## **Basic Concepts: Magnetism of electrons**

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- I. Spin and orbital moment of the electron
- 2. Paramagnetism of localized electrons
- 3. Precession and resonance
- 4. The free electron gas
- 5. Pauli paramagnetism
- 6. Landau diamagnetism





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This series of three lectures covers basic concepts in magnetism; Firstly magnetic moment, magnetization and the two magnetic fields are presented. Internal and external fields are distinguished. The main characteristics of ferromagnetic materials are briefly introduced. Magnetic energy and forces are discussed. SI units are explained, and dimensions are given for magnetic, electrical and other physical properties.

Then the electronic origin of paramagnetism of non-interacting electrons is calculated in the localized and delocalized limits. The multi-electron atom is analysed, and the influence of the local crystalline environment on its paramagnetism is explained.

Assumed is an elementary knowledge of solid state physics, electromagnetism and quantum mechanics.

# 1. Magnetism of the electron



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#### Einstein-de Hass Experiment

Demonstrates the relation between magnetism and angular momentum.



A ferromagnetic rod is suspended on a torsion fibre.

The field in the solenoid is reversed, switching the direction of magnetization of the rod.

An angular impulse is delivered due to the reversal of the angular momentum of the electronsconservation of angular momentum.

Ni has 28 electrons, moment per Ni is that of 0.6e

Three huge paradoxes; — Amperian surface currents

100 years ago

—Weiss molecular field

— Bohr - van Leeuwen theorem

## The electron

The magnetic properties of solids derive essentially from the magnetism of their electrons. (Nuclei also possess magnetic moments, but they are  $\approx 1000$  times smaller).





The same magnetic moment, the Bohr Magneton,

$$\mu_B = e\hbar/2m_e = 9.27 \ 10^{-24} \ Am^2$$

is associated with ½ħ of spin angular momentum or ħ of orbital angular momentum

On an atomic scale, magnetism is always associated with *angular momentum*. Charge is negative, hence the angular momentum and magnetic moment are oppositely directed

Spin

### **Origin of Magnetism**



At this point it seems that the whole of chemistry and much of physics is understood in principle. The problem is that the equations are much to difficult to solve..... P.A. M. Dirac

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### **Orbital and Spin Moment**



Magnetism in solids is due to the angular momentum of electrons on atoms.

Two contributions to the electron moment:

- Orbital motion about the nucleus
- Spin- the intrinsic (rest frame) angular momentum.

$$m = -(\mu_{\rm B}/\hbar)(l + 2s)$$

#### **Orbital moment**



\* Derivation can be generalized to noncircular orbits: m = IA for any planar orbit.

The g-factor is defined as the ratio of magnitude of m in units of  $\mu_B$  to magnitude of I in units of  $\hbar$ .

g = I for orbital motion

The Bohr model also provides us with a natural unit of length, the Bohr radius

$$a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$$
  $a_0 = 52.92 \text{ pm}$ 

and a natural unit of energy, the Rydberg  $R_0$ 

 $R_0 = (m/2\hbar^2)(e^2/4\pi\epsilon_0)^2$   $R_0 = 13.606 \text{ eV}$ 

### Spin moment

Spin is a relativistic effect.

Spin angular momentum **s** Spin quantum number **s** Spin magnetic quantum number m<sub>s</sub>

s =  $\frac{1}{2}$  for electrons  $m_s = \pm \frac{1}{2}$  for electrons

 $s_z = m_s \hbar$   $m_s = \pm \frac{1}{2}$  for electrons  $m_z = -(e/m_e)m_s \hbar = \pm \mu_B$   $m = -(e/m_e)s$ 

For spin moments of electrons we have:

$$\gamma = -e/m_e$$
  $g \approx 2$ 

More accurately, after higher order corrections: g = 2.0023  $m_z = 1.00116 \mu_B$ 

An electron will usually have both orbital and spin angular momentum

$$m = -(\mu_{\rm B}/\hbar)(I + 2s)$$

#### Quantized mechanics of spin

In quantum mechanics, we represent physical observables by operators – differential or matrix. e.g. momentum  $\mathbf{p} = -i\hbar\nabla$ ; energy  $\mathbf{p}^2/2m_e = -\hbar^2\nabla^2/2m_e$ 

n magnetic basis states  $\Rightarrow$  n x n Hermitian matrix,  $A_{ij} = A_{ji}^{*}$ Spin operator (for  $s = \frac{1}{2}$ )  $\mathbf{s} = \sigma \hbar/2$ Electron:  $s = \frac{1}{2} \Rightarrow m_{s} = \pm \frac{1}{2}$  i.e spin down and spin up states Represented by column vectors:  $|\downarrow\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} |\uparrow\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$   $\mathbf{s} = -(\hbar/2) |\uparrow\rangle; \quad \mathbf{s}|\downarrow\rangle = (\hbar/2)|\downarrow\rangle$   $\mathbf{s}^{2} = \mathbf{s}_{x}^{2} + \mathbf{s}_{y}^{2} + \mathbf{s}_{z}^{2} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} 3\hbar^{2}/4$ Eigenvalues of  $\mathbf{s}^{2}$ :  $\mathbf{s}(\mathbf{s}+\mathbf{l})\hbar^{2}$ 

The fundamental property of angular momentum in QM is that the operators satisfy the commutation relations:

$$[\hat{\boldsymbol{s}}_x, \hat{\boldsymbol{s}}_y] = i\hbar\hat{\boldsymbol{s}}_z, \quad [\hat{\boldsymbol{s}}_y, \hat{\boldsymbol{s}}_z] = i\hbar\hat{\boldsymbol{s}}_x, \quad [\hat{\boldsymbol{s}}_z, \hat{\boldsymbol{s}}_x] = i\hbar\hat{\boldsymbol{s}}_y. \qquad \text{or} \qquad \hat{\boldsymbol{s}}\times\hat{\boldsymbol{s}} = i\hbar\hat{\boldsymbol{s}}.$$

Where [A,B] = AB - BA and  $[A,B] = 0 \Rightarrow A$  and B's eigenvalues can be measured simultaneously  $[s^2,s_7] = 0$ 

#### Quantized spin angular momentum of the electron



The electrons have only two eigenstates, 'spin up' ( $\uparrow$ , m<sub>s</sub> = -1/2) and 'spin down' ( $\downarrow$ , m<sub>s</sub> = 1/2), which correspond to two possible orientations of the spin moment relative to the applied field.

# 2. Paramagnetism of localized electrons



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Populations of the energy levels are given by Boltzmann statistics;  $\propto \exp\{-E_i/k_BT\}$ . The thermodynamic average  $\langle m \rangle$  is evaluated from these Boltzmann populations.



In small fields,  $tanh(x) \approx x$ , hence the susceptibility

$$\chi = N\langle m \rangle / H$$
 (N is no of electrons m<sup>-3</sup>)  $I/\chi$   
 $\chi = \mu_0 N \mu_B^2 / k_B T$ 

This is the famous Curie law for susceptibility, which varies as  $T^{-1}$ .

In other terms

$$\chi = C/T$$
, where  $C = \mu_0 N \mu_B^2 / k_B$ 

is a constant with dimensions of temperature; Assuming an electron density N of 6 10<sup>28</sup> m<sup>-3</sup> gives a Curie constant  $C \approx 0.5$  K. The Curie law susceptibility at room temperature is of order 10<sup>-3</sup>.



## 3. Spin precession and resonance



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#### Electrons in a field; paramagnetic resonance



At room temperature there is a very slight difference in thermal populations of the two spin states (hence the very small spin susceptibility of  $10^{-3}$ ). The relative population difference is  $x = g\mu_0\mu_B H/2k_B T$ At resonance, energy is absorbed from the rf field until the populations are equalized.

The resonance condition is  $hf = g\mu_0\mu_BH$  $f/\mu_0H = g\mu_B/h$  [= geħ/2m<sub>e</sub>h = e/2  $\pi$  m<sub>e</sub>]

Spin resonance frequency is 28 GHz T<sup>-1</sup>

#### Electrons in a field - Larmor precession



 $d\mathbf{M}/dt = \gamma \mathbf{M} \times \mathbf{B} - \alpha \mathbf{e}_{M} \times d\mathbf{M}/dt$ 

28 GHz T<sup>-1</sup> for spin

#### Electrons in a field – Cyclotron resonance

Free electrons follow cyclotron orbits in a magnetic field. Electron has velocity  $\mathbf{v}$  then it experiences a Lorentz force

The electron executes circular motion about the direction of **B** (tracing a helical path if  $v_{||} \neq 0$ )

Cyclotron frequency  $f_c = v_{\perp}/2\pi r$ 

 $f_c = eB/2\pi m_e$ 

Electrons in cyclotron orbits radiate at the cyclotron frequency

Example: — Microwave oven

Since  $\gamma_e = -(e/m_e)$ , the cyclotron and Larmor and epr frequencies are all the same for electrons; 28.0 GHz T<sup>-1</sup>



## 4. The free electron gas



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We apply quantum mechanics to the electrons. They have spin  $\frac{1}{2}$ , and thus there are two magnetic states,  $m_s = \frac{1}{2}$  (spin up  $\uparrow$ ) and  $m_s = -\frac{1}{2}$  (spin down  $\downarrow$ ), for every electron.

Suppose the electrons are confined in a box of volume V, where the potential is constant,  $U_0$ Electrons are represented by a wavefunction  $\psi(\mathbf{r})$  where  $\psi^*(\mathbf{r})\psi(\mathbf{r})dV$  is the probability of finding an electron in a volume dV.





Only certain values of k are allowed. The boundary condition is that L is an integral number of wavelengths.

 $k_{\rm i} = 0, \pm 2\pi/L, \pm 4\pi/L, \pm 6\pi/L$  .....

The allowed states are represented by points in k-space

There is just one state in each volume  $(2\pi/L)^3$  of k-space, And at most two electrons, one spin up  $\uparrow$  and one spin down  $\downarrow$ , can occupy each state. Electrons are fermions.

The energy of an electron in the box is  $E = p^2/2m_e$ 

$$E_{\rm k} = (\hbar k)^2 / 2m_{\rm e} + U_0$$



The points in k-space are very closely spaced; There are N  $\sim 10^{22}$  electrons in a macroscopic sample, so k is effectively a continuous variable.

At temperature T = 0, we fill up all the lowest energy states, with two electrons per state, up to the Fermi level. The energy of the last electron is the Fermi energy  $E_{F}$ .

 $k_x$  The wavelength of the last electron is the Fermi wavelength  $k_F$ .

The N occupied states are contained within the Fermi surface. In the free-electron model this surface is a sphere.

We calculate  $E_{F} | N = (4\pi/3)k_F^3 \times 2/(2\pi/L)^3 \rightarrow k_F = (3\pi^2 N/V)^{1/3}$ 

$$(E_F - U_0) = (\hbar k_F)^2/2m = (\hbar^2/2m) (3\pi^2 n)^{2/3}$$
 where  $n = N/V$ 

For Cu,  $(E_F - U_0) \approx 7 \text{ eV}$ .

$$T_{\rm F}$$
 is defined by  $kT_{\rm F} = E_{\rm F}$ . For Cu,  $T_{\rm F} \approx 80,000$  K (1 eV =11605 K)

The Fermi velocity  $v_F = \hbar k_F/m$  For Cu,  $v_F \approx 1.6 \ 10^6 \ m \ s^{-1}$ 



The Fermi surface of copper.



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#### Electronic specific heat

Some physical properties can be explained solely in terms of the density of states at the Fermi level  $\mathcal{D}(\rm E_{F})$ 

Only electrons within ~  $k_BT$  of the Fermi level can be thermally excited. The number of these electrons is  $\mathcal{D}(E_F) k_BT$ The increase in energy U(T) - U(0) is ~  $\mathcal{D}(E_F) (k_BT)^2$ 

$$C_{el} = dU/dT \approx 2\mathcal{D}(E_F) k_B^2 T$$

 $\mathcal{D}(\mathsf{E})$ 

F



Note that the electronic entropy  $S_{el} = \int_0^T (C_{el}/T') dT'$  [recall  $\delta Q = T \delta S$ ]

According to the third law of thermodynamics,  $S \rightarrow 0$  as  $T \rightarrow 0$ 

### Pauli susceptibility

We now show the  $\uparrow$  and  $\downarrow$  density of states separately. They split in a field  $B = \mu_0 H$ 



The splitting is really very small, ~  $10^{-5}$  of the bandwidth in a field of 1 T.

 $M = \mu_{\rm B}(N_{\uparrow} - N_{\downarrow})/V \qquad \text{Note } M \text{ is magnetic moment per unit volume}$ At T = 0, the change in population in each band is  $\Delta N = \frac{1}{2} \mathcal{D}(E_{\rm F})\mu_0\mu_{\rm B}H$  $M = 2\mu_{\rm B}\Delta N = \mathcal{D}(E_{\rm F})\mu_0\mu_{\rm B}^2H \qquad \text{The dimensionless susceptibility } \chi = M/H$ 

 $\chi_{Pauli} = \mathcal{D}(E_F)\mu_0\mu_B^2$  It is ~ 10<sup>-5</sup> and independent of T

## Landau diamagnetism

In the free-electron model,  $\mathcal{D}(E_F) = (3/2)n/E_F$ 

Hence  $\chi_{Pauli} = \{3n\mu_0\mu_B^2/2E_F\}[I + cT^2 + ...]$  (Compare Curie law  $n\mu_0\mu_B^2/k_BT$ ) The ratio of electronic specific heat coefficient to Pauli susceptibility in the nearly-free, independent electron approximation should be a constant  $\mathcal{R}$ .

Free electron model was used by Landau to calculate the orbital diamagnetism of conduction electrons. The result is:

$$\chi_L = -n\mu_0\mu_B^2/2k_BT_F$$

exactly one third of the Pauli susceptibility, and opposite in sign.

The real band structure is taken into account in an approximate way by renormalizing the electron mass. Replace  $m_e$  by an effective mass  $m^*$ 

Then  $\chi_L = -(1/3)(m_e/m^*) \chi_P$ 

In some semimetals such as graphite or bismuth, m<sup>\*</sup> can be  $\approx 0.01 \text{ m}_{e}$ , hence the diamagnetism of the conduction electrons may sometimes be the dominant contribution to the susceptibility. ( $\chi_L = -4 \ 10^{-4}$  for graphite)

### Landau diamagnetism



### Density of states in other dimension



dot.

 $\mathcal{D}(\varepsilon) = \text{constant}$ 

 $\hat{\mathcal{D}}(\varepsilon) \propto \varepsilon^{-1/2}$ 

**Discreet** levels

#### Quantum oscillations

Let B = B<sub>z</sub>, **A** = (0, xB, 0), V(**r**) = 0 and m = m\* Canonical momentum **p** = **p** - q**A** Schrodinger's equation  $\frac{1}{2m^*} \left[ p_x^2 + (p_y + exB)^2 + p_z^2 \right] \psi = \varepsilon \psi,$  $\psi(x) e^{ik_y y} e^{ik_z z}.$  $\left[ -\frac{\hbar^2}{2m^*} \frac{d^2}{dx^2} + \frac{1}{2}m^* \omega_c (x - x_0)^2 \right] \psi(x) = E' \psi(x)$ 

$$\omega_{c} = eB/m^{*}, \quad x_{0} = -\hbar k_{y}/eB \quad E' = E - (\hbar^{2}/2m_{e})k_{z}^{2}$$
$$E' = E_{n} = (n + \frac{1}{2})\hbar\omega_{c}$$
$$E = \frac{\hbar^{2}k_{z}^{2}}{2m^{*}} + (n + \frac{1}{2})\hbar\omega_{c}$$



The motion is a plane wave along Oz, plus a simple harmonic oscillation at  $f_c = \omega_c/2$ , in the plane, where  $\omega_c = eB/m_e$ 

#### De Haas van Alfen effect

When a magnetic field is applied, the states in the Fermi sphere collapse onto a series of tubes. Each tube corresponds to one Landau level (n - value). As the field increases, the tubes expand and the outer one empties periodically as field increases. An oscillatory variation in  $I/B^2$  of magnetization (de Haas - van Alphen effect) or of conductivity (Shubnikov - de Haas effect) appears.



From the period, it is possible to deduce the cross section area of the Fermi surface normal to the tubes.



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Maxwell's equations relate magnetic and electric fields to their sources. The other fundamental relation of electrodynamics is the expression for the force on a moving particle with charge q,

 $\boldsymbol{F} = q(\boldsymbol{E} + \boldsymbol{v} \wedge \boldsymbol{B})$ 

The two terms are respectively the Coulomb and Lorentz forces. The latter gives the torque equation  $\Gamma = m \wedge B$  The corresponding Hamiltonian for the particle in a vector potential **A** representing the magnetic field B ( $B = \nabla \wedge A$ ) and a scalar potential  $\phi_{\epsilon}$  representing the electric field E ( $E = -\nabla \phi_{e}$ ) is  $\mathcal{H} = (1/2m)(p - qA)^2 + q\phi_{e}$ 

#### **Orbital moment**

The Hamiltonian of an electron with electrostatic potential energy  $V(\mathbf{r}) = -e\phi_e$  is  $\mathcal{H} = (1/2m)(\mathbf{p} + e\mathbf{A})^2 + V(\mathbf{r})$ Now  $(\mathbf{p} + e\mathbf{A})^2 = \mathbf{p}^2 + e^2\mathbf{A}^2 + 2e\mathbf{A}\cdot\mathbf{p}$  since  $\mathbf{A}$  and  $\mathbf{p}$  commute when  $\nabla \mathbf{A} = 0$ . So  $\mathcal{H} = [\mathbf{p}^2/2m + V(\mathbf{r})] + (e/m)\mathbf{A}\cdot\mathbf{p} + (e^2/2m)\mathbf{A}^2$   $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2$ where  $\mathcal{H}_0$  is the unperturbed Hamiltonian,  $\mathcal{H}_1$  gives the paramagnetic response of the orbital moment

where  $\mathcal{H}_0$  is the unperturbed Hamiltonian,  $\mathcal{H}_1$  gives the paramagnetic response of the orbital moment and  $\mathcal{H}_2$  describes the small diamagnetic response. Consider a uniform field B along z. Then the vector potential in component form is  $\mathbf{A} = (1/2)$  (-By, Bx, 0),

so 
$$\mathbf{B} = \nabla \wedge \mathbf{A} = \mathbf{e}_{z}(\partial A_{y}/\partial x - \partial A_{x}/\partial y) = \mathbf{e}_{z}\mathbf{B}$$
. More generally  
 $\mathbf{A} = (1/2)\mathbf{B} \wedge \mathbf{r}$  Now

 $(e/m)A.p = (e/2m)B \wedge r.p = (e/2m)B.r \wedge p = (e/2m)B.l$  since  $l = r \wedge p$ . The second terms in the Hamiltonian is then the Zeeman interaction for the orbital moment

$$\mathcal{H}_1 = (\mu_{\rm B}/\hbar) \boldsymbol{B}.\boldsymbol{l}$$

The third term is  $(e^2/8m) (B \wedge r)^2 = (e^2/8m^2)B^2(x^2+y^2)$ . If the orbital is spherically symmetric,  $\langle x^2 \rangle = \langle y^2 \rangle = \langle r^2 \rangle / 3$ . The corresponding energy  $E = (e^2B^2/12m) \langle r^2 \rangle$ . Since  $M = -\partial E/\partial B$  and susceptibility  $\chi = \mu_0 NM/B$ ,

It follows that the orbital diamagnetic susceptibility is  $\chi = \mu_0 Ne^2 \langle r^2 \rangle/6m$ .

#### Spin moment

The time-dependent Schrödinger equation

 $-(\hbar^2/2m)\nabla^2\psi + V\psi = i\hbar\partial\psi/\partial t$ 

is not relativistically invariant because the operators  $\partial/\partial t$  and  $\partial/\partial x$  do not appear to the same power. We need to use a 4-vector X = (ct, x, y, z) with derivatives  $\partial/\partial X$ .

Dirac discovered the relativistic quantum mechanical theory of the electron, which involves the Pauli spin operators  $\sigma_{I}$ , with coupled equations for electrons and positrons. The nonrelativistic limit of the theory, including the interaction with a magnetic field *B* represented by a vector potential **A** can be written as

$$\mathcal{H} = [(1/2m)(\mathbf{p} + e\mathbf{A})^2 + V(\mathbf{r})] - p^4/8m^3c^2 + (e/m)\mathbf{B}\mathbf{.s} + (1/2m^2c^2r)(dV/dr) - (1/4m^2c^2)(dV/dr) \partial/\partial r$$

•The second term is a higher-order correction to the kinetic energy

•The third term is the interaction of the electron spin with the magnetic field, so that the complete expression for the Zeeman interaction of the electron is

$$\mathcal{H}_{\rm Z} = (\mu_{\rm B}/\hbar) \boldsymbol{B} \cdot (\boldsymbol{l} + 2\boldsymbol{s})$$

#### Spin moment

The factor 2 is not quite exact. The expression is  $2(1 + \alpha/2\pi - ....) \approx 2.0023$ , where  $\alpha = e^2/4\pi\epsilon_0 hc \approx 1/137$  is the fine-structure constant.

• The fourth term is the spin-orbit ineteraction., which for a central potential  $V(r) = -Ze^2/4\pi\epsilon_0 r$  with Ze as the nuclear charge becomes  $-Ze^2\mu_0 \mathbf{l.s}/8\pi m^2 r^3$  since  $\mu_0\epsilon_0 = 1/c^2$ . In an atom  $<1/r^3> \approx (0.1 \text{ nm})^3$  so the magnitude of the spin-orbit coupling  $\lambda$  is 2.5 K for hydrogen (Z = 1), 60 K for 3d elements (Z  $\approx 25$ ), and 160 K for actinides (Z  $\approx 65$ ). In a noncentral potential, the spin-orbit interaction is  $(s \wedge \nabla V).p$ 

• The final term just shifts the levels when l = 0

The classification of interactions according to their relativistic character is based on the kinetic energy

$$E = mc^2 \sqrt{[1 + (v^2/c^2)]}$$

The order of magnitude of the velocity of electrons in solids is  $\alpha c$ . Expanding the equation in powers of c

$$E = mc^{2+} (1/2)\alpha^2 mc^2 - (1/8)\alpha^4 mc^2$$

Here the rest mass of the electron,  $mc^2 = 511$  keV; the second and third terms, which represent the order of magnitude of electrostatic and magnetostatic energies are respectively 13.6 eV and 0.18 meV. Magnetic dipolar interactions are therefore of order 2 K. (1 eV = 11605 K)



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