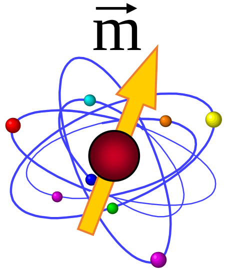
Lecture 2

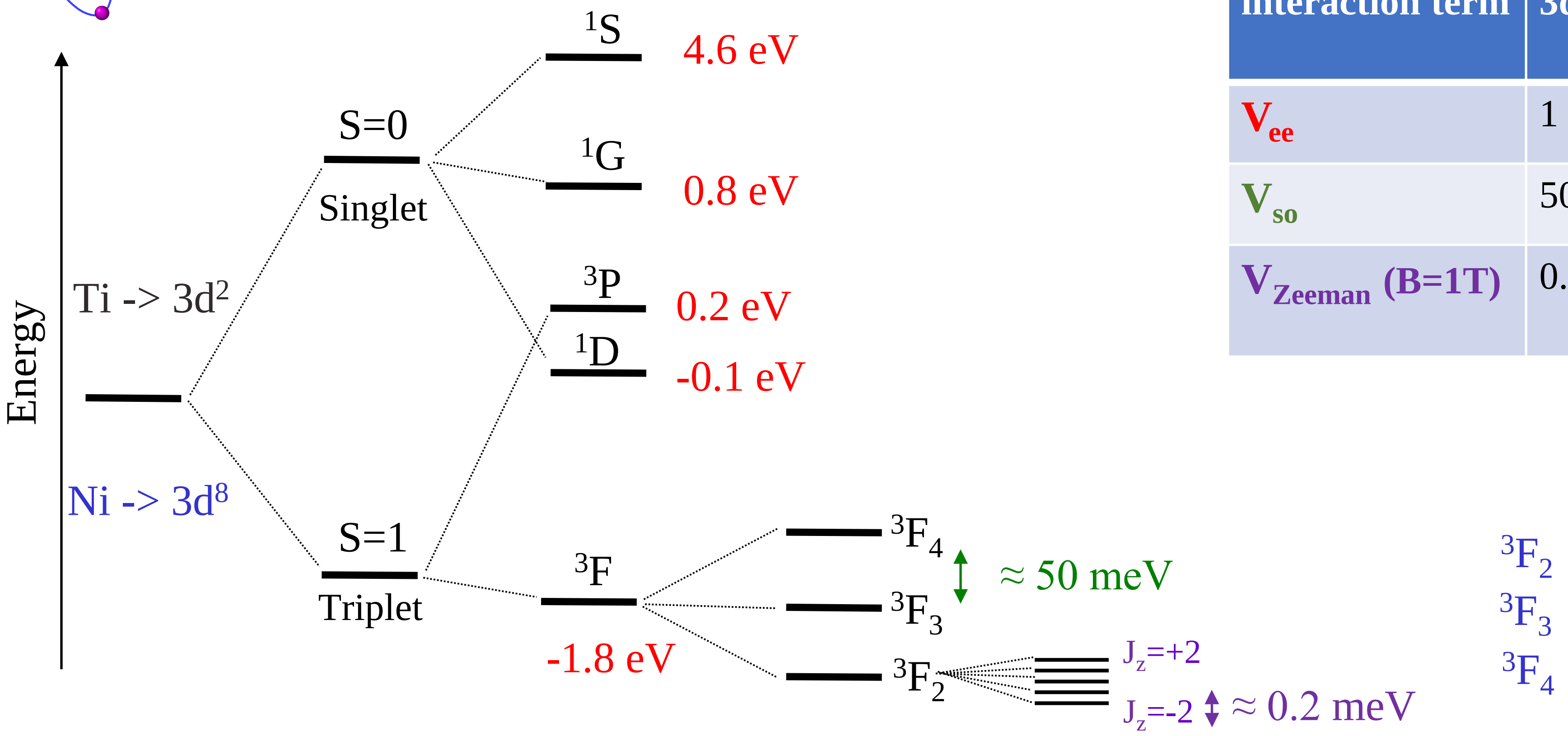
From atom to bulk magnetism

Energy spectrum of an isolated 3d atom



$$H_{atom} = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2me} + eV(r_i)\right) + \sum_{i<j}^{Z} \frac{e^2}{|r_i - r_j|} + \sum_{i=1}^{Z} (\boldsymbol{l}_i \cdot \boldsymbol{s}_i)\, \xi_{nl}(r_i) + \mu_B(\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{B} = H_C + V_{ee} + V_{so} + V_{Zeeman}$$

interaction term	3d transition metals	4f rare earths
V_{ee}	1 eV	1eV
V_{so}	50-100 meV	300-500 meV
V_{Zeeman} (B=1T)	0.1 -0.2 meV	0.1 -0.6 meV


Energy

Ti -> $3d^2$

Ni -> $3d^8$

S=0

Singlet

S=1

Triplet

^1S 4.6 eV

^1G 0.8 eV

^3P 0.2 eV

^1D -0.1 eV

^3F -1.8 eV

$^3F_4$

$^3F_3$

$^3F_2$

≈ 50 meV

$J_z=+2$

$J_z=-2$ ≈ 0.2 meV

$^3F_2$

$^3F_3$

$^3F_4$

$$V_{ee} = \sum_{i<j}^{Z} \frac{e^2}{|r_i - r_j|}$$

$$V_{SO} = \sum_{i=1}^{Z} (\boldsymbol{l}_i \cdot \boldsymbol{s}_i)\xi(r_i)$$

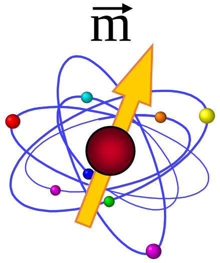
$$V_{Zee} = \mu_B(\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{B}$$

Hund's rules → max. S max. L min. J (band less than half filled) max. J (band more than half filled)

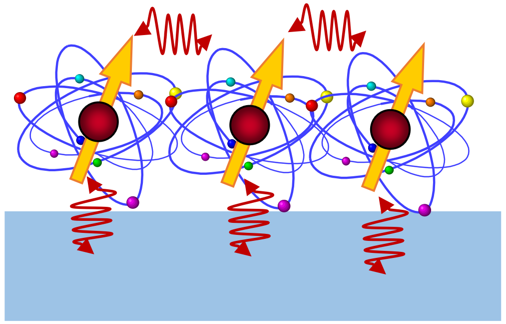
Spectroscopic notation of multiplets terms: $^{2S+1}X_J$ with X= S, P, D, F, G, H, I, … for L = 0, 1, 2, 3, 4, 5, 6, …

The spintronics “goose game”

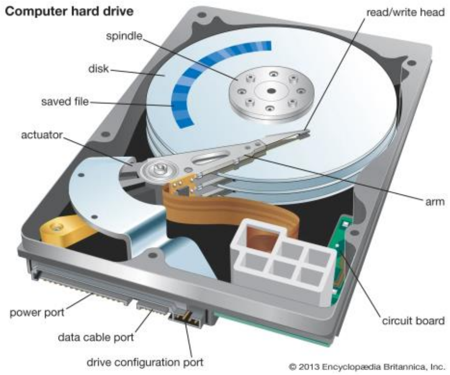
Atom magnetism

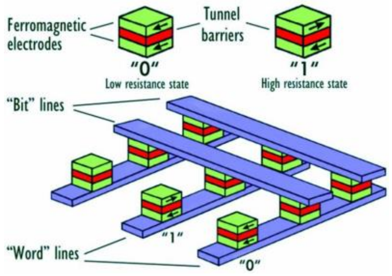


interactions between spins and with the supporting substrate

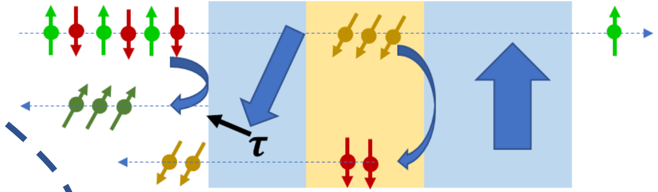


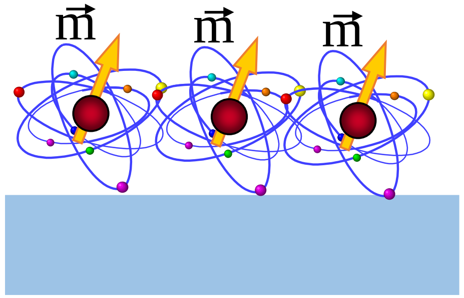
applications



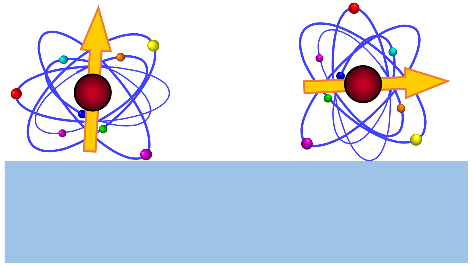


STT - SOT

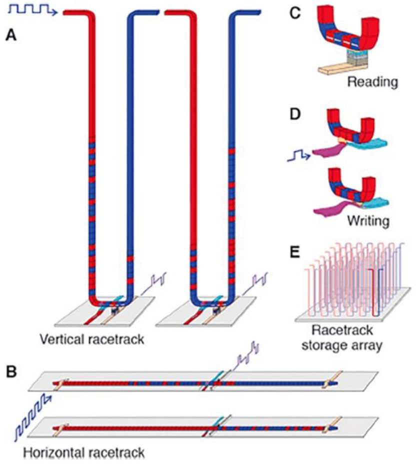




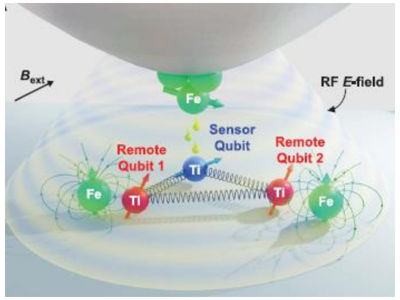
magnetic moment in a cluster and/or on a support

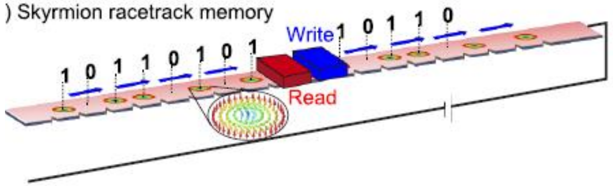


Magnetization easy axis



Future

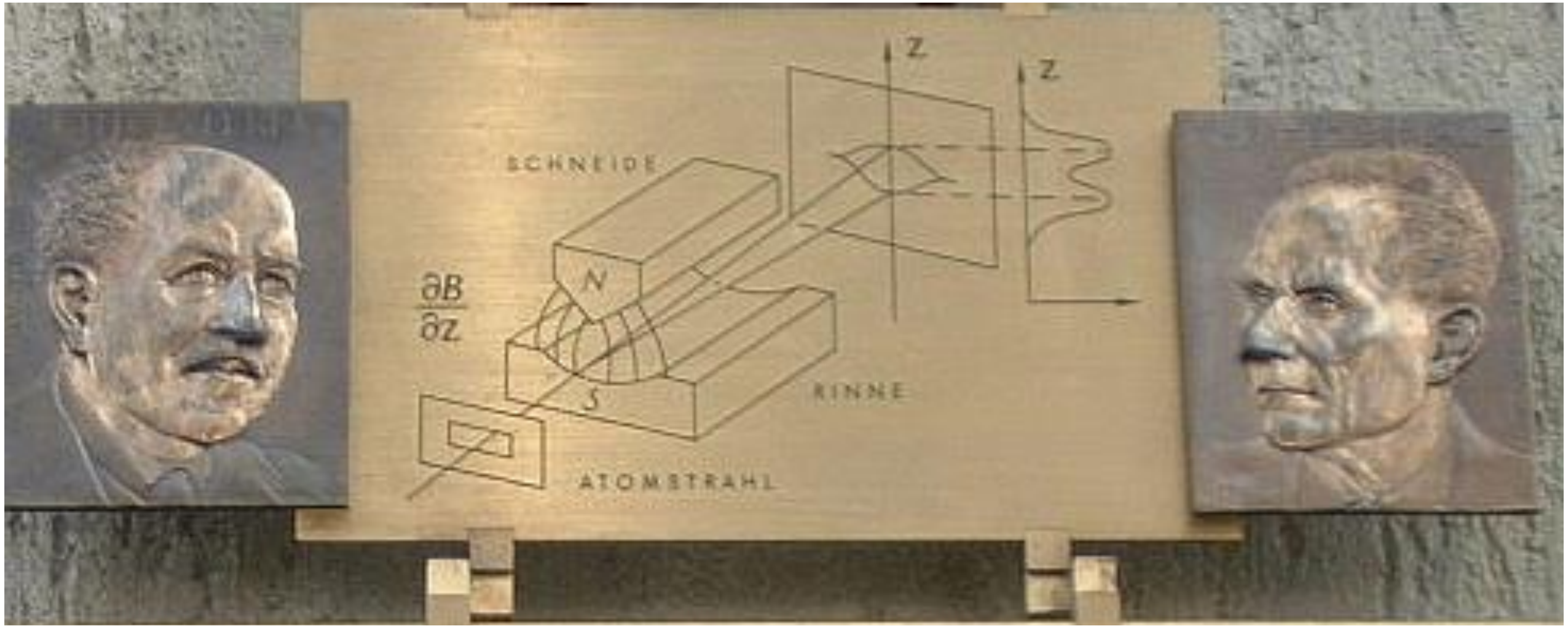




Stern-Gerlach experiment

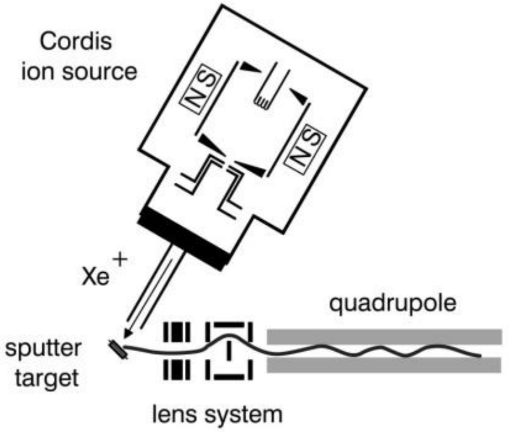
Beam of Ag atoms through a non-uniform magnetic field: the atoms deviate depending on their spin moment

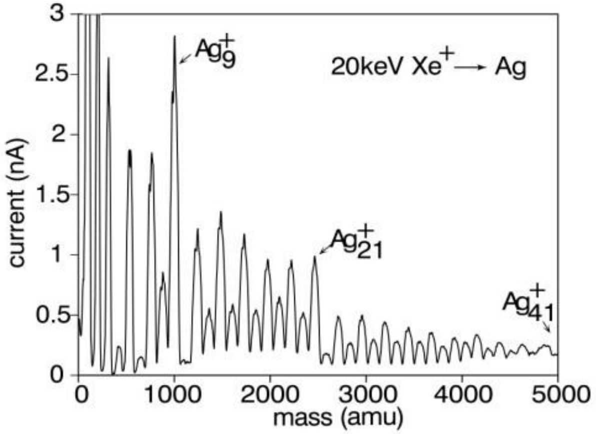
Ag: [Kr] $4d^{10}\ 5s^1$ → $L = 0;\ S = 1/2,\ S_z = J_z = \pm 1/2$

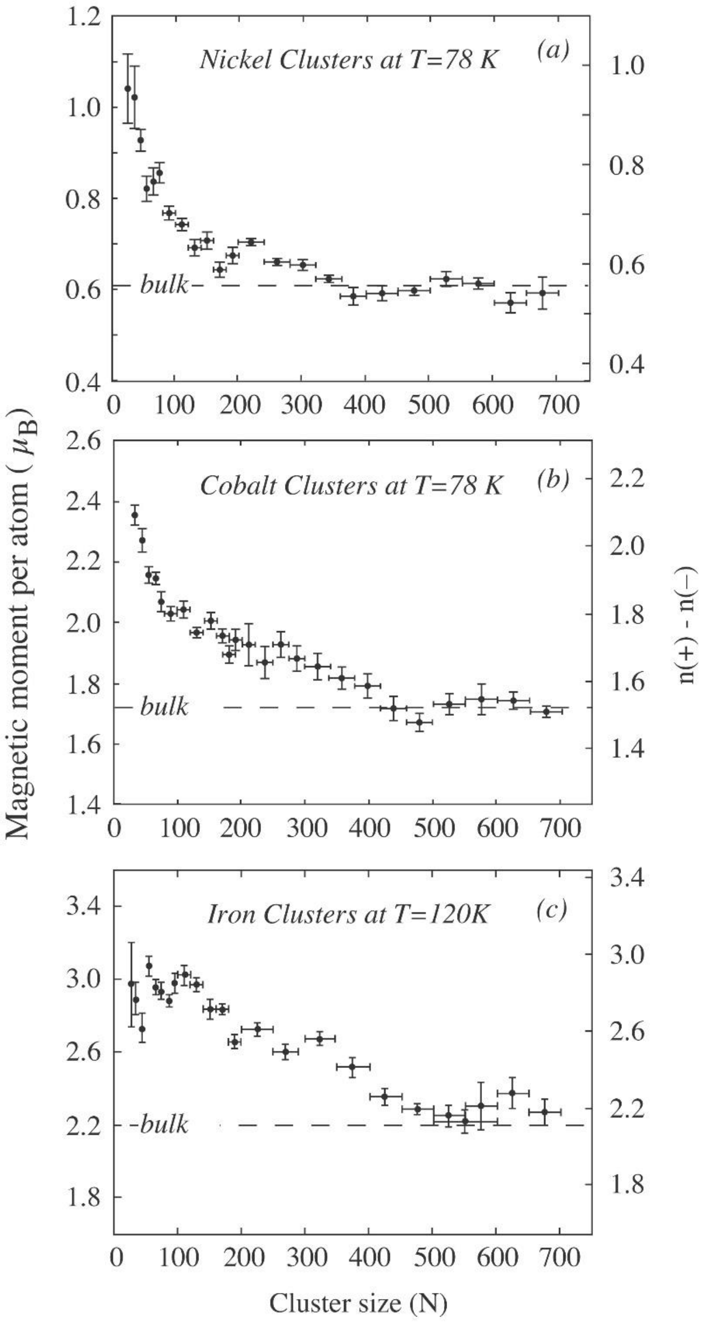


Same experiment with an Ag cluster would produce a single spot !!!

Stern-Gerlach experiment with 3d metals clusters



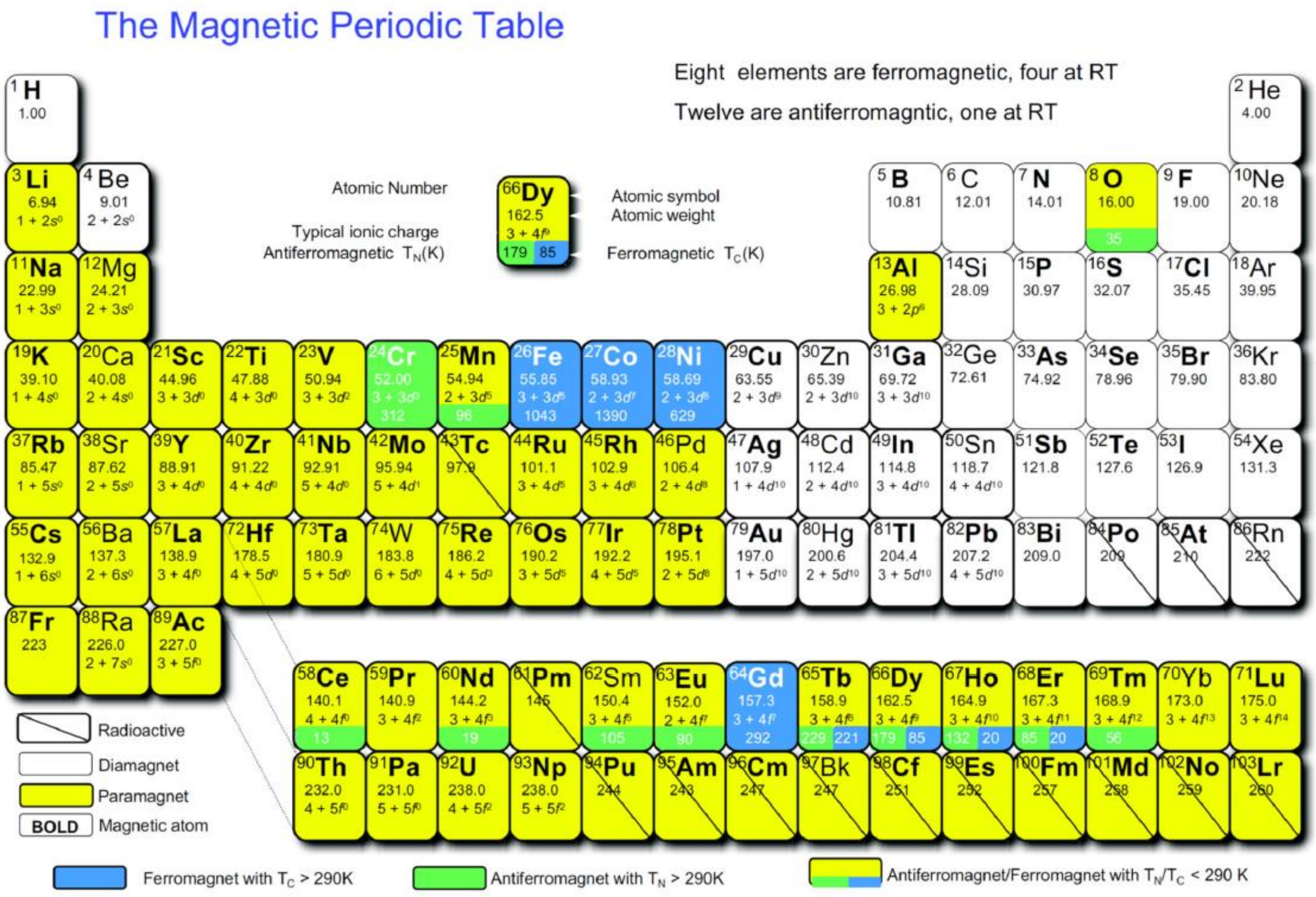




Below about 200-300 atoms per cluster the magnetic moment strongly increases with respect to bulk values

I.M.L. Billas, A. Châtelain, W.A. de Heer, Science **265**, 1682 (1994).

Magnetic moment in solids



The Magnetic Periodic Table

Eight elements are ferromagnetic, four at RT

Twelve are antiferromagntic, one at RT

Atomic Number
Typical ionic charge
Antiferromagnetic T_N(K)

66 Dy
162.5
3 + $4f^9$
179 85

Atomic symbol
Atomic weight
Ferromagnetic T_C(K)

1 **H** 1.00																	2 He 4.00
3 **Li** 6.94 1 + $2s^0$	4 Be 9.01 2 + $2s^0$											5 **B** 10.81	6 C 12.01	7 **N** 14.01	8 **O** 16.00 35	9 **F** 19.00	10 Ne 20.18
11 **Na** 22.99 1 + $3s^0$	12 Mg 24.21 2 + $3s^0$											13 **Al** 26.98 3 + $2p^6$	14 Si 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 Ar 39.95
19 **K** 39.10 1 + $4s^0$	20 Ca 40.08 2 + $4s^0$	21 **Sc** 44.96 3 + $3d^0$	22 **Ti** 47.88 4 + $3d^0$	23 **V** 50.94 3 + $3d^2$	24 **Cr** 52.00 3 + $3d^3$ 312	25 **Mn** 54.94 2 + $3d^5$ 96	26 **Fe** 55.85 3 + $3d^5$ 1043	27 **Co** 58.93 2 + $3d^7$ 1390	28 **Ni** 58.69 2 + $3d^8$ 629	29 **Cu** 63.55 2 + $3d^9$	30 Zn 65.39 2 + $3d^{10}$	31 **Ga** 69.72 3 + $3d^{10}$	32 Ge 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 Kr 83.80
37 **Rb** 85.47 1 + $5s^0$	38 Sr 87.62 2 + $5s^0$	39 **Y** 88.91 3 + $4d^0$	40 **Zr** 91.22 4 + $4d^0$	41 **Nb** 92.91 5 + $4d^0$	42 **Mo** 95.94 5 + $4d^1$	43 **Tc** 97.9	44 **Ru** 101.1 3 + $4d^5$	45 **Rh** 102.9 3 + $4d^6$	46 Pd 106.4 2 + $4d^8$	47 **Ag** 107.9 1 + $4d^{10}$	48 Cd 112.4 2 + $4d^{10}$	49 **In** 114.8 3 + $4d^{10}$	50 Sn 118.7 4 + $4d^{10}$	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 Xe 131.3
55 **Cs** 132.9 1 + $6s^0$	56 Ba 137.3 2 + $6s^0$	57 **La** 138.9 3 + $4f^0$	72 **Hf** 178.5 4 + $5d^0$	73 **Ta** 180.9 5 + $5d^0$	74 W 183.8 6 + $5d^0$	75 **Re** 186.2 4 + $5d^3$	76 **Os** 190.2 3 + $5d^5$	77 **Ir** 192.2 4 + $5d^5$	78 **Pt** 195.1 2 + $5d^8$	79 **Au** 197.0 1 + $5d^{10}$	80 Hg 200.6 2 + $5d^{10}$	81 **Tl** 204.4 3 + $5d^{10}$	82 **Pb** 207.2 4 + $5d^{10}$	83 **Bi** 209.0	84 **Po** 209	85 **At** 210	86 Rn 222
87 **Fr** 223	88 Ra 226.0 2 + $7s^0$	89 **Ac** 227.0 3 + $5f^0$															
				58 **Ce** 140.1 4 + $4f^0$ 13	59 **Pr** 140.9 3 + $4f^2$	60 **Nd** 144.2 3 + $4f^3$ 19	61 **Pm** 145	62 Sm 150.4 3 + $4f^5$ 105	63 **Eu** 152.0 2 + $4f^7$ 90	64 **Gd** 157.3 3 + $4f^7$ 292	65 **Tb** 158.9 3 + $4f^8$ 229 221	66 **Dy** 162.5 3 + $4f^9$ 179 85	67 **Ho** 164.9 3 + $4f^{10}$ 132 20	68 **Er** 167.3 3 + $4f^{11}$ 85 20	69 **Tm** 168.9 3 + $4f^{12}$ 56	70 Yb 173.0 3 + $4f^{13}$	71 **Lu** 175.0 3 + $4f^{14}$
				90 **Th** 232.0 4 + $5f^0$	91 **Pa** 231.0 5 + $5f^0$	92 **U** 238.0 4 + $5f^2$	93 **Np** 238.0 5 + $5f^2$	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 Bk 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 260

▨ Radioactive
☐ Diamagnet
🟨 Paramagnet
BOLD Magnetic atom

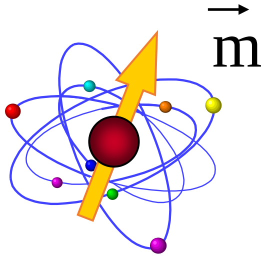
🟦 Ferromagnet with T_C > 290K
🟩 Antiferromagnet with T_N > 290K
🟨 Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

J.M.D. Coey, *Magnetism and magnetic materials* (Cambridge Univ. Press)

- Bulk (at room T): only a few elements (Fe, Co, and Ni) have a magnetic moment
- Atomic scale: all atoms except noble gas have a magnetic moment (due to unfilled electronic shells)

Atom *vs* bulk

atom



CF = 0
(the 3d orbitals are
degenerate)

d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{xy}, $d_{3z^2-r^2}$

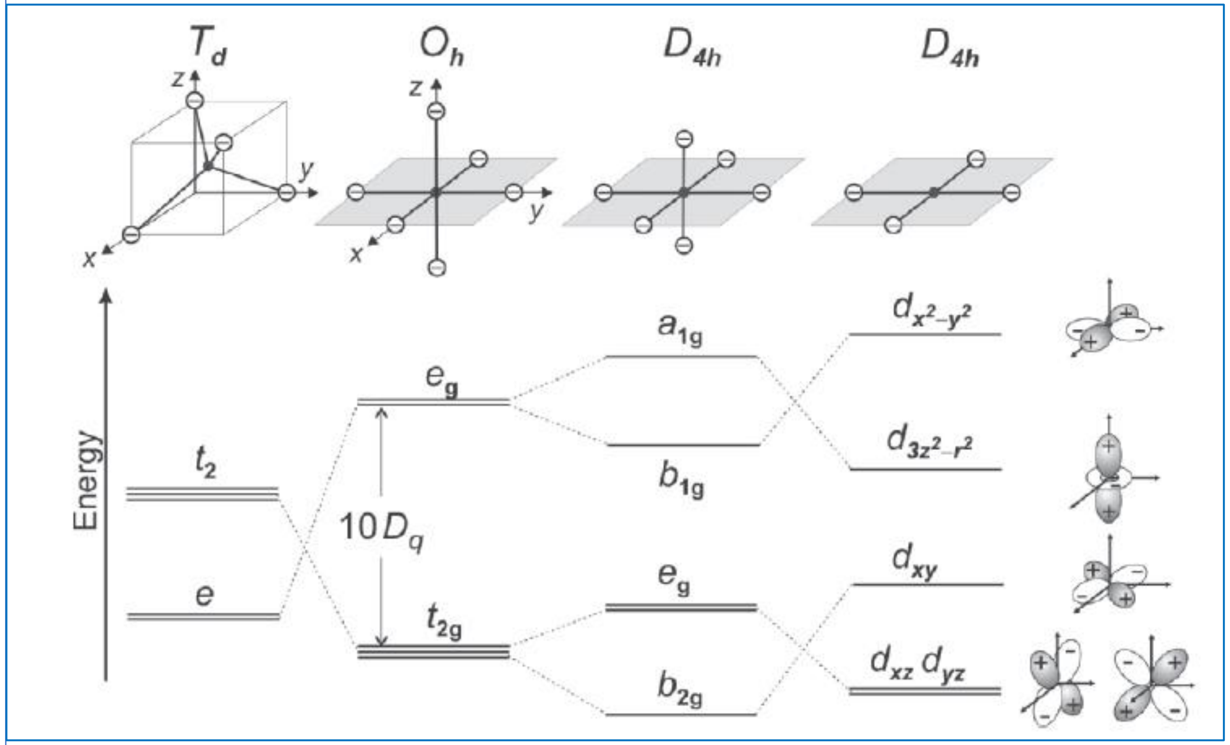
N.B.: $d_{3z^2-r^2} \Leftrightarrow d_{z^2}$

bulk

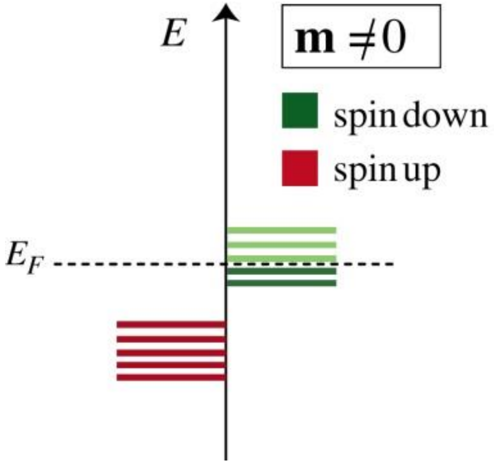
1) Crystal field (CF) : bond formation
- Broken orbital degeneracy
- Orbitals (real wave function)
- Quenching orbital moment: $L \approx 0$

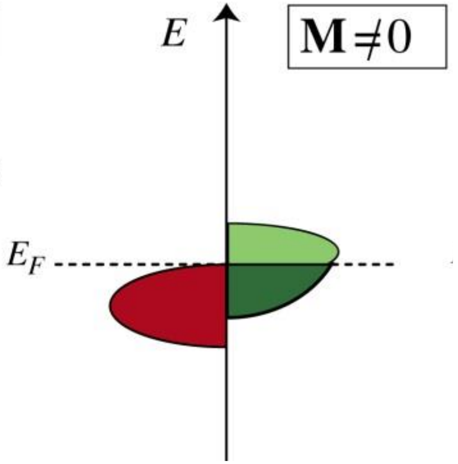
2) Electronic band formation

$d_{xz} = a\, Y_2^{1} + b\, Y_2^{-1}$ $d_{xy} = a\, Y_2^{-2} - b\, Y_2^{2}$



[St&Sie06]





Magnetism in materials: localized *vs* delocalized spins

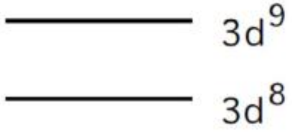
Ex: NiO
CoO
Fe_2O_3

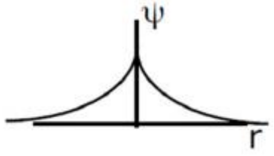
LOCALIZED MAGNETISM

Integral number of 3d or 4f electrons on the ion core; Integral number of unpaired spins; Discreet energy levels.

with

Ni^{2+} $3d^8$ $m = 2\ \mu_B$





$\psi \approx \exp(-r/a_0)$

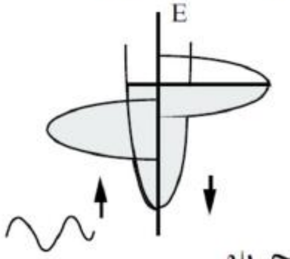
Boltzmann statistics

DELOCALIZED MAGNETISM

Nonintegral number of unpaired spins per atom.

Spin-polarized energy bands
strong correlations.

Ni $3d^{9.4}4s^{0.6}$ $m = 0.6\ \mu_B$



$\psi \approx \exp(-i\mathbf{k.r})$

Fermi-Dirac statistics

Ex: Ni, Co, Fe
(metallic)

4f metals	*localized electrons*
4f compounds	*localized electrons*
3d compounds	*localized/delocalized electrons*
3d metals	*delocalized electrons.*

Above the Curie temperature, neither localized nor delocalized moments disappear, they just become disordered in a paramagnetic state when $T > T_C$.

Ref: J.M.D. Coey, *Magnetism and magnetic materials* (Cambridge).

Local coordination: crystal (ligand) field

See exercise: 2.1

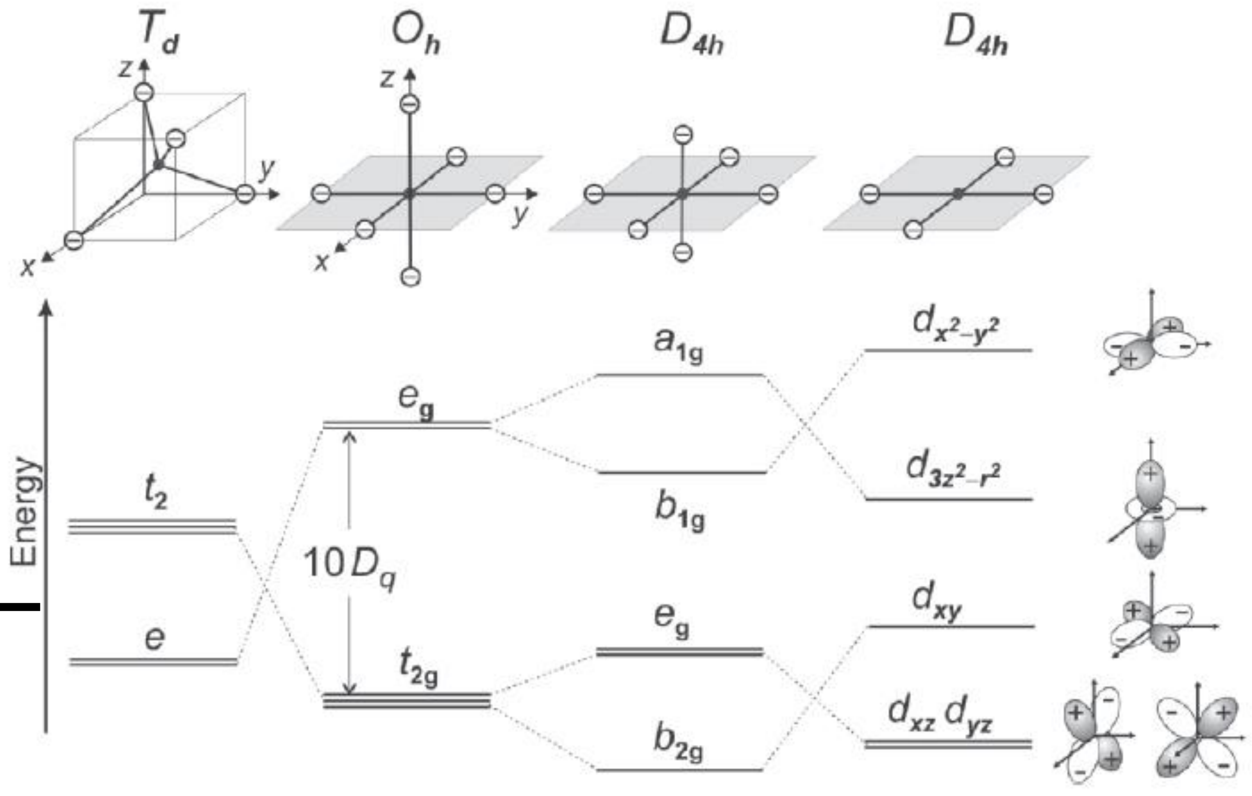
In the crystal (ligand) field theory the effect of the surrounding atoms is described by an effective potential (localized electrons)

$H = H_{free\ atom} + CF$

$CF = -e\,V(r)$

For example for an octahedral crystal field: $V(r) = \sum_{i=1}^{6} e\,Z_i / r_i$

d_{xz}, d_{yz},
$d_{x^2-y^2}$, d_{xy}, $d_{3z^2-r^2}$



e_g

t_{2g}

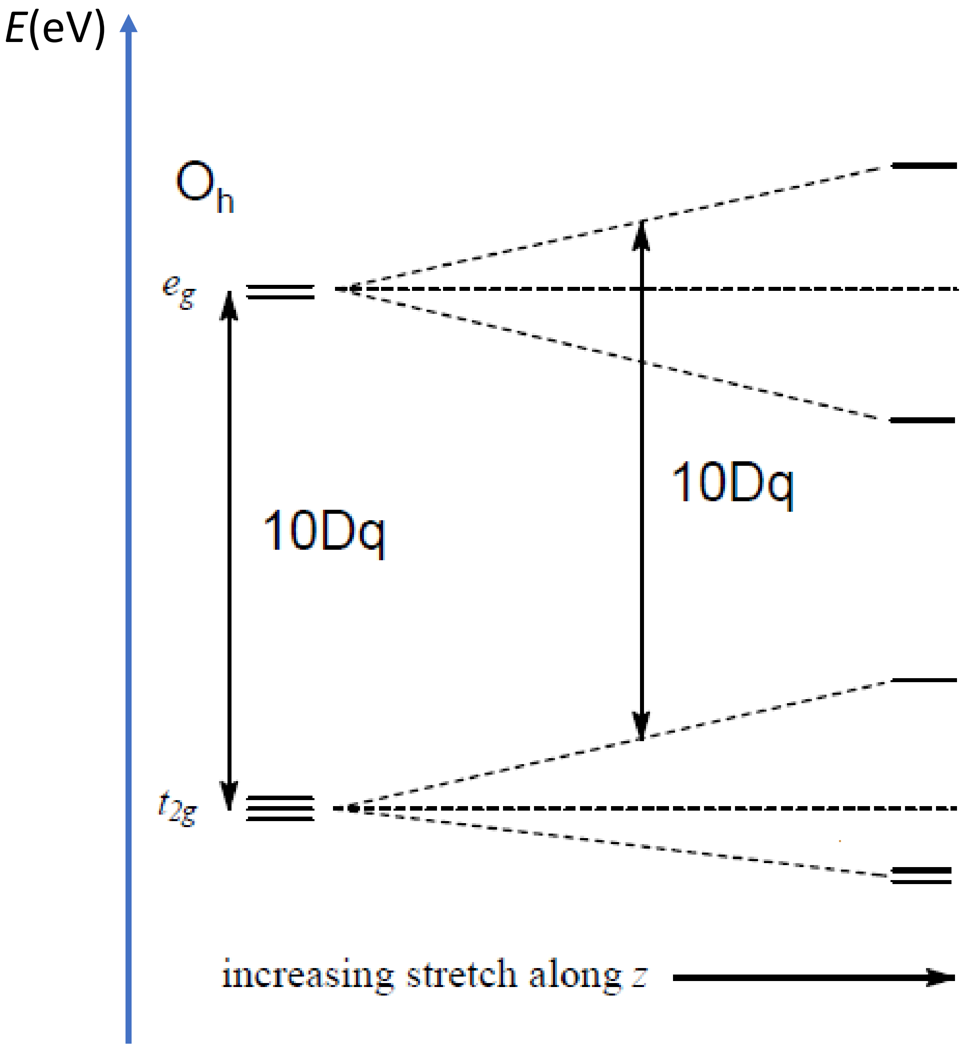
CF lifts the
d-orbital degeneracy

Qualitative arguments: the central atom orbitals pointing toward the ligand positions are higher in energy (due to Coulomb repulsion) than those orbitals avoiding the ligand positions:

- **t_{2g}** orbitals point towards the centres of the cube faces while the **e_g** orbitals point towards the centres of the cube edges.
- In T_d symmetry the latter points are closer to the ligands by a factor $\sqrt{2}$

St&Sie06

Crystal field splitting: parametrization

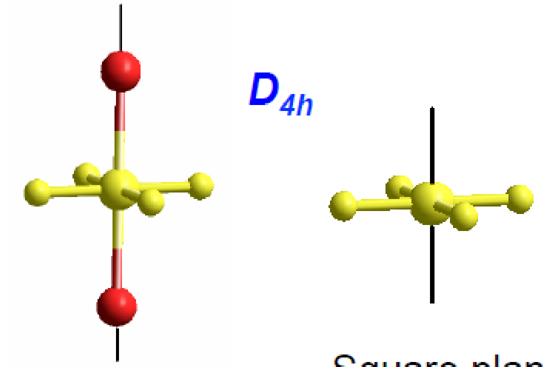


$d_{x^2-y^2}$ $6D_q + 2D_s - D_t$

$d_{3z^2-r^2}$ $6D_q - 2D_s - 6D_t$

d_{xy} $-4D_q + 2D_s - D_t$

d_{xz}, d_{yz} $-4D_q - D_s + 4D_t$



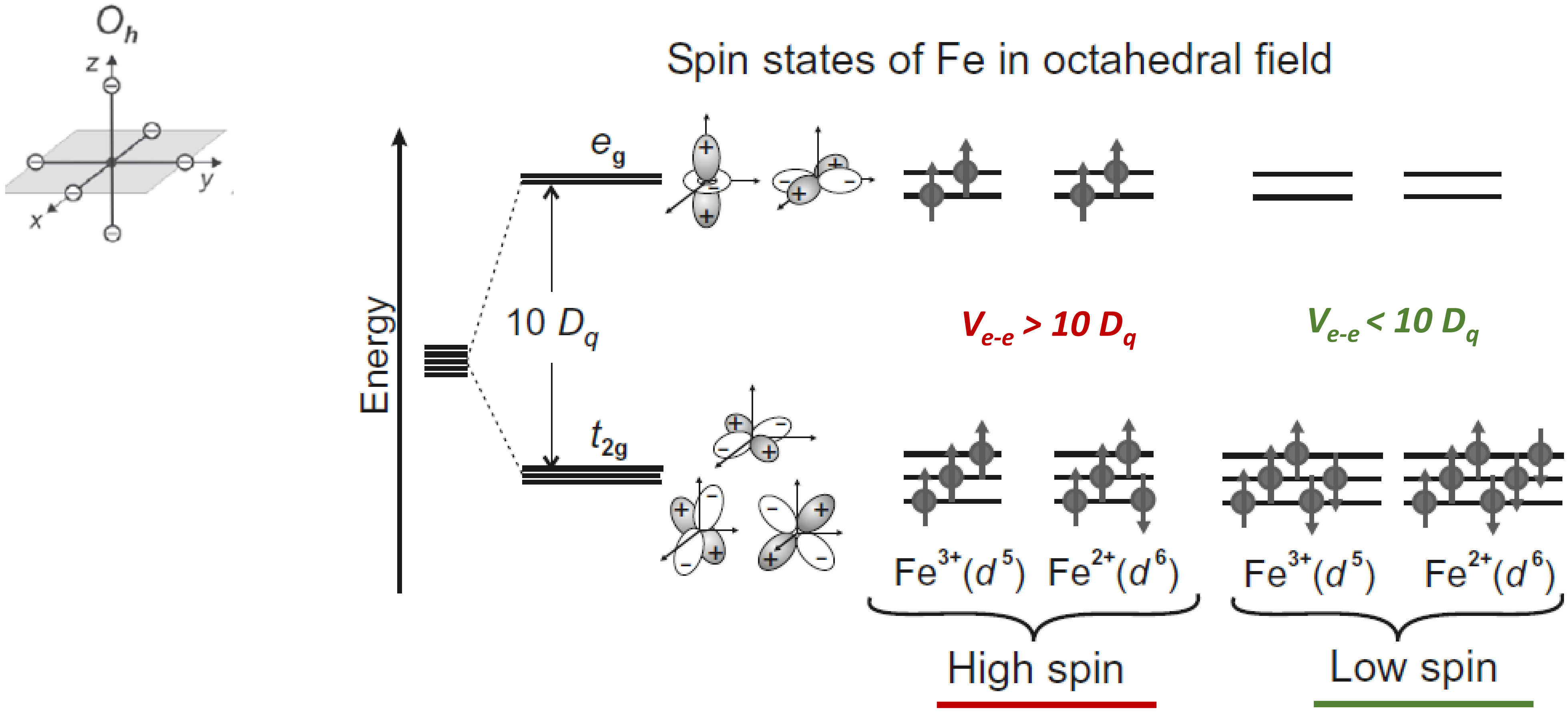
Elongated or compressed O_h along C_4 axis

Square planar

The parameters D_q, D_s and D_t are used to describe the splitting of the d-orbitals induced by the crystal field independently on the symmetry

Crystal field *vs* Coulomb interaction (V_{ee})

See exercise: 2.2

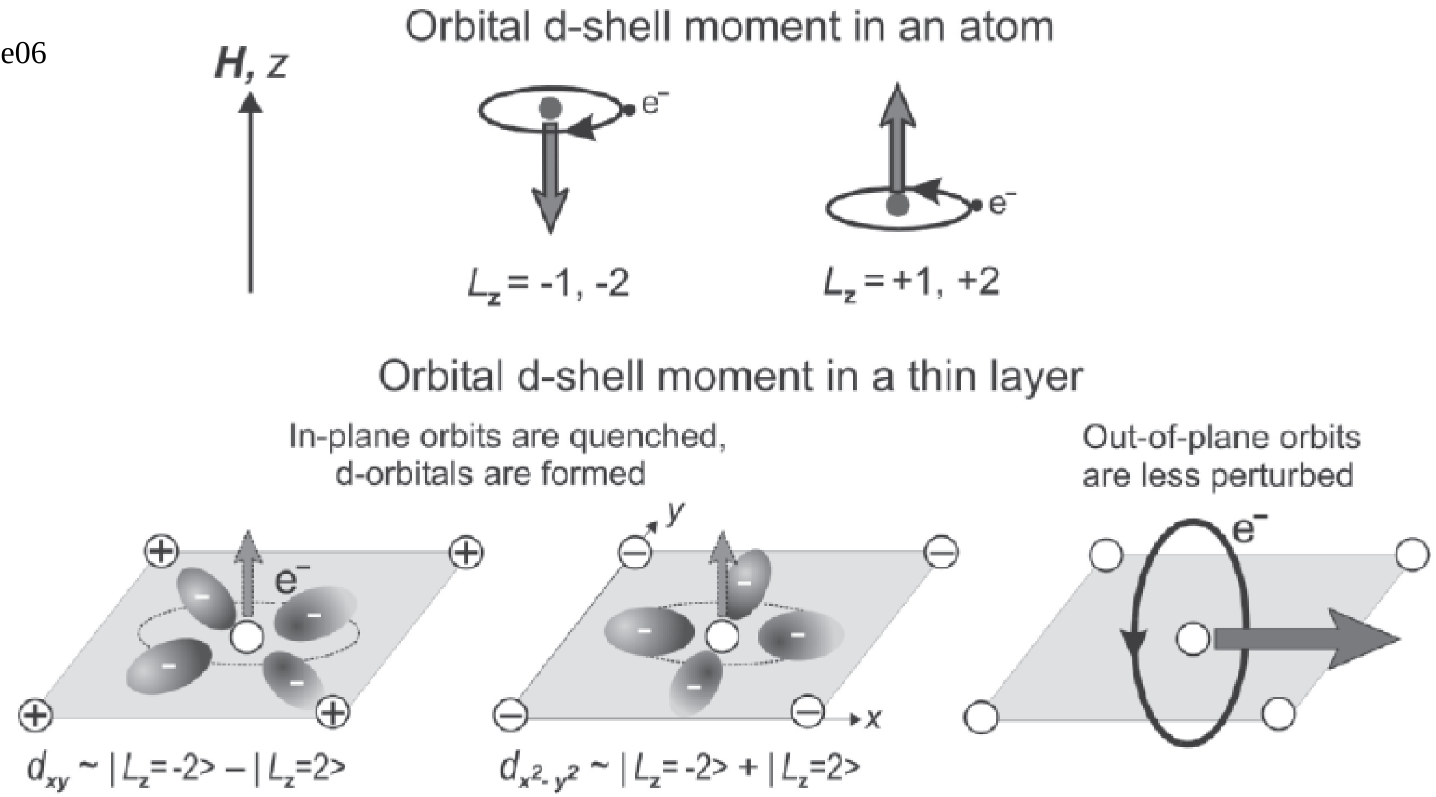


It is not anymore true that the spin *S* is maximized (failure of Hund's rules):
competition between e^--e^- interaction and CF

St&Sie06

Quenching of the orbital moment due to bond formation

St&Sie06



the orbital moment arises from the electron precession (Y_l^m)

-> bond formation stops the precession

A strong directional bonding generates a reduction in the component of *L* perpendicular to the bond direction

Central atom binds to four atoms in a plane.

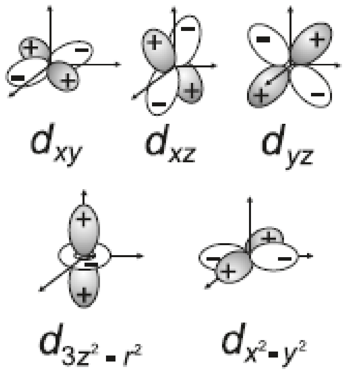
a) The *d* electron will form a standing wave with a spatial shape depending on the distribution of the electronic charge on the neighbouring atoms (i.e. orbital motion frozen by the formation of bonds with the neighbouring atoms) -> out-of-plane orbital moment is quenched

b) The orbital motion perpendicular to the bonding plane is less perturbed by the bonds -> in-plane orbital moment will stay unquenched

symmetry breaking implies **reduced** and **anisotropic** orbital moment

Quenching of the orbital moment by coordination

Wave function of an electron in one of the 3*d* orbitals (n=1..5): $\phi_n^\sigma = R_{3d} d_n \sigma$



$$\begin{aligned}
d_{xy} &= \sqrt{\frac{15}{4\pi}\frac{xy}{r^2}} &&= \frac{i}{\sqrt{2}}(Y_{2,-2} - Y_{2,+2}) \\
d_{xz} &= \sqrt{\frac{15}{4\pi}\frac{xz}{r^2}} &&= \frac{1}{\sqrt{2}}(Y_{2,-1} - Y_{2,+1}) \\
d_{yz} &= \sqrt{\frac{15}{4\pi}\frac{yz}{r^2}} &&= \frac{i}{\sqrt{2}}(Y_{2,-1} + Y_{2,+1}) \\
d_{x^2-y^2} &= \sqrt{\frac{15}{16\pi}\frac{(x^2-y^2)}{r^2}} &&= \frac{1}{\sqrt{2}}(Y_{2,-2} + Y_{2,+2}) \\
d_{3z^2-r^2} &= \sqrt{\frac{5}{16\pi}\frac{(3z^2-r^2)}{r^2}} &&= Y_{2,0}
\end{aligned}$$

$$\langle d_n|L_z|d_n\rangle = 0 \qquad \cancel{\Longrightarrow} \qquad L = 0$$

Similar for $L_{x,y}$

Easy argument frequently used to justify the quenching of the orbital moment in bulk but it is incorrect (in fact $\langle d_n|L_z^2|d_n\rangle \neq 0$)

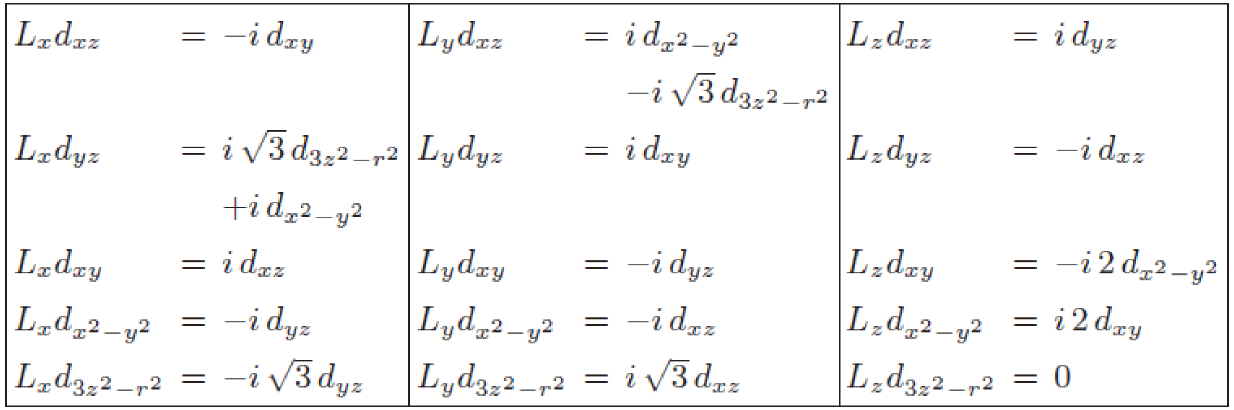
Matrix element in unit of $\hbar$

$L_x d_{xz} = -i\, d_{xy}$	$L_y d_{xz} = i\, d_{x^2-y^2} - i\sqrt{3}\, d_{3z^2-r^2}$	$L_z d_{xz} = i\, d_{yz}$
$L_x d_{yz} = i\sqrt{3}\, d_{3z^2-r^2} + i\, d_{x^2-y^2}$	$L_y d_{yz} = i\, d_{xy}$	$L_z d_{yz} = -i\, d_{xz}$
$L_x d_{xy} = i\, d_{xz}$	$L_y d_{xy} = -i\, d_{yz}$	$L_z d_{xy} = -i\,2\, d_{x^2-y^2}$
$L_x d_{x^2-y^2} = -i\, d_{yz}$	$L_y d_{x^2-y^2} = -i\, d_{xz}$	$L_z d_{x^2-y^2} = i\,2\, d_{xy}$
$L_x d_{3z^2-r^2} = -i\sqrt{3}\, d_{yz}$	$L_y d_{3z^2-r^2} = i\sqrt{3}\, d_{xz}$	$L_z d_{3z^2-r^2} = 0$

It simply implies that L_z is not an observable since the two states with $\pm L_z$ are degenerate and then the mean L_z value is $L_z = 0$

[Fig00]; Sugano, Tanabe, Kamimura: Multiplets of transition-metal ions in crystals (Academic Press 1970) p.155-156

L_z vs L_z^2



$L_x d_{xz} = -i\, d_{xy}$	$L_y d_{xz} = i\, d_{x^2-y^2} - i\sqrt{3}\, d_{3z^2-r^2}$	$L_z d_{xz} = i\, d_{yz}$
$L_x d_{yz} = i\sqrt{3}\, d_{3z^2-r^2} + i\, d_{x^2-y^2}$	$L_y d_{yz} = i\, d_{xy}$	$L_z d_{yz} = -i\, d_{xz}$
$L_x d_{xy} = i\, d_{xz}$	$L_y d_{xy} = -i\, d_{yz}$	$L_z d_{xy} = -i\, 2\, d_{x^2-y^2}$
$L_x d_{x^2-y^2} = -i\, d_{yz}$	$L_y d_{x^2-y^2} = -i\, d_{xz}$	$L_z d_{x^2-y^2} = i\, 2\, d_{xy}$
$L_x d_{3z^2-r^2} = -i\sqrt{3}\, d_{yz}$	$L_y d_{3z^2-r^2} = i\sqrt{3}\, d_{xz}$	$L_z d_{3z^2-r^2} = 0$

$$\xrightarrow{L_z}\quad \begin{array}{c|ccccc} & d_{z^2} & d_{xz} & d_{yz} & d_{xy} & d_{x^2-y^2} \\ \hline d_{z^2} & 0 & 0 & 0 & 0 & 0 \\ d_{xz} & 0 & 0 & -i & 0 & 0 \\ d_{yz} & 0 & i & 0 & 0 & 0 \\ d_{xy} & 0 & 0 & 0 & 0 & 2i \\ d_{x^2-y^2} & 0 & 0 & 0 & -2i & 0 \end{array}$$

$\langle d_n | L_z | d_n \rangle = 0$

$$\begin{array}{c|ccccc} & d_{z^2} & d_{xz} & d_{yz} & d_{xy} & d_{x^2-y^2} \\ \hline d_{z^2} & 0 & 0 & 0 & 0 & 0 \\ d_{xz} & 0 & 0 & -i & 0 & 0 \\ d_{yz} & 0 & i & 0 & 0 & 0 \\ d_{xy} & 0 & 0 & 0 & 0 & 2i \\ d_{x^2-y^2} & 0 & 0 & 0 & -2i & 0 \end{array} \quad x \quad \begin{array}{c|ccccc} & d_{z^2} & d_{xz} & d_{yz} & d_{xy} & d_{x^2-y^2} \\ \hline d_{z^2} & 0 & 0 & 0 & 0 & 0 \\ d_{xz} & 0 & 0 & -i & 0 & 0 \\ d_{yz} & 0 & i & 0 & 0 & 0 \\ d_{xy} & 0 & 0 & 0 & 0 & 2i \\ d_{x^2-y^2} & 0 & 0 & 0 & -2i & 0 \end{array} \quad \xrightarrow{L_z^2} \quad \begin{array}{c|ccccc} & d_{z^2} & d_{xz} & d_{yz} & d_{xy} & d_{x^2-y^2} \\ \hline d_{z^2} & 0 & 0 & 0 & 0 & 0 \\ d_{xz} & 0 & 1 & 0 & 0 & 0 \\ d_{yz} & 0 & 0 & 1 & 0 & 0 \\ d_{xy} & 0 & 0 & 0 & 4 & 0 \\ d_{x^2-y^2} & 0 & 0 & 0 & 0 & 4 \end{array}$$

$\langle d_n | L_z^2 | d_n \rangle \neq 0$

It simply implies that L_z is not an observable since the two states with $\pm L_z$ are degenerate: --
$\Rightarrow$ the mean L_z value is $L_z = 0$ but $\langle d_n | L_z^2 | d_n \rangle \neq 0$

Evaluation of the orbital moment

Orbital angular moment about an axis is associated to transformation by rotation of pairs of orbitals. This holds only if:

a) the two states of the pair are degenerate

b) the pair orbitals can be transformed one in the other by a rotation (matrix element $\neq 0$)

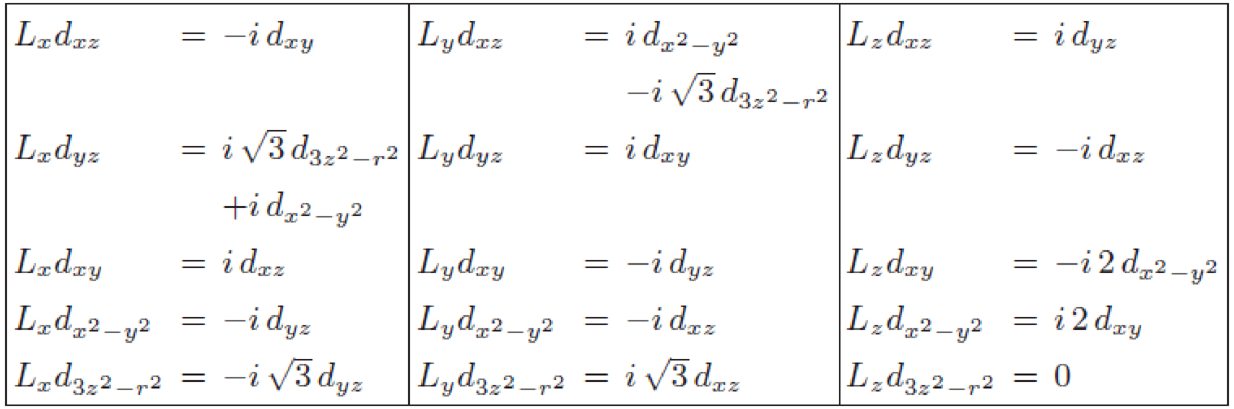
c) the second orbital must not contain an electron with the same spin as that in the first orbital (Pauli exclusion principle)

$\langle d_{xy} | L_z | d_{x^2-y^2} \rangle = -2i$ rotation by π/4 about the z axis transforming $d_{x2\text{-}y2}$ in d_{xy}

$\langle d_{yz} | L_z | d_{xz} \rangle = i$ rotation by π/2 about the z axis transforming d_{xz} in d_{yz}

$\langle d_n | L_z | d_{3z^2-r^2} \rangle = 0$ $d_{3z^2-r^2}$ cannot be transformed in any other orbital by a rotation about the *z* axis, thus no contribution to L_z

Matrix element in unit of $\hbar$



$L_x d_{xz} = -i\, d_{xy}$	$L_y d_{xz} = i\, d_{x^2-y^2} - i\sqrt{3}\, d_{3z^2-r^2}$	$L_z d_{xz} = i\, d_{yz}$
$L_x d_{yz} = i\sqrt{3}\, d_{3z^2-r^2} + i\, d_{x^2-y^2}$	$L_y d_{yz} = i\, d_{xy}$	$L_z d_{yz} = -i\, d_{xz}$
$L_x d_{xy} = i\, d_{xz}$	$L_y d_{xy} = -i\, d_{yz}$	$L_z d_{xy} = -i\, 2\, d_{x^2-y^2}$
$L_x d_{x^2-y^2} = -i\, d_{yz}$	$L_y d_{x^2-y^2} = -i\, d_{xz}$	$L_z d_{x^2-y^2} = i\, 2\, d_{xy}$
$L_x d_{3z^2-r^2} = -i\sqrt{3}\, d_{yz}$	$L_y d_{3z^2-r^2} = i\sqrt{3}\, d_{xz}$	$L_z d_{3z^2-r^2} = 0$

In a simple approximation we can use $|\langle d_i | L_{x(y,z)} | d_j \rangle|$ to evaluate the norm of the orbital angular momentum associated to the transformation by rotation of pairs of orbitals induced by the operators $L_{x(y,z)}$

[Fig00], p. 12-13, 241-243

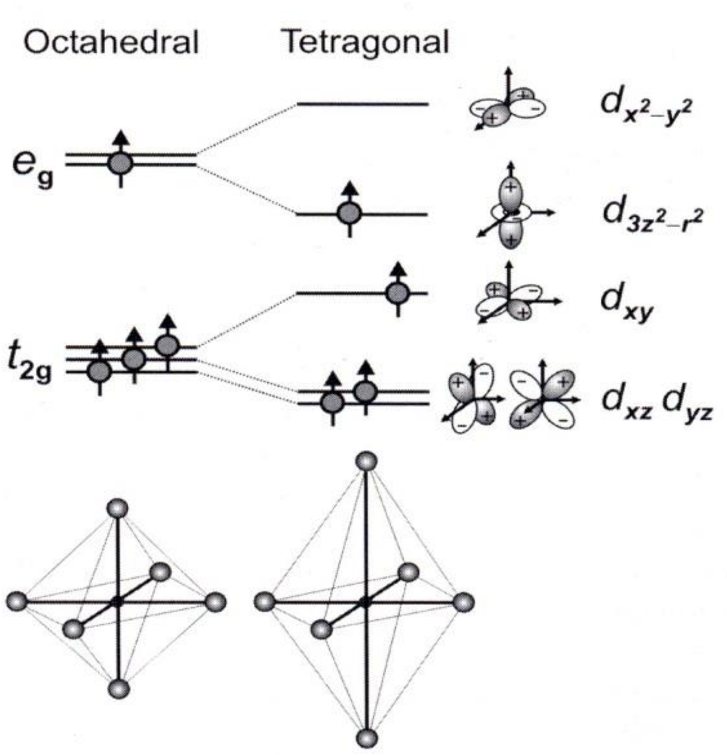
Quenching of the orbital moment by coordination

Orbital angular moment about an axis is associated to transformation by rotation of pairs of orbitals. This holds only if:
a) the two states of the pair are degenerate
b) there must not be an electron in the second orbital with the same spin as that in the first orbital

Ex: $3d^4$ in octahedral or tetragonal symmetry has $L = 0$:

- the $d_{x2\text{-}y2}$ and d_{xy} are split and hence do not contribute to the orbital moment (as a consequence of point a)

- the d_{yz} and d_{xz} are degenerate but can not be transformed by rotation (as a consequence of point b)

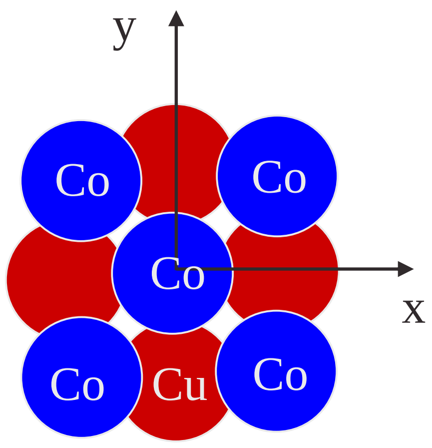


St&Sie06

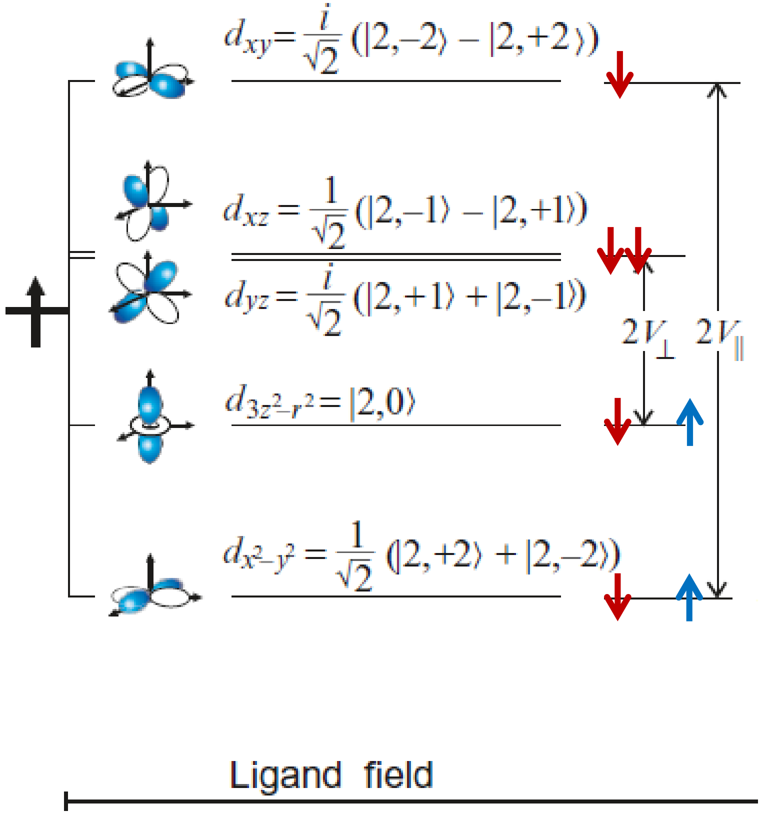
Ex: Co monolayer on Cu(100)

Co is a transition metal with electronic configuration given by [Ar] $4s^2\ 3d^7$
Assuming no charge transfer between Co and Cu, the d-orbital splitting due to the crystal field and occupation are:

Top view



Spin occupation



The Co d-orbitals pointing to another atom are higher in energy with respect to orbitals pointing to an empty space. Then, starting from the higher in energy:

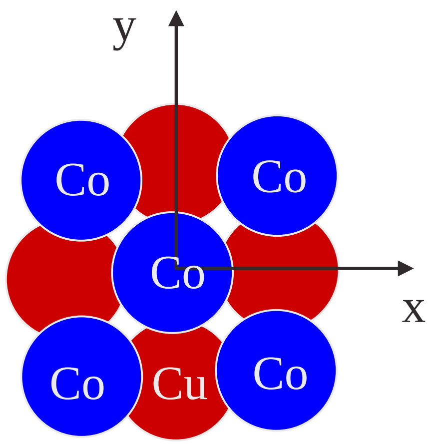
- d_{xy} is pointing directly against nearest Co neighbors and is the highest in energy
- d_{yz} d_{xz} are pointing in between two Cu atoms on the surface
- $d_{3z^2-r^2}$ is pointing in between 4 Cu atoms
- $d_{x^2-y^2}$ is flat on top of the Cu surface and it is not pointing against Co atoms (lowest in energy)

J. Stohr JMMM **200**, 470 (1999)

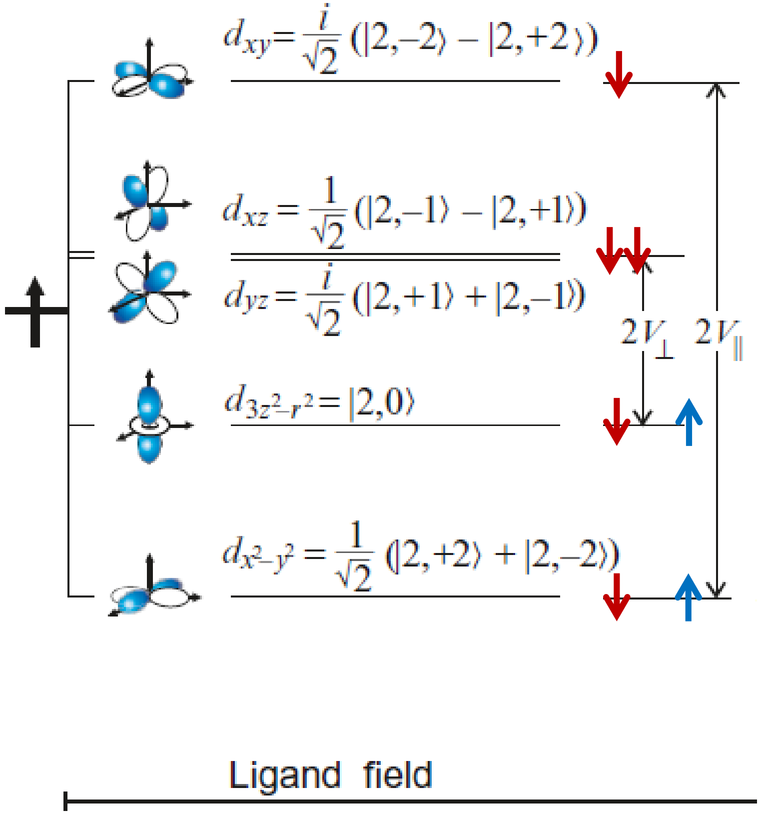
Ex: Co monolayer on Cu(100)

Co is a transition metal with electronic configuration given by [Ar] $4s^2\ 3d^7$
Assuming no charge transfer between Co and Cu, the d-orbital splitting due to the crystal field and occupation are:

Top view



Spin occupation

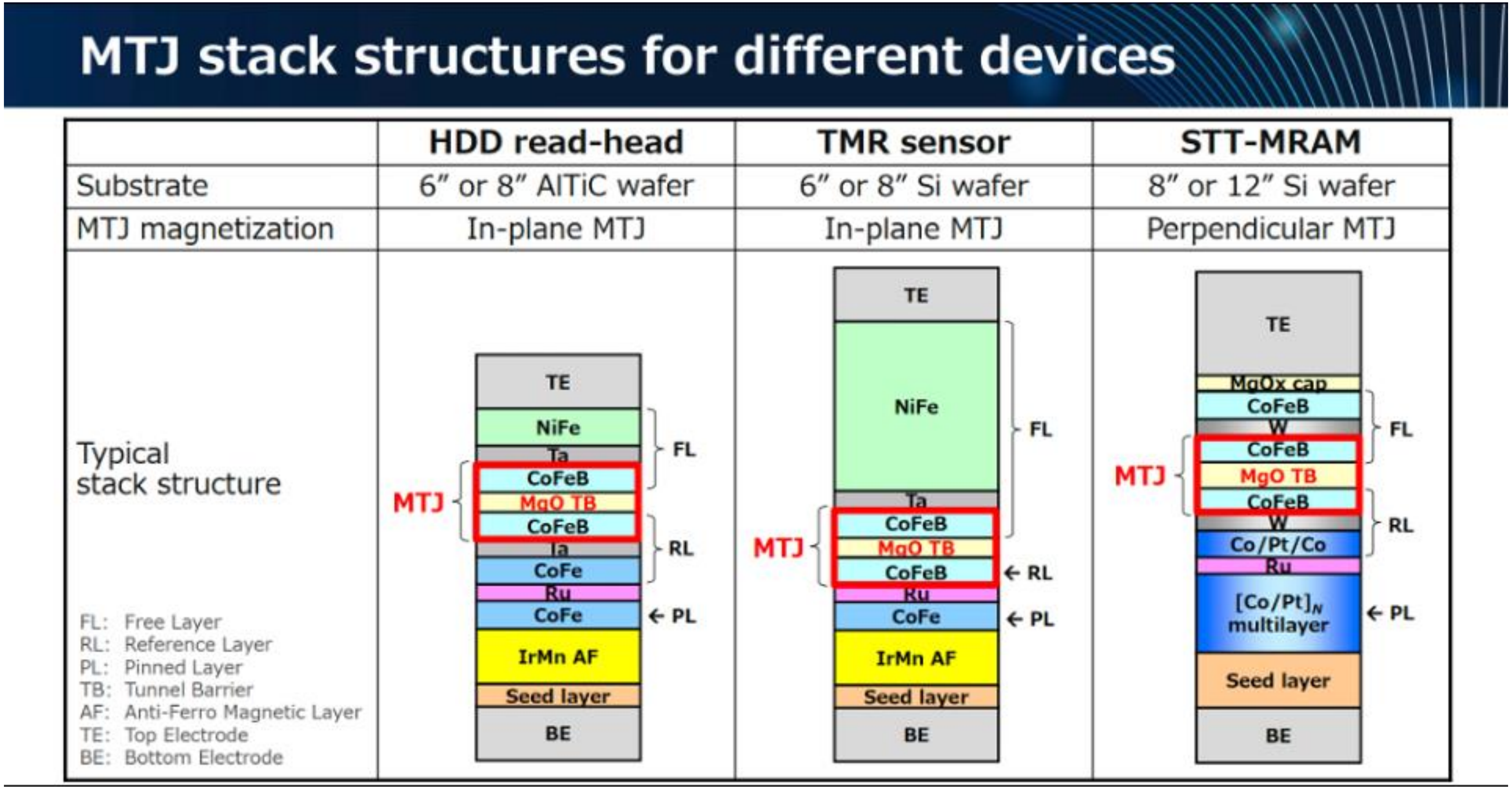


L = 0 because:

- $d_{3z^2-r^2}$ gives no contribution to *L*
- d_{xy} and $d_{x^2-y^2}$ can not transform one in the other because not degenerate
- d_{xz} and d_{yz} can not transform one in the other because they have the same spin

J. Stohr JMMM **200**, 470 (1999)

Co(Fe) /MgO interfaces are the base of spintronics



MTJ stack structures for different devices

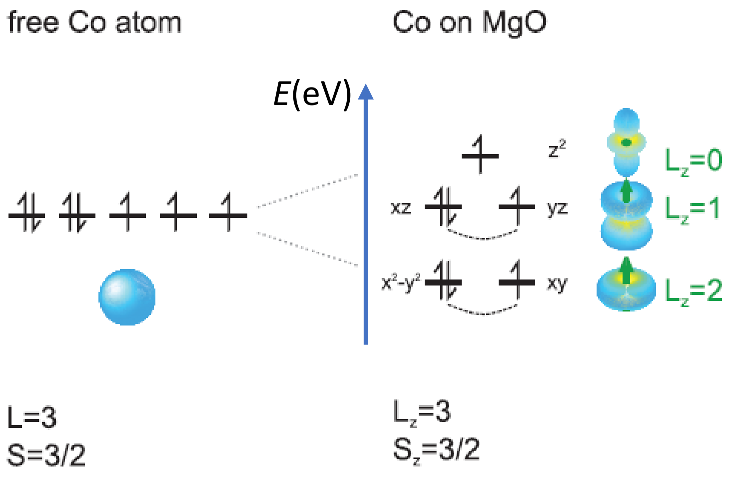
	HDD read-head	TMR sensor	STT-MRAM
Substrate	6″ or 8″ AlTiC wafer	6″ or 8″ Si wafer	8″ or 12″ Si wafer
MTJ magnetization	In-plane MTJ	In-plane MTJ	Perpendicular MTJ
Typical stack structure	TE NiFe Ta CoFeB MgO TB CoFeB Ta CoFe Ru CoFe IrMn AF Seed layer BE FL RL ← PL MTJ	TE NiFe Ta CoFeB MgO TB CoFeB Ru CoFe IrMn AF Seed layer BE FL ← RL ← PL MTJ	TE MgOx cap CoFeB W CoFeB MgO TB CoFeB W Co/Pt/Co Ru $[\text{Co/Pt}]_N$ multilayer Seed layer BE FL RL ← PL MTJ

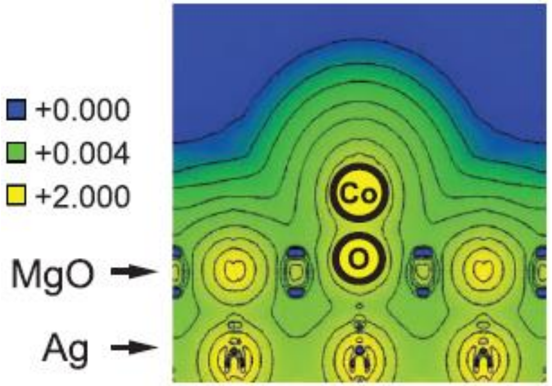
FL: Free Layer
RL: Reference Layer
PL: Pinned Layer
TB: Tunnel Barrier
AF: Anti-Ferro Magnetic Layer
TE: Top Electrode
BE: Bottom Electrode

https://www.forbes.com/sites/tomcoughlin/2024/08/20/the-2024-ieee-tmrc-reveals-the-future-of-mram-and-hamr/

Large orbital moment for Co_1/MgO(100)

See exercise: 2.3





- Co atom on MgO adsorbs on top of oxygen
- strong uniaxial bond preserves atomic values of *L* and *S*.

From XMCD: L_z = 2.9; S_z = 3/2

- The uniaxial bond generates a strong out-of-plane anisotropy

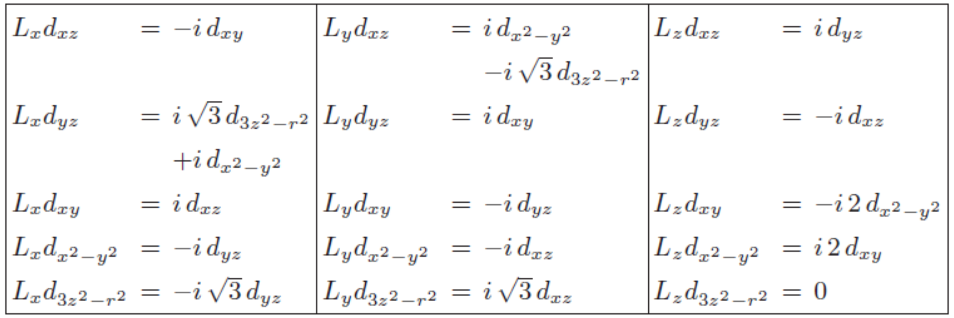
1) The orbital moment is **not always** quenched by CF
2) Strong anisotropy of the orbital moment

$$L_x(L_y) = 0$$

$$\langle d_n | L_x | d_{3z^2-r^2} \rangle = 0$$

$$\langle d_{yz} | L_x | d_{x^2-y^2} \rangle = 0$$

$$\langle d_{xz} | L_x | d_{xy} \rangle = 0$$



$L_x d_{xz} = -i\, d_{xy}$	$L_y d_{xz} = i\, d_{x^2-y^2} - i\sqrt{3}\, d_{3z^2-r^2}$	$L_z d_{xz} = i\, d_{yz}$
$L_x d_{yz} = i\sqrt{3}\, d_{3z^2-r^2} + i\, d_{x^2-y^2}$	$L_y d_{yz} = i\, d_{xy}$	$L_z d_{yz} = -i\, d_{xz}$
$L_x d_{xy} = i\, d_{xz}$	$L_y d_{xy} = -i\, d_{yz}$	$L_z d_{xy} = -i\, 2\, d_{x^2-y^2}$
$L_x d_{x^2-y^2} = -i\, d_{yz}$	$L_y d_{x^2-y^2} = -i\, d_{xz}$	$L_z d_{x^2-y^2} = i\, 2\, d_{xy}$
$L_x d_{3z^2-r^2} = -i\sqrt{3}\, d_{yz}$	$L_y d_{3z^2-r^2} = i\sqrt{3}\, d_{xz}$	$L_z d_{3z^2-r^2} = 0$

$$L_z = 3$$

$$\left| \langle d_n | L_x | d_{3z^2-r^2} \rangle \right| = 0$$

$$\left| \langle d_{xy} | L_z | d_{x^2-y^2} \rangle \right| = 2$$

$$\left| \langle d_{yz} | L_z | d_{xz} \rangle \right| = 1$$

Matrix elements are zero because d_{xy} and $d_{x^2-y^2}$ are not degenerate with d_{yz} and d_{xz}

Matrix elements are **non** zero because d_{xy} and $d_{x^2-y^2}$ are degenerate as well as d_{yz} and d_{xz}

I. Rau *et al.*, Science **344**, 988 (2014)

SOC partially restores orbital moment

Coordination frequently induces quenching of the orbital moment

However: H_{SO} mixes the ϕ_n^σ states and partially restores the orbital moment ($L \approx 0$)

In first approximation the wave function of a *d* electron becomes: $\Psi_n^+ = \phi_n^+ + \sum_i a_{n,i}\phi_i^+ + \sum_p b_{n,p}\phi_p^-$

Wave function of an electron in a 3*d* orbital (*i,p* =1…5): $\phi_n^\sigma = R_{3d} d_n \sigma$

$$a_{n,i} = \frac{\langle \phi_n^+ | H_{SO} | \phi_i^+ \rangle}{E_n - E_i} = \zeta \frac{\langle d_n^+ | \boldsymbol{L} \cdot \boldsymbol{S} | d_i^+ \rangle}{E_n - E_i}$$

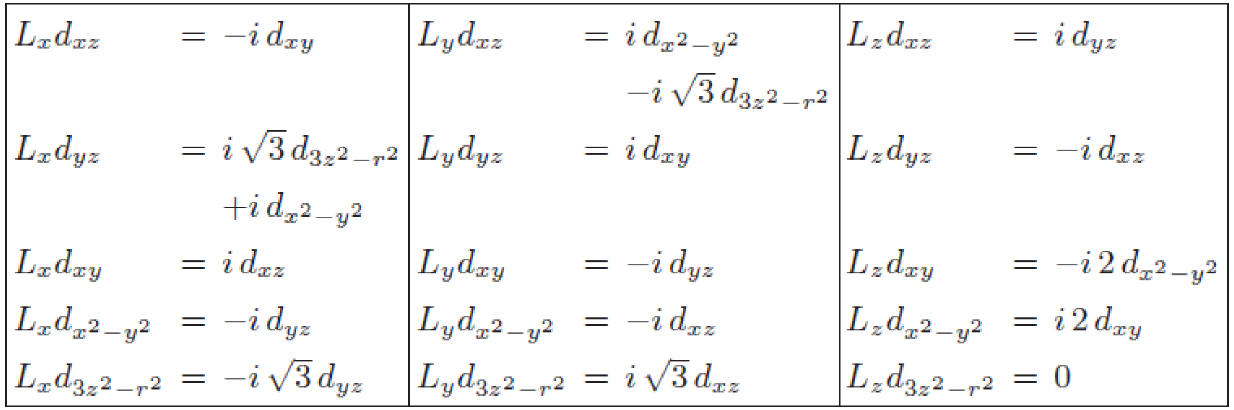
Orbital moment along direction α ($\alpha = x,y,z$) for the state d_n

$$L_{\alpha,n} = \langle \Psi_n^{+,-} | L_\alpha | \Psi_n^{+,-} \rangle \approx \zeta \sum_i \frac{|\langle d_n \sigma | L_\alpha | d_i \sigma \rangle|^2}{E_n - E_i}$$

$$\langle \Psi_n^\sigma | L_\alpha | \Psi_n^\sigma \rangle = \langle \phi_n^\sigma + \textstyle\sum_i a_{n,i}\phi_i^\sigma \, | L_\alpha | \phi_n^\sigma + \textstyle\sum_i a_{n,i}\phi_i^\sigma \rangle \approx \langle \phi_n^\sigma | L_\alpha | \textstyle\sum_i a_{n,i}\phi_i^\sigma \rangle$$

Total orbital moment along direction α

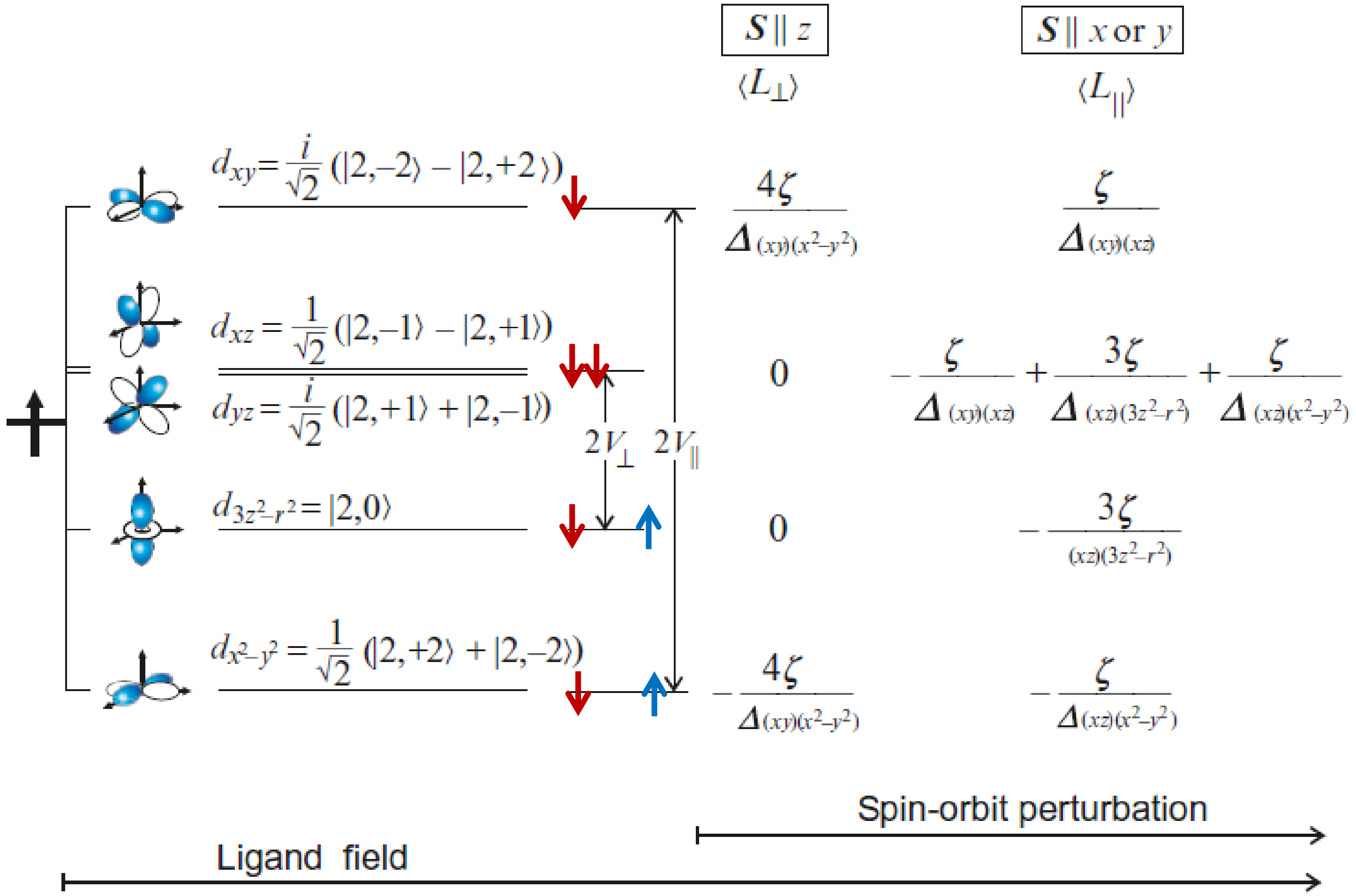
$$L_\alpha = \sum_n^{occ} \langle \Psi_n^{+,-} | L_\alpha | \Psi_n^{+,-} \rangle \approx \zeta \sum_n^{occ} \sum_i \frac{|\langle d_n \sigma | L_\alpha | d_i \sigma \rangle|^2}{E_n - E_i}$$



$L_x d_{xz} = -i\, d_{xy}$	$L_y d_{xz} = i\, d_{x^2-y^2}$ $-i\sqrt{3}\, d_{3z^2-r^2}$	$L_z d_{xz} = i\, d_{yz}$
$L_x d_{yz} = i\sqrt{3}\, d_{3z^2-r^2}$ $+i\, d_{x^2-y^2}$	$L_y d_{yz} = i\, d_{xy}$	$L_z d_{yz} = -i\, d_{xz}$
$L_x d_{xy} = i\, d_{xz}$	$L_y d_{xy} = -i\, d_{yz}$	$L_z d_{xy} = -i\, 2\, d_{x^2-y^2}$
$L_x d_{x^2-y^2} = -i\, d_{yz}$	$L_y d_{x^2-y^2} = -i\, d_{xz}$	$L_z d_{x^2-y^2} = i\, 2\, d_{xy}$
$L_x d_{3z^2-r^2} = -i\sqrt{3}\, d_{yz}$	$L_y d_{3z^2-r^2} = i\sqrt{3}\, d_{xz}$	$L_z d_{3z^2-r^2} = 0$

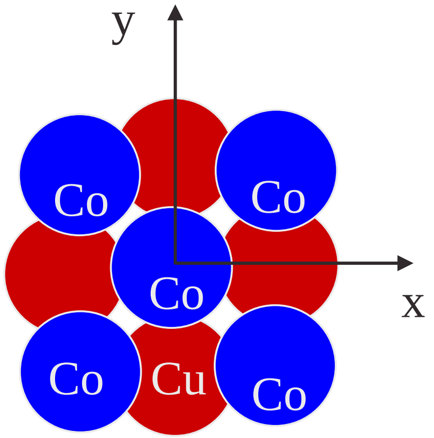
Ex: Co monolayer on Cu(100)

Co is a transition metal with electronic configuration given by
[Ar] $4s^2\,3d^7$
Assuming no charge transfer between Co and Cu, the level splitting due to the crystal field and occupation are:



J. Stohr JMMM **200**, 470 (1999)

Top view



Spin-orbit partially restores the orbital momentum destroyed by the CF

Ex.: $L_{z,xy} = \zeta \sum_i \frac{|\langle d_{xy}\sigma | L_z | d_i\sigma\rangle|^2}{E_{xy}-E_i} = \zeta \frac{|\langle d_{xy}+ | L_z | d_{x^2-y^2}+\rangle|^2}{E_{xy}-E_{x^2-y^2}}$

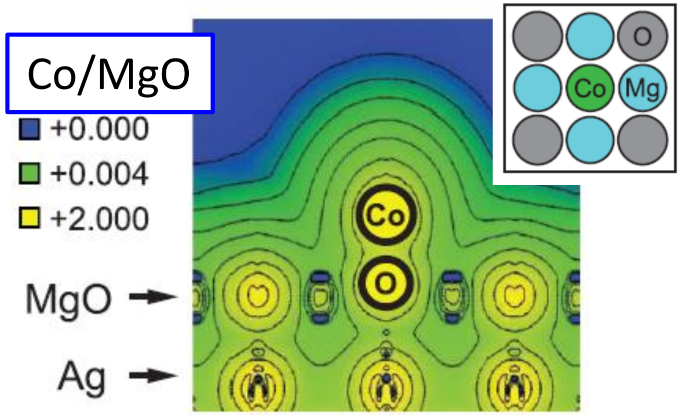
$$
\begin{array}{c|ccccc}
 & d_{z^2} & d_{xz} & d_{yz} & d_{xy} & d_{x^2-y^2} \\
d_{z^2} & 0 & 0 & 0 & 0 & 0 \\
d_{xz} & 0 & 0 & -i & 0 & 0 \\
d_{yz} & 0 & i & 0 & 0 & 0 \\
d_{xy} & 0 & 0 & 0 & 0 & 2i \\
d_{x^2-y^2} & 0 & 0 & 0 & -2i & 0
\end{array}
$$

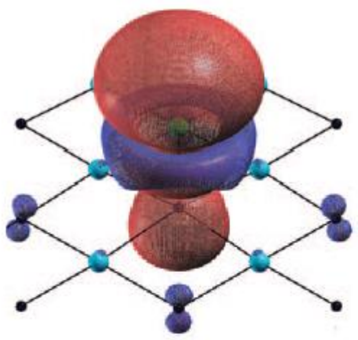
Co, Fe atoms on insulating substrates: MgO/Ag(100)

Charge distribution

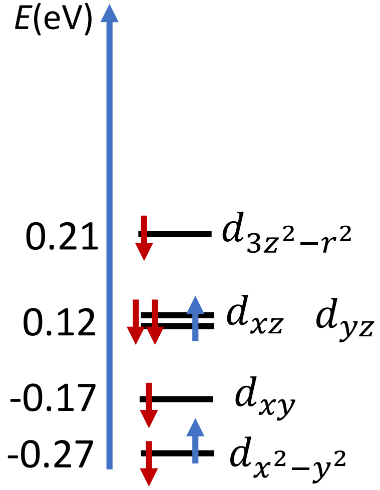
Spin distribution

Majority Minority





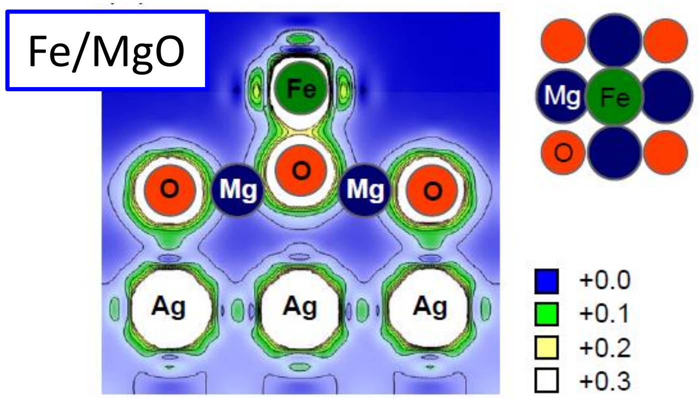
Axial (C_∞)
crystal field

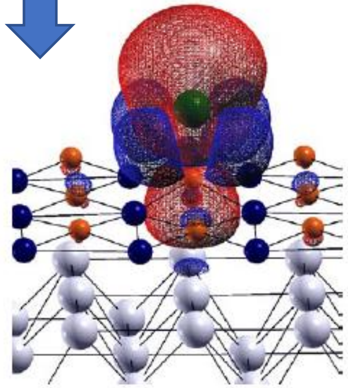


V_{ee}: $L_z = 2.9$ $S_z = 1.3$

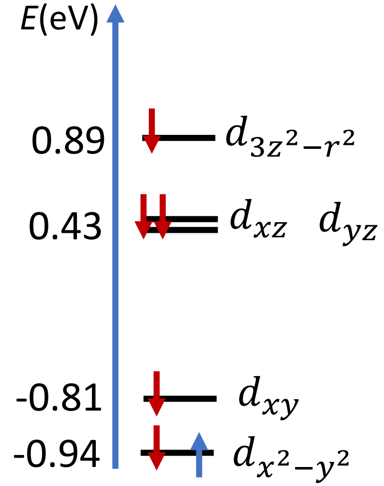
$V_{ee} + V_{SO}$: $L_z = 2.9$ $S_z = 1.3$

Different interactions with neighbors atoms for Co and Fe





C_{4v}
crystal field



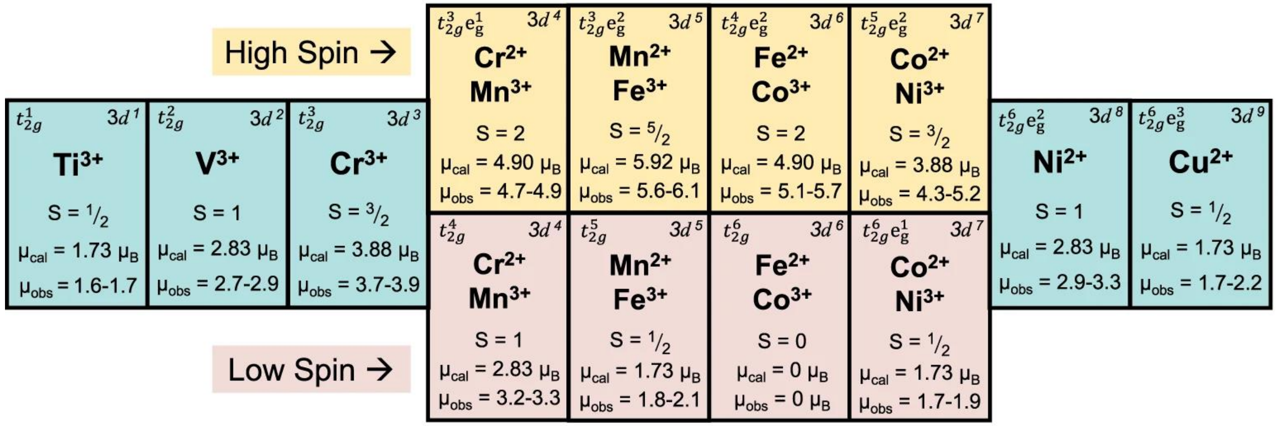
V_{ee}: $L_z = 0$ $S_z = 2$

$V_{ee} + V_{SO}$: $L_z = 1.25$ $S_z = 2$

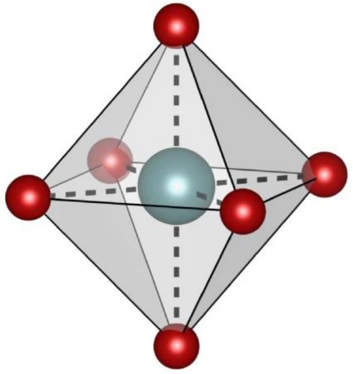
I.G. Rau *et al. Science* 988, **344** (2014); S. Baumann *et al.* Phys. Rev. Lett. **115**, 237202 (2015).

Magnetic properties of 3d ions

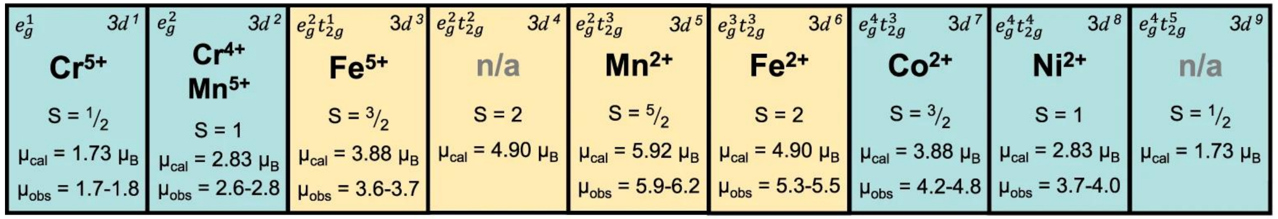
(a) Octahedral Ligand Field:



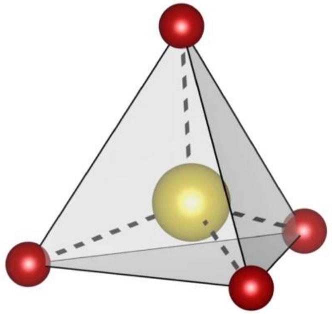
High Spin →	t_{2g}^1 $3d^1$ **Ti^{3+}** $S = 1/2$ $\mu_{cal} = 1.73\ \mu_B$ $\mu_{obs} = 1.6\text{-}1.7$	t_{2g}^2 $3d^2$ **V^{3+}** $S = 1$ $\mu_{cal} = 2.83\ \mu_B$ $\mu_{obs} = 2.7\text{-}2.9$	t_{2g}^3 $3d^3$ **Cr^{3+}** $S = 3/2$ $\mu_{cal} = 3.88\ \mu_B$ $\mu_{obs} = 3.7\text{-}3.9$	$t_{2g}^3 e_g^1$ $3d^4$ **Cr^{2+}** **Mn^{3+}** $S = 2$ $\mu_{cal} = 4.90\ \mu_B$ $\mu_{obs} = 4.7\text{-}4.9$	$t_{2g}^3 e_g^2$ $3d^5$ **Mn^{2+}** **Fe^{3+}** $S = 5/2$ $\mu_{cal} = 5.92\ \mu_B$ $\mu_{obs} = 5.6\text{-}6.1$	$t_{2g}^4 e_g^2$ $3d^6$ **Fe^{2+}** **Co^{3+}** $S = 2$ $\mu_{cal} = 4.90\ \mu_B$ $\mu_{obs} = 5.1\text{-}5.7$	$t_{2g}^5 e_g^2$ $3d^7$ **Co^{2+}** **Ni^{3+}** $S = 3/2$ $\mu_{cal} = 3.88\ \mu_B$ $\mu_{obs} = 4.3\text{-}5.2$	$t_{2g}^6 e_g^2$ $3d^8$ **Ni^{2+}** $S = 1$ $\mu_{cal} = 2.83\ \mu_B$ $\mu_{obs} = 2.9\text{-}3.3$	$t_{2g}^6 e_g^3$ $3d^9$ **Cu^{2+}** $S = 1/2$ $\mu_{cal} = 1.73\ \mu_B$ $\mu_{obs} = 1.7\text{-}2.2$
Low Spin →				t_{2g}^4 $3d^4$ **Cr^{2+}** **Mn^{3+}** $S = 1$ $\mu_{cal} = 2.83\ \mu_B$ $\mu_{obs} = 3.2\text{-}3.3$	t_{2g}^5 $3d^5$ **Mn^{2+}** **Fe^{3+}** $S = 1/2$ $\mu_{cal} = 1.73\ \mu_B$ $\mu_{obs} = 1.8\text{-}2.1$	t_{2g}^6 $3d^6$ **Fe^{2+}** **Co^{3+}** $S = 0$ $\mu_{cal} = 0\ \mu_B$ $\mu_{obs} = 0\ \mu_B$	$t_{2g}^6 e_g^1$ $3d^7$ **Co^{2+}** **Ni^{3+}** $S = 1/2$ $\mu_{cal} = 1.73\ \mu_B$ $\mu_{obs} = 1.7\text{-}1.9$		



(b) Tetrahedral Ligand Field:



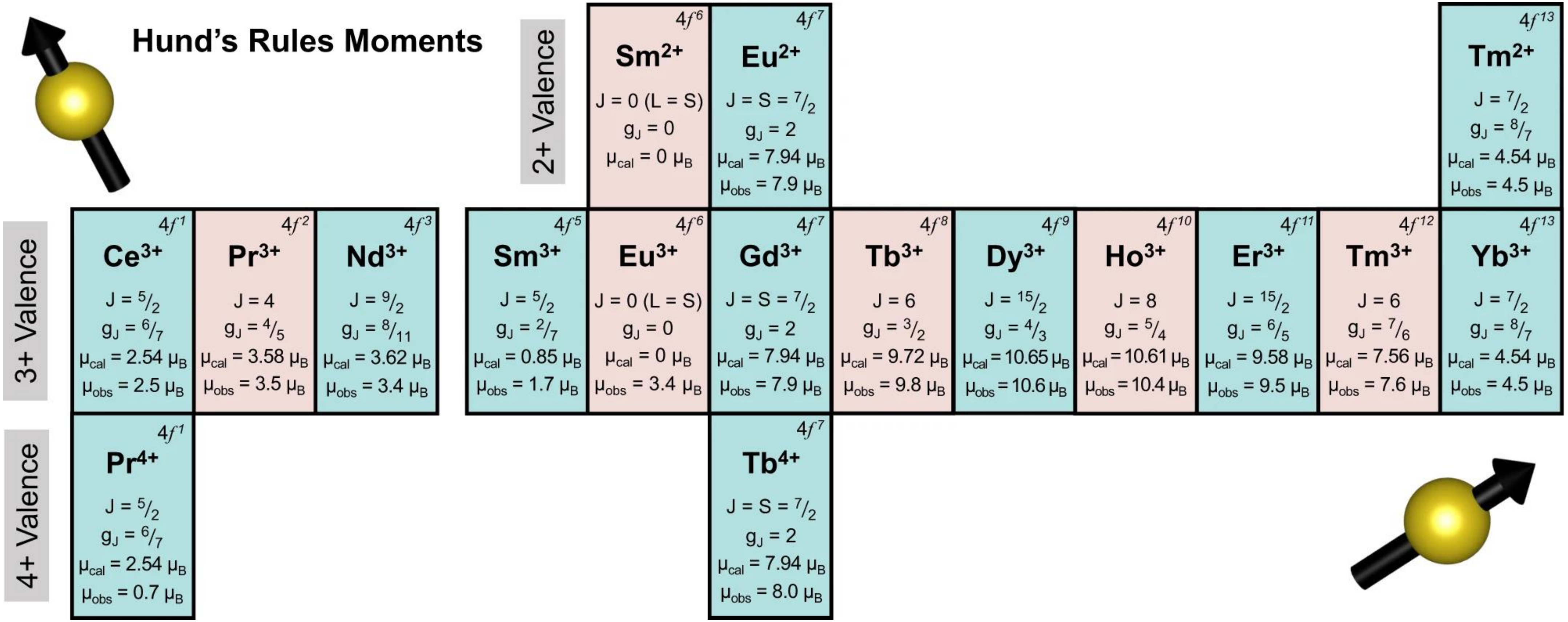
e_g^1 $3d^1$ **Cr^{5+}** $S = 1/2$ $\mu_{cal} = 1.73\ \mu_B$ $\mu_{obs} = 1.7\text{-}1.8$	e_g^2 $3d^2$ **Cr^{4+}** **Mn^{5+}** $S = 1$ $\mu_{cal} = 2.83\ \mu_B$ $\mu_{obs} = 2.6\text{-}2.8$	$e_g^2 t_{2g}^1$ $3d^3$ **Fe^{5+}** $S = 3/2$ $\mu_{cal} = 3.88\ \mu_B$ $\mu_{obs} = 3.6\text{-}3.7$	$e_g^2 t_{2g}^2$ $3d^4$ **n/a** $S = 2$ $\mu_{cal} = 4.90\ \mu_B$	$e_g^2 t_{2g}^3$ $3d^5$ **Mn^{2+}** $S = 5/2$ $\mu_{cal} = 5.92\ \mu_B$ $\mu_{obs} = 5.9\text{-}6.2$	$e_g^3 t_{2g}^3$ $3d^6$ **Fe^{2+}** $S = 2$ $\mu_{cal} = 4.90\ \mu_B$ $\mu_{obs} = 5.3\text{-}5.5$	$e_g^4 t_{2g}^3$ $3d^7$ **Co^{2+}** $S = 3/2$ $\mu_{cal} = 3.88\ \mu_B$ $\mu_{obs} = 4.2\text{-}4.8$	$e_g^4 t_{2g}^4$ $3d^8$ **Ni^{2+}** $S = 1$ $\mu_{cal} = 2.83\ \mu_B$ $\mu_{obs} = 3.7\text{-}4.0$	$e_g^4 t_{2g}^5$ $3d^9$ **n/a** $S = 1/2$ $\mu_{cal} = 1.73\ \mu_B$



Owing to quenching of orbital angular momentum, their calculated moments $\mu_{cal} = \frac{2\mu_B}{\hbar}\sqrt{S(S+1)}$ are best estimated from the spin-only, *S*, value with an isotropic Landé g-factor, *g* = 2, giving good agreement with the observed moments, μ_{obs}. When there are between four ($3d^4$) or seven ($3d^7$) electrons in the 3*d*-orbitals, either high-spin (yellow) or low-spin (pink) states can be observed for the octahedral case. The smaller crystal field splitting in the tetrahedral case means that high-spin states are always obtained, with very few exceptions. Observed moments that exceed the calculated moment, such as for Co^{2+}, imply an intermediate spin–orbit coupling and an incomplete quenching of orbital angular momentum.

https://doi.org/10.1038/s42005-022-00853-y

Magnetic properties of 4f ions



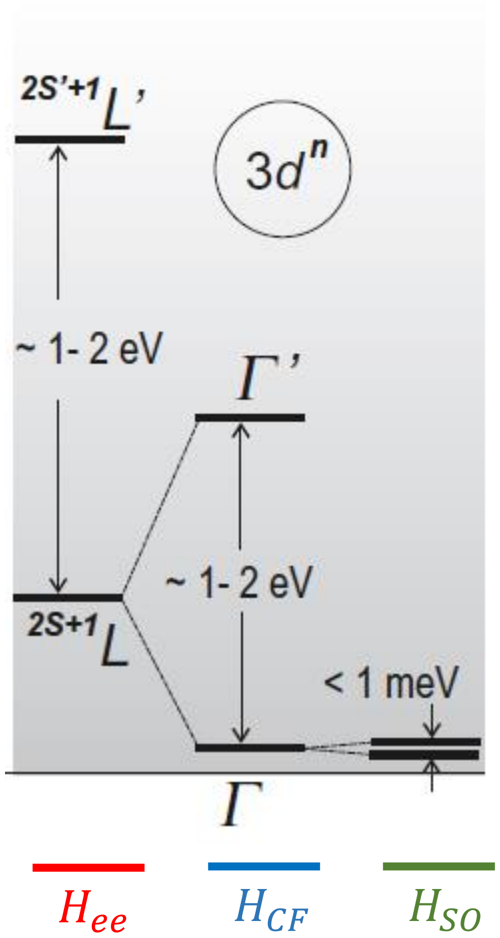
Hund's Rules Moments

2+ Valence					$4f^{6}$ **Sm^{2+}** J = 0 (L = S) $g_J = 0$ $\mu_{cal} = 0\ \mu_B$	$4f^{7}$ **Eu^{2+}** $J = S = 7/2$ $g_J = 2$ $\mu_{cal} = 7.94\ \mu_B$ $\mu_{obs} = 7.9\ \mu_B$						$4f^{13}$ **Tm^{2+}** $J = 7/2$ $g_J = 8/7$ $\mu_{cal} = 4.54\ \mu_B$ $\mu_{obs} = 4.5\ \mu_B$
3+ Valence	$4f^{1}$ **Ce^{3+}** $J = 5/2$ $g_J = 6/7$ $\mu_{cal} = 2.54\ \mu_B$ $\mu_{obs} = 2.5\ \mu_B$	$4f^{2}$ **Pr^{3+}** $J = 4$ $g_J = 4/5$ $\mu_{cal} = 3.58\ \mu_B$ $\mu_{obs} = 3.5\ \mu_B$	$4f^{3}$ **Nd^{3+}** $J = 9/2$ $g_J = 8/11$ $\mu_{cal} = 3.62\ \mu_B$ $\mu_{obs} = 3.4\ \mu_B$	$4f^{5}$ **Sm^{3+}** $J = 5/2$ $g_J = 2/7$ $\mu_{cal} = 0.85\ \mu_B$ $\mu_{obs} = 1.7\ \mu_B$	$4f^{6}$ **Eu^{3+}** J = 0 (L = S) $g_J = 0$ $\mu_{cal} = 0\ \mu_B$ $\mu_{obs} = 3.4\ \mu_B$	$4f^{7}$ **Gd^{3+}** $J = S = 7/2$ $g_J = 2$ $\mu_{cal} = 7.94\ \mu_B$ $\mu_{obs} = 7.9\ \mu_B$	$4f^{8}$ **Tb^{3+}** $J = 6$ $g_J = 3/2$ $\mu_{cal} = 9.72\ \mu_B$ $\mu_{obs} = 9.8\ \mu_B$	$4f^{9}$ **Dy^{3+}** $J = 15/2$ $g_J = 4/3$ $\mu_{cal} = 10.65\ \mu_B$ $\mu_{obs} = 10.6\ \mu_B$	$4f^{10}$ **Ho^{3+}** $J = 8$ $g_J = 5/4$ $\mu_{cal} = 10.61\ \mu_B$ $\mu_{obs} = 10.4\ \mu_B$	$4f^{11}$ **Er^{3+}** $J = 15/2$ $g_J = 6/5$ $\mu_{cal} = 9.58\ \mu_B$ $\mu_{obs} = 9.5\ \mu_B$	$4f^{12}$ **Tm^{3+}** $J = 6$ $g_J = 7/6$ $\mu_{cal} = 7.56\ \mu_B$ $\mu_{obs} = 7.6\ \mu_B$	$4f^{13}$ **Yb^{3+}** $J = 7/2$ $g_J = 8/7$ $\mu_{cal} = 4.54\ \mu_B$ $\mu_{obs} = 4.5\ \mu_B$
4+ Valence	$4f^{1}$ **Pr^{4+}** $J = 5/2$ $g_J = 6/7$ $\mu_{cal} = 2.54\ \mu_B$ $\mu_{obs} = 0.7\ \mu_B$					$4f^{7}$ **Tb^{4+}** $J = S = 7/2$ $g_J = 2$ $\mu_{cal} = 7.94\ \mu_B$ $\mu_{obs} = 8.0\ \mu_B$						

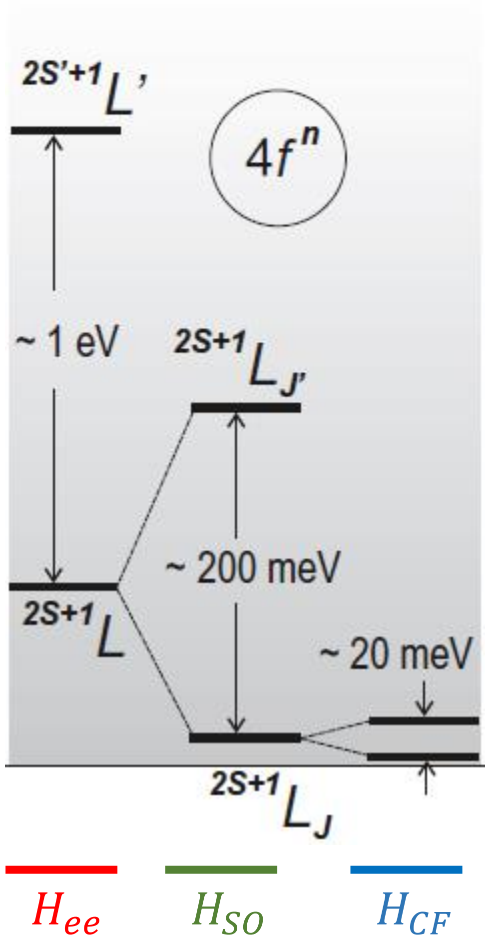
Excellent agreement between the calculated (Hund's rules) and observed moments is found for almost all rare earths. Poor agreement for Sm^{3+}, Eu^{3+}, and Pr^{4+} is due to the proximity of the next highest spin–orbit manifold. The blue shaded ions have an odd number of electrons and therefore Kramers ions, which are guaranteed to have at least a ground state doublet while the pink shaded ions are non-Kramers ions, where a non-magnetic singlet ground state is allowed by symmetry. Non-magnetic Ce^{4+} and Yb^{2+} are not included here.

https://doi.org/10.1038/s42005-022-00853-y

Strength of interactions in 3d and 4f solids



interaction term	3d transition metals	4f rare earths
V_{ee}	1 eV	1eV
V_{so}	50-100 meV	300-500 meV
V_{Zeeman} (B=1T)	0.1 -0.2 meV	0.1 -0.6 meV



The approximate size of the important interactions in solids for the $3d^n$ shell in transition metal ions and the $4f^n$ shell in rare earth ions, illustrated by the observed splitting in spectra of the ions in crystals.

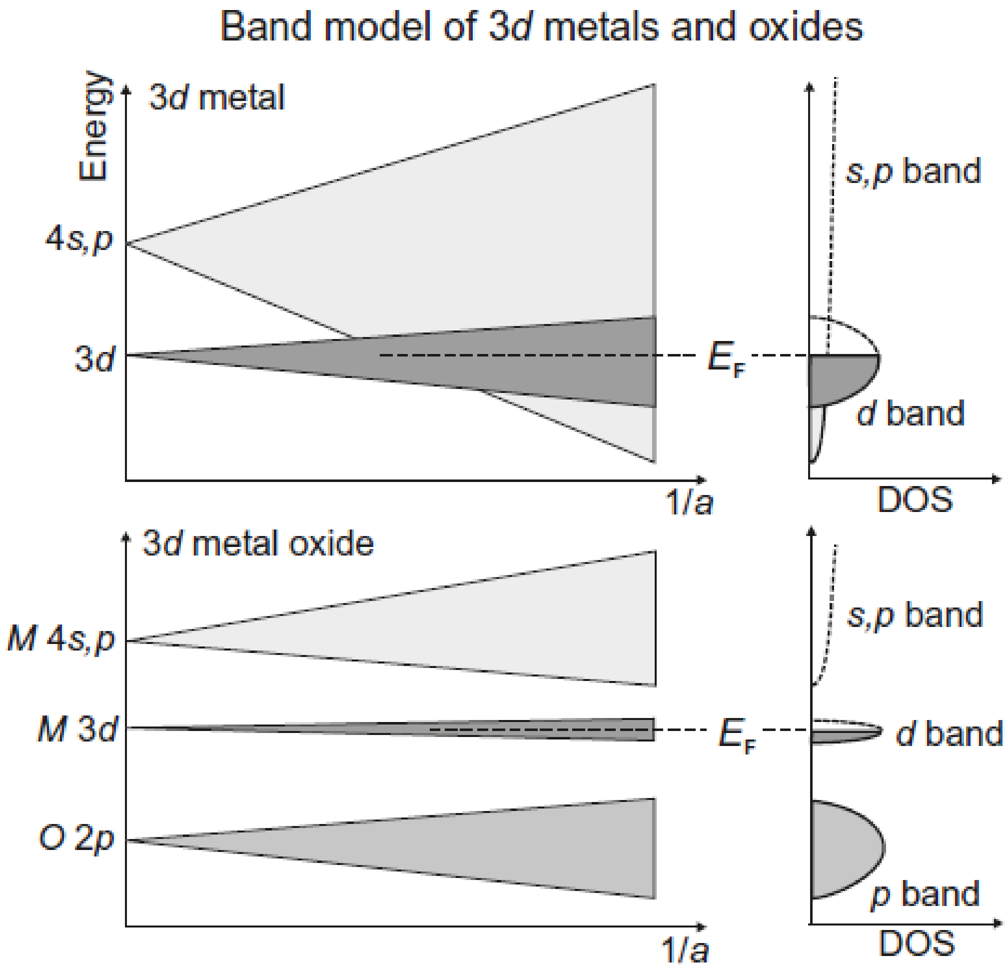
Note the opposite relative size of the CF and the spin–orbit splitting for the $3d$ and $4f$ systems.

Metals *vs* insulating compounds

Metals
Electrons are neither free nor entirely localized near the ion cores. Magnetic moments emerge from the balance of these two tendencies.

Insulating ionic compounds (e.g., transition-metal oxides)
The magnetic moment is determined by the type of atom and its ionic valence at each lattice site, site symmetry (crystal field).

St&Sie06



Large orbital overlap leads to delocalized electrons and large overlapping bands

Small orbital overlap leads to localized electrons (narrow electron bands)

- In a first approximation one may treat the valence orbitals of an insulating material, e.g., a transition metal oxide, as being localized on each ion. By knowing the number of electrons in unfilled shells, the atomic magnetic moment is derived using the Hund's rules.
- This procedure gives approximately correct results for the 4f ions, but fails to reproduce the correct moments for the 3d ions. The reason of this failure is mainly due to the quenching of the orbital component of the magnetic moment induced by the crystal field.

Band formation

The periodic potential of a crystal breaks up the atom states and redistributes the valence electrons in Bloch states
-> the quantum numbers *nlm* and atom position (***r***) are replaced by the band index *n,* orbital character (*lm*) and the wave vector *k*

In band theory, combining orbitals on different atoms corresponds to the formation of Bloch functions which, for the case of a linear chain of N atoms, are written as:

$$\phi_j(\boldsymbol{k}) = \sum_q d_j^{(q)} e^{i\boldsymbol{k}aq}$$

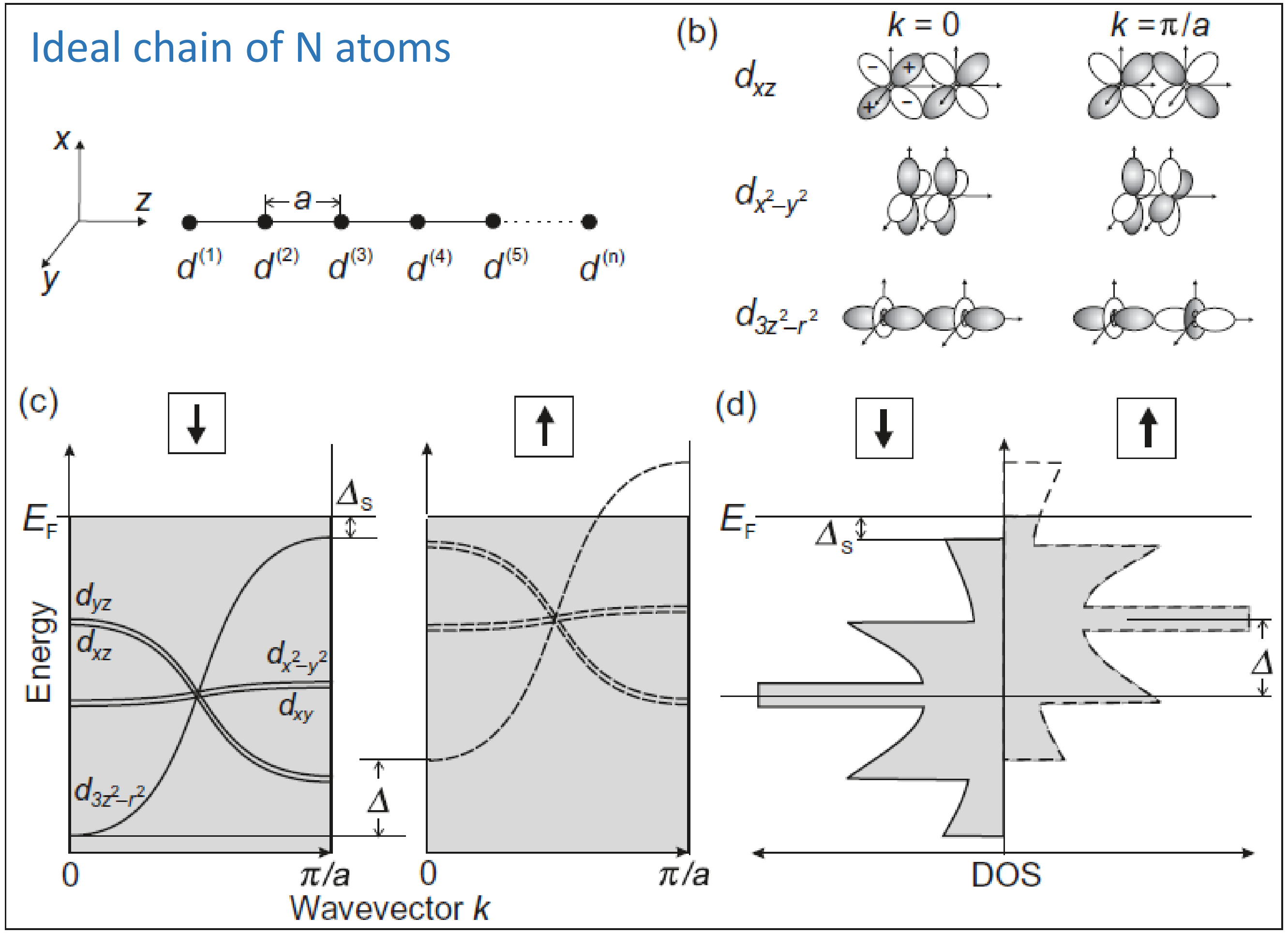
$d_j = d_{xy}, d_{xz}, \ldots$

For *k=0*

$$\phi_j(0) = \sum_q d_j^{(q)}$$

For *k=π/a*

$$\phi_j\left(\frac{\pi}{a}\right) = \sum_q (-1)^q d_j^{(q)}$$

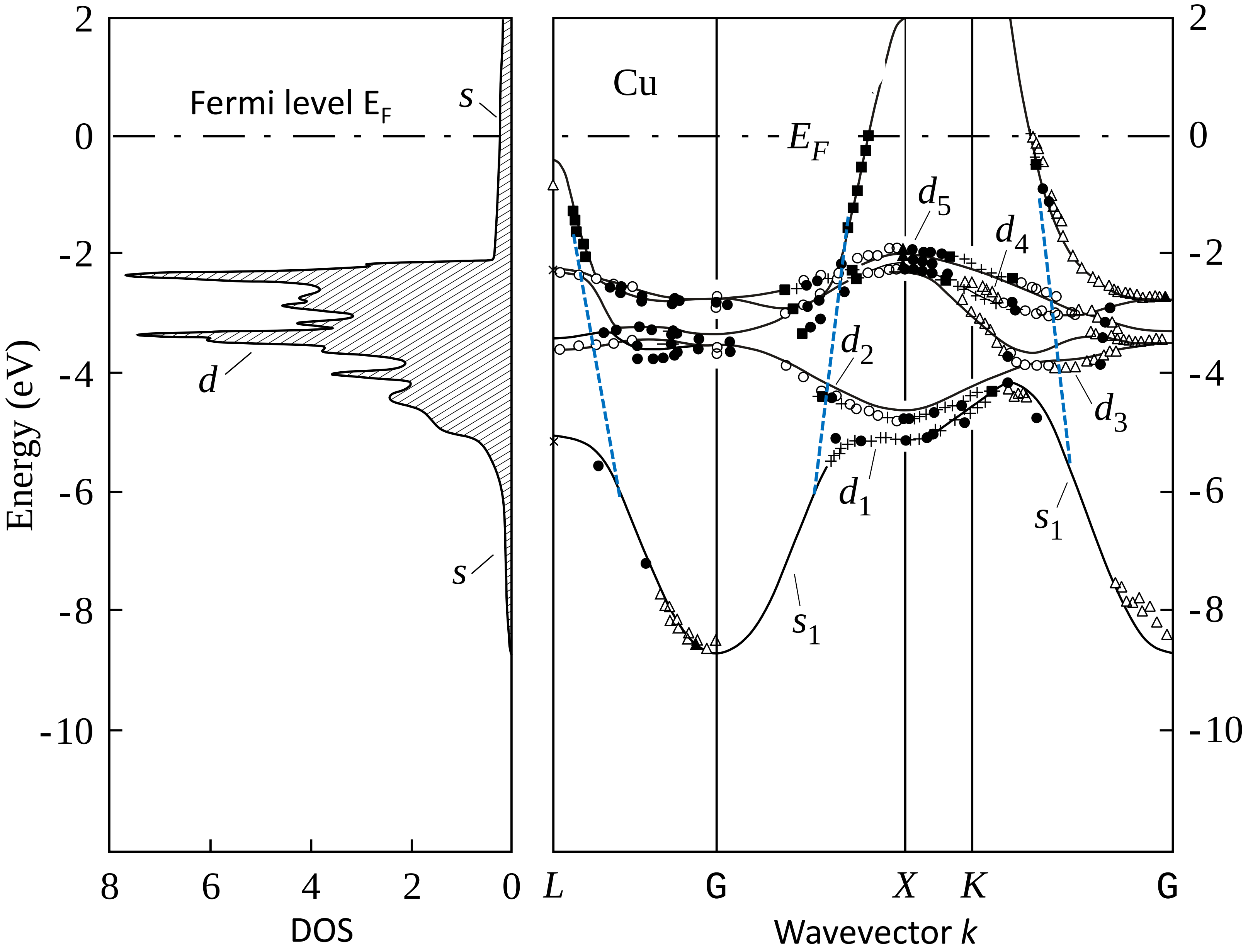

Ideal chain of N atoms

St&Sie06

Orbitals pointing at each other (strong interaction) show dispersion

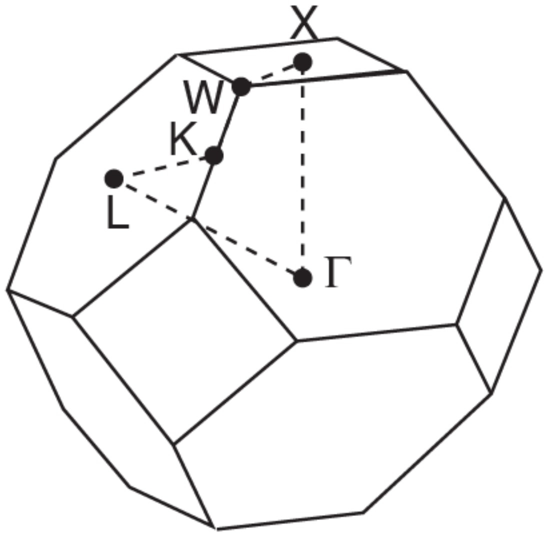
Orbitals parallelly aligned (poor interaction) do not disperse (mostly ***k***-independent)

Cu band structure and density of states (DOS)

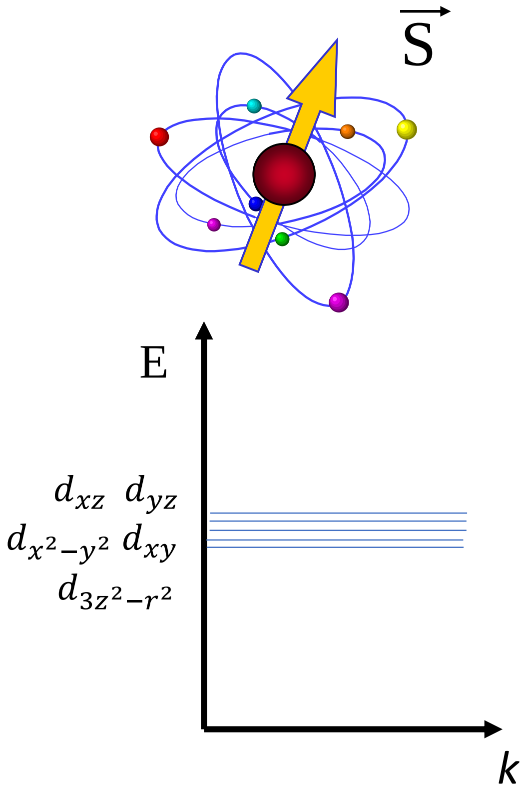


Cu: fcc crystal

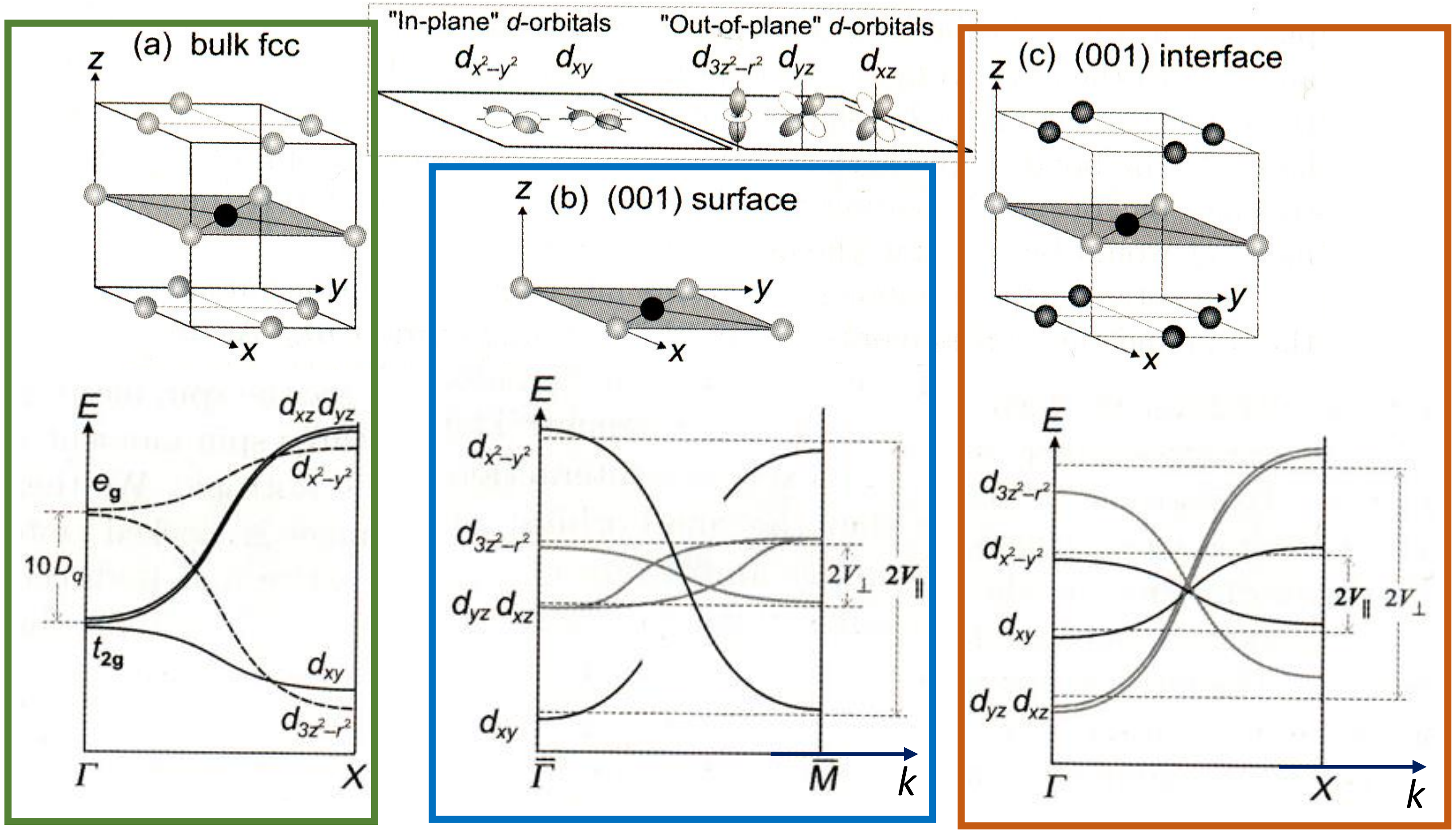
first Brillouin zone:



d-state dispersion *vs.* CF symmetry *vs.* *L* quenching



atom:
quantized, degenerate orbitals



Bulk: bands form due to overlapping of the wave functions of close atoms.

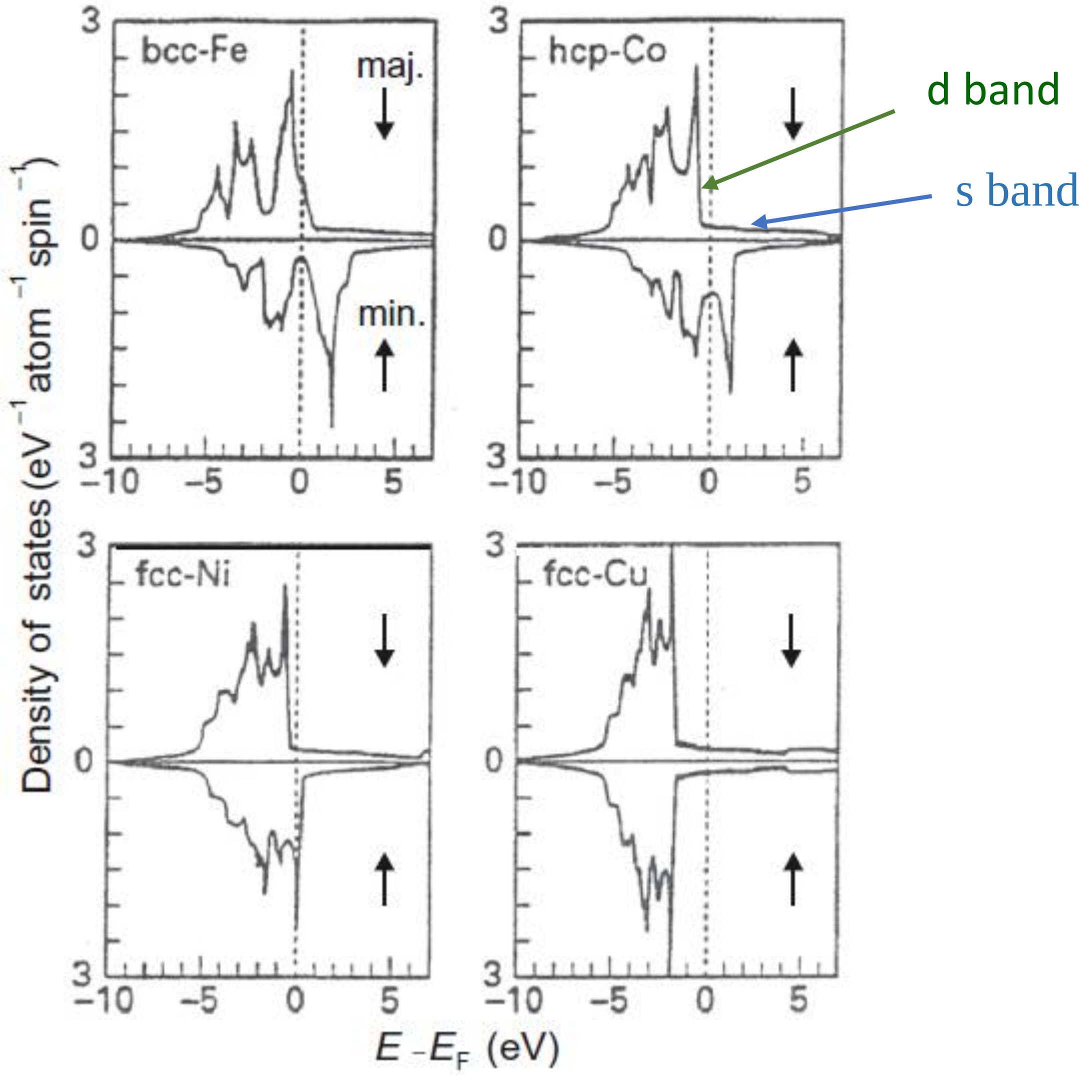
b) **free-standing monolayer**: mainly the in-plane d-orbitals feel the bonds and then show big splitting and dispersion in the (*E*,*k*) space while the out-of-plane d-orbitals stay mostly unperturbed **-> L_z quenched**

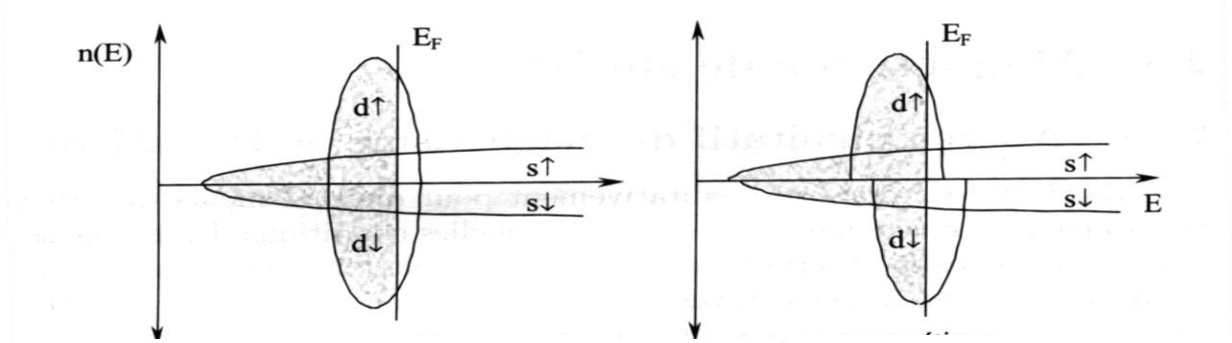
c) **multilayer** with stronger out-of-plane than in-plane bonds: the situation is reversed **-> $L_{x,y}$ quenched**

a) **cubic structure** in-plane and out-of-plane bonds have similar strength and then the dispersion of the d-orbitals is similar **-> $L_{x,y,z}$ quenched**

Band contribution to the spin moment

Spin moment is given by the unbalance
between spin up and down





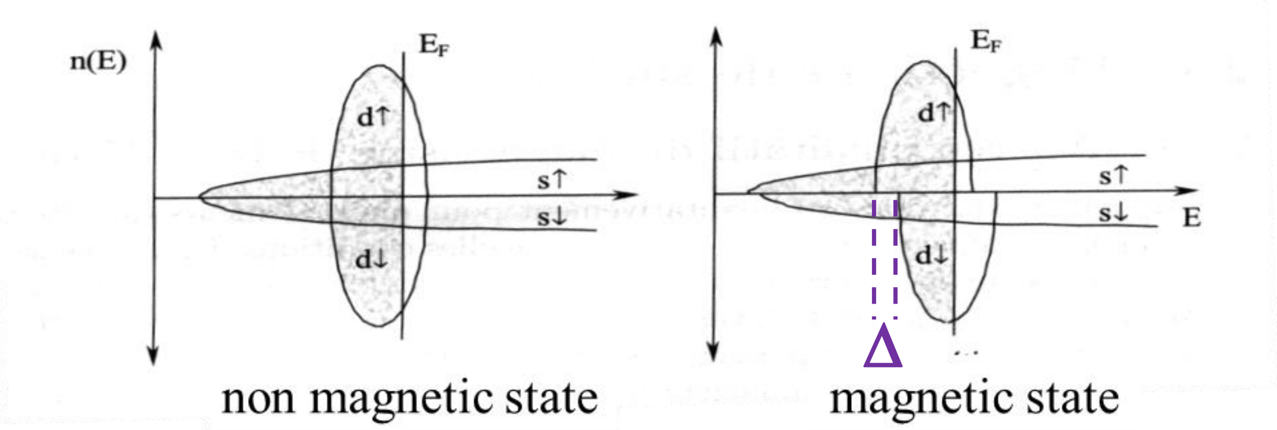
non magnetic state: $N_{up} = N_{dw}$ magnetic state $N_{up} \neq N_{dw}$

- s, p bands are extended (band width about 10 eV) -> contribute by about 5% to the total moment
- d bands are narrow (band width about 3 eV) -> their splitting determines the magnetism

St&Sie06; S. Blugel Phys. Rev. Lett. **68**, 851 (1992)

Stoner model for spontaneous magnetization: exchange splitting

The total electron energy of N electrons is given by the sum of the energies of all occupied states



non magnetic state

magnetic state

n(E) : density of states

Coulomb interaction: $V_{ee}\, N_{up}\, N_{down}$

$$N_{up} = N/2$$
$$N_{dw} = N/2$$

$$N_{up} = N/2 + n(E_F)\Delta/2$$
$$N_{dw} = N/2 - n(E_F)\Delta/2$$

Each band shifts by $\Delta/2$ in opposite directions;
N_{up} (N_{down}) increases (decreases) by $dN = n(E_F)\,\Delta/2$.
Gain (loss) in energy is = $dN * \Delta/2$

Kinetic energy variation = $\frac{\Delta}{2}\left(dN_{up} - dN_{dw}\right) = \frac{\Delta}{2}\left[n(E_F)\frac{\Delta}{2} - \left(-n(E_F)\frac{\Delta}{2}\right)\right] = \frac{\Delta^2}{2} n(E_F)$

Coulomb (e-e) interaction variation = $V_{ee}\left[\frac{N^2}{4} + n(E_F)\frac{\Delta}{2} * \frac{N}{2} - n(E_F)\frac{\Delta}{2} * \frac{N}{2} - \frac{\Delta^2}{4} n^2(E_F)\right] - V_{ee}\frac{N^2}{4} = -V_{ee}\frac{\Delta^2}{4} n^2(E_F)$

Total electron energy variation $dE = \frac{\Delta^2}{2} n(E_F) - V_{ee}\frac{\Delta^2}{4} n^2(E_F) = \frac{\Delta^2}{2} n(E_F)\left(1 - \frac{V_{ee}}{2} n(E_F)\right)$

If dE < 0 spontaneous magnetism appears -> $1 - \frac{V_{ee}}{2} n(E_F) < 0$ (Stoner criterion)

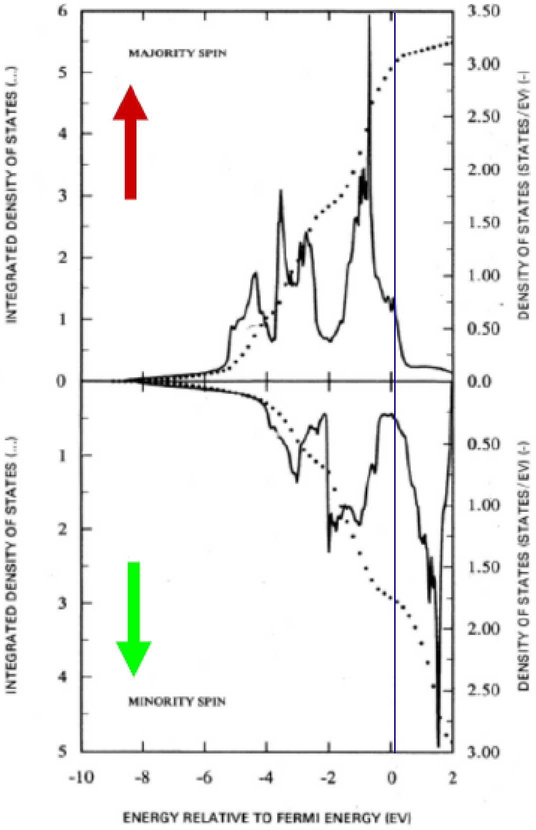
It depends on V_{ee} and $n(E_F)$ (both are material dependent)

St&Sie06; S. Blugel Phys. Rev. Lett. **68**, 851 (1992)

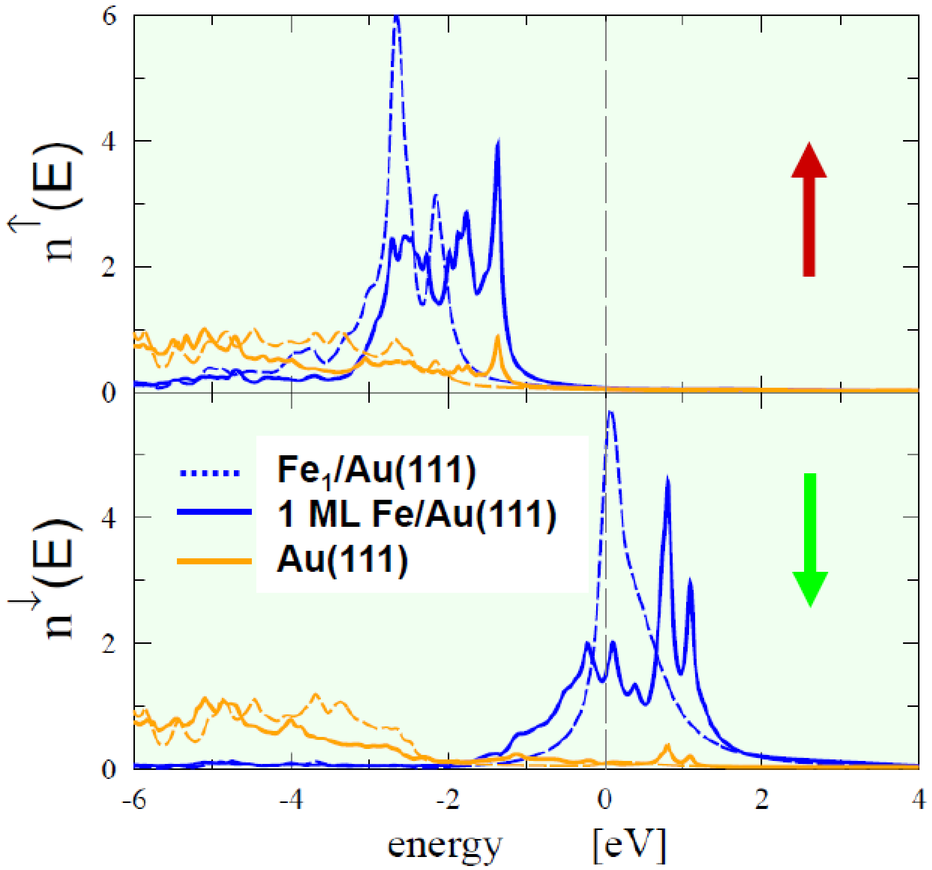
Band narrowing in low-dimension leads to increased exchange splitting

See exercise: 2.4

bulk Fe DOS



Moruzzi, Janak, and Williams,
Calculated electronic properties of metals
(Pergamon, 1978)

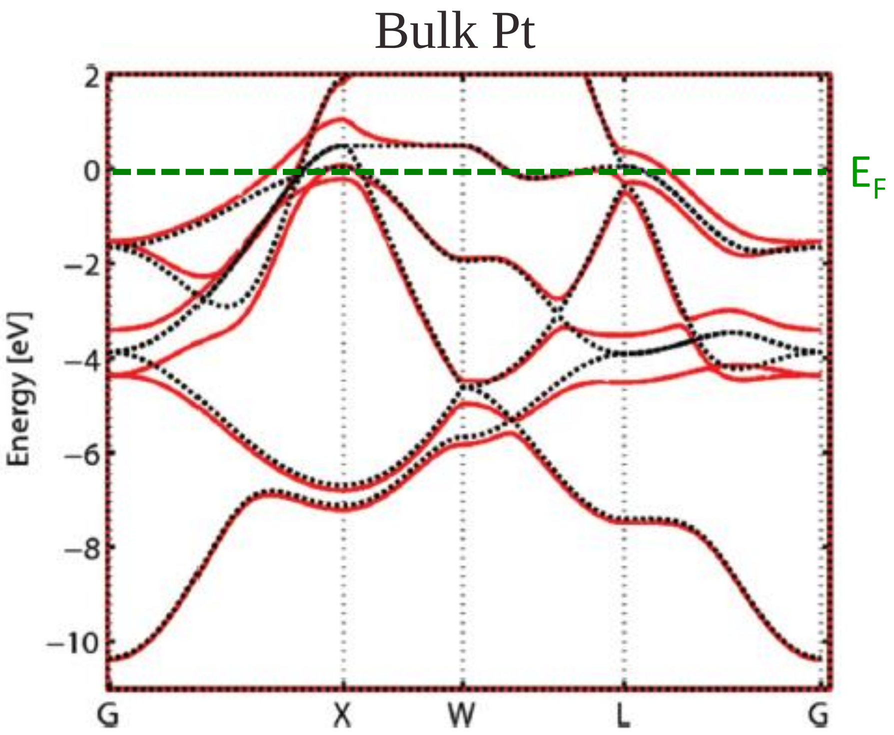


Sipr, Minar, and Ebert,
Europhys. Lett. 87, 67007(2009)

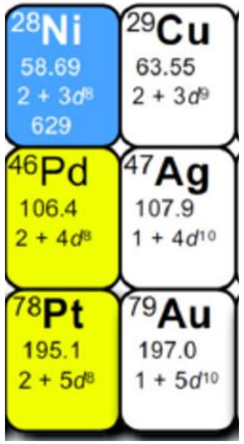
Fe_1 is one Fe atom at Au(111) surface

$m_S (Fe_1) > m_S (1ML) > m_S (Fe\ bulk)$

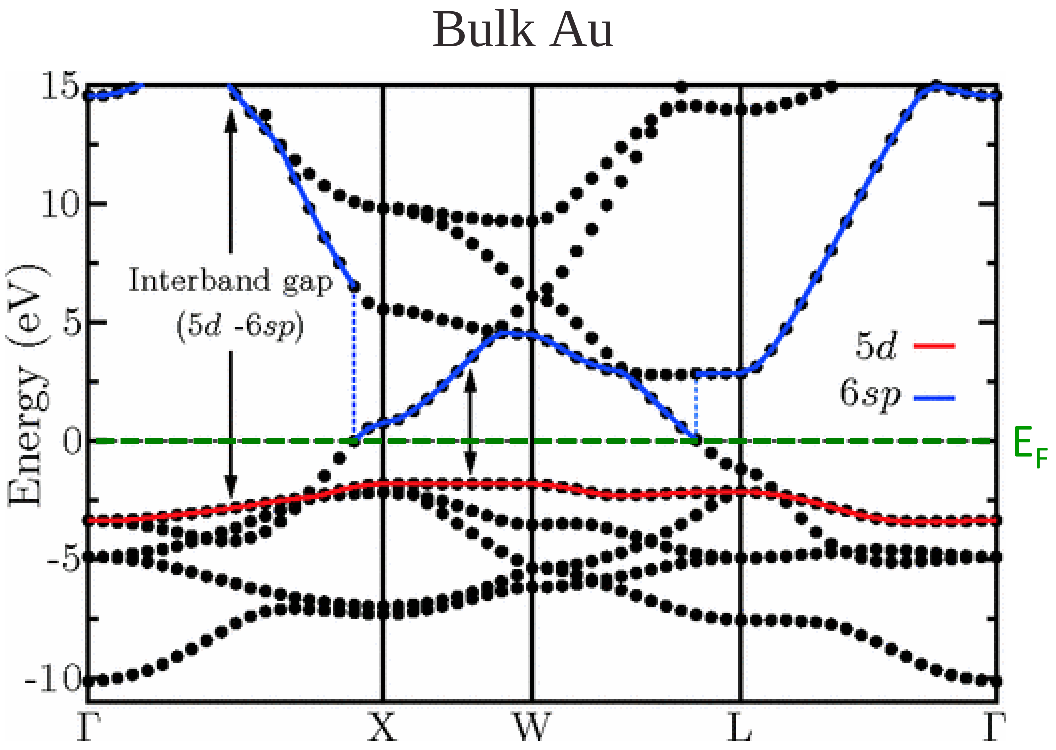
Band structure magnetism



Band structure of bulk Pt. Solid lines: with spin-orbit coupling, dotted lines: without spin-orbit coupling



^{28}Ni 58.69 2 + $3d^8$ 629	^{29}Cu 63.55 2 + $3d^9$
^{46}Pd 106.4 2 + $4d^8$	^{47}Ag 107.9 1 + $4d^{10}$
^{78}Pt 195.1 2 + $5d^8$	^{79}Au 197.0 1 + $5d^{10}$



Pt -> Fermi level crosses 5d band
-> close to show spontaneous magnetization
(need some extra interaction to promote band splitting)

Au-> 5d states well below Fermi level
-> difficult to induce magnetism
(big band splitting is necessary to have magnetism)

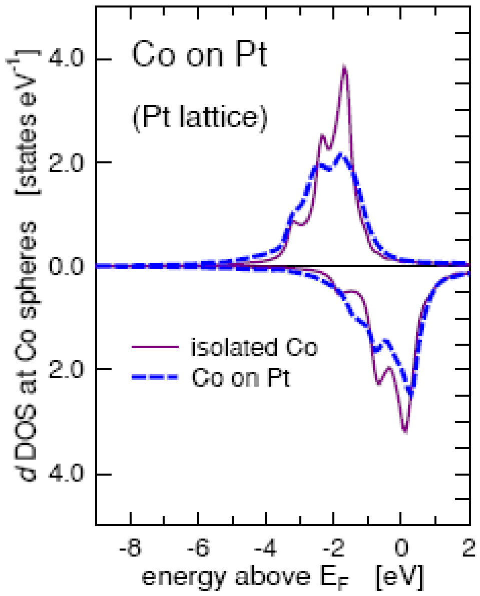
The same is true if we look at Pd and Ag

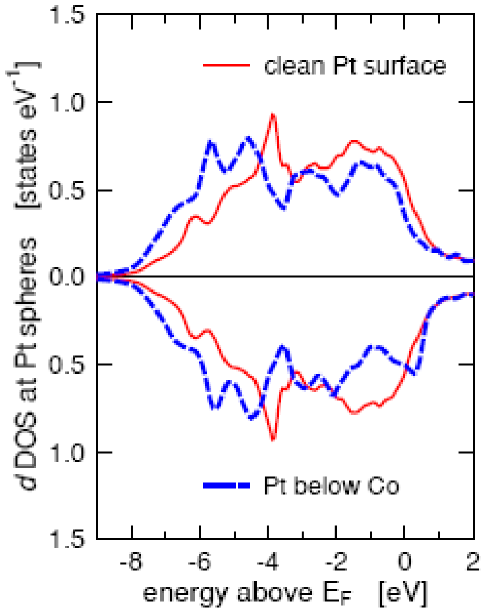
P.M. Haney *et al.*, Phys. Rev. B **88**, 214417 (2013); T. Rangel *et al.*, Phys. Rev. B **86**, 125125 (2012)

Hybridization and dimensionality effects

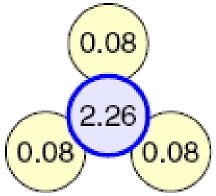
See exercise: 2.5

Co monomer on Pt: hybridization with the substrate





Asymmetry in the Pt LDOS at E_F when covered by Co->
induced magnetic moment in the Pt(111)

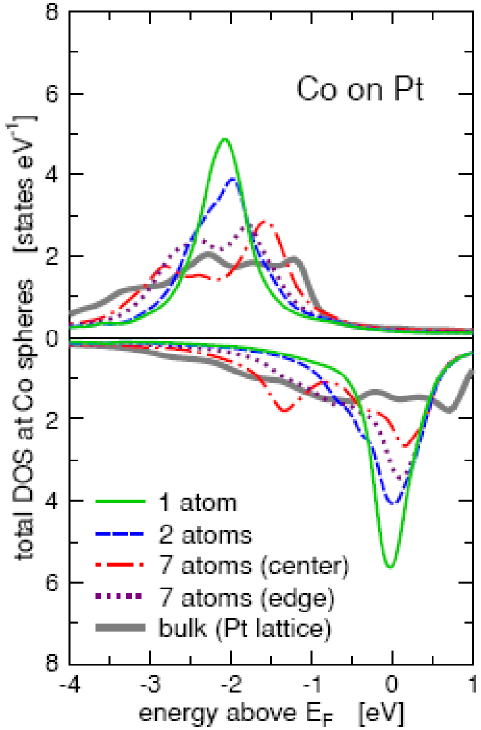


● Co atom

○ Pt atom

Size dependence

Reduced asymmetry by increasing the cluster size -> reduced magnetic moment

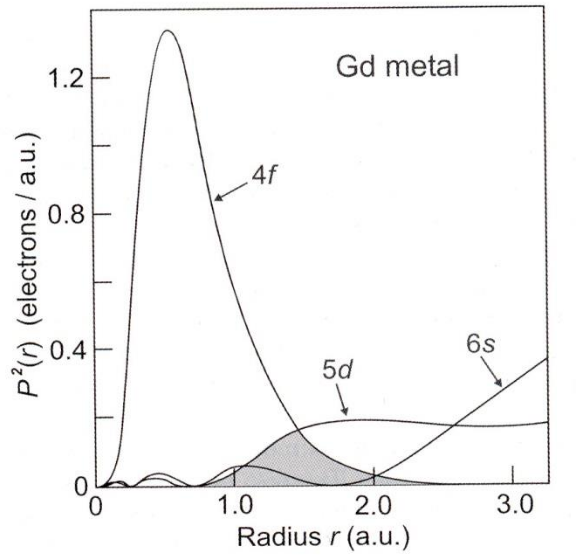


O. Sipr *et al.* J. Phys.: Condens. Matter. 19, 096203 (2007)

3d metals *vs* 4f lanthanides

Electronic configuration gas phase: [Xe] 6s^2 4f ^{N}

(exception for Gd: [Xe] 6s^1 5d^1 4f^7)

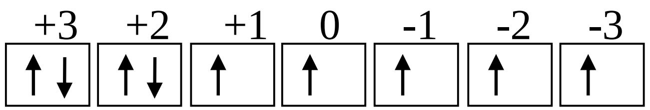


4f states are strongly localized ->
do not participate to bonding
CF ~ 10 meV
SOC ~ 200 meV
Coulomb repulsion ~ 1-10 eV

The difference between atomic and bulk case is the electronic configuration.
In bulk: [Xe] *4f $^{N-1}$ 5d^1 6s^2*
with the 3 electrons in the outer shells participating to bond formation

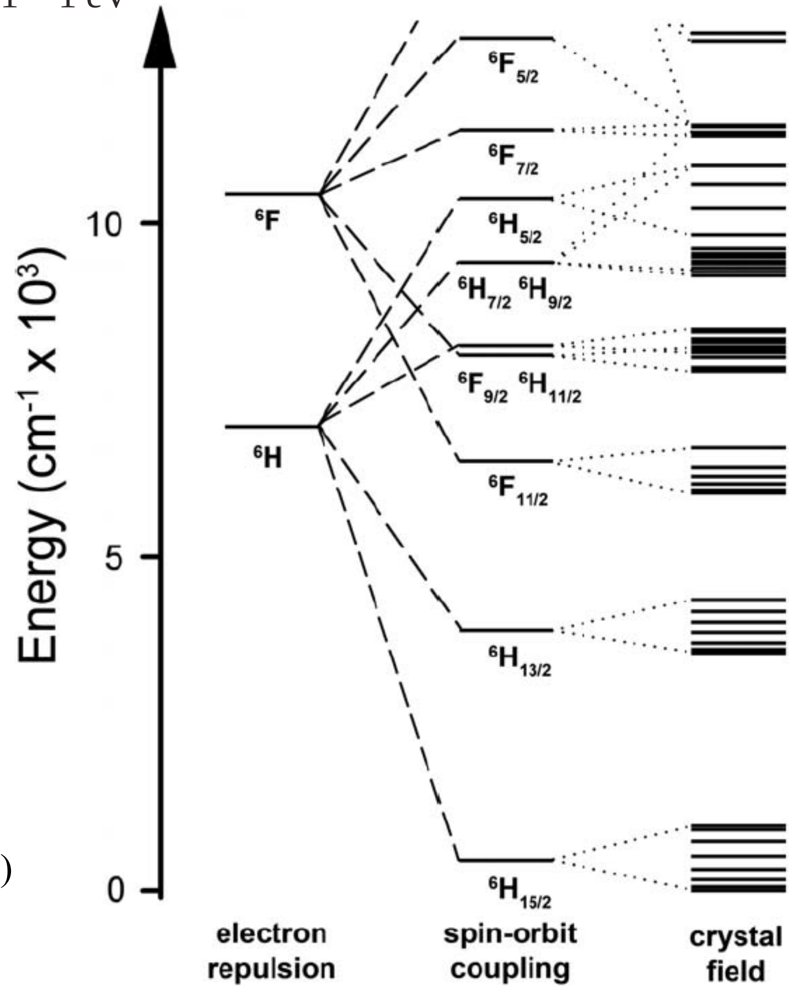
- Magnetic moment defined by the 4f states
- L unquenched (small CF for the 4f, Hund's rules hold)

Dy^{3+} (6s^0 4f ^{9})



L= 5; S=5/2 -> ground state $^6H_{15/2}$

8000 cm-1 ~ 1 eV



St&Sie-2006 J.D. Rinehart, *et al.* Chem. Sci., **2,** 2078 (2011)

Condensed summary

Single atom: $V_{ee} \Rightarrow \begin{matrix} \boldsymbol{S} \\ \boldsymbol{L} \end{matrix}$ ⇨ $V_{ee} + V_{SO} \Rightarrow$ ***J = S+L***

Ensemble of atoms: $V_{ee} \Rightarrow \begin{matrix} \boldsymbol{S} \\ \boldsymbol{L} \end{matrix}$ ⇨

3d $V_{ee} + V_{CF} \Rightarrow \begin{matrix} \boldsymbol{S} \\ \boldsymbol{L \approx 0} \end{matrix}$ $V_{ee} + V_{CF} + V_{SO} \Rightarrow \begin{matrix} \boldsymbol{L \geq 0} \\ \boldsymbol{J = S+L} \end{matrix}$

4f $V_{ee} + V_{SO} \Rightarrow$ ***J = S+L*** $V_{ee} + V_{SO} + V_{CF} \Rightarrow$ ***J = S+L***