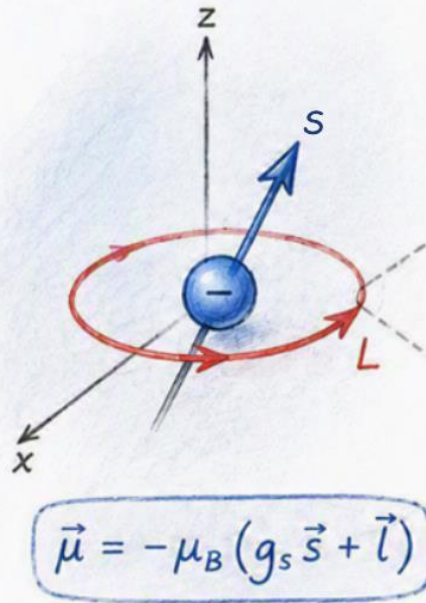
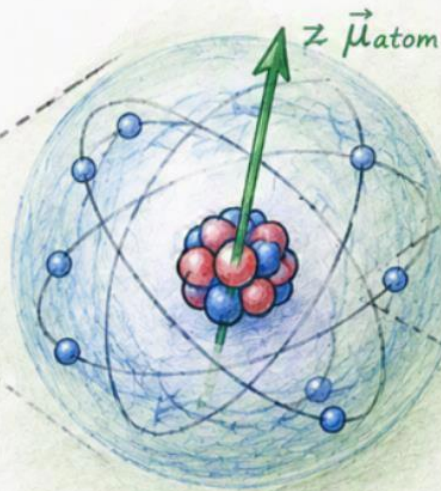


Magnetism from atoms to solids

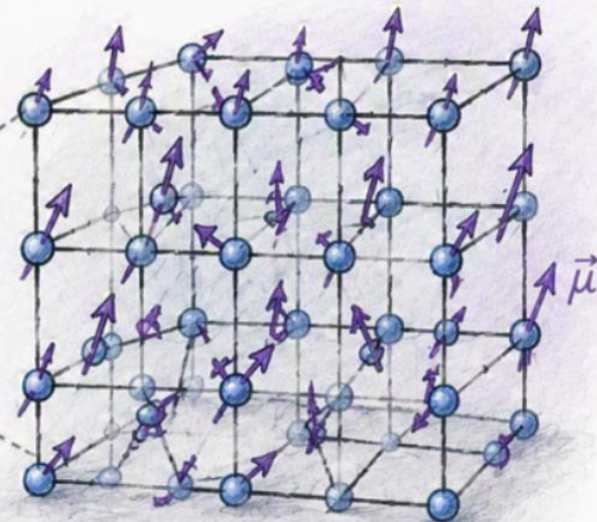
1. Electron level
spin and orbital moment



2. Atom level
many electrons
in an atom



3. Solid level
atoms in a solid
interacting



Graph generated by ChatGPT

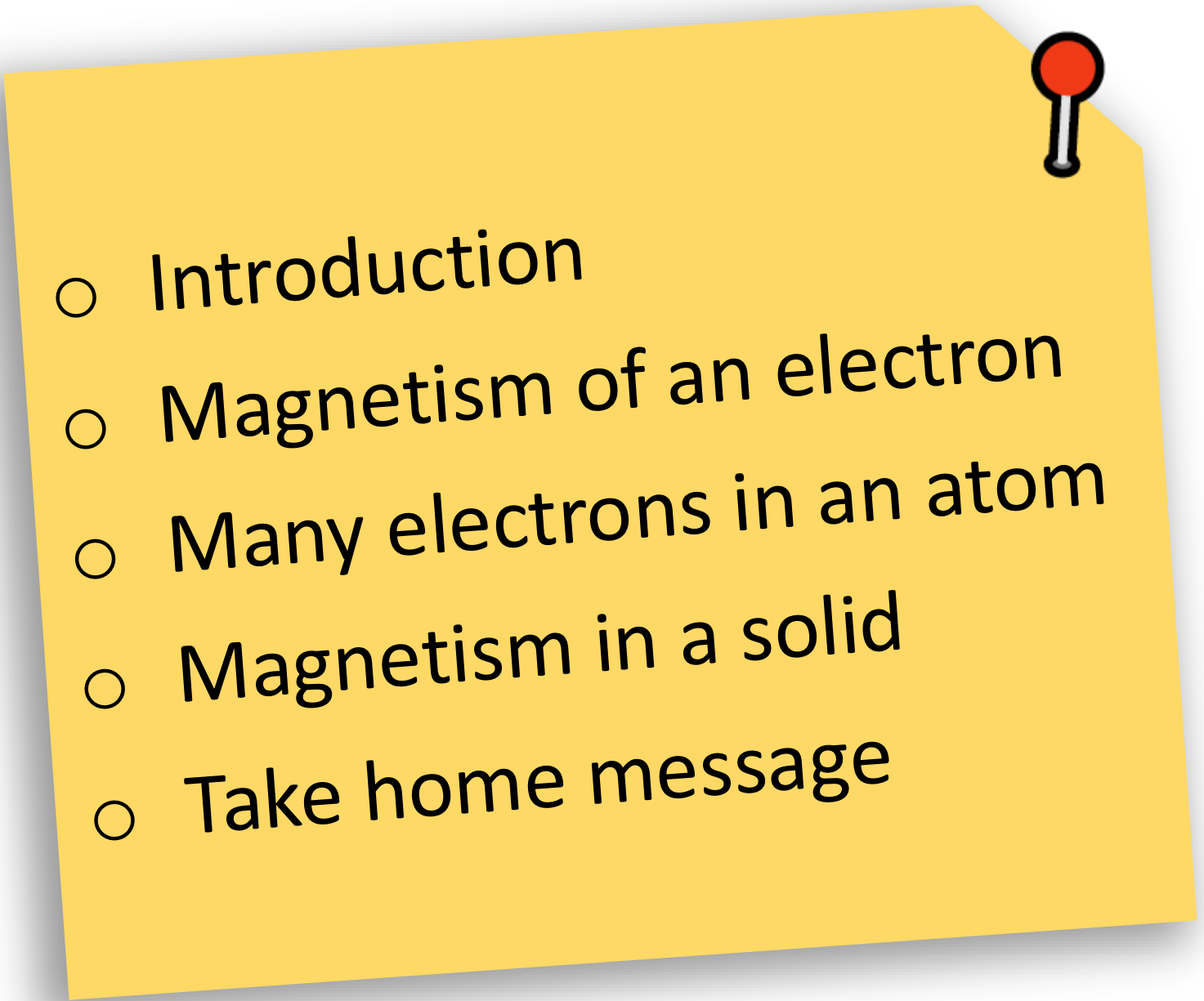
Dr. Heike Herper

Department of Physics and Astronomy, Uppsala University



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 $\rightarrow$ Equilibrium magnetization is zero

- The dependence on the magnetic field can be removed by changing the integration variable

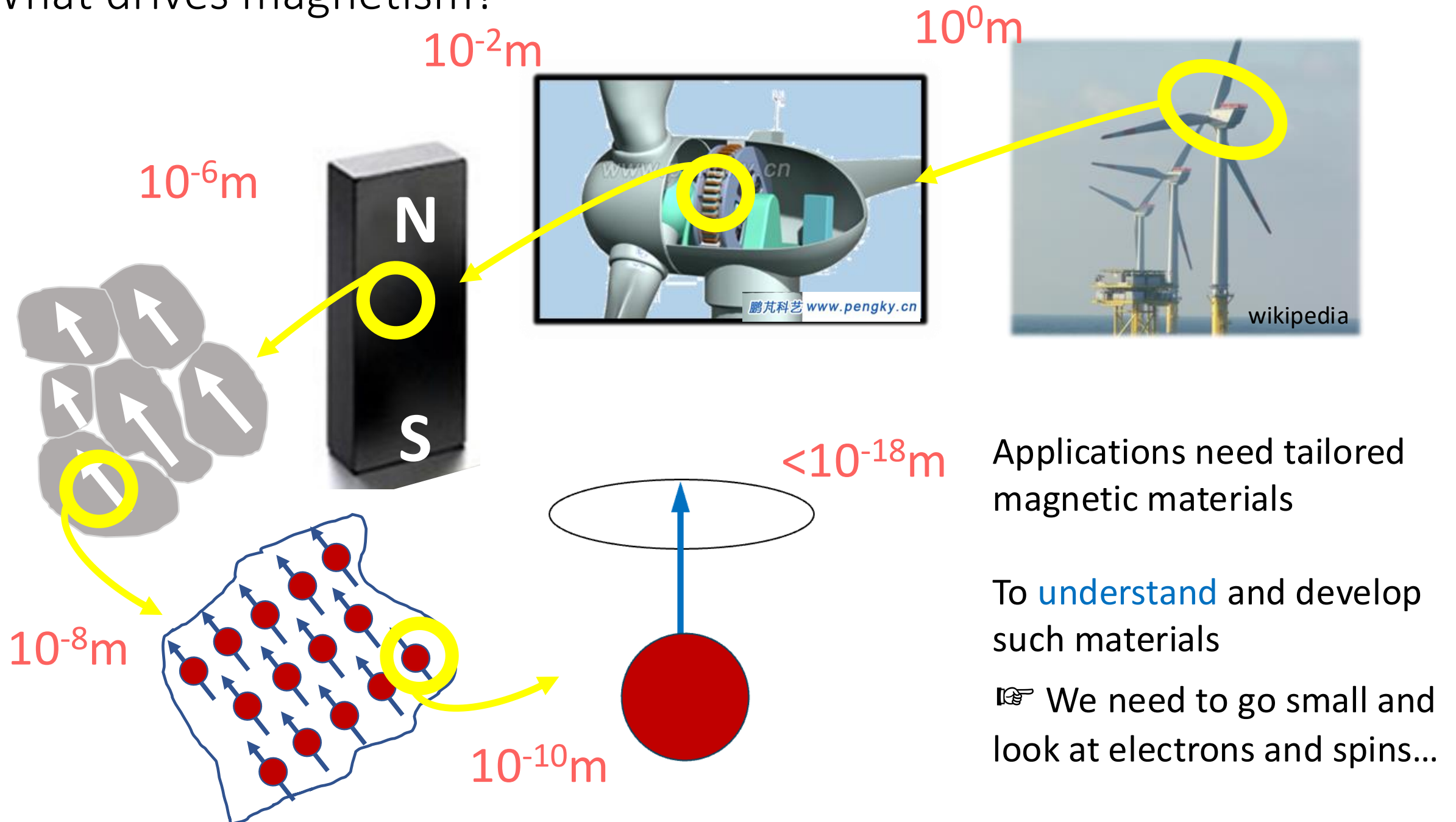
$\Rightarrow$ Consequently, no ferromagnetism, diamagnetism or other magnetic order exist

- Magnetism arises from the interaction of electrons

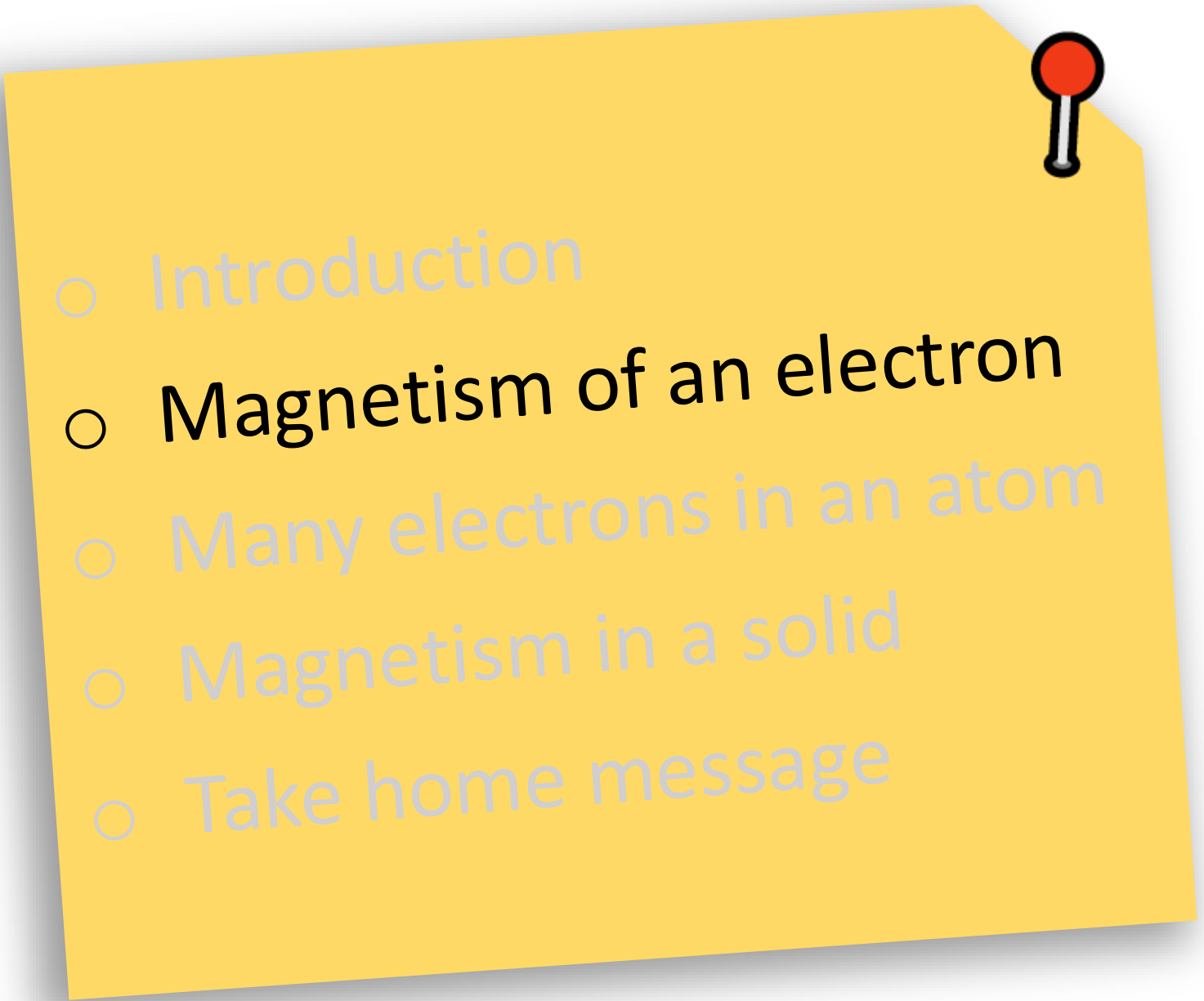
- Classical dipole picture does not hold

- What counts are the Pauli principle and the Coulomb repulsion between the electrons $\rightarrow E(\uparrow\uparrow) \neq E(\uparrow\downarrow)$

What drives magnetism?



Outline

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

Magnetism of the electron - The orbital momentum

An electron with velocity $\mathbf{v}$ creates a current $\mathbf{I}$ and a magnetic moment $\mathbf{m}$

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

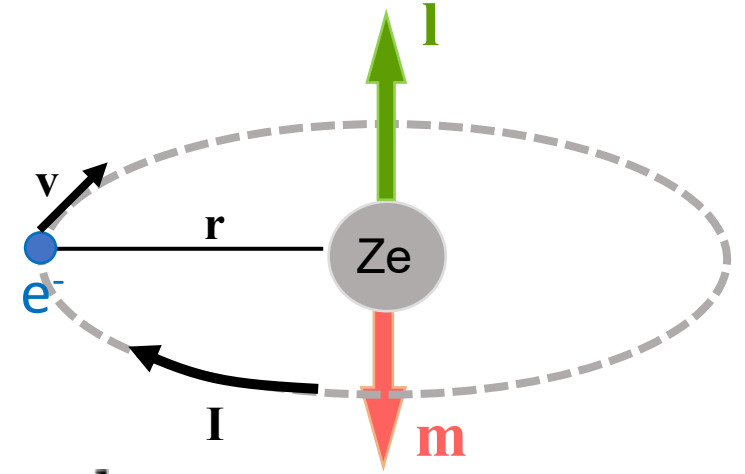
Bohr: Angular momenta are quantized – they are multiples of $\hbar = h/2\pi$

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

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 $\mathbf{m}$ $m_z = -\frac{e\hbar}{2m_e} m_l = -\mu_B m_l$
Bohr magneton

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



Circular orbit:

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

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

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

Magnetism of the electron - The orbital momentum

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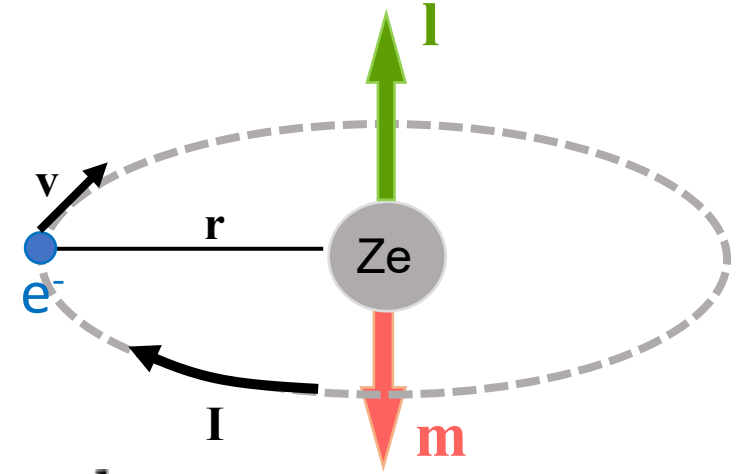
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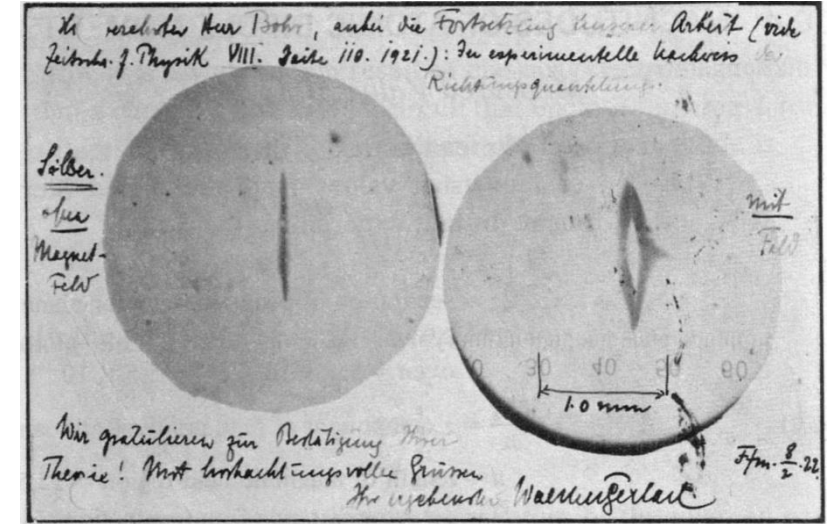
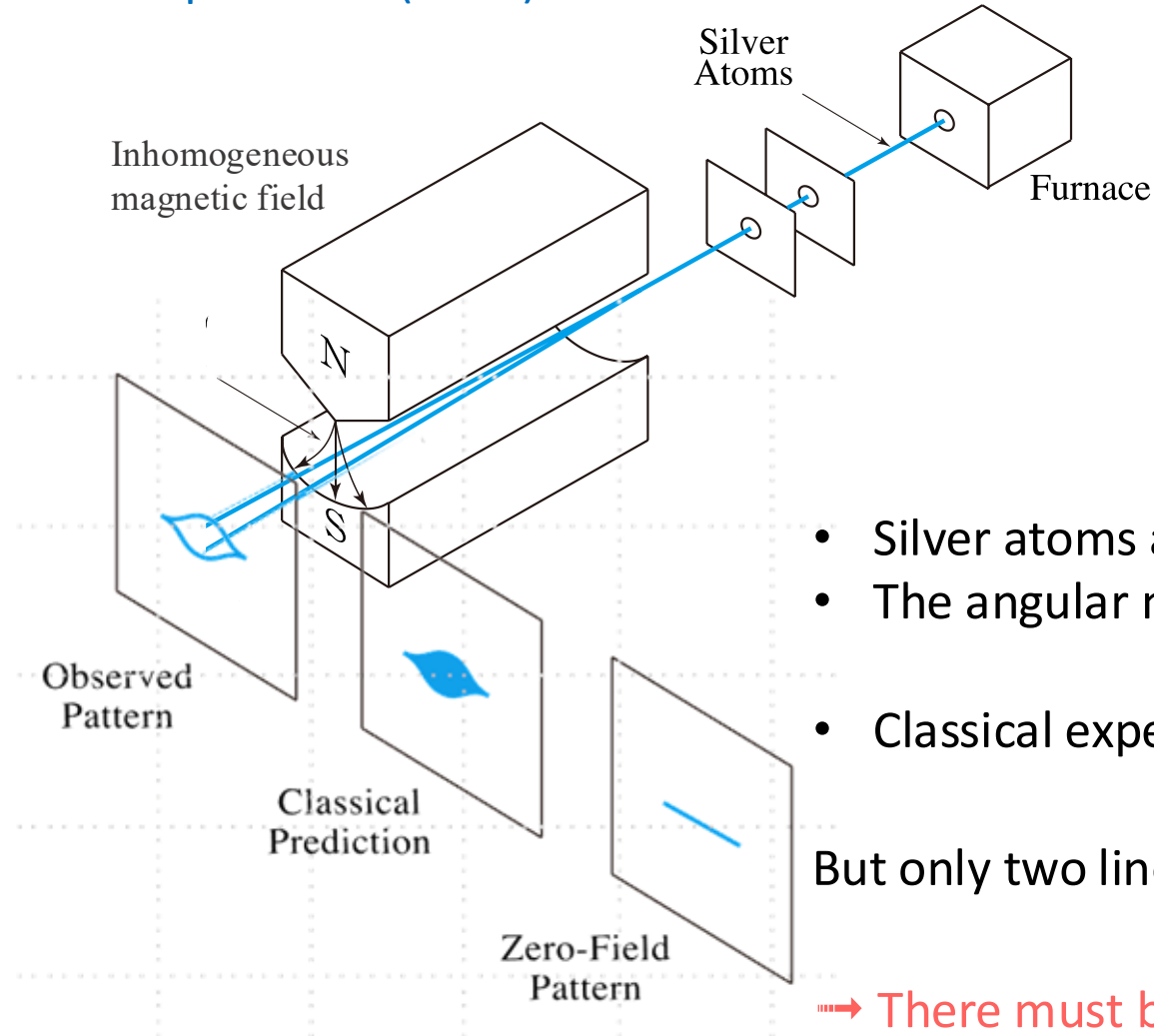
Ratio between $\mathbf{m}$ and $\mathbf{l}$:

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

$g = 1$ 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](https://doi.org/10.1063/1.1650229)

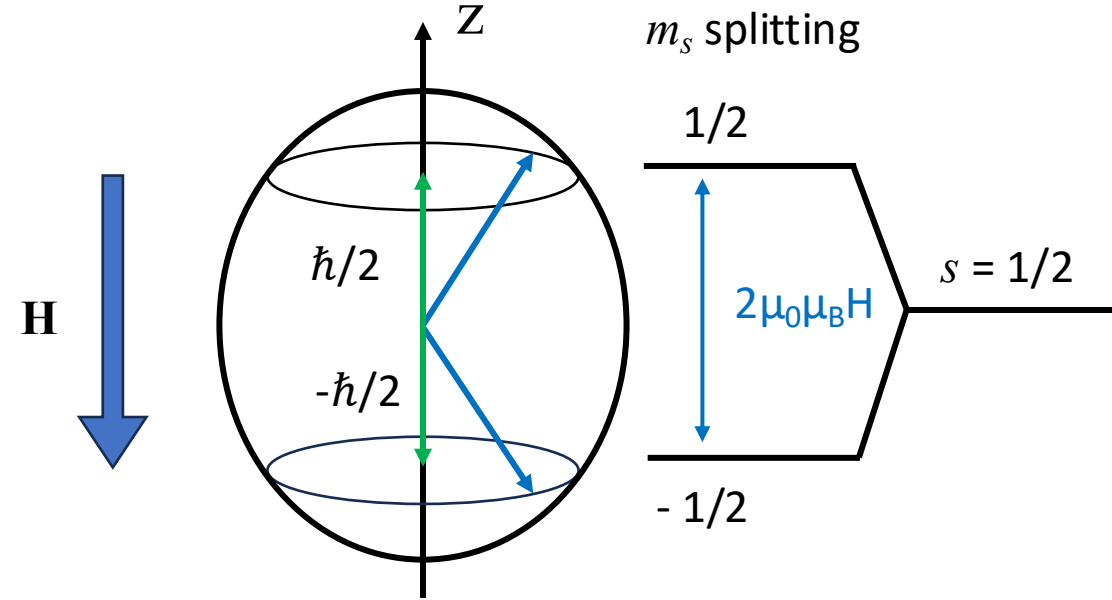
- Silver atoms are magnetic $\Rightarrow$ measure magnetic moment
- The angular momentum of silver atoms is zero
- Classical expectation $\Rightarrow$ homogenous distribution of moments

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

$\Rightarrow$ There must be more than the orbital angular momentum ...
 $\Rightarrow$ Experiment confirmed Bohr's prediction of the **spin**

Magnetism of the electron – The spin of the electron

$$s_z = m_s \hbar \quad m_s = \pm \frac{1}{2} \quad s = \frac{1}{2}$$
$$\mathbf{m} = -\frac{e}{m_e} \mathbf{s} \quad m_z = -\frac{e}{m_e} m_s \hbar = \pm \mu_B$$



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 $\mathbf{m}$ and $\mathbf{s}$:

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

$g = 2$ for spin !

Exact: $g = 2.0023$

Magnetism of the electron – the total moment

Spin and orbital moment are not independent!

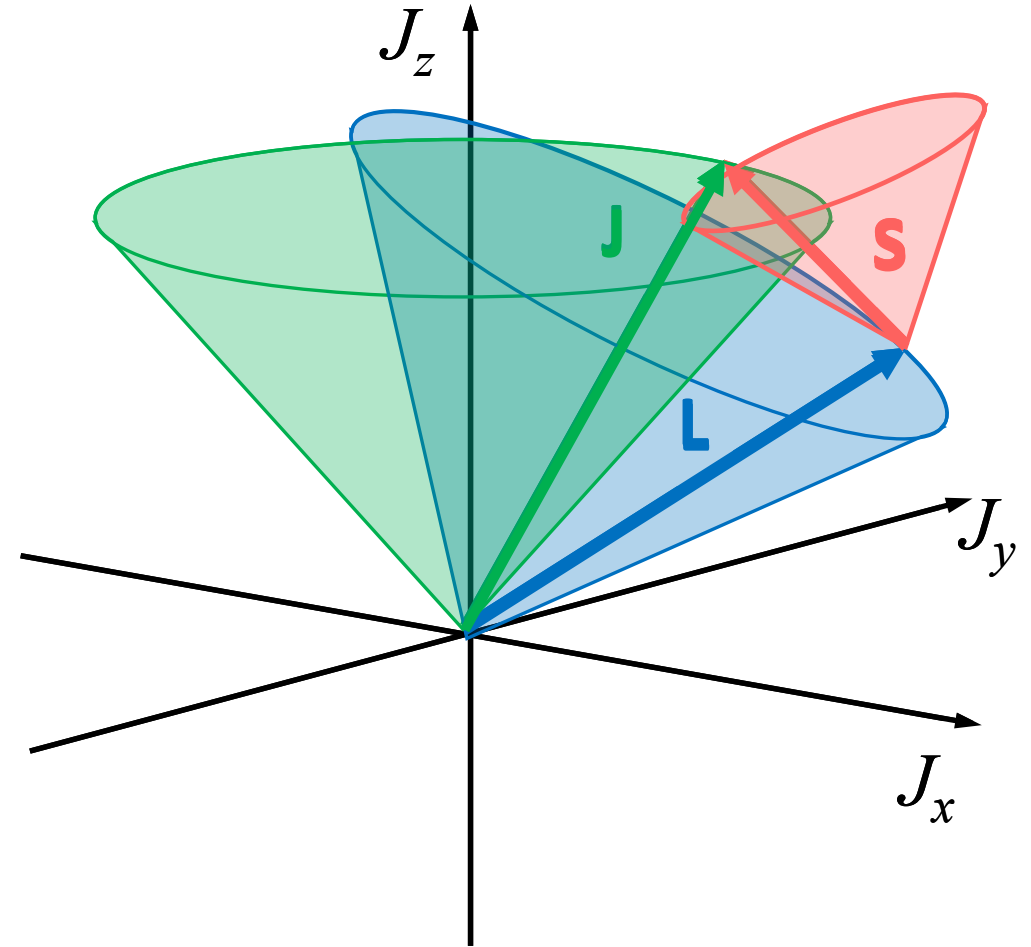
Total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$

Total magnetic moment

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

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

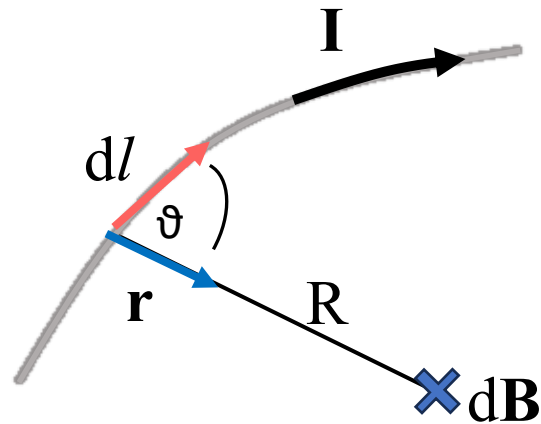
What influences the strength?



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 $\epsilon_{SO} = -\mathbf{m}\mathbf{B}$

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

$$\epsilon_{SO} = -\frac{\mu_0 \mu_B^2}{2\pi a_0^3} e Z^4$$

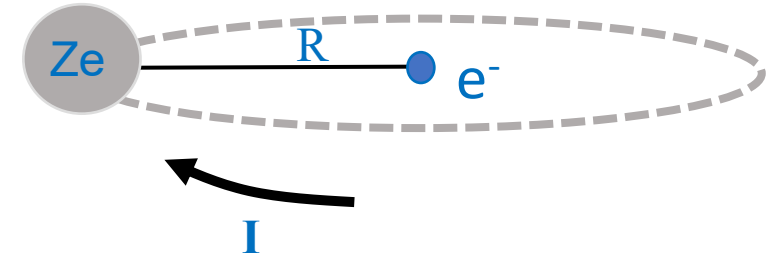
We know already that

$$I = \frac{Zev}{2\pi R} \quad \left\| \quad m_e v R \approx \hbar \quad \right\| \quad R \sim \frac{a_0}{Z} \quad \left\| \quad \mu_B = \frac{e\hbar}{2m_e} \quad \right\|$$

see 1 part e⁻ close to nuclei

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

Spin-orbit coupling constant λ



Periodic table

$$\epsilon_{SO} = -\frac{\mu_0 \mu_B^2}{2\pi a_0^3} e Z^4$$



crucial elements																		PubChem																																																																																																																																																																																									
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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

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

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

Solution

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

Laguerre Legendre
polynomials

Energy eigenvalues

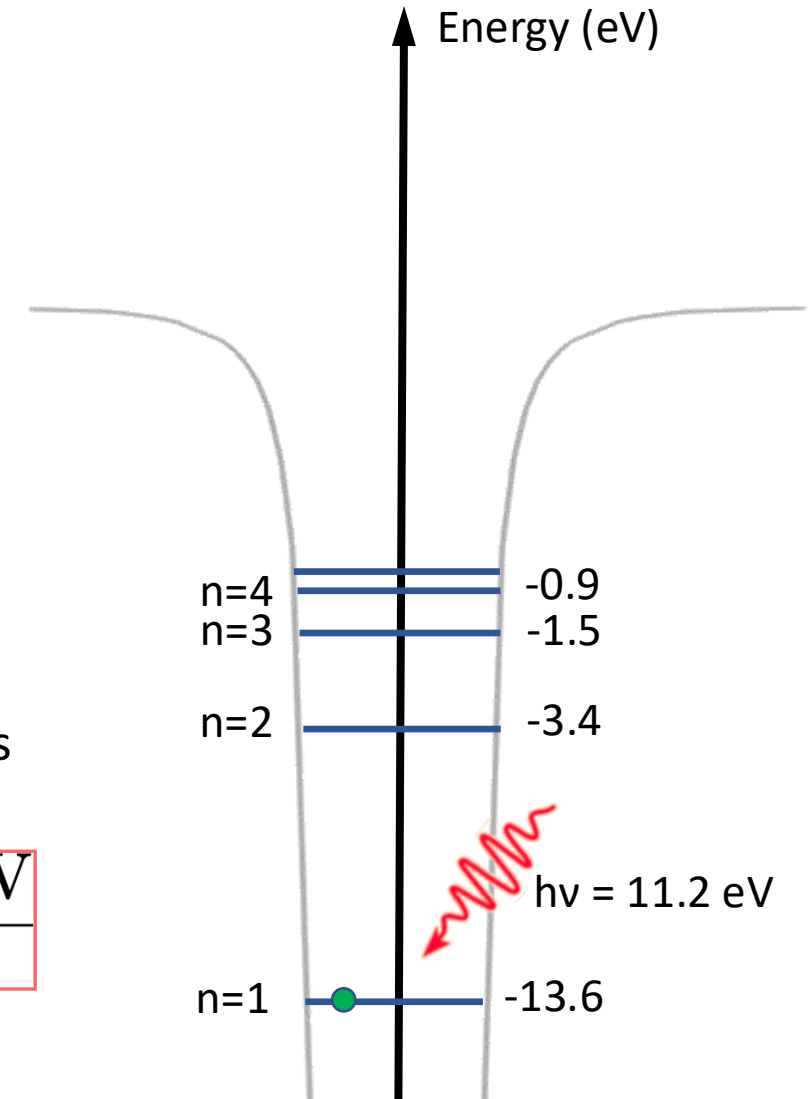
$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

Principle number $n = 1, 2, 3, \dots$

Angular momentum $l = 0, 1, \dots, n-1$

Magnetic quantum number $m = -l, -l+1, \dots, l$

Spin $s = -\frac{1}{2}, \frac{1}{2}$



Magnetism of the electron – a single electron atom

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

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

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

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

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

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

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

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad \text{Multiplicity: } |L - S|, |L - S + 1| \dots |L + S - 1|, |L + S|$$

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

Different J -states are called **multiplets** $2S+1 X_J$ X denotes L -quantum number according to
X = S, P, D, F, G, ...
for $L = 0, 1, 2, 3, 4, \dots$

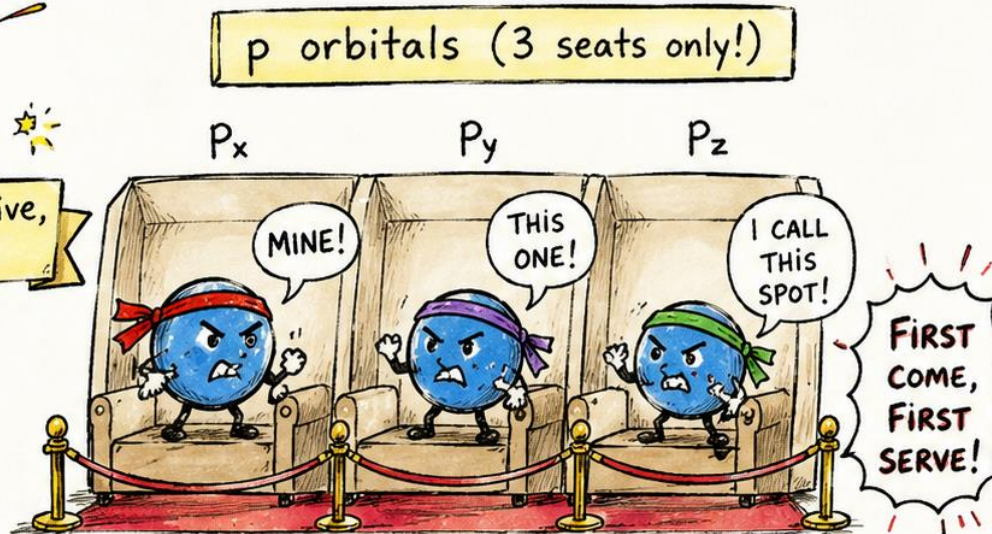
Total magnetic moment: $\mathbf{m}_J = -\frac{e}{2m_e} (\mathbf{L} + g\mathbf{S}) = -g_J \frac{e}{2m_e} \mathbf{J} = -g_J \frac{\mu_B}{\hbar} \mathbf{J}$

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

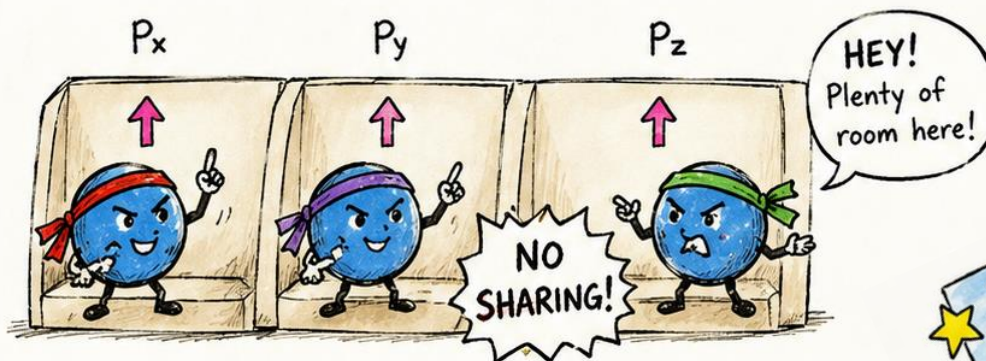
HUND'S RULES

Electrons are competitive, but they play fair!

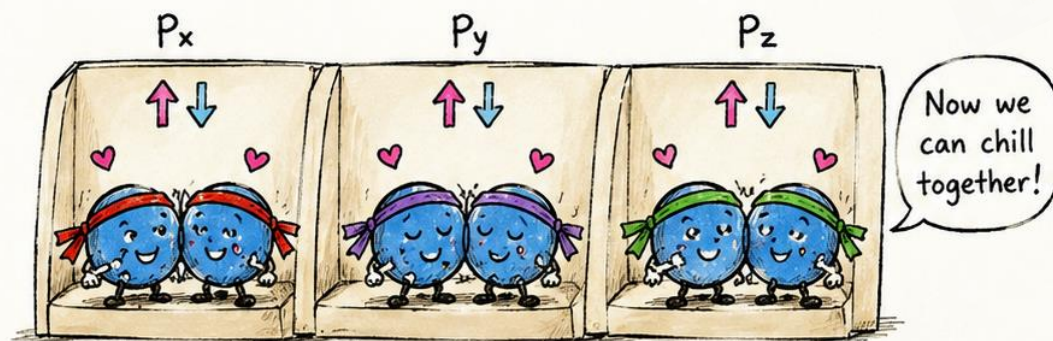
- 1 Electrons fill orbitals singly before pairing up.



- 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. ♥

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:

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

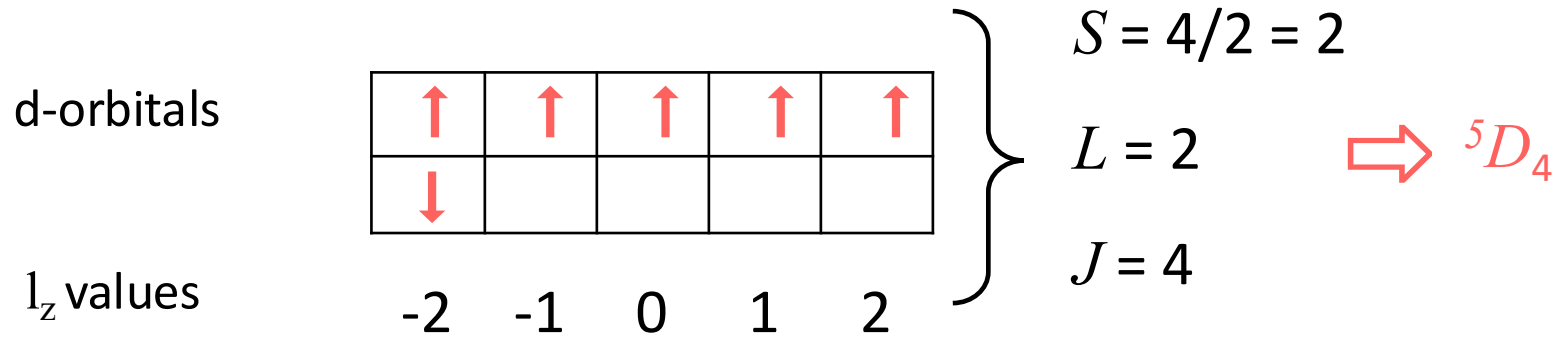
Example 1 Fe^{2+} ion $\Rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

d-orbitals	<table border="1"> <tr> <td>↑</td> <td>↑</td> <td>↑</td> <td>↑</td> <td>↑</td> </tr> <tr> <td>↓</td> <td></td> <td></td> <td></td> <td></td> </tr> </table>	↑	↑	↑	↑	↑	↓					Maximise S:	$S = 4/2 = 2$ $L = 2$ $J = 4$	$\Rightarrow {}^5D_4$
↑	↑	↑	↑	↑										
↓														
l_z values	-2 -1 0 1 2	Maximise L:												

$2S+1$
 L
 J

Atomic magnetism

Example 1 Fe^{2+} ion $\Rightarrow [\text{Ar}] \cancel{3d^6} 4s^2$



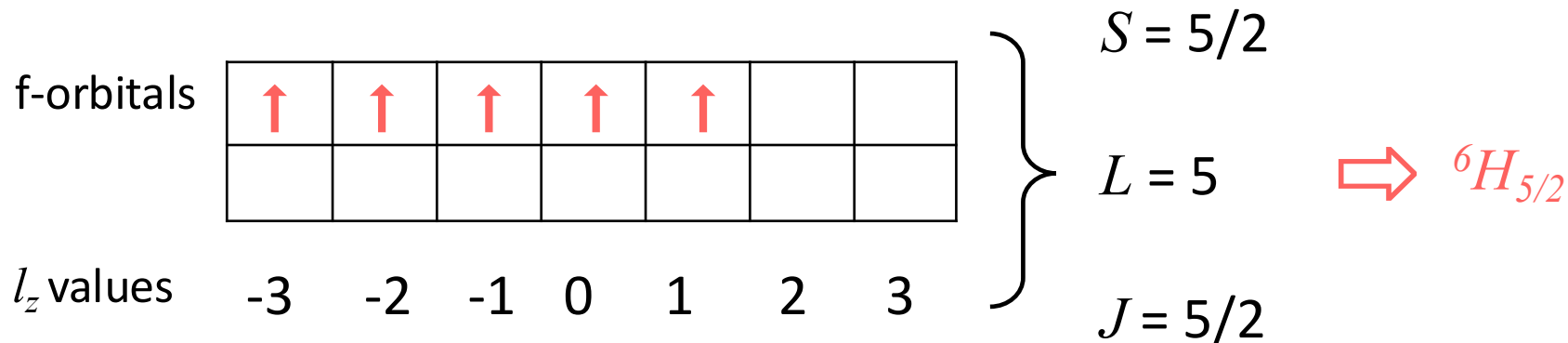
Maximize S

Maximize L

$J = \begin{matrix} L-S & \text{filling} < 1/2 \\ L+S & \text{filling} > 1/2 \\ 0 & 1/2 \text{ filled} \end{matrix}$

Example 2:

Sm^{3+} ion $\Rightarrow [\text{Xe}] \cancel{4f^5} \cancel{6s^2} \cancel{5d^1}$



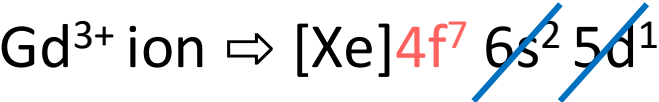
Try yourself:

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



f-orbitals

↑	↑	↑	↑	↑	↑	↑

-3 -2 -1 0 1 2 3

$S = ? , L = ? , J = ? , \text{notation} = ?$

1
H
Hydrogen
Nonmetal

3
Li
Lithium
Alkali Metal

4
Be
Beryllium
Alkaline Earth Metal

11
Na
Sodium
Alkali Metal

12
Mg
Magnesium
Alkaline Earth Metal

19
K
Potassium
Alkali Metal

20
Ca
Calcium
Alkaline Earth Metal

21
Sc
Scandium
Transition Metal

22
Ti
Titanium
Transition Metal

23
V
Vanadium
Transition Metal

24
Cr
Chromium
Transition Metal

25
Mn
Manganese
Transition Metal

26
Fe
Iron
Transition Metal

27
Co
Cobalt
Transition Metal

28
Ni
Nickel
Transition Metal

29
Cu
Copper
Transition Metal

30
Zn
Zinc
Transition Metal

31
Ga
Gallium
Post-Transition Metal

32
Ge
Germanium
Metalloid

33
As
Arsenic
Metalloid

34
Se
Selenium
Nonmetal

35
Br
Bromine
Halogen

36
Kr
Krypton
Noble Gas

37
Rb
Rubidium
Alkali Metal

38
Sr
Strontium
Alkaline Earth Metal

39
Y
Yttrium
Transition Metal

40
Zr
Zirconium
Transition Metal

41
Nb
Niobium
Transition Metal

42
Mo
Molybdenum
Transition Metal

43
Tc
Technetium
Transition Metal

44
Ru
Ruthenium
Transition Metal

45
Rh
Rhodium
Transition Metal

46
Pd
Palladium
Transition Metal

47
Ag
Silver
Transition Metal

48
Cd
Cadmium
Transition Metal

49
In
Indium
Post-Transition Metal

50
Sn
Tin
Post-Transition Metal

51
Sb
Antimony
Metalloid

52
Te
Tellurium
Metalloid

53
I
Iodine
Halogen

54
Xe
Xenon
Noble Gas

55
Cs
Cesium
Alkali Metal

56
Ba
Barium
Alkaline Earth Metal

57
La
Lanthanum
Lanthanide

58
Ce
Cerium
Lanthanide

59
Pr
Praseodymium
Lanthanide

60
Nd
Neodymium
Lanthanide

61
Pm
Promethium
Lanthanide

62
Sm
Samarium
Lanthanide

63
Eu
Europium
Lanthanide

64
Gd
Gadolinium
Lanthanide

65
Tb
Terbium
Lanthanide

66
Dy
Dysprosium
Lanthanide

67
Ho
Holmium
Lanthanide

68
Er
Erbium
Lanthanide

69
Tm
Thulium
Lanthanide

70
Yb
Ytterbium
Lanthanide

71
Lu
Lutetium
Lanthanide

72
Hf
Hafnium
Transition Metal

73
Ta
Tantalum
Transition Metal

74
W
Tungsten
Transition Metal

75
Re
Rhenium
Transition Metal

76
Os
Osmium
Transition Metal

77
Ir
Iridium
Transition Metal

78
Pt
Platinum
Transition Metal

79
Au
Gold
Transition Metal

80
Hg
Mercury
Transition Metal

81
Tl
Thallium
Post-Transition Metal

82
Pb
Lead
Post-Transition Metal

83
Bi
Bismuth
Metalloid

84
Po
Polonium
Metalloid

85
At
Astatine
Halogen

86
Rn
Radon
Noble Gas

87
Fr
Francium
Alkali Metal

88
Ra
Radium
Alkaline Earth Metal

89
Ac
Actinium
Actinide

90
Th
Thorium
Actinide

91
Pa
Protactinium
Actinide

92
U
Uranium
Actinide

93
Np
Neptunium
Actinide

94
Pu
Plutonium
Actinide

95
Am
Americium
Actinide

96
Cm
Curium
Actinide

97
Bk
Berkelium
Actinide

98
Cf
Californium
Actinide

99
Es
Einsteinium
Actinide

100
Fm
Fermium
Actinide

101
Md
Mendelevium
Actinide

102
No
Nobelium
Actinide

103
Lr
Lawrencium
Actinide

104
Rf
Rutherfordium
Transition Metal

105
Db
Dubnium
Transition Metal

106
Sg
Seaborgium
Transition Metal

107
Bh
Bohrium
Transition Metal

108
Hs
Hassium
Transition Metal

109
Mt
Meitnerium
Transition Metal

110
Ds
Darmstadtium
Transition Metal

111
Rg
Roentgenium
Transition Metal

112
Cn
Copernicium
Transition Metal

113
Nh
Nihonium
Post-Transition Metal

114
Fl
Flerovium
Post-Transition Metal

115
Mc
Moscovium
Post-Transition Metal

116
Lv
Livermorium
Post-Transition Metal

117
Ts
Tennessine
Halogen

118
Og
Oganesson
Noble Gas

Atomic Number

Symbol

Name

Chemical Group Block

PubChem

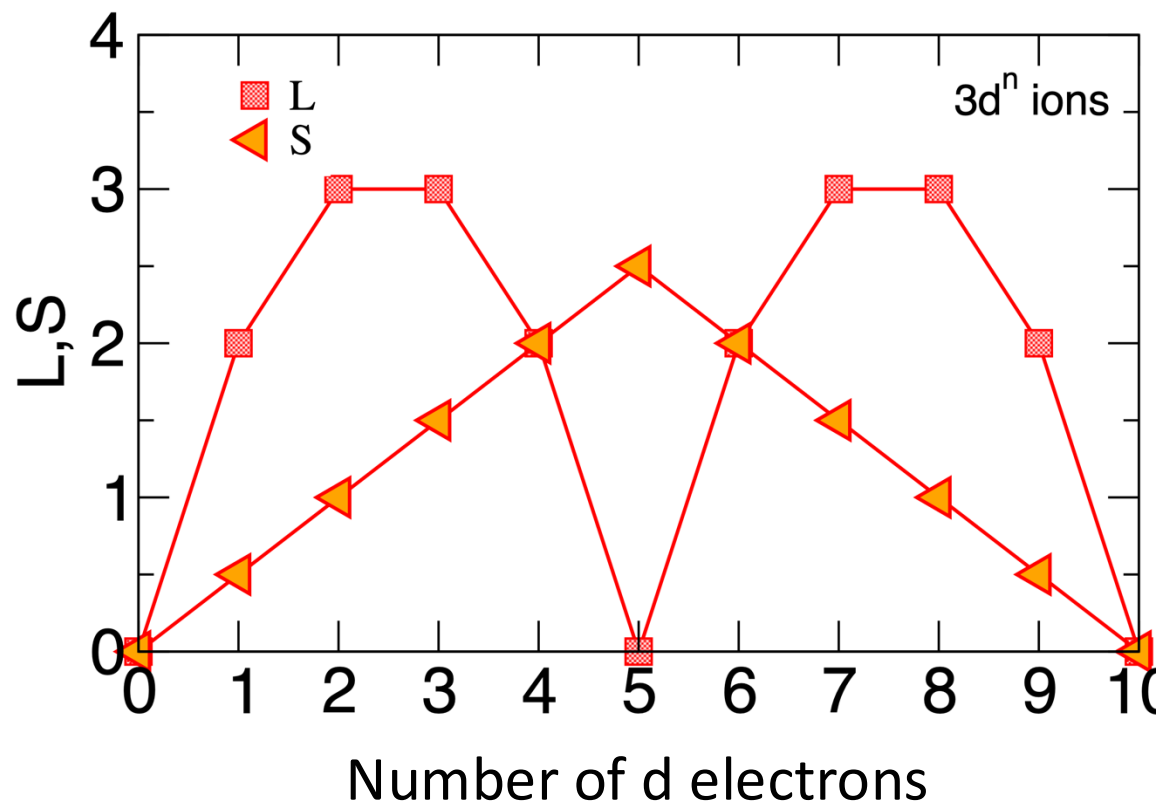
$S = 7/2$ $L = 0$ $J = 7/2$

$\Rightarrow {}^8S_{7/2}$

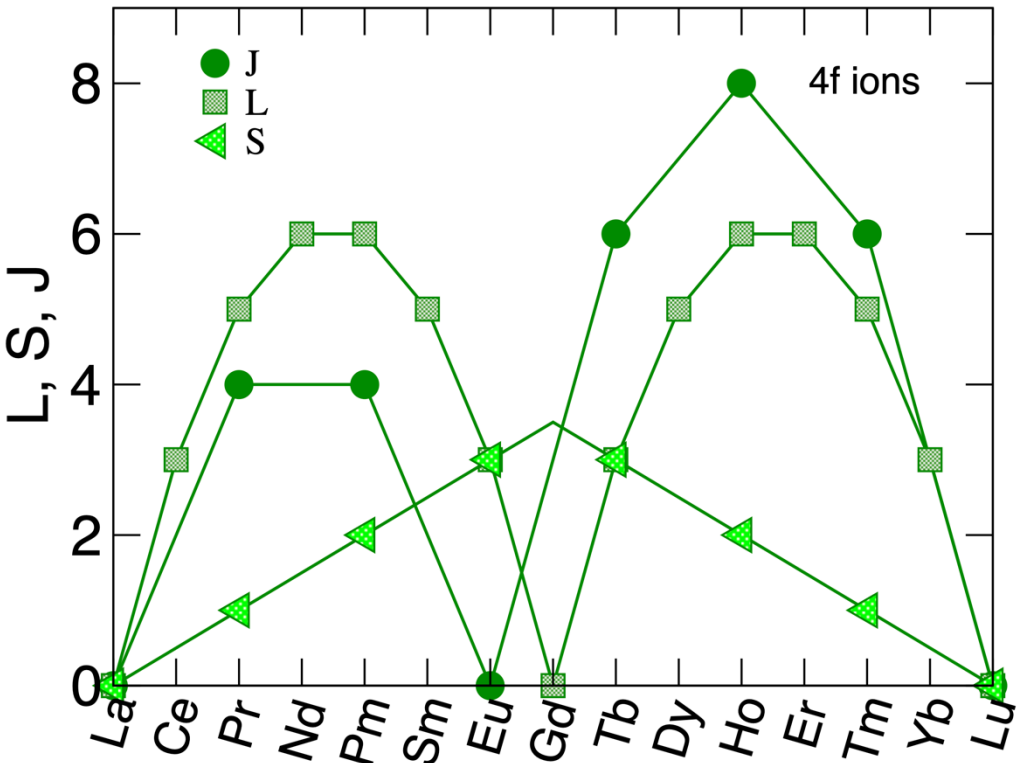
The full information about multiples for ions from the d and f shell can be found in Ashcroft & Mermin, Solid State Physics

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

1

H

Hydrogen

Nonmetal

3

Li

Lithium

Alkali Metal

4

Be

Beryllium

Alkaline Earth Metal

11

Na

Sodium

Alkali Metal

12

Mg

Magnesium

Alkaline Earth Metal

19

K

Potassium

Alkali Metal

20

Ca

Calcium

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37

Rb

Rubidium

Alkali Metal

38

Sr

Strontium

Alkaline Earth Metal

55

Cs

Cesium

Alkali Metal

56

Ba

Barium

Alkaline Earth Metal

87

Fr

Francium

Alkali Metal

88

Ra

Radium

Alkaline Earth Metal

1

H

Hydrogen

Nonmetal

Atomic Number

Symbol

Name

Chemical Group Block

2

He

Helium

Noble Gas

5

B

Boron

Metalloid

6

C

Carbon

Nonmetal

7

N

Nitrogen

Nonmetal

8

O

Oxygen

Nonmetal

9

F

Fluorine

Halogen

10

Ne

Neon

Noble Gas

13

Al

Aluminum

Post-Transition Metal

14

Si

Silicon

Metalloid

15

P

Phosphorus

Nonmetal

16

S

Sulfur

Nonmetal

17

Cl

Chlorine

Halogen

18

Ar

Argon

Noble Gas

31

Ga

Gallium

Post-Transition Metal

32

Ge

Germanium

Metalloid

33

As

Arsenic

Metalloid

34

Se

Selenium

Nonmetal

35

Br

Bromine

Halogen

36

Kr

Krypton

Noble Gas

49

In

Indium

Post-Transition Metal

50

Sn

Tin

Post-Transition Metal

51

Sb

Antimony

Metalloid

52

Te

Tellurium

Metalloid

53

I

Iodine

Halogen

54

Xe

Xenon

Noble Gas

81

Tl

Thallium

Post-Transition Metal

82

Pb

Lead

Post-Transition Metal

83

Bi

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Po

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85

At

Astatine

Halogen

86

Rn

Radon

Noble Gas

113

Nh

Nihonium

Post-Transition Metal

114

Fl

Flerovium

Post-Transition Metal

115

Mc

Moscovium

Post-Transition Metal

116

Lv

Livermorium

Post-Transition Metal

117

Ts

Tennessine

Halogen

118

Og

Oganesson

Noble Gas

*

21

Sc

Scandium

Transition Metal

22

Ti

Titanium

Transition Metal

23

V

Vanadium

Transition Metal

24

Cr

Chromium

Transition Metal

25

Mn

Manganese

Transition Metal

26

Fe

Iron

Transition Metal

27

Co

Cobalt

Transition Metal

28

Ni

Nickel

Transition Metal

29

Cu

Copper

Transition Metal

30

Zn

Zinc

Transition Metal

39

Y

Yttrium

Transition Metal

40

Zr

Zirconium

Transition Metal

41

Nb

Niobium

Transition Metal

42

Mo

Molybdenum

Transition Metal

43

Tc

Technetium

Transition Metal

44

Ru

Ruthenium

Transition Metal

45

Rh

Rhodium

Transition Metal

46

Pd

Palladium

Transition Metal

47

Ag

Silver

Transition Metal

48

Cd

Cadmium

Transition Metal

72

Hf

Hafnium

Transition Metal

73

Ta

Tantalum

Transition Metal

74

W

Tungsten

Transition Metal

75

Re

Rhenium

Transition Metal

76

Os

Osmium

Transition Metal

77

Ir

Iridium

Transition Metal

78

Pt

Platinum

Transition Metal

79

Au

Gold

Transition Metal

80

Hg

Mercury

Transition Metal

104

Rf

Rutherfordium

Transition Metal

105

Db

Dubnium

Transition Metal

106

Sg

Seaborgium

Transition Metal

107

Bh

Bohrium

Transition Metal

108

Hs

Hassium

Transition Metal

109

Mt

Meitnerium

Transition Metal

110

Ds

Darmstadtium

Transition Metal

111

Rg

Roentgenium

Transition Metal

112

Cn

Copernicium

Transition Metal

*

57

La

Lanthanum

Lanthanide

58

Ce

Cerium

Lanthanide

59

Pr

Praseodymium

Lanthanide

60

Nd

Neodymium

Lanthanide

61

Pm

Promethium

Lanthanide

62

Sm

Samarium

Lanthanide

63

Eu

Europium

Lanthanide

64

Gd

Gadolinium

Lanthanide

65

Tb

Terbium

Lanthanide

66

Dy

Dysprosium

Lanthanide

67

Ho

Holmium

Lanthanide

68

Er

Erbium

Lanthanide

69

Tm

Thulium

Lanthanide

70

Yb

Ytterbium

Lanthanide

71

Lu

Lutetium

Lanthanide

**

89

Ac

Actinium

Actinide

90

Th

Thorium

Actinide

91

Pa

Protactinium

Actinide

92

U

Uranium

Actinide

93

Np

Neptunium

Actinide

94

Pu

Plutonium

Actinide

95

Am

Americium

Actinide

96

Cm

Curium

Actinide

97

Bk

Berkelium

Actinide

98

Cf

Californium

Actinide

99

Es

Einsteinium

Actinide

100

Fm

Fermium

Actinide

101

Md

Mendelevium

Actinide

102

No

Nobelium

Actinide

103

Lr

Lawrencium

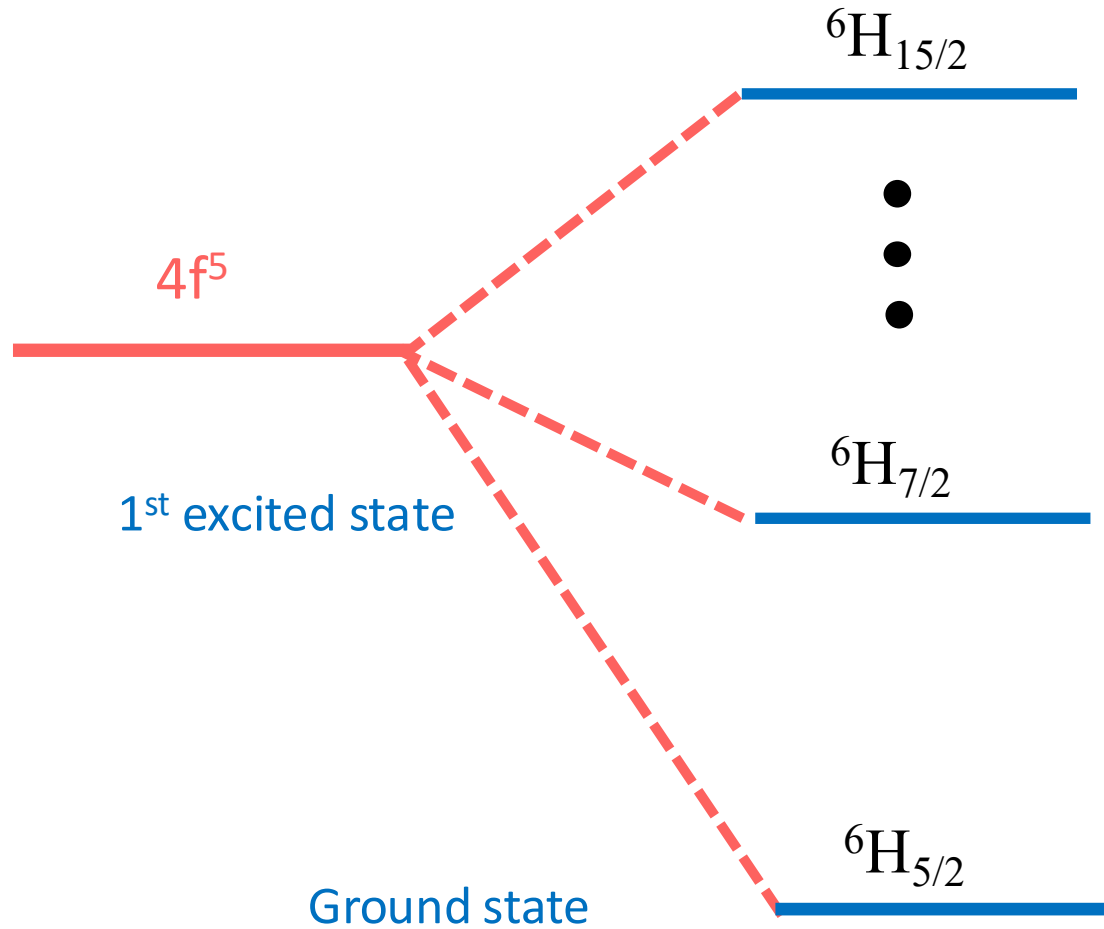
Actinide

PubChem

Many electrons in a free atom – LS coupling

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

LS splitting



Spin-orbit coupling

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

Λ spin-orbit coupling constant

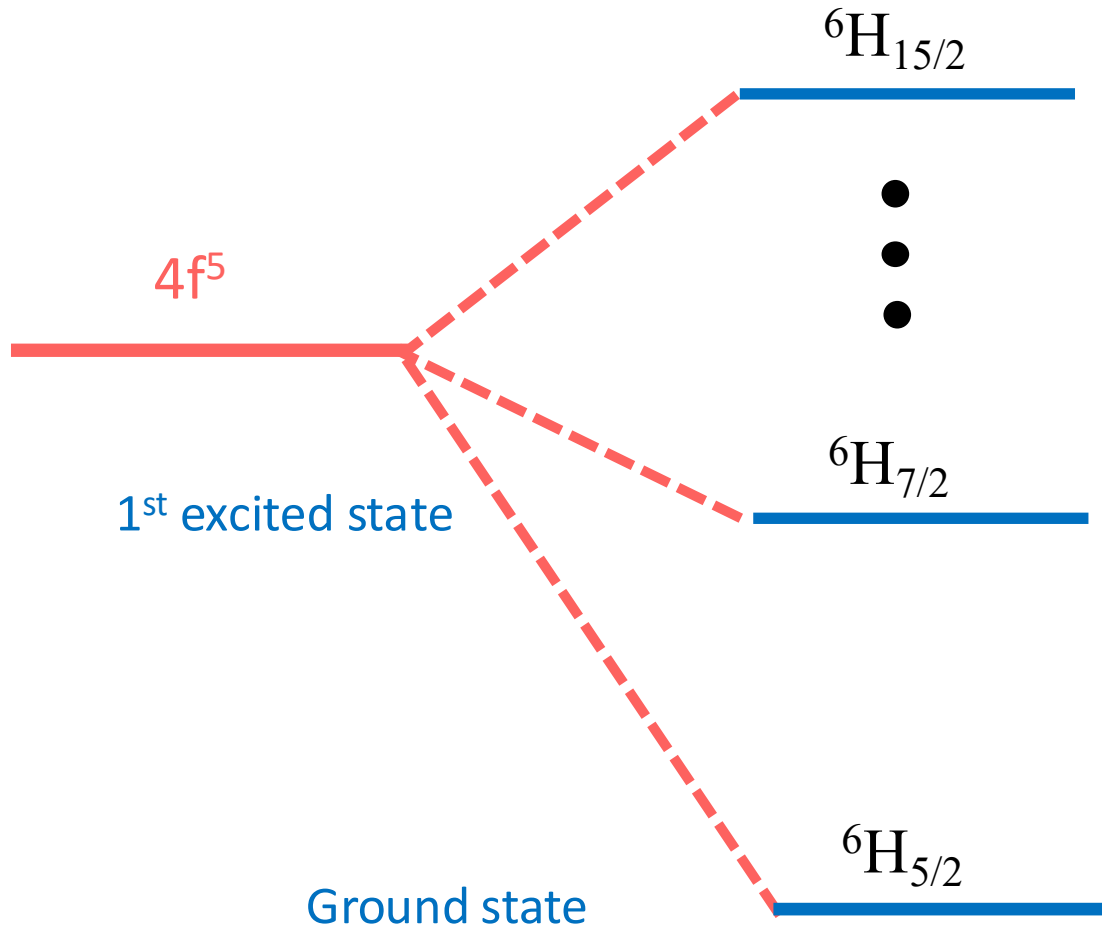
$$\Lambda = \pm \frac{\lambda}{2S}$$

$$\begin{aligned} \mathbf{L} \mathbf{S} &= \frac{1}{2} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \\ &= \frac{\hbar^2}{2} (J(J+1) - L(L+1) - S(S+1)) \end{aligned}$$

Extra slide

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

LS splitting



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

Experiment*: $4f^5 \Rightarrow p_{\text{exp}} = 1.74$

$$p_J = 3.32$$

Too big

$$p_J = 0.85$$

Too small

For Sm^{3+} the energy difference between ground state and 1st excited state is small.
 $\Rightarrow$ 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 $\mu_B = \frac{e\hbar}{2m_e}$

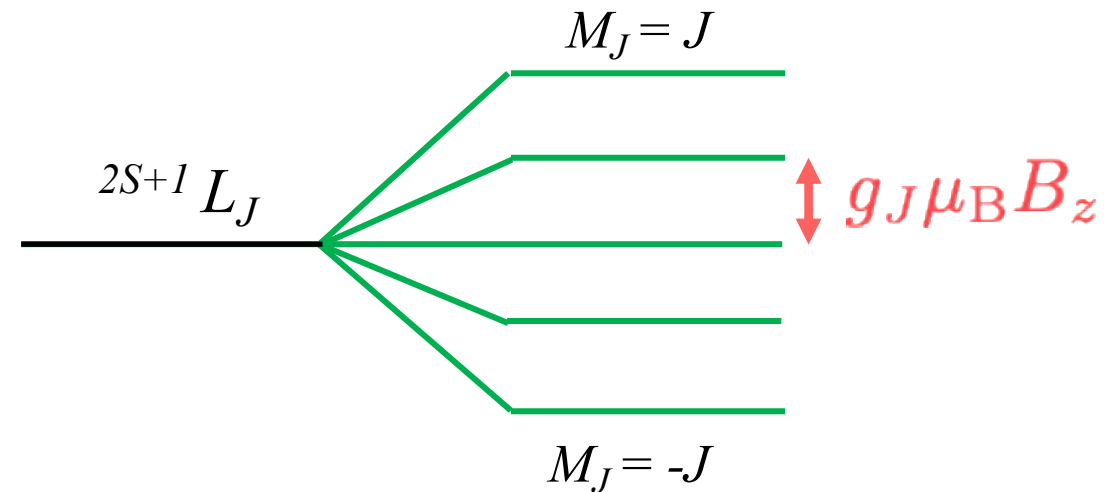
Change in energy due to applied magnetic field $E = -\mathbf{m}\mathbf{B}$, for $\mathbf{B} \parallel z$ we get

Zeeman energy

$$E_Z = g_J \frac{\mu_B}{\hbar} J_z B_z \equiv \mu_B M_J B_z$$

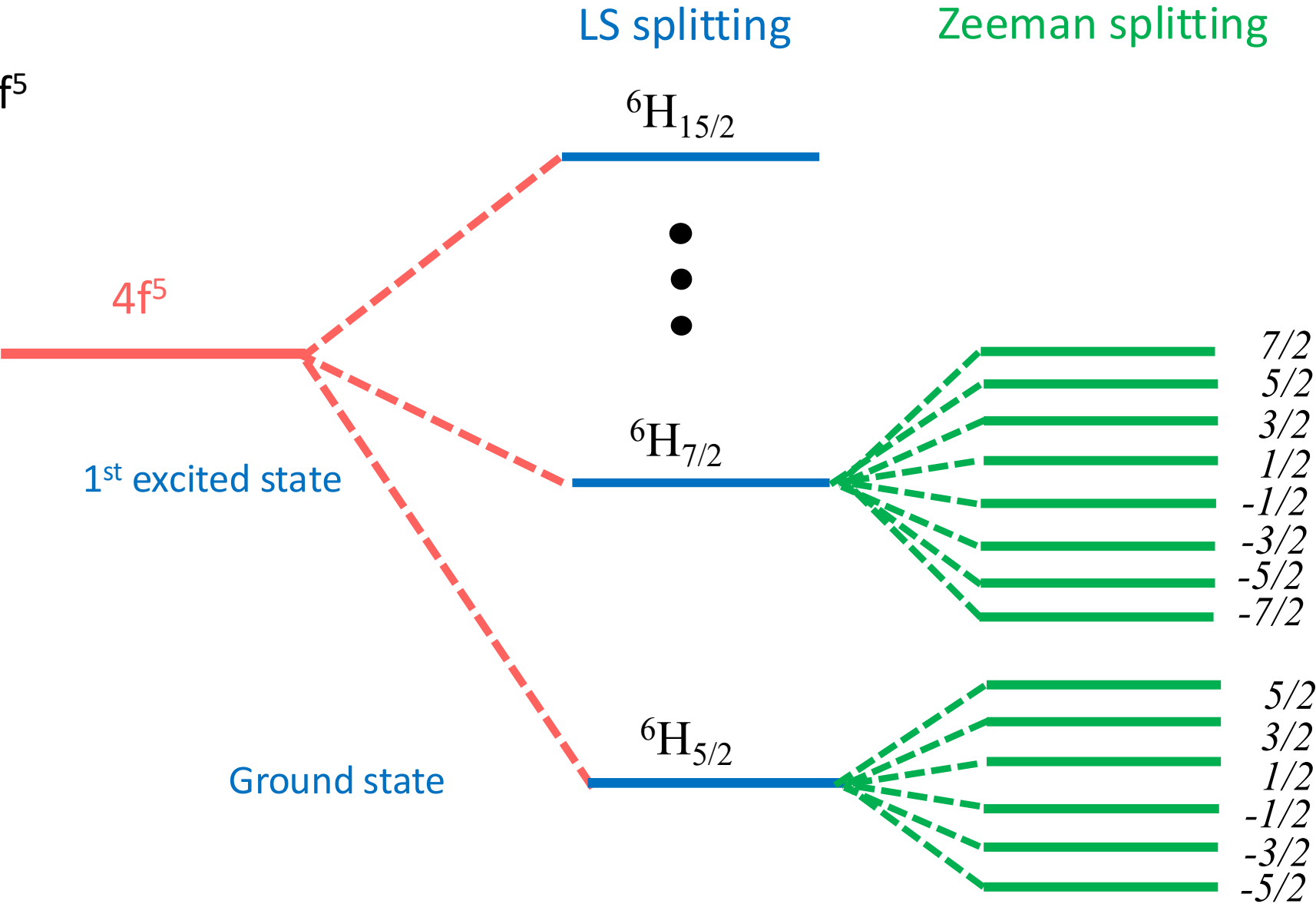
with $M_J = -J, -J + 1, \dots, J$

Degeneracy of $\mathbf{J}$ lifted



Many electrons in a free atom

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



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	¹ S ₀	0	0
Ce ³⁺	4f ¹	$\frac{1}{2}$	3	$\frac{5}{2}$	² F _{5/2}	2.54	2.51
Pr ³⁺	4f ²	1	5	4	³ H ₄	3.58	3.56
Nd ³⁺	4f ³	$\frac{3}{2}$	6	$\frac{9}{2}$	⁴ I _{9/2}	3.62	3.3-3.7
Pm ³⁺	4f ⁴	2	6	4	⁵ I ₄	2.68	-
Sm ³⁺	4f ⁵	$\frac{5}{2}$	5	$\frac{5}{2}$	⁶ I _{5/2}	0.85	1.74
Eu ³⁺	4f ⁶	3	3	0	⁷ F ₀	0.0	3.4
Gd ³⁺	4f ⁷	$\frac{7}{2}$	0	$\frac{7}{2}$	⁸ S _{7/2}	7.94	7.98
Tb ³⁺	4f ⁸	3	3	6	⁷ F ₆	9.72	9.77
Dy ³⁺	4f ⁹	$\frac{5}{2}$	5	$\frac{15}{2}$	⁶ H _{15/2}	10.63	10.63
Ho ³⁺	4f ¹⁰	2	6	8	⁵ I ₈	10.6	10.4
Er ³⁺	4f ¹¹	$\frac{3}{2}$	6	$\frac{15}{2}$	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	4f ¹²	1	5	6	³ H ₆	7.57	7.61
Yb ³⁺	4f ¹³	$\frac{1}{2}$	3	$\frac{7}{2}$	² F _{7/2}	4.53	4.5
Lu ³⁺	4f ¹⁴	0	0	0	¹ S 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 Sm³⁺ and Eu³⁺

→ LS coupling is small
 → Higher multiplets are partially occupied depending on B and T

* From paramagnetic salts, $k_B T \gg$ 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?

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 $F = -k_B T \ln Z$ and $Z = \text{Tr} e^{-\beta \mathcal{H}}$ and $\mathcal{H} = \sum_i^N g\mu_B m_{J_i} B$
Sum over atoms

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

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

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

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

Finally, the magnetization becomes:

$$\begin{aligned} M &= -\frac{\partial F}{\partial B} = N g \mu_{\text{B}} \left(\left(J + \frac{1}{2} \right) \coth \left(\beta g \mu_{\text{B}} B \left(J + \frac{1}{2} \right) \right) - \frac{1}{2} \coth \left(\frac{1}{2} g \mu_{\text{B}} B \right) \right) \\ &= N g \mu_{\text{B}} J B_J(\beta g \mu_{\text{B}} B J) \end{aligned}$$

Brillouin function

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

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

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

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

Limit of **large fields B or very low T**:

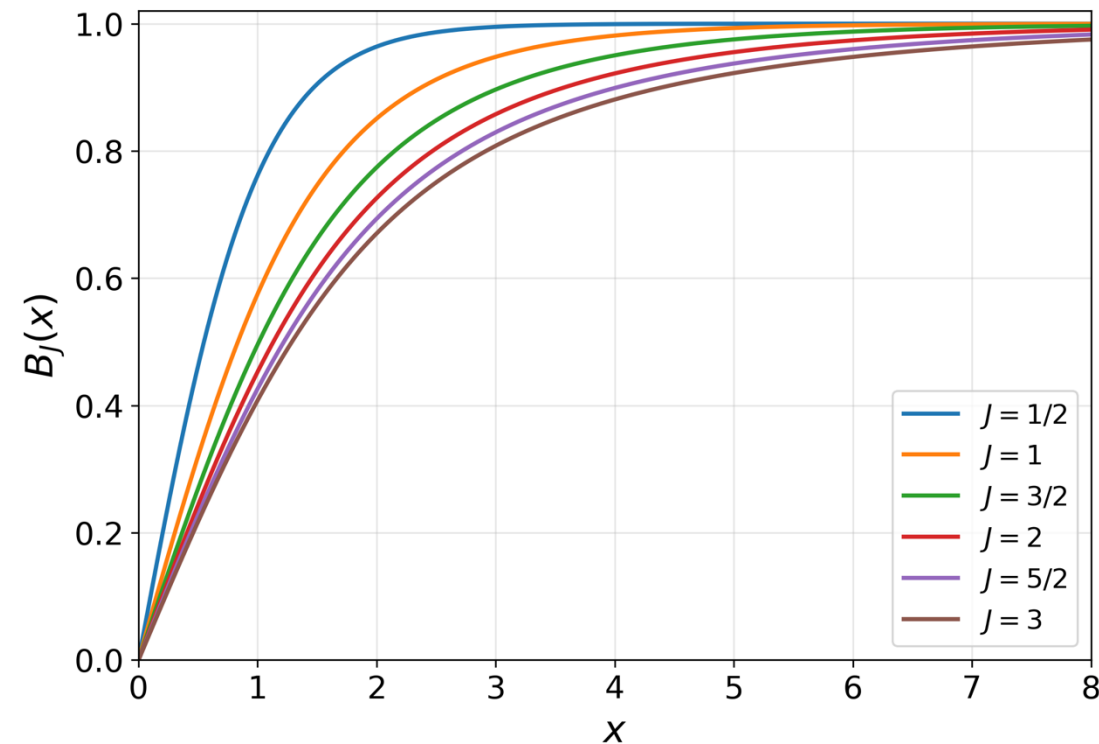
Saturation magnetisation $M \rightarrow N g \mu_B J$

Maximal value, all magnetic moments aligned with B

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

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

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



Many electrons in an atom - Hamiltonian

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

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

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

Hartree equation

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

Exchange term

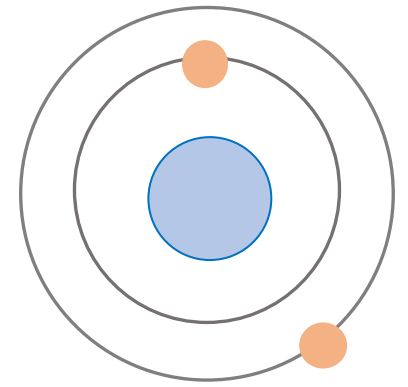
- Ensures antisymmetry
- Non-local term
- Angular momentum l no longer degenerated

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 degenerated

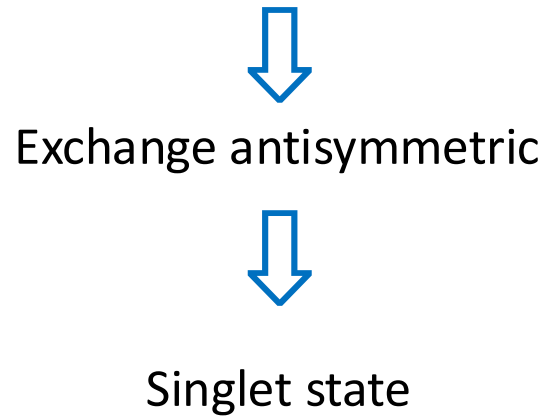
Which one is the ground state?

Many electrons in an atom - Hamiltonian

Aufbau principle

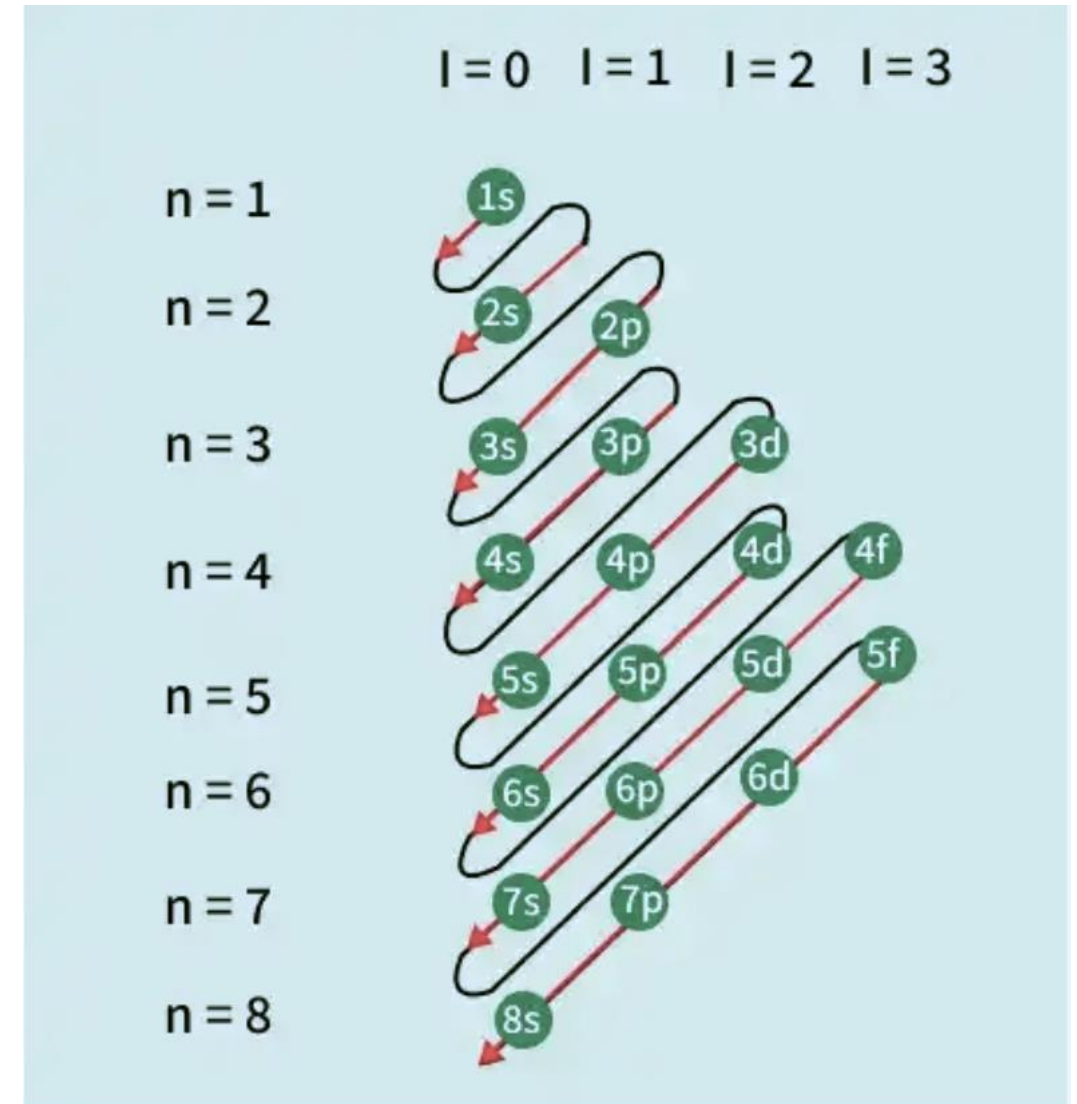
Ground state He:

Both electrons occupy the same spatial orbital



Aufbau rules: ?

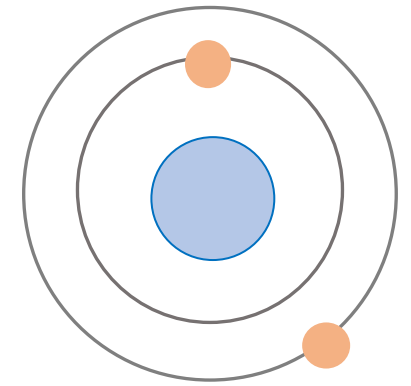
- Shell with smaller $(n+l)$ fill first
- Same $(n+l)$ of two shells $\Rightarrow$ the one with lower n fills first



Two electrons to start with...

Spin singlet wave function

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



ϕ_{nlm} = one electron wave function

Behaves like hydrogen-like atom with $Z = 2$

$$E_1 = E_2 = -Z^2 \cdot 13.6 \text{ eV} \Rightarrow E_1 + E_2 = -108.8 \text{ eV} \quad \Rightarrow \Leftarrow \quad \text{Experiment: } -79 \text{ eV}$$

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

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

Coulomb interaction

Exchange interaction

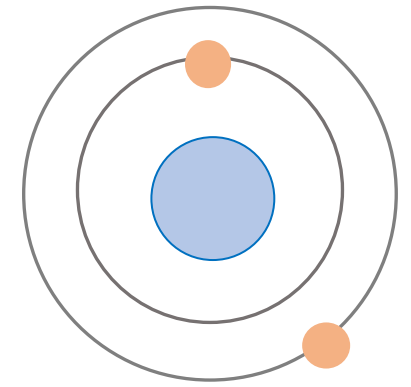
No classical counterpart

(Werner Heisenberg and Paul Dirac, 1926)

Coulomb corrected ground state: $E_1 + E_2 + J = -74.8 \text{ eV}$

Two electrons to start with...

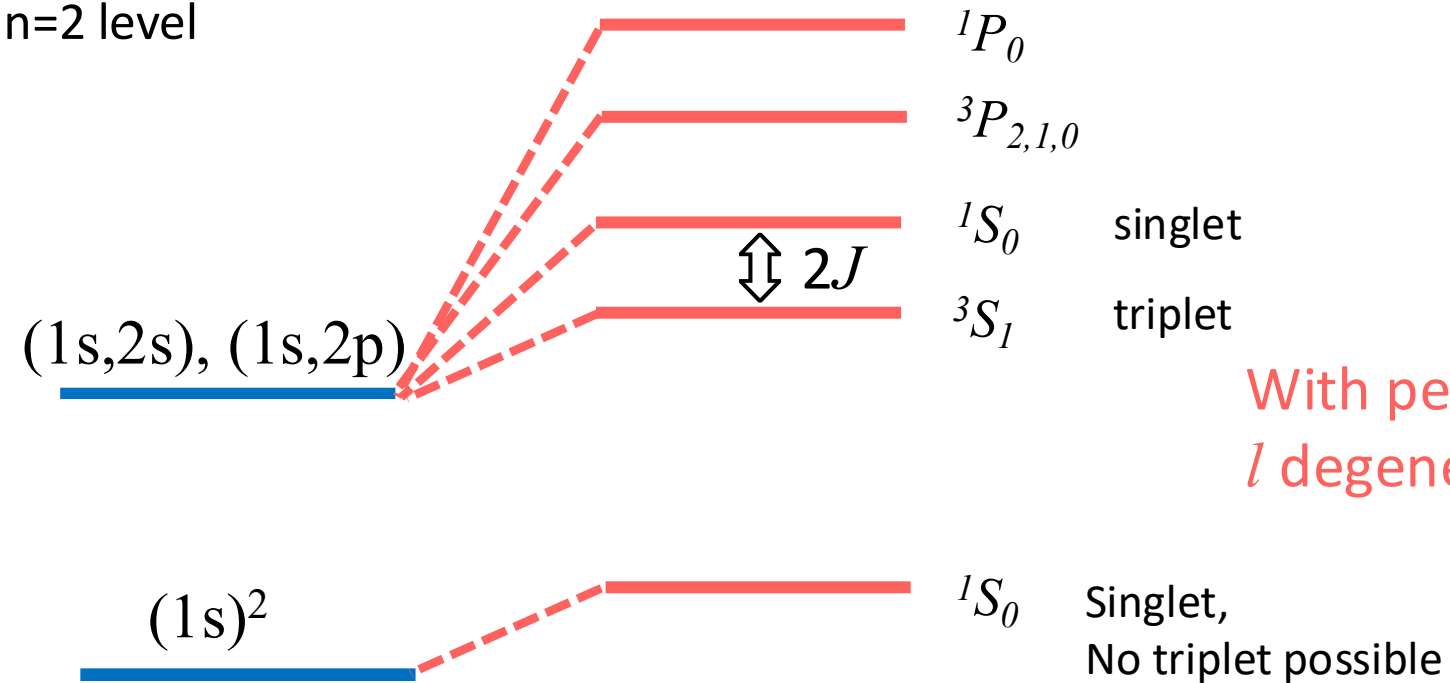
The energy shift due to the electron-electron interaction becomes $E_1 = V \pm J$



Excitation of 1 electron to the n=2 level

+ for singlet and – for triplet state

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: H independent of spin but $H + \text{Pauli principle}$ = 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

↑ = +1/2, ↓ = -1/2

Magnetic periodic table

Magnetic periodic table

Atomic Number → 66 **Dy** ← Atomic symbol
→ 162.5 ← Atomic weight
→ 3 + 4f⁹ ← Typical ionic change
→ 179 85 ← Antiferromagnetic T_N(K) 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 38.21 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 55.85 2 + 3d ⁵ 96	26 Fe 55.85 3 + 3d ⁶ 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 2 + 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 102.4 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 83.80				
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					

cd.ie/physics/r

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

- ☐ Nonmetal
- ☐ Metal
- ☐ Radioactive

- ☐ Diamagnet
- ☒ Paramagnet
- ☐ **BOLD** Magnetic atom

 Ferromagnet $T_C > 290K$
 Antiferromagnet with $T_N > 290K$
 Antiferromagnet/Ferromagnet with $T_N/T_C < 290 K$

- 
- 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)

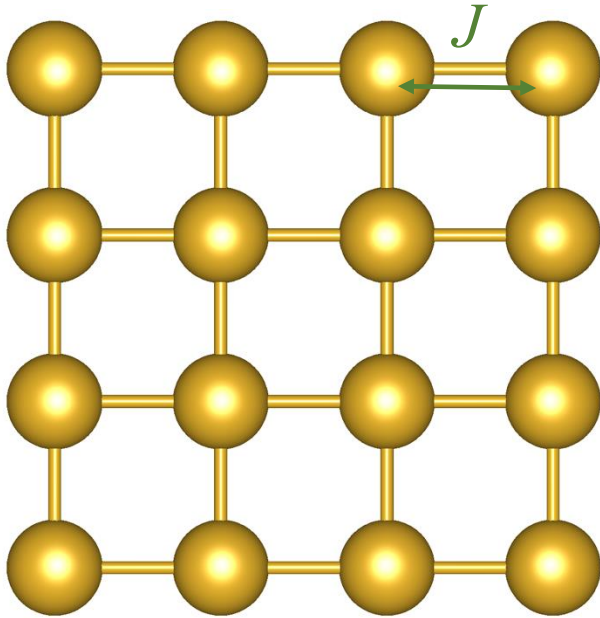
Macroscopic samples: Large numbers of electrons and ions ($\approx 10^{27}$)

⇒ Collective effects generate new phenomena

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

Exchange interaction

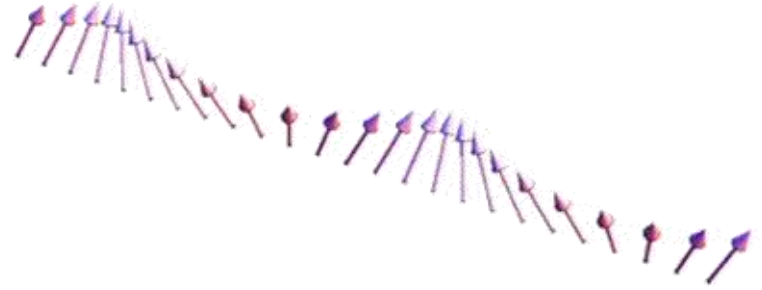
Beyond classical dipoles



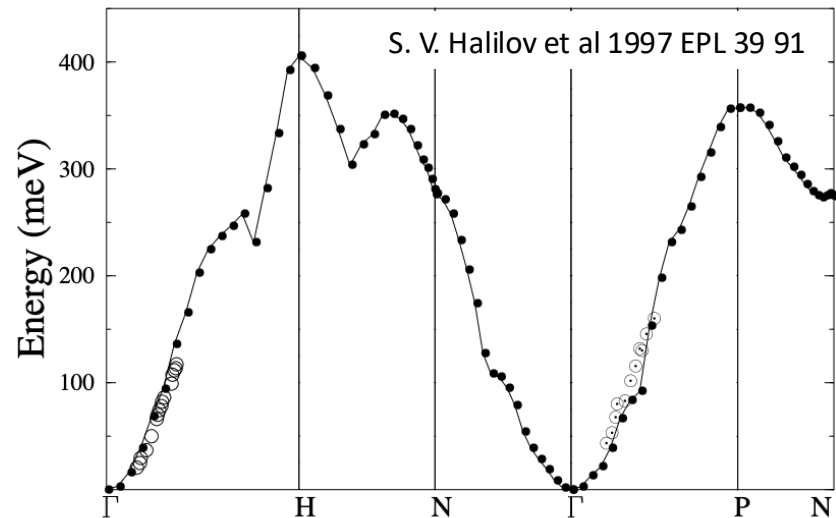
Heisenberg model

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

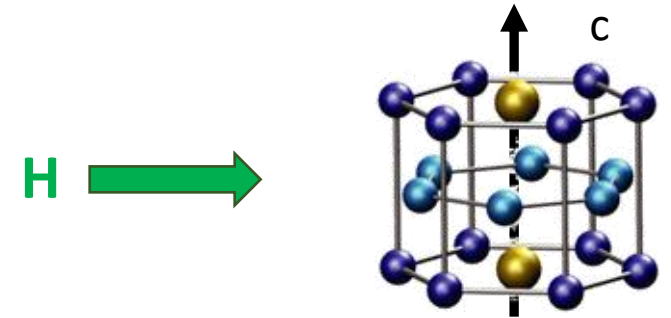
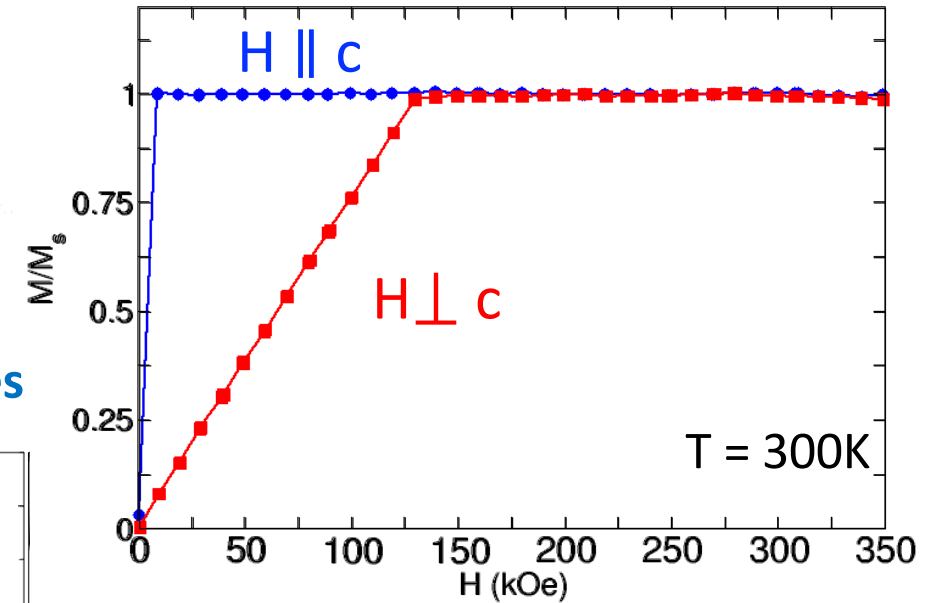
Spinwaves



Magnons - Quantised Spinwaves



Magnetocrystalline anisotropy

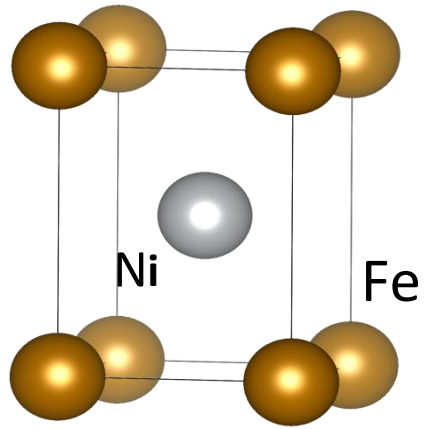


To be discussed in the following lectures

What do we do today in this lecture?

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

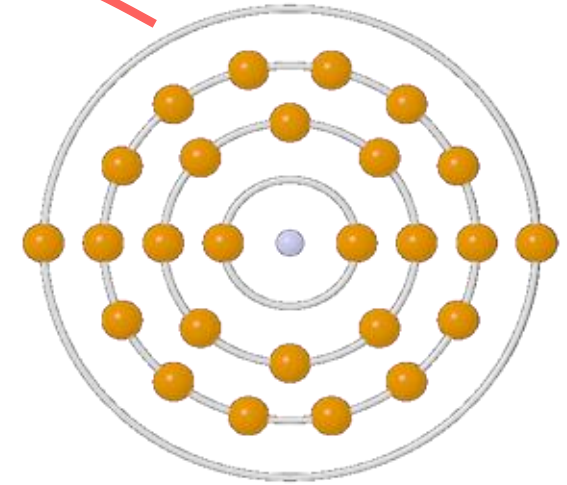
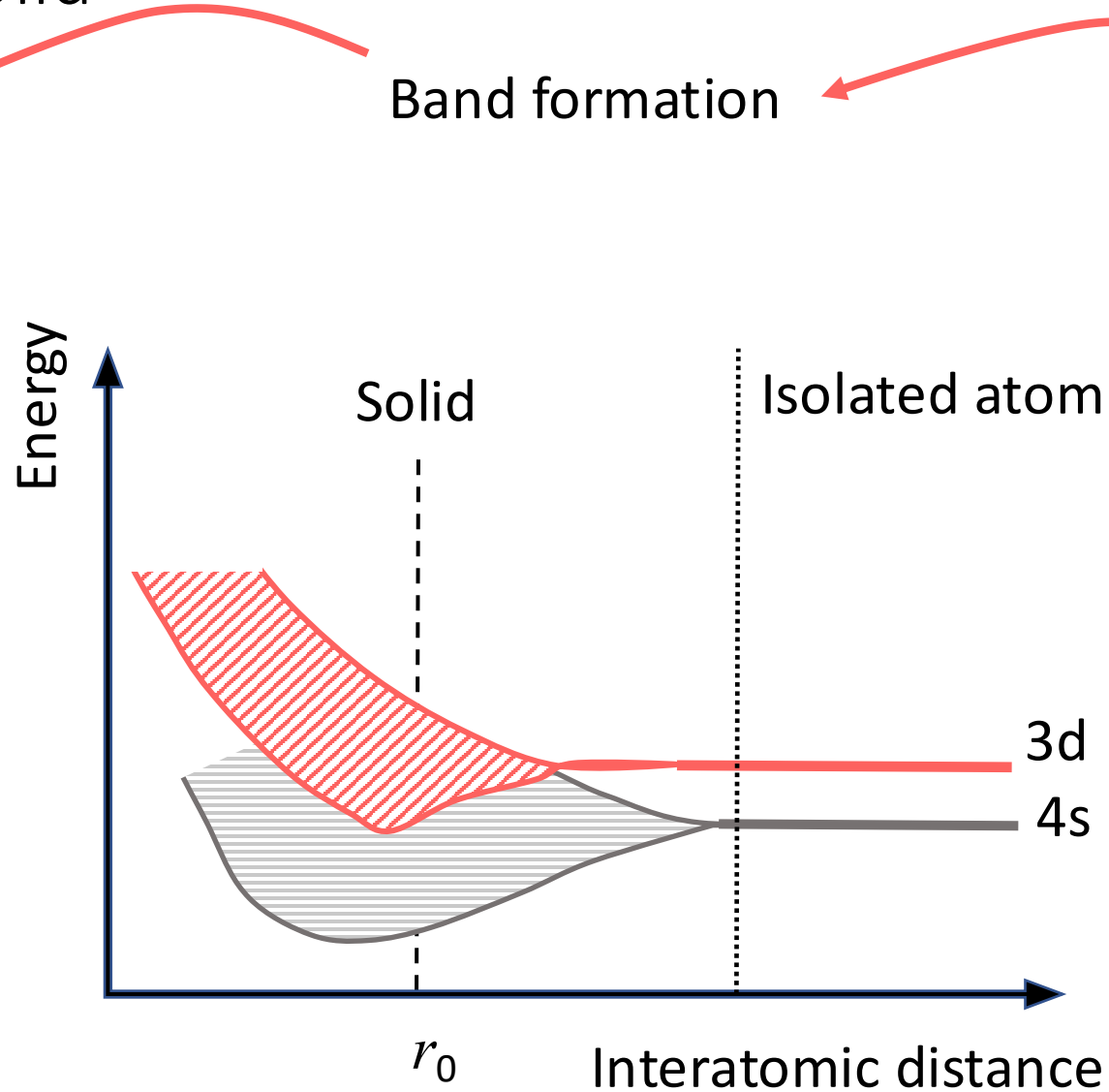
Magnetism in a solid



FeNi L1₀ (tetragonal)*

Transition metals:

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



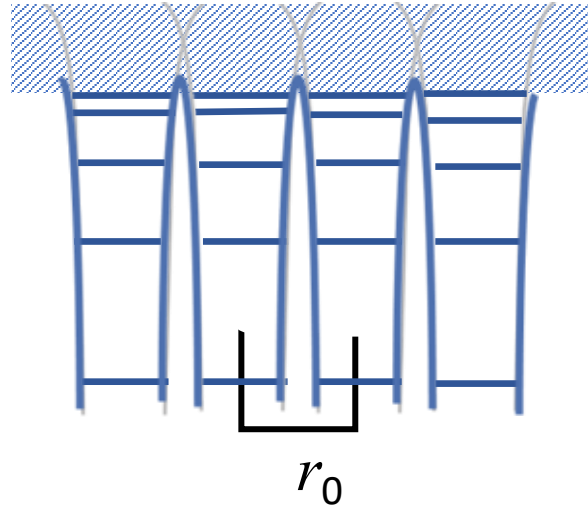
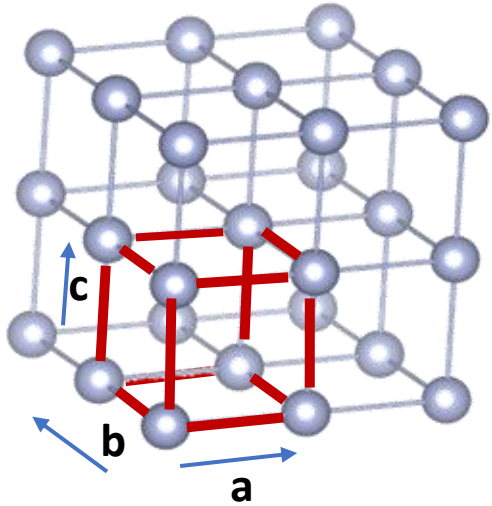
Fe atom

r_0 = equilibrium distance

(* 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

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

$\mathbf{k}$ = 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

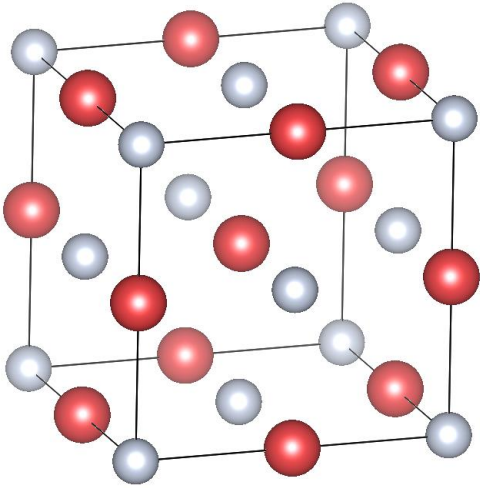
Substituting (*) and (**) in SEQ

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

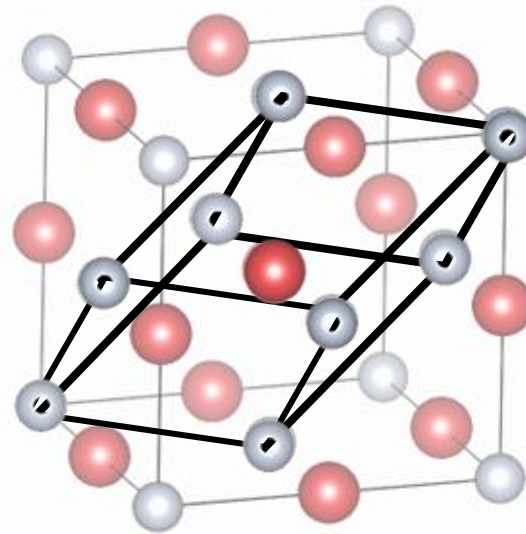
Band structure and periodic potential

Periodic potential:

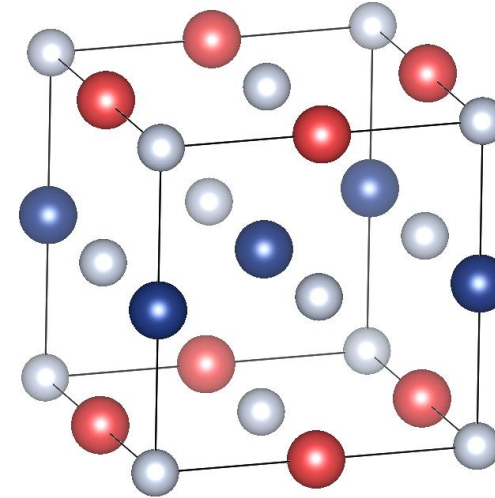
$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}) = \sum_G V_G e^{i\mathbf{G}\mathbf{r}}$$



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!)

Band structure and periodic potential

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



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

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

$$\sum_G c_{k-G} e^{-i\mathbf{G}\mathbf{r}}$$

Bloch theorem

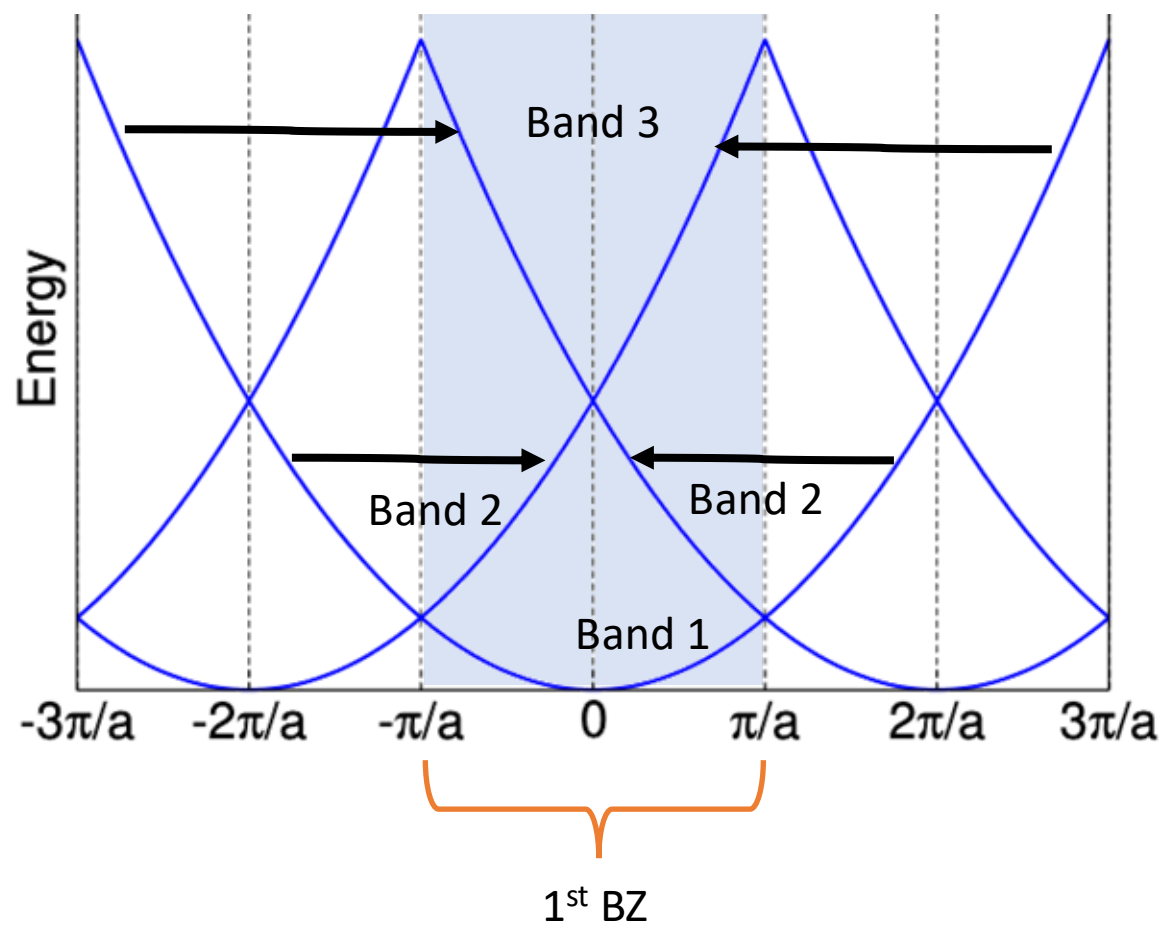
$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_k(\mathbf{r})$$

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

$\mathbf{T}$ = Bravais lattice vector

Band structure and periodic potential

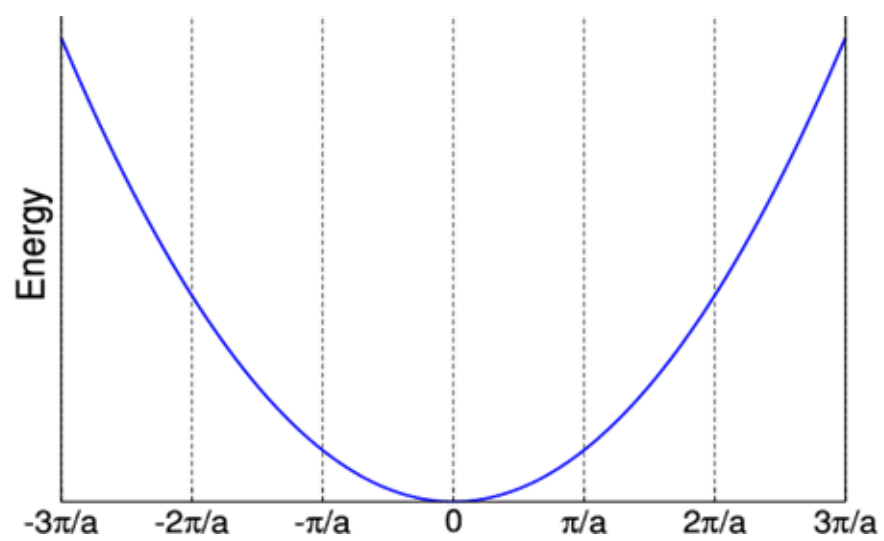
Free electron case



Inserting ψ and $V(r)$ to Schrödinger equation:

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

Coupled equations only if $k' = k \pm G$
 k runs over 1st Brillouin zone



Reduced
Zone
scheme

Band structure and periodic potential

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

↓

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}} = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}}$$

Lattice periodic function $u_{\mathbf{k}}(\mathbf{r})$

Bloch theorem

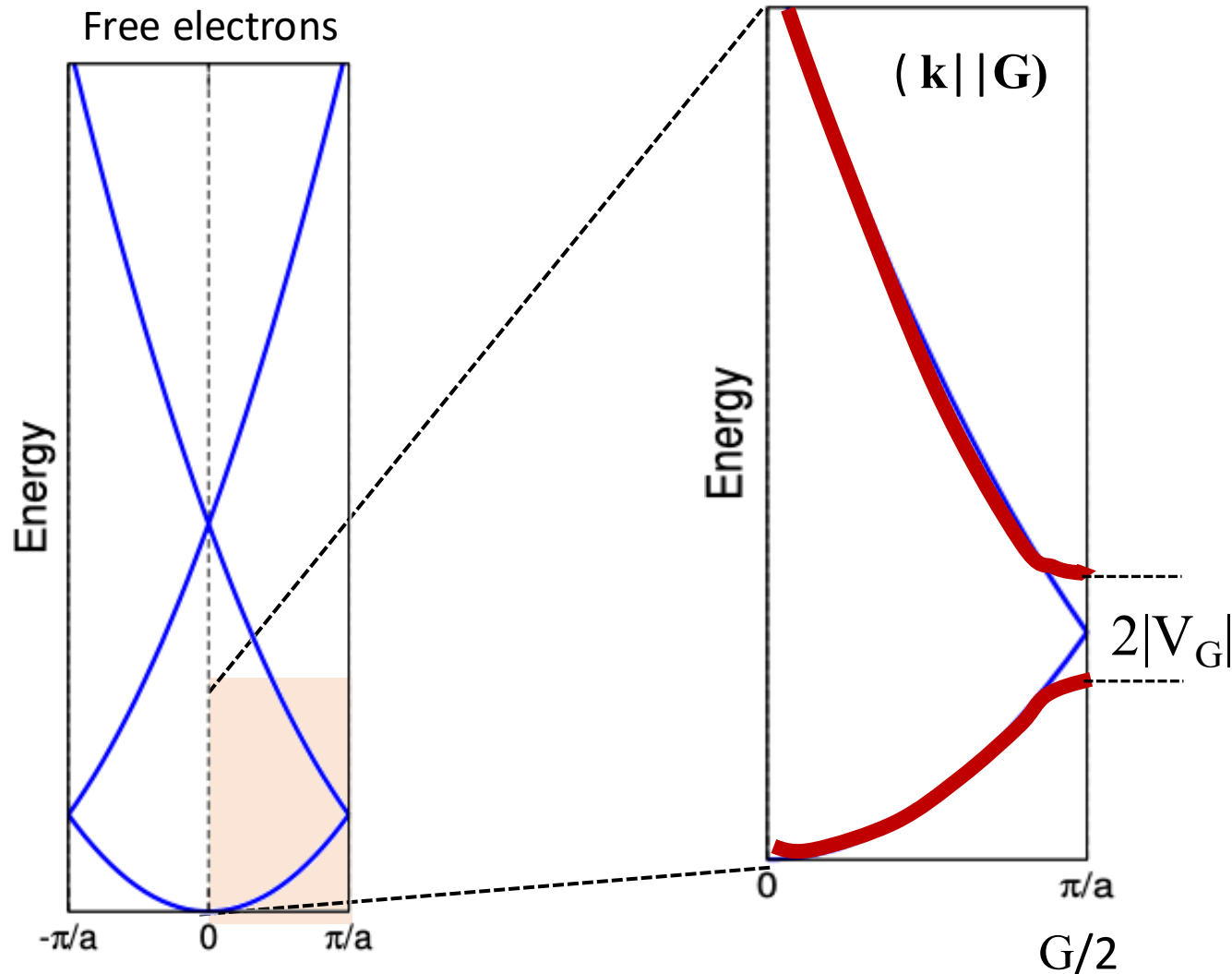
$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

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

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 $\psi_{n\mathbf{k}}(\mathbf{r})$; each value of $\mathbf{k}$ 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
 $V \ll |E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})|$

Perturbation theory

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

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

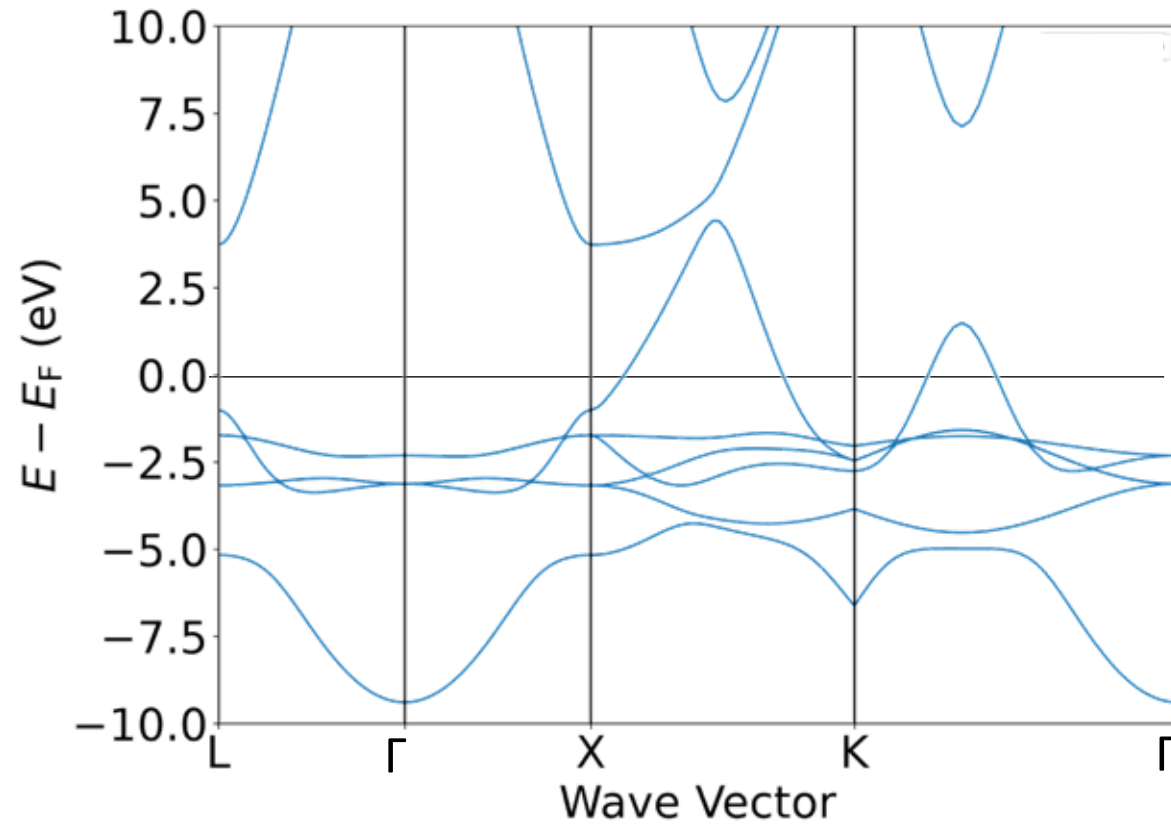
Solving the Schrödinger equation
 leads to a quadratic equation

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

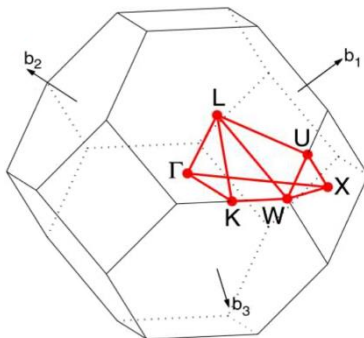
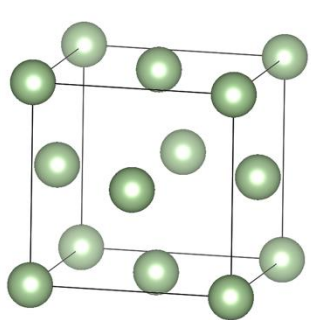
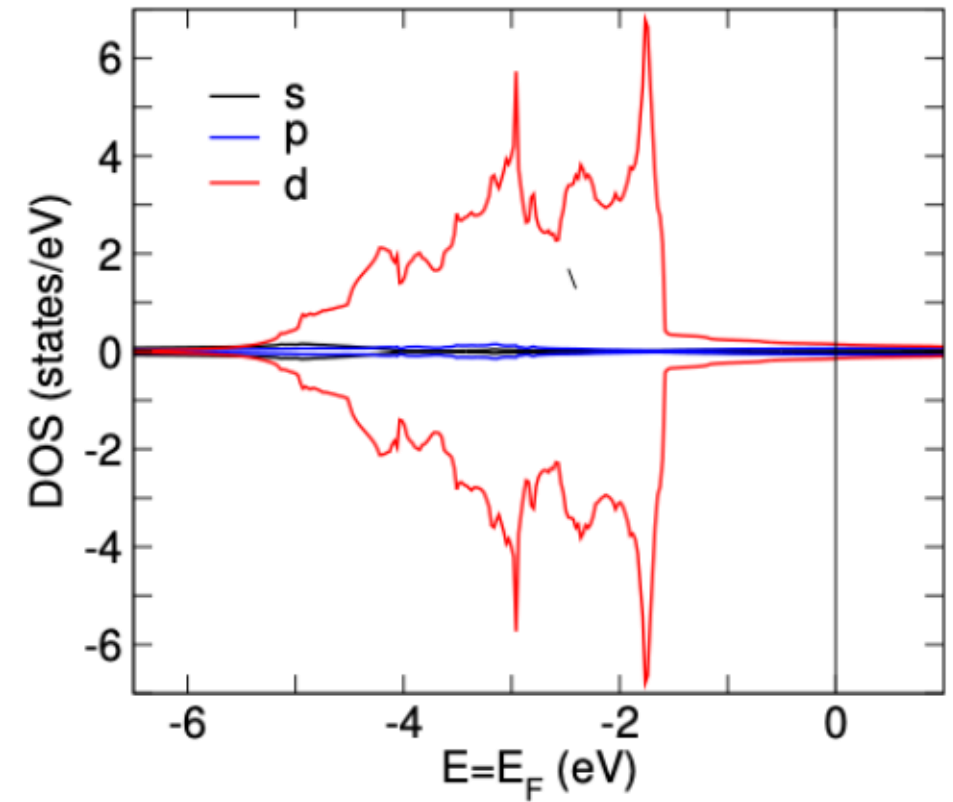
Density of states

Example: fcc Cu, (nonmagnetic)

Band structure



Density of states



Density of states (DOS)

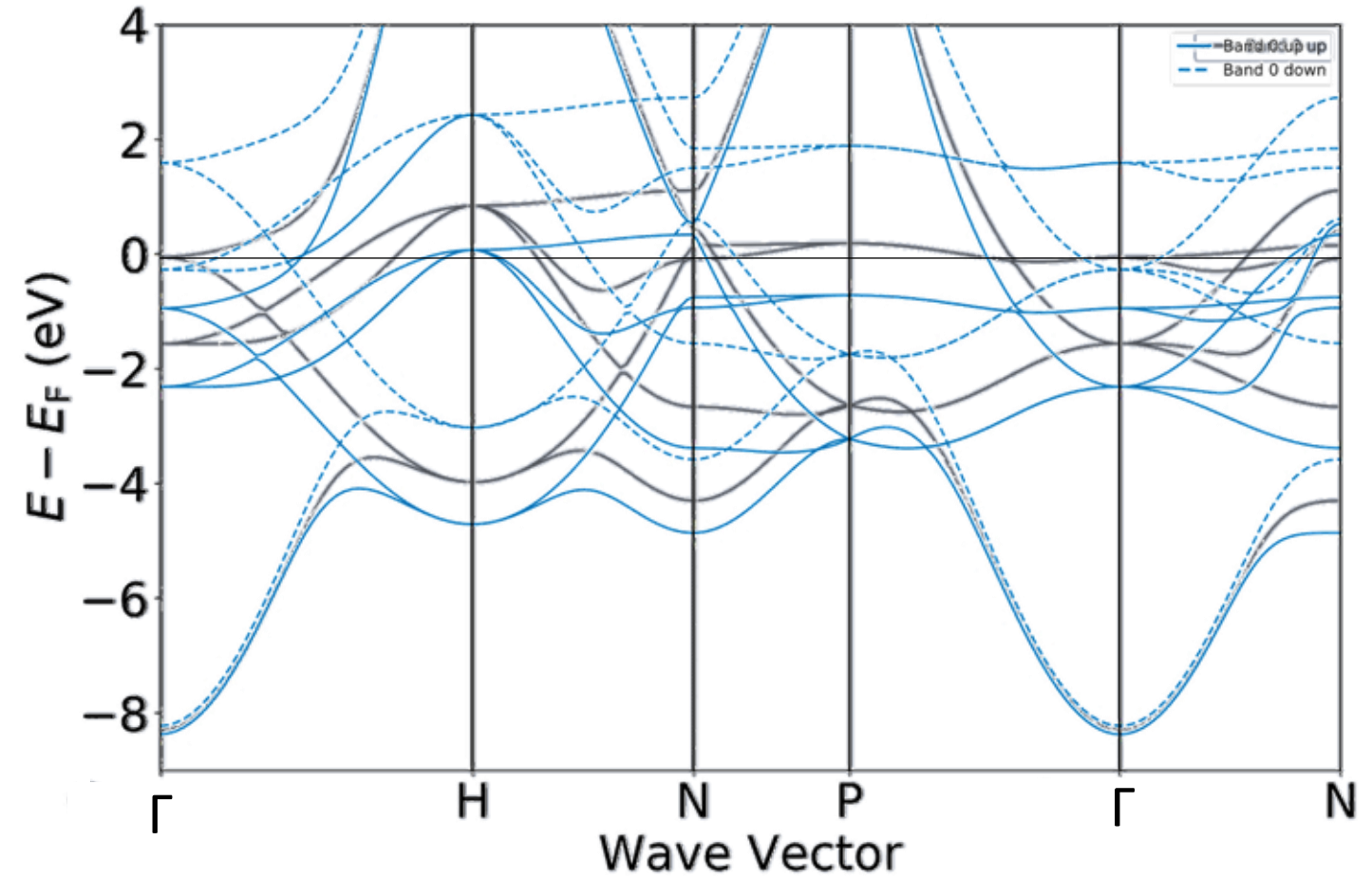
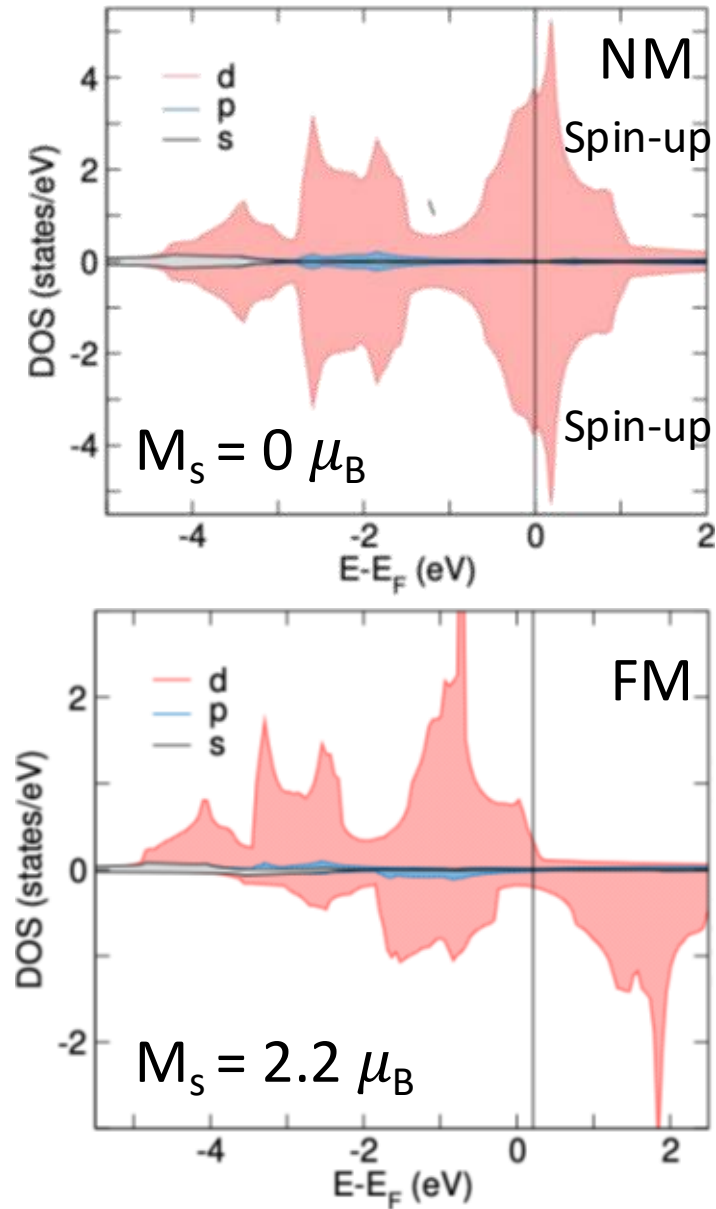
$$\rho(E) = \frac{1}{N} \sum_{n\mathbf{k}} \delta(E - E_n(\mathbf{k}))$$

Fermi level:

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

Density of states – bcc Fe

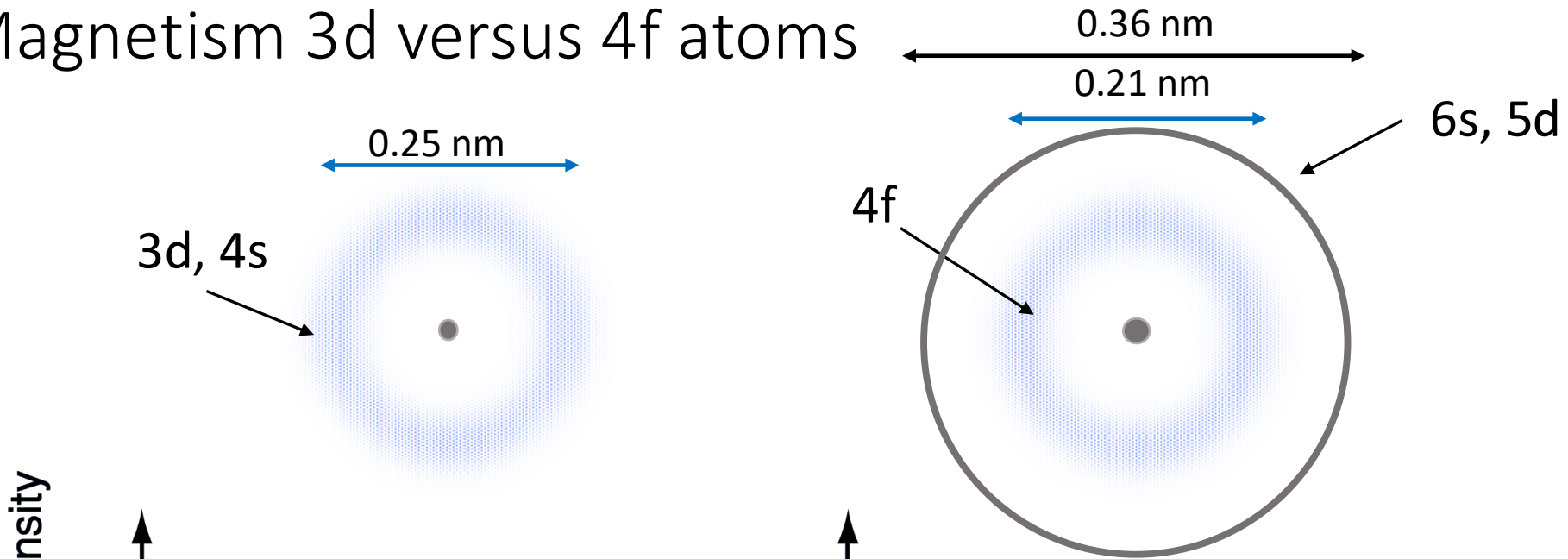
bcc Fe, NM and **spin-polarized, FM**



Exchange splitting : Relative shift of $DOS(\downarrow)$ vs. $DOS(\uparrow)$

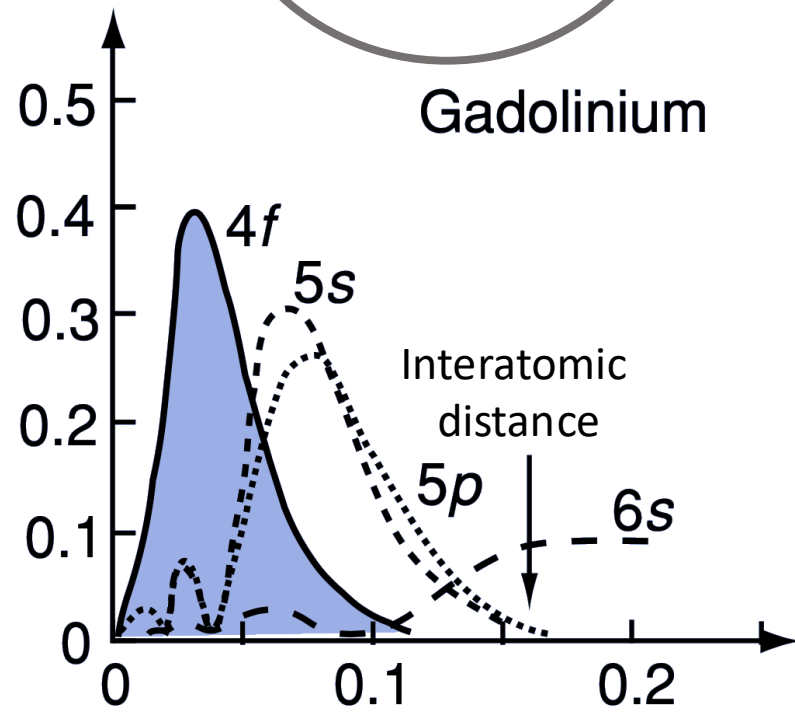
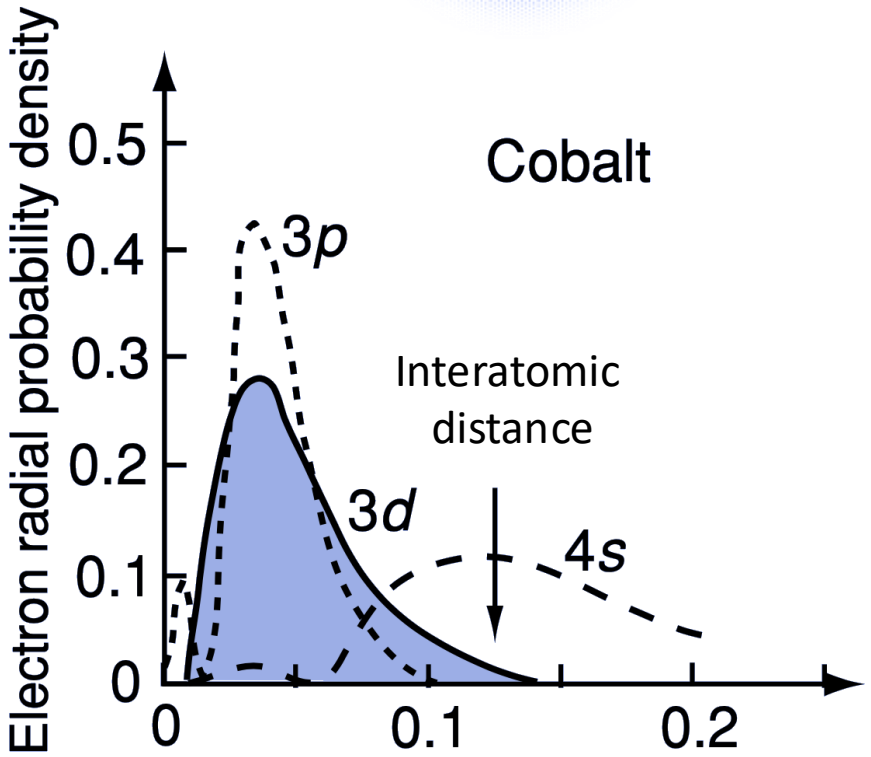
Magnetic moment $M_s \sim (n(\uparrow) - n(\downarrow))$

Magnetism 3d versus 4f atoms



3d ions
3d shell is the outer shell

4f ions
4f shell is buried below higher shells

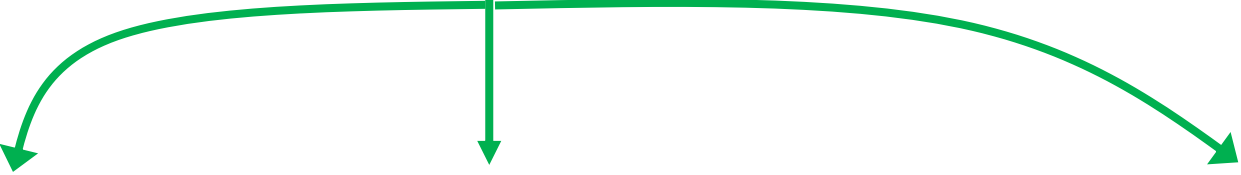


Magnetism of 4f ions is preserved even in solids
4f electrons are localized

3d ions are delocalized and magnetism depends on surrounding

Electron interactions

Present in an atom

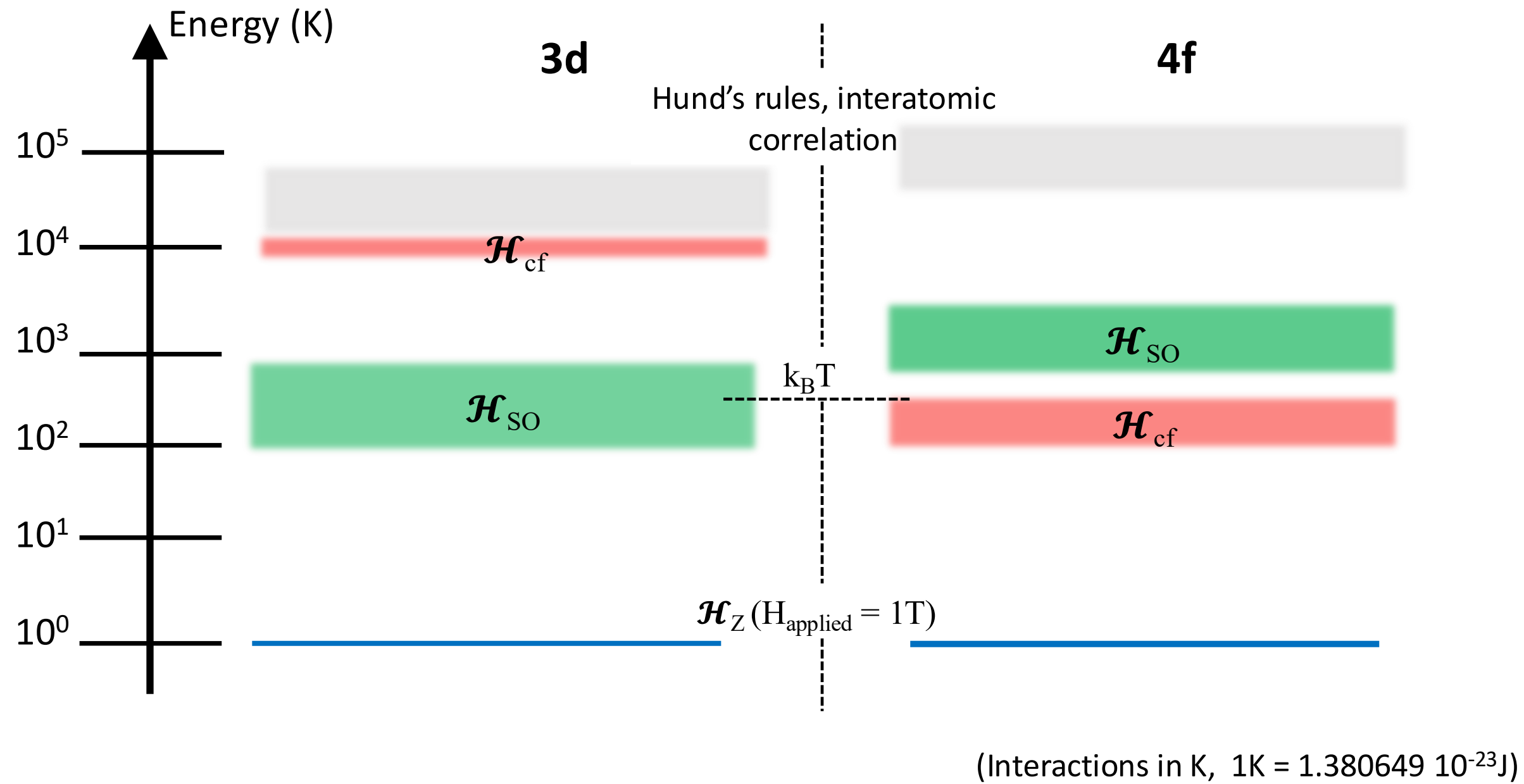

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{SO} + \mathcal{H}_{cf} + \mathcal{H}_Z$$

Coulomb	Spin-orbit	Crystal-field	Zeeman
$ \mathbf{L}, \mathbf{S}\rangle$	$\mathcal{H}_{SO} = \Lambda \mathbf{L} \mathbf{S}$	$\int \rho_0(r) V_{cf} d^3r$	$g\mu_B \mathbf{B} \mathbf{J}$

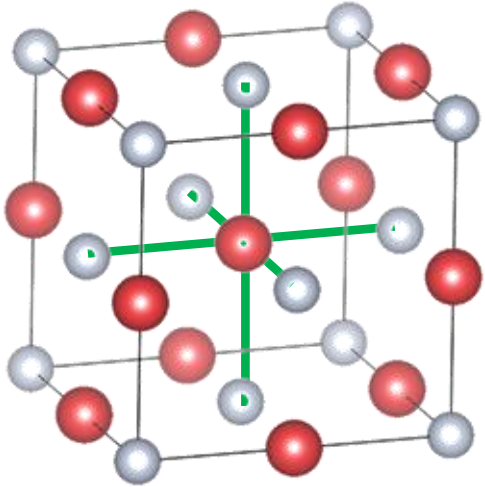
Not existing for
a single atom

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

Electron interactions



Crystal field



The eigenstates are different from the undisturbed potential

⇒ Use linear combinations of the unperturbed wavefunctions

⇒ Example d orbitals

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

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

Potential created by the charge distribution of the crystal

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

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

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

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

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

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 $\mathcal{H}_{\text{cf}}$

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

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

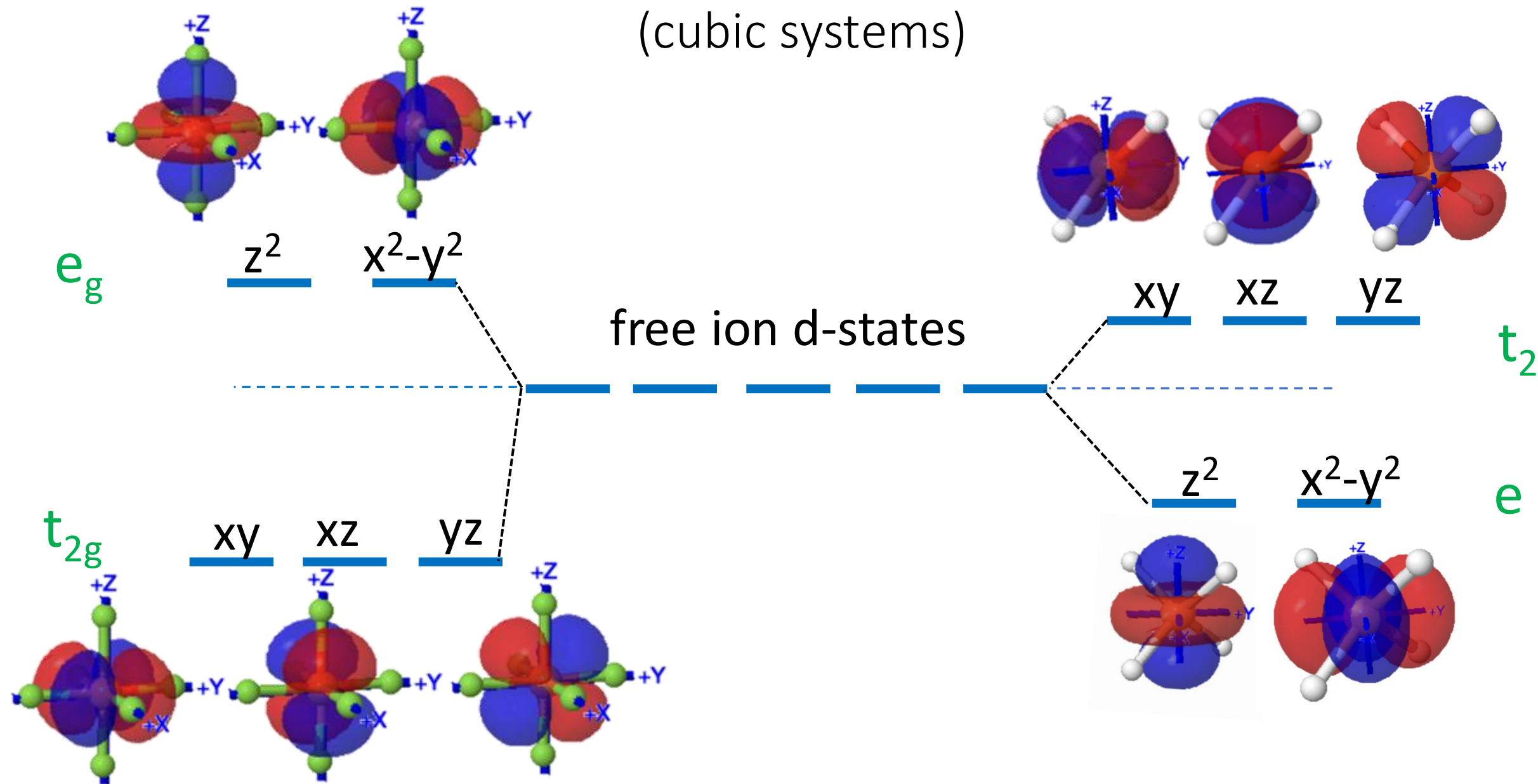
Angular momentum of e_g
states is fully quenched

$\Rightarrow$ Orbital moment quenched for 3d systems!

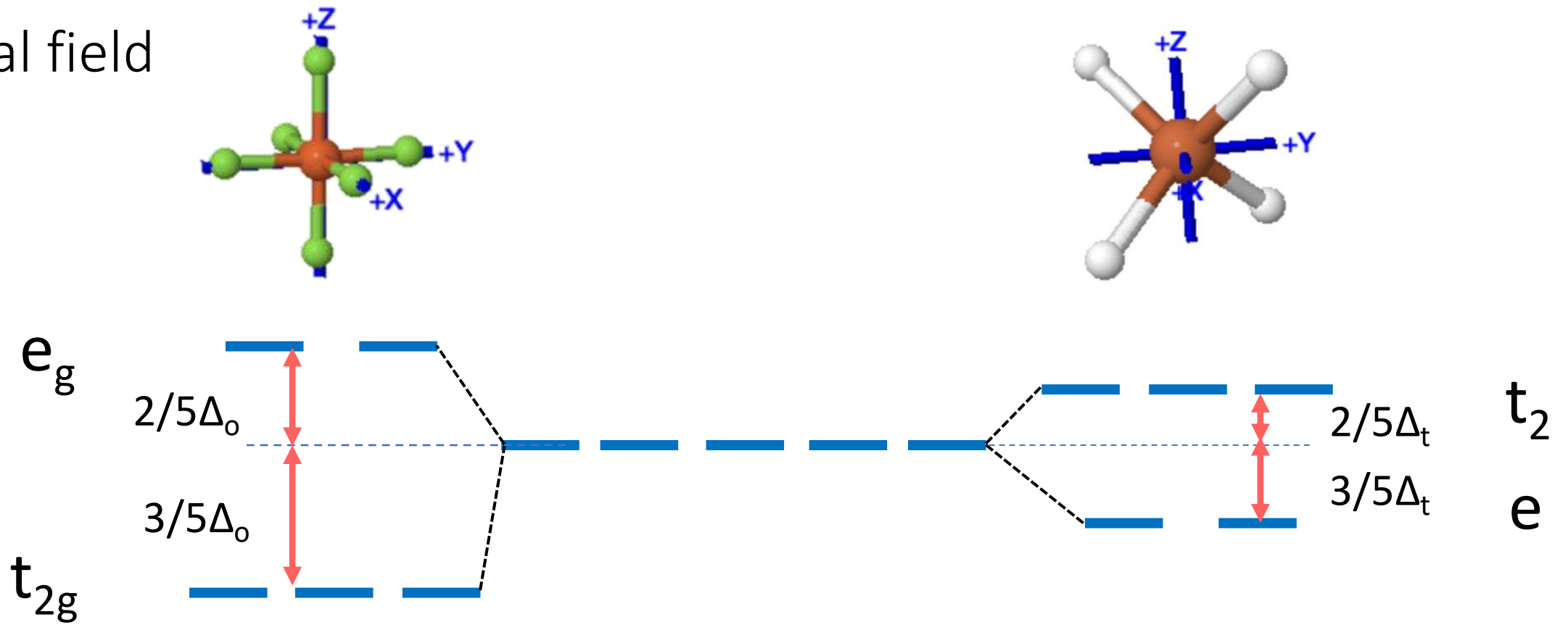
octahedral

Crystal field
(cubic systems)

tetrahedral



Crystal field

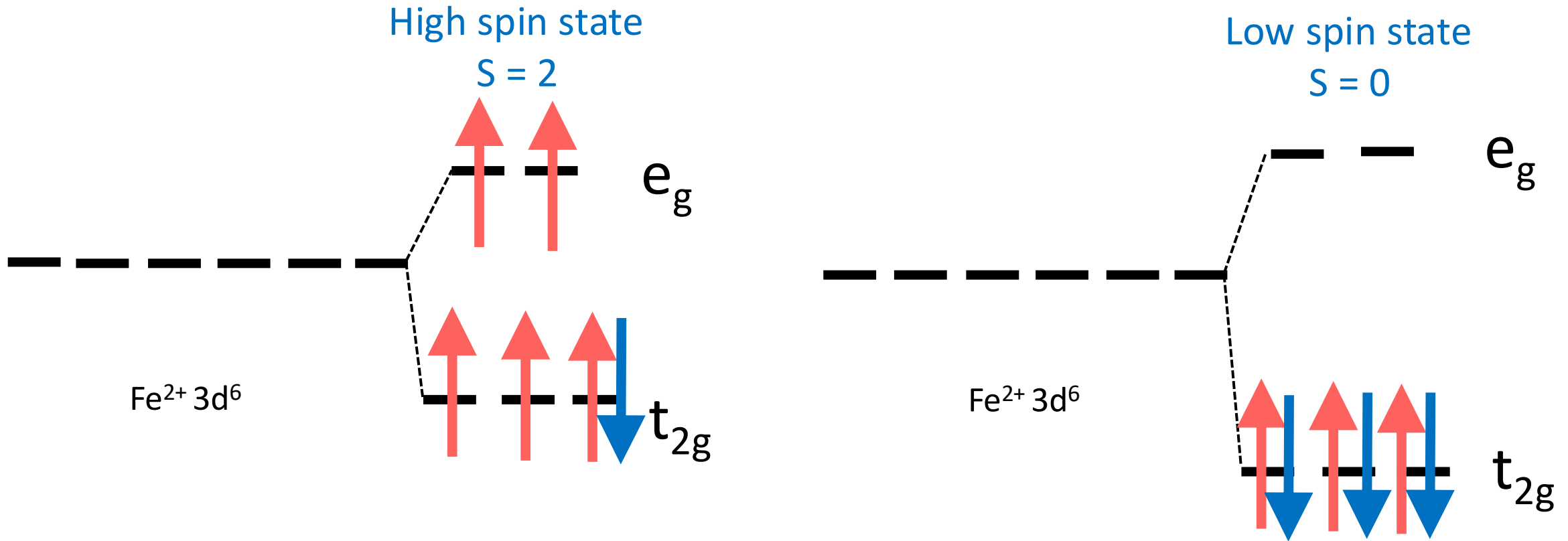


- The stronger the overlap with the neighbouring orbitals, the stronger is the electrostatic repulsion $\Rightarrow$ The higher the shift upwards in energy
- Octahedral splitting is larger $\Rightarrow \Delta_t = 4/9 \Delta_o$

Crystal field vs spin-orbit coupling

Crystal field is small: $\Delta_o \ll \Lambda_{LS} \Rightarrow$ Hund's rules apply

Crystal field large: $\Delta_o \gg \Lambda_{LS} \Rightarrow$ 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

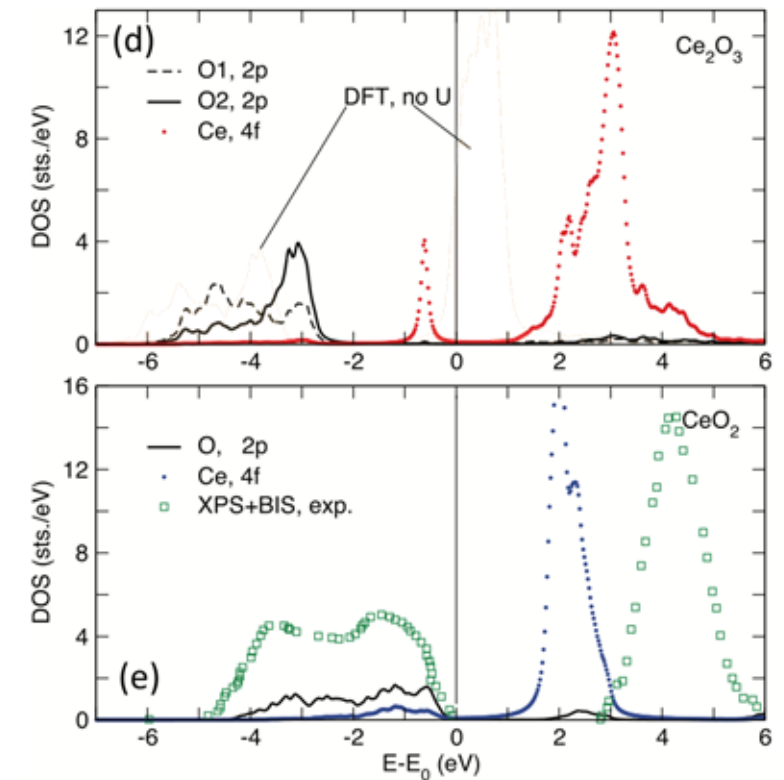
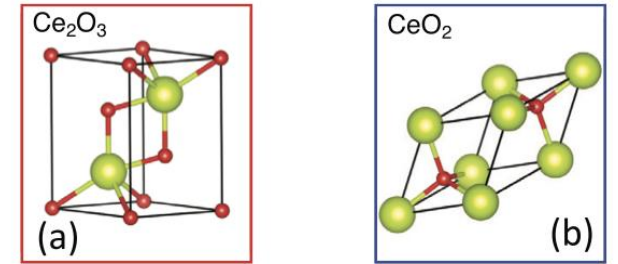
Collective phenomena possible due to delocalised atoms

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)

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