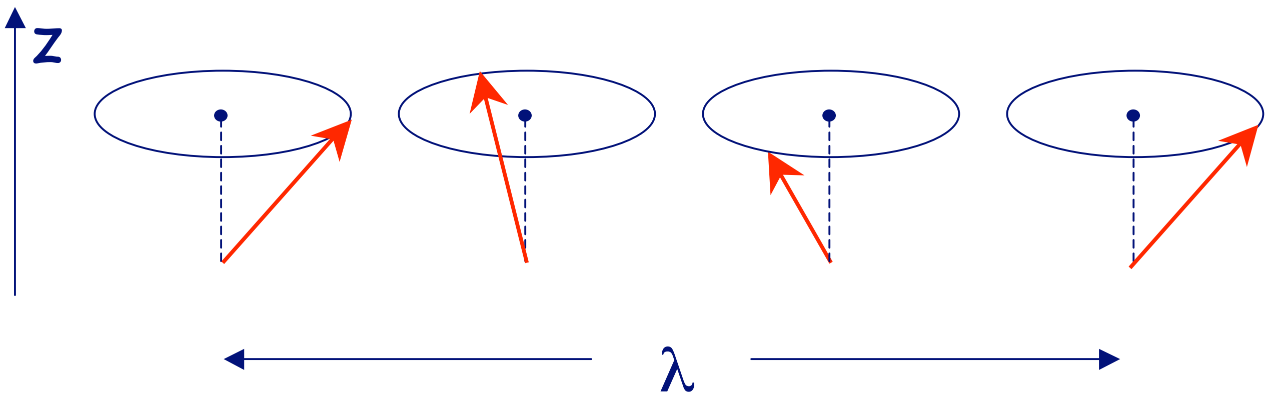
|k> rappresenta un'onda di spin

$$\left|k\right\rangle = \frac{1}{\sqrt{N}}\sum_j e^{i\vec{k}\cdot\vec{r}_j}\left|\downarrow_j\right\rangle$$

Si verifica facilmente che

- Gli autovalori di S_i^z e di $[(S_i^x)^2 + (S_i^y)^2]$ non dipendono dal tempo
- I valori di aspettazione di $[(S_i^x)^2 + (S_i^y)^2]$ non dipendono dal sito i
- I valori di aspettazione di S_i^x e di S_i^y sono nulli

Ciò corrisponde ad un moto di precessione attorno all'asse z, con una differenza di fase fra i siti determinata dal vettore d'onda k.



E_1 è l'energia del primo stato eccitato:

$$H|k\rangle = E_1|k\rangle$$

$$-\sum_i \sum_\delta J_{i\delta}\left[S_i^z S_{i+\delta}^z + \frac{1}{2}\left(S_i^+ S_{i+\delta}^- + S_i^- S_{i+\delta}^+\right)\right]\frac{1}{\sqrt{N}}\sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j} |\downarrow_j>$$

$$H|k\rangle = \frac{1}{\sqrt{N}}\sum_j e^{i\vec{k}\cdot\vec{r}_j}\left[-\frac{1}{4}\upsilon J(N-2)|\downarrow_j\rangle + \frac{1}{2}\upsilon J|\downarrow_j\rangle - \frac{1}{2}J\sum_\delta\left(|\downarrow_{j+\delta}\rangle + |\downarrow_{j-\delta}\rangle\right)\right]$$

rinumerando gli indici negli ultimi due termini:

$$H|k\rangle = \left[-\frac{1}{4}\upsilon JN + \upsilon J - \frac{1}{2}J\sum_\delta\left(e^{i\vec{k}\cdot\vec{r}_\delta} + e^{-i\vec{k}\cdot\vec{r}_\delta}\right)\right]\frac{1}{\sqrt{N}}\sum_j e^{i\vec{k}\cdot\vec{r}_j}|\downarrow_j\rangle$$

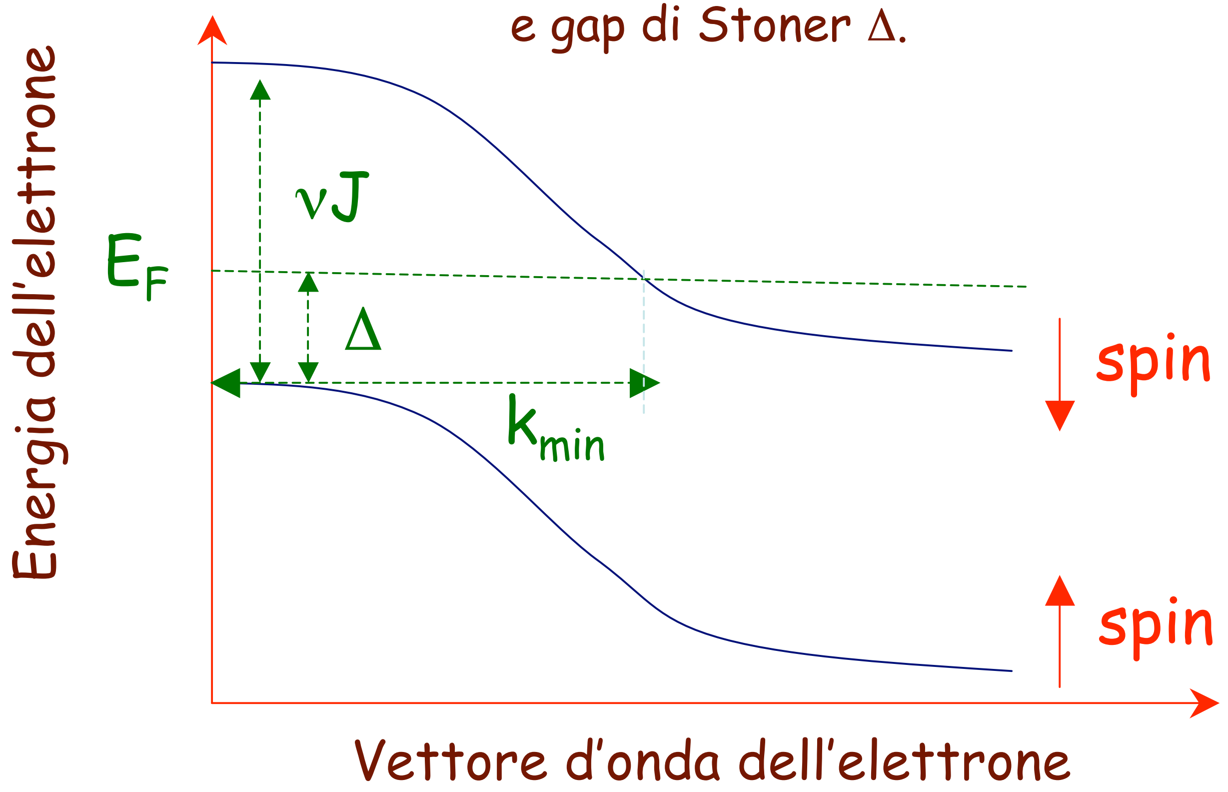
Dunque

$$E_1 - E_0 = J\left[\upsilon - \frac{1}{2}\sum_\delta\left(e^{i\vec{k}\cdot\vec{r}_\delta} + e^{-i\vec{k}\cdot\vec{r}_\delta}\right)\right] = J\left[\upsilon - \sum_\delta \cos\left(\vec{k}\cdot\vec{r}_\delta\right)\right]$$

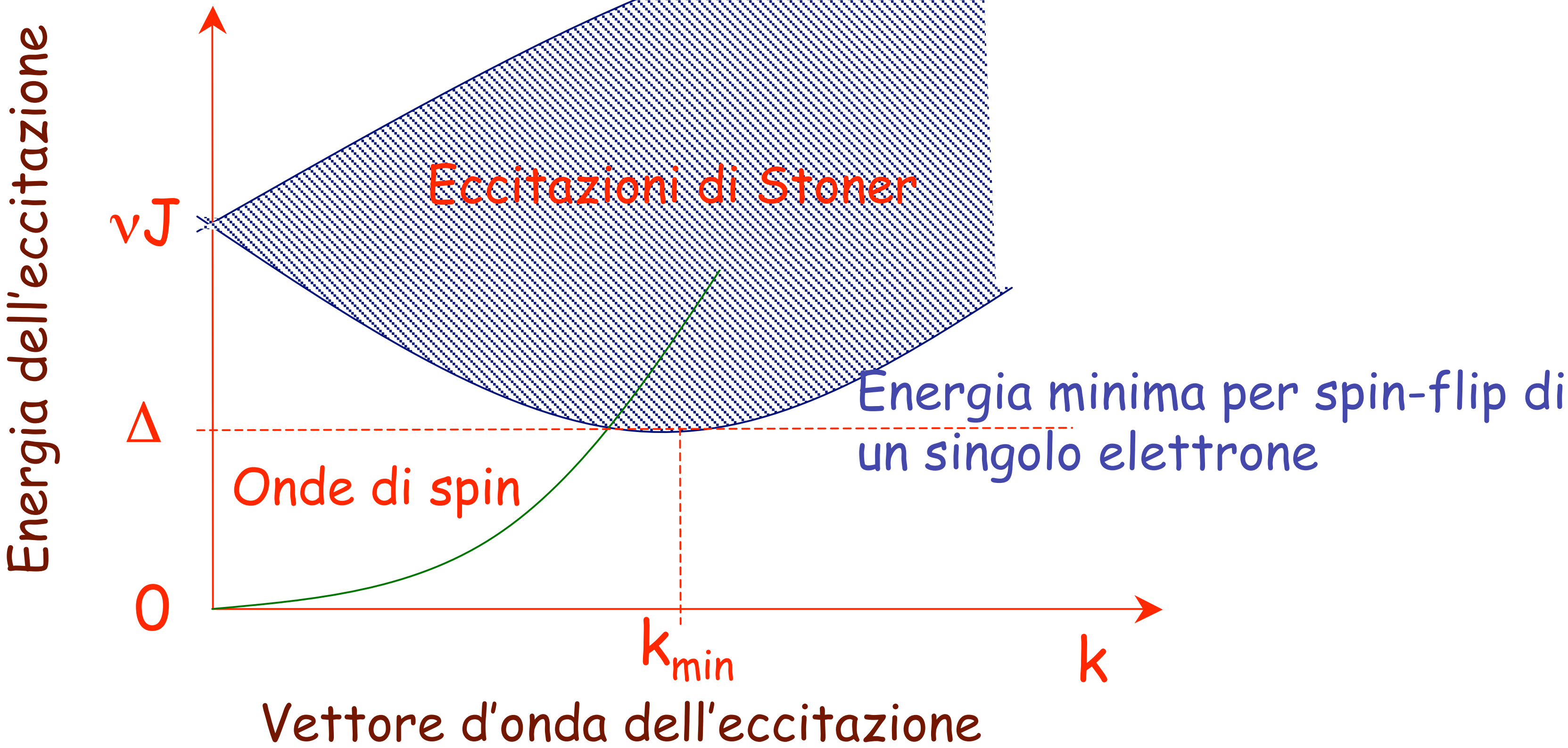
Per k piccolo

$$E_1 - E_0 = \frac{1}{2}J\sum_\delta\left(\vec{k}\cdot\vec{r}_\delta\right)^2$$

Struttura a bande modello, con splitting di scambio νJ e gap di Stoner Δ.



Dispersione delle onde di spin e spettro delle eccitazioni di elettrone singolo



Sezione d'urto per scattering da onde di spin

$$\frac{d^2\sigma}{d\Omega dE} = \frac{(\gamma r_0)^2}{2\pi\hbar}\frac{K_f}{Ki} N\left[\frac{1}{2} g f(\vec{Q})\right]^2 \sum_{\alpha,\beta}(\delta_{\alpha\beta} - \frac{Q_\alpha Q_\beta}{Q^2})e^{-2W} \times$$

$$\times \sum_{\ell} e^{i\vec{Q}\cdot\vec{\ell}} \int_{-\infty}^{\infty} dt e^{-i\omega t} < S_0^\alpha(0) S_\ell^\beta(t) >$$

Posto $\quad \langle\alpha,\beta\rangle = \langle S_0^\alpha(0) S_\ell^\beta(t)\rangle$

Si dimostra che

$$\langle +,+\rangle = \langle -,-\rangle = \langle +,z\rangle = \langle -,z\rangle = \langle z,+\rangle = \langle z,-\rangle = 0$$

$$\langle z,z\rangle, \quad \langle +,-\rangle, \quad \langle -,+\rangle \quad \neq \quad 0$$

$$<\lambda|\, S_0^z(0)\, S_e^z(t)\, |\lambda> \;=\; S^2 - \frac{2S}{N}\sum_{\mathbf{q}} <n_{\mathbf{q}}>$$

$$<S_0^+(0)\, S_e^-(t)> \;=\; \frac{2S}{N}\sum_{\mathbf{q}} e^{-\,i(\mathbf{q}\cdot e -\, \omega_q t)} <n_{\mathbf{q}} + 1>$$

$$<S_0^-(0)\, S_e^+(t)> \;=\; \frac{2S}{N}\sum_{\mathbf{q}} e^{\,i(\mathbf{q}\cdot e -\, \omega_q t)} <n_{\mathbf{q}}>$$

Il termine longitudinale <z,z> è indipendente da t e dà scattering elastico.
Lo scattering anelastico è dovuto ai termini trasversali, con α,β = x,y.
Esprimendo S^x ed S^y in termini di S^+ ed S^-, si ha

$$<S_0^x(0)\, S_e^x(t)> \;=\; <S_0^y(0)\, S_e^y(t)> \;=\; \frac{2S}{N}\sum_{\mathbf{q}} \{\, e^{-\,i(\mathbf{q}\cdot e -\, \omega_q t)} <n_{\mathbf{q}}+1> + e^{\,i(\mathbf{q}\cdot e -\, \omega_q t)} <n_{\mathbf{q}}> \,\}$$

$$<S_0^x(0)\, S_e^y(t)> \;=\; -\, <S_0^y(0)\, S_e^x(t)> \;=\; \frac{iS}{2N}\sum_{\mathbf{q}} \{\, e^{-\,i(\mathbf{q}\cdot e -\, \omega_q t)} <n_{\mathbf{q}}+1> - e^{\,i(\mathbf{q}\cdot e -\, \omega_q t)} <n_{\mathbf{q}}>\}$$

La somma dei termini <x,y> ed <y,x>, moltiplicati per lo stesso fattore Q_xQ_y/Q^2, si annulla. Rimane la somma dei termini <x,x> e <y,y>. Poiché

$$1 - \frac{Q_x^2}{Q^2} + 1 - \frac{Q_y^2}{Q^2} = 1 + \frac{Q_z^2}{Q^2}$$

$$\frac{d^2\sigma}{d\Omega dE} = (\gamma r_0)^2 \frac{K_f}{K_i} \frac{(2\pi)^3}{v_0} \left[\frac{1}{2} g f(\vec{Q})\right]^2 \frac{1}{2} S(1 + \frac{Q_z^2}{Q^2}) e^{-2W} \times$$
$$\times \sum_\tau \sum_{\vec{q}} \left\{ \delta(\vec{Q} - \vec{q} - \vec{\tau})\delta(\hbar\omega_q - \hbar\omega) < n_q + 1 > + \delta(\vec{Q} + \vec{q} - \vec{\tau})\delta(\hbar\omega_q + \hbar\omega) < n_q > \right\}$$

$$< n >= \frac{1}{e^{\hbar\omega/K_BT} - 1} \qquad < n + 1 >= \frac{e^{\hbar\omega/K_BT}}{e^{\hbar\omega/K_BT} - 1}$$

Lo scattering corrisponde alla creazione o alla annichilazione di un magnone. Il processo di scattering si verifica soltanto se

$$\frac{\hbar^2}{2m_n}(K_i^2 - K_f^2) = \pm\hbar\omega_q \qquad \vec{\mathrm{K}}_\mathrm{i} - \vec{\mathrm{K}}_\mathrm{f} = \vec{\tau} \pm \vec{\mathrm{q}}$$

Confronto intensità dovuta a scattering da un magnone o da un fonone:

❍ l'intensità per un magnone diminuisce col quadrato del fattore di forma

❍ l'intensità per un fonone cresce come Q^2

❍ le onde di spin sono presenti solo nella fase ordinata

❍ un campo magnetico esterno, sufficiente ad allineare gli eventuali domini magnetici fa cambiare l'intensità:

$$1 + \frac{Q_\eta^2}{Q^2} = \begin{cases} 1 & ; \mathbf{B} \perp \mathbf{Q} \\ 2 & ; \mathbf{B} \parallel \mathbf{Q} \end{cases}$$

Per B = 0, la media del fattore $(1+Q_\eta^2/Q^2)$ dipende dalla simmetria.

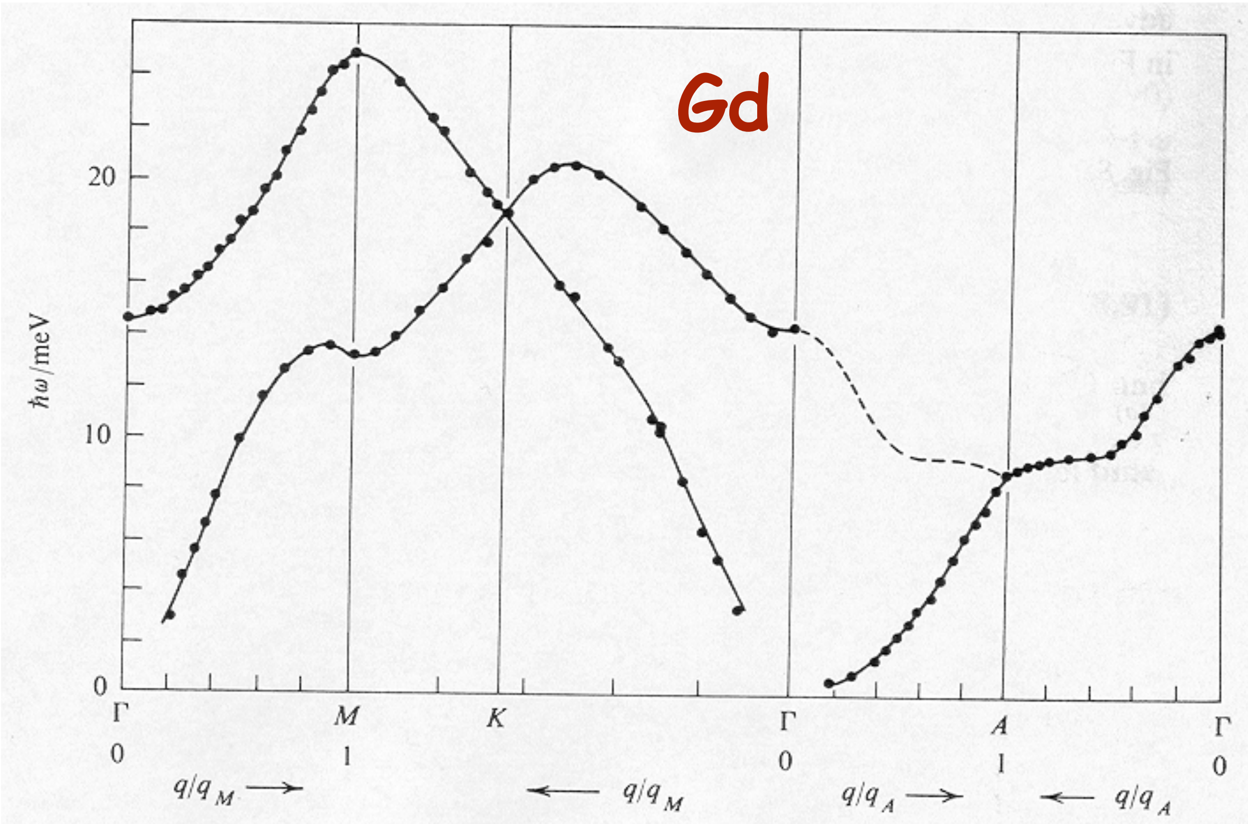
In un cristallo cubico vale 4/3.

Spin waves in a ferromagnet

$$S^{\perp}(\vec{\kappa},\omega)=\frac{S}{2}\{\delta(\varepsilon(\vec{\kappa})-\hbar\omega)(n(\hbar\omega)+1)+\delta(\varepsilon(\vec{\kappa})+\hbar\omega)n(\hbar\omega)\}$$

Magnon creation

Magnon destruction



Dispersion relation

$$\varepsilon(\vec{\kappa})=2S(J(0)-J(\vec{\kappa}))$$

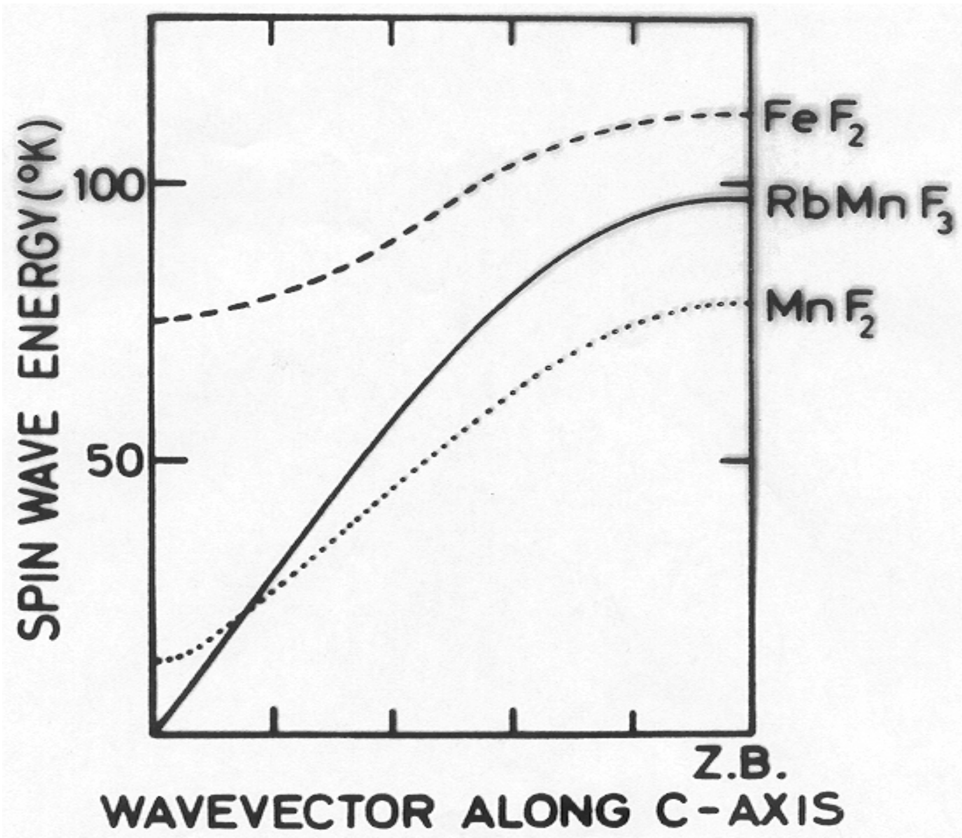
Magnon occupation prob.

$$n(E)=\frac{1}{\exp\left(E/k_BT\right)-1}$$

Spin waves in an antiferromagnet

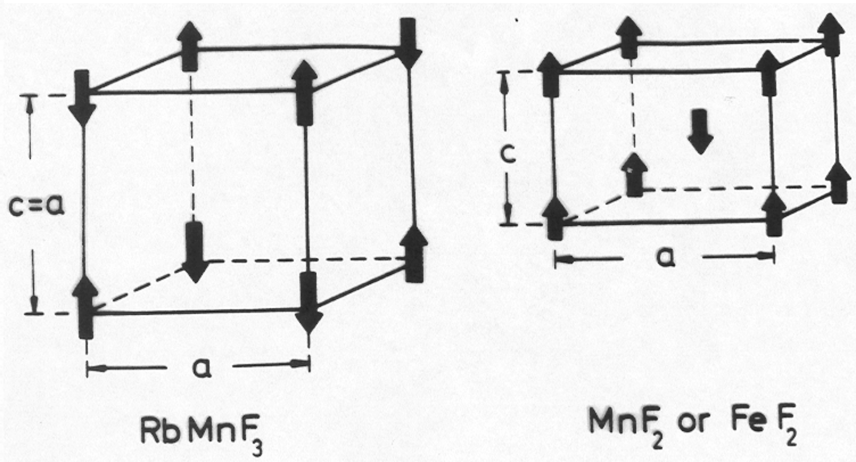
$$S^{\perp}(\vec{\kappa},\omega)=\frac{S}{2}\frac{J\left(1-\frac{1}{z}\sum_{\mathbf{d}}e^{i\vec{\kappa}\cdot\mathbf{d}}\right)}{\varepsilon(\vec{\kappa})}$$

$$\times\left\{\delta\left(\varepsilon(\vec{\kappa})-\hbar\omega\right)\left(n(\hbar\omega)+1\right)+\delta\left(\varepsilon(\vec{\kappa})+\hbar\omega\right)n(\hbar\omega)\right\}$$



<u>Dispersion relation</u>

$$\varepsilon(\vec{\kappa})=2S\sqrt{J(0)^2-J(\vec{\kappa})^2}$$



Exchange-coupled spins

Dinuclear systems

$$H_{ex} = \vec{S}_A \cdot \overline{D} \cdot \vec{S}_B$$

$$D_{ij} = \frac{1}{3}(D_{xx} + D_{yy} + D_{zz})\,\delta_{ij} + \frac{1}{2}(D_{ij} - D_{ji}) + \left(\frac{1}{2}(D_{ij} + D_{ji}) - \frac{1}{3}(D_{xx} + D_{yy} + D_{zz})\,\delta_{ij}\right)$$

$$J = -\frac{1}{3}(D_{xx} + D_{yy} + D_{zz})$$

$$d_{ij} = -d_{ji} = \frac{1}{2}(D_{ij} - D_{ji})$$

$$\vec{d} = (d_{yz}, d_{zx}, d_{xy})$$

$$D^0_{ij} = D^0_{ji} = \frac{1}{2}(D_{ij} + D_{ji}) + J$$

$$H_{ex} = -J\,\vec{S}_A \cdot \vec{S}_B + \vec{d} \cdot \left(\vec{S}_A \wedge \vec{S}_B\right) + \vec{S}_A \cdot \overline{D}^0 \cdot \vec{S}_B$$

$$-J\,\vec{S}_A \cdot \vec{S}_B = \text{ isotropic exchange}$$

$$\vec{d} \cdot \left(\vec{S}_A \wedge \vec{S}_B\right) = \text{ antisymmetric exchange}$$

$$\vec{S}_A \cdot \overline{D}^0 \cdot \vec{S}_B = \text{ asymmetric exchange}$$

Polynuclear clusters. Isotropic exchange

$$H_{Ex} = -\sum_{h=i}^{N}\sum_{k<h}^{N} J_{hk}\, S_h \cdot S_k$$

With N centres of spin S there are $(2S+1)^N$ energy levels

- If the isotropic exchange dominates the $(2S+1)^N$ states can be grouped as S_{tot}
- The magnetic anisotropy can be handled as a perturbation of the low lying S_{tot} states

Matrix elements are linear combinations of pair – interaction matrices :

$$< I \mid H^{iso} \mid J > = \sum_{h=1}^{N} \sum_{k>h}^{N} c_{hk} < I \mid \vec{S}_h \cdot \vec{S}_k \mid J >$$

with coefficients c_{hk} determined by exchange integrals $J_{hk.}$

Uncoupled basis states :

$$\mid I > = \mid S_1\, M_1 > \mid S_2\, M_2 > \cdots \mid S_N\, M_N >$$

A base with dimension $n = \prod_{1=1}^{N} (2\, S_i + 1)$ is obtained

$$\vec{S}_h \cdot \vec{S}_k = S_{hx} S_{kx} + S_{hy} S_{ky} + S_{hz} S_{kz} =$$

$$= \frac{1}{2} (S_{h+} S_{k-} + S_{h-} S_{k+}) + S_{hz} S_{kz}$$

The matrix elements are immediately obtained from the eigenvalues equations :

$$S_{h+} \mid S_h M_h \succ = \sqrt{(S_h + M_h + 1)(S_h - M_h)} \mid S_h M_h + 1 \succ$$

$$S_{h-} \mid S_h M_h \succ = \sqrt{(S_h - M_h + 1)(S_h + M_h)} \mid S_h M_h - 1 \succ$$

$$S_{hz} \mid S_h M_h \succ = M_h \mid S_h M_h \succ$$

Then:

$$S_{h+}\, S_{k-}\,|\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ =$$

$$= \sqrt{(S_h + M_h + 1)\,(S_h - M_h)}\,\sqrt{(S_k - M_k + 1)\,(S_k + M_k)} \times$$
$$\Big|\, S_1\, M_1 \cdots S_h\; M_h + 1 \quad S_k\; M_k - 1 \cdots S_N\, M_N \succ$$

$$S_{h-}\, S_{k+}\,\Big|\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ =$$

$$= \sqrt{(S_h - M_h + 1)\,(S_h + M_h)}\,\sqrt{(S_k + M_k + 1)\,(S_k - M_k)} \times$$
$$\Big|\, S_1\, M_1 \cdots S_h\; M_h - 1 \cdots S_k\; M_k + 1 \cdots S_N\, M_N \succ$$

$$S_{hz}\, S_{kz}\,\Big|\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ =$$

$$M_h\, M_k\,|\, S_1\, M_1 \cdots S_h\, M_h \cdots S_k\, M_k \cdots S_N\, M_N \succ$$

Diagonal Elements :

$$< \cdots S_h\, M_h \cdots S_k\, M_k \cdots |\, S_{hz}\, S_{kz} \,|\, \cdots S_h\, M_h \cdots S_k\, M_k \cdots > = M_h\, M_k\, \delta_{M_h^{'}\, M_h}\, \delta_{M_k^{'}\, M_k}$$

Non – Diagonal Elements :

$$< \cdots S_h\, M_h^{'} \cdots S_k\, M_k^{'} \cdots \big|\, S_{h+}\, S_{k-} \,\big|\, \cdots S_h\, M_h \cdots S_k\, M_k \cdots > =$$

$$\sqrt{(S_h + M_h + 1)\,(S_h - M_h)}\,\sqrt{(S_k - M_k + 1)\,(S_k + M_k)} \times \delta_{M_h^{'}\, M_h+1}\, \delta_{M_k^{'}\, M_k-1}$$

$$< \cdots S_h\, M_h^{'} \cdots S_k\, M_k^{'} \cdots |\, S_{h-}\, S_{k+} \,|\, \cdots S_h\, M_h \cdots S_k\, M_k \cdots > =$$

$$\sqrt{(S_h - M_h + 1)\,(S_h + M_h)}\,\sqrt{(S_k + M_k + 1)\,(S_k - M_k)} \times \delta_{M_h^{'}\, M_h-1}\, \delta_{M_k^{'}\, M_k+1}$$

The same result can be obtained using compound spherical tensors to build the scalar product:

$$\vec{S}_h \cdot \vec{S}_k = -\hat{S}_{h\,1,+1}\,\hat{S}_{k\,1,-1} + \hat{S}_{h\,1,0}\,\hat{S}_{k\,1,0} - \hat{S}_{h\,1,-1}\,\hat{S}_{k\,1,+1}$$

$$\begin{aligned} &\langle \cdots S_h\, M_h^{'} \quad S_k\, M_k^{'} \cdots \,|\, \vec{S}_h \cdot \vec{S}_k \,|\, \cdots S_h\, M_h \quad S_k\, M_k \cdots \rangle = \\ &= - \langle S_h\, M_h^{'} \,|\, \hat{S}_{h\,1,+1} \,|\, S_h\, M_h \rangle \langle S_k\, M_k^{'} \,|\, \hat{S}_{k\,1,-1} \,|\, S_k\, M_k \rangle + \\ &\qquad + \langle S_h\, M_h^{'} \,|\, \hat{S}_{h\,1,0} \,|\, S_h\, M_h \rangle \langle S_k\, M_k^{'} \,|\, \hat{S}_{k\,1,0} \,|\, S_k\, M_k \rangle - \\ &\qquad - \langle S_h\, M_h^{'} \,|\, \hat{S}_{h\,1,-1} \,|\, S_h\, M_h \rangle \langle S_k\, M_k^{'} \,|\, \hat{S}_{k\,1,+1} \,|\, S_k\, M_k \rangle \end{aligned}$$

using the Wigner – Eckart theorem

$$\prec \cdots S_h\, M_h^{'} \quad S_k\, M_k^{'} \cdots \left| \vec{S}_h \cdot \vec{S}_k \right| \cdots S_h\, M_h \quad S_k\, M_k \cdots \succ =$$

$$-\left[(-1)^{S_h-M'_h}\begin{pmatrix} S_h & 1 & S_h \\ -M_h^{'} & +1 & M_h \end{pmatrix}\left\langle S_h \,\|\vec{S}_h\|\, S_h\right\rangle\right]\left[(-1)^{S_k-M'_k}\begin{pmatrix} S_k & 1 & S_k \\ -M_k^{'} & -1 & M_k \end{pmatrix}\left\langle S_k \,\|\vec{S}_k\|\, S_k\right\rangle\right]+$$

$$+\left[(-1)^{S_h-M'_h}\begin{pmatrix} S_h & 1 & S_h \\ -M_h^{'} & 0 & M_h \end{pmatrix}\left\langle S_h \,\|\vec{S}_h\|\, S_h\right\rangle\right]\left[(-1)^{S_k-M'_k}\begin{pmatrix} S_k & 1 & S_k \\ -M_k^{'} & 0 & M_k \end{pmatrix}\left\langle S_k \,\|\vec{S}_k\|\, S_k\right\rangle\right]-$$

$$-\left[(-1)^{S_h-M'_h}\begin{pmatrix} S_h & 1 & S_h \\ -M_h^{'} & -1 & M_h \end{pmatrix}\left\langle S_h \,\|\vec{S}_h\|\, S_h\right\rangle\right]\left[(-1)^{S_k-M'_k}\begin{pmatrix} S_k & 1 & S_k \\ -M_k^{'} & +1 & M_k \end{pmatrix}\left\langle S_k \,\|\vec{S}_k\|\, S_k\right\rangle\right]$$

Use of the formulae for 3 j – symbols, recalling that $\langle J \| \vec{J} \| J \rangle = \sqrt{J(J+1)}$, gives

$$\prec \cdots S_h\, M_h^{'} \quad S_k\, M_k^{'} \cdots \left| \vec{S}_h \cdot \vec{S}_k \right| \cdots S_h\, M_h \quad S_k\, M_k \cdots \succ =$$

$$= M_h\, M_k\, \delta_{M_h^{'}\, M_h}\, \delta_{M_k^{'}\, M_k} +$$

$$+ \frac{1}{2} \sqrt{(S_h + M_h + 1)(S_h - M_h)} \sqrt{(S_k - M_k + 1)(S_k + M_k)} \times \delta_{M_h^{'}\, M_h+1}\, \delta_{M_k^{'}\, M_k-1} +$$

$$+ \frac{1}{2} \sqrt{(S_h - M_h + 1)(S_h + M_h)} \sqrt{(S_k + M_k + 1)(S_k - M_k)} \times \delta_{M_h^{'}\, M_h-1}\, \delta_{M_k^{'}\, M_k+1}$$

Homonuclear dimer

$$\text{Allowed spin states}: |S_A - S_B| \leqslant S \leqslant S_A + S_B$$

$$S^2 = \left(\vec{S}_A + \vec{S}_B\right)^2 = S_A^2 + S_B^2 + 2\,\vec{S}_A \cdot \vec{S}_B$$

$$H_{ex} = -\frac{1}{2}\,J\left(S^2 - S_A^2 - S_B^2\right)$$

Matrix Elements:

$$\langle S'\,M'\,|\,H_{ex}\,|\,SM\rangle = -\frac{1}{2}\,J[S\,(S+1) - S_A\,(S_A+1) - S_B\,(S_B+1)]\,\delta_{S'S}\;\;\delta_{M'M}$$

After translation by a constant, the eigenvalues are

$$\varepsilon_S = -\frac{1}{2}\,J\,S\,(S+1) \qquad\qquad 0 \le S \le 2S_A$$

Example $S_A = S_B = 1/2$

Basis states $\quad |m_A\, m_B> \; = \begin{pmatrix} |-\frac{1}{2}> \\ |\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |-\frac{1}{2}> \\ |\frac{1}{2}> \end{pmatrix} = \begin{pmatrix} |-\frac{1}{2}>|-\frac{1}{2}> \\ |-\frac{1}{2}>|\frac{1}{2}> \\ |\frac{1}{2}>|-\frac{1}{2}> \\ |\frac{1}{2}>|\frac{1}{2}> \end{pmatrix}$

Matrix elements

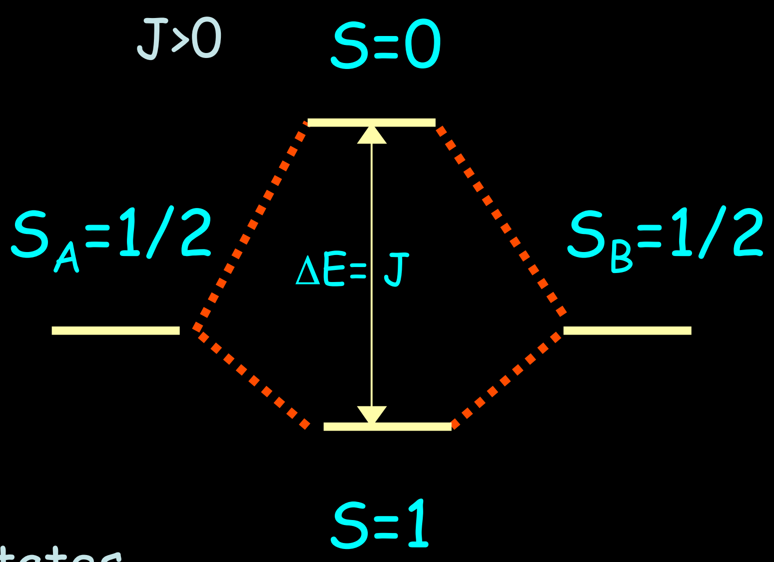
$$\langle m'_A\, m'_B | \mathbf{S}_A \cdot \mathbf{S}_B | m_A\, m_B \rangle = m_A\, m_B\, \delta_{m'_A m_A} \delta_{m'_B m_B} +$$

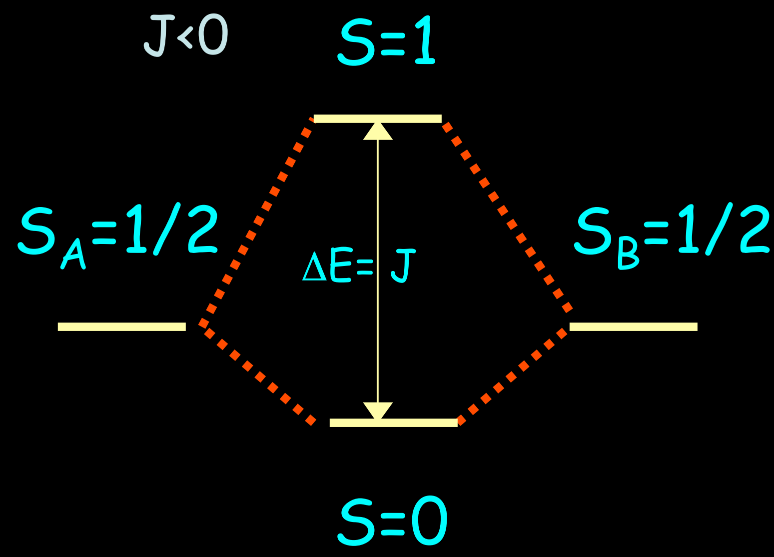
$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}+m_A+1\right)\left(\frac{1}{2}-m_A\right)}\sqrt{\left(\frac{1}{2}-m_B+1\right)\left(\frac{1}{2}+m_B\right)}\,\delta_{m'_A\, m_A+1}\,\delta_{m'_B\, m_B-1} +$$

$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}-m_A+1\right)\left(\frac{1}{2}+m_A\right)}\sqrt{\left(\frac{1}{2}+m_B+1\right)\left(\frac{1}{2}-m_B\right)}\,\delta_{m'_A\, m_A-1}\,\delta_{m'_B\, m_B+1}$$

	$\vert-\frac{1}{2}>\vert-\frac{1}{2}>$	$\vert-\frac{1}{2}>\vert\frac{1}{2}>$	$\vert\frac{1}{2}>\vert-\frac{1}{2}>$	$\vert\frac{1}{2}>\vert\frac{1}{2}>$
$<-\frac{1}{2}\vert<-\frac{1}{2}\vert$	$\frac{J}{4}$	0	0	0
$<-\frac{1}{2}\vert<\frac{1}{2}\vert$	0	$-\frac{J}{4}$	$\frac{J}{2}$	0
$<\frac{1}{2}\vert<-\frac{1}{2}\vert$	0	$\frac{J}{2}$	$-\frac{J}{4}$	0
$<\frac{1}{2}\vert<\frac{1}{2}\vert$	0	0	0	$\frac{J}{4}$

Eigenvalues $0, -J, -J, -J$





Eigenstates

$$|0,0> = \frac{1}{\sqrt{2}}\left(|\frac{1}{2}>|-\frac{1}{2}> - |-\frac{1}{2}>|\frac{1}{2}>\right)$$

$$|1,1> = |\frac{1}{2}>|\frac{1}{2}>$$

$$|1,0> = \frac{1}{\sqrt{2}}\left(|\frac{1}{2}>|-\frac{1}{2}> + |-\frac{1}{2}>|\frac{1}{2}>\right)$$

$$|1,-1> = |-\frac{1}{2}>|-\frac{1}{2}>$$

A magnetic field along the z – axis introduces the Zeeman term

$$H^Z = g_z \mu_B B S_z$$

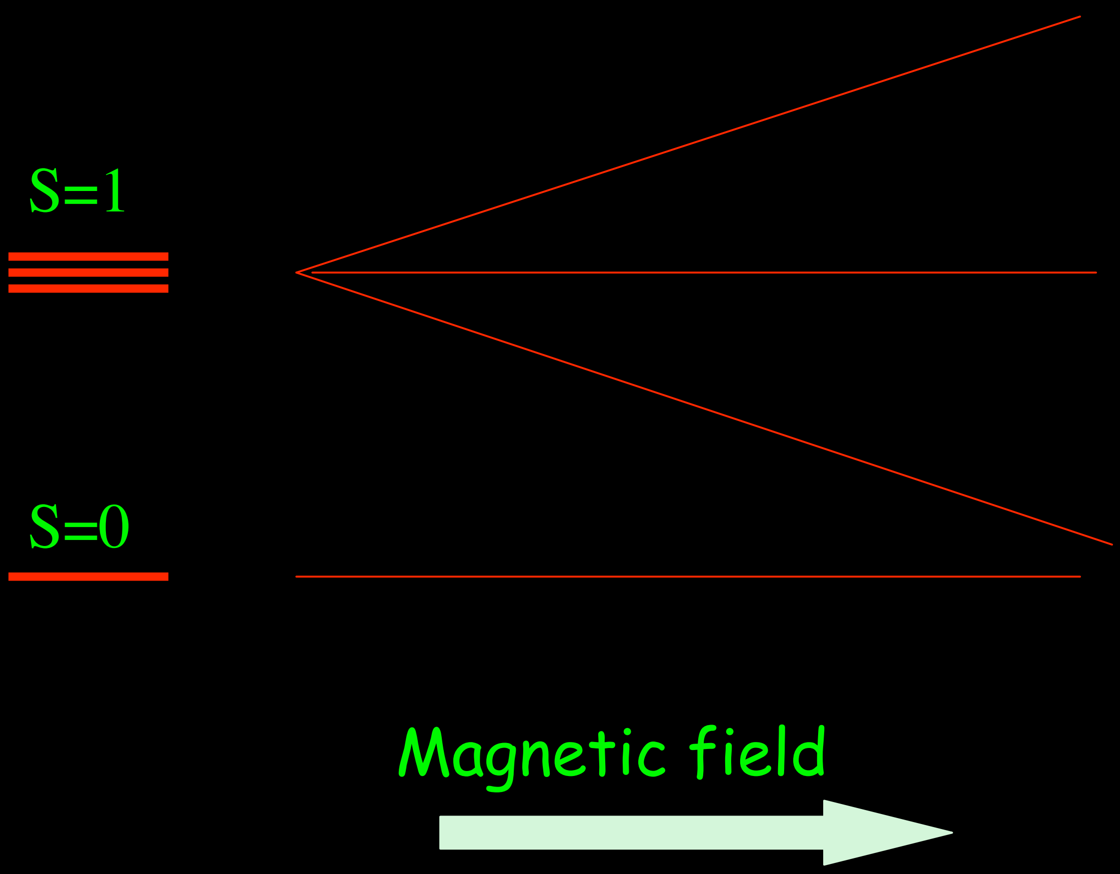
The total hamiltonian matrix is still diagonal, with eigenvalues

$$\varepsilon_S(B) = -\frac{1}{2} J S(S+1) + g_z \mu_B B M_S \qquad (M_S = -S, \ \ldots, S)$$

Example: $S_A = S_B = 1/2$

$\varepsilon_0 = 0$

$\varepsilon_1 = -J$



Etero – dinuclear spins.

Same eigenvalues as for omonuclear systems if $B = 0$:

$$\varepsilon_S = -\frac{1}{2} J\, S\,(S+1)$$

The situation changes when $B \neq 0$.

$\overline{g}_A,\ \overline{g}_B$ = local $\overline{g}$ tensors

$$H^{ex+Z} = -J\,\vec{S}_A \cdot \vec{S}_B + \mu_B\,\vec{B} \cdot \overline{g}_A \cdot \vec{S}_A \cdot + \mu_B\,\vec{B} \cdot \overline{g}_B \cdot \vec{S}_B$$

The matrix elements

$$H_{ij}^{ex+Z} = \langle i \mid H^{ex+Z} \mid j \rangle$$

are expressed in the basis of the $(2\,S_A + 1)\,(2\,S_B + 1)$ uncoupled spin states

$$\mid i \succ \; = \; \mid S_A\, M_A \succ \mid S_B\, M_B \succ$$

Alternatively, one can use the basis set of the coupled spin states

$$|I\succ = \left| S\,M \succ\right.$$

$$H^{ex+Z} = -\frac{J}{2}\left(\vec{S}^2 - \vec{S}_A^2 - \vec{S}_B^2\right) + \mu_B\,\vec{B}\cdot\overline{g}_S\cdot\vec{S}$$

with matrix elements

$$H_{IJ}^{ex+Z} = \left\langle I \middle| H^{ex+Z} \middle| J \right\rangle$$

The molecular g – tensor $\overline{g}_S$ is a linear combination of the local g – tensors :

$$\overline{g}_S = \frac{1}{2}(\overline{g}_A + \overline{g}_B) + \frac{S_A(S_A+1) - S_B(S_B+1)}{S(S+1)} \frac{1}{2}(\overline{g}_A - \overline{g}_B)$$

i.e.

$$\overline{g}_S = C_A \overline{g}_A + (1 - C_A)\overline{g}_B$$

with

$$C_A = \frac{S(S+1) + S_A(S_A+1) - S_B(S_B+1)}{2S(S+1)}$$

The Zeeman matrix is NO more diagonal:

$$\langle S\, M \,|\, H^Z \,|\, S'\, M\rangle \neq 0$$

making use of the irreducible tensor operator technique,

one obtains

$$\langle S_A\, S_B,\, S-1\;\, M \,|\, H^Z \,|\, S_A\, S_B,\, S\;\, M\rangle =$$

$$= (\overline{g}_A - \overline{g}_B)\, \mu_B\, B_z\, \langle S_A\, S_B,\, S-1\;\, M \,|\, S_{Az} \,|\, S_A\, S_B,\, S\;\, M\rangle =$$

$$= -(\overline{g}_A - \overline{g}_B)\, \mu_B\, B_z \sqrt{\frac{[S^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - S^2]\,(S^2 - M^2)}{4\, S^2\, (4\, S^2 - 1)}}$$

$$\langle S_A\, S_B,\, S+1\;\, M \,|\, H^Z \,|\, S_A\, S_B,\, S\;\, M\rangle =$$

$$= -(\overline{g}_A - \overline{g}_B)\, \mu_B\, B_z \sqrt{\frac{[(S+1)^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - (S+1)^2][(S+1)^2 - M^2]}{4\,(S+1)^2[4\,(S+1)^2 - 1]}}$$

Example: $A = Cu^{II}$ $(S_A = 1/2)$ $B = Ni^{II}$ $(S_B = 1)$

$$\Delta = \frac{g_{Cu} - g_{Ni}}{3} \qquad g_{1/2} = \frac{4\,g_{Ni} - g_{Cu}}{3} \qquad g_{3/2} = \frac{2\,g_{Ni} - g_{Cu}}{3}$$

$$\begin{array}{cccccc} |\tfrac{1}{2}\ -\tfrac{1}{2}> & |\tfrac{1}{2}\ \tfrac{1}{2}> & |\tfrac{3}{2}\ -\tfrac{3}{2}> & |\tfrac{3}{2}\ -\tfrac{1}{2}> & |\tfrac{3}{2}\ \tfrac{1}{2}> & |\tfrac{3}{2}\ \tfrac{3}{2}> \end{array}$$

$$H^{ex+Z} = \begin{pmatrix} -\frac{g_{1/2}}{2}\mu_B B & 0 & 0 & -\Delta\sqrt{2}\,\mu_B B & 0 & 0 \\ 0 & \frac{g_{1/2}}{2}\mu_B B & 0 & 0 & -\Delta\sqrt{2}\,\mu_B B & 0 \\ 0 & 0 & -\frac{3}{2}J - \frac{3\,g_{3/2}}{2}\mu_B B & 0 & 0 & 0 \\ -\Delta\sqrt{2}\,\mu_B B & 0 & 0 & -\frac{3}{2}J - \frac{g_{3/2}}{2}\mu_B B & 0 & 0 \\ 0 & -\Delta\sqrt{2}\,\mu_B B & 0 & 0 & -\frac{3}{2}J + \frac{g_{3/2}}{2}\mu_B B & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{3}{2}J + \frac{3\,g_{3/2}}{2}\mu_B B \end{pmatrix}$$

Eigenvalues

$$\left\{-\frac{3J}{2}-\frac{3}{2}Bg_{\frac{3}{2}}\mu_B,\ -\frac{3J}{2}+\frac{3}{2}Bg_{\frac{3}{2}}\mu_B,\right.$$

$$\frac{1}{8}\left(-6J+2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B-\sqrt{\left(6J-2Bg_{\frac{1}{2}}\mu_B-2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(-3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)}\right),$$

$$\frac{1}{8}\left(-6J+2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B+\sqrt{\left(6J-2Bg_{\frac{1}{2}}\mu_B-2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(-3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)}\right),$$

$$\frac{1}{8}\left(-6J-2Bg_{\frac{1}{2}}\mu_B-2Bg_{\frac{3}{2}}\mu_B-\sqrt{\left(6J+2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)}\right),$$

$$\left.\frac{1}{8}\left(-6J-2Bg_{\frac{1}{2}}\mu_B-2Bg_{\frac{3}{2}}\mu_B+\sqrt{\left(6J+2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)}\right)\right\}$$

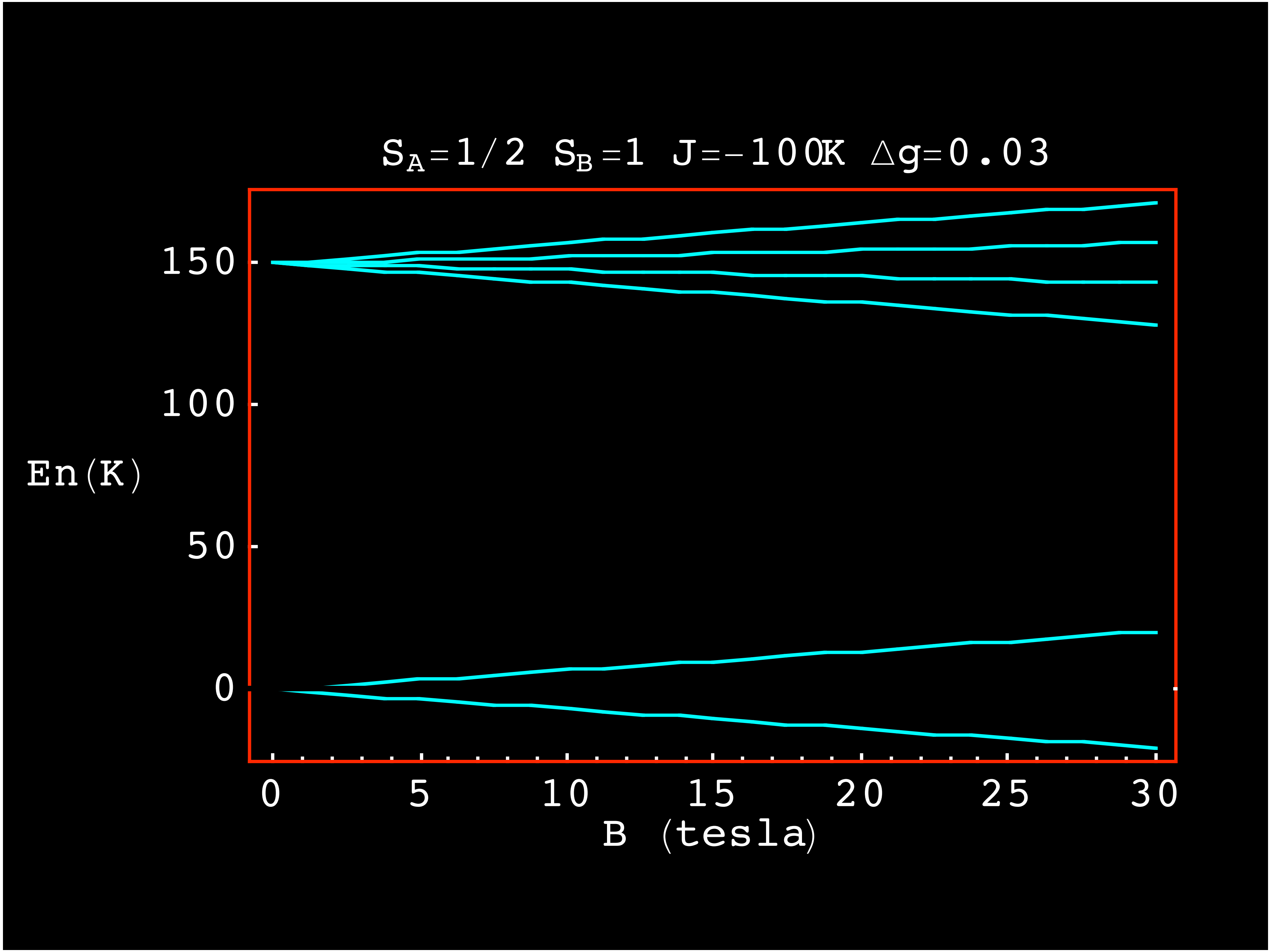
Eigenvectors

$$\left\{\{0,0,0,0,0,1\},\{0,0,1,0,0,0\},\left\{0,\frac{1}{8\sqrt{2}B\Delta\mu_B}\left(-6J-2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B+\sqrt{\left(\left(6J-2Bg_{\frac{1}{2}}\mu_B-2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(-3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)\right)}\right),\right.\right.$$

$$\left.0,0,1,0\right\},\left\{0,\frac{1}{8\sqrt{2}B\Delta\mu_B}\left(-6J-2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B-\sqrt{\left(\left(6J-2Bg_{\frac{1}{2}}\mu_B-2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(-3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)\right)}\right),0,0,1,0\right\},$$

$$\left\{-\frac{1}{8\sqrt{2}B\Delta\mu_B}\left(6J-2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B-\sqrt{\left(\left(6J+2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)\right)}\right),0,0,1,0,0\right\},$$

$$\left.\left\{-\frac{1}{8\sqrt{2}B\Delta\mu_B}\left(6J-2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B+\sqrt{\left(\left(6J+2Bg_{\frac{1}{2}}\mu_B+2Bg_{\frac{3}{2}}\mu_B\right)^2-16\left(3BJg_{\frac{1}{2}}\mu_B-8B^2\Delta^2\mu_B^2+B^2g_{\frac{1}{2}}g_{\frac{3}{2}}\mu_B^2\right)\right)}\right),0,0,1,0,0\right\}\right\}$$



S_A=1/2 S_B=1 J=-100K Δg=0.03
En(K)
150
100
50
0
0
5
10
15
20
25
30
B (tesla)

The INS pdcs for a dimer

$$S^{\alpha\beta}(\mathbf{q},\ \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda|s^{\alpha}_{n'}|\lambda'\rangle\langle\lambda'|\mathbf{s}^{\beta}_{n}|\lambda\rangle$$

$S_A = S_B = 1/2$

$|\lambda\rangle = |0\ 0\rangle, |1 -1\rangle, |1\ 0\rangle, |1\ 1\rangle$

$$S^{\alpha\beta}{}_{0\to 1} = \sum_{M}\Bigg(\sum_{n=A,B} p(E_0)\Big(\langle 00|s^{\alpha}{}_{n}|1\,M\rangle\langle 1\,M|\mathbf{s}^{\beta}{}_{n}|00\rangle +$$

$$+e^{i\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)}\langle 00|s^{\alpha}{}_{B}|1\,M\rangle\langle 1\,M|\mathbf{s}^{\beta}{}_{A}|00\rangle +$$

$$+e^{-i\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)}\langle 00|s^{\alpha}{}_{A}|1\,M\rangle\langle 1\,M|\mathbf{s}^{\beta}{}_{B}|00\rangle\Big)\Bigg)$$

$$|0,0> = \frac{1}{\sqrt{2}}\left(|\frac{1}{2}>|-\frac{1}{2}> - |-\frac{1}{2}>|\frac{1}{2}>\right)$$

$$|1,\ 1> = |\frac{1}{2}>|\frac{1}{2}>$$

$$|1,0> = \frac{1}{\sqrt{2}}\left(|\frac{1}{2}>|-\frac{1}{2}> + |-\frac{1}{2}>|\frac{1}{2}>\right)$$

$$|1,\ -1> = |-\frac{1}{2}>|-\frac{1}{2}>$$

Matrix elements

$$<1-1|\, s_A^x\, |00> = \frac{1}{2} < -\frac{1}{2} \ -\frac{1}{2}\left|(s_A^+ + s_A^-)\frac{1}{\sqrt{2}}\left(|\frac{1}{2} \ -\frac{1}{2}> - |-\frac{1}{2}\ \frac{1}{2}>\right) = \frac{1}{2\sqrt{2}}\right.$$

$$<1\,1|\, s_B^y\, |00> = \frac{-i}{2} < \frac{1}{2}\ \frac{1}{2}\left|(s_B^+ - s_B^-)\frac{1}{\sqrt{2}}\left(|\frac{1}{2} \ -\frac{1}{2}> - |-\frac{1}{2}\ \frac{1}{2}>\right) = \frac{-i}{2\sqrt{2}}\right.$$

Etc.

$$<1\ -1|\,s_A^x\,|00> = \frac{1}{2\sqrt{2}} \qquad <1\,0|\,s_A^x\,|00> = 0 \qquad <1\,1|\,s_A^x\,|00> = \frac{-1}{2\sqrt{2}}$$

$$<1\ -1|\,s_A^y\,|00> = \frac{i}{2\sqrt{2}} \qquad <1\,0|\,s_A^y\,|00> = 0 \qquad <1\,1|\,s_A^y\,|00> = \frac{i}{2\sqrt{2}}$$

$$<1\ -1|\,s_A^z\,|00> = 0 \qquad <1\,0|\,s_A^z\,|00> = \frac{1}{2} \qquad <1\,1|\,s_A^z\,|00> = 0$$

$$<1\ -1|\,s_B^x\,|00> = \frac{-1}{2\sqrt{2}} \qquad <1\,0|\,s_B^x\,|00> = 0 \qquad <1\,1|\,s_B^x\,|00> = \frac{1}{2\sqrt{2}}$$

$$<1\ -1|\,s_B^y\,|00> = \frac{-i}{2\sqrt{2}} \qquad <1\,0|\,s_B^y\,|00> = 0 \qquad <1\,1|\,s_B^y\,|00> = \frac{-i}{2\sqrt{2}}$$

$$<1\ -1|\,s_B^z\,|00> = 0 \qquad <1\,0|\,s_B^z\,|00> = -\frac{1}{2} \qquad <1\,1|\,s_B^z\,|00> = 0$$

Ex. Work out the above matrix elements

Substituting the above matrix elements into the pdcs, one has
(only the xx, yy and zz terms survive)

$$S^{xx}{}_{0\to1} = S^{yy}{}_{0\to1} = S^{zz}{}_{0\to1} = \frac{1}{2}[1-\cos\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)]$$

And finally

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{0\to1} = A(q)\sum_\alpha\left(1-\frac{q_\alpha q_\alpha}{q^2}\right)(S^{\alpha\alpha})_{0\to1}\,\delta(-J-\hbar\omega) =$$

$$= A(q)[1-\cos\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)]\,\delta(-J-\hbar\omega)$$

Note that there is no scattering 0-1 if **q** is parallel to the axis of the dimer.
For a polycrystalline sample

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{0\to1} = A(q)\frac{1}{4\pi}\int_{4\pi}[1-\cos\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)]\,d\Omega = A(q)\left(1-\frac{\sin(q|\mathbf{r}_A-\mathbf{r}_B|)}{q|\mathbf{r}_A-\mathbf{r}_B|}\right)$$

For a dimer with general spin values:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{S\to S'} = \frac{k_f}{k_i}(\gamma r_0)^2 |F(\mathbf{q})|^2 \exp(-2W(\mathbf{q}))\ \ p_S \sum_\alpha \left(1-\frac{q_\alpha^2}{q^2}\right)\times$$

$$\times\frac{2}{3}(2S+1)(2S'+1)S_A(S_A+1)(2S_A+1)\left(\begin{Bmatrix} S' & S & 1 \\ S_A & S_A & S_A \end{Bmatrix}\right)^2\times$$

$$\times\left[1+(-1)^{S'-S}\cos\mathbf{q}\cdot(\mathbf{r}_A-\mathbf{r}_B)\right]\delta(E_{S'}-E_S-\hbar\omega)$$

Or, for a polycrystal:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{S\to S'} = \frac{k_f}{k_i}(\gamma r_0)^2 |F(\mathbf{q})|^2 \exp(-2W(\mathbf{q}))\ \ p_S\times$$

$$\times\frac{4}{3}(2S+1)(2S'+1)S_A(S_A+1)(2S_A+1)\left(\begin{Bmatrix} S' & S & 1 \\ S_A & S_A & S_A \end{Bmatrix}\right)^2\times$$

$$\times\left[1+(-1)^{S'-S}\frac{\sin q|\mathbf{r}_A-\mathbf{r}_B|}{q|\mathbf{r}_A-\mathbf{r}_B|}\right]\delta(E_{S'}-E_S-\hbar\omega)$$

Trimers

Example. $S_1 = S_2 = S_3 = 1/2$ $\quad (8 \times 8)$ matrix

Basis states :

$$|S_A\, M_A\, S_B\, M_B\, S_C\, M_C \succ = \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} =$$

$$= \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}> \end{pmatrix} \otimes \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \end{pmatrix} =$$

$$= \begin{pmatrix} |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},-\frac{1}{2}> \\ |\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}>|\frac{1}{2},+\frac{1}{2}> \end{pmatrix}$$

$$H_{12} = -J_{12}\,\mathbf{S}_1 \cdot \mathbf{S}_2$$

$$\langle m'_1\, m'_2\, m'_3 | \mathbf{S}_1 \cdot \mathbf{S}_2 | m_1\, m_2\, m_3 \rangle = m_1\, m_2\, \delta_{m'_1 m_1}\, \delta_{m'_2 m_2}\, \delta_{m'_3 m_3} +$$

$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}+m_1+1\right)\left(\frac{1}{2}-m_1\right)}\sqrt{\left(\frac{1}{2}-m_2+1\right)\left(\frac{1}{2}+m_2\right)}\,\delta_{m'_1\, m_1+1}\,\delta_{m'_2\, m_2-1}\,\delta_{m'_3 m_3} +$$

$$+\frac{1}{2}\sqrt{\left(\frac{1}{2}-m_1+1\right)\left(\frac{1}{2}+m_1\right)}\sqrt{\left(\frac{1}{2}+m_2+1\right)\left(\frac{1}{2}-m_2\right)}\,\delta_{m'_1\, m_1-1}\,\delta_{m'_2\, m_2+1}\,\delta_{m'_3 m_3}$$

$$H_{12} = -J_{12}\begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & -\frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & -\frac{1}{4} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

$$H_{13} = -J_{13}\, S_1 \cdot S_3$$

$$H_{13} = -J_{13} \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & 0 & 0 & -\frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{4} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

$$H_{23} = -J_{23}\,\mathbf{S}_2 \cdot \mathbf{S}_3$$

$$H_{23} = -J_{23} \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{4} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{4} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} \end{pmatrix}$$

General triangle: $J_{12} \neq J_{13} \neq J_{23}$

$$H = \begin{pmatrix}
\frac{J_{12}}{4}+\frac{J_{13}}{4}+\frac{J_{23}}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{J_{12}}{4}-\frac{J_{13}}{4}-\frac{J_{23}}{4} & \frac{J_{23}}{2} & 0 & \frac{J_{13}}{2} & 0 & 0 & 0 \\
0 & \frac{J_{23}}{2} & -\frac{J_{12}}{4}+\frac{J_{13}}{4}-\frac{J_{23}}{4} & 0 & \frac{J_{12}}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{J_{12}}{4}-\frac{J_{13}}{4}+\frac{J_{23}}{4} & 0 & \frac{J_{12}}{2} & \frac{J_{13}}{2} & 0 \\
0 & \frac{J_{13}}{2} & \frac{J_{12}}{2} & 0 & -\frac{J_{12}}{4}-\frac{J_{13}}{4}+\frac{J_{23}}{4} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{J_{12}}{2} & 0 & -\frac{J_{12}}{4}+\frac{J_{13}}{4}-\frac{J_{23}}{4} & \frac{J_{23}}{2} & 0 \\
0 & 0 & 0 & \frac{J_{13}}{2} & 0 & \frac{J_{23}}{2} & \frac{J_{12}}{4}-\frac{J_{13}}{4}-\frac{J_{23}}{4} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{J_{12}}{4}+\frac{J_{13}}{4}+\frac{J_{23}}{4}
\end{pmatrix}$$

With the following definitions

$$J = \frac{1}{3}(J_{12} + J_{13} + J_{23})$$

$$\Delta = \sqrt{J_{12}^2 + J_{13}^2 + J_{23}^2 - J_{12}\,J_{23} - J_{13}\,J_{23} - J_{12}\,J_{13}}$$

$$a = J_{13}^2 - J_{12}\,J_{23} + J_{13}\,\Delta$$

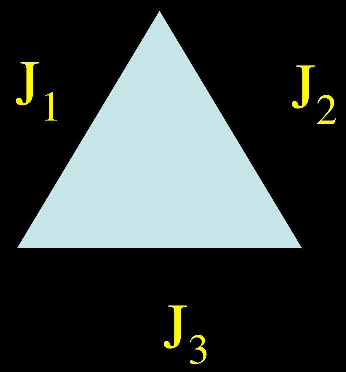
$$c = J_{AB}^2 - J_{13}\,J_{23} + J_{12}\,\Delta$$

$$b = J_{23}^2 - J_{12}\,J_{13} + J_{23}\,\Delta$$

$$A = J_{AC}^2 - J_{12}\,J_{23} - J_{13}\,\Delta$$

$$B = J_{12}^2 - J_{13}\,J_{23} - J_{12}\,\Delta$$

$$C = J_{BC}^2 - J_{12}\,J_{13} - J_{23}\,\Delta$$



Eigenvalues and eigenvectors are:

$$E(\lambda_0) = \frac{3J}{4}$$

$$\left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle$$

$$\left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle + \left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle + \left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle + \left|-\tfrac{1}{2}\right\rangle\left|+\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle + \left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle$$

$$E(\lambda_1) = -\left(\frac{3J}{4} + \frac{1}{2}\Delta\right)$$

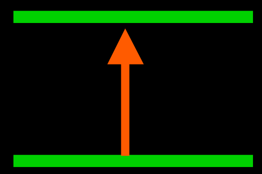
$$-\frac{a+c}{a}\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle + \frac{c}{a}\left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle + \left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle$$

$$-\frac{a+b}{a}\left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle + \frac{b}{a}\left|-\tfrac{1}{2}\right\rangle\left|+\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle + \left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle$$

$$E(\lambda_2) = -\left(\frac{3J}{4} - \frac{1}{2}\Delta\right)$$

$$-\frac{A+B}{A}\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle + \frac{B}{A}\left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle + \left|\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle$$

$$-\frac{A+C}{A}\left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\right\rangle + \frac{C}{A}\left|-\tfrac{1}{2}\right\rangle\left|+\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle + \left|\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle\left|-\tfrac{1}{2}\right\rangle$$



S=1/2

S=1/2

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda_1\rightarrow\lambda_2} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|\, F(\mathbf{q}) \,|^2 \exp(-2W(\mathbf{q})) \;\; p_{(\lambda_0)} \times$$

$$\times\frac{2}{3}\left[1 + \frac{(J_{12}-J_{23})(J_{13}-J_{12})}{\Delta^2}\;\frac{\sin(qR_{12})}{qR_{12}} + \right.$$

$$+\frac{(J_{12}-J_{23})(J_{23}-J_{13})}{\Delta^2}\;\frac{\sin(qR_{23})}{qR_{23}} +$$

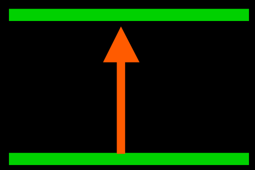
$$\left. + \frac{(J_{12}-J_{13})(J_{13}-J_{23})}{\Delta^2}\;\frac{\sin(qR_{13})}{qR_{13}}\right]\delta(\hbar\omega + E(\lambda_1) - E(\lambda_2))$$

$$
\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda_0\rightarrow\lambda_1} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|F(\mathbf{q})|^2 \exp(-2W(\mathbf{q}))\;\; p_{(\lambda_0)}\times
$$

$$
\times\frac{2}{3}\Big[2+\left(\frac{-a(a+b)}{a^2+b^2+ab}+\frac{-bc}{b^2+c^2-bc}\right)\frac{\sin(qR_{12})}{qR_{12}}+
$$

$$
+\left(\frac{ab}{a^2+b^2+ab}+\frac{b(c-b)}{b^2+c^2-bc}\right)\frac{\sin(qR_{13})}{qR_{13}}+
$$

$$
+\left(\frac{-b(a+b)}{a^2+b^2+ab}+\frac{-c(c-b)}{b^2+c^2-bc}\right)\frac{\sin(qR_{23})}{qR_{23}}\Big]\delta(\hbar\omega+E(\lambda_0)-E(\lambda_1))
$$



S=1/2 b

S=3/2

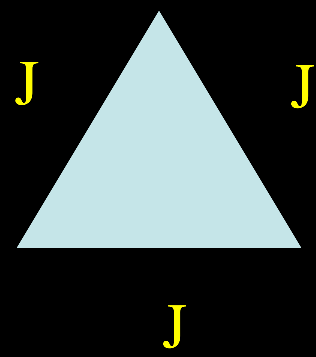
$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda_0\to\lambda_2} = \frac{k_f}{k_i}(\gamma r_0)^2\,|F(\mathbf{q})|^2\exp(-2W(\mathbf{q}))\;p_{(\lambda_0)}\times$$

$$\times\frac{2}{3}\Bigg[2+\left(\frac{-A(A+B)}{A^2+B^2+AB}+\frac{-BC}{B^2+C^2-BC}\right)\frac{\sin(qR_{12})}{qR_{12}}+$$

$$+\left(\frac{AB}{A^2+B^2+AB}+\frac{-BC}{B^2+C^2-BC}\right)\frac{\sin(qR_{13})}{qR_{13}}+$$

$$+\left(\frac{-B(A+B)}{A^2+B^2+AB}+\frac{-c(c-b)}{B^2+C^2-BC}\right)\frac{\sin(qR_{23})}{qR_{23}}\Bigg]\delta(\hbar\omega+E(\lambda_0)-E(\lambda_2))$$

Equilateral triangle: $J_{12} = J_{13} = J_{23} = J$

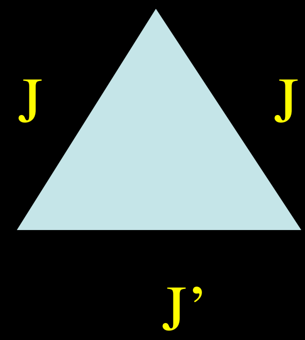


$$H = \begin{pmatrix} -\frac{3J}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{J}{4} & -\frac{J}{2} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & -\frac{J}{2} & \frac{J}{4} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{J}{4} & 0 & -\frac{J}{2} & -\frac{J}{2} & 0 \\ 0 & -\frac{J}{2} & -\frac{J}{2} & 0 & \frac{J}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & \frac{J}{4} & -\frac{J}{2} & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & -\frac{J}{2} & \frac{J}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{3J}{4} \end{pmatrix}$$

Eigenvalues : $\left\{-\frac{3J}{4}, -\frac{3J}{4}, -\frac{3J}{4}, -\frac{3J}{4}, \frac{3J}{4}, \frac{3J}{4}, \frac{3J}{4}, \frac{3J}{4}\right\}$

Two degenerate doublets S = 1/2 and one quartet S=3/2

Isosceles triangle : $J_{12} = J_{13} \quad J_{23} = J'$

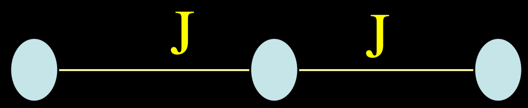


$$H = \begin{pmatrix} -\frac{J}{2}-\frac{J'}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{J'}{4} & -\frac{J}{2} & 0 & -\frac{J'}{2} & 0 & 0 & 0 \\ 0 & -\frac{J}{2} & \frac{J}{2}-\frac{J'}{4} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{J'}{4} & 0 & -\frac{J}{2} & -\frac{J'}{2} & 0 \\ 0 & -\frac{J'}{2} & -\frac{J}{2} & 0 & \frac{J'}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & \frac{J}{2}-\frac{J'}{4} & -\frac{J}{2} & 0 \\ 0 & 0 & 0 & -\frac{J'}{2} & 0 & -\frac{J}{2} & \frac{J'}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{J}{2}-\frac{J'}{4} \end{pmatrix}$$

Eigenvalues : $\left\{\frac{1}{4}(4J-J'), \frac{1}{4}(4J-J'), -\frac{J}{2}-\frac{J'}{4}, -\frac{J}{2}-\frac{J'}{4}, -\frac{J}{2}-\frac{J'}{4}, -\frac{J}{2}-\frac{J'}{4}, \frac{3J'}{4}, \frac{3J'}{4}\right\}$

$S = 1/2$, $S = 3/2$, $S = 1/2$

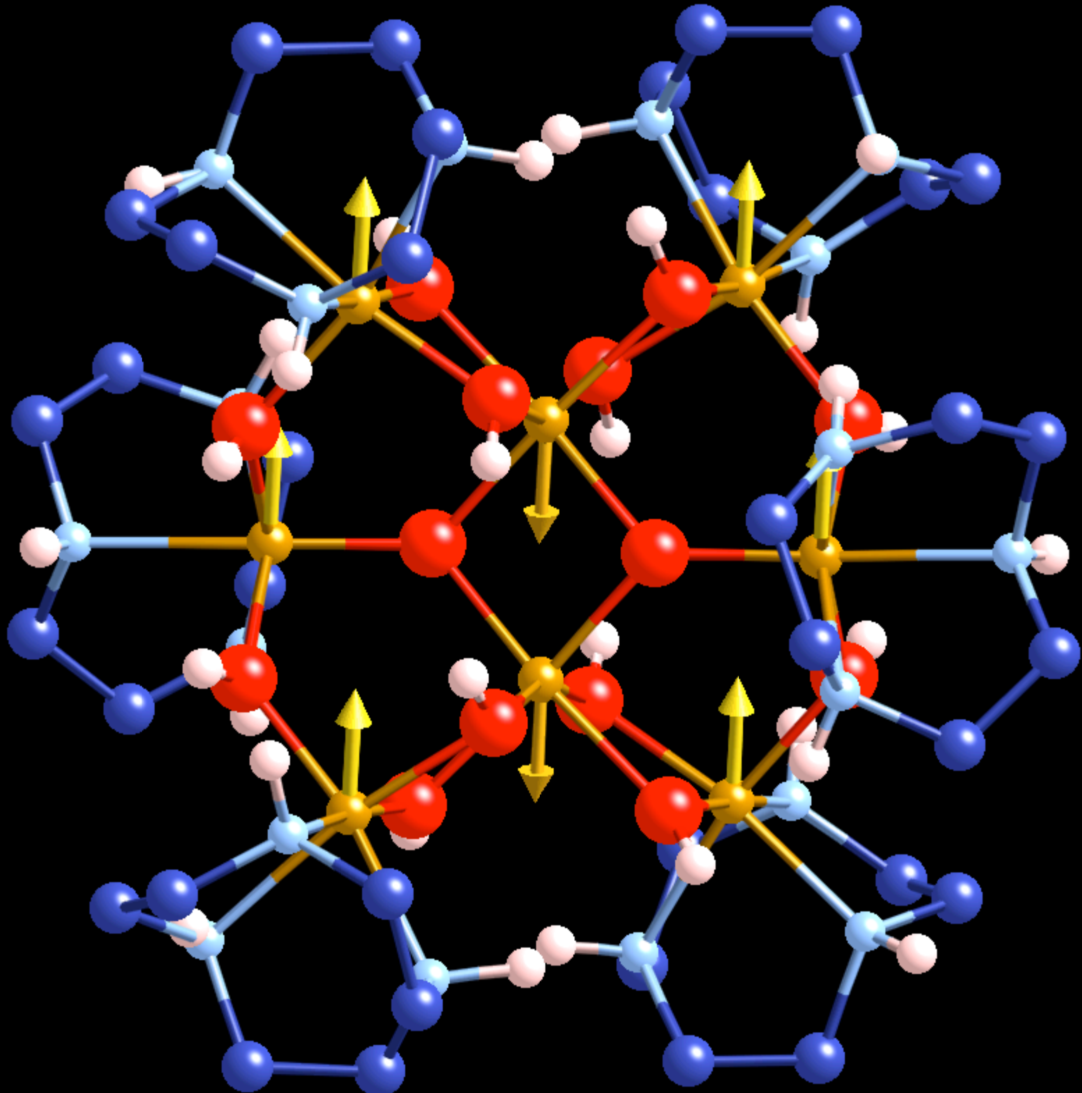
Linear Chain $1-2-3$

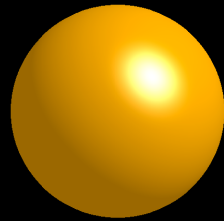


$$H=-J\left(H_{12}+H_{23}\right)=\begin{pmatrix} -\frac{J}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{J}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{J}{2} & \frac{J}{2} & 0 & -\frac{J}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{J}{2} & 0 & 0 \\ 0 & 0 & -\frac{J}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{J}{2} & 0 & \frac{J}{2} & -\frac{J}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{J}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{J}{2} \end{pmatrix}$$

$$\text{Eigenvalues}:\left\{0,0,-\frac{J}{2},-\frac{J}{2},-\frac{J}{2},-\frac{J}{2},J,J\right\}$$

$[Fe_8O_2(OH)_{12}(tacn)_6]Br_8\ 9H_2O$

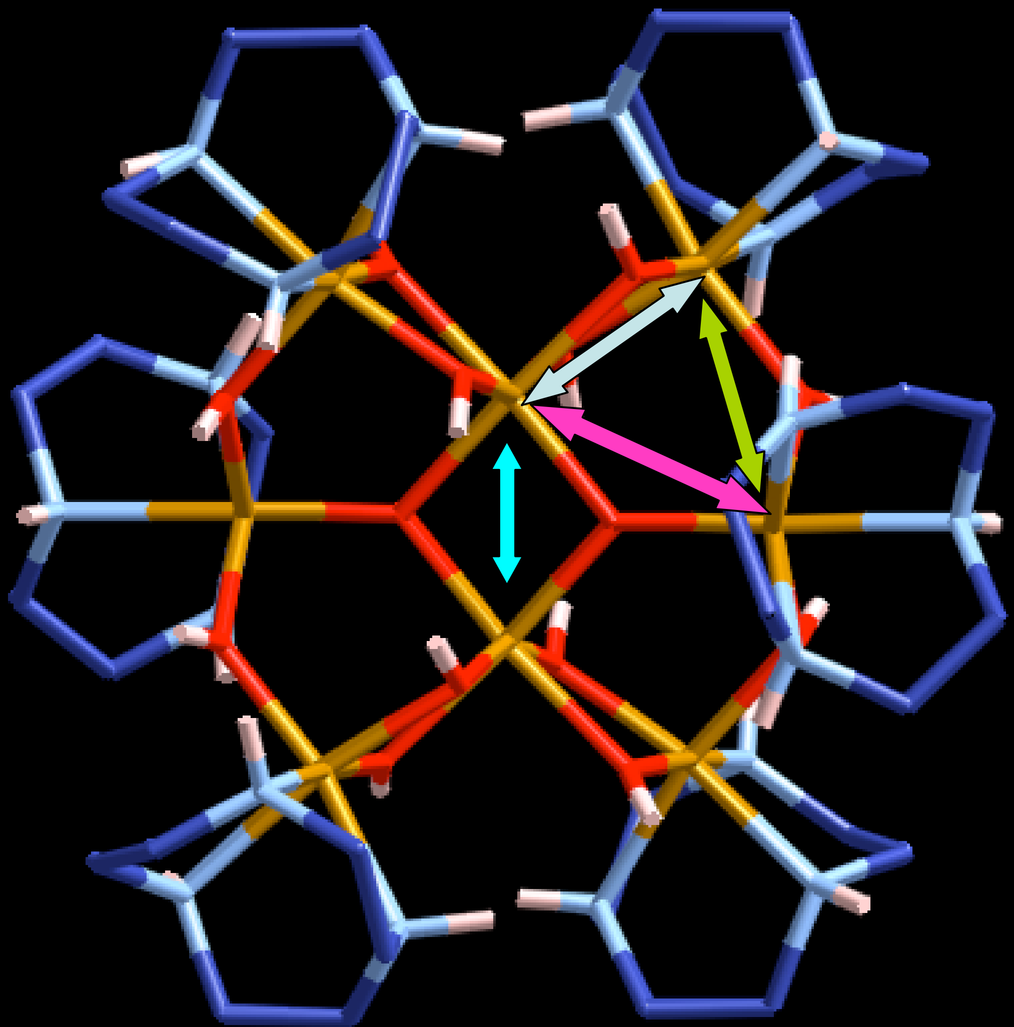


Fe^{3+} 

$s = 5/2$

$S = 10$

Exchange Interactions in Fe_8



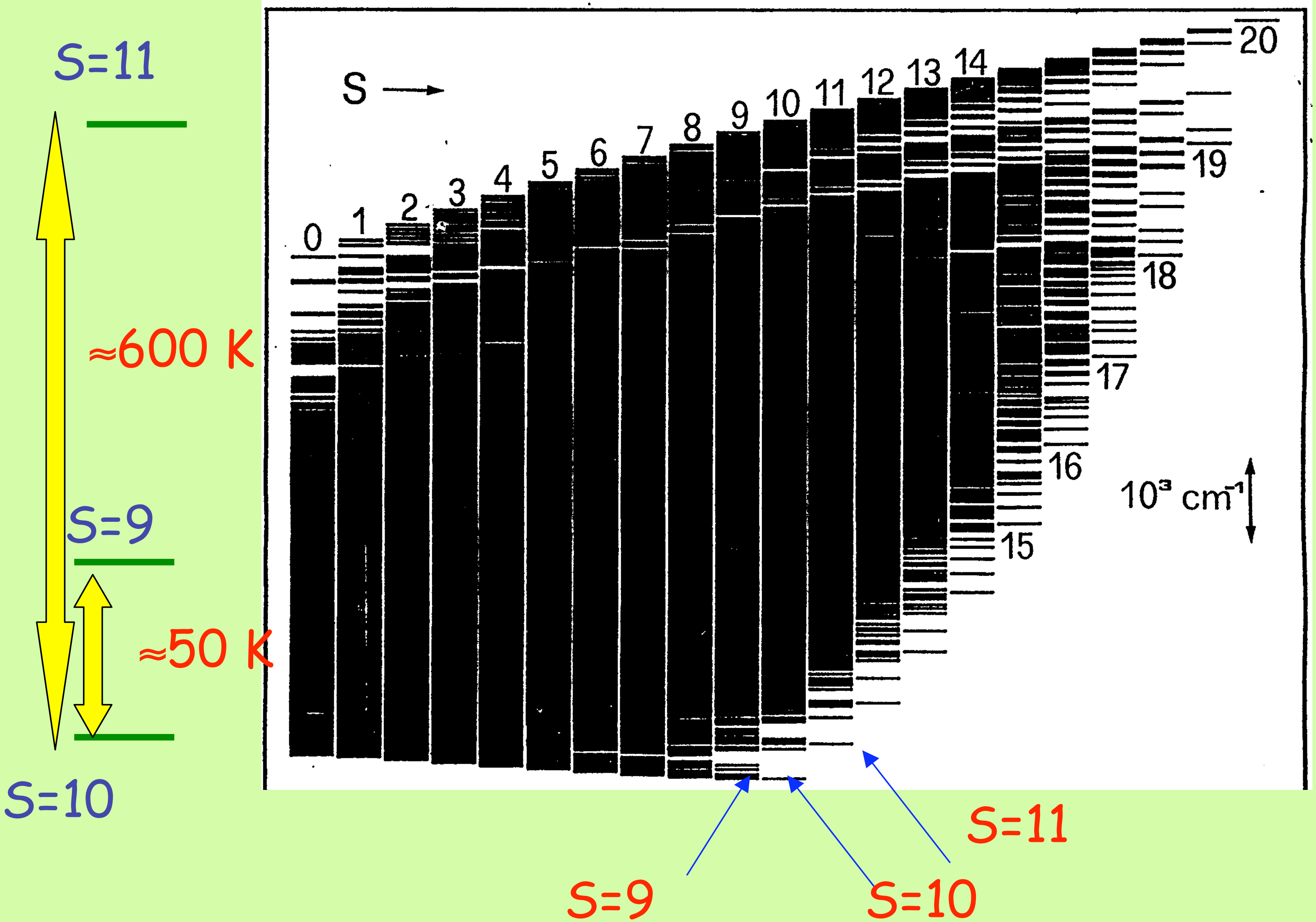
$J_1 = 25\ cm^{-1}$

$J_2 = 140\ cm^{-1}$

$J_3 = 18\ cm^{-1}$

$J_4 = 41\ cm^{-1}$

Energy levels in Fe_8



In the general case:

The Hamiltonian

$$H = \sum_{i<j} J_{ij}\,\hat{S}_i \cdot \hat{S}_j + \sum_{i} \hat{S}_i \cdot \overline{D}_i \cdot \hat{S}_i + \sum_{i<j} \hat{S}_i \cdot \overline{D}_{ij} \cdot \hat{S}_j + \mu_B \sum_{i} g_i\,\vec{B} \cdot \hat{S}_i$$

Isotropic exchange local ZFS Dipole-dipole interaction Zeeman term

$$\hat{S}_i \cdot \overline{D}_i \cdot \hat{S}_i = D_i\left(S_{iz}^2 - \frac{1}{3} S_i\,(S_i + 1)\right) + E_i\left(S_{ix}^2 - S_{iy}^2\right)$$

$$D = \frac{1}{2}\,(2\,\overline{D}_{zz} - \overline{D}_{xx} - \overline{D}_{yy}) \qquad E = \frac{1}{2}\,(\overline{D}_{xx} - \overline{D}_{yy})$$

The cluster spin states are linear combinations of basis states:

$$|\, S_1\, S_2\, (\tilde{S}_2)\, S_3\, (\tilde{S}_3) \cdots S_{N-1}\, (\tilde{S}_N)\, S_N,\ SM > \; = \; |\, (\tilde{S}),\ SM >$$

coupling scheme

i.e.
$$|\, \nu > \; = \sum_{(\tilde{S}),\, SM} |\, (\tilde{S}),\ SM > \; < (\tilde{S}),\ SM \,|\, \nu > \; =$$

$$= \sum_{(\tilde{S}),\, SM} |\, (\tilde{S}),\ SM > \; < (\tilde{S}),\ SM \,|\, \nu >$$

The coefficients $< (\tilde{S}),\ SM \,|\, \nu >$ are the solutions of the eigenvalues problem for the Hamiltonian H

The spin operators can be expressed in terms of ITOs components with k=1 and q = 0, ±1

$$s_x(i) = \frac{s^1_{-1}(i) - s^1_1(i)}{\sqrt{2}}$$

$$s_y(i) = i\,\frac{s^1_{-1}(i) + s^1_1(i)}{\sqrt{2}}$$

$$s_z(i) = s^1_0(i)$$

With matrix elements:

$$\langle SM|\,\hat{s}^1_q(i)\,|S'M'\rangle = \frac{1}{\sqrt{2S'+1}}\begin{pmatrix} S' & 1 & S \\ M' & q & M \end{pmatrix}\langle S\,\|\,\hat{s}^1(i)\,\|\,S'\rangle$$

Pdcs for a polycrystalline sample

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \frac{k_f}{k_i}(\gamma r_0)^2 \exp(-2W(\mathbf{q})) \sum_{nm} \frac{e^{-\frac{E_n}{k_B T}}}{Z} I_{nm}\,\delta(\hbar\omega + E_n - E_m)$$

$$I_{nm} = \sum_{i,j} F_i^*(q)\,F_j(q) \times \left\{ \frac{2}{3}\left[j_0(qR_{ij}) + C_0^2\, j_2(qR_{ij})\right] \tilde{s}_{z_i}\tilde{s}_{z_j} + \right.$$

$$+\frac{2}{3}\left[j_0(qR_{ij}) - \frac{1}{2}C_0^2\, j_2(qR_{ij})\right]\left(\tilde{s}_{x_i}\tilde{s}_{x_j} + \tilde{s}_{y_i}\tilde{s}_{y_j}\right) +$$

$$+\frac{1}{2} j_2(qR_{ij})\left[C_2^2\left(\tilde{s}_{x_i}\tilde{s}_{x_j} - \tilde{s}_{y_i}\tilde{s}_{y_j}\right) + C_{-2}^2\left(\tilde{s}_{x_i}\tilde{s}_{y_j} + \tilde{s}_{y_i}\tilde{s}_{x_j}\right)\right] +$$

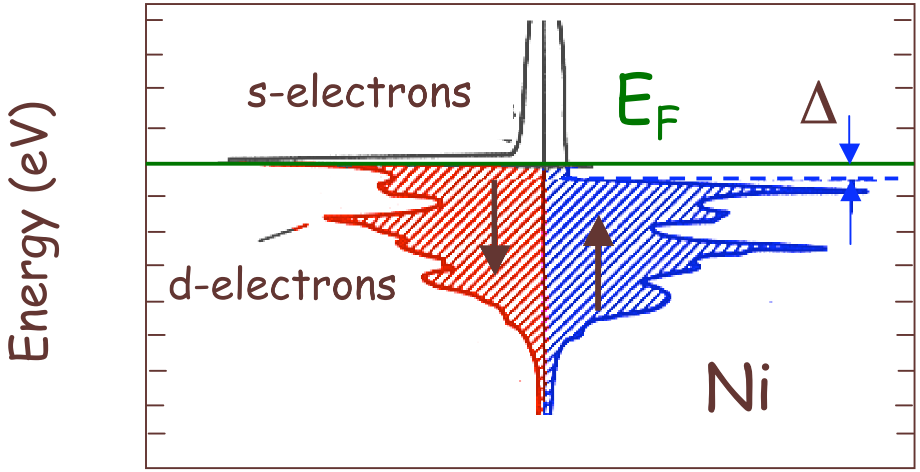
$$\left. + j_2(qR_{ij})\left[C_1^2\left(\tilde{s}_{z_i}\tilde{s}_{x_j} + \tilde{s}_{x_i}\tilde{s}_{z_j}\right) + C_{-1}^2\left(\tilde{s}_{z_i}\tilde{s}_{y_j} + \tilde{s}_{y_i}\tilde{s}_{z_j}\right)\right]\right\}$$

$$\tilde{s}_{\alpha_i}\tilde{s}_{\gamma_j} = \langle n | s_{\alpha_i} | m \rangle \langle m | s_{\gamma_j} | n \rangle \qquad (\alpha,\ \gamma = x,\ y,\ z)$$

$$C_0^2 = \frac{1}{2}\left[3\left(\frac{R_{ijz}}{R_{ij}}\right)^2 - 1\right] \quad C_2^2 = \frac{R_{ijx}^2 - R_{ijy}^2}{R_{ij}^2} \quad C_{-2}^2 = \frac{R_{ijx} R_{ijz}}{R_{ij}^2} \quad C_1^2 = 2\frac{R_{ijx} R_{ijy}}{R_{ij}^2} \quad C_{-1}^2 = \frac{R_{ijy} R_{ijz}}{R_{ij}^2}$$

Spin waves

Exchange interaction: a finite energy is required to flip an electron spin.
IN an itinerant system, a spin-flip process requires a minimum energy:
Stoner gap.
This is the difference between the highest energy in the majority band and the Fermi level.



We will consider excited states with one spin flipped in average over the entire crystal: collective excitation of the whole spin system. The excitation energy is < Δ, depends on **q** and can go to zero: Spin Waves

Exchenga Hamiltonian:

$$H = -\sum_i \sum_\delta J_{i\delta} \vec{S}_i \cdot \vec{S}_{i+\delta} =$$

$$-\sum_i \sum_\delta J_{i\delta} \left[S_i^z S_{i+\delta}^z + \frac{1}{2}\left(S_i^+ S_{i+\delta}^- + S_i^- S_{i+\delta}^+ \right) \right]$$

Using Pauli matrices we have

$$S^z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad S^x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S^y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$S^+ = S^x + iS^y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad S^- = S^x - iS^y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Ltets $|\alpha\rangle$ and $|\beta\rangle$ be eigenstates of S:

$$\begin{cases} S^z\left|\alpha\right\rangle = \frac{1}{2}\left|\alpha\right\rangle \\ S^z\left|\beta\right\rangle = -\frac{1}{2}\left|\beta\right\rangle \end{cases} \qquad \begin{cases} \left|\alpha\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \left|\beta\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{cases} \qquad \begin{cases} S^+\left|\alpha\right\rangle = 0 \\ S^+\left|\beta\right\rangle = \left|\alpha\right\rangle \end{cases} \qquad \begin{cases} S^-\left|\beta\right\rangle = 0 \\ S^-\left|\alpha\right\rangle = \left|\beta\right\rangle \end{cases}$$

J > 0 $\Rightarrow$ ferromagnetic coupling:

the spin in the ground state are aligned and have the same orientation

$$|0\rangle = \prod_i |\alpha\rangle_i$$

$$\begin{cases} S_i^z S_{i+\delta}^z |0\rangle = \frac{1}{4}|0\rangle \\ S_i^+ S_{i+\delta}^- |0\rangle = 0 \\ S_i^- S_{i+\delta}^+ |0\rangle = 0 \end{cases}$$

$$H|0\rangle = -\sum_i \sum_\delta J_{i\delta}\left[S_i^z S_{i+\delta}^z + \frac{1}{2}\left(S_i^+ S_{i+\delta}^- + S_i^- S_{i+\delta}^+\right)\right]|0\rangle = -\frac{1}{4}\upsilon JN|0\rangle$$

N = number of ions in the crystal, v = number of n.n. to the i-th ion

Hence, |0> is an eigenstate of H with eigenvalue

$$E_0 - \frac{1}{4}\upsilon JN$$

Spin on atom j flipped: excited state

$$|\downarrow_j\rangle = S_j^- |0\rangle = S_j^- \prod_n |\alpha\rangle_n$$

This is NOT an eigenstates of H

Indeed, the operators $S_j^+ S_{j+\delta}^-$ appearing in H move the flipped spin from the atom j to the atom j+δ: this is a different state!

To have an eigenstate of H we have to build a linear combination of th epossible states $|\downarrow_j\rangle$ with 1 spin reversed:

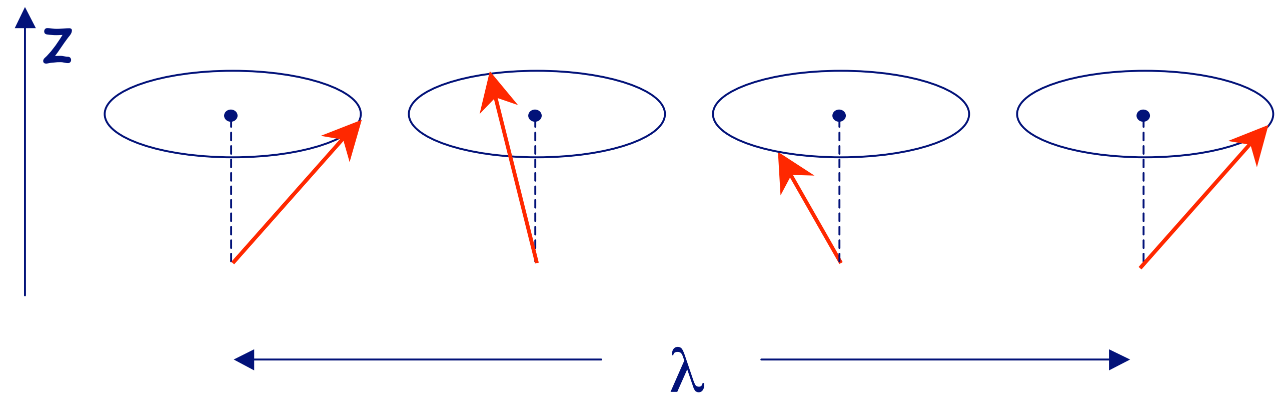
|k> represents a Spin Wave

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\cdot\vec{r}_j} |\downarrow_j\rangle$$

It is easy to verify that

- S_i^z and $[(S_i^x)^2 + (S_i^y)^2]$ eigenvalues are time independent
- $[(S_i^x)^2 + (S_i^y)^2]$ expectation values are site independent i
- S_i^x and S_i^y expectation values are zero

This situation is equivalent to a precession about the z axis, with a spatial phase difference determined by k.



Let's E_1 be the energy of the forst excited state:

$$H\left|k\right\rangle = E_1\left|k\right\rangle$$

$$-\sum_i \sum_\delta J_{i\delta}\left[S_i^z S_{i+\delta}^z + \frac{1}{2}\left(S_i^+ S_{i+\delta}^- + S_i^- S_{i+\delta}^+\right)\right]\frac{1}{\sqrt{N}}\sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \mid \downarrow_j >$$

$$H\left|k\right\rangle = \frac{1}{\sqrt{N}}\sum_j e^{i\vec{k}\cdot\vec{r}_j}\left[-\frac{1}{4}\upsilon J(N-2)\left|\downarrow_j\right\rangle + \frac{1}{2}\upsilon J\left|\downarrow_j\right\rangle - \frac{1}{2}J\sum_\delta\left(\left|\downarrow_{j+\delta}\right\rangle + \left|\downarrow_{j-\delta}\right\rangle\right)\right]$$

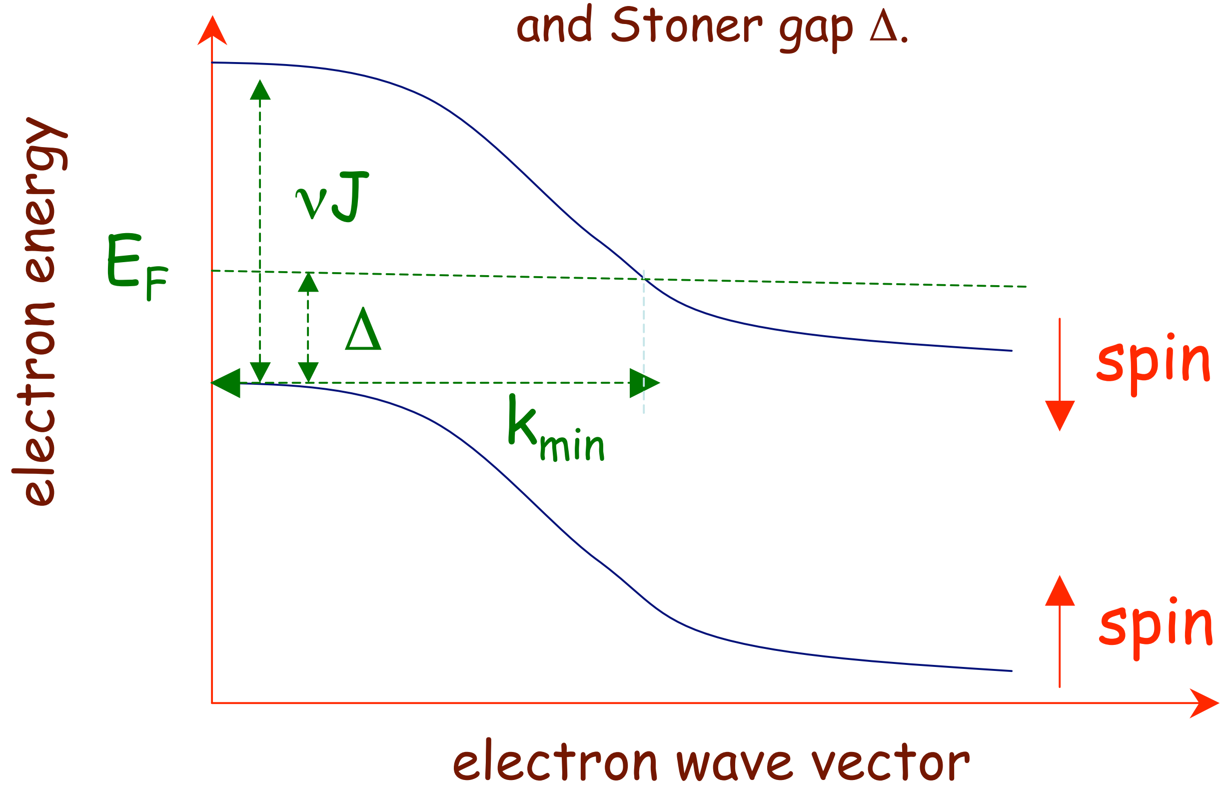
changing indices in the last two terms gives:

$$H\left|k\right\rangle = \left[-\frac{1}{4}\upsilon JN + \upsilon J - \frac{1}{2}J\sum_\delta\left(e^{i\vec{k}\cdot\vec{r}_\delta} + e^{-i\vec{k}\cdot\vec{r}_\delta}\right)\right]\frac{1}{\sqrt{N}}\sum_j e^{i\vec{k}\cdot\vec{r}_j}\left|\downarrow_j\right\rangle$$

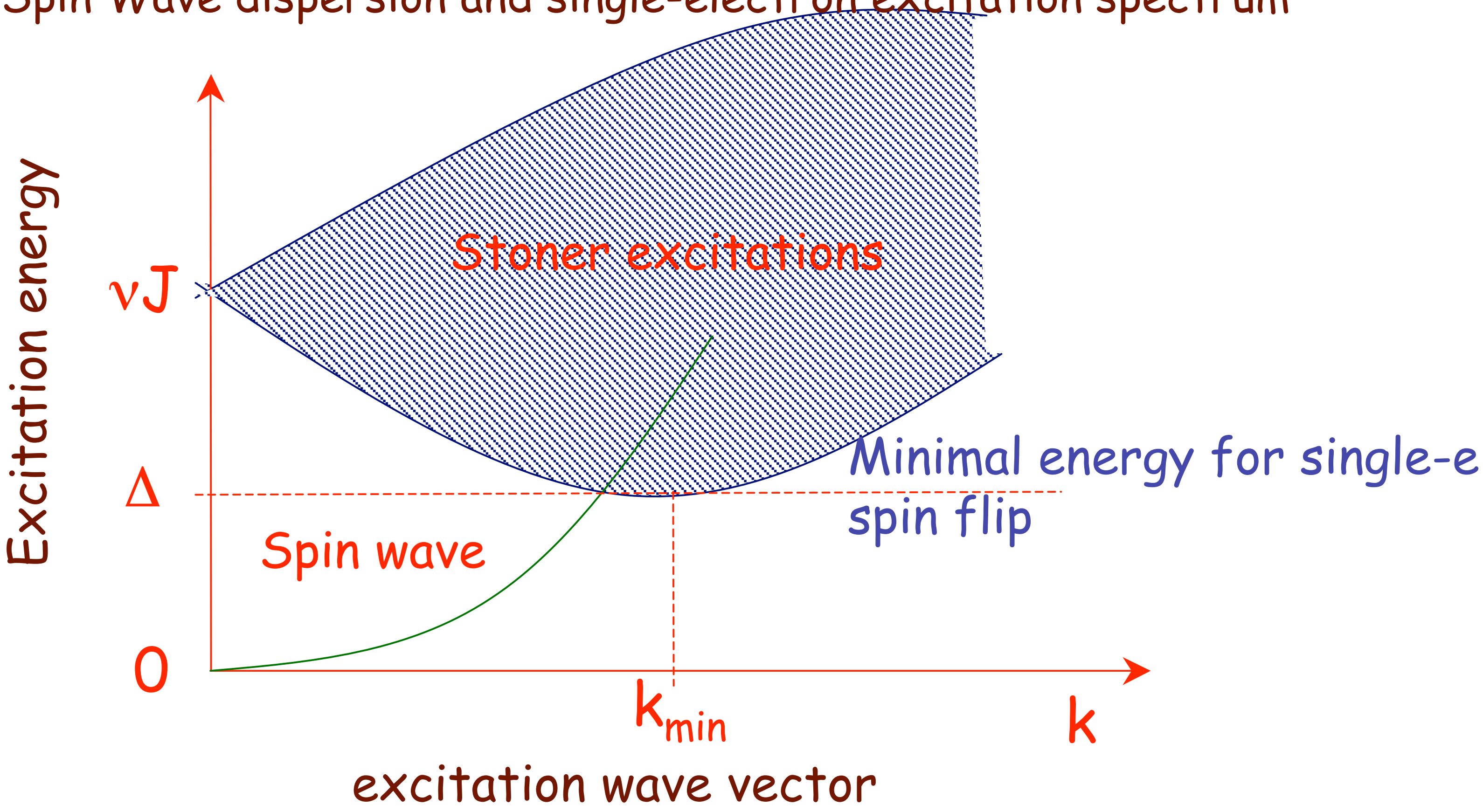
Then $$E_1 - E_0 = J\left[\upsilon - \frac{1}{2}\sum_\delta\left(e^{i\vec{k}\cdot\vec{r}_\delta} + e^{-i\vec{k}\cdot\vec{r}_\delta}\right)\right] = J\left[\upsilon - \sum_\delta \cos\left(\vec{k}\cdot\vec{r}_\delta\right)\right]$$

For k small: $$E_1 - E_0 = \frac{1}{2}J\sum_\delta\left(\vec{k}\cdot\vec{r}_\delta\right)^2$$

model band structure, with exchange splitting νJ and Stoner gap Δ.



Spin Wave dispersion and single-electron excitation spectrum



INS cross section for spin waves

$$\frac{d^2\sigma}{d\Omega dE} = \frac{(\gamma r_0)^2}{2\pi\hbar}\frac{K_f}{Ki}N\left[\frac{1}{2}gf(\vec{Q})\right]^2\sum_{\alpha,\beta}(\delta_{\alpha\beta}-\frac{Q_\alpha Q_\beta}{Q^2})e^{-2W}\times$$

$$\times\sum_{\ell}e^{i\vec{Q}\cdot\vec{\ell}}\int_{-\infty}^{\infty}dte^{-i\omega t} < S_0^{\alpha}(0)S_\ell^{\beta}(t) >$$

Posto $\quad \langle\alpha,\beta\rangle = \left\langle S_0^{\alpha}(0)S_\ell^{\beta}(t)\right\rangle$

It is possible to show that (G. Squires book for instance)

$$\langle +,+\rangle = \langle -,-\rangle = \langle +,z\rangle = \langle -,z\rangle = \langle z,+\rangle = \langle z,-\rangle = 0$$

$$\langle z,z\rangle, \quad \langle +,-\rangle, \quad \langle -,+\rangle \quad \neq \quad 0$$

$$<\lambda|\, S_0^z(0)\, S_e^z(t)\, |\lambda> = S^2 - \frac{2S}{N}\sum_{\mathbf{q}} <n_{\mathbf{q}}>$$

$$<S_0^+(0)\, S_e^-(t)> = \frac{2S}{N}\sum_{\mathbf{q}} e^{-i(\mathbf{q}\cdot e - \omega_q t)} <n_{\mathbf{q}} + 1>$$

$$<S_0^-(0)\, S_e^+(t)> = \frac{2S}{N}\sum_{\mathbf{q}} e^{i(\mathbf{q}\cdot e - \omega_q t)} <n_{\mathbf{q}}>$$

The longitudinal term <z,z> is time independent and gives elastic scattering.
Inelastic scattering is due to the transverse terms, with α,β = x,y.
One has:

$$<S_0^x(0)\, S_e^x(t)> = <S_0^y(0)\, S_e^y(t)> = \frac{2S}{N}\sum_{\mathbf{q}} \{ e^{-i(\mathbf{q}\cdot e - \omega_q t)} <n_{\mathbf{q}}+1> + e^{i(\mathbf{q}\cdot e - \omega_q t)} <n_{\mathbf{q}}> \}$$

$$<S_0^x(0)\, S_e^y(t)> = - <S_0^y(0)\, S_e^x(t)> = \frac{iS}{2N}\sum_{\mathbf{q}} \{ e^{-i(\mathbf{q}\cdot e - \omega_q t)} <n_{\mathbf{q}}+1> - e^{i(\mathbf{q}\cdot e - \omega_q t)} <n_{\mathbf{q}}>\}$$

The sum of <x,y> and <y,x> terms, multiplied by the same factor Q_xQ_y/Q^2, is zero. Only the sum of the terms <x,x> e <y,y> gives a contribution. As

$$1 - \frac{Q_x^2}{Q^2} + 1 - \frac{Q_y^2}{Q^2} = 1 + \frac{Q_z^2}{Q^2}$$

$$\frac{d^2\sigma}{d\Omega dE} = (\gamma r_0)^2 \frac{K_f}{K_i} \frac{(2\pi)^3}{v_0} \left[\frac{1}{2} g f(\vec{Q})\right]^2 \frac{1}{2} S(1 + \frac{Q_z^2}{Q^2}) e^{-2W} \times$$
$$\times \sum_{\tau} \sum_{\vec{q}} \left\{ \delta(\vec{Q} - \vec{q} - \vec{\tau}) \delta(\hbar\omega_q - \hbar\omega) < n_q + 1 > + \delta(\vec{Q} + \vec{q} - \vec{\tau}) \delta(\hbar\omega_q + \hbar\omega) < n_q > \right\}$$

$$< n > = \frac{1}{e^{\hbar\omega / K_B T} - 1} \qquad < n + 1 > = \frac{e^{\hbar\omega / K_B T}}{e^{\hbar\omega / K_B T} - 1}$$

The scattering correspond to the creation or to the annihilation of onr magnon. Scattering only occurs if

$$\frac{\hbar^2}{2m_n}(K_i^2 - K_f^2) = \pm\hbar\omega_q \qquad \vec{\mathrm{K}}_{\mathrm{i}} - \vec{\mathrm{K}}_{\mathrm{f}} = \vec{\tau} \pm \vec{\mathrm{q}}$$

Comparison of magnon and phonon scattering intensities:

- ❍ the intensity for magnon scattering decreases with the square of the form factor
- ❍ Phonon scattering intensity increases as Q^2
- ❍ SW excitations only in the magnetic ordered phase
- ❍ an external magnetic field, affect the intensity, provided it is strong enough to produce a domain reorientation:

$$1 + \frac{Q_\eta^2}{Q^2} = \begin{cases} 1 & ; \mathbf{B} \perp \mathbf{Q} \\ 2 & ; \mathbf{B} \parallel \mathbf{Q} \end{cases}$$

For B = 0, the directional average of $(1+Q_\eta{}^2/Q^2)$ depends on the symmetry. .

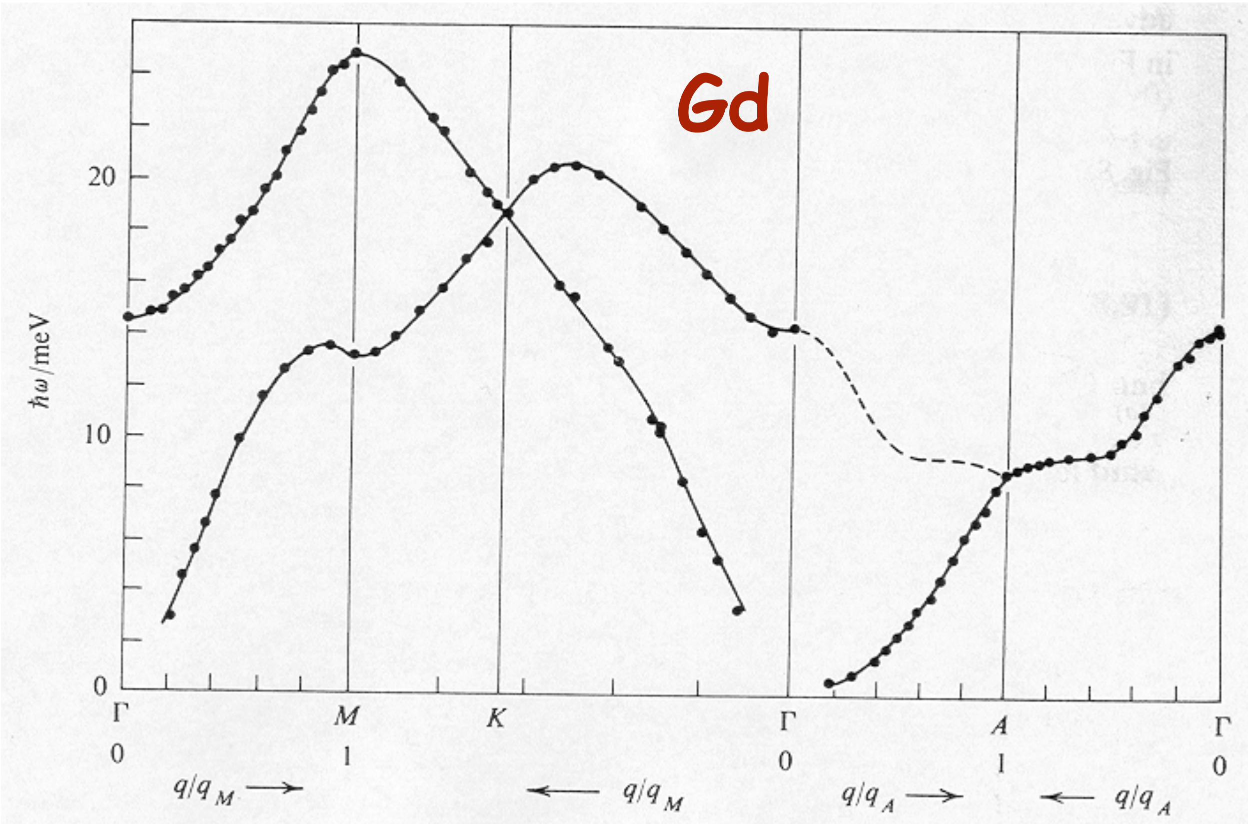
In a cubic crystal, the average is 4/3.

Spin waves in a ferromagnet

$$S^{\perp}(\vec{\kappa},\omega)=\frac{S}{2}\{\delta(\varepsilon(\vec{\kappa})-\hbar\omega)(n(\hbar\omega)+1)+\delta(\varepsilon(\vec{\kappa})+\hbar\omega)n(\hbar\omega)\}$$

Magnon creation

Magnon destruction



Dispersion relation

$$\varepsilon(\vec{\kappa})=2S(J(0)-J(\vec{\kappa}))$$

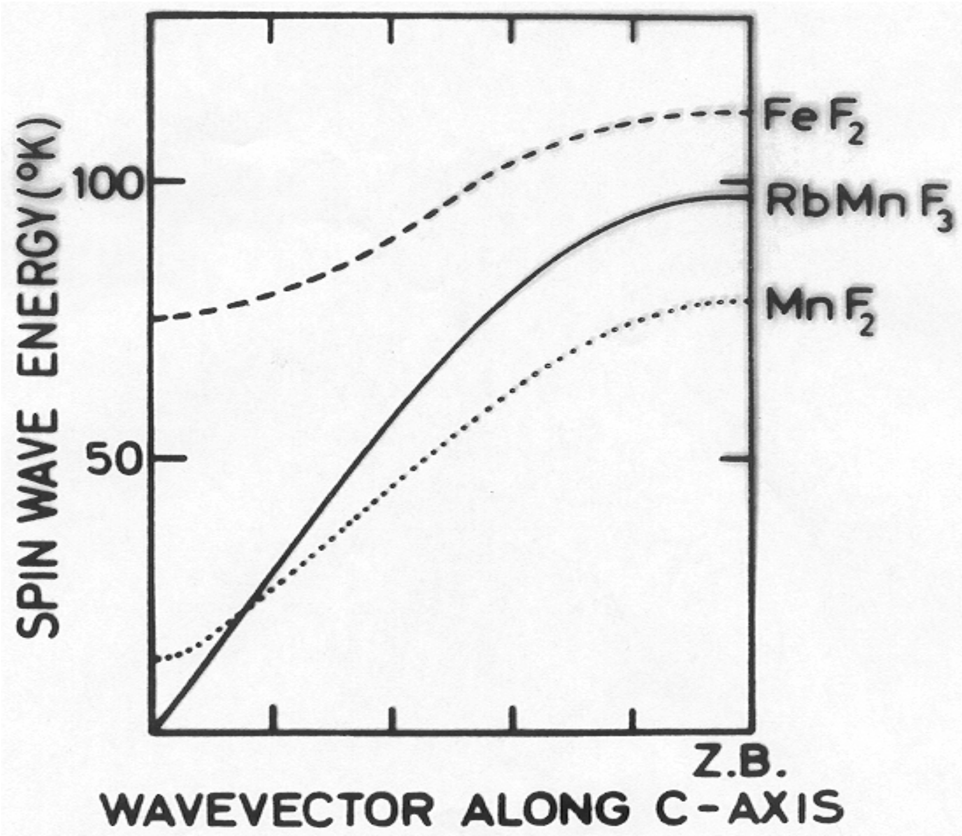
Magnon occupation prob.

$$n(E)=\frac{1}{\exp\left(E/k_BT\right)-1}$$

Spin waves in an antiferromagnet

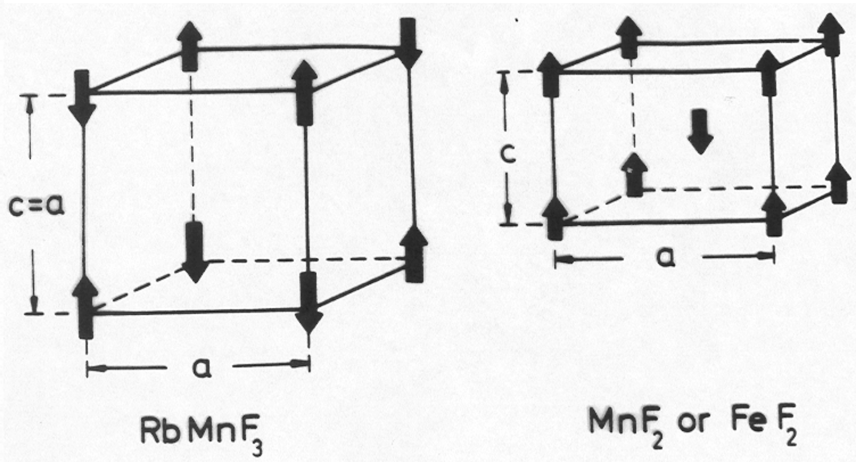
$$S^{\perp}(\vec{\kappa},\omega)=\frac{S}{2}\frac{J\left(1-\frac{1}{z}\sum_{\mathbf{d}}e^{i\vec{\kappa}\cdot\mathbf{d}}\right)}{\varepsilon(\vec{\kappa})}$$

$$\times\left\{\delta\left(\varepsilon(\vec{\kappa})-\hbar\omega\right)\left(n(\hbar\omega)+1\right)+\delta\left(\varepsilon(\vec{\kappa})+\hbar\omega\right)n(\hbar\omega)\right\}$$

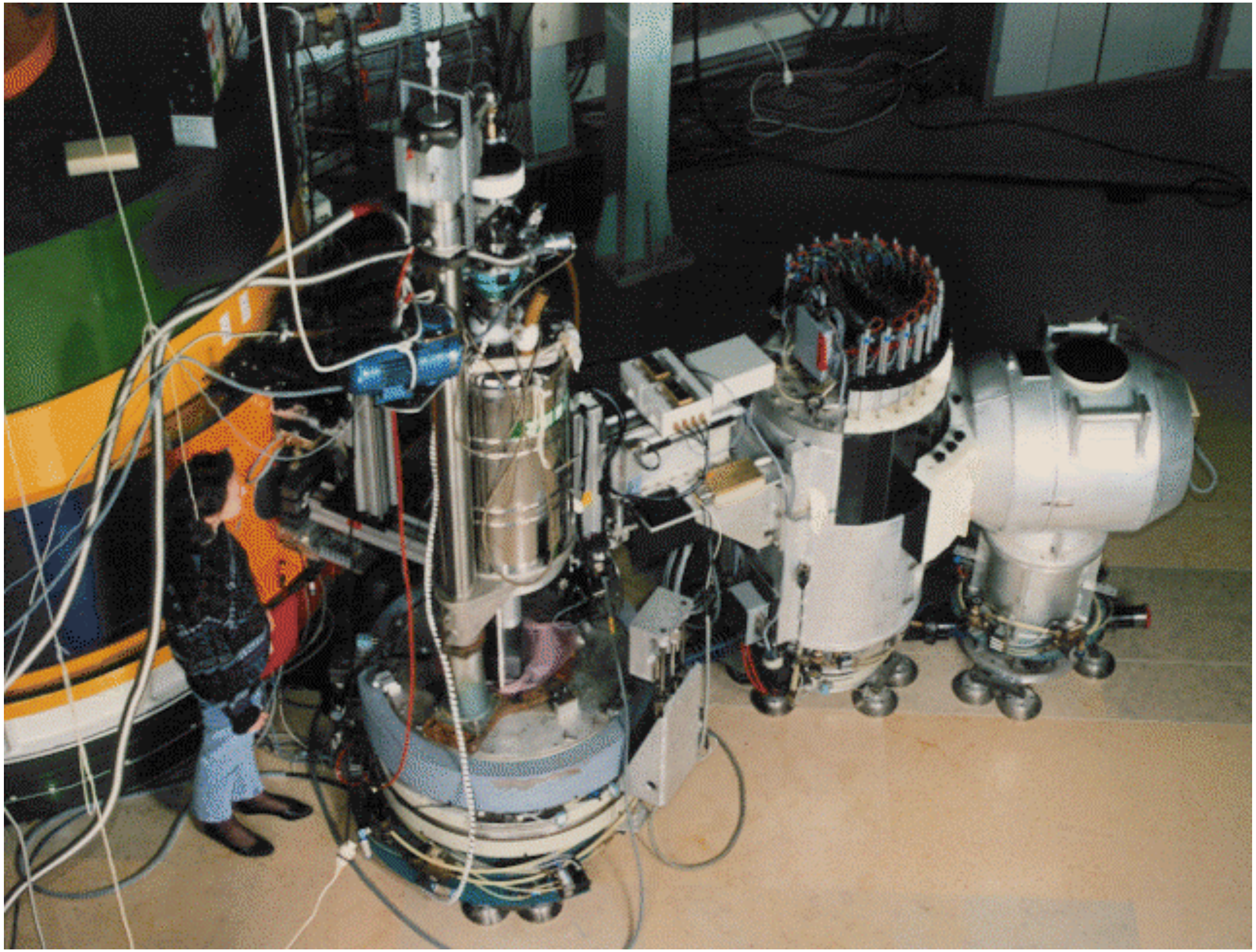


Dispersion relation

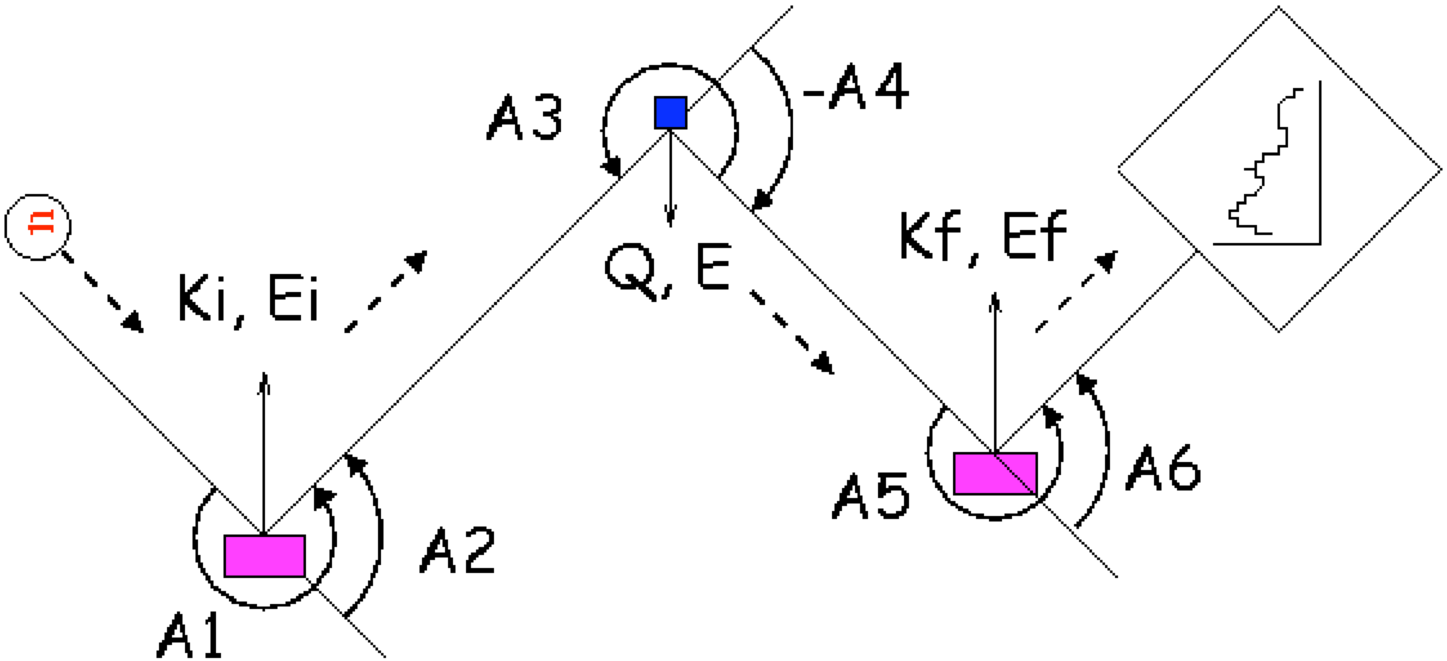
$$\varepsilon(\vec{\kappa})=2S\sqrt{\mathrm{J}(0)^2-\mathrm{J}(\vec{\kappa})^2}$$



The triple-axis spectrometer



- Possibility to perform constant **Q** or constant ω scans
- Flexibility
- Detailed studies at specified points in (Q,ω) space.



$K_i = \pi/d_M \sin(A_2/2)$
$E_i = \hbar^2 K_i^2/2m_n$

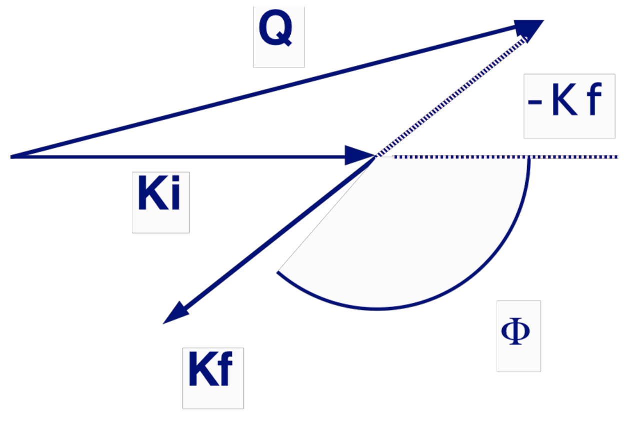
$K_f = \pi/d_A \sin(A_6/2)$
$E_f = \hbar^2 K_f^2/2m_n$

A_1: direction of $\mathbf{K}_i$ A_4: direction of $\mathbf{K}_f$
(typical horizontal collimation: 10′ -40′)
Resolution dependent on beam divergence

Momentum and Energy conservation:

$$\frac{\hbar^2 K_i^2}{2m_n} - \frac{\hbar^2 K_f^2}{2m_n} = \pm\hbar\omega$$

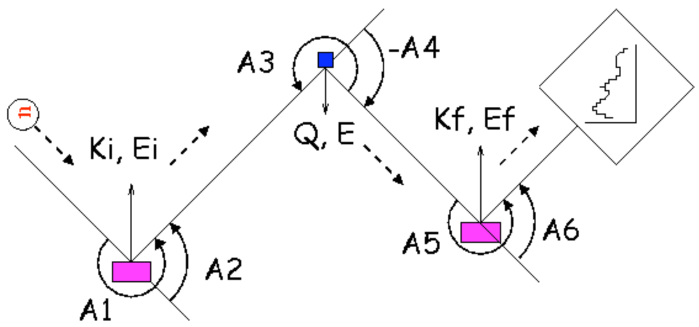
$$Q^2 = K_i^2 + K_f^2 - 2\, K_i K_f \cos\phi$$



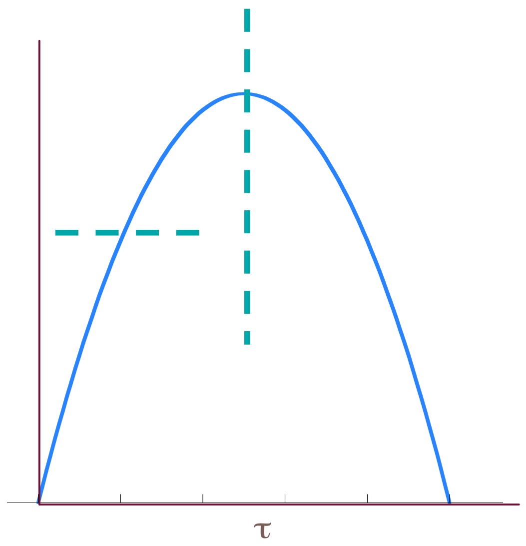
Triangolo di scattering

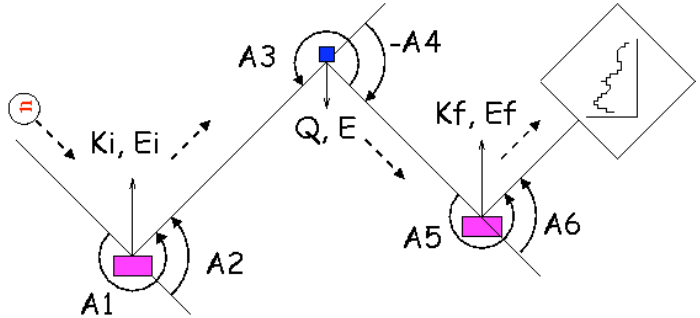
No solutions if

$$\hbar\omega \geq \frac{\hbar^2 Q^2}{2m_n \sin\phi}$$

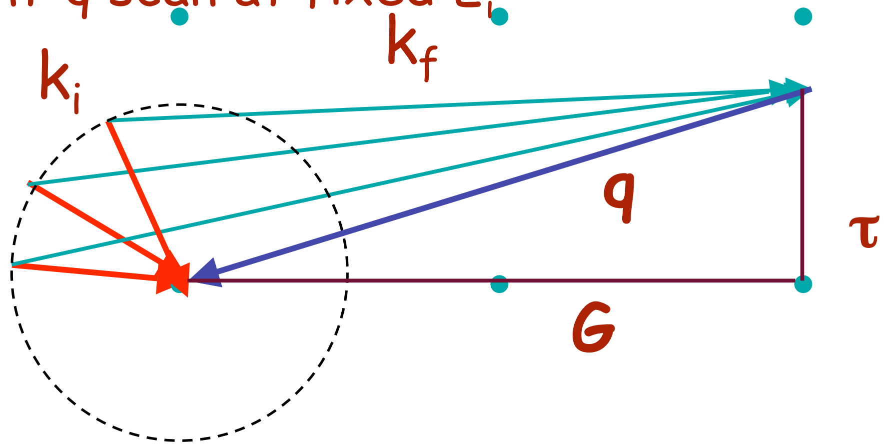


Probing a dispersion curve with a TAS

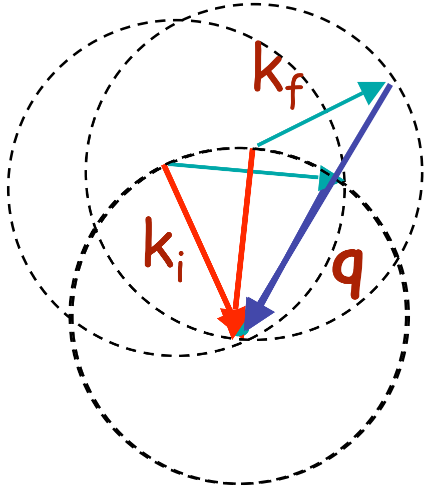




Constant-q scan at fixed E_i



Constant-E scan with q varying along a given direction



A given q-ω point can be probed using an infinite number of k_i-k_f combinations

Beware of spurions! (see the ILL 3-axis group web site)

Harmonic combinations

Bragg reflections on monochromator and analyzer can generate 2nd, 3rd, 4th order reflection when, measuring something at (Q,ω)

$k_i - k_f = Q$ $\qquad\qquad$ $nk_i - mk_f = Q'$

$k_i^2 - k_f^2 = a\,\omega$ $\qquad\qquad$ $n^2k_i^2 - m^2k_f^2 = a\,\omega'$

For given n and m, one can get an additional elastic signal ($\omega' = 0$), specially for $3k_i = 4k_f$ $\quad 2k_i = 3k_f$ $\quad k_i = 2k_f$

You will observe an excitation corresponding to 2k, 3k, ...

Test: changing k_i or k_f will make the spurion to move.

Solution: add an additional filter (PG or Be). Using a Si(111) or Ge(111) m/a will remove the 2nd-order.

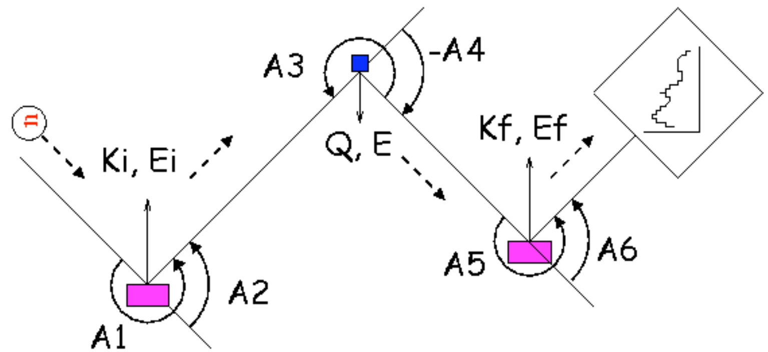
Aluminium contamination

The samples and cryostat often include some Al (or Cu) polycrystal parts, that will scatter neutrons at given A4 angles depending on k_i or k_f.

Test: the line doesn't move if A3 rotates. The monitor M2 signal increases
Solution: change k_i or k_f, or TAS configuration, so that A4 changes

Bragg/phonon contamination

As the (Q,ω) resolution ellipsoid of the TAS is tilted, the sides can still satisfy the $\omega=0$ Bragg condition when measuring something at non-zero (not too high) energy. This may generate an additional ghost Bragg peak. When observing a phonon, the ellipsoid may also touch an other phonon dispersion curve, and make a signal appear.
Test: the intensity of the spurion varies as exp(-a.Q) for Bragg, as a Bose signal for phonons.
Solution: use smaller k_i. Use thinner collimators to reduce the size of the ellipsoid.



Incoherent scattering of mono/analyzer

A small part (10^{-5}) of the incoming beam is always scattered incoherently by the monochromator or the analyzer$\Rightarrow$ reflection from the sample for this k_i or k_f.

Test A scan on A3 will have the width of a Bragg peak. Moving the monochromator or analyzer will make the 'good' signal to disappear; the incoherent contamination will remain.

Solution: changing k_i or k_f will make that peak move.

Protection leaks

For some spectrometer configurations, the detector can be in the axis of the incoming beam. Fast neutrons that may pass the protections will give an additional peak. Also, for small A4 angles, one can have an additional scattering from tubes lying in the incoming beam

Test: This peak is not sensible to the sample position, nor to the analyzer translation.

Solutions: Increase the protections

Vertical resolution, curved multi-slab analyzer

You may observe more that one Bragg signal.

Solution: Hide parts of the analyzer

Multiphonon processes

Multiphonon processes may be observed, specially for acoustic phonons near zone center.

Test: this will appear as a peak at 2ω, 3ω.. or a broad peak.

Curved dispersion surfaces

When observing highly anisotropic dispersion surfaces , the 'curvature' of the excitation will turn peaks to be asymmetric, usually with a quick raise with increasing energy, and slow decrease after.

Time of Flight Spectrometers

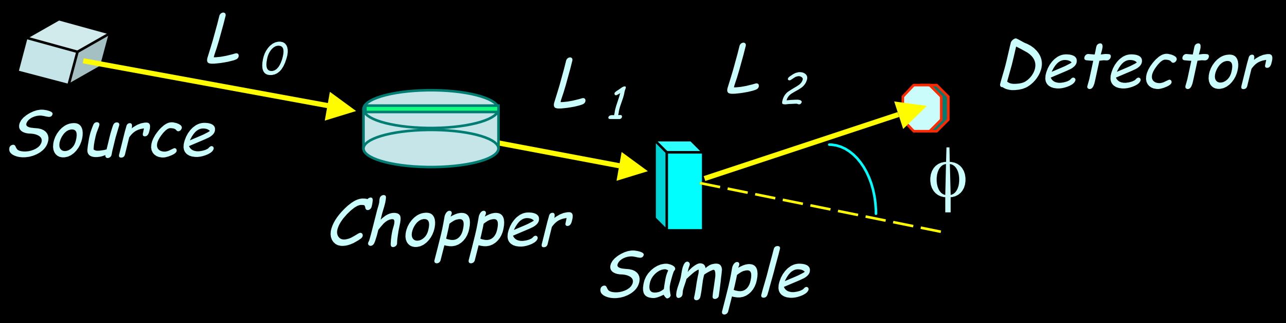
Thermal neutrons have velocity of the order of km/s

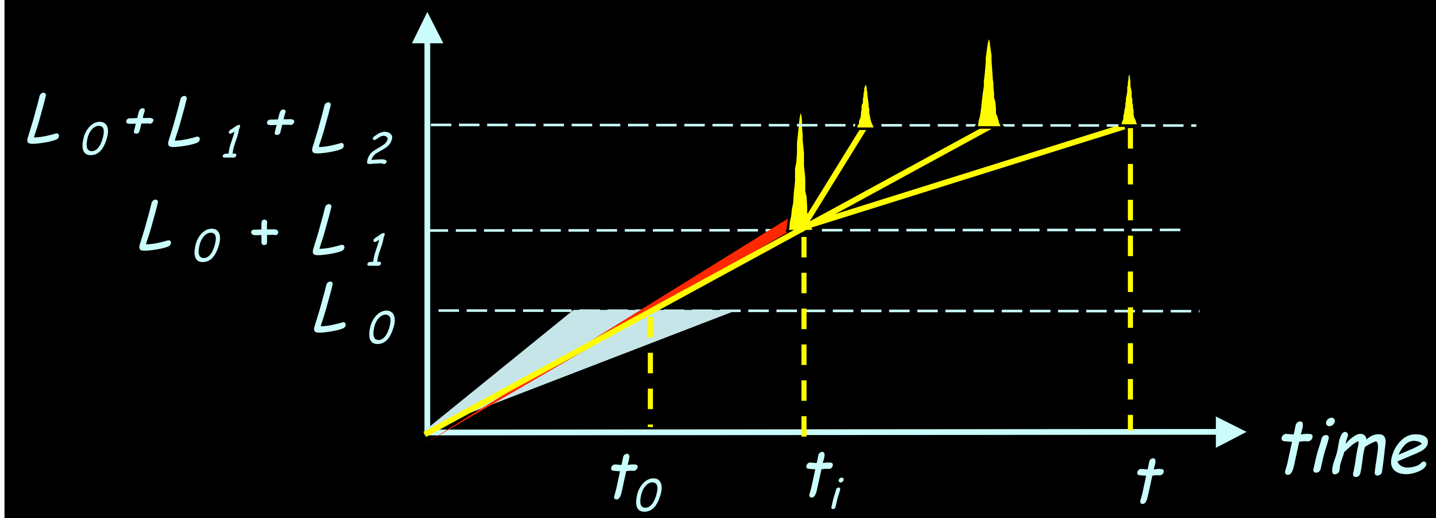
Their energy can be determined by measuring time-of-flight over a distance of a few metres.

Direct Geometry: the incident energy is defined by a crystal or a chopper and the incident energy is scanned by tof

Inverted Geometry: the final energy is defined by a crystal or a filter and the incident energy is scanned by tof

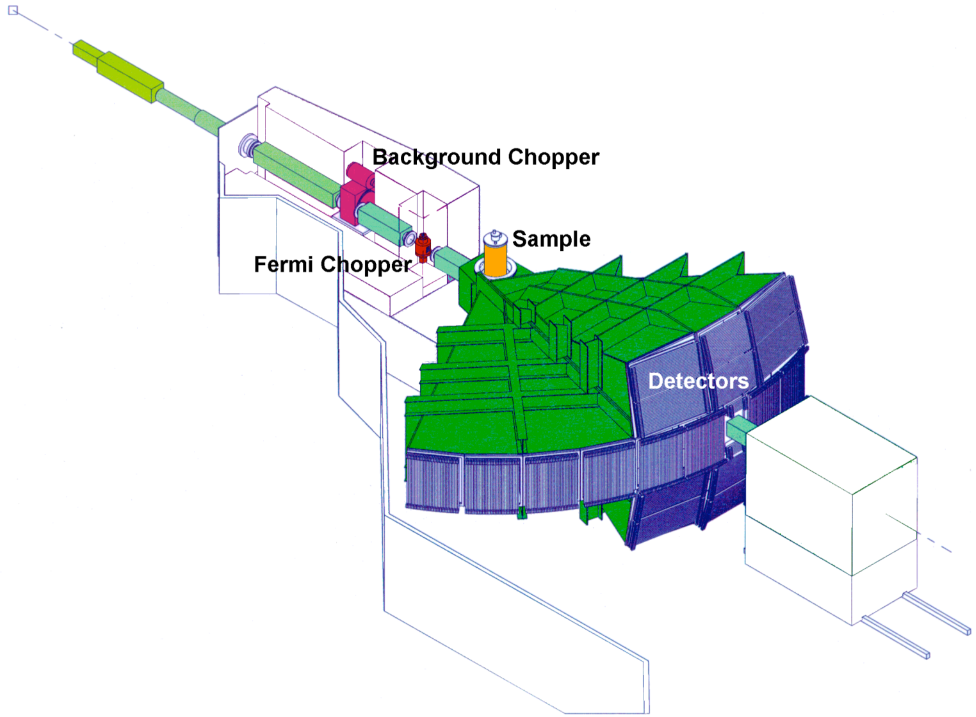
Direct Geometry Time-of-Flight Chopper Spectrometers





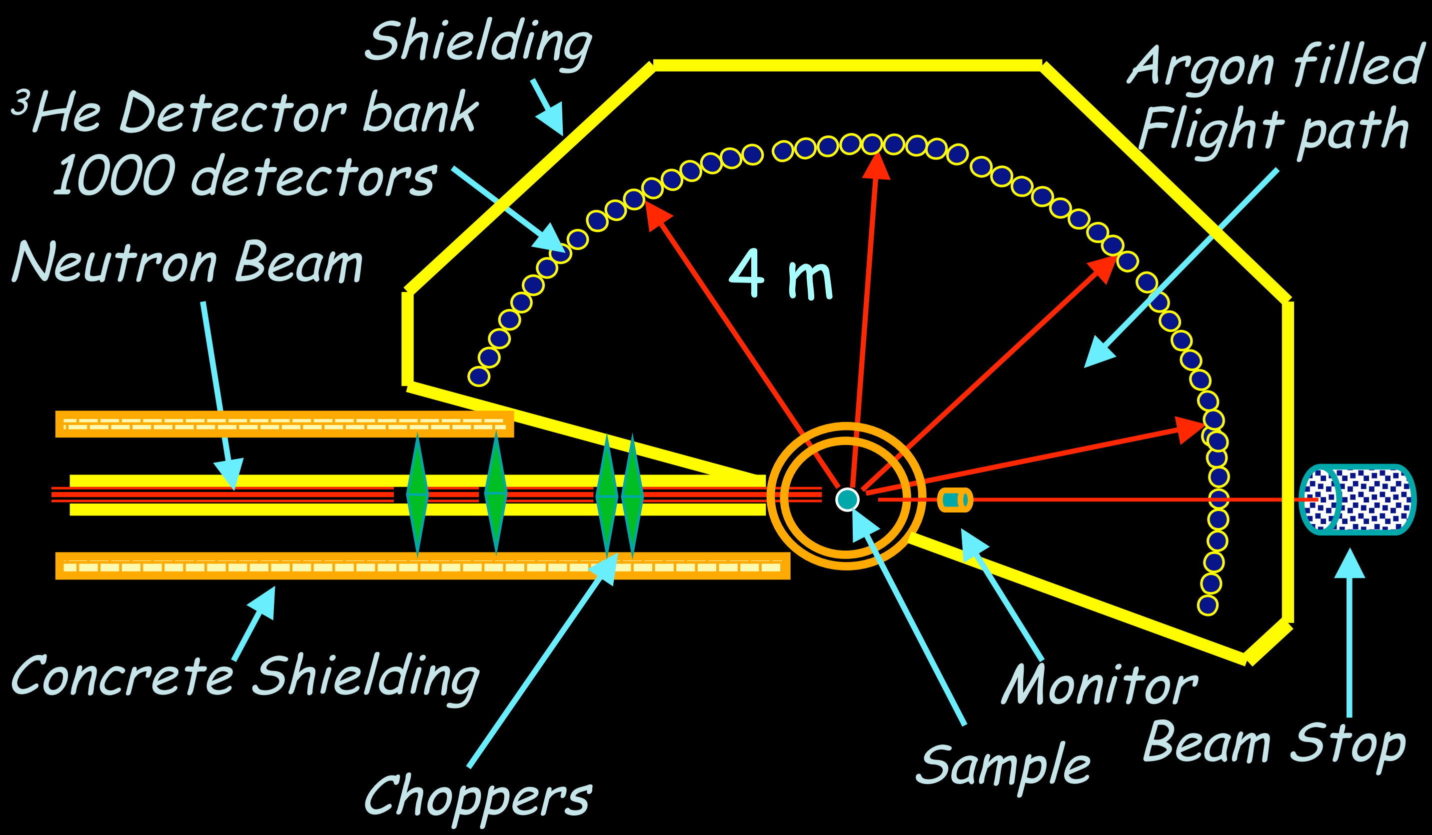
$$E_f = \frac{1}{2} m_n \frac{L_2^2}{(t - t_i)^2}$$

A chopper spectrometer

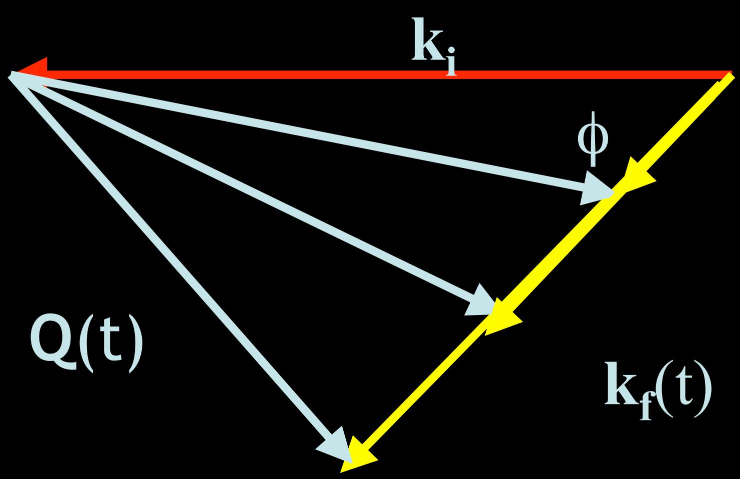


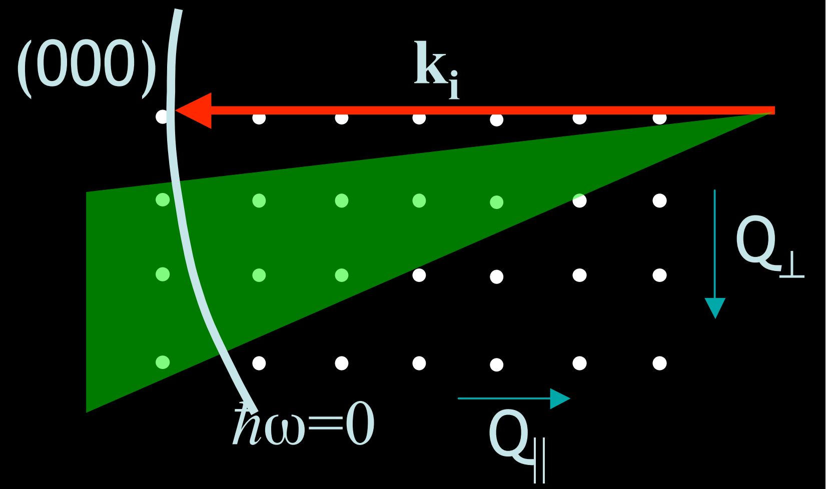
- Broad simultaneous coverage of (Q,ω) space
- Coupled measurement trajectories

IN5 at the Institut Laue Langevin



Trajectories





- From the scattering triangle we can see that an array of detectors will trace out a sector in reciprocal space

Apply the cosine rule

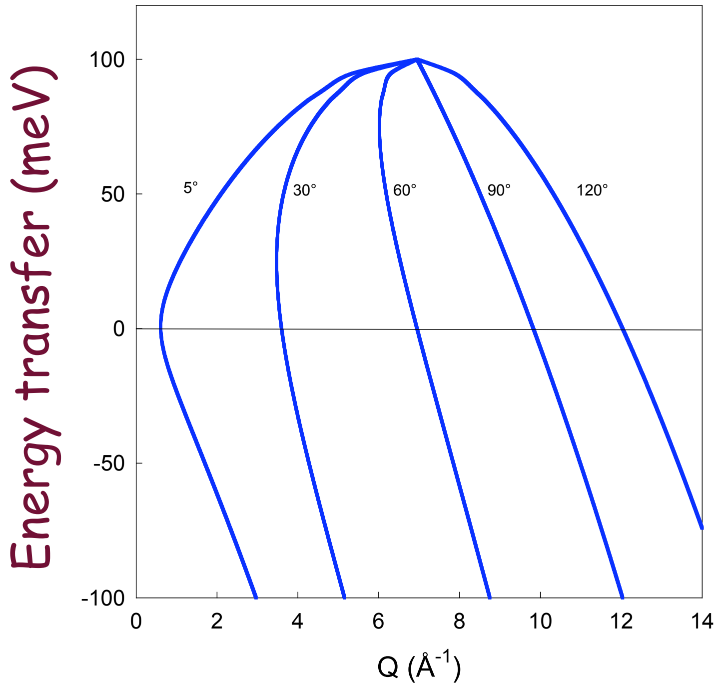
$$\mathbf{Q}^2 = \mathbf{k}_i^2 + \mathbf{k}_f^2 - 2\mathbf{k}_i\mathbf{k}_f\cos\phi$$

Convert to energy

$$\frac{\hbar^2\mathbf{Q}^2}{2m} = E_i + E_f - 2\left(E_iE_f\right)^{1/2}\cos\phi$$

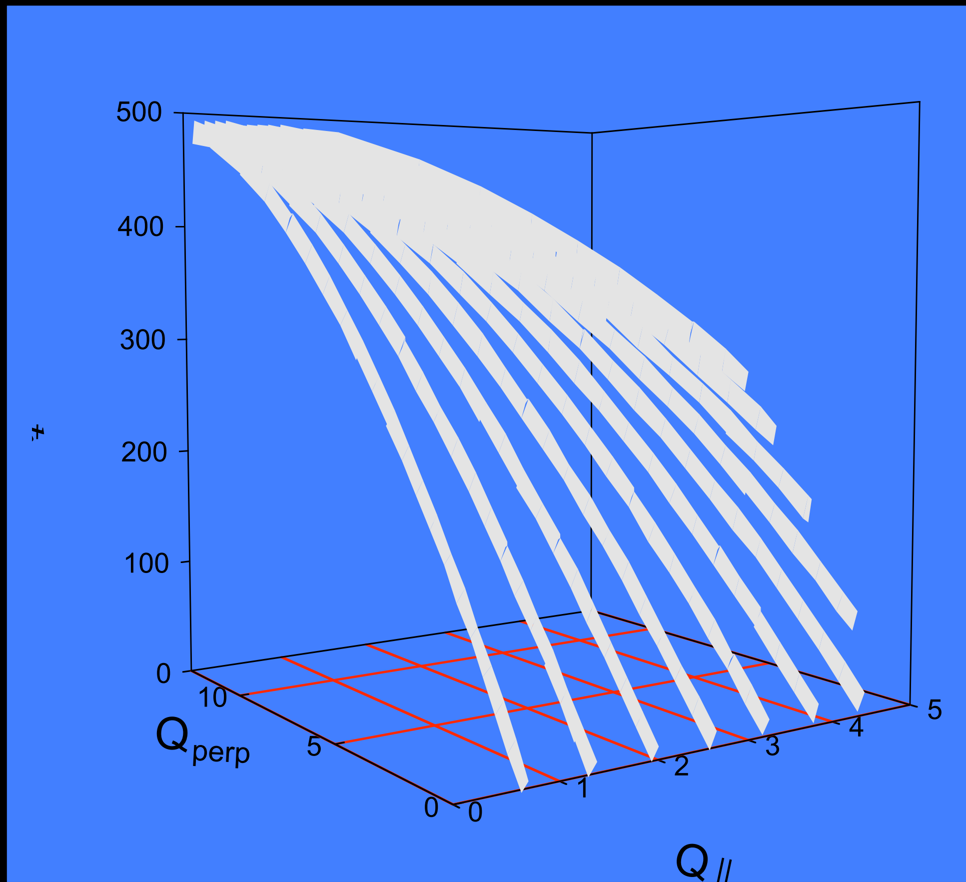
Eliminate E_f

$$\frac{\hbar^2\mathbf{Q}^2}{2m} = 2E_i - \hbar\omega - 2\cos\phi\left[E_i\left(E_i - \hbar\omega\right)\right]^{1/2}$$

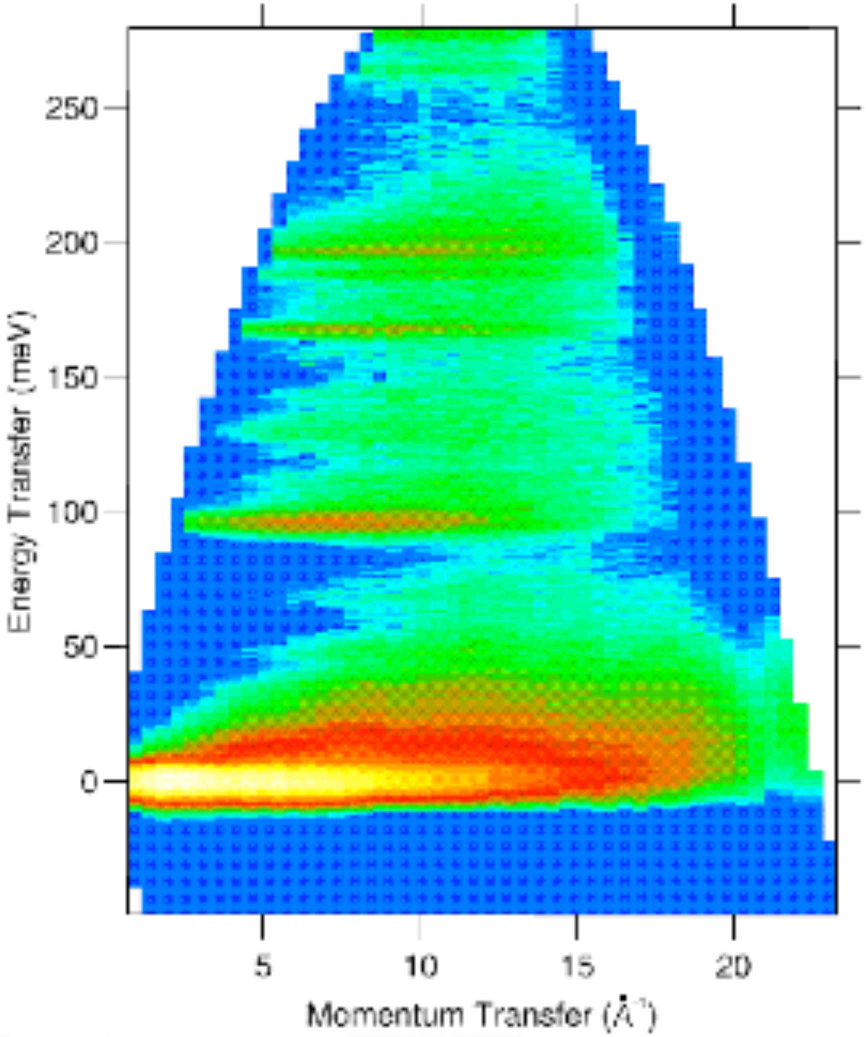


Each detector traces a parabolic trajectory trough (Q,ω) space

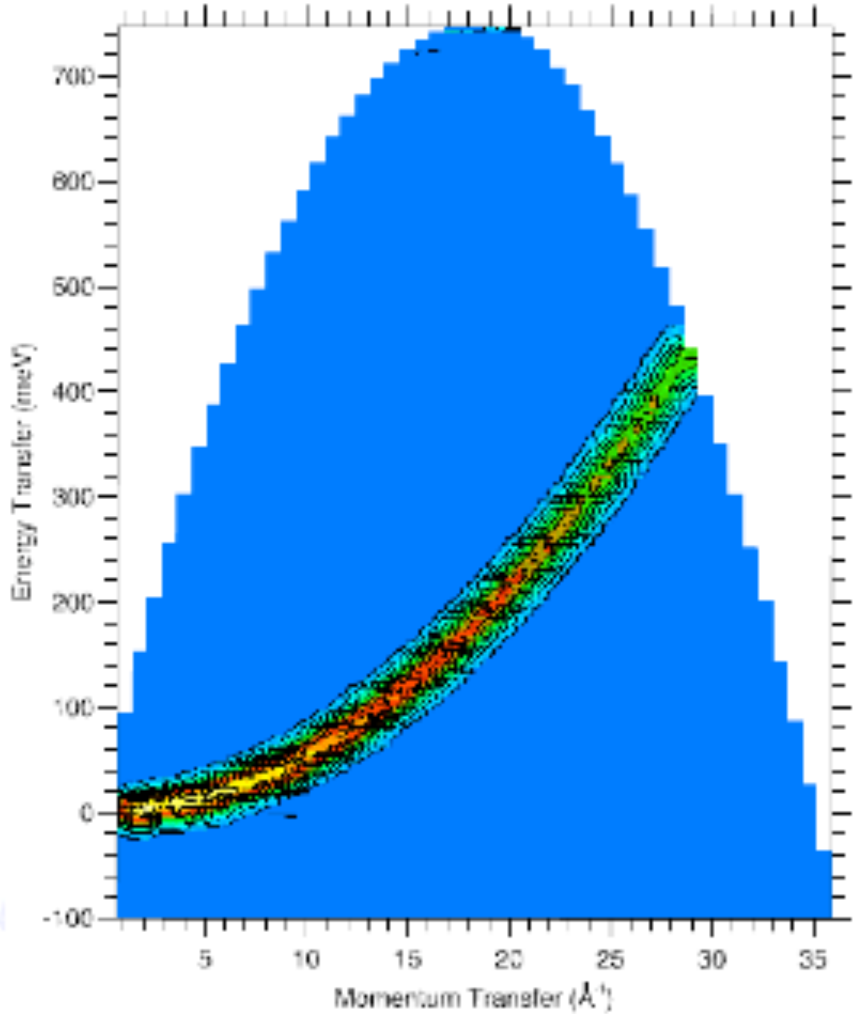
The detector array produces a surface in $(Q_{||}, Q_{\perp}, \omega)$ space



n-methyl acetamide (Fillaux)



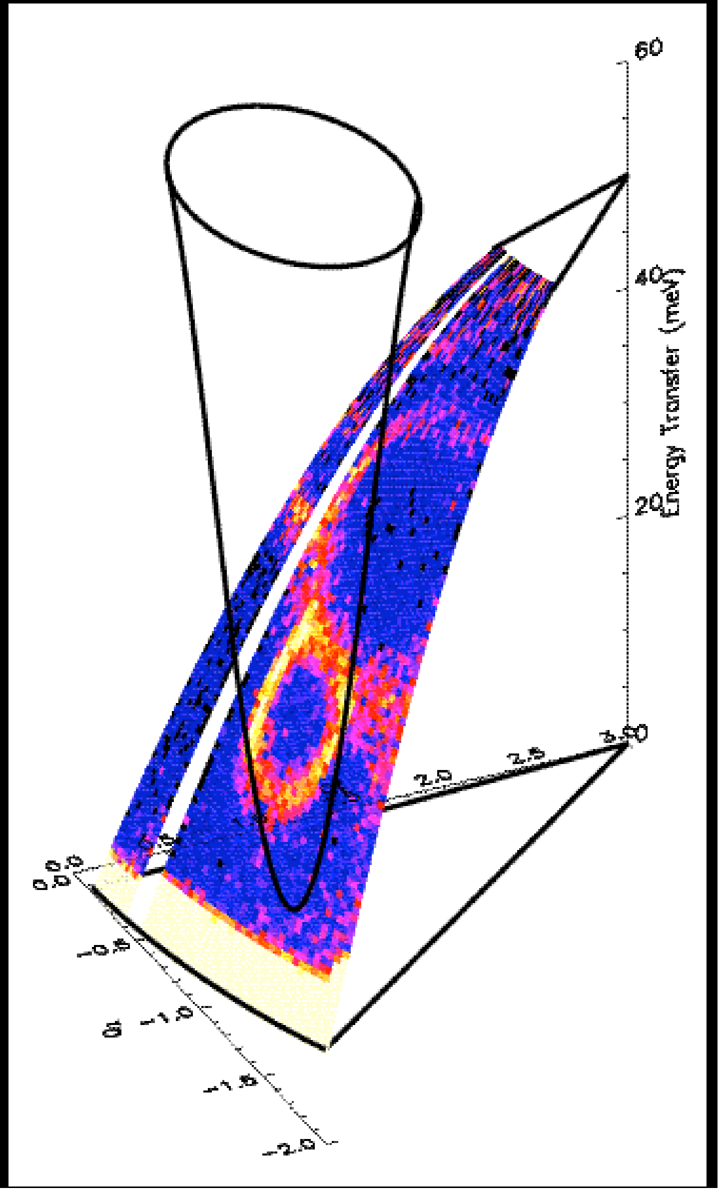
^{4}He (Stirling et al)



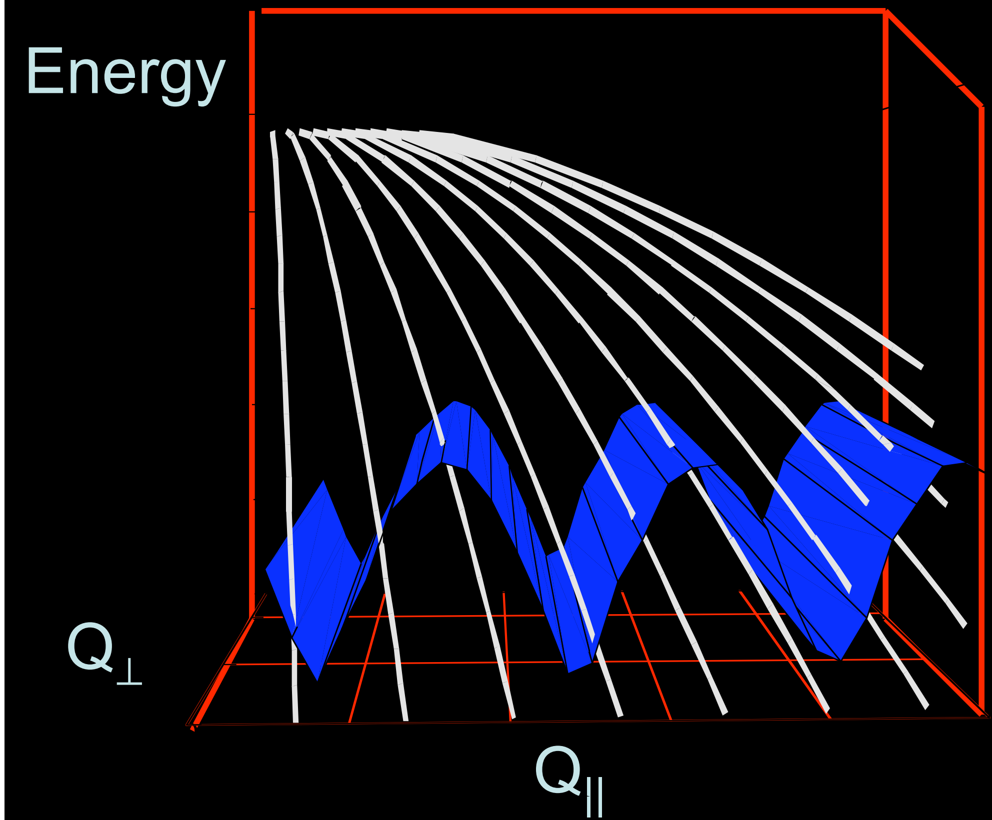
Ferromagnetic spin wave in a 3 dimensional magnetic system.
The spin wave will emerge like a 'cone' from a reciprocal lattice point.

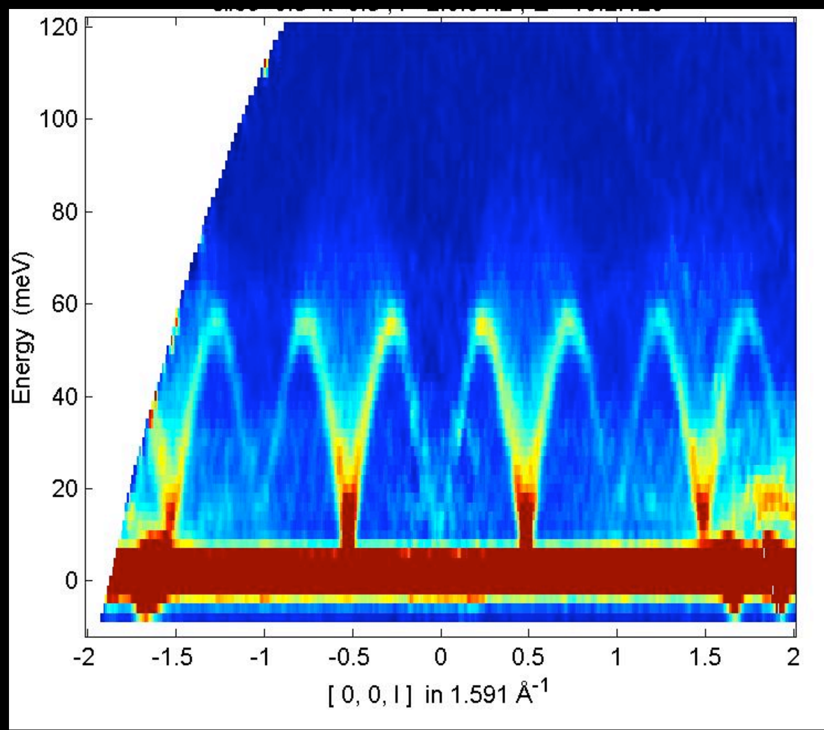
Where that 'cone' intersects with the surface in $(Q_{||},Q_{\perp},\omega)$ space, scattering will be observed.

'Cuts' can the be performed in software during data analysis.

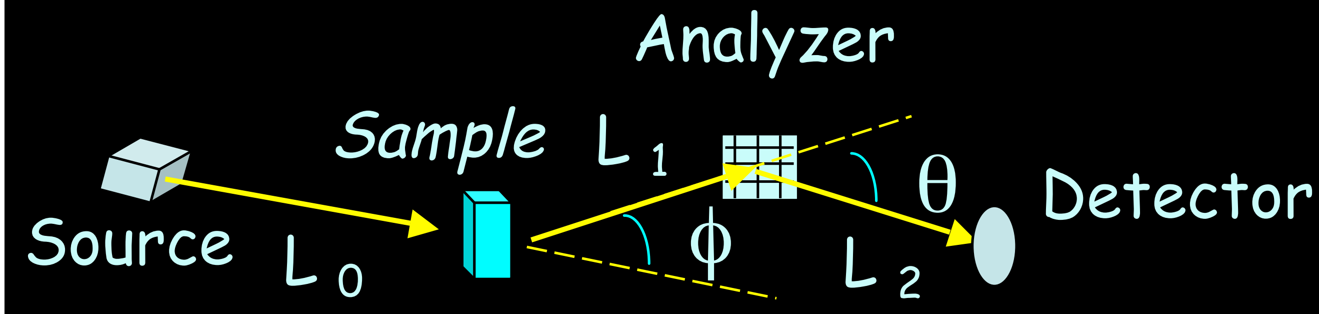


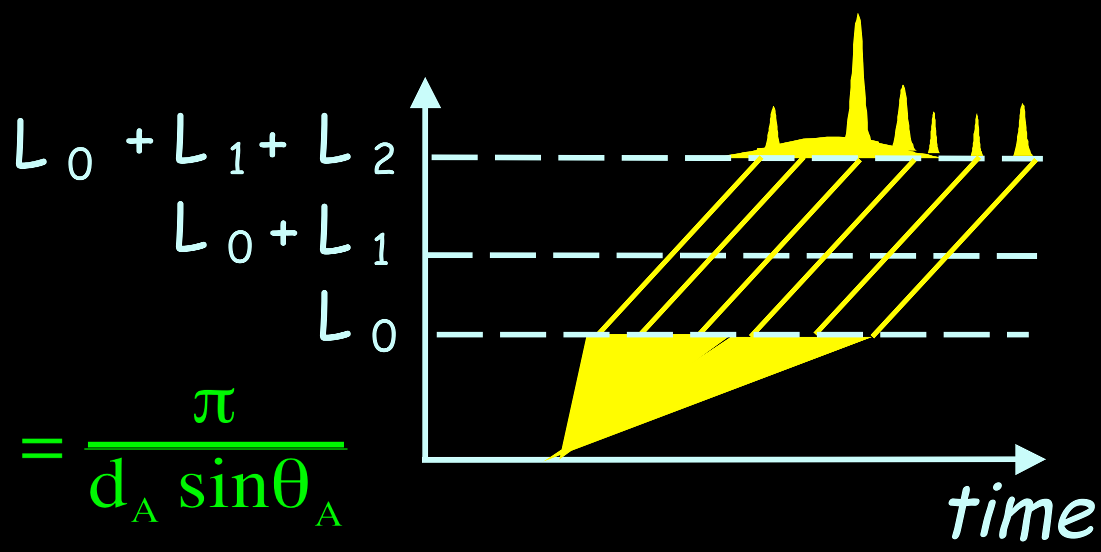
- In low dimensional magnetic systems, the crystal can be aligned with k_i parallel to the non-dispersive direction to provide a simultaneous measurement of the whole dispersion.





Inverse Geometry Chopper Spectrometers

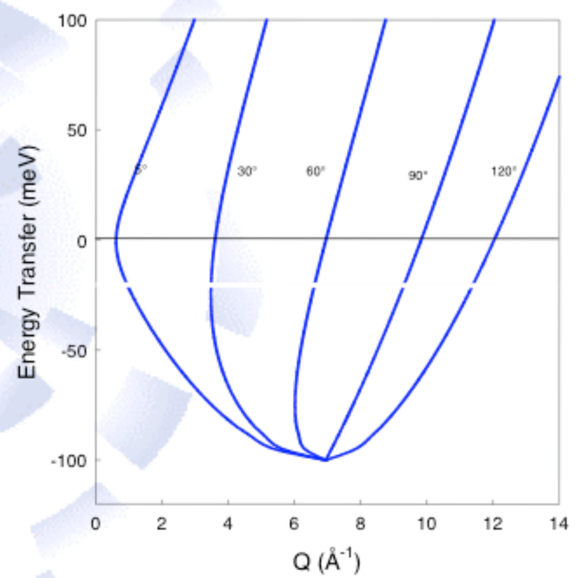




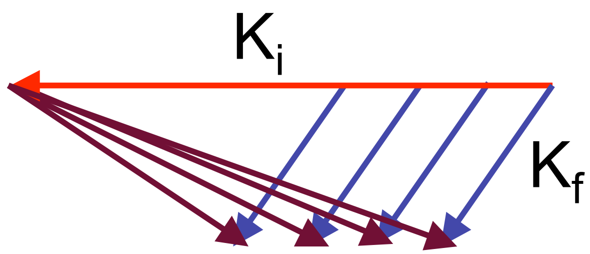
$$K_f = \frac{\pi}{d_A \sin\theta_A}$$

$$K_i = \frac{m_n L_0}{\hbar t - m_n (L_1 + L_2)\, d_A \sin\theta_A / \pi}$$

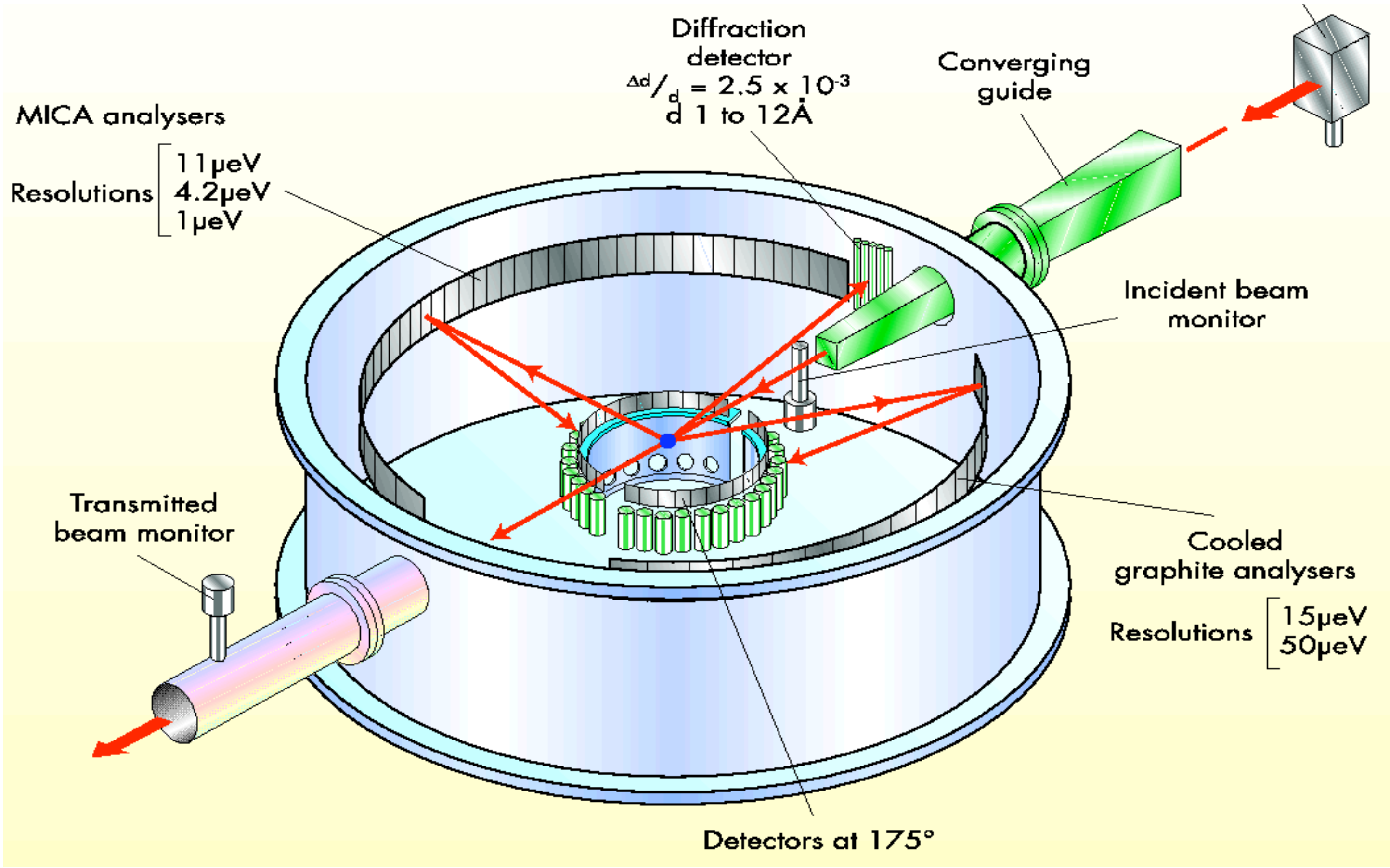
$$\frac{\hbar^2 \mathbf{Q}^2}{2m} = 2E_f + \hbar\omega - 2\cos\phi\left[E_f\left(E_f + \hbar\omega\right)\right]^{1/2}$$



IRIS, RAL

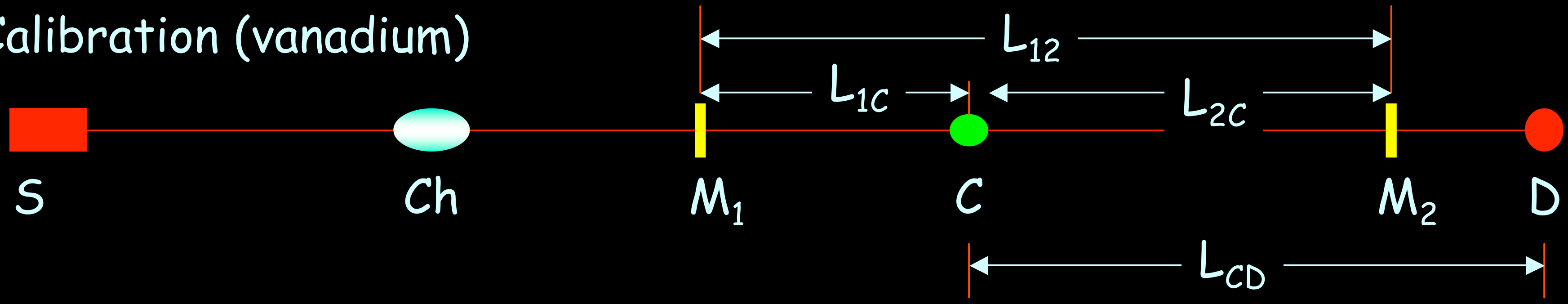


K_i
K_f



Diffraction detector
Δd/d = 2.5 x 10-3
d 1 to 12Å
Converging guide
MICA analysers
Resolutions
11μeV
4.2μeV
1μeV
Incident beam monitor
Transmitted beam monitor
Cooled graphite analysers
Resolutions
15μeV
50μeV
Detectors at 175°

Calibration (vanadium)



Incident wavevector: $$K_i = \frac{m_n}{\hbar}\,\frac{L_{12}}{t_2 - t_1} = 1.588\,\frac{L_{12}\,(\mathrm{mm})}{(t_2 - t_1)\,(\mu s)}$$

Time of arrival at the sample: $$t_C = t_1 + \frac{t_2 - t_1}{L_{12}}\,L_{1C}$$

Calibration of energy scale: the centre, t_e, of the vanadium elastic peak is determined first. The effective distance between the sample C and a given counter D is

$$L_{CD} = \frac{t_e - t_C}{t_2 - t_1}\,L_{12}$$

Wavevector and energy of neutrons detected at time t_j :

$$K_j = 1.588\,\frac{L_{CD}\,(\mathrm{mm})}{(t_j - t_C)\,(\mu s)}\,\text{Å}^{-1} \qquad E_j = 5.2131\,\frac{L_{CD}^2\,(\mathrm{mm}^2)}{(t_j - t_C)^2\,(\mu s)^2}\,\mathrm{meV}$$

Intensity calibration

Intensity histogram recorded with constant δt.
Time-to-energy conversion:

$$\delta E_j = -\frac{m_n L_{CD}^2}{(t_j - t_C)^3}\,\delta t$$

the cross-section is distorted

Counting strategy

C_j = counts in the j-th channel for sample +holder
H_j = counts in the j-th channel for holder
V_j = counts in the j-th channel for V standard
B_j = counts in the j-th channel for background
n_X = monitor counts (X = C, H, V, B)
$\eta_j(E)$ = detector efficiency
$\eta_M(E)$ = monitor efficiency

$$\frac{C_j}{n_C} - \frac{H_j}{n_H} = N_C \frac{d^2\sigma}{d\Omega dE_j} \Delta\Omega \, \Delta E_j \frac{\eta_j(E_j)}{\eta_M(E_0)}$$

$$\frac{V_j}{n_V} - \frac{B_j}{n_B} = N_V \left(\frac{d^2\sigma}{d\Omega dE_j}\right)_V \Delta\Omega \, \Delta E_j \frac{\eta_j(E_j)}{\eta_M(E_0)}$$

$$\sum_j \left(\frac{V_j}{n_V} - \frac{B_j}{n_B}\right) = N_V \left(\frac{d\sigma}{d\Omega}\right)_V \Delta\Omega \, \frac{\eta_j(E_0)}{\eta_M(E_0)}$$

$$\frac{d^2\sigma}{d\Omega dE_j} = \frac{N_V}{N_C}\,\frac{\dfrac{C_j}{n_C} - \dfrac{H_j}{n_H}}{\sum_j\left(\dfrac{V_j}{n_V} - \dfrac{B}{n_B}\right)}\left(\frac{d\sigma}{d\Omega}\right)_V \frac{\eta_j\,(E_j)}{\eta_M\,(E_0)}\,\frac{(t_j - t_C)^3}{m_n\,L_{CD}^2\,\delta t}$$

$$N_V = 0.70 \times 10^{23}\ \mathrm{at/cm^3}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_V = \frac{\sigma_V}{4\pi} = 0.3804\ \mathrm{barn/sr}$$

Polarisation analysis

s = neutron spin

$$s_z|\uparrow\rangle = \frac{\hbar}{2}|\uparrow\rangle \qquad s_z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle$$

$$|\chi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle \qquad \left(\alpha^2 + \beta^2 = 1\right)$$

Polarization of i-th neutron

$$\vec{P}_i = \frac{\langle\chi|\hat{s}_i|\chi\rangle}{\hbar/2} = \langle\chi|\hat{\sigma}|\chi\rangle =$$

$$\alpha^*\alpha\langle\uparrow|\hat{\sigma}|\uparrow\rangle + \beta^*\beta\langle\downarrow|\hat{\sigma}|\downarrow\rangle + \alpha^*\beta\langle\uparrow|\hat{\sigma}|\downarrow\rangle + \beta^*\alpha\langle\downarrow|\hat{\sigma}|\uparrow\rangle$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\vec{P}_i = \frac{2}{\hbar}(\alpha^*\beta + \beta^*\alpha)\hat{x} + \frac{2i}{\hbar}(\beta^*\alpha - \alpha^*\beta)\hat{y} + \frac{2}{\hbar}(\alpha^*\alpha - \beta^*\beta)\hat{z}$$

The polarisation unit vector gives the direction of the n magnetic moment; in general it has a transverse x-y component.

Polarisation of a neutron beam:

$$\vec{P} = \frac{1}{N}\sum_i \vec{P}_i$$

Polarisation in an external magnetic field

The equation of motion of the polarisation in an external magnetic field is

$$\frac{d\vec{P}}{dt} = -\gamma \vec{P} \times \vec{B}$$

B homogeneous $\Rightarrow$ precession of **P** about **B**, with a Larmor angular speed

$$\omega_L = |\gamma| B = 1.833 \cdot 10^8 B \quad \text{rad/tesla}$$

The angular precession of the spin of a neutron, with wavelength λ, travelling a distance Δx in a field B is

$$\Delta\phi/\Delta x \text{ (gradi/mm)} = 0.265\ \lambda B \text{ (ÅG)}.$$

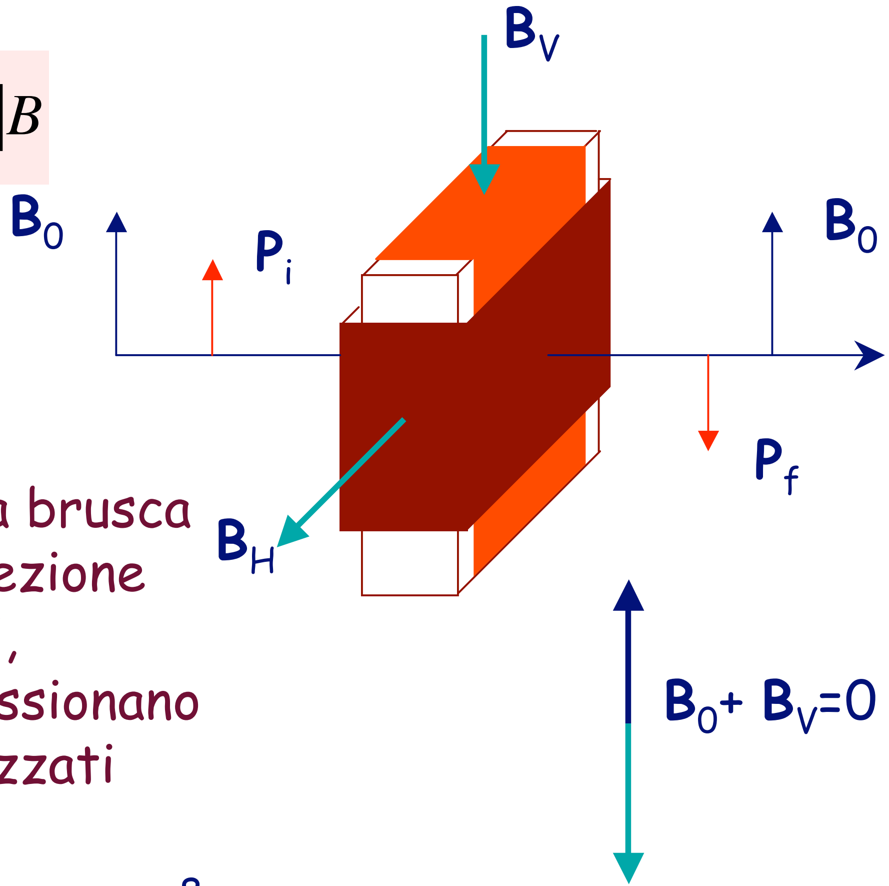
Se la direzione di B cambia lungo la traiettoria del fascio:

A) $d(\mathbf{B}/|\mathbf{B}|)/dt \ll \omega_L \Rightarrow P_z = \mathbf{P}\cdot\mathbf{B}/B$ si conserva (**rotazione adiabatica**)

B) $d(\mathbf{B}/|\mathbf{B}|)/dt \gg \omega_L \Rightarrow$ **passaggio non-adiabatico**; la direzione di **P** non segue quella del campo. Se θ_B è l'angolo fra **B**(x) e l'asse z, si ha un passaggio non-adiabatico se

$$\frac{d\theta_B}{dx}\frac{dx}{dt} >> |\gamma| B$$

Esempio: flipper di Mezei



$\mathbf{B}_0$ = campo guida esterno; $\mathbf{B}_V = -\mathbf{B}_0$.

Il dispositivo permette di realizzare una brusca rotazione del campo magnetico dalla direzione verticale a quella orizzontale. I neutroni, inizialmente polarizzati lungo $+\mathbf{B}_0$, precessionano di 180° attorno a $\mathbf{B}_H$ ed emergono polarizzati lungo $-\mathbf{B}_0$.

Se λ = 2.72Å, Δx = 10 mm, B_H = 25 gauss.

Sezione d'urto e polarizzazione finale per neutroni polarizzati

$$\sigma = NN^* + \vec{M}_\perp \cdot \vec{M}_\perp^* + \vec{P} \cdot \left(N^* \vec{M}_\perp + N\vec{M}_\perp^* + i\vec{M}_\perp^* \times \vec{M}_\perp \right)$$

$$\vec{P}_f \sigma = (\vec{M}_\perp N^* + \vec{M}_\perp^* N - i\vec{M}_\perp^* \times \vec{M}_\perp) + NN^* \vec{P} +$$
$$+ i\left(\vec{M}_\perp N^* - N\vec{M}_\perp^*\right) \times \vec{P} + \left(\vec{M}_\perp^* \cdot \vec{P}\right)\vec{M}_\perp + \left(\vec{M}_\perp \cdot \vec{P}\right)\vec{M}_\perp^* - \left(\vec{M}_\perp^* \cdot \vec{M}_\perp\right)\vec{P}$$

$$N = \frac{1}{\sqrt{N_0}} \sum_n b_n e^{i\vec{Q}\cdot\vec{R}_n}$$

$$\vec{M}_\perp = \frac{1}{\sqrt{N_0}} p \sum_m f_m(\vec{Q}) e^{i\vec{Q}\cdot\vec{R}_m} \left[\vec{M}_m - (\hat{Q} \cdot \vec{M}_m)\hat{Q} \right]$$

Per lo scattering anelastico

$$AB \rightarrow \frac{1}{\pi} \frac{1}{1 - e^{-\hbar\omega / k_B T}} \Im\left(i \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle A(t), B(0) \rangle \right)$$

L'esperimento più generale di scattering neutronico con fascio polarizzato ed analisi di polarizzazione permette di determinare 16 funzioni di correlazione reali.

$$\sigma = a + \vec{V}_1 \cdot \vec{P}$$

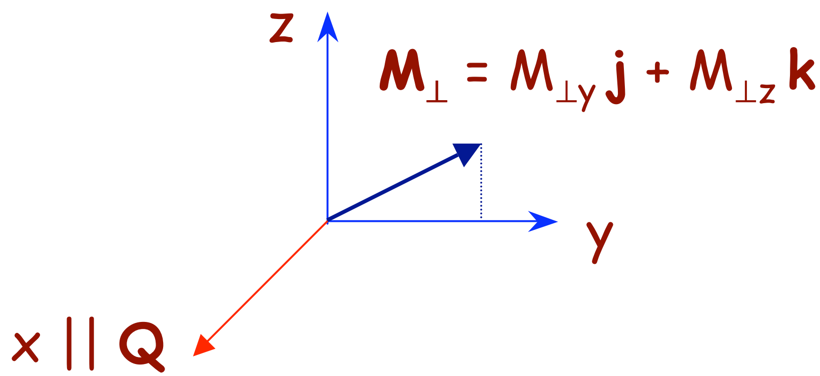
$$\vec{P}_f \sigma = \vec{V}_2 + \overleftrightarrow{T}\vec{P}$$

$$a = NN^* + \vec{M}_\perp \cdot \vec{M}_\perp^*$$

$$\vec{V}_1 = \left(N^* \vec{M}_\perp + N\vec{M}_\perp^*\right) + i\vec{M}_\perp^* \times \vec{M}_\perp$$

$$\vec{V}_2 = \left(N^* \vec{M}_\perp + N\vec{M}_\perp^*\right) - i\vec{M}_\perp^* \times \vec{M}_\perp$$

$$\overleftrightarrow{T} = \left(NN^* - \vec{M}_\perp \cdot \vec{M}_\perp^*\right)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + A_{MM} + iA_{MN}$$



$$A_{MM} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2M_{\perp y}M_{\perp y}^* & M_{\perp y}M_{\perp z}^* + M_{\perp z}M_{\perp y}^* \\ 0 & M_{\perp y}M_{\perp z}^* + M_{\perp z}M_{\perp y}^* & 2M_{\perp z}M_{\perp z}^* \end{pmatrix}$$

$$A_{MN} = \begin{pmatrix} 0 & M_{\perp z}^* N - M_{\perp z}N^* & M_{\perp y}N^* - M_{\perp y}^* N \\ M_{\perp z}N^* - M_{\perp z}^* N & 0 & 0 \\ M_{\perp y}^* N - M_{\perp y}N^* & 0 & 0 \end{pmatrix}$$

Initial polarization

Final polarization

$$\vec{P} = P_x\begin{pmatrix}1\\0\\0\end{pmatrix}$$

$$P_{fx}\sigma = -i\left(M_{\perp y}^* M_{\perp z} - M_{\perp z}^* M_{\perp y}\right) + NN^* P_x - \left(M_{\perp y}M_{\perp y}^* + M_{\perp z}M_{\perp z}^*\right)P_x$$

$$P_{fy}\sigma = \left(N^* M_{\perp y} + NM_{\perp y}^*\right) + i\left(M_{\perp z}N^* - M_{\perp z}^* N\right)P_x$$

$$P_{fz}\sigma = \left(N^* M_{\perp z} + NM_{\perp z}^*\right) + i\left(M_{\perp y}^* N - M_{\perp y}N^*\right)P_x$$

$$\vec{P} = P_y\begin{pmatrix}0\\1\\0\end{pmatrix}$$

$$P_{fx}\sigma = -i\left(M_{\perp y}^* M_{\perp z} - M_{\perp z}^* M_{\perp y}\right) + i\left(M_{\perp z}^* N - M_{\perp z}N^*\right)P_y$$

$$P_{fy}\sigma = \left(N^* M_{\perp y} + NM_{\perp y}^*\right) + NN^* P_y + \left(M_{\perp y}M_{\perp y}^* - M_{\perp z}M_{\perp z}^*\right)P_y$$

$$P_{fz}\sigma = \left(N^* M_{\perp z} + NM_{\perp z}^*\right) + \left(M_{\perp y}M_{\perp z}^* + M_{\perp z}M_{\perp y}^*\right)P_y$$

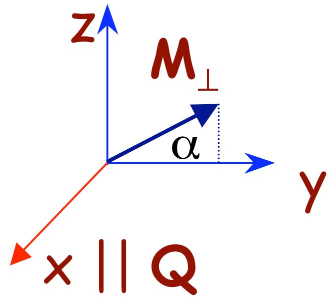
$$\vec{P} = P_z\begin{pmatrix}0\\0\\1\end{pmatrix}$$

$$P_{fx}\sigma = -i\left(M_{\perp y}^* M_{\perp z} - M_{\perp z}^* M_{\perp y}\right) + i\left(M_{\perp y}N^* - M_{\perp y}^* N\right)P_z$$

$$P_{fy}\sigma = \left(N^* M_{\perp y} + NM_{\perp y}^*\right) + \left(M_{\perp y}M_{\perp z}^* + M_{\perp z}M_{\perp y}^*\right)P_z$$

$$P_{fz}\sigma = \left(N^* M_{\perp z} + NM_{\perp z}^*\right) + NN^* P_z + \left(M_{\perp z}M_{\perp z}^* - M_{\perp y}M_{\perp y}^*\right)P_z$$

Es.: N ed $\mathbf{M}_\perp$ in fase (entrambi reali o immaginari)



$$\vec{P}_f = \begin{pmatrix} N^2 - M_\perp^2 & 0 & 0 \\ 0 & N^2 + M_\perp^2 \cos 2\alpha & M_\perp^2 \sin 2\alpha \\ 0 & M_\perp^2 \sin 2\alpha & N^2 - M_\perp^2 \cos 2\alpha \end{pmatrix} \frac{\vec{P}}{N^2 + M_\perp^2 + 2N\vec{P}\cdot\vec{M}_\perp} +$$

$$+ \begin{pmatrix} 0 \\ \cos\alpha \\ \sin\alpha \end{pmatrix} \frac{2NM_\perp}{N^2 + M_\perp^2 + 2N\vec{P}\cdot\vec{M}_\perp}$$

Se il fascio incidente non è polarizzato, P = 0, il fascio scatterato è polarizzato nella direzione di $\mathbf{M}_\perp$:

$$\vec{P}_f = \frac{2N\vec{M}_\perp}{N^2 + M_\perp^2}$$

$P_f = \pm 1$ se $N = \pm M_\perp$

La situazione $N=-M_\perp$ si verifica per la riflessione (111) della lega di Heusler Cu_2MnAl: monocromatori polarizzatori.

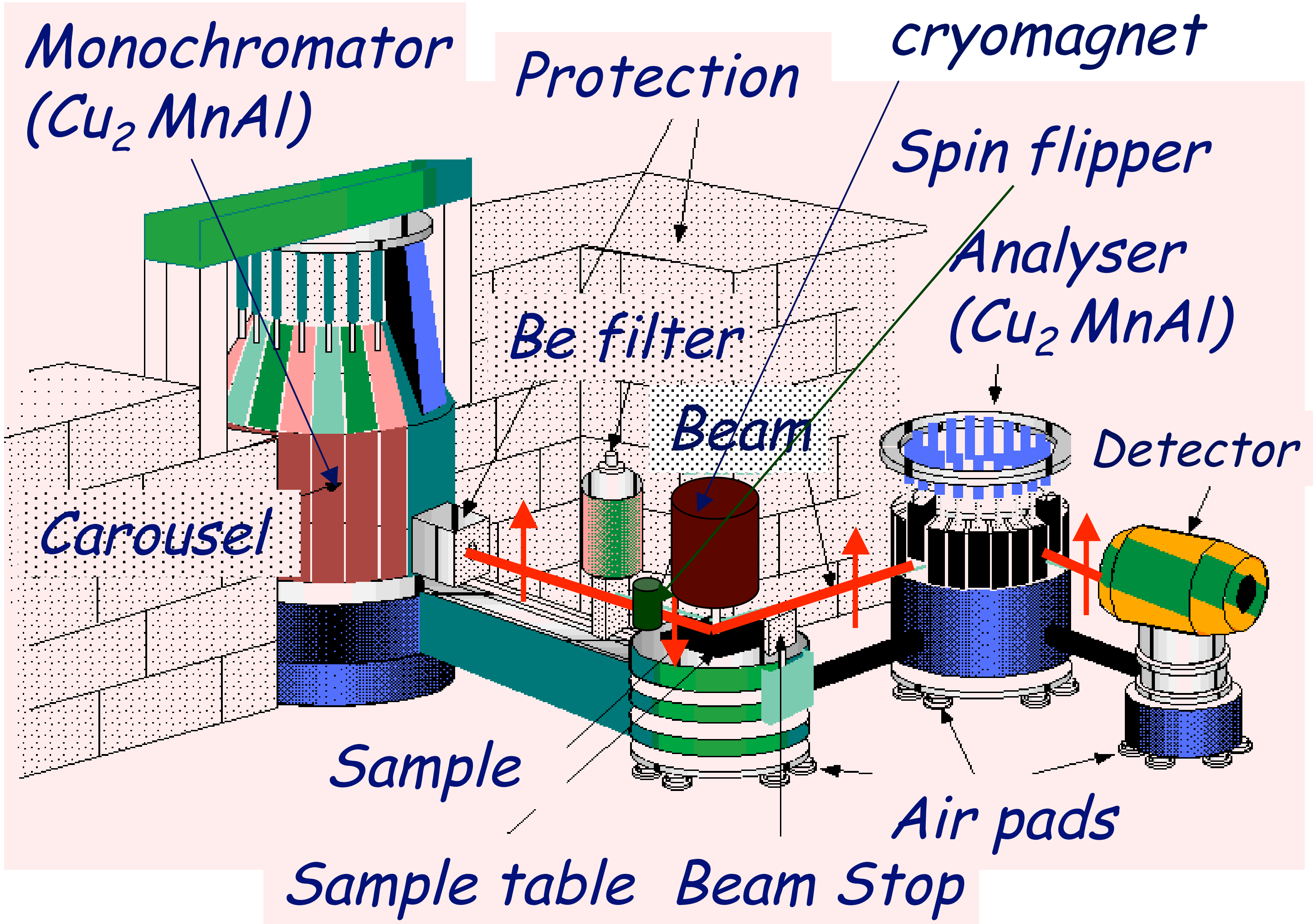
Se **n** è la direzione della magnetizzazione, la sezione d'urto è

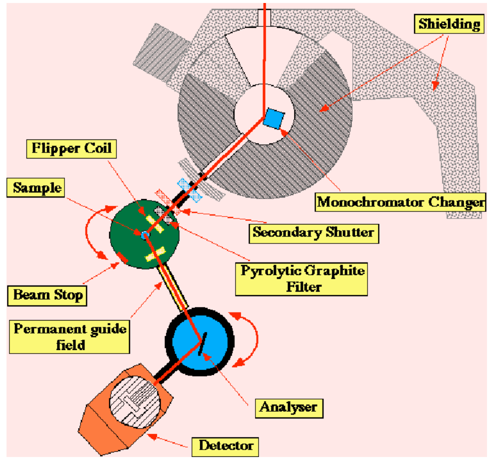
$$\sigma = 2N^2\left(1 - \vec{P}\cdot\vec{n}\right) = \begin{cases} 0, & \vec{P}\cdot\vec{n} = 1 \\ 4N^2, & \vec{P}\cdot\vec{n} = -1 \end{cases}$$

Analisi uniassiale della polarizzazione:

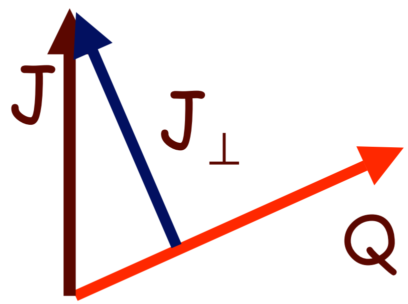
si analizza la proiezione di $\mathbf{P}_f$ lungo la direzione di un campo guida.

Si ottengono 4 sezioni d'urto parziali due spin-flip e due non-spin-flip





$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\sigma_f\sigma_i} \sim \left|\langle C_f|\sum_j e^{i\vec{Q}\cdot\vec{r}_j} U_j^{\sigma_f\sigma_i}|C_i\rangle\right|^2$$



$$U_j^{\sigma_f\sigma_i} = \langle\sigma_f|(b_j - p_j \vec{J}_{\perp j}\cdot\vec{\sigma} + B_j \vec{I}_{\perp j}\cdot\vec{\sigma}\,|\sigma_i\rangle$$

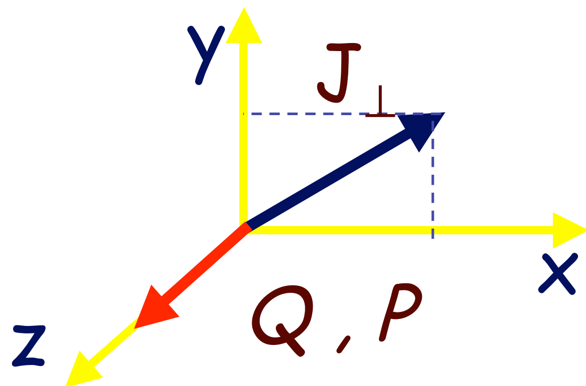
$p \propto g\, f(Q)$

$$U^{-+} = -p(J_{\perp x} - iJ_{\perp y}) + \frac{B}{2}(I_{\perp x} - iI_{\perp y})$$

$$U^{+-} = -p(J_{\perp x} + iJ_{\perp y}) + \frac{B}{2}(I_{\perp x} + iI_{\perp y})$$

$$U^{++} = b - pJ_{\perp z} + \frac{B}{2} I_z$$

$$U^{--} = b + pJ_{\perp z} - \frac{B}{2} I_z$$



***P** parallelo a **Q**: $J_{\perp z} = 0$ e lo scattering magnetico è solo SF*

I(NSF) = <u>nucleare</u> + incoerente/3

I(SF) = <u>magnetico</u> + incoerente x 2/3

Analisi di polarizzazione triassiale

Si tratta di una strategia di misura basata su applicazioni successive di analisi uniassiale lungo tre direzioni mutuamente perpendicolari: Si misura la proiezione di $\mathbf{P}_f$ lungo un campo guida orientato prima lungo X, poi lungo Y ed infine lungo Z

E' possibile misurare 10 delle 16 funzioni di correlazione:

a, V_1, V_2 e gli elementi diagonali del tensore T.

Non è possibile misurare le componenti trasverse della polarizzazione.

La sezione d'urto per il cristallo analizzatore è infatti

$$\sigma = 2N^2\left(1-\vec{P}\cdot\vec{n}\right) = \begin{cases} 0, & \vec{P}\cdot\vec{n} = 1 \\ 4N^2, & \vec{P}\cdot\vec{n} = -1 \end{cases}$$

Non è quindi possibile distinguere una rotazione di **P** da una depolarizzazione (riduzione del modulo di **P**)