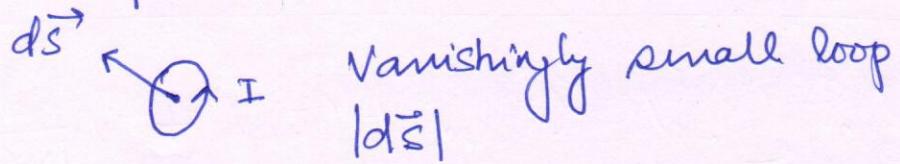


Magnetism

What is magnetism? How does it arise in different magnetic systems?

Magnetic moment?

We can equate with a current loop:



Magnetic moment: $d\vec{\mu} = I d\vec{S}$

I is the current, which is also the flow charge.

There charges are associated with particles (e) which have mass.

Consider the angular momentum vector \vec{L}

$\vec{\mu}$ — parallel or anti-parallel to \vec{L} .

Now consider a loop of finite size



$$\vec{\mu} = \int d\vec{\mu} = I \int d\vec{S}$$

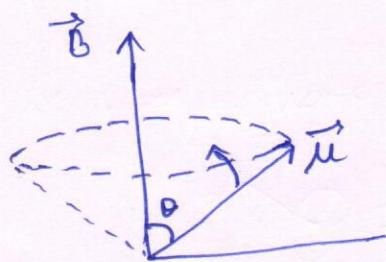
when we sum up the contributions from these infinitesimal loops — left with current around the perimeter of the loop.

connection with angular momentum

$$\vec{\mu} = \gamma \vec{L}$$

γ = gyromagnetic ratio (a constant)

$E = -\vec{\mu} \cdot \vec{B}$ energy of a magnetic dipole in the presence of a magnetic field



The torque acting on the magnetic moment is

$$\vec{\tau} = \vec{\mu} \times \vec{B},$$

$$\vec{\tau} = \frac{d\vec{\mu}}{dt} \Rightarrow \gamma \vec{\tau} = \frac{d\gamma \vec{\mu}}{dt} = \frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}$$

$$\boxed{\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}}$$

The magnetic field causes the direction of $\vec{\mu}$ to precess around \vec{B} .

The Bohr Magneton



$$\text{current } I = \frac{-e}{2\pi r/\sigma} = -\frac{ev}{2\pi r}$$

Magnitude of the angular momentum
 $m_e v r = \hbar$,

Now

$$\mu = \pi r^2 I = \pi r^2 \left(\frac{-ev}{2\pi r} \right) = \left(\frac{-e}{2me} \right) (m_e v r) = -\frac{eh}{2me} = -M_B.$$

$$\Rightarrow \boxed{M_B = \frac{eh}{2me} = 9.274 \times 10^{-24} \text{ Am}^2}$$

$$\gamma = \frac{e}{2me}$$

Larmor frequency

Larmor frequency $\omega_L = |\gamma|B = \frac{eB}{2me}$

Magnetism

\vec{M} — magnetic moment per unit volume

Magnetic solid — atoms — magnetic moments

$|\vec{M}| = 0$ in free space

$$\vec{B} = \mu_0 \vec{H} \quad \mu_0 = 4\pi \times 10^{-7} \text{ H/m} \quad \text{permeability of free space}$$

Magnetic material

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

now $\vec{M} \propto \vec{H} \Rightarrow \vec{M} = \chi \vec{H}$; χ is the magnetic susceptibility.

$$\Rightarrow \vec{B} = \mu_0(1+\chi) \vec{H} = \mu_0 \mu_r \vec{H}$$

μ_r = relative permeability of the material.

Consider a charged particle with charge q , mass m moving in the presence of an electric field \vec{E} and magnetic field \vec{B} .

$$\text{Lorentz force } \vec{F} = q(\vec{E} + \vec{v} \times \vec{B}).$$

How the momentum of a charged particle in a magnetic field is modified?

$$\vec{F} = m \frac{d\vec{v}}{dt}; \quad \vec{B} = \vec{\nabla} \times \vec{A} \text{ and } \vec{E} = -\vec{\nabla} V - \frac{\partial \vec{A}}{\partial t},$$

where \vec{A} is magnetic vector potential.

$$\Rightarrow m \frac{d\vec{v}}{dt} = -q \vec{\nabla} V - q \frac{\partial \vec{A}}{\partial t} + q \vec{v} \times (\vec{\nabla} \times \vec{A})$$

$$\boxed{\vec{v} \times (\vec{\nabla} \times \vec{A}) = \vec{\nabla}(\vec{v} \cdot \vec{A}) - \vec{v} \cdot \vec{\nabla} \vec{A}},$$

$$\Rightarrow m \frac{d\vec{v}}{dt} + q \left[\frac{\partial \vec{A}}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \vec{A} \right] = -q \vec{\nabla}(V - \vec{v} \cdot \vec{A}).$$

$\underbrace{\frac{d\vec{A}}{dt}}$

$$\Rightarrow \frac{d}{dt} (m\vec{v} + q\vec{A}) = -q \vec{\nabla}(V - \vec{v} \cdot \vec{A}).$$

Canonical momentum

$$\vec{p} = m\vec{v} + q\vec{A}$$

$$\text{and } V_{\text{eff}} = V - \vec{v} \cdot \vec{A}.$$

$$\begin{aligned} \text{The kinetic energy} &= \frac{1}{2} m v^2 \\ &= \frac{1}{2} m (\vec{p} - q\vec{A})^2. \end{aligned}$$

δM . K.E. operator

$$\frac{1}{2} m (-i\hbar \vec{\nabla} - q\vec{A})^2.$$

Orbital and spin angular momentum

Orbital angular momentum depends on the electronic state occupied by the electron.

Recall you deal with quantum numbers l and m_l .

Component along a fixed axis : $m_l \hbar$

Magnitude of the orb. ang. mom : $\sqrt{l(l+1)} \hbar$

What is the component of the magnetic moment along the z-axis : $-m_l M_B$

Total magnetic dipole moment : $\sqrt{l(l+1)} M_B$.

Let's summarize

operators	eigenvalues
\hat{L}^2	$l(l+1)\hbar^2$
\hat{L}_z	$m_l \hbar$
\hat{M}^2	$l(l+1) M_B$
\hat{M}_z	$-m_l M_B$

Spin - an intrinsic angular momentum, so it leads to an intrinsic magnetic moment.

Therefore, the total angular momentum is $\vec{J} = \vec{L} + \vec{S}$.

Consider an spin with a spin quantum number δ .

For an electron $\delta = \frac{1}{2}$.

choose an axis, the components of the spin intrinsic angular momentum will have $(2\delta+1)$ possible values.

$\delta\hbar, (\delta-1)\hbar, \dots, -\delta\hbar$.

$m_s\hbar$

For an electron $\delta = \frac{1}{2}$, therefore $m_s = \pm \frac{1}{2}$.

$\frac{1}{2}$ up and $-\frac{1}{2}$ down.

So the components of magnetic moment along a particular axis $-g\mu_B m_s$.

Total magnitude $\sqrt{\delta(\delta+1)} g \mu_B = \frac{\sqrt{3}}{2} g \mu_B$, where

g is a constant and is called the g -factor.

$g \approx 2$. Dirac's theory predicts $g=2$, but it is not

exactly 2.

$$g = 2 \left(1 + \frac{\alpha}{\pi} + \dots \right)$$

$$= 2.0023\dots$$

where α is the fine structure constant $\alpha = \frac{e^2}{4\pi\epsilon_0 c} = \frac{1}{137.0}$

Therefore the energy in a magnetic field B (along z-axis) is given by

$$E = g \mu_B m_s B.$$

The energy levels of an electron will split in a magnetic field $g\mu_B B$. Zeeman splitting.

Our goal is study the different kind of magnetic behaviors that shows up in condensed matter systems / solids.

Here our focus would be on some of the intrinsic magnetic properties of solids: the magnetic moments they exhibit in the presence and sometimes even in the absence of applied magnetic fields.

We will start our discussion with the magnetic properties of insulating solids. The observed magnetic behavior can be explained in terms of the properties of their individual atoms, or ions; however, if required, we can introduce suitable modifications to take into account effects of the surroundings/crystalline environment.

We will ignore the interaction between different magnetic moments on different atoms or between the magnetic moment and their surroundings.

$$\begin{matrix} \uparrow & \nearrow & \downarrow & \nearrow & \uparrow \\ \times & \nearrow & \uparrow & \nearrow & \rightarrow \end{matrix}$$

So we will be concerned with the physics of isolated atoms and their interaction with an applied magnetic field.

Therefore, consider an atom (or an ion) in a magnetic field.

Electron spin will interact with the magnetic field and will give rise to the following energy contribution

$$E = g M_B B m_s,$$

where $g \approx 2$ and $m_s = \pm \frac{1}{2}$. Therefore, $E \approx \pm M_B B$.

Now consider the orbital angular momentum part. Let there be 2 electrons in the atom.

Let \vec{r}_i and \vec{p}_i represent the position and the linear momentum of the i th electron. Therefore, we can write

$$\vec{\tau} L = \sum_i \vec{r}_i \times \vec{p}_i,$$

where the summation is over all the electrons in an atom.

The hamiltonian for this system in the absence of a magnetic field can be written as

$$H_0 = \sum_{i=1}^Z \left(\frac{\vec{p}_i^2}{2m_e} + V_i \right),$$

where V_i some potential.

Let us apply a magnetic field B , characterized by

$$\vec{B} = \vec{\nabla} \times \vec{A} \text{ and } \vec{A}(\vec{r}) = \frac{\vec{B} \times \vec{r}}{2}.$$

Therefore, the Hamiltonian in the presence of a magnetic field is given by

$$\begin{aligned} H &= \sum_{i=1}^Z \left(\frac{\vec{p}_i^2}{2m_e} + e\vec{A}(\vec{r}_i) \right)^2 + V_i + g\mu_B \vec{B} \cdot \vec{s} \\ &= \sum_{i=1}^Z \left(\frac{\vec{p}_i^2}{2m_e} + \frac{e^2}{8m_e} (\vec{B} \times \vec{r}_i)^2 + \frac{2e\vec{p}_i \cdot \vec{B} \times \vec{r}_i}{2} + V_i \right) + g\mu_B \vec{B} \cdot \vec{s} \\ &= \sum_{i=1}^Z \left(\frac{\vec{p}_i^2}{2m_e} + V_i \right) + \frac{e\hbar}{2m_e} \vec{L} \cdot \vec{B} + g\mu_B \vec{B} \cdot \vec{s} + \frac{e^2}{8m_e} (\vec{B} \times \vec{r}_i)^2 \end{aligned}$$

Note

$$\vec{p}_i \cdot \vec{B} \times \vec{r}_i = \underbrace{\vec{r}_i \times \vec{p}_i}_{\vec{\tau} L} \cdot \vec{B}$$

The field dependent terms in the Hamiltonian
 $H = H_0 + \Delta H$, where

$$\Delta H = \mu_B (\vec{L} + g\vec{s}) \cdot \vec{B} + \frac{e^2}{8m_e} \sum_{i=1}^Z (\vec{B} \times \vec{r}_i)^2.$$

Generally the energy shift produced by ΔH is quite small on the scale of atomic excitation energies, even for the highest presently attainable laboratory field.

This observation allows us to compute the changes in the energy levels induced by the field with ordinary perturbation theory.

We are interested in susceptibility χ , which is a second derivative w.r.t. the field ($\chi \sim \partial^2 / \partial B^2$); therefore, we must retain terms up to second order in H . Thus, we use the second-order perturbation theory result

$$E_n \Rightarrow E_n + \Delta E_n, \text{ where}$$

$$\Delta E_n = \langle n | \Delta H | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \Delta H | n' \rangle|^2}{E_n - E_{n'}}.$$

Substitute for the ΔH and retain terms only up to second order in B .

$$\Delta E_n = \mu_B \langle n | (\vec{L} + g\vec{s}) \cdot \vec{B} | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \mu_B (\vec{L} + g\vec{s}) \cdot \vec{B} | n' \rangle|^2}{E_n - E_{n'}}$$

term 1 term 2

$$+ \frac{e^2}{B m_e} B^2 \langle n | \sum_{i=1}^2 (x_i^2 + y_i^2) | n \rangle$$

term 3

The above equation will be the starting point for our discussion of theories of the magnetic susceptibility of individual atoms, ions or molecules.

This also helps with the susceptibilities of those solids that can be represented as a collection of only slightly deformed individual ions, i.e; ionic and molecular solids. Note that in such cases the susceptibility is computed ion by ion.

Observations

Term 1 will always be the dominant term, of course, unless it vanishes. This is true even if the applied magnetic field is very strong (LT).

If the term L_2 is not vanishing, $\langle n | L_2 + g \vec{S}_2 | n \rangle$ will be of order unity so that

$$\mu_B \vec{B} \cdot \langle n | \vec{L} + g \vec{s} | n \rangle = D(\mu_B B) \sim \frac{eB\hbar}{2m_e} \sim \hbar\omega_c$$

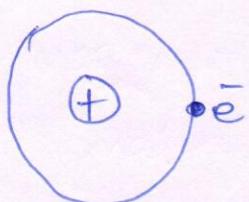
$\sim 10^{-4}$ eV when B is 1 Tesla.

This is very small compared to the atomic energies.
The energy shifts are small.

Estimation of term 3

$\langle n | x_i^2 + y_i^2 | n \rangle$ will be of the order of the square of typical atomic dimensions.

$$\frac{e^2}{8me} B^2 \langle n | \sum_i (x_i^2 + y_i^2) | n \rangle = O\left(\left[\frac{eB}{2me}\right]^2 m a_0^2\right)$$



$$\frac{\hbar^2}{ma_0^2} \sim \frac{e^2}{4\pi\epsilon_0 a_0}$$

we are just doing an order of magnitude estimation

$$\text{A0 } (\hbar\omega_L)^2 \frac{ma_0^2}{\hbar^2} = \hbar\omega_L \left(\frac{\hbar\omega_L}{e^2/4\pi\epsilon_0 a_0} \right) \sim \hbar\omega_L \times 10^{-5}$$

$$\text{and } \frac{e^2}{4\pi\epsilon_0 a_0} \sim 27 \text{ eV} \quad \left. \begin{array}{l} \hbar\omega_L \sim 10^4 \text{ eV} \\ \text{This tells us that the term 3 is smaller than term 1 by a factor of about } 10^5 \end{array} \right\} \text{about } 10^{-5} \text{ (at a large field strength of 1 T).}$$

Estimation of term 2

$$|\langle n | \mu_B (\vec{l} + g\vec{s}) \cdot \vec{B} | n \rangle|^2 / E_n - E_{n'}$$

$$\sim \hbar\omega_L \frac{\hbar\omega_L}{\Delta}; \quad \Delta = \min |E_n - E_{n'}| \text{ is the typical atomic excitation energy}$$

In most of the cases, Δ is large enough to make ratio $\hbar\omega_L/\Delta$ very small.

Diamagnetic moment

$$\mathcal{H} = \mathcal{H}_0 + M_B (\vec{I} + g \vec{S}) \cdot \vec{B} + \frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2$$

Dominant perturbation
paramagnetism

Diamagnetism

Let us assume that no unfilled electronic shells are present, so the paramagnetic term drops out.
Also now assume that \vec{B} is parallel to the z -axis.

$$\vec{B} \times \vec{r}_i = -y_i B \hat{x} + x_i B \hat{y} + 0 \hat{z}$$

$$= B (-y_i, x_i, 0)$$

$$(\vec{B} \times \vec{r}_i)^2 = B^2 (x_i^2 + y_i^2)$$

$$\mathcal{H}_d = \frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2$$

Such an atom/ion has zero spin & orbital angular momentum in its ground state $|0\rangle$. The G-state of closed-shell ion is spherically symmetric.

$$J|0\rangle = L|0\rangle = S|0\rangle = 0.$$

Let $|0\rangle$ denote the ground state wavefunction in the absence of the field.

Only the term 3 will lead to a shift in the ground state energy.

We are interested in the change in the ground state energy.

To the first order the change in the ground state energy is given by

$$\Delta E_0 = \frac{e^2 B^2}{8m_e} \sum_{i=1}^Z \langle 0 | (x_i^2 + y_i^2) | 0 \rangle.$$

If we assume that the atom is spherically symmetric, then we have

$$\langle x_i^2 \rangle = \langle y_i^2 \rangle = \frac{1}{3} \langle r_i^2 \rangle.$$

$$\Rightarrow \boxed{\Delta E_0 = \frac{e^2 B^2}{12m_e} \sum_i \langle 0 | r_i^2 | 0 \rangle.}$$

Our sample or the solid is composed of N atoms (or ions) and it occupies a volume V .

The free energy is then

$$F = E - TS,$$

where T is the temperature and S the entropy.

Also, recall

$$dE = TdS - pdV - MdB$$

$$dF = -SdT - pdV - MdB.$$

Magnetization at $T=0$

$$F = E$$

$$M = -\frac{\partial F}{\partial B} = -\left(\frac{N}{V}\right) \frac{\partial \Delta E_0}{\partial B} \quad \frac{N}{V} = n$$

\Rightarrow

$$M = -\frac{Ne^2 B}{6meV} \sum_i^Z \langle r_i^2 \rangle.$$

Susceptibility

$$\chi = \lim_{H \rightarrow 0} \frac{\partial M}{\partial H}$$

$$B = M_0 H$$

$$\chi = \frac{M}{H} \approx \frac{M_0 M}{B}$$

$$\Rightarrow \chi = -\frac{N}{V} \frac{e^2 M_0}{6me} \sum_{i=1}^Z \langle r_i^2 \rangle$$

Diamagnetic susceptibility.

This is the mag. susceptibility of insulators with all shells closed, also called the Larmor diamagnetic susceptibility. Also called the Langevin susceptibility.

The term diamagnetism is applied to cases of negative susceptibility, i.e., cases in which the induced moment is opposite to the applied field.

A uniform vector field \vec{F}_0 can be expressed as

(a) an irrotational field

$$\vec{F}_0 = -\nabla V,$$

where $V(\vec{r}) = -\vec{r} \cdot \vec{F}_0$.

(b) a solenoidal field

$$\vec{F}_0 = \vec{\nabla} \times \vec{A}$$

where $\vec{A}(\vec{r}) = -\frac{1}{2}(\vec{r} \times \vec{F}_0)$.

Consider the i th component of $\vec{\nabla}V$ and $\vec{\nabla} \times \vec{A}$ respectively, and recalling that the F_{0i} are spatially constant, give:

(a) $\nabla_i(\vec{r} \cdot \vec{F}_0) = \nabla_i(r_j F_{0j}) = F_{0j} \nabla_i r_j = F_{0j} \delta_{ij}$, which contracts to F_{0i} as required.

(b) $(\vec{\nabla} \times \vec{A})_i = -\frac{1}{2} \epsilon_{ijk} \nabla_j (\vec{r} \times \vec{F}_0)_k = -\frac{1}{2} \epsilon_{ijk} \epsilon_{klm} F_{0m} \nabla_j r_l$
 $= -\frac{1}{2} (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) F_{0m} \delta_{jl}$.

Contracting subscripts gives F_{0i} as required.

Comments

- (i) The results $V(\vec{r}) = -\vec{r} \cdot \vec{F}_0$ and $A(\vec{r}) = -\frac{1}{2}(\vec{r} \times \vec{F}_0)$ are often conveniently potentials for representing uniform electrostatic and magnetostatic fields respectively.
- (ii) Because a uniform field does not satisfy the conditions of Helmholtz's theorem (it does not tend to zero at infinity), \vec{F}_0 has no unique representation. It is easily verified that \vec{F}_0 can be expressed as a linear combination of ① and ② in infinitely many ways.

(Very closely follows Ashcroft/Mermin)

What is the magnetic behavior of solids which contain some ions with partially filled electronic shells?

To comment on this question using the expression for ΔE_n derived earlier, we must gather/recall the basic facts about the low-lying states of such ions.

So we are interested in knowing about the ground-state of ions with a partially filled shell, which can be understood using a set of rules called the Hund's rule.

Let us consider a free atom or ion in which all electronic shells are filled or empty except for one, whose one-electron levels are characterized by orbital angular momentum l .

For a given value of l , its projection along a particular axis say l_z can take $2l+1$ values ($l, l-1, l-2, \dots, -l$). Moreover, for each l_z there two possible spin orientations.

Therefore, such a shell will contain $2(2l+1)$ one-electron levels.

Now if the electrons did not interact with one another, the resulting ionic ground state would be degenerate. Thus, there would be a large number of ways of putting n electrons into more than n levels.

However, this degeneracy is considerably ~~lifted~~, though in general not completely, lifted by electron-electron Coulomb interactions as well as by the electron spin-orbit interaction.

If the spin-orbit coupling is not strong, the lowest-lying levels after the degeneracy is lifted can be described by a ^{simple} set of rules, simplified both by complex calculations and by the analysis of atomic spectra.

Note that for very heavy ions spin-orbit coupling is very strong.

The angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together in many varied ways.

Following three types of interactions can occur.

- * spin-Spin coupling;
- * orbit-orbit coupling;
- * Spin-orbit coupling.

There are two principal coupling schemes that are used:

- * Russell-Saunders (or L-S) coupling;
- * j-j coupling.

In the Russell-Saunders scheme the strength of the couplings are as follows:

Spin-Spin coupling \gg orbit-orbit coupling \gg Spin-orbit coupling

It has been found that this scheme gives a good approximation for the first row transition series where j-j coupling can be ignored. However, for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling is med.

The total angular momentum J is always a good quantum number for an atom or ion, but L and S are good quantum numbers only to the extent that spin-orbit coupling is unimportant.

If this is the case, then the following commutations hold

$$[H, J] = 0 ; [H, L] = 0 ; [H, S] = 0 ,$$

where H is the Hamiltonian of the atom or ion, \vec{S} the total spin, \vec{L} the total electron orbital angular momentum and $\vec{J} = \vec{L} + \vec{S}$ the total electronic angular momentum.

Thus, the states of the ions can be described by quantum numbers L, L_z, S, S_z, J and J_z , indicating that they are eigenstates of the operators $\hat{L}^2, \hat{L}_z, \hat{S}, \hat{S}_z, \hat{J}$ and \hat{J}_z with eigenvalues $L(L+1), L_z, S(S+1), S_z, J(J+1)$, and J_z , respectively.

Now since filled shells have zero orbital, spin and total angular momentum, these quantum numbers describe the electronic state configuration of the partially filled shell, as well as the ion as a whole.

The ground state of these ions obey Hund's rule.

1. Subject to Pauli exclusion principle, the total spin \vec{S} is maximized.
2. Subject to Pauli exclusion principle, and to Hund's first rule, the orbital angular momentum \vec{L} is maximized.
3. \vec{L} and \vec{S} are parallel, with $J = |\vec{L} + \vec{S}|$ if the shell is more than half-filled, and they are anti-parallel, with $J = |\vec{L} - \vec{S}|$ for the case of less-than-half-filled shells.

Let us analyse these rules in some more details.

Hund's first rule

Let's say there are n electrons that have to be accommodated into the $2(2l+1)$ levels of the partially filled shell. We have to describe the ground state.

Consider $n \leq 2l+1$.

Then all electrons can have parallel spins with different l_z .

$$\therefore S = \frac{1}{2}n.$$

If $n = 2l+1$, then the maximum value of $S = l + \frac{1}{2}$.

Consider $n > 2l+1 \rightarrow$ spins will start pairing up.

After the $(2l+1)^{\text{th}}$ electron, the subsequent ones will have their spin opposite to the spins of the first $(2l+1)$ as required by the Pauli exclusion principle. S will start getting reduced by half a unit from its maximum for each electron after the $(2l+1)^{\text{th}}$.

Hund's second rule

This concerns with the orbital angular momentum.

Ground state has the largest total orbital angular momentum and it should be consistent with the first rule and the exclusion principle.

Note that the largest value is equal to the largest magnitude L_z can have.

Therefore the first electron will go into a level with $|L_z|$ equal to its maximum value l .

The second must have the same sign spin as the first, and is therefore forbidden by the exclusion principle from having the same value of L_z . The best it can do is to have $|L_z| = l-1$, the total L of $l+(l-1) = 2l-1$.

So, for a shell which is less than half filled,

$$L = l + (l-1) + \dots + [l - (n-1)].$$

For $n = 2l+1$, precisely half-filled, all values of L_z must be assumed, $L = 0$.

If the shell is more than ~~than~~ half-filled, we repeat the process but with spin opposite to the earlier ones, so as to be consistent with the exclusion principle.

Hund's third rule

The first and second rule allowed us to determine the value of \vec{S} and \vec{L} assumed by the ground state or the states of lowest energy.

Now L can have $2L+1$ values and S can have $2S+1$ values. Therefore, the degeneracy is $(2L+1)(2S+1)$.

For further classification we look at the values of the total angular momentum $\vec{J} = \vec{L} + \vec{S}$.

Following the basic rules of angular momentum addition J can take all integral values between $|L-S|$ and $L+S$.

Note that the above degeneracy, there are $(2L+1)(2S+1)$ degenerate states, is lifted by the spin-orbit interaction/coupling, which, within this set of states, can be represented by a term in the Hamiltonian of the form $\mathcal{H}(L \cdot S)$. (SOC)

- SOC will favor maximum J (parallel orbital and spin angular momenta) if \mathcal{H} is negative.
- It favors minimum J (antiparallel orbital and spin angular momenta) if \mathcal{H} is positive.
- It so happens that \mathcal{H} is positive for shells that are less than half filled and negative for shells that are more than half filled.

→ Therefore, in states of lowest energy J has values

$$J = |L-S|, \quad n \leq (2l+1),$$

$$J = |L+S| \quad n \geq (2l+1),$$

Representation

Lowest lying J -multiplet is known as a term.

For ions in a solid we encounter only 22 cases of interest:

- 1 to 9 electrons in a d-shell ($l=2$) or
- 1 to 13 electrons in an f-shell ($l=3$).

For historical reasons the ground-state multiplet is described as follows.

* L is given by a letter, according to the spectroscopic code

$$\begin{array}{ccccccc} L & = & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\ & & S & P & D & F & G & H & I \end{array}$$

* The spin is specified by affixing the number $2S+1$ (the multiplicity) to the letter as a superprefix

and

* J is given as the number J , affixed as a right subscript.

* The lowest-lying J -multiplet is described by the symbol: $(2S+1)X_J$.

Examples

Dy³⁺ → outer shell 4f⁹

f electrons have $\ell=3 \rightarrow (2\ell+1)=7$.

1st rule $S = 7 \times \frac{1}{2} - 2 \times \frac{1}{2} = 5/2 \Rightarrow (2S+1) = 6$.

• $\ell=3$

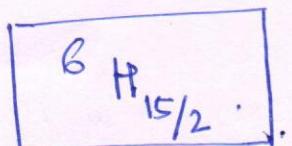
3	2	1	0	-1	-2	-3
↑	↑	↑	↑	↑	↑	↑
↓	↓					

$$L = 3 + 2 + 1 + 0 + (-1) + (-2) + (-3) + 3 + 2$$

$$= 5$$

∴ more than half-filled, $J < 0$.

$$J = |5 + 5/2| = 15/2$$



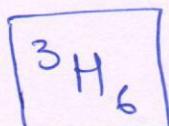
Tm³⁺ (4f¹²)

$$S = \frac{7}{2} - \frac{5}{2} = 1$$

8

$$L = 5$$

$$J = |1 + 5| = 6$$



Susceptibility of insulators containing ions with a partially filled shell : Paramagnetism

1. Consider the following example.

An ion with $n=4$ electrons in the d-shell — $\ell=2$.

We have $2(2\ell+1)=10$, so the shell is just one electron short of being half-filled.

$$S = \frac{1}{2} \times 4 = 2 \quad \begin{matrix} 2 & 1 & 0 & -1 & 2 \end{matrix}$$

$$L = 2 + 1 + 0 + (-1) = 2$$

$$J = |L-S| = |2-2| = 0.$$

$J(L, S)$

$J > 0$ — less than half filled
L & S antiparallel

→ If $J=0$, then the ground state is non-degenerate, as in the case of a filled shell.

→ In this case the linear term in the energy shift expression will vanish.

→ The second term ~~will~~ ^{need} not vanish.

→ Therefore, the shift of energy in the ground-state energy is

$$\Delta E_0 = - \sum_n \frac{|\langle 0 | M_B \vec{B} \cdot (\vec{L} + g \vec{S}) | n \rangle|^2}{E_n - E_0} + \frac{e^2}{8m_e} B^2 \langle 0 | \sum_i (x_i^2 + y_i^2) | 0 \rangle.$$

Assume that the solid contains N/V such ions per unit volume,

What is the magnetization M ?

The susceptibility is

$$\begin{aligned}\chi &= -\frac{N}{V} \frac{\partial^2 E_0}{\partial H^2} \\ &= -\frac{N}{V} \left[\frac{e^2 \mu_0}{4m_e} \langle 0 | \sum_i (x_i^2 + y_i^2) | 0 \rangle \right. \\ &\quad \left. - \sum_n 2\mu_B^2 \mu_0 \frac{|\langle 0 | L_z + g s_z | n \rangle|^2}{E_n - E_0} \right] \\ &= -\frac{N}{V} \frac{e^2 \mu_0}{4m_e} \langle 0 | \sum_i (x_i^2 + y_i^2) | 0 \rangle \\ &\quad + \sum_n 2\mu_B^2 \mu_0 \frac{|\langle 0 | L_z + g s_z | n \rangle|^2}{E_n - E_0}\end{aligned}$$

Note that the first term is just the Larmor diamagnetic susceptibility.

The second term has a sign opposite to that of the first (since the energies of excited states necessarily exceed that of the ground state).

It therefore favors alignment of the moment parallel to the field, a behavior known as paramagnetism, $\chi > 0$.

This paramagnetic correction to the Larmor diamagnetic susceptibility is known as Van Vleck paramagnetism.