Atomic Magnetic Moment

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Introduction
One-electron magnetic moment at the atomic scale
Classical to Quantum
Many-electron: Hund’s rules and spin-orbit coupling
Non interacting moments under magnetic field
Diamagnetism and paramagnetism
Localized versus itinerant electrons
Conclusion

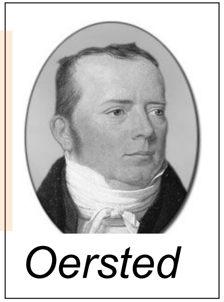
Introduction

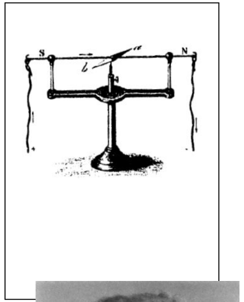
A bit of history

Lodestone-magnetite Fe_3O_4 known in antic Greece and ancient China (spoon-shape compass)
Described by Lucrecia in *de natura rerum*

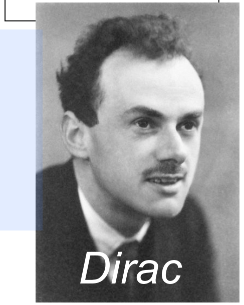
Medieval times to seventeenth century:
Pierre de Maricourt (1269), B. E. W. Gilbert (1600), R. Descartes (≈1600)…
Properties of south/north poles, earth is a magnet, compass, perpetual motion

Modern developments:
H. C. Oersted, A. M. Ampère, M. Faraday, J. C. Maxwell, H. A. Lorentz…
Unification of magnetism and electricity, field and forces description





20th century: P. Curie, P. Weiss, L. Néel, N. Bohr, W. Heisenberg, W. Pauli, P. Dirac…
Para-ferro-antiferro-magnetism, molecular field, domains,
(relativistic) quantum theory, spin…



Introduction

Magnetism:

science of cooperative effects of orbital and spin moments in matter

➔Wide subject expanding over physics, chemistry, geophysics, life science.

At fundamental level: Inspiring or verifying lots of model systems, especially in theory of phase transition and concept of symmetry breaking (ex. Ising model)

Large variety of behaviors: dia/para/ferro/antiferro/ferrimagnetism, phase transitions, spin liquid, spin glass, spin ice, skyrmions, magnetostriction, magnetoresistivity, magnetocaloric, magnetoelectric effects, multiferroism, exchange bias…
in different materials: metals, insulators, semi-conductors, oxides, molecular magnets,.., films, nanoparticles, bulk...

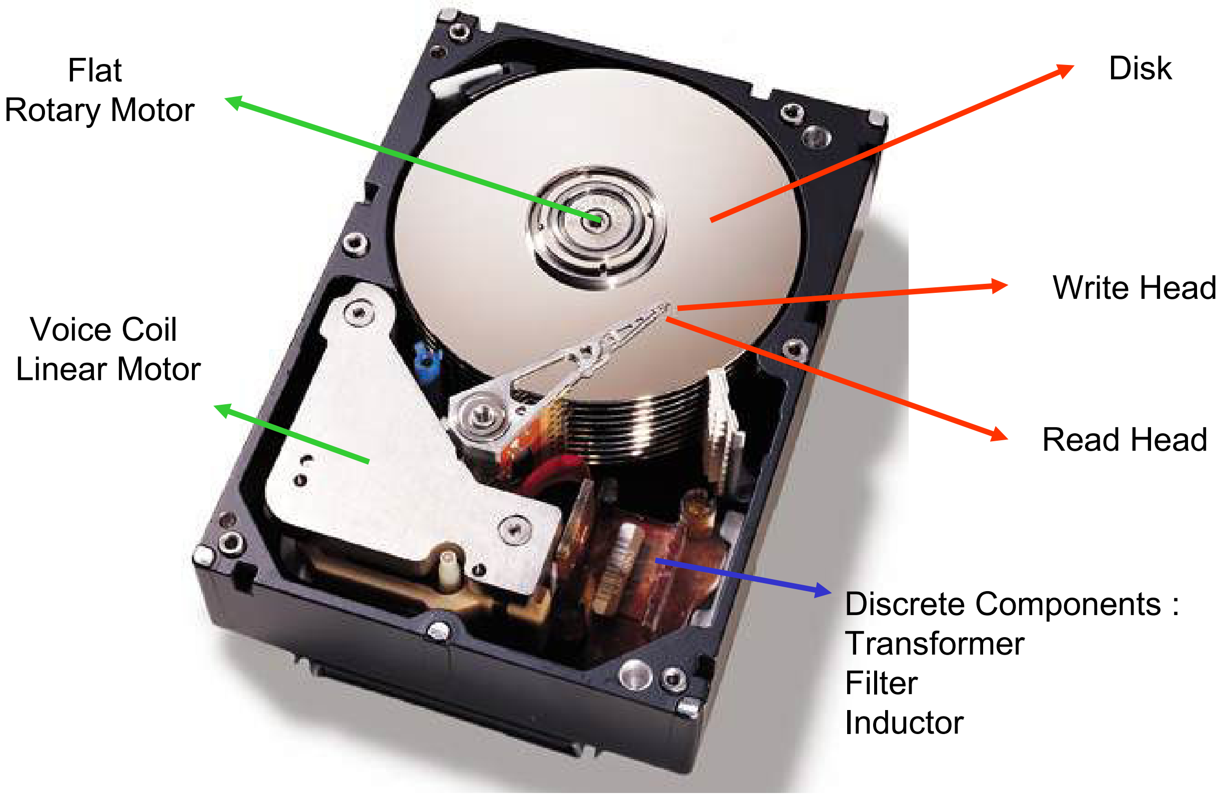
Magnetism is a quantum phenomenon but phenomenological models are commonly used to treat classically matter as a continuum

Many applications in everyday life

Introduction

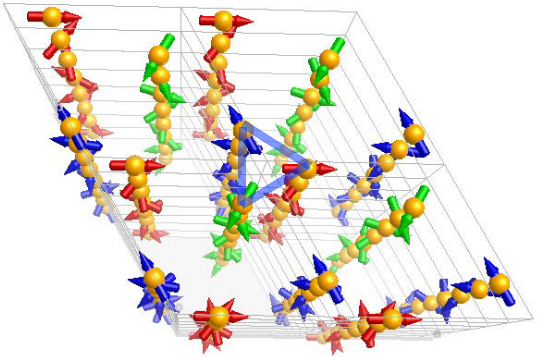
Magnetic materials all around us : the earth, cars, audio, video, telecommunication, electric motors, medical imaging, computer technology…

Hard Disk Drive

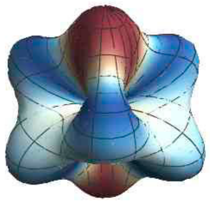


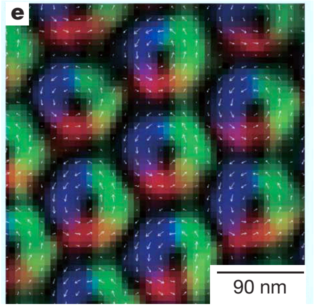
Introduction

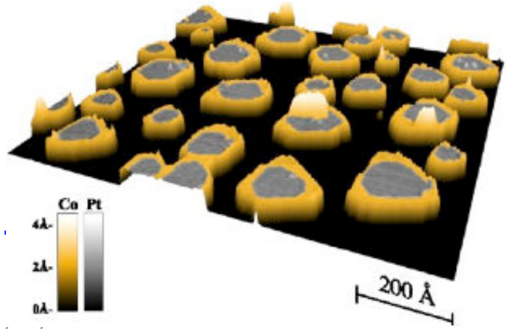
Topical research fields in magnetism



- Magnetic frustration: complex magnetic (dis)ordered ground states
- Molecular magnetism: photo-switchable, quantum tunneling
- Mesoscopic scale (from quantum to classical) ➔ quantum computer
- Quantum phase transition (at T=0)
- Low dimensional systems: Haldane, Bose-Einstein condensate, Luttinger liquids
- Magnetic topological matter
- Multiferroism: coexisting ferroic orders (magnetic, electric…)
- Magnetism and superconductivity
- Nanomaterials: thin films, multilayers, nanoparticles
- Spintronics: use of the spin of the electrons in electronic devices
- Skyrmionics: new media for encoding information
- Magnetic fluids: ferrofluids
- Magnetoscience: magnetic field effects on physics, chemistry, biology …



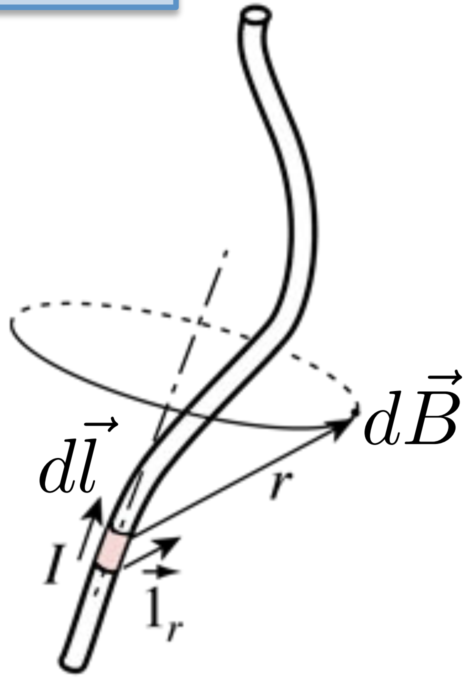




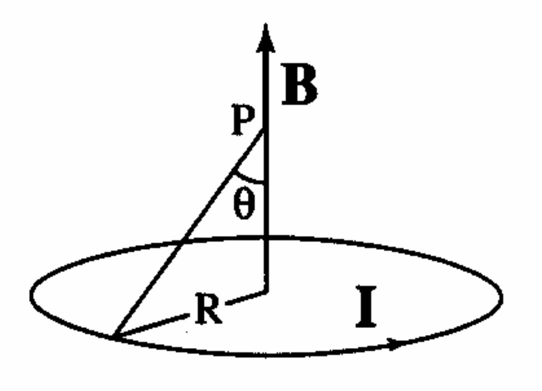
Atomic magnetic moment: classical

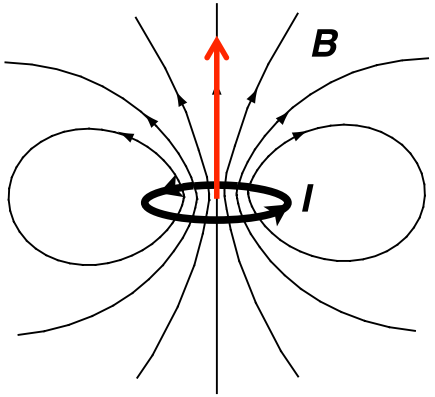
✔An electric current is the source of a magnetic field B

$$\vec{B} = \frac{\mu_0}{4\pi} \int_C \frac{I d\vec{l}}{r^2} \times \frac{\vec{r}}{r} \qquad \mu_0/4\pi = 10^{-7}$$



✔ Magnetic moment/magnetic field generated by a single-turn coil





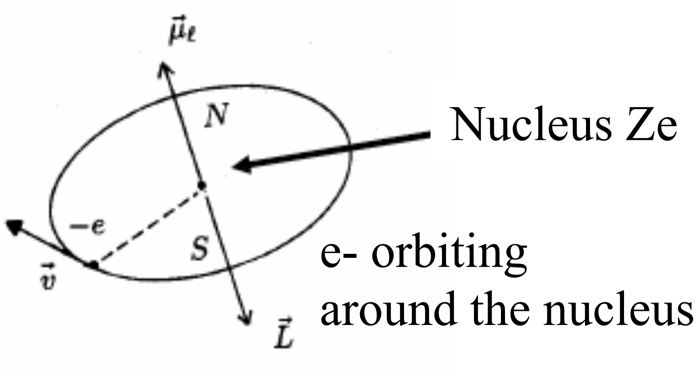
Magnetic moment

$$\vec{B} = \frac{\mu_0}{4\pi}[3\frac{(\vec{m}.\vec{r})\vec{r}}{r^5} - \frac{\vec{m}}{r^3}] \quad \text{with} \quad \vec{m} = IS\vec{n}$$

Atomic magnetic moment: classical

✔ Orbiting electron is equivalent to a magnetic moment

$$\vec{\mu}_\ell = I.\vec{S} = \frac{-ev}{2\pi r}\pi r^2\vec{n} = \frac{-evr}{2}\vec{n}$$



Nucleus Ze

e- orbiting
around the nucleus

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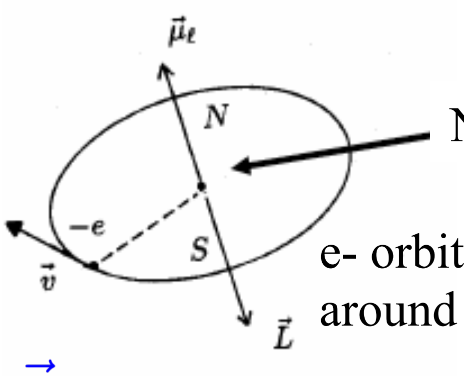


Nucleus Ze

e- orbiting
around the nucleus

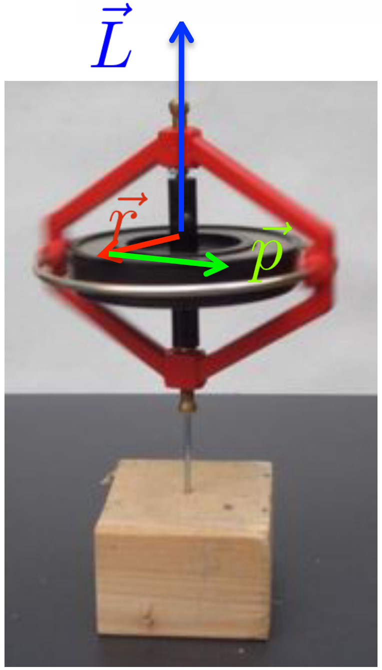
- ✔ The magnetic moment is related to the angular momentum

$$\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times m\vec{v}$$

$$\vec{\mu}_\ell = \frac{-e}{2m}\vec{L} = \gamma\vec{L}$$

Orbital magnetic moment

Gyromagnetic ratio



gyroscope

https://en.wikipedia.org/Wiki/Angular_momentum

Atomic magnetic moment: classical

✔ Orbiting electron is equivalent to a magnetic moment

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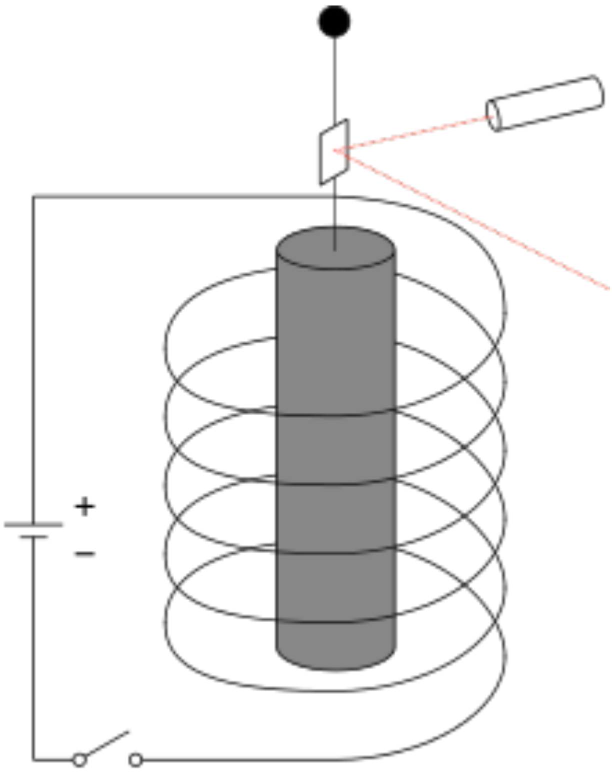


https://fr.wikipedia.org/wiki/Effet_Einstein-de_Haas

Einstein-de Haas effect (1915): suspended ferromagnetic rod magnetized by magnetic field → rotation of rod to conserve total angular momentum

Atomic magnetic moment: classical

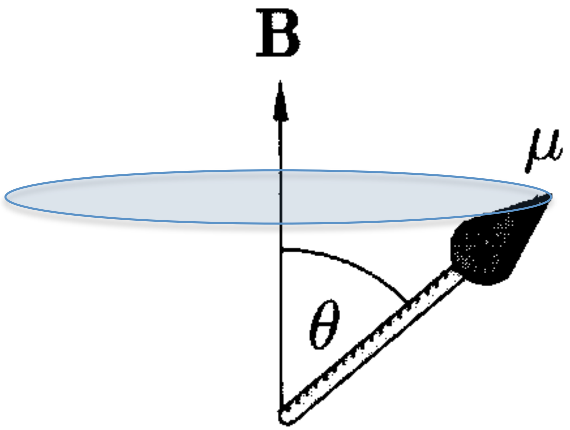
✔ The magnetic moment is related to the angular momentum: consequence Larmor precession.

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

Torque applied to the moment $\vec{G} = \vec{\mu} \times \vec{B}$

Equation of motion →
Variation of the magnetic moment (hyp. no dissipation)

$$\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu} \times \vec{B}$$



✔ The magnetic moment precesses about the field at the Larmor frequency $\omega_L = |\gamma|B$

Atomic magnetic moment: classical to quantum

Consequences:

✔ Orbital motion, magnetic moment and angular momentum are antiparallel

✔ Calculations with magnetic moment using formalism of angular momentum

No work produced by a magnetic field on a moving e- hence a magnetic field cannot modify its energy and cannot produce a magnetic moment.

$$\vec{f} = -e(\vec{v} \times \vec{B})$$

Atomic magnetic moment: classical to quantum

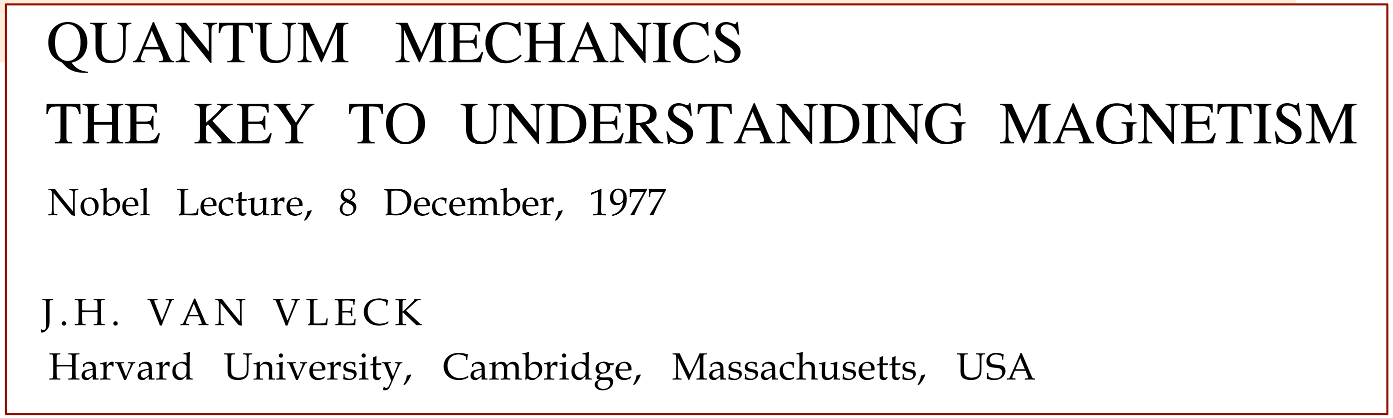
Consequences:

✔ Magnetic moment and angular momentum are antiparallel

✔ Calculations with magnetic moment using formalism of angular momentum

In a classical system, there is no thermal equilibrium magnetization!
(Bohr-van Leeuwen theorem)

→ **Need of quantum mechanics**



QUANTUM MECHANICS
THE KEY TO UNDERSTANDING MAGNETISM

Nobel Lecture, 8 December, 1977

J.H. VAN VLECK
Harvard University, Cambridge, Massachusetts, USA

Atomic magnetic moment: classical to quantum

Reminder of Quantum Mechanics

Wavefunction ψ and operator $\hat{A}$

$$|\psi|^2 = \psi^*\psi$$

$$\hat{A}\phi_i = a_i\phi_i \qquad \langle\hat{A}\rangle = \int d\tau\psi^*\hat{A}\psi$$

$$\psi = \sum_i c_i\phi_i \qquad \langle\hat{A}\rangle = \sum_i |c_i|^2 a_i$$

Commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

Schrödinger equation $\hat{\mathcal{H}}\psi = i\hbar\frac{d\psi}{dt}$ $\qquad \hat{\mathcal{H}}\phi_i = E_i\phi_i$

Angular momentum operator $\hbar\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = -i\hbar\hat{\vec{r}} \times \nabla$

Perturbation theory $E \approx E_k + \langle\phi_k|\hat{V}|\phi_k\rangle + \sum_{i\neq k}\frac{|\langle\phi_i|\hat{V}|\phi_k\rangle|^2}{E_k - E_i}$

Atomic magnetic moment: quantum

Magnetism in quantum mechanics:

Distribution of electrons on atomic orbitals, which minimizes the energy
→ *Building of atomic magnetic moments*

The electronic wavefunction $\Psi_{n\ell m_\ell}$ is characterized by 3 quantum numbers (spin ignored)

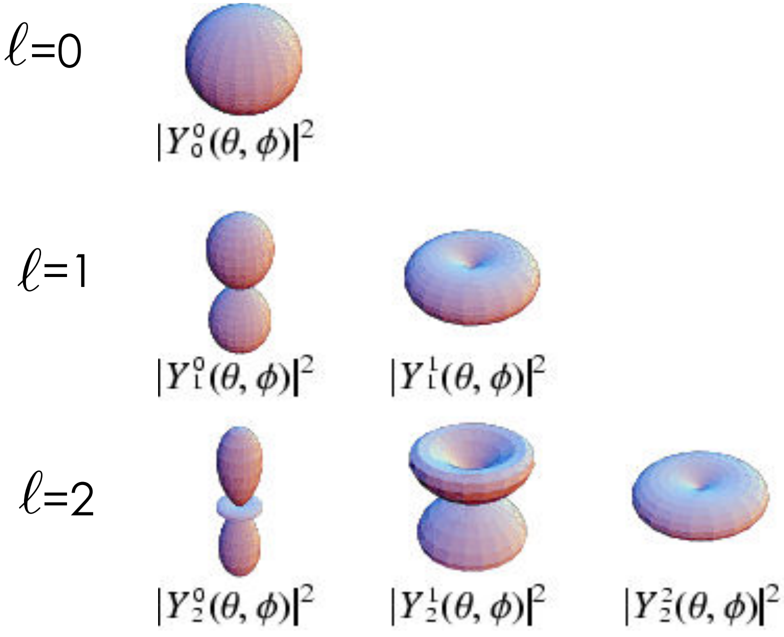
$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\mathcal{H}\Psi_i = E_i\Psi_i$$

$$\Psi_{n\ell m_\ell}(\vec{r}) = R_{n\ell}(r).Y_\ell^m(\theta,\phi)$$

Radial part

Spherical harmonics



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The electronic wavefunction $\Psi_{n\ell m_\ell}$ is characterized by 3 quantum numbers (spin ignored)

n : principal quantum number (electronic shell)
ℓ : orbital angular momentum quantum number $0 < \ell < n - 1$

ℓ	0	1	2	3
	s	p	d	f

m_ℓ : magnetic quantum number $-\ell < m_\ell < +\ell$

Atomic magnetic moment: quantum

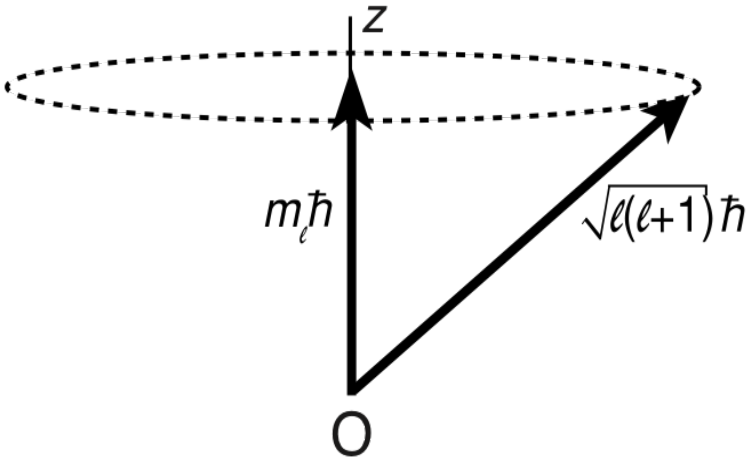
Magnetism in quantum mechanics: quantized orbital angular momentum

$\vec{\ell}$ is the angular momentum operator

Electronic orbitals are eigenstates of ℓ^2 and ℓ_z

$$\ell^2 \Psi_{n\ell m_\ell} = \hbar^2 \ell(\ell+1)\Psi_{n\ell m_\ell}$$

$$\ell_z = \hbar m_\ell \Psi_{n\ell m_\ell}$$



The magnitude of the orbital momentum is $\hbar\sqrt{\ell(\ell+1)}$

The component of the orbital angular momentum along the z axis is $\hbar m_\ell$

Atomic magnetic moment: quantum

Magnetism in quantum mechanics: quantized orbital angular momentum

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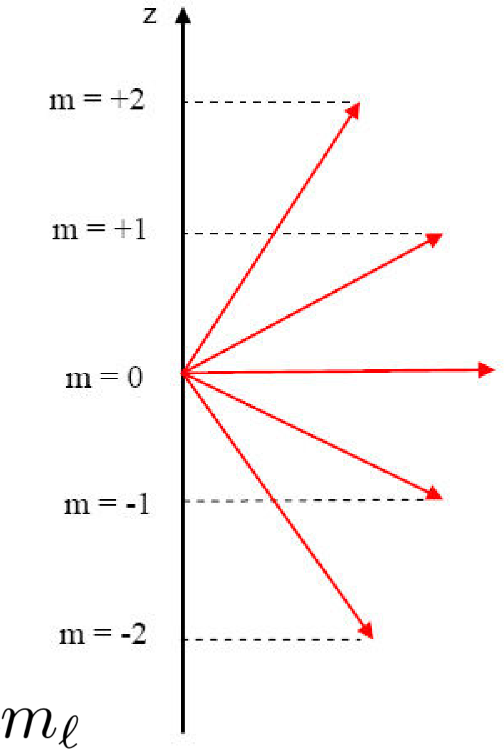
Ex. vector model for ℓ=2



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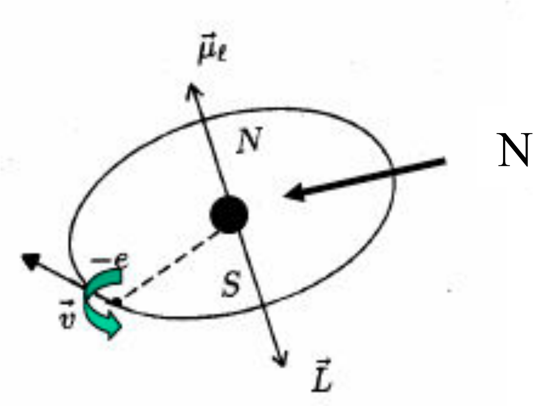
The component of the orbital angular momentum along the z axis is $\hbar m_\ell$

Degeneracy $2\ell+1$, can be lifted by magnetic field (Zeeman effect)

Atomic magnetic moment: quantum

Magnetism in quantum mechanics: spin angular momentum of pure quantum origin $\vec{s}$

$$s^2\Psi_s = \hbar^2 s(s+1)\Psi_s$$
$$s_z\Psi_s = \hbar m_s \Psi_s$$



Nucleus Ze

With the quantum numbers :

$$s = 1/2, m_s = -1/2, +1/2$$

The magnitude of the spin angular momentum is $\hbar\sqrt{s(s+1)} = \hbar\sqrt{3/4}$

The component of the spin angular momentum along the z axis is $\hbar m_s$

Atomic magnetic moment: quantum

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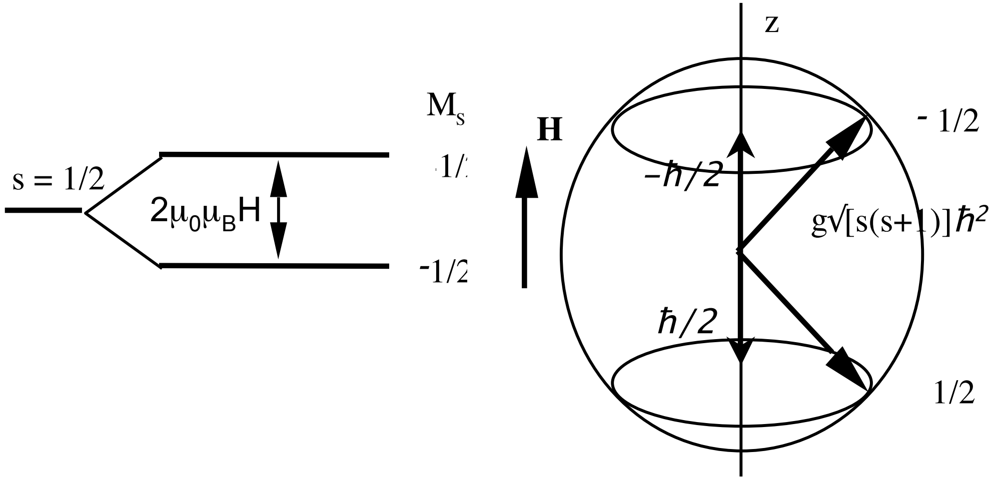

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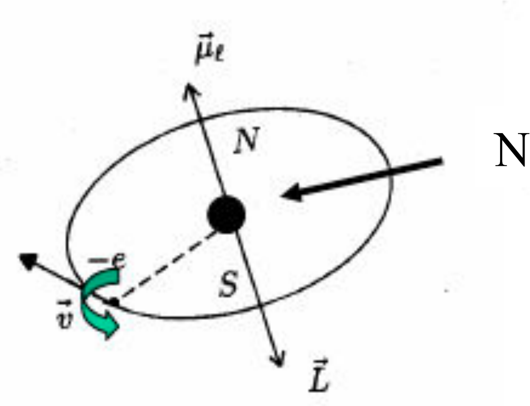
Degeneracy $2s+1=2$, can be lifted by magnetic field

Atomic magnetic moment: quantum

Magnetism in quantum mechanics:

Magnetic moment associated to 1 electron in the atom
Two contributions: spin and orbit



Nucleus Ze

Magnetic moments

$$\vec{\mu}_\ell = -g_\ell \mu_B \vec{l}$$

$$\vec{\mu}_s = -g_s \mu_B \vec{s}$$

With $g_\ell = 1$ and $g_s = 2 + \mathcal{O}(10^{-3})$

and the Bohr magneton $\mu_B = \dfrac{\hbar e}{2m_e} = 9.27.10^{-24} J.T^{-1}$

Atomic magnetic moment: quantum

Magnetism in quantum mechanics: several e- in an atom

Ex : $4f^2$

m_l	-3	-2	-1	0	1	2	3
m_s		↑					

? ←

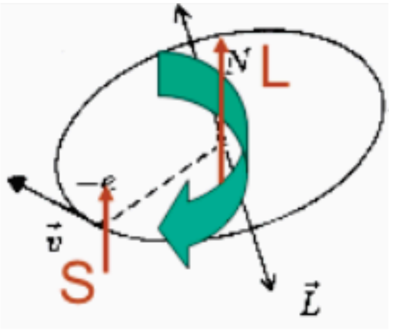
↑

Atomic magnetic moment: quantum

Magnetism in quantum mechanics: several e- in an atom

$$\vec{L} = \sum_{ne^-} \vec{\ell} \qquad \vec{S} = \sum_{ne^-} \vec{s}$$

Combination of the orbital and spin angular momenta of the different electrons:
related to the filling of the electronic shells in order to minimize
the electrostatic energy and fulfill the Pauli exclusion principle (one e- at most in quantum state)



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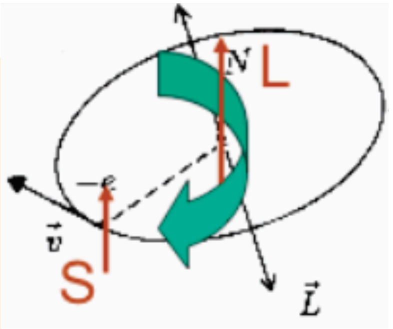
Spin-orbit coupling: $\lambda \vec{L}.\vec{S}$

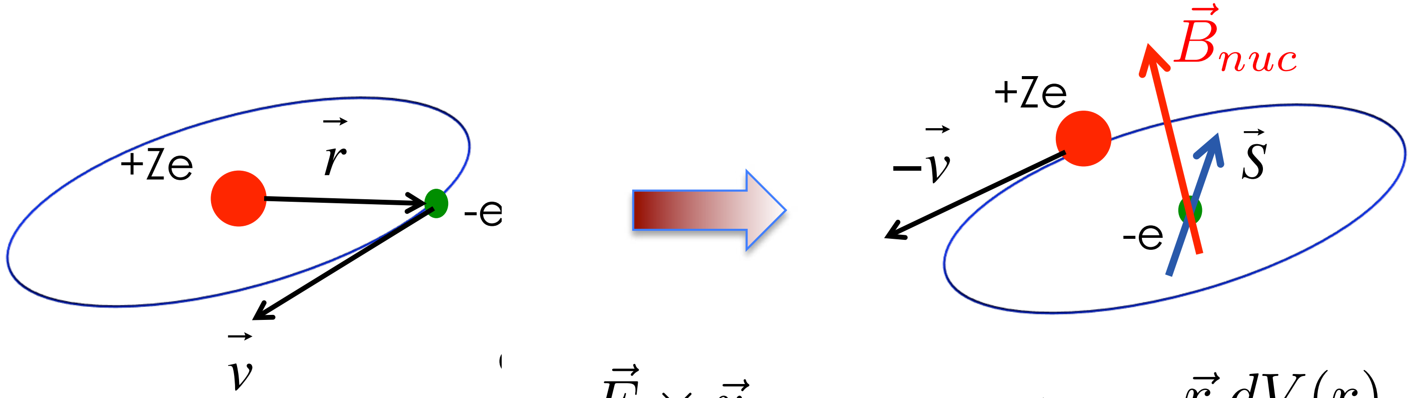


Total angular momentum $\vec{J} = \vec{L} + \vec{S}$

A given atomic shell (multiplet) is defined by 4 quantum numbers :
L, S, J, M_J with $-J < M_J < J$

Atomic magnetic moment: quantum

Origin of spin-orbit coupling: change of rest frame + special relativity



$$\vec{B}_{nuc} = \frac{\vec{E} \times \vec{v}}{c^2} \quad \text{with} \quad \vec{E} = -\frac{\vec{r}}{r}\frac{dV(r)}{dr}$$

$$\mathcal{H}_{so} = \mu_B \vec{S}.\vec{B}_{nuc} = \mu_B \frac{1}{c^2 r}\frac{dV(r)}{dr}\vec{S}(\vec{r}. \times \vec{v}) = \mu_B \frac{\hbar}{mc^2 r}\frac{dV(r)}{dr}\vec{S}.\vec{L}$$

Spin-orbit Hamiltonian $\mathcal{H}_{so} = \lambda \vec{S}.\vec{L}$

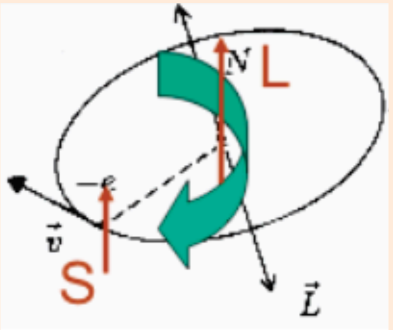
λ increases with atomic number Z^4

Consequence: m_ℓ and m_s are no longer good quantum numbers (L, S, J, M_J instead)

Atomic magnetic moment: quantum

Magnetism in quantum mechanics: several e- in an atom

Hund's rules for the ground state



1st rule $S = M_S = \sum_{ne^-} m_s$ maximum

2nd rule $L = M_L = \sum_{ne^-} m_\ell$ maximum in agreement with the 1st rule

3rd rule from spin-orbit coupling $\mathcal{H}_{so} = \lambda \vec{S}.\vec{L}$

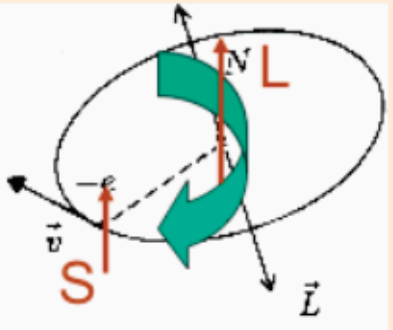
$$J = |L - S| \qquad\qquad J = |L + S|$$

for less than ½ filled shell for more than ½ filled shell

Atomic magnetic moment: quantum

Magnetism in quantum mechanics: several e- in an atom

Hund's rules for the ground state



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3rd rule from spin-orbit coupling $\mathcal{H}_{so} = \lambda \vec{S}.\vec{L}$

$J = |L - S|$ for less than ½ filled shell

$J = |L + S|$ for more than ½ filled shell

Degeneracy *2J+1*, can be lifted by a magnetic field

Atomic term
labeling the ground state:

$$^{2S+1}L_J$$

With $L = S, P, D...$

Atomic magnetic moment: quantum

Application of Hund's rule : L and S are zero for filled shells

Ex. Lu^{3+} is $4f^{14}$, 14 electron to put in 14 boxes ($\ell = 3$)

m_ℓ	-3	-2	-1	0	1	2	3
$m_s = \frac{1}{2}$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
$m_s = -\frac{1}{2}$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$

so $L = 0$ and $S = 0$, $J = 0$

Atomic magnetic moment: quantum

Application of Hund’s rule : L and S are zero for filled shells

Example of unfilled shell

Ce^{3+} is 4f^1, 1 electron to put in 14 boxes ($\ell = 3$)

m_ℓ	-3	-2	-1	0	1	2	3
$m_s = \frac{1}{2}$	↑						
$m_s = -\frac{1}{2}$							

so $L = 3$ and $S = 1/2$

The spin-orbit coupling applies for less than ½ filled shell $J = |L - S|$

so $J = 5/2$ and $-5/2 < M_J < 5/2$

The ground state is 6-fold degenerate

$$E_{so} = \langle LS|\mathcal{H}_{so}|LS\rangle = \lambda\left[\sum_{i,up}\langle \vec{L}_i.\vec{S}_{\|}\rangle - \xcancel{\sum_{i,down}\langle \vec{L}_i.\vec{S}_{\|}\rangle}\right]$$

Atomic magnetic moment: quantum

Application of Hund’s rule : L and S are zero for filled shells

Example of unfilled shell

Tb^{3+} is 4f^8, 8 electrons to put in 14 boxes ($\ell = 3$)

m_ℓ	-3	-2	-1	0	1	2	3
$m_s = \frac{1}{2}$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
$m_s = -\frac{1}{2}$	$\downarrow$						

so $L = 3$ and $S = 3$

The spin-orbit coupling applies for more than ½ filled shell $J = |L + S|$

so $J = 6$ and $-6 < M_J < 6$

The ground state is 13-fold degenerate

$$E_{so} = \langle LS|\mathcal{H}_{so}|LS\rangle = \lambda \left[\cancel{\sum_{i,up} \langle \vec{L}_i.\vec{S}_{\parallel} \rangle} - \sum_{i,down} \langle \vec{L}_i.\vec{S}_{\parallel} \rangle \right]$$

Atomic magnetic moment: quantum

The Zeeman interaction:

Hyp. $\mathcal{H}_Z << \mathcal{H}_{so}$ Wigner-Eckart theorem (projection theorem), 1st order perturbation theory

$$\vec{\mu} = -\mu_B(\vec{L} + 2\vec{S})$$

$$\mathcal{H}_z = \mu_B(\vec{L} + 2\vec{S}).\vec{B} \approx \mu_B g_J \vec{J}.\vec{B}$$ In the *J* multiplet basis

With the **Landé g_J-factor** $g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

Hence the Zeeman energy is $E_z = g_J \mu_B M_J B$ with $M_J \in \{-J, J\}$

and the level separation with $\Delta M_J = \pm 1$ is $g_J \mu_B B$

of the order of 1 K ≈ 0.1 meV

Atomic magnetic moment: quantum

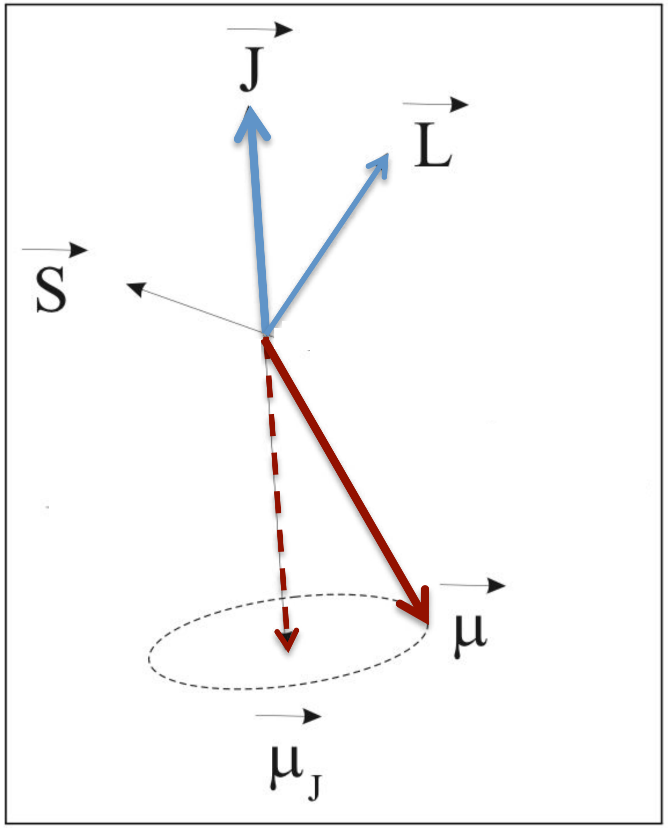
Summary: Total magnetic moment of the unfilled shell

$$\vec{\mu} = -\mu_B(\vec{L} + 2\vec{S})$$

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

$$\vec{\mu}_J = -g_J \mu_B \vec{J}$$

Example Tb^{3+}, J=6, g_J= 3/2
so that the magnetic moment is 9 μ_B



Atomic magnetic moment: quantum

Summary of atomic magnetism

- Electrons in central potential (nucleus + central part of e-e interactions)

  → fundamental electronic configuration, degeneracy $2n^2$, energies labeled by n

  $\Delta E \approx 10^8$ K
- Add non-central part of e-e interactions

  →separates the energies in different terms labeled by (L, S), degeneracy $(2L+1)(2S+1)$

  $\Delta E \approx 10^4$ K
- Add spin-orbit coupling

  → each term decomposed in multiplets characterized by J (and L, S), degeneracy $2J+1$

  $\Delta E \approx$100-1000 K for 3d ions, 1000-10000 K for 4f ions
- Add magnetic field: lift multiplet's degeneracy, $\Delta E \approx 1$ K

Atomic magnetic moment: quantum

Summary of atomic magnetism

Ex. free ion Co^{2+} $3d^7$, S=3/2, L=3, J=9/2

$\ell = 2$, 10 boxes to fill

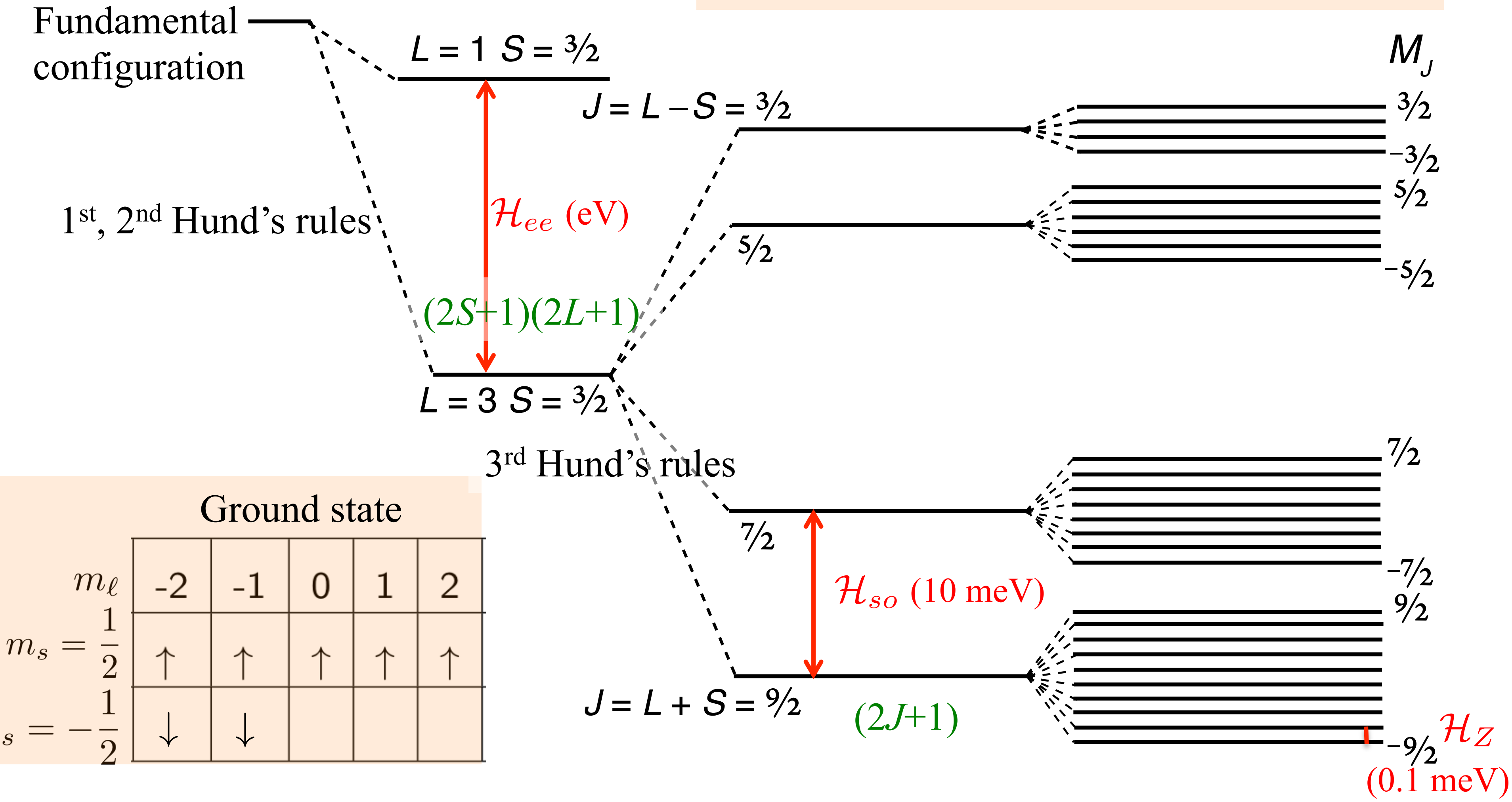
Ground state

m_ℓ	-2	-1	0	1	2
$m_s = \frac{1}{2}$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
$m_s = -\frac{1}{2}$	$\downarrow$	$\downarrow$			

Atomic magnetic moment: quantum

Summary of atomic magnetism

Ex. free ion Co^{2+} $3d^7$, S=3/2, L=3, J=9/2



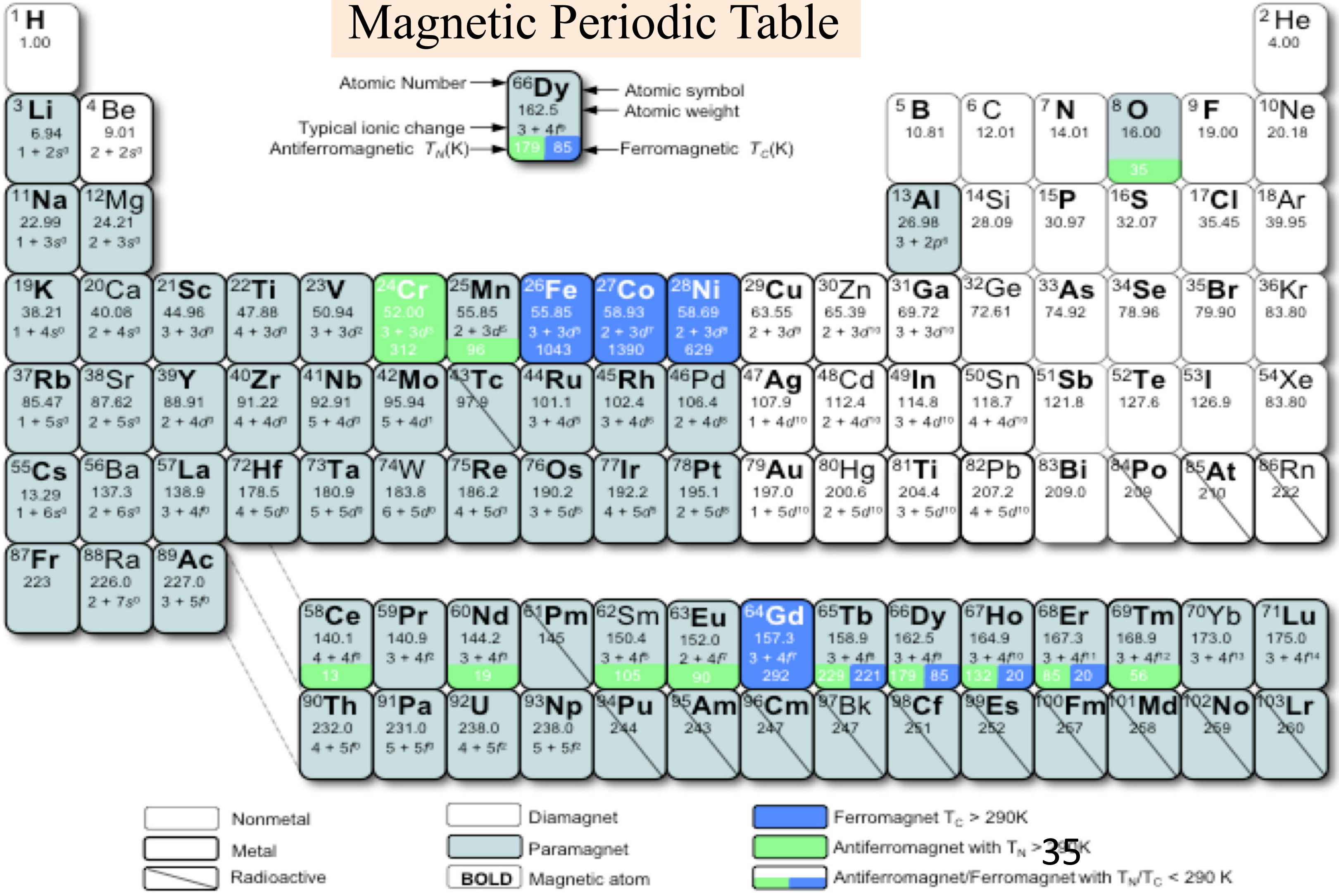
Ground state

m_ℓ	-2	-1	0	1	2
$m_s = \frac{1}{2}$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
$m_s = -\frac{1}{2}$	$\downarrow$	$\downarrow$			

Atomic magnetic moment in matter

Magnetism is a property of unfilled electronic shells:
Most atoms (bold) are concerned but ≈22 are magnetic in condensed matter

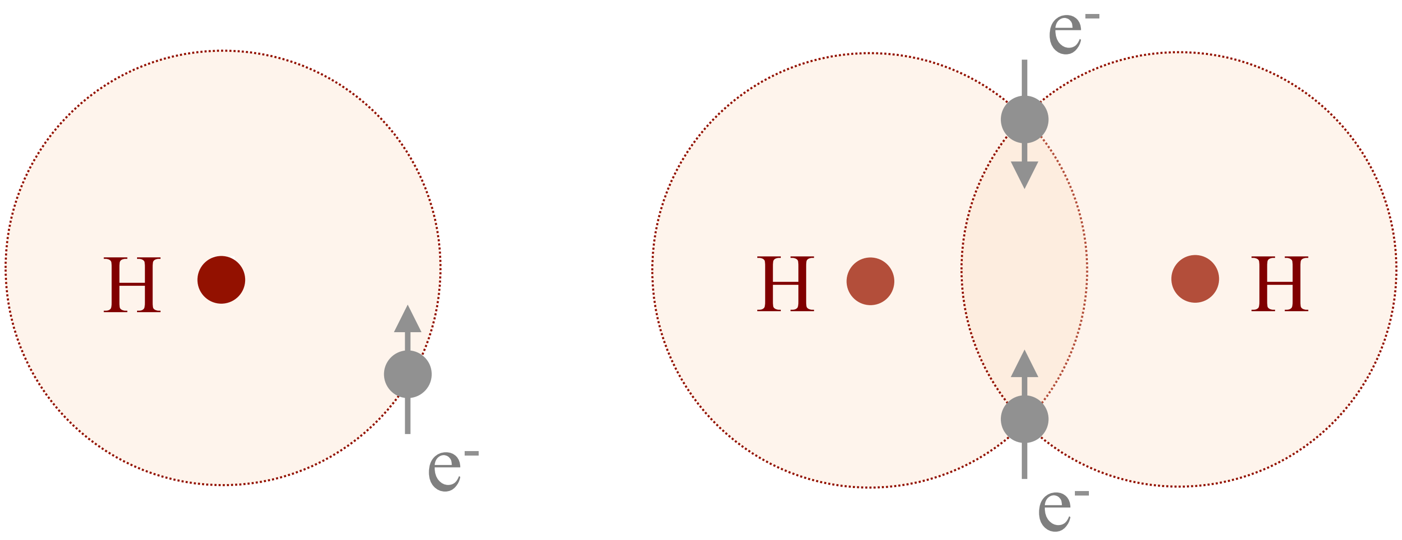
Magnetic Periodic Table



Atomic magnetic moment in matter

Atom in matter:

✔ Chemical bonding ➔ filled e- shells : no magnetic moments



Magnetic

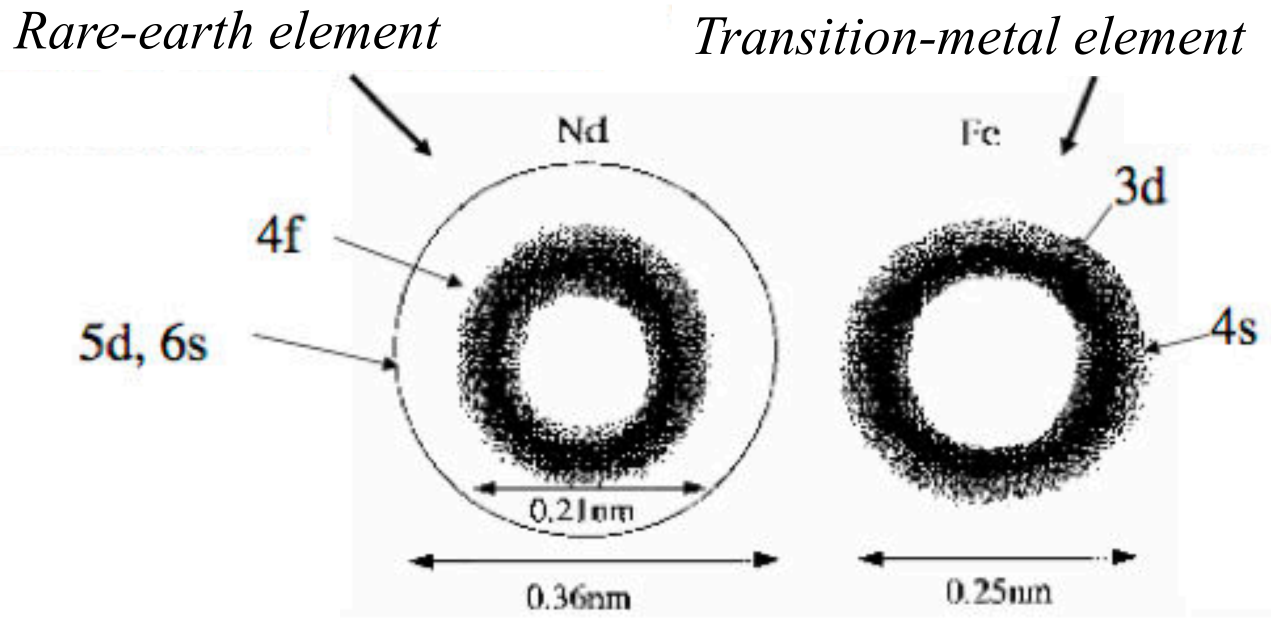
Non Magnetic

Atomic magnetic moment in matter

Atom in matter:

✔ Chemical bonding ➔ filled e- shells : no magnetic moments, exceptions:

Rare-earth element *Transition-metal element*



4f electrons: inner shell (localized moment)
3d electrons: outer shell (more delocalized, less screened)

Atomic magnetic moment in matter

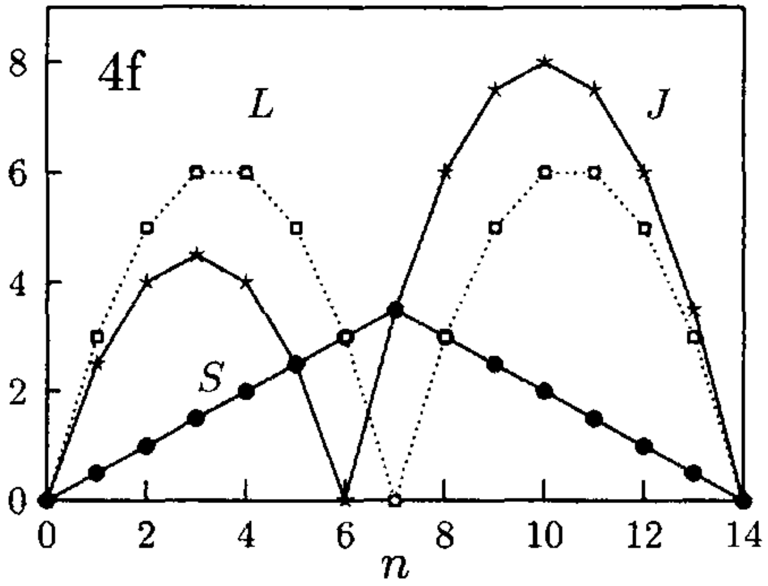
Validity of empirical Hund's rules:

L-S (Russel-Saunders) coupling scheme assumes spin-orbit coupling << electrostatic interactions:
L and S combined separately, then apply spin-orbit coupling.

No more valid for high Z (large spin-orbit coupling)→ j-j coupling scheme:
s and ℓ coupled first for each e-, then couple each electronic j.

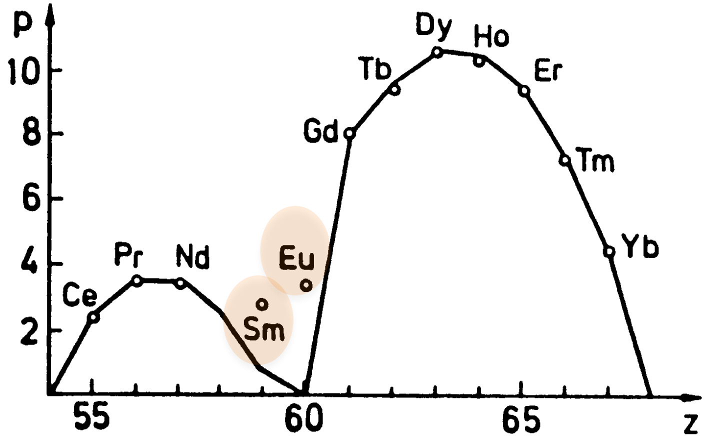
Atomic magnetic moment in matter

Validity of empirical Hund's rules: good for 4f



La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu^{3+}

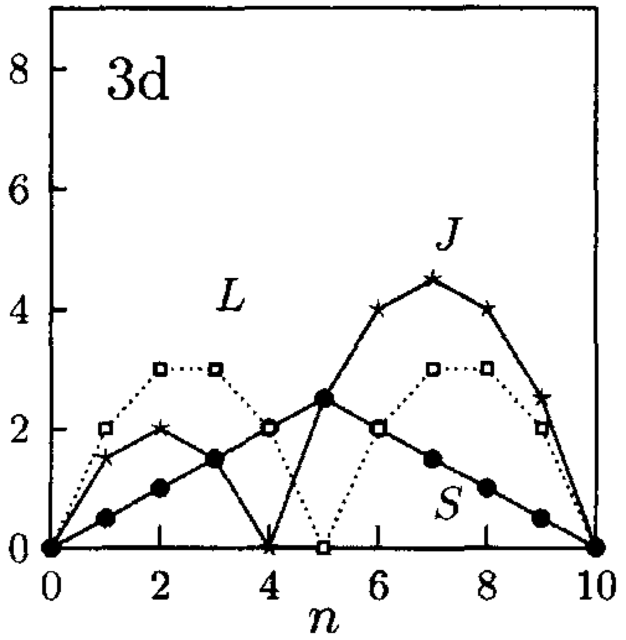
$$p_{eff} = g_J \sqrt{J(J+1)}\mu_B$$



except forEu, Sm: contribution from higher (L, S) levels

Atomic magnetic moment in matter

Validity of empirical Hund's rules: good for 4f but less good for 3d (due to crystal field)



Sc Ti V Cr Mn Fe Co Ni Cu Zn^{2+}

For 3d ions works better if *J* is replaced by *S* *(influence of crystal field)*

Atomic magnetic moment in matter

Summary

- ✓ Magnetism is a quantum phenomenon
- ✓ Magnetic moments are associated to angular momenta
- ✓ Orbital and Spin magnetic moments can be coupled (spin-orbit coupling) yielding the total magnetic moment (Hund’s rules)
- ✓ Magnetic moment in 3d and 4f atoms have different behaviors

Assembly of non-interacting magnetic moments

Measurable quantities:

Magnetization : magnetic moment per unit volume (A/m)
derivative of the free energy w. r. t. the magnetic field

$$M = -\frac{\partial F}{\partial B}$$

Susceptibility: derivative of magnetization w. r. t. magnetic field,
alternatively, ratio of the magnetization on the field in the linear regime (unitless)

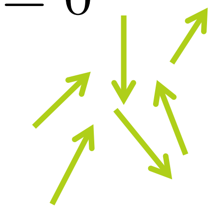
$$\chi = \mu_0 \frac{\partial M}{\partial B} \approx \mu_0 \left(\frac{M}{B}\right)_{lin}$$

$$\mu_0 = 4\pi 10^{-7}$$

Assembly of non-interacting magnetic moments

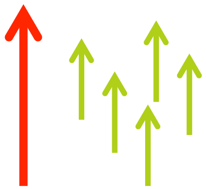
N atomic moments in a magnetic field B

$\vec{B} = 0$



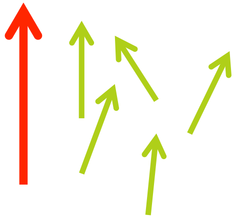
Non-interacting
magnetic moments

$\vec{B}$



At T=0 K
M=M_s saturated magnetization

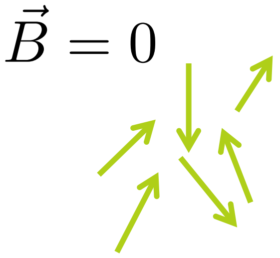
$\vec{B}$



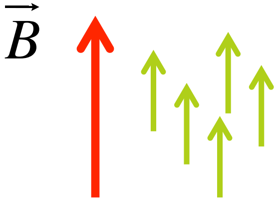
At T≠0 K, M<M_s, competition
between Zeeman energy
and entropy term

Assembly of non-interacting magnetic moments

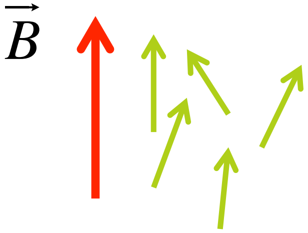
N atomic moments in a magnetic field B



Non-interacting
magnetic moments



At T=0 K
M=M_s saturated magnetization



At T≠0 K, M<M_s, competition
between Zeeman energy
and entropy term

Calculation of magnetization and susceptibility
Thermal average (Boltzmann statistics) + perturbation theory

$$M_\alpha = \frac{N}{V}\sum_j -\frac{\partial E_j}{\partial B_\alpha}\frac{\exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)} \qquad \text{with} \quad \beta = 1/k_B T$$

Assembly of non-interacting magnetic moments

One atomic moment in a magnetic field B

$$\mathcal{H} = \sum_{i=1}^{Z} \left(\frac{(\vec{p_i} - e\vec{A}(\vec{r_i}))^2}{2m_e} + V_i(r_i) \right) + g\mu_B \vec{B}.\vec{S} \qquad \vec{B} = \nabla \times \vec{A}$$

With the magnetic vector potential (Coulomb gauge) $\vec{A}(\vec{r}) = \frac{\vec{B} \times \vec{r}}{2}$

$$\mathcal{H} = \sum_i \left(\frac{p_i^2}{2m_e} + V_i(r_i) \right) + \boxed{\mu_B(\vec{L} + 2\vec{S}).\vec{B}} + \boxed{\frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r_i})^2}$$

Zeeman hamiltonian: coupling of total magnetic moment with the magnetic field

Diamagnetic hamiltonian: induced orbital moment by the external magnetic field

Assembly of non-interacting magnetic moments

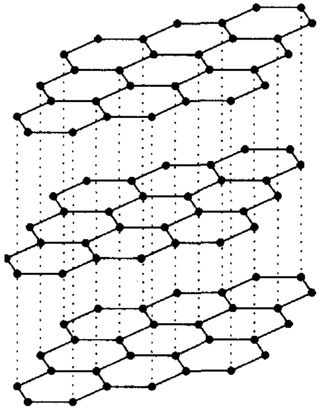
Energy: $$\mathcal{H}_B = \boxed{\mu_B(\vec{L}+2\vec{S}).\vec{B}} + \boxed{\frac{e^2}{8m_e}\sum_i(\vec{B}\times\vec{r_i})^2}$$

Diamagnetic term for N atoms:

$$\chi = -\frac{N}{V}\mu_0\frac{e^2}{4m_e} < r_\perp^2 >$$

→ perpendicular to the field

due to the induced moment by the magnetic field



➔ **Larmor diamagnetism**

➔ negative weak susceptibility, concerns all e- of the atom, T-independent

➔ Large anisotropic diamagnetism found in planar systems with delocalized e- (ex. graphite, benzene)

Assembly of non-interacting magnetic moments

Energy: $$\mathcal{H}_B = \boxed{\mu_B(\vec{L}+2\vec{S}).\vec{B}} + \boxed{\frac{e^2}{8m_e}\sum_i(\vec{B}\times\vec{r_i})^2}$$

Paramagnetic term for N atoms :

$$M = \frac{N}{V} g_J J \mu_B B_J(x) \qquad \text{with} \qquad x = \frac{g_J J \mu_B B}{k_B T}$$

and the Brillouin function:

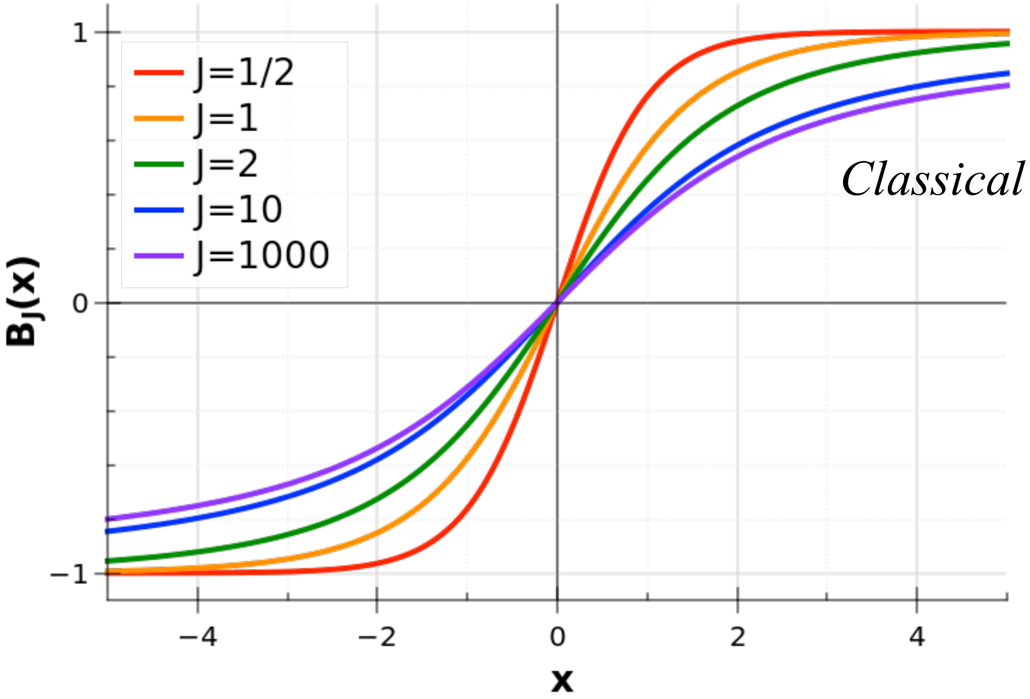
$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

Assembly of non-interacting magnetic moments

Paramagnetic term

Brillouin functions for different *J* values,

$$M = \frac{N}{V} g_J J \mu_B B_J(x)$$



Classical limit

Limit $x >> 1$ i.e. $B >> k_B T$

Saturation magnetization $M_s = \frac{N}{V} g_J J \mu_B$

https://fr.wikipedia.org/wiki/ Fichier:Brillouin_Function.svg

Assembly of non-interacting magnetic moments

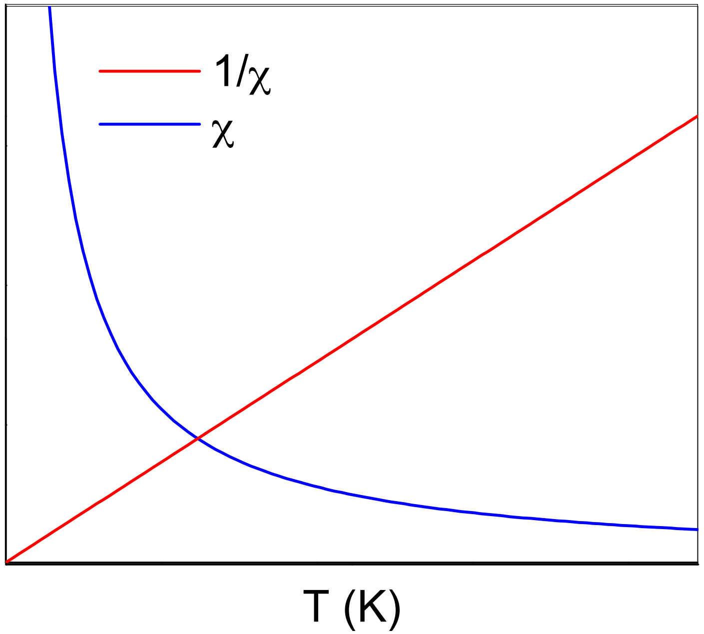
Paramagnetic term

Limit $x << 1$ i.e. $k_B T >> B$ $$B_J(x) = \frac{(J+1)x}{3J} + \mathcal{O}(x^3)$$

Curie law: $$\chi = \frac{N}{V}\frac{(\mu_B g_J)^2 J(J+1)}{3k_B T} = \frac{N}{V}\frac{p_{eff}^2}{3k_B T} = \frac{C}{T}$$

with C the Curie constant
and the effective moment

$$p_{eff} = g_J \sqrt{J(J+1)}\mu_B$$

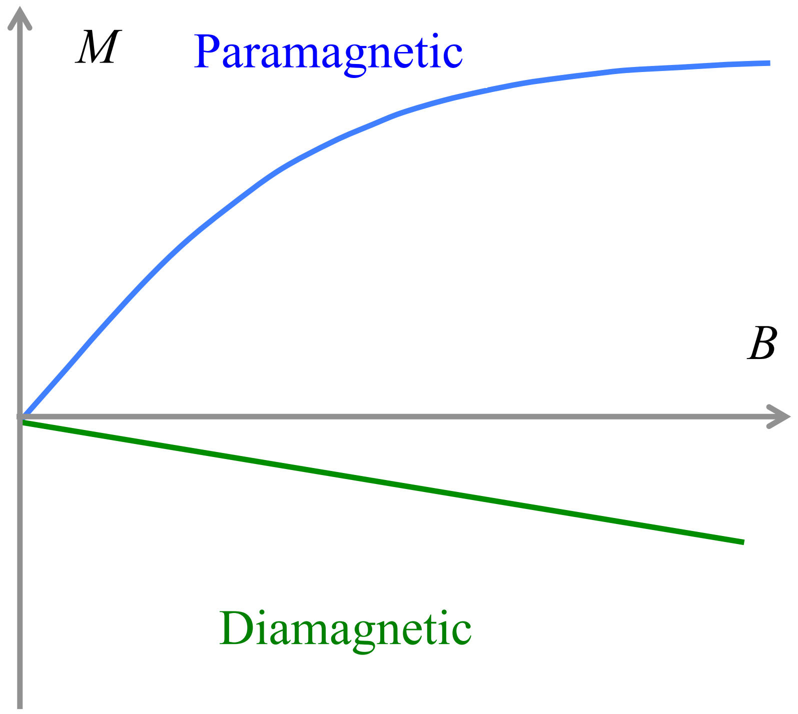


It works well for magnetic moments without interactions and negligible CEF: ex. Gd^{3+}, Fe^{3+}, Mn^{2+} (L=0)

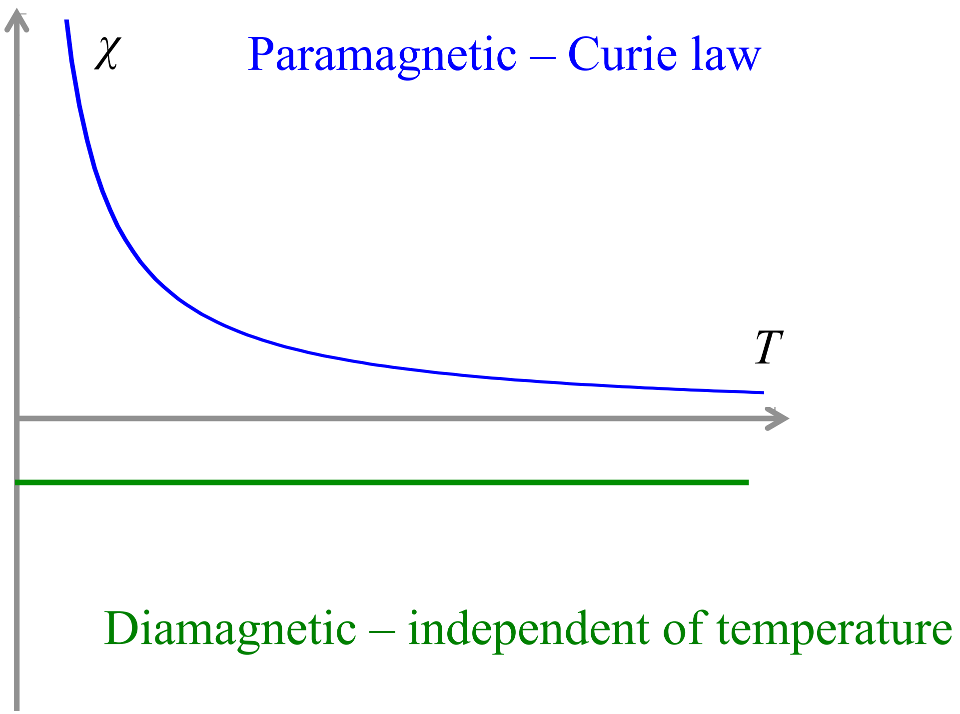
Assembly of non-interacting magnetic moments

Summary of magnetic field response of non-interacting atomic moments

versus magnetic field



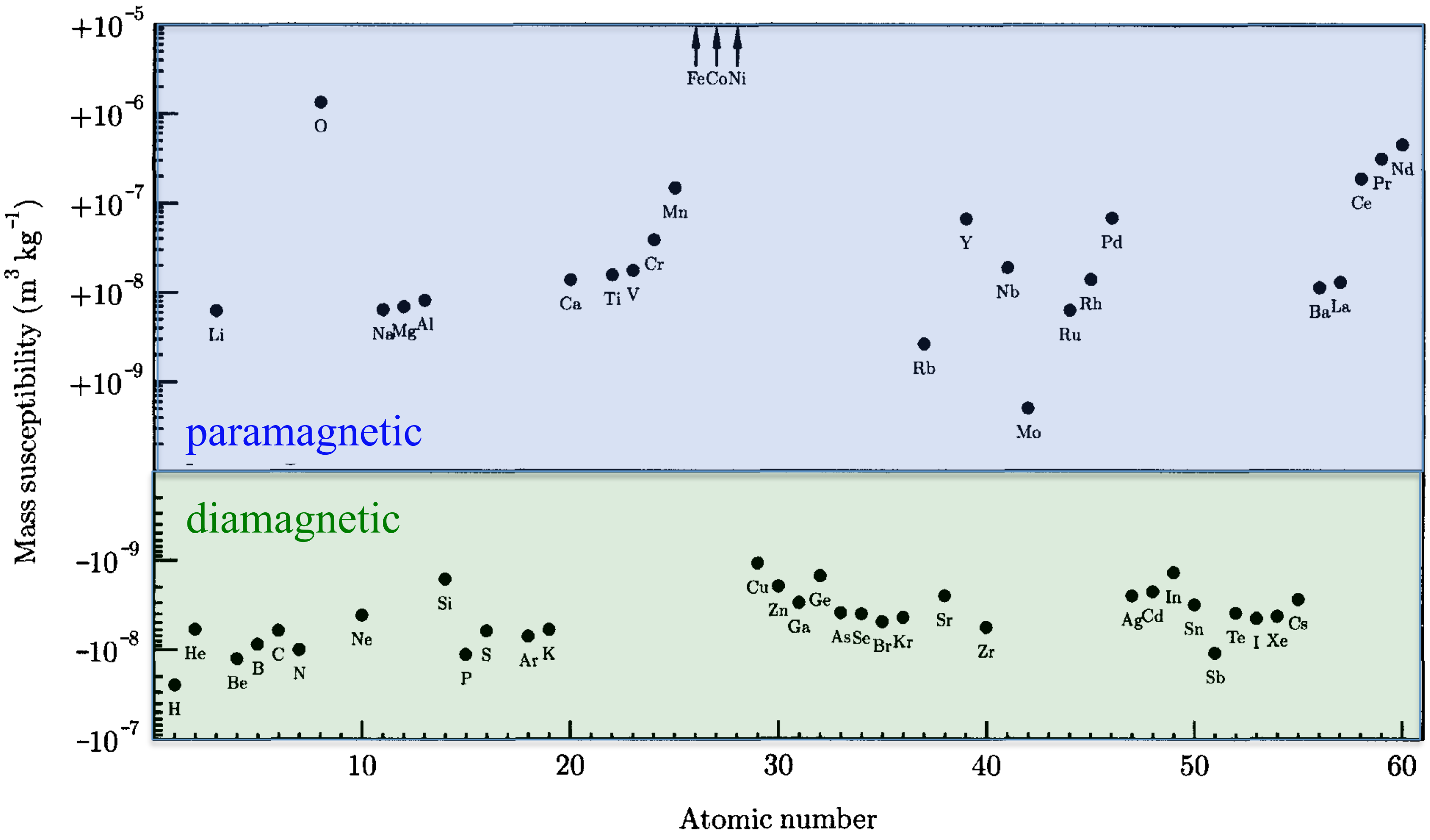
versus temperature



Rmq: Another source of paramagnetism (2^{nd} order perturbation theory, mixing with excited states)
Van Vleck paramagnetism → weak positive and temperature independent

Assembly of non-interacting magnetic moments

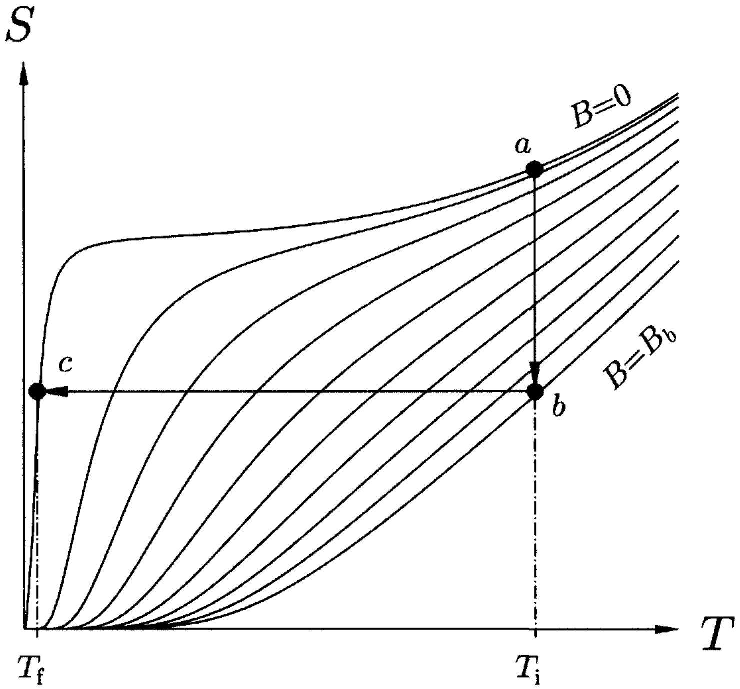
Summary of magnetic field response of non-interacting atomic moments



Assembly of non-interacting magnetic moments

Adiabatic demagnetization: cooling a sample down to mK

The entropy is a monotonically decreasing function of *B/T*
Two steps:
a-b isothermal magnetization by applying a magnetic field → reduces the entropy
b-c Removing the magnetic field adiabatically (at constant entropy)→ lower the temperature

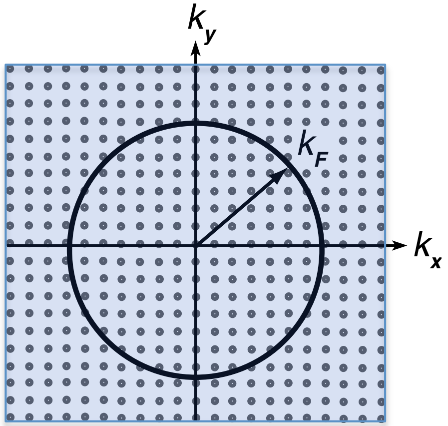


Itinerant electrons

Magnetism in metals

Starting point: the free electron model, properties of Fermi surface, Fermi-Dirac statistics, electronic band structure

Non-interacting electron waves confined in a box



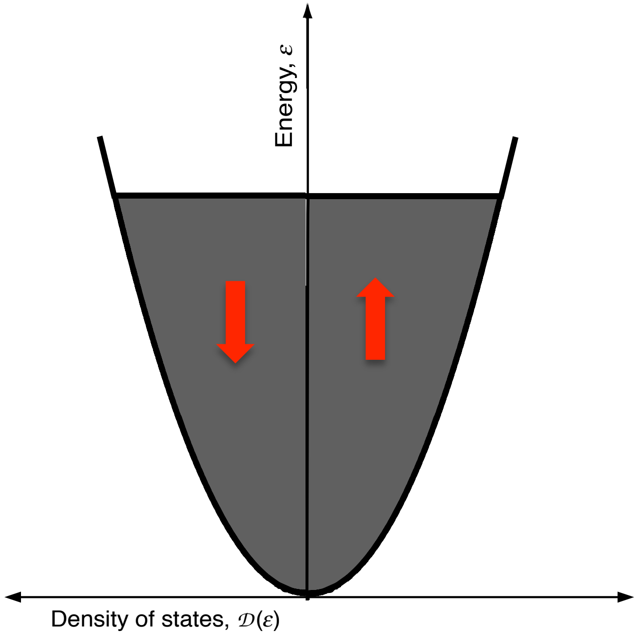
Fermi wavevector

$$k_F = (3\pi^2 n)^{\frac{1}{3}}$$

Density of states at Fermi level (T=0)

$$\mathcal{D}_{\uparrow,\downarrow}(E_F) = \frac{3n}{4E_F}$$

k-space:
Each points is a possible state for one spin up and down



For a non-magnetic metal: same number of spins ↑ and ↓ electrons at Fermi level

Itinerant electrons

Magnetism in metals

Applying a magnetic field
(at T=0)

$$E_z = g\mu_B B m_s$$

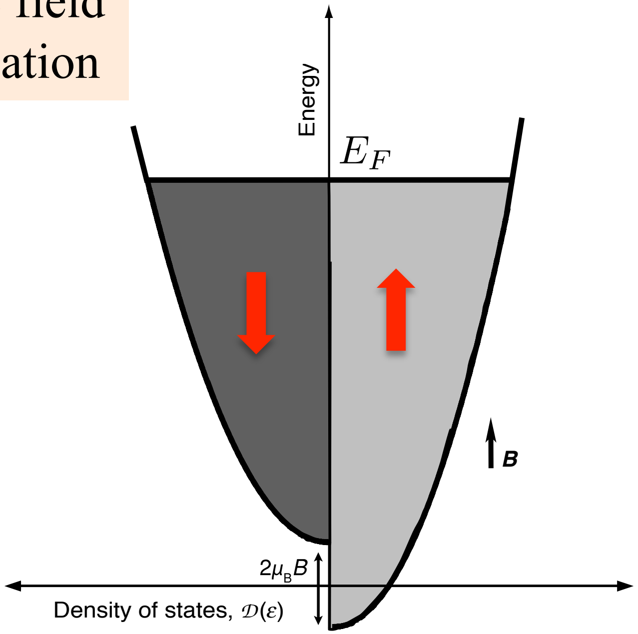
$$\Delta E = 2\mu_B B \approx 10^{-4} eV$$

$$M = \frac{g\mu_B(n\uparrow - n\downarrow)}{2}$$

$$M = \mu_B^2 \mathcal{D}(E_F) B$$

$$\chi_P = \mu_0 \mu_B^2 \mathcal{D}(E_F)$$

Spin-split bands
by magnetic field
→ magnetization



Pauli paramagnetism (effect associated to spin of e-)
Temperature independent > 0, weak effect.
Small correction at finite temperature $\propto T^2$

Itinerant electrons

Magnetism in metals

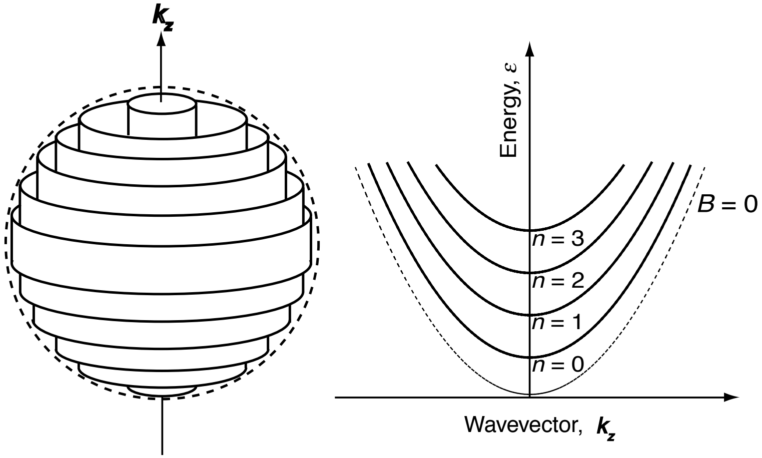
Applying a magnetic field

Pauli paramagnetism
associated to spin of electrons

$$\chi_P = \mu_0 \mu_B^2 \mathcal{D}(E_F)$$

Orbital response of e$^-$ gas to magnetic field

The applied magnetic field results in Landau tubes of electronic states



→ Landau diamagnetism,
Temperature independent < 0

$$\chi_L = -\frac{1}{3}\left(\frac{m_e}{m^*}\right)^2 \chi_P$$

→ Oscillations of the magnetization (de Haas-van Alphen effect)

Conclusion

Summary

- ✓ Magnetism is a quantum phenomenon
- ✓ Magnetic moments are associated to angular momenta
- ✓ Orbital and Spin magnetic moments can be coupled (spin-orbit coupling) yielding the total magnetic moment (Hund's rules)
- ✓ Magnetic moment in 3d and 4f atoms have different behaviors
- ✓ Various responses of non-interacting magnetic moments in applied magnetic field, different for localized or delocalized electrons:
  →Curie-law/Pauli paramagnetism, Larmor/Landau diamagnetism

But… does not explain spontaneous magnetization/magnetic order in absence of magnetic field, 3d ions magnetism and anisotropic behaviors…

→ Next lectures will introduce missing ingredients: **magnetic interactions** and influence of the environment (**crystal field**)

Further reading

- Material borrowed from presentations of D. Givord, L. Ranno, Y. Gallais, Thanks to them!
- “**Magnetism in Condensed Matter**” by Stephen Blundell, *Oxford University press (2003)*
- “**Introduction to magnetism**” by Laurent Ranno, *collection SFN 13, 01001 (2014), EDP Sciences, editors V. Simonet, B. Canals, J. Robert, S. Petit, H. Mutka*,

  free access DOI: http://dx.doi.org/10.1051/sfn/20141301001
- “**Magnetism and Magnetic Materials**” by J.M.D. Coey, Cambridge Univ. Press (2009)
- **Lectures of Yann Gallais Website**: www.mpq.univ-paris-diderot.fr/spip.php?rubrique260
- Any questions: virginie.simonet@neel.cnrs.fr