PHYS 342/555 Condensed Matter in a Nutshell

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Bohr-van Leeuwen Theorem

 $\langle \mathbf{M} \rangle = \langle \gamma \mathbf{L} \rangle = \mathbf{0}$ according to classical statistics.

 \rightarrow magnetism obeys quantum statistics.

Main contribution for free atoms:

- paramagnetism
- orbital angular momenta of electrons
- Induced orbital moments

spins of electrons

diamagnetism

Electronic structure	Moment
H: 1s	$\mathbf{M} \sim \mathbf{S}$
He: $1s^2$	$\mathbf{M} = 0$
unfilled shell	$\mathbf{M} \neq 0$
All filled shells	$\mathbf{M} = 0$

Magnetization M = magnetic moment per unit volume

Magnetic subsceptibility per unit volume $\chi = \frac{M}{H}$ In vacuum, H = B.

 $\chi_M =$ molar subsceptibility

$$\sigma$$
 = specific subsceptibility

nuclear moments $\sim 10^{-3}$ electronic moments

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Langevin diamagnetism equation

The diamagnetic susceptibility per unit volume is,

$$\chi = -\frac{NZe^2}{6mc^2} \langle r^2 \rangle;$$

where N is the number of atoms per unit volume, $\langle r^2 \rangle$ is the mean square distance of the electrons from the nucleus, Z is number of electrons in each nuclei.



Lenz's Law

When an emf is generated by a change in magnetic flux according to <u>Faraday's Law</u>, the polarity of the induced emf is such that it produces a current whose magnetic field opposes the change which produces it. The induced magnetic field inside any loop of wire always acts to keep the magnetic flux in the loop constant. In the examples below, if the B field is increasing, the induced field acts in opposition to it. If it is decreasing, the induced field acts in the direction of the applied field to try to keep it constant.



Diamagnetism

The orbital motion of electrons creates tiny atomic current loops, which produce magnetic fields. When an external magnetic field is applied to a material, these current loops will tend to align in such a way as to oppose the applied field. This may be viewed as an atomic version of Lenz's law: induced magnetic fields tend to oppose the change which created them. Materials in which this effect is the only magnetic response are called diamagnetic. All materials are inherently diamagnetic, but if the atoms have some net magnetic moment as in paramagnetic materials, or if there is long-range ordering of atomic magnetic moments as in ferromagnetic materials, these stronger effects are always dominant. Diamagnetism is the residual magnetic behavior when materials are neither paramagnetic nor ferromagnetic. Any conductor will show a strong diamagnetic effect in the presence of changing magnetic fields because circulating currents will be generated in the conductor to oppose the magnetic field changes. A superconductor will be a perfect diamagnet since there is no resistance to the forming of the current loops.

In a magnetic field *H*, the precession of the *Z* electrons within the atom is equivalent to a current equal to $-Z(e/c)(\omega_L/2\pi)$ in electromagnetic units. Here e/c is the magnitude of the electronic charge in emu, and ω_L is the angular Larmor frequency, where *m* is the electronic mass.

$$\omega_L = \frac{-eH}{2mc}$$

The magnetic moment μ arising from this induced current is equal to the product of the current and the area of the current loop, as in Eq. (3), where

$$\mu = \frac{-Ze}{c} \frac{\omega_L}{2\pi} \overline{\rho^2}$$

 ρ^2 is the statistical average, over a large number of atoms, of the square of the perpendicular distance of an electron from the field axis. This average is equivalent to $x^2 + y^2$ if *H* is along *z*. For a random assembly of atoms, since $x^2 = y^2 = z^2$, one may write Eq. (4), where r^2 is the

$$\overline{\rho^2} = 2/3\left(\overline{x^2} + \overline{y^2} + \overline{z^2}\right) = 2/3 \ \overline{r^2}$$

mean-square distance of the electron from the nucleus. Thus, the diamagnetic susceptibility of N atoms is given by Eq. (5). This is P. Langevin's result, as

$$\chi_d = \frac{N\mu}{H} = -\frac{Ze^2N}{6mc^2} \ \overline{r^2}$$

Larmor Precession

$$\mathbf{A} = \frac{1}{c} \int d^3 x' \frac{\mathbf{J}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}$$

Magnetic (dipole) moment:
$$\mathbf{m} = \frac{1}{2c} \int d^3 x' \, \mathbf{x}' \times \mathbf{J}(\mathbf{x}') \qquad \mathbf{A} = \frac{\mathbf{m} \times \mathbf{x}}{r^3}$$

For a current loop: $\mathbf{J} d^3 x = I d\mathbf{I}$ $\mathbf{m} = \frac{1}{2c} \oiint \mathbf{x} \times I d\mathbf{I} = \frac{I}{c} Area$

For a charge moving in a loop: $\mathbf{J}(\mathbf{x}) = q \mathbf{v} \delta(\mathbf{x} - \mathbf{x}_q)$ (charge at \mathbf{x}_q)

$$\mathbf{m} = \frac{1}{2c} \int d^3 x' \, \mathbf{x}' \times q \, \mathbf{v} \, \delta \left(\mathbf{x}' - \mathbf{x}_q \right) = \frac{q}{2c} \mathbf{x}_q \times \mathbf{v} = \frac{q}{2mc} \mathbf{L} = \gamma \, \mathbf{L}$$

Caution: we'll set \mathbf{L} to $\eta \mathbf{L}$ in the quantum version

Classical gyromagnetic ratio $\gamma = \frac{q}{2 m c}$ $\mu_B = \frac{e \hbar}{2 m c}$

Torque on **m** in magnetic field: $\Gamma = \frac{d \mathbf{L}}{d t} = \mathbf{m} \times \mathbf{B} = \gamma \mathbf{L} \times \mathbf{B}$

 $\rightarrow \mathbf{L} \text{ precesses about } \mathbf{B} \text{ with the Larmor frequency} \qquad \omega_L = \gamma B = \frac{q B}{2 m c}$ Lorentz force: $m \frac{d \mathbf{v}}{dt} = \frac{q}{c} \mathbf{v} \times \mathbf{B} \qquad \rightarrow \text{ cyclotron frequency} \qquad \omega_c = \frac{q B}{m c} = 2\omega_L$

Langevin Diamagnetism Equation

Diamagnetism ~ Lenz's law: induced current opposes flux changes. $\gamma < 0$ Larmor theorem: weak **B** on e in atom \rightarrow precession with freq $\omega_L = \frac{eB}{2mc} = \frac{1}{2}\omega_C$ $I = \left(-Ze\right)\frac{\omega_L}{2\pi} = -\frac{Ze^2B}{4\pi mc} \qquad \qquad \mu = \frac{1}{c}I\pi\left\langle \rho^2\right\rangle = -\frac{Ze^2B}{4mc^2}\left\langle \rho^2\right\rangle$ Larmor precession of Z e's: $\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle \qquad \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \longrightarrow \langle r^2 \rangle = \frac{3}{2} \langle \rho^2 \rangle$ For *N* atoms per unit volume: $\chi = \frac{N \mu}{R} = -\frac{N Z e^2}{6 m c^2} \langle r^2 \rangle$ Langevin diamagnetism same as QM result Ne Kr Xe He Ar Good for inert gases and dielectric solids χ_M in CGS in 10^{-6} cm³/mole: -1.9-7.2-19.4-28.0-43.0

experiment

Failure: conduction electrons (Landau diamagnetism & dHvA effect)

1. Diamagnetic susceptibility of atomic hydrogen. The wave function of the hydrogen atom in its ground state (1s) is $\psi = (\pi a_0^3)^{-1/2} \exp(-r/a_0)$, where $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}$ cm. The charge density is $\rho(x, y, z) = -e|\psi|^2$, according to the statistical interpretation of the wave function. Show that for this state $\langle r^2 \rangle = 3a_0^2$, and calculate the molar diamagnetic susceptibility of atomic hydrogen $(-2.36 \times 10^{-6} \text{ cm}^3/\text{mole})$.

Paramagnetism

Electronic paramagnetism:

1. Atoms, molecules, and lattice defects possessing an odd number of electrons.

2. Free atoms and ions with a partly filled inner shell: transition elements; ions isoelectronic with transition elements; rare earth and actinide elements.

3. A few compounds with an even number of electrons, including molecular oxygen and organic biradicals.

4. Metals.

Quantum Theory of Paramagnetism









The energy levels of the system in a magnetic field are $U = -\vec{\mu} \cdot \vec{B} = m_J g \mu_B B$, where m_J is the azimuthal quantum number and has the values

J, J-1, ..., -J. For a single spin with no orbital moment we have $m_J = \pm 1/2$ and g = 2, $U = \pm \mu_B B$.



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If a system has only two levels the equilibrium populations are, with

$$\tau = k_B T$$

$$\frac{N_1}{N} = \frac{\exp(\mu B / \tau)}{\exp(\mu B / \tau) + \exp(-\mu B / \tau)};$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B / \tau)}{\exp(\mu B / \tau) + \exp(-\mu B / \tau)}$$
Here N_1, N_2 are the populations of the lower and upper levels.
 $N = N_1 + N_2$ is the total number of atoms.



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The projection of the total magnetization for N atoms per unit volume is, with $x \equiv \mu B / k_B T$,

$$M = (N_1 - N_2)\mu = N\mu \frac{e^x - e^{-x}}{e^x + e^{-x}} = N\mu \tanh x.$$

Here $x \ll 1$, $\tanh x \cong x$, and we have $M \cong N \mu (\mu B / k_B T)$.

In a magnetic field an atom with angular momentum quantum number J has 2J + 1 equally spaced energy levels. The magnetization (Fig. 4) is given by

$$M = NgJ\mu_B B_J(x) , \qquad (x = gJ\mu_B B/k_B T) , \qquad (19)$$

where the **Brillouin function** B_I is defined by

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh}\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \operatorname{ctnh}\left(\frac{x}{2J}\right) \,. \tag{20}$$

Equation (17) is a special case of (20) for $J = \frac{1}{2}$. For $x = \mu B/k_BT \ll 1$, we have

$$\operatorname{ctnh} x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \cdots, \qquad (21)$$

and the susceptibility is

$$\frac{M}{B} \approx \frac{NJ(J+1)g^2\mu_B^2}{3k_BT} = \frac{Np^2\mu_B^2}{3k_BT} = \frac{C}{T}$$
(22)

Here p is the effective number of Bohr magnetons, defined as

$$p \equiv g[J(J+1)]^{1/2} . \tag{23}$$

Rare Earth Ions

and a second	erwalen of the second second second second second and the second s		(Near room temperature)									
íon	Configuration	Basic level	p(calc) = $g[J(J + 1)]^{1/2}$	p(exp), approximate								
Ce ³⁺	$4f^{1}5s^{2}p^{6}$	${}^{2}F_{5/2}$	2.54	2.4								
Pr ³⁺	$4f^25s^2p^6$	${}^{3}H_{4}$	3.58	3.5								
Nd^{3+}	$4f^{3}5s^{2}p^{6}$	⁴ I _{9/2}	3.62	3.5								
Pm ³⁺	$4f^{4}5s^{2}p^{6}$	${}^{5}I_{4}$	2.68									
3m ³⁺	$4f^{5}5s^{2}p^{6}$	⁶ H _{5/2}	0.84	1.5								
Eu ³⁺	$4f^{6}5s^{2}p^{6}$	F_0	0	3.4								
Gd^{3+}	$4f^{7}5s^{2}p^{6}$	⁸ S _{7/2}	7.94	8.0								
Γb^{3+}	$4f^85s^2p^6$	7F_6	9.72	9.5								
Dy ³⁺	$4f^95s^2p^6$	${}^{6}H_{15/2}$	10.63	10.6								
Ho ³⁺	$4f^{10}5s^2p^6$	⁵ I ₈	10.60	10.4								
≤r ³⁺	$4f^{11}5s^2p^6$	⁴ I _{15/2}	9.59	9.5								
Րm ³⁺	$4f^{12}5s^2p^6$	${}^{3}H_{a}$	7.57	7.3								
(b^{3+})	$4f^{13}5s^2p^6$	${}^{2}F_{7/2}$	4.54	4.5								
	on Ce^{3+} $2r^{3+}$ Vd^{3+} $2m^{3+}$ $2m^{3+}$ Cu^{3+} Cd^{3+} Cd^{3+} Cy^{3+} Er^{3+} Er^{3+} Cm^{2	on Configuration Ce^{3+} $4f^{1}5s^{2}p^{6}$ $2r^{3+}$ $4f^{2}5s^{2}p^{6}$ Nd^{3+} $4f^{3}5s^{2}p^{6}$ $2m^{3+}$ $4f^{4}5s^{2}p^{6}$ $2m^{3+}$ $4f^{4}5s^{2}p^{6}$ $2m^{3+}$ $4f^{6}5s^{2}p^{6}$ $2m^{3+}$ $4f^{6}5s^{2}p^{6}$ Cd^{3+} $4f^{7}5s^{2}p^{6}$ Cb^{3+} $4f^{8}5s^{2}p^{6}$ Cy^{3+} $4f^{9}5s^{2}p^{6}$ Er^{3+} $4f^{10}5s^{2}p^{6}$ Er^{3+} $4f^{11}5s^{2}p^{6}$ Em^{3+} $4f^{12}5s^{2}p^{6}$ Cm^{3+} $4f^{13}5s^{2}p^{6}$	on Configuration Basic level $\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$								

Table 1 Effective magneton numbers p for trivalent lanthanide group ions

4f radius ~ 0.3A

Perturbation from higher states significant because splitting between L-S multiplets $\sim k_B T$

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Chapter 11-19

Hund's rules

Suppose we have 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. Since for given l there are 2l + 1 values l_ can have (l, l-1, l-2, ..., -l) and two possible spin directions for each l_{2} , such a shell will contain 2(2l+1) one-electron levels. Let n be the number of electrons in the shell, with 0 < n < 2(2l+1). If the electrons did not interact with one another, the ionic ground state would be degenerate, reflecting the large number of ways of putting *n* electrons into more than *n* levels. However, this degeneracy is considerably lifted by electron-electron Coulomb interactions as well as by the electron spin-orbit interaction.

1. Russel-Saunder coupling To a good approximation the Hamiltonian of the atom or ion can be taken to commute with the total electronic spin and orbital angular momenta, \vec{S} and \vec{L} , as well as with the total electronic angular momentum $\vec{J} = \vec{L} + \vec{S}$.

2. Hund's first rule Out of the many states one can form by placing n electrons into the 2(2l+1) levels of partially filled shells, those that lie lowest in energy have the largest total spin S that is consistent with the exclusion principle.

3. Hund's second rule The total orbital angular momentum L of the lowest-lying states has the largest value that is consistent with Hund's first rule, and with the exclusion principle.

4. Hund's third rule The first two rules determine the values of L and S assumed by the states of lowest energy. This still leaves (2L+1)(2S+1)possible states. These can be further classified according to their total angular momentum J, which, according to the basic rules of angular momentum composition, can take on all integral values between |L-S| and L+S. The degeneracy of the set of (2L+1)(2S+1) states is lifted by the spin-orbit coupling, which, within this set of states, can be represented by a term in the Hamiltonian of the simple form $\lambda(\vec{L}\cdot\vec{S})$. Spin-orbit coupling will favor maximum J if λ is negative, and minimum J if λ is positive. λ is positive for shells that are less than half filled and negative for shells that are more than half filled. $J = |L - S|, n \le (2l + 1),$ $J = L + S, n \ge (2l + 1).$

Hund's Rules

For filled shells, spin orbit couplings do not change order of levels.

Hund's rule (L-S coupling scheme):

Outer shell electrons of an atom in its ground state should assume

- 1. Maximum value of S allowed by exclusion principle.
- 2. Maximum value of L compatible with (1).
- 3. J = |L-S| for less than half-filled shells.

J = L + S for more than half-filled shells.

Causes:

- 1. Parallel spins have lower Coulomb energy.
- 2. e's meet less frequently if orbiting in same direction (parallel Ls).
- 3. Spin orbit coupling lowers energy for $L \cdot S < 0$.

Mn²⁺:
$$3d^{5}$$
 (1) $\rightarrow S = 5/2$ exclusion principle $\rightarrow L = 2+1+0-1-2 = 0$

Ce³⁺: $4f^1$ $L = 3, S = \frac{1}{2}$ (3) $\rightarrow J = |3 - \frac{1}{2}| = \frac{5}{2}$ ${}^2F_{5/2}$

Pr³⁺: 4f² (1) → S = 1 (2) → L = 3+2 = 5 (3) → J = |5-1| = 4 ³H₄

a-	shell $(l = 2$)								
n	$l_z = 2$,	1,	0,	-	1,	-2	S	$L = \Sigma l_z $	J	SYMBOL
1	Ļ						1/2	2	3/2	² D _{3/2}
2	1	1					1	3	$\begin{vmatrix} 2 \\ 1 \end{vmatrix} = \begin{vmatrix} I \\ -S \end{vmatrix}$	³ F ₂
3	1	Ļ	Ļ				3/2	3	3/2 - L - 3	⁴ F _{3/2}
4	1	1	Ļ		1		2	2	0)	⁵ D ₀
5	1 I	1	Ļ		1	Ļ	5/2	0	5/2	6S5/2
6	11	1	1		t	t	2	2	4	⁵ D ₄
7	tt.	11	1		1	t	3/2	3	$9/2 _{I = I + S}$	4F _{9/2}
8	tt (11	ţţ,		t	Ť	1	3	$ 4 \begin{cases} J = L + 3 \\ J = -L + 3 \end{cases}$	3F4
9	tt.	1t	ļ†		1t	t	1/2	2	5/2	² D _{5/2}
0	tt.	1t	ţ1		1t	ţţ.	0	0	0	¹ S ₀
f.	shell $(l = 3$)								
f. n	shell $(l = 3$ $l_z = 3, 2$) 	0, -	- 1, -	- 2,	-3	S	$L = \Sigma l_z $	J	
f - n 1	shell $(l = 3$ $l_z = 3, 2$ \downarrow) 	0, -	- 1, -	- 2,	- 3	S	$L = \Sigma l_z $	J 5/2	² F _{5/2}
f - n 1 2	shell $(l = 3$ $l_z = 3, 2$ \downarrow \downarrow) , 1,	0, -	- 1, -	- 2,	_ 3	S 1/2 1	$L = \Sigma l_z $ 3 5	<i>J</i>	${}^{2}F_{5/2}$ ${}^{3}H_{4}$
$f \cdot \frac{n}{1}$	shell $(l = 3$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow) 	0, -	- 1, -	- 2,	- 3	S 1/2 1 3/2	$L = \left \Sigma l_z \right $ $\begin{array}{c} 3\\ 5\\ 6 \end{array}$	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \end{array} $ $I = L - S $	${}^{2}F_{5/2}$ ${}^{3}H_{4}$ ${}^{4}I_{9/2}$
f. n 1 2 3 4	shell $(l = 3$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow) , 1, ↓	0,	- 1, -	- 2,	3	S 1/2 1 3/2 2	$L = \left \Sigma l_z \right $ 3 5 6 6	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \end{array} $ $ J = L - S $	${}^{2}F_{5/2}$ ${}^{3}H_{4}$ ${}^{4}I_{9/2}$ ${}^{5}I_{4}$
f. n 1 2 3 4 5	shell $(l = 3$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow) , 1, ↓ ↓	0, - ↓ ↓	<u>- 1, -</u>	- 2,	-3	S 1/2 1 3/2 2 5/2	$L = \left \Sigma l_z \right $ $\begin{array}{c} 3 \\ 5 \\ 6 \\ 6 \\ 5 \end{array}$	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \end{array} \bigg J = L - S $	$\begin{array}{r}{}^{2}F_{5/2}\\{}^{3}H_{4}\\{}^{4}I_{9/2}\\{}^{5}I_{4}\\{}^{6}H_{5/2}\end{array}$
f · n 1 2 3 4 5 6	shell $(l = 3$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow) , 1, ↓ ↓	0,	<u>-1, -</u> ↓	-2, 1	_ 3	S 1/2 1 3/2 2 5/2 3	$L = \Sigma l_z $ 3 5 6 6 5 3	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \end{array} \right\} J = L - S $	$\begin{array}{c} {}^{2}F_{5/2} \\ {}^{3}H_{4} \\ {}^{4}I_{9/2} \\ {}^{5}I_{4} \\ {}^{6}H_{5/2} \\ {}^{7}F_{0} \end{array}$
f · n 1 2 3 4 5 6 7	shell $(l = 3)$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow) 	0,	- 1, - ↓ ↓	-2, 1	3	S 1/2 1 3/2 2 5/2 3 7/2	$L = \left \Sigma l_z \right $ $\begin{array}{c} 3 \\ 5 \\ 6 \\ 6 \\ 5 \\ 3 \\ 0 \end{array}$	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \\ 7/2 \end{array} $ $ J = L - S $	$\begin{array}{c} {}^{2}F_{5/2} \\ {}^{3}H_{4} \\ {}^{4}I_{9/2} \\ {}^{5}I_{4} \\ {}^{6}H_{5/2} \\ {}^{7}F_{0} \\ {}^{8}S_{7/2} \end{array}$
f · n 12345678	shell $(l = 3)$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow		0,	1, ↓ ↓ ↓	-2, ↓ ↓	3	S 1/2 1 3/2 2 5/2 3 7/2 3	$L = \Sigma l_z $ 3 5 6 6 5 3 0 3	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \\ 7/2 \\ 6 \\ \end{array} $	$\begin{array}{c} {}^{2}F_{5/2}\\ {}^{3}H_{4}\\ {}^{4}I_{9/2}\\ {}^{5}I_{4}\\ {}^{6}H_{5/2}\\ {}^{7}F_{0}\\ {}^{8}S_{7/2}\\ {}^{7}F_{6}\end{array}$
f - n 1 2 3 4 5 6 7 8 9	shell $(l = 3)$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow) - - - - - - - - - - - - - - - - - - -	0,	-1,- ↓ ↓ ↑ ↑	-2, 1 1	3	S 1/2 1 3/2 2 5/2 3 7/2 3 5/2	$L = \Sigma l_z $ 3 5 6 6 5 3 0 3 5	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \\ 7/2 \\ 6 \\ 15/2 \end{array} $	$\begin{array}{r}{}^{2}F_{5/2}\\{}^{3}H_{4}\\{}^{4}I_{9/2}\\{}^{5}I_{4}\\{}^{6}H_{5/2}\\{}^{7}F_{0}\\{}^{8}S_{7/2}\\{}^{7}F_{6}\\{}^{6}H_{15/2}\end{array}$
f n 1234567890	shell $(l = 3)$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow) , 1, ↓ ↓ ↓ ↓ ↑ ↑	0,	-1,- ↓ ↓ ↑ ↑	, 	3	S 1/2 1 3/2 2 5/2 3 7/2 3 5/2 2	$L = \Sigma l_{z} $ 3 5 6 6 5 3 0 3 5 6	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \\ 7/2 \\ 6 \\ 15/2 \\ 8 \\ J = L + S \end{array} $	$\begin{array}{c} {}^{2}F_{5/2} \\ {}^{3}H_{4} \\ {}^{4}I_{9/2} \\ {}^{5}I_{4} \\ {}^{6}H_{5/2} \\ {}^{7}F_{0} \\ {}^{8}S_{7/2} \\ {}^{7}F_{6} \\ {}^{6}H_{15/2} \\ {}^{5}I_{8} \end{array}$
f n 12345678901	shell $(l = 3)$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow) , 1, ↓ ↓ ↓ ↓ ↓ ↑ ↑ ↑	0,	-1,- ↓ ↓ ↑ ↑ ↑	-2, ↓ † † †	3	S 1/2 1 3/2 2 5/2 3 7/2 3 5/2 2 3/2	$L = \Sigma l_{z} $ 3 5 6 6 5 3 0 3 5 6 6 6	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \\ 7/2 \\ 6 \\ 15/2 \\ 8 \\ 15/2 \\ 8 \\ 15/2 \\ J = L + S \end{array} $	$\begin{array}{c} {}^{2}F_{5/2} \\ {}^{3}H_{4} \\ {}^{4}I_{9/2} \\ {}^{5}I_{4} \\ {}^{6}H_{5/2} \\ {}^{7}F_{0} \\ {}^{8}S_{7/2} \\ {}^{7}F_{6} \\ {}^{6}H_{15/2} \\ {}^{5}I_{8} \\ {}^{4}I_{15/2} \end{array}$
f - n 1 2 3 4 5 6 7 8 9 0 1 2	shell $(l = 3)$ $l_{z} = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow		0,	-1,- ↓ ↓ ↑ ↑ ↓	-2, ↓ † † † †	3	S 1/2 1 3/2 2 5/2 3 7/2 3 5/2 2 3/2 1	$L = \Sigma l_z $ 3 5 6 6 5 3 0 3 5 6 6 5 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 5 6 6 5 3 0 3 5 6 6 5 5 6 6 5 5 6 6	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \\ 7/2 \\ 6 \\ 15/2 \\ 8 \\ 15/2 \\ 6 \end{array} $ $J = L + S$	$\begin{array}{c} {}^{2}F_{5/2}\\ {}^{3}H_{4}\\ {}^{4}I_{9/2}\\ {}^{5}I_{4}\\ {}^{6}H_{5/2}\\ {}^{7}F_{0}\\ {}^{8}S_{7/2}\\ {}^{7}F_{6}\\ {}^{6}H_{15/2}\\ {}^{5}I_{8}\\ {}^{4}I_{15/2}\\ {}^{3}H_{6}\\ \end{array}$
f - n 1 2 3 4 5 6 7 8 9 10 11 2 13	shell $(l = 3)$ $l_z = 3, 2$ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow		0, ↓ ↓ ↑ ↑ ↓ ↓ ↓	-1,- ↓ ↓ ↑ ↑ ↓ ↓	-2, ↓ ↓ ↑ ↑ ↑		S 1/2 1 3/2 2 5/2 3 7/2 3 5/2 2 3/2 1 1/2	$L = \Sigma l_z $ 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 0 3 5 6 6 5 3 8 8 8 8 8 8 8 8 8	$ \begin{array}{c} J \\ 5/2 \\ 4 \\ 9/2 \\ 4 \\ 5/2 \\ 0 \\ 7/2 \\ 6 \\ 15/2 \\ 8 \\ 15/2 \\ 6 \\ 7/2 \end{array} \right\} J = L + S$	$\begin{array}{c} {}^{2}F_{5/2}\\ {}^{3}H_{4}\\ {}^{4}I_{9/2}\\ {}^{5}I_{4}\\ {}^{6}H_{5/2}\\ {}^{7}F_{0}\\ {}^{8}S_{7/2}\\ {}^{7}F_{6}\\ {}^{6}H_{15/2}\\ {}^{5}I_{8}\\ {}^{4}I_{15/2}\\ {}^{3}H_{6}\\ {}^{2}F_{7/2}\end{array}$

2 Table 31.2

The orbital angular momentum

L is given by a letter,

L = 0123456

$$X = SPDFGHI$$

2.3 The principal terms in the electronic Hamiltonian

- 1. The electron kinetic energy
- 2. The electron potential energy \longrightarrow free ion potential energy V_0 (the field due to the nucleus and
 - other inner electrons)
 - crystalline potential $V_{\rm cryst}$ (the field due to charges outside the atom)
- 3. The spin-orbit coupling energy

An electron moves at a velocity $v = \frac{p}{m}$, in an electrostatic field *E* created by the proton. In the electron frame, a magnetic field $B' = -\frac{1}{C^2}v \times E$ appears. Since an electron possesses an intrinsic magnetic moment $\mu = -\frac{e}{2m}\hbar\hat{S}$, it experiences a coupling energy of the spin to the orbital **motion:** $\hat{H}_{SO} = -\mu \cdot B' = \frac{e\hbar}{2m^2c^2}\hat{S} \cdot [E \times \hat{p}]$

Often the electric field in an atom points radially outward and is a function of *r* only, so that $E(r) = -\frac{1}{e} \frac{dV(r)}{dr} = \frac{e}{r^2} (V(r)) = -\frac{e^2}{r}$ directs a radial direction.

$$\square \searrow E \times \hat{p} = \frac{1}{r} E(r) \hat{r} \times \hat{p} = \frac{\hbar}{r} E(r) \hat{L}$$

position vector momentum vector angular momentum

$$\Box > H_{so} = \lambda \hat{L} \cdot \hat{S}$$

$$\lambda = \frac{1}{2} Z \left(\frac{\hbar e}{mc}\right)^2 \frac{1}{\langle r^3 \rangle}$$

atomic number (average) nucleus-electron separation

 $\implies \hat{J} = \hat{S} + \hat{L}$ (total angular momentum)

Lande g factor

 \hat{L} : total orbital angular momentum of the electrons of an atom $\left(=\sum_{i} \hat{L}i\right)$ \hat{S} : total spin angular momentum $\left(=\sum_{i} \hat{S}i\right)$ $\hat{J} = \hat{L} + \hat{S}$

The eigenstates of the atomic Hamiltonian:

$$\hat{\mathcal{H}}|E_0, L, S, J, M\rangle = E_0|E_0, L, S, J, M\rangle$$
$$\hat{L}^2 \to \hbar^2 L(L+1), \hat{S}^2 \to \hbar^2 S(S+1), \hat{J}^2 \to \hbar^2 J(J+1), \hat{J}_z \to \hbar M$$

Recursion relation:

$$\hat{J}_{\pm}|E_0, L, S, J, M\rangle = \hbar \sqrt{J(J+1) - M(M \pm 1)}|E_0, L, S, J, M \pm 1\rangle$$

$$M = \underbrace{J, J-1, \dots - J}_{2J+1}$$
degenerate multiplets





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- 4. The coupling of the electron spin and orbital magnetic moments to an external magnetic field
- 5. The magnetic coupling of the nuclear spin to the electronic spin and orbital moments.

6. The coupling of the nuclear electrical quadruple moment to the electronic charge.

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9.2.3 Total Angular Momentum and Total Magnetic Moment

The total angular momentum of an atom is given by

$$J = L + S.$$
 (9.25)

The total magnetic moment is given by

$$\mathbf{m} = -\mu_{\mathbf{B}} \left(\mathbf{L} + 2\mathbf{S} \right). \tag{9.26}$$

In quantum mechanics the components of \mathbf{J} , \mathbf{L} , and \mathbf{S} are operators that satisfy commutation relations. As we learned in quantum mechanics, it is possible to diagonalize J^2 and J_z simultaneously.

$$J^{2}|j, j_{z}\rangle = j(j+1)|j, j_{z}\rangle; \ j = 0, \frac{1}{2}, \frac{3}{2}, \dots$$
 (9.27)

$$J_z |j, j_z\rangle = j_z |j, j_z\rangle; \quad -j \le j_z \le j$$

$$(9.28)$$

Note that $j_z = 0, \pm 1, \ldots, \pm j$ or $j_z = \pm \frac{1}{2}, \pm \frac{3}{2}, \ldots, \pm j$. We can write that

$$m = -\hat{g}\mu_B J.$$
 (9.29)

This defines the operator \hat{g} because we have $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and

$$\hat{g}J = L + 2S.$$
 (9.30)

We can use these definitions to show that

$$\mathbf{J} \cdot \mathbf{J} = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S}$$
(9.31)

and

$$\hat{\mathbf{j}}\mathbf{J}\cdot\mathbf{J} = (\mathbf{L}+\mathbf{S})\cdot(\mathbf{L}+2\mathbf{S}) = \mathbf{L}^2 + 2\mathbf{S}^2 + 3\mathbf{L}\cdot\mathbf{S}.$$
 (9.32)

We can eliminate $\mathbf{L} \cdot \mathbf{S}$ and obtain

$$g_{\rm L} = \frac{3}{2} + \frac{1}{2} \frac{s(s+1) - l(l+1)}{j(j+1)}$$
(9.33)

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This eigenvalue of \hat{g} is called the Landé g-factor.

EXAMPLE

Consider an ion of Fe²⁺; it has 6 electrons in the 3*d* level. We can put 5 of them in spin up states (since *d* means l = 2 and m_l can be -2, -1, 0, 1, 2) and to maximize *S*, hence,

```
\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow \downarrow \text{ gives } S = 2.
```

The maximum value of L-value is given by

$$L = -2 - 1 + 0 + 1 + 2 + 2 = 2.$$

The *J*-value (since it is over half-filled) is

J = L + S = 4.

Therefore we have

$$g = \frac{3}{2} + \frac{1}{2} \frac{2(3) - 2(3)}{4(5)} = \frac{3}{2}.$$

One can work out some examples listed in Table 9.1. The ground state notation is ${}^{2S+1}L_J$, where $L = 0, 1, 2, 3, 4, \ldots$ are denoted by the letters S, P, D, F, G, \ldots , respectively.

Curie's law in solids

Insulating crystals containing rare earth ions are found to obey Curie's law. One frequently writes the law in:

$$\chi = \frac{1}{3} \frac{N}{V} \frac{\mu_B^2 p^2}{k_B T},$$

where *p* is the "effective Bohr magneton number",

$$p = g(JLS)[J(J+1)]^{1/2}.$$

In all cases the magnetism of rare earth ions in an insulating solid is well described by treating them as isolated ions. For transition metal ions from the iron group, one finds that although Curie's law is obeyed, the value of p is still given by above equation only if one assumes that although S is given by Hund's rules, L is zero and J=S. This is known as the quenching of the orbital angular momentum.

Table 31.3 CALCULATED AND MEASURED EFFECTIVE MAGNETON NUMBERS p FOR RARE EARTH IONS^a

ELEMENT (TRIPLY IONIZED)	BASIC ELECTRON CONFIGURATION	GROUND-STATE TERM	CALCULATED ^b p	MEASURED ^c p
La	$4f^0$	¹ S	0.00	diamagnetic
Ce	$4f^1$	${}^{2}F_{5/2}$	2.54	2.4
Pr	$4f^2$	${}^{3}H_{4}$	3.58	3.5
Nd	$4f^{3}$	4I9/2	3.62	3.5
Pm	$4f^4$	⁵ I ₄	2.68	
Sm	$4f^{5}$	⁶ H _{5/2}	0.84	1.5
Eu	$4f^6$	$^{7}F_{0}$	0.00	3.4
Gd	$4f^7$	⁸ S _{7/2}	7.94	8.0
Tb	$4f^8$	7F6	9.72	9.5
Dy	$4f^9$	6H15/2	10.63	10.6
Ho	$4f^{10}$	⁵ <i>I</i> ₈	10.60	10.4
Er	$4f^{11}$	4115/2	9.59	9.5
Tm	$4f^{12}$	${}^{3}H_{6}$	7.57	7.3
Yb	$4f^{13}$	${}^{2}F_{7/2}$	4.54	4.5
Lu	$4f^{14}$	¹ S	0.00	diamagnetic

Table 31.4 CALCULATED AND MEASURED EFFECTIVE MAGNETON NUMBERS p FOR THE IRON (3d) GROUP IONS^a

ELEMENT (AND IONIZATION)	BASIC ELECTRON CONFIGURATION	GROUND- STATE TERM	(J = S)	$(J = L \pm S)$	MEASURED ^c p
$ \begin{array}{c} \text{Ti}^{3+} \checkmark \\ \text{V}^{4+} \\ \text{V}^{3+} \checkmark \\ \text{V}^{2+} \\ \text{Cr}^{3+} \checkmark \end{array} $	$3d^{1}$ $3d^{1}$ $3d^{2}$ $3d^{3}$ $3d^{3}$	${}^{2}D_{3/2}$ ${}^{2}D_{3/2}$ ${}^{3}F_{2}$ ${}^{4}F_{3/2}$ ${}^{4}F_{3/2}$	1.73 1.73 2.83 3.87 3.87	1.55 1.55 1.63 0.77 0.77	1.8 2.8 3.8 3.7
Mn^{4+} Cr^{2+} Mn^{3+} Mn^{2+} Fe^{3+}	$3d^{3}$ $3d^{4}$ $3d^{4}$ $3d^{5}$ $3d^{5}$ $3d^{6}$	${}^{4}F_{3/2}$ ${}^{5}D_{0}$ ${}^{5}D_{0}$ ${}^{6}S_{5/2}$ ${}^{6}S_{5/2}$ ${}^{5}D_{4}$	3.87 4.90 4.90 5.92 5.92 4.90	0.77 0 0 5.92 5.92 6.70	4.0 4.8 5.0 5.9 5.9 5.9 5.4
Fe2+ Co2+ Ni2+ Cu2+	3d ⁷ 3d ⁸ 3d ⁹	${}^{4}F_{9/2}$ ${}^{3}F_{4}$ ${}^{2}D_{5/2}$	3.87 2.83 1.73	6.54 5.59 3.55	4.8 3.2 1.9

* 14. C tha

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Crystal field splitting

Crystal field splitting is unimportant for rare earth ions, because their partially filled 4 f shells lie deep inside the ion. In contrast to this, the partially filled d-shells of transition metal ions are the outermost electronic shells, and are therefore far more strongly influenced by their crystalline environment. The interaction of the paramagnetic ions with the crystal field has two major effects: the coupling of L and S vectors is largely broken up, so that the states are no longer specified by their J values; the 2L+1 sublevels belonging to a given L which are degenerate in the free ion may now be split by the crystal field.



2.4 Example of spin-orbit coupling and crystalline fields

Crystal Field Splitting

Rare earth group: 4f shell lies within 5s & 5p shells

 \rightarrow behaves like in free atom.

Iron group: 3d shell is outer shell

- \rightarrow subject to crystal field (E from neighbors).
- → L-S coupling broken-up; J not good quantum number. Degenerate 2L+1 levels splitted ; their contribution to moment diminished.



Consider a two-level system with an energy splitting $k_B \Delta$ between upper and lower states; the splitting may arise from a magnetic field or in other ways. Show that the heat capacity per system is:

$$C = \left(\frac{\partial U}{\partial T}\right)_{\Delta} = k_B \frac{\left(\Delta/T\right)^2 e^{\Delta/T}}{\left(1 + e^{\Delta/T}\right)^2}.$$

Peaks of this type in the heat capacity are often known as Schottky anomalies.