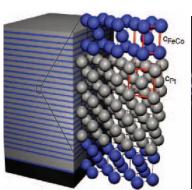
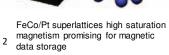


Magnetism

Not only permanent ferromagnets, many applications:

motors, transformers, imaging, data storage (probably just as important as semiconductors for modern computers)

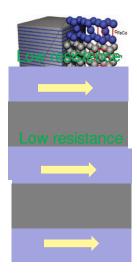




Giant magnetoresistance (GMR) is a quantum mechanical effect that occurs in multilayers of alternating ferromagnetic and non-magnetic conductive layers. The discovery of GMR received the 2007 Nobel Prize in Physics (Albert Fert and Peter Grünberg).

In the GMR effect there is a significant change in the electrical resistance depending on whether the magnetization of adjacent ferromagnetic layers are in a parallel or an antiparallel alignment. For a parallel alignment, the resistance is low while for an antiparallel alignment it is high.

The magnetization can be controlled by applying an external magnetic field. This effect occurs because the resistance depends on electron scattering, and this depends on the spin orientation. The discovery of GMR in 1988 spawned the field of spintronics which can be thought of as a new type of electronics where both the electrons charge and spin are manipulated.



High resistance

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Magnetism

Magnetism is an extremely active area of research with many still unanswered questions.

Condensed matter physics uses magnetism as a testing ground for understanding complex quantum and statistical physics.

- How do solids react to an external field?
- What is the cause of spontaneous magnetic ordering?

Most magnetic phenomena caused by quantum mechanical behaviour of the electrons.

Magnetic properties

- Magnetic moments in atoms
- Weak magnetism in solids (paramagnetism, diamagnetism)
- Magnetic ordering (ferromagnetism, antiferromagnetism, ferrimagnetism)

Weak magnetism in solids can largely be understood by atomic properties, magnetic ordering cannot - cannot describe it as ordering of totally localised moments on atoms because these have to "talk" to each other, otherwise there is no ordering in the first place.

- Nuclei also have magnetic moments, and can contribute to magnetism.
- Magnitude is typically much less than that of electrons, by a factor of ~2000, since magnetic moment of electron is $\mu = \frac{e\hbar}{2m}$ with m the electron mass; mass of nucleus ~2000 electron mass.

Oxford Basics Ch. 19, Ashcroft and Mermin Ch. 31, 32

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Basic definitions of types of magnetism

For a small magnetic field, the magnetization of a system \mathbf{M} (moment per unit volume) is typically related linearly to the applied magnetic field \mathbf{H} by a (magnetic) susceptibility χ

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

The field ${\bf B}$ that any electron in the sample experiences is related to the applied field ${\bf H}$ via

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$$

Permeability of free space $\mu_0 = 4\pi x 10^7$ (SI units: Newton per ampere², N/A²)

Substituting in for $\mathbf{M}=\chi\mathbf{H}$ in the above equation we get,

M=χH →
$$\mathbf{B} = \mu_0 (1 + \chi)\mathbf{H}$$
 or $\mathbf{B} = \mu\mathbf{H}$; $\mu = \mu_0 (1 + \chi)$; $\mu_r = 1 + \chi$ relative magnetic permeability

(Real crystals anisotropic, and susceptibility is a second-rank tensor; ignore such effects)

Basic definitions of types of magnetism: units

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = \mathbf{B}_0 + \mu_0 \mathbf{M}$$

- Both ${\bf B}$ and ${\bf B}_0$ are measured in Tesla (T).
- 1 T is a strong field. The magnetic field of the earth is only of the order of 10⁻⁵ T.

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Types of magnetism

All magnetic materials may be grouped into three magnetic classes depending on the magnetic ordering and the sign and magnitude of the magnetic susceptibility:

Diamagnetic: the magnetic susceptibility is negative – the magnetization is opposite to the applied magnetic field. Usually its magnitude is \sim -10⁻⁶ to -10⁻⁵. In diamagnetic materials the susceptibility nearly has a constant value, dependent on temperature.

Examples: ionic crystals and inert gases, zinc, copper, gold, water, NaCl, Glass.

Paramagnetic: χ is positive, i.e. **M** is parallel to **H**. The susceptibility is also very small: $\sim 10^{-4}$ to 10^{-5} .

Examples: ions of the transition and rare-earth ions, platinum, chromium, sodium.

Ferromagnetic: very large positive χ (e.g. 10^5), spontaneous magnetization below a certain temperature; also antiferromagnetism, ferrimagnetism. Examples: iron, cobalt, nickel. *(more later)*

Diamagnetism

Potential energy
$$\,U=Vrac{|\chi_{
m m}|}{2\mu_0}B_0^2\,$$

Increase in potential energy for higher field, unfavourable.

Diamagnetism is caused by "currents" induced by the external field.
 According to Lenz' law, these currents always lead to a field opposing the external field.

Paramagnetism

Potential energy
$$U=-Vrac{|\chi_{
m m}|}{2\mu_0}B_0^2$$

The potential energy is lowered when moving the magnetized bodies to a higher field strength

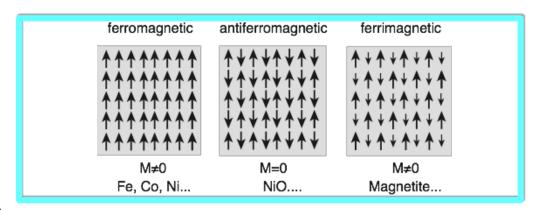
 Paramagnetism is caused by aligning some dipoles, which are already present, with the magnetic field

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Ferromagnetism

A **ferromagnet** is a material where **M** can be nonzero even in the absence of an applied magnetic field.

Magnetism is said to be spontaneous when it occurs even in the absence of an externally applied magnetic field, as in the case of a ferromagnet.



Ferromagnetism

The best-known examples – transition metals Fe, Co, and Ni. Also, other elements and alloys involving transition or rare-earth elements, such as the rare-earth metals Gd, Dy, and the insulating transition metal oxides (CrO₂). Gadolinium, Dysprosium

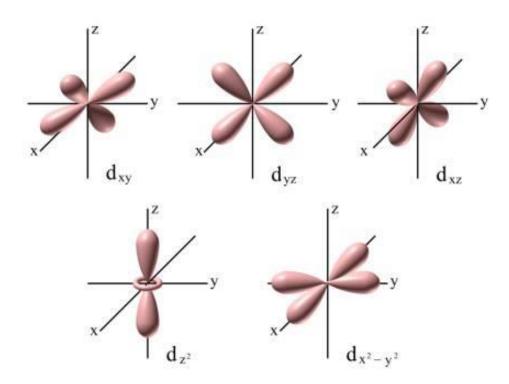
The phenomenon is restricted to transition and rare-earth elements -> it is related to the unfilled 3d and 4f shells in these substances.

Ferromagnetism involves the alignment of a significant fraction of the molecular magnetic moments in some favorable direction in the crystal.

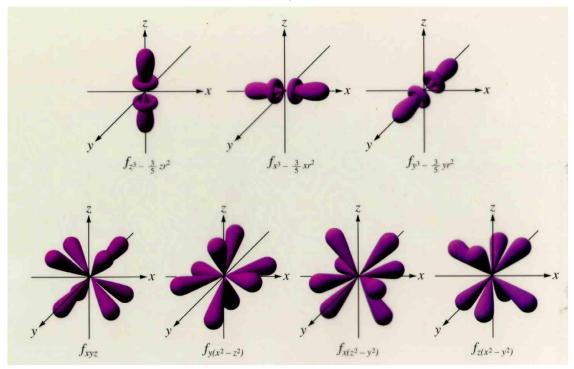
Ferromagnetism appears only below a certain temperature, which is known as the *ferromagnetic transition temperature* or simply as the *Curie temperature* (depends on the substance).

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For a given shell with d-states, there are five d-electron orbitals, and each can accommodate two electrons, so 10 d-electrons.



For a given shell with f-states, there are seven *f*-electron orbitals, and each can accommodate two electrons, so 14 *f*-electrons.



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Isolated atoms

- The magnetic moment of a free atom has three main sources:
- 1. the spin of the electrons
- 2. the electron orbital angular momentum about the nucleus
- 3. the change in orbital moment induced by an applied magnetic field.
- In classical picture, electrons orbit around nucleus.
- Each orbit like a loop of electric current.
- A loop of current produces a magnetic field, so electrons in an atom generate a magnetic field.
- Quantum numbers n, l, m_l and m_s label the electrons in an atom (alternatively called n, l, l_z , σ_z).

Corresponding to: the principal quantum number, angular momentum, *z*-component of angular momentum and *z*-component of the spin.

Hund's rules for isolated atoms

Start with some fundamentals of electrons in isolated atoms.

Set of rules – Hund's rules – that determines how electrons fill orbitals. Recall from QM, an electron in an atomic orbital can be labelled by four quantum numbers:

 $|n,l,l_z,\sigma_z\rangle$

Principal quantum number $n = 1, 2, \dots$

Angular momentum $l = 0, 1, \dots, n-1$

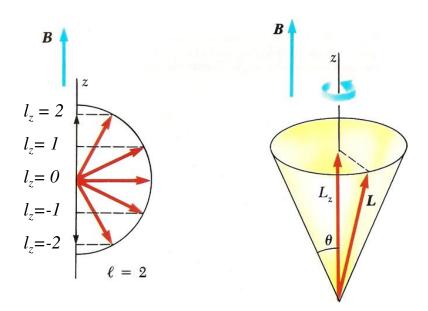
z-component of ang. mom. $l_z = -l, \ldots, l$

z-component of spin $\sigma_z = -1/2 \text{ or } +1/2$

Sometimes the angular momentum shells l=0,1,2,3 are known as s,p,d,f,\ldots and can accommodate $2,6,10,14,\ldots$ electrons, respectively.

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Hund's rules for isolated atoms



z-component of ang. mom.

Hund's rules for isolated atoms

Hund's 0th rule (Aufbau principle): shells filled starting with lowest available energy state. An entire shell filled before another started.

Madelung Rule: energy ordering is from lowest value of n+1 to largest; when two shells have the same n+1, fill one with smallest n first.

Two examples:
Nitrogen (N) 7 electrons, filled 1s shell with 2 electrons spin-up and spin-down, 2 electrons in the 2s shell with 2 electrons spin-up and spin-down 3 electrons in the 2p shell
$$1s^22s^22p^3$$

Praseodymium (Pr) 59 electrons

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3\pmb{p}^{-10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^3$$
 or as $[\mathrm{Xe}] 6s^2 4f^3$

: : : : : :

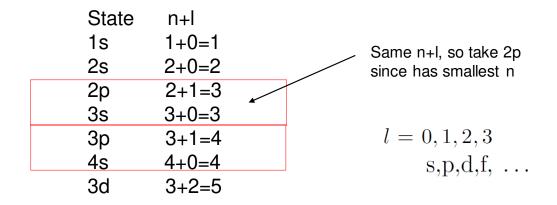
5f

6h

Hund's rules for isolated atoms

Madelung Rule: energy ordering is from lowest value of n+1 to largest; when two shells have the same n+1, fill one with smallest n first.

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, \dots$$



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Hund's rules for isolated atoms

The shell filling sequence is the rule which defines the overall structure of the periodic table.

When shells are partially filled need to describe which of the orbitals are filled in these shells and which spin states are filled.



(1) Electrons try to align their spins, i.e. the electrons should occupy the orbitals such that the maximum possible value of the total spin S is realized.

Consider Pr as example $[\rm Xe]6s^24f^3$ - the 3 valence electrons will have spins that point in same direction giving S=3/2.

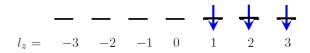
For f shell so l=3, and 2l+1 values of l_z

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Hund's rules for isolated atoms

(2) The electrons should occupy the orbitals such that the maximum of L (sum over I_z), consistent with S, is realized.

For Pr, this means $\,l_z=3\,\,l_z=2\,\,l_z=1$ giving $\,L_z=6$ so we have $\,S=3/2\,$ and $\,L=6$

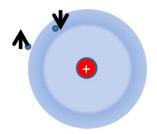


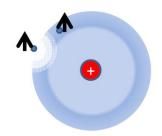
- (3) The total angular momentum J is calculated such that:
- If the sub-shell is less than half-full J=L-S
- If the sub-shell is more than half full J=L+S
- If the sub-shell is half full, L=0 and J=S

For Pr, since shell less than half-full (have 3 electrons, shell can hold 14 electrons) we use J=L-S=6-3/2=9/2

Why moments align

Preference for spins to align comes from the Coulomb interaction energy between the electron and nucleus.





For spins anti-aligned, electrons are closer and the nucleus is partially screened by the negative charge of the other electron.

For spins aligned the electrons repel each other and see the full positive charge of the nucleus, so greater Coulomb attraction.

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Another example: Cr3+

Cr electronic configuration is: [Ar] 3d⁵ 4s¹ Cr³⁺ has lost 3 electrons; the configuration is: [Ar] 3d³

- The first of Hund's rules requires S=3/2.
- The possible I_z values for the 3d shell are -2,-1,0,1,2. Hund's second rule requires to choose the largest possible value of L, i.e. to choose $I_z = 0,1,2$, so L=3.
- Since the sub-band is less than half filled, J=L-S=3-3/2=3/2.

Hund's rules

The allowed spectroscopic code:

L = 0.123456X = SPDFGHI

The spin is specified by affixing the number 2S+1 (known as the multiplicity) to the letter as a superprefix, and only J is given as the number J, affixed as a right subscript. Thus the lowest lying J-multiplet is described by the symbol: ${}^{(2S+1)}X_J$.

d	-shell ($l =$	2)						1 1	
n	$l_z = 2$,	1,	0,	-1,	-2	S	$L = \Sigma l_z $	J	SYMBOL
1	1					1/2	2	3/2)	$^{2}D_{3/2}$
2	1	1				1	3	2 7 17 8	3F2
3	1	1	1			3/2	3	$\left \frac{2}{3/2} \right J = L - S $	$^{4}F_{3/2}$
4	1	1	1	1		2	2	0	5D0
5	1	1	1	1	1	5/2	0	5/2	6S _{5/2}
6	11	1	1	1	†	2	2	4	5 D4
7	11	11	1	1	†	3/2	3	9/2 $J = L + S$	$^{4}F_{9/2}$
8	11	11	11	1	†	1	3	$4 \int_{0}^{3} = L + 3$	3F4
9	11	11	11	11	†	1/2	2	5/2	$^{2}D_{5/2}$
10	11	17	11	11	11	0	0	0	¹ S ₀

Ashcroft & Mermin Ch. 31

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Hund's rules

GROUND STATES OF IONS WITH PARTIALLY FILLED 4- OR f-SHELLS, AS CONSTRUCTED FROM HUND'S RULES"

	f-	shell (l	=	3)									
×	n	$l_z = 3$,	2,	1,	0, -	-1,-	-2,	-3	S	$L = \Sigma l_z $		J
	1	1								1/2	3	5/2	
	2	1		1						1	5	4	
l	3	1		1	1					3/2	6	9/2	J = L - S
	4	1		1	1	1				2	6	4	J = L - S
	5	1		1	1	1	1			5/2	5	5/2	
	6	1		1	1	1	1	1		3	3	0)
	7	1		1	1	1	1	1	Ţ	7/2	0	7/2	
l	8	1	1	1	1	1	1	†	1	3	3	6	-
l	9	1	1	17	1	1	1	1	1	5/2	5	15/2	
l	10	1	1	11	17	1	1	1	1	2	6	8	7 7 . 6
	11	1	1	17	17	11	1	1	1	3/2	- 6	15/2	J = L + S
	12	1		11	17	#	11	1	1	1	5	6	
	13	1		11	17	#	11	17	1	1/2	3	7/2	
	14	1		17	17	11	11	11	11	0	0	0	
	14	1	ľ	ħ.	t.	4	भ	ħ	†I	0	0	0	7

Coupling of electrons in atoms to an external field

Seen how electron orbital and spin can align with each other, now consider how electrons couple to an external magnetic field.

First recall:

particle in electromagnetic field

change the momentum (operator)

$$\mathbf{p} o \mathbf{p} - q \mathbf{A}$$
 for electrons $q = -e$

Oxford Basics, Ch. 19.3

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Coupling of electrons in atoms to an external field

In absence of a magnetic field the Hamiltonian for an electron in an atom is: $V_0 = \frac{{\bf p}^2}{2m} + V({\bf r})$ potential from the nucleus

In presence of a magnetic field:

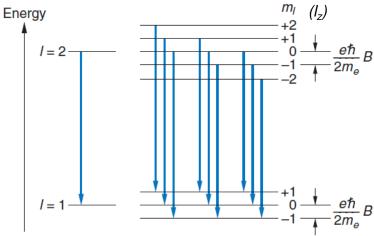
$$\mathcal{H} = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + g\mu_B \mathbf{B} \cdot \boldsymbol{\sigma} + V(\mathbf{r})$$
Kinetic energy term
$$+ g\mu_B \mathbf{B} \cdot \boldsymbol{\sigma} + V(\mathbf{r})$$
Attraction to the nuclei spin and the field of electron points in same direction as magnetic field

where σ is the electron spin, g is the electron g-factor (about 2) and the Bohr magneton is $\mu_B=e\hbar/(2m)$

(Since the electron charge is negative, the electron spin magnetic moment is anti-aligned with its spin.)

Zeeman effect

Energy level splitting in the normal Zeeman effect for singlet levels 1=2 and 1=1



Splitting of spectral lines when atom is placed in an external magnetic field predicted by Lorentz, first observed by Zeeman.

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Coupling of electrons in atoms to an external field

For a uniform magnetic field, we can take ${\bf A}=\frac{1}{2}{\bf B}\times{\bf r}$ and $\nabla\times{\bf A}={\bf B}$ and so

$$\mathcal{H} = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + g\mu_B \mathbf{B} \cdot \boldsymbol{\sigma} + V(\mathbf{r})$$

can be written as:

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{e}{2m}\mathbf{p} \cdot (\mathbf{B} \times \mathbf{r}) + \frac{e^2}{2m} \frac{1}{4} |\mathbf{B} \times \mathbf{r}|^2 + g\mu_B \mathbf{B} \cdot \boldsymbol{\sigma}$$

First two terms just Hamiltonian in absence of field, \mathcal{H}_0 .

Can rewrite 3rd term as:

$$\frac{e}{2m}\mathbf{p}\cdot(\mathbf{B}\times\mathbf{r}) = \frac{e}{2m}\mathbf{B}\cdot(\mathbf{r}\times\mathbf{p}) = \mu_B\mathbf{B}\cdot\mathbf{l}$$

where $\,\hbar {f l} = {f r} imes {f p}\,$ is the angular momentum of the electron.

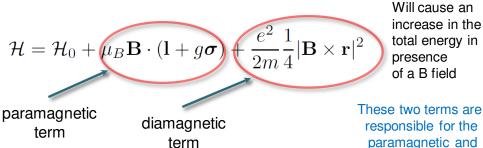
Coupling of electrons in atoms to an external field

With 3rd term as
$$\frac{e}{2m}\mathbf{p}\cdot(\mathbf{B}\times\mathbf{r})=\frac{e}{2m}\mathbf{B}\cdot(\mathbf{r}\times\mathbf{p})=\mu_{B}\mathbf{B}\cdot\mathbf{l}$$

Can combine with 5th term of below

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{e}{2m}\mathbf{p} \cdot (\mathbf{B} \times \mathbf{r}) + \frac{e^2}{2m}\frac{1}{4}|\mathbf{B} \times \mathbf{r}|^2 + g\mu_B \mathbf{B} \cdot \boldsymbol{\sigma}$$

To obtain final expression:



Coupling of field to total magnetic moment of electron diamagnetic response of atoms – orbital moment - $\mu_{\rm B}$ I and spin moment - $g\mu_{\rm B}\sigma$

responsible for the paramagnetic and to external magnetic fields

Free spin (Curie or Langevin) paramagnetism

It describes the reorientation of free spins in an atom

Consider the paramagnetic term in previous equation – generalize to multiple electrons in the atom; want to find the susceptibility, Curie's Law.

$$\mathcal{H} = \mu_B \mathbf{B} \cdot (\mathbf{L} + g\mathbf{S})$$
 L and S, orbital and spin components of all electrons, and $\mathbf{J} = \mathbf{L} + \mathbf{S}$

Can write as:
$$\mathcal{H}= ilde{g}\mu_B\mathbf{B}\cdot\mathbf{J}$$
 Called the effective g-factor, known as the Landé g-factor

$$\begin{array}{ll} \text{where} & \tilde{g} = \frac{1}{2}(g+1) + \frac{1}{2}(g-1) \left[\frac{S(S+1) - L(L+1)}{J(J+1)} \right] & \text{(see Solid State Basics for derivation or } \\ \text{The partition function is} & Z = \sum_{J_z = -J}^{J} e^{\beta \tilde{g} \mu_B B J_z} & \text{Appendix P} \end{array}$$

And the corresponding free energy is $F = -k_BT \log Z$ $\beta = 1/k_BT$

Free spin (Curie or Langevin) paramagnetism

Given the free energy $F = -k_B T \log Z$

The magnetic moment per spin is $M=-\frac{\partial F}{\partial \mathcal{P}}$ $(M=\chi H = \chi B/\mu_0)$

Oxford Basics, Ch. 19.4 (derivation Ex. 19.7)

Curie constant

$$\chi = \lim_{B \to 0} \frac{\partial M}{\partial B} \, \mu_0$$

Assuming a density n of these atoms it can be shown that the susceptibility is:

 $\chi = \frac{n\mu_0(\tilde{g}\mu_B)^2}{3} \frac{J(J+1)}{k_B T} = \frac{C}{T}$

Curie's Law

Called "Curie paramagnetism" or "Langevin paramagnetism"

Larmor diamagnetism

Consider now diamagnetic term – coupling of the orbital motion to the magnetic field.

Curie paramagnetism dominant when $J \neq 0$, so can only observe diamagnetism when J=0.

For example, filled shell configurations like noble gases:

$$L = S = J = 0$$

[Or if J=0, but L and S not equal to zero. This occurs when shell has one electron fewer than being half full]

The expectation of the diamagnetic term, for **B** in the z direction is:

Recall, we had
$$\mathcal{H} = \mathcal{H}_0 + \mu_B \mathbf{B} \cdot (\mathbf{l} + g\boldsymbol{\sigma}) + \frac{e^2}{2m} \frac{1}{4} |\mathbf{B} \times \mathbf{r}|^2$$

$$\delta E = \frac{e^2}{8m} \langle |\mathbf{B} \times \mathbf{r}|^2 \rangle = \frac{e^2 B^2}{8m} \langle x^2 + y^2 \rangle$$

Larmor diamagnetism

The atom is rotationally symmetric: $\langle x^2+y^2\rangle=\frac{2}{3}\langle x^2+y^2+z^2\rangle=\frac{2}{3}\langle r^2\rangle$ So we have $\delta E=\frac{e^2B^2}{12m}\langle r^2\rangle$

and the magnetic moment per electron is: $-\frac{dE}{dB} = -\left[\frac{e^2}{6m}\langle r^2\rangle\right]B$

(can see the magnetic moment is proportional to the area $~=\chi\,B/~\mu_0$ enclosed by the orbit of the electron)

Assume density ρ of electrons, can write:

Larmor Diamagnetism

$$\chi = -\frac{\rho e^2 \mu_0 \langle r^2 \rangle}{6m}$$

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[Advanced only]

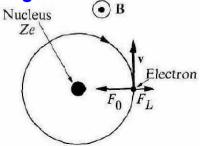
Classical consideration: diamagnetism

Can obtain the same formula classically:

Consider an electron rotating about the nucleus in a circular orbit; let a magnetic field be applied.

Before this field is applied, we have, according to Newton's second law,

 $F_0 = m\omega_0^2 r$



 F_0 is the attractive Coulomb force between the nucleus and the electron, and ω_0 is the angular velocity.

Applied field \rightarrow an additional force: the *Lorentz force* $F_L = -e(\mathbf{v} \times \mathbf{B})$

$$F_L = -eB\omega r \implies F_0 - eB\omega r = m\omega^2 r$$
 $\omega = \omega_0 - \frac{eB}{2m}$

Reduction in frequency \rightarrow corresponding change in the magnetic moment.

The change in the frequency of rotation is equivalent to the change in the current around the nucleus: $\Delta I = (\text{charge}) \times (\text{revolutions per unit time})$

[Advanced only]

$$\Delta I = -Ze \frac{1}{2\pi} \frac{eB}{2m}$$

The magnetic moment of a circular current is given by the product (current) x (area of orbit)

$$\Delta \mu = -e \frac{1}{2\pi} \frac{eB}{2m} \pi \left\langle r_{xy}^{2} \right\rangle = -\frac{e^{2} \left\langle r_{xy}^{2} \right\rangle}{4m} B$$

Here $\langle r_{xy}^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$. The mean square distance of the electrons from the nucleus is $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$.

For a spherically symmetrical charge distribution $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \langle r^2 \rangle / 3$

$$\Rightarrow \left\langle {r_{xy}}^2 \right\rangle = \frac{2}{3} \left\langle {r^2} \right\rangle \quad \Rightarrow \quad \Delta \mu = -\frac{e^2 \left\langle {r^2} \right\rangle}{6m} B \quad \Rightarrow \quad \chi = -\frac{\mu_0 e^2 NZ \left\langle {r^2} \right\rangle}{6m}$$

Diamagnetism in ionic crystals and crystals composed of inert gas atoms: they have atoms or ions with complete electronic shells.

Another class of diamagnetics is noble metals, which will be discussed later.

End