Magnetism of Atoms and Ions

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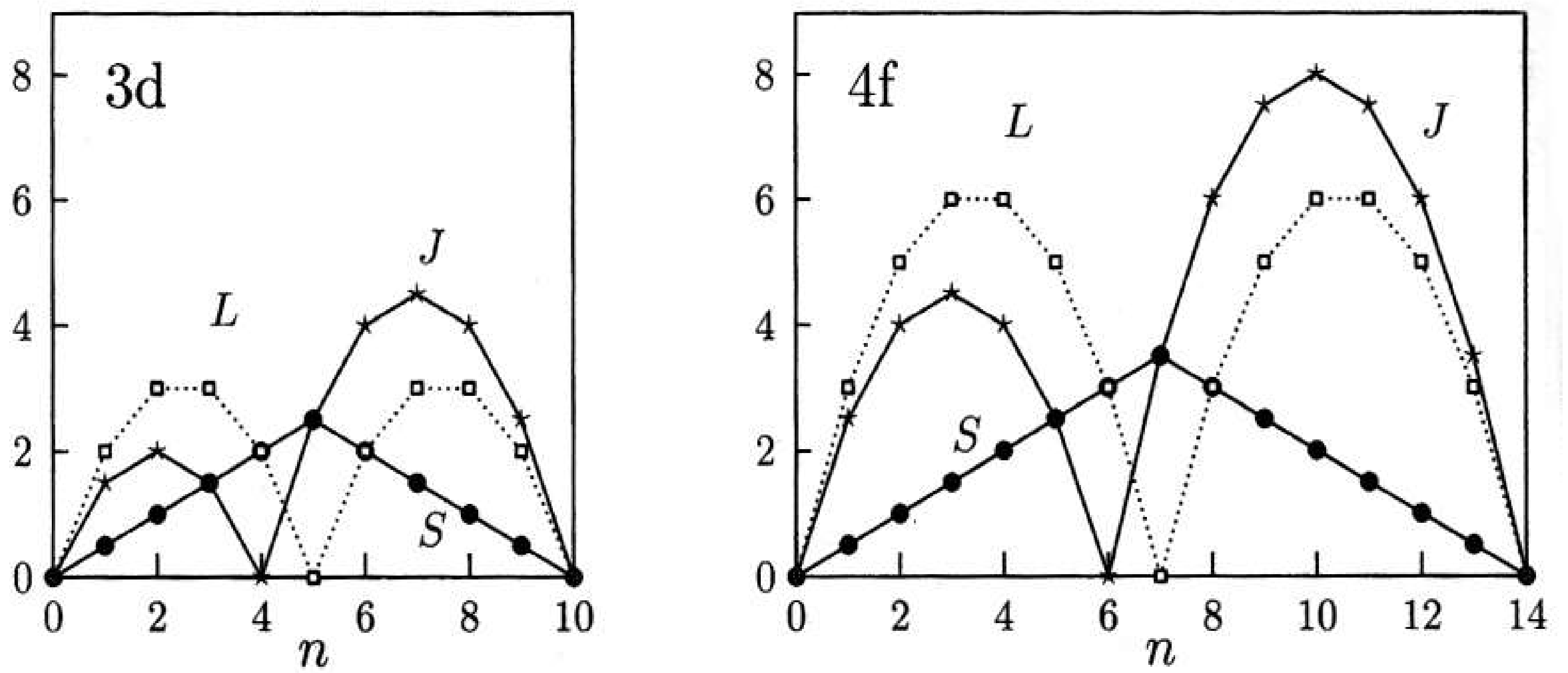


Literature

J.M.D. Coey, Magnetism and Magnetic Materials,
Cambridge University Press, 628 pages (2010).
Very detailed

Stephen J. Blundell, Magnetism in Condensed Matter,
Oxford University Press, 256 pages (2001).
Easy to read, gives a condensed overview

C. Kittel, Introduction to Solid State Physics,
John Whiley and Sons (2005).
Solid state aspects

Chapters of the two lectures

1. A quick refresh of quantum mechanics
2. The Hydrogen problem, orbital and spin angular momentum
3. Multi electron systems
4. Paramagnetism
5. Dynamics of magnetic moments and EPR
6. Crystal fields and zero field splitting
7. Magnetization curves with crystal fields

The equation of motion

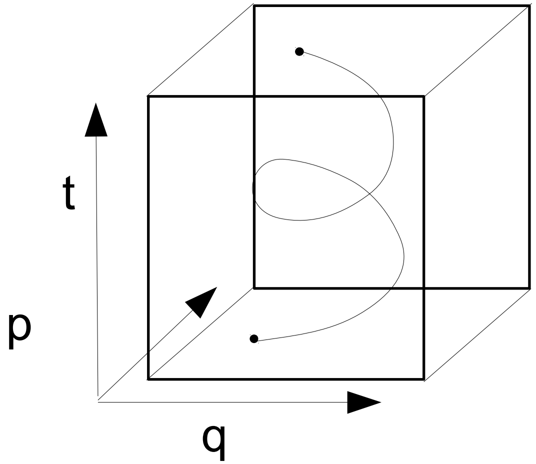
The Hamilton function: $H = T + V = f(p_i, q_i)$

with T the kinetic energy and V the potential, q the positions and p the momenta gives the

equations of motion: $\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}, \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}$

Hamiltonian gives **second order** differential equation of motion and thus p(t) and q(t)

Initial conditions needed for $q, p = m\dot{q}$
Classical equations need information on the past!

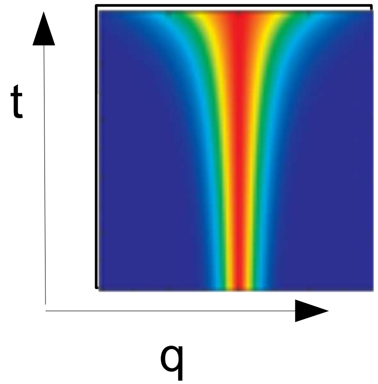


The Schrödinger equation

Quantum mechanics replacement rules for Hamiltonian:
$$p_i \rightarrow \hat{p}_i = -i\hbar \frac{\partial}{\partial q_i}$$
$$q_i \rightarrow \hat{q}_i = q_i$$

Equation of motion transforms into Schrödinger equation:
$$i\hbar \frac{\partial}{\partial t} \Psi(q,t) = \hat{H}\Psi(q,t)$$

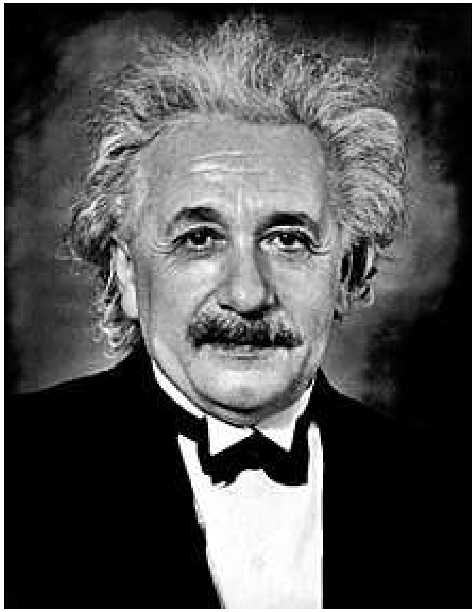
Schrödinger equation operates on wave function (**complex** field in space) and is of **first order** in time. Absolute square of the wave function is the probability density to find the particle at selected position and time.

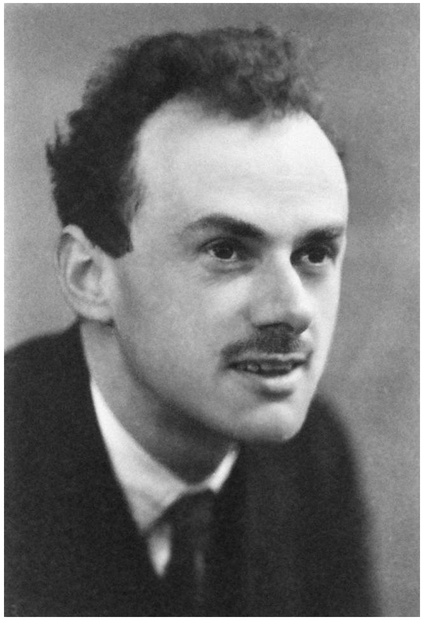


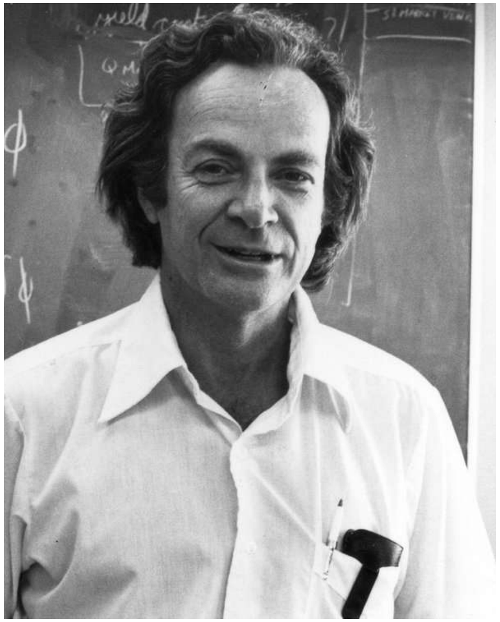
Initial conditions needed for $\Psi(q,t_0)$
Schrödinger equation does not need information on the past!

How is that possible? We know that the past influences the present!

Limits of knowledge







Eigenstates

To determine an observable quantity O (for example average position q) you calculate:

$$O = <\Psi|\hat{O}|\Psi> = \int \Psi^*(x,t)\hat{O}\Psi(x,t)dV$$

In case the Hamiltonian is no function of the time, you get the time independent equation:

$\hat{H}\psi(q) = E\psi$ and the energy is conserved

The Schrödinger equation usually has more than one solution with different energies
Solutions with a particular energy are called eigenstates of the system

For an eigenstate you find: $\Psi_n(q,t) = \psi_n(q)e^{-i\frac{E_n}{\hbar}t}$

For all eigenstates, expectation values of observables (that do not explicitly depend on time) are time independent and the energy has no spread (sharp value)

Quantum numbers

Often, the Hamiltonian does not change under particular transformations (change of time, position, rotation in space, etc.)

Each of these "symmetries" gives conserved quantities (just like time translation and energy)

See→ Noether theorem

Especially, if H and O commute, you can find states that are eigenstates of both H and O

$$\hat{H}\hat{O} - \hat{O}\hat{H} = [\hat{H}, \hat{O}] = 0$$

$$\hat{H}|\psi_{nm}> = E_n|\psi_{nm}>, \hat{O}|\psi_{nm}> = O_m|\psi_{nm}>$$

Quantum numbers

A complete set of commuting operators (commute pairwise) gives a full basis set of eigenfunctions of the quantum mechanical problem

There is no need to write down the wave function, you can characterize it by giving the eigenvalues of the complete set of operators

Since we are "lazy", we will use this nomenclature and only show pictures

Any quantum state can than be written by a superposition of eigenstates and it is sufficient to give the complex coefficients

$$\Psi(q,t) = \sum_j c_j \psi_j(q) e^{-i\frac{E_j}{\hbar}t}$$

Since eigenstates and coefficients do not depend on time, all time dependence comes from the energy of the eigenstates

Central potentials and the angular moment

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(|r|)$$

Neither the kinetic energy nor the potential energy changes, if we rotate the coordinate system around the origin
Two rotation angles are needed to describe this → we expect two conserved quantities

Angular momentum $\hat{l} = \hat{r} \times \hat{p}$ $[\hat{l}^2, \hat{l}_z] = 0$

Standard choice of set of commutating operators is l^2 and l_z

$$[\hat{l}^2, \hat{l}_z] = 0, [\hat{l}^2, \hat{H}] = 0, [\hat{l}_z, \hat{H}] = 0$$

Solutions of the angular part of the Schrödinger equation are the spherical harmonics

$Y_{lm}(\theta, \phi)$ with $l = 0, 1, 2, \ldots, m = -l, -l+1, \ldots l-1, l$

Spherical harmonics

Eigenvalues are:

$$\hat{l}_z|Y_{lm}> = \hbar m|Y_{lm}>$$

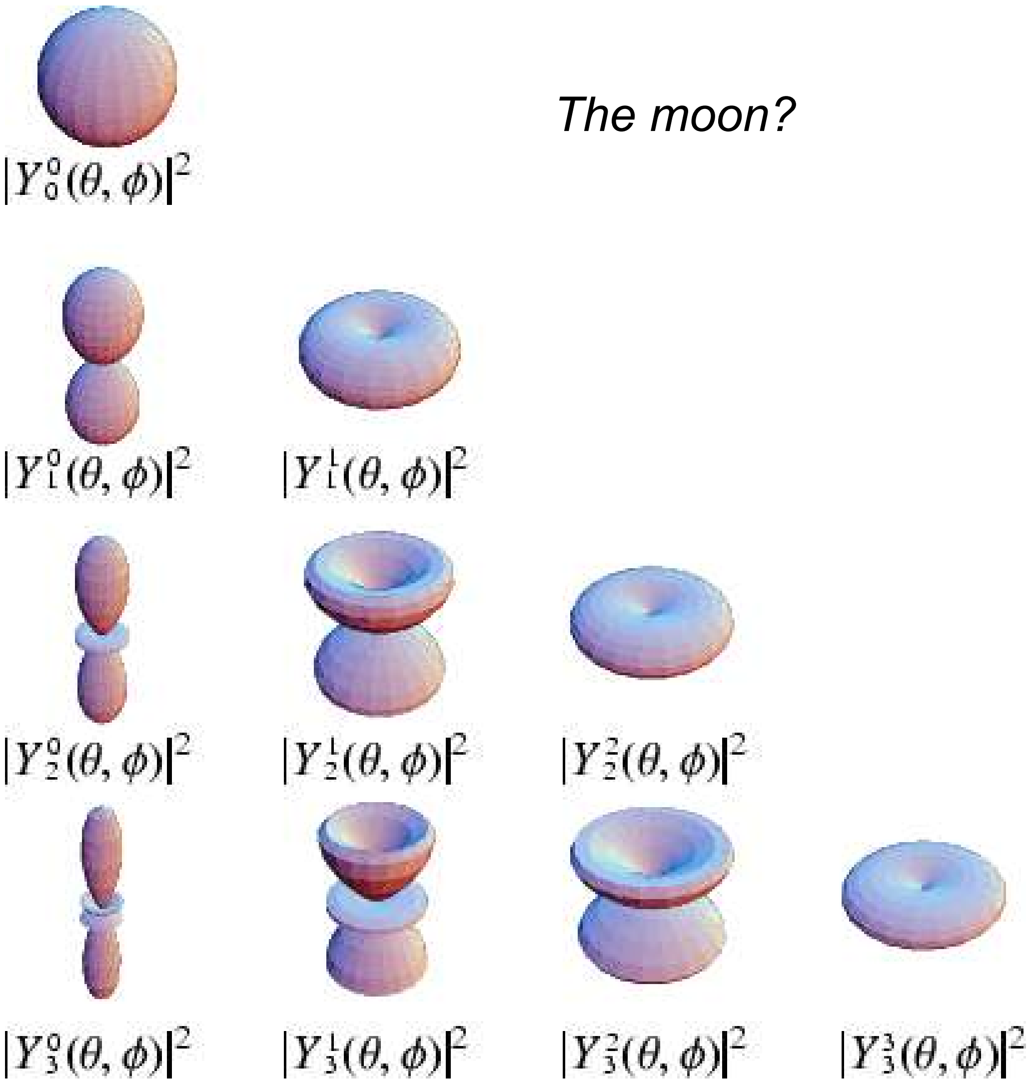
$$\hat{l}^2|Y_{lm}> = \hbar^2 l(l+1)|Y_{lm}>$$

Phase of Y_{lm}:

$$Y_{lm}(\theta,\phi) = f_{l|m|}(\theta)_{\mathbb{R}} e^{im\phi}$$

Useful: $$\sum_m |Y_{lm}|^2 = \text{const}$$

i.e. like s-orbital, no angular momentum



The moon?

Central potentials and the angular moment

Individual components of l do not commute

Y_{lm} has an exact value for l^2 and l_z, i.e. you can measure them exactly and at the same time

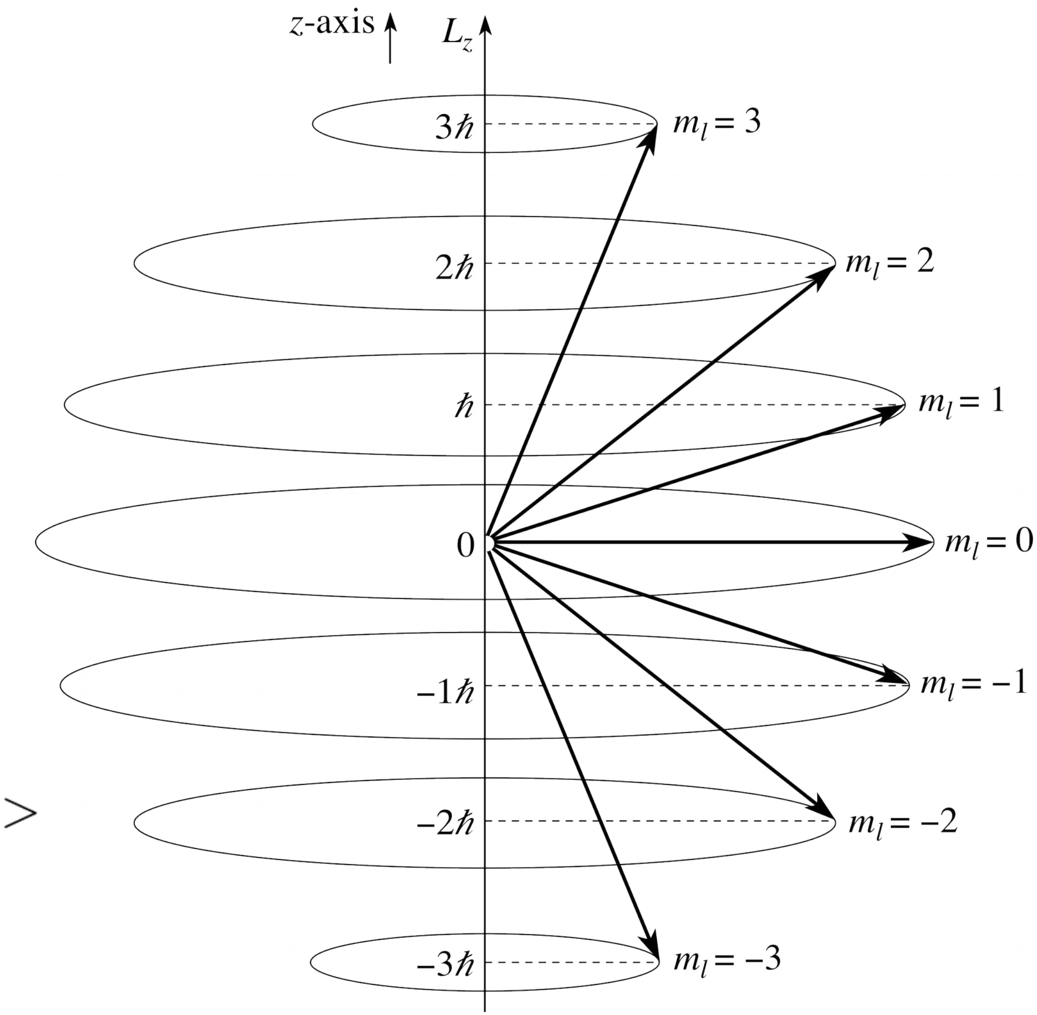
The x and y components are widely spread on circles, when you measure them but the average value, i.e. the expectation value, vanishes

$$l_{\pm} = l_x \pm i l_y$$

$$l_{\pm}|Y_{lm}> = \hbar\sqrt{l(l+1) - m(m \pm 1)}|Y_{lm\pm1}>$$

$$<Y_{lm}|l_{\pm}|Y_{lm}> = 0$$

$$<Y_{lm}|l_x|Y_{lm}> = 0 = <Y_{lm}|l_y|Y_{lm}>$$

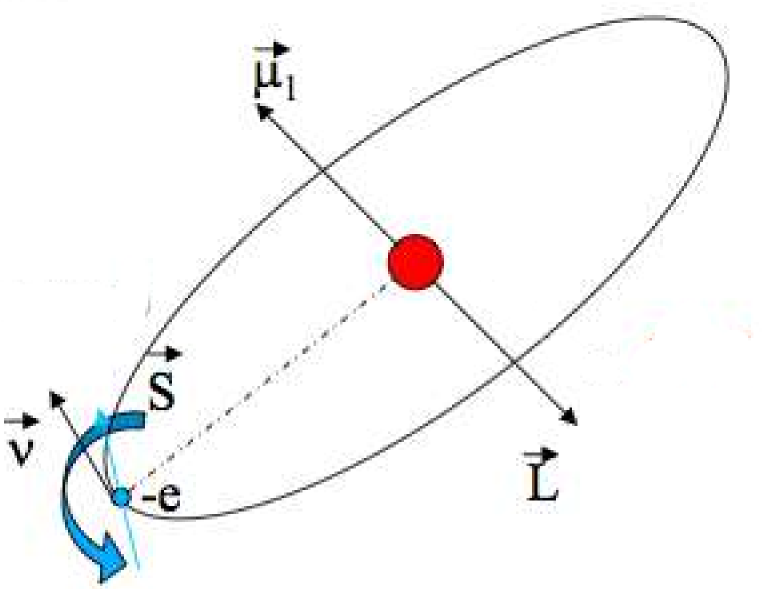


Correspondence ?

The orbital magnetic moment

Magnetic moment of ring current (orbital moment)

$$\vec{\mu} = I\vec{A} = -ev\pi r^2 = \frac{-e}{2m}(m\omega r^2) = \frac{-e}{2m}\vec{l}$$



Quantum mechanics

$$\hat{\mu} = \frac{-e}{2m}\hat{l}$$

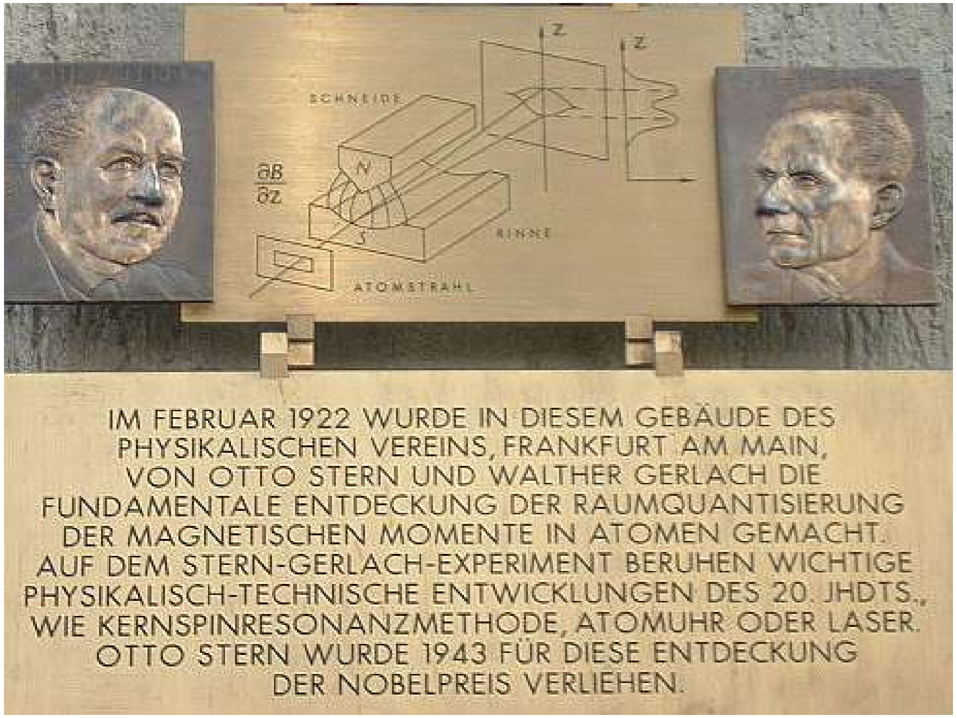
$$\mu_z = -\mu_B m$$

$$|\mu| = \sqrt{l(l+1)}\mu_B$$

Bohr magneton $\mu_B = \frac{e\hbar}{2\mathrm{m}} = 9.27 \times 10^{-24} J/T$

Attention: The magnetic moment behaves like an angular momentum

The spin magnetic moment



IM FEBRUAR 1922 WURDE IN DIESEM GEBÄUDE DES PHYSIKALISCHEN VEREINS, FRANKFURT AM MAIN, VON OTTO STERN UND WALTHER GERLACH DIE FUNDAMENTALE ENTDECKUNG DER RAUMQUANTISIERUNG DER MAGNETISCHEN MOMENTE IN ATOMEN GEMACHT. AUF DEM STERN-GERLACH-EXPERIMENT BERUHEN WICHTIGE PHYSIKALISCH-TECHNISCHE ENTWICKLUNGEN DES 20. JHDTS., WIE KERNSPINRESONANZMETHODE, ATOMUHR ODER LASER. OTTO STERN WURDE 1943 FÜR DIESE ENTDECKUNG DER NOBELPREIS VERLIEHEN.

Stern Gerlach experiment

Atomic Ag beam in inhomogeneous magnetic field leads to sorting of atoms with respect to the z-component of their magnetic moment

Two spots found

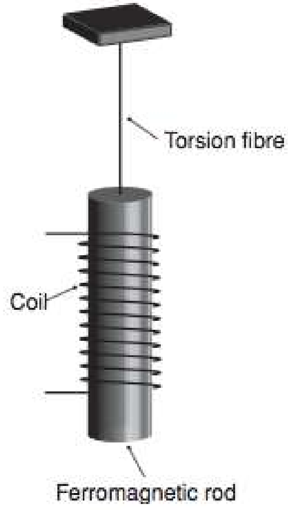
(Spin) angular momentum s=½ with s_z = +- ½

$$\hat{\mu}_s = \mu_B g_s \hat{s}$$

Landé factor of the electron $g_S = 2.0023 \approx 2$

g_S=2 for relativistic Dirac equation

Einstein de Haas experiment: g=1 (data fiddled)

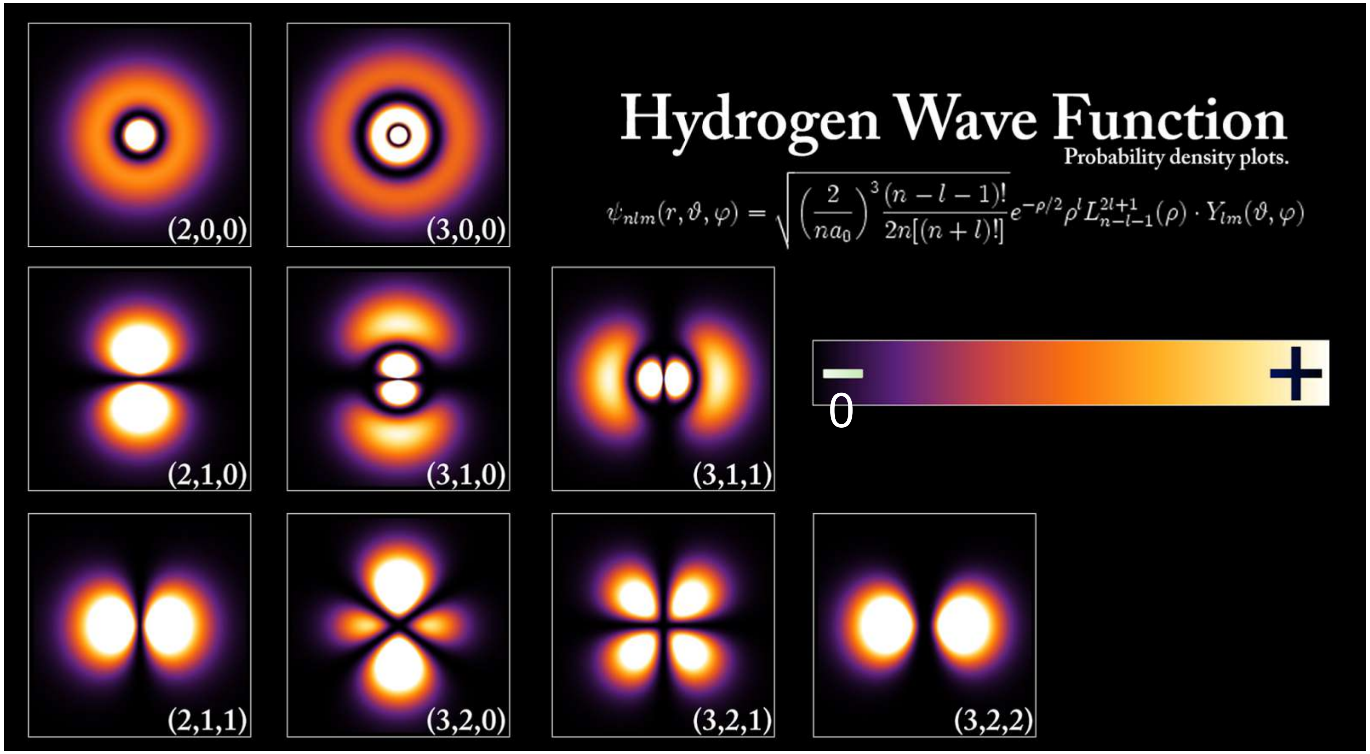


The Hydrogen problem

We still need to solve the radial part of the Schrödinger equation with 1/r potential
We find radial wave functions with principal quantum number n and energy

$$E_n = -R_H \frac{1}{n^2}$$

Radial wave function has (n-1)-l nodes, l<n



Relativistic corrections

In the rest frame of the electron, a proton current circulates creating a magnetic field that acts on the spin moment of the electron (+other relativistic effects)

A small energy shift arises depending on the direction of s with respect to l

l and s couple to total angular momentum j

$$\hat{j} = \hat{l} + \hat{s} \qquad j_z = l_z + s_z = \hbar(m_l + m_s), j = l \pm \frac{1}{2}$$

For the ls-coupled states we find an intermediate g-factor between 1 and 2

$$g_{jls} = 1 + \frac{j(j+1)s(s+1) - l(l+1)}{2j(j+1)}$$

Pauli principle

The many particle wave function $\psi(r_1, s_1, r_2, s_2, \ldots)$
of Fermions needs to be antisymmetric under exchange of each pair of electrons

Example: $\Psi(1,2) = -\Psi(2,1)$

If both electrons have the very same quantum numbers including spin:

$\Psi(1,1) = -\Psi(1,1) = 0$ This cannot happen!

Wave function of electron is a product of spatial and spin part: $\Psi(1) = \Psi(r_1) \times \vec{\sigma}(1)$

For antiparallel spins (singlet): $\sigma(1,2) = \frac{1}{\sqrt{(2)}}(\uparrow\downarrow - \downarrow\uparrow)$ antisymmetric

For parallel spins (triplet) : $\sigma(1,2) = \uparrow\uparrow, \frac{1}{\sqrt{(2)}}(\uparrow\downarrow + \downarrow\uparrow), \downarrow\downarrow$ symmetric

→ Spatial part ans pin part of wave function have opposite symmetry

Exchange energy

$$\Psi(r_{1,}r_2)=\frac{1}{\sqrt{2}}(\Psi_a(r_1)\Psi_b(r_2)+\Psi_a(r_2)\Psi_b(r_1))$$

symmetric for singlet

$$\Psi(r_{1,}r_2)=\frac{1}{\sqrt{2}}(\Psi_a(r_1)\Psi_b(r_2)-\Psi_a(r_2)\Psi_b(r_1))$$

antisymmetric for triplet

For the antisymmetric wave function : $\Psi(r_{1,}r_2)=-\Psi(r_{2,}r_1)$

In case $r_1=r_2$ follows : $\Psi(r,r)=0$

→ Coulomb repulsion of two electrons in He is lower for antisymmetric spatial wave function and thus its energy Is lower than that of the symmetrical spatial wave function
Spin triplet states are lower in energy

Exchange energy

Exchange interaction between two spins: difference of the coulomb energy due to symmetry

$$E_S - E_T = 2\int \Psi_a^*(r_1)\Psi_b^*(r_2)\frac{e^2}{4\pi\epsilon_0|r_1 - r_2|}\Psi_a(r_2)\Psi_b(r_1)\,dr_1\,dr_2$$

$$\Delta E = -2E_{Ex}S_1S_2$$

For He, the ground state is easy to find:

We can put two electrons in the 1s state only with opposite m_s, same m_s not allowed

We can put one electron in the 1s and the second in the 2s and make the wave function antisymmetric

Here the exchange favours the triplet state

Exchange is smaller than difference between 1s and 2s energy

Problems of many electron states

Problems of many electron states

Let us put n electrons in the system, e.g. Fe with 26 electrons

Alone the spin part of the wave function has 2^{26} = 67.108.864 combinations / dimensions

Nobody can write down, calculate or store this totally antisymmetric wave function

We need an educated guess with some simplified quantum numbers

Angular and spin momenta of all electrons add up $\hat{L} = \sum_i \hat{l}_i, \hat{S} = \sum_i \hat{s}_i, \hat{J} = \hat{L} + \hat{S}$

We only care for the lowest energy states and determine the number of electrons in a shell and the spin, orbital and total angular momentum

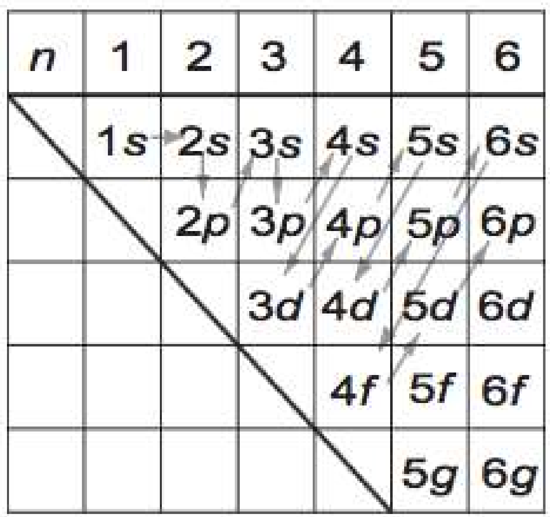
We are left with a J multiplet with J(J+1) states

Hund´s rule

A complete atomic shell has one electron for each spin and each magnetic state
For complete shells, we have only one choice to fill the states

→ Both the total spin and orbital angular momentum vanish, as well as J
Complete shells have no magnetic moment

Hund´s rules describe how to fill in the electrons with spin-orbit interaction in incomplete shells and take into account the exchange interaction



n	1	2	3	4	5	6
	1s	2s	3s	4s	5s	6s
		2p	3p	4p	5p	6p
			3d	4d	5d	6d
				4f	5f	6f
					5g	6g

Bare in mind that in e.g. in Fe the 1s, to 4s shells are full (20 electrons)
To store the wave function requires for the principle quantum number (1...4)=3^{20},
angular momentum (0 or 1)=2^{20},
magnetic quantum number (-1,1,0)=3^{12}
an spin (+-1/2)=2^{20} coefficient…..... This is about 10^{35} complex numbers!

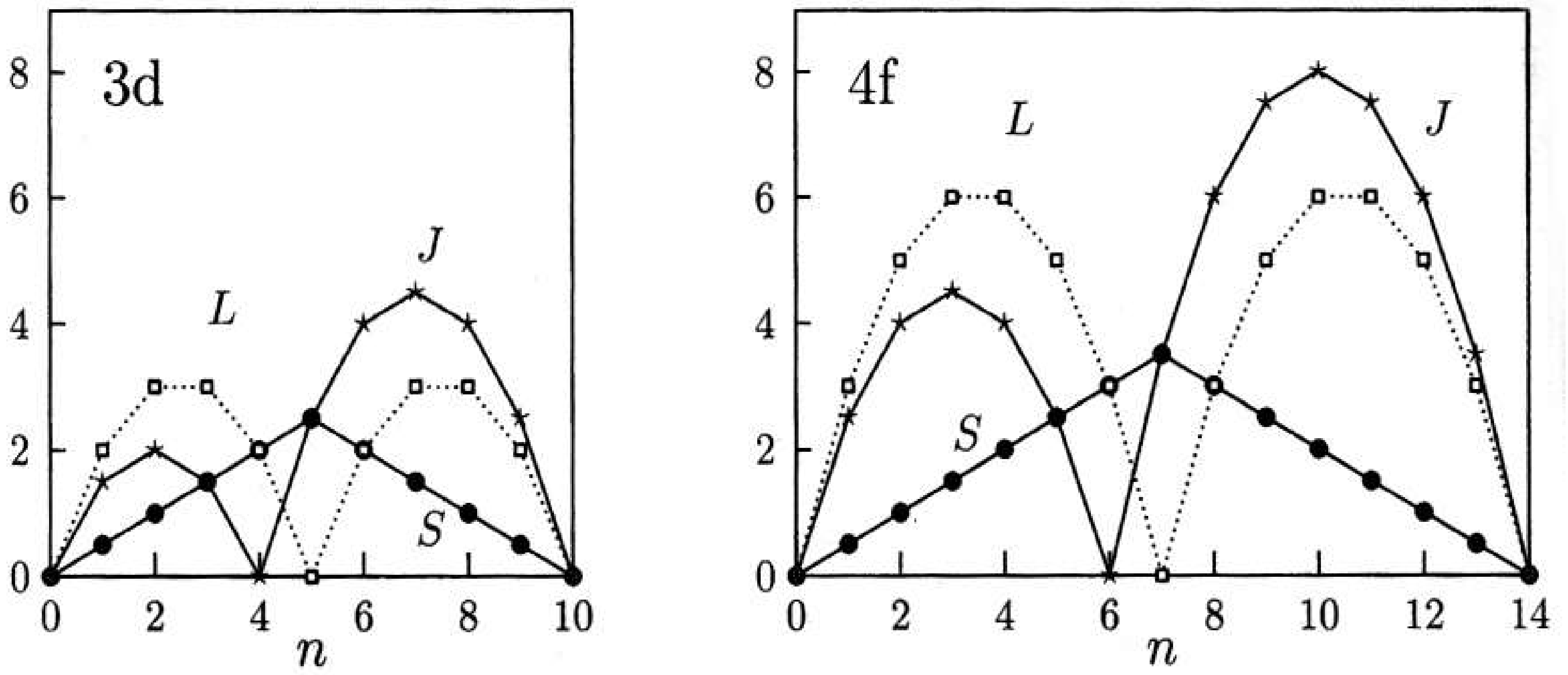
Hund´s rule

1. Hund´s rule: **Ground state has maximal S**,
because for maximal S, spins are mostly parallel, i.e. symmetric spin part and antisymmetric spatial part of wave function, where electrons cannot be at same position minimizing Coulomb repulsion

2. Hund´s rule: **Ground state has maximal L**,
because Coulomb repulsion is smaller, if electrons orbit in the same rotation sense (sign of magnetic quantum number) around the nucleus

3. Hund´s rule: **For less than half filled shells J=|L-S| and for more J=|L+S|**,
because spin-orbit interaction is given by $\lambda \vec{L}\vec{S}$, in which λ changes sign from positive to negative at half filled shell

Hund´s rule



Side note: Half filled shells have L=0 and shells with one less electron have J=0.

from: Blundell

Hund´s rule

Example: Fe $3d^6$

half full

1. Hund´s rule	m_s :	½	½	½	½	½	-½	-½	-½	-½	-½
2. Hund´s rule	m_l :	2	1	0	-1	-2	2	1	0	-1	-2
3. Hund´s rule	J :	|L-S|					|L+S|				

Spectroscopic term $^{(2S+1)}L_J$

$$3d^6 = {}^5D_6$$

$S=½(5-1)=2$
$L=0+2=2$
$J=|L+S|=4$, $g=3/2$
$\mu=6\mu_B$

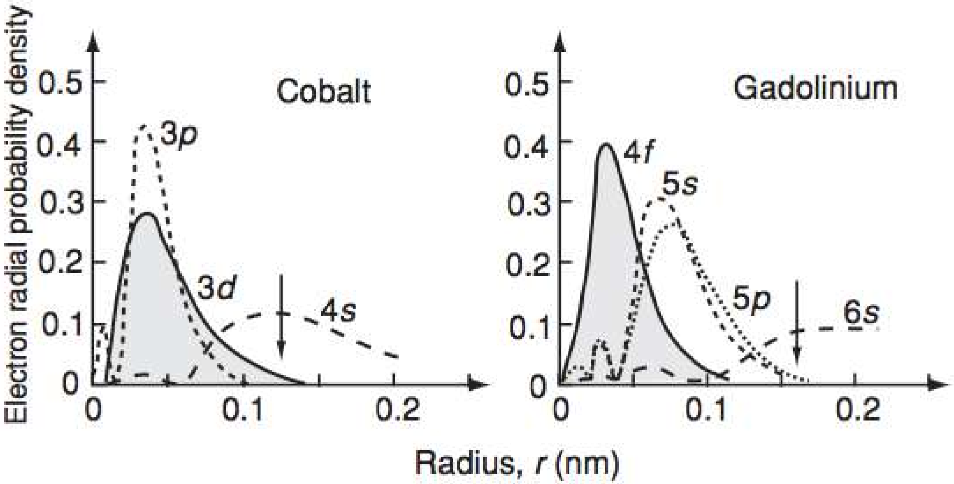
bcc Fe with 2 atoms per unit cell of $(286\ \text{pm})^3$ leads to $M = 12\ \mu_B / (286\ \text{pm})^3 = 4{,}75\ \text{MA/m}^2$
But experimental value is $1.71\ \text{MA/m}^2$

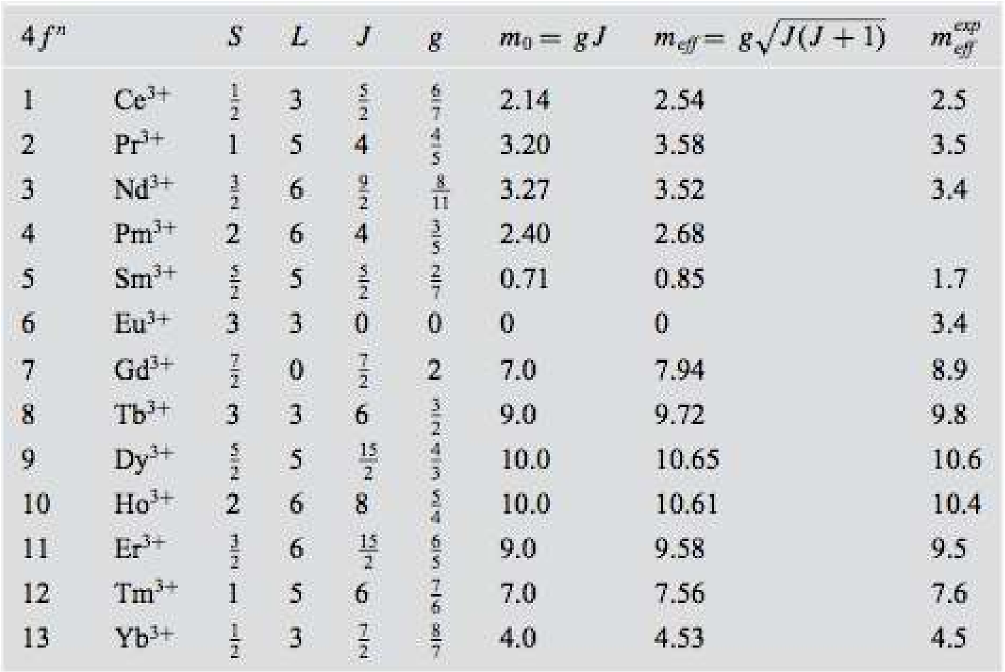
Problems with Hund´s rules

Hund's rules work well for free atoms and ions
- fails for 3d atoms/ions in matter due to exposure of 3d wave functions to neighboring atoms, quenching of orbital momentum

Hund´s rule work well for rare earth atoms and ions
- 4f electrons are shielded from neighboring atoms and spin-orbit interaction is strong

Hund’s rule fails near half filled shells minus one (second order corrections)





$4f^n$		S	L	J	g	$m_0 = gJ$	$m_{eff} = g\sqrt{J(J+1)}$	m_{eff}^{exp}
1	Ce^{3+}	$\frac{1}{2}$	3	$\frac{5}{2}$	$\frac{6}{7}$	2.14	2.54	2.5
2	Pr^{3+}	1	5	4	$\frac{4}{5}$	3.20	3.58	3.5
3	Nd^{3+}	$\frac{3}{2}$	6	$\frac{9}{2}$	$\frac{8}{11}$	3.27	3.52	3.4
4	Pm^{3+}	2	6	4	$\frac{3}{5}$	2.40	2.68	
5	Sm^{3+}	$\frac{5}{2}$	5	$\frac{5}{2}$	$\frac{2}{7}$	0.71	0.85	1.7
6	Eu^{3+}	3	3	0	0	0	0	3.4
7	Gd^{3+}	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.0	7.94	8.9
8	Tb^{3+}	3	3	6	$\frac{3}{2}$	9.0	9.72	9.8
9	Dy^{3+}	$\frac{5}{2}$	5	$\frac{15}{2}$	$\frac{4}{3}$	10.0	10.65	10.6
10	Ho^{3+}	2	6	8	$\frac{5}{4}$	10.0	10.61	10.4
11	Er^{3+}	$\frac{3}{2}$	6	$\frac{15}{2}$	$\frac{6}{5}$	9.0	9.58	9.5
12	Tm^{3+}	1	5	6	$\frac{7}{6}$	7.0	7.56	7.6
13	Yb^{3+}	$\frac{1}{2}$	3	$\frac{7}{2}$	$\frac{8}{7}$	4.0	4.53	4.5

from Coey

The Zeeman effect

Magnetic moment of atom couples to external field (along z-axis)

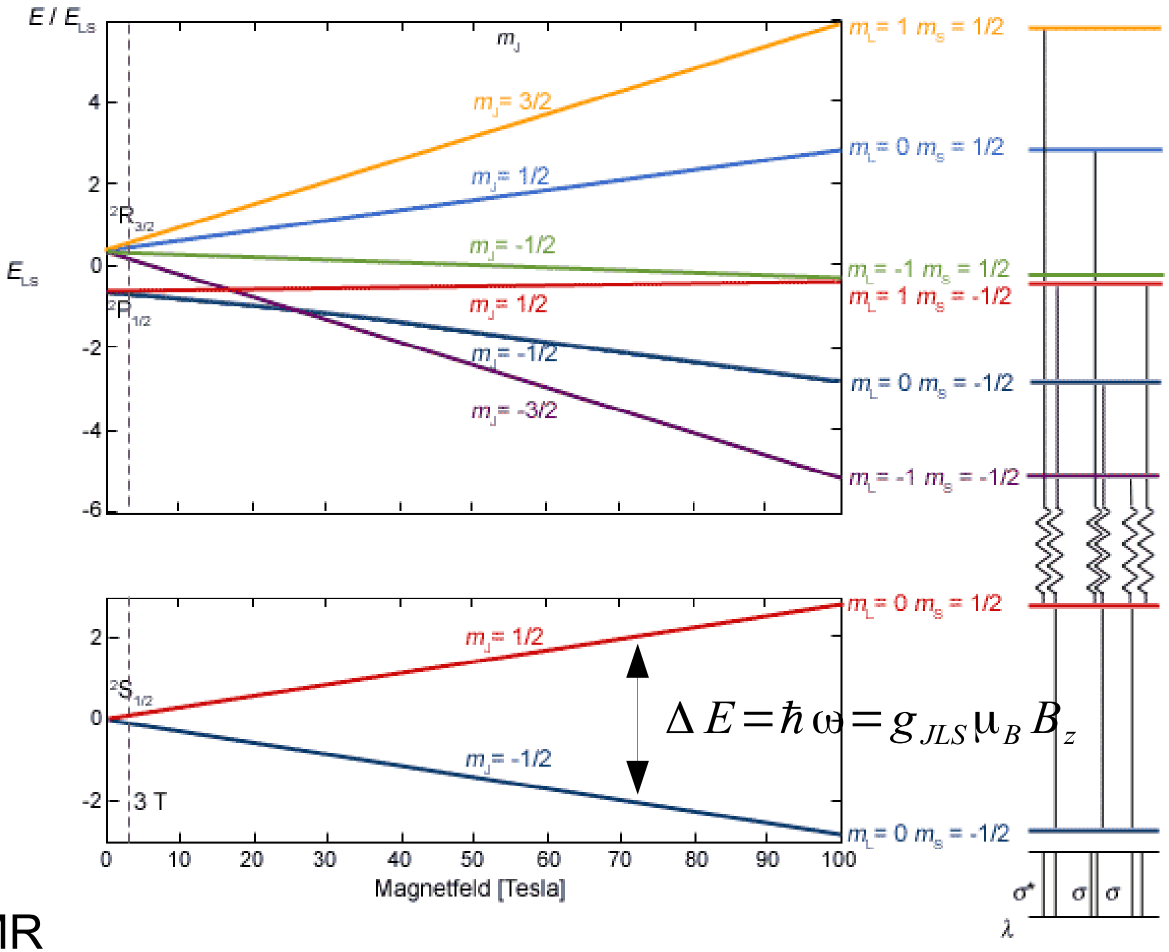
$$E = -\vec{\mu}\vec{B}$$

$$\hat{H}_Z = -\hat{\mu}B = g_{JLS}\mu_B \frac{\hat{J}_z}{\hbar} B_z$$

Zeeman operator commutes as it is proportional to J_z

Splitting of the states

Atom can be excited by microwaves (magnetic dipole approx.) when you hit the right frequency → ESR/EPR/NMR



$$\Delta E = \hbar\omega = g_{JLS}\mu_B B_z$$

The Zeeman energy and the Brillouin function

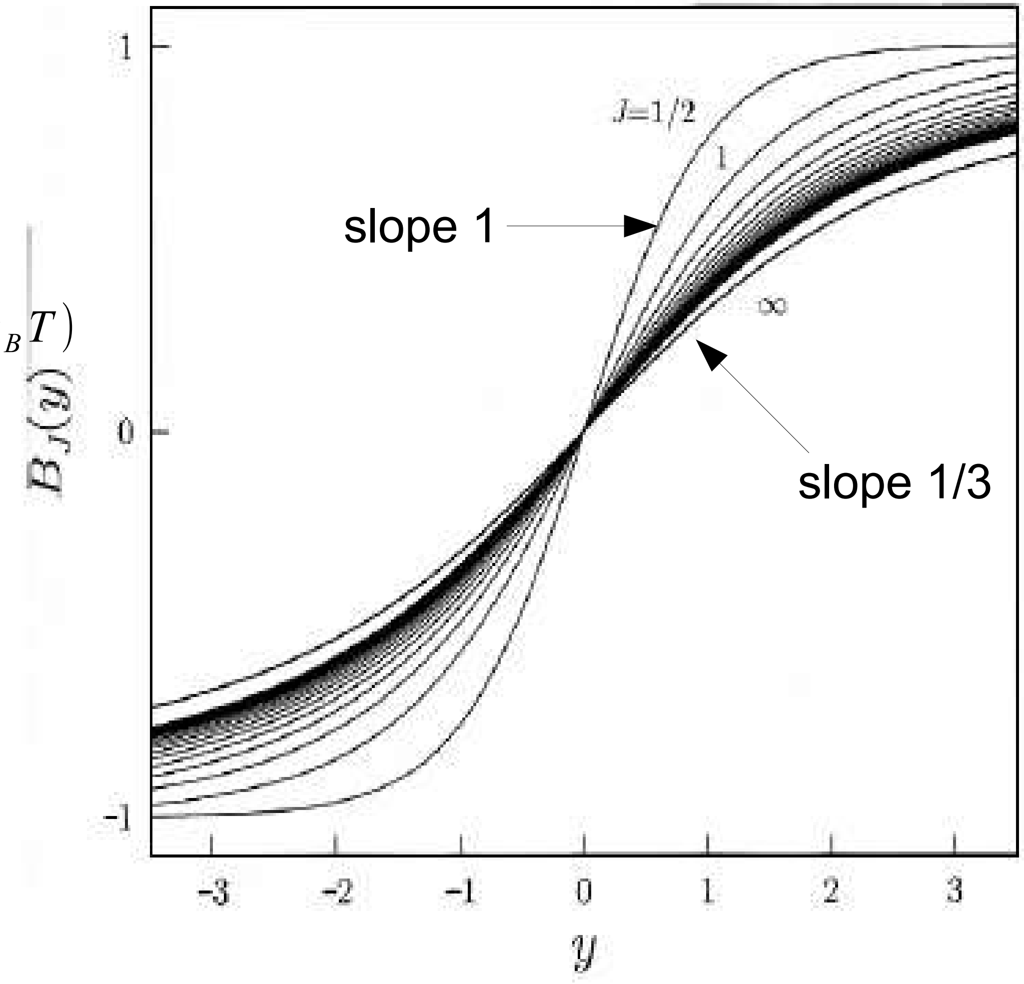
With partition function Z, the expectation value of m_J can be calculated

$$Z = \sum_{m_J=-J}^{+J} e^{m_J g_{JLS} \mu_B B / k_B T}$$

$$< m_J > = -k_B T \frac{d \ln(Z)}{d B} = g_{JLS} \mu_B J \times B_J(g_{JLS} \mu_B J B / k_B T)$$

$$B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} y\right) - \frac{1}{2J} \coth\left(\frac{y}{2J}\right)$$

$$y = \frac{g \mu_B J B}{k_B T}$$

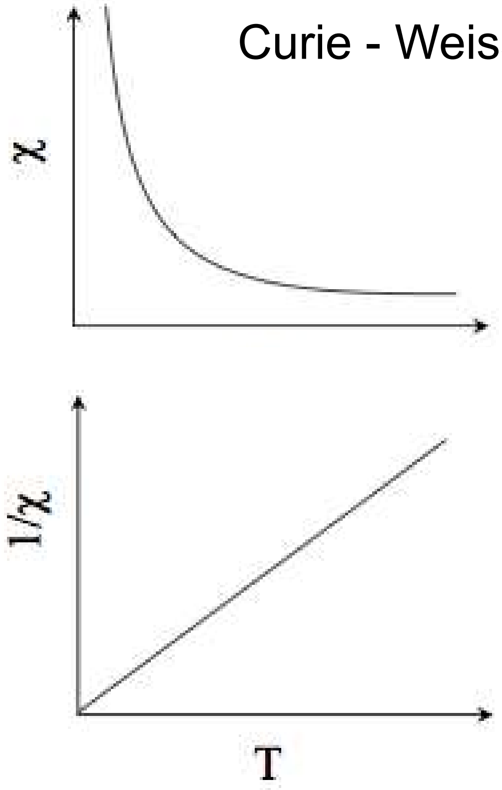


slope 1

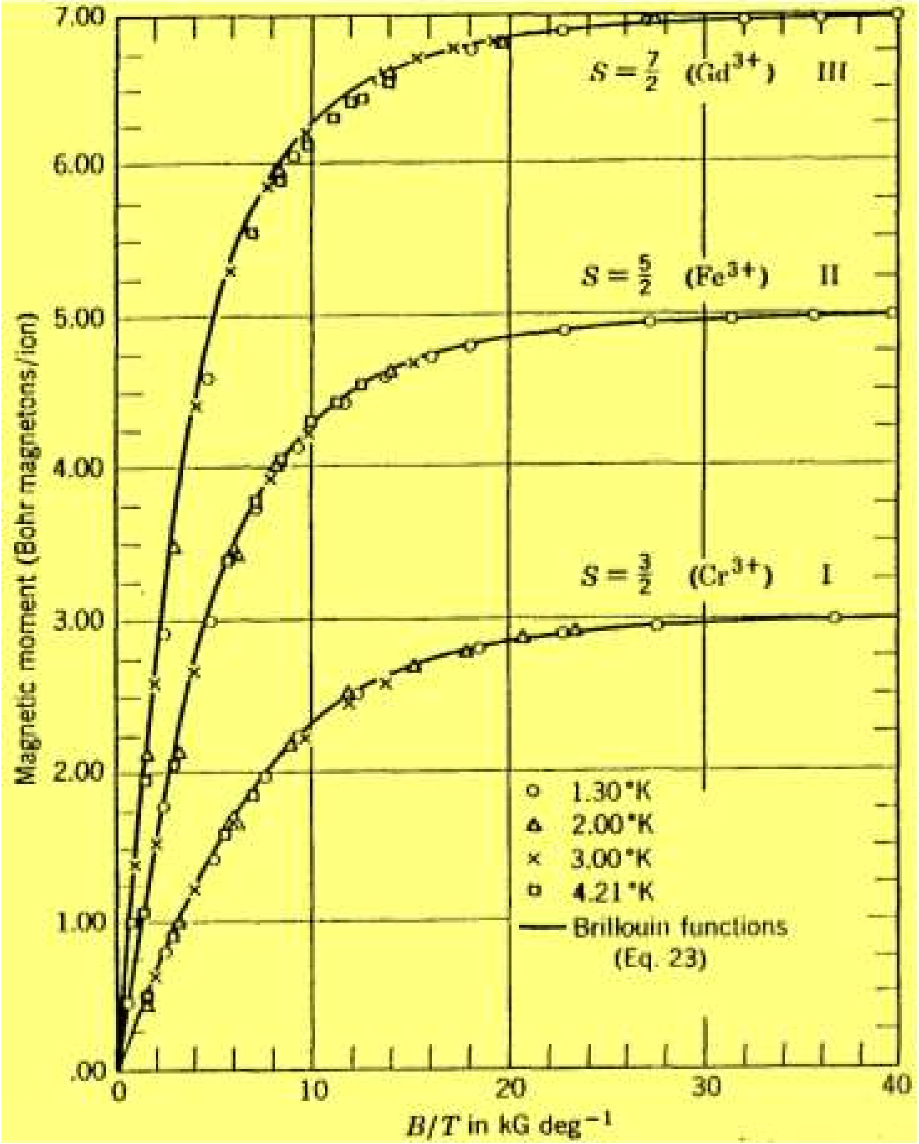
slope 1/3

The Zeeman energy and the Brillouin function

$$y=\frac{g\,\mu_B J\,B}{k_B T}$$

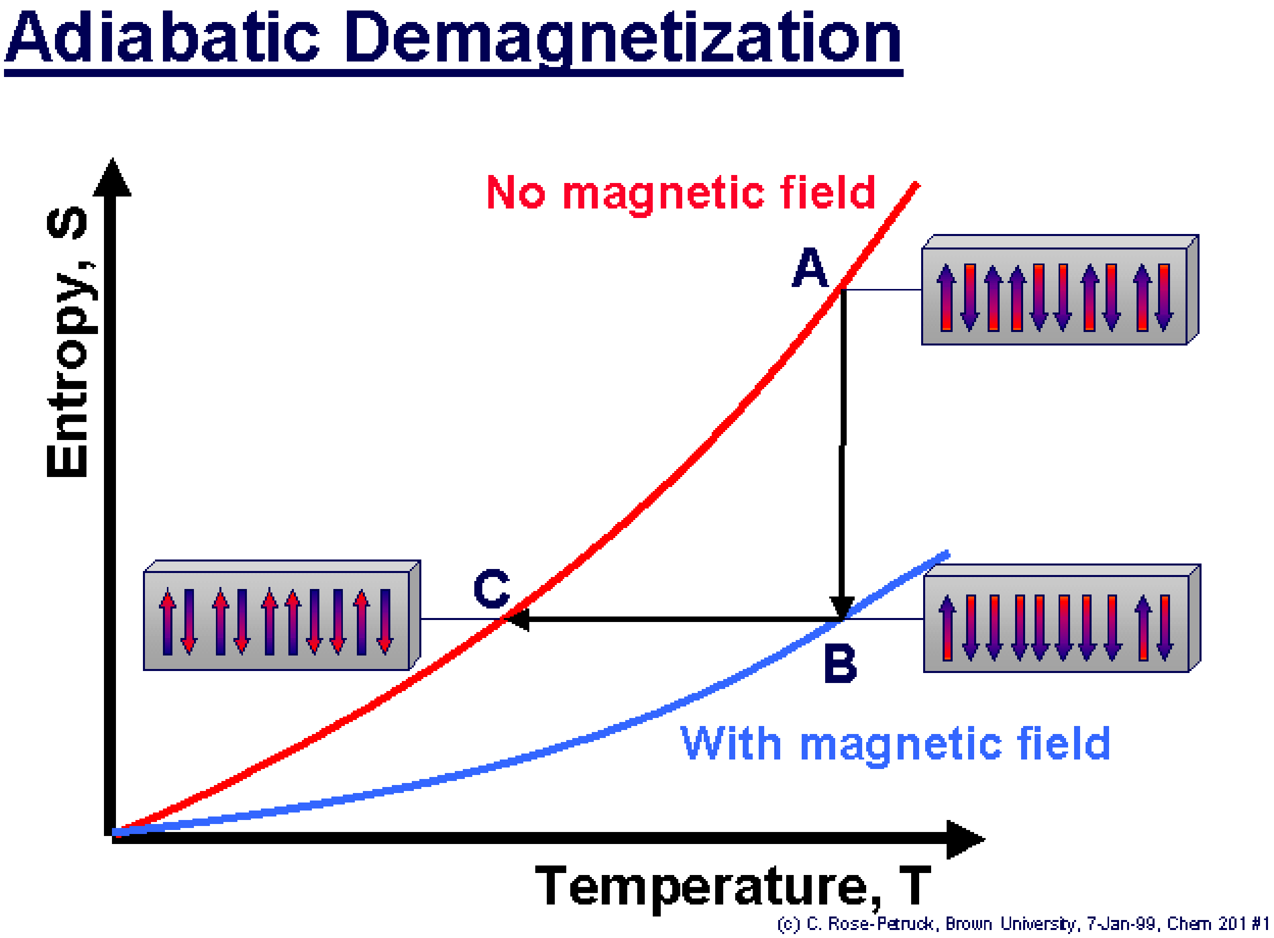


Curie - Weiss



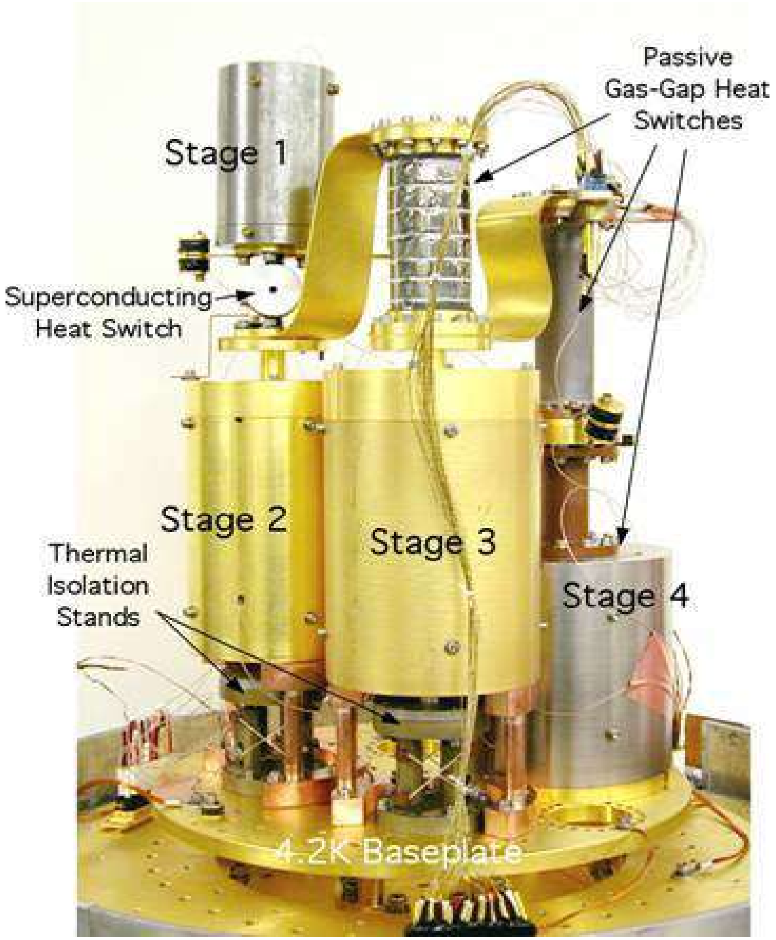
from: Kittel

Adiabatic demagnetization

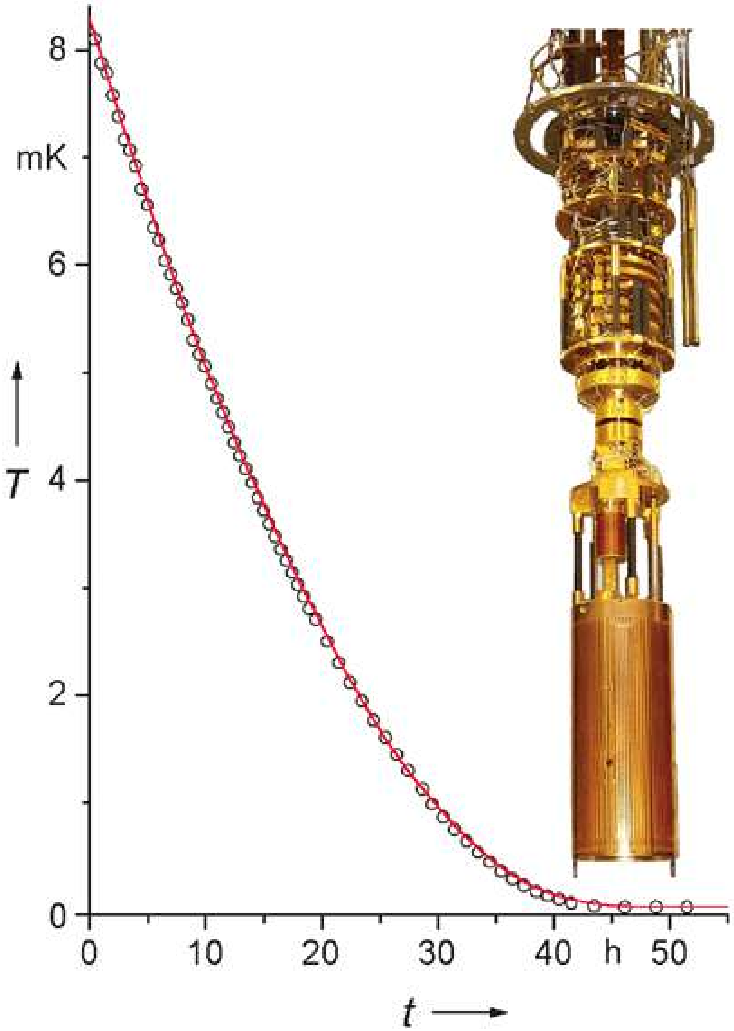


(c) C. Rose-Petruck, Brown University, 7-Jan-99, Chem 201 #1

Adiabatic demagnetization



NASA: X-ray calorimeter of the international X-ray observatory



PTB: Micro-Kelvin nuclear demagnetization of Cu

Superposition states

Eigenstates have trivial dynamics with a mere phase change of the wave function

$$\Psi = |Jm_J\!> e^{-\frac{g_{JLS} m_J B_z}{\hbar} t}$$

What about superposition states?

Example: spin ½

$$\psi = \frac{|\uparrow> + |\downarrow>}{\sqrt{2}}$$

$$< \psi|\hat{s}_z|\psi > = \frac{1}{2}\,(\,<\uparrow|\hat{s}_z|\uparrow> + \cancel{<\uparrow|\hat{s}_z|\downarrow>} + \cancel{<\downarrow|\hat{s}_z|\uparrow>} + <\downarrow|\hat{s}_z|\downarrow>\,)$$

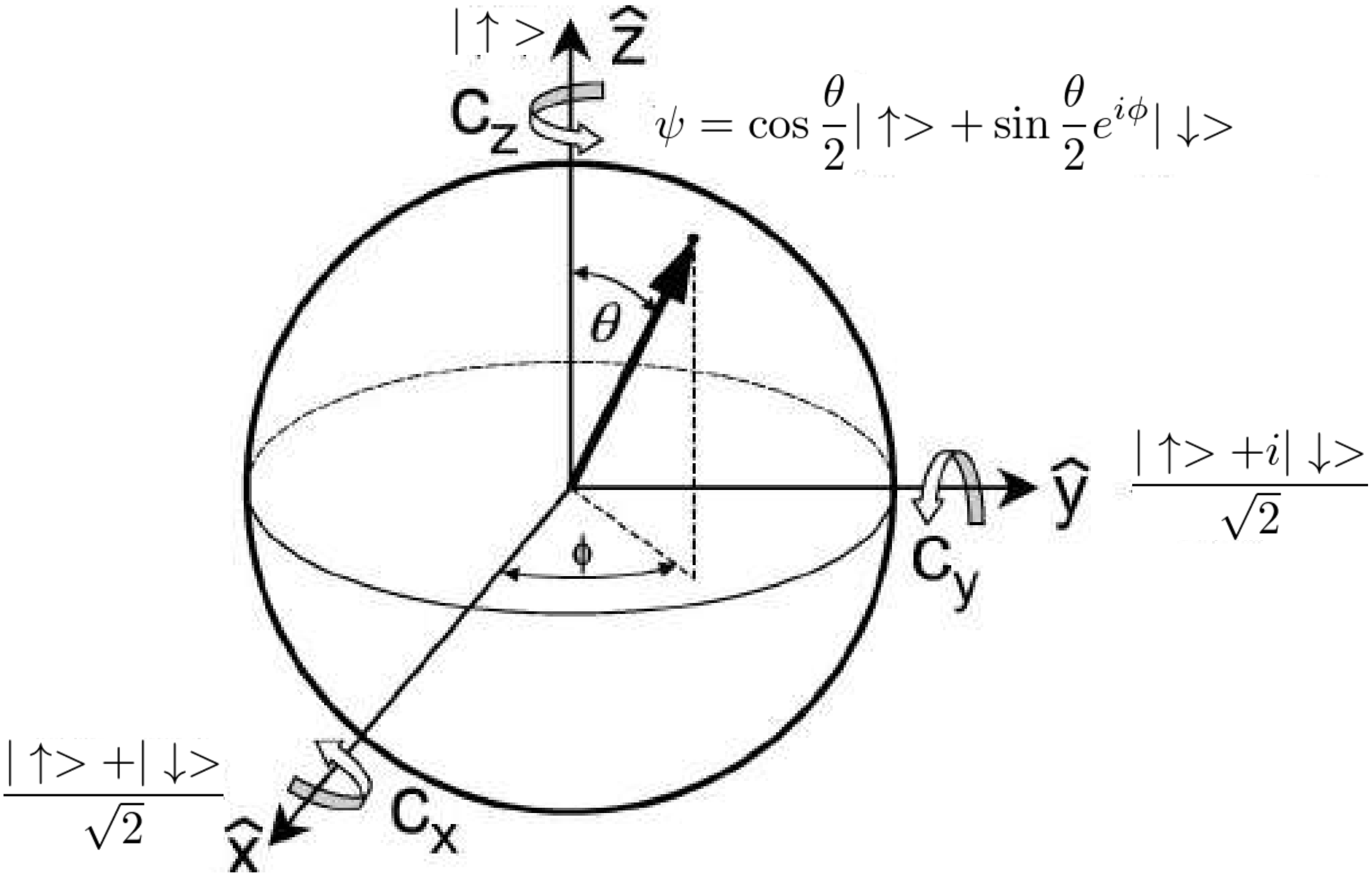
$$= \frac{1}{2}\hbar\,(1/2 + 0 + 0 - 1/2\,) = 0$$

But with $\hat{s}_x = \dfrac{\hat{s}_+ + \hat{s}_-}{2}$

$$< \psi|s_x|\psi > = \frac{1}{4}\,(\,<\uparrow|\cancel{\hat{s}_+} + \cancel{\hat{s}_-}|\uparrow> + <\uparrow|\hat{s}_+ + \cancel{\hat{s}_-}|\downarrow> + <\downarrow|\cancel{\hat{s}_+} + \hat{s}_-|\uparrow> + <\downarrow|\cancel{\hat{s}_+} + \cancel{\hat{s}_-}|\downarrow>\,)$$

$$= \frac{1}{4}\hbar\,(0 + 0 + 1 + 0 + 0 + 1 + 0 + 0\,) = \frac{1}{2}\hbar \qquad < \psi|s_y|\psi > = 0$$

Bloch sphere



$$\psi = \cos\frac{\theta}{2}|\uparrow> + \sin\frac{\theta}{2}e^{i\phi}|\downarrow>$$

Bloch sphere

Precession in magnetic field:

$$\Psi(t) = e^{-i\frac{E_\uparrow}{\hbar}t}\left(\cos\frac{\theta}{2}|\uparrow> + \sin\frac{\theta}{2}e^{i\phi_0}e^{-i\frac{E_\downarrow - E_\uparrow}{\hbar}t}|\downarrow>\right)$$

$$\phi(t) = \phi_0 - \frac{E_\downarrow - E_\uparrow}{\hbar}t = \phi_0 - \frac{g\mu_B B_z}{\hbar}t$$

Note that when you measure an ensemble of spins, you will see two effects:

- longitudinal relaxation, i.e. relaxation to the ground state by dissipation with lifetime T_1
- dephasing of the individual precession by e.g. slightly different environments with T_2

Electron paramagnetic resonance: you induce transitions between magnetic states m_J in a magnetic filed B_z and study time evolvement of superposition states

The crystal field

The electric fields of neighboring atoms can perturb the centro-symmetric potential of the free atom

The new eigenstates are thus mixtures of the free atom eigenstates

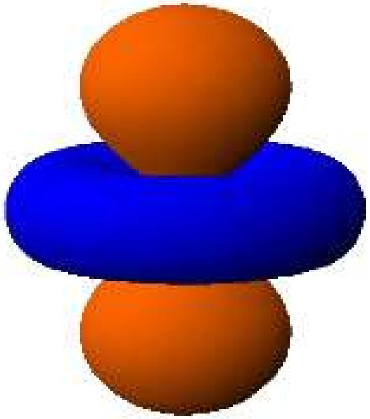
In 3d elements, the crystal field is typically larger than the spin-orbit interaction and you need to go back to L and S states

In 4f elements, the crystal field is typically smaller than the spin-orbit interaction and you can keep the J states

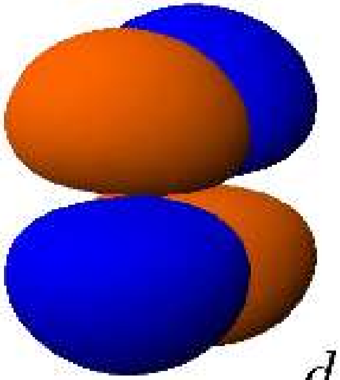
If crystal field is not too strong, the orbital states in the presence of a crystal field are states with a good L^2 but not with a good L_z

The orbital states in a cubic crystal field

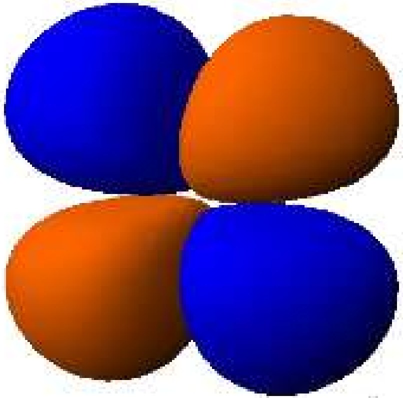
$m = 0$ $m = \pm 1$ $m = \pm 2$



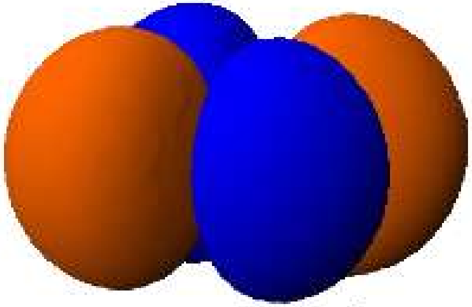
$d_{z^2} = Y_{20}$



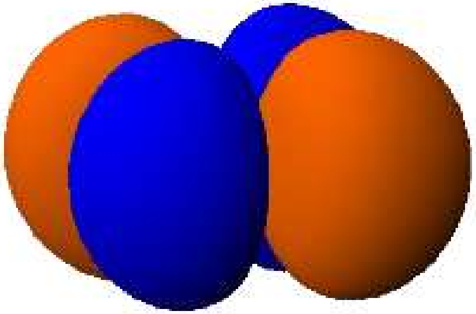
$d_{yz} = \frac{i}{\sqrt{2}}(Y_{21} - Y_{2-1})$



$d_{xz} = \frac{1}{\sqrt{2}}(-Y_{21} + Y_{2-1})$



$d_{xy} = \frac{i}{\sqrt{2}}(Y_{22} - Y_{2-2})$



$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_{22} + Y_{2-2})$

Quenching of the orbital momentum

While L^2 is not influenced $<d_{xy}|L^2|d_{xy}>=\hbar^2 L(L+1)$

L$_z$ is quenched $<d_{xy}|L_z|d_{xy}>=\frac{1}{2}(<Y_{22}|L_z|Y_{22}>+<Y_{2-2}|L_z|Y_{2-2}>)=\frac{1}{2}(2-2)=0$

So, if you apply a magnetic field along z, you see to first order no magnetic moment along z
In second order perturbation theory, you see eventually an orbital momentum

Perturbation: $V_i=\mu_B L_i B_i$ $\mu_i^o=\frac{-\delta E^o}{\delta B_i}$ $<L_i>=\frac{\delta E^o}{\mu_B \delta B_i}$

$$\vec{L}=\sum_n^{\text{excited}}\left(\frac{-2\mu_B B_x|<\psi_0|L_x|\psi_n>|^2}{E_n-E_0}\vec{x}-\frac{2\mu_B B_y|<\psi_0|L_y|\psi_n>|^2}{E_n-E_0}\vec{y}-\frac{2\mu_B B_z|<\psi_0|L_z|\psi_n>|^2}{E_n-E_0}\vec{z}\right)$$

Ψ_n : multi-electron wave function

Quenching of the orbital momentum

A closer look:

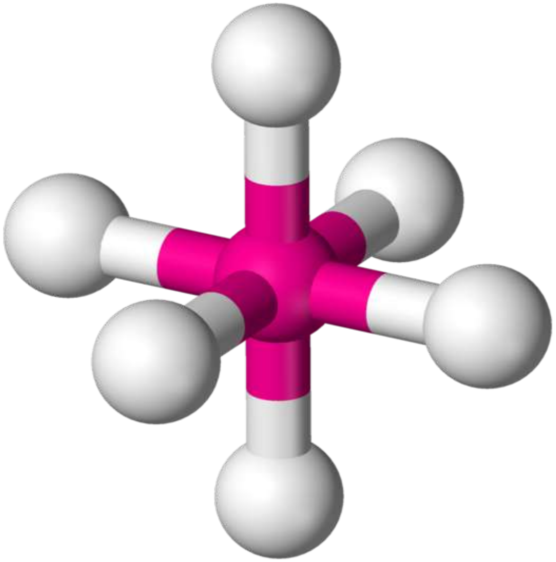
$$\vec{L} = \sum_n^{\text{excited}} \left(\frac{-2\mu_B B_x |\langle\psi_0|L_x|\psi_n\rangle|^2}{E_n - E_0}\vec{x} - \frac{2\mu_B B_y |\langle\psi_0|L_y|\psi_n\rangle|^2}{E_n - E_0}\vec{y} - \frac{2\mu_B B_z |\langle\psi_0|L_z|\psi_n\rangle|^2}{E_n - E_0}\vec{z} \right)$$

L_z can only be caused by mixing of states that contain same L_z components

d_{xz}, d_{yz} and $d_{xy}, d_{x^2-y^2}$

L_x or L_y can only be caused by mixing of states that contain L_z components that differ by one as L_x and L_y can be written as superpositions of L_- and L_+

Crystal field splitting in an octahedral crystal field



e_g:

$$e_1 = d_{z^2} = Y_{20}$$

$$e_2 = d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_{22} + Y_{2-2})$$

fully quenched

t_{2g}:

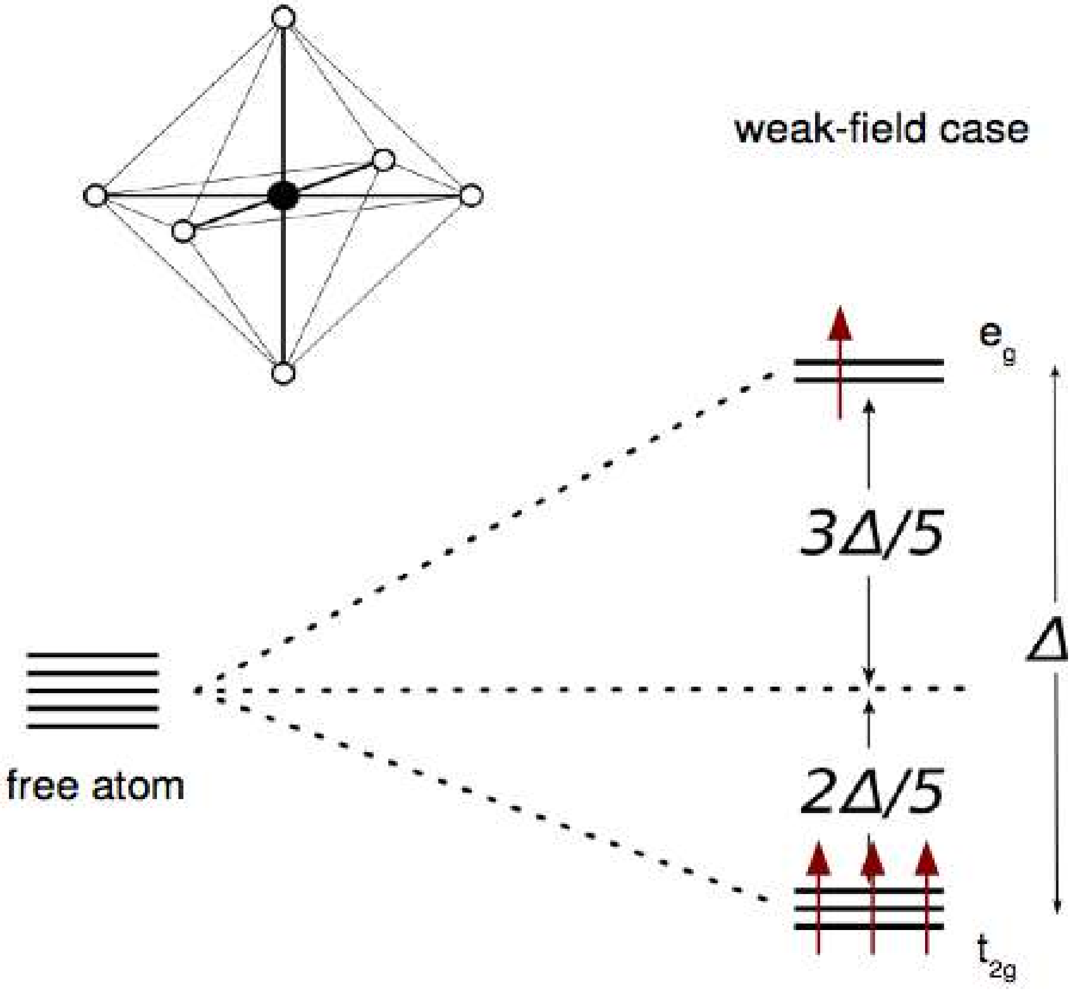
$$t_1 = \frac{1}{\sqrt{2}}(d_{xz} - id_{yz}) = Y_{2-1}$$

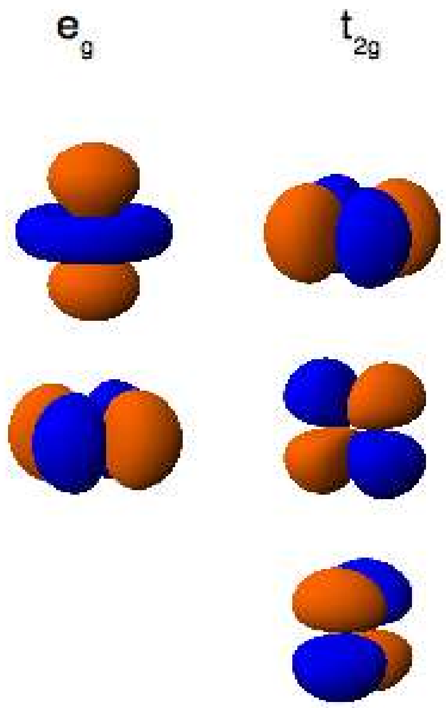
$$t_2 = \frac{1}{\sqrt{2}}(-id_{xz} + d_{yz}) = Y_{21}$$

$$t_3 = d_{xy} = \frac{-i}{\sqrt{2}}(Y_{22} - Y_{2-2})$$

partially quenched

Weak octahedral crystal field

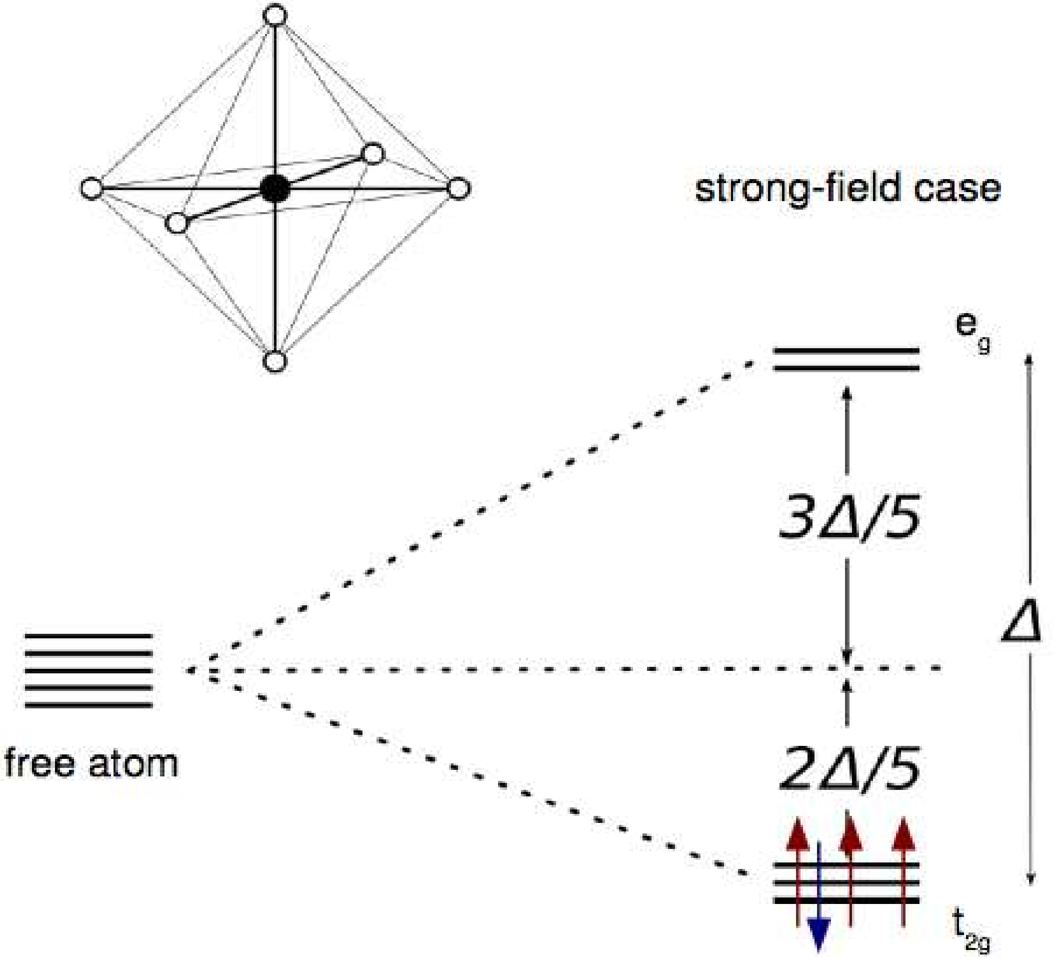


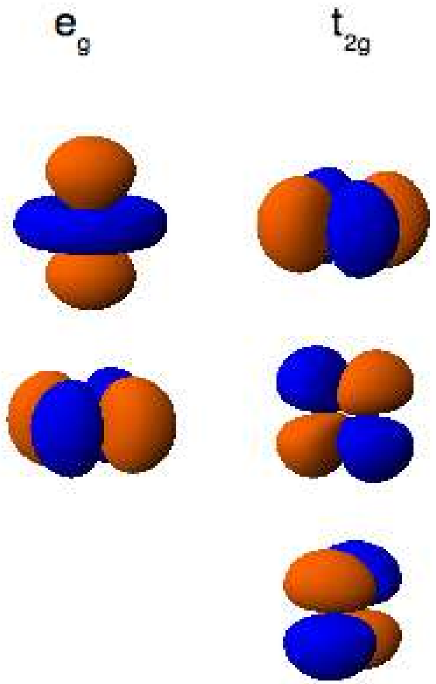


L quenched

Hund´s rules hold: S=2

Strong octahedral crystal field



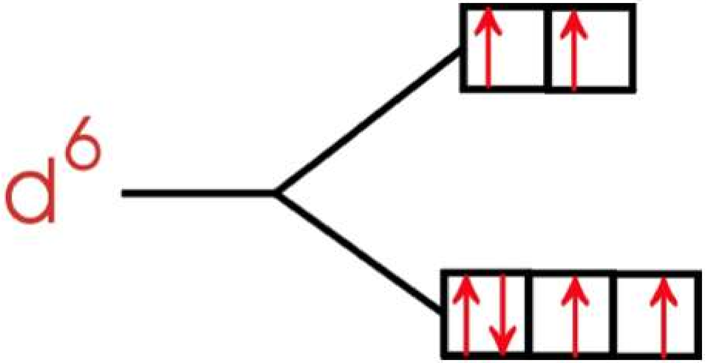


Degenerate ground state!
L is not fully quenched

Hund´s rules fail: S=1

High-spin low-spin transitions

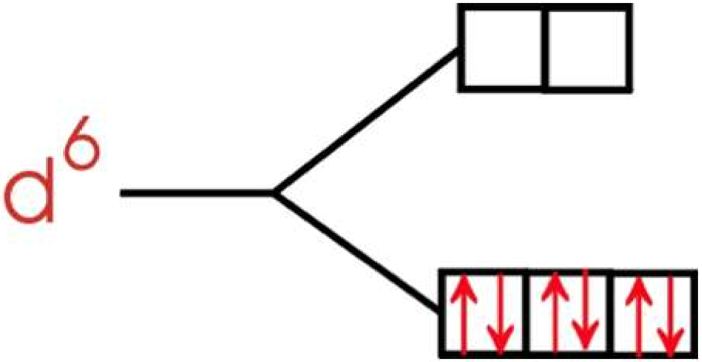
High spin



S=2

Fe^{2+}

Low spin



S=0

Stevens operators

$$H_{CF} = -e\sum_{i=1}^{N} V\left(\vec{r}_i\right) \Longrightarrow H_{CF} = \sum_{n=0}^{\infty}\left(B_n^0 O_n^0 + \sum_{m=1}^{n} B_n^m O_n^m + \sum_{m=1}^{n} \tilde{B}_n^m \tilde{O}_n^m\right)$$

$B_n^m, \tilde{B}_n^m$: Crystal field parameters O_n^0: only J_z up to power n (and J)

$O_n^m, \tilde{O}_n^m$: Stevens' Operators $O_n^m, \tilde{O}_n^m$: also $\left(J_\pm\right)^m$

Which terms contribute?

- No terms with odd n (time reversal symmetry)
- No terms with n>2J (2J+1 states in the multiplet)
- 3d: choose J=S, n=4 / 4f: choose J, n=6
- No terms with n>2l (crystal field acts on l)
- Specific symmetry of the crystal field
- Mirror plane eliminates all $\tilde{O}_n^m$

Stevens operators

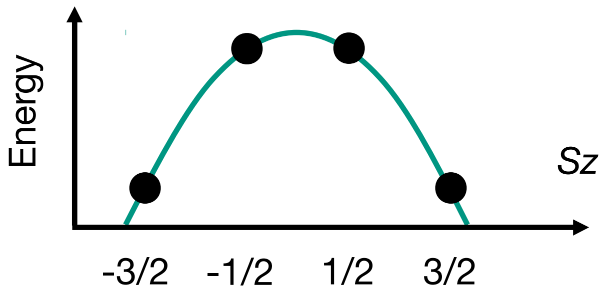
$$
\begin{aligned}
O^s_{22} &= \frac{-i}{2}[J_+^2 - J_-^2] = J_xJ_y + J_yJ_x = 2P_{xy} \\
O^s_{21} &= \frac{-i}{4}[J_z(J_+ - J_-) + (J_+ - J_-)J_z] = \frac{1}{2}[J_yJ_z + J_zJ_y] = P_{yz} \\
O_{20} &= [3J_z^2 - X] \\
O_{21} &= \frac{1}{4}[J_z(J_+ + J_-) + (J_+ + J_-)J_z] = \frac{1}{2}[J_xJ_z + J_zJ_x] = P_{xz} \\
O_{22} &= \frac{1}{2}[J_+^2 + J_-^2] = J_x^2 - J_y^2
\end{aligned}
$$

$$
\begin{aligned}
O^s_{44} &= \frac{-i}{2}[(J_+^4 - J_-^4] \\
O^s_{43} &= \frac{-i}{4}[(J_+^3 - J_-^3)J_z + J_z(J_+^3 - J_-^3)] \\
O^s_{42} &= \frac{-i}{4}[(J_+^2 - J_-^2)(7J_z^2 - X - 5) + (7J_z^2 - X - 5)(J_+^2 - J_-^2)] \\
O^s_{41} &= \frac{-i}{4}[(J_+ - J_-)(7J_z^3 - (3X+1)J_z) + (7J_z^3 - (3X+1)J_z)(J_+ - J_-)] \\
O_{40} &= [35J_z^4 - (30X - 25)J_z^2 + 3X^2 - 6X] \\
O_{41} &= \frac{1}{4}[(J_+ + J_-)(7J_z^3 - (3X+1)J_z) + (7J_z^3 - (3X+1)J_z)(J_+ + J_-)] \\
O_{42} &= \frac{1}{4}[(J_+^2 + J_-^2)(7J_z^2 - X - 5) + (7J_z^2 - X - 5)(J_+^2 + J_-^2)] \\
O_{43} &= \frac{1}{4}[(J_+^3 + J_-^3)J_z + J_z(J_+^3 + J_-^3)] \\
O_{44} &= \frac{1}{2}[(J_+^4 + J_-^4]
\end{aligned}
$$

$$
\begin{aligned}
O^s_{66} &= \frac{-i}{2}[J_+^6 - J_-^6] \\
O^s_{65} &= \frac{-i}{4}[(J_+^5 - J_-^5)J_z + J_z(J_+^5 - J_-^5)] \\
O^s_{64} &= \frac{-i}{4}[(J_+^4 - J_-^4)(11J_z^2 - X - 38) + (11J_z^2 - X - 38)(J_+^4 - J_-^4)] \\
O^s_{63} &= \frac{-i}{4}[(J_+^3 - J_-^3)(11J_z^3 - (3X+59)J_z) + (11J_z^3 - (3X+59)J_z)(J_+^3 - J_-^3)] \\
O^s_{62} &= \frac{-i}{4}[(J_+^2 - J_-^2)\{33J_z^4 - (18X+123)J_z^2 + X^2 + 10X + 102\} + \{\ldots\}(J_+^2 - J_-^2)] \\
O^s_{61} &= \frac{-i}{4}[(J_+ - J_-)\{33J_z^5 - (30X-15)J_z^3 + (5X^2 - 10X + 12)J_z\} + \{\ldots\}(J_+ - J_-)] \\
O_{60} &= [231J_z^6 - (315X - 735)J_z^4 + (105X^2 - 525X + 294)J_z^2 - 5X^3 + 40X^2 - 60X] \\
O_{61} &= \frac{1}{4}[(J_+ + J_-)\{33J_z^5 - (30X-15)J_z^3 + (5X^2 - 10X + 12)J_z\} + \{\ldots\}(J_+ + J_-)] \\
O_{62} &= \frac{1}{4}[(J_+^2 + J_-^2)\{33J_z^4 - (18X+123)J_z^2 + X^2 + 10X + 102\} + \{\ldots\}(J_+^2 + J_-^2)] \\
O_{63} &= \frac{1}{4}[(J_+^3 + J_-^3)(11J_z^3 - (3X+59)J_z) + (11J_z^3 - (3X+59)J_z)(J_+^3 + J_-^3)] \\
O_{64} &= \frac{1}{4}[(J_+^4 + J_-^4)(11J_z^2 - X - 38) + (11J_z^2 - X - 38)(J_+^4 + J_-^4)] \\
O_{65} &= \frac{1}{4}[(J_+^5 + J_-^5)J_z + J_z(J_+^5 + J_-^5)] \\
O_{66} &= \frac{1}{2}[J_+^6 + J_-^6]
\end{aligned}
$$

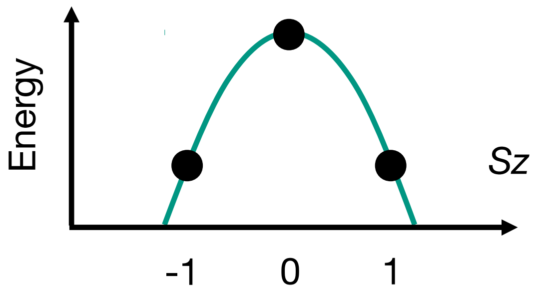
Zero filed splitting

Co^{2+}, S = 3/2 (4 states)



$$O_2^0 \propto \hat{S}_z^2$$

Ni^{2+}, S = 1 (3 states)



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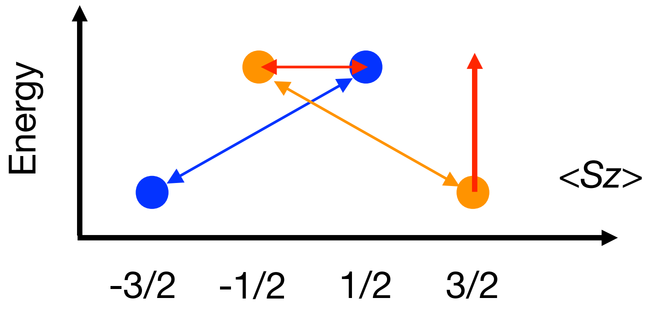
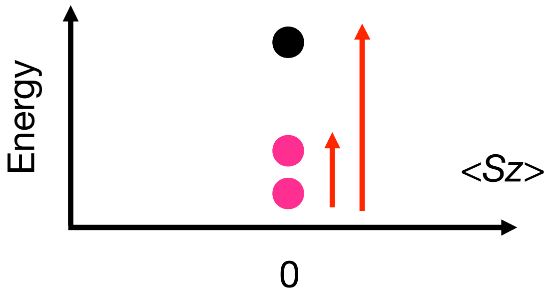


$$O_2^2 \propto \hat{S}_+^2 + \hat{S}_-^2$$

$\Delta Sz = \pm 2$



Ways to determine the crystal field parameters

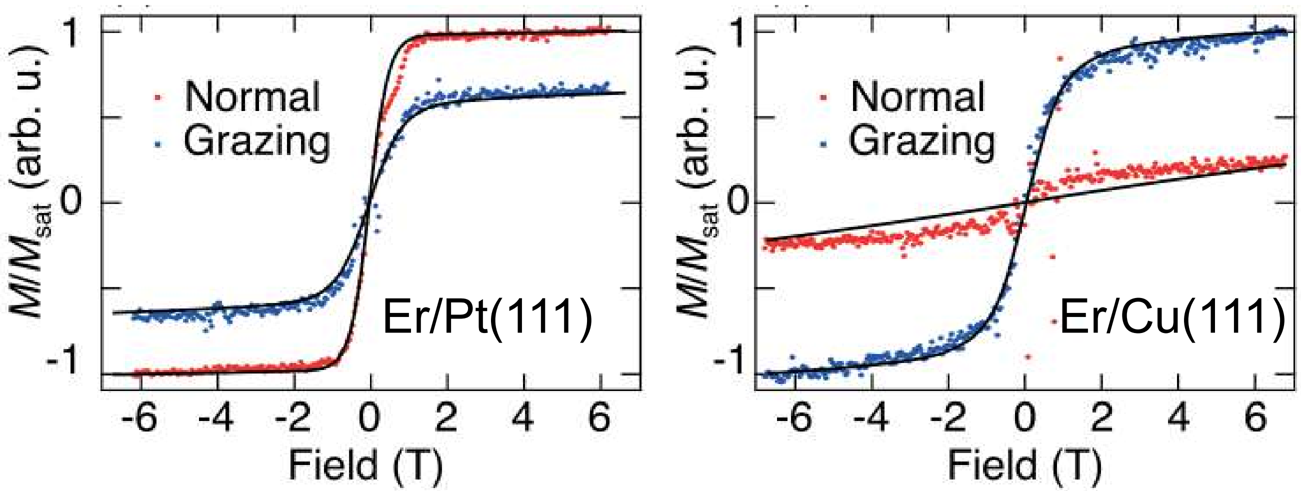
Solve the crystal field + Zeeman Hamiltonian: $\hat{H}_J = \hat{H}_{CF} + g_{JLS}\mu_B \frac{\hat{J}}{\hbar} B$

Compute partition function: $Z = \sum_{2J+1} e^{\frac{E_i}{K_B T}}$

Compute magnetic moment: $<\mu> = -k_B T \frac{\partial ln(Z)}{\partial B}$

Fit to experimental data of magnetization

Use different directions of magnetic field (easy and hard directions)



B^2_0=-96μeV for Pt(111)
Easy axis along z

B^2_0=96μeV for Cu(111)
Easy plane

Donatti et al. PRL 2014