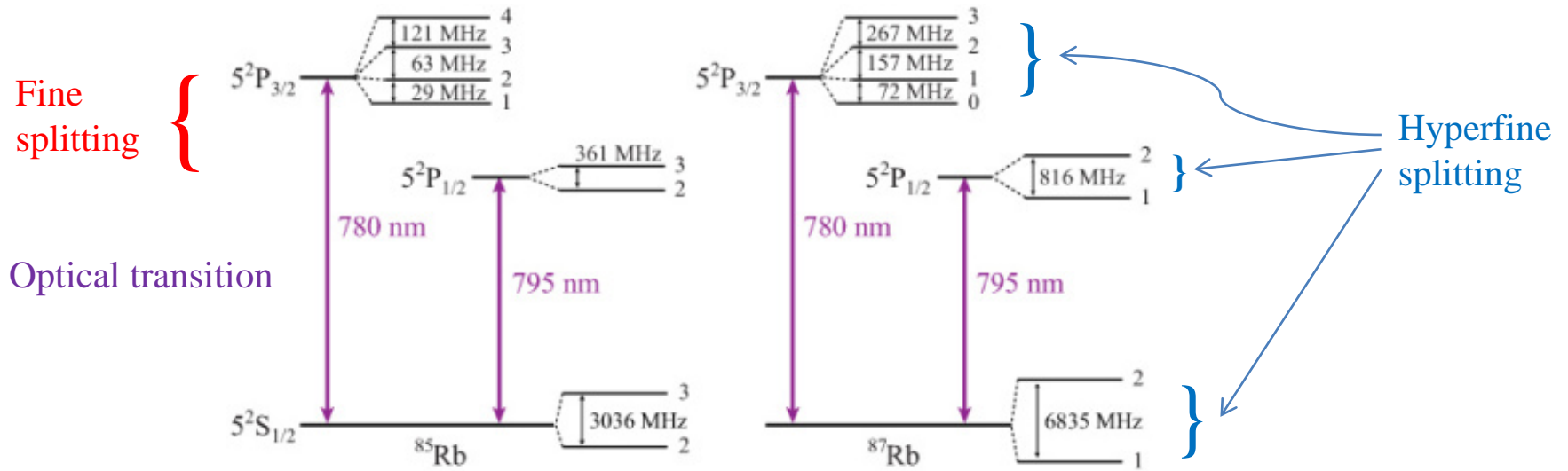


# V. Spectra of alkali atoms

Alkali atoms: single valence electron; spectra are like that of the hydrogen atom.



Optical transition: Coulomb interactions.

Fine splitting: spin-orbit coupling for the valence electron.

Hyperfine splitting: interacting of magnetic momenta of the electron and the nucleus.

## Spin-orbit coupling for the electron (fine structure)

Energy of a magnetic moment in a magnetic field:  $U = -\boldsymbol{\mu} \cdot \mathbf{B}$

Magnetic momentum of an electron:  $\hat{\boldsymbol{\mu}} = g_S \mu_B \hat{\mathbf{S}}$

Bohr magneton: in SI units:  $\mu_B = \frac{\hbar |e| \hbar}{2m_e}$  (in CGS units:  $\mu_B = \frac{\hbar |e| \hbar}{2m_e c}$  )

Gyromagnetic factor for the electron spin:  $g_S = -2$

To calculate the magnetic field experienced by the valence electron, consider **classical picture** in the reference frame where the electron is at the rest and the core (the nucleus & other electrons) rotates around. The core has the charge  $+|e|$ , and its velocity  $\mathbf{v}_c = -\mathbf{v}_e$ .

The latter velocity  $|\mathbf{v}_e| \ll c$ .

Then, in this reference frame the magnetic field (in SI units!) is

$$\mathbf{B} \approx -c^{-2} \mathbf{v}_e \times \mathbf{E} = -\frac{\mathbf{p}_e \times \mathbf{E}}{m_e c^2}$$

where  $\mathbf{E} = \frac{e\mathbf{r}}{4\pi\epsilon_0 r^3}$  is the Coulomb field,

$\mathbf{r}$  is directed from the nucleus to the electron,  $\mathbf{r} \times \mathbf{p}_e = \hbar \mathbf{L}$  .

Recall that in SI units  $c = \frac{1}{\sqrt{\epsilon_0 \mu_0}}$

Finally, we arrive at the following quantum-mechanical (operator) expression for the spin-orbit interaction energy:

$$\hat{H}_{so} = \frac{1}{2} \frac{\mu_0}{4\pi} \left( \frac{\hbar e}{m_e} \right)^2 \frac{1}{r^3} \hat{\mathbf{L}} \hat{\mathbf{S}}$$

Factor  $1/2$  is due to the **Thomas precession** (a relativistic effect that arises in **rotating** frames of reference), which was not taken into account in the previous (simplified) derivation.

In CGS system of units  $\mu_0/(4\pi)$  must be replaced by  $c^{-2}$ .

The spin-orbit coupling is zero for states with  $L = 0$  (e.g., an alkali atom ground state).

For the states with  $L = 1, 2, 3, \dots$

$$\left\langle \frac{1}{r^3} \right\rangle = 4\pi \int_0^\infty dr r^2 [R_{nL}(r)]^2 r^{-3}$$

is finite, since the radial wave function  $R_{nL}(r) \propto r^L$ ,  $r \rightarrow 0$ .

$\langle r^{-3} \rangle$  decreases with increasing  $L$ .

In general, the fine-structure splitting of an atomic state is given by the spin-orbit interaction

$$\hat{H}_{so} = a_{fs} \hat{\mathbf{L}} \hat{\mathbf{S}}$$

$a_{fs}$  depends on the particular electronic state ( $n, L$ ).

The electron orbital and spin momenta are coupled to the full electron angular momentum:

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

$$\hat{\mathbf{L}}\hat{\mathbf{S}} = \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)$$

The eigenvalues:  $\hat{\mathbf{L}}\hat{\mathbf{S}} = \frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$

For atomic states with  $S = 1/2$ , like in alkali atoms,  $J = L \pm 1/2$  for  $L = 1, 2, 3, \dots$

The fine splitting between the states with  $J = L + 1/2$  and  $J = L - 1/2$  is  $a_{fs} (2L + 1)/2$ .

Prove for arbitrary  $L$  and  $S$ , that the fine splitting does not shift the „center of gravity“ of the multiplet with respect to the energy of the electron state, i.e., the weighted sum of all the eigenenergies of the spin-orbit coupling Hamiltonian is zero, the weight of the state with the total electron momentum  $J$  being equal to  $(2J + 1)$ .

Use summation formulae

$$\sum_{k=1}^n k = \frac{n(n+1)}{2}, \quad \sum_{k=1}^n k^2 = \frac{n(n+1)(2n+1)}{6}, \quad \sum_{k=1}^n k^3 = \frac{n^2(n+1)^2}{4}.$$

$$\sum_{k=m}^n f(k) = \sum_{k=1}^n f(k) - \sum_{k=1}^{m-1} f(k)$$

## Magnetic momentum of a valence electron in an alkali atom

$$\hat{\boldsymbol{\mu}} = -\mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) = -\mu_B (\hat{\mathbf{J}} + \hat{\mathbf{S}}) = -\mu_B (2\hat{\mathbf{J}} - \hat{\mathbf{L}})$$

Its matrix elements within a manifold of sublevels of a certain component of the fine structure are, according to the Wigner-Eckart theorem:

$$\langle LSJM' | \hat{\mu}_{1\kappa} | LSJM \rangle = -\mu_B \frac{C_{JM1\kappa}^{JM'}}{\sqrt{2J+1}} \left( \langle LSJ \| \hat{L}_1 \| LSJ \rangle + 2 \langle LSJ \| \hat{S}_1 \| LSJ \rangle \right)$$

On the other hand,

$$\langle LSJM' | \hat{J}_{1\kappa} | LSJM \rangle = \frac{C_{JM1\kappa}^{JM'}}{\sqrt{2J+1}} \langle LSJ \| \hat{J}_1 \| LSJ \rangle$$

Therefore, for the processes when an atom remains in the same sublevel manifold of a certain fine structure component, we may write

$$\hat{\boldsymbol{\mu}} = g_J \mu_B \hat{\mathbf{J}}$$

$$\begin{aligned} g_J &= - \frac{\langle LSJ \| \hat{L}_1 \| LSJ \rangle + 2 \langle LSJ \| \hat{S}_1 \| LSJ \rangle}{\langle LSJ \| \hat{J}_1 \| LSJ \rangle} = \\ &= -1 - \frac{\langle LSJ \| \hat{S}_1 \| LSJ \rangle}{\langle LSJ \| \hat{J}_1 \| LSJ \rangle} = -2 + \frac{\langle LSJ \| \hat{L}_1 \| LSJ \rangle}{\langle LSJ \| \hat{J}_1 \| LSJ \rangle} \end{aligned}$$

An easy way to derive  $g_J$

$$\hat{\mu} = -\mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) = -\mu_B (\hat{\mathbf{J}} + \hat{\mathbf{S}}) = g_J \mu_B \hat{\mathbf{J}}$$

$$g_J \mu_B \hat{\mathbf{J}}^2 = -\mu_B (\hat{\mathbf{J}}^2 + \hat{\mathbf{S}} \hat{\mathbf{J}})$$

$$\hat{\mathbf{S}} \hat{\mathbf{J}} = \frac{1}{2} [\hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - (\hat{\mathbf{J}} - \hat{\mathbf{S}})^2] = \frac{1}{2} [\hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2]$$

Eigenvalues :

$$\hat{\mathbf{S}} \hat{\mathbf{J}} = \frac{J(J+1) + S(S+1) - L(L+1)}{2}$$

$$g_J = - \left[ 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right]$$

For alkali atoms  $S=1/2$ .

To obtain the same result strictly from

$$g_J = -1 - \frac{\langle LSJ \| \hat{S}_1 \| LSJ \rangle}{\langle LSJ \| \hat{J}_1 \| LSJ \rangle}$$

we need to derive the necessary reduced matrix elements and find the way to calculate matrix elements for operators acting on a subsystem (e.g., spin) of the whole system.

## Calculation of $\langle LSJ \| \hat{\mathbf{J}}_1 \| LSJ \rangle$

The total momentum operator does not change  $J$  (as well as  $L$  and  $S$ ):

$$\langle LSJ' M | \hat{\mathbf{J}}_{10} | LSJM \rangle = \delta_{JJ'} M$$

← Why?

On the other hand,

$$\langle LSJ' M | \hat{\mathbf{J}}_{10} | LSJM \rangle = \frac{C_{JM10}^{J'M}}{\sqrt{2J'+1}} \langle LSJ' \| \hat{\mathbf{J}}_1 \| LSJ \rangle$$

Comparing to the value of the respective CG coefficient (e.g., from the tables in the book by Varshalovich, Moskalev & Khersonsky),

$$C_{JM10}^{JM} = \frac{M}{\sqrt{J(J+1)}}$$

we find finally

$$\langle LSJ' \| \hat{\mathbf{J}}_1 \| LSJ \rangle = \delta_{JJ'} \sqrt{J(J+1)(2J+1)}$$

Now we need to express  $\langle LSJ \| \hat{\mathbf{S}}_1 \| LSJ \rangle$  through  $\langle S \| \hat{\mathbf{S}}_1 \| S \rangle = \sqrt{S(S+1)(2S+1)}$



Here spin is free, not coupled with the orbital momentum

# Matrix elements of operators acting on one subsystem

(Example: spin coupled to orbital momentum)

$$\begin{aligned} \langle n'_1 j'_1 n'_2 j'_2 j' m' | \hat{P}_{\alpha\alpha}(1) | n_1 j_1 n_2 j_2 j m \rangle &= \\ &= \delta_{j'_2 j_2} \delta_{n'_2 n_2} (-1)^{j+j'_1+j_2-a} \Pi_j C_{j m \alpha}^{j' m'} \begin{Bmatrix} j_1 & j_2 & j \\ j' & a & j'_1 \end{Bmatrix} \langle n'_1 j'_1 | \hat{P}_\alpha(1) | n_1 j_1 \rangle \end{aligned} \quad (\text{V.*})$$

$$\Pi_{ab\dots c} \equiv \sqrt{(2a+1)(2b+1)\dots(2c+1)}$$

We start the proof by noticing that

$$\langle n'_1 j'_1 m'_1; n'_2 j'_2 m'_2 | \hat{P}_{\alpha\alpha}(1) | n_1 j_1 m_1; n_2 j_2 m_2 \rangle = \delta_{n'_2 n_2} \delta_{j'_2 j_2} \delta_{m'_2 m_2} \langle n'_1 j'_1 m'_1 | \hat{P}_{\alpha\alpha}(1) | n_1 j_1 m_1 \rangle$$

$$\text{By definition, } |n_1 j_1 n_2 j_2 j m \rangle = \sum_{m_1 m_2} C_{j_1 m_1 j_2 m_2}^{j m} |n_1 j_1 m_1; n_2 j_2 m_2 \rangle$$

$$\text{Then } \langle n'_1 j'_1 n'_2 j'_2 j' m' | \hat{P}_{\alpha\alpha}(1) | n_1 j_1 n_2 j_2 j m \rangle =$$

$$= \sum_{m_1, m'_1, m_2} \frac{(-1)^{2a}}{\sqrt{2j'_1+1}} C_{j'_1 m'_1 j_2 m_2}^{j' m'} C_{j_1 m_1 j_2 m_2}^{j m} C_{j_1 m_1 \alpha}^{j'_1 m'_1} \langle n'_1 j'_1 | \hat{P}_\alpha(1) | n_1 j_1 \rangle$$



The latter formula contains three CG coefficients. We also know that

$$\sum_{\substack{j_1 m_1, j_2 m_2, j_3 m_3 \\ j_1 m_1, j_2 m_2, j_3 m_3}} C_{j_1 m_1 j_2 m_2}^{j m} C_{j_1 m_1 j_2 m_2}^{j_{12} m_{12}} C_{j_1 m_1 j_2 m_2}^{j' m'} C_{j_2 m_2 j_3 m_3}^{j_{23} m_{23}} = \delta_{j j'} \delta_{m m'} (-1)^{j_1 + j_2 + j_3 + j} \sqrt{(2j_{12} + 1)(2j_{23} + 1)} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix} \quad (\text{V.**})$$

(sum over all projections, except of  $m$  and  $m'$ ).

From Eq. (V.\*) [a particular case of the Wigner-Eckart theorem] we see that

$$\sum_{m, \alpha} C_{j m \alpha}^{j' m'} \langle n_1' j_1' n_2' j_2' j' m' | \hat{P}_{\alpha\alpha}(1) | n_1 j_1 n_2 j_2 j m \rangle \quad \text{does not depend on } m'.$$

Now we calculate

$$\sum_{\substack{m_1, m_1', m_2 \\ m, \alpha}} \frac{(-1)^{2a}}{\sqrt{2j_1' + 1}} C_{j_1' m_1' j_2 m_2}^{j' m'} C_{j_1 m_1 j_2 m_2}^{j m} C_{j_1 m_1 \alpha}^{j_1' m_1'} C_{j m \alpha}^{j' m'} \quad (\text{V.***)}$$

Eq. (V.\*\*\*) is reduced to (V.\*\*\*) if we interchange the lower index pairs in  $\underline{\quad}$  and  $\underline{\quad}$ .

Then we recall that

$$C_{\alpha\alpha}^{c\gamma}{}_{b\beta} = (-1)^{a+b-c} C_{b\beta}^{c\gamma}{}_{\alpha\alpha}$$

$$\begin{aligned}
\sum_{\substack{m_1, m_1', m_2, \\ m, \alpha}} \frac{(-1)^{2a}}{\sqrt{2j_1'+1}} C_{j_1' m_1' j_2 m_2}^{j' m'} C_{j_1 m_1 j_2 m_2}^{j m} C_{j_1 m_1 a \alpha}^{j_1' m_1'} C_{j m a \alpha}^{j' m'} = \\
= (-1)^{a+2j_1+j_2+j-j_1'} \delta_{j j'} \delta_{m m'} \sqrt{2j+1} \begin{Bmatrix} a & j_1 & j_1' \\ j_2 & j' & j \end{Bmatrix} = \\
= (-1)^{j+j_1'+j_2-a} \delta_{j j'} \delta_{m m'} \sqrt{2j+1} \begin{Bmatrix} j_1 & j_2 & j \\ j' & a & j_1' \end{Bmatrix}
\end{aligned}$$

In the last equality we use the symmetry property of the  $6j$ -symbol and the fact that, according to the triangle rule,  $j_1 + a - j_1'$  is an integer number. The last equality proves that

$$\begin{aligned}
\langle n_1' j_1' n_2' j_2' j' m' | \hat{P}_{a\alpha}(1) | n_1 j_1 n_2 j_2 j m \rangle = \\
= \delta_{j_2' j_2} \delta_{n_2' n_2} (-1)^{j+j_1'+j_2-a} \Pi_j C_{j m a \alpha}^{j' m'} \begin{Bmatrix} j_1 & j_2 & j \\ j' & a & j_1' \end{Bmatrix} \langle n_1' j_1' | \hat{P}_a(1) | n_1 j_1 \rangle
\end{aligned}$$

where  $\Pi_j = \sqrt{2j+1}$

$$\langle LSJM' | \hat{S}_{1\kappa} | LSJM \rangle = (-1)^{L+S+J-1} \sqrt{2J+1} C_{JM1\kappa}^{JM'} \begin{Bmatrix} S & L & J \\ J & 1 & S \end{Bmatrix} \langle S || \hat{S}_1 || S \rangle$$

$$\langle S || \hat{S}_1 || S \rangle = \sqrt{S(S+1)(2S+1)}$$

$$\begin{Bmatrix} S & L & J \\ J & 1 & S \end{Bmatrix} = (-1)^{S+L+J+1} \frac{J(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)(2J+1)S(S+1)(2S+1)}}$$

$$\langle LSJ || \hat{S}_1 || LSJ \rangle = \sqrt{\frac{2J+1}{J(J+1)} \frac{J(J+1) + S(S+1) - L(L+1)}{2}}$$

$$g_J = - \left[ 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right]$$

## Hyperfine structure

Interaction of electronic and nuclear magnetic momenta

$$\hat{\boldsymbol{\mu}}_e = -\mu_B(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \quad \hat{\boldsymbol{\mu}}_n = g_I\mu_N\hat{\mathbf{I}} \leftarrow \text{Operator of the spin of the nucleus}$$

Nuclear magneton:

$$\mu_N = \frac{e\hbar}{2m_p} \quad (\text{SI}) \quad \mu_N = \frac{e\hbar}{2m_p c} \quad (\text{CGS})$$

Nuclear magneton is by 3 orders of magnitude smaller than the Bohr magneton. The hyperfine interaction (compared to the fine structure) can be considered as a perturbation.

Hamiltonian of the hyperfine interaction

$$\hat{H}_{hf} = \frac{\mu_0}{4\pi} \frac{2g_I\mu_N\mu_B}{r^3} \left[ \hat{\mathbf{L}}\hat{\mathbf{I}} + [3(\hat{\mathbf{S}}\mathbf{n})(\hat{\mathbf{I}}\mathbf{n}) - \hat{\mathbf{S}}\hat{\mathbf{I}}] \right]$$

Here  $\mathbf{n} = \mathbf{r} / r$ . In CGS units,  $\mu_0/(4\pi)$  is replaced by 1 [the factor  $c^{-2}$  is „absorbed“ by the Bohr and nuclear magnetons].

The 1st term is the coupling of the nuclear spin to the orbital motion of the electron. It is analogous to the fine structure, but by a factor  $\sim 0.001$  smaller.

The 2nd term is the magnetic interaction of the electron and nuclear spin at a distance  $r$ . It can be written in the tensor form as

$$\hat{H}_{SI} = \frac{\mu_0}{4\pi} \frac{2g_I\mu_N\mu_B}{r^3} \sum_{i,l=x,y,z} \left[ \frac{1}{2}(\hat{S}_i\hat{I}_l + \hat{S}_l\hat{I}_i) - \frac{1}{3}\delta_{il}(\hat{\mathbf{S}}\hat{\mathbf{I}}) \right] [3n_i n_l - \delta_{il}]$$

Symmetric tensor with zero trace, i.e., IR tensor of the rank 2, composed of electron and nuclear spin operators

Symmetric tensor with zero trace, i.e., IR tensor of the rank 2, acting on electr. orb. degrees of freedom and denoted by  $\hat{\mathcal{Q}}$

$$\hat{H}_{SI} \propto \{ \{ \hat{S}_1 \otimes \hat{I}_1 \}_2 \otimes \hat{\mathcal{Q}}_2 \}_0$$

A scalar product (defined only for two tensors of the same rank) is equal, up to a numerical factor, to the IR tensor product of the rank 0:

$$(\mathfrak{M}_J \cdot \mathfrak{N}_J) = (-1)^{-J} \sqrt{2J+1} \{ \mathfrak{M}_J \otimes \mathfrak{N}_J \}_{00},$$

$$(\tilde{\mathfrak{M}}_J \cdot \tilde{\mathfrak{N}}_J) = \sqrt{2J+1} \{ \tilde{\mathfrak{M}}_J \otimes \tilde{\mathfrak{N}}_J \}_{00}.$$

Matrix elements of a scalar product of two operators acting on different subsystems:

$$\begin{aligned} & \langle n'_1 j'_1 n'_2 j'_2 j' m' | (\hat{\mathbf{P}}_a(1) \cdot \hat{\mathbf{Q}}_a(2)) | n_1 j_1 n_2 j_2 j m \rangle = \\ & = \delta_{j' j} \delta_{m' m} (-1)^{j+j_1+j'_2} \begin{Bmatrix} j'_1 & j_1 & a \\ j_2 & j'_2 & j \end{Bmatrix} \langle n'_1 j'_1 | \hat{\mathbf{P}}_a(1) | n_1 j_1 \rangle \langle n'_2 j'_2 | \hat{\mathbf{Q}}_a(2) | n_2 j_2 \rangle \end{aligned}$$

Matrix element of an IR tensor product in a general case:

$$\begin{aligned} & \langle n'_1 j'_1 n'_2 j'_2 j' m' | \{ \hat{\mathbf{P}}_a(1) \otimes \hat{\mathbf{Q}}_b(2) \}_{c\gamma} | n_1 j_1 n_2 j_2 j m \rangle = \\ & = (-1)^{2c} \Pi_{c_j} C_{j m c \gamma}^{j' m'} \begin{Bmatrix} a & b & c \\ j'_1 & j'_2 & j' \\ j_1 & j_2 & j \end{Bmatrix} \langle n'_1 j'_1 | \hat{\mathbf{P}}_a(1) | n_1 j_1 \rangle \langle n'_2 j'_2 | \hat{\mathbf{Q}}_b(2) | n_2 j_2 \rangle \end{aligned}$$

## 9j-symbols [Wigner; Fano]

$$\begin{aligned} \langle j_1 j_2 (j_{12}) j_3 j_4 (j_{34}) j m | j_1 j_3 (j_{13}) j_2 j_4 (j_{24}) j' m' \rangle = \\ = \delta_{j j'} \delta_{m m'} [(2j_{12} + 1) (2j_{13} + 1) (2j_{24} + 1) (2j_{34} + 1)]^{\frac{1}{2}} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} \end{aligned}$$

It follows from the definition that

$$\begin{aligned} \sum_{m_1 m_2 m_3 m_4} C_{j_1 m_1 j_2 m_2}^{j_{12} m_{12}} C_{j_3 m_3 j_4 m_4}^{j_{34} m_{34}} C_{j_{12} m_{12} j_{34} m_{34}}^{j m} C_{j_1 m_1 j_3 m_3}^{j_{13} m_{13}} C_{j_2 m_2 j_4 m_4}^{j_{24} m_{24}} C_{j_{13} m_{13} j_{24} m_{24}}^{j' m'} = \\ = \delta_{j j'} \delta_{m m'} [(2j_{12} + 1) (2j_{13} + 1) (2j_{24} + 1) (2j_{34} + 1)]^{\frac{1}{2}} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix}. \end{aligned}$$

However, there is the problem with the both interaction terms  $\hat{H}_{LI} \propto \hat{\mathbf{L}}\hat{\mathbf{I}}$

and  $\hat{H}_{SI} \propto \{ \{ \hat{S}_1 \otimes \hat{I}_1 \}_2 \otimes \hat{Q}_2 \}_0$  . They yield zero splitting for states with

$L = 0$ . But the hyperfine splitting of the ground states of alkali metals ( $L=0$ ) is observed.

The reason is the Fermi contact interaction.

Consider an uniformly charged, rotating sphere. The magnetic field outside is dipole, the magnetic field inside the sphere is homogeneous, the magnetic induction is proportional to the angular velocity of rotation.

Fermi's idea: an electron inside the nucleus interacts via its magnetic moment with a homogeneous magnetic field. The corresponding Hamiltonian is

$$\hat{H}_{Fermi} = \frac{4}{3} \mu_0 g_I \mu_N \mu_B \delta(\mathbf{r}) \hat{\mathbf{S}}\hat{\mathbf{I}}, \text{ it gives non-zero contribution for } L=0 \text{ states only.}$$

Finally, since the hf interaction is only a perturbation to the fine structure, its effective Hamiltonian is

$$\hat{H}_{hf} = \mathcal{A}_{hf} \hat{\mathbf{J}}\hat{\mathbf{I}}$$

Its eigenvalues:  $\frac{1}{2} \mathcal{A}_{hf} [F(F+1) - J(J+1) - I(I+1)]$

Why for  $^{87}\text{Rb}$  ground state the  $F = 2$  sublevel has higher energy than the  $F = 1$  sublevel?



# VI. Spherical functions

Eigenvalue problem:

$$\hat{L}^2 Y_{lm}(\vartheta, \varphi) = l(l+1) Y_{lm}(\vartheta, \varphi)$$

$$\hat{L}_z Y_{lm}(\vartheta, \varphi) = m Y_{lm}(\vartheta, \varphi),$$

$$\left[ \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} + l(l+1) \right] Y_{lm}(\vartheta, \varphi) = 0,$$

$$\left[ i \frac{\partial}{\partial \varphi} + m \right] Y_{lm}(\vartheta, \varphi) = 0.$$

Boundary conditions

$$Y_{lm}(\vartheta, \varphi \pm 2\pi n) = Y_{lm}(\vartheta, \varphi),$$

$$\frac{\partial}{\partial \varphi} Y_{lm}(\vartheta, \varphi) \Big|_{\vartheta=0} = \frac{\partial}{\partial \varphi} Y_{lm}(\vartheta, \varphi) \Big|_{\vartheta=\pi} = 0.$$

Normalization

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta \sin \vartheta Y_{l'm'}^*(\vartheta, \varphi) Y_{l''m''}(\vartheta, \varphi) = \delta_{ll''} \delta_{mm''}$$

Phase condition:

$$Y_{l0}(0, 0) = \sqrt{\frac{2l+1}{4\pi}}$$

$$Y_{lm}^*(\vartheta, \varphi) = Y_{lm}(\vartheta, -\varphi) = (-1)^m Y_{l-m}(\vartheta, \varphi)$$

Modified spherical functions:

$$\tilde{Y}_{lm}(\vartheta, \varphi) = i^l Y_{lm}(\vartheta, \varphi),$$

$$Y_{lm}^*(\vartheta, \varphi) = (-1)^{l+m} \tilde{Y}_{l-m}(\vartheta, \varphi)$$

$$Y_{lm}(\vartheta, \varphi) = e^{im\varphi} \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \vartheta)$$

$$|m| \leq l$$

Associated Legendre polynomial

$$Y_{lm}(\vartheta, \varphi) = (-1)^m e^{im\varphi} \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l+m)!}{(l-m)!}} \left(\text{tg} \frac{\vartheta}{2}\right)^m \sum_s (-1)^s \frac{(l+s)!}{(l-s)!} \cdot \frac{\left(\sin \frac{\vartheta}{2}\right)^{2s}}{s!(s+m)!}$$

Sum over all  $s$  yielding non-negative arguments of the factorial.

$$Y_{lm}(\vartheta, \varphi) = e^{im\varphi} \sqrt{\frac{2l+1}{4\pi} \frac{(l+m)!}{(l-m)!}} \times$$

$\left[ \begin{array}{l} \times \\ \times \end{array} \right.$

$$\sum_{s=|m|, |m|+2, \dots}^l (-1)^{\frac{s+m}{2}} \frac{(l+s)!}{(s+m)! (s-m)!} \cdot \frac{(l+m)! (l-m)!}{(l+s)! (l-s)!} (\sin \vartheta)^s$$

$l-m$  even

$$\cos \vartheta \sum_{s=|m|, |m|+2, \dots}^{l-1} (-1)^{\frac{s+m}{2}} \frac{(l+s)!}{(s+m)! (s-m)!} \cdot \frac{(l+m-1)! (l-m-1)!}{(l+s-1)! (l-s-1)!} (\sin \vartheta)^s$$

$l-m$  odd

Spin functions – columns with  $(2S+1)$  components [or  $(2I+1)$  components].  
 Their addition to  $L$  (that yields  $J$  and  $F$ ) – using CG coefficients.