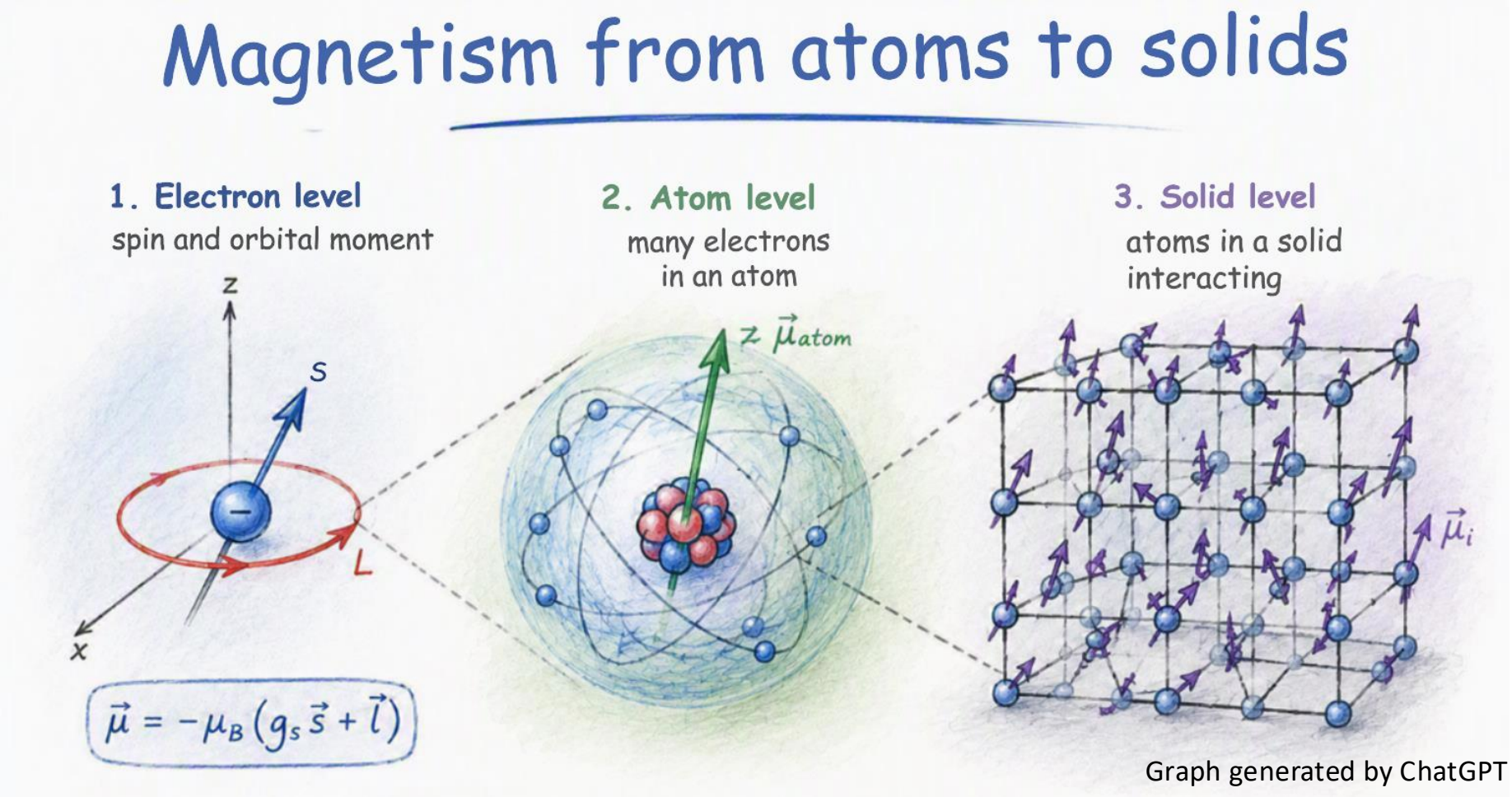
School on Magnetism 2026



Graph generated by ChatGPT

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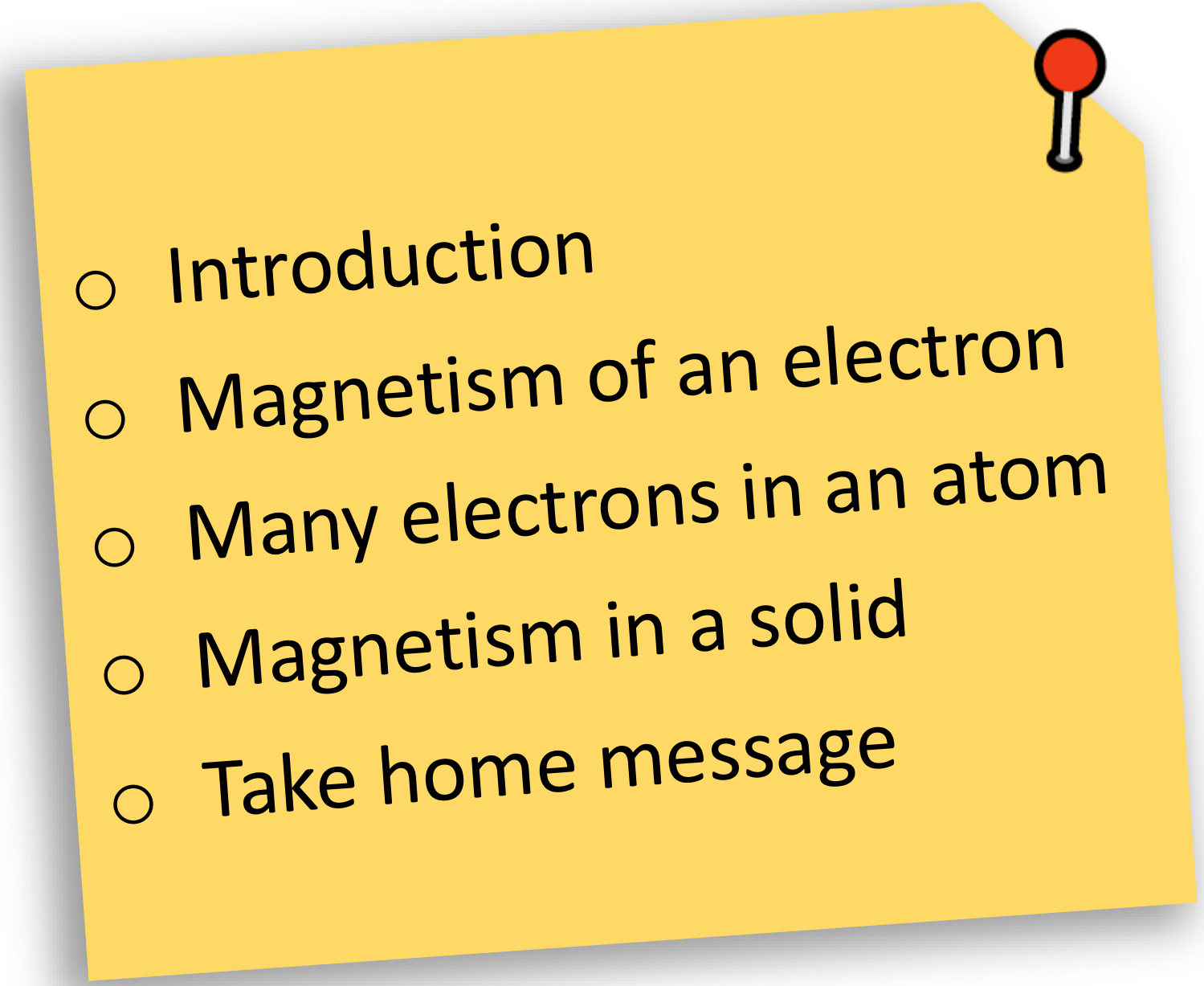
UPPSALA UNIVERSITET

Outline


Introduction
Magnetism of an electron
Many electrons in an atom
Magnetism in a solid
Take home message

Magnetism is a quantum phenomenon

- Bohr-van Leeuwen theorem:

  - Classical Physics ➜ Equilibrium magnetization is zero
  - The dependence on the magnetic field can
    be removed by changing the integration variable

  ⇨ Consequently, no ferromagnetism, diamagnetism or other magnetic order exist

- Magnetism arises from the interaction of electrons

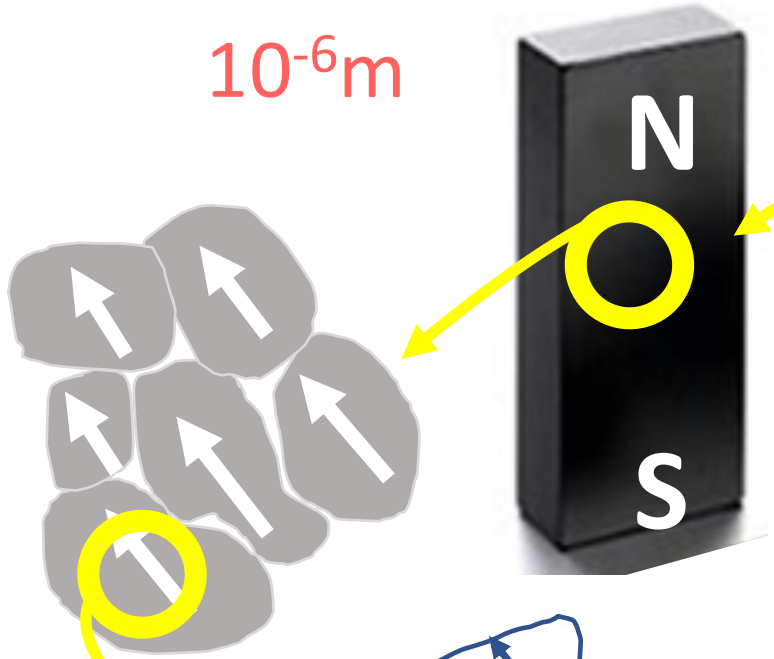
  - Classical dipole picture does not hold
  - What counts are the Pauli principle and the Coulomb repulsion between the electrons ➜ $E(\uparrow\uparrow) \neq E(\uparrow\downarrow)$

What drives magnetism?

10^{0}m

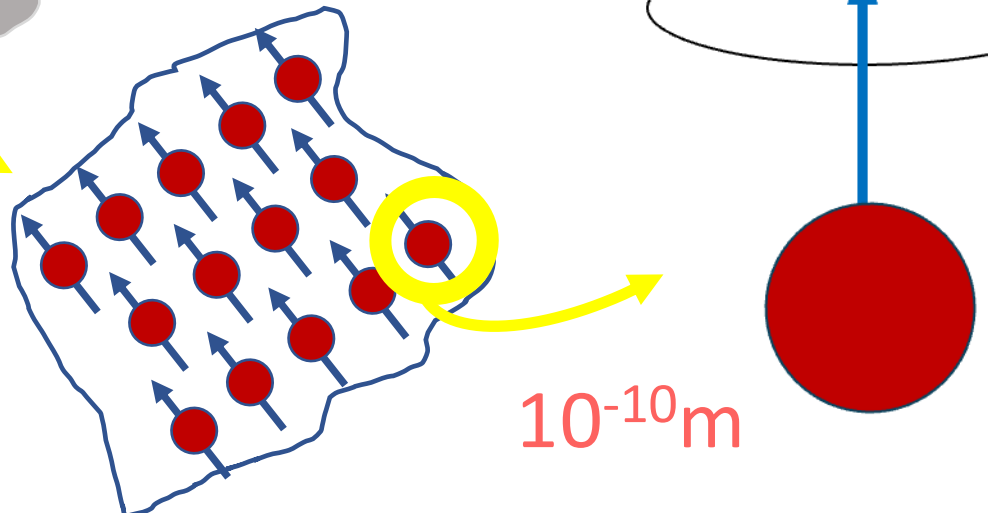
10^{-2}m

10^{-6}m



$<10^{-18}$m

10^{-8}m



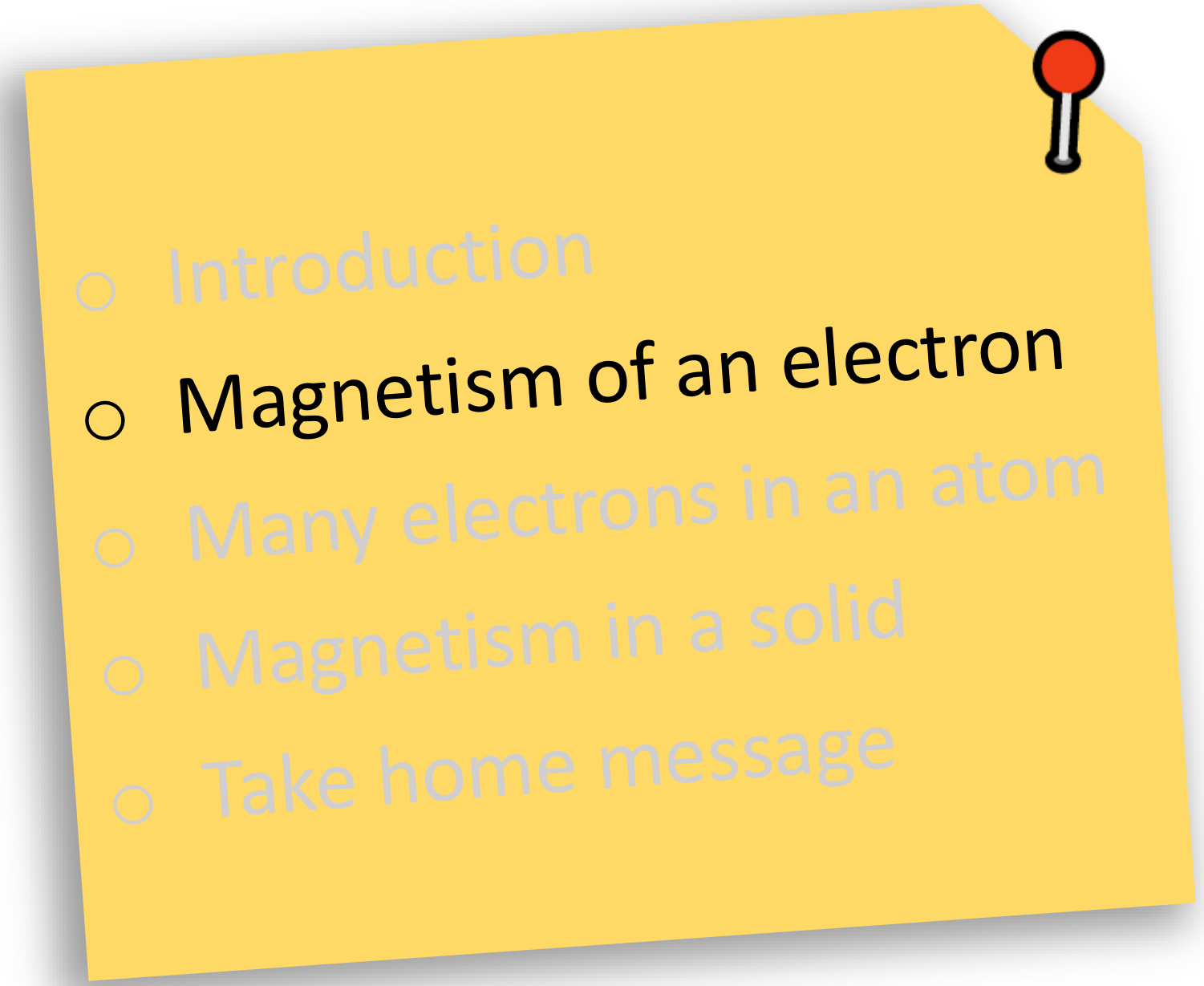
10^{-10}m

Applications need tailored magnetic materials

To understand and develop such materials

☞ We need to go small and look at electrons and spins…

Outline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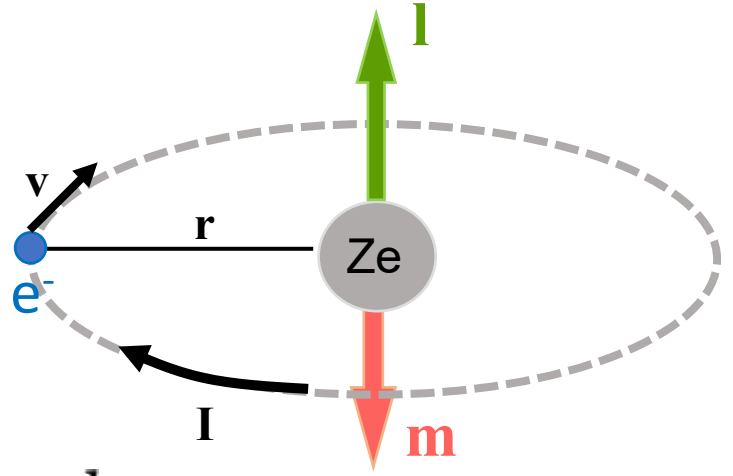
Magnetism of the electron - The orbital momentum

An electron with velocity **v** creates a current **I** and a magnetic moment **m**



Angular momentum $\mathbf{l} = m_e \mathbf{r} \times \mathbf{v}$

Bohr: Angular momenta are quantized – they are multiples of ħ = h/2π

z-component $l_z = m_l \hbar$ with $m_l = -l, \ldots, -1, 0, 1, \ldots, +l$

Magnetic moment $\mathbf{m} = \mathbf{I}\mathcal{A} = -\frac{e}{2}\mathbf{r} \times \mathbf{v} = -\frac{e}{2m_e}\mathbf{l}$

z-component of **m** $m_z = -\frac{e\hbar}{2m_e} m_l = -\mu_B m_l$

Bohr magneton

$\mu_B = 9.274 \cdot 10^{-24}$ J/T

Circular orbit:

$$I = -\frac{e}{\tau} = -\frac{ev}{2\pi r}$$

$$\mathcal{A} = \pi r^2$$

$$\rightarrow \quad m = -\frac{evr}{2}$$

Magnetism of the electron - The orbital momentum

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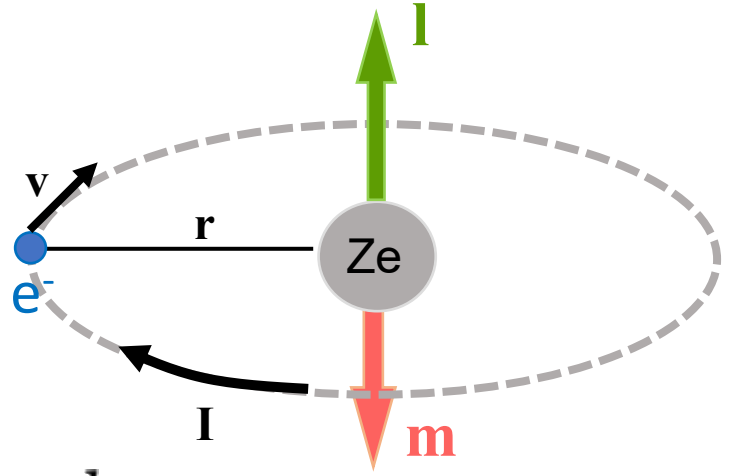

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Bohr magneton

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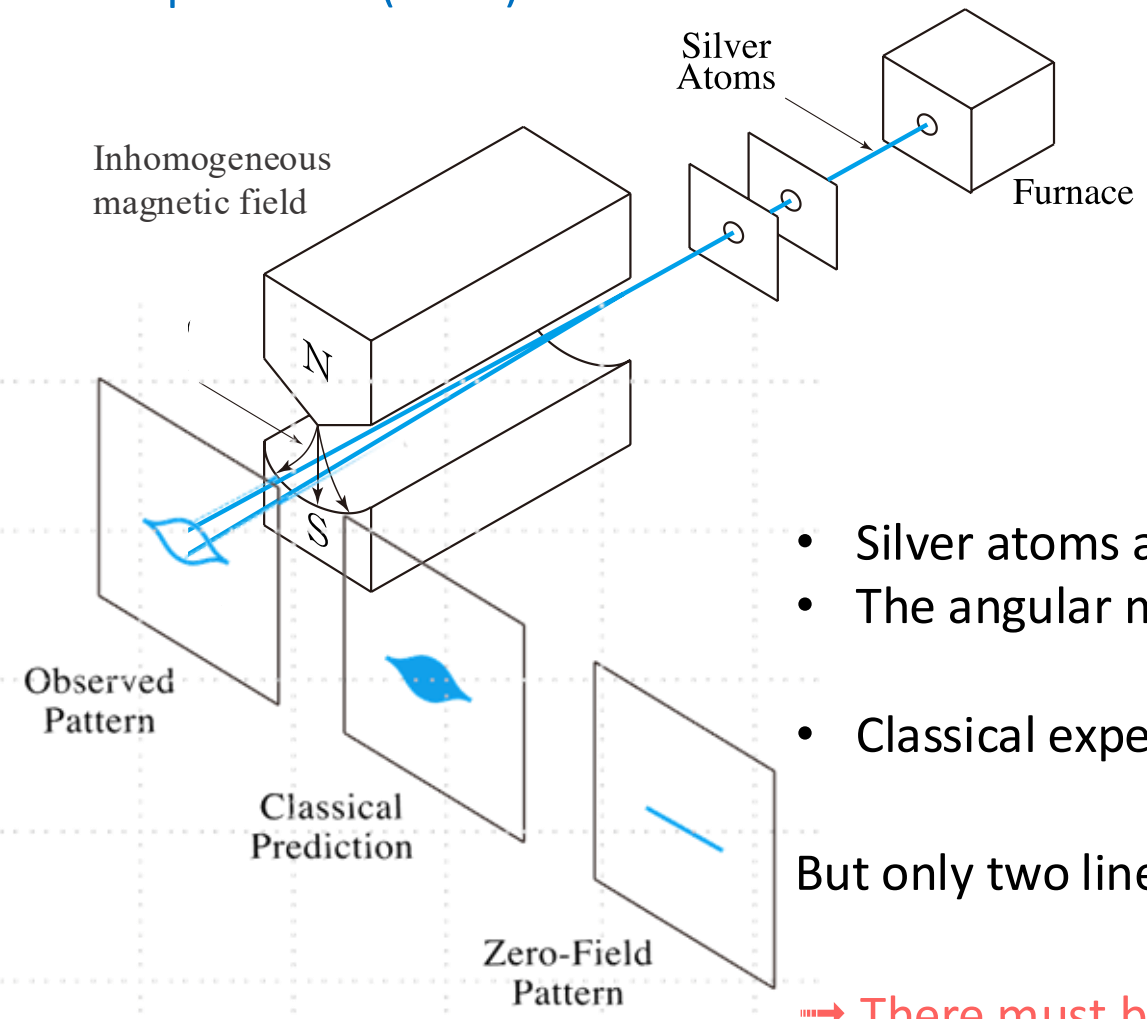
Ratio between **m** and **l**:

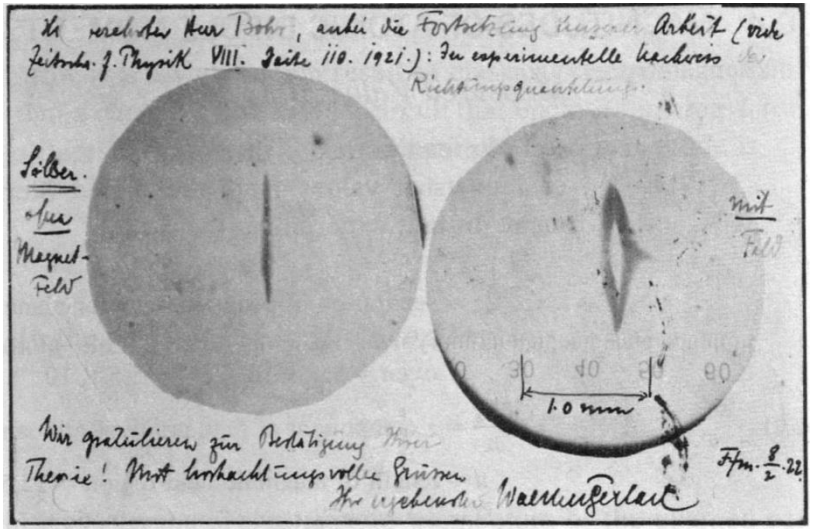
$$\left(\frac{\mathbf{m}}{\mu_B}\right) = g\left(\frac{\mathbf{l}}{\hbar}\right)$$

g = 1 for orbital motion (classical value)

Magnetism of the electron – The spin of the electron

Stern – Gerlach experiment (1922)





Postcard from Gerlach to Bohr, DOI: 10.1063/1.1650229

- Silver atoms are magnetic ⇢ measure magnetic moment
- The angular momentum of silver atoms is zero

- Classical expectation ⇢ homogenous distribution of moments

But only two lines were observed ⇢ two quantum numbers: $\pm\frac{1}{2}$

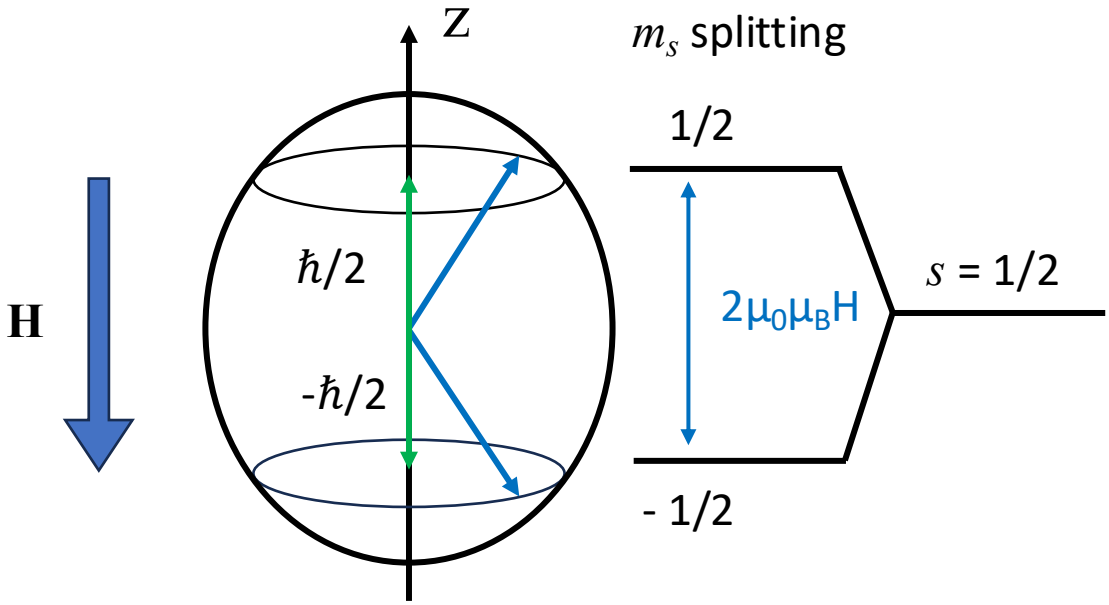
⇢ There must be more than the orbital angular momentum …
⇢ Experiment confirmed Bohr's prediction of the **spin**

Graphics adapted from https://en.namu.wiki/w/슈테른-게를라흐%20실험

Magnetism of the electron – The spin of the electron

$$s_z = m_s\hbar \qquad m_s = \pm\frac{1}{2} \qquad s = \frac{1}{2}$$

$$\mathbf{m} = -\frac{e}{m_e}\mathbf{s} \qquad m_z = -\frac{e}{m_e}m_s\hbar = \pm\mu_B$$



The spin and angular momentum contribute to the total magnetic moment of the electron

$$\mathbf{m} = -\frac{\mu_B}{\hbar}(\mathbf{l} + 2\mathbf{s})$$

Ratio between **m** and **s:**

$$\left(\frac{\mathbf{m}}{\mu_B}\right) = g\left(\frac{\mathbf{s}}{\hbar}\right)$$

g = 2 for spin !

Exact: g = 2.0023

Magnetism of the electron – the total moment

Spin and orbital moment are not independent!

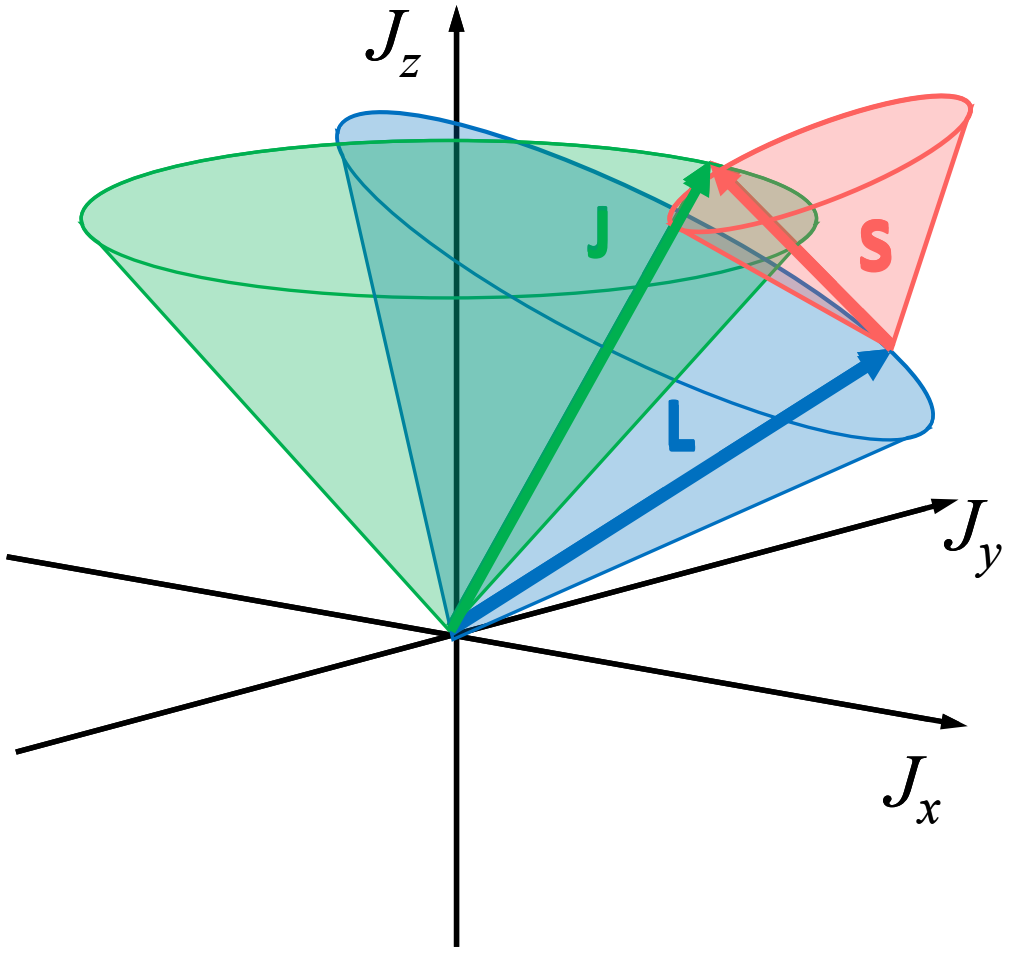
Total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$

Total magnetic moment

$$\mathbf{m} = -\frac{e}{2m_e}(\mathbf{l} + 2\mathbf{s})$$

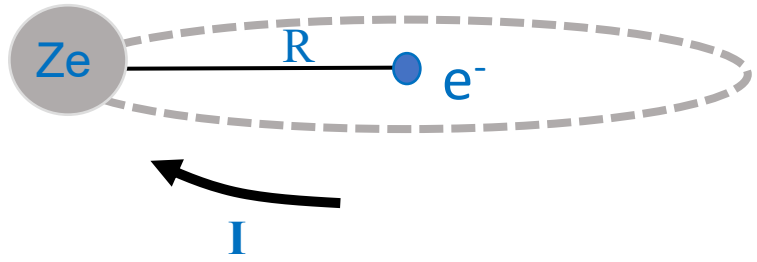
How strong is the coupling between $\mathbf{l}$ and $\mathbf{s}$?

What influences the strength?

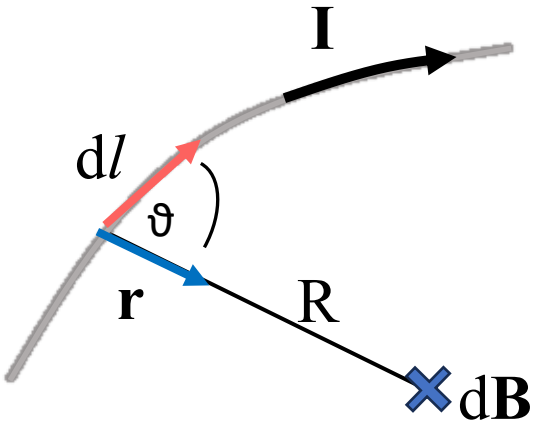


Magnetism of the electron – spin-orbit coupling

Invert the reference system – take the electron's point of view



Biot-Savart law $d\mathbf{B} = \frac{\mu_0}{4\pi} \mathbf{I} \frac{\mathbf{r} \times d\mathbf{l}}{R^3}$



Here: $\mathbf{r} \perp d\mathbf{l} \Rightarrow d\mathbf{B} = \frac{\mu_0}{4\pi} \mathbf{I} \frac{d\mathbf{l}}{R^2} \Rightarrow \mathbf{B} = \frac{\mu_0 \mathbf{I}}{4\pi R^2} \underbrace{\oint d\mathbf{l}}_{2\pi r} = \frac{\mu_0 \mathbf{I}}{2R}$

Energy of the magnetic field $\epsilon_{SO} = -\mathbf{mB}$

Assume: $m = 1\mu_B$ than the spin-orbit coupling energy becomes:

$$\epsilon_{SO} = -\frac{\mu_0 \mu_B^2}{2\pi a_o^3} e Z^4$$

We know already that

$I = \frac{Zev}{2\pi R}$ see l part | $m_e v R \approx \hbar$ | $R \sim \frac{a_0}{Z}$ e- close to nuclei | $\mu_B = \frac{e\hbar}{2m_e}$

Hamiltonian: $\mathcal{H}_{SO} = \lambda \mathbf{ls}$

Spin-orbit coupling constant λ

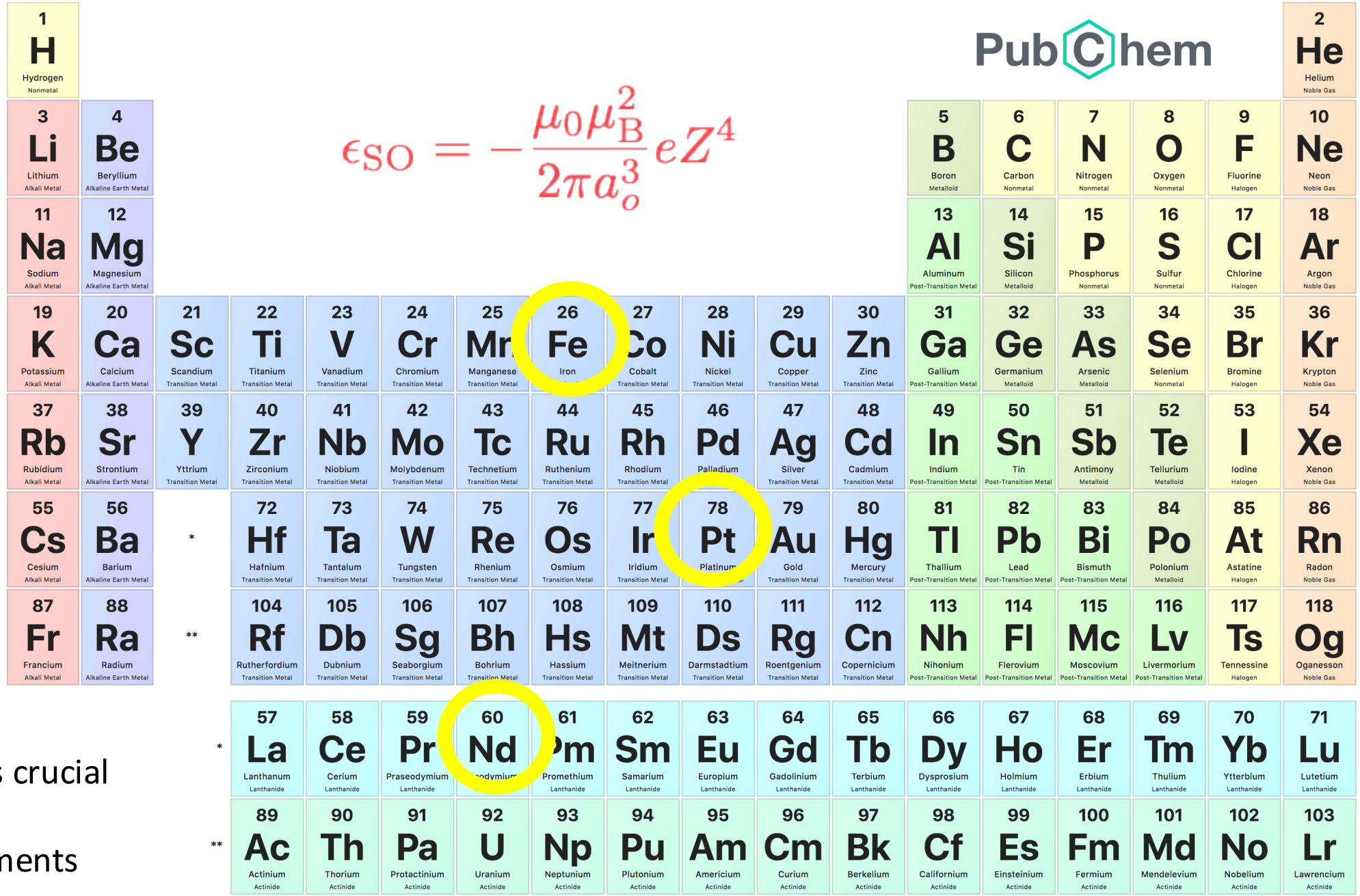
Periodic table

$$\epsilon_{SO} = -\frac{\mu_0 \mu_B^2}{2\pi a_o^3} e Z^4$$

Fe ϵ_{SO}^{Fe}

Nd $28 \cdot \epsilon_{SO}^{Fe}$

Pt $81 \cdot \epsilon_{SO}^{Fe}$



Spin-orbit coupling is crucial for heavy elements such as 4f or 5d elements

Magnetism of the electron – a single electron atom

Time independent Schrödinger equation

$$\left(\left[-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{1}{\hbar^2 r^2}\mathbf{l}^2\right)\right]-\frac{e^2}{4\pi\epsilon_0 r}\right)\Psi_n = E_n\Psi_n$$

With $$\mathbf{l}^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Solution

$$\Psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)Y_l^{m_l}(\theta,\phi)$$

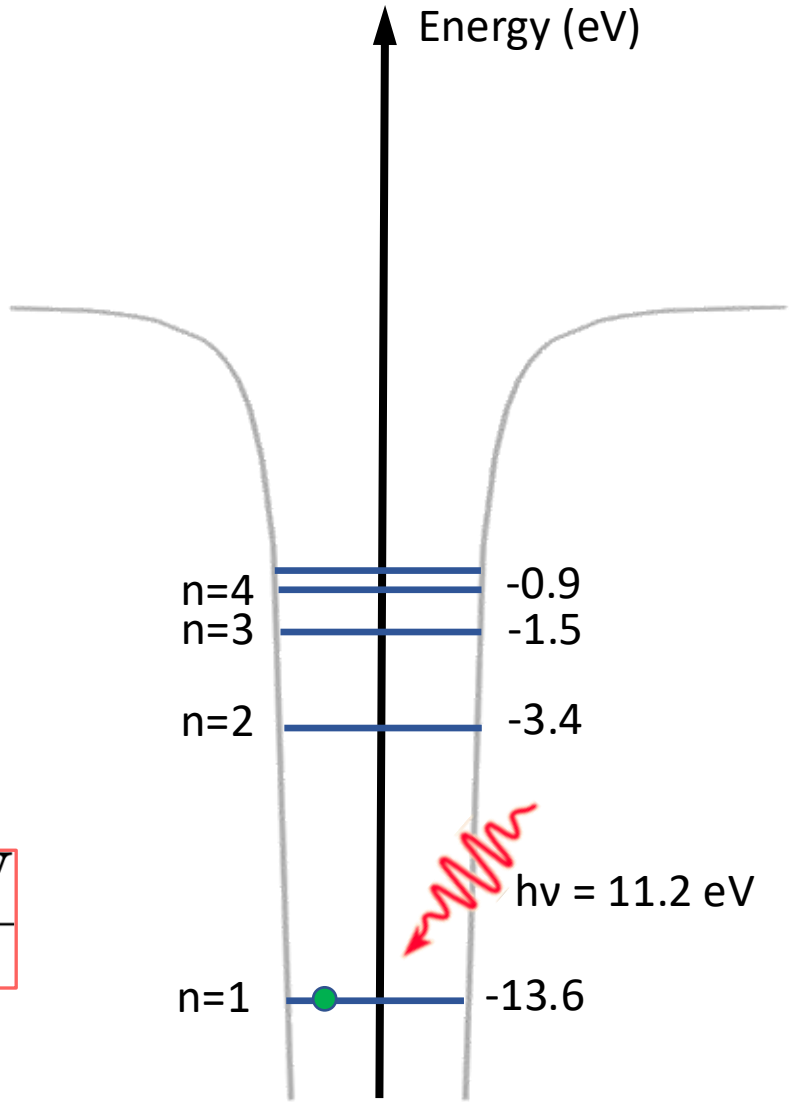
Laguerre Legendre

polynomials

Energy eigenvalues

$$E_n = -\frac{13.6\,\text{eV}}{n^2}$$

Principle number n = 1,2,3,..
Angular momentum l = 0,1,..,n-1
Magnetic quantum number m = -l,-l+1,...,l
Spin s = -½, ½



Magnetism of the electron – a single electron atom

$$\Psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)Y_l^{m_l}(\theta,\phi)$$

s: $Y_0^0 = \sqrt{\frac{1}{4\pi}}$

p: $Y_1^0 \sim \cos\theta$ $Y_1^{\pm 1} \sim \pm \sin\theta e^{\pm i\phi}$

d: $Y_2^0 \sim (\cos^3\theta - 1)$ $Y_2^{\pm 1} \sim \pm \sin\theta\cos\theta e^{\pm i\phi}$ $Y_2^{\pm 2} \sim \pm \sin^2\theta\cos\theta e^{\pm i\phi}$

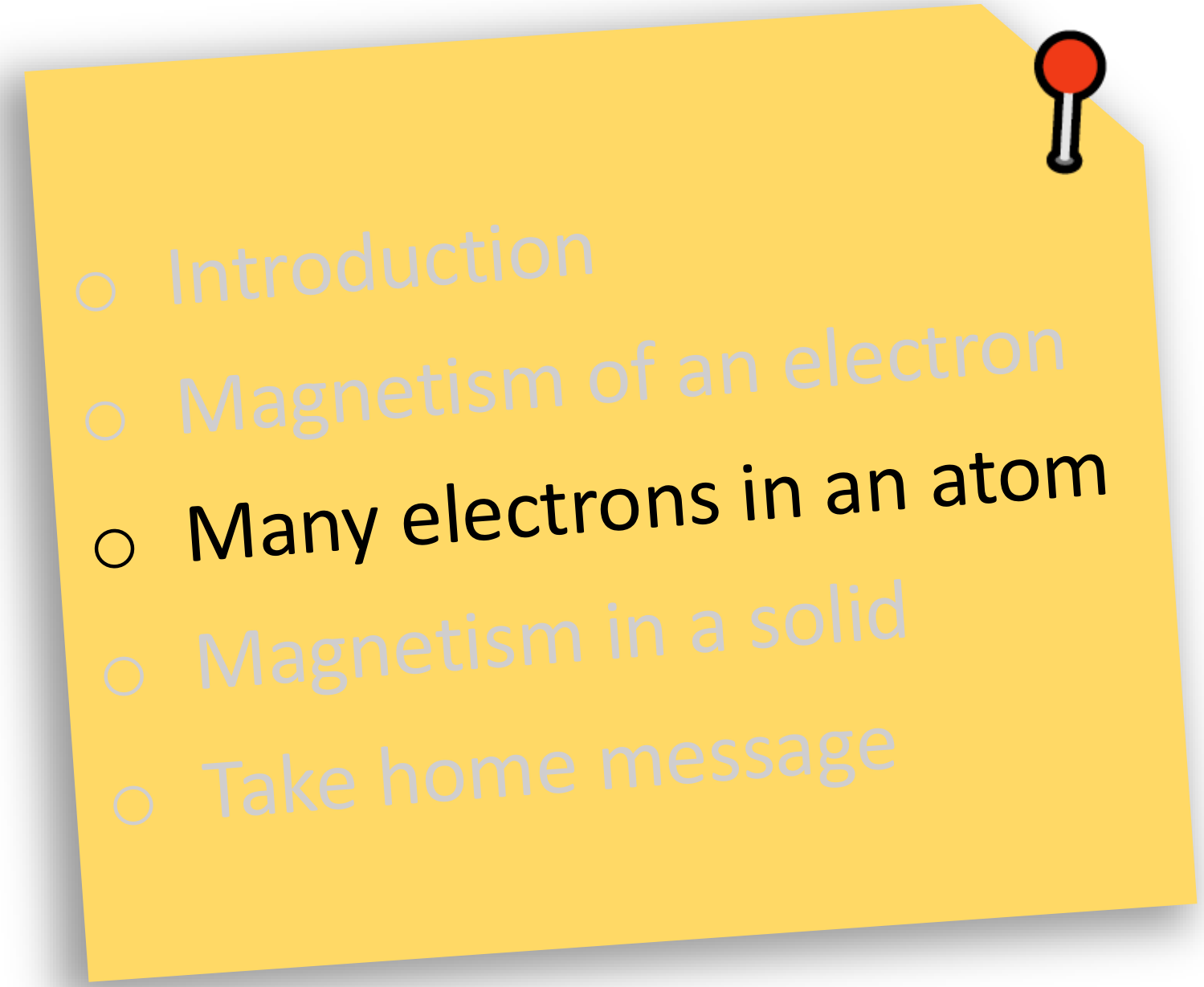
In general: $Y_l^{m_l} \sim P_l^{m_l} e^{\pm i m_l \phi}$

Summary 1

- Magnetism is a quantum effect – spin is essential to explain magnetic observations (Stern-Gerlach experiment; gyromagnetic factor)

- The total magnetic moment is given by $\mathbf{m} = -\frac{e}{2m_e}(\mathbf{l} + 2\mathbf{s})$

- The spin orbit coupling energy is proportional to Z^4
  ⇨ spin-orbit coupling increasingly important for heavy elements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Atomic magnetism

$$L = \sum_i l_i \quad M_l = \sum_i m_{li} \quad S = \sum_i s_i \quad M_s = \sum_i m_{si} \qquad J = ?$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

Multiplicity: $|L - S|, |L - S + 1| ... |L + S - 1|, |L + S|$

z-component and magnetic quantum number: $J_z = m_j \hbar, \quad m_j = -J, J - 1, ..., J$

Different J-states are called multiplets $\quad {}^{2S+1}X_J$

X denotes L-quantum number according to

X = S, P, D, F, G, …

for L = 0, 1, 2, 3, 4,….

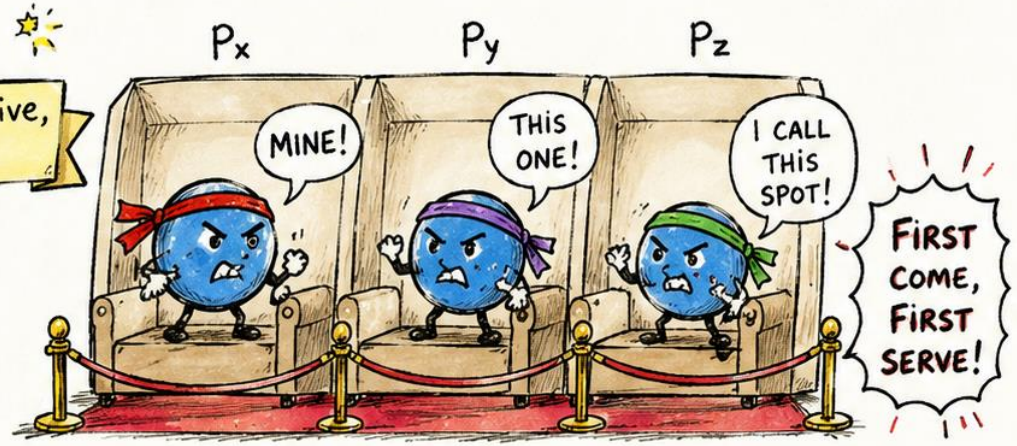
Total magnetic moment: $\mathbf{m}_J = -\frac{e}{2m_e}(\mathbf{L} + g\mathbf{S}) = -g_J \frac{e}{2m_e}\mathbf{J} = -g_J \frac{\mu_B}{\hbar}\mathbf{J}$

Landé-factor: $g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$

HUND'S RULES

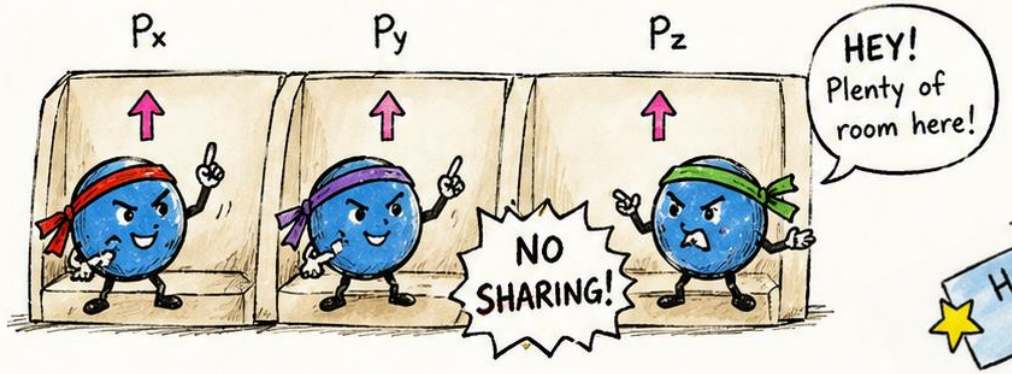
Electrons are competitive, but they play fair!

p orbitals (3 seats only!)

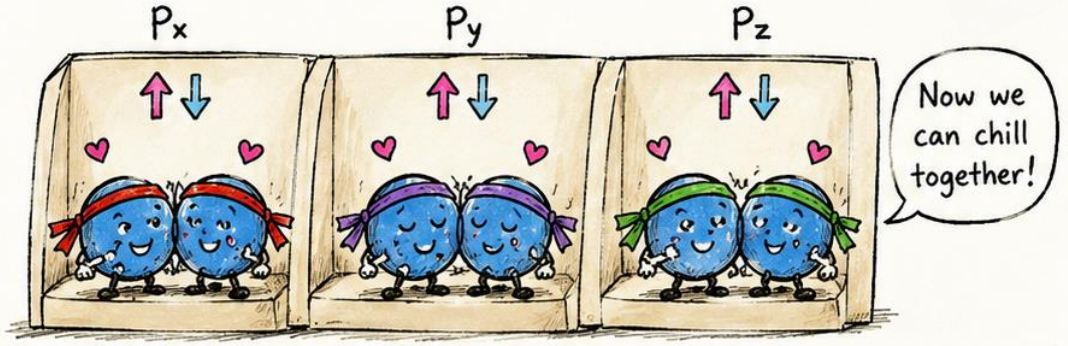


1. Electrons fill orbitals singly before pairing up.

2. Electrons with the same spin prefer to occupy separate orbitals (maximize their space).



3. Only after all orbitals are singly occupied do electrons pair up (and then they can share).



Hund's Rules: Electrons are competitive, but also kind of social.

Sketch generated by ChatGPT

Atomic magnetism – How to fill the orbitals

Hund's rules:

1. Maximise S for the given configuration of orbitals
2. Maximise L consistent with S
3. Minimise spin-orbit energy and couple S and L such that:

$$J = \begin{cases} L-S & \text{if the shell is less than half filled} \\ L+S & \text{if the shell is more than half filled} \\ 0 & \text{if the shell is half filled} \end{cases}$$

Example 1 Fe^{2+} ion ⇨ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ \cancel{4s^2}$

d-orbitals

↑	↑	↑	↑	↑
↓				

l_z values: -2 -1 0 1 2

Maximise S: $S = 4/2 = 2$

Maximise L: $L = 2$

$J = 4$

⇨ $^5D_4$

$2S+1$, L, J

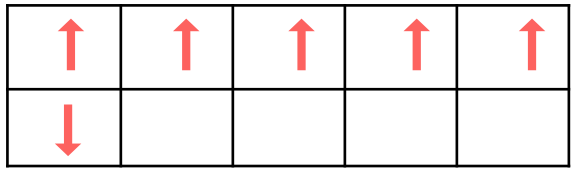
Atomic magnetism

Maximize S
Maximize L

	L-S	filling < 1/2
J =	L+S	filling > 1/2
	0	1/2 filled

Example 1 Fe^{2+} ion ⇨ [Ar] $3d^6$ $4s^2$

d-orbitals



l_z values -2 -1 0 1 2

$S = 4/2 = 2$

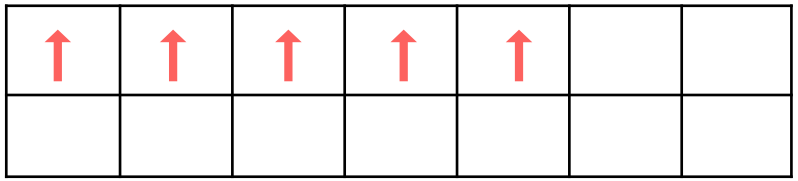
$L = 2$ ⇨ $^5D_4$

$J = 4$

Example 2:

Sm^{3+} ion ⇨ [Xe]$4f^5$ $6s^2$ $5d^1$

f-orbitals



l_z values -3 -2 -1 0 1 2 3

$S = 5/2$

$L = 5$ ⇨ $^6H_{5/2}$

$J = 5/2$

Try yourself:

Fe^{3+} S=5/2, L = 0, J =5/2; $^6S_{5/2}$

Co^{2+} S=3/2, L=3,J=9/2, $^3F_{9/2}$

Nd^{3+} S=3/2, L=6,J=6/2, $^7I_{9/2}$

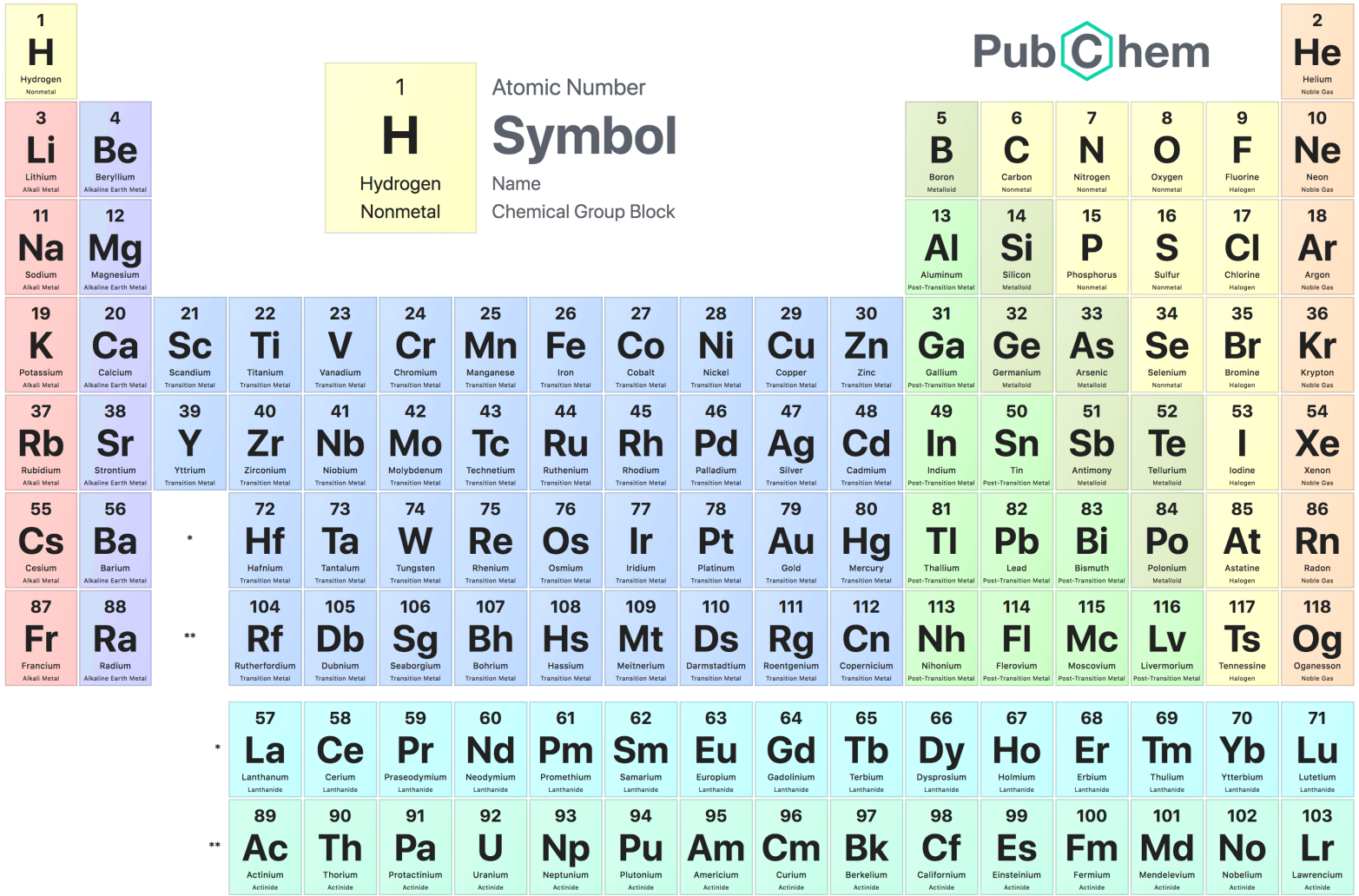
Extra slide

Gd^{3+} ion ⇨ $[Xe]4f^7$ ~~$6s^2$~~ ~~$5d^1$~~

f-orbitals

↑	↑	↑	↑	↑	↑	↑

-3 -2 -1 0 1 2 3



S = ?, L = ?, J = ? , notation = ?

$S = 7/2$

$L = 0$

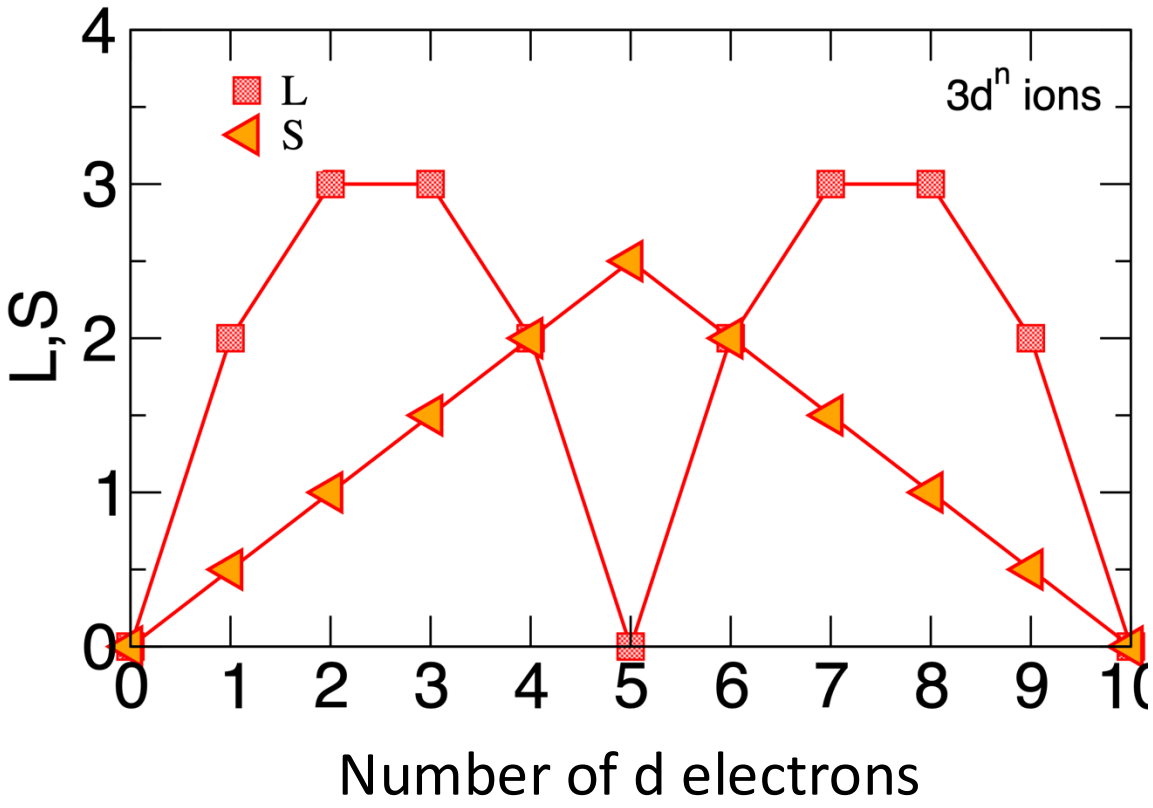
$J = 7/2$

⇨ $^8S_{7/2}$

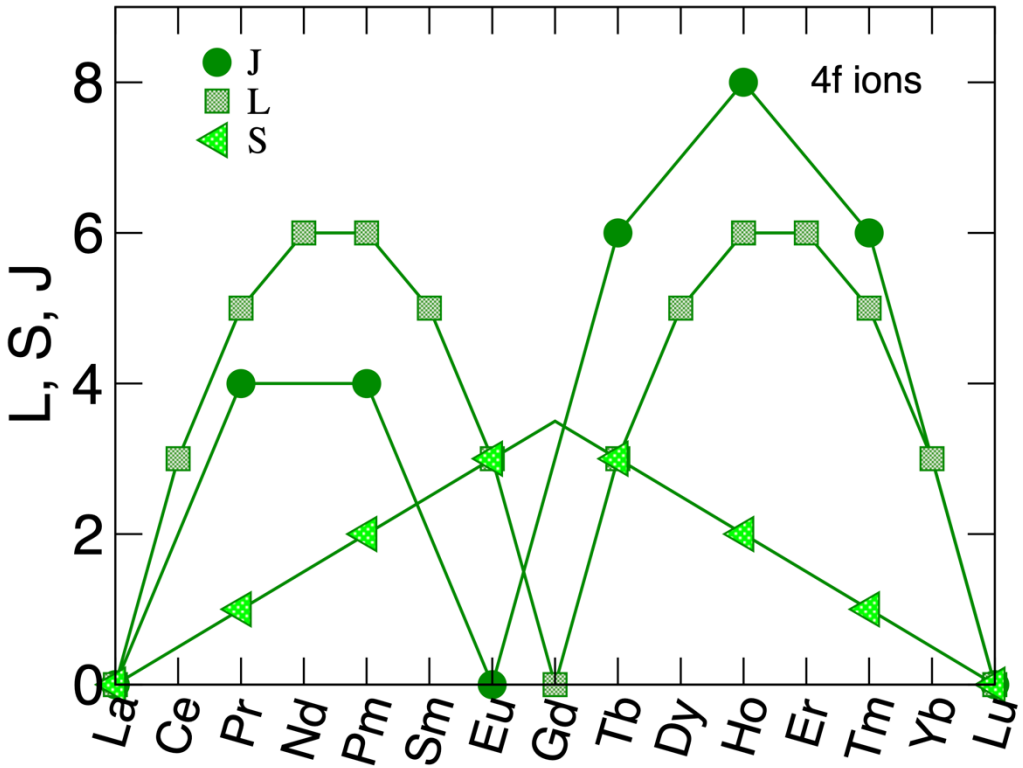
The full information about multiples for ions from the d and f shell can be found in Ashcroft & Mermin, Solid State Physics

Atomic magnetism

Transition metal ions - 3d shell



Rare earths ions – 4f shell



Most free atoms carry a magnetic moment

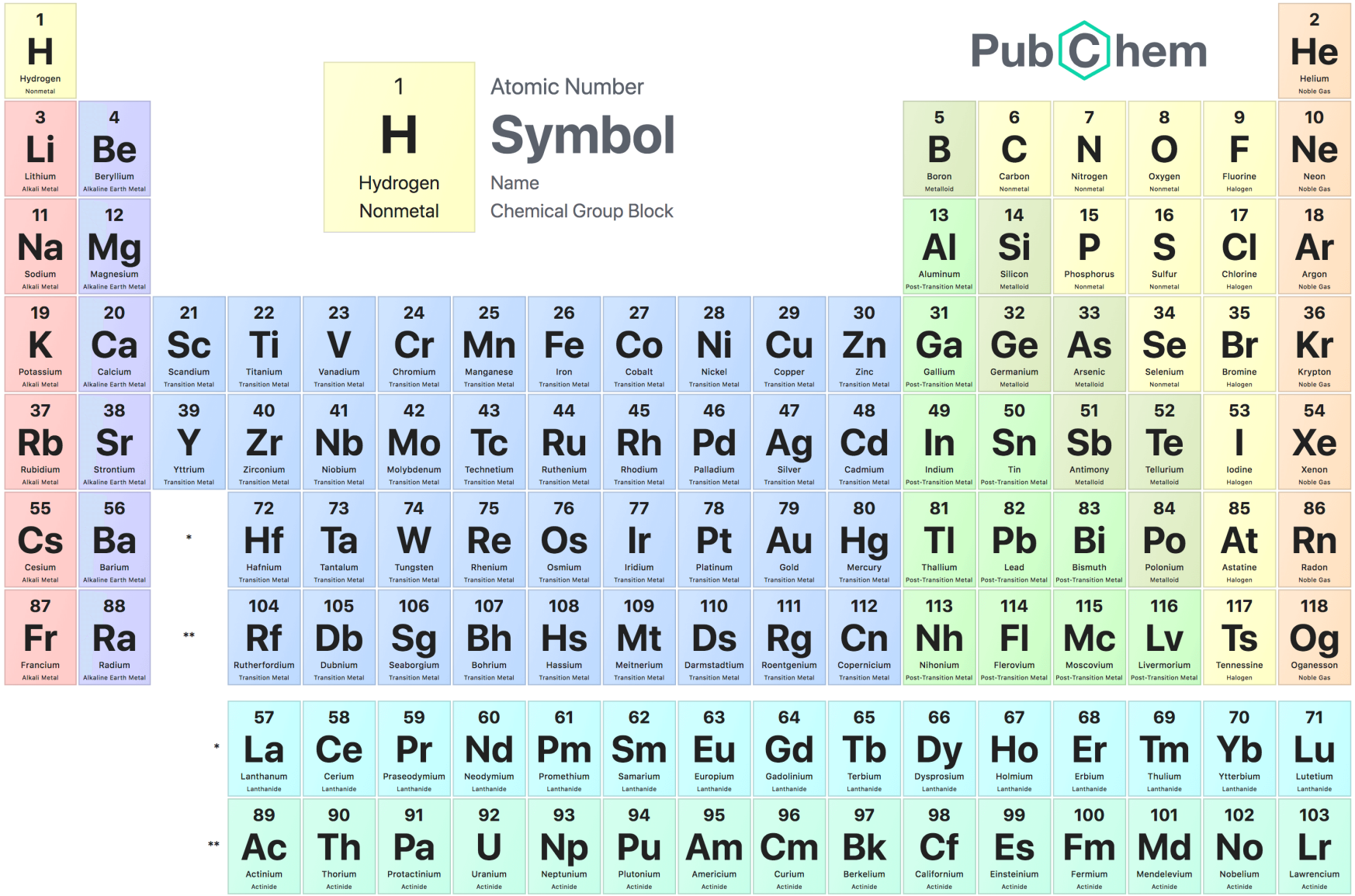
Many electrons in a free atom – atomic magnetism

What happens to the angular momenta L in an external field ?

Impact of LS-coupling on energy levels?

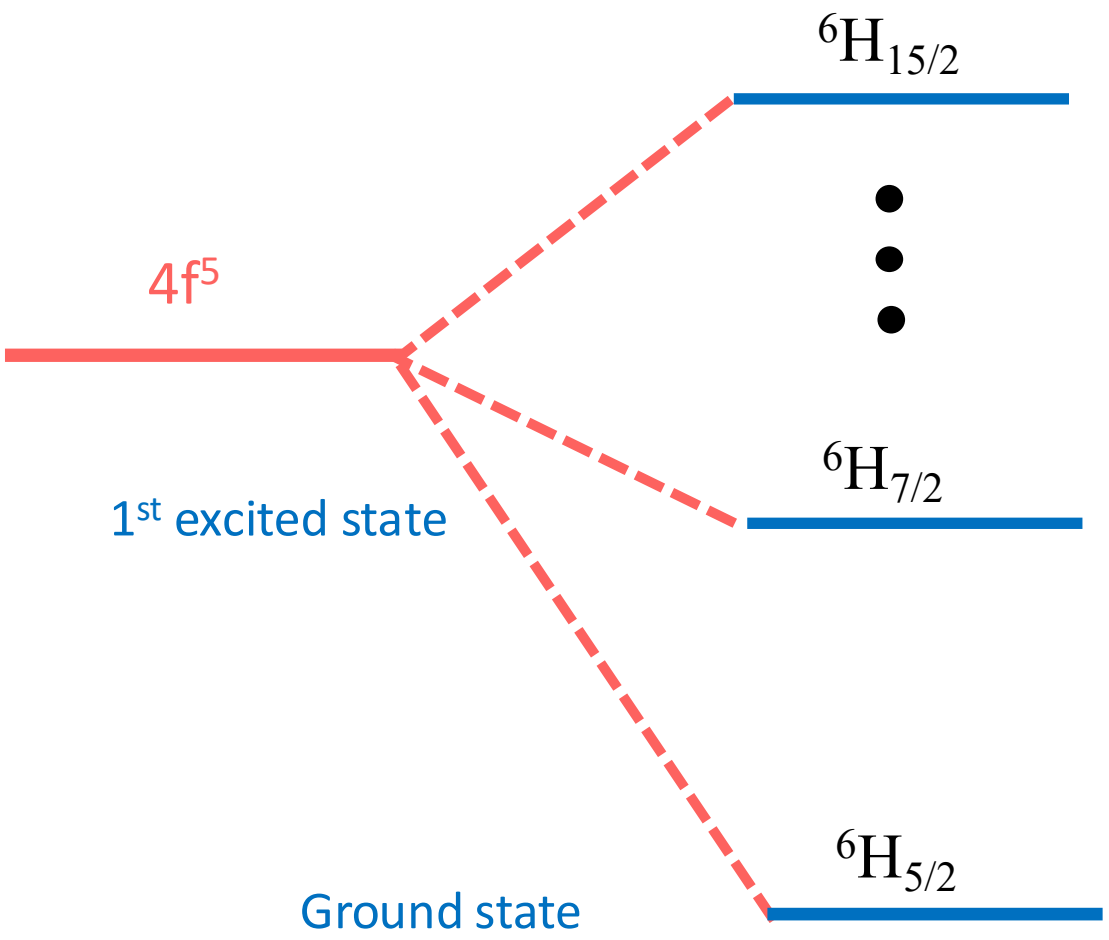
Every electron counts

⇨ l degeneracy lifted



Many electrons in a free atom – LS coupling

Example: Sm^{3+}, $4f^5$



Spin-orbit coupling

$$\mathcal{H}_{SO} = \Lambda \mathbf{LS}$$

Λ spin-orbit coupling constant

$$\Lambda = \pm \frac{\lambda}{2S}$$

$$\mathbf{LS} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$

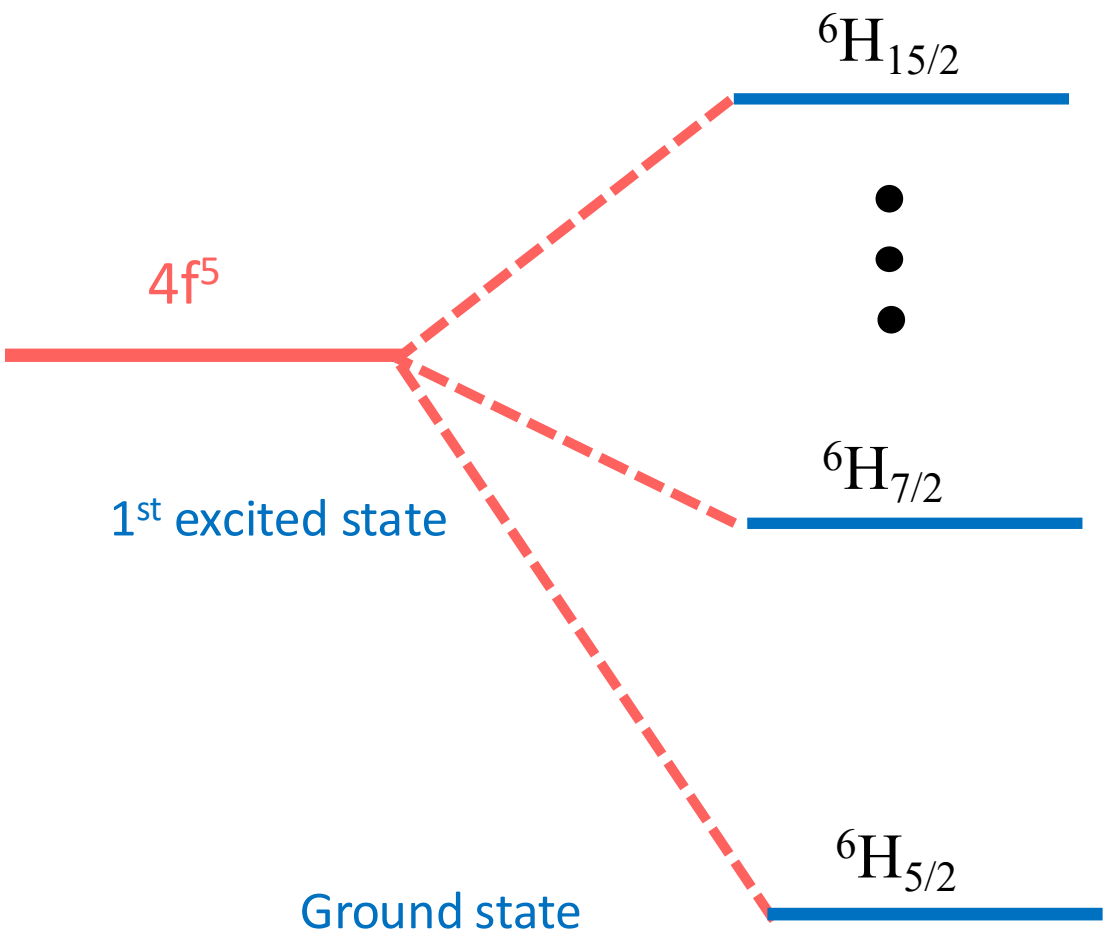
$$= \frac{\hbar^2}{2}(J(J+1) - L(L+1) - S(S+1))$$

Extra slide

$$\frac{m_J}{\mu_B} = p_J = g_J\sqrt{(J(J+1)}$$

Example: Sm^{3+}, $4f^5$

LS splitting



Experiment*: $4f^5$ ⇨ p_{exp} = 1.74

p_J = 3.32 Too big

p_J = 0.85 Too small

For Sm^{3+} the energy difference between ground state and 1st excited state is small.
⇨ Both are partially occupied.

*Measured at paramagnetic salts

Many electrons in a free atom – Zeeman effect

With $\mathbf{M}_J = -\frac{e}{2m_e}(\mathbf{L}+2\mathbf{S}) = -g_J\frac{e}{2m_e}\mathbf{J}$ and $J_z = M_J\hbar$ and $\mu_B = \frac{e\hbar}{2m_e}$

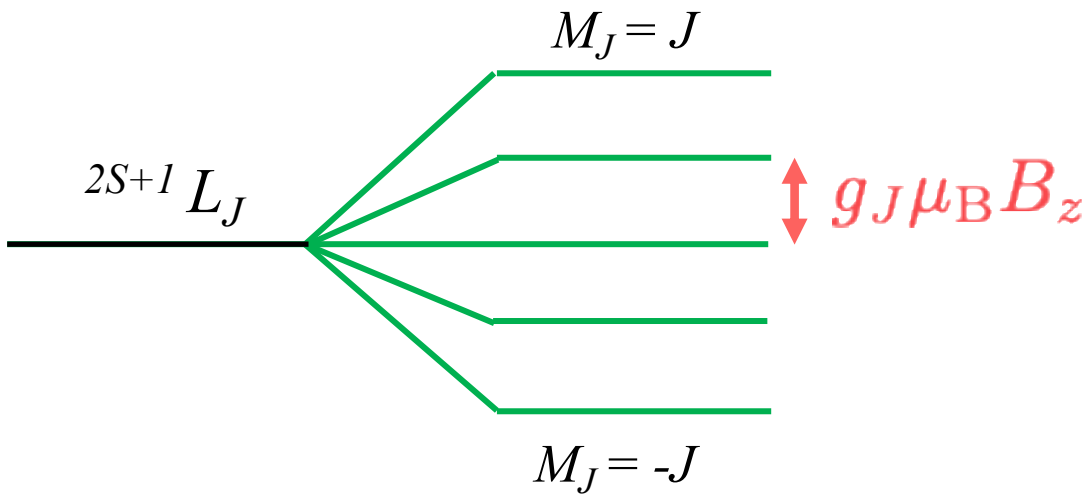
Change in energy due to applied magnetic field $E = -\mathbf{mB}$, for B || z we get

Zeeman energy

$$E_z = g_J\frac{\mu_B}{\hbar}J_zB_z \equiv \mu_B M_J B_z$$

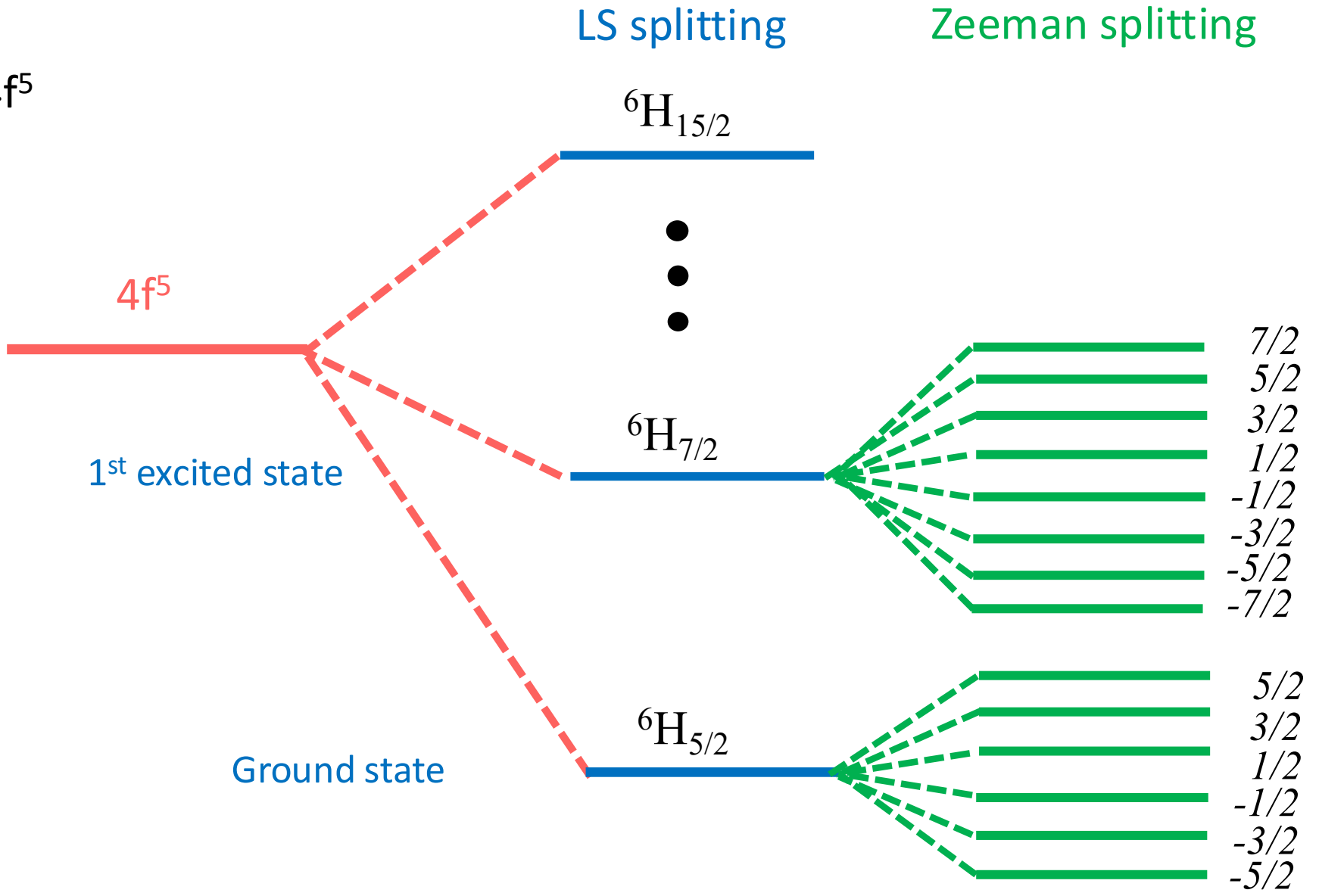
with $M_J = -J, -J+1, \ldots, J$

Degeneracy of **J** lifted



Many electrons in a free atom

Example: Sm^{3+}, $4f^5$



Many electrons in a free atom - magnetic moment of 4f ions

ion	shell	S	L	J	term	p_J	p_{exp} *
La^{3+}	$4f^0$	0	0	0	$^1S_0$	0	0
Ce^{3+}	$4f^1$	$\frac{1}{2}$	3	$\frac{5}{2}$	$^2F_{5/2}$	2.54	2.51
Pr^{3+}	$4f^2$	1	5	4	$^3H_4$	3.58	3.56
Nd^{3+}	$4f^3$	$\frac{3}{2}$	6	$\frac{9}{2}$	$^4I_{9/2}$	3.62	3.3-3.7
Pm^{3+}	$4f^4$	2	6	4	$^5I_4$	2.68	-
Sm^{3+}	$4f^5$	$\frac{5}{2}$	5	$\frac{5}{2}$	$^6I_{5/2}$	0.85	1.74
Eu^{3+}	$4f^6$	3	3	0	$^7F_0$	0.0	3.4
Gd^{3+}	$4f^7$	$\frac{7}{2}$	0	$\frac{7}{2}$	$^8S_{7/2}$	7.94	7.98
Tb^{3+}	$4f^8$	3	3	6	$^7F_6$	9.72	9.77
Dy^{3+}	$4f^9$	$\frac{5}{2}$	5	$\frac{15}{2}$	$^6H_{15/2}$	10.63	10.63
Ho^{3+}	$4f^{10}$	2	6	8	$^5I_8$	10.6	10.4
Er^{3+}	$4f^{11}$	$\frac{3}{2}$	6	$\frac{15}{2}$	$^4I_{15/2}$	9.59	9.5
Tm^{3+}	$4f^{12}$	1	5	6	$^3H_6$	7.57	7.61
Yb^{3+}	$4f^{13}$	$\frac{1}{2}$	3	$\frac{7}{2}$	$^2F_{7/2}$	4.53	4.5
Lu^{3+}	$4f^{14}$	0	0	0	$^1S_0$	0	0

$$p_J = g_J\sqrt{J(J+1)}$$

- Hund's 3rd rule correctly predicts the magnetic moment
- J is a good quantum number

- Deviation for Sm^{3+} and Eu^{3+}

  → LS coupling is small

  → Higher multiplets are partially occupied depending on B and T

* From paramagnetic salts, $k_B T >>$ crystal field

(Table taken from: L. Paolasini, Lectures on Magnetism, ESRF)

Many electrons in a free atom - magnetic moment of 3d ions

ions	shell	S	L	J	term	p_J	p_{exp}	p_S
Ti^{3+}, V^{4+}	$3d^1$	$\frac{1}{2}$	2	$\frac{3}{2}$	$^2D_{3/2}$	1.55	1.70	1.73
V^{3+}	$3d^2$	1	3	2	$^3F_2$	1.63	2.61	2.83
Cr^{3+}, V^{2+}	$3d^3$	$\frac{3}{2}$	3	$\frac{3}{2}$	$^4F_{3/2}$	0.77	3.85	3.87
Mn^{3+}, Cr^{2+}	$3d^4$	2	2	0	$^5D_0$	0	4.82	4.90
Fe^{3+}, Mn^{2+}	$3d^5$	$\frac{5}{2}$	0	$\frac{5}{2}$	$^6S_{5/2}$	5.92	5.82	5.92
Fe^{2+}	$3d^6$	2	2	4	$^5D_4$	6.70	5.36	4.90
Co^{2+}	$3d^7$	$\frac{3}{2}$	3	$\frac{9}{2}$	$^4F_{9/2}$	6.63	4.90	3.87
Ni^{2+}	$3d^8$	1	3	4	$^3F_4$	5.59	3.12	2.83
Cu^{2+}	$3d^9$	$\frac{1}{2}$	2	$\frac{5}{2}$	$^2D_{5/2}$	3.55	1.83	1.73
Zn^{2+}	$3d^{10}$	0	0	0	$^1S_0$	0	0	0

$$p_J = g_J\sqrt{J(J+1)}$$

$$p_S = g_s\sqrt{S(S+1)}$$

- Hund's 3rd rule fails
- The paramagnetic moment **does not** agree with experiment
- Orbital moment is quenched
- S is a good quantum number

Why is this different from 4f ion behaviour?

(Table taken from: L. Paolasini, Lectures on Magnetism, ESRF)

Many electrons in a free atom – paramagnetism (of localized moments)

Apply a homogeneous magnetic field to an ensemble of N atoms – how does this change the magnetisation?

The total magnetization is the change of the free energy with the magnetic field $M = -\frac{\partial F}{\partial B}$

with $F = -k_{\mathrm{B}} T \ln Z$ and $Z = \mathrm{Tr}\, e^{-\beta \mathcal{H}}$ and $\mathcal{H} = \sum_i^N g \mu_{\mathrm{B}} m_{J_i} B$

Sum over atoms

$$Z = \mathrm{Tr}\, e^{-\beta \mathcal{H}} = \prod_i^N \sum_{m_J=-J}^{J} e^{-\beta g \mu_{\mathrm{B}} B m_J} = \prod_i^N e^{-\beta g \mu_{\mathrm{B}} B J} \frac{1 - e^{-\beta g \mu_{\mathrm{B}} B (2J+1)}}{1 - e^{-\beta g \mu_{\mathrm{B}} B}}$$

$$F = -k_{\mathrm{B}} T \ln Z = -k_{\mathrm{b}} T N \ln \left(\frac{e^{\beta g \mu_{\mathrm{B}} B (J+\frac{1}{2})} - e^{-\beta g \mu_{\mathrm{B}} B (J+\frac{1}{2})}}{e^{\beta g \mu_{\mathrm{B}} B \frac{1}{2}} - e^{-\beta g \mu_{\mathrm{B}} B \frac{1}{2}}} \right)$$

Many electrons in a free atom – paramagnetism (of localized moments)

$$F = -k_{\mathrm{B}}T \ln Z = -k_{\mathrm{b}}TN \ln \left(\frac{e^{\beta g \mu_{\mathrm{B}} B (J+\frac{1}{2})} - e^{-\beta g \mu_{\mathrm{B}} B (J+\frac{1}{2})}}{e^{\beta g \mu_{\mathrm{B}} B \frac{1}{2}} - e^{-\beta g \mu_{\mathrm{B}} B \frac{1}{2}}} \right)$$

Finally, the magnetization becomes:

$$M = -\frac{\partial F}{\partial B} = N g \mu_{\mathrm{B}} \left(\left(J + \frac{1}{2} \right) \coth \left(\beta g \mu_{\mathrm{B}} B \left(J + \frac{1}{2} \right) \right) - \frac{1}{2} \coth \left(\frac{1}{2} g \mu_{\mathrm{B}} B \right) \right)$$

$$= N g \mu_{\mathrm{B}} J B_J (\beta g \mu_{\mathrm{B}} B J)$$

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

$x = \beta g \mu_{\mathrm{B}} B J$

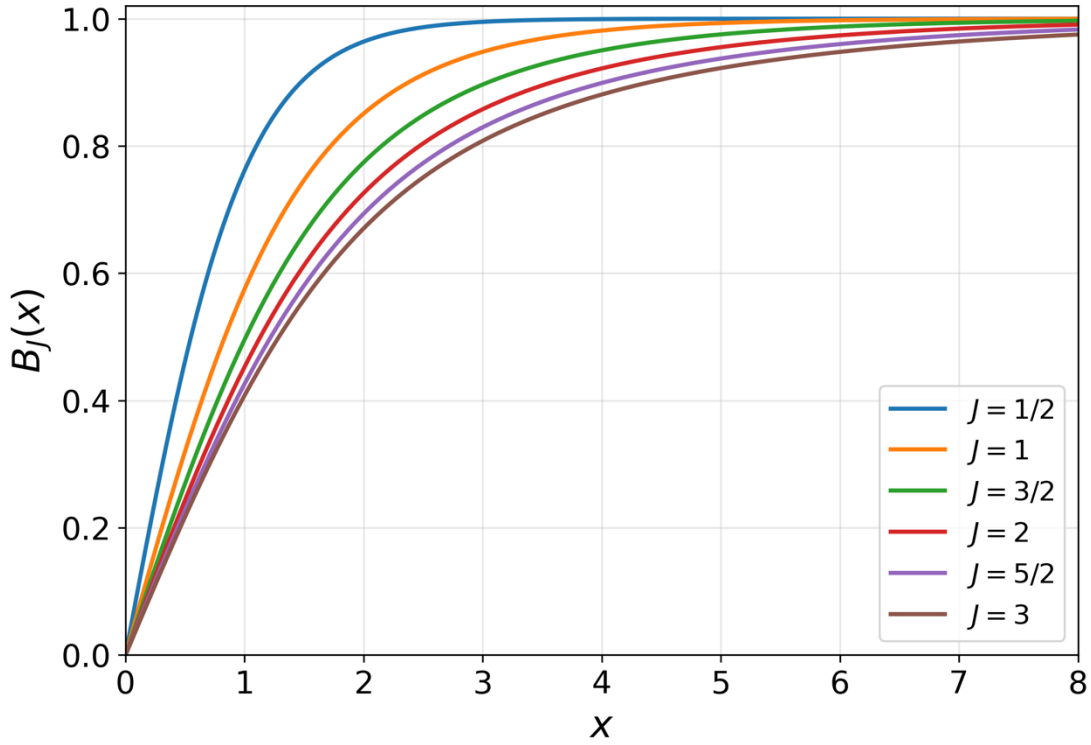
Many electrons in a free atom – paramagnetism (of localized moments)

Brillouin function $B_J(x) = \frac{2J+1}{2J}\left(\coth\left(\frac{2J+1}{2J}x\right)\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)$, $x = \beta g \mu_B B J$

Limit of large fields B or very low T:

Saturation magnetisation $M \to N g \mu_B J$

Maximal value, all magnetic moments aligned with B



Limit of small fields B or very high T: $B_J \approx \left(1 + \frac{1}{J}\right)\frac{x}{3}$

$$M \approx N\frac{(g\mu_B)^2 J(J+1)}{3k_B T}B = N\frac{M_{eff}^2 \mu_B^2}{3k_B T}B$$

$$\chi = \frac{\partial M}{\partial B}|_{B\to 0} = \frac{N(g\mu_B)^2 J(J+1)}{3k_B}\frac{1}{T} = \frac{C}{T}$$ Curie law

Many electrons in an atom - Hamiltonian

To include the quantum effect of exchange in the Hamiltonian Fock extended the Harterr model:

$$\mathcal{F}\psi_k(\mathbf{x}) = \epsilon_k \psi_k(\mathbf{x})$$ Fock operator **F**

$$\mathcal{F}\psi_k(\mathbf{x}) = \left[\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{\mathbf{r}-\mathbf{R}_n} + \sum_{l=1}^{N}\int dx' |\psi_l(\mathbf{x}')|^2 \frac{1}{\mathbf{r}-\mathbf{r}'}\right]\psi_k(\mathbf{x})$$

Coulomb potential

Hartree equation

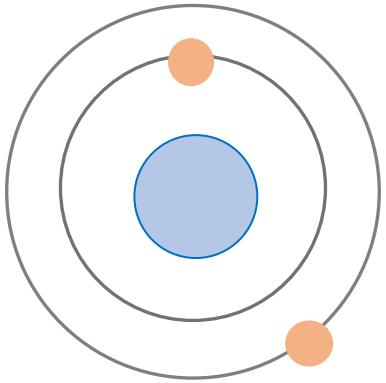
$$-\sum_{l=1}^{N}\int dx' \psi_l^\star(\mathbf{x}')\frac{1}{\mathbf{r}-\mathbf{r}'}\psi_k(\mathbf{x}')\psi_l(\mathbf{x})$$

Exchange term

- Ensures antisymmetry
- Non-local term
- Angular momentum l no longer degenerated

Notation: $e = \hbar = 1$

Two electrons to start with…



- Hamiltonian for a system with 2 electrons (e.g. He atom)

$$\hat{H} = \underbrace{\frac{p_1^2}{2m} - \frac{Ze^2}{r_1}}_{\hat{H}_1} + \underbrace{\frac{p_2^2}{2m} - \frac{Ze^2}{r_2}}_{\hat{H}_2} + \underbrace{\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}}_{\text{e-e--interaction}}$$

Without the e-e interaction

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = -\Psi(\mathbf{r}_2, s_2; \mathbf{r}_1, s_1) = \phi(\mathbf{r}_1, \mathbf{r}_2)\chi(s_1, s_2)$$

Possible spin configurations

$$\chi(s_1, s_2) = |\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

Triplet (S = 1)
symmetric

Singlet (S=0)
antisymmetric

2s+1 degenerted

Which one is the ground state?

Many electrons in an atom - Hamiltonian

Ground state He:

Both electrons occupy the same spatial orbital

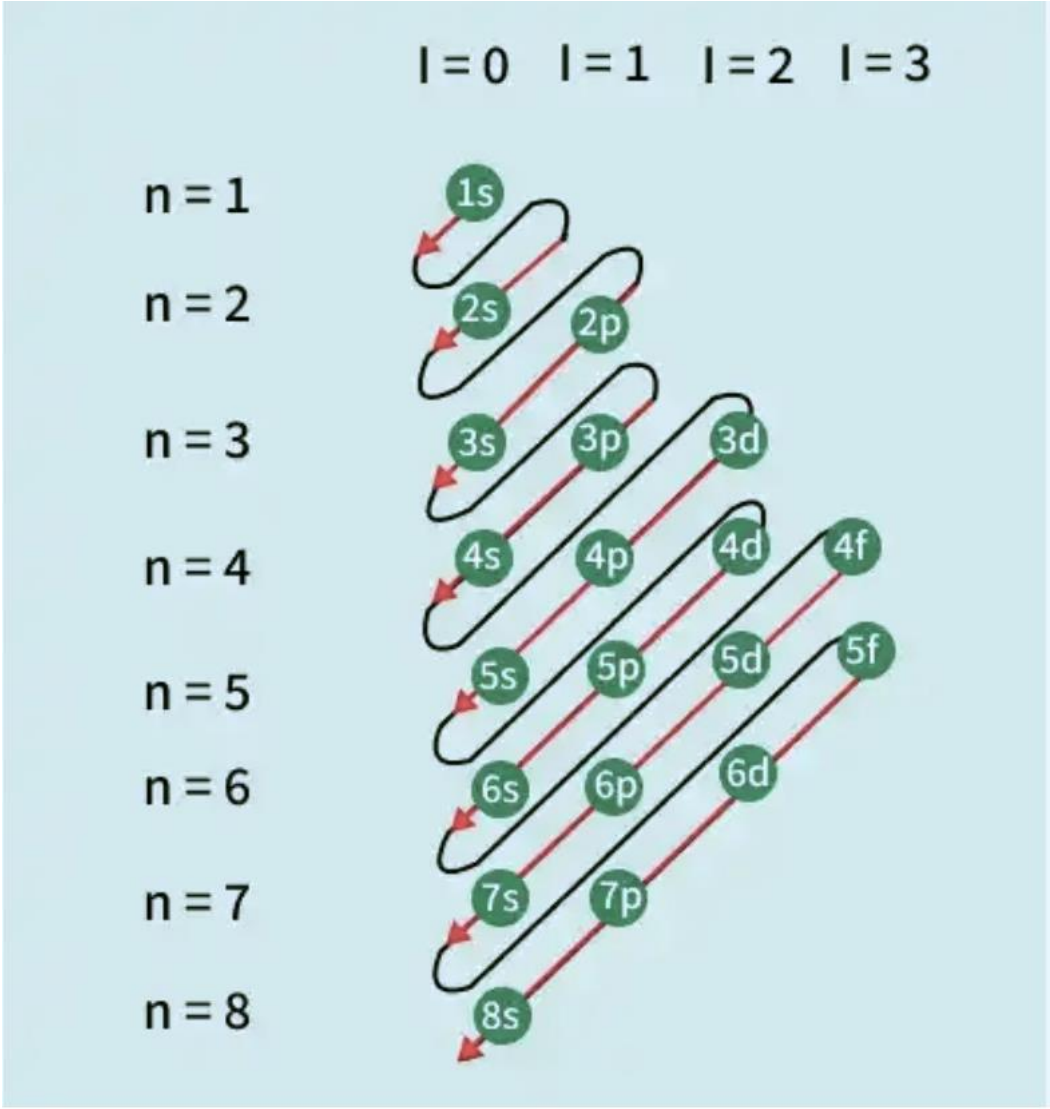
⇩

Exchange antisymmetric

⇩

Singlet state

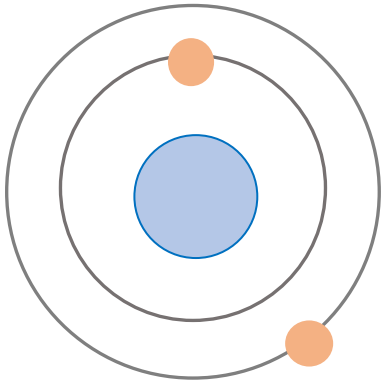
Aufbau principle



Aufbau rules: ?

- Shell with smaller $(n+l)$ fill first
- Same $(n+l)$ of two shells ⇨ the one with lower n fills first

Two electrons to start with…



Spin singlet wave function

$$\Psi = \frac{1}{\sqrt{2}}\left[\phi_{nlm}(\mathbf{r}_1)\chi_{1,\sigma}\phi_{n'l'm'}(\mathbf{r}_2)\chi_{2,\sigma'} - \phi_{nlm}(\mathbf{r}_2)\chi_{2,\sigma}\phi_{n'l'm'}(\mathbf{r}_1)\chi_{1,\sigma'}\right]$$

ϕ_{nlm} = one electron wave function

Behaves like hydrogen-like atom with Z = 2

$E_1 = E_2 = -Z^2 \cdot 13.6$ eV ⇨ $E_1 + E_2 = -108.8$ eV ⇒⇐ Experiment: −79 eV

Electron-Electron interaction (from 1st order perturbation theory):

$$V = \int\int |\phi_{nlm}|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\phi_{n'l'm'}|^2 \qquad J = \int\int \phi^*_{nlm}\phi_{n'l'm'} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi^*_{n'l'm'}\phi_{nlm}$$

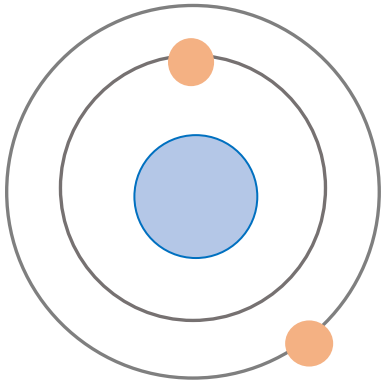
Coulomb interaction

Exchange interaction

No classical counterpart
(Werner Heisenberg and Paul Dirac, 1926)

Coulomb corrected ground state: $E_1 + E_2 + J = -74.8$ eV

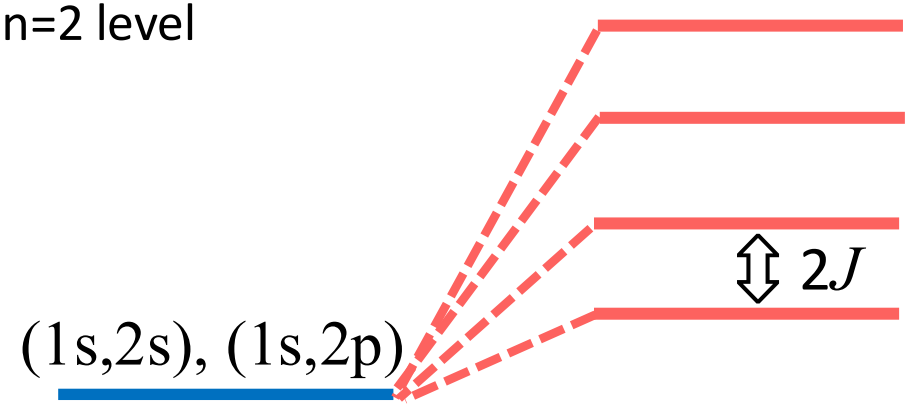
Two electrons to start with…



The energy shift due to the electron-electron interaction becomes $E_1 = V \pm J$

+ for singlet and – for triplet state

Excitation of 1 electron to the n=2 level



With perturbation, l degeneracy lifted

No perturbation

- Splitting of energy levels by different interactions into L=0 and L=1
- Further splitting through exchange interaction into singlet and triplet

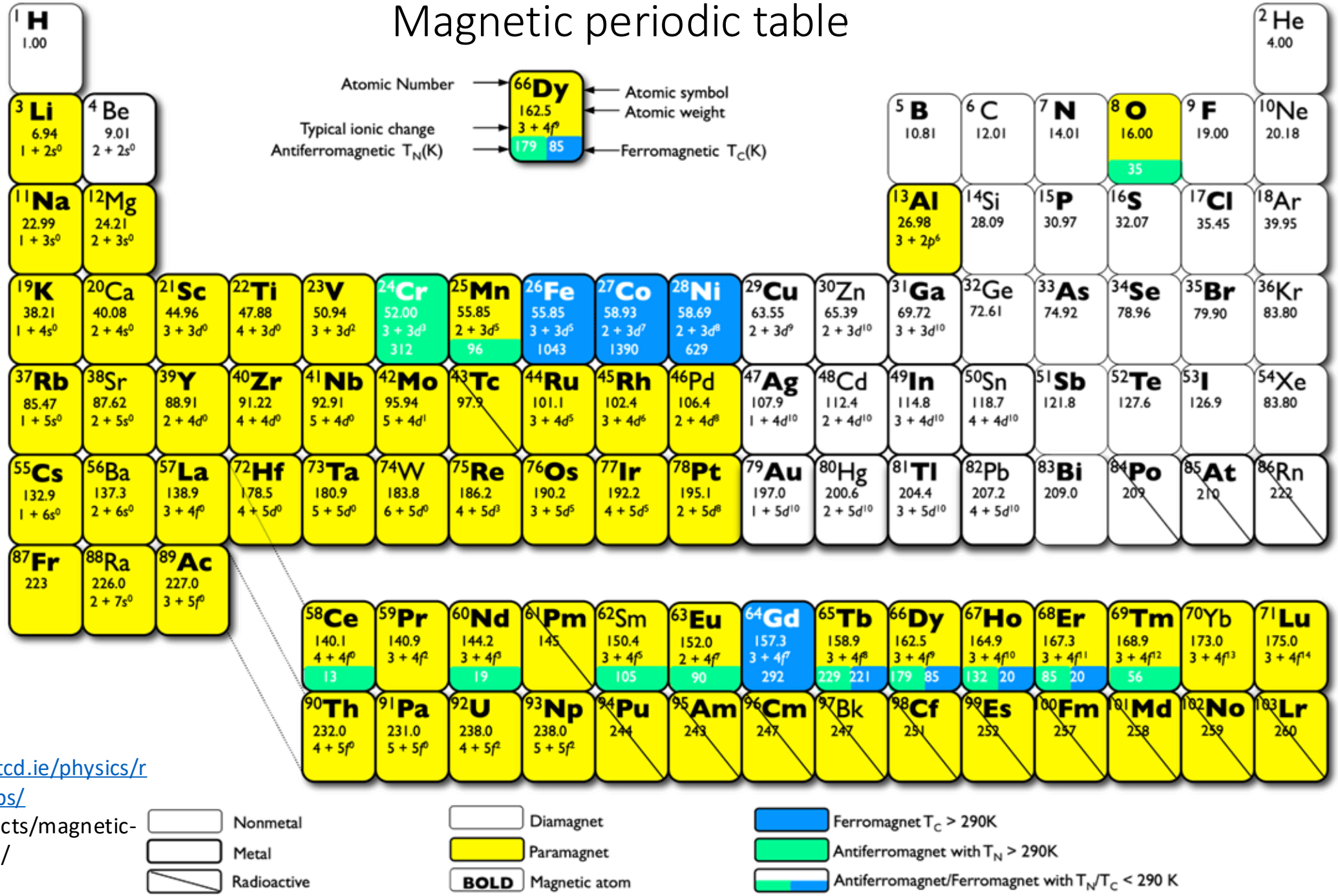
Many electrons in an atom

- Hund's rules – how to fill orbitals
- Pauli principle
  ⇨Two electrons in the same orbital must have antiparallel spins!
  - Degeneracy of the angular momentum is lifted due to
    - External fields (Zeeman)
    - LS-coupling
    - Exchange splitting
- Note: $\boldsymbol{H}$ independent of spin but $\boldsymbol{H}$ + Pauli principle = spin-dependent energy

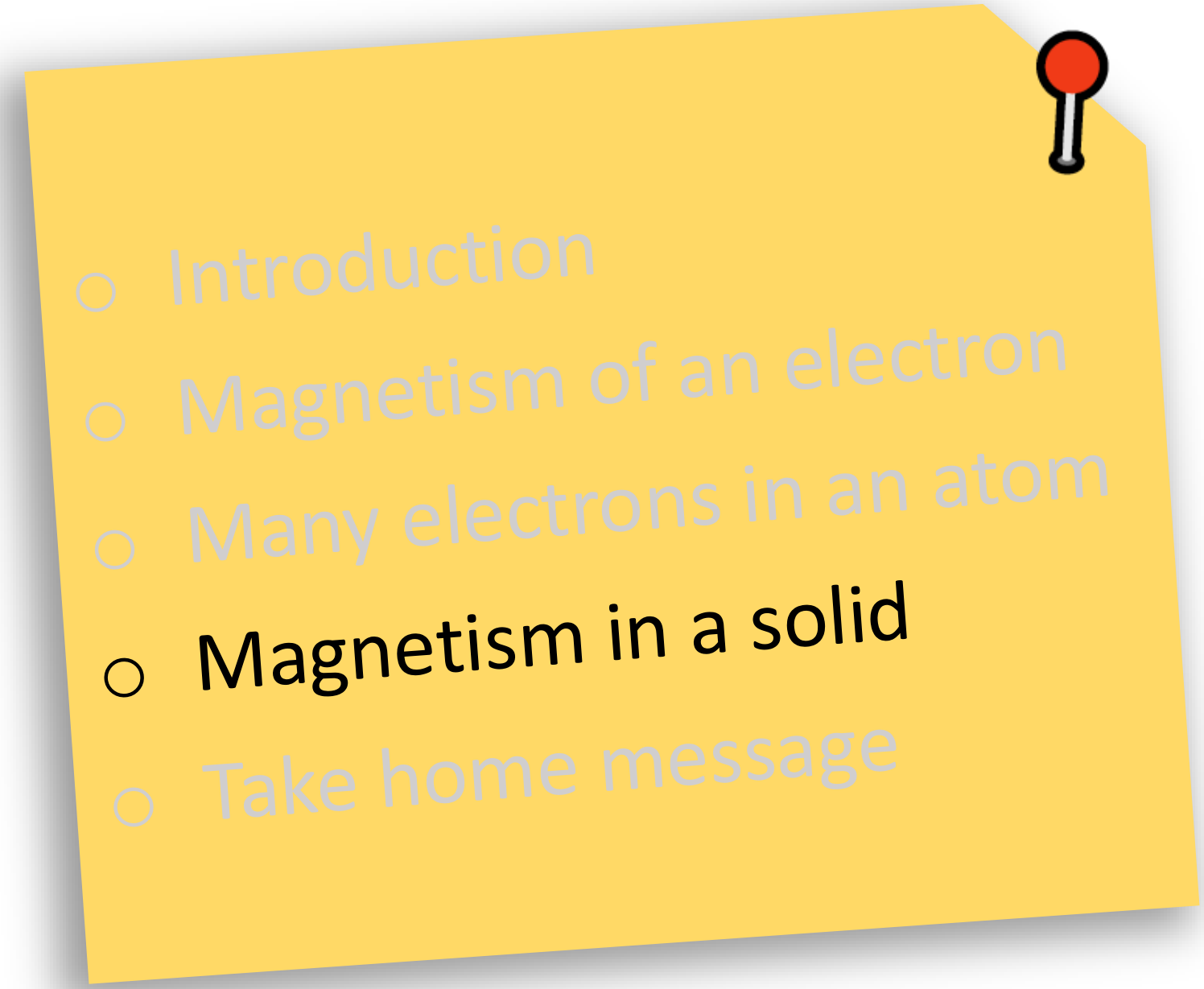
	n	l	m_l							s		#
1s	1	0				0				↑	↓	2
2s	2	0				0				↑	↓	2
2p	2	1			-1	0	+1			↑	↓	6
3s	3	0				0				↑	↓	2
3p	3	1			-1	0	+1			↑	↓	6
3d	3	2		-2	-1	0	+1	+2		↑	↓	10
4s	4	0				0				↑	↓	2
4p	4	1			-1	0	+1			↑	↓	6
4d	4	2		-2	-1	0	+1	+2		↑	↓	10
4f	4	3	-3	-2	-1	0	+1	+2	+3	↑	↓	14

$\uparrow = +1/2, \uparrow = -1/2$

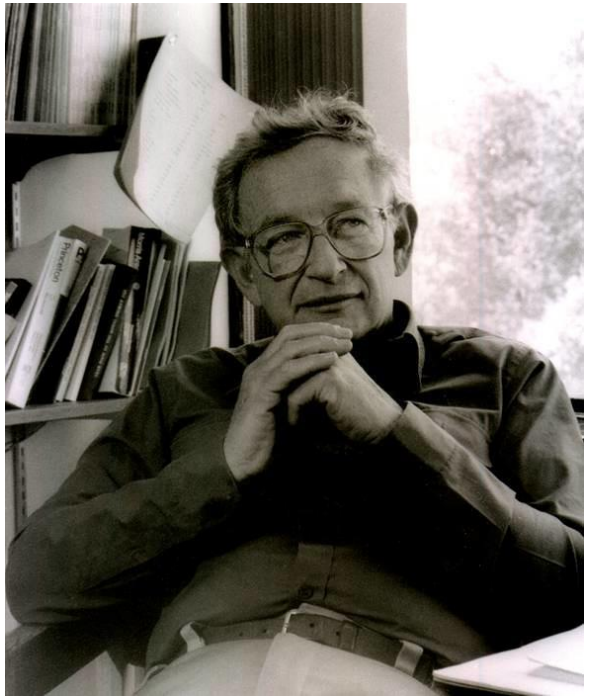
Magnetic periodic table



https://www.tcd.ie/physics/research/groups/magnetism/facts/magnetic-periodic-table/


Introduction
Magnetism of an electron
Many electrons in an atom
Magnetism in a solid
Take home message

“ More is different”



P.W. Anderson (source:Wikipedia)

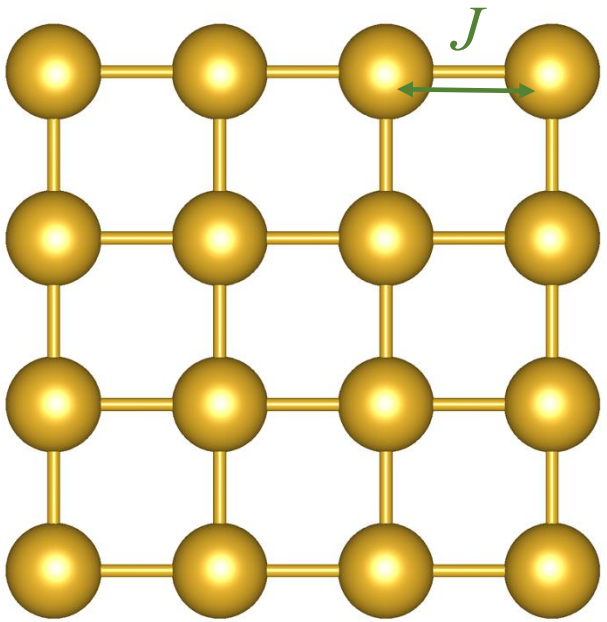
Macroscopic samples: Large numbers of electrons and ions ($\approx 10^{27}$)

⇨ Collective effects generate new phenomena

Magnetism in a solid – What change compared to the atom?

Exchange interaction

Beyond classical dipoles

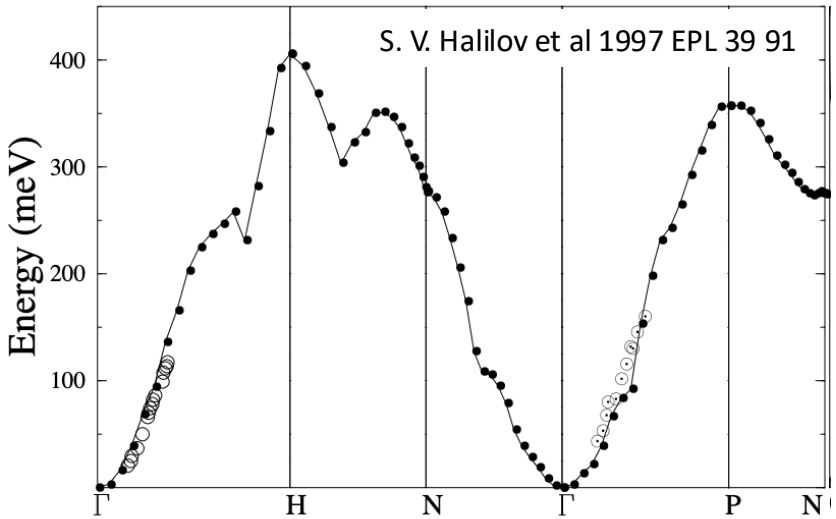


Heisenberg model

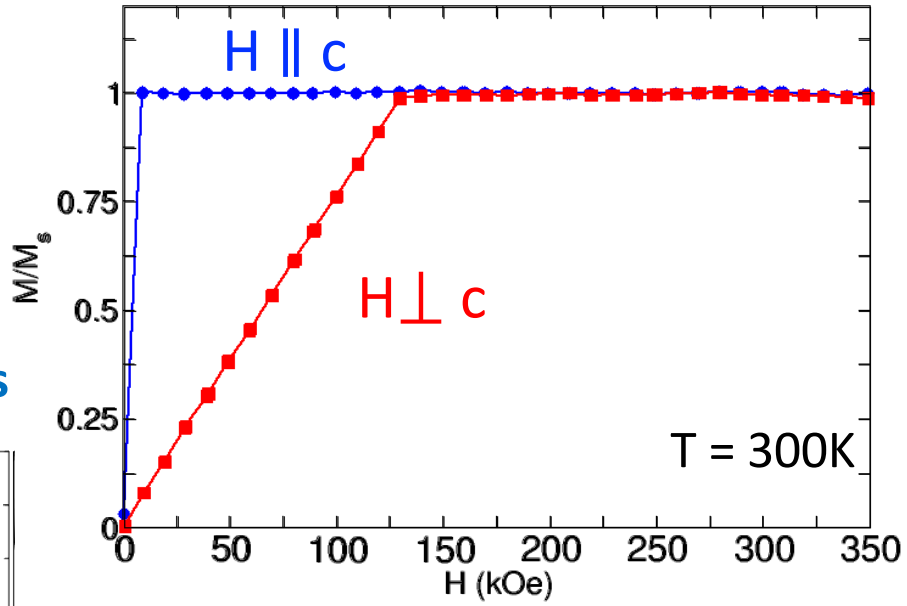
$$\hat{H} = -2\sum_{i>j} J_{ij}\hat{\mathbf{S}}_i\hat{\mathbf{S}}_j$$

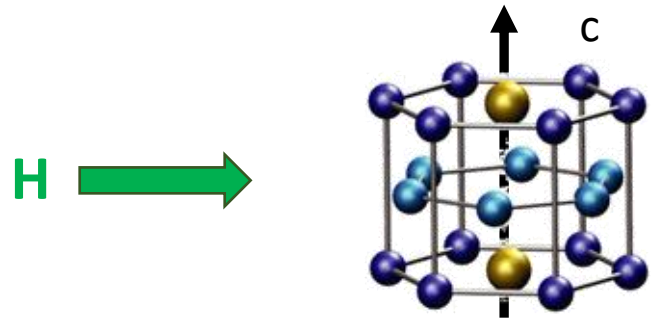
Spinwaves

Magnons - Quantised Spinwaves



Magnetocrystalline anisotropy



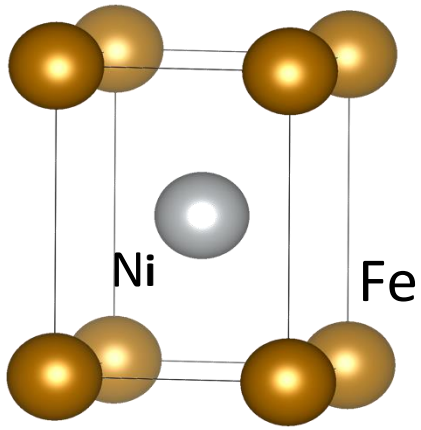


To be discussed in the following lectures

What do we do today in this lecture?

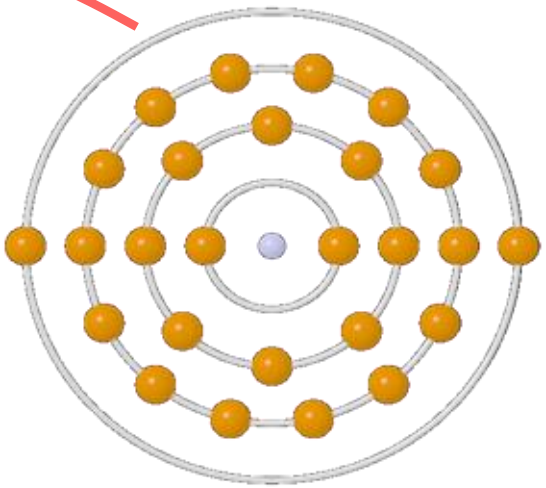
- Band structure and density of states
- 4f vs 3d magnetism
- Crystal field effects

Magnetism in a solid

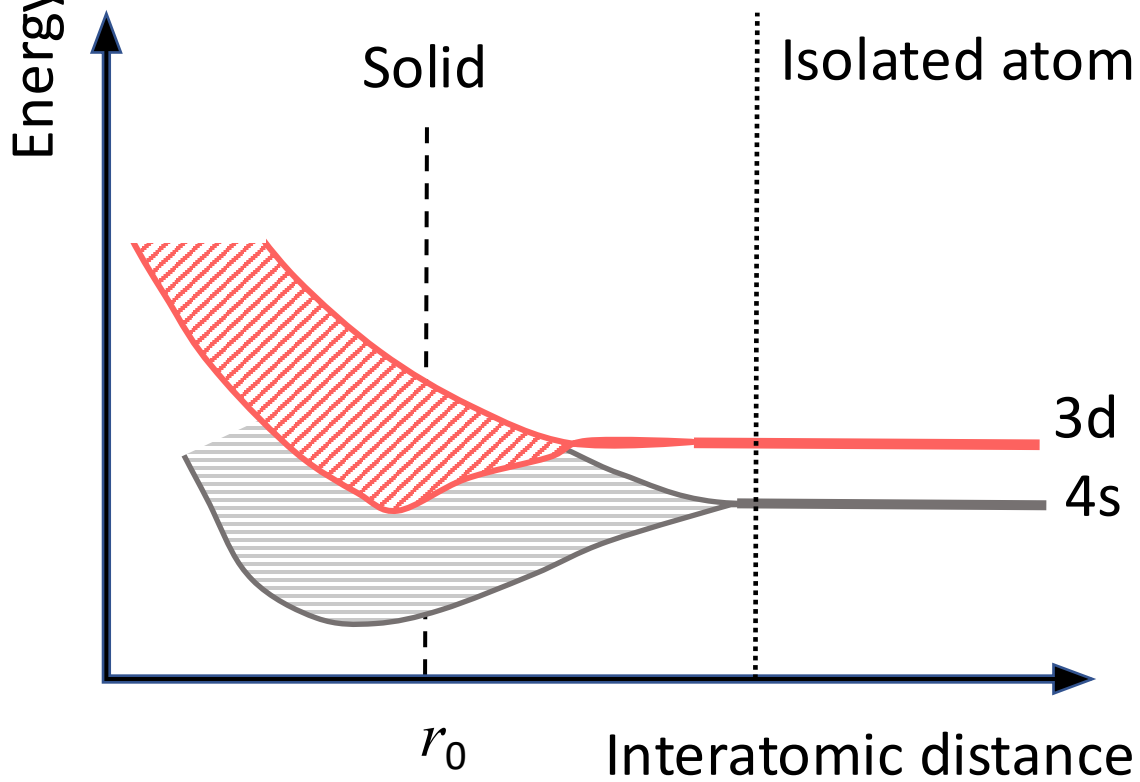


FeNi $L1_0$ (tetragonal)*

Band formation



Fe atom



r_0 = equilibrium distance

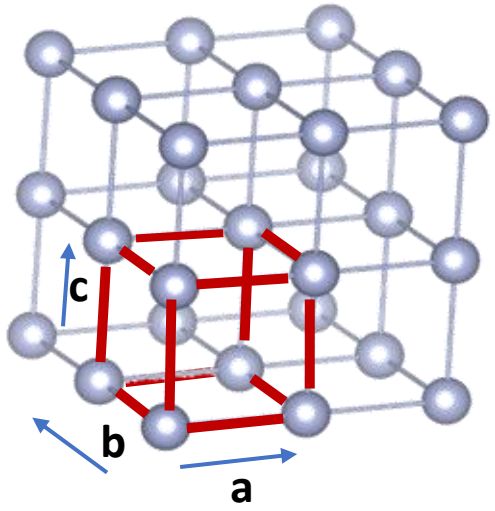
Transition metals:

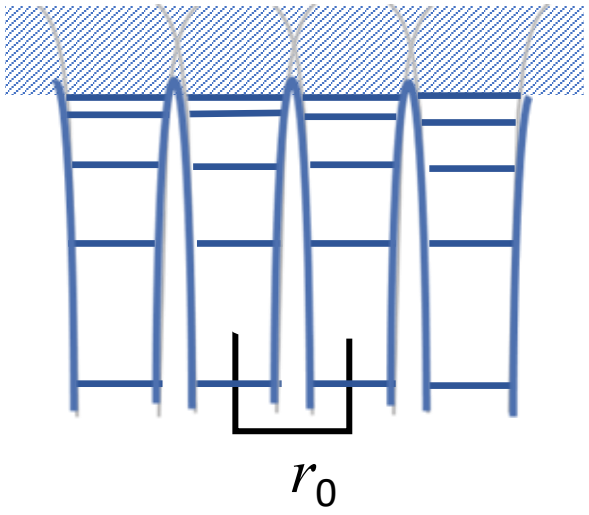
- d-shell is partly filled
- electrons are mobile (weakly bonded)
- Collective phenomena
- Exchange interactions occur (⇨next lecture)

(* Generated with VESTA, https://jp-minerals.org/vesta/en/)

Band structure and periodic potential

Magnetism dictates periodicity





Periodic potential:

$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R}) = \sum_G V_G e^{i\mathbf{G}\mathbf{r}} \quad (*)$$

Periodic boundary conditions

$$\left.\begin{aligned} \psi(x_1,x_2,x_3) &= \psi(x_1+L,x_2,x_3) \\ k_{x_1} &= \frac{2\pi n_{x_i}}{L} \end{aligned}\right\} \forall x_i$$

$\mathbf{k}$ = vector in reciprocal space

V_G = Fourier coefficients of the potential

Schrödinger equation non-interacting electrons (1 electron)

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Wave functions:

$$\psi(\mathbf{r}) = \sum_k c_k e^{i\mathbf{k}\mathbf{r}} \quad (**)$$

Fourier series, generalization of free particle solution

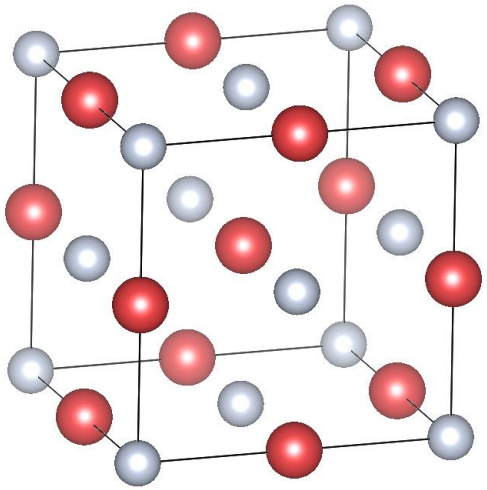
Substituting (*) and (**) in SEQ

$$\sum_k \left\{ \left(\frac{1}{2}k^2 - E\right) c_k + \sum_G V_G c_{k-G} \right\} = 0$$

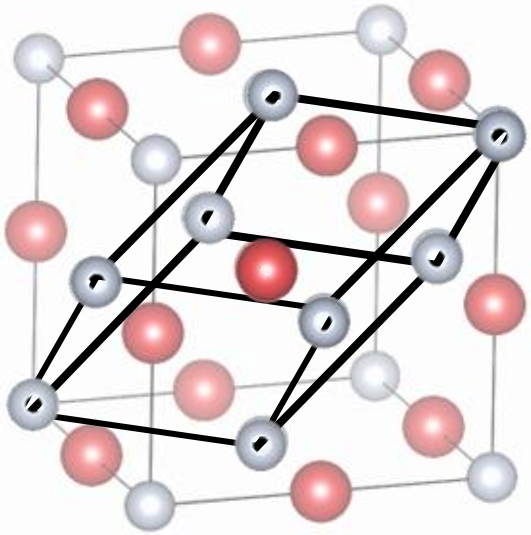
Band structure and periodic potential

Periodic potential:

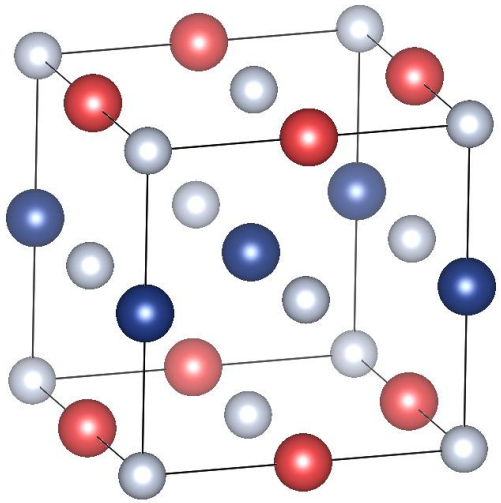
$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R}) = \sum_G V_G e^{i\mathbf{G}\mathbf{r}}$$



fcc structure with 2 sublattices, space group 225 , e.g. SmN, NiO



Smallest possible unit, primitive cell, orthorhombic cell



2-atom primitive cell does not work

AFM

Spin-down

Spin-up

Magnetism alters lattice periodicity – size of primitive cell
(Often neglected fact in (ab initio) databases!

Structures made by VESTA

Band structure and periodic potential

$$\psi(\mathbf{r}) = \sum_k c_k e^{i\mathbf{kr}}$$

$$\psi_k(\mathbf{r}) = \sum_G c_{k-G} e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}} = e^{i\mathbf{kr}} \sum_G c_{k-G} e^{-i\mathbf{Gr}}$$

Lattice periodic function $u_k(\mathrm{r})$

Bloch theorem

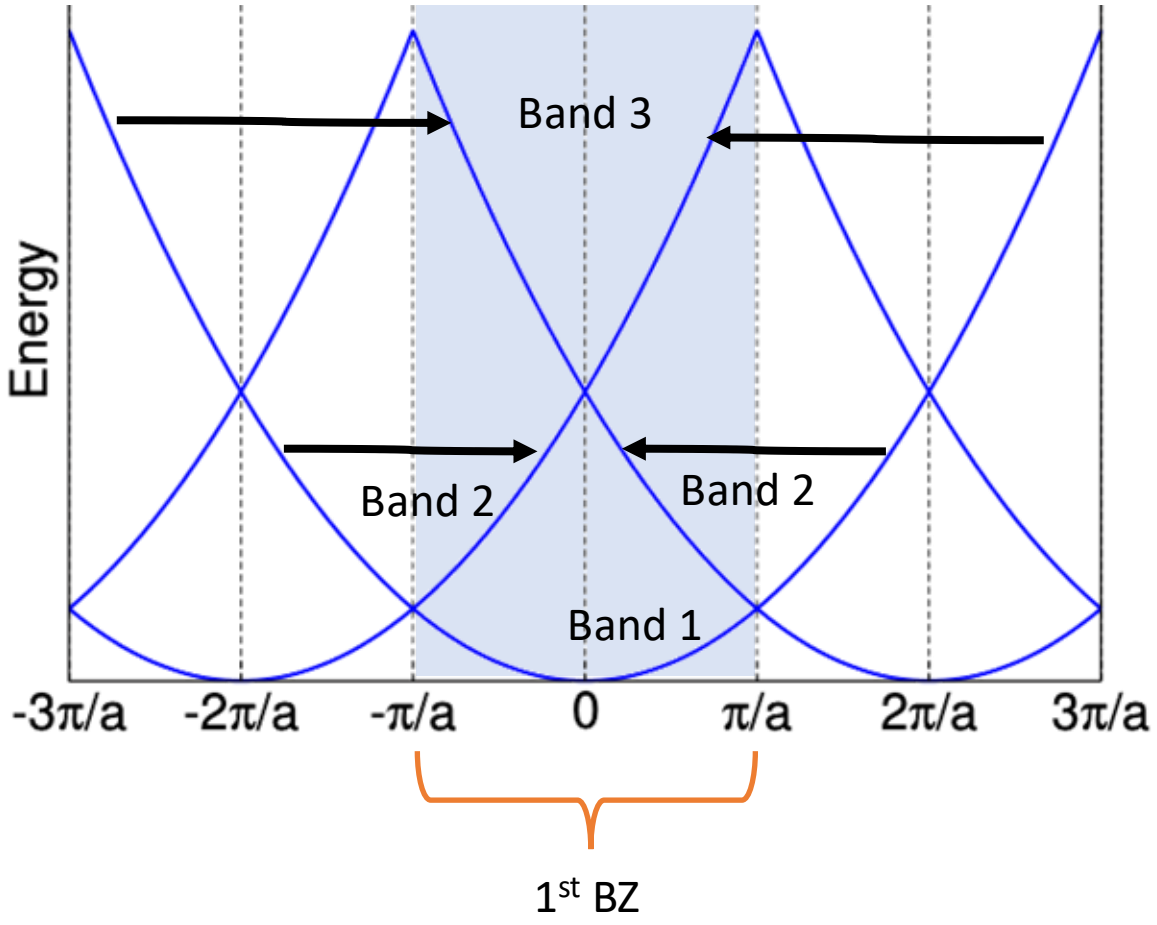
$$\psi_k(\mathbf{r}) = e^{i\mathbf{kr}} u_k(\mathbf{r})$$

with $u_k(\mathbf{r}) = u_k(\mathbf{r}+\mathbf{T})$

$\mathbf{T}$ = Bravais lattice vector

Band structure and periodic potential

Free electron case



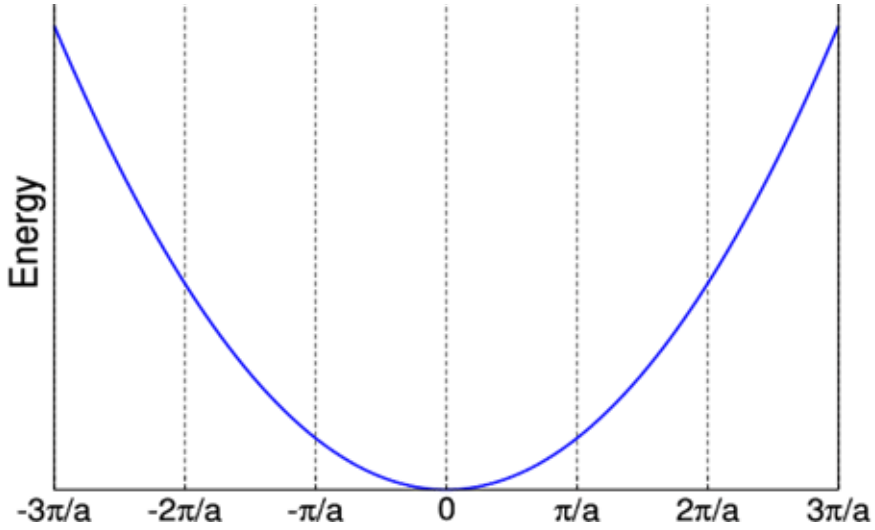
Inserting ψ and V(r) to Schrödinger equation:

$$\sum_k \left\{ \left(\frac{1}{2}k^2 - E \right) c_k + \sum_G V_G c_{k-G} \right\} = 0$$

=0

Coupled equations only if $k' = k \pm G$

k runs over 1st Brillouin zone



Reduced Zone scheme

Band structure and periodic potential

$$\psi(\mathbf{r}) = \sum_k c_k e^{i\mathbf{kr}}$$

$$\psi_k(\mathbf{r}) = \sum_G c_{k-G} e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}} = e^{i\mathbf{kr}} \sum_G c_{k-G} e^{-i\mathbf{Gr}}$$

Lattice periodic function $u_k(r)$

Bloch theorem

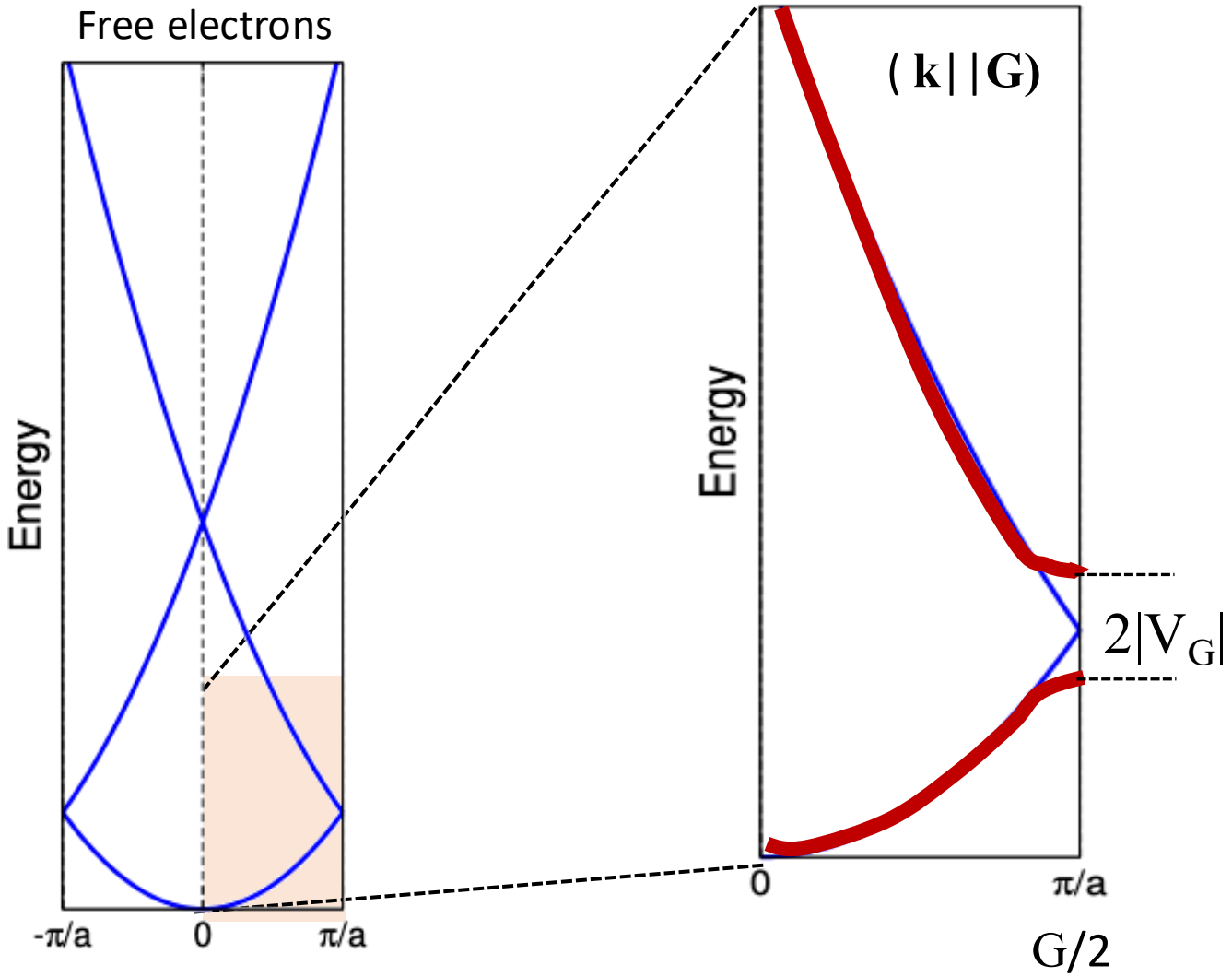
$$\psi_k(\mathbf{r}) = e^{i\mathbf{kr}} u_k(\mathbf{r})$$

with $$u_k(\mathbf{r}) = u_k(\mathbf{r}+\mathbf{T})$$

Consequences:

1) All wave vectors can be folded back to the 1st BZ calculations can be restricted to the 1st BZ
2) Formation of energy bands, BZ has a fixed volume → band index n
3) Bloch function $\psi_{nk}(\mathbf{r})$; each value of k and n defines an orbital with energy $E_n(\mathbf{k})$

Band structure and periodic potential



$$\sum_k \left\{ \left(\frac{1}{2}k^2 - E \right) c_k + \sum_G V_G c_{k-G} \right\} = 0$$

Switch on the potential assuming
$V << |E^0(\mathbf{k})-E^0(\mathbf{k-G})|$

Perturbation theory
$E(\mathbf{k}) = E^0(\mathbf{k}) + \sum_G (V_G)^2/|E^0(\mathbf{k})-E^0(\mathbf{k-G})|$

Switch on the potential assuming
$V \geq |E^0(\mathbf{k})-E^0(\mathbf{k-G})|$

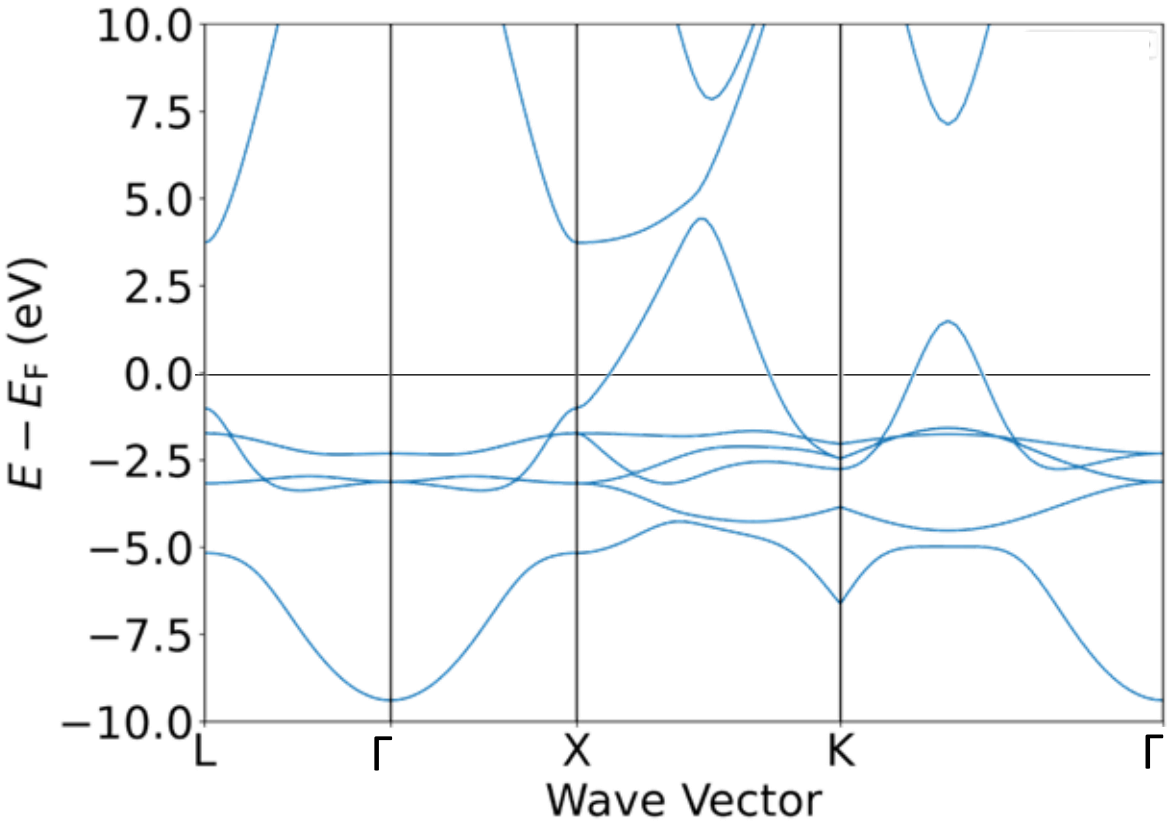
Solving the Schrödinger equation leads to a quadratic equation

$$(E^0(\mathbf{k}) - E)(E^0(\mathbf{k-G}) - E) - |V_G|^2 = 0$$

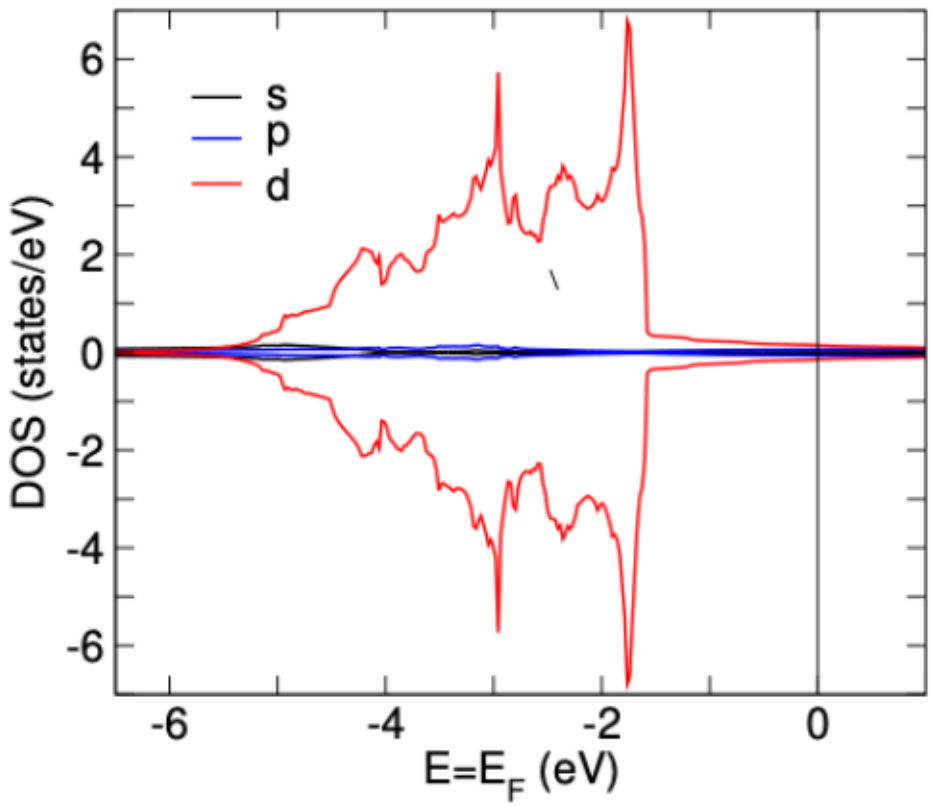
Density of states

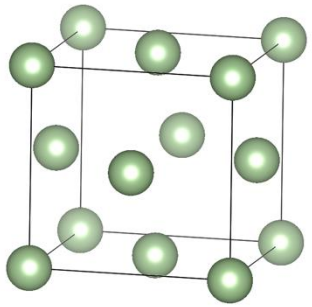
Example: fcc Cu, (nonmagnetic)

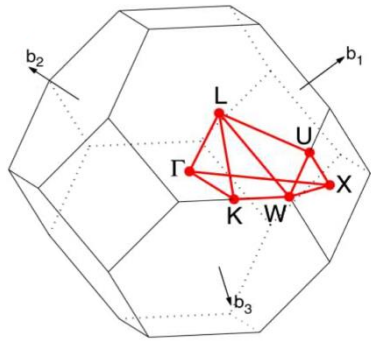
Band structure



Density of states







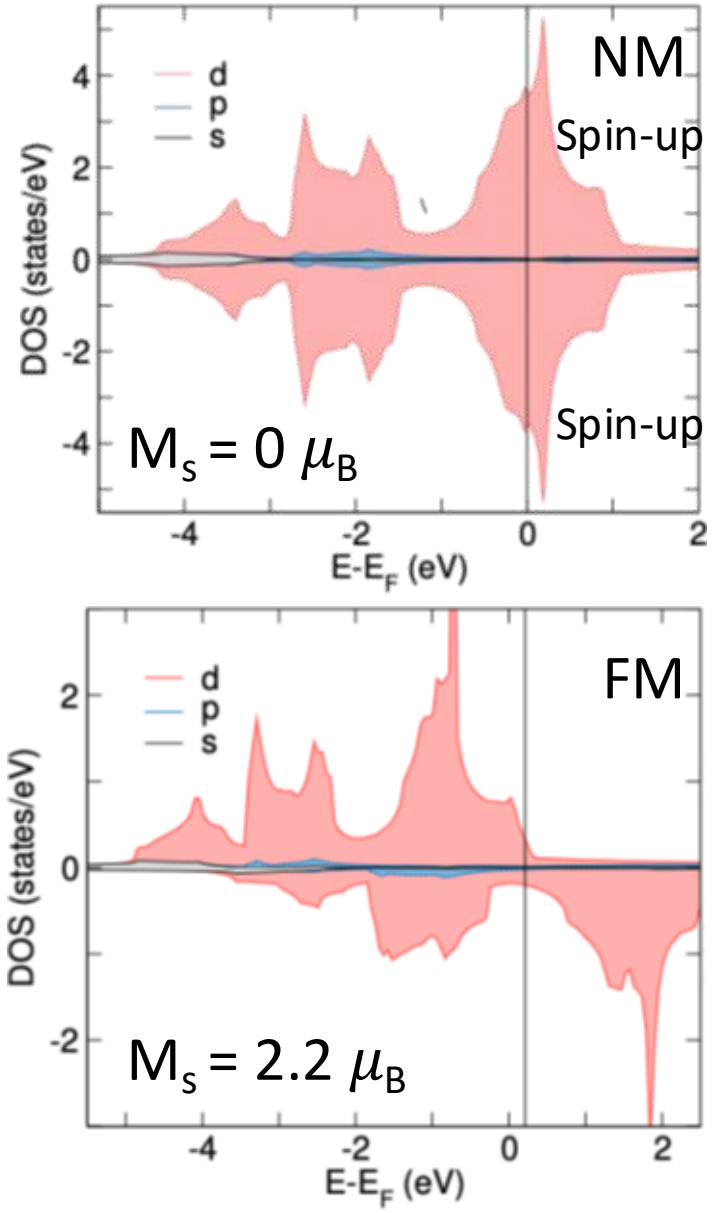
Density of states (DOS)

$$\rho(E) = \frac{1}{N}\sum_{n\mathbf{k}} \delta(E - E_n(\mathbf{k}))$$

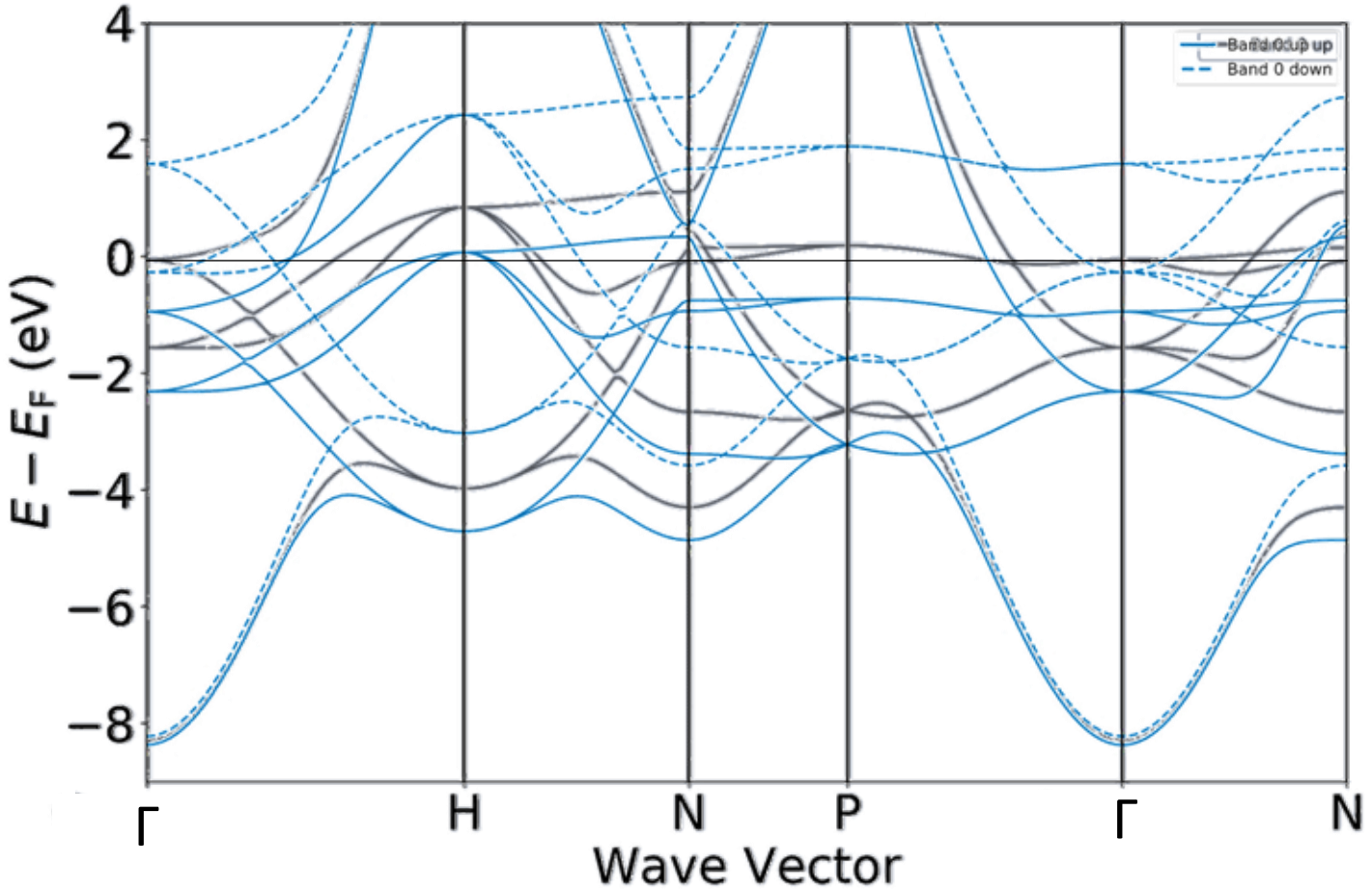
Fermi level:

$$\int_{-\infty}^{E_F} dE\, \rho(E) = Z_e$$

Density of states – bcc Fe



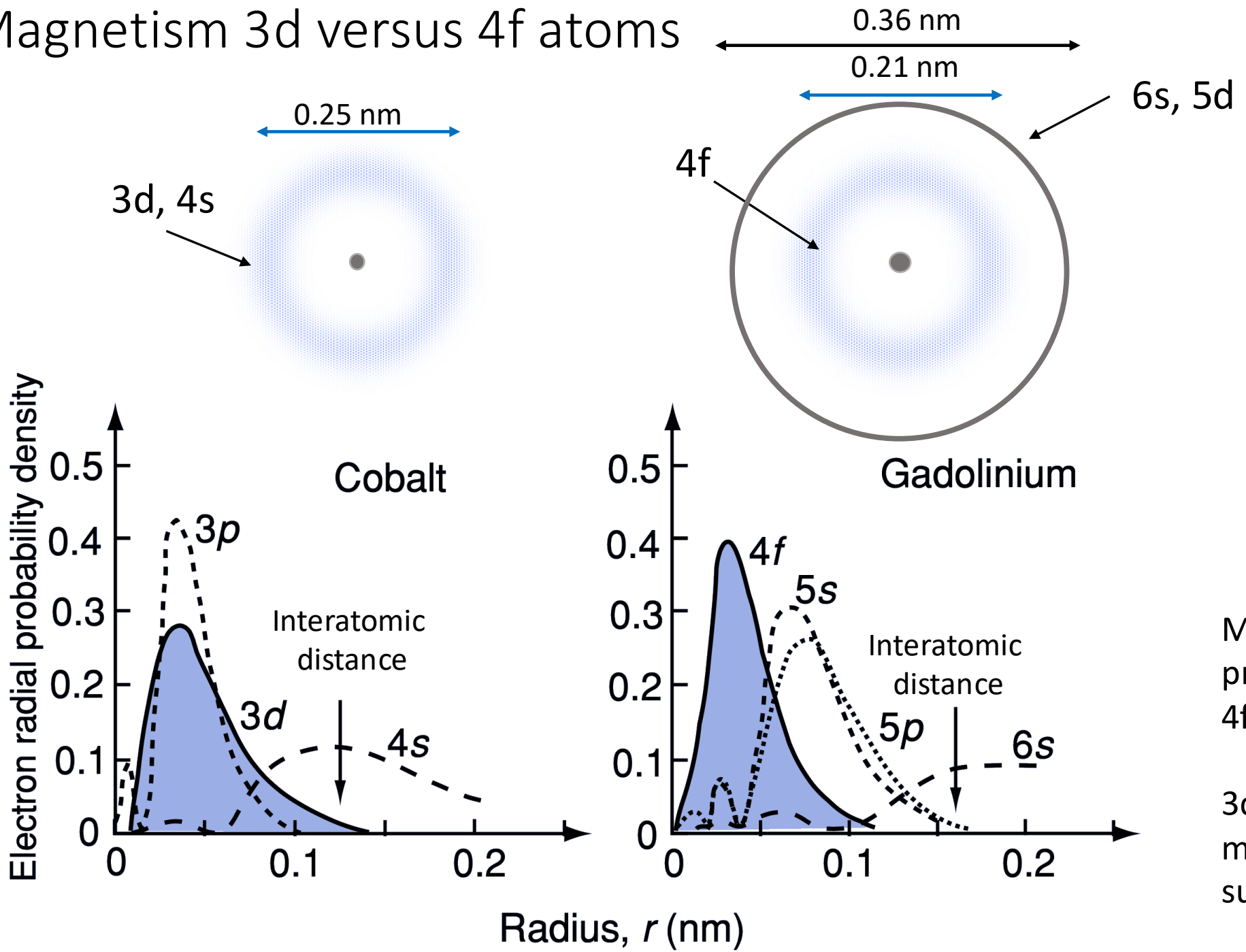
bcc Fe, NM and spin-polarized, FM



Exchange splitting : Relative shift of DOS(⇩) vs. DOS(⇧)

Magnetic moment $M_s \sim (n(\Uparrow) - n(\Downarrow))$

Magnetism 3d versus 4f atoms



3d ions

3d shell is the outer shell

4f ions

4f shell in buried below higher shells

Magnetism of 4f ions is preserved even is solids
4f electrons are localized

3d ions are delocalized and magnetism depends on surrounding

Electron interactions

Present in an atom

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\mathrm{SO}} + \mathcal{H}_{\mathrm{cf}} + \mathcal{H}_Z$$

Coulomb

$|\mathbf{L}, \mathbf{S}\rangle$

Spin-orbit

$\mathcal{H}_{SO} = \Lambda \mathbf{L}\mathbf{S}$

Crystal-field

$$\int \rho_0(r)\, V_{\mathrm{cf}}\, \mathrm{d}^3 r$$

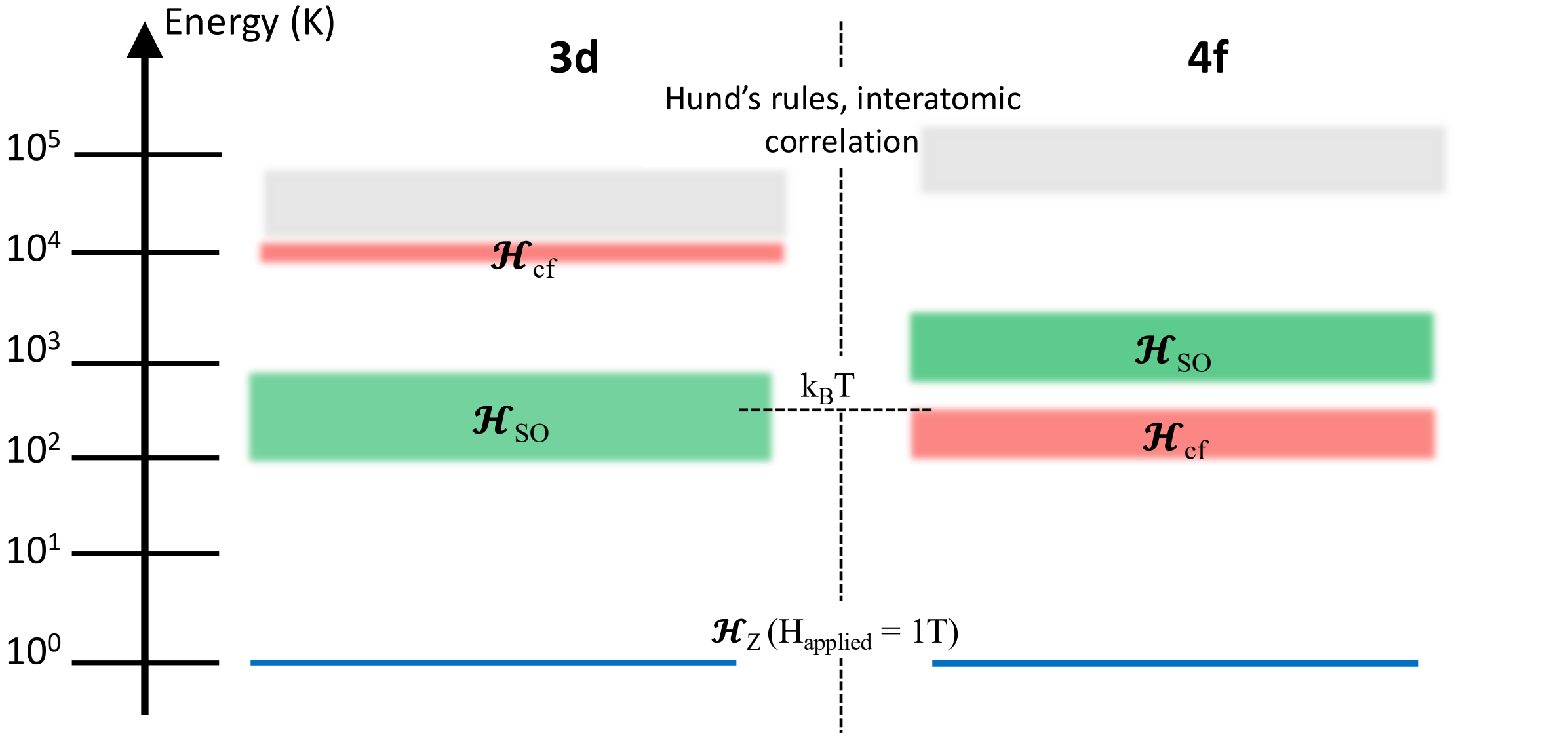
Not existing for
a single atom

Zeeman

$g\mu_{\mathrm{B}}\mathbf{B}\mathbf{J}$

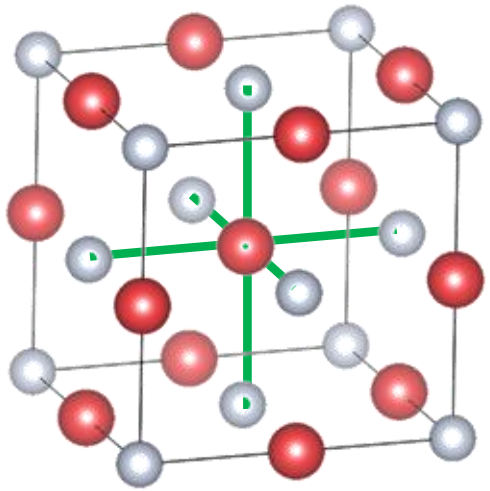
Interaction of the electronic density with the potential created by the other ions

Electron interactions



(Interactions in K, 1K = 1.380649 10^{-23}J)

Crystal field



Crystal field Hamiltonian $\mathcal{H}_{\mathrm{cf}} = \int \rho_0(r) V_{\mathrm{cf}}(r) \mathrm{d}^3 r$

with $V_{\mathrm{cf}}(r) = \int \frac{\rho(r')}{4\pi\epsilon_0} \mathrm{d}^3 r'$

Potential created by the charge distribution of the crystal

The eigenstates are different from the undisturbed potential

⇨ Use linear combinations of the unperturbed wavefunctions

⇨ Example d orbitals

$$d_{xy} = \frac{1}{\sqrt{2}}(\Psi^2 - \Psi^{-2}) = R(r)\sin^2\theta\sin(2\phi)$$

$$d_{yz} = \frac{1}{\sqrt{2}}(\Psi^1 - \Psi^{-1}) = R(r)\sin\theta\cos\theta\sin\phi$$

$$d_{z^2} = \Psi^0 = R(r)(3\cos^2\theta - 1)$$

$$d_{zx} = \frac{1}{\sqrt{2}}(\Psi^1 + \Psi^{-1}) = R(r)\sin^2\theta\sin(2\phi)$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(\Psi^2 + \Psi^{-2}) = R(r)\sin^2\theta\cos(2\phi)$$

Crystal field

Angular momentum z- component $L_z = -i\hbar\frac{\partial}{\partial\phi}$

Expectation value $\langle L_z\rangle = \int_0^{\pi}\int_0^{2\pi} \Psi^*(\phi,\theta)\left(-i\hbar\frac{\partial}{\partial\phi}\right)\Psi(\phi,\theta)d\theta d\phi$

$\langle L_z\rangle$ Vanishes for eigenfunctions of $\mathcal{H}_{cf}$

Example: $d_{xy} = R(r)\sin^2\theta\sin(2\phi)$

(r-integral skipped)

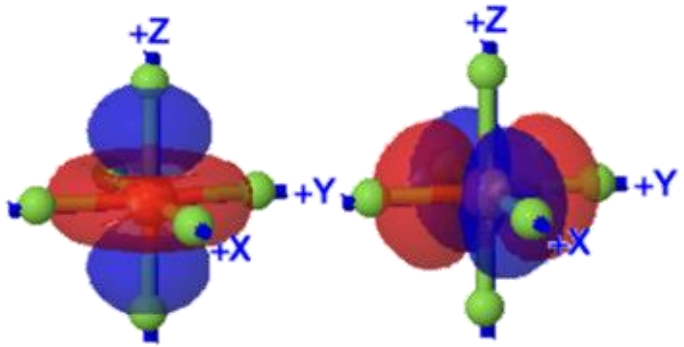
$$\langle L_z\rangle = R(r)\int_0^{\pi}\int_0^{2\pi}\sin^2\theta\sin(2\phi)\frac{-i\hbar\partial}{\partial\phi}\sin^2\theta\sin(2\phi)d\phi d\theta$$
$$= i2\hbar R(r)\int_0^{\pi}\int_0^{2\pi}\sin^4\theta\sin(2\phi)\cos(2\phi)d\phi d\theta$$
$$= i\frac{1}{2}\hbar R(r)\int_0^{2\pi}\sin^4\theta d\theta(\sin^2(2\phi))|_0^{\pi}d\theta$$

Angular momentum of e_g states is fully quenched

⇨ Orbital moment quenched for 3d systems!

Crystal field (cubic systems)

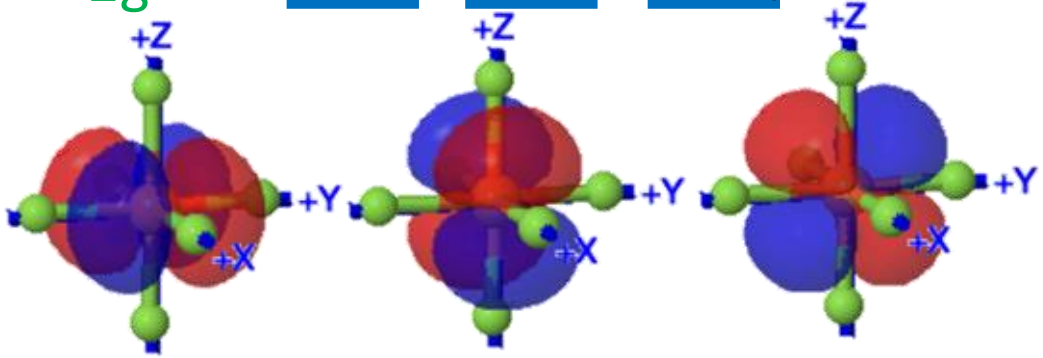
octahedral



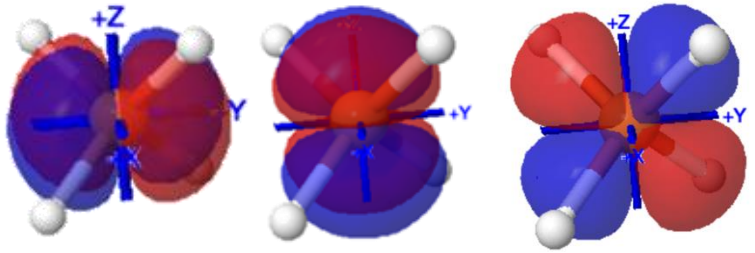
e_g z^2 x^2-y^2

free ion d-states

t_{2g} xy xz yz

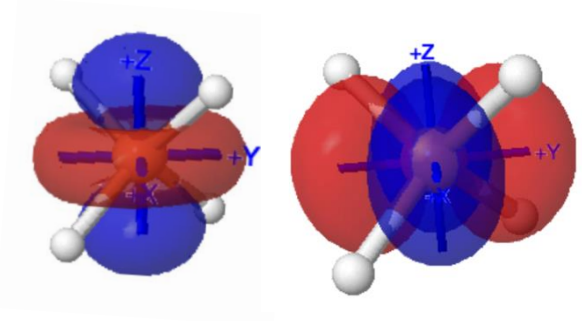


tetrahedral



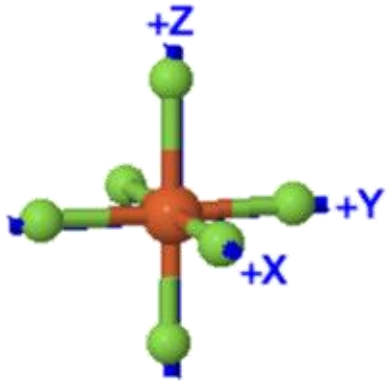
xy xz yz t_2

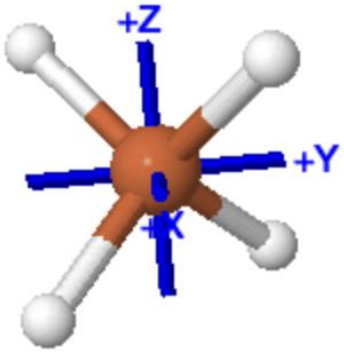
z^2 x^2-y^2 e



Made with JSmol, http://wwwchem.uwimona.edu.jm/courses/CFT_Orbs.html

Crystal field





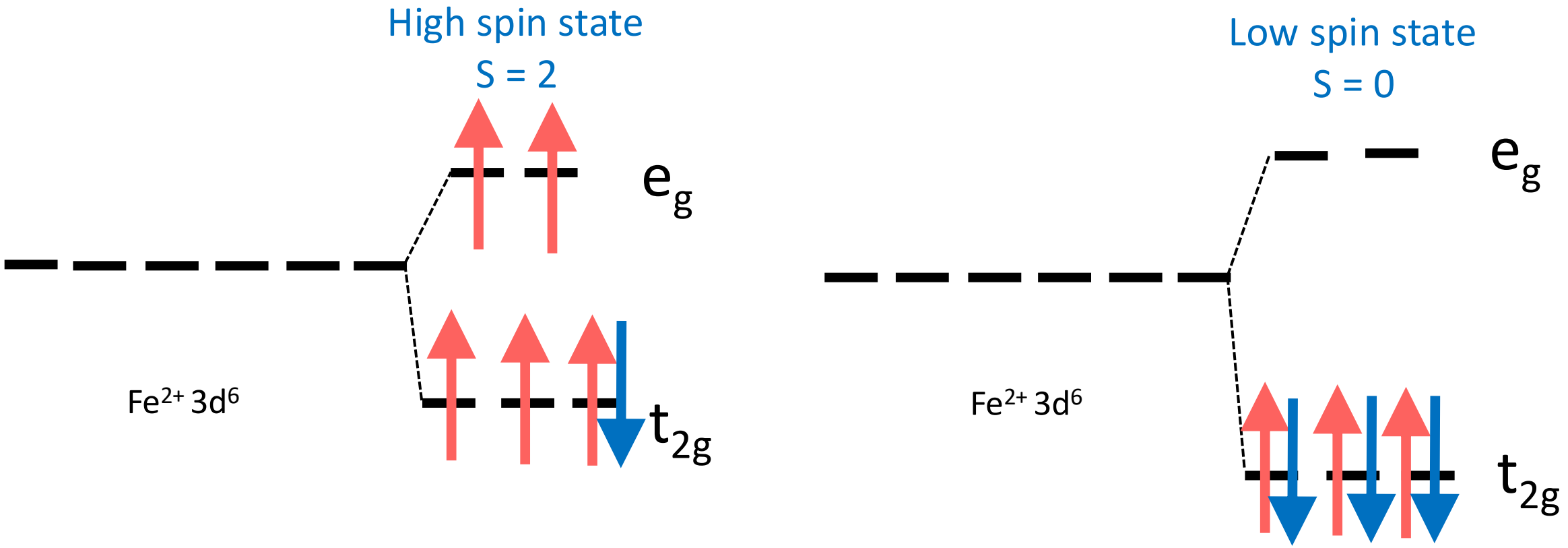
- The stronger the overlap with the neighbouring orbitals,
  the stronger is the electrostatic repulsion ⇨ The higher the shift upwards in energy

- Octahedral splitting is larger ⇨ $\Delta_t = 4/9\ \Delta_o$

Crystal field vs spin-orbit coupling

Crystal field is small: Δ_o. << ΛLS ⇨ Hund's rules apply

Crystal field large: Δ_o. >> ΛLS ⇨ Only lowest energy level s occupied



- Jahn-Teller effect
- Verwey transition in Fe_3O_4 - Magnetite

Take home message – magnetism in solids

The presence of other atoms changes all

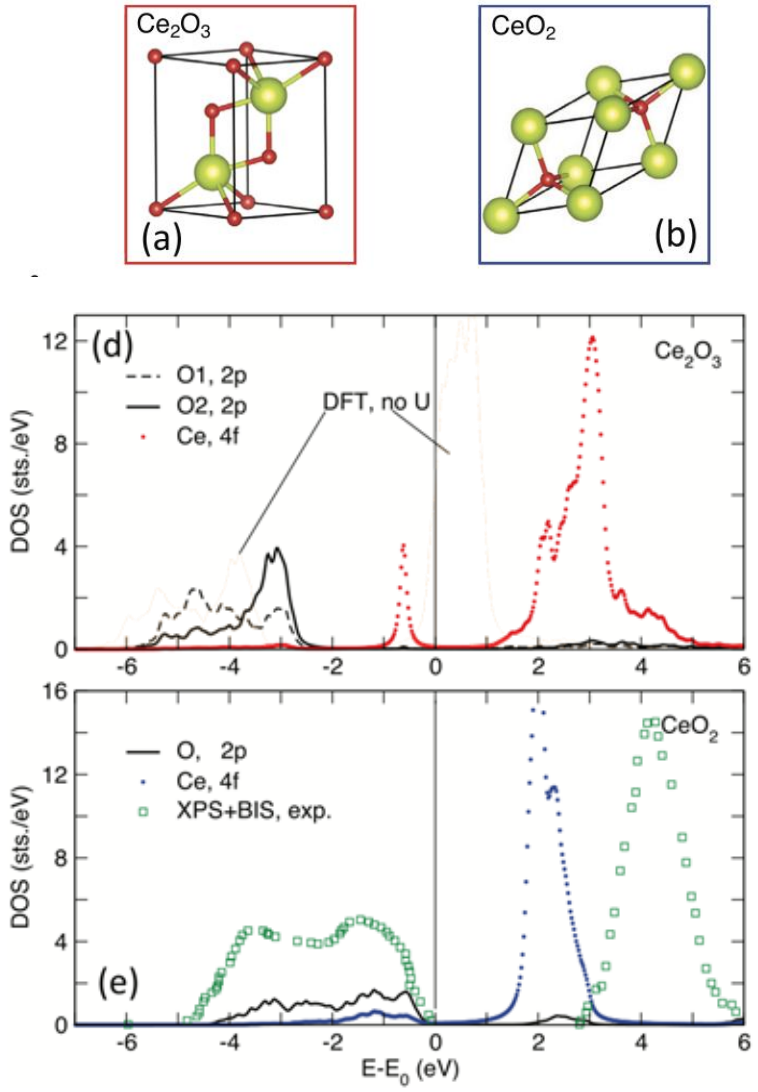
Collective phenomena possible due to delocalised atoms

Bandstructure and density of states

- Spin-polarization shifts bands and DOS Exchange splitting

Significant difference between 3d and 4f magnetism

- Atomic magnetism (almost) conserved for 4f systems (there are exceptions)
- Magnetism in 3d systems driven by crystal field effects
- CF and LS are competing interactions



The End

Further reading

Fundamentals, broad overview:

J. M. D. Coey, *Magnetism and Magnetic Materials,* Cambridge University Press (2009)

Theory of magnetism:

J. Kübler, Theory of Itinerant Electron Magnetism, Oxford, International Series of Monographs on Physics (2009)