3 Summation of angular momentum

For systems with rotational invariance, the total angular momentum is conserved. In the case of many-particle systems (e.g. atoms), the total angular momentum can consist of the angular momenta of the single-particle subsystems. Even for one-particle system, the total angular momentum can consist of, say, an orbital angular momentum $\vec{L}$ and a spin $\vec{S}$, $\vec{J} = \vec{L} + \vec{S}$. Hence, we have to learn how to add angular momenta. This is not as easy in quantum mechanics as in classical mechanics (where only classical 3-vectors have to be added), but the combination of different state spaces have to be mapped onto the state space of the total angular momentum.

3.1 Special properties of angular momentum

Let us first recall basic facts about angular momentum, as known from QM 1. The components of angular momentum satisfy

$$[J_i, J_j] = i\hbar \varepsilon_{ijk} J_k \qquad (3.1)$$

In the following, we will choose the convention

$\underline{\hbar = 1}$ for notational simplicity.

The maximum set of compatible operators consists, for instance, of $\vec{J}^2$ and J_z with corresponding eigenvalue equations

$$\begin{aligned} \vec{J}^2 |jm\rangle &= j(j+1)\, |jm\rangle \quad , j \in \tfrac{1}{2}\mathbb{N}_0 \\ J_z |jm\rangle &= m\, |jm\rangle \quad , m = -j, \dots, j \end{aligned} \tag{3.2}$$

The eigenstates can be generated from the ladder operators

$$J_\pm = J_x \pm i J_y \quad , \quad J_-^\dagger = J_+ \tag{3.3}$$

which act on the eigenstates as follows

$$J_\pm |jm\rangle = C^\pm_{jm} |j, m\pm 1\rangle$$

where $$C^\pm_{jm} = \sqrt{j(j+1) - m(m\pm 1)} \,. \tag{3.4}$$

The quantum number j classifies the $(2j+1)$-dimensional irreducible representation of the angular momentum algebra. Let us denote the representation space as $\mathcal{H}_j$,

3.2 Summation of angular momentum

Let us consider two angular momenta $\vec{J}_1$ and $\vec{J}_2$ (representing, e.g., orbital $\vec{J}_1 = \vec{L}$ and spin $\vec{J}_2 = \vec{S}$ angular momentum of one electron, or two orbital angular momenta of two electrons in a helium atom) with eigenstates $|j_1 m_1\rangle$ and $|j_2, m_2\rangle$.

The total state space can be understood as a product space: $\mathcal{H}_{j_1 j_2} = \mathcal{H}_{j_1} \otimes \mathcal{H}_{j_2}$ with basis

$$|j_1 m_1\, j_2 m_2\rangle = |j_1 m_1\rangle \otimes |j_2 m_2\rangle \qquad (3.5)$$

This space has dimension

$$\dim(\mathcal{H}_{j_1 j_2}) = \dim(\mathcal{H}_{j_1}) \cdot \dim(\mathcal{H}_{j_2}) \qquad (3.6)$$
$$= (2j_1+1)(2j_2+1)$$

The product states are eigenstates of $\vec{J}_1^2$, $\vec{J}_2^2$, J_{1z} and J_{2z},

$$\vec{J}_1^2 |j_1 m_1 j_2 m_2\rangle = j_1(j_1+1)\, |j_1 m_1 j_2 m_2\rangle, \quad J_{1z}|j_1 m_1 j_2 m_2\rangle = m_1 |j_1 m_1 j_2 m_2\rangle$$

$$\vec{J}_2^2 |j_1 m_1 j_2 m_2\rangle = j_2(j_2+1)\, |j_1 m_1 j_2 m_2\rangle, \quad J_{2z}|j_1 m_1 j_2 m_2\rangle = m_2 |j_1 m_1 j_2 m_2\rangle \qquad (3.7)$$

The total angular momentum

$$\vec{J} = \vec{J}_1 + \vec{J}_2 \tag{3.8}$$

also satisfies the angular momentum algebra (as $\vec{J}_1$ and $\vec{J}_2$ trivially commute, i.e. the act on different spaces). Hence the must be a basis, in which $\vec{J}^2$ and J_z are diagonal. Furthermore, $\vec{J}_1^2$ and $\vec{J}_2^2$ comute with $\vec{J}$, hence

$$\vec{J}^2, J_z, \vec{J}_1^2, \vec{J}_2^2 \tag{3.9}$$

form a basis of compatible operators. Let us denote the corresponding orthonormalized eigenstates by $|j_1 j_2 j m\rangle$,

$$\vec{J}^2 |j_1 j_2 j m\rangle = j(j+1) |j_1 j_2 j m\rangle \,, \; J_z |j_1 j_2 j m\rangle = m |j_1 j_2 j m\rangle$$

$$\vec{J}_1^2 |j_1 j_2 j m\rangle = j_1(j_1+1) |j_1 j_2 j m\rangle \quad \vec{J}_2^2 |j_1 j_2 j m\rangle = j_2(j_2+1) |j_1 j_2 j m\rangle \tag{3.10}$$

The sets of states $|j_1 m_1 j_2 m_2\rangle$, $|j_1 j_2 j m\rangle$ now form two base systems of one and the same space: $\mathcal{H}_{j_1 j_2}$. Hence, one set should be representable as a linear combination of the othe set:

e.g.

$$|j_1 j_2 j m\rangle = \sum_{m_1 m_2} \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle \quad |j_1 m_1 j_2 m_2\rangle \tag{3.11}$$

Here, we have taken into account that all states are eigenstates of $\vec{J}_1^2$ and $\vec{J}_2^2$. Hence, the associated eigenvalues must be equal in order for the scalar product not to vanish. These scalar products, or matrix elements,

$$\langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle$$

are also called Clebsch-Gordan coefficients.

(Different notations are used in the literature,

$$\langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle \equiv \langle j_1 m_1 j_2 m_2 | j m\rangle = C^{jm}_{j_1 m_1 j_2 m_2} \tag{3.12}$$

)

Let us derive some important properties of these coefficients. As $J_z = J_{1z} + J_{2z}$ is hermitean,

$$m \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle = \langle j_1 m_1 j_2 m_2 | J_z | j_1 j_2 j m\rangle = (m_1 + m_2)\langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle$$

Hence, the coefficients are only non-vanishing, (3.13)

if the selection rule

$$m = m_1 + m_2 \tag{3.14}$$

holds. Hence (3.11) reduces to

$$|j_1 j_2 jm\rangle = \sum_{m=m_1+m_2} \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle \; |j_1 m_1 j_2 m_2\rangle \tag{3.15}$$

The eigenvalue m has, in fact, a degeneracy which is equal to the number of possible pairs (m_1, m_2) satisfying $m_1 + m_2 = m$.

Without loss of generality, let us assume $j_1 \geq j_2$ in the following.

The maximal value of m is not degenerate, since

$$\max m = j_1 + j_2 \tag{3.16}$$

The corresponding state is $|j_1 j_1\rangle \otimes |j_2 j_2\rangle$ with maximal $J_{z1,2}$ eigenvalues. This state is annihilated by both ladder operators $J_{+1,2}$.

Since

$$\vec{J}^2 = (\vec{J}_1 + \vec{J}_2)^2 = \vec{J}_1^2 + \vec{J}_2^2 + 2\,\vec{J}_1 \cdot \vec{J}_2$$

$$= \vec{J}_1^2 + \vec{J}_2^2 + 2 J_{1z} J_{2z} + J_{1+} J_{2-} + J_{1-} J_{2+} \,, \qquad (3.17)$$

This state is also eigenstate of $\vec{J}^2$:

$$\vec{J}^2 |j_1 j_1 j_2 j_2\rangle = \vec{J}^2 |j_1 j_1\rangle \otimes |j_2 j_2\rangle$$

$$= \underbrace{\left(j_1(j_1+1) + j_2(j_2+1) + 2 j_1 j_2\right)}_{|j_1 j_1 j_2 j_2\rangle} + \Big(\underbrace{J_{1+} |j_1 j_1\rangle}_{=0} \otimes J_{2-} |j_2 j_2\rangle + J_{1-} |j_1 j_1\rangle \otimes \underbrace{J_{2+} |j_2 j_2\rangle}_{=0} \Big)$$

$$= (j_1 + j_2)(j_1 + j_2 + 1) \qquad (3.18)$$

Hence $|j_1 j_1\rangle \otimes |j_2 j_2\rangle$ is obviously the state with angular momentum quantum number $j = j_1 + j_2$ and magnetic quantum number $m = j$: $|j_1 j_1 j_2 j_2\rangle \equiv |j_1 j_2\, j\, (j_1 + j_2)\rangle$

Applying the ladder operator $J_- = J_x - i J_y$ to this state generates the $2j+1$ eigenstates

$$|j_1 j_2\, j\, m\rangle \quad \text{with} \quad j = j_1 + j_2 \,, \; -j \le m \le j \qquad (3.19)$$

Hence the total system contains a "multiplet" with angular momentum $j = j_1 + j_2$.

Is this all there is?

No: we already know that there is a degeneracy of states with eigenvalue m. In particular there must be two states in the total system with eigenvalue $m = j_1 + j_2 - 1$ corresponding to the two pairs $(m_1 = j_1,\ m_2 = j_2 - 1)$ and $(m_1 = j_1 - 1,\ m_2 = j_2)$, but the multiplett (3.19) contains only one such state with eigenvalue $m = j_1 + j_2 - 1$.

Hence there must be another state with this eigenvalue, which is now the maximal remaing magnetic quantum number of that part of the system that we still don't know. The corresponding state is annihilated by J_+ (as there is no state left with a higher magnetic quantum number). It must therefore constitute the state of maximal magnetic quantum number of another multiplett with $j = j_1 + j_2 - 1$. Constructing this multiplett by applying J_-, the remaing states again have a state with maximum magnetic quantum numbe $m = j_1 + j_2 - 2$ belonging to a further multiplett with $j = j_1 + j_2 - 2$, and so on.

This leads to the construction of multiplets with

$$j = j_1+j_2 \,,\; j_1+j_2-1 \,,\; \dots \,,\; |j_1-j_2| \tag{3.20}$$

which exhausts the degeneracy of the magnetic quantum number m. We conclude that the total angular-momentum quantum number obeys the rule

$$|j_1-j_2| \le j \le j_1+j_2 \tag{3.21}$$

It is easy to verify that this exhaust all possible states by comparing the dimensionality (# of states) of all these multiplets:

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1) \tag{3.22}$$

$$\dim h_{j_1 j_2} = \dim h_{j_1} \dim h_{j_2}$$

Thus we have proved that the tensor product of two representations h_{j_1} and h_{j_2} of two angular momentum algebras contains a number of representations of the total angular momentum algebra:

$$h_{j_1} \otimes h_{j_2} = h_{j_1+j_2} \oplus h_{j_1+j_2-1} \oplus \dots \oplus h_{|j_1-j_2|} . \qquad (3.23)$$

In group theory, the multiplets are often abbreviated by their dimension. For instance, the triplet of three spin-1 states $|j,m\rangle = \{|1,-1\rangle, |1,0\rangle, |1,1\rangle\}$ would be called simply $\underline{3}$. Adding two different spin-1 multiplets, i.e. forming the tensor product of these states, leads to 9 different states $|j_1 m_1 j_2 m_2\rangle$ which can be decomposed into a quintet, triplet and singlet of the total angular momentum:

$$\underset{\uparrow\, j_1=1}{\underline{3}} \otimes \underset{\uparrow\, j_1=1}{\underline{3}} = \underset{\uparrow\, j=2}{\underline{5}} + \underset{\uparrow\, j=1}{\underline{3}} + \underset{\uparrow\, j=0}{\underline{1}} \qquad (3.24)$$

Correspondingly, a product of two independent spin-$\frac{1}{2}$ states can be understood as a linear combination of a triplet and a singlet,

$$\underline{2} \otimes \underline{2} = \underline{3} \oplus \underline{1} \qquad (3.25)$$

3.3 Determination of Clebsch-Gordan coefficients

Apart from trivial phase conventions, the CG coefficients can be inferred from recursion rules. In the following, we derive these rules and apply them to a specific example. Let us first recall that we have introduced the CG coefficients by means of a change of basis in (3.11):

$$|j_1 j_2\, jm\rangle = \sum_{m_1+m_2=m} \langle j_1 m_1 j_2 m_2 | j_1 j_2\, jm\rangle \; |j_1 m_1 j_2 m_2\rangle \tag{3.26}$$

Projection onto $\langle j_1 j_2\, j'm'|$ yields

$$\delta_{jj'}\delta_{mm'} = \sum_{m_1+m_2=m} \langle j_1 m_1 j_2 m_2 | j_1 j_2 jm\rangle \langle j_1 j_2 j'm' | j_1 m_1 j_2 m_2\rangle \tag{3.27}$$

For $j=j'$ and $m=m'$, this implies

$$\sum_{m_1+m_2=m} |\langle j_1 m_1 j_2 m_2 | j_1 j_2 jm\rangle|^2 = 1 \tag{3.28}$$

With hindsight, we can choose all CG coefficients real,

$$\langle j_1 m_1 j_2 m_2 | j_1 j_2 jm\rangle \in \mathbb{R} \tag{3.29}$$

We can also perform an inverse base change,

$$|j_1 j_2 m_2\rangle = \sum_{j, m=m_1+m_2} \langle j_1 j_2 j m | j_1 m_1 j_2 m_2\rangle \; |j_1 j_2 j m\rangle \tag{3.30}$$

with the inverse CG coefficients $\langle j_1 j_2 j m | j_1 m_1 j_2 m_2\rangle$ which due to (3.29) obey

$$\langle j_1 j_2 j m | j_1 m_1 j_2 m_2\rangle = \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\rangle \tag{3.31}$$

Projection of (3.30) onto $\langle j_1 m_1' j_2 m_2'|$ yields

$$\sum_{j, m=m_1+m_2} \langle j_1 j_2 j m | j_1 m_1 j_2 m_2\rangle \langle j_1 m_1' j_2 m_2' | j_1 j_2 j m\rangle$$

$$= \delta_{m_1 m_1'} \delta_{m_2 m_2'} \tag{3.32}$$

Note that the j-sum in (3.30) and (3.32) has to satisfy the constraint (3.21).

The recursion relations now follow from the matrix elements of $J_\pm = J_{1\pm} + J_{2\pm}$ (using $J_\pm^\dagger = J_\mp$).

$$C_{jm}^{\pm} \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m\pm 1\rangle = \langle j_1 m_1 j_2 m_2 | J_\pm | j_1 j_2 j m\rangle$$

$$= C_{j_1 m_1}^{\mp} \langle j_1 m_1 \mp 1 \; j_2 m_2 | j_1 j_2 j m\rangle + C_{j_2 m_2}^{\mp} \langle j_1 m_1 \; j_2 m_2 \mp 1 | j_1 j_2 j m\rangle$$

(3.33)

where we have used the property (3.4) of the ladder operator. The transposed matrix elements yield another recursion formula,

$$C^{\pm}_{jm} \langle j_1 j_2 j m \pm 1 | j_1 m_1 j_2 m_2 \rangle = \langle j_1 j_2 j m | J_{\mp} | j_1 m_1 j_2 m_2 \rangle$$

$$= C^{\mp}_{j_1 m_1} \langle j_1 j_2 j m | j_1 m_1 \mp 1 \; j_2 m_2 \rangle + C^{\mp}_{j_2 m_2} \langle j_1 j_2 j m | j_1 m_1 j_2 m_2 \mp 1 \rangle$$

(3.34)

The initial condition for the recursion relation can be provided by our observation in (3.18) that

$$| j_1 j_2 j_2 j_2 \rangle = | j_1 j_2 \; (j_1 + j_2) \; (j_1 + j_2) \rangle \qquad (3.35)$$

such that

$$1 = \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle$$

$$\text{for } j = j_1 + j_2 \;, m_1 = j_1 \;, m_2 = j_2 \qquad (3.36)$$

$$m = m_1 + m_2 = j$$

Also the CG coefficients have to obey the normalization (3.28).

Let us apply these recursion relations to compute the CG coefficients for a coupling of an orbital angular momentum $j_1 = l$ and a spin $j_2 = \frac{1}{2}$.

Since

$$h_0 \otimes h_{1/2} = h_{1/2} \quad , h_\ell \otimes h_{1/2} = h_{\ell-\frac{1}{2}} \otimes h_{\ell+\frac{1}{2}} \tag{3.37}$$

the total angular momentum j of an s shell electron is $j=\frac{1}{2}$, of a p shell electron $j=+\frac{1}{2}$ or $j=\frac{3}{2}$, and of a d shell electron $j=\frac{3}{2}$ or $j=\frac{5}{2}$, and so on.

The case $\ell=0$ is almost trivial:

$$\langle 0\ 0\ \tfrac{1}{2}\ m_s \mid \tfrac{1}{2}\ m\rangle = \delta_{m,m_s} \tag{3.38}$$

These are the complete set of CG coefficients for this case.

For $\ell>0$, i.e. $\ell\geq 1$, we have $j=\ell\pm\frac{1}{2}$. Using (3.36) for this case, implies

$$1 = \langle \ell\ \ell\ \tfrac{1}{2}\ \tfrac{1}{2} \mid \ell+\tfrac{1}{2}\ \ell+\tfrac{1}{2}\rangle \tag{3.39}$$

In (3.38) and (3.39) we have used the reduced notation $\langle j_1\ m_1\ j_2\ m_2 \mid j\ m\rangle$ for the CG coefficients.

Now, we apply the recursion relation (3.33) with the lower sign to (3.39) (using $j_2=m_2=\frac{1}{2}$):

$$C^{-}_{jm} \langle l\, m_l\, \tfrac{1}{2}\tfrac{1}{2} \mid j\, m-1\rangle = C^{+}_{l m_l} \langle l\, m_l+1\, \tfrac{1}{2}\tfrac{1}{2} \mid j\, m\rangle \qquad (3.40)$$

The second term on the RHS vanishes as a state with $j_s = \frac{1}{2}$ and $m_s = \frac{3}{2}$ doesn't exist. Using the selection rule $m_l + \frac{1}{2} = m - 1 \Rightarrow m_l = m - \frac{3}{2}$ and shifting $m \to m+1$, we get ($\overset{\text{use}}{j} = l + \frac{1}{2}$)

$$\sqrt{(l+\tfrac{1}{2})(l+\tfrac{3}{2}) - (m+1)m}\ \langle l\, m-\tfrac{1}{2}, \tfrac{1}{2}\tfrac{1}{2} \mid l+\tfrac{1}{2}\, m\rangle$$

$$= \sqrt{l(l+1) - (m-\tfrac{1}{2})(m+\tfrac{1}{2})}\ \langle l\, m+\tfrac{1}{2}\ \tfrac{1}{2}\tfrac{1}{2} \mid l+\tfrac{1}{2}\, m+1\rangle \qquad (3.41)$$

or

$$\langle l\, m-\tfrac{1}{2}\ \tfrac{1}{2}\tfrac{1}{2} \mid l+\tfrac{1}{2}\, m\rangle = \sqrt{\frac{l+m+\frac{1}{2}}{l+m+\frac{3}{2}}}\ \langle l, m+\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2} \mid l+\tfrac{1}{2}\ m+1\rangle \qquad (3.42)$$

where we divided by the common factor $(l-m+\frac{1}{2})^{1/2}$.

Iterating (3.42) until we hit (3.39), we find

$$\langle l, m-\tfrac{1}{2}, \tfrac{1}{2}\tfrac{1}{2} \mid l+\tfrac{1}{2}, m\rangle = \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} \qquad (3.43)$$

Analogously, we can compute the CG coefficients for the $j = l - \frac{1}{2}$ states. The result can be summarized in a table.

$j \backslash m_s$	$1/2$	$-1/2$
$l+\frac{1}{2}$	$\sqrt{\frac{l+m+1/2}{2l+1}}$	$\sqrt{\frac{l-m+1/2}{2l+1}}$
$l-\frac{1}{2}$	$-\sqrt{\frac{l-m+1/2}{2l+1}}$	$\sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}$

(3.44)

3.4 Tensor operators

3.4.1 Scalar operators

Scalar operators such as the Hamiltonian, the kinetic energy or the spin-orbit coupling $\vec{L}\cdot\vec{S}$ are invariant under rotations. More formally, let S be a scalar operator,

$$\Gamma(U)\, S\, \Gamma(U^{-1}) = S \quad \text{or} \quad [\vec{J}, S] = 0, \tag{3.45}$$

where $U \in SU(2)$ represents a quantum mechanical rotation, and $\Gamma(U)$ is its representation on the Hilbert space on which S acts.

From (3.45), we deduce that

$$\langle jm | [\vec{J}^2, S] | j'm' \rangle = 0$$
$$\text{and} \quad \langle jm | [J_z, S] | j'm' \rangle = 0 \,, \tag{3.46}$$

implying that

$$\langle jm | S | jm' \rangle = \delta_{jj'} \delta_{mm'} \langle jm | S | jm \rangle \tag{3.47}$$

This simple selection rule means that S acting on a certain total angular momentum eigenstate does not modify the angular momentum quantum numbers. Hence, matrix elements of a scalar operator between states of different angular momenta vanish.

We can prove another important property. Consider

$$\langle jm | \underbrace{J_+ S}_{= S J_+} J_- | jm \rangle = (C_{jm}^-)^2 \langle jm-1 | S | jm-1 \rangle$$

$$= \langle jm | S J_+ J_- | jm \rangle = \underbrace{C_{jm-1}^+ C_{jm}^-}_{\equiv (C_{jm}^-)^2} \langle jm | S | jm \rangle \tag{3.48}$$

This implies that the matrix elements

$$\langle jm | S | jm \rangle \tag{3.49}$$

of a scalar operator cannot depend on the

magnetic quantum number

$$\langle jm|S|jm'\rangle = \delta_{jj'}\delta_{mm'}\langle j\|S\|j\rangle \qquad (3.50)$$

where the notation of the reduced matrix element $\langle j\|S\|j\rangle$ simply means that (in practise) one can use any convenient (often $m=j$) value for m to compute this matrix element.

Similar simplifications hold for vector or more generally tensor operators.

3.42 Tensor operators

Selection rules play an important role for computing matrix elements, for instance, for atomic spectra. E.g., the dipole vector operator is responsible for emission, absorption and scattering of electromagnetic radiation.

Let us first recall, how eigenstates of angular momentum respond under rotations. As constant global rotations do not change the modulus of the angular momentum

the rotated state can be spanned by the complete basis for fixed quantum number j:

$$\Gamma(U)\,|jm\rangle = \sum_{m'} D^{j}_{m'm}\,|jm'\rangle\,, \qquad (3.51)$$

where the coefficients

$$D^{j}_{m'm} = \langle jm'|\,\Gamma(U)\,|jm\rangle \qquad (3.52)$$

form a $2j+1$-dimensional unitary representation of $SU(2)$ on the subspace $\mathcal{H}_j$. Product states transform accordingly

$$\Gamma(U)\,|j_1 m_1 j_2 m_2\rangle = \sum_{m_1' m_2'} D^{j_1}_{m_1' m_1} D^{j_2}_{m_2' m_2}\,|j_1 m_1' j_2 m_2'\rangle \qquad (3.53)$$

Now, we define a tensor T^{j}_{m} as an object which transforms according to

$$\Gamma(U)\,T^{j}_{m}\,\Gamma^{-1}(U) = \sum_{m'} D^{j}_{m'm}(U)\,T^{j}_{m'}\,, \qquad U \in SU(2) \qquad (3.54)$$

To be precise, T^{j}_{m} are the "normal components" of an irreducible tensor operator of rank j.

As a consequence, the states $T^j_M |jm\rangle$ transform similar to product states, as

$$\Gamma(U)\, T^j_M |jm\rangle = \Gamma(U) T^J_n \underbrace{\Gamma^{-1}(U)\Gamma(U)}_{=\mathbb{1}} |jm\rangle$$

$$= \sum_{M',m'} D^J_{M'M} D^j_{m'm} T^J_{M'} |jm'\rangle, \qquad (3.55)$$

Hence, we expect that the states $T^J_M |jm\rangle$ also group in multiplets with angular momenta ranging from $J+j$ to $|J-j|$.

Using $U = e^{i\vec{\alpha}\cdot\vec{J}}$ and expanding (3.54) infinitesimally, we find together with (3.52) that

$$[J_\pm, T^j_m] = C^\pm_{jm} T^j_{m\pm1}, \quad [J_3, T^j_m] = m T^j_m. \qquad (3.56)$$

Roughly speaking, the T^j_m behave very similar to the states $|jm\rangle$. The last commutator implies

$$J_3 T^J_M |jm\rangle = T^J_n J_3 |jm\rangle + M T^j_m = (m+M) T^J_n |jm\rangle. \qquad (3.57)$$

As the normal component of T^J_M increase the eigenvalue of J_3 by M, we find a

first selection rule:

$$m \neq M+m' \Rightarrow \langle jm | T^J_M | j'm' \rangle = 0 . \qquad (3.58)$$

(A difference between T^J_m and the states $|jm\rangle$ is that $T^J_M |jm\rangle$ are generally not eigenstates of $\vec{J}^2$.)

Let us now study matrix elements of the first commutator in (3.56):

$$\langle jm | J_\mp T^J_M - T^J_M J_\mp - c^\mp_{JM} T^J_{M\mp1} | j'm' \rangle = 0 \qquad (3.59)$$

This leads to the recursion relations

$$c^\pm_{jm} \langle jm\pm1 | T^J_M | j'm' \rangle$$

$$= c^\mp_{JM} \langle jm | T^J_{M\mp1} | j'm' \rangle + c^\mp_{j,m\pm1} \langle jm | T^J_M | j'm'\mp1 \rangle$$

(3.60)

These are also the recursion relations for the inverse CG coefficients (3.34). We conclude that the matrix element $\langle jm | T^J_M | j'm' \rangle$ and those CG coefficients are identical up to a global factor which has to be independent of the magnetic quantum numbers.

This is the content of the Wigner-Eckart theorem:

$$\langle jm | T^J_M | j'm' \rangle = \langle jm | JM, j'm' \rangle \cdot \langle j \| T^J \| j' \rangle \tag{3.61}$$

The proportionality factor $\langle j \| T^J \| j' \rangle$ is indeed fixed by, e.g., the matrix element with maximum possible magnetic quantum numbers. In any case, it is a reduced matrix element which cannot depend on the magnetic quantum numbers involved.

The theorem implies another selection rule:

$$\langle jm | T^J_M | j'm' \rangle = 0 \tag{3.62}$$

$$\text{for} \quad j \neq \{ j'+J, j'+J-1, \ldots, |j'-J| \}.$$

So far, we worked with the normal components T^J_M of a tensor operator. In many cases, we are interested also in a cartesian representation. For instance, for integer j, $\Gamma(U)$ is a representation of the rotation group $SO(3)$, $\Gamma(U) \equiv \Gamma(R)$ where $R \in SO(3)$. The cartesian components $T^j_{i_1 \ldots i_j}$ then transform as

$$\Gamma(R)\; T^{j}_{i_1 \dots i_j}\; \Gamma(R^{-1})$$

$$= R_{i i_1} \dots R_{j i_j}\, T^{i}_{i_1 \dots i_j} \quad , R \in SO(3) \qquad (3.63)$$

Note that in $\mathbb{R}^3$, the irreducible tensor T^j can only have $2j+1$ linearly independent components. Except for scalar and vector operators, there are generally algebraic relations between cartesian components of tensor operators.

For a vector operator the change from cartesian to normal components is similar to the transition from (x,y,z) coordinates to spherical harmonics,

$$Y_{11} = -\frac{c}{\sqrt{2}}(x+iy)\,, \quad Y_{10} = c\cdot z \quad , \quad Y_{1-1} = \frac{c}{\sqrt{2}}(x-iy)\,, \qquad (3.64)$$

where $c = \sqrt{\frac{3}{4\pi}}\,\frac{1}{r}$, and the spherical harmonics transform as $|1\,m\rangle$. Analogously, the normal components of a vector are

$$V_1 = -\frac{1}{\sqrt{2}}(V_x + iV_y)\,, \quad V_0 = V_z\,, \quad V_{-1} = \frac{1}{\sqrt{2}}(V_x - iV_y)\,. \qquad (3.65)$$

The standard commutation relations for a cartesian vector operator,

$$[J_i, V_j] = i\varepsilon_{ijk} V_k \tag{3.66}$$

are equivalent to (3.56) for $j=1$ and the normal components V_m given in (3.65). For a vector operator, the Wigner-Eckart theorem reads

$$\langle jm | V_M | j'm' \rangle = \langle jm | 1\, M\, j'm' \rangle \langle j \| V \| j' \rangle . \tag{3.66}$$

As an application of these rather formal considerations, let us first compute the reduced matrix elements of the angular momentum operator with normal components,

$$J_1 = -\frac{1}{\sqrt{2}} J_+ \quad , J_0 = J_z \, , \; J_{-1} = \frac{1}{\sqrt{2}} J_- . \tag{3.67}$$

(3.66) then yields

$$\langle jm | J_M | j'm' \rangle = \langle jm | 1 M j'm' \rangle \langle j \| J \| j' \rangle \tag{3.68}$$

The left-hand side vanishes for $j \neq j'$, hence:

$$\langle j \| J \| j' \rangle = 0 \quad \text{for} \quad j \neq j' \tag{3.69}$$

For $j = j'$, let us choose $M=0$ and $m-m' = j$,

$$\Rightarrow \quad \underbrace{\langle jj|J_0|jj\rangle}_{= j\langle j,1|jj\rangle = j} = \langle jj|10\,jj\rangle \langle j\|J\|j\rangle . \qquad (3.70)$$

Here, we need the CG coefficient $\langle jj|10\,jj\rangle$ which occurs when coupling an arbitrary j-plet with a spin-1 angular momentum. The result is

$$\langle jj\,|\,10\,jj\rangle = \frac{j}{\sqrt{j(j+1)}} . \qquad (3.71)$$

The reduced matrix element thus gives

$$\langle j\|J\|j\rangle = \sqrt{j(j+1)} \qquad (3.72)$$

We use this to rewrite (3.68) as $(j=j')$

$$\langle jm\,|\,J_M\,|\,j\,m'\rangle = \langle jm\,|\,1M\,jm\rangle \sqrt{j(j+1)} \qquad (3.73)$$

Since the matrix element ~~on~~ the RHS occurs in the Wigner-Eckart theorem for a general vector operator (3.66), we deduce

$$\langle jm|V_M|jm'\rangle = \langle jm|J_M|jm'\rangle \frac{\langle j\|V\|j\rangle}{\sqrt{j(j+1)}} . \qquad (3.74)$$

Since the relation between normal and cartesian components is linear, this is equivalent to

$$\langle jm|\vec{V}|jm'\rangle = \langle jm|\vec{J}|jm'\rangle \frac{\langle j\|V\|j\rangle}{\sqrt{j(j+1)}}. \qquad (3.75)$$

The reduced matrix element is actually easy to get: multiply by $\langle jm'|\vec{J}|jm''\rangle$ and sum over m',

$$\langle jm|\vec{V}\cdot\vec{J}|jm''\rangle = \underbrace{\langle jm|\vec{J}^2|jm''\rangle}_{=\delta_{mm''}\, j(j+1)} \frac{\langle j\|V\|j\rangle}{\sqrt{j(j+1)}} \qquad (3.76)$$

$$= \delta_{mm''}\sqrt{j(j+1)}\,\langle j\|V\|j\rangle .$$

We finally obtain for (3.75):

$$\langle jm|\vec{V}|jm'\rangle = \langle jm|\vec{J}|jm'\rangle \frac{\langle jm|\vec{V}\cdot\vec{J}|jm\rangle}{j(j+1)}$$

$$= \langle jm|\vec{J}|jm'\rangle \frac{\langle j\|\vec{V}\cdot\vec{J}\|j\rangle}{j(j+1)}, \qquad (3.77)$$

where we have used (3.50) as $\vec{V}\cdot\vec{J}$ is a scalar operator.

We conclude that the matrix elements of an arbitrary vector operator $\vec{V}$ are equal to those of $\vec{J}$ on the subspace h_j up to j-dependent factors. This does <u>not</u> mean that the operators $\vec{J}$ and $\vec{V}$

are proportional to each other. For instance, whereas $\langle jm | \vec{J} | j \pm 1\ m' \rangle$ vanishes, this is generally not true for an arbitrary vector operator $\vec{V}$.

3.4.3 Landé factors

As an application of the Wigner-Eckart theorem, we compute the Landé factors. The latter are proportionality constants ~~of the~~ characterizing the level splitting of degenerate energy levels where the degeneracy is lifted by an external magnetic field.

Let $\vec{L} = \vec{L}_1 + \ldots + \vec{L}_N$ be the total orbital angular momentum of an N electron atom. Similarly $\vec{S} = \vec{S}_1 + \ldots \vec{S}_N$ is the total spin. For a vanishing nuclear spin, the total angular momentum is

$$\vec{J} = \vec{L} + \vec{S} \tag{3.78}$$

Let H_0 be the Hamiltonian of the system without an external magnetic field.
We assume that a maximal set of compatible operators is given by

$$H_0 , \vec{L}^2 , \vec{S}^2 , \vec{J}^2 , J_z . \tag{3.78}$$

Let $|E_0 L S J M\rangle$ denote the simultaneous eigen-basis of all operators with eigenvalues

$$H_0 \to E_0 , \ \vec{L}^2 \to L(L+1) , \ \vec{S}^2 \to S(S+1) , \ \vec{J}^2 \to J(J+1) , J_z \to M .$$

(NB: This assumption holds at least for light atoms.) (3.80)

Since by definition $[H_0, \vec{J}] = 0$, all $2J+1$ states

$$|E_0 L S J M\rangle \quad \text{with } M = -J , \dots , J \tag{3.81}$$

in an irreducible J-multiplet have the same energy.

Let $\mathcal{H}(E_0, L, S, J, M)$ denote the state space that is spanned by the eigenvectors $|E_0 L S J M\rangle$.

In the presence of an external magnetic field $\vec{B} = B \hat{e}_z$, the (perturbed) Hamilton operator becomes

$$H = H_0 + H_1 \ , \text{ where } \ H_1 = \omega_L (L_z + 2 S_z) . \tag{3.82}$$

The factor 2 in front of S_z arises from the gyromagnetic ratio of the electron spin. We have also introduced the Larmor-Frequency ω_L ,

$$\omega_L = - \frac{q B}{2m} = - \frac{\mu_B}{\hbar} B , \tag{3.83}$$

where μ_B is Bohr's magneton.

Let us compute the level splitting to first order in the perturbative expansion, i.e., we need the matrix elements of H_1 on the subspace $\mathcal{H}(E_0, L, S, J)$.

On this subspace, we have according to the theorem (3.77):

$$\vec{L} = \vec{J} \quad \frac{\langle \vec{L}\cdot\vec{J}\rangle_{E_0 L S J M}}{J(J+1)}$$

$$\vec{S} = \vec{J} \quad \frac{\langle \vec{S}\cdot\vec{J}\rangle_{E_0 L S J M}}{J(J+1)} \qquad (3.84)$$

involving the reduced matrix elements of $\vec{L}\cdot\vec{J}$ and $\vec{S}\cdot\vec{J}$, which do not depend on M. These can be computed by observing that

$$\vec{L}\cdot\vec{J} = \vec{L}\cdot(\vec{L}+\vec{S}) = \vec{L}^2 + \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right) \qquad (3.85)$$

$$\vec{S}\cdot\vec{J} = \vec{S}\cdot(\vec{L}+\vec{S}) = \vec{S}^2 + \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$$

and consequently

$$\langle \vec{L}\cdot\vec{J}\rangle_{E_0 L S J M} = L(L+1) + \frac{1}{2}\left(J(J+1) - L(L+1) - S(S+1)\right)$$

$$\langle \vec{S}\cdot\vec{J}\rangle_{E_0 L S J M} = S(S+1) + \frac{1}{2}\left(J(J+1) - L(L+1) - S(S+1)\right)$$

(3.86)

Inserting this into (3.84) and then into (3.82), we get

$$\langle H_1 \rangle_{\text{EOESIM}} = g_J \omega_L J_z \tag{3.87}$$

where we have introduced the Landé factor

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} . \tag{3.88}$$

We conclude that the first-order correction due to the magnetic field leads to a level splitting/shift of

$$\Delta E_1 = \hbar \omega_L g_J M . \tag{3.89}$$

So the magnetic field lifts the degeneracy of the angular momentum multiplets completely and leads to $2J+1$ equidistant energy levels. This generalizes earlier results from QM I on the Zeeman effect.

3.5 The real (more realistic) hydrogen atom

In the introductory QM course, we have solved the idealized hydrogen atom, defined by a Hamiltonian

$$H = \frac{\vec{p}^2}{2\mu} - \frac{Ze^2}{r} \qquad (3.90a)$$

with eigenvalues $E_n = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2}$.

Here μ is the reduced mass $\mu = \frac{M m_e}{M + m_e}$

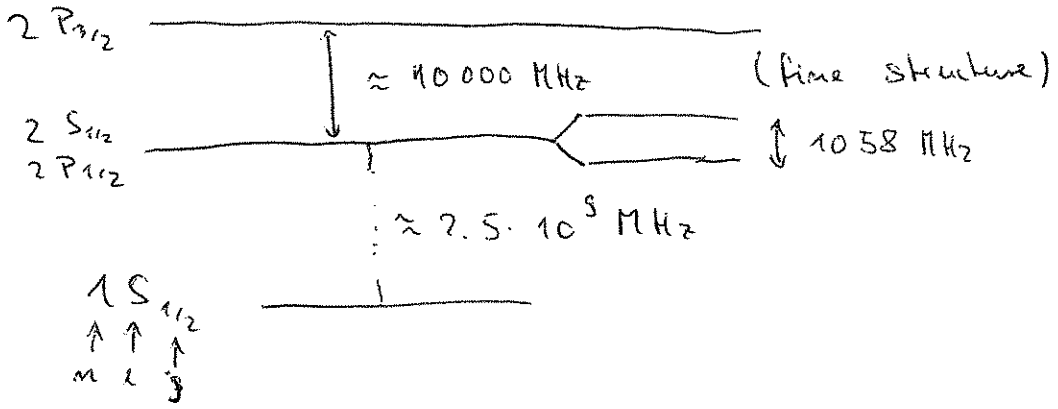
where M is the proton mass and m_e the electron.

For hydrogen ($M \triangleq 935$ MeV), we have

$$\frac{\mu}{m_e} = \frac{M}{M+m_e} = \frac{1}{1+\frac{m_e}{M}} \simeq 1 - \frac{m_e}{M} \simeq 1 - 5.4 \cdot 10^{-4} \qquad (3.90b)$$

The spectrum has an $2 \cdot n^2$-fold degeneracy, where the factor 2 is due to the spin degree of freedom, and n^2 counts the number of different angular momentum states belonging to the principal quantum number n. If this was exact, all photons emitted from an $n=2$ states (by relaxing) to the $n=1$ states would have to have the same

frequency. First signatures of level splitting were already observed by Michelson (1887). Precise data was taken by G. Hansen (1925) using Zeiss instruments. This level splitting can be understood in terms of the following scheme



The main part of the splitting (fine structure) will be discussed in the following. The small splitting between $2S_{1/2}$ and $2p_{1/2}$ was discovered in 1947 by Lamb and Retherford (Lamb shift). Its understanding requires knowledge about the quantized radiation field (which will not be discussed in these lecture notes).

3.5.1 Fine structure

The fine structure of atomic spectra arises from different sources: spin-orbit interactions and relativistic corrections. Relativistic corrections, in turn, occur as corrections to the kinetic energy and as a particular new term (Darwin term) arising from the Dirac equation, a relativistic quantum mechanical wave equation for spin-$\frac{1}{2}$ particles. The latter correction applies for $l=0$ states and will be discussed later.

Let us first start with relativistic corrections to the kinetic energy (see problem sheet 01).

The classical expression for the relativistic kinetic energy is

$$T = \sqrt{(\vec{p}c)^2 + (m_e c^2)^2} - m_e c^2$$

$$\simeq \frac{\vec{p}^2}{2m_e} - \frac{1}{8}\frac{(\vec{p}^2)^2}{m_e^3 c^2} + \dots$$

$$= T_0 + T_1 \,, \qquad (3.90c)$$

where T_0 is the standard non-relativistic Hamiltonian, and T_1 can be treated as a correction

within perturbation theory:

$$T_1 = -\frac{1}{2m_e c^2}\left(\frac{\hat{p}^2}{2m_e}\right)^2 = -\frac{1}{2m_e c^2}\left(H_0 + \frac{Ze^2}{r}\right)\left(H_0 + \frac{Ze^2}{r}\right) \qquad (3.91)$$

where, this time, the reduced mass in H_0 has to be replaced by the electron mass. To first order in perturbation theory, we need to compute the expectation value of T_1 WRT the (usual) hydrogen states $|nlm\rangle$:

$$\begin{aligned}\langle nlm|T_1|nlm\rangle &= -\frac{1}{2m_e c^2}\left(E_n^2 + 2E_n Ze^2\langle nlm|\frac{1}{r}|nlm\rangle \right.\\ &\qquad \left. + Z^2e^4\langle nlm|\frac{1}{r^2}|nlm\rangle\right)\\ &= E_n(Z\alpha)^2\left(\frac{1}{n(l+\frac{1}{2})} - \frac{3}{4n^2}\right),\end{aligned} \qquad (3.92)$$

where $E_n = -\frac{m_e c^2}{2}\frac{(Z\alpha)^2}{n^2}$.

Here, we have used the expectation values of $\frac{1}{r}$ and $\frac{1}{r^2}$ as known from the non-relativistic case. Since these expectation values are l-dependent, this relativistic correction already induces a level-splitting between, e.g., s and p electrons.

The second (more interesting) correction arises from spin-orbit interactions:

The electron spin goes along with a magnetic moment

$$\vec{\mu} = -\frac{e g}{2 m_e c} \vec{S} \,, \qquad (3.93)$$

where g is the gyromagnetic ratio. In the following, we will use $g \simeq 2$ (as predicted by the Dirac equation). Corrections due to the quantized radiation field lead to slight deviations from $g = 2$ (but will not be discussed here).

Classically, a moving electron does not only see the Coulomb field of the nucleus,

$$\vec{E} = -\vec{\nabla}\phi(r) \,, \quad \phi = -\frac{Ze}{r} \qquad (3.94)$$

but also – in its rest frame – a magnetic component. For a uniform motion of the electron at a speed $\vec{v} = \frac{\vec{p}}{m_e}$ relative to the nucleus, the magnetic field to first order in $\vec{v}/c$ in the electrons rest frame is

$$\vec{B} = -\frac{\vec{v}}{c} \times \vec{E} \,. \qquad (3.95)$$

The corresponding energy of the magnetic moment in this field is

$$-\vec{\mu} \cdot \vec{B} = \frac{eg}{2m_e c} \vec{S} \cdot \vec{B} \overset{g=2}{=} -\frac{e}{m_e c^2} \vec{S} \cdot (\vec{v} \times \vec{E})$$

$$= \frac{e}{m_e^2 c^2} \vec{S} \cdot (\vec{p} \times \vec{\nabla} \phi)$$

$$= \frac{e}{m_e^2 c^2} \vec{S} \cdot \underbrace{(\vec{p} \times \vec{r})}_{= -\vec{L}} \frac{1}{r} \frac{d\phi}{dr}$$

$$= -\frac{e}{m_e^2 c^2} \vec{S} \cdot \vec{L} \frac{1}{r} \frac{d\phi}{dr} \qquad (3.96)$$

However, the electron is not moving uniformly but "circulates" around the nucleus. This leads (relativistically) to a precession of the electron spin. Taking this "Thomas-precession" into account, reduces the spin-orbit interaction by a factor $\frac{1}{2}$:

$$H_{so} = -\frac{e}{2m_e^2 c^2} \vec{S} \cdot \vec{L} \frac{1}{r} \frac{d\phi}{dr} \,. \qquad (3.97)$$

Again, we compute the corrections induced by this spin-orbit coupling to first order

within perturbation theory. As H_{so} does not commute with H_0 due to the appearance of $\vec{L}$, the states $|n\ell m\rangle$ tensor multiplied with the spin eigenstates $|\frac{1}{2} m_s\rangle$ no longer are eigenstates of the complete system. But since

$$\vec{S}\cdot\vec{L} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right), \tag{3.98}$$

the eigenstates of $(\vec{J}^2, \vec{L}^2, \vec{S}^2, J_z)$ are eigenstates of the complete Hamiltonian $H_0 + H_{so}$. As the product space $\mathcal{H}_\ell \otimes \mathcal{H}_{1/2}$ can be decomposed into

$$\mathcal{H}_\ell \otimes \mathcal{H}_{1/2} = \mathcal{H}_{\ell+\frac{1}{2}} \oplus \mathcal{H}_{\ell-1/2} \tag{3.99}$$

(for $\ell > 0$), a proper basis is given by

$$|n\ell\tfrac{1}{2} jm\rangle \quad \text{where} \quad j = \ell \pm \tfrac{1}{2} \tag{3.100}$$

Within perturbation theory, we need to compute

$$\langle n\ell\tfrac{1}{2} jm | H_{so} | n\ell\tfrac{1}{2} jm\rangle$$

$$= -\frac{Ze^2}{2m_e^2 c^2}\langle \ell\tfrac{1}{2} jm|\vec{S}\cdot\vec{L}|\ell\tfrac{1}{2} jm\rangle \int dr\, r^2 f_{n\ell}^2(r)\frac{1}{r^3}, \tag{3.101}$$

where we have used $\frac{1}{r}\frac{d\Phi}{dr} = \frac{Ze}{r^2}$ and radial parts of the hydrogen wave functions $f_{n\ell}(r)$.

For $\ell > 0$ the radial integral yields

$$\int dr\, r^2\, f_{nl}^2(r)\, \frac{1}{r^3} = \frac{Z^3}{a_0^3}\, \frac{1}{n^3\, l(l+\frac{1}{2})(l+1)}$$

for $l > 0$. (3.102)

The corresponding matrix element of H_{so} reads

$$\langle n\, l\tfrac{1}{2}\, jm | H_{so} | n\, l\tfrac{1}{2}\, jm\rangle = -E_n \left(\frac{Z\alpha}{\hbar}\right)^2 \frac{\langle l\tfrac{1}{2}\, jm | \vec{S}\cdot\vec{L} | l\tfrac{1}{2} jm\rangle}{n\, l(l+\frac{1}{2})(l+1)}$$

(3.103)

(for $l > 0$). Depending on $j = l \pm \frac{1}{2}$, this yields

$$\Delta E_{so} = -E_n\, \frac{Z^2\alpha^2}{2n}\, \frac{1}{(l+\frac{1}{2})(l+1)} \qquad \text{for } j = l+\tfrac{1}{2}$$

$$\Delta E_{so} = E_n\, \frac{Z^2\alpha^2}{2n}\, \frac{1}{l(l+\frac{1}{2})} \qquad \text{for } j = l-\tfrac{1}{2}.$$

(3.104)

Adding up the relativistic correction (3.92) and the spin-orbit coupling (3.104), we find a remarkably simple formula for the fine structure

$$\Delta E_{FS} = E_n\, (Z\alpha)^2\, \frac{1}{n} \left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \qquad (3.105)$$

which holds for both cases $j = l \pm \frac{1}{2}$. In this derivation we have confined ourselves to the case $l > 0$, since the radial integral diverges for $l = 0$ (the s shell wave functions are finite at the origin).

However, this divergence is an artefact which is removed by the Darwin term mentioned above arising from the Dirac equation. As a result, this form of ΔE_{FS} also holds for $l = 0$.

We observe that the level splitting does not depend on l but only on j.

To this order, the states $2s_{1/2}$ and $2p_{1/2}$ should have the same energy. This is "almost" true apart from the Lamb shift mentioned above.

3.5.2 Hyperfine structure

Another step closer to realistic atom spectra is taken by considering also the magnetic dipole moment of the nucleus. For instance, the hydrogen nucleus is a spin-$\frac{1}{2}$ proton with magnetic dipole moment

$$\vec{\mu} = \frac{q}{2m_p c} g_p \vec{I} \quad \text{, where } g_p \cong 5.585 \tag{3.106}$$

Due to the occurrence of the heavy proton mass in the denominator, the nuclear magnetism is less important than the electron magnetism. Still, the coupling between nuclear magnetic moment and electron spin leads to a further small splitting of the energy levels. This "hyperfine" splitting has an enormeous practical relevance in various fields of physics (astronomy, cold atom gases) as the electromagnetic transition frequencies are often easily accessible (e.g. the 21 cm line in radio astronomy).

Let us more generally consider the magnetic moment of a nucleus with charge Z_q, mass m_N and gyromagnetic ratio g_N

$$\vec{\mu} = \frac{Z_q}{2m_N c} g_N \vec{I} \qquad (3.107)$$

This point-like magnetic dipole induces a magnetic field which can be parametrized by a vector potential

$$\vec{A}(\vec{x}) = -\frac{1}{4\pi}(\vec{\mu} \times \vec{\nabla})\frac{1}{r} = \frac{1}{4\pi}\frac{\vec{\mu} \times \vec{x}}{r^3} \qquad (3.108)$$

The associated magnetic field is

$$\vec{B} = \vec{\nabla} \times \vec{A} = -\frac{1}{4\pi}\vec{\mu}\vec{\nabla}^2\frac{1}{r} + \frac{1}{4\pi}\vec{\nabla}(\vec{\mu}\cdot\vec{\nabla})\frac{1}{r} \qquad (3.109)$$

Since $\frac{1}{r}$ is the Green's function of the Laplace operator, we have $-\frac{1}{4\pi}\vec{\nabla}^2\frac{1}{r} = \delta(r)$, such that

$$B_i = \mu_i \delta(r) + \frac{1}{4\pi}\mu_j \frac{\partial^2}{\partial x_i \partial x_j}\frac{1}{r} \qquad (3.110)$$

The interaction between the electron magnetic dipole and the nuclear magnetic dipole giving rise to (3.110) leads to a contribution to the

Hamiltonian

$$H_{HF} = -\vec{\mu}_e \cdot \vec{B} \quad , \text{ where } \vec{\mu}_e \approx \frac{e}{m_e c} \vec{S} . \qquad (3.111)$$

Using the representation (3.110) of the magnetic field, we get

$$H_{HF} = -\vec{\mu}_e \cdot \vec{\mu} \, \delta(r) - \frac{1}{4} \mu_{ei} \left(\frac{\partial^2}{\partial x_i \partial x_j} \frac{1}{r} \right) \mu_j . \qquad (3.112)$$

Let us in the following concentrate on the level splitting of the s electrons (for which the wave functions are nonzero at $r = 0$). As the corresponding wave functions are spherically symmetric, i.e. $Y_{00} = \frac{1}{\sqrt{4\pi}} = \text{const.}$, the associated expectation value of H_{HF} contains

spherical symmetry

$$\int d^3x \, f_{n0}^2(r) \frac{\partial^2}{\partial x_i \partial x_j} \frac{1}{r} = \frac{1}{3} \delta_{ij} \int d^3x \, f_{n0}^2(r) \vec{\nabla}^2 \frac{1}{r}$$

$$= -\frac{4\pi}{3} \delta_{ij} \int d^3x \, f_{n0}^2(r) \, \delta^{(3)}(\vec{x})$$

$$= -\frac{4\pi}{3} \left(\frac{Z}{a_0 n} \right)^3 \qquad (3.113)$$

where we have used the explicit form of the normalized radial wave function $f_{n0}(r)$, cf. an introductory course on the ideal hydrogen atom.

In total the 2nd term of (3.112) is $-\frac{1}{3}$ x the 1st term, and we get

$$\langle n\,00|H_{HF}|n\,00\rangle = -\frac{2}{3}\cdot\frac{4}{n^3}\frac{Z^3}{a_0^3}\vec{\mu}_e\cdot\vec{\mu}$$

$$\overset{(3.107)}{=} \frac{4}{3}\left(\frac{e^2}{a_0}\right) g_N\left(\frac{m_e}{m_N}\right)\left(\frac{\alpha^2}{n^3}\right) Z^4\left(\frac{\vec{S}\cdot\vec{I}}{\hbar^2}\right) \qquad (3.114)$$

Let us define the total spin of the nucleus-electron system

$$\vec{F} = \vec{S} + \vec{I} \qquad (3.115)$$

such that

$$\frac{2}{\hbar^2}\vec{S}\cdot\vec{I} = \frac{1}{\hbar^2}\left(\vec{F}^2 - \vec{S}^2 - \vec{I}^2\right)$$

$$= F(F+1) - \frac{3}{4} - I(I+1)$$

$$= \begin{cases} I & \text{for } F = I + \frac{1}{2} \\ -I-1 & \text{for } F = I - \frac{1}{2} \end{cases} \qquad (3.116)$$

We conclude the the level splitting for vanishing orbital angular momentum is

$$\Delta E_{HF}$$
$$= \Delta \langle n\,0\,0 | H_{HF} | n\,0\,0 \rangle$$

$$= \frac{4}{3} \left(\frac{e^2}{a_0}\right) g_N \left(\frac{m_e}{m_N}\right) \left(\frac{\alpha^2}{n^3}\right) Z^4 \left(I + \frac{1}{2}\right). \qquad (3.117)$$

For the hydrogen atom, where $g_N = g_p$, $I = \frac{1}{2}$, we get for this hyperfine splitting:

$$\Delta E_{HF} = \frac{4}{3} \left(\frac{e^2}{a_0}\right) g_p \left(\frac{m_e}{m_N}\right) \alpha^2 \qquad (3.118)$$

This corresponds to a wave length of 21 cm in the microwave regime. This spectral transition line being emitted from the triplet state $F = 1$ towards the singlet state $F = 0$ is very important in radio astronomy (for measuring Doppler shifts or hydrogen distributions).