

**AMS43101**

**(Introduction to)  
Magnetic properties of  
materials**

**Ch. 3 Magnetism of electrons**

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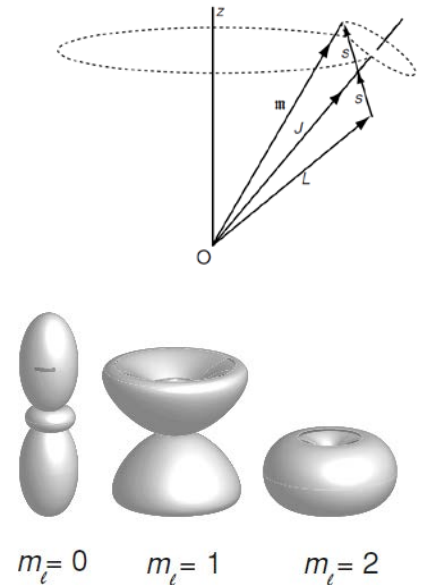
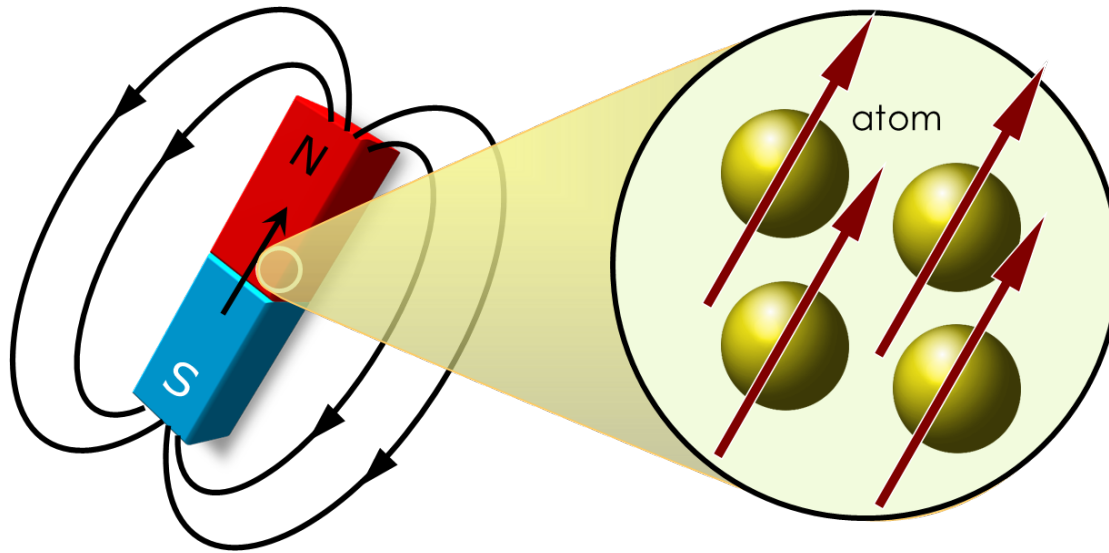
**Class Lab.**

**Materials Science and Engineering  
Nano Materials Engineering Track**



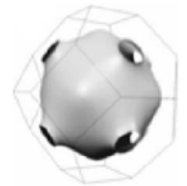
**Creative Lab. for  
Advanced Spin System**

# Goal of this class



## 3 Magnetism of electrons

- 3.1 Orbital and spin moments
- 3.2 Magnetic field effects
- 3.3 Theory of electronic magnetism
- 3.4 Magnetism of electrons in solids



**Magnetic moment**

## 4 Magnetism of localized electrons on the atom

- 4.1 The hydrogenic atom and angular momentum
- 4.2 The many-electron atom
- 4.3 Paramagnetism
- 4.4 Ions in solids; crystal-field interactions

# Goal of this chapter

The magnetic moments in solids are associated with electrons.

The microscopic theory of magnetism is based on the quantum mechanics of electronic angular momentum, which has two distinct sources – orbital motion and spin.

They are coupled by the spin–orbit interaction.

**Free electrons** follow **cyclotron orbits** in a magnetic field, whereas **bound electrons** undergo **Larmor precession**, which gives rise to orbital diamagnetism.

The description of magnetism in solids is fundamentally different depending on whether the electrons are **localized on ion cores**, or **delocalized in energy bands**.

A starting point for discussion of magnetism in metals is the free-electron model, which leads to temperature-independent Pauli paramagnetism and Landau diamagnetism.

By contrast, localized noninteracting electrons exhibit Curie paramagnetism.

# Basics on electrons

$$p = h/\lambda_e$$

This de Broglie relation, combined with Niels Bohr's postulate that the angular momentum of electrons in atoms was quantized in multiples of

$$\hbar, |\mathbf{r} \times \mathbf{p}| = n\hbar$$

led to the idea that the allowed orbits of electrons in atoms were stationary states with an integral number of de Broglie wavelengths. This opened the door to the development of quantum physics.

Two basic approaches are wave mechanics, due to Schrödinger, and matrix mechanics, due to Heisenberg.

$$\mathcal{H}\Psi = \varepsilon\Psi \qquad \mathcal{H}\Psi = i\hbar \frac{\partial\Psi}{\partial t}$$

$$\Psi^*(\mathbf{r})\Psi(\mathbf{r})\delta^3 r$$

# Basics on electrons

$$\mathcal{H}\Psi = \varepsilon\Psi$$

eigenstates

eigenvalues

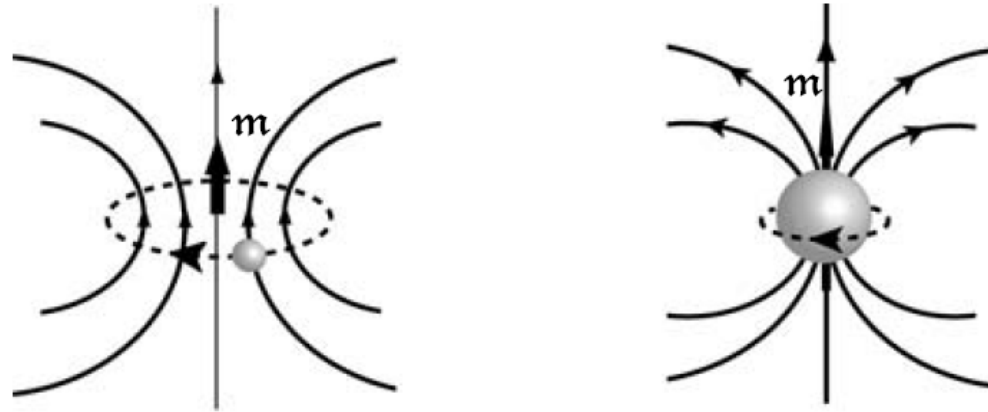
The eigenfunctions are orthogonal and form a basis of the system

The Heisenberg formulation which is especially useful in magnetism when only a small number of eigenstates are relevant, uses an  $n \times n$  matrix representation for the Hamiltonian.

All physical observables can be represented by matrix operators. The eigenstates are  $n \times 1$  column vectors, and the eigenvalues are real numbers. The procedure to determine them often involves diagonalizing a matrix to find its eigenvalues.

Corrections due to small additional terms in the Hamiltonian are deduced from perturbation theory.

# 3.1 Orbital and spin moments



Magnetism is intimately connected with angular momentum of elementary particles, so the quantum theory of magnetism is closely linked to the quantization of angular momentum.

Protons, neutrons and electrons possess an intrinsic angular momentum

$\frac{1}{2}\hbar$  known as spin,

Nuclear spin creates much smaller magnetic moments than electronic spin because of the much greater nucleon mass.

Electrons are the main source of magnetic moments in solids.

# 3.1 Orbital and spin moments

**Table 3.1.** Properties of the electron

Mass	$m_e$	$9.109 \times 10^{-31}$ kg
Charge	$-e$	$-1.6022 \times 10^{-19}$ C
Spin quantum number	$s$	1/2
Spin angular momentum	$\frac{1}{2}\hbar$	$5.273 \times 10^{-34}$ J s
Spin g-factor	$g$	2.0023
Spin magnetic moment	$m$	$-9.285 \times 10^{-24}$ A m <sup>2</sup>
Classical radius $\mu_0 e^2 / 4\pi m_e$	$r_e$	$2.818 \times 10^{-15}$ m

# 3.1.1 Orbital moment

The orbital moment can be introduced in terms of the Bohr model of the atom, where electrons revolve around a nucleus of charge  $Ze$  in circular orbits under the influence of the Coulomb potential

$$\varphi_e = -Ze/4\pi\epsilon_0 r$$

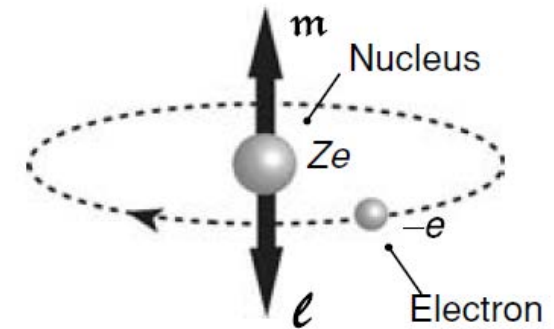
$$\tau = 2\pi r/v$$

$$I = -e/\tau$$

$$-\frac{1}{2}er \times v$$

$$m = -\frac{e}{2m_e} \ell.$$

$$m = \gamma \ell$$



$$m = IA$$

angular momentum

$$\ell = m_e r \times v$$

$\gamma$  is  $-(e/2m_e)$

the proportionality factor  $\gamma$  is known as the gyromagnetic ratio.



# 3.1.1 Orbital moment

The orbital angular momentum is quantized in units of  $\hbar$ , in such a way that the component of  $m$  in some particular direction, chosen as the  $z$ -direction, is

$$m_z = -\frac{e}{2m_e} m_\ell \hbar, \quad \text{where } m_\ell = 0, \pm 1, \pm 2, \dots$$

The natural unit for electronic magnetism is therefore the **Bohr magneton**, defined as

$$\mu_B = \frac{e\hbar}{2m_e};$$

$$1 \mu_B = 9.274 \times 10^{-24} \text{ A m}^2$$

The remarkable difference between an electron in a quantum-mechanical stationary state and a classical charged particle is that the former can circulate indefinitely in its orbit as some sort of perpetual motion or electronic supercurrent – whereas the classical particle, or an electron in an unquantized orbit, must radiate energy on account of its continuous centripetal acceleration. Classical orbital motion will soon cease as a result of radiation loss.

# 3.1.1 Orbital moment

## g-factor

the ratio of the magnitude of the magnetic moment in units of  $\mu_B$  to the magnitude of the angular momentum in units of  $\hbar$ :

$$(|\mathbf{m}|/\mu_B) = (g|\ell|/\hbar)$$

*Hence g is exactly 1 for orbital motion.*

The Bohr model, a simplified version of the quantum mechanics of the atom, provides us with the natural units of length and energy for atomic physics.

$$e^2/4\pi\epsilon_0 r^2 = m_e v^2/r$$

$$m_e v r = n\hbar,$$

$$r = n^2 a_0$$

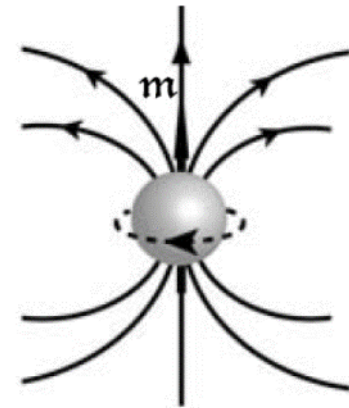
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \cdot \text{the Bohr radius}$$

## 3.1.2 Spin moment

The electron possesses intrinsic spin angular momentum with quantum number

$$s = \frac{1}{2}$$

There is an associated intrinsic magnetic moment, unrelated to any orbital motion, which can only adopt one of two discrete orientations relative to a magnetic field.



the image of a spinning ball  
of charge is ultimately misleading

The mysterious built-in angular momentum emerges as a consequence of relativistic quantum mechanics

## 3.1.2 Spin moment

All fermions have spin and an associated magnetic moment. It turns out that the magnetic moment associated with the electron spin is not a half, but almost exactly one Bohr magneton.

The gyromagnetic ratio  $\gamma$  is  $-(e/m_e)$

$g$ -factor is close to 2

$$\mathbf{m} = -\frac{e}{m_e} \mathbf{s}.$$

The spin magnetic quantum number is  $m_s = \pm \frac{1}{2}$

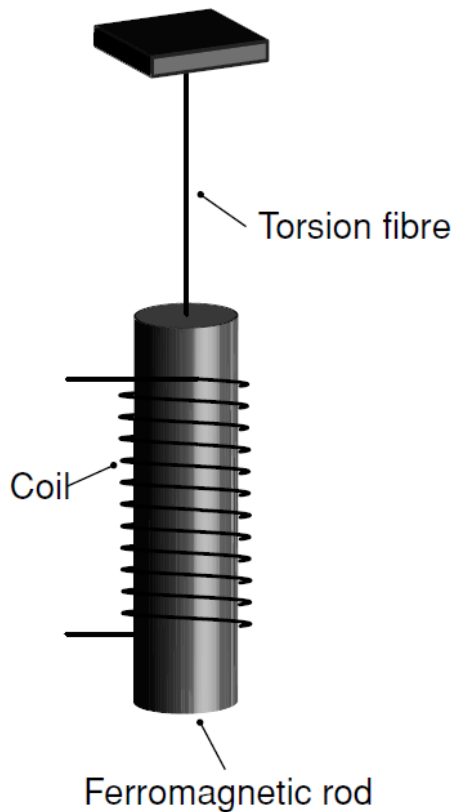
so there are only the two possible angular momentum states.

The component of spin along any axis is

$$\pm \frac{1}{2} \hbar$$

$$m_z = -\frac{e}{m_e} m_s \hbar \quad \text{with } m_s = \pm \frac{1}{2}.$$

# 3.1.2 Spin moment



The reality of the link between magnetism and angular momentum, known as the **Einstein-de Haas effect**, was demonstrated in an experiment carried out by John Stewart in 1917.

the spontaneous magnetization  $M_s = 1710 \text{ kA m}^{-1}$

the  $g$ -factor 2.09

the magnitude of the ferromagnetic moment is only  $2.2\mu\text{B}$  per atom.

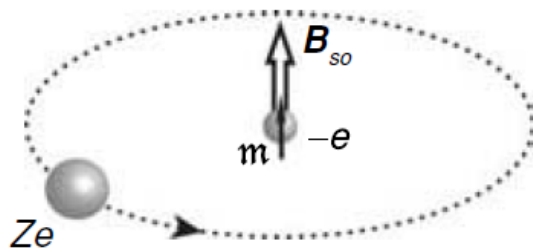
the ferromagnetic moment of iron corresponds to the spin moment of barely two of them.  
All the others form pairs with oppositely aligned spins, and contribute nothing.

# 3.1.3 Spin-orbit coupling

Generally, an atomic electron possesses both spin and orbital angular momentum.

They may be coupled by spin-orbit interaction to create a total electronic angular momentum  $\mathbf{j}$ , with resultant magnetic moment

$$\mathbf{m} = \gamma \mathbf{j}.$$



Spin-orbit interaction from the viewpoint of the electron.

$$I_n = Zev/2\pi r$$

$$\mu_0 I_n / 2r$$

$$B_{so} = \mu_0 Zev / 4\pi r^2$$

The electron's magnetic moments associated with  $l$  and  $s$  are oppositely aligned.

$$\epsilon_{so} = -\mu_B B_{so}$$

$$\epsilon_{so} \approx -\frac{\mu_0 \mu_B^2 Z^4}{4\pi a_0^3}.$$

## 3.1.3 Spin-orbit coupling

$$\varepsilon_{so} \approx -\frac{\mu_0 \mu_B^2 Z^4}{4\pi a_0^3}.$$

The  $Z$  variation means that the spin-orbit interaction, while weak for light elements becomes much more important for heavy elements and especially for inner shells.

The associated magnetic field is of order 10 T

The correct version of the spin-orbit interaction, resulting from a relativistic calculation, is given in §3.3.3.

The expression (3.12) is modified by a factor 2

the spin-orbit Hamiltonian

$$\mathcal{H}_{so} = \lambda \hat{l} \cdot \hat{s},$$

## 3.1.4 Quantum mechanics of angular momentum

The Bohr model is an oversimplification of the quantum theory of angular momentum. In quantum mechanics, physical observables are represented by differential operators or matrix operators, which we denote by bold symbols with a hat.

$$\hat{\mathbf{p}} = -i\hbar\nabla$$

$$\hat{\mathbf{p}}^2/2m = -\hbar^2\nabla^2/2m$$

$$\hat{\mathbf{O}}\psi_i = \lambda_i\psi_i$$

The allowed values of a physical observable

the eigenvalues,  $\lambda_i$

the possible observable states of the system.

$\psi_i$  are the eigenfunctions,

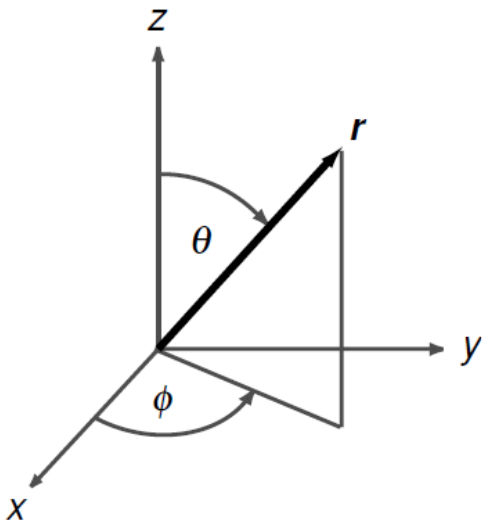


## 3.1.4 Quantum mechanics of angular momentum

The angular momentum operator

$$\hat{\mathbf{l}} = \mathbf{r} \times \hat{\mathbf{p}},$$

$$\hat{\mathbf{l}} = -i\hbar(y\partial/\partial z - z\partial/\partial y)\mathbf{e}_x - i\hbar(z\partial/\partial x - x\partial/\partial z)\mathbf{e}_y - i\hbar(x\partial/\partial y - y\partial/\partial x)\mathbf{e}_z.$$



$$\hat{l}_x = i\hbar(\sin\phi\partial/\partial\theta + \cot\theta\cos\phi\partial/\partial\phi),$$

$$\hat{l}_y = i\hbar(-\cos\phi\partial/\partial\theta + \cot\theta\sin\phi\partial/\partial\phi),$$

$$\hat{l}_z = -i\hbar(\partial/\partial\phi).$$

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 = -\hbar^2 \left( \frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right).$$

## 3.1.4 Quantum mechanics of angular momentum

An alternative way of representing angular momentum operators, which is invaluable when considering the spin of electrons, is with matrices.

### Square hermitian matrices

The magnetic systems have a small number  $\nu$  of magnetic basis states, each denoted by a different magnetic quantum number  $m_i$ , and they can be represented by  $\nu \times \nu$  square hermitian matrices.

For orbital angular momentum with quantum number  $l$ ,

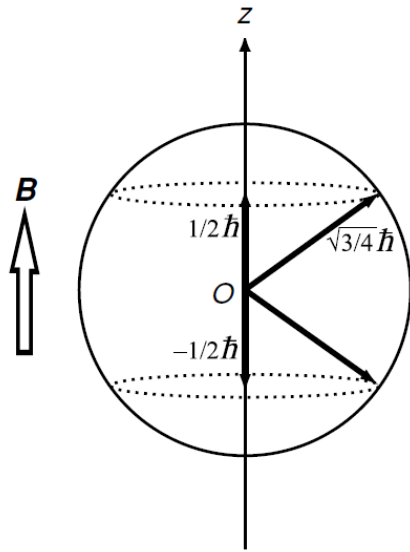
$$\nu \text{ is } (2l + 1)$$

Similarly for spin, the electron with

$$s = \frac{1}{2} \quad m_s = \pm \frac{1}{2}$$

$$2 \times 2 \text{ spin operator } \hat{\mathbf{S}} \quad \hat{\mathbf{S}}_x, \hat{\mathbf{S}}_y, \hat{\mathbf{S}}_z$$

# 3.1.4 Quantum mechanics of angular momentum



$$\hat{S}_x, \hat{S}_y, \hat{S}_z$$

$$s = \frac{1}{2}$$

$$m_s = \pm \frac{1}{2}$$

2 × 2 spin operator  $\hat{S}$

The eigenvalues  $\frac{1}{2}\hbar$  and  $-\frac{1}{2}\hbar$

The eigenvectors

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

'spin-up'

$$|\downarrow\rangle$$

$$\begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

'spin-down'

$$|\uparrow\rangle$$

The arrow indicates the direction of the magnetic moment.

The negative charge of the electron means (somewhat confusingly) that  $\uparrow$  is spin down and vice versa.

## 3.1.4 Quantum mechanics of angular momentum

The Pauli spin matrices:

$$\hat{s}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \frac{1}{2}\hbar$$

$$\hat{s}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \frac{1}{2}\hbar$$

$$\hat{s}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \frac{1}{2}\hbar$$

$$\hat{\mathbf{s}} = (s_x, s_y, s_z)$$

The eigenvalues  $\frac{1}{2}\hbar$  and  $-\frac{1}{2}\hbar$

The eigenvectors  $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$   $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$   
spinors.

$$\hat{\boldsymbol{\sigma}} = \hat{\mathbf{s}} \times 2/\hbar = \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right).$$

## 3.1.4 Quantum mechanics of angular momentum

The fundamental property of angular momentum in quantum mechanics is that the operators representing the x, y, and z components satisfy the **commutation rules**

$$[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z, \quad [\hat{s}_y, \hat{s}_z] = i\hbar\hat{s}_x, \quad [\hat{s}_z, \hat{s}_x] = i\hbar\hat{s}_y.$$

$$[\hat{s}_x, \hat{s}_y] = \hat{s}_x\hat{s}_y - \hat{s}_y\hat{s}_x$$

$\hat{s}_x$ ,  $\hat{s}_y$  and  $\hat{s}_z$  satisfy the commutation rule,  
eigenvalues  $\pm\frac{1}{2}\hbar$

These operators have to be **Hermitian** so that their eigenvalues are real. A neat way of summarizing the commutation relations is

$$\hat{s} \times \hat{s} = i\hbar\hat{s}.$$

## 3.1.4 Quantum mechanics of angular momentum

The differential operators for orbital angular momentum, (3.15), also obey these commutation rules, as all angular momentum operators must. Two operators are said to commute if their commutator is zero.

$$[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z, \quad [\hat{s}_y, \hat{s}_z] = i\hbar\hat{s}_x, \quad [\hat{s}_z, \hat{s}_x] = i\hbar\hat{s}_y.$$

In quantum mechanics, **only those physical quantities whose operators commute can be measured simultaneously.**

The three components of angular momentum do not commute and therefore cannot be measured at the same time.

A precise measurement of the z component, for example, means that the x and y components are indeterminate.

However, **it is possible to measure the total angular momentum and any one of its components** (but conventionally the z component) simultaneously.

The square of the total spin angular momentum,

$$\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} 3\hbar^2/4.$$

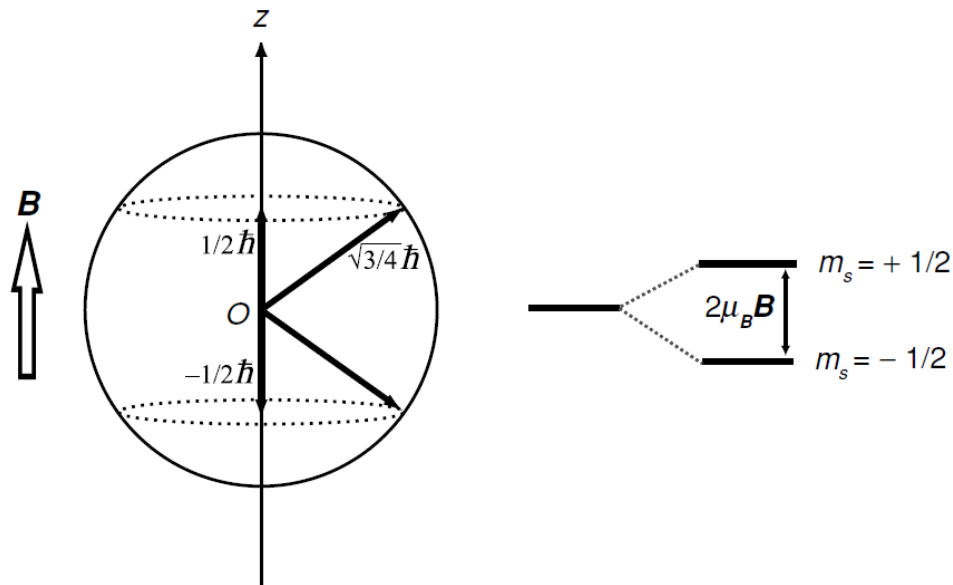
$\hat{s}^2$  with eigenvalues  $s(s + 1)\hbar^2$   
It commutes with  $\hat{s}_x$ ,  $\hat{s}_y$  and  $\hat{s}_z$

# 3.1.4 Quantum mechanics of angular momentum

The eigenvalue of the square of the total angular momentum

$$\langle \hat{\mathbf{S}}^2 \rangle = \langle i | \hat{\mathbf{S}}^2 | i \rangle \text{ is } 3\hbar^2/4 \text{ for both eigenstates } \begin{bmatrix} 1 \\ 0 \end{bmatrix} \text{ and } \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

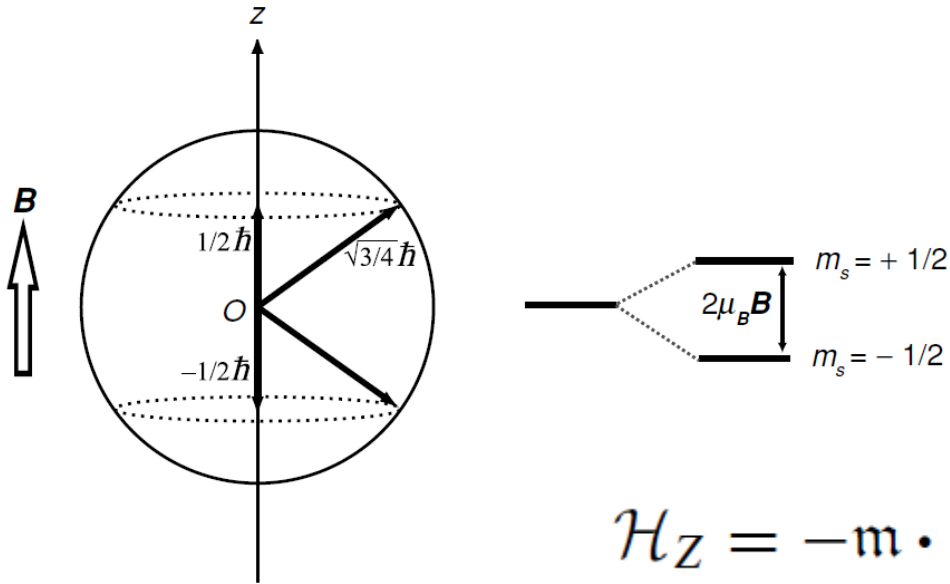
$\hat{\mathbf{S}}_z$  and  $\hat{\mathbf{S}}^2$  are diagonal, and diagonal matrices always commute.



In the Dirac notation,  $\langle i | \hat{a} | j \rangle$  is the  $i, j$  matrix element of the operator  $\hat{a}$ . The diagonal components are  $\langle i | \hat{a} | i \rangle$ . When the matrix has only diagonal terms, which can always be achieved by a suitable transformation if the matrix is Hermitian, the diagonal matrix elements are the eigenvalues. If  $\hat{a}$  is the Hamiltonian, the eigenvalues are the energy levels of the system.  $|i\rangle$ , known as the ‘ket’, is the eigenfunction – a column vector in the matrix representation.  $\langle i|$ , known as the ‘bra’, is the complex conjugate row vector. Their product, the Dirac bracket,  $\langle i | i \rangle = 1$  for normalized eigenfunctions.



## 3.1.4 Quantum mechanics of angular momentum



The two states with  $m_s = \pm \frac{1}{2}$  have opposite magnetic moments and a Zeeman splitting of the two energy levels develops in a magnetic field  $\mathbf{B}$ .

$$\mathcal{H}_Z = -\mathbf{m} \cdot \mathbf{B} = (e/m_e)\hat{\mathbf{s}} \cdot \mathbf{B}$$

$$\text{eigenvalues } g\mu_B m_s B \approx \pm \mu_B B$$

To summarize, an electron with spin quantum number  $s = \frac{1}{2}$  has total angular momentum  $\sqrt{3}\hbar/2$ . There are two spin states,  $m_s = \pm \frac{1}{2}$  with a projection of the angular momentum along a specified direction  $Oz$  of  $\pm \frac{1}{2}\hbar$ . The states are degenerate in zero field, but split in a magnetic field. Alternative notations for the two spin states of the electron are  $|\frac{1}{2}\rangle$  and  $|-\frac{1}{2}\rangle$ ,  $|\downarrow\rangle$  and  $|\uparrow\rangle$ , or  $\alpha$  and  $\beta$ .

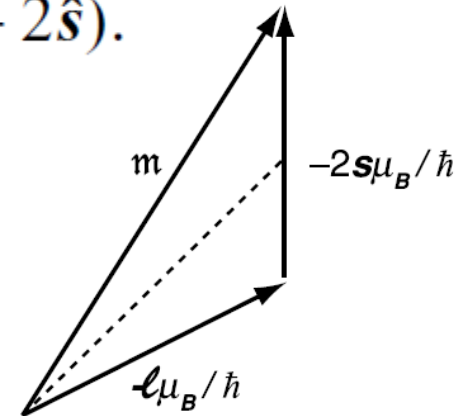
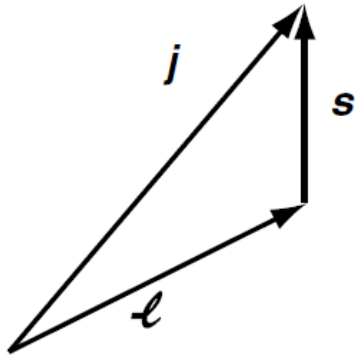
# 3.1.4 Quantum mechanics of angular momentum

The magnetic moment operator of the electron ( $\hat{m}$ , in units of Bohr magnetons) is proportional to the associated angular momentum (in units of  $\hbar$ ) and can be represented by a similar matrix, with the proportionality factor (g-factor) of 1 for orbital and 2 for spin moments.

The total magnetic moment of an electron is generally a vector sum of the spin and orbital magnetic moments:

$$m = -\frac{e}{2m_e}\ell.$$
$$m = -\frac{e}{m_e}s.$$

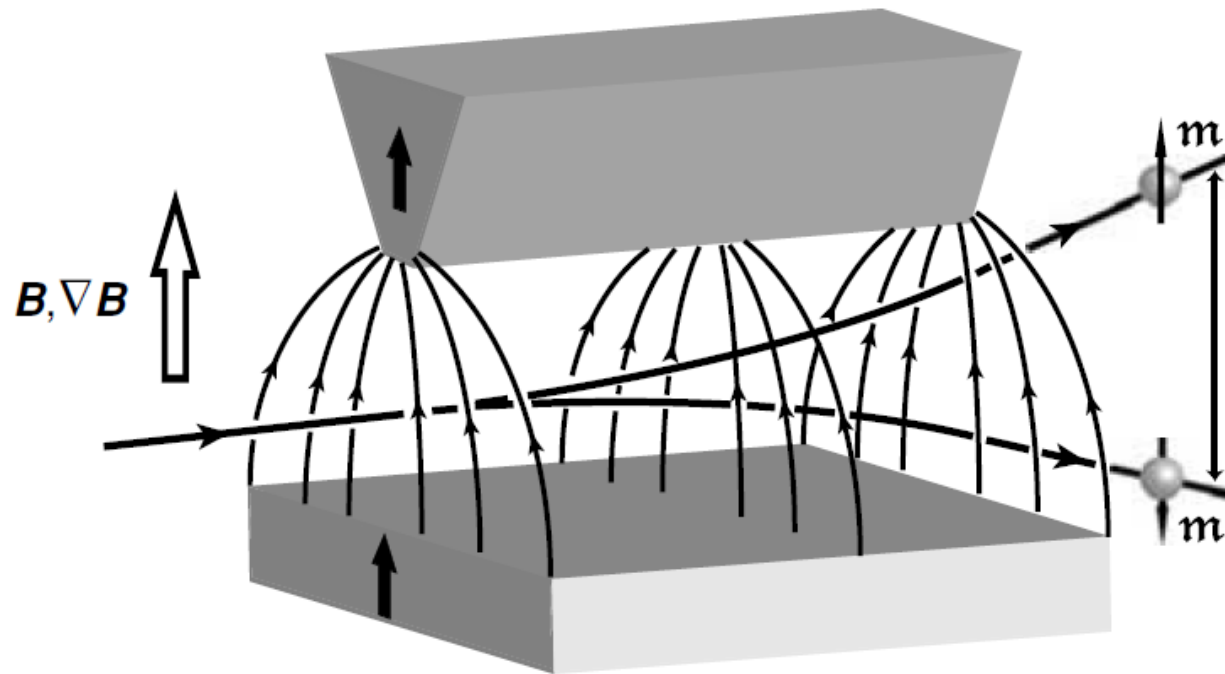
$$\hat{m} = -(\mu_B/\hbar)(\hat{I} + 2\hat{S}).$$



The Zeeman interaction of these moments with an applied field  $B$

$$\mathcal{H}_Z = (\mu_B/\hbar)(\hat{I} + 2\hat{S}) \cdot B.$$

# The Stern–Gerlach experiment



## 3.2 Magnetic field effects

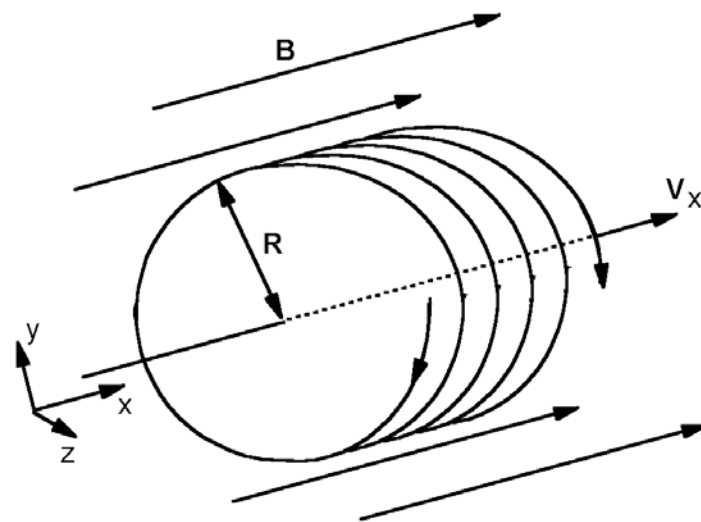
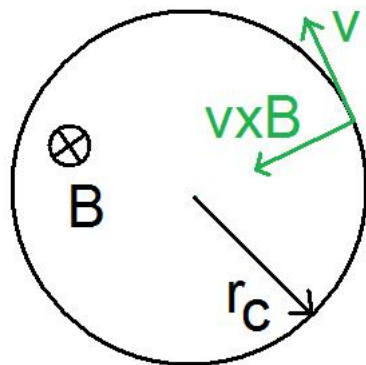
The effects of a magnetic field on an electron are to modify its linear or angular motion, and to induce some magnetization in the direction of the field, as a result of Boltzmann population of the energy levels obtained from (3.21).

In this section, we discuss the effects of a magnetic field on the electron motion semiclassically.

## 3.2.1 Cyclotron orbits

The Lorentz force

$$-e\mathbf{v} \times \mathbf{B}$$



Newton's second law

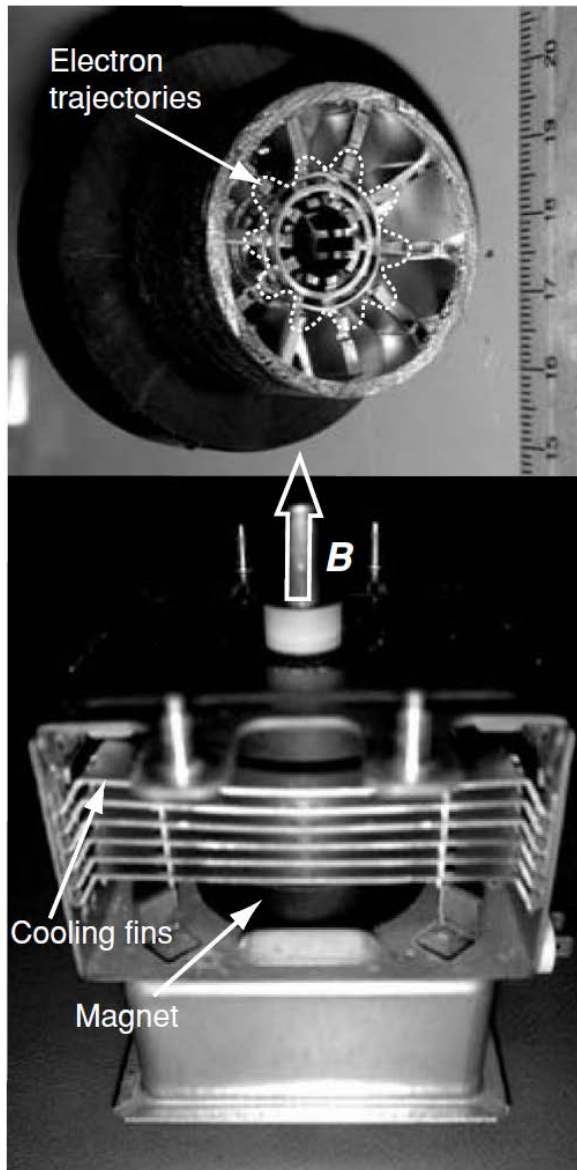
$$f = m_e v_{\perp}^2 / r = e v_{\perp} B$$

the cyclotron frequency

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

$$f_c = \frac{eB}{2\pi m_e}$$

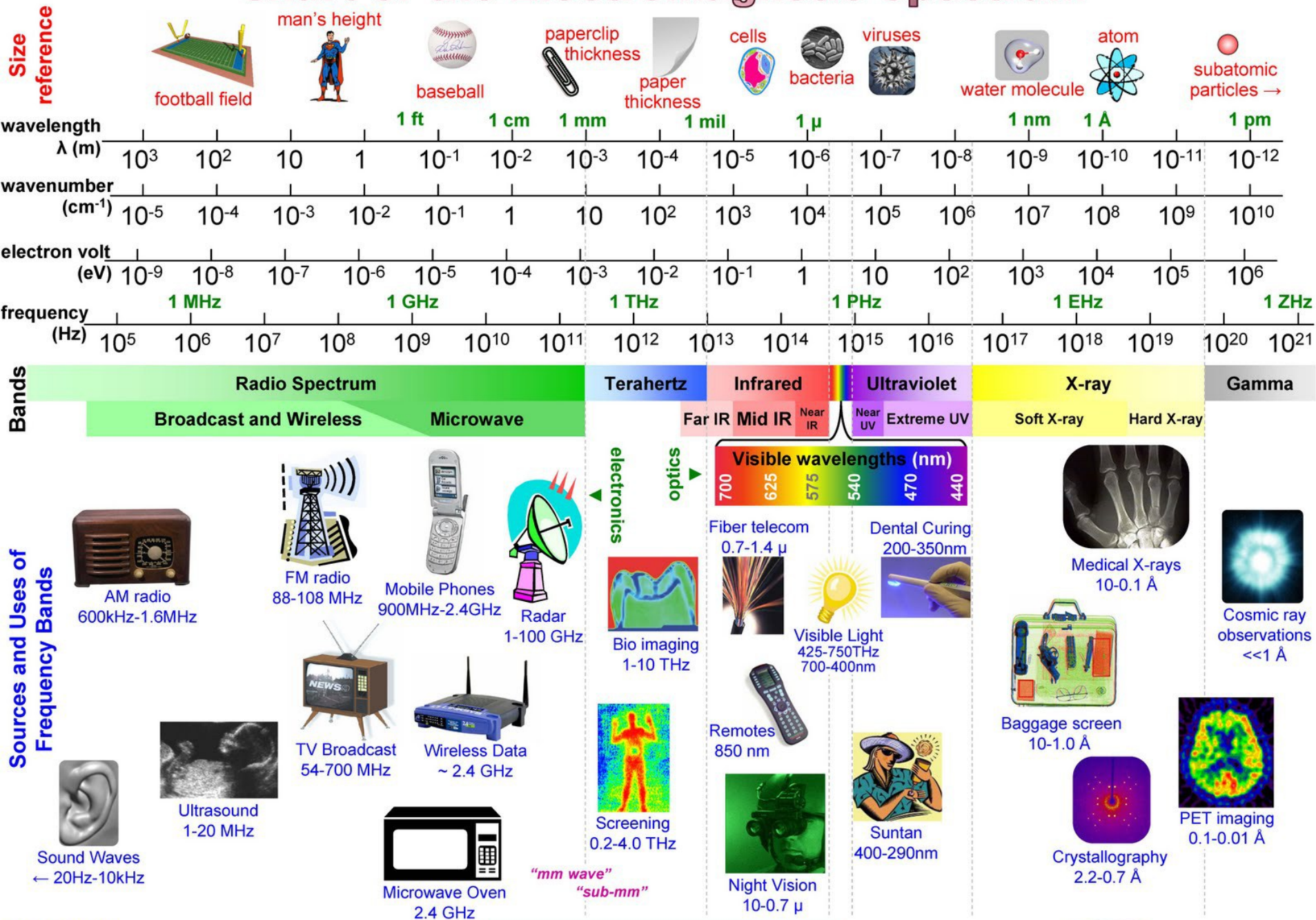
## 3.2.1 Cyclotron orbits



Percy Spencer, the inventor of the first microwave oven, perceived his idea after World War II from radar technology developed during the war. Named the *Radarange*, it was first sold in 1947. Raytheon later licensed its patents for a home-use microwave oven that was first introduced by Tappan in 1955, but these units were still too large and expensive for general home use. The countertop microwave oven was first introduced in 1967 by the Amana Corporation, which was acquired in 1965 by Raytheon.



# Chart of the Electromagnetic Spectrum



$$\lambda = 3 \times 10^8 / \text{freq} = 1 / (\text{wn} * 100) = 1.24 \times 10^{-6} / \text{eV}$$

## 3.2.2 Larmor precession

If an electron is constrained somehow to move in an orbit, it has an associated magnetic moment

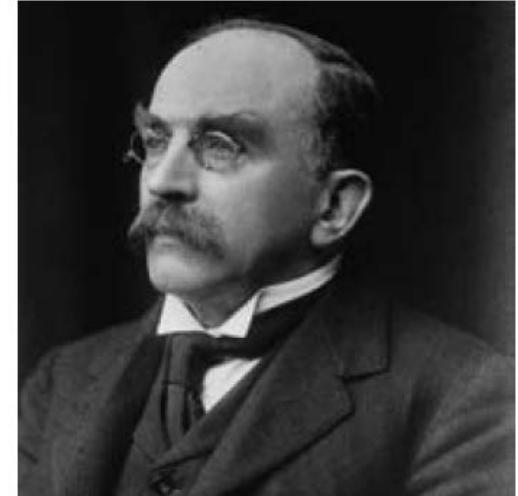
$$\mathbf{m} = \gamma \boldsymbol{\ell}$$

$\gamma$  is the gyromagnetic ratio

The effect of the magnetic field is to exert a torque

$$\boldsymbol{\Gamma} = \mathbf{m} \times \mathbf{B}$$

$$\frac{d\mathbf{m}}{dt} = \gamma \mathbf{m} \times \mathbf{B}.$$



Joseph Larmor, 1857-1942.

$$\boldsymbol{\Gamma} = d\boldsymbol{\ell}/dt$$

When  $\mathbf{B}$  is along the  $z$ -axis, the vector product in Cartesian coordinates gives

$$\frac{dm_x}{dt} = \gamma m_y B \quad \frac{dm_y}{dt} = -\gamma m_x B \quad \frac{dm_z}{dt} = 0.$$

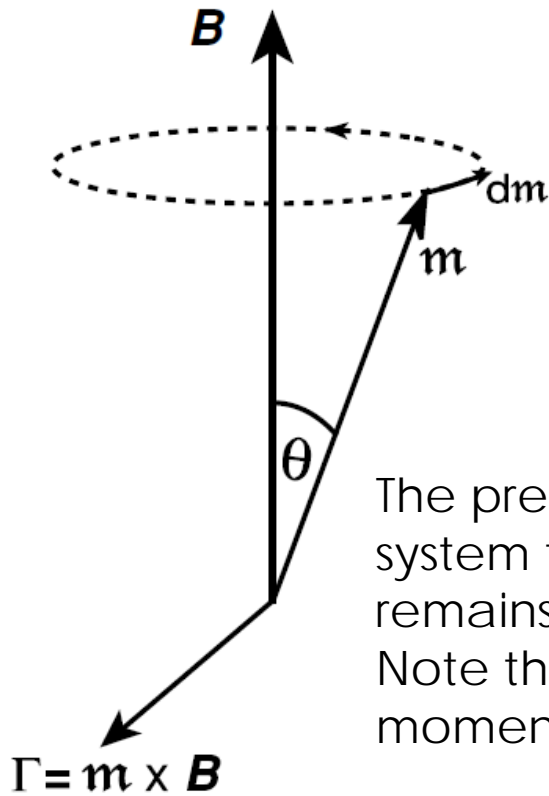


## 3.2.2 Larmor precession

$$\frac{dm_x}{dt} = \gamma m_y B \quad \frac{dm_y}{dt} = -\gamma m_x B \quad \frac{dm_z}{dt} = 0.$$

$$\mathbf{m}(t) = (m \sin \theta \sin \omega_L t, m \sin \theta \cos \omega_L t, m \cos \theta),$$

$$\omega_L = \gamma B$$



The magnetic moment  $m$  therefore precesses around the applied field direction at the Larmor frequency

$$f_L = \frac{\gamma B}{2\pi}.$$

The precession continues indefinitely if there is no way for the system to dissipate energy, and the angular momentum remains constant.

Note that the Larmor precession frequency for an orbital moment is just half the cyclotron frequency,

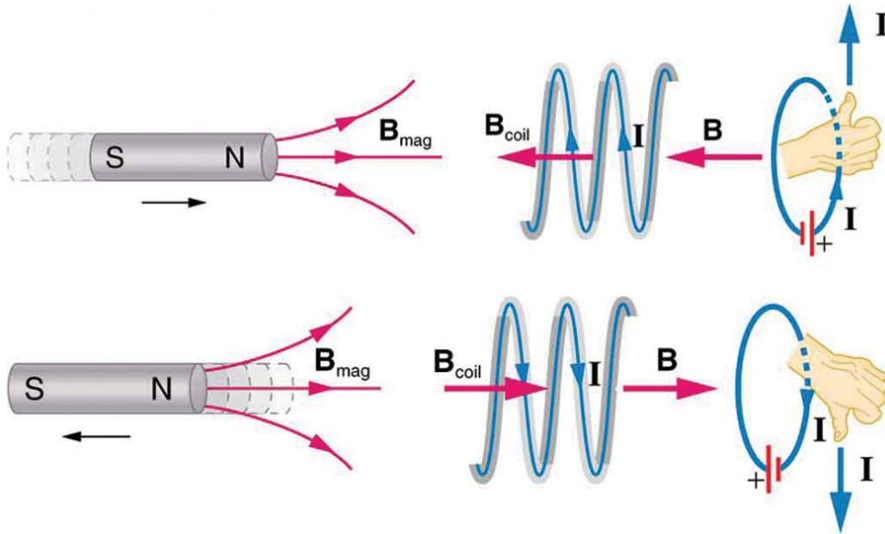
$$\gamma = -e/2m_e \quad \gamma = -e/m_e$$

whereas it is equal to the cyclotron frequency for a spin moment

# 3.2.3 Orbital diamagnetism

There is some angular momentum, and therefore a magnetic moment is associated with the precession of the electron orbit induced by the magnetic field.

By Lenz's law, the induced moment is expected to oppose the applied field.



The induced angular momentum  $m_e \omega_L \langle \rho^2 \rangle$

$$\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$$

the mean square radius of the electron's orbit projected onto the plane perpendicular to  $B$ .

$$\omega_L = \gamma B$$

$$m = \gamma \ell$$

$$m = -\gamma^2 m_e \langle \rho^2 \rangle B$$

$$\gamma = -(e/2m_e)$$

$$\langle r^2 \rangle = (3/2) \langle \rho^2 \rangle$$

a susceptibility  $\mu_0 M/B$

$$\chi = -n \mu_0 e^2 \langle r^2 \rangle / 6m_e$$

# 3.2.3 Orbital diamagnetism

**Table 3.2.** Diamagnetic susceptibilities  $\chi_m$  of common ions. Units are  $10^{-9} \text{ m}^3 \text{ kg}^{-1}$  (after Sellwood, 1956)

H <sup>+</sup>	0	Be <sup>2+</sup>	0.6	Sc <sup>3+</sup>	1.7	C <sup>4+</sup>	0.1	F <sup>-</sup>	7.2
Li <sup>+</sup>	1.1	Mg <sup>2+</sup>	1.6	Y <sup>3+</sup>	1.8	Si <sup>4+</sup>	0.4	OH <sup>-</sup>	8.8
Na <sup>+</sup>	2.7	Ca <sup>2+</sup>	2.5	La <sup>3+</sup>	1.8	Ge <sup>4+</sup>	1.2	Cl <sup>-</sup>	9.2
K <sup>+</sup>	4.2	Sr <sup>2+</sup>	2.1	Lu <sup>3+</sup>	1.2	Sn <sup>4+</sup>	1.7	Br <sup>-</sup>	5.6
Rb <sup>+</sup>	2.9	Ba <sup>2+</sup>	2.9			Pb <sup>4+</sup>	1.4	I <sup>-</sup>	5.1
Cs <sup>+</sup>	2.9			B <sup>3+</sup>	0.2				
Cu <sup>+</sup>	2.4	Zn <sup>2+</sup>	1.9	Al <sup>3+</sup>	0.9	Ti <sup>4+</sup>	1.3	O <sup>2-</sup>	9.4
Ag <sup>+</sup>	2.8	Cd <sup>2+</sup>	2.5	Ga <sup>3+</sup>	1.4	Zr <sup>4+</sup>	1.4	S <sup>2-</sup>	14.8
Au <sup>+</sup>	2.5	Hg <sup>2+</sup>	2.3	In <sup>3+</sup>	2.1	Hf <sup>4+</sup>	1.1	Se <sup>2-</sup>	7.6
NH <sub>4</sub> <sup>+</sup>	8.0	Pb <sup>2+</sup>	1.7			U <sup>6+</sup>	1.0	Te <sup>2-</sup>	6.8

In atoms, the effect is dominated by the outer electron shells, which have the largest orbital radii.

Negative ions therefore tend to have the largest diamagnetic susceptibility

The order of magnitude of the orbital diamagnetic susceptibility  $\chi$  for an element with

$n \approx 6 \times 10^{28} \text{ atoms m}^{-3}$

$\sqrt{\langle r^2 \rangle} \approx 0.2 \text{ nm}$

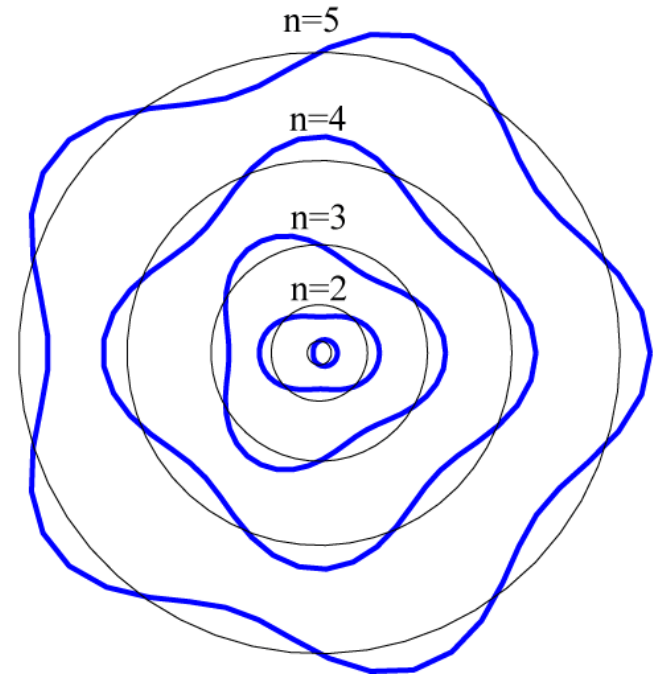
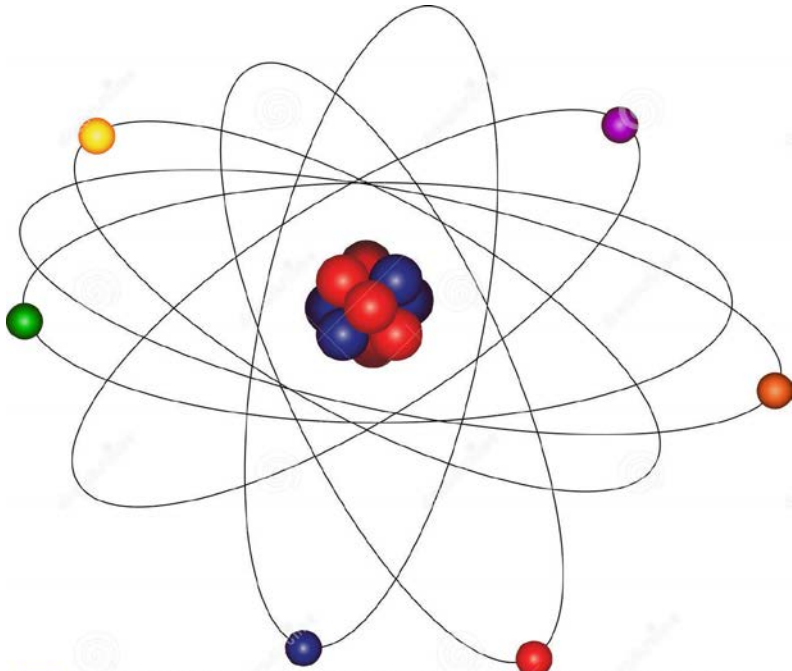
mass susceptibility  $\chi_m = \chi/d$ ,  $10^{-9} \text{ m}^3 \text{ kg}^{-1}$

## 3.2.3 Orbital diamagnetism

Orbital diamagnetism is a small effect, present to some extent for every element and molecule.

It is the dominant susceptibility when there are no partially filled shells, which produce a larger paramagnetic contribution due to unpaired electron spins.

Relatively large diamagnetic susceptibilities are observed for aromatic organic materials.



# the Bohr–van Leeuwen theorem

Unfortunately, there is an underlying problem with classical calculations of the response of electrons to magnetic fields. Since the magnetic force  $\mathbf{f} = -e(\mathbf{v} \times \mathbf{B})$  is perpendicular to the electron velocity, the magnetic field does no work on a moving electron, and cannot modify its energy.

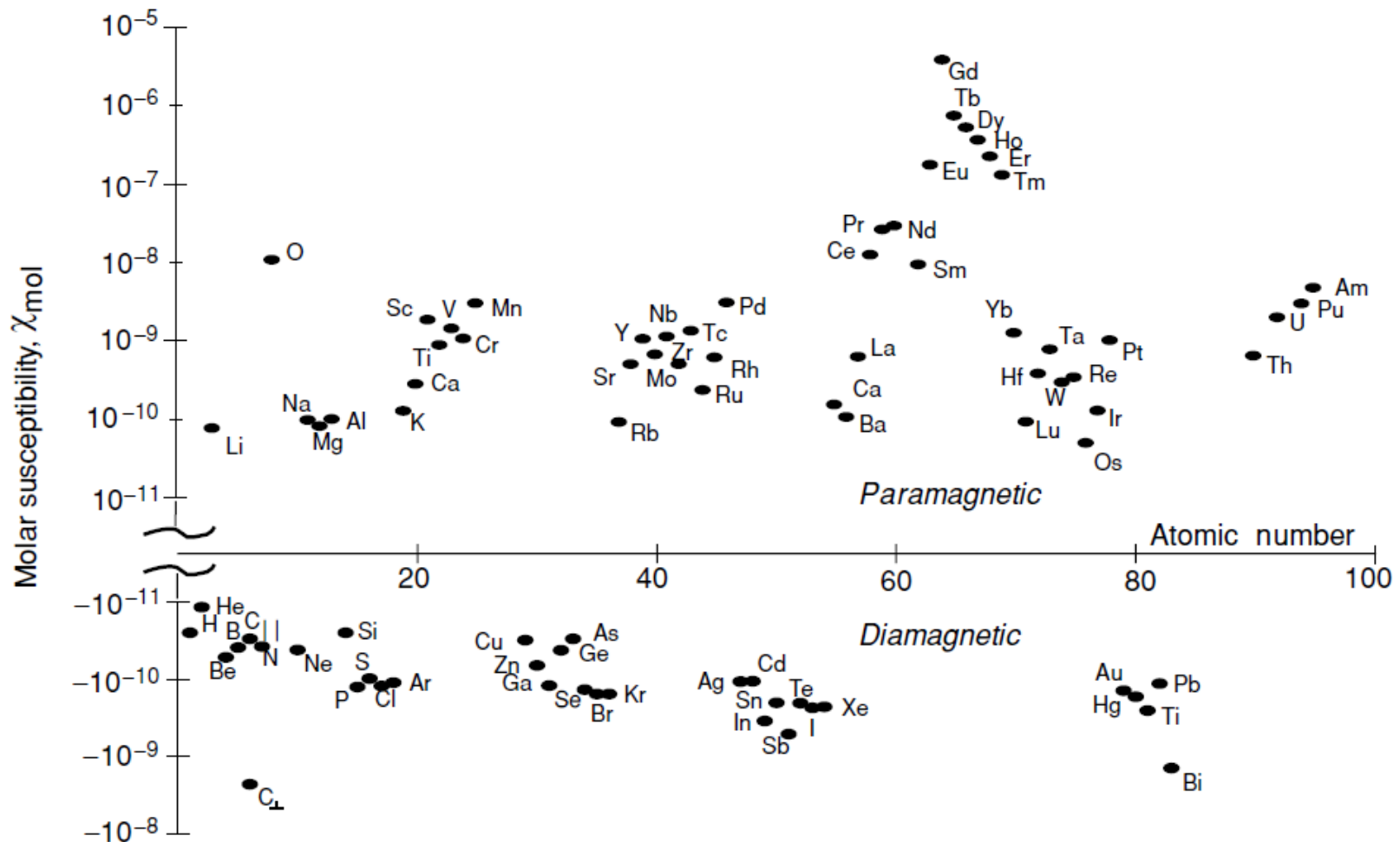
Hence  $\delta w'$  is zero in (2.92), and it follows that there can be no change of magnetization.

The idea was set out in the Bohr–van Leeuwen theorem, a famous and disconcerting result of classical statistical mechanics which states that

*at any finite temperature and in all finite electric or magnetic fields, the net magnetization of a collection of electrons in thermal equilibrium vanishes identically.*

**Every sort of magnetism is impossible for electrons in classical physics!**

The semiclassical calculation of the orbital diamagnetism works only because we have assumed that there is a fixed magnetic moment associated with the orbit.



The diamagnetic susceptibility of more than half the elements in the periodic table is overwhelmed by a positive paramagnetic contribution.

## 3.2.4 Curie-law paramagnetism (localized e)

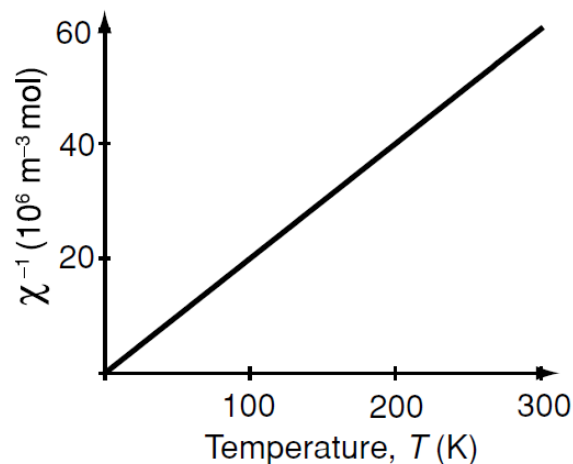
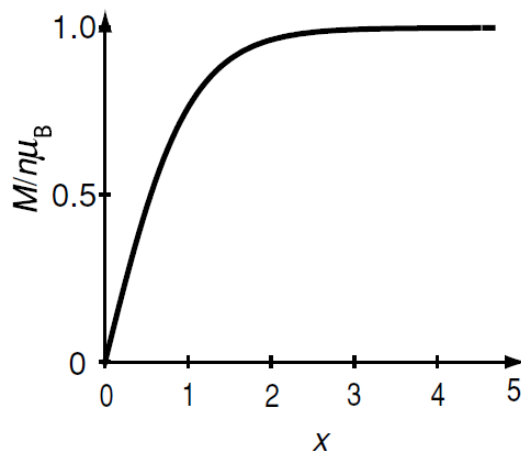
We now grant the electron its intrinsic spin moment, and examine how paramagnetic susceptibility arises in the **two extreme models of magnetism**, those of localized and delocalized electrons.

The Curie law is

$$\chi = C/T$$

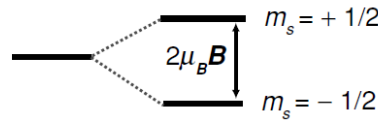
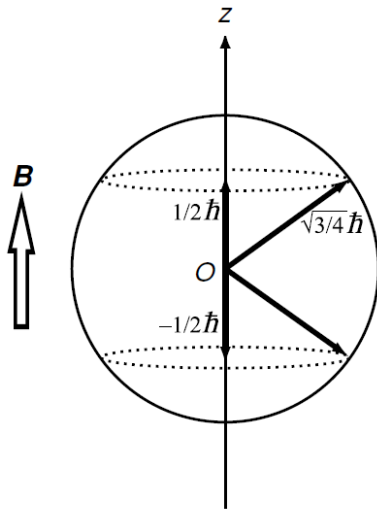
The Curie constant

$$C = n\mu_0\mu_B^2/k_B$$





### 3.2.4 Curie-law paramagnetism (localized e)



electrons per unit volume

$$n = (n^\uparrow + n^\downarrow)$$

the induced magnetization along Oz

$$(n^\uparrow - n^\downarrow)\mu_B$$

The Boltzmann populations of the two energy levels which are proportional to

$$\exp(\pm\mu_B B/k_B T)$$

$$M = c\mu_B[\exp(\mu_B B/k_B T) - \exp(-\mu_B B/k_B T)]$$

$$n = c[\exp(\mu_B B/k_B T) + \exp(-\mu_B B/k_B T)]$$

## 3.2.4 Curie-law paramagnetism (localized e)

The average z-component of the moment per atom

$$\langle m_z \rangle = \frac{(n^\uparrow - n^\downarrow)\mu_B}{(n^\uparrow + n^\downarrow)}$$

$$\langle m_z \rangle = \frac{[\exp(x) - \exp(-x)]\mu_B}{[(\exp(x) + \exp(-x))],}$$

$$x = \mu_B B / k_B T$$

$$M = n\mu_B \tanh x$$

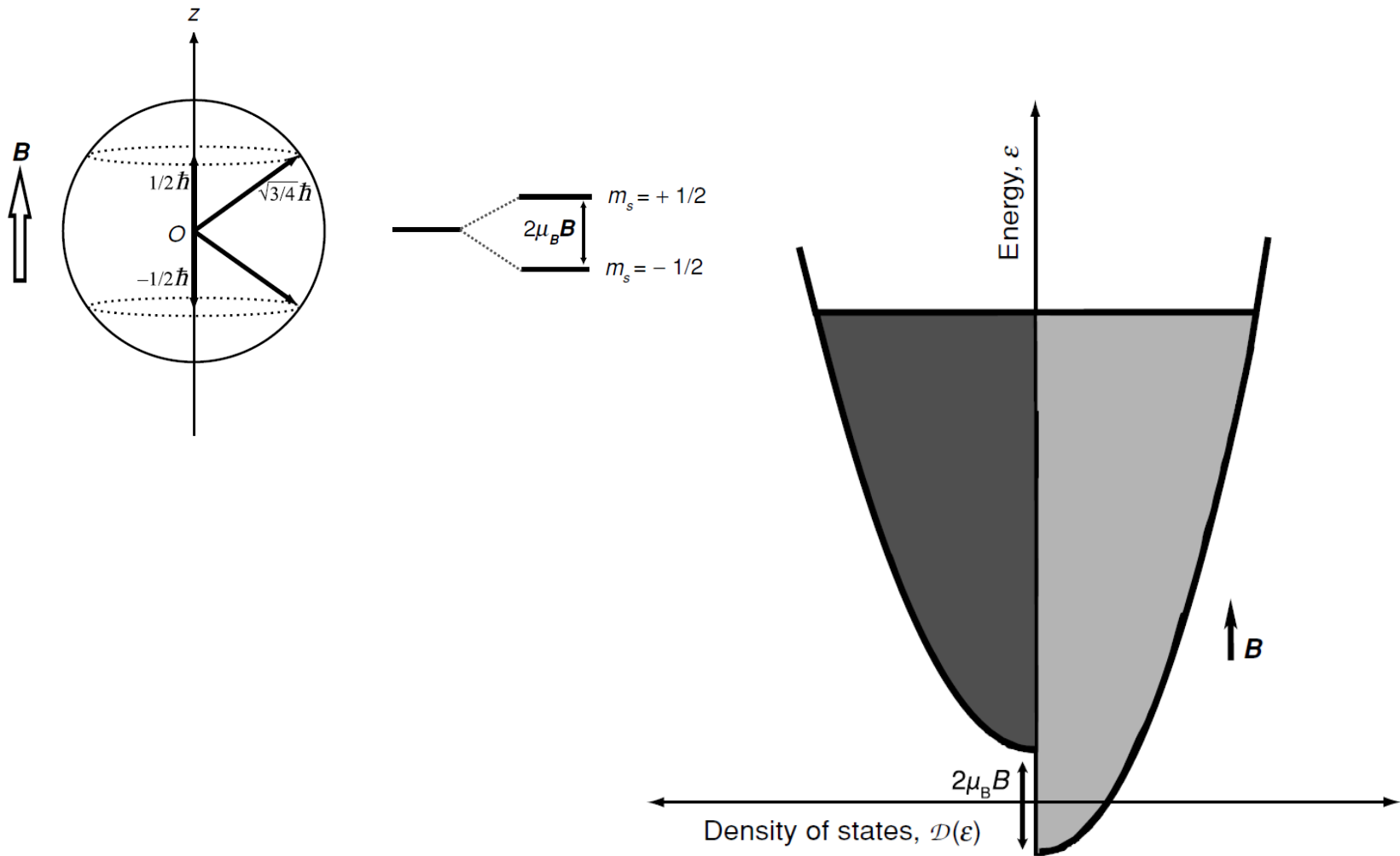
At room temperature  $\mu_B B \ll k_B T$

$$\tanh x \approx x$$

$$\chi = \mu_0 M / B$$

$$\chi = n\mu_0\mu_B^2 / k_B T$$

## 3.2.5 The free-electron model



## 3.2.5 The free-electron model

In order to calculate the susceptibility in the opposite, delocalized, limit we introduce the simplest possible delocalized-electron model for a solid.

The electrons are described as noninteracting waves confined in a box of dimension  $L$ .

The Hamiltonian is the sum of terms representing the kinetic and potential energy:

$$\mathcal{H} = [(p^2/2m_e) + V(\mathbf{r})]$$

$$\hat{p} = -i\hbar\nabla$$

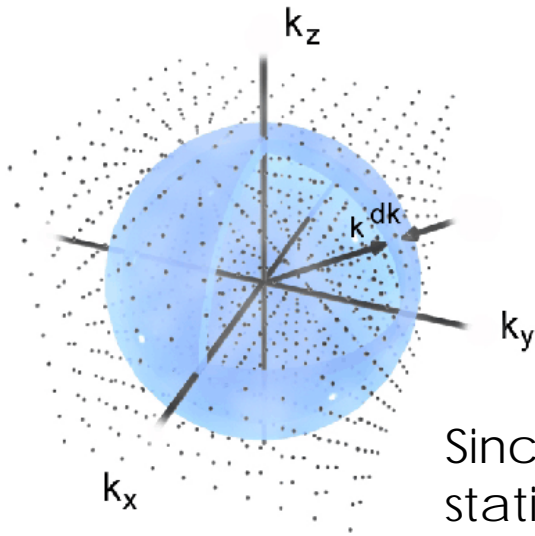
$$-(\hbar^2/2m_e)\nabla^2\psi = \varepsilon\psi$$

$$\psi = L^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r})$$

$$\mathbf{p} = \hbar\mathbf{k}$$

$$\varepsilon = \hbar^2 k^2 / 2m_e$$

## 3.2.5 The free-electron model



The boundary conditions, which are periodic for free-electron waves, restrict the allowed values of  $\mathbf{k}$  so that the components

$$k_i (i = x, y, z) = \pm 2\pi n_i / L$$

Since indistinguishable electrons obey Fermi–Dirac statistics, each quantum state represented by the integers  $n_x, n_y, n_z$  can accommodate at most two electrons one  $\uparrow$ , the other  $\downarrow$

Each state has two-fold spin degeneracy.

At zero temperature the  $N = nL^3$  electrons in the box occupy all the lowest available energy states, which occupy a sphere of radius  $k_F$ , the Fermi wavevector.

$$\frac{4}{3}\pi k_F^3 = (N/2)(2\pi/L)^3$$

## 3.2.5 The free-electron model

**Table 3.3.** Properties of the free-electron gas

Fermi wavevector	$k_F$	$(3\pi^2 n)^{1/3}$	$1.2 \times 10^{10}$	$\text{m}^{-1}$
Fermi velocity	$v_F$	$\hbar k_F / m_e$	$1.4 \times 10^6$	$\text{m s}^{-1}$
Fermi energy	$\varepsilon_F$	$(\hbar k_F)^2 / 2m_e$	$9 \times 10^{-19}$	J
Fermi temperature	$T_F$	$\varepsilon_F / k_B$	$6.5 \times 10^4$	K
Density of states	$\mathcal{D}_{\uparrow, \downarrow}(\varepsilon_F)$	$3n / 4\varepsilon_F$	$5 \times 10^{46}$	$\text{m}^{-3} \text{J}^{-1}$
Pauli susceptibility	$\chi_P$	$3\mu_0 \mu_B^2 n / 2\varepsilon_F$	$1.1 \times 10^{-5}$	
Hall coefficient	$R_h$	$1 / ne$	$1.0 \times 10^{-10}$	$\text{m}^3 \text{C}^{-1}$

Numerical values are for  $n = 6 \times 10^{28} \text{ m}^{-3}$ . Density of states is for one spin.

$$\varepsilon_F = (\hbar^2 / 2m_e)(3\pi^2 n)^{2/3}$$

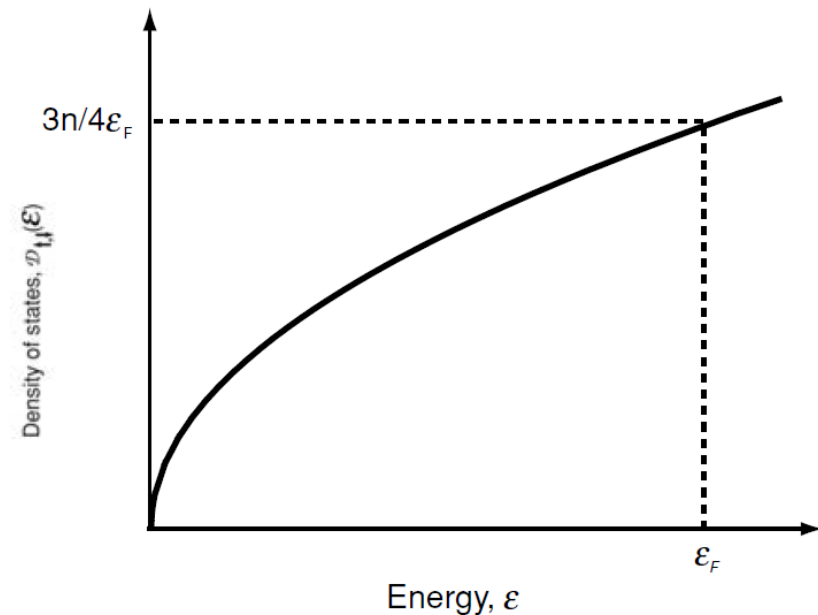
The surface separating occupied and unoccupied states is the **Fermi surface**, which in the free electron model is a sphere.

## 3.2.5 The free-electron model

The density of states  $\text{m}^{-3} \text{J}^{-1}$

$$\mathcal{D}_{\uparrow,\downarrow}(\varepsilon) = \frac{1}{2} \text{d}n/\text{d}\varepsilon$$

$$\mathcal{D}_{\uparrow,\downarrow}(\varepsilon) = (1/4\pi^2)(2m_e/\hbar^2)^{3/2} \varepsilon^{1/2}$$



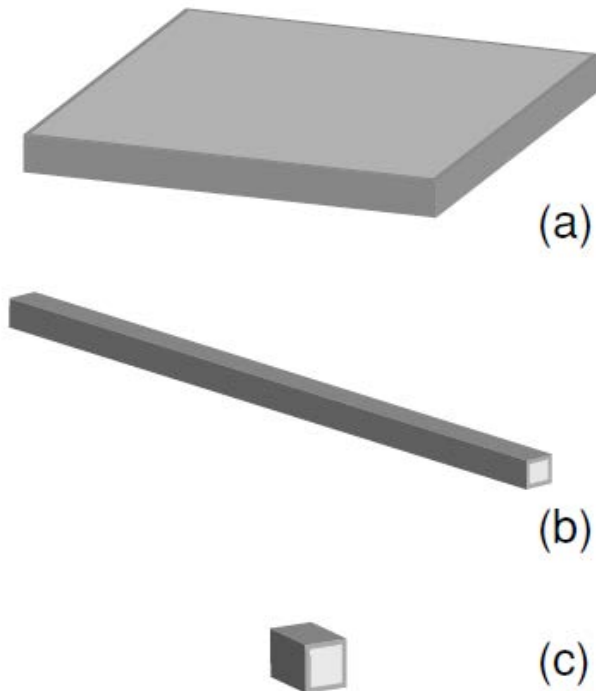
the density of states at the Fermi level for our sample with  $n$  electrons per unit volume can be written

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

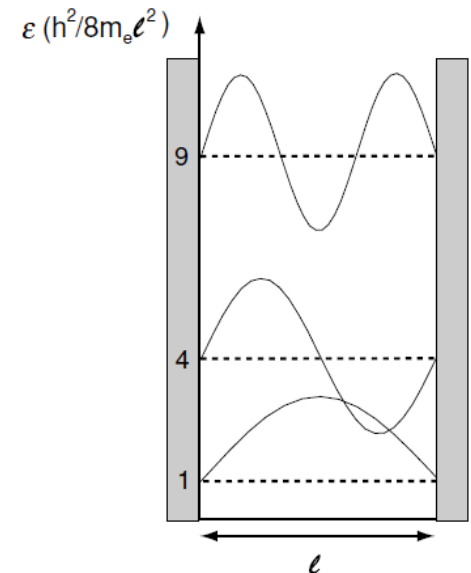
## 3.2.5 The free-electron model

Provided the dimensions of the box are macroscopic, the electron states are very closely spaced in energy, and the expression for the density of states does not depend on  $L$  or on the shape of the box.

However, the energy structure and density of states are drastically modified when the electron gas is confined in one or more directions on a nanometre length scale. Generations of miniaturization have made electron transport in such confined dimensions the focus of modern electronics.



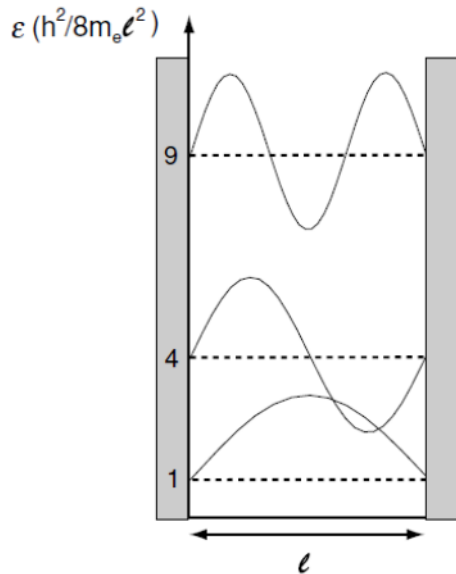
Confinement leads to a coarse-grained momentum and energy structure, which follows from the de Broglie relation





## 3.2.5 The free-electron model

A two-dimensional electron gas



$$\varepsilon_i = \frac{\hbar^2}{2m_e} \left[ k_x^2 + k_y^2 + \left( \frac{\pi n_i}{l} \right)^2 \right]$$

$$\pi k_F^2 = (N/2)(2\pi/L)^2$$

$$N = nL^2$$

The Fermi energy  $\varepsilon_F$

$$(\hbar^2/2m_e)2\pi n$$

$$\mathcal{D}_{\uparrow,\downarrow}(\varepsilon_F) = (1/4\pi)(2m_e/\hbar^2)$$

a quantum wire

$$\varepsilon_{ij} = \frac{\hbar^2}{2m_e} \left[ k_x^2 + \left( \frac{\pi n_i}{l} \right)^2 + \left( \frac{\pi n_j}{l} \right)^2 \right]$$

$$\mathcal{D}_{\uparrow,\downarrow}(\varepsilon_F) = (m_e/2\pi\hbar)(1/2m_e\varepsilon_F)^{1/2}$$

## 3.2.5 The free-electron model

Electrons moving in the lattice of a crystalline solid are subject to the periodic potential of the nuclei screened by their tightly bound ion cores. According to **Bloch's theorem**, the electronic states

$$\psi(\mathbf{r}) \approx \exp(i\mathbf{k} \cdot \mathbf{r})u_k(\mathbf{r})$$

$$u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R})$$

$$\mathbf{R} = p\mathbf{a}_1 + q\mathbf{a}_2 + r\mathbf{a}_3$$

a general lattice vector defined as a sum of the primitive lattice vectors

When the wavevector for an electron moving in some direction in  $k$ -space satisfies the **Bragg condition**,

$$2\mathbf{k} \cdot \mathbf{G} = G^2,$$

it will be reflected and a series of singularities will appear in the free-electron dispersion relation, which can lead to sharp structure and even gaps in the density of states.

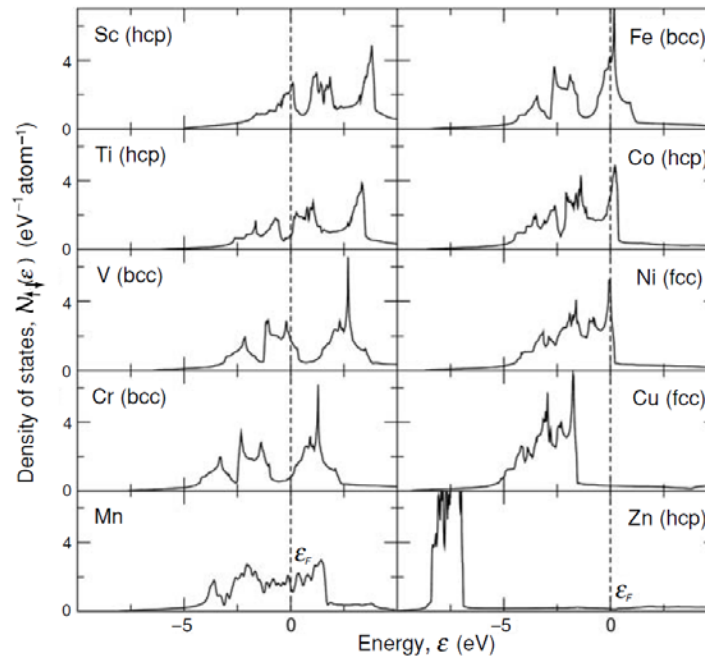
## 3.2.5 The free-electron model

$$2\mathbf{k} \cdot \mathbf{G} = G^2,$$

Here  $\mathbf{G}$  is a lattice vector of the reciprocal lattice of the crystal in  $k$ -space, whose lattice points are

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

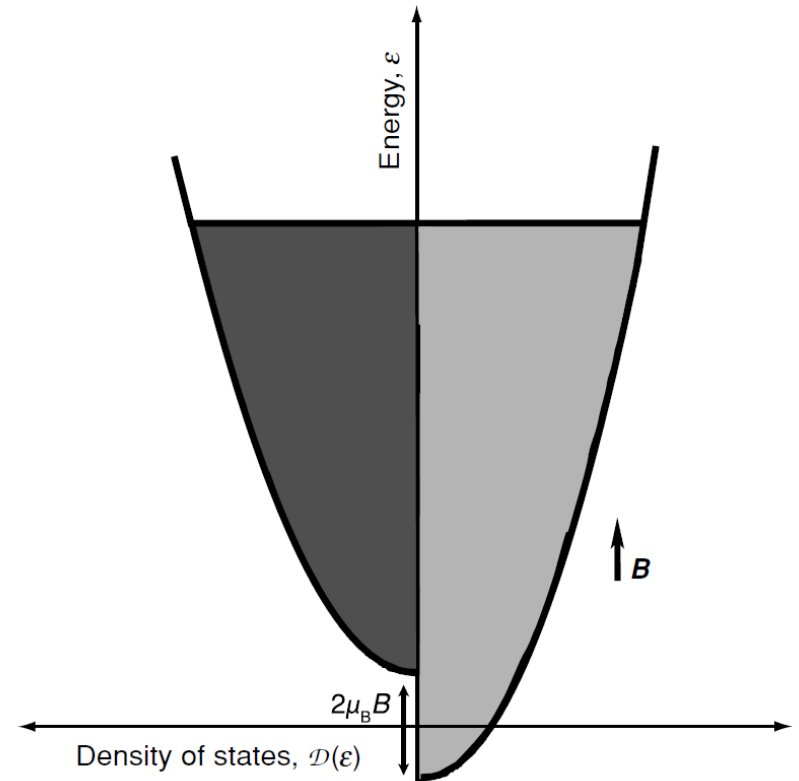
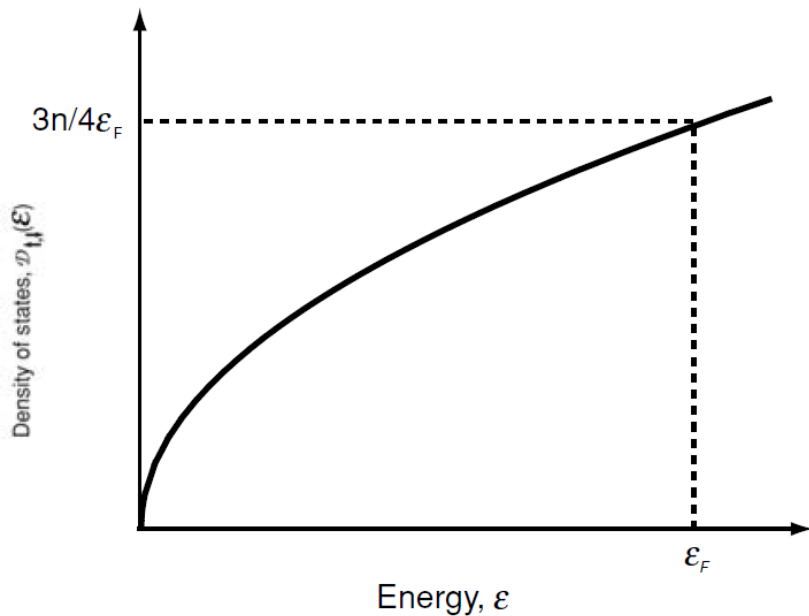
$$\mathbf{b}_1 = 2\pi(\mathbf{a}_2 \times \mathbf{a}_3)/(\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3))$$



## 3.2.6 Pauli susceptibility

The effect of an applied magnetic field  $B$  acting on the spin moment is to shift the two subbands by

$$\pm \mu_B B$$

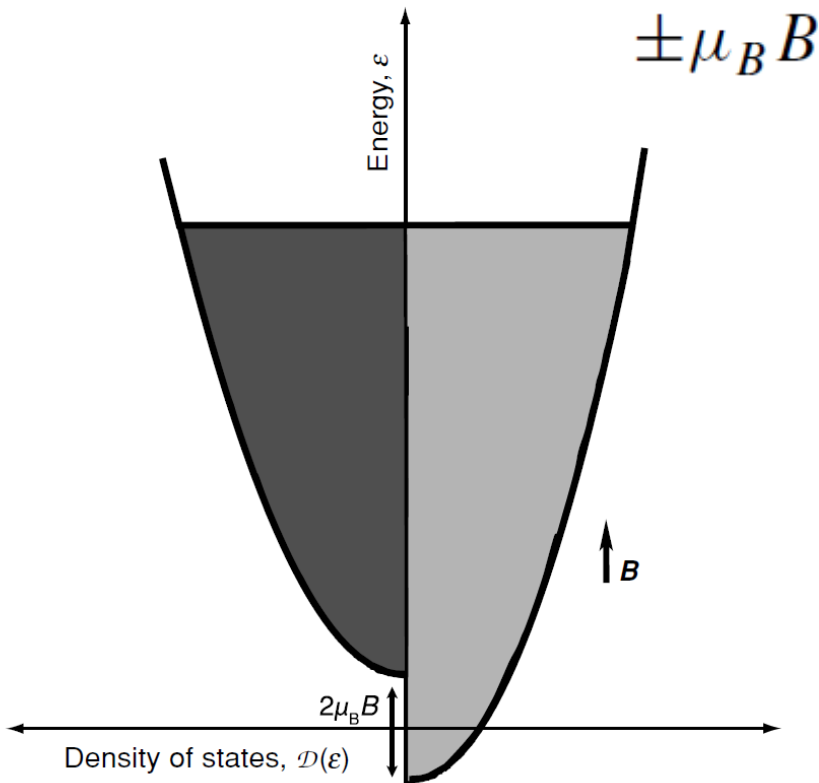


$$M = (n^{\uparrow} - n^{\downarrow})\mu_B$$

$$2\mathcal{D}_{\uparrow,\downarrow}(\varepsilon_F)\mu_B^2 B$$

## 3.2.6 Pauli susceptibility

The effect of an applied magnetic field  $B$  acting on the spin moment is to shift the two subbands by



$$\pm\mu_B B$$

$$M = (n^\uparrow - n^\downarrow)\mu_B$$

$$2\mathcal{D}_{\uparrow,\downarrow}(\epsilon_F)\mu_B^2 B$$

$$\chi_P = \mu_0 M / B$$

$$\chi_P = 2\mu_0\mu_B^2 \mathcal{D}_{\uparrow,\downarrow}(\epsilon_F).$$

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

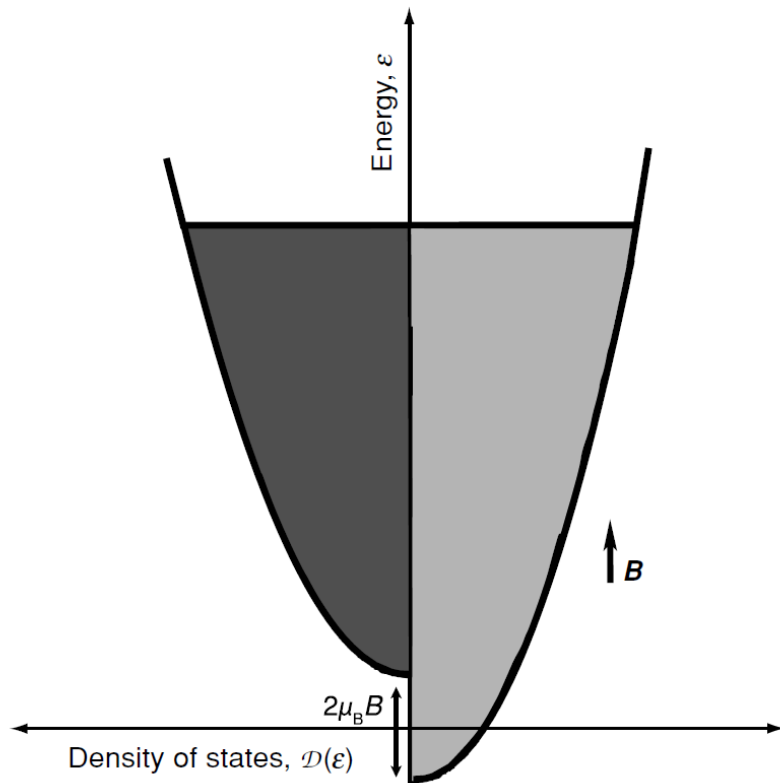
$$\epsilon_F = k_B T_F$$

$$\chi_P = \frac{3n\mu_0\mu_B^2}{2k_B T_F}.$$

The Pauli susceptibility is temperature-independent to first order. about two orders of magnitude smaller than the Curie susceptibility at room temperature.

## 3.2.6 Pauli susceptibility

At finite temperature, the occupancy of the states given by  $D(\varepsilon)$  is determined by the Fermi-Dirac distribution function:



$$f(\varepsilon) = \frac{1}{\{\exp[(\varepsilon - \mu)/k_B T] + 1\}},$$

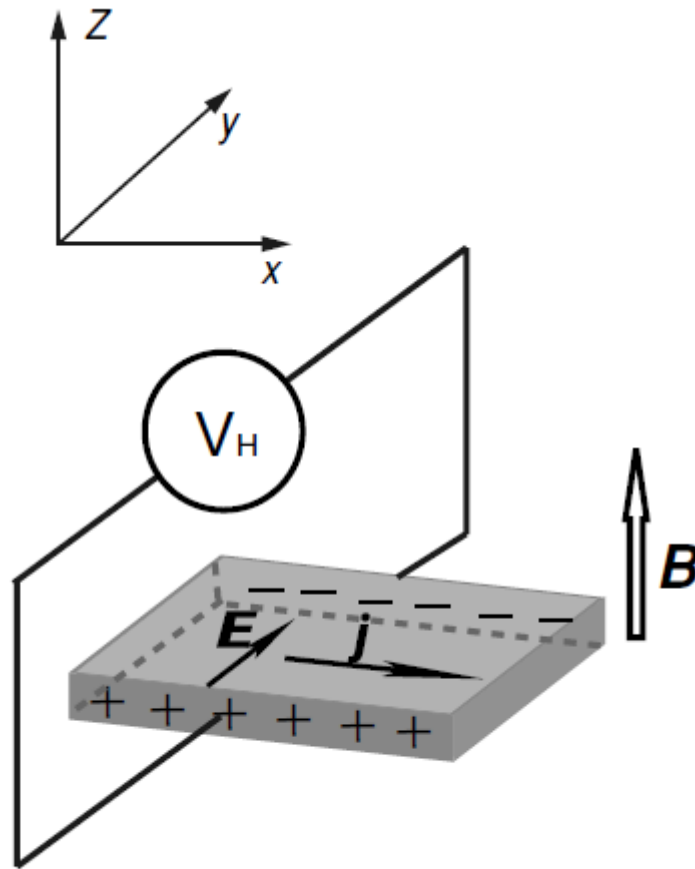
where  $\mu$  is the **chemical potential**.  
At  $T = 0$  K,  $\mu = \varepsilon_F$ .

$$\mu = \varepsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \dots \right].$$

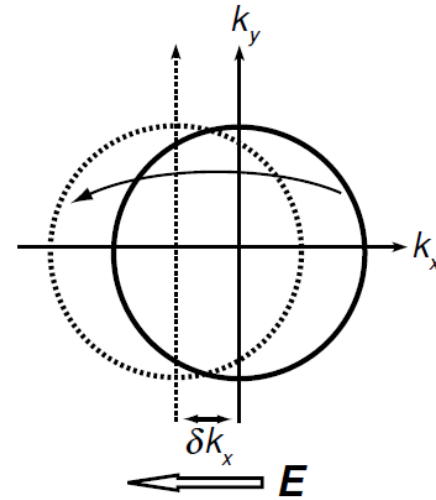
$$\chi_P = \frac{3n\mu_0\mu_B^2}{2k_B T_F}.$$

$$\chi_P = \frac{3n\mu_0\mu_B^2}{2k_B T_F} \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \dots \right]$$

## 3.2.7 Electrical conduction



The Hall effect.



The Fermi surface of copper.

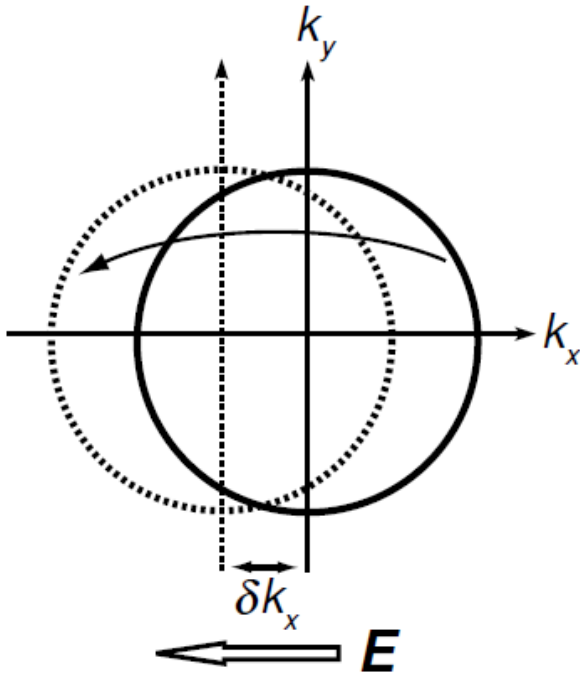
$$\mathbf{E} = \varrho \mathbf{j},$$

$$\hat{\varrho} = \begin{bmatrix} \varrho_{xx} & -\varrho_{xy} & 0 \\ \varrho_{xy} & \varrho_{xx} & 0 \\ 0 & 0 & \varrho_{zz} \end{bmatrix},$$

$$\varrho_{xy} \propto B \text{ and } \varrho_{xx} = \varrho_{zz} + \alpha B^2.$$

## 3.2.7 Electrical conduction

We will now consider electrical conduction in the free electron model of a metal, and how it is influenced by a magnetic field.



$$\mathbf{j} = \sigma \mathbf{E},$$

where  $\sigma$  is the electrical conductivity in  $\text{S m}^{-1}$ .

$$\mathbf{E} = \varrho \mathbf{j},$$

where  $\varrho = 1/\sigma$  is the resistivity in  $\Omega \text{ m}$ .

$$R = \varrho l/a.$$

$$E = V/l,$$

$$I = ja,$$

$$V = IR$$

Ohm's law can be written in terms of the chemical potential, which is the change of energy when one extra electron is added to the metal. In an electric potential

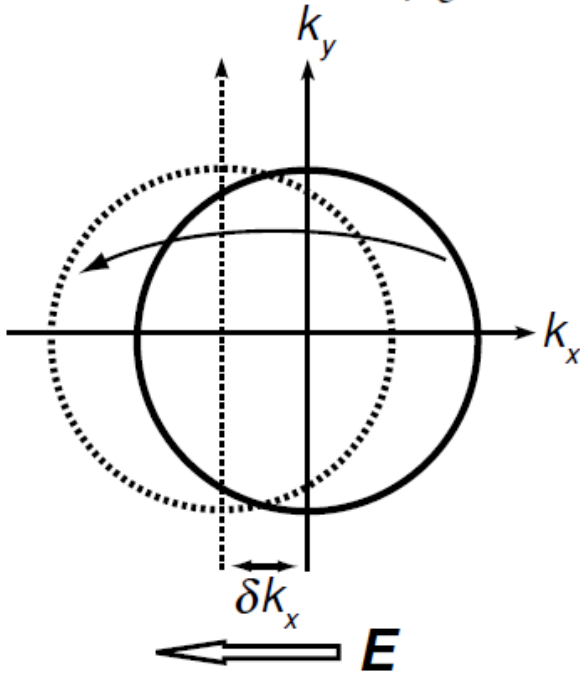


## 3.2.7 Electrical conduction

Ohm's law can be written in terms of the chemical potential, which is the change of energy when one extra electron is added to the metal. In an electric potential  $\varphi_e$

$$\mu = \mu_0 - e\varphi_e,$$

where  $\mu_0$  is the constant chemical potential in the absence of an electric field.



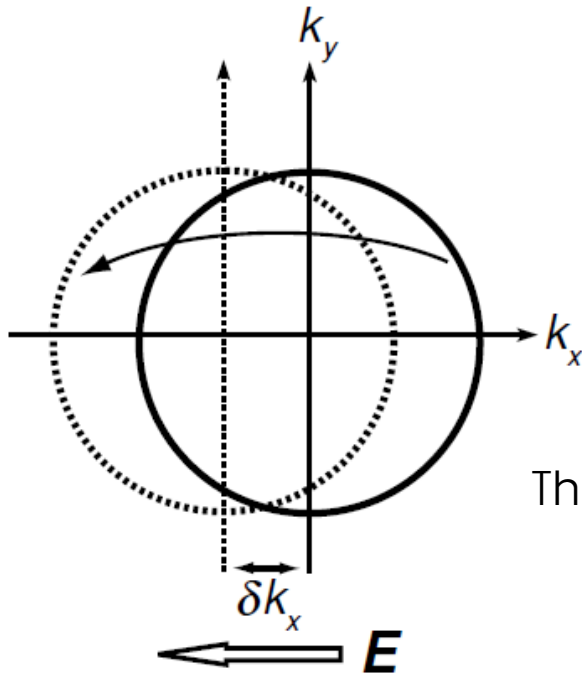
$$\mathbf{E} = -\nabla\varphi_e = \nabla(\mu/e),$$

$$\mathbf{j} = \frac{\sigma}{e}\nabla\mu.$$

A constant gradient of chemical potential is therefore associated with a flow of current in a conductor. The electrons are guided down the wire by a gradient of charge density at the surface of the conductor.

## 3.2.7 Electrical conduction

The entire Fermi surface is very slightly shifted in the direction of  $\mathbf{E}$  as the electrons acquire a drift velocity  $v_d$  in the field direction.



$$\mathbf{j} = -nev_d$$

Mobility, defined as

$$\mu = v_d / E$$

$$\mathbf{j} = \sigma \mathbf{E},$$

$$\sigma = ne\mu.$$

The conductivity of copper at room temperature

$$\sigma = 60 \times 10^6 \Omega^{-1} \text{ m}$$

$$n = 8.45 \times 10^{28} \text{ m}^{-3}$$

$$\mu = 4 \times 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

$$\mathbf{j} = 1 \text{ A mm}^{-2}$$

$$v_d = 0.07 \text{ mm s}^{-1}$$

Electrons drift at the proverbial snail's pace, but their instantaneous Fermi velocity is an astonishing ten orders of magnitude greater.

## 3.2.7 Electrical conduction

The conduction process involves electrons being accelerated by the force

$$-e\mathbf{E}$$

in a direction opposite to the field for a time  $\tau$ , on average, before they are scattered across the Fermi surface into states where their velocity is randomized

Newton's second law gives  $eE\tau = m_e v_d$

$$\sigma = \frac{ne^2\tau}{m_e}.$$

The **mean free path** travelled by an electron in time  $\tau$  between collisions is

$$\lambda = v_F\tau$$

In our example of copper,

$$\tau = 2.5 \times 10^{-14} \text{ s}$$

$$\lambda = 40 \text{ nm.}$$

## 3.2.7 Electrical conduction

The free-electron model is quite a good approximation for metals like copper with a half-filled s-band and an almost-spherical Fermi surface. It can be extended to other metals with nonparabolic densities of states by defining an effective mass for the electrons as

$$m^* = \hbar^2 (\partial^2 \varepsilon / \partial k^2)_{\varepsilon_F}^{-1}.$$

Hence, narrow bands have high effective mass and low mobility,

$$\mu = e\tau / m^*.$$

Generally, the conductivity or resistivity in Ohm's law (3.47) is a diagonal tensor, which reduces to the familiar scalar for cubic crystals or polycrystalline material.

## 3.2.7 Electrical conduction

Generally, the conductivity or resistivity in Ohm's law (3.47) is a diagonal tensor, which reduces to the familiar scalar for cubic crystals or polycrystalline material.

$$\mathbf{j} = \sigma \mathbf{E},$$

When a magnetic field is applied in the z-direction, the diagonal components

$$\rho_i = \rho_{xx}, \rho_{yy}, \rho_{zz}$$

of the resistivity may change.

$$\hat{\rho} = \begin{bmatrix} \rho_{xx} & -\rho_{xy} & 0 \\ \rho_{xy} & \rho_{xx} & 0 \\ 0 & 0 & \rho_{zz} \end{bmatrix}$$

### Magnetoresistance

$$\Delta\rho/\rho = [\rho_i(B) - \rho_i(0)]/\rho_i(0).$$

The resistance of a metal is inversely proportional to the mean free path.

The change of resistance in an applied magnetic field results from the curtailing of the mean free path in the current direction when the electrons complete a significant fraction of a cyclotron orbit before they are scattered.

## 3.2.7 Electrical conduction

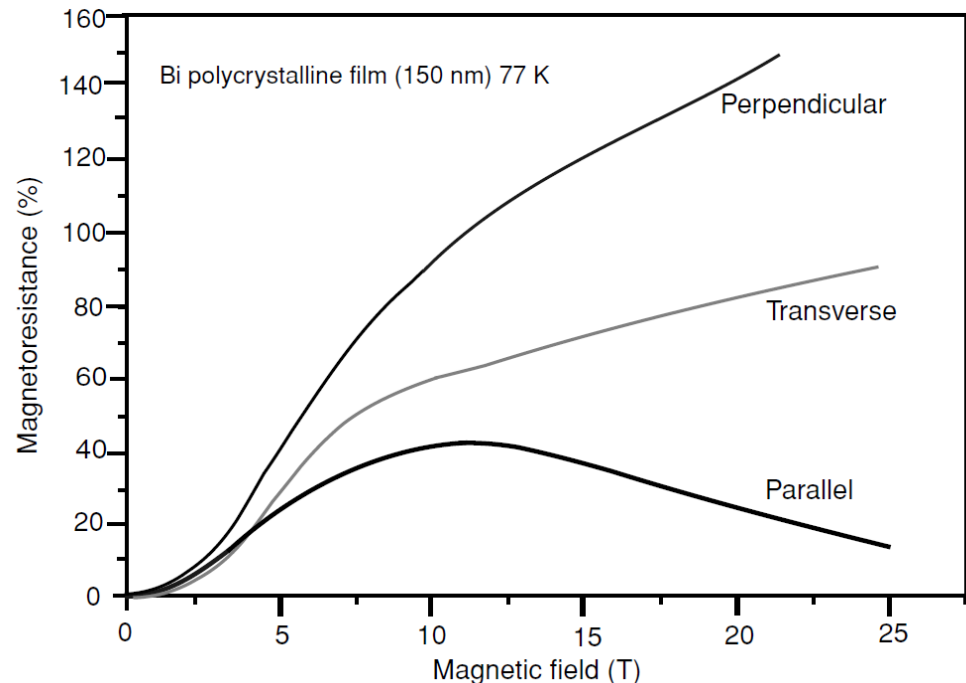
Magnetoresistance effects associated with cyclotron motion can be significant when

$$\omega_c \tau \gtrsim 1$$

The effect is initially quadratic in B.

$$\Delta \rho \propto B^2$$

The magnetoresistance is small ( $\approx 1\%$  in 1 T) in metals where scattering is strong, but it may be much larger in semimetals and semiconductors, where the electron mobility is high.



## 3.2.7 Electrical conduction

Furthermore, off-diagonal terms appear which are due to the Lorentz force. This leads to the Hall effect. When an electric current  $j_x$  of electrons moving with drift velocity  $v$  in the negative  $x$ -direction flows in a conductor, and a transverse magnetic field  $B_z$  is applied, the electrons are deflected and accumulate at the edge of the sample until the electric field  $E_y$  they create is just sufficient to balance the Lorentz force.

$$E_y = v_x B_z$$

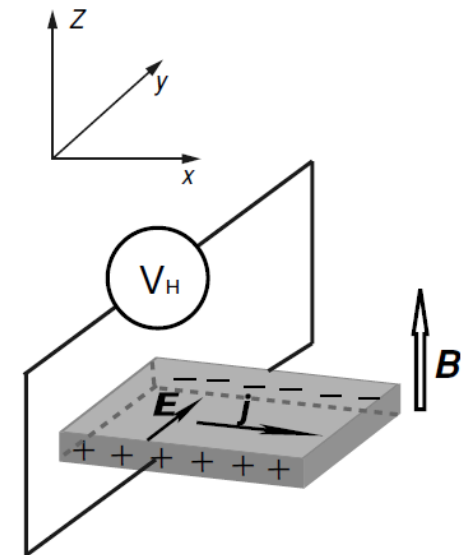
$$j_x = -nev_x,$$

$$E_y = -(1/ne)j_x B_z$$

the Hall coefficient

$$R_h = -(1/ne)$$

$$\rho_{xy} = R_h B_z$$



The Hall effect.

The Hall effect is inversely proportional to electron density, so it is large when  $n$  is small, as in semiconductors.

## 3.2.7 Electrical conduction

$$\hat{\varrho} = \begin{bmatrix} \varrho_{xx} & -\varrho_{xy} & 0 \\ \varrho_{xy} & \varrho_{xx} & 0 \\ 0 & 0 & \varrho_{zz} \end{bmatrix}$$

$$\varrho_{xy} \propto B$$

$$\varrho_{xx} = \varrho_{zz} + \alpha B^2$$

The form of the resistivity is determined by the Onsager principle, which requires that the off-diagonal terms in a response function satisfy

$$\sigma_{ij}(B) = -\sigma_{ji}(B) = \sigma_{ji}(-B)$$

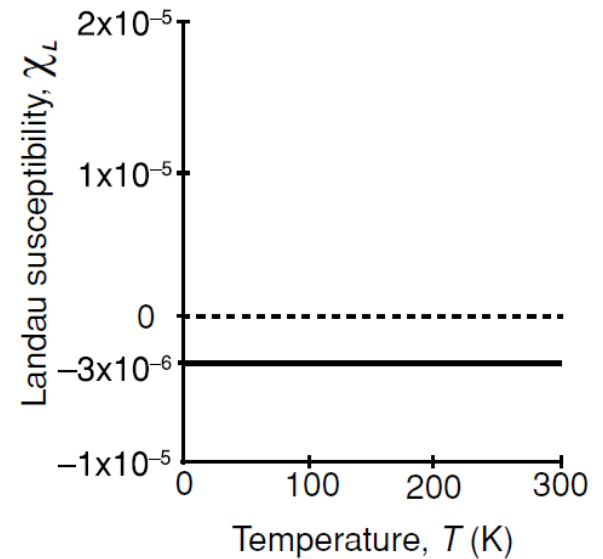
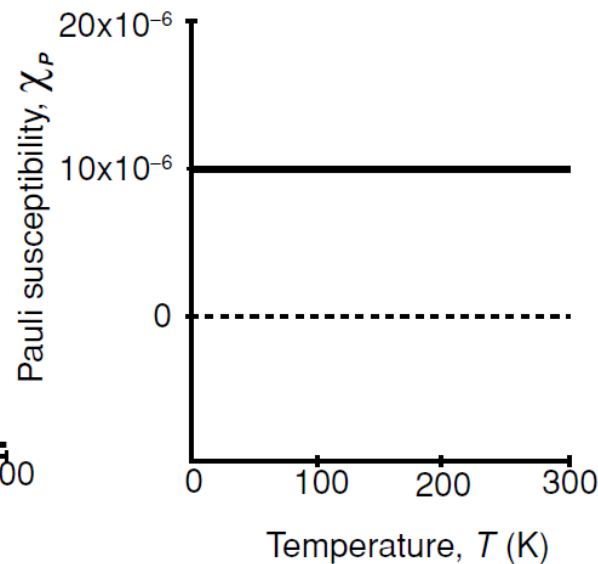
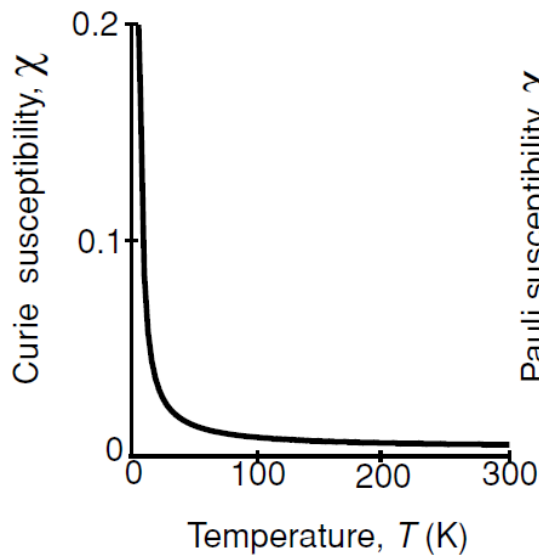


## 3.2.8 Landau diamagnetism

The free-electron model was used by Landau to calculate the susceptibility due to orbital diamagnetism of the conduction electrons. The result is

$$\chi_L = -n\mu_0\mu_B^2/2k_B T_F$$

which is exactly one third of the Pauli paramagnetism, but of opposite sign



## 3.2.8 Landau diamagnetism

$$\chi_L = -n\mu_0\mu_B^2/2k_B T_F \qquad \chi_P = \frac{3n\mu_0\mu_B^2}{2k_B T_F}.$$

the real band structure of solids is approximately taken into account, by using the effective mass

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

For some semiconductors, and semimetals such as graphite or bismuth,

$$m^* \approx 0.01m_e$$

## 3.4 Magnetism of electrons in solids

The free-electron model provides a fair account of the outermost electrons in a metal or semiconductor.

A better understanding of the magnetism of electrons in solids is achieved by considering first the situation for free atoms.



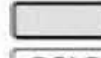
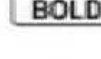
The electronic moments are completely paired for some of the elements with even atomic number  $Z$  such as the alkaline earths or the noble gases, but most elements retain a magnetic moment in the atomic state.

Electrons in filled shells have paired spins and no net orbital moment. Only unpaired spins in unfilled shells, usually the outermost one, contribute to the atomic moment.

# The Magnetic Periodic Table

Atomic Number → **66** Dy ← Atomic symbol  
 Atomic weight → 162.5  
 Typical ionic charge → 3 + 4f ←  
 Antiferromagnetic  $T_M$ (K) → 179 ← Ferromagnetic  $T_C$ (K) → 85

<b>1</b> H 1.00																	<b>2</b> He 4.00				
<b>3</b> Li 6.94 1 + 2s <sup>1</sup>	<b>4</b> Be 9.01 2 + 2s <sup>2</sup>															<b>5</b> B 10.81	<b>6</b> C 12.01	<b>7</b> N 14.01	<b>8</b> O 16.00 35	<b>9</b> F 19.00	<b>10</b> Ne 20.18
<b>11</b> Na 22.99 1 + 3s <sup>1</sup>	<b>12</b> Mg 24.30 2 + 3s <sup>2</sup>															<b>13</b> Al 26.98 3 + 2p <sup>1</sup>	<b>14</b> Si 28.09	<b>15</b> P 30.97	<b>16</b> S 32.07	<b>17</b> Cl 35.45	<b>18</b> Ar 39.95
<b>19</b> K 39.10 1 + 4s <sup>1</sup>	<b>20</b> Ca 40.08 2 + 4s <sup>2</sup>	<b>21</b> Sc 44.96 3 + 3d <sup>1</sup>	<b>22</b> Ti 47.87 4 + 3d <sup>2</sup>	<b>23</b> V 50.94 3 + 3d <sup>2</sup>	<b>24</b> Cr 52.00 3 + 3d <sup>5</sup> 312	<b>25</b> Mn 54.94 2 + 3d <sup>5</sup> 96	<b>26</b> Fe 55.85 3 + 3d <sup>6</sup> 1043	<b>27</b> Co 58.93 2 + 3d <sup>7</sup> 1300	<b>28</b> Ni 58.69 2 + 3d <sup>8</sup> 629	<b>29</b> Cu 63.55 2 + 3d <sup>10</sup>	<b>30</b> Zn 65.39 2 + 3d <sup>10</sup>	<b>31</b> Ga 69.72 3 + 3d <sup>10</sup>	<b>32</b> Ge 72.64	<b>33</b> As 74.92	<b>34</b> Se 78.96	<b>35</b> Br 79.90	<b>36</b> Kr 83.80				
<b>37</b> Rb 85.47 1 + 5s <sup>1</sup>	<b>38</b> Sr 87.62 2 + 5s <sup>2</sup>	<b>39</b> Y 88.91 3 + 4d <sup>1</sup>	<b>40</b> Zr 91.22 4 + 4d <sup>2</sup>	<b>41</b> Nb 92.91 5 + 4d <sup>4</sup>	<b>42</b> Mo 95.94 5 + 4d <sup>5</sup>	<b>43</b> Tc 97.9	<b>44</b> Ru 101.1 3 + 4d <sup>7</sup>	<b>45</b> Rh 102.9 3 + 4d <sup>8</sup>	<b>46</b> Pd 106.4 2 + 4d <sup>10</sup>	<b>47</b> Ag 107.9 1 + 4d <sup>10</sup>	<b>48</b> Cd 112.4 2 + 4d <sup>10</sup>	<b>49</b> In 114.8 3 + 4d <sup>10</sup>	<b>50</b> Sn 118.7 4 + 4d <sup>10</sup>	<b>51</b> Sb 121.8	<b>52</b> Te 127.6	<b>53</b> I 126.9	<b>54</b> Xe 131.3				
<b>55</b> Cs 132.9 1 + 6s <sup>1</sup>	<b>56</b> Ba 137.3 2 + 6s <sup>2</sup>	<b>57</b> La 138.9 3 + 4f <sup>1</sup>	<b>72</b> Hf 178.5 4 + 5d <sup>2</sup>	<b>73</b> Ta 180.9 5 + 5d <sup>3</sup>	<b>74</b> W 183.8 6 + 5d <sup>4</sup>	<b>75</b> Re 186.2 4 + 5d <sup>5</sup>	<b>76</b> Os 190.2 3 + 5d <sup>6</sup>	<b>77</b> Ir 192.2 4 + 5d <sup>7</sup>	<b>78</b> Pt 195.1 2 + 5d <sup>9</sup>	<b>79</b> Au 197.0 1 + 5d <sup>10</sup>	<b>80</b> Hg 200.6 2 + 5d <sup>10</sup>	<b>81</b> Tl 204.4 3 + 5d <sup>10</sup>	<b>82</b> Pb 207.2 4 + 5d <sup>10</sup>	<b>83</b> Bi 209.0	<b>84</b> Po 209	<b>85</b> At 210	<b>86</b> Rn 222				
<b>87</b> Fr 223	<b>88</b> Ra 226.0 2 + 7s <sup>2</sup>	<b>89</b> Ac 227.0 3 + 5f <sup>1</sup>																			
			<b>58</b> Ce 140.1 4 + 4f <sup>1</sup> 13	<b>59</b> Pr 140.9 3 + 4f <sup>2</sup>	<b>60</b> Nd 144.2 3 + 4f <sup>3</sup> 19	<b>61</b> Pm 145	<b>62</b> Sm 150.4 3 + 4f <sup>6</sup> 105	<b>63</b> Eu 152.0 2 + 4f <sup>7</sup> 90	<b>64</b> Gd 157.3 3 + 4f <sup>7</sup> 292	<b>65</b> Tb 158.9 3 + 4f <sup>9</sup> 209 221	<b>66</b> Dy 162.5 3 + 4f <sup>9</sup> 178 85	<b>67</b> Ho 164.9 3 + 4f <sup>10</sup> 132 20	<b>68</b> Er 167.3 3 + 4f <sup>11</sup> 85 20	<b>69</b> Tm 168.9 3 + 4f <sup>12</sup> 55	<b>70</b> Yb 173.0 3 + 4f <sup>14</sup>	<b>71</b> Lu 175.0 3 + 4f <sup>14</sup>					
			<b>90</b> Th 232.0 4 + 5f <sup>1</sup>	<b>91</b> Pa 231.0 5 + 5f <sup>2</sup>	<b>92</b> U 238.0 4 + 5f <sup>3</sup>	<b>93</b> Np 237.0 5 + 5f <sup>4</sup>	<b>94</b> Pu 244	<b>95</b> Am 243	<b>96</b> Cm 247	<b>97</b> Bk 247	<b>98</b> Cf 251	<b>99</b> Es 252	<b>100</b> Fm 257	<b>101</b> Md 258	<b>102</b> No 259	<b>103</b> Lr 262					

-  Radioactive
-  Diamagnet
-  Paramagnet
-  **BOLD** Magnetic atom

 Ferromagnet with  $T_C > 290K$      Antiferromagnet with  $T_M > 290K$      Antiferromagnet/Ferromagnet with  $T_M/T_C < 290 K$

## 3.2.8 Landau diamagnetism

Assembling the atoms together to form a solid is a traumatic process for the atomic moments. Magnetism tends to be destroyed by chemical interactions of the outermost electrons, which can occur in various ways:

- Electron transfer to form filled shells in ionic compounds;
- covalent bond formation in semiconductors;
- band formation in metals.