Electronic Structure and Magnetism of Nanoparticles

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1 Preview

The electronic structure and magnetic properties of nanoparticles differ from those of molecules on the one hand and solids on the other hand. This leads to a number of applications, some already realized, other expected.¹

List of some of them:

1.1 Magnetic nanoparticles

- magnetically soft nanoparticles (Fe₃O₄, superparamagnetic Co)
  - can be drawn out of solution, or even within a living organism, by a strong magnet
  - can be protected against corrosion by layers of graphene or of (Si-containing) polymer
  - active molecules are attached to it, for example
    - catalysts – to be recovered by a magnet and re-used many times
    - complexing ligands – to remove heavy metals from contaminated water
    - anticancer drug or radionuclide atoms – for local treatment of a tumor, without damaging surrounding tissue
  - are used as contrast enhancers (controlling spin relaxation rates) for MRI (magnetic resonance imaging)
  - can be heated from distance with alternating (AC) magnetic fields for hyperthermal therapy of tumors

- magnetically hard nanoparticles (FePt)
  - may be used for future ultra-high capacity computer disk

1.2 Magnetic nanostructures (nano-thin multilayer structures)

- giant magnetoresistance GMR
- tunneling magnetoresistance TMR

2 Band structure of solids

2.1 The free electron model

2.1.1 Energies and wavefunctions

This model is a very coarse approximation, applicable to gain a first insight into materials where electrons are free to move, in metals. It is an independent electron model – it neglects the interactions between the electrons. It then assumes that the potential is constant (no force) within the metal, and infinite (electron cannot leave) outside. It corresponds to an electron in a box, the solutions for which you know how to derive, either from the de Broglie relation

\[ \Lambda = \frac{h}{p} \]  

or from the Schrödinger equation (1 dimension, length \( L \), \( V(x) = 0 \) inside, \( \infty \) outside).

\[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) = E \Psi(x) \]  

The solutions are (box length \( L \))

\[ \Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \]  

\[ E_n = \frac{\hbar^2}{8mL^2} n^2 \quad n = 1, 2, 3, \ldots \]

The boundary condition requires for \( \lambda_n \), the full wavelength of the electron in the \( n \)-th state, that

\[ \frac{n\lambda_n}{2} = L \]  

In 3D (electron in a cube) we have

\[ \Psi_{n, n, n}(x, y, z) = A \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi y}{L}\right) \sin\left(\frac{n\pi z}{L}\right) \]

This formula describes standing waves in the cube.

The energies are

\[ E = \frac{\hbar^2}{8mL^2} \left( n_x^2 + n_y^2 + n_z^2 \right) \]

---

\(^2\) see for example P. M. Fishbane, S. Gasiorowicz, S. T. Thornton, Physics for Scientists and Engineers, 2nd ed., Prentice Hall
2.1.2 Surface electrons in a 2D square well

The 2D spatial shape of the electron density in a given state can be imaged by Scanning Tunneling Microscopy (STM), as has been shown very nicely for surface electrons in a square well in Ref. 3.

First a square well with dimensions about \( L_x \times L_y = 9 \text{ nm} \times 10 \text{ nm} \) was made out of 28 Mn atoms on a Ag(111) surface. This well confines a small number of “surface electrons” – electrons which are confined to a very thin layer in the \( z \) dimension. A voltage \( V \) is then applied to the substrate with respect to the STM tip. A negative bias thus means that electrons pass from the occupied states of substrate to the tip. A larger (in absolute magnitude) negative bias probes deeper states. Larger electron density is manifested by a larger \( \frac{dI}{dV} \) signal. \( \frac{dI}{dV} \) is the derivative of the STM tip current with small AC variations of the bias voltage.

\[
\Psi_{n_x, n_y}(x, y) = A \sin \left(n_x \frac{\pi x}{L_x}\right) \sin \left(n_y \frac{\pi y}{L_y}\right)
\]

with \((n_x, n_y = 1, 1)\). At a bias of -100 mV the Mn atoms defining the well are well visible, but there is no density within the well. At a bias of -50 mV the deepest state is reached and a spot is seen in the middle of the well, corresponding to the density of the lowest 2D state, with a wavefunction

\[
\Psi_{n_x, n_y}(x, y) = A \sin \left(n_x \frac{\pi x}{L_x}\right) \sin \left(n_y \frac{\pi y}{L_y}\right)
\]

with \((n_x, n_y = 1, 1)\). At a bias of -30 mV two spots are seen arranged vertically in the well, corresponding to the density of the next 2D state, \((n_x, n_y = 1, 2)\). The next state, \((n_x, n_y = 2, 1)\), is energetically very close and can not be completely separated. The next image, 1 in Figure 1, therefore shows not only the \((n_x, n_y = 2, 1)\) state, but also partly the lower-lying \((n_x, n_y = 1, 2)\) state. The states at higher biases, images m-p in Figure 1, are more complex because they show superpositions of unresolved states. A tendency toward higher number of nodes is evident, however.

---

2.1.3 Impulse

In a bachelor course you learned the wavefunction for a free electron with an impulse $p$:

$$\Psi_p(x) = A e^{\frac{i p x}{\hbar}} = A \left( \cos \frac{p}{\hbar} x + i \sin \frac{p}{\hbar} x \right) \tag{9}$$

Comparison with equation 3 tells us that

$$\frac{n \pi}{L} = \frac{p}{\hbar} \tag{10}$$

$$p = \frac{\pi \hbar}{n} \tag{11}$$

(There is, of course, a difference between equation 3 and equation 9, in that the former is real, the latter complex. Equation 3 describes a standing wave – a superposition of particles moving left and right, with impulses $-p$ and $+p$. Equation 9 describes particles moving only right, with impulse $+p$. But the absolute magnitude of the impulse is always $p$.)

2.1.4 The wavevector

In solid state science it is customary to describe the wavefunction (and many other things) in terms of a wavevector $\vec{k}$ with the three components $k_x$, $k_y$, $k_z$. Equation 3 is written as

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin(n \pi x) \tag{12}$$

Comparison of equations 3 and 12 tells us what $k_x$ is:

$$k_x = \frac{n \pi}{L} = \frac{2 \pi}{\lambda_n} = 2 \pi \tilde{\lambda}_n \tag{13}$$

(equation 5 was used in the 2nd step)

You see that the wavevector is proportional to the wavenumber, with which you are familiar. Its dimension is also [m$^{-1}$].

Comparison of equations 12 and 9 reveals that $k_x$ is closely related to impulse $p_x$ (similarly for $y$ and $z$).

$$p_x = \hbar k_x \quad \text{(etc. for } y \text{ and } z) \tag{14}$$

$$\tilde{p} = \hbar \vec{k} \tag{15}$$

Since the dimension of $k$ is reciprocal meter, we say that the $k$ vectors, the wavevectors, span the reciprocal space. Each state, defined by $n_x$, $n_y$, $n_z$ has a corresponding point in the reciprocal space; together these points form the reciprocal lattice.
As the last thing, let’s express the energy in function of $k$. Start with equation 4 and substitute from equation 13:

$$E_n = \frac{\hbar^2}{2m} k_n^2$$

The dependence is quadratic. A diagram is shown in Figure 2.

![Figure 2. Dependence of $E$ on $k$ for an electron in a box (the free electron model).](image)

This may appear trivial, but you’ll see below that this diagram will be changed in an interesting way when the electrons are not entirely free, but in a periodic lattice like in a real solid.

### 2.1.5 The Fermi level

Now let’s fill our levels, equation 16, with $N$ electrons ($N$ is an even number). Only two electrons will fit into each level, one with spin up, the other spin down. They will fill the levels up to an energy $E_F$, called the Fermi energy

$$E_F = \frac{\hbar^2}{2m} k_F^2$$

How high is this energy? We can not simply resolve the above equation because $k$ is a vector with the components $k_x$, $k_y$, $k_z$ and $k^2 = k_x^2 + k_y^2 + k_z^2$. We need a more complicated argument.

Consider the reciprocal space with the axis $k_x$, $k_y$, $k_z$. All the occupied states will have $k$ smaller then $k_F$, i.e.,

$$k^2 = k_x^2 + k_y^2 + k_z^2 \leq k_F^2$$

That is, they will lie within a sphere with the radius $k_F$ in the reciprocal space, shown in Figure 3.
Equation 13 tells us that the one-electron states (orbitals) are equidistant in the reciprocal space, spaced by $\pi / L$. There is thus one state for each small volume $(\pi / L)^3$. The volume of the sphere in Figure 3 (in the reciprocal space) is $(4/3)\pi k_F^3$ and we want to take only 1/8 of it, the octant where $k_x, k_y, k_z$ are all positive. The number of orbitals within the Fermi surface can thus be calculated as the ratio of the two volumes in the reciprocal state, and will be set equal to $N/2$, because $N/2$ of the orbitals are required to accommodate $N$ electrons

$$\frac{(1/8)(4/3)\pi k_F^3}{(\pi L)^3} = \frac{L^3}{6\pi^2}k_F^3 = \frac{N}{2}$$

(19)

We thus obtain, with the volume of the cubic potential box being $V = L^3$ (this time in real space)

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

(20)

Substituting into equation 17 we obtain for the Fermi energy

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

(21)

For a macroscopic box there will be very many very closely spaced orbitals; they will be nearly continuous.

2.1.6 Density of states (DOS)

A very important quantity in solid state science is how many orbitals (one electron states) there are within a small energy interval – it is called the density of states (DOS), $D(E) = dN/dE$. 
For the free electron model we can calculate it from the expression 21. Imagine that we vary the number \( N \) of electrons – they will occupy the orbitals up to an energy \( E \) given by equation 21. We reformulate it to obtain the number \( N \) as a function of \( E \)

\[
N = \frac{V}{3\pi^2} \left( \frac{2mE}{\hbar^2} \right)^{3/2}
\]  

(22)

and now we calculate the DOS

\[
D(E) = \frac{\Delta N}{\Delta E} = \frac{V}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}
\]

(23)

It is proportional to \( \sqrt{E} \).

The results until now are summarized in Figure 4.

\[\text{Figure 4. Schematics of energy as a function of } k \text{ (left) and of density of states (right) for a free electron gas.}\]

\[\text{Figure 5. DOS of aluminum. Solid line: detailed theory, dashed: free electron model. Note that the x, y axis are exchanged with respect to those of Figure 4. Another difference is that the origin of the energy scale is placed at the Fermi Energy. From E. C. Snow, Phys. Rev. 158 (1967) 683.}\]
The DOS in real materials sometimes resemble that of the free electron model, for example in Al (Figure 5), but often it is very different.

2.2 Electrons in periodic potentials

In reality the potential in a solid is not constant at the bottom as we assumed so far, but is periodically varying at the positions of the atoms. It is deeper near the nuclei and higher in-between.

Let the distance between atoms be $a$. The Bloch’s theorem tells us that the (one-electron) wavefunction can be written as

$$\Psi_k(x) = e^{ikx} u(x)$$

where the first part is the same as for a free electron, equation 9, modulated by some periodic function $u(x)$, which has the same periodicity as the potential. For the flat-bottom square well potential which we treated until now, $u(x)$ is constant. A schematic drawing with a periodic potential is in Figure 6.

The consequence of the periodic potential is to distort the parabola on the left of Figure 4, to cut-out sections in such a way as to introduce “forbidden bands”, energy ranges where there are no orbitals. It can be seen in Figure 7. The ranges of $k$ where continuous allowed bands are found are called the Brillouin zones.
Figure 7. (a) Energy band diagram for a simple periodic potential (the Kröning-Penny model). (b) Reduced-zone scheme of the energy band diagram.

Figure 7 is only in one dimension. The Brillouin zones can have complex shapes in 3D.

Figure 8. The first Brillouin zone of (a) a body-centered cubic lattice and (b) a face-centered cubic lattice in real space. From Ref.4.

The energy diagram then also becomes complicated – it shows the dependence of $E$ on $k$ in several directions (labeled $\Lambda$, $\Sigma$, etc.) from the origin $\Gamma$. An example for Si is shown in Figure 9.

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2.3 Chemist’s view of band structure

A beautiful and readable explanation of band structure, designed for chemists, was given by Roald Hoffmann.\textsuperscript{5} The following discussion and diagrams follow his article. He considers the solid to be a big molecule and constructs (very large) molecular orbitals as linear combination of atomic orbitals the way we are used to do for molecules.

**One-dimensional case:**
Take an infinitely long chain of atoms, say H-atoms, or CH groups whose $\pi$-orbitals can make a long polyene:

---

To avoid problems with boundary conditions at the ends, make the atoms go on a cycle. You know the MOs of the small cycles by heart. The long cycle can be intuitively extrapolated:

![Figure 10. MOs of cyclic molecules. From Ref. 5.](image)

It turns out that the MOs of the cycles can be obtained from a simple formula:

$$
\Psi_k = \sum_n c_n \chi_n = \sum_n e^{i k n a} \chi_n
$$

(25)

where $\chi_n$ are the basis functions, $a$ the distance between the atoms and $c_n = e^{i k n a}$ the MO coefficients. Note the similarity of this with the Bloch function, eq. 24. The $x$
coordinate is \( x = na \). For each of the lowest orbitals in Figure 10 \( k = 0 \). The highest orbital is obtained when \( c_n = e^{ikna} \) changes sign for each increment of \( n \), i.e., when \( ka = \pi \), that is, when
\[
 k = \frac{\pi}{a} \tag{26}
\]
This is the end of the meaningful range of \( k \), the end of the Brillouin zone. The meaningful range of \( k \) goes from \(-\pi/a\) to \(+\pi/a\), whereby the energy of \( k \) and \(-k\) is the same – it is the degenerate orbital pair in Figure 10. If energy of the orbital is plotted against \( k \), we obtain the following:

![Figure 11](image)

**Figure 11.** Band structure of a long cyclic molecule. Discrete levels for not-so-long chain (a nanoparticle) is shown on the left, a quasi-continuum situation for a very long chain is shown as a rectangle. From Ref. 5

Note that it is nearly the same curve as the “lowest allowed band” on the right of Figure 7, except that the part with negative \( k \) is not shown (it is symmetric anyway).

But we have much more chemical understanding now. We see intuitively what determines how wide a band will be (whether it will have a “large dispersion” in the terminology of solid state science) – it depends on the overlap of the AOs, the \( \beta \) in Hückel theory, which depends on the interatomic separation, as shown in the following diagram:
Figure 12. The band structure of a chain of H atoms where the overlap of the AOs is tuned by varying the interatomic distance $a$. Large $a$ means small overlap and a narrow band, on the left. Note that the bands, in particular the one on the right, is asymmetric, it extends further up than down. The energy of an isolated atom is -13.6 eV. From Ref. 5.

We see that a band can be made of $p$ orbitals instead of $s$ orbitals:

$$
\Psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots
$$

$$
\Psi_{-\Pi} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots
$$

Figure 13. A band made of $p_z$ orbitals from Ref. 5.

We see immediately that the orbital with $k = 0$ has now the highest energy – it has the highest number of nodes: we say that the band “runs down”. Note that it is the same picture as the “second lowest allowed band” on the right side of Figure 7.

A typical material thus has many bands, see Ref. 5.

2.4 DOS

The individual states (orbitals) are equidistant on the $k$ scale, that is, the density of states becomes
2.5 Band structure and conductivity

An electron in an entirely filled band is ‘locked’ in a given orbital, its probability density is fixed, it cannot respond to an applied voltage, and is thus immobile. This is the case when the Fermi level is in a band gap, in insulators (on the right in Figure 15).

An electron in a partly filled band can be promoted to a higher orbital with an infinitesimally small amount of energy in response to an applied voltage and becomes mobile. (In terms of time-dependent QM it is promoted to a non stationary state where it is described by a wave packet which moves.) The result is a conductor, as on the left side of Figure 15.

A semiconductor does not conduct a priori, but the gap is small, the electrons from the Fermi level can be promoted to the conduction band thermally, by light, or by doping, inducing conduction.
3 Optical properties of nanomaterials

3.1 Excitons

You learned about excited states in molecules: electrons are excited from occupied to unoccupied orbitals. Similarly, electrons can be excited from the valence band to the conduction band in solids, leading to a hole and a mobile electron.

3.1.1 Wannier exciton

In a material with a high dielectric constant, there is little Coulomb attraction between the hole and the electron. The hole and the electron will be able to move nearly freely and independently, the pair will be delocalized.

3.1.2 Frenkel exciton

In a material with a low dielectric constant, there is large Coulomb attraction between the hole and the electron and the pair will remain localized.

3.2 Electron DOS in 0D materials (nanodots)

When a particle has nanometer dimensions in all 3 dimensions we speak of nanodots. The energies may be approximated by the “electron in a 3D box” model, equation 7, except that the $x$, $y$, $z$, dimensions need not be the same. The DOS is not quasicontinuous as in macroscopic solid, but a series of discrete lines.

![Figure 16. Electron DOS in 0D materials (nanodots).](image)

For the transition energy $E_B$ from the highest occupied orbital of the valence band to the empty levels of the conduction band (Figure 15) we thus obtain
where $E_g$ is the gap energy in bulk samples and $m^*_e$ is the effective mass of the electron, a concept which takes into account the effect of the periodic potential by formally modifying the mass of the electron.

The energies are now discrete, like those of a large molecule. The advantage over a molecule is that it is possible to tune the energies of the transitions by changing the sizes of the nanoparticles. By combining different materials and sizes, it is possible to cover the entire visible range plus near IR and UV. Examples are given in Figure 17. The nanodots are also efficient light emitters, they show intense fluorescence.

Figure 17. (A) Size- and material-dependent emission spectra of several surfactant-coated semiconductor nanocrystals in a variety of sizes. The blue series represents different sizes of CdSe nanocrystals with diameters of 2.1, 2.4, 3.1, 3.6, and 4.6 nm (from right to left). The green series is of InP nanocrystals with diameters of 3.0, 3.5, and 4.6 nm. The red series is of InAs nanocrystals with diameters of 2.8, 3.6, 4.6, and 6.0 nm. (B) A true-color image of a series of silica-coated core (CdSe), (ZnS or CdS) nanocrystal probes in aqueous buffer, all illuminated simultaneously with a handheld ultraviolet lamp. From Ref. 6.

For many applications nanodots are better than “classical” molecular chromophores. Examples are fluorescent labels as described in Ref. 6, or as light capturing devices which promise to greatly improve the performance of digital cameras (Refs. 7,8,9).

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The later application is illustrated in Figure 18. In the sensors used in today’s cameras, most of the light-sensitive silicon area is covered by the metal stripes making electrical connections, only 25% of the light is collected. Furthermore, the bandgap of Si does not match well the visible photon’s energies. The “Quantumfilm” layer, containing nanodots, ‘harvests’ visible photons and carries the energy to the Si layer.

![Schematic of a pixel of a typical digital camera and the pixel using the light-harvesting “Quantumfilm” with nanodots.](http://news.cnet.com/8301-30685_3-20000786-264.html#ixzz13Pj2w5Zo)

**Figure 18.** Schematics of a pixel of a typical digital camera (left) and the pixel using the light-harvesting “Quantumfilm” with nanodots. Read more: [http://news.cnet.com/8301-30685_3-20000786-264.html#ixzz13Pj2w5Zo](http://news.cnet.com/8301-30685_3-20000786-264.html#ixzz13Pj2w5Zo)

### 3.3 Electron DOS in 1D materials (nanowires)

When the material has nanometer size in 2 dimensions we speak of nanowires. The electron moves freely in the $z$ direction and is confined in the $x$, $y$ dimensions. The energies may be approximated by the “electron in a 2D box” model.

$$ E_b = E_g + \frac{\hbar^2}{8m^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) $$

(28)

The DOS is a series of discrete lines, and on them superimposed a (rapidly decreasing) quasicontinuum due to motion in the $z$ direction (Figure 19).

---

Figure 19. Electron DOS in 1D materials (nanowires). \( l, m \) are the \( n_x, n_y \) of equation 4.

This DOS leads to quantized conductance (Figure 20). The conductance passes by the peaks in DOS in Figure 19. As the wire is made thinner and thinner, the sharp peaks in DOS in Figure 19 drift farther and farther apart and the number of peaks below a certain energy, available for conductance, decreases one by one. The conductance (Figure 20) decreases stepwise each time a peak in DOS crosses the threshold.

Figure 20. The conductance of a Cu wire as its width is being slowly decreased by electrochemical etching. The stepwise change is due to conductance quantization. From Ref. 10

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3.4 Electron DOS in 2D materials (nanosheet or a quantum well)

The particle now moves freely in the two directions and is confined in the \( z \) dimension. The energies in the \( z \) dimension may be approximated by the “electron in a 1D box” model.

\[
E_B = E_g + \frac{\hbar^2}{8m_e} \left( \frac{n_z^2}{L_z^2} \right)
\]  

(29)

Each of the discrete energies increases stepwise the DOS. Superimposed on the steps is a flat quasicontinuum due to motion in the \( x, y \) directions (Figure 21).

This DOS leads to an absorption spectrum shown in Figure 22. The bottom spectrum is that of a nearly macroscopic object, a step with an onset at the band gap energy. Structures due to quantization in the \( z \) direction appear for thin layers. The separation of the structures increases for thinner layers (smaller \( L_z \)) as indicated by equation 29.
Figure 22. Transition from quasi-three-dimensional to quasi-two-dimensional behavior can be seen in these linear absorption spectra of InGaAs-InAlAs structures with different thickness $L_z$. Bottom to top: 600 nm, 20 nm, 10 nm, 7.5 nm. From Ref. 11.

4 Magnetism

The space between the poles of a magnet has a property which we call magnetic field $\vec{B}$

unit: Tesla [T], dimension $\frac{\text{kg}}{\text{C} \cdot \text{s}}$

Common non SI unit: Gauss (10'000 Gauss = 1 T)

Magnetic field exerts a force $\vec{F}$ on a charge $q$ moving with the velocity $\vec{v}$

$$\vec{F} = q \, \vec{v} \times \vec{B} \tag{30}$$

($\times$ stands a vector product)

The “total amount of magnetic field flowing through a given area $A$ perpendicular to the field” is the magnetic flux

$$\Phi_B = B \, A \tag{31}$$

4.1 Magnetic dipole moment

How “magnetic” is a little magnet (like a compass needle), or a loop of wire with electric current, is expressed by their magnetic dipole moments $\vec{\mu}$

A loop of wire with current $I$ and an area $A$ will have a magnetic dipole moment with a magnitude $\mu = |\vec{\mu}|$

$$\mu = I \, A \tag{32}$$

When such a magnetic dipole is placed in a magnetic field, the field will exert a “turning force” – a torque $\vec{\tau}$ (Drehmoment, moment de force) on it

$$\vec{\tau} = \vec{\mu} \times \vec{B} \tag{33}$$

for example, the magnetic field of the earth will turn the needle of a compass until it points toward the North pole, i.e., until $\vec{\mu}$ and $\vec{B}$ are aligned

If you have an unknown magnetic field, you can measure its strength by putting a known magnetic dipole moment into it and measure the torque.

If you rotate the magnetic dipole against the torque, you have to invest energy – a magnetic dipole $\vec{\mu}$ in a magnetic field $\vec{B}$ has a potential energy

$$U(\phi) = -\vec{\mu} \cdot \vec{B} = -\mu \cos \phi \tag{34}$$

where $\cdot$ stands for scalar product

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12 see for example P. M. Fishbane, S. Gasiorowicz, S. T. Thornton „Physics for Scientists and Engineers, 2nd ed., Prentice Hall

13 to confuse things, some people call it „flux density“
4.2 How to make magnetic field

Magnetic field can be made with a loop of wire:

- the field in the center of the loop is

\[ B = \mu_0 \frac{I}{2R} \]  

(35)

where \( \mu_0 \) is the permeability of free space (magnetische Feldkonstante)

\[ \mu_0 = 4\pi \times 10^{-7} \, \text{Tm/A} \]

What is not so nice about a field generated by a loop of wire: the field is not the same across the loop.

Magnetic field can be made even better with a solenoid:

- the field (for a long solenoid) is now

\[ B = \mu_0 n I \]  

(36)

where \( n \) is the number of solenoid turns per unit length of the solenoid,

\[ n = N/l \]

The field is now homogenous, it is the same not only in the center, but anywhere within the solenoid, even off-centre.

4.3 The effect of materials

4.3.1 The magnetic susceptibility

Until now the discussion was for vacuum. If you put some material into the solenoid, the field will generally change. With an iron core it will be strongly amplified14 - see Figure 23.

![Figure 23. (a) A solenoid that carries a current has a magnetic field. (b) When it is filled with an iron core, the magnetic field is greatly amplified. (From Ref.12)](image)

\[ ^{14} \text{for simplicity let’s call it amplified even when the material makes the field weaker – the „amplification“ is then less than 1.} \]
The field for our solenoid is now

$$B = \mu_0 n I + \mu_0 \chi_m n I$$

(37)

The field is now a sum of two terms. The first term is what the field would be without the iron core (eq. 36), the second term is the additional field brought by the material. Both terms are proportional to the electric current $I$ in the solenoid which is somehow the “driving force” for generating the magnetic field. The product $nI$ is obviously very important, so we shall give it a new name – the **magnetic intensity** $H$. For a long solenoid, $H = nI$.

$$B = \mu_0 H(1 + \chi_m)$$

(38)

The factor $\chi_m$ (chi) is called the **magnetic susceptibility**. It has no dimension, and expresses to what degree is a given material capable of “amplifying” the “basic” magnetic field $\mu_0 H$ (which is what the magnetic field would be without the material). A positive value of $\chi_m$ indicates that this material makes the field stronger, a negative value of $\chi_m$ indicates that this material makes the field weaker.

There are several other common variables:

### 4.3.2 The magnetization

The product $\chi_m \bar{H}$ in equation 38 is called the **magnetization** $\bar{M}$.

$$\bar{M} = \chi_m \bar{H} = \frac{d\bar{\mu}}{dV}$$

(39)

The way to picture this is that the electric current in the solenoid, that is, the magnetic intensity $H$, causes the material to become a magnetic dipole moment $\bar{\mu}$. The magnetization $\bar{M}$ expresses how large this magnetic dipole moment $\bar{\mu}$ is, per unit volume of the material. If you want, you can now write equation 38 as

$$\bar{B} = \mu_0 \left( \bar{H} + \bar{M} \right)$$

(40)

*i.e.*, the final magnetic field is given by the “driving force” $H$ plus the “amplifying effect” of the material $M$.

Note that our way to define the magnetic susceptibility $\chi_m$ is, with reference to equation 39, “per volume”. It is therefore called in some books the “volume susceptibility”. To confuse things, other people define other susceptibilities, for example the molar susceptibility.
4.3.3 The magnetic permeability

We can give the product $\mu_0(1+\chi_m)$ in equation 38 a new name and call it the permeability $\mu$.

$$\mu = \mu_0(1+\chi_m) = \mu_0 \mu_r \tag{41}$$

We then define the relative permeability $\mu_r$. It is just a number – it has no dimension. Like $\chi_m$ it expresses how much does a given material “amplify” a magnetic field. But, for a completely “nonmagnetic” material, $\chi_m = 0$ and $\mu_r = 1$.

4.4 Classification of magnetic properties of materials

Let us have a look at the measured susceptibilities of some materials:

<table>
<thead>
<tr>
<th>material</th>
<th>$\chi_m$</th>
<th>class</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>-9.1$\cdot$10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-9.6$\cdot$10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>-24$\cdot$10$^{-6}$</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>diamant</td>
<td>-22$\cdot$10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>-170$\cdot$10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>+7.2$\cdot$10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>+7.2$\cdot$10$^{-6}$</td>
<td>paramagnetic</td>
</tr>
<tr>
<td>liquid O$_2$</td>
<td>+3500$\cdot$10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>5.5$\cdot$10$^3$</td>
<td></td>
</tr>
<tr>
<td>permalloy (55%Fe45%Ni)</td>
<td>25$\cdot$10$^3$</td>
<td>ferromagnetic</td>
</tr>
<tr>
<td>Mu-metal (NiFeCuCr)</td>
<td>100$\cdot$10$^3$</td>
<td></td>
</tr>
<tr>
<td>ferrimagnet</td>
<td>5.5$\cdot$10$^3$</td>
<td></td>
</tr>
<tr>
<td>MnZn(Fe$_2$O$_4$)$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Susceptibilities of some materials.

Table 1 indicates that the majority of materials affect the magnetic field only very weakly, they are nearly “nonmagnetic” in the common sense of the word. Large part of them makes the field weaker by a very small amount – we call them diamagnetic. Some of them make the field stronger by a small amount – we call them paramagnetic. Some materials make the field dramatically stronger – we call them ferromagnetic. A particularity of ferromagnetic material is that the dependence of $B$ on $H$ is strongly
non-linear $- \chi_m$ depends on $H$. Saturation is reached in point 1 in Figure 24. Another particularity is the hysteresis (Figure 24).

![Figure 24](image1.png)

**Figure 24.** A magnetization curve illustrating the phenomenon of hysteresis in ferromagnetic materials. The freshly made material starts at the origin with zero magnetization. When a current in the solenoid is turned on and a magnetic intensity $H$ is applied, the material responds by becoming magnetic and is magnetic even when $H$ is returned to zero again.

The hysteresis is more pronounced in some materials than in others, and we distinguish between magnetically hard (suitable to make permanent magnets) and magnetically soft materials (magnetized only in the presence of electric current in the solenoid; the magnetization disappears when the current is turned off).

![Figure 25](image2.png)

**Figure 25.** Hysteresis loops for magnetically hard (left) and magnetically soft materials (right).

We would like to understand the atomic origins of the various magnetic behaviors. For that we need to learn about the electronic structure of solids – the band structure.
5 Magnetic properties of materials

5.1 Angular momentum and magnetic dipole moment\(^{15}\)

A charged particle with an angular momentum corresponds classically to a circling charge\(^{16}\), \textit{i.e.}, circular electric current, and has a magnetic dipole moment \(\vec{\mu}\). Its magnitude depends only on the angular momentum, and is independent of the details of the orbital shape or of chemical surroundings.

\[ \vec{\mu} = g \frac{-e}{2m_e} \vec{L} \quad (42) \]

\(-e\) and \(m_e\) are electron charge and mass, resp., \(\vec{L}\) is angular momentum, \(|\vec{L}| = h\sqrt{l(l+1)}\).

\[ \mu = g \frac{-e}{2m_e} h\sqrt{l(l+1)} \quad (43) \]

For the constant \(\mu_b = \frac{e}{2m_e} h\) we introduce the name \textit{Bohr magneton}. The only point to bear in mind is that orbital angular momentum and spin angular momentum behave differently, they have different \(g\) values: \(g = 1\) for orbital motion and \(g = 2\) for spin\(^{17}\). Important here is the \(z\)-component, \(\mu_z\). For spin, with \(g = 2\), we have:

\[ \mu_z^S = -2\mu_B m_S \quad (44) \]

where \(m_S\) is the spin quantum number, \(-\frac{1}{2}\) or \(\frac{1}{2}\).

The magnetic moment produced by one electron with \(m_S = \frac{1}{2}\) is then

\[ \mu_z^S = -\mu_B \quad (45) \]

for orbital motion \(g = 1\):

\[ \mu_z = -\mu_B m_l \quad (46) \]

where \(m_l\) is the magnetic quantum number, \(m_l = -l, \ldots, 0, \ldots, +l\)


\(^{16}\) For spin, the picture of actual mechanical rotation is not correct – an electron has an inherent angular momentum and magnetic moment.

\(^{17}\) Strictly speaking, 2.0023.
5.2 Diamagnetic materials

In these materials all orbital and spin moments are paired, there is no net angular momentum, and the only magnetic effect is a small and negative susceptibility as already explained.

5.3 Paramagnetic materials

Here the individual particles do have magnetic moments, but the directions of these magnetic moments are only very weakly coupled, they are independent of each other. Thermal motion makes them to point in arbitrary directions, which is thermally changing all the time. The net magnetic moment is thus zero, the material is “nonmagnetic” in the common sense of the word.

When an external magnetic field is applied, the magnetic moments of the atoms become oriented, because their energy is lowest when they are parallel to the external field (equation 34). But the interaction is weak, they become oriented only to a very small degree – the coupling between the external field and the magnetic moments of the atoms is much weaker than $kT$. The induced magnetization $M$ is therefore very small and depends inversely on temperature $T$. The behavior is described by the Curie law:

$$\vec{M} = C \frac{\vec{B}}{T}$$     \hspace{1cm} (47)

or, for the susceptibility we have

$$\chi_m = \mu_0 \frac{C}{T}$$     \hspace{1cm} (48)

where $C$ is a material-specific Curie constant.

5.4 Ferromagnetic materials

5.4.1 Exchange interaction

The strong ferromagnetism is brought about by spontaneous orientation of the electron’s magnetic moments. Magnetic moments interact by their magnetic fields, as expressed by equation 34, these forces tend to orient the magnetic moments in antiparallel fashion. But these forces are very small and can be neglected.

The strong forces responsible for the spontaneous orientation are due to exchange interactions. You already learned about these interactions in Bachelor courses, when you learned about Hund’s rule and the singlet-triplet splitting. You learned that, in
case of degenerate orbitals like the $\pi^*$ orbitals in $\text{O}_2$, the state with parallel electrons (the $^3\Sigma_g^-$ ground state) is lower in energy by about 1 eV than the singlet state with the same orbital occupation. This energy difference is much larger than magnetic interactions.

You learned that the cause lies in two principles:
- Coulomb repulsion between electrons.
- The Pauli exclusion principle.

The Pauli principle, or the requirement that the total electron wavefunction is antisymmetric in respect to exchange of the coordinates of two electrons, affects the multielectron wavefunction in such a way that the electrons are on the average closer together in the state with antiparallel spins, and farther apart in the state with parallel spins. The Coulomb repulsion is thus smaller in the latter case, making it energetically lower.

### 5.4.2 Spin-resolved DOS

Let’s draw the DOS for electrons with spin up and spin down separately. We just saw that the exchange interaction favors parallel spins, that is, makes the electrons flow from one side to the other such as to have more electrons on the spin down side. Since the Fermi energy $E_F$ is a global quantity, the bands on the majority spin side will shift down, so as to reach the situation on the right in Figure 26.\(^{18}\)

![Figure 26](image)

**Figure 26.** Band structure of a ferromagnet before (left) and after (right) spontaneous magnetization. The DOS of the d band is split by the exchange interaction.

This releases some exchange energy $E_{\text{ex}}$ dependent on the difference of the number of majority and minority spin electrons, \(i.e.,\) the number of unpaired electrons \(m = N_\downarrow - N_\uparrow\). The energy thus gained is written as

\[
E_{\text{ex}} = -\frac{1}{4} I m^2
\]

\(^{18}\) The figure could have, of course, been drawn as to have more spin-up electrons.
where $I$ is called the Stoner exchange parameter.

There is a cost for that, however. As the electrons flow to the majority spin side, they have to occupy orbitals higher and higher in the band, orbitals which are higher in energy than those from which they came – and this costs energy. The equilibrium magnetization is reached when the two effects are offset.\textsuperscript{19}

It is evident from the Figure 26 that conditions favorable to the electron transfer, and thus for ferromagnetism, is when $I$ and the DOS at the Fermi level are both large. The condition is given by the Stoner criterion $I \cdot \text{DOS}(E_F) > 1.19$

\textbf{Figure 27.} (a) DOS of Fe (bcc) which is artificially forced to have all electrons paired (solid and dashed lines are two different theoretical models). (b) Spin-resolved DOS, when the flow of electrons is allowed. The dotted vertical line shows the Fermi level. From Ref. \textsuperscript{19}.

Iron is an example; on the left of Figure 27 the Fermi level passes through the highest peak in the DOS spectrum. In a calculation which allows the flow of the electrons and balances the exchange energy and the orbital occupation, shown in Figure 27 on the right, majority spin (bottom) and the minority spin (top) are shifted.

\subsection*{5.4.3 Magnetic anisotropy}

From what has been said so far, one could not yet make a permanent magnet – the spins become spontaneously, collectively, parallel oriented, but the orientation of the ensemble is not fixed, it can change easily. We need that an energy barrier is involved in changing the orientation, as shown in Figure 28 so that it does not happen spontaneously. There are various mechanisms for the anisotropy, such as coupling with the crystal orientation (magneto-crystalline anisotropy), or with the shape of a nanoparticle – ellipsoidal particles tend to be magnetized more easily along the longer axis.

5.4.4 Curie temperature

As temperature is increased, the tendency of spins for self-alignment is overcome by the thermal disorder and the material becomes paramagnetic, that is, “non-magnetic” in the common sense of the word. The transition is not gradual – it is a (second order) phase transition, the susceptibility changes abruptly at the Curie temperature. As an example, the Curie temperature of Fe is 770°C. The effect has many applications, for example to make a thermostat.

5.4.5 Magnetic domains and superparamagnetism

Where is the limit to the tendency of the spins to spontaneously orient themselves parallel? When the piece of space (the domain), where they are parallel, becomes large, it develops a large magnetic dipole moment, and generates a large magnetic field around it. But magnetic field contains energy, so further growing of the domain is energetically unfavorable. To avoid this, the material breaks up into domains (about 0.1 mm large) in order to reduce its magnetostatic energy by decreasing the spatial extent of its external field – the magnetic moments of the domains cancel towards the outside.

---

When external field is applied, the domains parallel to the applied field grow at the expense of other domains – a net magnetization $M$ results, responsible for the high susceptibility $\chi_m$.

Domains are separated by domain walls. These cannot be infinitely thin – their thickness is a compromise between two tendencies. Making them too thin leads to unfavorable exchange interaction (antiparallel spins!) making them too thick leads to too many electrons in an unfavorable orientation with respect to magnetic anisotropy (Figure 28). The actual domain wall width is the result of a compromise between these two trends.

As the particle’s dimensions are decreased, to below 3-50 nm, the formation of domain walls becomes energetically expensive. In this case, the particle will not form distinct domains. All the spins are now oriented in one direction and are coherent – a “macro-spin”.
Because of the nanoparticle’s magnetic anisotropy, the magnetic moment has usually only two stable orientations antiparallel to each other, separated by an energy barrier (Figure 28). The stable orientations define the nanoparticle’s “easy axis”. At a finite temperature, there is a finite probability for the magnetization to flip and reverse its direction. The flipping rate increases rapidly with decreasing particle size (Figure 32) and, of course with temperature.

![Relaxation time in magnetite ellipsoids as a function of grain size.](http://magician.ucsd.edu/Essentials/WebBookse22.html)

When the flipping rate is sufficiently large, a measurement will record only the average magnetization which is zero. When external field is applied, magnetization sets in – the particles behave as a paramagnet, except that the susceptibility $\chi_m$ is much larger. The effect is therefore called superparamagnetism. The great difference to paramagnetism is the large $\chi_m$ and that the effect is size-dependent.

The great difference to ferromagnetism is that there is no hysteresis (Figure 25). This behavior is an advantage, for medical applications (targeted drug delivery, contrast agents for Magnetic Resonance Imaging (MRI), magnetic hyperthermia, magnetic separation: cell-, DNA-, protein- separation, RNA fishing) for catalyst removal. Other applications are ferrofluids (used for example as liquid seals in hard disk drives and other places21).

But the absence of hysteresis is also a problem – for data storage on magnetic disks, where permanent magnetization of very small particles is required. The absence of hysteresis in small particles thus limits the storage density - the so-called “superparamagnetic limit”.

At low temperature, below the blocking temperature (which also depends on the time-scale of the measurement), the flipping rate becomes slow and the orientation of magnetization becomes blocked in one direction.

5.5 Antiferromagnetic coupling

In some cases where the magnetic ions do not touch directly, but are connected by intermediate nonmagnetic ligands like O$^{2-}$ in magnetite Fe$_3$O$_4$, or $\gamma$-Fe$_2$O$_3$. The distance between the ions is large and the exchange interaction described above is weak. But there is an exchange interaction mediated by the ligand, called the superexchange interaction. The interaction is such that it favors antiparallel spin orientation rather than parallel and is consequently called negative exchange, or antiferromagnetic interaction.

![Antiferromagnetic interaction](image)

This leads to antiferromagnet, with no net magnetization, when all the magnetic centers are equivalent. When there are two different ions, chemically, or because they occupy two different sets of lattice sites, then a permanent magnetization occurs and it is a ferrimagnet. Ferrimagnets behave like ferromagnets but have some interesting properties for applications, they are often nonconductors, thus reducing energy losses due to induced currents in transformers etc.

5.6 Giant magnetoresistance (GMR)$^{22}$

A cornerstone for understanding GMR is the ‘two currents’ conduction concept to explain specific behaviors in the conductivity of the ferromagnetic metals Fe, Ni, Co and their alloys. In such ‘itinerant ferromagnets’ both the 4$s$ and 3$d$ electron bands contribute to the density of states at the Fermi level $E_F$ (Figure 26 and Figure 34). Because of the strong exchange interaction favoring parallel orientation of electron spins, the ‘spin-up’ and ‘spin-down’ 3$d$ bands are shifted in energy. This band
splitting creates the imbalance between numbers \( n_{\text{up}} \) and \( n_{\text{down}} \) of \( 3d \) electrons that is at the origin of the ferromagnetic moment (\( \mu \approx -(n_{\text{up}} - n_{\text{down}}) \mu_B/\text{atom} \) (c.f. equation 45), where \( \mu_B \) is the Bohr magneton), whereas the conduction is dominated by the unsplit \( 4s \) band, the \( 4s \) electrons having a much higher mobility.

However, the spin-conserving \( s \)-to-\( d \) transitions are the main source of \( s \)-electron scattering. This has two chief consequences for transport: the spin-imbalanced density of states for \( 3d \) electrons at \( E_F \) results in strongly spin-dependent scattering probabilities. Scattering hinders the conduction, so that conduction happens in parallel through two spin channels that have very different conductivities (Figure 35). The spin-dependent scattering probability results in very different mean free paths \( \lambda_{\text{up}} \) and \( \lambda_{\text{down}} \). In usual thin metallic layers they scale from a few nanometres to a few tens of nanometres, with highly variable \( \lambda_{\text{down}}/\lambda_{\text{up}} \) ratios: some impurities have strongly spin-dependent cross sections, so that in Ni, for example, the ratio \( \lambda_{\text{down}}/\lambda_{\text{up}} \) can reach 20.

The crucial step in the design of the giant magnetoresistance device is to build magnetic multilayers with individual thicknesses comparable to the mean free paths, so that evidence can be seen for spin-dependent electron transport. The principle is
schematized in Figure 36 for the simplest case of a triple-layer film of two identical ferromagnetic layers F1 and F2 sandwiching a non-magnetic metal spacer layer M. We assume $\lambda_{\text{up}}^{F} >> \lambda_{\text{down}}^{F}$, with $\lambda_{\text{up}}^{F} > t_{F} > \lambda_{\text{down}}^{F}$, for the thickness $t_{F}$ of the magnetic layer and $t_{M} << \lambda_{M}$ for the thickness $t_{M}$ of the spacer layer. When the two magnetic layers are magnetized parallel (P), the spin-up electrons can travel through the sandwich nearly unscattered, providing a conductivity shortcut and a low resistance. On the contrary, in the antiparallel (AP) case, both spin-up and spin-down electrons undergo collisions in one F layer or the other, giving rise to a high resistance. The relative magnetoresistance $\Delta R/R = (R_{\text{AP}} - R_{P})/R_{P}$ can reach 100% or more in multilayers with a high number of F/M periods. Elaborate theories must of course take into account other effects such as interfacial scattering and quantum confinement of the electrons in the layers. The GMR is an outstanding example of how structuring materials at the nanoscale can bring to light fundamental effects that provide new functionalities.

![Figure 36. Principle of the GMR device. From Ref. 22](image)

And indeed the amplitude of the GMR immediately triggered intense research, soon achieving the definition of the spin-valve sensor. In its simplest form, the spin valve is just a trilayer film of the kind displayed in Figure 37 in which one layer (for example, F2) has its magnetization pinned along one orientation. The rotation of the free F1 layer magnetization then ‘opens’ (in P configuration) or ‘closes’ (in AP configuration) the flow of electrons, acting as a sort of valve.
The pinning of the one layer is achieved by coupling with an antiferromagnetic layer. Antiferromagnetism thus plays a crucial role in giant magnetoresistance. Exchange bias is a crucial effect linked to an interface, here between a ferromagnetic and antiferromagnetic layer: the antiferromagnetic layer has no net magnetic moment that could be sensitive to an applied field, but may retain a large magnetic anisotropy, which, transferred to the ferromagnetic layer through interfacial exchange interaction, contributes to stabilizing the orientation of its magnetization. This effect gained wide application in the spin valve and magnetic tunnel junctions for pinning the magnetization of the reference magnetic layer.

5.7 Tunnel magnetoresistance (TMR)

The device is constructed similarly to that for GMR: two identical ferromagnetic layers F1 and F2 sandwich a non-magnetic spacer layer A – except that the spacer is now an insulator like Al2O3. Electrons tunnel through the spacer in a spin dependent way. Electrons from the spin-up band tunnel only to the spin up band and similarly for spin down, as shown in Figure 38. The tunneling rate depends on the product of the DOSs at Fermi level of the left and right ferromagnetic layers. The total tunneling rate is the sum of the rates for the up and down spin electrons. This sum is larger for the parallel orientation of the magnetizations of the ferromagnetic layers, because it involves a transfer from a wide band to a wide band. For the antiparallel

orientation there are two unfavorable wide-to-narrow and narrow-to-wide contributions (Figure 38).

![Figure 38](image)

**Figure 38.** Spin-dependent tunneling of electrons. From Ref. 4.

The Fe layers are made from magnetically hard Fe, but the “degree of hardness” is not the same. The initial orientation is parallel, the resistance is low (in the center of Figure 39). When the magnetic intensity $H$ is increased, such as to reverse the magnetization of the Fe layers to the opposite direction, first the “less hard” material reverses its magnetization, leading to antiparallel magnetization – and the resistance rises. At even higher $H$ both Fe layers reverse their magnetizations, then they are parallel again, and the resistance drops again (above about 60 Oe in Figure 39).

![Figure 39](image)

**Figure 39.** From Ref. 4.