Course Outline

1. Symmetry, Group Theory, and Electronic Structure

2. Ground State Spectroscopic Methods

2.1 Nuclear Magnetic Resonance

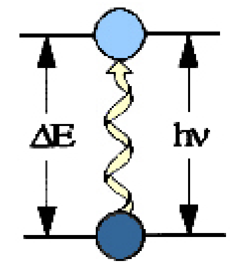
2.2 Electron Paramagnetic Resonance

2.3 Mössbauer Spectroscopy

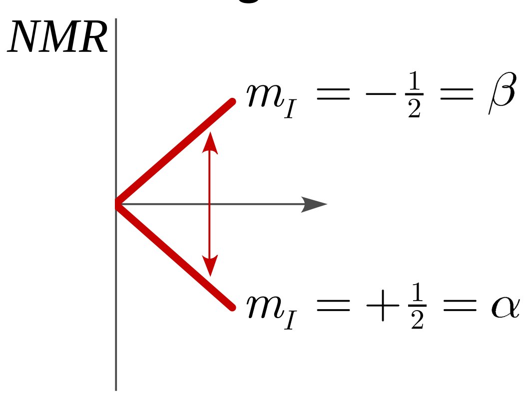
3. Excited State Spectroscopic Methods

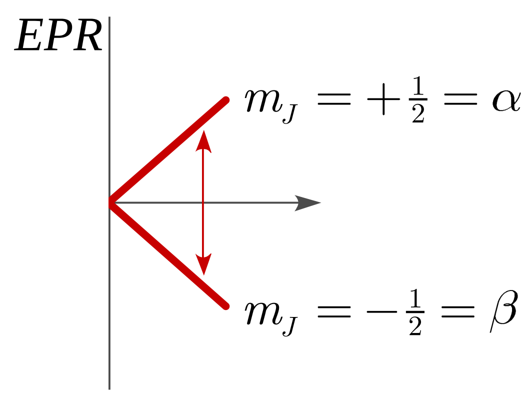
4. Other Physical Methods

EPR basics



- *a.k.a.* Electron Spin Resonance (ESR)
- exactly the same phenomenon as NMR!
  - splitting of angular momentum states in presence of magnetic field
  - but instead of nuclear spin states, look at *electron spin states*
  - splitting is much greater for electrons since γ is much greater
  - particle charges are different $\rightarrow$ ordering of spin states differs





$$\Delta E_{\alpha\rightarrow\beta} = h\nu = \gamma\hbar B_{eff}$$
$\sim$ RF energies

$$\Delta E_{\alpha\rightarrow\beta} = h\nu = g_{eff}\mu_B B_0$$
$\sim$ MW energies

2.2 Electron Paramagnetic Resonance

- the Zeeman effect, revisited…
  - Hamiltonian for electronic Zeeman effect: $H'_{Zeeman} = -\vec{\mu}_J \cdot \vec{B} = -\hbar\gamma_e \vec{J} \cdot \vec{B}$
  - energy levels:

$$E_{Zeeman} = -\gamma_e \hbar \left|\vec{B}\right| \cdot \left\langle \Psi_J \left| \vec{J} \right| \Psi_J \right\rangle = -\gamma_e \hbar B_0 m_J \;\Rightarrow\; E_{Zeeman} = \pm \tfrac{1}{2} \gamma_e \hbar B_0$$

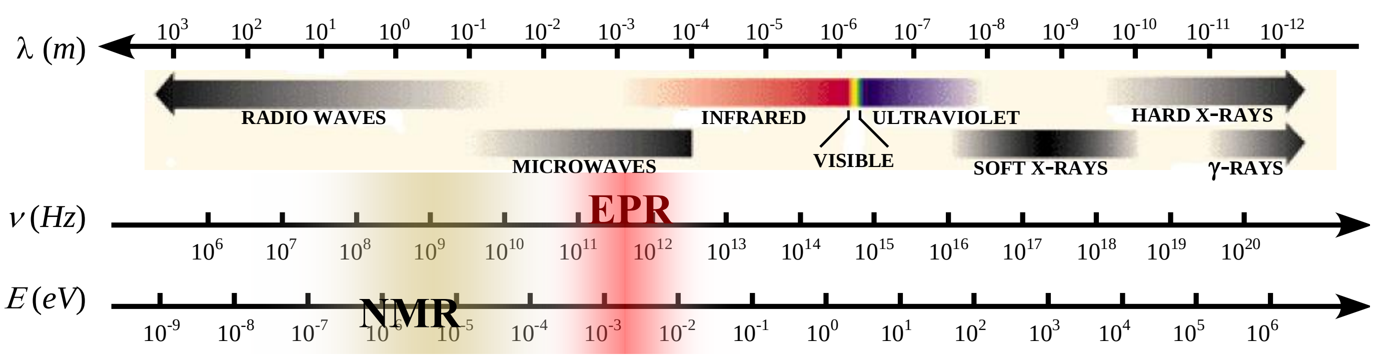
  - energy splitting is therefore $\Delta E = h\nu = -\hbar\gamma_e B_0 = g\mu_B B_0$

$$\mu_B = \beta = \text{Bohr magneton} = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} JT^{-1}$$

  - differences between NMR and EPR:
    - NMR: use gyromagnetic ratio $\gamma_e = \frac{g_e}{\hbar}\mu_e$
    - EPR: use Landé Factor (*g* factor)
    - basically a slightly different way to express gyromagnetic ratio
    - gyromagnetic ratio for electron is **negative** $\rightarrow$ opposite splitting from nuclei
  - for an isolated (free) electron: $g = \frac{\gamma_e \hbar}{\beta} = 2.0023$

The EPR Experiment

- just as with NMR, there are three main possibilities:
  1. fixed magnetic field, tunable electromagnetic radiation source
  2. fixed EM source, tunable magnetic field
  3. pulsed experiments
- tuning microwave source is <u>*very*</u> difficult –option 1 never used
  - CW-EPR = sweep magnetic field at fixed MW frequency
  - Pulsed EPR = fun with MW pulses in a fixed magnetic field
- again, like NMR – the resonance condition depends on $h\nu$
  - several types of EPR experiments depending on the MW source...

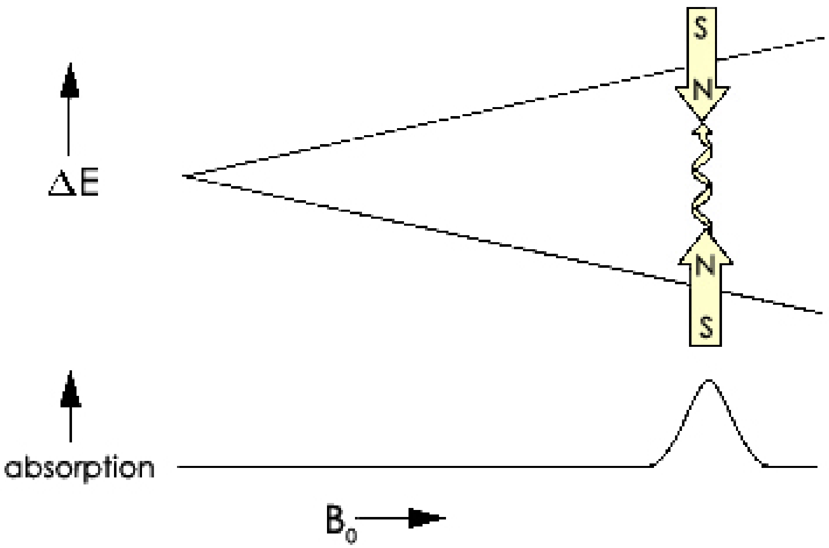


2.2 Electron Paramagnetic Resonance

- Spectrometer frequencies used in EPR:

Microwave Band	ν (*GHz*)	$B_{res}(T)$
L	1.1	0.0392
S	3.0	0.1070
X	9.75	0.3480
Q	34.0	1.2000
W	94.0	3.4000

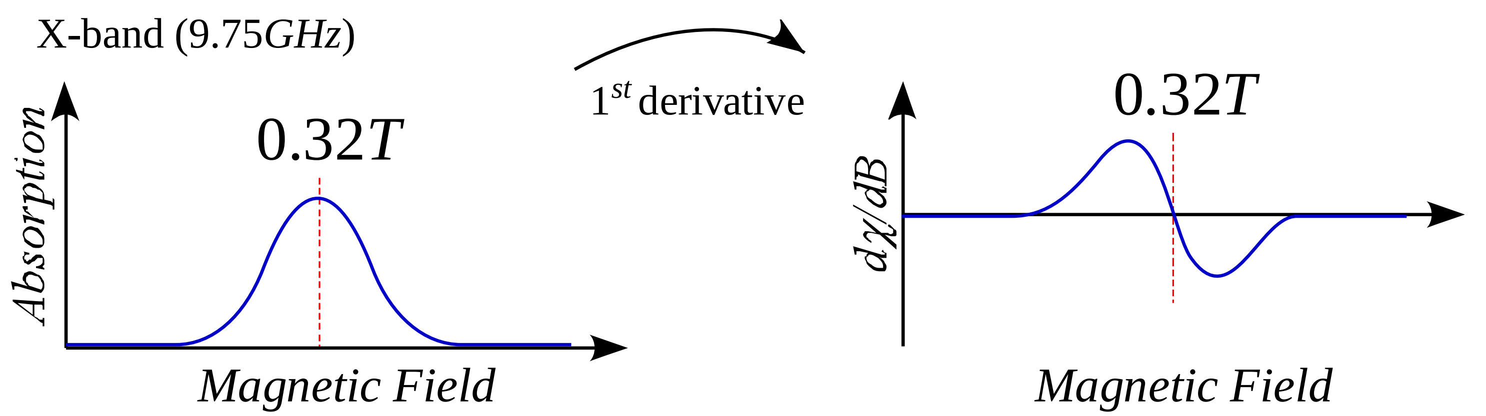
↑ for free electron (g = 2.00)



$$g = \frac{h\nu}{\beta B_0} = 0.71448 \times \frac{\nu(MHz)}{B_0(Gauss)}$$

The EPR Spectrum

- selection rules for EPR transitions → $\text{for } \vec{B}_{MW} \perp \vec{B}_0 \rightarrow \Delta M_J = \pm 1$; $\text{for } \vec{B}_{MW} \parallel \vec{B}_0 \rightarrow \Delta M_J = 0$
    - therefore need magnetic field vector of incident MW radiation (B_{MW}) to be perpendicular to magnetic field (B_0) to observe standard EPR transitions...
    - standard EPR instruments use this "perpendicular mode"
- for better resolution, spectra are shown as *derivative spectra*



Effect of Chemical Environment on EPR Experiment

- unpaired electrons in atoms/molecules are affected by chemical environment

NMR

- chemical shift (δ_{ppm}) gives frequency shift ($\Delta\nu = \nu_i - \nu_0$) from reference
- ν_i is considered to come from modifications in the *effective magnetic field* (B_{eff})
- but could also think of it as *effective magnetogyric ratio* (γ_{eff})

$$\nu_i = \frac{\gamma}{2\pi} B_{eff} = \frac{\gamma}{2\pi} B_0 (1 - \sigma_i) = \frac{\gamma(1-\sigma_i)}{2\pi} B_0 = \frac{\gamma_{eff}}{2\pi} B_0$$

EPR

- use *g*-factor to define changes in response to the incident magnetic field (B_0)
- Δg thus provides chemical shift 'information'
- Δg is thus *analogous* to δ_{ppm} in NMR
- *g*-factor is also field independent (same value for all EPR experiments...)
- electron environment is usually anisotropic (non spherical)

Contribution to shifts in g-values (why isn't g always 2.0023?)

- The influence of ***shielding*** is very small in atoms/molecules
  - Unpaired electrons are near surface of molecule
  - Transition energies are much larger than NMR in 2.4*T* magnetic field →

^{1}H resonates at ~ 140 *MHz*
e^- resonates at ~ 94 *GHz*

- Spin-Orbit Coupling (*L*•*S*)
  - interaction between *electron spin* (*S*) and *orbital angular momentum* (*L*)
  - magnitude of SOC depends on
    - SOC parameter for the orbital (ζ) → element specific
    - amount of orbital angular momentum in orbital containing *unpaired electron*
    - mechanisms for indirect transfer of SOC to unpaired electron
  - in molecules, direct SOC is usually quenched by low symmetry
  - not true in atoms → in spherical symmetry – easy to calculate *g*-value

Landé Factor

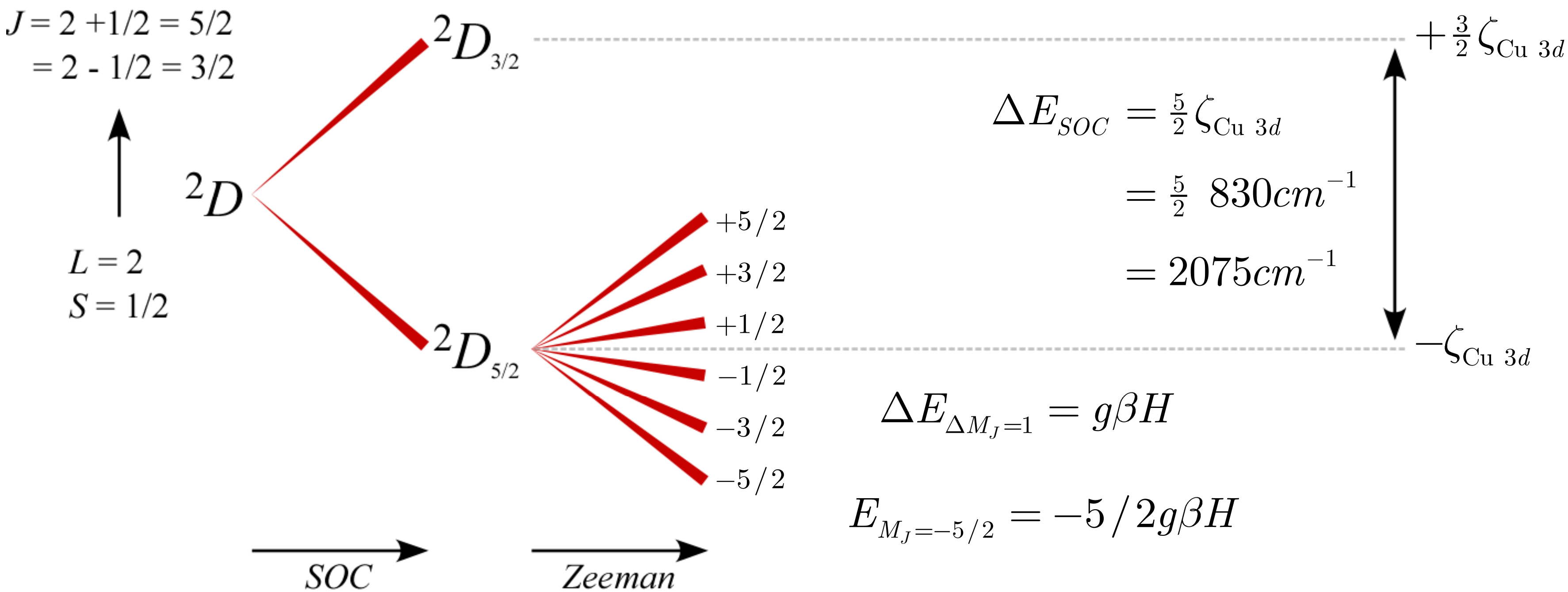
$$g = 1 + \frac{J\ \ J+1\ -L\ \ L+1\ +S\ \ S+1}{2J\ \ J+1}$$

Effect of SOC on Unpaired Electrons in Atoms

Cu^{II} ($3d^9$)

$$g = 1 + \frac{\frac{5}{2}\ \frac{5}{2}+1\ - 2\ 2+1\ + \frac{1}{2}\ \frac{1}{2}+1}{2\,\frac{5}{2}\ \frac{5}{2}+1}$$

$$= 1 + \frac{\frac{35}{4} - \frac{24}{4} + \frac{3}{4}}{\frac{35}{2}} = 1 + \frac{7}{35} = \boxed{1.2}$$



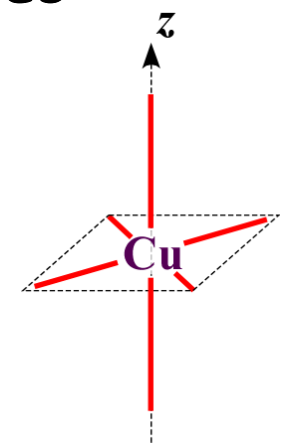
g-factor Anisotropy

- for isolated electron $\rightarrow$ orientation of electron in B_0 doesn't matter
  - spherically symmetric environment = isotropic environment ($x = y = z$)
  - isotropic environment can also occur in atoms/molecules (in high symmetry)
- but... the chemical environment is often *anisotropic* (asymmetric)
  - axial ($x = y \neq z$)
  - rhombic ($x \neq y \neq z$)

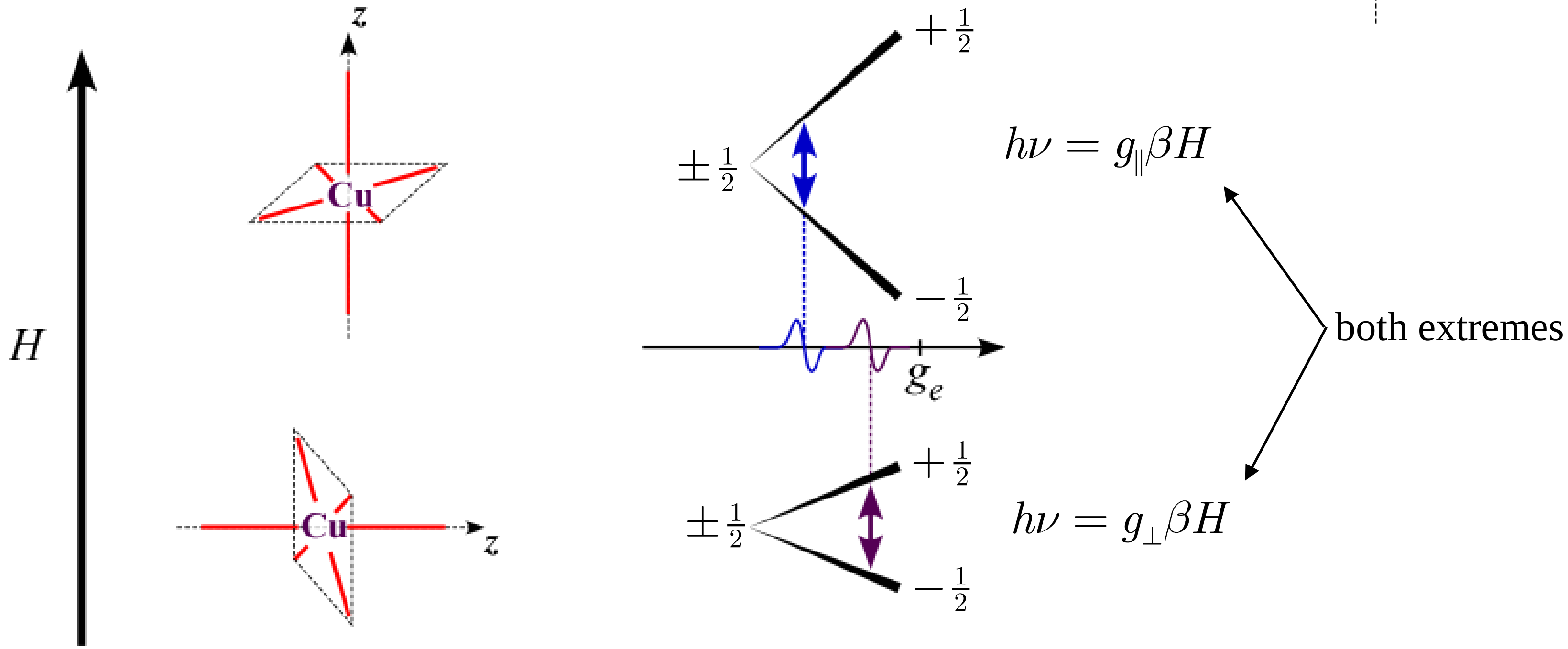
limiting cases for magnetic anisotropy

- asymmetric chemical environment generates ***g-anisotropy*** in EPR
  - more than one *g*-value is observed
  - the *g*-tensor is different depending which way you look at the molecule

Anisotropic g-values – example: Cu^{II} complexes



- *e.g.*, 6 coordinate Cu^{II} ($3d^9$) complexes
  - D_{4h} axial elongation due to Jahn-Teller effect
  - chemical environment is thus different along *z* axis



Anisotropic g-values – single crystal spectrum

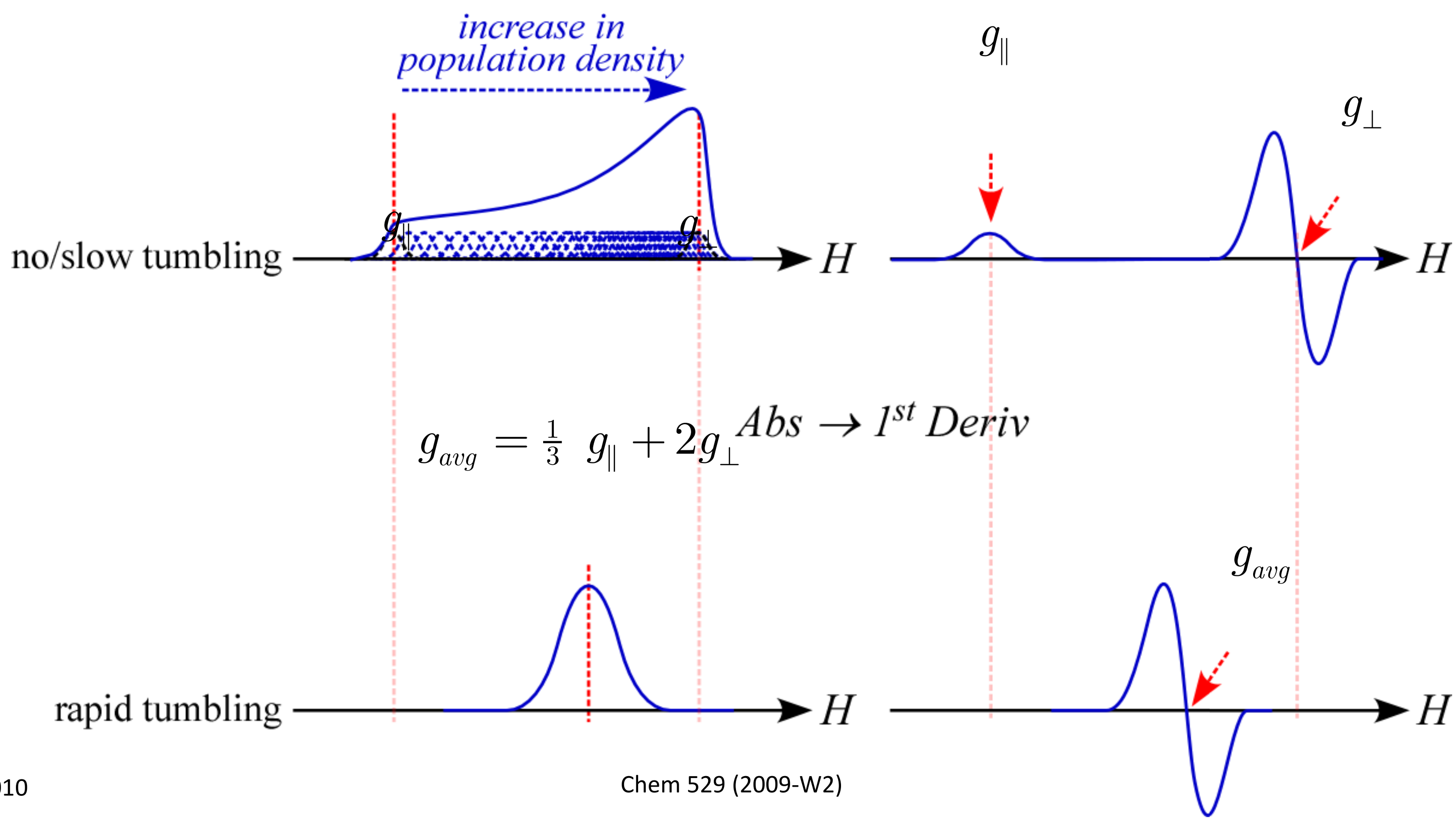
- in perfect system $\rightarrow$ 1 molec/unit cell oriented along crystal axes
  - spectrum along *z*-direction will give peak at $g_{\parallel}$
  - spectrum along x,y-direction will give peak at $g_{\perp}$
  - for any given angle relative to *H*, the transition will appear at projected weighted average of the two components of the *g*-tensor:

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$$

- but situation is usually more complicated...
  - molecular axes don't correspond with unit cell
  - more than one molecule per unit cell
  - need a single crystal!
  - however: single-crystal EPR is very powerful even if not perfect!

Anisotropic g-values – Axial "powder pattern" spectrum

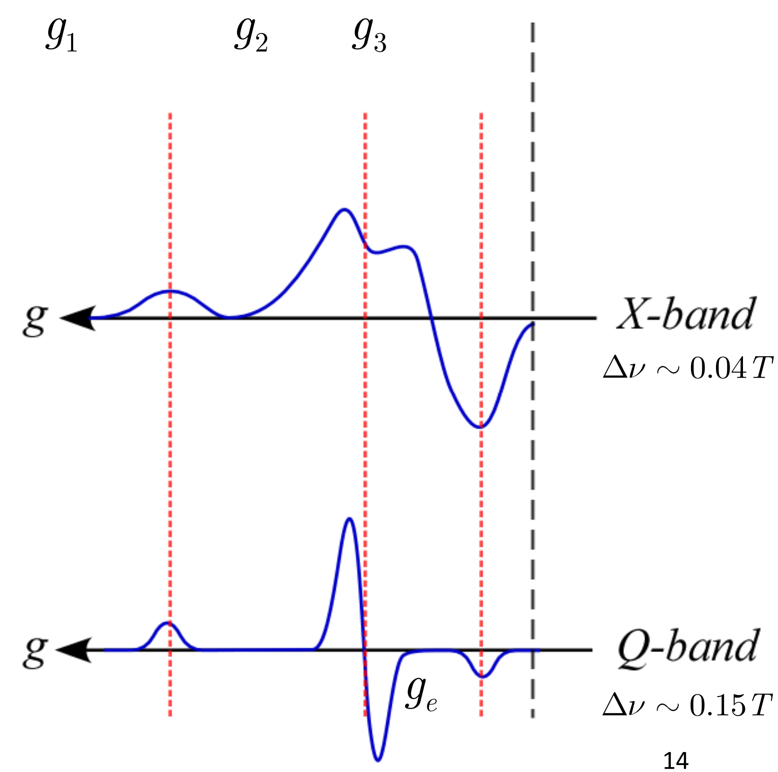
- normally: solution, frozen glass, or dilute polycrystalline solids
- random orientation of molecules relative to *magnetic field (H)*



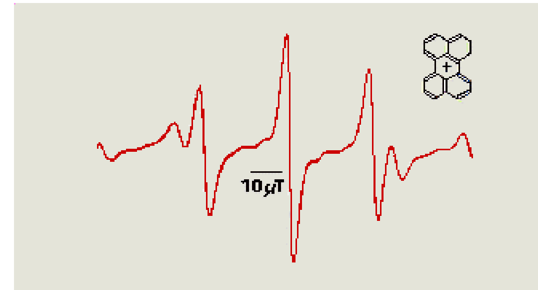
Anisotropic g-values – Rhombic "powder" spectrum

- occurs in low symmetry complexes where $x \neq y \neq z$
- result is that each direction of the *g*-tensor is different $\rightarrow g_x \neq g_y \neq g_z$
- derivative spectrum will now show three components...
  - often, a rhombic X-band spectrum will be difficult to resolve
  - using a higher frequency MW Band will better resolve the *g*-tensor components
  - larger magnetic field range = better resolution

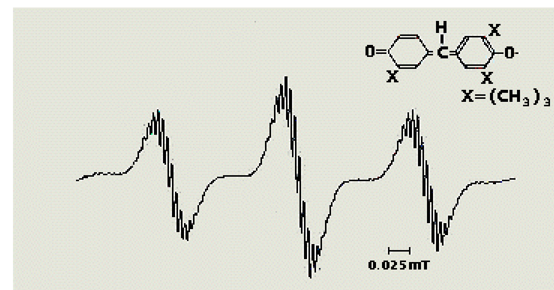
$$h\nu_Q \approx 3.9 h\nu_X$$



EPR of Organic Radicals



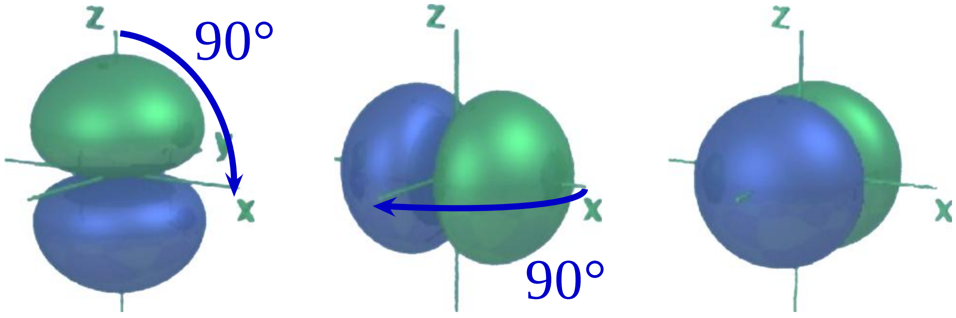
- usually, SOC is very small... (< 100cm^{-1})
- get "spin-only" contributions
  - for single unpaired electron → S = ½, *g* ~ 2.0023
- organic radicals have very sharp peaks centred at *g* = 2
- but other contributions to spectra...
  - hyperfine interactions
  - superhyperfine interactions
  - *due to* coupling of e^- spin with other angular momenta in molecule (*vide infra*)



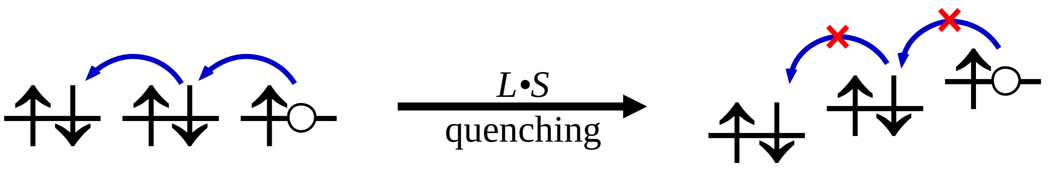
- EPR of Radical Species with large Spin-Orbit Coupling
  - broader signals
  - larger deviations from *g* = 2
  - *next*: we look at TM complexes and the origin of *g*-shifts in these systems

LFT of g values (where do g-shifts come from?)

- orbital angular momentum results from ability to rotate degenerate orbitals into each other, e.g. 2*p* orbitals (*L* = 1)

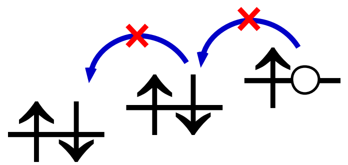


- but *orbital angular momentum* (*L*) is usually quenched by low symmetry
- interactions will lift degeneracy and quench *L*•*S*
  - direct overlap with orbitals from other atoms (covalent)
  - indirect electrostatic interactions (ionic)

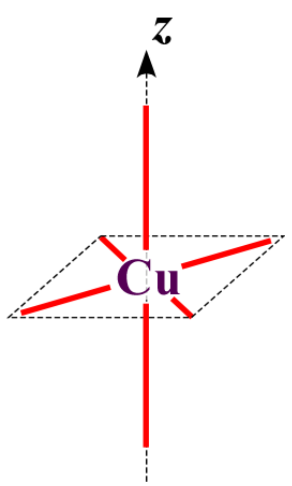


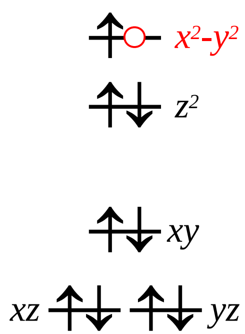
Spin-Orbit Coupling through Electronic Excited States

- although SOC is not directly possible
  - some interaction with electronic excited states
  - can get *symmetry allowed spin-orbit mixing*
  - mixing of other orbital components into ground state wavefunction

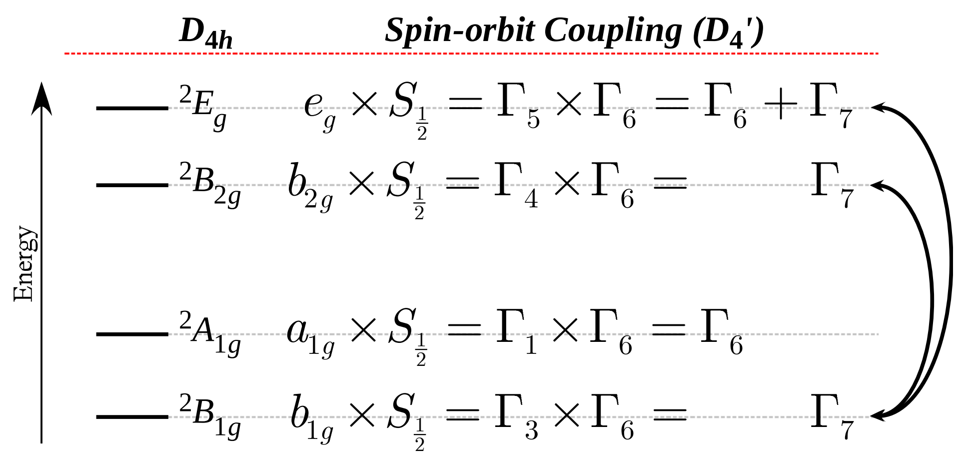


- *e.g.*, elongated 6-coordinate D_{4h} Cu^{II} ($3d^9$) complex





MO diagram



state diagram

no longer a pure $^2B_{1g}$ spin state!

2.2 Electron Paramagnetic Resonance

- must use symmetry of spin-orbit wavefunctions
  - product of orbital symmetry with spin symmetry $\Psi_{GS} = \psi_{orbital} \cdot \psi_{electron}$

- augment point group to include this – *double group* rep
  - add a new symmetry operation that accounts for spin symmetry $\rightarrow$ $\bar{E} \equiv R \Rightarrow \text{do nothing except flip the spin...}$
  - this effectively "doubles" the size of the point group
  - every irrep (called a *spinor*) is doubly-degenerate (includes spin symmetry)
  - spin flip is always represented by *E*' spinor (first additional spinor)

- *e.g.* $D_{4h} \rightarrow D_4 + S \rightarrow D_4'$
  - only need to use rotational subgroup to include spin-orbit effects

- *e.g.* $D_{4h} \rightarrow D_4 + S \rightarrow D_4'$ (only need to use rotational subgroup)

D_{4h}	D_4	D_4'	E	R	$2C_{2(z)}$	$2C_2R$	$2C_{4(z)}$	$2C_4R$	$4C_2','' $	$4C_2','' R$	
A_{1g}	A_1	Γ_1	+1	-1	+1	+1	+1	+1	+1	+1	x^2+y^2, z^2
A_{2g}	A_2	Γ_2	+1	-1	+1	+1	+1	+1	-1	-1	z, R_z
B_{1g}	B_1	Γ_3	+1	-1	+1	+1	-1	+1	+1	-1	x^2-y^2
B_{2g}	B_2	Γ_4	+1	-1	+1	+1	-1	+1	-1	+1	xy
E_g	E	Γ_5	+2	-2	-2	-2	0	0	0	0	(x,y), (R_x, R_y), (xz, yz)
	E'	Γ_6	+2	-2	0	0	$+\sqrt{2}$	$-\sqrt{2}$	0	0	$\boldsymbol{S}$
	E''	Γ_7	+2	-2	0	0	$-\sqrt{2}$	$+\sqrt{2}$	0	0	

Effect of Excited State Spin-Orbit Coupling on g-values

$$\lambda_{GS} = \frac{\pm\zeta}{2S}$$

- ground state wavefunction is now a mixture of orbital configurations due to spin-orbit coupling:
  - complete wavefunction should include contributions from all possible excited states!
  - we know from GT that only two LF states will contribute: $|xy\rangle \,\&\, |xz,yz\rangle$
  - use ***perturbation theory*** to determine contribution from each excited state to the ground state →

    $$\text{effect of E on G} \sim \frac{k\left\langle E\middle|\hat{O}\middle|G\right\rangle}{\Delta E_{GE}}|E\rangle$$

    - thus we get...

$$\left|{}^2B_{1g}\right\rangle = \left|x^2-y^2\right\rangle + \frac{\lambda\left\langle xy\middle|\vec{L}\cdot\vec{S}\middle|x^2-y^2\right\rangle}{E_{x^2-y^2}-E_{xy}}|xy\rangle + \frac{\lambda\left\langle xz,yz\middle|\vec{L}\cdot\vec{S}\middle|x^2-y^2\right\rangle}{E_{x^2-y^2}-E_{xz,yz}}|xz,yz\rangle$$

- apply field **and** turn on Zeeman splitting...
  - $$E_{Zeeman} = \beta\vec{B}\cdot\left\langle {}^2B_{1g}\middle|\vec{L}+2\vec{S}\middle|{}^2B_{1g}\right\rangle = g\beta\vec{B}$$

    ($\vec{L}$ ← $\hat{L}_x + \hat{L}_y + \hat{L}_z$)

  - what is symmetry of $L_{x,y,z}$ operators in D_{4h} ?

New Hamiltonian Operator for Zeeman Splitting:

$$H'_{Zeeman} = \beta\vec{B}\cdot\ \vec{L}+2\vec{S}$$

$$O_h\Big|\ \hat{L}_x,\hat{L}_y,\hat{L}_z \equiv R_x,R_y,R_z \equiv t_{1g} \rightarrow D_{4h}\Big|\ \begin{matrix}\hat{L}_z \equiv R_z \equiv a_{2g} \\ \hat{L}_x,\hat{L}_y \equiv R_x,R_y \equiv e_g\end{matrix}$$

anisotropic!

Look at effect of excited state SOC for H || z

- for *H* || *z* $\rightarrow$ evaluate L_z term only $\lambda\ \vec{L}\cdot\vec{S}\ = \lambda\ \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z\ = \lambda\hat{L}_z\hat{S}_z$
- use group theory to determine what *L* terms will be non-zero:
  - what will give us $\left\langle \Gamma_i \middle| \hat{L}_z \middle| x^2-y^2 \right\rangle \neq 0$ in D_{4h} symmetry? $\left.\begin{matrix}\Gamma_i \times a_{2g} \times b_{1g} \equiv a_{1g} \\ \Gamma_i \times b_{2g} \equiv a_{1g}\end{matrix}\right| \Gamma_i = b_{2g}$
  - along the *z*-axis, only B_{2g} excited states will contribute to *g*-value

$$\left|{}^2B_{1g}\right\rangle = \left|x^2-y^2\right\rangle + \underbrace{\frac{\lambda\left\langle xy\middle|\vec{L}\cdot\vec{S}\middle|x^2-y^2\right\rangle}{E_{x^2-y^2}-E_{xy}}}_{\text{only need to evaluate this term!}}\left|xy\right\rangle + \frac{\lambda\left\langle xz,yz\middle|\vec{L}\cdot\vec{S}\middle|x^2-y^2\right\rangle}{E_{x^2-y^2}-E_{xz,yz}}\left|xz,yz\right\rangle \rightarrow 0$$

- we can now evaluate the true nature of Ψ_{GS} with SOC for *H* || *z*

$$\boxed{\left|{}^2B_{1g}\right\rangle = \left|x^2-y^2,\ \pm\tfrac{1}{2}\ \right\rangle + \frac{\lambda\ +2i\ \ M_S}{E_{x^2-y^2}-E_{xy}}\left|xy,\ \pm\tfrac{1}{2}\ \right\rangle}$$

2.2 Electron Paramagnetic Resonance

- here's the complete evaluation of the GS wavefunction...

$$\left|{}^2B_{1g}\right\rangle = \left|\overset{orbital}{B_{1g}}\;;\overset{spin}{\alpha,\beta}\right\rangle$$ → *wavefunction has either α or β spin*

$$= \left|x^2-y^2;\alpha,\beta\right\rangle + \frac{\lambda\left\langle xy;\alpha,\beta\left|\hat{L}\cdot\hat{S}\right|x^2-y^2;\alpha,\beta\right\rangle}{E_{x^2-y^2}-E_{xy}}\left|xy;\alpha,\beta\right\rangle$$

evaluate along z-direction

$$\lambda\;\vec{L}\cdot\vec{S} = \lambda\;\hat{L}_x\hat{S}_x+\hat{L}_y\hat{S}_y+\hat{L}_z\hat{S}_z = \lambda\hat{L}_z\hat{S}_z$$

$$= \left|x^2-y^2;\alpha,\beta\right\rangle + \frac{\lambda\left\langle xy;\alpha,\beta\left|\hat{L}_z\hat{S}_z\right|x^2-y^2;\alpha,\beta\right\rangle}{E_{x^2-y^2}-E_{xy}}\left|xy;\alpha,\beta\right\rangle$$

separate integral

$\hat{L}_z \mapsto$ orbital function only

$\hat{S}_z \mapsto$ spin function only

$$= \left|x^2-y^2;\alpha,\beta\right\rangle + \frac{\lambda\left\langle xy\left|\hat{L}_z\right|x^2-y^2\right\rangle\left\langle\alpha,\beta\left|\hat{S}_z\right|\alpha,\beta\right\rangle}{E_{x^2-y^2}-E_{xy}}\left|xy;\alpha,\beta\right\rangle$$

evaluate integrals

$$= \left|x^2-y^2;\alpha,\beta\right\rangle + \frac{\lambda\left\langle xy\right|+2i\left|xy\right\rangle M_S}{E_{x^2-y^2}-E_{xy}}\left|xy;\alpha,\beta\right\rangle$$

$$= \left|x^2-y^2;\alpha,\beta\right\rangle + \frac{2\lambda i M_S}{E_{x^2-y^2}-E_{xy}}\left|xy;\alpha,\beta\right\rangle$$

$$\left.\begin{aligned}\left\langle\alpha\left|\hat{S}_z\right|\alpha\right\rangle &= +\tfrac{1}{2}\langle\alpha|\alpha\rangle\\ \left\langle\beta\left|\hat{S}_z\right|\beta\right\rangle &= -\tfrac{1}{2}\langle\beta|\beta\rangle\end{aligned}\right| = M_S$$

excited state must have same spin as ground state

$$\hat{L}_z\left|d_{x^2-y^2}\right\rangle = 2i\left|d_{xy}\right\rangle$$

2.2 Electron Paramagnetic Resonance

- what happens to each of the d orbitals under the $L_{x,y,z}$ operators...

$$\hat{L}_x\left|d_{xz}\right\rangle = -i\left|d_{xy}\right\rangle \qquad \hat{L}_y\left|d_{xz}\right\rangle = i\left|d_{x^2-y^2}\right\rangle - \sqrt{3}i\left|d_{z^2}\right\rangle \qquad \hat{L}_z\left|d_{xz}\right\rangle = i\left|d_{yz}\right\rangle$$

$$\hat{L}_x\left|d_{yz}\right\rangle = \sqrt{3}i\left|d_{z^2}\right\rangle + i\left|d_{x^2-y^2}\right\rangle \qquad \hat{L}_y\left|d_{yz}\right\rangle = i\left|d_{xy}\right\rangle \qquad \hat{L}_z\left|d_{yz}\right\rangle = -i\left|d_{xz}\right\rangle$$

$$\hat{L}_x\left|d_{xy}\right\rangle = -i\left|d_{xz}\right\rangle \qquad \hat{L}_y\left|d_{xy}\right\rangle = -i\left|d_{yz}\right\rangle \qquad \hat{L}_z\left|d_{xy}\right\rangle = -2i\left|d_{x^2-y^2}\right\rangle$$

$$\hat{L}_x\left|d_{x^2-y^2}\right\rangle = -i\left|d_{yz}\right\rangle \qquad \hat{L}_y\left|d_{x^2-y^2}\right\rangle = -i\left|d_{xz}\right\rangle \qquad \hat{L}_z\left|d_{x^2-y^2}\right\rangle = 2i\left|d_{xy}\right\rangle$$

$$\hat{L}_x\left|d_{z^2}\right\rangle = -\sqrt{3}i\left|d_{yz}\right\rangle \qquad \hat{L}_y\left|d_{z^2}\right\rangle = \sqrt{3}i\left|d_{xz}\right\rangle \qquad \hat{L}_z\left|d_{z^2}\right\rangle = 0$$

2.2 Electron Paramagnetic Resonance

- can now get Zeeman energy $\rightarrow$ $E_{Zeeman} = \beta \vec{H}_z \left\langle {}^2B_{1g}, \pm\tfrac{1}{2} \left| \vec{L}_z + 2\vec{S}_z \right| {}^2B_{1g}, \pm\tfrac{1}{2} \right\rangle$

where $\left| {}^2B_{1g} \right\rangle = \left| x^2 - y^2, \pm\tfrac{1}{2} \right\rangle + \dfrac{\lambda \ {+2i} \ M_S}{E_{x^2-y^2} - E_{xy}} \left| xy, \pm\tfrac{1}{2} \right\rangle$

$$E_{Zeeman} = \beta \vec{H}_z \left\langle x^2 - y^2, \pm\tfrac{1}{2} \left| \vec{L}_z^{\,\nearrow 0} + 2\vec{S}_z \right| x^2 - y^2, \pm\tfrac{1}{2} \right\rangle \rightarrow 2\beta \vec{H}_z M_S$$

$$+ 2\beta \vec{H}_z \left(\frac{\lambda \ 2i \ M_S}{E_{x^2-y^2} - E_{xy}} \right) \left\langle xy, \pm\tfrac{1}{2} \left| \vec{L}_z \, (+2i) + 2\vec{S}_z^{\,\nearrow 0} \right| x^2 - y^2, \pm\tfrac{1}{2} \right\rangle \rightarrow \left(\frac{8\lambda}{E_{x^2-y^2} - E_{xy}} \right) \beta \vec{H}_z M_S$$

$$+ \text{ very small term in } \left(\frac{\lambda}{E_{x^2-y^2} - E_{xy}} \right)^2 \rightarrow \textit{ignore}$$

$$E_{Zeeman}\left(\vec{H} \parallel z\right) = \left(2 + \frac{8\lambda}{E_{x^2-y^2} - E_{xy}} \right) \beta \vec{H} M_S$$

$$\boxed{g_{\parallel} = 2 + \frac{8\lambda}{E_{x^2-y^2} - E_{xy}}}$$

What about for magnetic field along x,y direction?

- symmetry of $L_{x,y}$ is e_g in D_{4h} such that $\left\langle \Gamma_i \middle| \hat{L}_{x,y} \middle| x^2 - y^2 \right\rangle \neq 0$

- only contributions from E_g states

$$\left. \begin{array}{r} b_{1g} \times e_g \times \Gamma_i \equiv a_{1g} \\ e_g \times \Gamma_i \equiv a_{1g} \end{array} \right| \quad \Gamma_i = e_g$$

- Zeeman operator simplifies to

$$\lambda \ \vec{L} \cdot \vec{S} = \lambda \ \hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z = \lambda \ \hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y$$

- after evaluation, we find that

$$\boxed{g_\perp = 2 + \frac{2\lambda}{E_{x^2-y^2} - E_{xz,yz}}}$$

General expression for g-values of S=1/2 systems

- obtained from perturbation theory

$$g_i = 2\left(1 - k^2 \lambda \sum_{n \neq 0} \frac{\langle \psi_0 | L_i | \psi_n \rangle \langle \psi_n | L_i | \psi_0 \rangle}{E_n - E_0}\right)$$

due to Zeeman effect

due to Spin-Orbit Coupling with Excited States

$k =$ Steven's orbital reduction factor

$\lambda = \pm\zeta / 2S =$ spin-orbit coupling term

$\psi_0 =$ ground state wavefunction (energy E_0)

$\psi_n =$ excited state wavefunction (energy E_n)

$\hat{L}_i =$ orbital angular momentum operator ($i = x, y, z$)

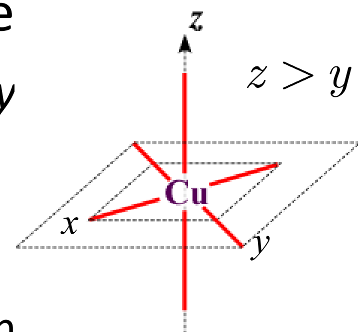
Dependence of g values on geometry

depends on whether system involves electrons (+) or holes (-)

- for elongated D_{4h} Cu^{II} complex $\Rightarrow -\zeta_{\mathrm{Cu}\,3d} = -830 cm^{-1}$

$$\Delta E = \text{positive} \qquad g_{\parallel} > g_{\perp} > 2.0$$

- what happens if symmetry is lowere
  - *e.g.*, $D_{4h} \rightarrow D_{2h}$ (elongation along the *y*
    - symmetry is now *rhombic*
    - SOC different along *x,y*
    - *xz,yz* orbitals split
    - z^2 and x^2-y^2 have same symmetry (can ...x,



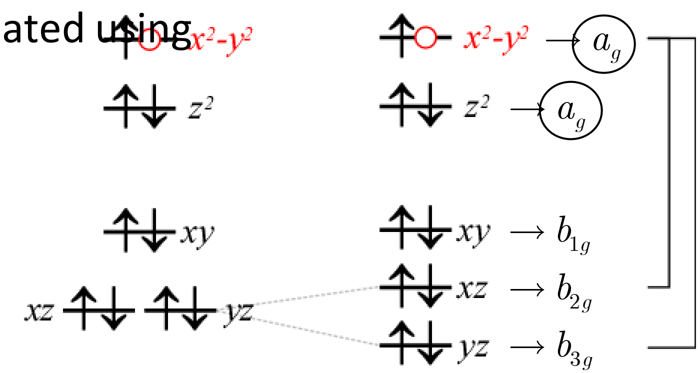
$$z > y > x$$

$$D_{4h} \rightarrow D_{2h}$$

$$\underbrace{L_x, L_y}_{e_g} \rightarrow \underbrace{L_x}_{b_{2g}} \neq \underbrace{L_y}_{b_{3g}}$$

$$|\psi_{GS}\rangle = a|x^2 - y^2\rangle - b|z^2\rangle \text{ where } a^2 + b^2 = 1 \text{ and } a \gg b$$

- $g_{x,y}$ are therefore different and can be calculated using the formalisms developed earlier...
  - but must evaluate for contributions to both x^2-y^2 and z^2 components
  - thankfully, not too difficult...

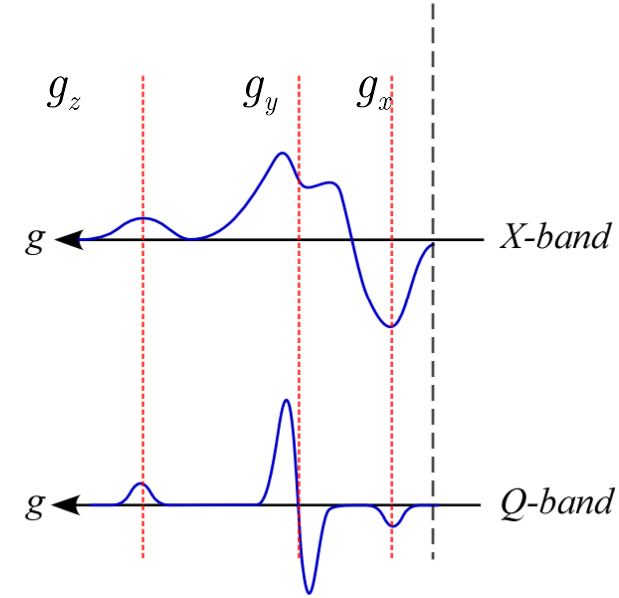


D_{2h} Cu^{II} Complex – Rhombic EPR Spectrum

$$g_x = 2 + \frac{2\lambda\left(a - \sqrt{3}b\right)^2}{E_{x^2-y^2} - E_{yz}}$$

$$g_y = 2 + \frac{2\lambda\left(a + \sqrt{3}b\right)^2}{E_{x^2-y^2} - E_{xz}}$$

$$\rightarrow \boxed{g_x < g_y}$$



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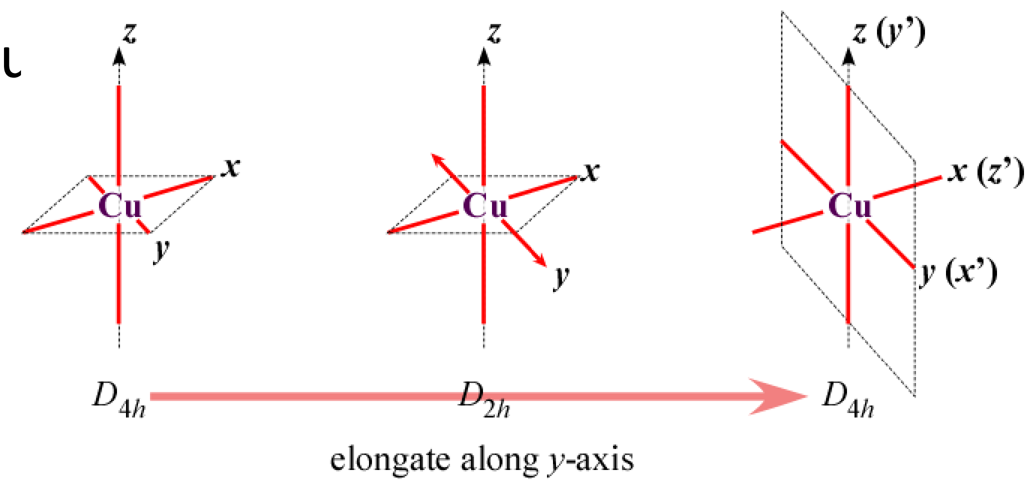
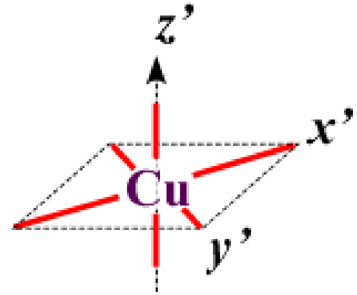


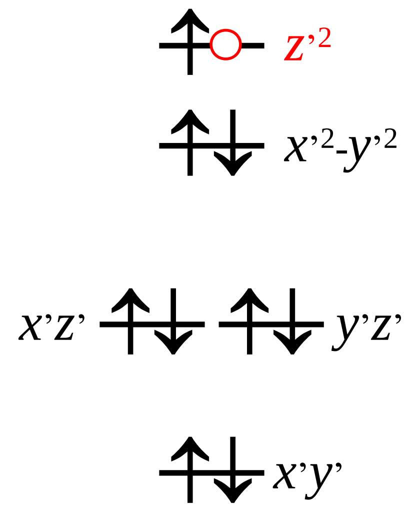
will get back to D_{4h}
(compressed z'-axis)

Compressed D_{4h} Cu^{II} Complex – Another Axial EPR Spectrum

- axes have been redefined... $^2A_{1g}$
- ground state is different →
  - need new equations for A_{1g}
  - use general expression

$$g_i = 2\left[1 - k^2\lambda \sum_{n\neq 0} \frac{\langle\psi_0|L_i|\psi_n\rangle\langle\psi_n|L_i|\psi_0\rangle}{E_n - E_0}\right]$$

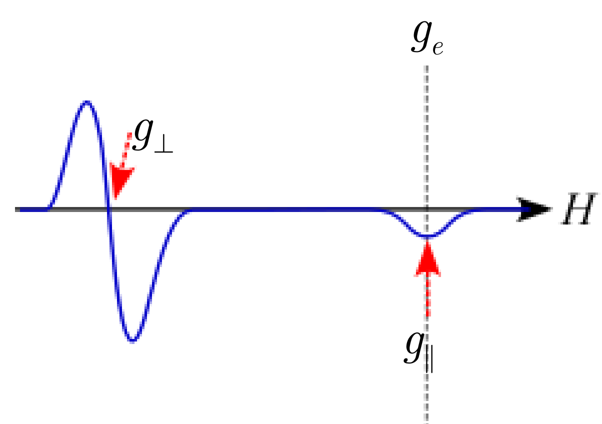




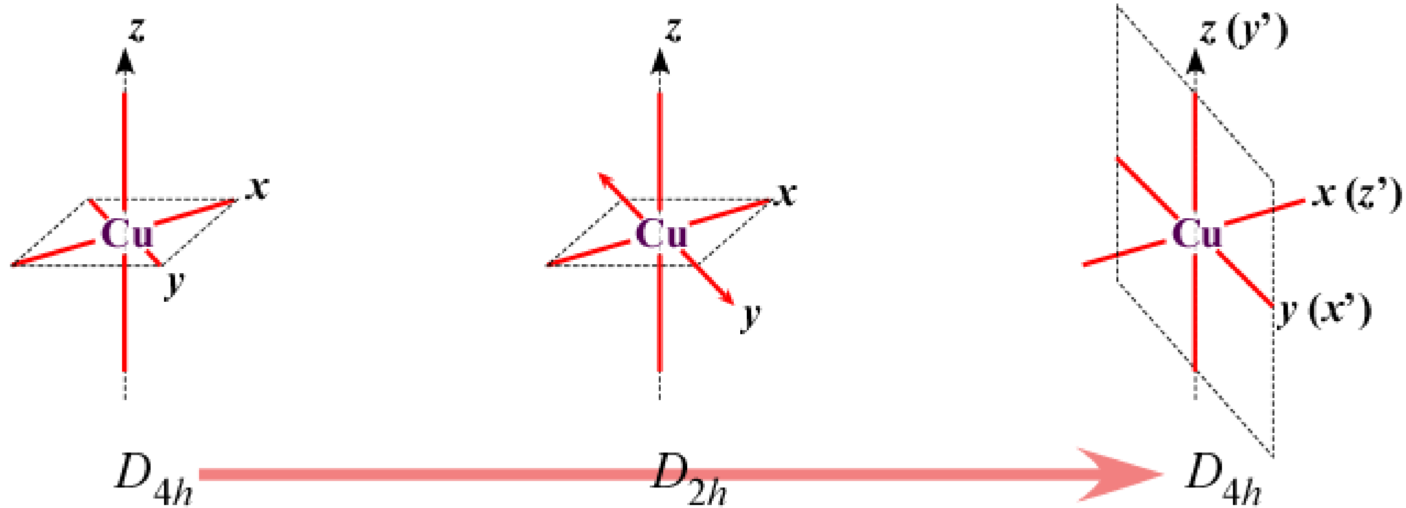
to obtain the following

$$g_\parallel = 2$$

$$g_\perp = 2 + \frac{6\lambda}{E_{z'^2} - E_{x'z',y'z'}} \rightarrow \boxed{g_\perp > g_\parallel}$$

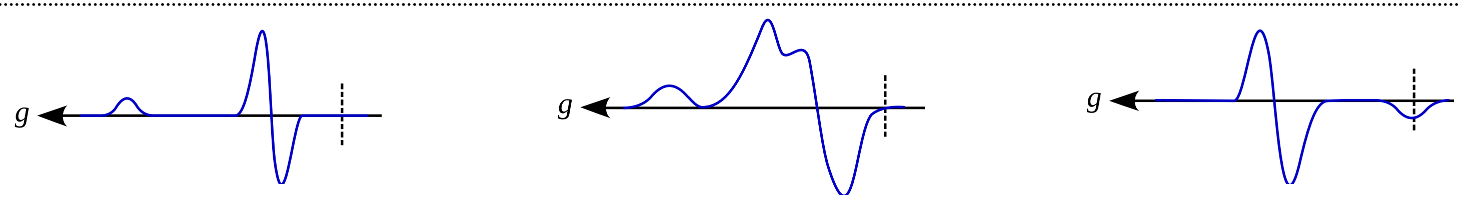


EPR is very sensitive to geometry...



axes	$x = y < z$	$x < y < z$	$x < y = z \mid z' < x' = y'$
ψ_{GS}	$\lvert 3d_{x^2-y^2}\rangle$	$a\lvert 3d_{x^2-y^2}\rangle - b\lvert 3d_{z^2}\rangle$	$\lvert 3d_{z'^2}\rangle = 0.866\lvert 3d_{x^2-y^2}\rangle - 0.500\lvert 3d_{z^2}\rangle$ (75%, 25%)
g	$g_{\parallel} > g_{\perp} > 2.00$	$g_z > g_y > g_x > 2.00$	$g_{\perp} > g_{\parallel} = 2.00$

spectra



Effect of electron delocalization and covalency on g values

- thus far, effect of ligands has been limited to changing *energy* of the magnetic orbitals
  - qualitatively → gives reasonable description of *g*-values
  - quantitatively → not very good
    - look at D_{4h} $[CuCl_4]^{2-}$ ($^2B_{1g}$ ground state) → Δg too large

	LFT Calc	Exp
$g_\parallel$	2.743	2.221
$g_\perp$	2.117	2.040

- LFT predicts too much orbital angular momentum
  - assumes pure 3*d* orbitals (no covalency)
  - ligand orbitals normally don't carry any orbital angular momentum
  - delocalization onto ligand orbitals will thus decrease the effective SOC contribution

$\hat{L} \to k\hat{L}$ where $k < 1$

$k_\parallel < k_\perp$ and $k_{av} \sim 0.57$

$$g_\parallel = 2 + \frac{8\lambda k^2}{E_{x^2-y^2} - E_{xy}}$$

$$g_\perp = 2 + \frac{2\lambda k^2}{E_{x^2-y^2} - E_{xz,yz}}$$

- use Steven's orbital reduction factor (*k*)
  - modified equations for *g* values
  - fit to match exp →

Using theoretical methods to obtain g values

- LFT approach still doesn't account for
  - anisotropic electron delocalization (anisotropic covalency)
  - ligand orbital angular momentum
  - ligand spin-orbit coupling
  - charge transfer mixing into ground state from bonding MOs
- in the end – complete MO model has many more parameters than observables
  - need approaches to calculating *g*-values from first principles
- Density Functional (DFT) methods are most often used
  - extremely good accuracy for radical species with small SOC
  - good results for TM systems involving *S* = ½
- experimental *g* values provide an effective approach to testing

Hyperfine Coupling in EPR

- coupling of *spin angular momentum* with *nuclear spin* of metal ion

$$H'_{hyperfine} = A\hat{S}\cdot\hat{I}$$

- new terms in spin Hamiltonian

$$H' = \lambda\hat{L}\cdot\hat{S} + \underbrace{\beta B_0\cdot(\hat{L}+2\hat{S})}_{\text{Zeeman splitting}} + \underbrace{A\hat{S}\cdot\hat{I}}_{\text{Hyperfine coupling}} + \underbrace{\beta_N B_0\cdot\hat{I}}_{\text{nuclear Zeeman}}$$

spin-orbit coupling

- generally use a strong magnetic field to ensure that

$$H'_{Zeeman} \gg H'_{hyperfine}$$

- *A*-tensor can also be anisotropic → depends on orientation relative to magnetic field

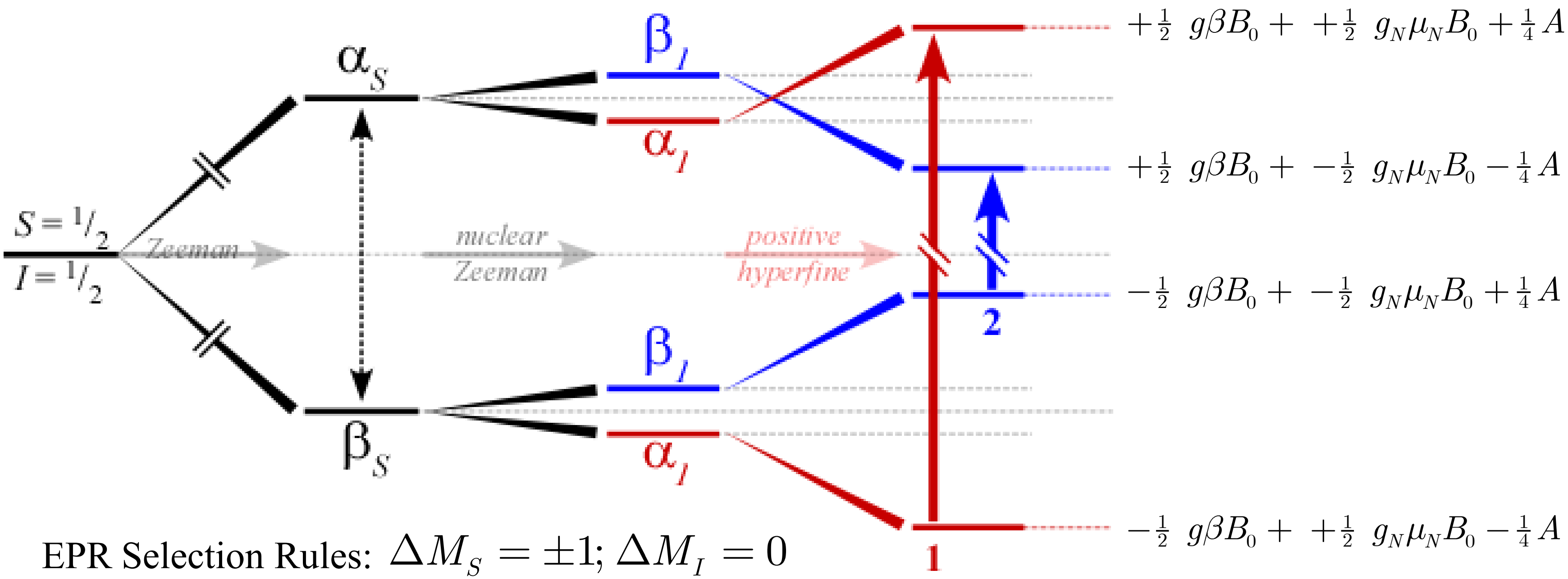
$$H'_{hf} = A_z\hat{S}_z\hat{I}_z + A_x\hat{S}_x\hat{I}_x + A_y\hat{S}_y\hat{I}_y$$

- for axial system:

$$H'_{hf} = A_{\parallel}\hat{S}_z\hat{I}_z + A_{\perp}\ \hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y$$

$$H'_{hf\ z} = A_z m_S m_I$$

Effect of Hyperfine Coupling in High Magnetic Field Limit



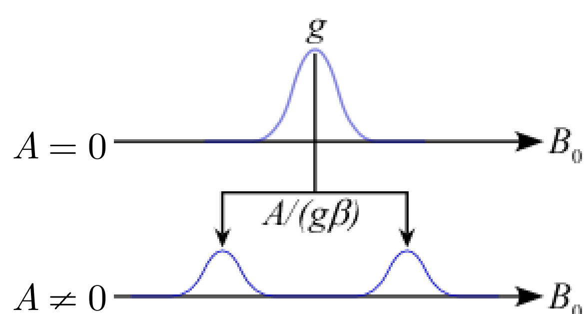
EPR Selection Rules: $\Delta M_S = \pm 1; \Delta M_I = 0$

$$\Delta E_1 = g\beta B_0 + \tfrac{1}{2} A_{SI}$$

$$\Delta E_2 = g\beta B_0 - \tfrac{1}{2} A_{SI}$$

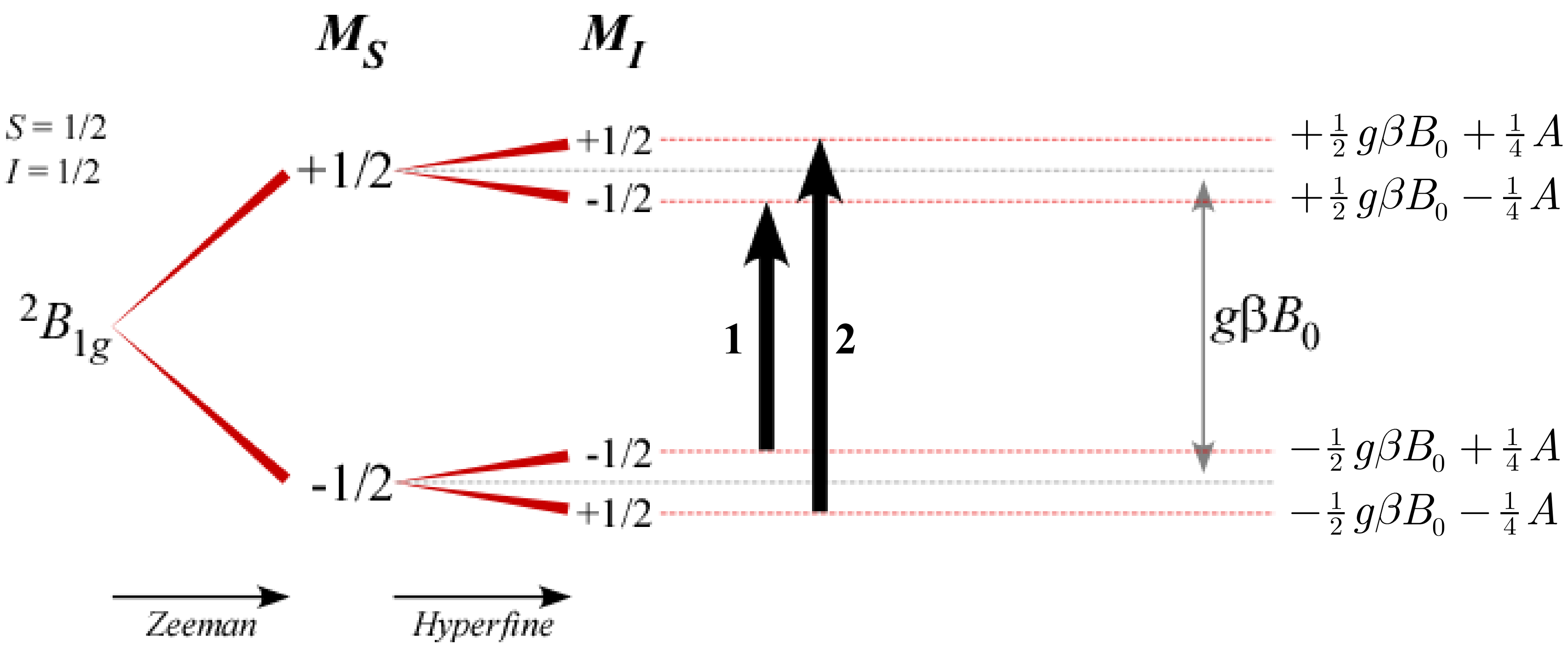
$$\Delta\Delta E_{12} = A_{SI}$$

in terms of g-values $\rightarrow \boxed{A_{SI}/\beta B_0}$



2.2 Electron Paramagnetic Resonance

- Energy diagram for EPR hyperfine coupling is often simplified
  - nuclear Zeeman is so tiny that you ignore it... (eZ >> A >> nZ)
  - it doesn't contribute to the EPR energy splittings (1,2) anyways



Effect of Hyperfine Coupling in a small Magnetic Field

- $A\hat{S}\cdot\hat{I}$ term does not require a magnetic field
  - coupling still occurs when B_0 = 0 → coupling occurs even without a magnetic field!

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

  - just like scalar coupling

$$E_F = \frac{1}{2} A \left[F(F+1) - S(S+1) - I(I+1) \right]$$

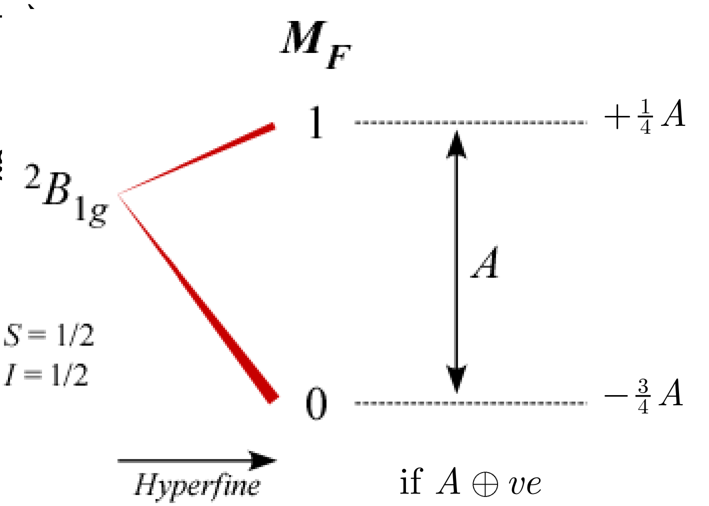
    - new angular momentum quantum number (F) →

$$M_F = F, F-1, \ldots -F$$

    - energies of states depend on I, S, and F
    - each F angular momentum state has de

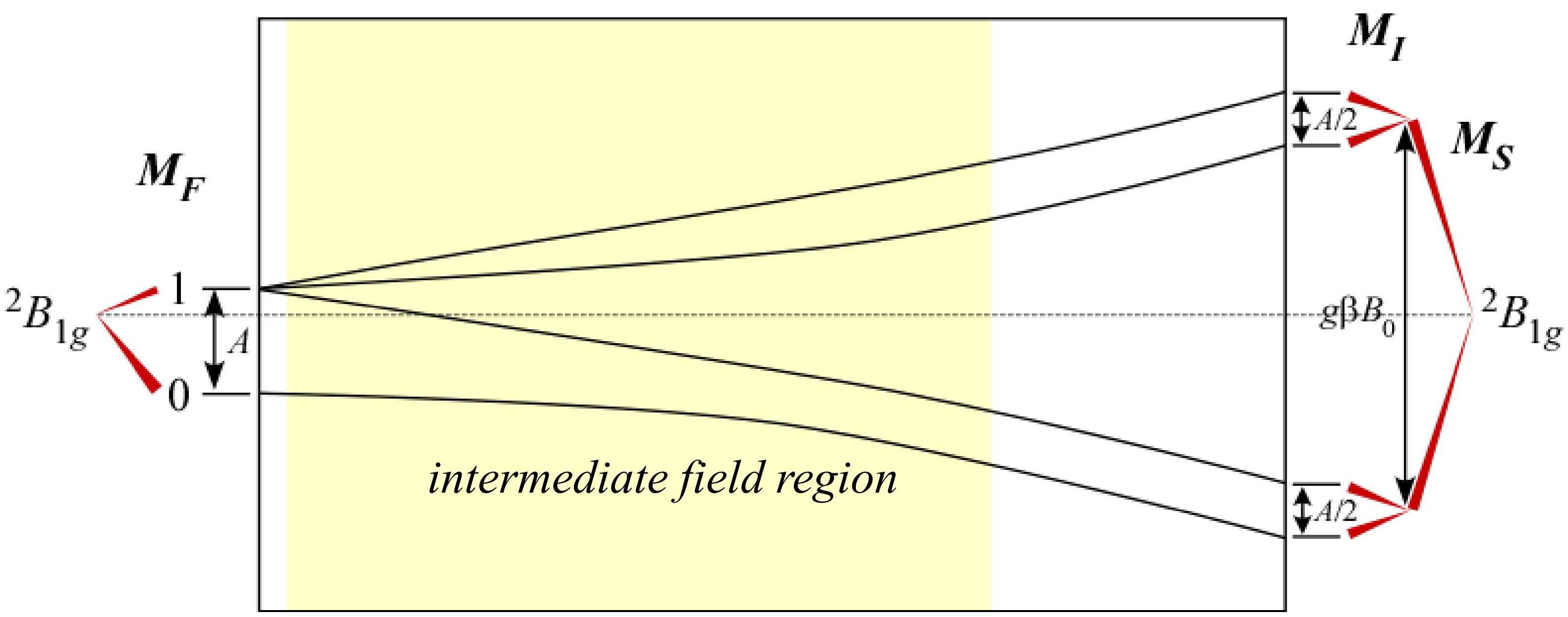
$$S = \frac{1}{2}, I = \frac{1}{2} \quad \left| \begin{array}{ll} F = 1 & E_1 = +\frac{1}{4}A \\ F = 0 & E_0 = -\frac{3}{4}A \end{array} \right.$$

- *e.g.*



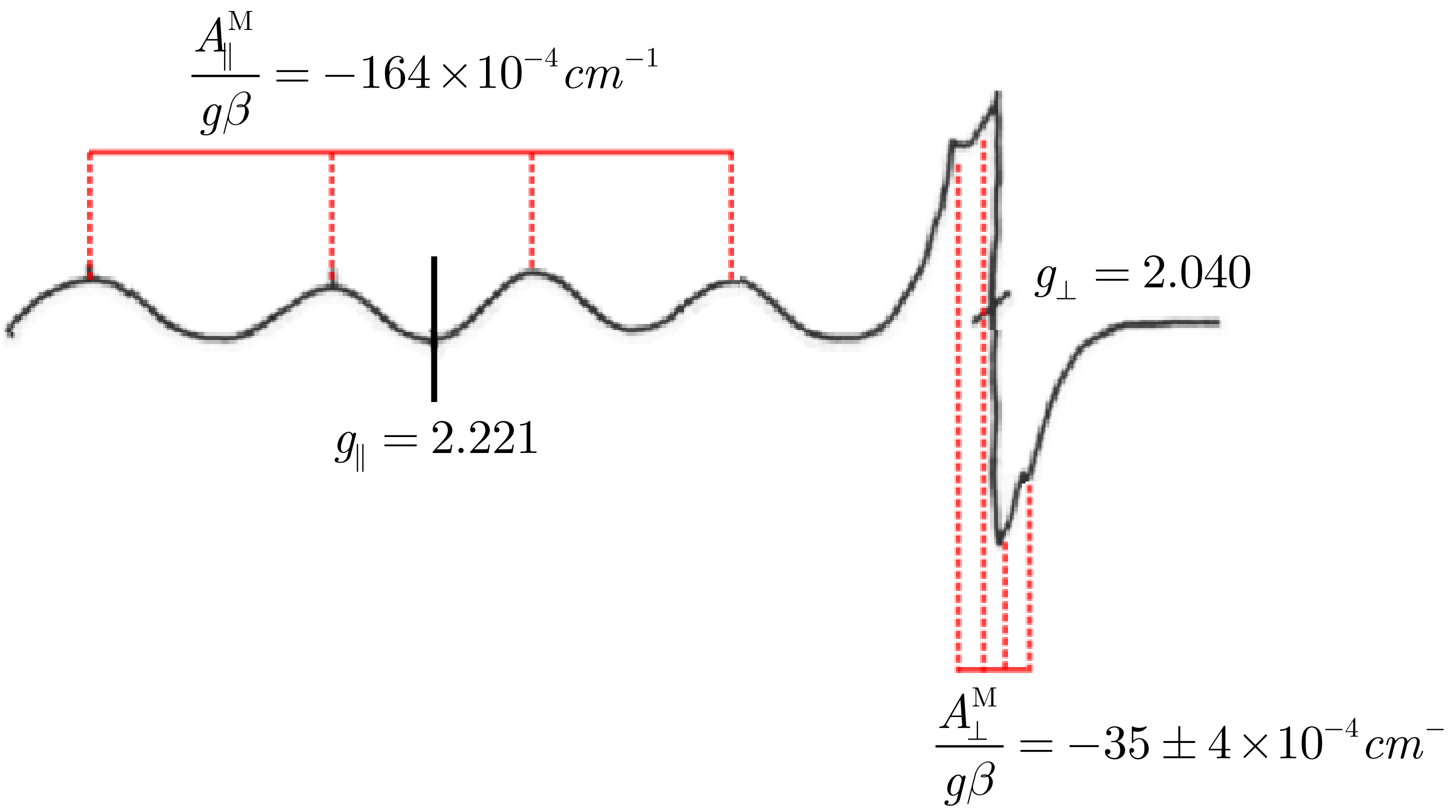
Hyperfine Splitting Correlation Diagram (Briet-Rabi Diagram)

- in each limit the correct QN for the states is different



Example of Metal Hyperfine Interactions

- D_{4h} $[CuCl_4]^{2-}$ ($3d^9$) $S=\frac{1}{2}, I=\frac{3}{2} \quad \rightarrow \quad 2nI+1=2\ 1\left(\frac{3}{2}\right)+1=4$ hyperfine lines



Ligand Field Contributions to Metal Hyperfine Coupling

- *Fermi Contact (Scalar Coupling)*
  - direct overlap of electronic wavefunction with atomic nucleus
  - proportional to contributing magnetogyric ratios
  - can only directly occur with *s*-type orbitals
  - can contribute indirectly through spin polarization of core *s*-electrons

$$A^{Fermi} = \frac{8\pi}{3} g_e \beta_e g_n \beta_n \left|\Psi_g^{r=0}\right|^2$$

- *Spin (or Direct) Dipolar Coupling*
  - through space interaction of two dipoles
  - strong dependence on average r_{eN}
  - depends on orientation of orbital and B_0
  - generally averages to zero in solution but can be anisotropic

$$A^{SD} = \underbrace{\frac{g_e \beta_e g_n \beta_n}{\left\langle r^3 \right\rangle_{3d}}}_{Pd} \left\langle 3\cos^2\alpha - 1 \right\rangle_{3d} \quad 3\cos^2\theta - 1$$

energy contribution $\propto r^{-3}$

relaxation contribution $\propto \left(r^{-3}\right)^2 = \boxed{r^{-6}}$

- *Orbital (or Indirect) Dipolar Coupling*
  - coupling of nuclear spin with orbital angular momentum → $\hat{A}^{OD} = Pd\hat{L} \cdot \hat{I}$
  - very comparable to spin-orbit contributions
    - difficult to calculate → must include excited state contributions
    - directly related to experimental *g*-values
    - includes both isotropic and anisotropic contributions..
  - often called *Pseudo Contact Term*

$$A_{\parallel}^{OD} = Pd\Delta g_{\parallel}$$

$$A_{\perp}^{OD} = Pd\Delta g_{\perp}$$

$$A_{ave}^{OD} = \frac{A_{\parallel} + 2A_{\perp}}{3} = Pd\left[\frac{\Delta g_{\parallel} + 2\Delta g_{\perp}}{3}\right] \neq 0$$

Effect of Metal-Ligand Covalency on Hyperfine Coupling

- just as with effect on *g*-values... must introduce correction because $\psi_{GS} \neq \left|x^2 - y^2\right\rangle \rightarrow \boxed{\psi_{GS} = \alpha\left|x^2 - y^2\right\rangle - \sqrt{1-\alpha^2}\,|L\rangle}$

  for D_{4h} $[CuCl_4]^{2-}$

- ligand contributions to the wavefunction do not contribute significantly to the
  hyperfine coupling term since the ligands are too far from the metal nucleus
  - *Fermi Contact* $\rightarrow$ almost no ligand electron density at metal nucleus
  - *Spin Dipolar* $\rightarrow$ distance is too large (remember: effective $1/r^6$ behaviour)
    $k \sim \alpha^2$
  - *Orbital Dipolar* $\rightarrow$ also highly depends on distance + ligand SOC

Superhyperfine Coupling in EPR

- Actual spectra have even more structure than just *g*-values + hyperfine

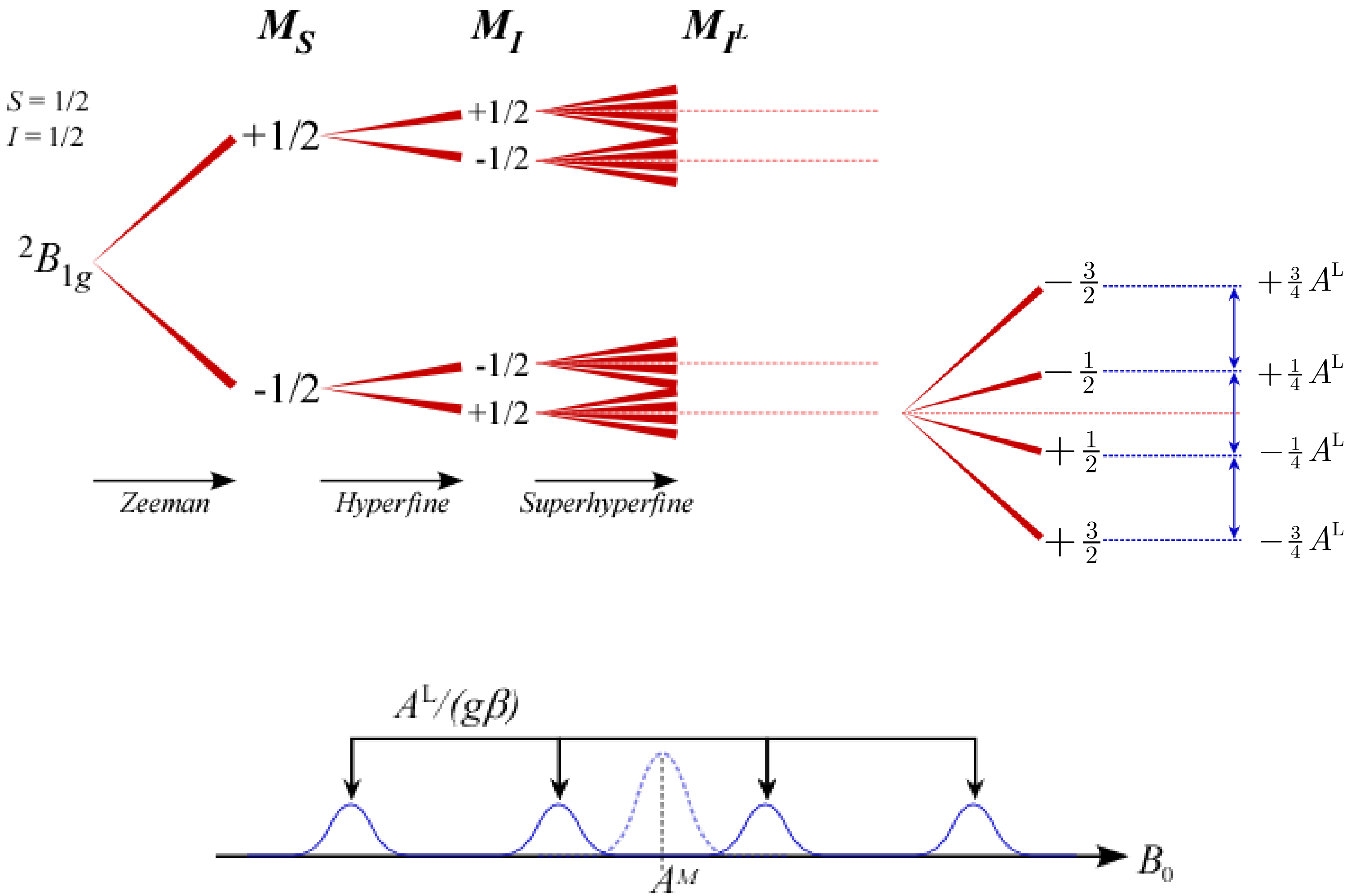
$$H' = \underbrace{\lambda \hat{L}\cdot\hat{S} + \beta B_0\cdot(\hat{L}+2\hat{S})}_{\text{SOC+Zeeman}} + \underbrace{A^{\mathrm{M}}\hat{S}\cdot\hat{I}}_{\text{hyperfine}} + \underbrace{A^{\mathrm{L}}\hat{S}\cdot\hat{I}}_{\text{superhyperfine}}$$

- ligands with nuclear spin can also couple to electron spin → *superhyperfine coupling*

$$\beta B_0\cdot(\hat{L}+2\hat{S}) >> A^{\mathrm{M}}\hat{S}\cdot\hat{I} > A^{\mathrm{L}}\hat{S}\cdot\hat{I}$$

- phenomenon is exactly identical to hyperfine coupling
- usually much smaller than hyperfine
  - delocalization onto ligands is generally small $\dfrac{A^{\mathrm{L}}}{g\beta}$
  - electron doesn't see I^L as much as I^M
  - allows us to treat each effect separately

2.2 Electron Paramagnetic Resonance



Ligand Field Theory of Superhyperfine Coupling

- basically the same as hyperfine coupling (and coupling in NMR!)
- Fermi contact (scalar coupling)

$$\psi_{GS} = \alpha\left|x^2 - y^2\right\rangle - \sqrt{1-\alpha^2}\,|L\rangle$$

$$A^{L-Fermi} \propto \sqrt{1-\alpha^2}$$

  - directly correlates with covalency of M-L bond
  - large if delocalisation over ligands is large
- Spin Dipolar coupling

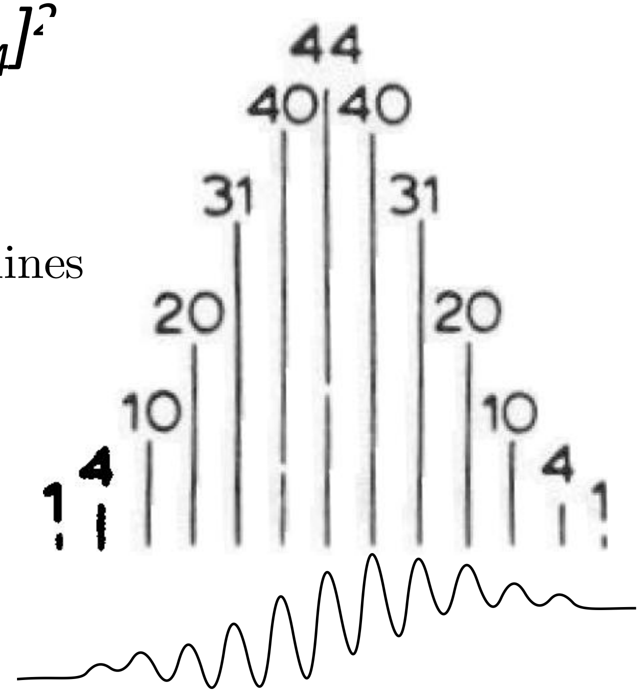
$$A^{L-SD} = g_e\beta_e g_n\beta_n \frac{3\cos^2\theta - 1}{r^3}$$

  - similar to spin dipolar hyperfine interactions
  - does not depend on orbital orientation
  - small and anisotropic
  - does not require metal-ligand overlap (covalency)
- Orbital Dipolar coupling
  - requires strong SOC in ligand orbitals involved in bonding

Superhyperfine Coupling in D_{4h} $[CuCl_4]^{2}$

- 4 equivalent Cl ligands with I^L = 3/2

$$2nI^L + 1 = \left(2\ 4\ \frac{3}{2} + 1\right) = 13 \text{ superhyperfine lines}$$

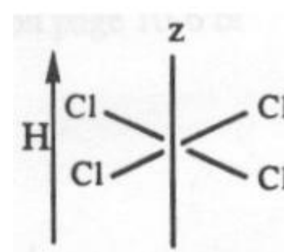


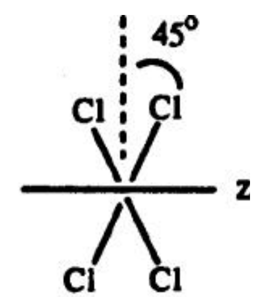
- depends on orientation (anisotropic!)
  - axes used to define A^L are generally chosen along the M-L bond
  - not the same as molecular axes

$$\beta^2 = \sqrt{1-\alpha^2} = 0.36$$

$$\alpha^2 = k = 0.61$$

$$\alpha^2 = k = 0.7$$





- Electron Delocalization →
  - from *g*-values →
  - from A^M →

What do we know from EPR of D_{4h} $[CuCl_4]^{2-}$?

$$\alpha^2 = k = 0.61$$

$$\text{from } g_\parallel \rightarrow \Delta E_{3d_{xy} - 3d_{x^2-y^2}}$$
$$\text{from } g_\perp \rightarrow \Delta E_{3d_{xz,yz} - 3d_{x^2-y^2}}$$

- *from g values:*

$$\alpha^2 = 0.7$$

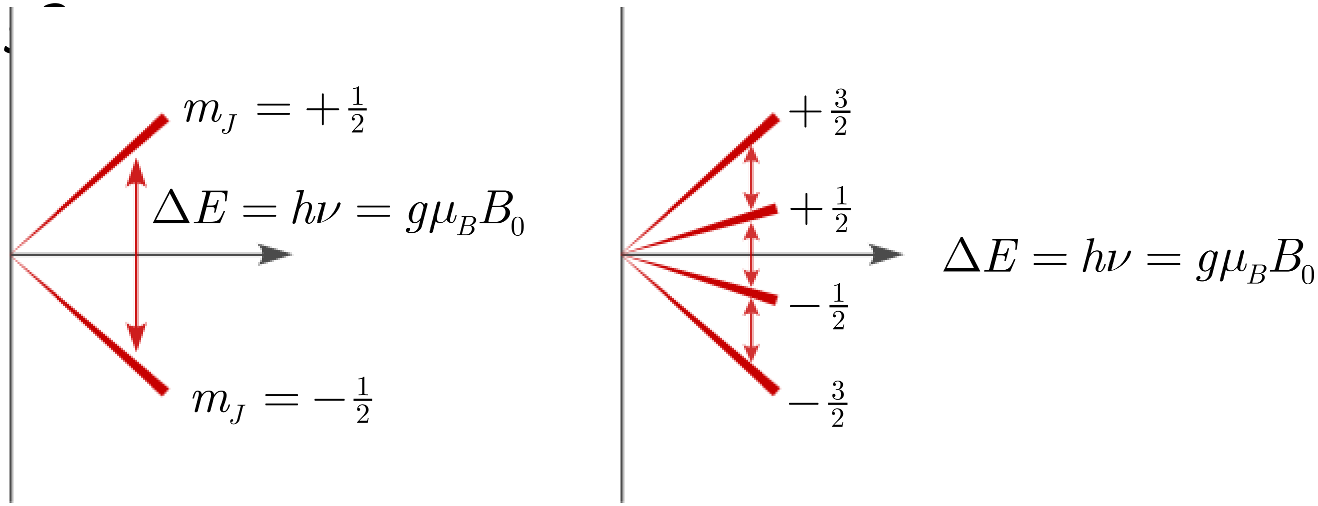
- *from hyperfine coupling:*

$$\beta^2 = 0.36$$

- *from superhyperfine coupling:*

- EPR provides a broad range of information on the ground state of transition metal complexes (and other radical species)

Shouldn't the whole thing be the same for S > 1/2 System



- no obvious reason why things should be different for *S* = 3/2 system...

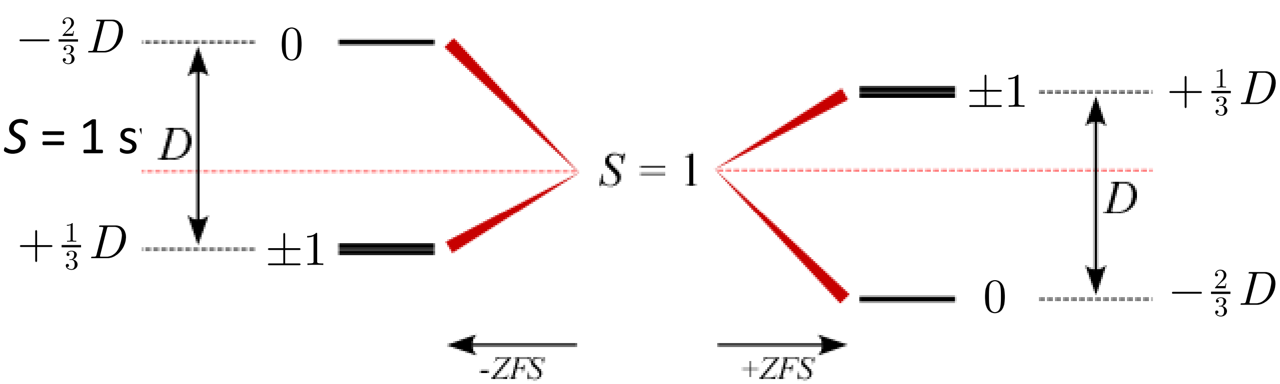
Zero Field Splitting (ZFS) → level splitting in lower symmetry

- splitting of levels in lower than cubic symmetries
  - anything below O_h and/or T_d
- forces us to add a new term in the *effective spin Hamiltonian*

$$\mathcal{H}_{ZFS} = D\left[S_z^2 - \frac{1}{3}S(S+1)\right]$$

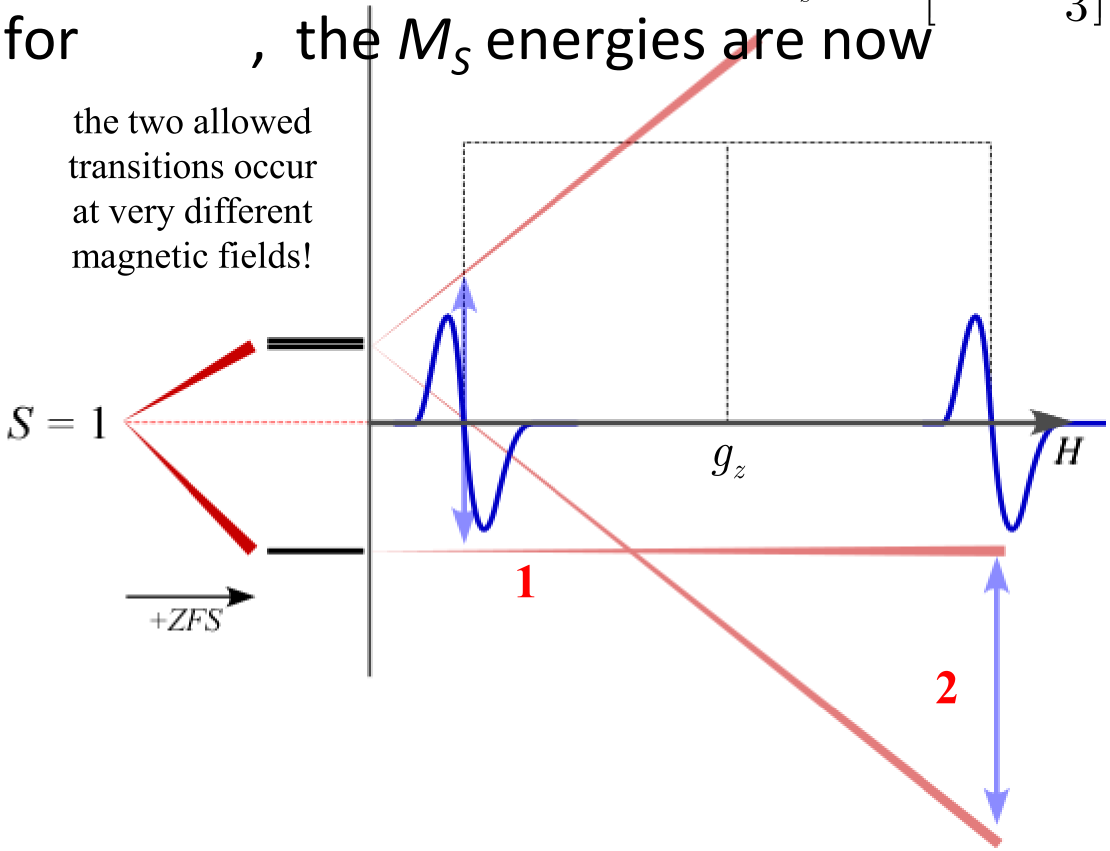
D is the *axial* ZFS parameter

  - for an axial system: $E'_{M_S} = D\left[M_S^2 - \frac{2}{3}\right]$
  - for S = 1 s



Effect of Axial ZFS on Zeeman Splitting and EPR Spectrum

- $$\hat{\mathfrak{H}}' = \hat{\mathfrak{H}}_{ZFS} + \hat{\mathfrak{H}}_{Zeeman} = D\left[S_z^2 - \frac{1}{3}S\ \ S+1\ \right] + \beta\vec{H}\cdot(\hat{L}+2\hat{S})$$
- for $\vec{H} \parallel z$, the M_S energies are now $E'_{M_S} = D\left[M_S^2 - \frac{2}{3}\right] + g_z\beta\vec{H}M_S$



$$E'_{\pm 1} = +\frac{1}{3}D \pm g_z\beta\vec{H}$$
$$E'_0 = -\frac{2}{3}D$$

1 $\quad h\nu = g_z\beta H_1 + D$

2 $\quad h\nu = g_z\beta H_2 - D$

$$H_1 = \frac{h\nu - D}{g_z\beta}$$
$$H_2 = \frac{h\nu + D}{g_z\beta}$$

2.2 Electron Paramagnetic Resonance

- in general:
  - 2*S*+1 degenerate ground state will give 2*S*+1 non-degenerate levels with different energy splitting between each level
  - intensity of transitions:

$$I \propto \left|\langle M_S+1|S_x|M_S\rangle\right|^2 \qquad S_x = \tfrac{1}{2}\ S_+ + S_-$$

based on raising & lowering operators

$$\text{where } S_+|M_S\rangle = \sqrt{S+M_S+1\quad S-M_S}\;|M_S+1\rangle$$

$$\boxed{I_{M_S\to\ M_S+1} \propto \sqrt{S+M_S+1\quad S-M_S}}$$

assuming similar Boltzmann populations

$$\frac{I_{0\to 1}}{I_{-1\to 0}} = 1$$

  - so for *S* = 1: there are 2 transitions with

$$|{-1}\rangle > |0\rangle$$

  - importantly – we can get |*D*| from splitting but not its sign
    - sign is obtained from intensity distribution at very low *T*

What happens when $\vec{H} \parallel x$?

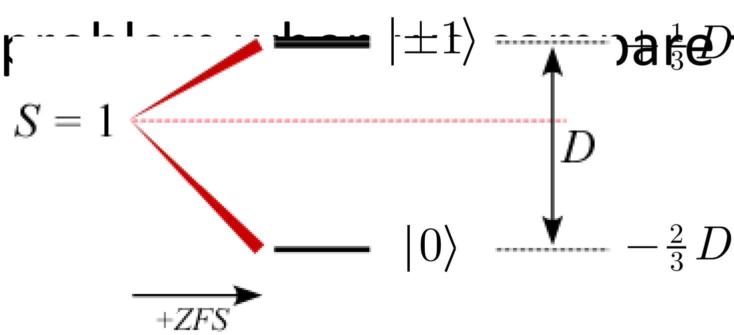
- $$\hat{\mathfrak{H}}'_x = \hat{\mathfrak{H}}_{ZFS} + \hat{\mathfrak{H}}_{Zeeman} = D\left[S_z^2 - \frac{1}{3}S\ \ S+1\ \right] + g_x\beta\vec{H}_x\hat{S}_x$$

$$E'_{M_S} = D\left[M_S^2 - \frac{2}{3}\right] + g_x\beta\vec{H}M_S \longrightarrow$$

$$E'_{\pm 1} = -\tfrac{1}{6}D \pm \sqrt{\tfrac{1}{4}D^2 + g_x^2\beta^2\vec{H}^2}$$
$$E'_0 = +\tfrac{1}{3}D$$

- which gives

- problem when compare to ZFS at H = 0...



once we apply H_x, it is $M_S = 0$ that should be at $+D/3$...

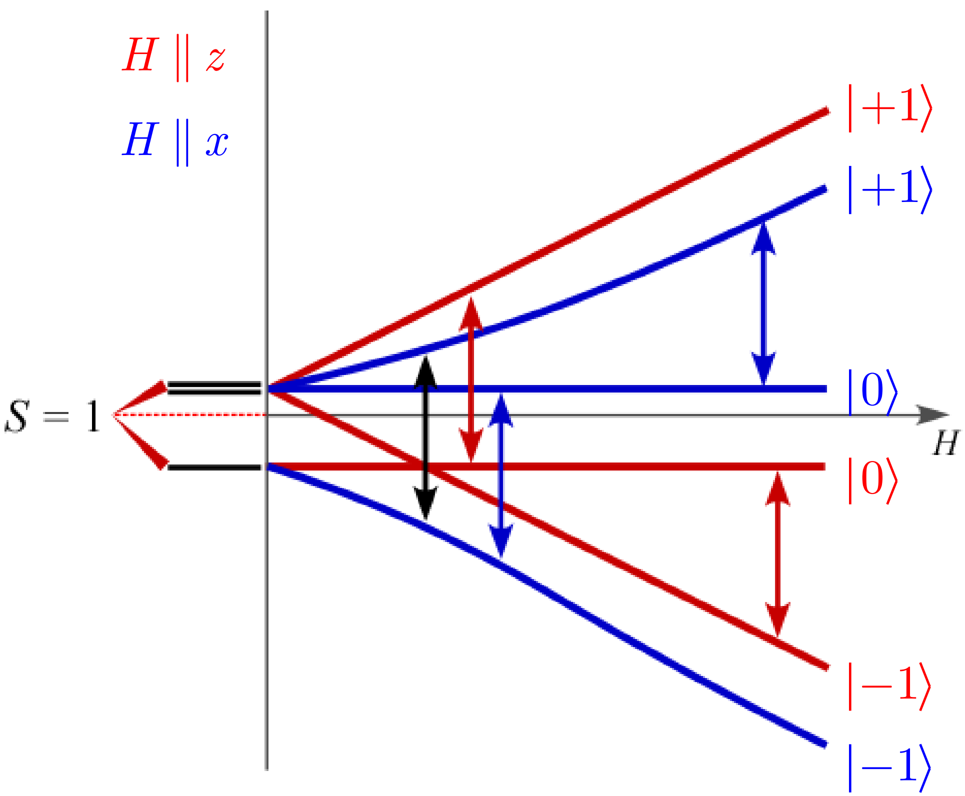
Reason: the wavefunctions change when applying field

- M_S quantized along H if $g\beta H \gg |D|$

- M_S quantized along ZFS if $g\beta H \ll |D|$

- at intermediate fields – *all hell breaks loose*

2.2 Electron Paramagnetic Resonance



Completely different spectrum along perpendicular direction!

So what happens in a frozen glass and/or polycrystalline solid?

General Orientation Dependence of ZFS-EPR Spectrum

- in general, for any $S > 1$ where $g\beta H \gg D$ with the field at an angle θ

$$E'_{M_S} = g_{eff}\beta \vec{H} M_S + \underbrace{\frac{D}{2}\left[3\left(\frac{g_z}{g_{eff}}\right)^2 \cos^2\theta - 1\right]}_{\Delta/2}\left[M_S^2 - \frac{1}{3}S\ S+1\right]$$

$$g_{eff} = g_z^2 \cos^2\theta + g_x^2 \sin^2\theta$$

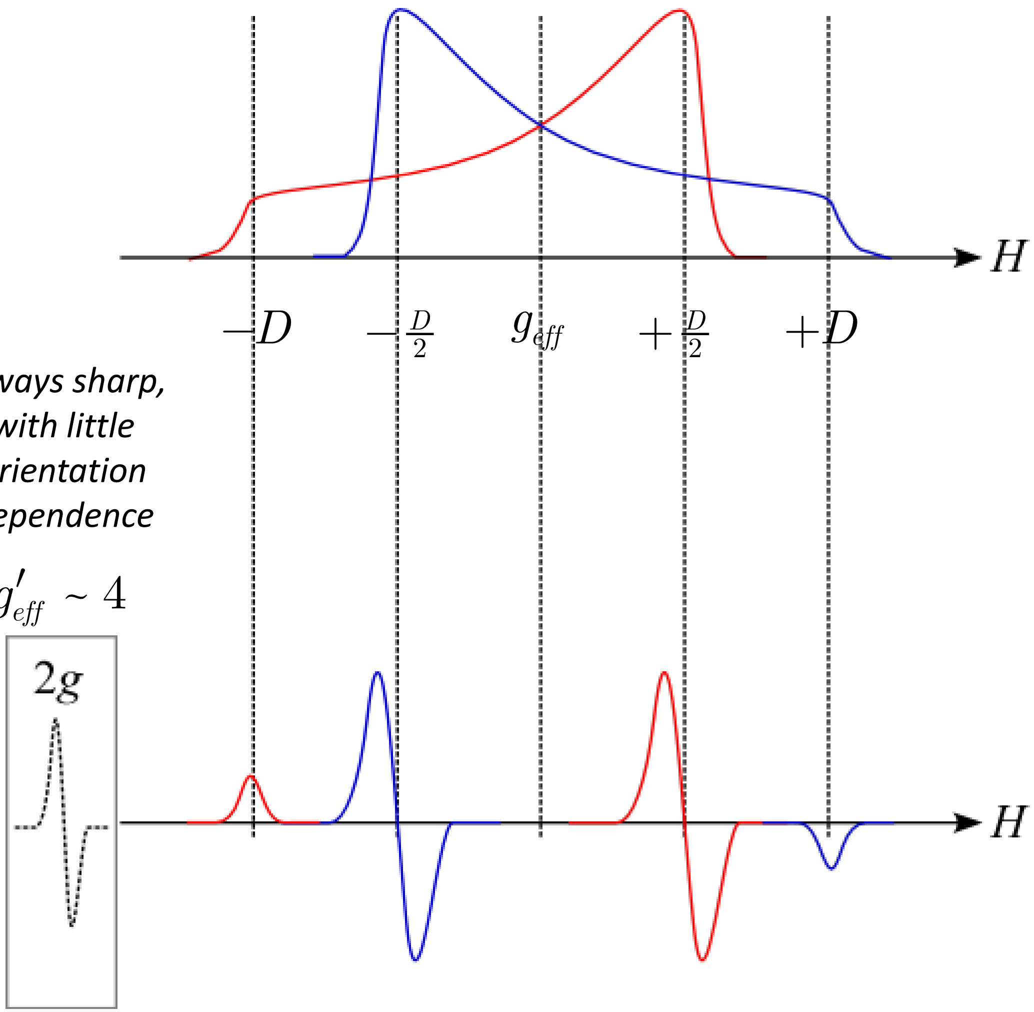
- from this equation, we find that for *S* = 1

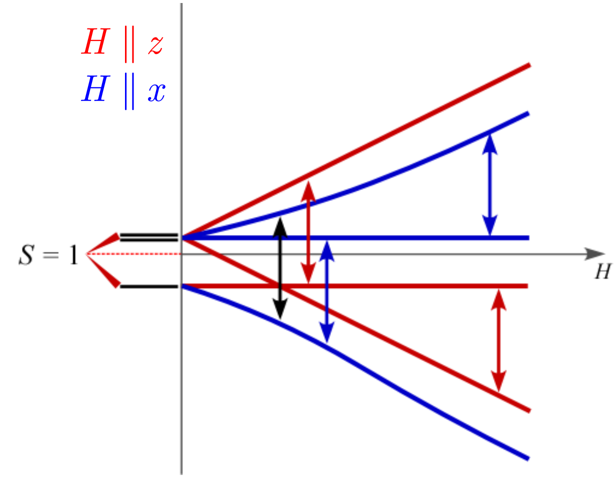
$$\frac{D}{g_{eff}\beta}\left[3\left(\frac{g_z^2}{g_{eff}^2}\right)\cos^2\theta - 1\right] = 2\left(\frac{\Delta}{2}\right)\left(\frac{1}{g_{eff}\beta}\right)$$

  - two transitions, split by

$$\begin{cases} \text{for } \vec{H} \parallel z \rightarrow \theta = 0^\circ \rightarrow \Delta E = +2D \\ \text{for } \vec{H} \perp z \rightarrow \theta = 90^\circ \rightarrow \Delta E = -D \end{cases}$$

ZFS-EPR for frozen solution with S = 1 (for small D)



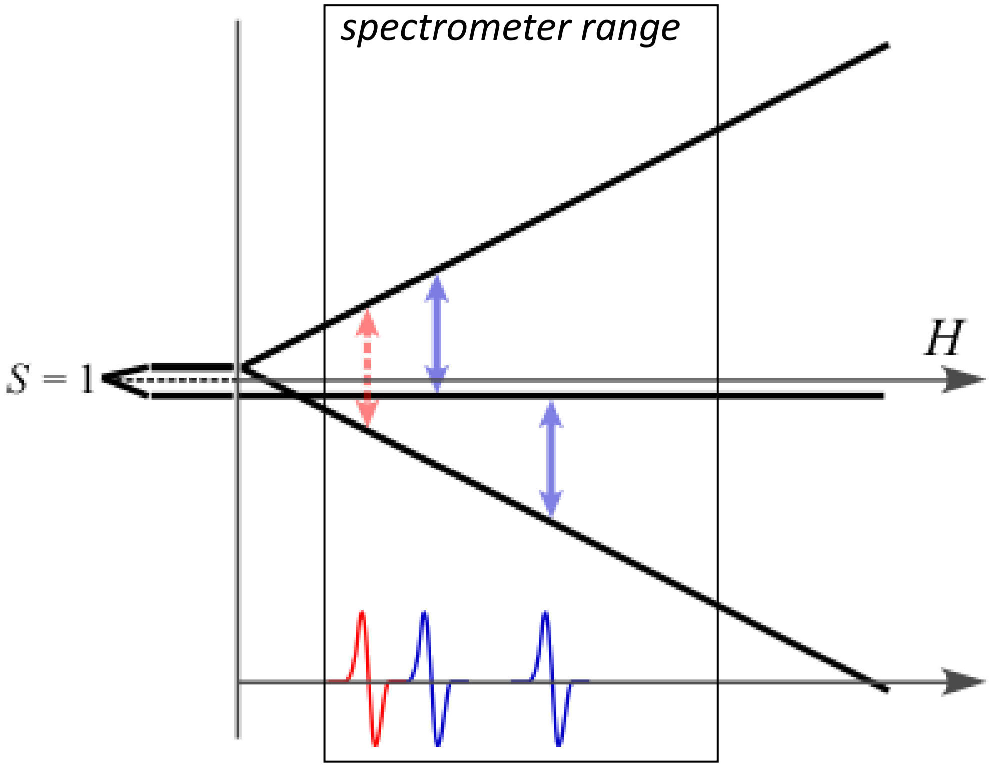


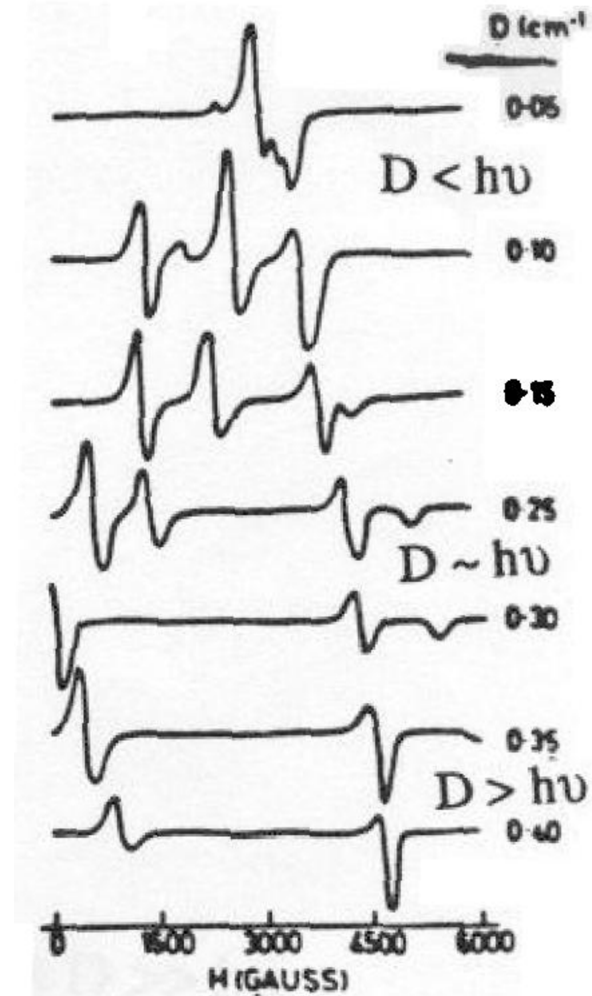
T will affect relative intensity of each transition

But what happens in axial distortion (*D*) is very large?

$$i.e. \quad D \gg h\nu$$

Spectra at the Large Axial ZFS Limit





- lose $\Delta M_S = 1$ components

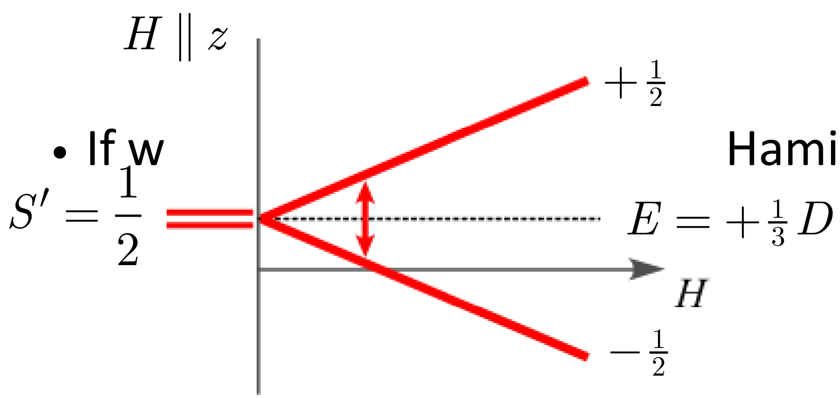
Effective Spin Hamiltonian for S' = ½

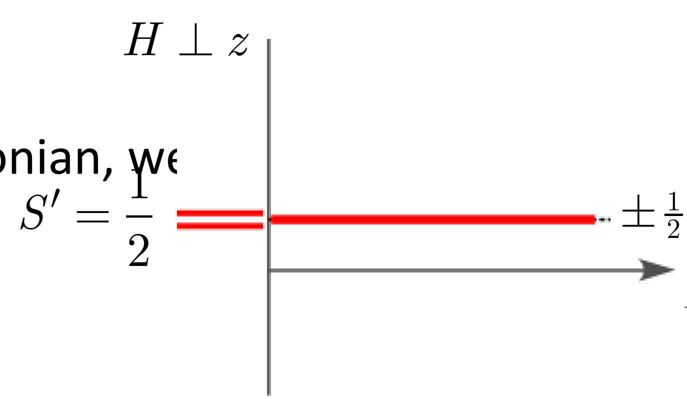
- use same equations for $|-1\rangle \rightarrow |+1\rangle$ as for $|-\tfrac{1}{2}\rangle \rightarrow |+\tfrac{1}{2}\rangle$
- intensity complicated since it relies on mixing from $M_s = 0$ state

$$\mathcal{H}_{Zeeman} = g'_{\parallel}\beta H_z \hat{S}_z + g'_{\perp}\beta H_{\perp}\left(\hat{S}_x + \hat{S}_y\right)$$

with very unusual *g* values...

- If w … Hamiltonian, we … :





$$\Delta E = g'_{\parallel}\beta H_z \quad \rightarrow \quad g'_{\parallel} \sim 4.00$$

$$\Delta E = g'_{\perp}\beta H_{\perp} \quad \rightarrow \quad g'_{\perp} = 0$$

Effect of Rhombic ZFS on Zeeman Splitting and EPR Spectrum

$x \neq y \neq z$

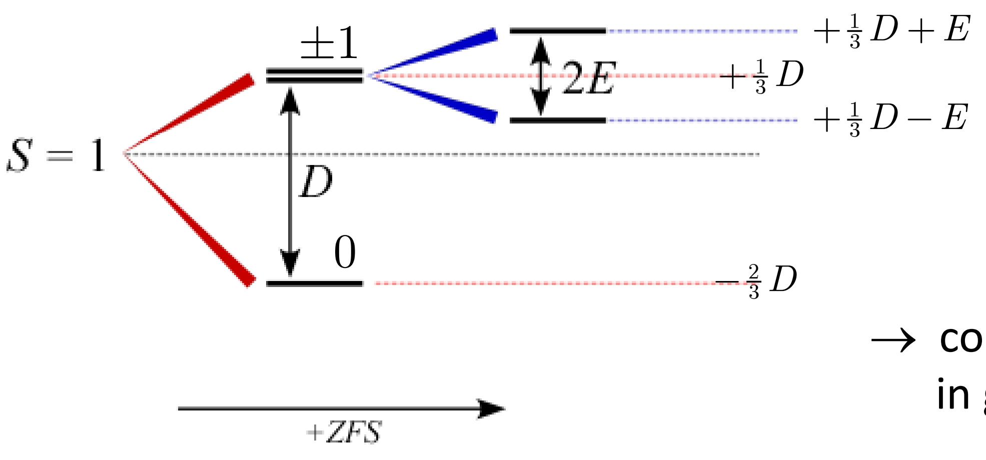
- what happens if the symmetry is lowered even more such that

  i.e. rhombic system

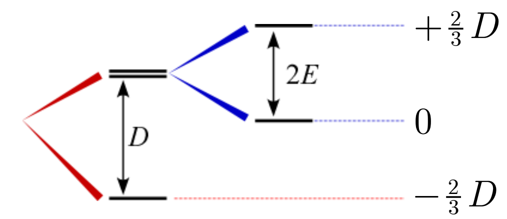
- new term in the spin Hamiltonian (*E*):

$$\hat{\mathcal{H}}_{ZFS} = D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E\left[\hat{S}_x^2 - \hat{S}_y^2\right] \quad \text{where} \quad |E| \leq \tfrac{1}{3}D$$

*ensures that effect of **D** > effect of **E***



Note: if *E* = *D*/3, then



$\rightarrow$ completely removes degeneracy in ground state!

= *loss of EPR signals...*

Kramers vs. non-Kramers ions...

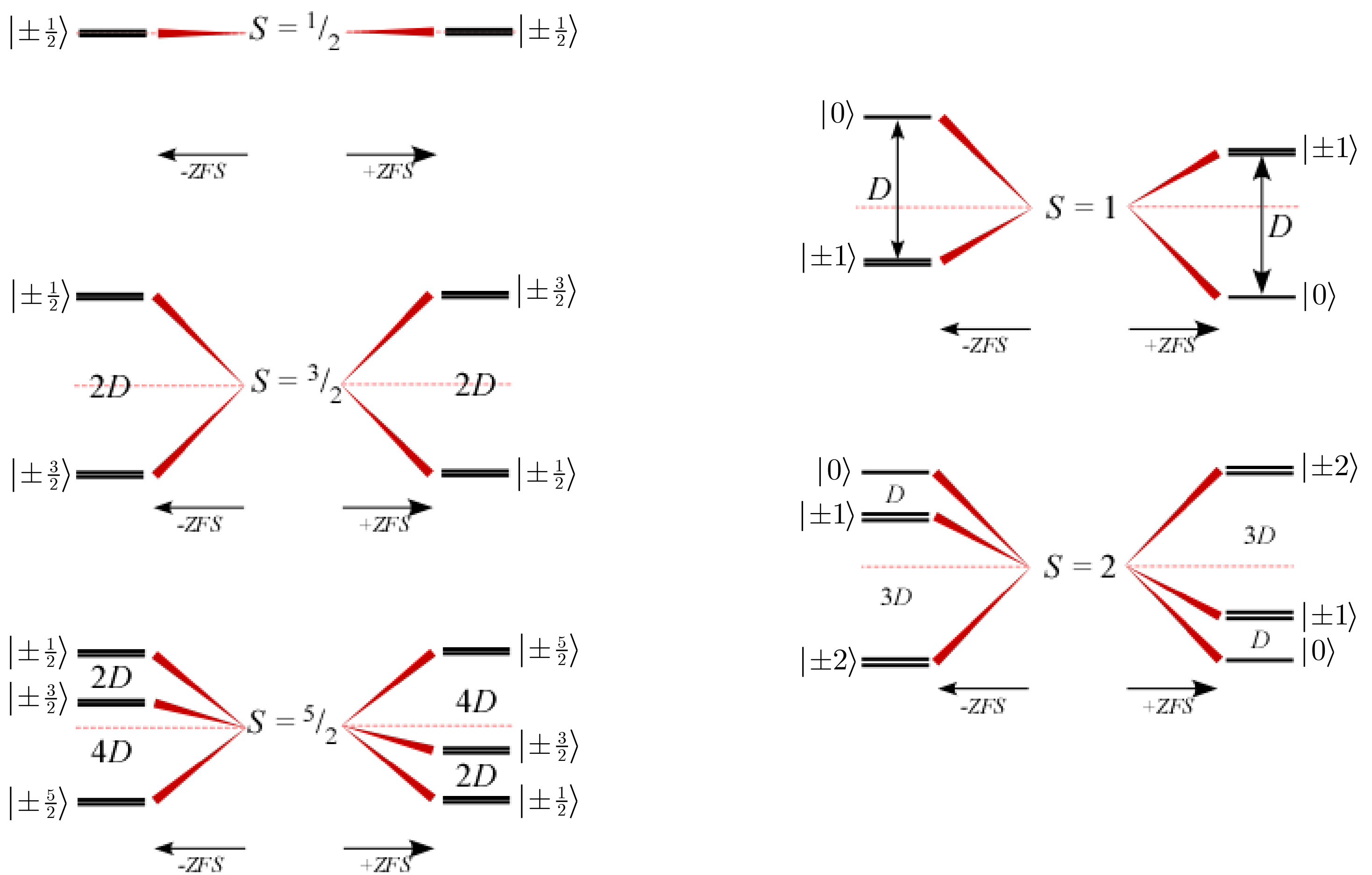
- Kramers ions are non-integer spin systems (*S* = 1/2, 3/2, 5/2, 7/2...)

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

  - generally easily observed in EPR
  - can usually see even with ZFS

- non-Kramers ions are integer spin systems (*S* = 1, 2, 3 ...)
  - usually difficult to observe by normal EPR
  - effect of rhombic splitting usually makes possible EPR transitions invisible
  - often need other techniques to investigate magnetic properties of these systems
    - Magnetic Circular Dichroism (MCD)

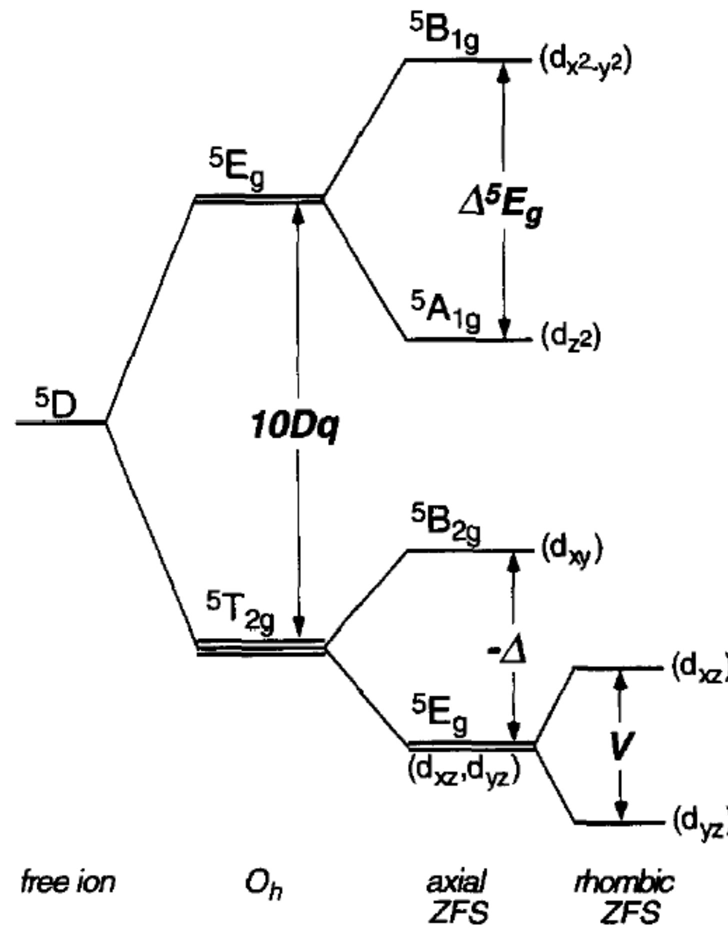
Axial ZFS Splitting Patterns for different spin systems



Correlation between ZFS and Ligand Field Theory

- the effect of ZFS can be interpr
  splittings of the metal *d*-orbital

- application of Ligand Field Thec
  this problem allows quantitativ
  evaluation of the state splitting
  diagram for a particular d^n conf
  - not easily done
  - but provides direct measure of *d*-orbital energies for complex systems

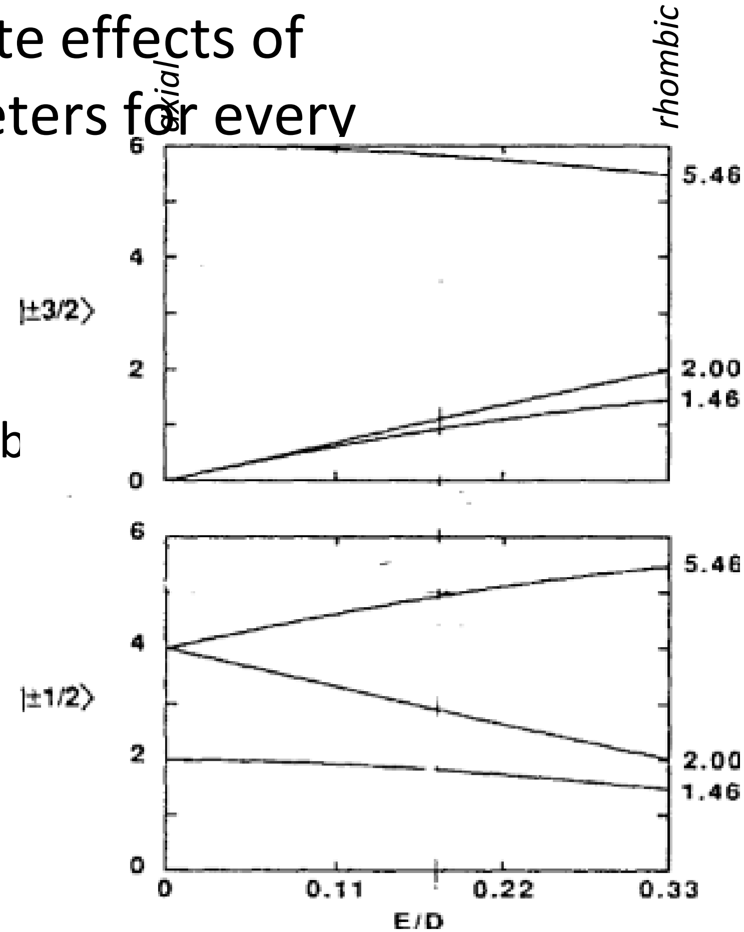


- *e.g.* in HS Fe^{II} complexes,

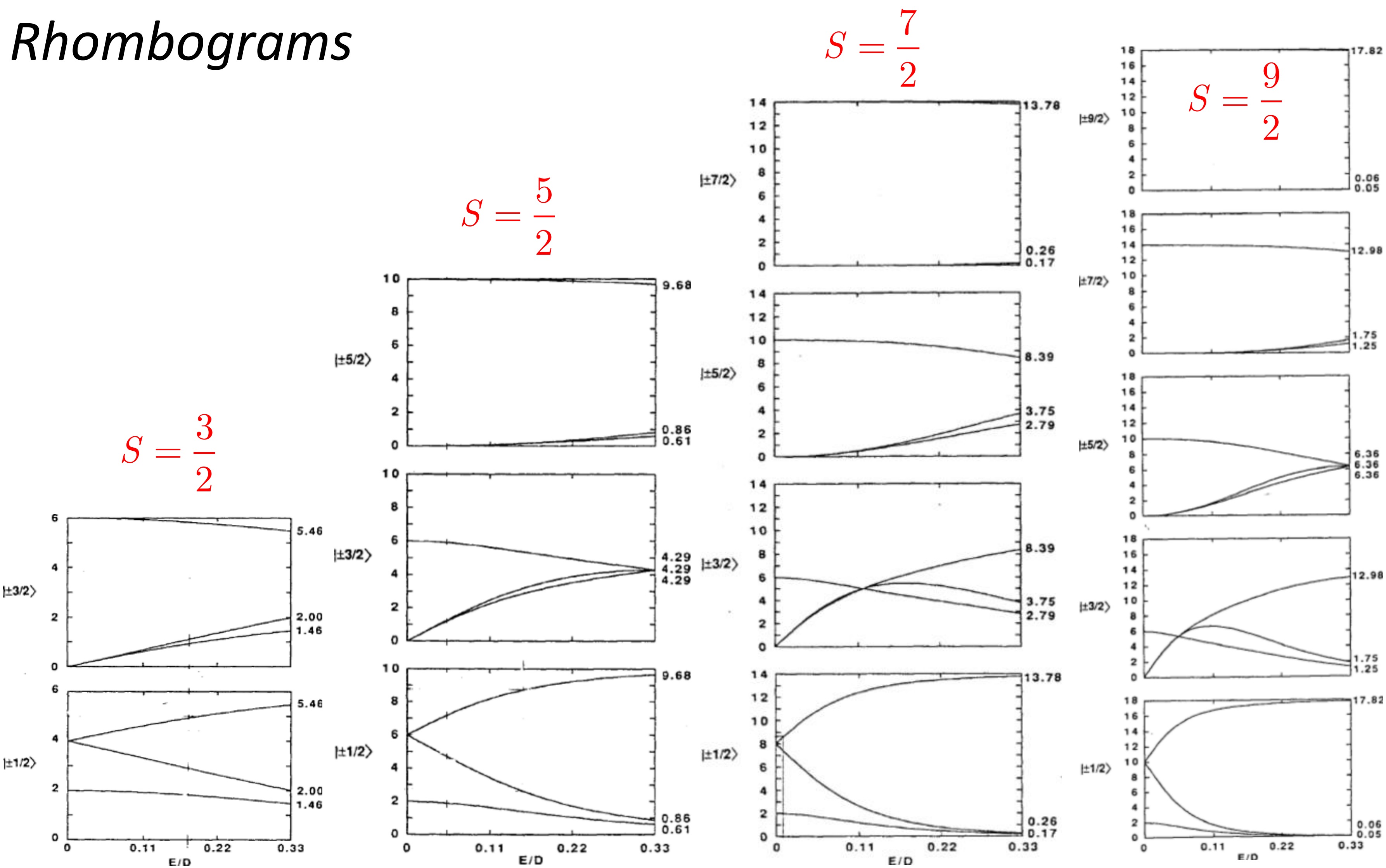
Rhombograms...

- rather annoying to have to calculate effects of different Spin Hamiltonian parameters for every system
    - it has already been done it for you... in the form of ***rhombograms***...
    - Assumes "isolated" effective spin doub

$$S = \frac{3}{2}$$

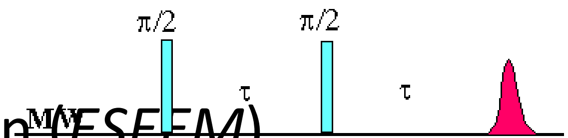


Rhombograms



Pulsed EPR Methods

- pulsed techniques offer additional insights into
  - electronic structure
  - geometric structure
  - spin dynamics
  - chemical dynamics/exchange



- Electron Spin Echo Envelope Modulation (*ESEEM*)
  - ESEEM is exactly the same as NMR spin echo experiments...
- Electron Nuclear Double Resonance (*ENDOR*)
  - coupling of EPR with NMR – better resolution for hyperfine and superhyperfine information
  - allows for high resolution measurement of hyperfine/superhyperfine interactions