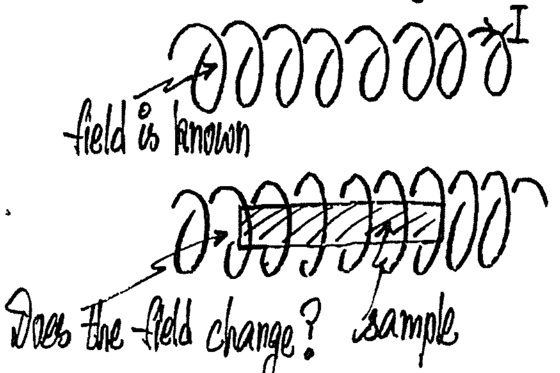
XV. Magnetic Properties

The question is: What happens when a solid is placed in a magnetic field?



Most materials: Only tiny changes / virtually no effect

Large changes only in a few materials⁺

— Magnetic Materials

(e.g. Fe, Co, Ni, Fe_3O_4)

Large changes ~ field near sample may change by a factor of 10^2 to 10^3.

⁺ Comparing the number of magnetic and non-magnetic materials, magnetic materials are rare, but they form an important class of materials for both academic and practical reasons.

A. Magnetic Susceptibility, χ

- The magnetic effects of materials is quantified by the magnetic susceptibility χ

$$\boxed{\vec{M} = \chi \vec{H}}$$

$\vec{H}$ → also called magnetic field intensity (Am^{-1}) SI units → Macroscopic magnetic field within the sample

χ → dimensionless

$\vec{M}$ → Magnetization → magnetic moment per unit volume $\left(\frac{m^2 \cdot A}{m^3} = Am^{-1}\right)$

- $\chi < 0$ diamagnetic [usually $|\chi| \ll 1$ for diamagnetic materials e.g. $\chi \sim -8.1 \times 10^{-6}$ for ice]

- $\chi > 0$ paramagnetic or ferromagnetic

paramagnetic → alignments of permanent magnetic moments by external field against thermal effect (e.g. $CuSO_4$ $\underbrace{\chi \sim 3.8 \times 10^{-4}}_{\text{typical of paramagnetic materials}}$ at $T = 300K$)

ferromagnetic → due to interactions between permanent dipole moments ⇓ alignment of moments at low temp. even without an applied field (spontaneous magnetization)

$$\vec{M} = \chi \vec{H}$$

- χ carries no units
- But sometimes, it is referred to as "the susceptibility per unit volume" or "volume susceptibility". Even so, it is dimensionless.
- Databook sometimes give
  - susceptibility per unit mass or mass susceptibility

    $$\frac{\chi}{\underset{\uparrow}{\rho}} \leftarrow \text{mass density } \left(\frac{\text{mass}}{\text{volume}}\right)$$

  - susceptibility per mole or molar susceptibility

    $$\chi_{molar} = \chi V_m \leftarrow \text{molar volume } (m^3 mol^{-1})$$

- χ_{SI} is related to χ_{cgs} by

  $$\underset{\text{SI units}}{\underset{\uparrow}{\chi_{SI}}} = 4\pi \underset{\text{cgs units}}{\underset{\uparrow}{\chi_{cgs}}}$$

$\chi_M = \chi_{Molar}$ for solid elements at room temperature ($m^3 mol^{-1}$)

UNDERSTANDING THE PROPERTIES OF MATTER: WEB CHAPTER 2

Table W2.1 Molar magnetic susceptibility of the elements at around room temperature. The data are summarised in Figure W2.3. The shading in the table corresponds to the shading in Figure and highlights elements with a large susceptibilities.

d

f

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Z	Element, atomic mass (u) and density (kg m⁻³)			χ_M (m³ mol⁻¹)
1	Hydrogen, H	1.008	89	—
2	Helium, He	4.003	120	—
3	Lithium, Li	6.941	533	1.78×10^{-10}
4	Beryllium, Be	9.012	1846	-1.17×10^{-10}
5	Boron, B	10.81	2466	-8.43×10^{-11}
6	Carbon, C	12.01	2266	-7.57×10^{-11}
7	Nitrogen, N	14.01	1035	—
8	Oxygen, O	16	1460	—
9	Fluorine, F	19	1140	—
10	Neon, Ne	20.18	1442	-8.48×10^{-11}
11	Sodium, Na	22.99	966	2.02×10^{-10}
12	Magnesium, Mg	24.31	1738	1.65×10^{-10}
13	Aluminium, Al	26.98	2698	2.08×10^{-10}
14	Silicon, Si	28.09	2329	-5.06×10^{-11}
15	Phosphorus, P	30.97	1820	-3.41×10^{-10}
16	Sulphur, S	32.06	2086	-1.95×10^{-10}
17	Chlorine, Cl	35.45	2030	—
18	Argon, A	39.95	1656	—
19	Potassium, K	39.1	862	2.62×10^{-10}
20	Calcium, Ca	40.08	1530	5.61×10^{-10}
21	Scandium, Sc	44.96	2992	3.96×10^{-9}
22	Titanium, Ti	47.9	4508	1.92×10^{-9}
23	Vanadium, V	50.94	6090	3.20×10^{-9}
24	Chromium, Cr	52	7194	2.31×10^{-9}
25	Manganese, Mn	54.94	7473	6.59×10^{-9}
26	Iron, Fe	55.85	7873	Ferro
27	Cobalt, Co	58.93	8800	Ferro
28	Nickel, Ni	58.7	8907	Ferro
29	Copper, Cu	63.55	8933	-6.87×10^{-11}
30	Zinc, Zn	65.38	7135	-1.44×10^{-10}
31	Gallium, Ga	69.72	5905	-2.72×10^{-10}
32	Germanium, Ge	72.59	5323	-9.64×10^{-11}
33	Arsenic, As	74.92	5776	-6.87×10^{-11}
34	Selenium, Se	78.96	4808	-3.16×10^{-10}
35	Bromine, Br	79.9	3120	—
36	Krypton, Kr	83.8	3000	—
37	Rubidium, Rb	85.47	1533	2.13×10^{-10}
38	Strontium, Sr	87.62	2583	1.16×10^{-9}
39	Yttrium, Y	88.91	4475	2.40×10^{-9}
40	Zirconium, Zr	91.22	6507	1.53×10^{-9}
41	Niobium, Nb	92.91	8578	2.56×10^{-9}
42	Molybdenum, Mo	95.94	10222	1.15×10^{-9}
43	Technetium, Tc	97	11496	3.01×10^{-9}
44	Ruthenium, Ru	101.1	12360	5.43×10^{-10}
45	Rhodium, Rh	102.9	12420	1.40×10^{-9}
46	Palladium, Pd	106.4	11995	7.13×10^{-9}
47	Silver, Ag	107.9	10500	-2.45×10^{-10}
48	Cadmium, Cd	112.4	8647	-2.48×10^{-10}
49	Indium, In	114.8	7290	-8.04×10^{-10}
50	Tin, Sn	118.7	7285	-4.75×10^{-10}
51	Antimony, Sb	121.7	6692	-1.22×10^{-9}
52	Tellurium, Te	127.6	6247	-4.98×10^{-10}
53	Iodine, I	126.9	4953	-5.58×10^{-10}
54	Xenon, Xe	131.3	3560	-5.51×10^{-10}
55	Caesium, Cs	132.9	1900	3.72×10^{-10}
56	Barium, Ba	137.3	3594	2.61×10^{-10}
57	Lanthanum, La	138.9	6174	1.53×10^{-9}
58	Cerium, Ce	140.1	6711	3.04×10^{-8}
59	Praseodymium, Pr	140.9	6779	6.30×10^{-8}
60	Neodymium, Nd	144.2	7000	7.07×10^{-8}
61	Promethium, Pm	145	7220	—
62	Samarium, Sm	150.4	7536	2.29×10^{-8}
63	Europium, Eu	152	5248	4.27×10^{-7}
64	Gadolinium, Gd	157.2	7870	Ferro
65	Terbium, Tb	158.9	8267	1.83×10^{-6}
66	Dysprosium, Dy	162.5	8531	1.30×10^{-6}
67	Holmium, Ho	164.9	8797	9.05×10^{-7}
68	Erbium, Er	167.3	9044	5.57×10^{-7}
69	Thulium, Tm	168.9	9325	3.21×10^{-7}
70	Ytterbium, Yb	173	6966	3.13×10^{-9}
71	Lutetium, Lu	175	9842	2.28×10^{-9}
72	Hafnium, Hf	178.5	13276	9.46×10^{-10}
73	Tantalum, Ta	180.9	16670	1.94×10^{-9}
74	Tungsten, W	183.9	19254	7.36×10^{-10}
75	Rhenium, Re	186.2	21023	8.49×10^{-10}
76	Osmium, Os	190.2	22580	1.24×10^{-10}
77	Iridium, Ir	192.2	22550	3.21×10^{-10}
78	Platinum, Pt	195.1	21450	2.54×10^{-9}
79	Gold, Au	197	19281	-3.51×10^{-10}
80	Mercury, Hg	200.6	13546	—
81	Thallium, Tl	204.4	11871	-6.40×10^{-10}
82	Lead, Pb	207.2	11343	-2.88×10^{-10}
83	Bismuth, Bi	209	9803	-3.52×10^{-9}
84	Polonium, Po	209	9400	—
85	Astatine, At	210	—	—
86	Radon, Rn	222	4400	—
87	Francium, Fr	223	—	—
88	Radium, Ra	226	5000	—
89	Actinium, Ac	227	10060	—
90	Thorium, Th	232	11725	1.67×10^{-9}
91	Protactinium, Pa	231	15370	—
92	Uranium, U	238	19050	5.14×10^{-9}
93	Neptunium, Np	237	20250	—
94	Plutonium, Pu	244	19840	7.73×10^{-9}
95	Americium, Am	243	13670	1.22×10^{-8}

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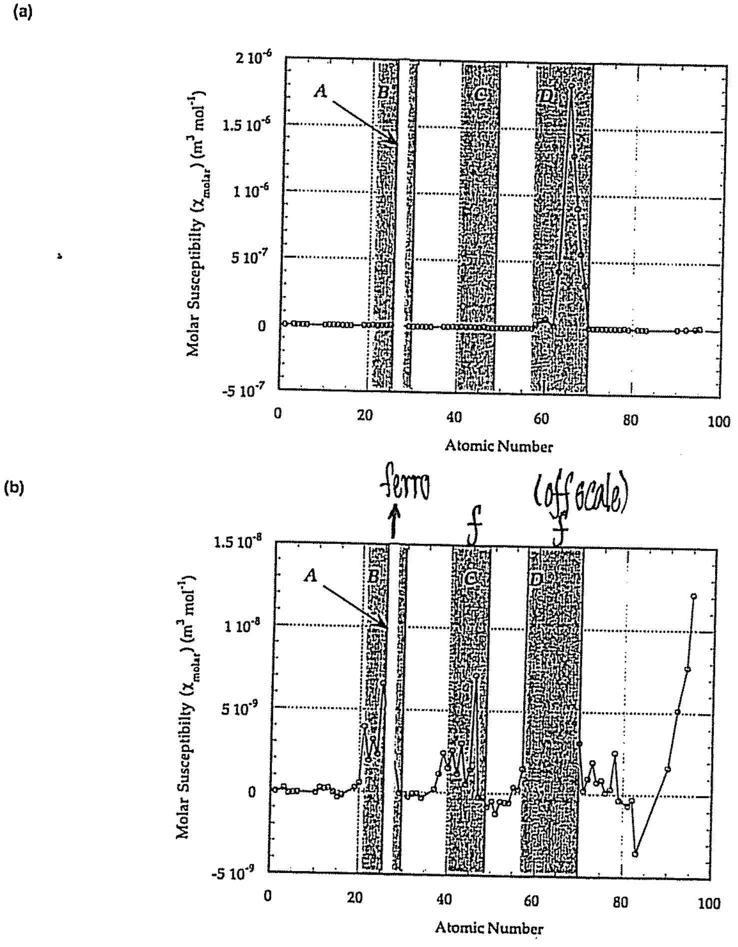
- Most elemental solids: paramagnetic or diamagnetic
- Only a few are ferromagnetic.

Figure W2.3 Summary of molar magnetic susceptibility data for the solid elements shown (a) at a large scale and (b) on a detailed scale. The bands *B*, *C* and *D* mark the first and second row of transition elements, and the lanthanide series. The band *A* marks the ferromagnetic elements Fe, Co and Ni. **Note:** points greater than zero correspond to a paramagnetic response and points less than zero correspond to a diamagnetic response.



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free space

$\vec{B}, \vec{H}$ ← due to some source (current) outside

$\vec{B} = \mu_0 \vec{H}$

"magnetic induction"

$\vec{B} = ?$

$$\vec{B} = \mu_0 \vec{H} + \mu_0 \vec{M} = \mu_0 (\vec{H} + \vec{M})$$

$\vec{B}$ is altered by presence of material

$$\vec{B} = \mu_0 (\vec{H} + \chi \vec{H}) = \mu_0 (1+\chi) \vec{H}$$

$$\equiv \mu_0 \mu_r \vec{H} = \mu \vec{H}$$

permeability

$\mu_r = 1 + \chi$

relative permeability

magnetic susceptibility

For para and dia magnetic materials, $|\chi| \ll 1$

$\Rightarrow \mu_r \approx 1$ or $\mu \approx \mu_0$

B. Magnetic Moment of an atom

- The magnetic properties of materials come from:
  - magnetic moments of the atoms (or group of atoms)
  - interaction between moments and interaction between moments and applied field.

(a) Electron Spin[+]

Recall: Spin angular momentum $\vec{S}$

$$S = \text{magnitude of spin } \vec{S} = \sqrt{s(s+1)}\,\hbar$$

Electrons: $s = \frac{1}{2}$ ("spin-½ particle")

$$S_z = m_s \hbar \quad \text{where } m_s = \frac{1}{2}, -\frac{1}{2}$$

so that

$$S_z = \frac{\hbar}{2} \quad \text{or} \quad \frac{-\hbar}{2} \quad \text{for an electron}$$

- Associated with $\vec{S}$ is a magnetic moment $\vec{\mu}_{spin}$:

$$\boxed{\vec{\mu}_{spin} = -\frac{e}{m_e}\vec{S}}$$

Writing $\vec{\mu}_{spin} = \frac{-e}{2m_e} g_s \vec{S}$, we have $g_s = 2$

[+] Spin or Spin angular momentum has no classical analogy. Hence, the origin of magnetism is entirely Quantum in nature.

- Since S_z can only be $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$, a measurement of μ_z along any direction can only yield one of the two values

$$\underbrace{+\frac{e\hbar}{2m_e}}_{\substack{\equiv \\ +\mu_B}} \quad \text{or} \quad \underbrace{-\frac{e\hbar}{2m_e}}_{\substack{\equiv \\ -\mu_B}}$$

$$\boxed{\mu_B = \text{"Bohr Magneton"} = \frac{e\hbar}{2m_e} = 9.27\times10^{-24}\,\overset{\text{or J/Tesla}}{\overbrace{A\cdot m^2}}}$$

$$= 5.79\times10^{-5}\ \text{eV/Tesla}$$

Remarks:

- We use $g_s = 2$. Note that "spin" is not included in non-relativistic QM (Schrödinger). The search of a theory from which g_s can be calculated had led to the establishment of QED. The accuracy of g_s, when compared with high precision experimental value, obtained by QED calculations is the most accurate calculation from a theory of physics.
- We have protons and neutrons (spin-½) in a nucleus. But $\vec{\mu}_{spin}$ is much smaller than that of electrons.

(b) Orbital Magnetic Moment

Electron in an atom has orbital angular momentum $\vec{L}$

$$L = \text{magnitude of } \vec{L} = \sqrt{l(l+1)}\,\hbar$$

$$L_z = m_l \hbar \quad \text{with } m_l = l, l-1, \cdots, -l$$

Associated with $\vec{L}$ is an orbital magnetic moment $\vec{\mu}_{orb}$

$$\boxed{\vec{\mu}_{orb} = \frac{-e}{2m_e}\vec{L}}$$

∴ The component of $\vec{\mu}_{orb}$ along a direction can take on one of the $(2l+1)$ values.

Remarks

- Spin angular momentum or simply "spin" is an intrinsic property of a particle, just like the charge and mass.
- Orbital angular momentum is an extrinsic property, i.e., it depends on the state of the electron, e.g. an electron in a hydrogen atom can be in $s\,(l=0)$, $p\,(l=1)$, $d\,(l=2)$, $f\,(l=3)$ states or in a state with no definite value of $\vec{L}$.

- Writing $\vec{\mu}_{spin}$ and $\vec{\mu}_{orb}$ in the same form:

$$\vec{\mu} = \frac{-e}{2m_e}\, g \,(\text{corresponding angular momentum})$$

↳ $\vec{S}$ or $\vec{L}$

$g = 2$ spin angular momentum

$g = 1$ orbital angular momentum

- But spin and orbital effects may be coupled (spin-orbit interaction)[+]

↳ Russell-Saunders coupling scheme

↳ add up $\vec{L}$ of electrons, add up $\vec{S}$ of electrons, then couple

$$\vec{J} = \vec{L} + \vec{S} \qquad (\text{total angular momentum})$$

$$|\vec{J}| = \sqrt{j(j+1)}\,\hbar$$

Write:

$$|\mu_J| = \frac{-e}{2m_e}\, g\, |\vec{J}|$$

$$= \frac{-e\hbar}{2m_e}\, g \sqrt{j(j+1)}$$

$$= -\mu_B\, g \sqrt{j(j+1)}$$

g = Lande g-factor

Note:

$$\vec{\mu} = \vec{\mu}_{spin} + \vec{\mu}_{orb}$$

$$\propto (2\vec{S} + \vec{L})$$

is not parallel to $\vec{J}$

[+] Another scheme of coupling is to get $\vec{J}$ for each electron first and then couple the $\vec{J}$'s (JJ coupling).

(c) Multi-electron Atoms

- Each electron has $\vec{S}$ and $\vec{L}$ ($\vec{\mu}_{spin}$ and $\vec{\mu}_{orb}$)
- Pauli Exclusion Principle ⇒ each atomic orbital can hold at most two electrons with opposite spin.
- Complete (filled/full) shells do not contribute to the magnetic moment of the atom.
- Only incomplete shells and unpaired electrons contribute to atomic magnetic moment. +
  - Transition metals have incomplete shell (d-shell) and have the strongest moment.
    [Hund's rule for isolated ions]

Atoms with Zero magnetic moment: Diamagnetism

Atoms with non-zero magnetic moment:
Paramagnetism or Ferromagnetism.

+ There are also contributions due to spin and orbital response of conduction electrons.

C. General Picture

In a solid, there are

- electrons in the filled core orbitals (core electrons)
- electrons in partially filled orbitals (also "core electrons") that belong to the ions
- conduction electrons (metals)

and electron responds to $\vec{H}$ in two ways:

- spin response
- orbital response

} may couple into $\vec{J}$

	Spin Response	Orbital response
Core Electrons (filled shells)	No response (all cancelled)	Diamagnetic (Larmor/Langevin)
Core Electrons (partially filled shells)	Paramagnetic (Curie)	Paramagnetic (Curie)
	may couple into $\vec{J}$ (Paramagnetic) (Curie)	
Conduction electrons (metal)	Paramagnetic (Pauli)	Diamagnetic (Landau)

Experimentally, one measures the combined net effect.

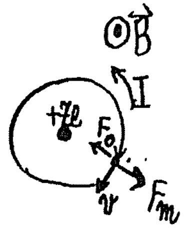
D. Diamagnetism

- Observed in solids in which the basic entities have closed shell structure (e.g., Ne, Ar, Kr, ions in ionic crystals)
- But the diamagnetic effect is actually there for all core electrons
  - become apparent when ions/atoms do not have magnetic moment (full shell)
  - masked by other effects (e.g. paramagnetic) when ions/atoms have magnetic moment.
- It stems from Lenz Law

(i) Classical Description

Consider an electron (-e) in circular orbit around a fixed nucleus (+Ze)

ω_0 = angular speed



charge (-e)

$\vec{\mu}_0 = \frac{e\omega_0}{2} r^2 \hat{z}$

$\vec{B}=0, \quad F_0 = \frac{Ze^2}{4\pi\varepsilon_0 r^2} = m\omega_0^2 r$

$\vec{B} = B\hat{z},$

$F_0 - F_m = m\omega^2 r$

$m\omega_0^2 r - eBr\omega = m\omega^2 r$

modified due to $\vec{B}$

$\Rightarrow \omega \approx \omega_0 - \frac{eB}{2m}$

(for small field)

$\vec{\mu} = \frac{e}{2}\left(\omega_0 - \frac{eB}{2m}\right) r^2 \hat{z}$

$= \vec{\mu}_0 - \frac{e^2 r^2}{4m} B\hat{z}$

$= \vec{\mu}_0 + \Delta\vec{\mu}$

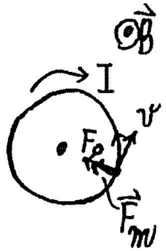
$\Delta\vec{\mu} = -\frac{e^2 r^2}{4m} B\hat{z}$

$= -\frac{e^2 r^2}{4m} \vec{B}$

antiparallel to $\vec{B}$

$\Downarrow$

diamagnetic response



$\vec{\mu}_0 = \frac{e}{2}\omega_0 r^2 (-\hat{z})$

$\vec{B} = B\hat{z}$

$F_0 + F_m = m\omega^2 r$

$m\omega_0^2 r + eBr\omega = m\omega^2 r$

modified due to $\vec{B}$

$\Rightarrow \omega \approx \omega_0 + \frac{eB}{2m}$

(for small field)

$\vec{\mu} = -\frac{e}{2}\left(\omega_0 + \frac{eB}{2m}\right)\hat{z}$

$= \vec{\mu}_0 - \frac{e^2 r^2}{4m} B\hat{z}$

$= \vec{\mu}_0 + \Delta\vec{\mu}$

$\Delta\vec{\mu} = -\frac{e^2 r^2}{4m} B\hat{z}$

antiparallel to $\vec{B} = +B\hat{z}$

$\Downarrow$

diamagnetic response

- Every orbiting electron is expected to respond as

$$\Delta\mu = -\frac{e^2 r^2}{4m} B \qquad (*)$$

- A better estimation:
  - QM: orbitals in 3D (not 2D)
  - "r^2" in (*) $\approx \langle x^2 \rangle + \langle y^2 \rangle$ in QM

$$\approx \frac{2}{3}\langle r^2 \rangle \quad \text{in QM}$$

$$= \frac{2}{3}\overline{r^2}$$

∴ every orbiting electron is expected to respond as

$$\Delta\mu = -\frac{e^2}{6m}\overline{r^2} B$$

- Counting:

N_e = number of electrons in atom (Z) / ion

$$N = \frac{\mathcal{N}_{at}}{V} = \frac{\text{number of atoms in volume } V}{V}$$

$$\therefore N_e \cdot N = N_e \cdot \frac{\mathcal{N}_{at}}{V} = \#\text{ electrons per unit volume}$$

$$\vec{M} = -\left(\frac{e^2}{6m}\overline{r^2}\right) \cdot N_e \cdot \frac{\mathcal{N}_{at}}{V} \vec{B} = \text{magnetic moment per unit volume}$$

$\vec{B} = \mu\vec{H} \approx \mu_0 \vec{H}$ (since expect χ to be small compared to 1)

$$\vec{M} = \underbrace{-\frac{\mu_0 e^2}{6m} \cdot N_e \cdot \frac{\mathcal{N}_{at}}{V}\overline{r^2}}_{\text{a negative magnetic susceptibility}} \vec{H} \qquad \mu_0 = 4\pi \times 10^{-7}\,\text{N}\cdot\text{Amp}^{-2}$$

$$\boxed{\chi = -\frac{\mu_0 e^2}{6m} \cdot N_e \cdot \frac{\mathcal{N}_{at}}{V}\overline{r^2}}$$

Larmor diamagnetic susceptibility

Estimate:

Typical:	Solid Argon: (at 4K)
$\frac{\mathcal{N}_{at}}{V} \cong 10^{29}\,\text{m}^{-3}$	$\frac{\mathcal{N}_{at}}{V} = 2.66 \times 10^{28}\,\text{m}^{-3}$
$N_e \cong 10$	$N_e = 18$
$\overline{r^2} \sim \text{Å}^2 \sim 10^{-20}\,\text{m}^2$	$\overline{r^2} \sim 10^{-20}\,\text{m}^2$
$\chi \approx -10^{-5}$ $(\ll 1)$	$\chi \approx -1.08 \times 10^{-5}$ $(\ll 1)$

$|\mu_0 M| \sim |\chi| B \sim 10^{-5} B \ll B$ (a weak response)

$$\chi_{molar} = \chi \cdot V_{molar} = \chi \cdot \underbrace{\left(\frac{V}{\mathcal{N}_{at}} \cdot N_A\right)}_{\sim 10^{-6}}$$

N_A ← Avogadro's number

$$\Rightarrow \chi_{molar} \sim -10^{-11}\,\text{m}^3\,\text{mol}^{-1}$$

	χ		χ
He	-1.9×10^{-6}	Li^+	0.7×10^{-6}
Ne	-7.6	Na^+	6.1
Ar	-19	K^+	14.6
Kr	-29	Mg^{2+}	4.3
Xe	-44	Ca^{2+}	10.7
F^-	-9.4	Sr^{2+}	18.0
Cl^-	-24.2		
Br^-	-34.5		

- Some data on diamagnetic materials
- Observe that χ is more negative when there are more electrons in the closed shell structure
- This diamagnetic response is there for <u>every</u> <u>core electron</u>

  ↖ <u>note</u>: electrons involved in covalent bonds or $\underbrace{\text{metallic bonds}}_{\text{conduction electrons}}$ have orbits very different from what we considered!

- $\chi \sim (-10^{-5}) - (-10^{-6}) \ll 1$

  When there are other responses, this small diamagnetic response is usually covered up!

(ii) <u>Diamagnetism</u> : <u>Quantum Mechanical Description</u>

- Spin is something extra in non-relativistic QM. In the presence of a field $\vec{B}$, there is an <u>interaction</u> (potential) <u>energy</u>

  $(-\vec{\mu}_{spin} \cdot \vec{B})$ in the Hamiltonian

  ↳ $\vec{\mu}_{spin} = -\frac{e}{2m_e} g_s \vec{S}$ with $g_s = 2$ for most purposes

- How about $\vec{\mu}_{orb}$?

  - taken care of by properly handling the <u>kinetic energy term</u> in the Hamiltonian

    $\vec{B} = \vec{\nabla} \times \vec{A}$ ↜ vector potential

- particle of mass m and <u>charge q</u>:

  $$K.E. = \frac{1}{2}mv^2 = \frac{1}{2m}(\vec{p} - q\vec{A})^2$$

  ↑ • <u>NOT</u> the mechanical momentum
  • the <u>canonical momentum</u>
  ↳ the $\vec{p}$ that becomes $-i\hbar\vec{\nabla}$ in QM

- For an electron ($q=-e$) in an external magnetic induction $\vec{B}$:

  $$\boxed{\hat{H} = \frac{1}{2m_e}(\hat{\vec{p}} + e\vec{A})^2 - \vec{\mu}_{spin} \cdot \vec{B} + V_{atom}(\vec{r})} \quad (1)$$

- For $\vec{B} = B\hat{z}$, a possible choice is $\vec{A} = \left(-\frac{By}{2}, \frac{Bx}{2}, 0\right)$ Coulomb gauge

- Eq.(1) includes the effects of applied magnetic field (not only diamagnetic response)
- More properly, include $V_{atom}(\vec{r})$ for an atom and $V(\vec{r})$ for a crystal
- Here, we focus on the extra terms due to $\vec{B}$

Write $\hat{H}$ out:

$$\hat{H} = \underbrace{\frac{p^2}{2m_e} + V_{atom}(\vec{r})}_{\hat{H}_0(\vec{B}=0)} + \underbrace{\frac{eB}{2m_e}\overbrace{(xp_y - yp_x)}^{L_z} + \overbrace{\frac{e^2B^2}{8m_e}(x^2+y^2)}^{\text{leads to diamagnetic response}} + \overbrace{\frac{eB}{m_e}S_z}^{\text{due to spin}}}_{\hat{H}_1 \text{ (perturbation due to } \vec{B})}$$

For an atom/ion with Ne electrons:

$$\hat{H}_1 = \frac{eB}{2m_e}\sum_{j=1}^{N_e}(L_z(j) + 2S_z(j)) + \frac{e^2B^2}{8m_e}\sum_{j=1}^{N_e}(x_j^2+y_j^2)$$

$$= \underbrace{\frac{eB}{2m_e}(L_z + 2S_z)}_{\sim B} + \underbrace{\frac{e^2B^2}{8m_e}\sum_{j=1}^{N_e}(x_j^2+y_j^2)}_{\sim B^2}$$

where $L_z = \sum_{j=1}^{N_e} L_z(j)$; $S_z = \sum_{j=1}^{N_e} S_z(j)$

(z-component of total orbital angular momentum) (z-component of total spin angular momentum)

$$\hat{H}_1 = \underbrace{\frac{eB}{2m_e}(L_z + 2S_z)}_{\sim B\ (-\vec{\mu}_L\cdot\vec{B} - \vec{\mu}_S\cdot\vec{B})\ \text{(paramagnetic)}} + \underbrace{\frac{e^2B^2}{8m_e}\sum_{j=1}^{N_e}(x_j^2+y_j^2)}_{\sim B^2\ \text{(diamagnetic)}}$$

- Only when paramagnetic term does not contribute, the diamagnetic term will be apparent.

- When $\vec{B}=0$, $\underbrace{\hat{H}_0|\Psi_0\rangle}_{\text{ground state}} = \overset{\uparrow}{\underset{\text{ground state energy}}{\mathcal{E}_0}}|\Psi_0\rangle$

- $\vec{B} \neq 0$, ground state energy is shifted by

$$\langle\Psi_0|\hat{H}_1|\Psi_0\rangle \quad \text{(1st order perturbation theory)}$$

- Closed shell (e.g. full p-shell, full s-shell)

$\Rightarrow \langle\Psi_0|L_z|\Psi_0\rangle = 0$ and $\langle\Psi_0|S_z|\Psi_0\rangle = 0$

(ground state has zero magnetic moment, since it is spherically symmetric)

thus, $\sim B$ term does not contribute.

In this case, the shift in energy is

$$\frac{e^2B^2}{8m_e}\langle\Psi_0|\sum_{j=1}^{N_e}(x_j^2+y_j^2)|\Psi_0\rangle$$

$$= \frac{e^2B^2}{8m_e}\cdot\frac{2}{3}\langle\Psi_0|\sum_{j=1}^{N_e}(x_j^2+y_j^2+z_j^2)|\Psi_0\rangle$$

$$= \frac{e^2B^2}{12m_e}\langle\Psi_0|\sum_{j=1}^{N_e}r_j^2|\Psi_0\rangle$$

$$\equiv \frac{e^2B^2}{12m_e}\cdot N_e\langle r^2\rangle = \frac{e^2B^2}{12m_e}\cdot N_e\overline{r^2}$$

$$\therefore \mathcal{E}_{0,\text{perturbed}} = \mathcal{E}_0 + \underbrace{\frac{e^2B^2}{12m_e}\cdot N_e\overline{r^2}}_{\sim B^2 \text{ correction}}$$

Induced magnetic moment (in an atom/ion)

$$= \mu_z = -\frac{\partial}{\partial B}\left(\frac{e^2B^2}{12m_e}\cdot N_e\overline{r^2}\right)$$

$$= -\frac{e^2}{6m_e}\cdot N_e\cdot\overline{r^2}\cdot B$$

diamagnetic

this is the same result as obtained by classical treatment

E. Atoms with a Partially filled shell

- leads to paramagnetism and ferromagnetism

Now $\langle\Psi_0|(L_z+2S_z)|\Psi_0\rangle \neq 0$ (see (*) on p. XIV-⑫)

and the atom has a permanent magnetic moment

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

where $\vec{L} = \sum_i \vec{l}_i$

sum over electrons in atom

$\vec{S} = \sum_i \vec{s}_i$

[Note: Contribution of a closed shell = 0]

- $\boxed{\text{In general, there is spin-orbit interaction.}}$

In this case, useful to form

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

total angular momentum

LS coupling: energy states of atom are simultaneous eigenstates of J^2, J_z, L^2, S^2

(instead of L^2, L_z, S^2, S_z)

Quantum physics:

$$\hat{J}^2\,|J, m_J, L, S\rangle = J(J+1)\hbar^2\,|J, m_J, L, S\rangle$$

$$\hat{L}^2\,|J, m_J, L, S\rangle = L(L+1)\hbar^2\,|J, m_J, L, S\rangle$$

$$\hat{S}^2\,|J, m_J, L, S\rangle = S(S+1)\hbar^2\,|J, m_J, L, S\rangle$$

$$\hat{J}_z\,|J, m_J, L, S\rangle = m_J\hbar\,|J, m_J, L, S\rangle$$

where m_J can only take on

$$m_J = \underbrace{J, J-1, \cdots, -J+1, -J}_{(2J+1)\text{ values for given } J}$$

- From QM consideration, values of L, S, J for <u>the states of lowest energy</u> (work for isolated atoms or ions in weak applied fields) are determined by <u>Hund's rules</u>. These rules should be applied <u>one by one in order</u>.

<u>HR1</u>: S takes the maximum value allowed by the Pauli Exclusion Principle — as many as possible of the electrons must have parallel spins.
[Each electron, up to half the number of states in the shell, gives $+\frac{1}{2}$ to S. Beyond half-fill, each contributes $-\frac{1}{2}$ to S.]

<u>HR2</u>: L takes the maximum value consistent with the value of S — the electrons have their orbital angular momentum as well aligned as possible.

<u>HR3</u>: $J = |L-S|$ for a shell less than half-full

$J = L+S$ for a shell more than half-full

<u>Examples</u>:

		V^{3+}	l_z	Fe^{2+}
	Number of 3d electrons	2		6
	Occupancy of states as given by Hund's rules	—↑—— —↑—— ———— ———— ————	2 1 0 −1 −2	—↑—↓— —↑—— —↑—— —↑—— —↑——
HR1	Hund's rule 1: determination of S. Make as many spins parallel as possible	$S = \frac{1}{2} + \frac{1}{2}$ $= 1$		$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2}$ $= 2$
HR2	Hund's rule 2: determination of L. Make $\sum l_z$ as large as possible	$L = \sum l_z$ $= 2 + 1 = 3$		$L = 2 + 1 + 0 - 1 - 2 + 2$ $= 2$
HR3	Hund's rule 3: determination of J.	Shell less than half-full $J = \lvert L - S \rvert = 2$		Shell more than half-full $J = L + S = 4$
	Spectroscopic notation, $^{2S+1}L_J$	$^3F_2$		$^5D_4$ $\quad ^{2S+1}L_J$

Use of Hund's rules to calculate the quantum numbers S, L and J of the ground states of the V^{3+} and Fe^{2+} ions. The 3d shell has $l = 2$ so there are $2l + 1$ sublevels corresponding to $l_z = -2, -1, 0, 1, 2$ as indicated. In the spectroscopic notation, values of L of 0, 1, 2, 3, 4, 5, 6, ... are indicated by letters S, P, D, F, G, H, I, ..

Remarks:

- HR1 and HR2, which determine the values of L and S, are robust [∵ associated with Coulomb interaction between electrons]
- HR3, which determines the value of J, is not as robust.
  It works for isolated atoms/ions and weak applied fields.
  [∵ associated with spin-orbit interaction, and thus with an internal magnetic field generated by relative motion of electron and nucleus]
  - May fail in a large applied field and/or under the influence of neighboring ions in a solid.

F. Interaction of a permanent dipole moment with an applied magnetic field

- partially filled shells: magnetic moment
- $\vec{J} = \vec{L} + \vec{S}$
  ↑ useful because $\vec{L}$ and $\vec{S}$ couple and they are no longer good quantum numbers
  $[J, m_J, L, S]$ instead of $[L, L_z, S, S_z]$

Note: $\vec{\mu}_{total} = -\frac{\mu_B}{\hbar}(\vec{L} + 2\vec{S})$ is NOT parallel to $\vec{J}$

- Key idea:
  Due to L-S coupling, the atoms/ions react to an applied field $\vec{B} = B\hat{z}$ as if they have an effective magnetic dipole moment $\vec{\mu}_{eff}$ corresponding to the component of $\vec{\mu}_{total}$ parallel to $\vec{J}$.

Write: $\boxed{\vec{\mu}_{eff} = -\frac{\mu_B}{\hbar}\, g\, \vec{J}}$

↑ Landé g-factor

The Landé g-factor: A classical description+

$$\vec{\mu}_{total} \propto \vec{L}+2\vec{S} = -\frac{\mu_B}{\hbar}(\vec{L}+2\vec{S})$$

Need the projection of $\vec{L}+2\vec{S}$ in the direction of $\vec{J}$

$\therefore$ Want to get

$$\vec{\mu}_{eff} = \left(\vec{\mu}_{total}\cdot\frac{\vec{J}}{J}\right)\underbrace{\frac{\vec{J}}{J}}_{\text{unit vector in } \vec{J}} \equiv -\frac{\mu_B}{\hbar} g \vec{J}$$

$$\therefore \boxed{g = (\vec{L}+2\vec{S})\cdot\frac{\vec{J}}{J^2}}$$

$$g = (\vec{L}+\vec{S}+\vec{S})\cdot\frac{\vec{J}}{J^2} = (\vec{J}+\vec{S})\cdot\frac{\vec{J}}{J^2} = 1 + \frac{\vec{J}\cdot\vec{S}}{J^2}$$

$$\because \vec{L}+\vec{S}=\vec{J} \Rightarrow \vec{L}=\vec{J}-\vec{S} \Rightarrow L^2 = J^2+S^2-2\vec{J}\cdot\vec{S}$$

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

$$\therefore \boxed{g = 1 + \frac{J^2+S^2-L^2}{2J^2} = \frac{3}{2} - \frac{(L^2-S^2)}{2J^2}} \quad \text{classical}$$

QM : $J^2 \rightarrow J(J+1)\hbar^2$; $S^2 \rightarrow S(S+1)\hbar^2$; $L^2 \rightarrow L(L+1)\hbar^2$

$$\boxed{g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} = \frac{3}{2} - \frac{L(L+1)-S(S+1)}{2J(J+1)}}$$

+ See Ashcroft and Mermin, "Solid State Physics" (Appendix P) for a quantum mechanical treatment.

- Given atoms/ions: ↙ Atomic Physics
  - (i) Hund's rules ⇒ S, L, J
  - (ii) S, L, J ⇒ Landé g factor
  - (iii) $\vec{\mu}_{eff} = -\frac{\mu_B}{\hbar} g \vec{J}$

- In the presence of an applied field $\vec{B}$:

  an extra term $\boxed{-\vec{\mu}_{eff}\cdot\vec{B}}$ appears in the Hamiltonian (c.f. Zeeman effect)

  For $\vec{B} = B\hat{z}$, the extra term becomes:

$$-\vec{\mu}_{eff}\cdot\vec{B} = \frac{\mu_B}{\hbar} g \vec{J}\cdot\hat{z} B = \frac{\mu_B}{\hbar} g B J_z$$

  In QM, this becomes an operator

$$\boxed{\frac{\mu_B}{\hbar} g B \hat{J}_z} \quad \Big| \; \hat{J}_z \text{ has eigenvalues } m_J\hbar$$

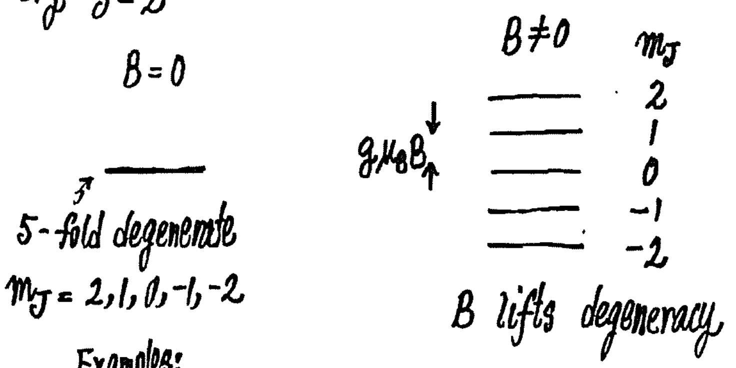
- In a state with $|J, m_J, L, S\rangle$, it is also an eigenstate of $\frac{\mu_B}{\hbar} g B \hat{J}_z$

$$\frac{\mu_B}{\hbar} g B \hat{J}_z |J, m_J, L, S\rangle = \overset{\propto B}{(\mu_B g B m_J)} |J, m_J, L, S\rangle$$

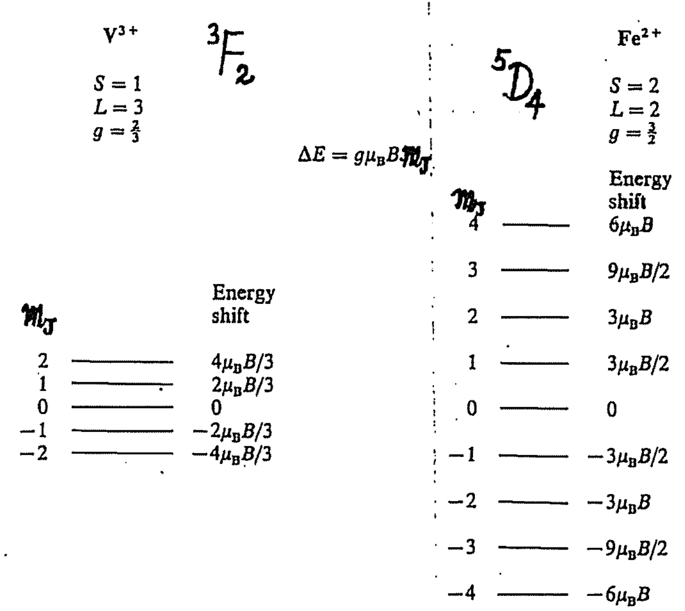
extra term in energy eigenvalue · depends on m_J

$\therefore \vec{B}$ lifts the degeneracy in m_J

e.g. $J=2$



Examples:



Splitting of ground state degeneracy by $\vec{B}$

Note: The lowest energy corresponds to the <u>maximum possible alignment of $\vec{\mu}_{eff}$ with $\vec{B}$</u>

- paramagnetism and ferromagnetism

G. <u>Paramagnetism</u>

- Calculate the Magnetization of paramagnetic ions

• If permanent dipoles in a solid <u>behave independently</u> of each other (N non-interacting atoms/ions), then $\vec{M}$ can be readily evaluated by simple statistical mechanics (non-interacting system)

<u>Physical argument</u>:

- Relative occupation of the energy levels ($g\mu_B m_J B$) is given by the Boltzmann factor

$$e^{-(-\vec{\mu}_{eff}\cdot\vec{B})/k_BT} = e^{-g\mu_B m_J B/k_BT}$$

$$\because \mu_{eff,z} = -\frac{\mu_B}{\hbar} g J_z = -\mu_B g m_J \qquad (\vec{B} = B\hat{z})$$

For n moments per unit volume, the Magnetization $\vec{M}$ is:

$$M = \frac{n\sum_{m_J=-J}^{+J} (-\mu_B g m_J)\, e^{-g\mu_B m_J B/k_BT}}{\sum_{m_J=-J}^{+J} e^{-g\mu_B m_J B/k_BT}}$$

Define: $z = \sum_{m_J=-J}^{+J} e^{-g\mu_B m_J B/k_BT} = \sum_{m_J=-J}^{+J} e^{-\beta g\mu_B m_J B}$

(i) $M = n\left(\frac{1}{\beta}\frac{\partial \ln z}{\partial B}\right)$

(ii) Sum up z

Call $\beta g\mu_B J B \equiv x$

$$z = \sum_{m_J=-J}^{+J} e^{-x\, m_J/J} = e^{x}\sum_{m_J=-J}^{+J} e^{-x\, m_J/J}\, e^{-x}$$

$$= e^{x}\sum_{m_J=-J}^{J} e^{-\frac{x}{J}(m_J+J)}$$

$$= e^{x}\sum_{n=0}^{2J}\left(e^{-\frac{x}{J}}\right)^{n}$$

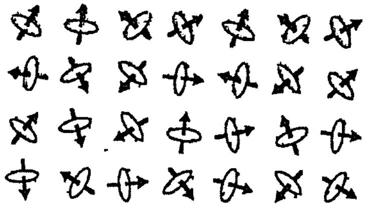
$$= e^{x}\,\frac{1-e^{-\frac{x}{J}(2J+1)}}{1-e^{-x/J}}$$

$$\sum_{n=0}^{N} x^{n} = \frac{1-x^{N+1}}{1-x}$$

(geometric series)

$$= \frac{\sinh\left[\left(\frac{2J+1}{2J}\right)\cdot x\right]}{\sinh\left(\frac{x}{2J}\right)} \quad ; \quad x \equiv \beta g\mu_B J B$$

An illustration of the random orientations of permanent magnetic moments on atoms. The magnetic moment is represent schematically by an arrow and a loop indicating the sense in which an equivalent current would flow.



Physics:
- independent moments
- B wants to align $\vec{\mu}$
- k_BT tends to randomize $\vec{\mu}$

$$\therefore M = n\,\frac{1}{\beta}\frac{\partial}{\partial B}\ln\left(\frac{\sinh\left[\left(\frac{2J+1}{2J}\right)\cdot x\right]}{\sinh\frac{x}{2J}}\right) \quad ; \quad x = \beta g\mu_B J B$$

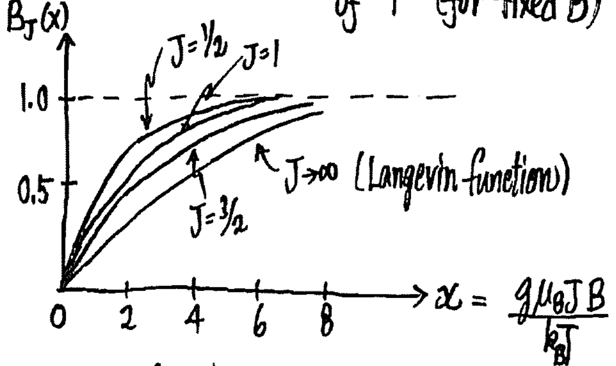
$$= \left(n g\mu_B J\right)\cdot\underbrace{\left(\frac{2J+1}{2J}\coth\left[\left(\frac{2J+1}{2J}\right)\cdot x\right] - \frac{1}{2J}\coth\frac{x}{J}\right)}\quad (Ex)$$

$$= \underbrace{n g\mu_B J}_{M_s}\ \underbrace{B_J(x)}$$

← Brillouin Function

M_s = saturation magnetization ($M \to M_s$ as $\underbrace{x \gg 1}$) high B or low T

Gives M as a function of B (for fixed T)
of T (for fixed B)



(i) High field / Low Temp: $x = \frac{g\mu_B J B}{k_BT} \gg 1$; $B_J(x) \approx 1$

$$M \approx M_s = \underbrace{n g\mu_B J}$$

each atom gives maximum contribution to magnetic moment

(ii) Low field / high temp: $x = \frac{g\mu_B J B}{k_B T} \ll 1$

$$\left(\coth x \approx \frac{1}{x} + \frac{1}{3}x + O(x^3)\ ;\ x \ll 1\right)$$

$$B_J(x) \approx \frac{(J+1)}{3J}\,x \sim x \propto B \qquad (\text{Ex.})$$

$$\therefore M \cong n g\mu_B J \cdot \frac{(J+1)}{3J} \cdot \frac{g\mu_B J B}{k_B T}$$

$$= \frac{n(g\mu_B)^2}{3k_B T} \cdot J(J+1)\,B \qquad B = \mu H \approx \mu_0 H$$

$$= \frac{\mu_0 n \mu_B^2}{3k_B T} g^2 J(J+1)\ H$$

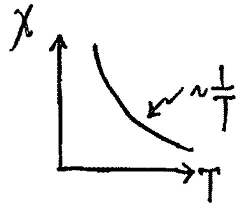
$$= \chi H$$

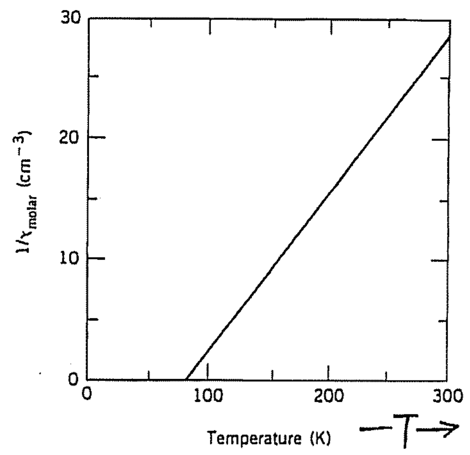
$$\chi = \frac{n\mu_0 \mu_B^2 g^2 J(J+1)}{3k_B T} \equiv \frac{\overset{\text{Curie constant}}{C}}{T} \sim \frac{1}{T} \quad \text{Curie's law}$$

$$= \frac{n\mu_0\mu_B^2 p^2}{3k_B} \cdot \frac{1}{T}$$

$p \equiv$ effective number of Bohr magnetons per atom (ion)

- measure χ vs $T \Rightarrow$ extract C and thus p
- $p_{\text{theory}} = \underset{\text{Landé g-factor}}{g}\sqrt{J(J+1)}$





$\chi \sim \frac{1}{T}$

slope gives the value of exptal p

The reciprocal of the molar susceptibility (in Gaussian units) as a function of temperature for EuO. The line represents theoretical values for noninteracting ions in states with $L' = 0$ and $S' = \frac{7}{2}$, while the dots represent experimental values. The linearity of the plot attests to the validity of the Curie law.

$$p^2 = g^2 J(J+1) \quad (\text{theoretically})$$

Effective Number of Bohr Magnetons p for Rare Earth and Transition Metal Ions (Experimentally Determined)

rare earth ions (4f shell)

Ion	Number of Electrons in Shell	L'	S'	J'	Expt p	(theory)
Cerium(3+)	1	3	$\frac{1}{2}$	$\frac{5}{2}$	2.39	(2.54)
Praseodymium(3+)	2	5	1	4	3.60	(3.58)
Neodymium(3+)	3	6	$\frac{3}{2}$	$\frac{9}{2}$	3.62	(3.62)
Promethium(3+)	4	6	2	4	[illegible]	(2.68)
Samarium(3+)	5	5	$\frac{5}{2}$	$\frac{5}{2}$	1.54	(0.84)
Europium(3+)	6	3	3	0	3.61	0
Gadolinium(3+)	7	0	$\frac{7}{2}$	$\frac{7}{2}$	8.2	(7.94)
Terbium(3+)	8	3	3	6	9.6	(9.72)
Dysprosium(3+)	9	5	$\frac{5}{2}$	$\frac{15}{2}$	10.5	(10.63)
Holmium(3+)	10	6	2	8	10.5	(10.60)
Erbium(3+)	11	6	$\frac{3}{2}$	$\frac{15}{2}$	9.5	(9.59)
Thulium(3+)	12	5	1	6	7.2	(7.57)
Ytterbium(3+)	13	3	$\frac{1}{2}$	$\frac{7}{2}$	4.4	(4.54)
Vanadium(2+)	3	3	$\frac{3}{2}$	$\frac{3}{2}$	3.8	
Chromium(2+)	4	2	2	0	4.9	
Manganese(2+)	5	0	$\frac{5}{2}$	$\frac{5}{2}$	5.9	
Iron(2+)	6	2	2	4	5.4	
Cobalt(2+)	7	3	$\frac{3}{2}$	$\frac{9}{2}$	4.8	
Nickel(2+)	8	3	1	4	3.2	
Copper(2+)	9	2	$\frac{1}{2}$	$\frac{5}{2}$	1.9	

Remarks:

- The J-value (follows from the Hund's rules) and the Landé g-factor (with S and L determined by Hund's rules) give predicted values of $p = g\sqrt{J(J+1)}$ that, in general, agree with exp'tal values in rare-earth ions (4f shell).
- There are a few cases that the predicted values are way off!
  e.g. Eu^{3+} p(measured) = 3.6 p(theory) = 0

Comparison of experimental and theoretical values of p for transition metal ions. The experimental values agree much better with $2[S(S+1)]^{1/2}$ than with $g[J(J+1)]^{1/2}$, indicating that the orbital angular momentum is quenched.

transition metal ions (3d shell)

Ion	Number of 3d electrons	Hund's rule ground state	Measured p	theory p $g[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
K^+	0	$^1S_0$	0	0	0
V^{4+}	1	$^2D_{3/2}$	1.8	1.55	1.73
V^{3+}	2	$^3F_2$	2.8	1.63	2.83
V^{2+}	3	$^4F_{3/2}$	3.8	0.77	3.87 †
Cr^{3+}	3	$^4F_{3/2}$	3.7	0.77	3.87 †
Mn^{4+}	3	$^4F_{3/2}$	4.0	0.77	3.87 †
Cr^{2+}	4	$^5D_0$	4.8	0	4.90 †
Mn^{3+}	4	$^5D_0$	5.0	0	4.90 †
Mn^{2+}	5	$^6S_{5/2}$	5.9	5.92	5.92
Fe^{3+}	5	$^6S_{5/2}$	5.9	5.92	5.92
Fe^{2+}	6	$^5D_4$	5.4	6.70	4.90
Co^{2+}	7	$^4F_{9/2}$	4.8	6.54	3.87 †
Ni^{2+}	8	$^3F_4$	3.2	5.59	2.83 †
Cu^{2+}	9	$^2D_{5/2}$	1.9	3.55	1.73 †

† In transition metal ions, there are many cases that the theoretical prediction doesn't work. Instead, the ions behave as if $L = 0$, and thus $p = 2\sqrt{S(S+1)}$. This feature is called the quenching of orbital angular momentum (due to crystal field).

H. Pauli Paramagnetism

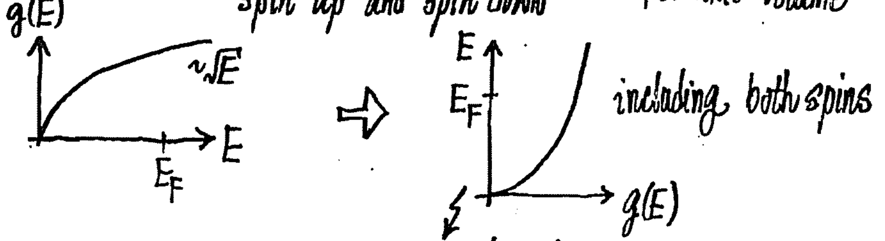
– Magnetism in metals

- free electrons (conduction electrons)
- electron: spin-½ particles (spin response)
- Recall: electron DOS per unit volume in 3D

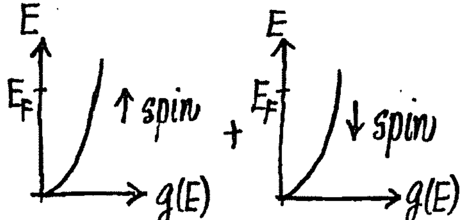
$$g(E) = 2 \cdot \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$

No factor of V because DOS per unit volume

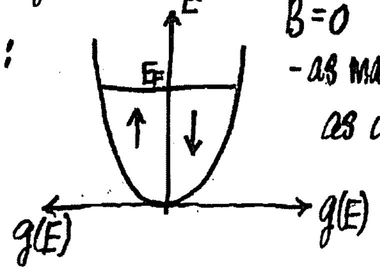
spin up and spin down



separate into "spin-up" and "spin-down" contributions



Draw them back to back:



$\vec{B} = 0$
– as many up spins as down spins

(temp. $T \ll T_F$ ⇒ tiny temp. effect)

"Spin-up" and "Spin-down" Vs "moment-up" and "moment-down"?

$$\vec{\mu}_{spin} = -\frac{e}{m_e}\vec{S}$$

- With $\vec{B} = B\hat{z}$, the extra energy due to $\vec{\mu}_{spin}$ is:

$$-\vec{\mu}_{spin}\cdot\vec{B} = \frac{e}{m_e}\vec{S}\cdot\vec{B} = \frac{e}{m_e}BS_z$$

$S_z = m_s\hbar$ where $m_s = \pm\frac{1}{2}$

Some tend to call $\begin{cases} m_s = +\frac{1}{2} & \text{"spin-up"} \\ m_s = -\frac{1}{2} & \text{"spin-down"} \end{cases}$

(i) $$-\vec{\mu}_{spin}\cdot\vec{B} = \begin{cases} \frac{e\hbar}{2m_e}B = \mu_B B & \text{for } m_s = +\frac{1}{2} \text{ "spin-up"} \\ -\frac{e\hbar}{2m_e}B = -\mu_B B & \text{for } m_s = -\frac{1}{2} \text{ "spin-down"} \end{cases}$$

$m_s = -\frac{1}{2}$ has lower energy than $m_s = +\frac{1}{2}$

(ii) $\mu_{spin,z}$ = z-component of $\vec{\mu}_{spin} = \frac{-e}{m_e}S_z$

"moment-up"

$$\therefore \mu_{spin,z} = \begin{cases} \frac{e\hbar}{2m_e} = \overset{\downarrow}{+}\mu_B & \text{for } m_s = -\frac{1}{2} \text{ "spin-down"} \\ \frac{-e\hbar}{2m_e} = \underset{\uparrow}{-}\mu_B & \text{for } m_s = +\frac{1}{2} \text{ "spin-up"} \end{cases}$$

($\hat{z}$-component opposite to field)
("moment-down": higher energy)

$\therefore$ $\underbrace{\mu_{spin,z} \parallel B}$ has energy LOWERED by $\mu_B B$

Sometimes, people refer to these electrons as "spin-up" (actually "moment-up" or "moment-parallel") and label them ↑

$\underbrace{\mu_{spin,z} \text{ antiparallel to } B}$ has energy RAISED by $\mu_B B$

Sometimes, people refer to these electrons as "spin-down" (actually "moment-down" or "moment-antiparallel") and label them ↓

Effect of $\vec{B} = B\hat{z}$ on free electrons

$\begin{cases} \text{States of "moment-up": lower energy} \\ \text{States of "moment-down": higher energy} \end{cases}$

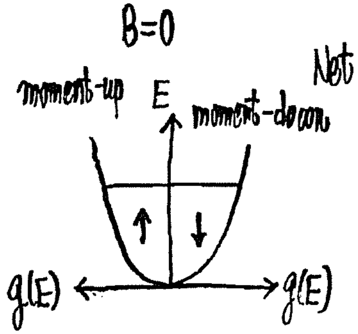
→ fill electrons into states (should fill to some energy)

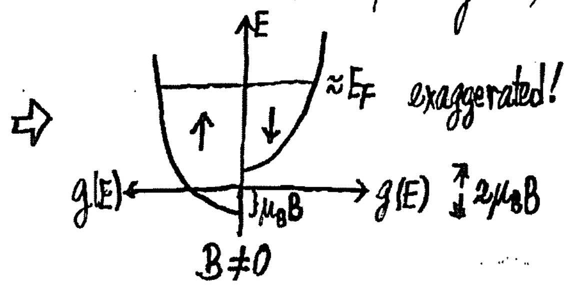
⇓

more "moment-up" electrons than "moment-down" electrons

⇓

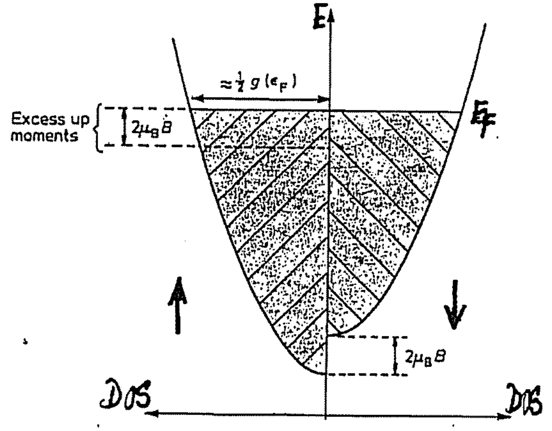
Net moment ($\parallel$ B) for $B \neq 0$ (paramagnetic)





exaggerated!

Estimate[†] the Magnetization [due to spins of free electrons]



← Must fill to the same energy

Note:
$\mu_B = 9.27 \times 10^{-24}\,J/Tesla$
$= \underbrace{5.79 \times 10^{-5}\,eV/Tesla}$
$\Downarrow$
$\mu_B B \ll E_F$ (for practical value of B)

Number of <u>extra electrons</u> per unit volume with "moment-up" (people usually refer to as "spin-up") $= n_\uparrow$

$$= \left(\frac{1}{2} g(E_F)\right) \cdot \mu_B B$$

Number of missing electrons per unit volume with "moment-down" (usually refer to as "spin-down")

$$= n_\downarrow = \left(\frac{1}{2} g(E_F)\right) \mu_B B$$

i.e. take $n_\downarrow$ electrons → change them from $(-\mu_B)$ to $(+\mu_B)$ → $n_\uparrow$ excess electrons

$$M = \frac{1}{2} g(E_F) \mu_B B \cdot 2\mu_B = \mu_B^2 g(E_F) \cdot B$$

[†] The argument here is similar to that of getting the electronic heat capacity.

Ignoring any possible difference of applied field and local field:

$$M = \mu_B^2 g(E_F) B = \mu_B^2 g(E_F) H \mu_0$$
$$= \underbrace{\mu_B^2 \mu_0 g(E_F)} H$$
$$= \underbrace{\chi_{Pauli}} H$$

↳ <u>Pauli spin susceptibility</u>

$$\therefore \boxed{\begin{aligned} \chi_{Pauli} &= g(E_F) \mu_B^2 \mu_0 \\ &= \frac{3n}{2E_F} \mu_B^2 \mu_0 \end{aligned}} \quad \propto g(E_F)$$

since $g(E_F) = \frac{3n}{2E_F}$
$\uparrow$
DOS <u>per unit volume</u>.

(i) $\chi_{Pauli} > 0 \Rightarrow$ <u>paramagnetic</u> contribution (from spins of free electrons)

(ii) χ_{Pauli} has <u>NO</u> temperature-dependence

[c.f. Curie law for distinguishable non-interacting moments $\chi_{Curie} \sim \frac{C}{T}$]

(iii) If the electrons WERE not free and WERE treated as localized $\vec{\mu}_{spin}$ ($+\mu_B$ or $-\mu_B$), then we would have obtained a Curie-law χ as: [$S = ½$, $L = 0$, $J = ½$; $g = 2$]

$$\chi = \frac{n}{k_B T} \mu_B^2 \mu_0$$

Comparing the two expressions, χ_{Pauli} is only $\left(\frac{T}{T_F}\right)$ of what one would expected for localized electrons, i.e.

$$\chi_{\text{Pauli}} = \frac{3n}{2E_F}\mu_B^2\mu_0 = \frac{3n}{2k_BT_F}\mu_B^2\mu_0 = \frac{3}{2}\underbrace{\left(\frac{n}{k_BT}\mu_B^2\mu_0\right)}_{\text{if electrons were localized}}\underbrace{\left(\frac{T}{T_F}\right)}_{\text{for metals, } \lesssim 0.01}$$

[suppression due to Pauli Exclusion principle]

(iv) For metals, χ_{Pauli} is small $(\sim 10^{-5})$

	Li	Na	K	Rb	Cs
$10^5 \times \chi_P$ (experiment)	2.5	1.4	1.1	1.0	1.0
$10^5 \times \chi_P$ (theory)	1.01	0.83	0.67	0.63	0.58

(v) Further Remark (Optional): χ_{Pauli} assumes free electrons. Electrons may also "feel" the magnetic field produced by other electrons (spins), i.e. they interact. If this interaction is sufficiently strong, the ↑-band and ↓-band may be split ("spin-split bands") spontaneously (i.e. $B=0$), leading to <u>band ferromagnetism</u> (or <u>itinerant ferromagnetism</u>). (Related to ferromagnetism in metals)

I. Susceptibility χ_{Landau} due to motion of free electrons in a magnetic field (Optional)

Solving: $\frac{(\vec{p}+e\vec{A})^2}{2m}\psi = E\psi$ ← effect due to orbiting motion of conduction electrons

⇒ Landau levels

$B=0$

$$E(\vec{k}) = \frac{\hbar^2k_x^2}{2m} + \frac{\hbar^2k_y^2}{2m} + \frac{\hbar^2k_z^2}{2m}$$

$B\neq 0$ $(\vec{B}\parallel\hat{z})^{+}$ (Uniform field)

$$E = \frac{\hbar^2k_z^2}{2m} + \left(l+\frac{1}{2}\right)\hbar\omega_c, \qquad \omega_c = \frac{eB}{m}$$

The point is:

- Different DOS for $B=0$ and $B\neq 0$
- Fill in electrons ⇒ $E(B=0) \neq E(B\neq 0)$ with

$$\Delta E = E(B\neq 0) - E(B=0) = \frac{Vk_Fe^2B^2}{24\pi^2m} = -\underset{\text{motion}}{\vec{\mu}}\cdot\vec{B}$$

due to motion

$$\chi_{\text{Landau}} = -\frac{\mu_0}{V}\frac{\partial^2\Delta E}{\partial B^2} = -\frac{1}{3}\left(\frac{e\hbar}{2m}\right)^2\left(\frac{mk_F}{\pi^2\hbar^2}\right)\mu_0 = -\frac{1}{3}g(E_F)\mu_B^2\mu_0$$

Landau diamagnetic susceptibility of a free electron metal

$$\chi_{\text{Landau}} = -\frac{1}{3}\chi_{\text{Pauli}}$$

[+] See, for example, 曾謹言: 量子力学 (卷I)(第三版) 第七章. Liboff, "Introductory Quantum Mechanics", Ch. 10.

Summary

	Spin Response	Orbital Response
Core Electrons (full shells) $S_{total} = 0$ $L_{total} = 0$	No response (all cancelled)	Diamagnetic (Larmor) $\chi = -\frac{\mu_0 e^2}{6m} \cdot N_e \cdot \frac{N_{at}}{V} \overline{r^2}$ $\sim -10^{-5}$ $\chi_{molar} \sim -10^{-11}\ m^3\ mol^{-1}$
Core electrons (partially filled) shells	Paramagnetic (Curie) may couple into $\vec{J}$ independent moments $\chi \sim \frac{1}{T}$	Paramagnetic (Curie)
Conduction electrons (metals)	Pauli Paramagnetism $\chi_{Pauli} = \mu_0 \mu_B^2 g(E_F)$	Landau diamagnetism $\chi_{Landau} = -\frac{1}{3} \chi_{Pauli}$

Ferromagnetism?

- Need magnetic moments to interact among themselves

References:

Kittel: Ch.11

Michael de Podesta www.physicsofmatter.com