

PHY404- Solid State Physics II

MAGNETISM-PartII

Assoc.Prof.Dr. Yeşim MOĞULKOÇ

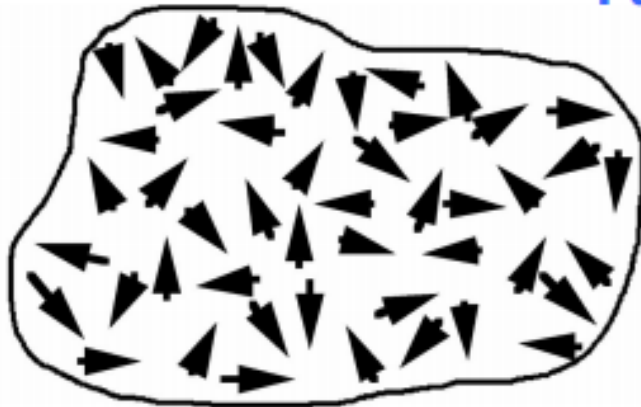
Contents

- Definition of paramagnetism
- Quantum theory of paramagnetism
- Zeeman splitting
- Hund rules
- The periodic table and the electron configurations
- Pauli spin magnetism in metals

Paramagnetism is the attraction of material while in a magnetic field, and diamagnetism is the repulsion of magnetic fields.

- An unpaired electron is called paramagnetic.
- *Paramagnetic materials* have a small, positive susceptibility to magnetic fields.

Paramagnetism



Spins are randomized by thermal energy.



Spins are aligned with or against an applied magnetic field.

Atoms with unpaired \uparrow electrons are called ***paramagnetic***.

- Paramagnetic atoms are attracted to a magnet.

Atoms with paired $\uparrow\downarrow$ electrons are called ***diamagnetic***.

- Diamagnetic atoms are repelled by a magnet.

Quantum theory of paramagnetism

Consider the effect of the first term on an ion in a ground state which can be described by quantum numbers L, S, J and J_z , where \mathbf{J} is the total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$; and J_z is the projection of this momentum into a quantization axis.

It can be shown that $\langle LSJJ_z | \mathbf{L} + 2\mathbf{S} | LSJJ'_z \rangle = g \langle LSJJ_z | \mathbf{J} | LSJJ'_z \rangle$

where g is the g -factor, given by
$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

This relation is valid only within the $(2J+1)$ -dimensional set of states that make up the degenerate atomic ground state in zero field, i.e. only for matrix elements taken between states that are diagonal in J, L , and S .

** g factor gives us Landé equation.

Zeeman splitting

If the splitting between the zero-field atomic ground state multiplet and the first excited multiplet is large compared with $k_B T$ (as is frequently the case), then only the $(2J + 1)$ states in the ground-state multiplet will contribute appreciably to the energy.

In that case the first term in the Hamiltonian leads to the energy $E = -\boldsymbol{\mu} \cdot \mathbf{B}$

Magnetic moment of an ion is proportional to the total angular momentum of the ion: $\boldsymbol{\mu} = -g\mu_B \mathbf{J}$

The applied magnetic field lifts degeneracy of the ground state multiplet and splits it into $2J+1$ equidistant levels - *Zeeman splitting*.

The energies of these levels are given by $E_{J_z} = g\mu_B B J_z$

J_z is an quantized and has values from $-J$ to J .

If thermal energy is less or comparable with the Zeeman splitting, these levels will be populated differently and give a different contribution to the magnetic moment of the ion.

$\mathbf{M} = N\langle\boldsymbol{\mu}\rangle$, where N is the concentration of ions in the solid;

$\langle\boldsymbol{\mu}\rangle$ - value of magnetic moment averaged over the Boltzmann distribution:

$$\mathbf{M} = N\langle\boldsymbol{\mu}\rangle = -Ng\mu_B \frac{\sum_{J_z=-J}^J J_z e^{\frac{g\mu_B B J_z}{k_B T}}}{\sum_{J_z=-J}^J e^{\frac{g\mu_B B J_z}{k_B T}}}$$

The summation can be done using the geometric progression formula.

Result for the magnetization: $M = NgJ\mu_B B_J(x)$ where $x = \frac{g\mu_B JB}{kT}$

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

- the Brillouin function

At relatively low fields and not too low temperatures we can expand the $\coth(x)$ assuming that $x \ll 1$:

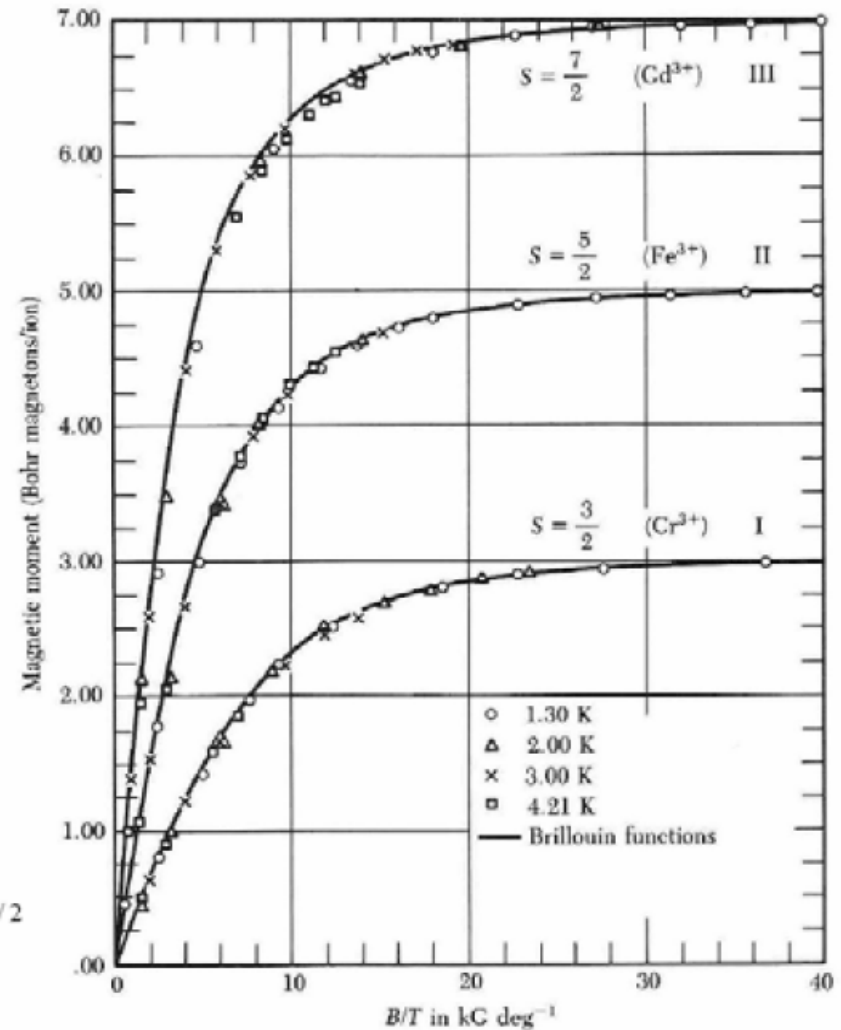
$$\coth(x) \approx \frac{1}{x} + \frac{x}{3}$$

Get for the susceptibility:

$$\chi = \mu_0 \frac{M}{B} = \frac{NJ(J+1)g^2\mu_B^2}{3k_B T} = \frac{\mu_0 N p^2 \mu_B^2}{3k_B T} = \frac{C}{T} \quad \text{Curie Law}$$

where p is the effective number of Bohr magnetons, defined as $p = g[J(J+1)]^{1/2}$

C is the Curie constant



Hund Rules

- 1) The maximum value of the total spin S allowed by the exclusion principle;
- 2) The maximum value of the orbital angular momentum L consistent with this value of S ;
- 3) The value of the total angular momentum J is equal to $|L-S|$ when the shell is less than half full and to $L+S$ when the shell is more than half full.

This is due to the spin-orbit interaction the constant of which has opposite sign depending on whether is less than half full or more than half full.

When the shell is just half full, the application of the first rule gives $L = 0$, so that $J = S$.

Example: carbon. Two electrons in the $2p$ shell ($L=1$). Rule #1 $\Rightarrow S = 1$;

Maximum $L = 1$. Shell is less than half-full $\Rightarrow J = |L-S| = 0$. No paramagnetism.

The periodic table and electron configurations

- The number of orbitals per n level is given by n^2 .
- The maximum number of electrons per n level is $2n^2$.

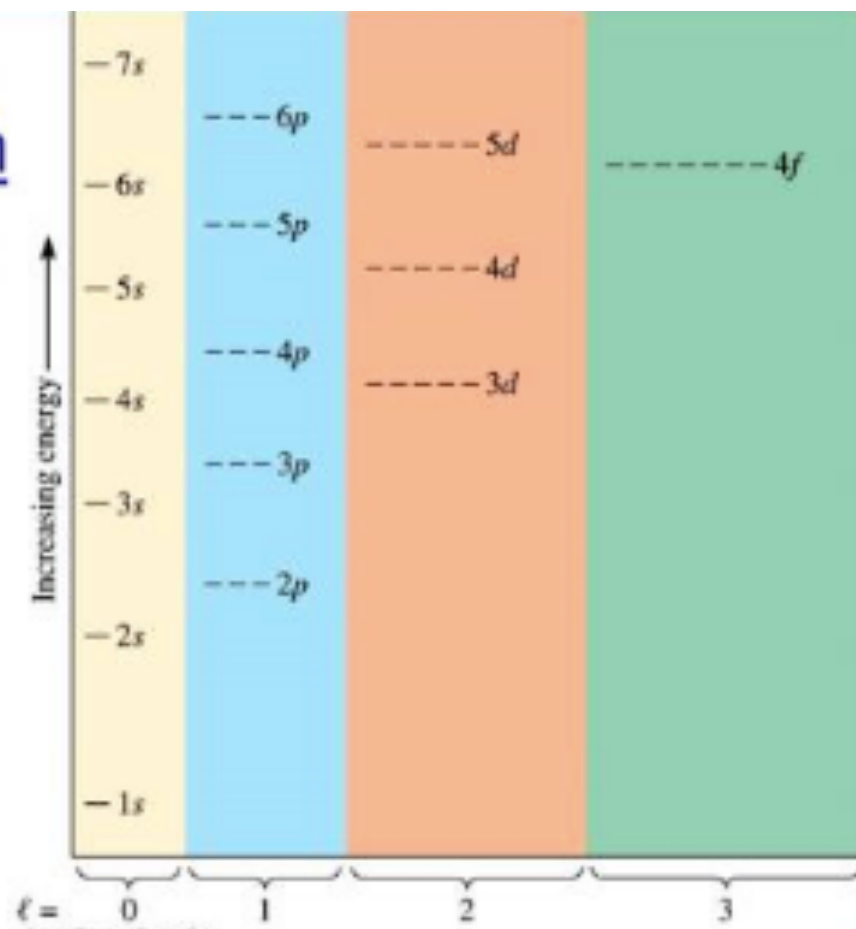
<u>Energy Level</u>	<u># of Orbitals</u>	<u>Max. # of e⁻</u>
n	n^2	$2n^2$
1	1	2
2	4	8
3	9	18
4	16	32

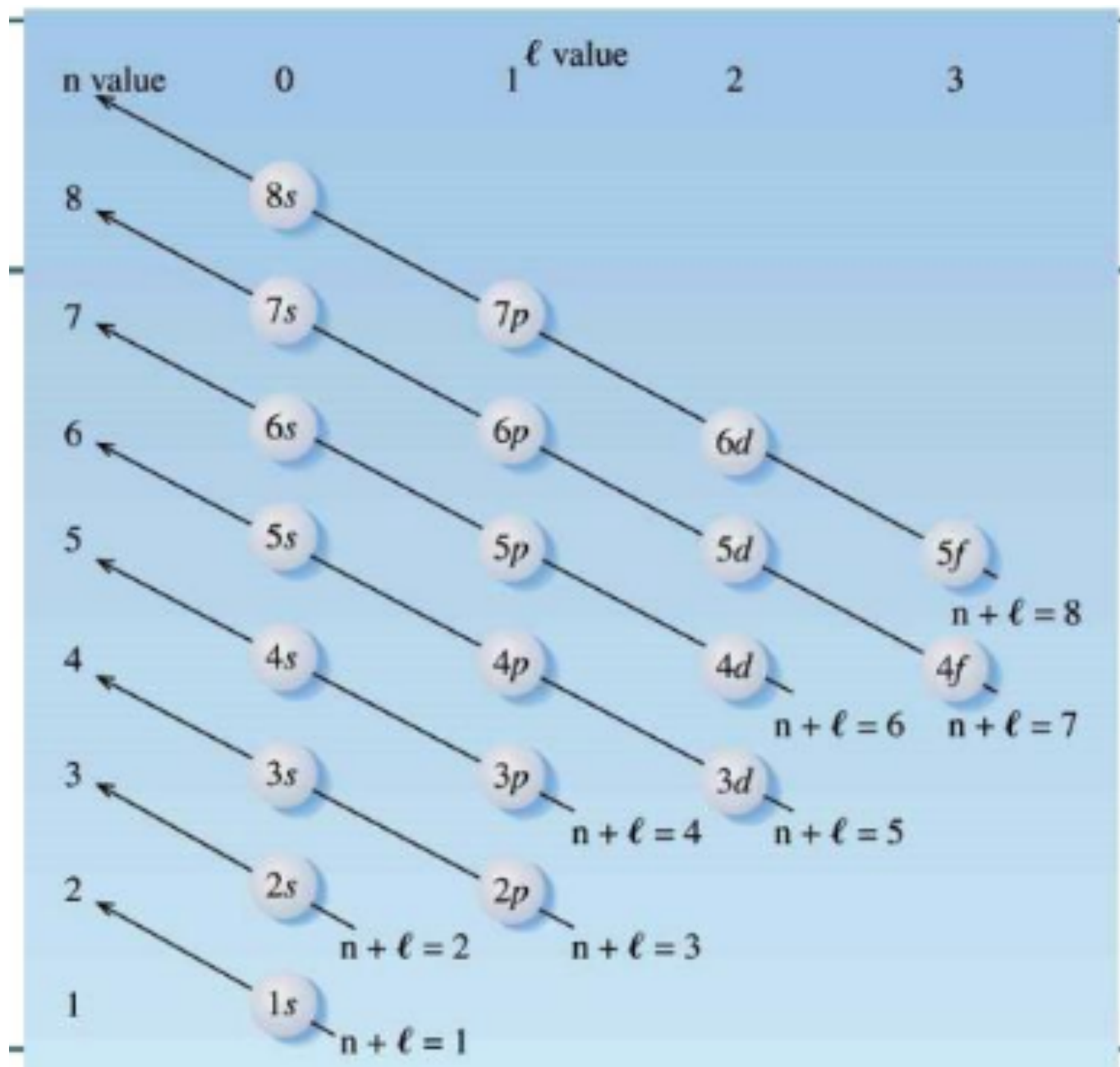
The periodic table and electron configurations

- The principle that describes how the periodic chart is a function of electronic configurations is the **Aufbau Principle**.
- The electron that distinguishes an element from the previous element enters the lowest energy atomic orbital available.

The periodic table and electron configurations

- The Aufbau Principle describes the electron filling order in atoms.





The periodic table and electron configurations

- 1st row elements

	<u>1s</u>	<u>Configuration</u>
₁ H	<u>↑</u>	1s ¹

	<u>1s</u>	<u>Configuration</u>
₁ H	<u>↑</u>	1s ¹
₂ He	<u>↑↓</u>	1s ²

- 2nd row elements

	<u>1s</u>	<u>2s</u>	<u>2p</u>	<u>Configuration</u>
₃ Li	<u>↑↓</u>	<u>↑</u>	___	1s ² 2s ¹
₄ Be	<u>↑↓</u>	<u>↑↓</u>	___	1s ² 2s ²
₅ B	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u> __	1s ² 2s ² 2p ¹
₆ C	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u> <u>↑</u> _	1s ² 2s ² 2p ²
₇ N	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u> <u>↑</u> <u>↑</u>	1s ² 2s ² 2p ³
₈ O	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u> <u>↑</u> <u>↑</u>	1s ² 2s ² 2p ⁴
₉ F	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u> <u>↑↓</u> <u>↑</u>	1s ² 2s ² 2p ⁵
₁₀ Ne	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u> <u>↑↓</u> <u>↑↓</u>	1s ² 2s ² 2p ⁶

Pauli Spin paramagnetism in metals

Arises from the fact that each conduction electron carries a spin magnetic moment which tends to align with the field.

An electron has spin $\frac{1}{2}$ - might expect a Curie-type paramagnetic contribution to the magnetization of the metal with $J=S = 1/2$:
$$\chi = \frac{\mu_0 N \mu_B^2}{k_B T}$$

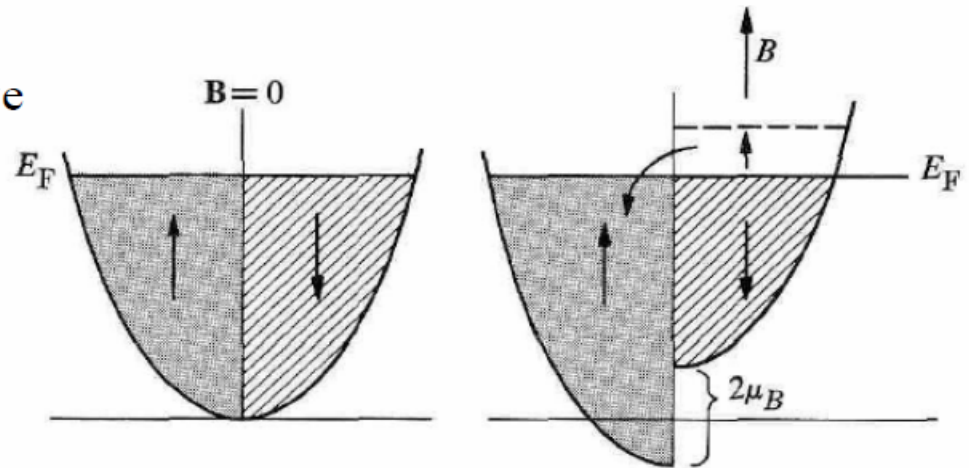
However, experiments show, that spin susceptibilities in metals are essentially independent of temperature, and the observed values are also considerably smaller.

Source of this discrepancy:

the above formula was derived on the basis of localized electrons obeying the Boltzmann distribution, whereas the conduction electrons are delocalized and satisfy the Fermi distribution.

The proper treatment must taking this into account.

➔ No field: half the electrons have spins along $+z$, the other half – spins along $-z$ direction \Rightarrow vanishing net magnetization.



➔ Field is applied along the z -direction:

the energy of the spins $\parallel \mathbf{B}$ is lowered by the amount $\mu_B B$;
the energy of spins opposite to \mathbf{B} is raised by the same amount.

\Rightarrow some electrons near the Fermi level begin to transfer from the opposite-spin half to the parallel-spin one, leading to a net magnetization.

Note that only relatively few electrons near the Fermi level are able to flip their spins and align with the field. The other electrons, lying deep within the Fermi distribution, are prevented from doing so by the exclusion principle.

We can now estimate the magnetic susceptibility.

The electrons participating in the spin flip occupy an energy interval $\sim \mu_B B$

\Rightarrow their concentration is $N_{eff} = \frac{1}{2} D(E_F) \mu_B B$,

where $D(E_F)$ - the density of states at the Fermi energy level

Each spin flip increases the magnetization by $2\mu_B$ (from $-\mu_B$ to $+\mu_B$)

\Rightarrow the net magnetization $M = N_{eff} 2\mu_B = \mu_B^2 D(E_F) B$

leading to a paramagnetic susceptibility $\chi = \mu_B^2 D(E_F)$

\Rightarrow susceptibility is determined by the density of states at the Fermi level.

$\Rightarrow \chi$ is essentially independent of temperature. (Temperature has only a small effect on the Fermi-Dirac distribution of the electrons)

\Rightarrow the derivation remains valid.

If we apply the results for free electrons: $D(E_F) = \frac{3N}{2E_F} = \frac{3N}{2k_B T_F}$,

then

$$\chi = \frac{3N\mu_B^2}{2k_B T_F}$$

T_F - Fermi temperature ($E_F = k_B T_F$).

T_F is very large (often 30,000°K or higher), $\Rightarrow \chi$ is smaller by factor of $\sim 10^2$ - in agreement with experiment.

Summary

- ❖ Langevin paramagnetism: if an atom has moment μ , then classical paramagnetic susceptibility $\chi = \frac{\mu_0 N \mu^2}{3k_B T}$
quantum treatment \rightarrow same result for $\mu = g[J(J+1)]^{1/2} \mu_B$
- ❖ In metals, conduction electrons make a spin paramagnetic contribution: $\chi = \mu_B^2 D(E_F)$ - independent on T
- ❖ Conduction electrons also exhibit diamagnetism due to the cyclotron motion, which is equal to 1/3 of the spin paramagnetic contribution.

HW: Introduction to Solid State Physics,
Chapter 11, Problem 2, Hund rules.

You do not need to send to me. Please study this question by yourself to better understand the Hund Rules.