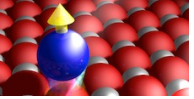


# 8.1 Energy schemes in CF with different symmetries

Make a qualitative plot (highlighting split doublets and states belonging to the same family) of the energy scheme characterizing a magnetic atom in the following situations (assuming B = 0) :

1) J=15/2 in a CF with $C_{2v}$ symmetry
2) J=8 in a CF with $C_{3v}$ symmetry
3) J=7 in a CF with $C_{4v}$ symmetry

4) In which of the three cases we can have QTM?
5) In which of the three cases we can have TA-QTM?

Adapted from: C. Hubner *et al.*, Phys. Rev.B **90**, 155134 (2014)

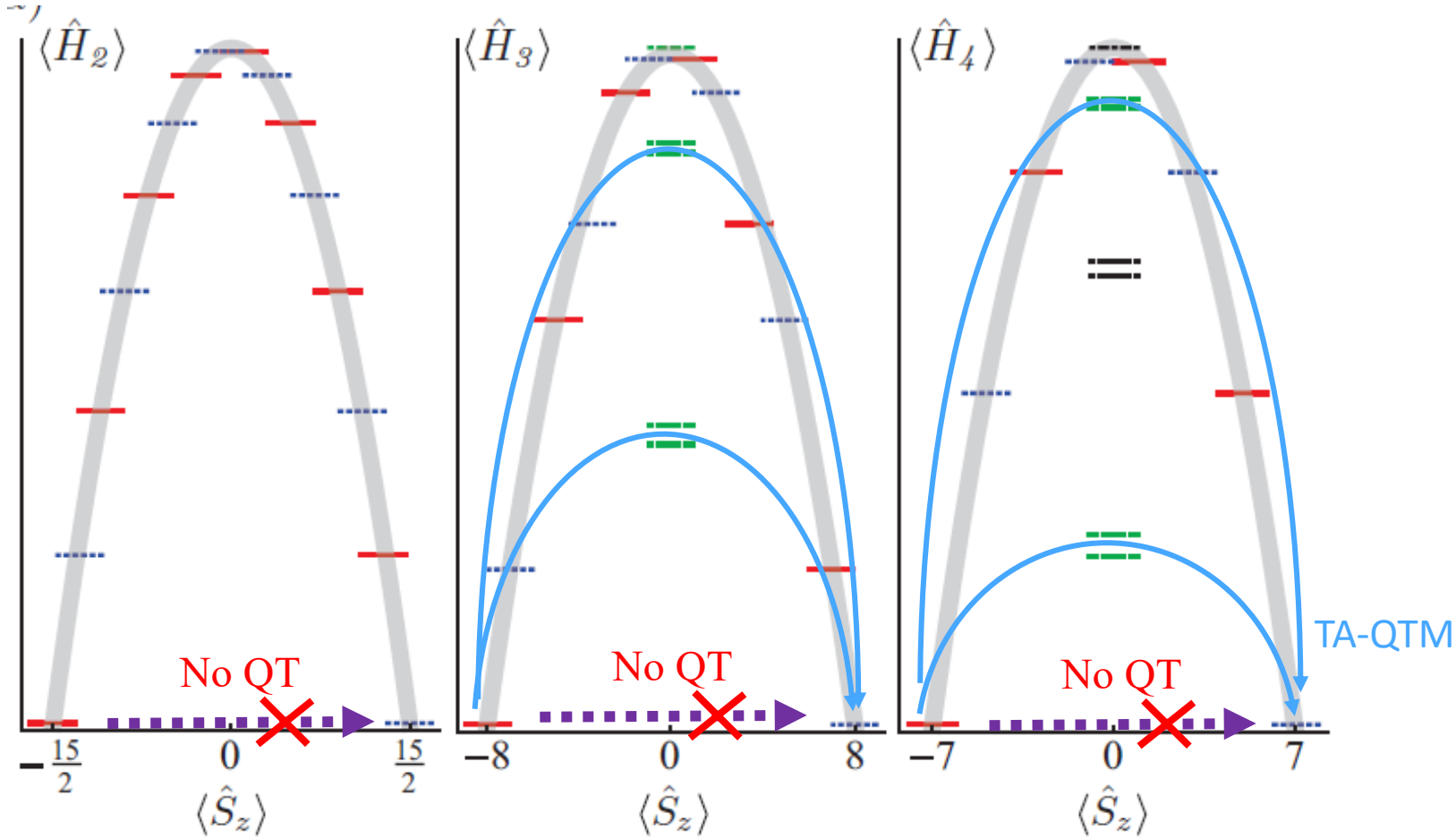
# 8.1 Energy schemes in CF with different symmetries - Solution

1) In a CF with $C_{2v}$ symmetry all states having a $J_z$ differing by 2 are mixed $\Rightarrow$ 2 families of states. In addition $J_z^+ - J_z^- \neq 2$ for all doublets $\Rightarrow$ no split doublets i.e. no TA-QTM
2) In a CF with $C_{3v}$ symmetry all states having a $J_z$ differing by 3 are mixed $\Rightarrow$ 3 families of states. In addition $J_z^+ - J_z^- = 3i$ for $J_z = 6\ and\ 3 \Rightarrow$ two split doublets and two paths for TA-QTM
3) In a CF with $C_{4v}$ symmetry all states having a $J_z$ differing by 4 are mixed $\Rightarrow$ 4 families of states. In addition $J_z^+ - J_z^- = 4i$ for $J_z = 6\ and\ 2 \Rightarrow$ two split doublets and two paths for TA-QTM

1) CF with $C_{2v}$ symmetry

2) CF with $C_{3v}$ symmetry

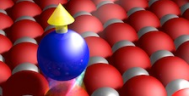
3) CF with $C_{4v}$ symmetry




States belonging to the same family are shown with the same color

4) No QTM in all three cases-> magnetization preserved without external perturbation

5) TA-QTM only in case 2) and 3)



# 8.2 Perturbation of a two-levels system

Consider an atom with total angular momentum *J* and thus 2*J*+1 $J_z$ states. The interaction with a CF breaks the degeneracy of the $J_z$ states.
In a perfect axial CF ($C_{\infty v}$) all eigenstates are pure and characterized by one of the 2*J*+1 values of $J_z$. In a CF with reduced symmetry, transverse terms ($O_k^m\ m \neq 0$) appear in the Hamiltonian and produce the splitting of the doublets characterized by $\Delta J_z = m$.
We want to calculate such splitting.
For simplicity we consider a system that has only two eigenstates described by an Hamiltonian $H = H^0 + H^1$, where $H^0$ describes the axial terms and $H^1$ the transverse terms. We denote with $|1\rangle$ and $|2\rangle$ the eigenstates of $H^0$ having energies $E_1$ and $E_2$, respectively i.e.
$H^0 |a\rangle = E_a |a\rangle$ $a$ = 1, 2.
Assuming that $H^1$ is a perturbation to the axial part, demonstrate that:

1) the eigenvalues of the Hamiltonian *H* are given by $E_\pm = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4\varepsilon^2}$ where $\varepsilon^2 = H_{12}^1 H_{21}^1$ and $H_{ij}^1 = \langle i|H^1|j\rangle$
2) how the difference in energy $E_+ - E_-$ depends on $E_1 - E_2$?
3) the eigenstates of the Hamiltonian *H* are given by $|+\rangle \approx |1\rangle - \frac{H_{12}^1}{E_2 - E_1}|2\rangle$ and $|-\rangle \approx |2\rangle + \frac{H_{12}^1}{E_2 - E_1}|1\rangle$

N.B.: the same arguments apply to the discussion of the hot spots in the DOS as source of the MAE (see lecture 4, slide 13). In that case the SOC play the role of the perturbation

# 8.2 Perturbation of a two-levels system - Solution

The wavefunctions of the true system differ only slightly from those of the model system, and we can hope to solve the equation

$$H\psi = E\psi \tag{2}$$

in terms of them by writing

$$\psi = a_1\psi_1^{(0)} + a_2\psi_2^{(0)} \tag{3}$$

where $a_1$ and $a_2$ are constants.

To find the constants $a_m$ we insert the linear combination into the Schrödinger equation and obtain (using ket notation)

$$a_1(H - E)|1\rangle + a_2(H - E)|2\rangle = 0$$

When this equation is multiplied from the left by the bras $\langle 1|$ and $\langle 2|$ in turn, and use is made of the orthonormality of the two states, we obtain the two equations

$$a_1(H_{11} - E) + a_2H_{12} = 0 \qquad a_1H_{21} + a_2(H_{22} - E) = 0 \tag{4}$$

where $H_{mn} = \langle m|H|n\rangle$.

The condition for the existence of non-trivial solutions of this pair of equations is that the determinant of the coefficients of the constants $a_1$ and $a_2$ should disappear:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

This condition is satisfied for the following values of $E$:

$$E_\pm = \tfrac{1}{2}(H_{11} + H_{22}) \pm \tfrac{1}{2}\{(H_{11} - H_{22})^2 + 4H_{12}H_{21}\}^{1/2} \tag{5}$$

In the special but common case of a perturbation for which the diagonal matrix elements are zero ($H_{mm}^{(1)} = 0$), this expression simplifies to

$$E_\pm = \tfrac{1}{2}(E_1 + E_2) \pm \tfrac{1}{2}\{(E_1 - E_2)^2 + 4\varepsilon^2\}^{1/2} \tag{6}$$

where $\varepsilon^2 = H_{12}^{(1)}H_{21}^{(1)}$. Because $H^{(1)}$ is hermitian, we can write $\varepsilon^2 = |H_{12}^{(1)}|^2$. When the perturbation is absent, $\varepsilon = 0$ and $E_+ = E_1$, $E_- = E_2$, the two unperturbed energies.

The variation of the energies of the system as the separation of the states of the model system is increased is illustrated in Fig. 6.1. As can be seen, the lower of the two levels is lowered in energy whereas that of the upper level is raised. In other words, the effect of the perturbation is to drive the energy levels apart and to prevent their crossing. This **non-crossing rule** is a common feature of all perturbations. A second general feature can also be seen from the illustration: the effect of the perturbation is greater the smaller the energy separation of the unperturbed levels. For instance, when the two original energies have the same energy ($E_1 = E_2$), then

$$E_+ - E_- = 2\varepsilon$$

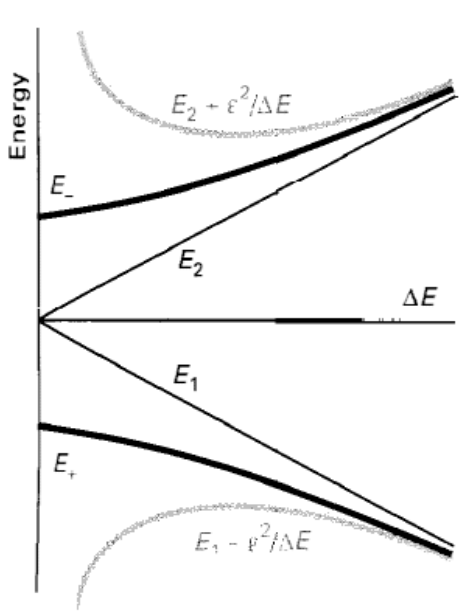



**Fig. 6.1** The variation of the energies of a two-level system with a constant perturbation as the separation of the unperturbed levels is increased. The pale lines show the energies according to second-order perturbation theory.

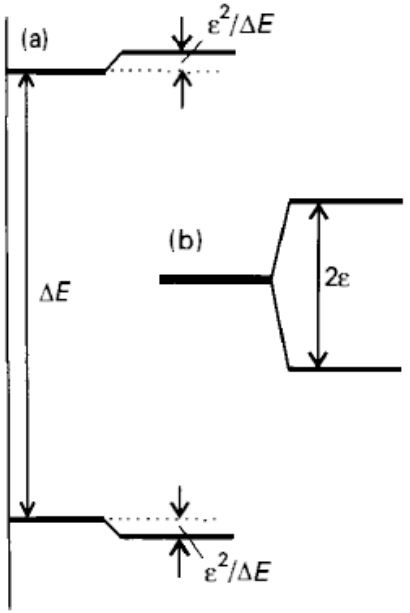
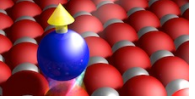



**Fig. 6.2** (a) When the unperturbed levels are far apart in energy, the shift in energ caused by a perturbation of strength $\varepsilon$ is $\pm\varepsilon^2/\Delta E$. (b) If the levels are initially degenerate, then the shift in energy is much larger, and is equal to $\pm\varepsilon$.



# 8.2 Perturbation of a two-level system - Solution

Equation 6.6 also shows that the stronger the perturbation, the stronger the effective repulsion of the levels (Fig. 6.2). In summary:

1. When a perturbation is applied, the lower level moves down in energy and the upper level moves up.
2. The closer the unperturbed states are in energy, the greater the effect of a perturbation.
3. The stronger the perturbation, the greater the effect on the energies of the levels.

The effect of the perturbation can be seen in more detail by considering the case of a perturbation that is weak compared with the separation of the energy levels in the sense that $\varepsilon^2 \ll (E_1 - E_2)^2$. When this condition holds, eqn 6.6 can be expanded by making use of $(1+x)^{1/2} = 1 + \frac{1}{2}x + \ldots$, to obtain

$$E_\pm = \tfrac{1}{2}(E_1 + E_2) \pm \tfrac{1}{2}(E_1 - E_2)\left(1 + \frac{2\varepsilon^2}{\Delta E^2} + \ldots\right)$$

where $\Delta E = E_2 - E_1$. Then, to second-order in $\varepsilon$ we have

$$E_+ \approx E_1 - \frac{\varepsilon^2}{\Delta E} \qquad E_- \approx E_2 + \frac{\varepsilon^2}{\Delta E} \tag{7}$$

These two solutions converge on the exact solutions when $(2\varepsilon/\Delta E)^2 \ll 1$, as shown in Fig. 6.1. A general feature of all perturbation theory calculations is that the shifts in energy are of the order of $\varepsilon^2/\Delta E$.

The perturbed wavefunctions are obtained by solving eqn 6.4 for the coefficients setting in turn $E = E_+$ (to obtain $\psi_+$) and $E = E_-$ (to obtain $\psi_-$). A convenient way to express the solutions is to write

$$\psi_+ = \psi_1^{(0)} \cos\zeta + \psi_2^{(0)} \sin\zeta \qquad \psi_- = -\psi_1^{(0)} \sin\zeta + \psi_2^{(0)} \cos\zeta \tag{8}$$

and then it is found that[1]

$$\tan 2\zeta = \frac{2|H_{12}^{(1)}|}{E_1 - E_2} \tag{9}$$

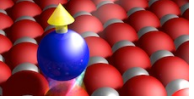
For a degenerate model system ($E_1 = E_2$), we have $\tan 2\zeta = \infty$, corresponding to $\zeta = \pi/4$. In this case the perturbed wavefunctions are

$$\psi_+ = \frac{1}{\sqrt{2}}\left(\psi_1^{(0)} + \psi_2^{(0)}\right) \qquad \psi_- = -\frac{1}{\sqrt{2}}\left(\psi_1^{(0)} - \psi_2^{(0)}\right) \tag{10}$$

It follows that each perturbed state is a 50 per cent mixture of the two model states. In contrast, for a perturbation acting on two widely separated states we can write $\tan 2\zeta \approx 2\zeta = -2|H_{12}^{(1)}|/\Delta E$. Furthermore, because $\sin\zeta \approx \zeta$ and $\cos\zeta \approx 1$, it follows that

$$\psi_+ \approx \psi_1^{(0)} - \frac{|H_{12}^{(1)}|}{\Delta E}\psi_2^{(0)} \qquad \psi_- \approx \psi_2^{(0)} + \frac{|H_{12}^{(1)}|}{\Delta E}\psi_1^{(0)} \tag{11}$$

We see that each model state is slightly contaminated by the other state.



# 8.3 Fe atom in a $C_{4v}$ CF

Consider an Fe atom adsorbed on a site with $C_{4v}$ symmetry, like the one shown in the figure, in a magnetic field ***B*** applied along the ***z*** axis.

1) Write the most general spin Hamiltonian that can be used to describe the energy scheme.
2) For the CF part, let's use a spin Hamiltonian with a minimum number of terms, $H_{CF} = B_2^0 O_2^0 + B_4^4 O_4^4$ with $O_2^0 = 3S_z^2$ (neglecting the $S(S+1)$ term which just generates a shift in energy) and $O_4^4 = \frac{1}{2}(S_+^4 + S_-^4)$; we also assume no magnetic field. Calculate the energy scheme assuming $B_2^0 = -1$ and a negligible transverse term i.e. $B_4^4 = 0$
3) Calculate the energy scheme assuming $B_2^0 = -1$ and a small transverse term i.e. $B_4^4 = 0.01$. Express the wave functions of the two states forming the ground doublet
4) At which value of the magnetic field the two states of the ground multiplet become almost pure (assuming $g = 2$)?

# 8.3 Fe atom in a $C_{4v}$ CF - Solution

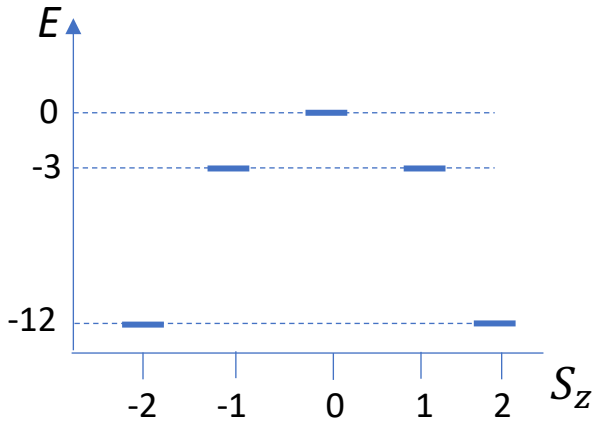
1) Fe is a $3d_6$ transition metal with the magnetism originating from the 3d states i.e. $l = 2$ and $S=2$ . The most general spin Hamiltonian in an external magnetic field along the *z* direction with a $C_{4v}$ CF is then

$$H_{eff} = g\mu_B S_z B + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4.$$

2) With the given conditions, the spin Hamiltonian becomes $H_{eff} = B_2^0 O_2^0 = -3S_z^2$

We need to calculate $H_{eff} \left| S, S_z \right\rangle = -3S_z^2 \left| S, S_z \right\rangle \Rightarrow$

$H_{eff} \left| S, \pm 2 \right\rangle = -12 \left| S, \pm 2 \right\rangle$; $H_{eff} \left| S, \pm 1 \right\rangle = -3 \left| S, \pm 1 \right\rangle$; $H_{eff} \left| S, 0 \right\rangle = 0$



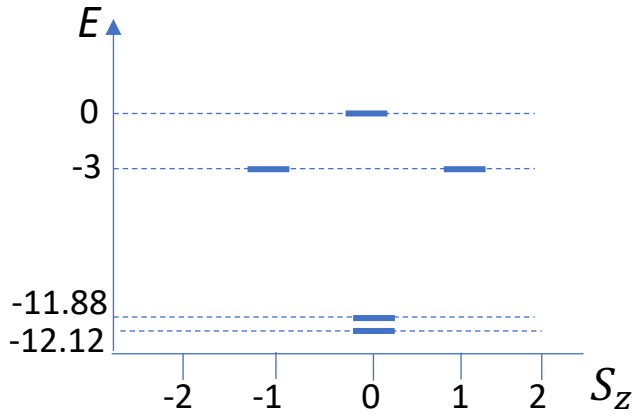

3) The spin Hamiltonian becomes $H_{eff} = B_2^0 O_2^0 + B_4^4 O_4^4 = -3S_z^2 + 0.01\frac{1}{2}(S_+^4 + S_-^4)$.

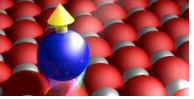
We can consider the effect of the $O_4^4$ as a perturbation of the previous energy scheme given the relative intensity of the $B_k^m$ coefficients weighting the effect of the operators ($B_4^4 = \frac{1}{100} B_2^0$).

We have that $S_+^4 \left| S, -2 \right\rangle = \sqrt{4} S_+^3 \left| S, -1 \right\rangle = \sqrt{4}\sqrt{6}\, S_+^2 \left| S, 0 \right\rangle = \sqrt{4}\, 6\, S_+ \left| S, 1 \right\rangle = 24 \left| S, 2 \right\rangle$ and similarly for the $S_-^4$ term. Thus the transverse term mixes the two states $\left| 1 \right\rangle = \left| S, -2 \right\rangle$ and $\left| 2 \right\rangle = \left| S, 2 \right\rangle$ of the ground multiplet. All the other states are not affected since they can not be projected onto one of the other states by the $O_4^4$operator.

To evaluate the splitting we can use the result of the previous exercise showing that two degenerate states split by $2\varepsilon$ with $\varepsilon = H_{12} = B_4^4 \frac{1}{2} S_+^4 = 0.12$. Then the new energy scheme is the one shown on the side.

The wave functions of the two mixed states are $\left| S, \pm \right\rangle = \frac{1}{\sqrt{2}} ( \left| S, -2 \right\rangle \pm \left| S, 2 \right\rangle )$





# 8.3 Fe atom in a $C_{4v}$ CF - Solution

4) In an applied magnetic field, the two states of the ground multiplet are not anymore degenerate and their difference in energy depends on *B*; thus the effect of the perturbation generated by the transverse term of the CF is to add a correction to the energy $E_{1,2}(B) = g\mu_B S_z B + B_2^0 O_2^0$ of the pure states of the order of

$\delta E_{\pm}(B) = \frac{\pm\varepsilon^2}{E_1 - E_2} = \frac{\pm\varepsilon^2}{2g\mu_B|S_z|B}$ with the g-factor g = 2 and $|S_z| = 2$.

The field dependence of the mixed states is then given by $E_{\pm}(B) = E_{1,2}(B) + \delta E_{\pm}(B)$

We can assume that the two states of the ground multiplet become almost pure when

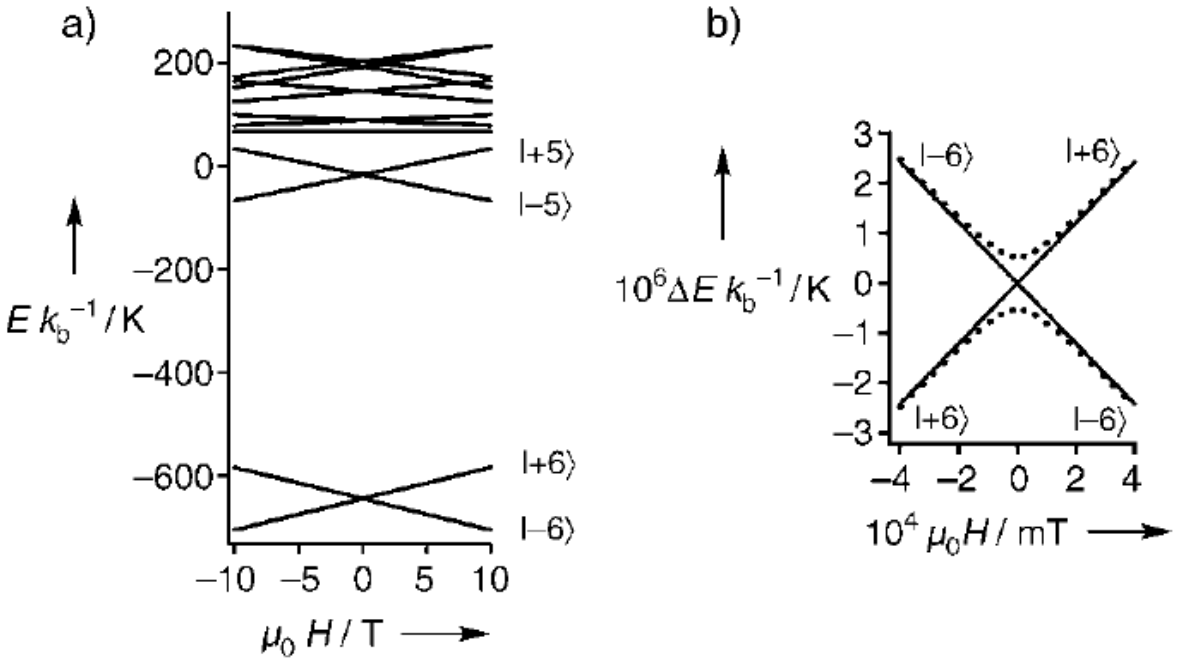
$\frac{2\delta E_{\pm}(B)}{E_1(B) - E_2(B)} = 2\left(\frac{\varepsilon}{2g\mu_B|S_z|B}\right)^2 = 0.01 \quad \Rightarrow 2g\mu_B|S_z|B \approx 14\,\varepsilon \Rightarrow B \approx 3.5\,T$ (with $\mu_B \approx 0.06$ meV/T)

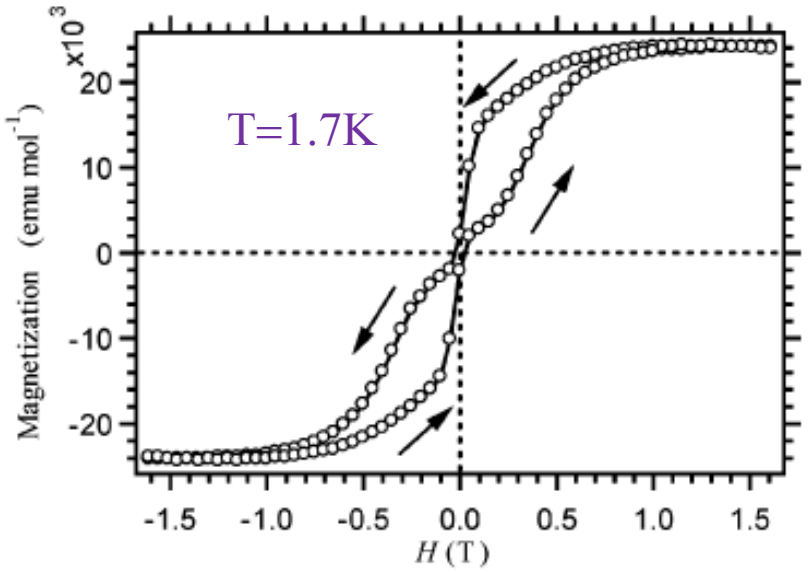
At this field $|+\rangle \approx |1\rangle - \frac{\varepsilon}{E_1 - E_2}|2\rangle \approx |1\rangle - 0.07\,|2\rangle$ i.e. there is only a $0.07^2 = 5 \cdot 10^{-3}$ weight of state $|2\rangle$ in state $|+\rangle$

# 8.4 Butterfly shaped magnetization curve of $TbPc_2$

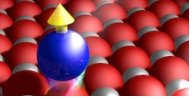
From the crystallographic structure of the $TbPc_2$ molecule we know that the Tb atom is in a $C_{4v}$ crystal field.

1) Write the Spin Hamiltonian that describe the Tb atom
2) From a series of different measurements, the energy scheme shown in the figure has been deduced. This simplified energy scheme (nuclear spin effects are not shown) qualitatively explain the magnetization curve of the $TbPc_2$ molecules showing a butterfly shape characterized by fast relaxation for $B \approx 0$. Qualitatively, at which magnetic field fast relaxation should set in according to this scheme?
3) Always neglecting the nuclear spin effects, what should be the zero-field splitting of the ground doublet to have a fast relaxation starting at $B \approx 50\ mT$ as seen in the magnetization curve shown in the figure?




Adapted from 10.1002/anie.200462638



# 8.4 Butterfly shaped magnetization curve of $TbPc_2$ - Solution

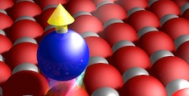
1) Tb is a rare earth element with the magnetism originating from the 4f states i.e. $l = 3$ and $J = 6$ . The most general spin Hamiltonian in an external magnetic field along the $z$ direction with a $C_{4v}$ CF is then

$$H_{eff} = g\mu_B J_z B + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4.$$

2) From the figures we see that the two states of the ground multiplet mix for fields smaller than about $4 \cdot 10^{-4}$ mT, with a zero-field splitting of about $9 \cdot 10^{-8}$ meV. Then fast relaxation via QTM should set in for fields smaller than $4 \cdot 10^{-4}$ mT,

3) We have seen in the previous exercises that the states start to mix when $\frac{\Delta E_{\pm}(B)}{E_1(B) - E_2(B)} = 2\left(\frac{\varepsilon}{2g_J\mu_B|J_z|B}\right)^2 = 0.01 \Rightarrow \varepsilon = 2\sqrt{0.005}\, g_J\mu_B|J_z|\mathrm{B}$

With $g_J = 1.5$ we find that $\varepsilon = 0.0038$ meV



# 8.5 Spin dynamics

Consider an atom of Dy adsorbed on a crystal surface and assume that the CF defined by the interaction with the surrounding atoms has a $C_{6v}$ symmetry. The Dy electronic configuration is similar to the one it has in gas phase : [Xe] $6s^2$ $4f^{10}$.

1) Write the most general spin Hamiltonian describing the energy scheme of the Dy atom

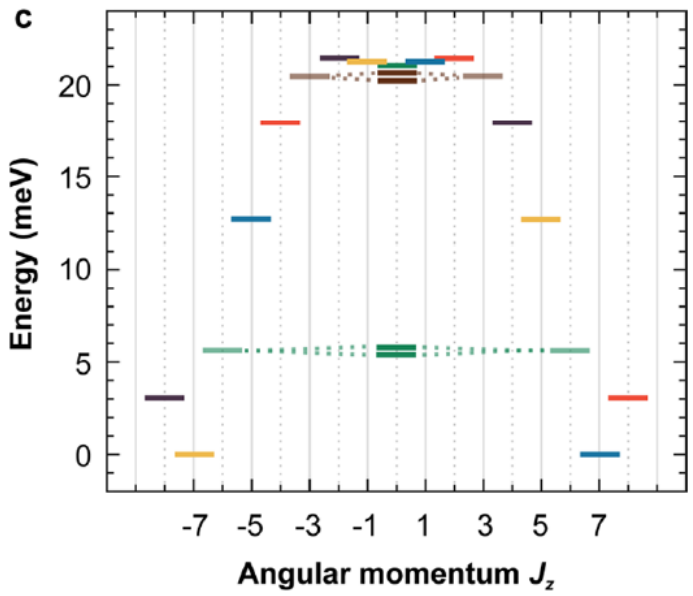
Assuming a ground doublet with maximum $J_z$ and absence of magnetic field, what is the minimum number of scattering events for spin relaxation of a fully occupied $J_z$ = -8 state assuming that:

2) the spin can relax only via spin-electron scattering. Sketch the possible paths.

3) the spin can relax only via spin-phonon scattering. Sketch the possible paths.

Consider the energy scheme shown in the figure which correspond to Dy adsorbed on graphene.

4) Repeat point 2) and 3) for this configuration. What happens in a small magnetic field, just large enough to avoid split doublets?



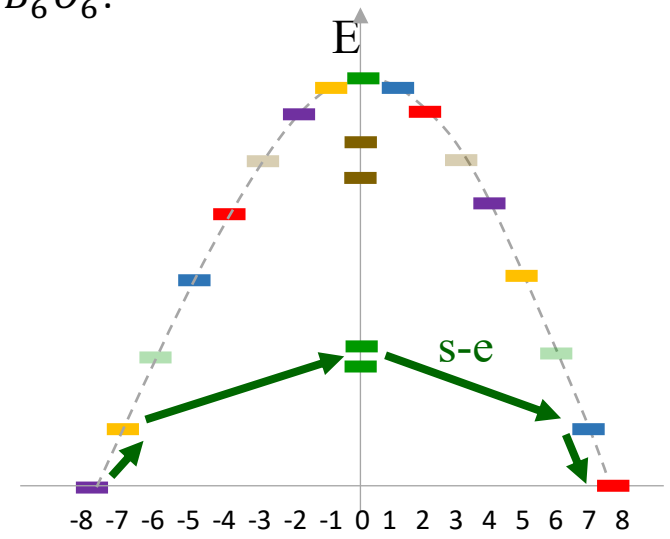

R. Baltic *et al.*, Nano Letters **16**, 7610 (2016)

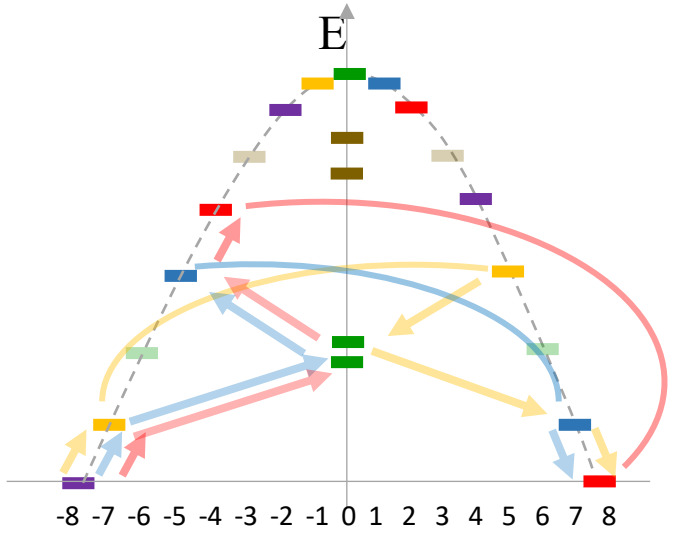
# 8.5 Spin dynamics - Solution

1) Dy is a rare earth element with the magnetism originating from the 4f states i.e. $l = 3$ and from the electronic configuration we deduce $J = 8$ . The most general spin Hamiltonian in an external magnetic field along the $z$ direction with a $C_{6v}$ CF is then

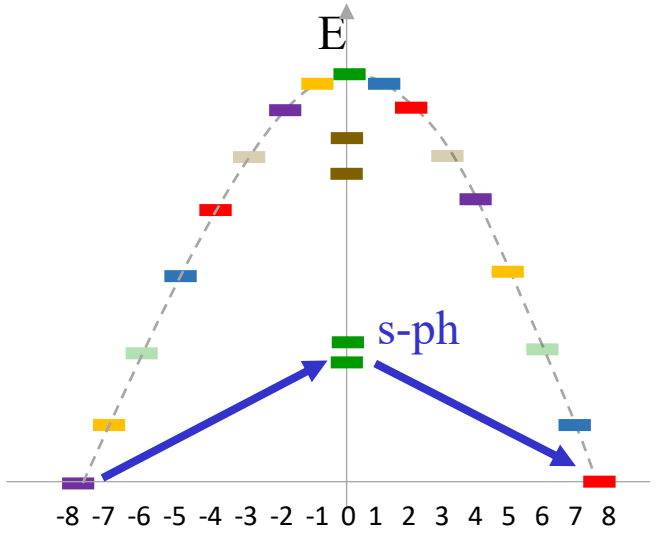
$$H_{eff} = g\mu_B J_z B + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6.$$

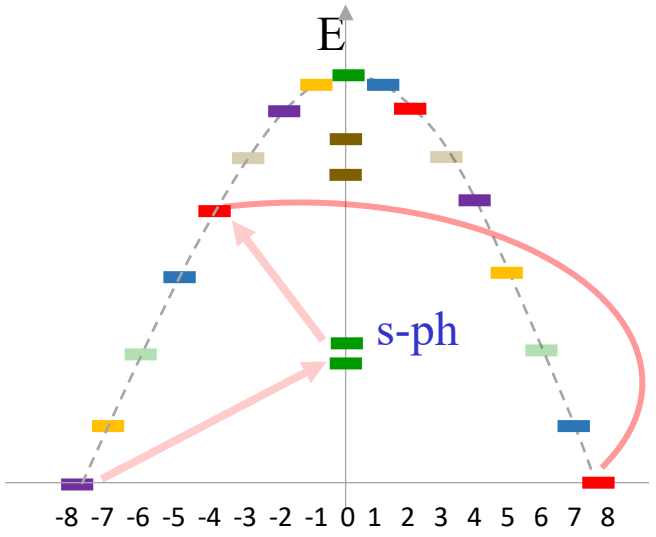
2) Since $H_{spin\text{-}electron} = J_{exc}\, J_z\, \sigma_z + 1/2\, J_{exc}\, (J_+ \sigma_- + J_- \sigma_+)$ a minimum of 4 spin-electron scattering are needed. The path using QTM via the split doublet is the fastest one. Other three paths exist but they are less probable since the mixing of non degenerate states is much smaller




3) Since $H_{spin\text{-}phonon} = a\,(J_+, J_-) + b\,(J_+^2, J_-^2)$ a minimum of 2 spin-phonon scattering are needed. Also in this case the path using QTM via the split doublet is the fastest one. Another path exists but it is less probable since the mixing of non degenerate states is much smaller



# 8.5 Spin dynamics - Solution

4) In case of spin-phonon scattering a single scattering is enough but the probability is low. The most probable spin-phonon scattering path passes via the spilt doublet and it requires two scattering events.
In case of spin-electron, a minimum of 2 scattering events are needed.

In an applied field, the reversal paths are the same but the one via the split doublet is not anymore the most probable. Two calculate the probability of each path one need to calculate the matrix elements and consider the electron (phono) density as well as the electron (phonon) population ( given by the Fermi-Dirac (Bose-Einstein) function)