FoP3B Part I Lecture 6: Multi-electron atoms and Hund's rules

The magnetic moment $\boldsymbol{\mu}$ and angular momentum are related by $\boldsymbol{\mu}$ = -γ$\mathbf{l}$. At the same time the Bohr-van Leeuwen theorem predicts zero magnetisation for electrons obeying classical statistical physics. This hints that angular momentum in quantum mechanics behaves rather differently to the classical world. In this lecture we will explore electron angular momentum in multi-electron atoms using quantum mechanics, and show how it leads to magnetism in solids.

Quantum Mechanical Angular Momentum

From $\mathbf{l}$ = $\mathbf{r}$ x $\mathbf{p}$ the **orbital angular momentum** operator is defined as $\hat{l} = \mathbf{r} \times \left(-i\hbar\vec{\nabla}\right) = -i\hbar\mathbf{r} \times \vec{\nabla}$. It can be shown that:

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$$
$$[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x$$
$$[\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y$$

The square brackets represent the commutator[1]. In quantum mechanics any two operators with zero commutator represent *compatible measurements*, i.e. the two operators share a common electron wavefunction, so that the properties represented by the two operators can both be measured simultaneously with no error. From the above it is clear that no two components of the orbital angular momentum can be known simultaneously. However, $[\hat{l}^2, \hat{l}_x] = [\hat{l}^2, \hat{l}_y] = [\hat{l}^2, \hat{l}_z] = 0$, i.e. it is possible to know both the magnitude and only *one* component (say the z-component) of $\mathbf{l}$.
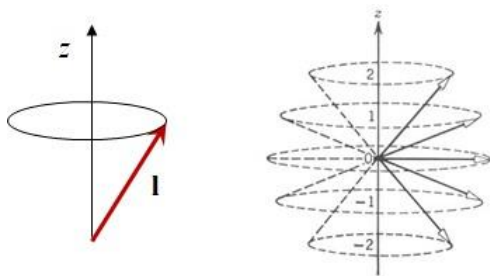

Figure 1

Figure 1 (left) illustrates the situation; the length of the vector $\mathbf{l}$ and its projection along z are known. The vector $\mathbf{l}$ precesses about the z-axis, consistent with the fact that the x,y components are unknown.

Furthermore, we have the following relationships:
$$|\mathbf{l}| = \sqrt{l(l+1)}\hbar$$
$$l_z = m_l\hbar$$
$$m_l = l, l-1, \dots, 0, -1, \dots, -l$$

l and m_l are quantum numbers that can take only integer values. The former determines the magnitude of $\mathbf{l}$, while the latter determines the z-component. An example for $l = 2$ is shown in Figure 1 (right). Note that vector magnitude is constant, but its orientation changes depending on the m_l value. For $l = 2$ there are only five orientations (w.r.t. z-axis); this behaviour is very different to classical angular momentum which is a continuous variable.

The magnetic moment due to orbital angular momentum is $\boldsymbol{\mu}_l = -\gamma\mathbf{l}$ so that $\mu_{lz} = -\gamma l_z = -(\gamma\hbar)m_l = -\mu_B m_l$. The energy in a magnetic field is therefore $E = -\boldsymbol{\mu}_l \cdot \mathbf{B} = \mu_B B m_l$.

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[1] For any two operators A and B [A,B] = AB – BA. Operators with non-zero commutator cannot be measured simultaneously, e.g. position and momentum in Heisenberg's uncertainty principle.

Apart from orbital angular momentum electrons also possess an intrinsic **spin angular momentum**, **s**, that has no classical equivalent[2]. The quantum mechanical conditions for **s** are similar to **l**:

$$|\mathbf{s}| = \sqrt{s(s+1)}\hbar \quad (s = \frac{1}{2})$$

$$s_z = m_s \hbar$$

$$m_s = s, s - 1 = \frac{1}{2}, -\frac{1}{2}$$

Note that the spin quantum number s can only take the value of ½, so that there are only two values for m_s, i.e. +½, -½, corresponding to spin up and spin down electrons. The magnetic moment due to spin angular momentum is $\boldsymbol{\mu}_s = -\gamma g_s \mathbf{s}$, where g_s is the Landé g-factor ($g_s \approx 2$).

The orbital and spin angular momentum can couple in what is called **spin-orbit interaction**. This is illustrated in Figure 2.
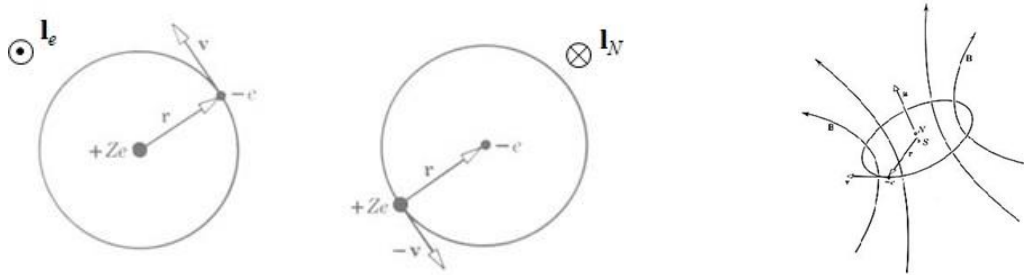

Figure 2: electron orbiting the nucleus (left) and the same situation as viewed from the electron frame of reference (middle) resulting in an internal **B**-field (right)

The electron orbits the nucleus, but when viewed from its own frame of reference the electron sees the nucleus orbiting around it. The nuclear orbital angular momentum $\mathbf{l}_N$ is anti-parallel to that of the electron $\mathbf{l}_e$. There will be a magnetic moment, $\boldsymbol{\mu}_N = -\gamma \mathbf{l}_N$, associated with $\mathbf{l}_N$, which generates a strong *internal* magnetic **B**-field that is parallel to $\mathbf{l}_e$. The electron spin angular momentum **s** therefore has a potential energy $\Delta E = -\boldsymbol{\mu}_s \cdot \mathbf{B}$ due to the internal **B**-field arising from the orbital angular momentum. It can be shown that the spin-orbit interaction energy:

$$\Delta E = \frac{1}{2mc^2 r} \frac{dV(r)}{dr} \mathbf{s} \cdot \mathbf{l}$$

where $V(r)$ is the potential due to the atomic nucleus and c is the speed of light. The spin-orbit interaction is greater for heavy atoms with large $V(r)$. Since the **B**-field causing spin-orbit interaction is internal, there are no external torques, meaning that angular momentum is conserved and $\mathbf{j} = \boldsymbol{l} + \mathbf{s}$. The quantum rules for angular momentum **j** are:

$$|\mathbf{j}| = \sqrt{j(j+1)}\hbar \; ; \; j = l + s, |l - s|$$
$$j_z = m_j \hbar \; ; \; m_j = j, j - 1, \dots, -j$$

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[2] Spin arises from relativistic quantum mechanics, i.e. Dirac's theory of the electron.

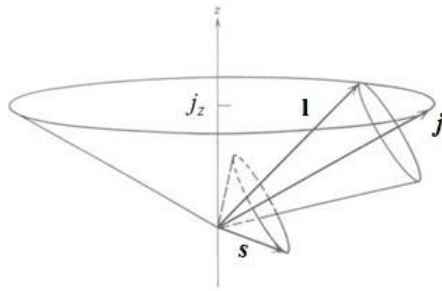Note that these rules are similar for **l** and **s** apart from the values for the j quantum number[3].

Figure 3

The spin-orbit interaction is illustrated in Figure 3: **l** and **s** precess together about **j** due to torques induced by the internal **B**-field. **j** can lie anywhere on the cone with constant j_z. Note that m_l and m_s are no longer good quantum numbers, i.e. the z-components of **l** and **s** are not known after spin-orbit coupling.

Consider now the spin-orbit interaction energy ΔE which depends on $\mathbf{s} \cdot \mathbf{l}$. From $\mathbf{j} = \mathbf{l} + \mathbf{s}$,

$$|\mathbf{j}|^2 = |\mathbf{l}|^2 + |\mathbf{s}|^2 + 2\mathbf{s}$$

Or $j(j + 1)\hbar = l(l + 1)\hbar + s(s + 1)\hbar + 2\mathbf{s} \cdot \mathbf{l}$ which gives:

$$\mathbf{s} \cdot \mathbf{l} = \frac{\hbar}{2}[j(j + 1) - l(l + 1) - s(s + 1)]$$

The Spin-orbit energy is therefore expected to increases with j. Spin-orbit energies are of the order 10^{-4} eV for light atoms (i.e. much smaller than the few eV spacing between energy levels in an atom).

Multi-electron atoms and Hund's rules

The electron configuration in a multi-electron atom must be such that the energy is minimised. The energy is due to: (i) Coulomb interaction and (ii) spin-orbit interaction. For light atoms the former is dominant and must be minimised first. This is known as ***LS* or Russel-Saunders coupling**. Coulomb energy has contributions from both spin and orbital angular momentum. Parallel spins are favoured (Figure 4a), since from the Pauli exclusion principle these are spaced far apart, thereby reducing the Coulomb energy. Hence the total spin angular momentum $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \dots$ must be maximised, where $\mathbf{s}_1$, $\mathbf{s}_2$, are the spin angular momenta of the individual electrons. Similarly, the total orbital angular momentum $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \dots$ must also be maximised; in Figure 4b if the two electrons both move in the same sense (i.e. clockwise or counter-clockwise) around the loop they stay far apart, whereas if they move in opposite senses they cross paths, thereby increasing the Coulomb energy. The **S** and **L** angular momenta can spin-orbit couple to give a new angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

Anti-parallel spins (singlet)

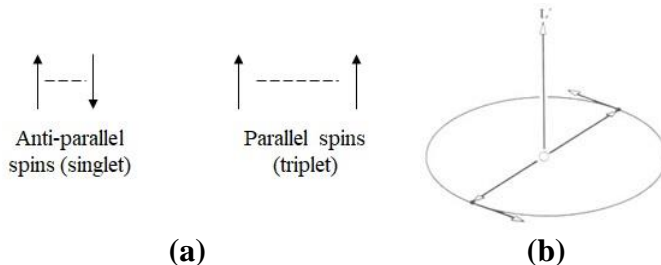Parallel spins (triplet)

(a)

(b)

Figure 4: (a) distance between parallel and anti-parallel spins and (b) two electrons in a circular orbit. Coulomb energy is minimised for parallel spins in (a) and electrons orbiting in the same sense in (b).

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[3] The rules for adding any two angular momenta **q** and **r** are as follows (note that **q**, **r** could represent two orbital or two spin momenta or alternatively one each of orbital and spin momenta): the z-component of $\mathbf{p} = \mathbf{q} + \mathbf{r}$ is conserved, i.e. $p_z = q_z + r_z$. Since $|\mathbf{p}| = \sqrt{p(p + 1)}\hbar$ and $p_z = m_p\hbar$ ($m_p = p, p - 1, \dots, -p$) and similarly for **q** and **r** this means that the maximum value for p is $(q+r)$. p can therefore take values $q+r$, $q+r-1$, $q+r-2\dots$ etc. The terminating point for the series is determined by the vector inequality $|\mathbf{q+r}| \geq ||\mathbf{q}| - |\mathbf{r}||$, which gives a minimum value for p of $|q-r|$. For $\mathbf{j} = \mathbf{l} + \mathbf{s}$ there are thus only two values for j (i.e. $l+s$ and $|l-s|$) because $s = \frac{1}{2}$.

Hund's rules govern the minimum energy electron configuration in atoms where *LS* coupling is present. The procedure for determining the electron configuration is as follows: (i) First maximise **S**, (ii) next maximise **L,** followed by (iii) selecting **J** that gives the smallest spin-orbit interaction energy (this is $J = |L - S|$ if the band is less than half-full and $J = L + S$ for a band more than half-full[4]). Note that the larger Coulomb energy is minimised first before minimising the smaller spin-orbit interaction energy.

m_l	$m_s = \frac{1}{2}$	$m_s = -\frac{1}{2}$
3	●	●
2	●	●
1	●	
0	●	
-1	●	
-2	●	
-3	●	

Figure 5

As an example Figure 5 shows Hund's rules applied to a Dy^{3+} ion with a $4f^9$ shell (NB: $l = 3$ for a *f*-shell)[5]. It can be seen that $L = \Sigma m_l = 5$ and $S = \Sigma m_s = 5/2$. Strictly speaking, $\Sigma m_l = m_L$, where $L_z = m_L \hbar$ and m_L can take any value of $L, L-1,...,-L$. However, since **L** is maximised by Hund's rules we must have $m_L = L$ and therefore $L = \Sigma m_l$. Similar arguments apply to $S = \Sigma m_s$.

Since the band is more than half-full $J = L + S = 15/2$. The electronic configuration is denoted by $^{2S+1}L_J$. $(2S + 1)$ is the spin multiplicity. L is denoted using the relevant letter from the table below:

L	0	1	2	3	4	5	6
	S	P	D	F	G	H	I

The electronic configuration of Dy^{3+} is therefore $^6H_{15/2}$. This is also known as the **term symbol**.

Magnetism in multi-electron atoms

The magnetic Hamiltonian terms for a multi-electron atom is:

$$\sum_i \gamma \mathbf{B} \cdot (\mathbf{l_i} + g_s \mathbf{s_i}) + \left(\begin{array}{c}\text{spin} - \text{orbit} \\ \text{interaction}\end{array}\right) + \frac{e^2}{8m}(\mathbf{B} \times \mathbf{r_i})^2$$

For an atom with *LS* coupling:

$$\sum_i \gamma \mathbf{B} \cdot (\mathbf{l_i} + g_s \mathbf{s_i}) + \left(\begin{array}{c}\text{spin} - \text{orbit} \\ \text{interaction}\end{array}\right) = \gamma \mathbf{B} \cdot (\mathbf{L} + g_s \mathbf{S}) + \left(\begin{array}{c}\text{spin} - \text{orbit} \\ \text{interaction}\end{array}\right) = \gamma g_J \mathbf{B} \cdot \mathbf{J}$$

where g_J is a Landé *g*-factor for J : $g_J = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)}$. For a full shell **L, S** and $\mathbf{J} = 0$, so that only the diamagnetic term remains (i.e. atoms/ions with filled shells show diamagnetic behaviour). On the other hand, for an incomplete shell **L, S** and $\mathbf{J} \neq 0$, so that there will also be a paramagnetic contribution.

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[4] We showed earlier that the spin-orbit interaction should generally increase with *J*. The minimum value of *J* is |*L-S*|, so we expect Hund's rules to always favour $J = |L-S|$. However, this condition only holds when the band is less than half-full.

[5] Hund's rules are typically always satisfied in Lanthanide ions, since the 4f shell is screened from the rest of the solid by the 5s and 5p shells. In 3d transition metal ions the screening is not as strong, so that Hund's rules may break down in transition metal solids. In these solids a phenomenon known as 'orbital quenching' occurs where the favoured value of *L* is $L = 0$.