## 2. Magnetism of free atoms and ions

The study of magnetism starts with small systems - atoms, ions and molecules - where many of the mechanisms that give rise to magnetic ordering are already active as soon as there are two interacting electrons. The tendency to form a high spin ground state in a small system is related to a ferromagnetic state in a solid, the tendency to align antiparallel and form a spin singlet is related to antiferromagnetism. On the other hand, when electrons are essentially localized to ions, the properties of the isolated ions are directly relevant also for the solid, as is the case for rare earth ions.

### 2.1 Hartree approximation for the electron shell

We cannot exactly solve the many-body problem of a nucleus with many electrons. In the simplest non-trivial approximation, the Hartree approximation, a given electron moves in a potential resulting from the nucleus and the average density of the other electrons; it is important that the selfinteraction, the interaction of the electron with its own averaged charge density is excluded. The total potential is

$$
\begin{equation*}
V_{\text {eff }}(\vec{r})=-\frac{1}{4 \pi \epsilon_{0}} \frac{Z e^{2}}{r}-\frac{1}{4 \pi \epsilon_{0}} \int d^{3} r^{\prime} \frac{e \rho_{\mathrm{r}}\left(\vec{r}^{\prime}\right)}{\left|\overrightarrow{\mathrm{r}}-\overrightarrow{\mathrm{r}}^{\prime}\right|} \tag{2.1}
\end{equation*}
$$

where Z is the atomic number of the nucleus, the electron charge is $-\mathrm{e}<0$, and $\rho_{\vec{r}}\left(\overrightarrow{\mathrm{r}}^{\prime}\right)<0$ is the charge density at $\overrightarrow{\mathrm{r}}^{\prime}$ of the other electrons if the given electron is at $\vec{r}$. $V_{\text {eff }}(\vec{r})$ is spherically symmetric due to the isotropy of space, but $\rho_{\vec{r}}\left(\overrightarrow{\mathrm{r}}^{\prime}\right)$ as a function of $\overrightarrow{\mathrm{r}}^{\prime}$ is not spherically symmetric except for $\vec{r}=0$. For the electron at $\vec{r}$ we solve the single-particle Schrödinger equation

$$
\begin{equation*}
\left(\frac{p^{2}}{2 m}+V_{\text {eff }}(\stackrel{\rightharpoonup}{r})\right) \psi(\stackrel{\rightharpoonup}{r})=E \psi(\stackrel{\rightharpoonup}{r}) \tag{2.2}
\end{equation*}
$$

From a separation of variables and using the spherical symmetry, the eigenfunctions are

$$
\begin{equation*}
\psi_{\mathfrak{n l m}}(\vec{r})=R_{n l}(r) Y_{l m}(\vartheta, \phi) \tag{2.3}
\end{equation*}
$$

with principal quantum number $\mathfrak{n}=1,2,3, \ldots$, orbital angular momentum quantum number $\mathfrak{l}=0,1,2, \ldots, \mathfrak{n}-1$ and magnetic quantum number $\mathfrak{m}=$ $-l,-l+1, \ldots, l$. The angular part is the same for any spherically symmetric potential and is given by the spherical harmonics $Y_{l m}(\vartheta, \phi)$. Eigenenergies $\epsilon_{n, l}$ only depend on $n, l$ in the present approximation. Including a factor of 2 from spin $s=1 / 2$, the $\epsilon_{n, l}$ are $2(2 l+1)$-fold degenerate. Completely full shells comprising all orbitals with a given quantum number $n, l$ have $\left\langle\sum_{i} \overrightarrow{\mathfrak{l}}_{\mathfrak{i}}\right\rangle=0$ and $\left\langle\sum_{i} \vec{s}_{i}\right\rangle=0$, i.e. vanishing total angular moment because for every electron there is another one with opposite $\left\langle\overrightarrow{\mathfrak{l}}_{i}\right\rangle,\left\langle\vec{s}_{i}\right\rangle$. The total magnetic moment of filled shells also vanishes. Therefore, magnetic ions require incompletely filled shells.
In the ground states, we need to fill the Hartree orbitals starting from the lowest in energy. For a shell containing $p$ electrons (with $p<2(2 l+1)$ ), the number of possibilities of doing this is given by

$$
\binom{2(2 l+1)}{p} .
$$

This represents the degeneracy of the many-particle state. For a filled state, we get no degeneracy:

$$
\binom{2(2 l+1)}{2(2 l+1)}=1 .
$$

### 2.2 Beyond the Hartree approximation

The large degeneracy we found is partially lifted by the Coulomb repulsion beyond the Hartree approximation. The Coulomb interaction

$$
\begin{equation*}
\mathrm{V}_{\mathrm{C}}=\frac{1}{4 \pi \epsilon_{0}} \frac{1}{2} \sum_{i \neq j} \frac{e^{2}}{\left|\overrightarrow{\vec{r}_{i}}-\overrightarrow{\mathrm{r}_{j}}\right|} \tag{2.4}
\end{equation*}
$$

commutes with the total orbital angular momentum of the shell $\overrightarrow{\mathrm{L}}=\sum_{\bar{S}_{i}} \vec{l}_{i}$ as $\mathrm{V}_{\mathrm{C}}$ is spherically symmetric, and with the total spin of the shell $\overline{\mathrm{S}}=$ $\sum_{i} \vec{s}_{i}$ as well because the Hamiltonian doesn't depend on it:

$$
\begin{equation*}
[\overrightarrow{\mathrm{S}}, \mathrm{H}]_{-}=0, \quad[\stackrel{\rightharpoonup}{\mathrm{~L}}, \mathrm{H}]_{-}=0 \tag{2.5}
\end{equation*}
$$

The Hamiltonian also commutes with $\overrightarrow{\mathrm{L}}^{2}$ and with $\overrightarrow{\mathrm{S}}^{2}$. Furthermore, the total angular momentum of the shell

$$
\begin{equation*}
\overrightarrow{\mathrm{J}}=\overrightarrow{\mathrm{L}}+\overrightarrow{\mathrm{S}} \tag{2.6}
\end{equation*}
$$

commutes with the Hamiltonian

$$
\begin{equation*}
[\stackrel{\rightharpoonup}{\mathrm{J}}, \mathrm{H}]_{-}=0 . \tag{2.7}
\end{equation*}
$$

Physically, this means that

$$
\begin{equation*}
\mathrm{L}=\sum_{i=1}^{p} m_{l}^{(i)}, S=\sum_{i=1}^{p} m_{s}^{(i)}, J \tag{2.8}
\end{equation*}
$$

are good quantum numbers; $\mathfrak{m}_{l}^{(i)}$ and $\mathfrak{m}_{s}^{(i)}$ are the magnetic quantum numbers of the electrons. We can also say that there exists a simultaneous set of eigenstates for the operators

$$
\mathrm{H}, \mathrm{~J}^{2}, \mathrm{~J}_{z}, \mathrm{~L}^{2}, \mathrm{~L}_{z}, \mathrm{~S}^{2}, \mathrm{~S}_{z},
$$

and states can be labeled by the corresponding quantum numbers

$$
\begin{equation*}
|\ldots\rangle=\left|\mathrm{J}, \mathrm{M}_{\mathrm{J}}, \mathrm{~L}, \mathrm{M}_{\mathrm{L}}, \mathrm{~S}, \mathrm{M}_{\mathrm{S}}\right\rangle \tag{2.9}
\end{equation*}
$$

Here, S is the maximum possible value of $\left\langle\mathrm{S}_{z}\right\rangle$, L is the maximum possible value of $\left\langle\mathrm{L}_{z}\right\rangle$. For example,

$$
\begin{array}{rlrl}
\mathrm{J}^{2}|\ldots\rangle & =\hbar^{2} \mathrm{~J}(\mathrm{~J}+1)|\ldots\rangle & \mathrm{J}_{z}|\ldots\rangle=\hbar M_{\mathrm{J}}|\ldots\rangle \\
\mathrm{J} & =|\mathrm{L}-\mathrm{S}|, \ldots, \mathrm{L}+\mathrm{S} & & -\mathrm{J} \leqslant \mathrm{M}_{\mathrm{J}} \leqslant+\mathrm{J} \tag{2.10}
\end{array}
$$

The other angular momentum operators act in similar fashion. The energy eigenvalues of the Hamiltonian

$$
\begin{equation*}
\mathrm{H}|\ldots\rangle=\mathrm{E}_{\mathrm{JLS}}^{(0)}|\ldots\rangle \tag{2.11}
\end{equation*}
$$

will depend on J, L, S, but in the absence of a magnetic field, they will be degenerate with respect to $M_{J}, M_{L}$ and $M_{S}$.
If we apply the raising operator $\mathrm{L}^{+}=\mathrm{L}_{x}+i \mathrm{~L}_{y}$ to $|\psi\rangle$ and obtain a $\left|\psi^{\prime}\right\rangle$ with $M_{\mathrm{L}}^{\prime}=M_{\mathrm{L}}+1$, we reach a new state that has the same energy as the old one because $\left[\mathrm{H}, \mathrm{L}^{+}\right]=0$. There are $(2 \mathrm{~L}+1)(2 \mathrm{~S}+1)$ states that are connected by $L^{ \pm}$and by $S^{ \pm}\left(S^{-}=S_{x}-i S_{y}, S^{+}=S_{x}+i S_{y}\right)$; the $\binom{2(2 l+1)}{p}$-fold degenerate states split into multiplets with fixed $S$ and L and degeneracies $(2 L+1)(2 S+1)$. Typically, energy splitting between multiplets are much larger than 1 eV so that for magnetic problems, we only need to know the ground state multiplet.

### 2.2.1 Hund's rules for LS coupling

We assume here that the Coulomb interaction $\mathrm{H}_{\mathrm{C}}$ is significantly larger than the spin-orbit coupling $\mathrm{H}_{\mathrm{SO}}$

$$
\mathrm{H}_{\mathrm{C}} \gg \mathrm{H}_{\mathrm{SO}}
$$

which leads us to the Russell-Saunders- or LS-coupling. This is relevant for light nuclei.
The empirical Hund's rules tell us how to build the ground-state LS multiplet for given $L$ and $S$, and for $p$ electrons filled into a shell with orbital angular momentum quantum number $l$ :

1st Hund's rule: The ground state multiplet has the largest possible $S$. (The maximum $S$ corresponds to the largest possible value of $\left\langle\mathrm{S}_{z}\right\rangle$ ).

$$
S=\frac{1}{2}[(2 l+1)-|2 l+1-\mathfrak{p}|]
$$

2nd Hund's rule: If the 1st Hund's rule leaves several possibilities, the state with maximum $L$ is lowest in energy:

$$
L=S|2 l+1-p|
$$

(The maximum $L$ corresponds to the largest possible value of $\left\langle L_{z}\right\rangle$ ).
A short qualitative explanation for the 1st Hund's rule is that the same spin together with the Pauli principle means that the electrons are on average further apart, reducing the Coulomb repulsion. Also the aligned orbital momenta, i.e. rotation in the same sense, of the second rule optimizes distance between electrons and reduces Coulomb energy.
The multiplets are labeled as ${ }^{2 S+1} \mathrm{~L}$ where a letter is used for L :

$$
\begin{array}{ccccccccc}
\mathrm{L}= & 0 & 1 & 2 & 3 & 4 & 5 & 6 & \ldots \\
\hline \mathrm{X}= & \mathrm{S} & \mathrm{P} & \mathrm{D} & \mathrm{~F} & \mathrm{G} & \mathrm{H} & \mathrm{I} & \text { continuing alphabetically }
\end{array}
$$

We can count the number of distinct states within the LS multiplets as

$$
\begin{equation*}
\sum_{J=|L-S|}^{\mathrm{L}+\mathrm{S}}(2 \mathrm{~J}+1)=(2 \mathrm{~S}+1)(2 \mathrm{~L}+1) \tag{2.12}
\end{equation*}
$$

Often (not always), these states are ordered according to the

Table 2.1: Atomic term scheme for an $f$ shell occupied by $p$ electrons. $\uparrow$ represents spin projection $1 / 2, \downarrow$ represents spin projection $-1 / 2$.

| p | $\mathrm{m}_{l}$ |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 3 | 2 | 1 | 0 | -1 | -2 | -3 | S | L | J | term |
| 1 | $\uparrow$ |  |  |  |  |  |  | $1 / 2$ | 3 | $5 / 2$ | ${ }^{2} \mathrm{~F}_{5 / 2}$ |
| 2 | $\uparrow$ | $\uparrow$ |  |  |  |  |  | 1 | 5 | 4 | ${ }^{3} \mathrm{H}_{4}$ |
| 3 | $\uparrow$ | $\uparrow$ | $\uparrow$ |  |  |  |  | $3 / 2$ | 6 | $9 / 2$ | ${ }^{4} \mathrm{I}_{9 / 2}$ |
| 4 | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |  |  |  | 2 | 6 | 4 | ${ }^{5} \mathrm{I}_{4}$ |
| 5 | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |  |  | $5 / 2$ | 5 | $5 / 2$ | ${ }^{6} \mathrm{H}_{5 / 2}$ |
| 6 | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |  | 3 | 3 | 0 | ${ }^{7} \mathrm{~F}_{0}$ |
| 7 | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $7 / 2$ | 0 | $7 / 2$ | ${ }^{8} \mathrm{~S}_{7 / 2}$ |
| 8 | $\uparrow \downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | 3 | 3 | 6 | ${ }^{7} \mathrm{~F}_{6}$ |
| 9 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $5 / 2$ | 5 | $15 / 2$ | ${ }^{6} \mathrm{H}_{15 / 2}$ |
| 10 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | 2 | 6 | 8 | ${ }^{5} \mathrm{I}_{8}$ |
| 11 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $3 / 2$ | 6 | $15 / 2$ | ${ }^{4} \mathrm{I}_{15 / 2}$ |
| 12 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $\uparrow$ | 1 | 5 | 6 | ${ }^{3} \mathrm{H}_{6}$ |
| 13 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $1 / 2$ | 3 | $7 / 2$ | ${ }^{2} \mathrm{~F}_{7 / 2}$ |
| 14 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | 0 | 0 | 0 | ${ }^{1} \mathrm{~S}_{0}$ |

3rd Hund's rule: For the total angular momentum of the shell, $\vec{J}=|\overrightarrow{\mathrm{L}}-\overrightarrow{\mathrm{S}}|$ in case the shell is less than half filled $(p \leqslant(2 l+1))$,
$\overrightarrow{\mathrm{J}}=\overrightarrow{\mathrm{L}}+\overrightarrow{\mathrm{S}}$ in case the shell is more than half filled $(\mathrm{p} \geqslant(2 l+1))$,
which means

$$
\mathrm{J}=\mathrm{S}|2 \mathrm{l}-\mathrm{p}|
$$

Table 2.1 gives the terms for an $\mathbf{f}$ shell (e.g. $4 \mathbf{f}$, relevant for rare earths), occupied by $p$ electrons.

### 2.3 Spin-orbit coupling

Experimentally, the magnetic moment of an electron is

$$
\stackrel{\rightharpoonup}{m}_{s}=-g \mu_{B} \frac{\stackrel{\rightharpoonup}{s}}{\hbar}
$$

with $\mathrm{g} \approx 2.0023$. This cannot be explained with a classical calculation. A classical estimate of $g$ based on the assumption that an electron is a spinning charged sphere with angular momentum $\vec{s}$ would only lead to
$\mathrm{g}=1$. However, relativistic Dirac quantum theory gives $\mathrm{g}=2$, and the remaining $\approx 0.0023$ are due to small corrections arising from the interaction of the electronic charge with the electromagnetic field it generates; this can be calculated precisely with quantum electrodynamics.
We will see now that also for the many-particle states of ions, a relativistic description is necessary. The starting point for the derivation is the nonrelativistic $v \ll c$ limit of the Dirac equation which gives rise to the twocomponent Pauli theory. However, we have to go further in perturbation theory, including terms of the order $\frac{v^{2}}{c^{2}}$. This higher order approximation is done formally correctly using the Foldy-Wouthuysen transformation. A static electric potential $\phi$ of the nucleus is considered. One obtains the following Hamiltonian in spinor space:

$$
\begin{equation*}
\mathrm{H}=\frac{\mathrm{p}^{2}}{2 \mathrm{~m}}+\phi(\overrightarrow{\mathrm{r}})-\frac{\mathrm{p}^{4}}{8 \mathrm{~m}_{e}^{3} \mathrm{c}^{2}}+\frac{\hbar^{2}}{2 \mathrm{~m}_{e}^{2} \mathrm{c}^{2}} \frac{1}{r} \frac{\partial \phi}{\partial \mathrm{r}} \overrightarrow{\mathrm{~s}} \cdot \vec{l} \cdot \frac{\hbar^{2}}{8 \mathrm{~m}_{e}^{2} \mathrm{c}^{2}} \nabla^{2} \phi \tag{2.13}
\end{equation*}
$$

Here, the first two terms are the non-relativistic $\mathrm{H}_{0}$, the third term is a relativistic correction to the kinetic energy, the fourth term contains the spin-orbit coupling $\mathrm{H}_{\mathrm{SO}}$, and the last term is a correction to the potential, known as the Darwin term.
We will now consider the spin-orbit coupling term for the central potential of the nucleus

$$
\mathrm{H}_{\mathrm{SO}}=-\frac{\hbar^{2}}{2 \mathrm{~m}_{e}^{2} \mathrm{c}^{2}} \frac{Z e^{2}}{4 \pi \epsilon_{0}} \frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}} \frac{1}{\mathrm{r}} \cdot \stackrel{\rightharpoonup}{\mathrm{~s}} \cdot \overrightarrow{\mathrm{l}}=\frac{\hbar^{2}}{2 \mathrm{~m}_{e}^{2} \mathrm{c}^{2}} \frac{Z e^{2}}{4 \pi \epsilon_{0}} \frac{\overrightarrow{\mathrm{~s}} \cdot \overrightarrow{\mathrm{l}}}{\mathrm{r}^{3}}=\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z \frac{\overrightarrow{\mathrm{~s}} \cdot \overrightarrow{\mathrm{l}}}{\mathrm{r}^{3}},
$$

where we assume $\mathrm{g}=2$ and use $\mu_{\mathrm{B}}=\frac{e \hbar}{2 \mathrm{~m}_{e}}$ and $\mathrm{c}=\frac{1}{\mu_{0} \epsilon_{0}}$.
The operator of spin-orbit coupling for several electrons in an incompletely filled shell is then

$$
\begin{equation*}
H_{S O}=\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z \sum_{i} \frac{\vec{s}_{i} \cdot \vec{l}_{i}}{r_{i}^{3}} . \tag{2.14}
\end{equation*}
$$

In principle, not only the bare nuclear potential but the full effective potential of the Hartree approximation should be taken into account; however, this is done in practice by replacing the atomic number $Z$ by an effective $Z_{\text {eff }}<Z$. Next, we treat $H_{S O}$ as a weak perturbation to $H_{0}$ and evaluate the contribution of the spin-orbit coupling to the energy:

$$
\begin{equation*}
\mathrm{E}_{\mathrm{SO}}:=\left\langle\mathrm{H}_{\mathrm{SO}}\right\rangle=\frac{\mu_{0}}{4 \pi} \mathrm{~g} \mu_{\mathrm{B}}^{2} Z \sum_{i}\left\langle\frac{\left.{\stackrel{\rightharpoonup}{s_{i}} \cdot \vec{l}_{i}}_{r_{i}^{3}}\right\rangle . . . . . . .}{}\right. \tag{2.15}
\end{equation*}
$$

For free ions, the radial wave function $R_{n l}$ for all orbitals of the nl shell is the same; therefore

$$
\begin{equation*}
E_{S O}=\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z \sum_{i}\left\langle\frac{1}{r^{3}}\right\rangle_{n l}\left\langle\vec{s}_{i} \cdot \vec{l}_{i}\right\rangle . \tag{2.16}
\end{equation*}
$$

Now we call electrons with spin parallel to $\vec{S}$ spin up $(\uparrow)$ and the others spin down $(\downarrow)$. Also, the $\vec{s}_{i}$ and $\overrightarrow{\mathfrak{l}}_{i}$ commute. Thus

$$
E_{S O}=\frac{\mu_{0}}{4 \pi} g \mu_{B}^{2} Z \sum_{i}\left\langle\frac{1}{r^{3}}\right\rangle_{n l}\left(\sum_{\substack{i \\ \text { spin up }}}\left\langle\frac{\vec{S} \cdot \vec{l}_{i}}{2 S}\right\rangle-\sum_{\substack{i \\ \text { spin up }}}\left\langle\frac{\vec{S} \cdot \vec{l}_{i}}{2 S}\right\rangle\right) .
$$

We distinguish three cases:
(i) If the shell is less than half filled ( $\boldsymbol{n}_{\mathfrak{n l}}<2 l+1$ ), all spins are aligned and the spin down sum doesn't contain any terms:

$$
\begin{equation*}
E_{S O}=\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z\left\langle\frac{1}{r^{3}}\right\rangle_{n l} \frac{1}{2 S}\left\langle\overrightarrow{\mathrm{~S}} \cdot \sum_{i} \overrightarrow{\mathrm{l}}_{\mathrm{i}}\right\rangle=\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z\left\langle\frac{1}{r^{3}}\right\rangle_{\mathfrak{n l}} \frac{1}{2 S}\langle\overrightarrow{\mathrm{~S}} \cdot \overrightarrow{\mathrm{~L}}\rangle=: \lambda\langle\overrightarrow{\mathrm{S}} \cdot \overrightarrow{\mathrm{~L}}\rangle \tag{2.17}
\end{equation*}
$$

with

$$
\lambda=\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z\left\langle\frac{1}{\mathrm{r}^{3}}\right\rangle_{\mathrm{nl}} \frac{1}{2 S} .
$$

(ii) If the shell is more than half filled $\left(n_{n l}>2 l+1\right)$, the spin up sum vanishes because it contains

$$
\sum_{\mathfrak{m}_{\imath}=-l}^{l}\left\langle\mathfrak{l m}_{\mathfrak{l}}\right| \vec{l}\left|m_{l}\right\rangle=0
$$

and we obtain

$$
\begin{equation*}
\mathrm{E}_{S O}=-\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z\left\langle\frac{1}{\mathrm{r}^{3}}\right\rangle_{\mathrm{nl}} \frac{1}{2 S}\langle\overrightarrow{\mathrm{~S}} \cdot \overrightarrow{\mathrm{~L}}\rangle=: \lambda\langle\overrightarrow{\mathrm{S}} \cdot \overrightarrow{\mathrm{~L}}\rangle \tag{2.18}
\end{equation*}
$$

with

$$
\lambda=-\frac{\mu_{0}}{4 \pi} g \mu_{\mathrm{B}}^{2} Z\left\langle\frac{1}{\mathrm{r}^{3}}\right\rangle_{\mathfrak{n l}} \frac{1}{2 \mathrm{~S}} .
$$

(iii) If the shell is half filled $\left(n_{n l}=2 l+1\right)$, both spin up and spin down sums vanish and we get $\mathrm{E}_{\text {SO }}=0$. Note that at higher orders in perturbation theory, there is a nonzero contribution.

In summary, the spin-orbit coupling in a free ion behaves, within perturbation theory, like a term $\mathrm{H}_{\mathrm{SO}}=\lambda\langle\overrightarrow{\mathrm{S}} \cdot \overrightarrow{\mathrm{L}}\rangle$ in the Hamiltonian, with $\lambda>0$ for less than half filled shells and $\lambda<0$ for more than half filled shells.
As a consequence of spin-orbit coupling $\mathrm{H}_{\text {SO }}$, even in the absence of an external magnetic field $\left(\overrightarrow{\mathrm{B}}_{0}=0\right) \vec{l}$ and $\stackrel{\rightharpoonup}{s}$ do not commute with the Hamiltonian.
One can show that

$$
[\vec{l} \cdot \vec{s}, \vec{l}]_{-}=i \hbar(\vec{l} \times \vec{s})=-[\vec{l} \cdot \vec{s}, \vec{s}]_{-} .
$$

On the other hand,

$$
[\vec{l} \cdot \vec{s}, \vec{j}]_{-}=0 \quad \text { with } \overrightarrow{\mathfrak{j}}=\overrightarrow{\mathrm{l}}+\overrightarrow{\mathrm{s}}
$$

Furthermore,

$$
\left[\overrightarrow{\mathrm{l}} \cdot \overrightarrow{\mathrm{~s}}, \vec{j}^{2}\right]_{-}=\left[\overrightarrow{\mathrm{l}} \cdot \overrightarrow{\mathrm{~s}}, \overrightarrow{\mathrm{l}}^{2}\right]_{-}=\left[\overrightarrow{\mathrm{l}} \cdot \overrightarrow{\mathrm{~s}}, \overrightarrow{\mathrm{~s}}^{2}\right]_{-}=0 .
$$

This means that the energy eigenstates can be classified by $\mathfrak{j}, \mathfrak{m}_{\mathfrak{j}}, l$ and $s$ (which are good quantum numbers) but not by $\mathfrak{m}_{l}$ and $\mathfrak{m}_{s}$. $\mathrm{H}_{\mathrm{SO}}$ couples, i.e. hybridizes the states with different $\mathfrak{m}_{l}$ and $\mathfrak{m}_{s}$.
$\mathrm{H}_{\text {SO }}$ partially lifts the degeneracy of the LS-multiplet (here the doublet as our treatment is for one electron, $\mathfrak{j}=l \pm 1 / 2$ ). Due to

$$
\overrightarrow{\mathfrak{j}}=\overrightarrow{\mathrm{l}}+\overrightarrow{\mathrm{s}} \curvearrowright 2(\overrightarrow{\mathrm{l}} \cdot \overrightarrow{\mathrm{~s}})=\overrightarrow{\mathfrak{j}}^{2}-\overrightarrow{\mathrm{l}}^{2}-\overrightarrow{\mathrm{s}}^{2}
$$

$H_{S O}$ produces a fine structure of the energy terms

$$
\begin{equation*}
E_{n l j}^{(0)}=E_{n l}^{(0)}+\lambda_{\mathfrak{n l}} \hbar^{2}[j(j+1)-l(l+1)-s(s+1)] \tag{2.19}
\end{equation*}
$$

with energy $E_{n l j}^{(0)}$ in the absence of spin-orbit coupling. The constant $\lambda_{n l}$ is

$$
\lambda_{\mathrm{nl}}=-\frac{e}{2 \mathrm{~m}_{e}^{2} \mathrm{c}^{2}}\langle\mathrm{nls}| \frac{1}{\mathrm{r}} \frac{\mathrm{~d} \phi}{\mathrm{dr}}|\mathrm{nls}\rangle .
$$

Thus, terms with $\mathfrak{j}=l \pm 1 / 2$ have different energies for $l \neq 0$ while the $2 \boldsymbol{j}+1$-fold degeneracy due to $\boldsymbol{m}_{\mathfrak{j}}$ remains.

### 2.4 Magnetic moments of ions

A problem arises when we want to calculate the magnetic moment of an ion with quantum number $S, L, J$ : Using $g=2$ for the $g$ factor of the electron, the magnetic moment is

$$
\vec{m}_{J}=\vec{m}_{S}+\overrightarrow{\mathrm{m}}_{\mathrm{L}}=-2 \mu_{\mathrm{B}} \overrightarrow{\mathrm{~S}}-\mu_{\mathrm{B}} \overrightarrow{\mathrm{~L}}=-\mu_{\mathrm{B}}\left((2 \overrightarrow{\mathrm{~S}}+\overrightarrow{\mathrm{L}})=-\mu_{\mathrm{B}}(\overrightarrow{\mathrm{~J}}+\overrightarrow{\mathrm{S}})\right.
$$

But $\vec{m}_{J}$ does not commute with the Hamiltonian because of the spin-orbit coupling term $\lambda \overrightarrow{\mathrm{L}} \cdot \overrightarrow{\mathrm{S}}(\overrightarrow{\mathrm{J}}$ does commute but $\overrightarrow{\mathrm{S}}$ does not). Therefore, $\overrightarrow{\mathrm{J}}$ is a constant of motion but $\vec{m}_{\mathrm{J}}$ is not; we can think of $\vec{S}$ and $\overrightarrow{\mathrm{L}}$ and thus $\overrightarrow{\mathrm{m}}_{\mathrm{J}}$ as rotating around the fixed vector $\vec{J}$ (see Figure 2.1).

Figure 2.1: Neither $\vec{L}, \vec{S}$ nor $\vec{m}_{J}$ are constants of motion, only $\stackrel{\rightharpoonup}{\mathrm{J}}$.


The typical time scale of this rotation should be $\frac{h}{|\lambda|}$. For "slow" experiments like magnetization measurements, only a time averaged $\overrightarrow{\mathrm{m}}_{\text {obs }}$ will be observable. We can determine it by projecting $\overrightarrow{\mathrm{m}}_{\mathrm{J}}$ on the direction of the constant $\overrightarrow{\mathrm{J}}$ :

$$
\begin{align*}
\stackrel{\rightharpoonup}{m}_{\text {obs }} & =\frac{\left(\vec{m}_{\mathrm{J}} \cdot \overrightarrow{\mathrm{~J}}\right) \overrightarrow{\mathrm{J}}}{\overrightarrow{\mathrm{~J}} \cdot \overrightarrow{\mathrm{~J}}}=-\mu_{\mathrm{B}} \frac{[(\overrightarrow{\mathrm{~J}}+\overrightarrow{\mathrm{S}}) \cdot \overrightarrow{\mathrm{J}}] \overrightarrow{\mathrm{J}}}{\overrightarrow{\mathrm{~J}} \cdot \overrightarrow{\mathrm{~J}}}=-\mu_{\mathrm{B}} \overrightarrow{\mathrm{~J}}-\mu_{\mathrm{B}} \frac{(\overrightarrow{\mathrm{~S}} \cdot \overrightarrow{\mathrm{~J}}) \overrightarrow{\mathrm{J}}}{\overrightarrow{\mathrm{~J}} \cdot \overrightarrow{\mathrm{~J}}} \\
& =-\mu_{\mathrm{B}} \overrightarrow{\mathrm{~J}}+\frac{\mu_{\mathrm{B}}}{2} \frac{(\overrightarrow{\mathrm{~J}}-\overrightarrow{\mathrm{S}})^{2}-\overrightarrow{\mathrm{J}} \cdot \overrightarrow{\mathrm{~J}}-\overrightarrow{\mathrm{S}} \cdot \overrightarrow{\mathrm{~S}}_{\overrightarrow{\mathrm{S}}} \overrightarrow{\mathrm{~J}} \text { and with } \overrightarrow{\mathrm{J}}-\overrightarrow{\mathrm{S}}=\overrightarrow{\mathrm{L}}}{\overrightarrow{\mathrm{~J}} \cdot \overrightarrow{\mathrm{~J}}} \\
\overrightarrow{\mathrm{~m}}_{\text {obs }} & =-\mu_{\mathrm{J}} \overrightarrow{\mathrm{~J}}-\frac{\mu_{\mathrm{B}}}{2} \frac{\mathrm{~J}(\mathrm{~J}+1)+\mathrm{S}(\mathrm{~S}+1)-\mathrm{L}(\mathrm{~L}+1)}{\mathrm{J}(\mathrm{~J}+1)}=:-\mathrm{g}_{J} \mu_{B} \overrightarrow{\mathrm{~J}} \tag{2.20}
\end{align*}
$$

after introducing the Landé g factor

$$
\begin{equation*}
g_{J}=1+\frac{\mathrm{J}(\mathrm{~J}+1)+\mathrm{S}(\mathrm{~S}+1)-\mathrm{L}(\mathrm{~L}+1)}{2 \mathrm{~J}(\mathrm{~J}+1)} \tag{2.21}
\end{equation*}
$$

$g_{\mathrm{J}}$ satisfies $0 \leqslant \mathrm{~g}_{\mathrm{J}} \leqslant 2$ and can be smaller than the orbital value $\mathrm{g}_{\mathrm{L}}=1$.

