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Solid State Theory I

Quantum Magnetism + Superconductivity

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Literature:

Ibach, Lüth : An introduction to solid-state physics (Springer)

Ashcroft, Mermin : Solid State Physics (Thomson)

Mahan : Condensed Matter in a Nutshell (Princeton University Press)

Simon : The Oxford Solid State Basics (Oxford University Press)

Mohn : Magnetism in the Solid State - an introduction (Springer)

Tinkham : Introduction to Superconductivity (Dover)

(A) Quantum Magnetism

- Magnetism is a central topic of solid state / many-body physics
- magnetic phase transitions are central to statistical field theory and the renormalization group
- the interplay of magnetism and superconductivity is an active research topic
- magnetic effects like e.g. giant magnetoresistance are of current technological relevance
- In China and in Greece magnetism was known ≈ 1000 B.C. through the magnetic properties of magnetite (Fe_3O_4)

Magnetization and magnetic Susceptibility

Applying a magnetic field $\vec{H}$ to a sample results in a magnetization $\vec{M}$ (magnetic moment per unit volume).
For small fields $\vec{H}$, we have

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

χ is the magnetic susceptibility
The susceptibility is defined in terms of $\vec{H}$
In the sample, we have $\vec{B} = \mu_0(\vec{H} + \vec{M}) = \mu_0(1+\chi)\vec{H}$
or, if χ is small, $\chi \ll 1$, $\vec{B} = \mu_0 \vec{H}$ and $M = \frac{\chi}{\mu_0} B$

- χ is dimensionless (in SI units)
- the range of possible values of χ is extremely large

<u>diamagnetic</u> substances: $\chi < 0$

"typical" values $\approx -10^{-6}$

perfect diamagnetism is superconductors

$$\chi = -\frac{1}{4\pi}$$

$\rightarrow$ magnetic force can outnumber gravitational force

a diamagnet repels the field that creates it

A <u>diamagnet</u> is a material where $\chi < 0$, i.e., the resulting magnetization is opposite to the direction of the applied field.

A <u>paramagnet</u> is a mateial where $\chi > 0$, i.e. the resulting magnetization is in the same direction as the applied field.

A <u>ferromagnet</u> is a material where $\vec{M}$ can be non-zero even in the absence of any applied field.

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A slightly more general definition of χ is

$$\chi = \mu_0 \frac{\partial M}{\partial B}$$

At $T=0$, the magnetization of a homogeneous system of volume V is a uniform magnetic field is

$$M(T=0, B) = -\frac{1}{V} \frac{\partial E_0(B)}{\partial B} \qquad (\mu_0 \stackrel{!}{=} 1)$$

where $E_0(B)$ is the ground state energy of the system in the presence of B.

Therefore,

$$\chi(T=0, B) = -\frac{1}{V} \frac{\partial^2 E_0(B)}{\partial B^2}$$

$\rightarrow$ If the curvature of $E_0(B)$ versus B is positive, χ is negative and vice versa.

If $E_0(B) \sim B^2 \rightarrow \chi$ is independent of the strength of the field.

At finite temperatures,

$$M(T, B) = -\frac{1}{V} \frac{\partial F(T, B)}{\partial B}$$

where F is the free energy

$$F = -k_B T \ln Z = -k_B T \ln \sum_n e^{-E_n(B)/k_B T}$$

Boltzmann constant

partition function

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$$\Rightarrow M(T,B) = -\frac{1}{V} \frac{\sum_n \frac{\partial E_n(B)}{\partial B} e^{-E_n(B)/k_B T}}{\sum_n e^{-E_n(B)/k_B T}}$$

$\rightsquigarrow$ The magnetization is just the thermal equilibrium average of the magnetization of each pure state of the system

χ becomes $\quad \chi = -\frac{1}{V} \frac{\partial^2 F(T,B)}{\partial B^2}$

Magnetic behavior of atoms - Hund's Rules

An electronic state of an atom is characterized by 4 quantum numbers: $|n, L, L^z, S^z\rangle$

principal quantum number $n = 1, 2, 3, \dots$

angular quantum number: an integer between 0 and $n-1$ describes the shape of the atomic orbital

magnetic quantum number an integer between $-L$ and $+L$ orientation in space of a particular orbital

electron spin projection

To understand the net magnetic moment of partially filled atomic shells, we need to understand which of the available L^2 and S^2 for given n and L will be filled.

$\rightarrow$ <u>Hund's Rules</u>

Hund's First Rule:

Electrons try to align their spin

(The Coulomb energy can be lowered when the spin part of the wavefunction is symmetric)

Example: Praseodymium has 3 electrons in its outer shell which is an f-shell $\Rightarrow L=3$

$L=3 \Rightarrow 2L+1$ possible values for L^2

and S^2 has two possible values

(as $S=\frac{1}{2} \rightsquigarrow 2S+1=2$ values, $S^2=+S$ or $S^2=-S$)

$\rightarrow$ all electron spins will have $S^2=+\frac{1}{2}$ or $S^2=-\frac{1}{2}$

Hund's Second Rule:

Electrons try to maximize their total orbital angular momentum, consistent with Hund's first rule.

$\rightarrow L^2=3,\ L^2=2,\ L^2=1$ for Pr

$$\begin{array}{cccccccc} & - & - & - & - & \uparrow & \uparrow & \uparrow \\ L^2= & -3 & -2 & -1 & 0 & 1 & 2 & 3 \end{array} \quad \rightarrow L=6,\ S=\frac{3}{2}$$

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Hund's Third Rule

Given Hund's first and second rules, the orbital and spin angular momentum either align or antialign, so that the total angular is $J = |L \pm S|$ with the sign being determined by whether the shell of orbitals is more than half filled (+) or less than half filled (−).

This rules arises from spin-orbit coupling, which is a term $\propto \vec{L} \cdot \vec{S}$ in the Hamiltonian.
If the shell is less than half filled, all spins are aligned and we have $\propto \vec{L} \cdot \vec{S} = \propto \sum_i \vec{l}_i \cdot \vec{s}_i$
which is minimized for
anti alignment.
If the shell is half filled : $L^2 = 0$ and $S^2 = \frac{2L+1}{2}$
adding more electrons : spins have to antialign with
$S^2 = \frac{2L+1}{2}$ because of Pauli's principle
For the half-filled shell $\propto \vec{L} \cdot \vec{S} = 0$
For the spins added to the half-filled shell, spin-orbit anti-aligns their spin s_i and their angular momentum l_i
But most of the total spin is anti-aligned to the additional s_i and therefore L and S align for more than half-filled shells.

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The magnetic moment associated with the valence shell of isolated atoms is clearly a quantum phenomenon as the orbitals arise as solutions of Schrödinger's equation.
In fact, magnetism is only possible because of quantum mechanics, it is a quantum phenomenon.

The Bohr-van Leeuwen Theorem

The Bohr-van Leeuwen theorem states that from purely classical arguments the magnetic susceptibility of any dynamical system is rigorously zero.

The theorem applies to any system (interacting or not) whose Hamiltonian depends exclusively on the positions and momenta of the particles (i.e. no internal degrees of freedom like spin should be present).

Proof:
We start from the classical partition function:

$$Z_{cl} = \int dq_1\, dq_2 \dots dp_1\, dp_2 \dots dp_{3N}\ \exp\left[-H_0(\vec{q}_i, \vec{p}_i)/k_B T\right]$$

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In the presence of a magnetic field, described by the vector potential $\vec{A}(r)$, each momentum $\vec{p}_i$ must be replaced by $\underline{\vec{p}}_i = \vec{p}_i + \left(\frac{e}{c}\right)\vec{A}(\vec{r}_i)$

→ The term containing the vector potential can be eliminated by a simple shift in the momentum integration.

In quantum mechanics, the presence of the spin degree of freedom $\vec{S}$ alters this result, as a magnetic field $\vec{B}$ also couples to $\vec{S}$:

magnetic moment $\vec{\mu} = g \frac{e}{2mc} \vec{S}$

→ additional term in the Hamiltonian

$$-\vec{\mu}\cdot\vec{B} = -g \frac{e}{2mc} \vec{S}\cdot\vec{B} = \mu_B \, \vec{\sigma}\cdot\vec{B}$$

where $g = 2.002 \approx 2$ and $\mu_B = \frac{|e|\hbar}{2mc} > 0$

is Bohr's magneton

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Here, $\vec{\sigma} = \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}$ and $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, and

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The Hamiltonian for an electron in a magnetic field $\vec{B}$:

$$\mathcal{H} = \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} - \frac{e\hbar}{2mc}\,\vec{\sigma}\cdot\vec{B} + \underbrace{\frac{\hbar^2}{4m^2c^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\vec{\ell}\cdot\vec{\sigma}}_{\text{spin-orbit coupling}}$$

$V(\vec{r})$ is e.g. the atomic or the solid state potential

choose $\underline{B} = (0, 0, B)$

so that $\underline{A} = \frac{1}{2}(\underline{B} \times \underline{r}) = \frac{1}{2}(-By, Bx, 0)$

we then can write

$$(\vec{p} - \frac{e}{c}\vec{A})^2 = \vec{p}^{\,2} - \frac{e}{c}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{e^2}{c^2}\vec{A}^2$$

$$= \vec{p}^{\,2} + \frac{eB}{c}(p_x y + y p_x - p_y x - x p_y) + \frac{e^2 \vec{B}^2}{4c^2}(x^2 + y^2)$$

and

$$H = \frac{p^2}{2m} + \mu_B(\ell_z + \sigma_z)\cdot B + \frac{e^2 B^2}{8mc^2}(x^2 + y^2) + \frac{\hbar^2}{4m^2c^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\vec{\ell}\cdot\vec{\sigma}$$

$$+ V(r) \qquad (*)$$

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where $L_z = x p_y - y p_x = \frac{\hbar}{i}\underbrace{\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)}_{i l_z} - \hbar l_z$

$$S_z = \frac{\hbar}{2}\sigma_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The magnetic field couples to both the angular momentum and the spin of the electrons.

What is the magnetization?

$$\vec{M} = \langle \vec{\mu} \rangle = Tr\{\rho\, \vec{\mu}\} = -\frac{\partial}{\partial \vec{B}} F_s$$

ρ: density matrix

$$= -\mu_B \langle \vec{l} + \vec{\sigma} \rangle = \frac{e\hbar}{2mc} \langle \vec{l} + \vec{\sigma} \rangle$$

and as before, the static magnetic susceptibility follows from

$$\chi_{\alpha\beta} = \frac{\partial M_\alpha}{\partial B_\beta} = -\frac{\partial}{\partial B_\beta}\frac{\partial}{\partial B_\alpha} F_s$$

$$\vec{M} = -\frac{\partial F_s}{\partial \vec{B}} = -\frac{1}{\underbrace{\sum_n e^{-E_n/kT}}_{Z}} \sum_n \frac{\partial E_n}{\partial \vec{B}} e^{-E_n/kT}$$

$$\chi_{zz} = \frac{\partial}{\partial B} M_z$$

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$$\chi_{zz} = \frac{1}{Z}\sum_n \left(\frac{1}{k_B T}\left(\frac{\partial E_n}{\partial B}\right)^2 - \frac{\partial^2 E_n}{\partial B^2}\right) e^{-E_n/kT} - \frac{1}{Z^2}\frac{1}{k_B T}\left(\sum_n \frac{\partial E_n}{\partial B} e^{-\frac{E_n}{kT}}\right)^2$$

From the Hamiltonian (*) we find for the terms containing the magnetic field in 2nd order perturbation theory

$$E_n = E_n^0 + \mu_B \langle n | l_z + \sigma_z | n\rangle B + \frac{e^2 B^2}{8mc^2}\langle n|(x^2+y^2)|n\rangle$$

$$+ \mu_B^2 \sum_{m\neq n} \frac{|\langle n| l_z + \sigma_z | m\rangle|^2}{E_n^0 - E_m^0} B^2$$

and therefore

$$\left.\frac{\partial E_n}{\partial B}\right|_{B=0} = \mu_B \langle n | l_z + \sigma_z | n\rangle$$

$$\left.\frac{\partial^2 E_n}{\partial B^2}\right|_{B=0} = \frac{e^2}{4mc^2}\langle n | x^2+y^2 | n\rangle + 2\mu_B^2 \sum_{m\neq n} \frac{|\langle n| l_z + \sigma_z | m\rangle|^2}{E_n^0 - E_m^0}$$

For $B \to 0$, we find

$$M_z = -\frac{1}{Z}\sum_n \frac{\partial E_n}{\partial B} e^{-E_n/k_B T} = -\frac{1}{Z}\sum_n \mu_B \langle n | l_z + \sigma_z | n\rangle e^{-\beta E_n^0}$$

$$= \langle \mu_z \rangle = 0$$

since positive and negative magnetic moments appear with identical probabilities.

For χ_{zz} we can write

$$\chi_{zz} = \chi_c + \chi_{vV} + \chi_{dia}$$

where

$$\chi_c = \frac{\mu_B^2}{k_B T} \frac{\sum_n \langle n| l_z + \sigma_z |n\rangle e^{-E_n^0/kT}}{\sum_n e^{-E_n^0/kT}} = \frac{\langle \mu_z^2 \rangle}{k_B T}$$

$$\chi_{vV} = -\frac{2}{Z} \sum_{m \neq n} \mu_B \frac{|\langle n| l_z + \sigma_z |m\rangle|^2}{E_n^0 - E_m^0} e^{-E_n^0/k_B T}$$

$$\chi_{dia} = -2 \frac{e^2}{8mc^2} \langle x^2 + y^2 \rangle = -\frac{e^2}{6mc^2} \langle r^2 \rangle$$

χ_c is positive and temperature dependent

$$\chi_c = \frac{C}{T} \qquad \text{"Curie law"}$$

whee the Curie constant is given by

$$C = \frac{\mu_B^2}{k_B} \frac{1}{Z} \sum_n \langle n| l_z + \sigma_z |n\rangle^2 e^{-E_n^0/kT}$$

Notice that $\frac{1}{Z} \sum_n \langle n| l_z + \sigma_z |n\rangle^2 e^{-\frac{E_n}{kT}}$ is the thermodynamic average of the square of the diagonal matrix elements of the magnetic moments.

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$\chi_c > 0$, and therefore a paramagnetic contribution: The magnetization is parallel to the applied field.

Notice that χ_c requires the presence of magnetic moments: $\langle n | l_z + \sigma_z | n \rangle \neq 0$

χ_{vV} is the van Vleck contribution. The van Vleck susceptibility is at low temperatures approximately temperature independent

$$\chi_{vV} = -\frac{2}{Z} \mu_B \sum_{\substack{m,n \\ m \neq n}}' \frac{|\langle n | l_z + \sigma_z | m \rangle|^2}{E_n^0 - E_m^0} e^{-\beta E_n^0}$$

and – at low temperatures – is a paramagnetic contribution (i.e. $\chi_{vV} > 0$), as $E_n^0 - E_m^0 < 0$ for the groundstate ($n=0$)

From $\chi_{vV} = \frac{2}{Z} \mu_B e^{-\beta E_0^0} \sum_n e^{-\beta (E_n^0 - E_0^0)} \sum_{m \neq n} \frac{|\langle n | l_z + \sigma_z | m \rangle|^2}{E_m^0 - E_n^0}$

we see that for $E_n^0 - E_0^0 \gg k_B T$ the contribution is temperature independent

at high temperatures, where $k_B T \gg E_m^0 - E_n^0$, χ_{vV} displays a $\frac{1}{T}$ behavior:

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$$\chi_{vv} = \frac{2}{Z} \sum_{m \neq n} \mu_B \frac{|\langle n| l_z + \sigma_z |m\rangle|^2}{E_m^0 - E_n^0} e^{-E_n^0/kT}$$

$$= -\frac{2}{Z} \sum_{m \neq n} \mu_B \frac{|\langle n| l_z + \sigma_z |m\rangle|^2}{E_m^0 - E_n^0} e^{-E_m^0/kT}$$

or

$$\chi_{vv} = \frac{1}{Z} \sum_{m \neq n} \mu_B \frac{e^{-E_n^0/kT} - e^{-E_m^0/kT}}{E_m^0 - E_n^0} |\langle n| l_z + \sigma_z |m\rangle|^2$$

$$\overset{E_m^0 - E_n^0 \ll kT}{\sim} \frac{1}{Z} \sum_{, m \neq n} e^{-E_n^0/kT} \frac{|\langle n| l_z + \sigma_z |m\rangle|^2}{k_B T}$$

χ_{dia} is alway negativ; it is a diamagnetic contibution: the magnetization is oriented opposite to the field

elementary explanation: the magnetic field induces currents whose moments are opposite to the field according to Lenz' law

<u>but</u>: recall the Bohr-van Leeuwen theorem such an induced current relaxes back to zero, i.e., to equilibrium.

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χ_{dia} has its origin in the minimal coupling

$$\vec{p} \rightarrow \vec{p} - \frac{e}{c}\vec{A}$$

- typically, the paramagnetic contributions dominate in the susceptibility, unless $l_z + \sigma_z = 0$

Our considerations were for a single electron but the analysis can be straightforwardly generalized to a system of N non-interacting electrons.

Paramagnetism of localized magnetic moments

Consider N atoms or ions with partially filled electron shells. These could e.g. be magnetic impurities in an insulator or semiconductor.

The total angular momentum $\vec{J} = \vec{L} + \vec{S}$ of all electrons in the partially filled shell leads to a magnetic moment $\vec{\mu} = -g \frac{e}{2mc} \vec{J}$, $\quad g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

In a magnetic field $\vec{B}$, we can write

$$\mathcal{H} = -\sum_i^N \vec{\mu}_i \cdot \vec{B}(\vec{R}_i) = \sum_i g \mu_B m_{J_i} B$$

i^{th} magnetic moment

location of i^{th} moment

magn. quantum number of i^{th} atom/ion

where we assumed a homogenous magnetic field in z-direction: $\vec{B}(\vec{R}_i) = \vec{B} = (0, 0, B)$

From the Hamiltonian we obtain the partition function which in turn determines the free energy and $\vec{M}$ and χ:

$$Z = \mathrm{Tr}\{ e^{-\beta \mathcal{H}} \} = \mathrm{Tr}\{ e^{-\beta \sum_i g \mu_B B m_{J_i}} \}$$

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$$Z = \mathrm{Tr}\left\{ e^{-\beta \sum_i g \mu_B B m_{J_i}} \right\} = \prod_i^N \sum_{m_J=-J}^{+J} e^{-\beta g \mu_B B m_J}$$

$$K := g \mu_B B \beta$$

$$\rightarrow Z = \prod_i^N e^{KJ} \frac{1 - e^{-K(2J+1)}}{1 - e^{-K}} = \prod_i^N \frac{e^{(J+\frac{1}{2})K} - e^{-(J+\frac{1}{2})K}}{e^{\frac{K}{2}} - e^{-\frac{K}{2}}}$$

so that $F = -k_B T \ln Z$

$$= -N k_B T \ln \frac{e^{(J+\frac{1}{2})K} - e^{-(J+\frac{1}{2})K}}{e^{K/2} - e^{-K/2}}$$

and the total magnetization is given by

$$M = -\frac{\partial}{\partial B} F = N g \mu_B \left[(J + \tfrac{1}{2}) \coth\left(\beta g \mu_B B (J+\tfrac{1}{2})\right) - \tfrac{1}{2} \coth\left(\tfrac{\beta}{2} g \mu_B B\right) \right]$$

$$= N g \mu_B J B_J (g J \mu_B B \beta)$$

where the <u>Brillouin function</u> $B_J(x)$ is given by

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

$B_J(x \to \infty) \to 1$ (or $M \to N g \mu_B J$)

$B_J(x \ll 1) \sim x$ i.e. $B_J(x) \approx (1 + \frac{1}{J}) \frac{x}{3}$

(or $M \approx N \frac{(g\mu_B)^2 J(J+1)}{3 k_B T} B \longrightarrow x \sim \frac{1}{T}$)

In a magnetic field, Zeeman splitting occurs
→ at low T (compared to Zeeman splitting):
spins accumulate at the lowest level with
the spin parallel to the field which leads
to an increase of magnetization