

Photoemission from 4f shell of rare-earth compounds

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0.1 4f shell Hamiltonian and its eigenstates

This text is a brief collection of information, which is needed to calculate angle-resolved 4f photoemission spectra of lanthanides.

1 Total 4f-shell Hamiltonian

The total 4f-shell Hamiltonian is

$$\hat{H} = \hat{H}_{CF} + \hat{H}_{ES} + \hat{H}_{SO} + \hat{H}_{CI} + \hat{H}_{CEF} + \hat{H}_{mag} + \dots \quad (1.1)$$

Here, \hat{H}_{CF} is a Hamiltonian of a central-field approximation. \hat{H}_{CF} is the most important part of the generic Hamiltonian. Other parts only make corrections that violate sphericity and splitting levels. \hat{H}_{ES} separate the different terms and other parts of the Hamiltonian give rise to the fine structure of the terms.

The nonrelativistic electrostatic part, which takes into account Coulomb interaction between electrons, is

$$\hat{H}_{ES} = \sum_{k=0,2,4,6} F^k(nf, nf) \hat{f}_k = \sum_{k=0}^3 \hat{e}_k E^k$$

Where $F^k(nf, nf)$ is the integral responsible for the angular component and \hat{f}_k is the Slater integral responsible for the radial component. Its good quantum numbers are $LM_S M_S$. The \hat{e}_k represent the angular part while the E^k are linear combinations of the Slater radial integrals $F^{(k)}$. The matrix elements are discussed in section 7. The matrices \hat{e}_k are tabulated in [1] for all f^n configurations, so there is no need to calculate them.

The spin-orbit interaction is

$$\hat{H}_{SO} = \sum_i \xi(r_i) \vec{l}_i \cdot \vec{s}_i$$

Its good quantum numbers are JM_J . Calculation of its matrix elements is discussed in section 8.

The free-ion configuration interaction (CI) Hamiltonian consists of two parts with two-body and three-body corrections:

$$\hat{H}_{CI} = \alpha \hat{L}^2 + \beta \hat{G}(G_2) + \gamma \hat{G}(R_7) + \sum_{i=2,3,4,6,7,8} T^i \hat{t}_i,$$

where α , β and γ are linear combinations of radial integrals and $\hat{G}(G_2)$ and $\hat{G}(R_7)$ are Casimir's operators for groups G_2 and R_7 . The respective matrix elements are discussed in section 9. The last term is a Judd's three-body correction, which is neglected and not discussed here.

\hat{H}_{CEF} is a crystal electric field term, which is absent in the case of free ion. Its matrix elements are discussed in section 10.

The part \hat{H}_{mag} takes into account influence of magnetization and external magnetic field (Zeeman term). Magnetization is temperature-dependent and must be calculated in a self-consistent way based on certain approximations. This is discussed in sections 11-13.

In order to calculate the total Hamiltonian matrix the following parameters are required (see [2]):

- E^1, E^2, E^3 – electrostatic parameters (it is assumed that $E^0 = 0$, since it gives only a constant energy shift),
- ξ – SO parameter,
- α, β, γ – Trees CI parameters,
- $T^2, T^3, T^4, T^6, T^7, T^8$ – Casimir three-body CI parameters (ignored here),
- M0, M2, M4, P2, P4, P6 – Judd parameters (ignored here),
- \vec{B} – external magnetic field (interacts with both orbital and spin moments),
- \vec{B}_M – effective exchange magnetic field. It interacts only with spin moments, however, if mixing of different J is neglected, the exchange field acts similarly to the external field, because spin moment is proportional to the total moment (see section 13).
- B_k^q – CEF parameters.

Most of these parameters are usually estimated from experimental data (e.g. optical absorption [2]).

2 Nonrelativistic electrostatic Hamiltonian and determinantal product states

The nonrelativistic Hamiltonian of an atom with N electrons is

$$H_{atom} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} + \sum_{i<j}^N \frac{e^2}{r_{ij}}$$

if the nuclear mass is assumed to be infinite. Exact solution is possible only for $N = 1$. The most common approximation is the central field approximation, where the electron moves in the spherically averaged potential of other electrons. Then the Hamiltonian becomes

$$H_{CF} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right]$$

The difference $H_{atom} - H_{CF}$ is treated as a perturbation electrostatic potential

$$H_{atom} - H_{CF} = H_{ES} = \sum_{i=1}^N \left[-\frac{Ze^2}{r_i} \nabla_i^2 - U(r_i) \right] + \sum_{i < j}^N \frac{e^2}{r_{ij}}$$

The Shrödinger equation for the central field

$$\sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] \Psi = E_{CF} \Psi$$

can be separated by choosing a solution such that

$$\Psi = \sum_{i=1}^N \phi_i(a^i) \quad \text{and} \quad E_{CF} = \sum_{i=1}^N E_i.$$

Each electron moving in the central field will then satisfy equations of the type

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(r) \right] \phi_i(a^i) = E(a^i) \phi_i(a^i)$$

where a^i is described by a set of quantum numbers $\{nlm\}$ of the i^{th} electron. After introducing the spin coordinate σ , which may equal $\pm\frac{1}{2}$, and a spin function $\delta(m_s, \sigma)$ satisfying the orthonormality relation

$$\sum_{\sigma} \delta(m_s, \sigma) \delta(m'_s, \sigma) = \delta(m_s, m'_s),$$

the one-electron eigenfunctions become

$$\phi(nlmm_s) = \delta(m_s, \sigma) r^{-1} R_{nl}(r) Y_l^m(\theta, \phi).$$

Here, we write r^{-1} separately to avoid r^2 in the radial matrix elements. The N -electron wave function then can be written as

$$\Psi = \sum_{i=1}^N \phi(k_i)$$

where k_i is a set of quantum numbers $\{nlmm_s\}$ of the i^{th} electron. To satisfy Pauli exclusion principle, we must choose an antisymmetric linear combination of these solutions. Thus, we arrive to the Slater determinant wave function, which is

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi(k_1, r_1) & \phi(k_2, r_1) & \dots & \phi(k_N, r_1) \\ \phi(k_1, r_2) & \phi(k_2, r_2) & \dots & \phi(k_N, r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi(k_1, r_N) & \phi(k_2, r_N) & \dots & \phi(k_N, r_N) \end{vmatrix}$$

For the $4f^N$ shell we have $4l + 2 = 14$ orbitals, N of which are occupied by electrons. The number of possible states is the number of possibilities to occupy N orbitals. It is given by the binomial coefficient

$$\binom{4l+2}{N} = \frac{(4l+2)!}{N!(4l+2-N)!}.$$

For example, for Gd $4f^7$ shell there are 3432 possible basis states. Each Slater determinant can be written using the following short notation

$$\{k_1, k_2, \dots k_N\}.$$

Obviously, when the two functions (or coordinates) of two electrons are interchanged, the phase factor of $(-1)^p$ appears, where p is the number of permutations, e.g.

$$\{k_1, k_2, k_3\} = -\{k_2, k_1, k_3\} = \{k_2, k_3, k_1\}.$$

Determinantal product states usually are not the eigenstates of the Hamiltonian, but they form a complete basis in which any eigenstate can be expanded. This basis is used in the program LANTHANIDE [3], which is able to calculate the eigenstates of the $4f$ shell Hamiltonian.

3 Matrix elements for determinantal product states

See [4], p. 17.

4 Angular momentum operators and states

One-particle orbital angular momentum operator is

$$\vec{l} = \vec{r} \times \vec{p} = -i\hbar \vec{r} \times \vec{\nabla}$$

Alternatively,

$$l_x = yp_z - zp_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (4.1)$$

$$l_y = zp_x - xp_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad (4.2)$$

$$l_z = xp_y - yp_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (4.3)$$

From these expressions it is easy to obtain the following commutation relation

$$[l_x, l_y] = l_x l_y - l_y l_x = i\hbar l_z$$

The general commutation relations valid for any (orbital and spin) angular momentum operator are

$$[j_x, j_y] = i\hbar j_z \quad (4.4)$$

$$[j_y, j_z] = i\hbar j_x \quad (4.5)$$

$$[j_z, j_x] = i\hbar j_y \quad (4.6)$$

The shift (ladder) operators are defined as

$$J_{\pm} \equiv J_x \pm iJ_y.$$

The eigenfunctions of the angular momentum operators satisfy the following relations

$$J_z|j, m\rangle = \hbar m|j, m\rangle \quad (4.7)$$

$$J^2|j, m\rangle = \hbar^2 j(j+1)|j, m\rangle \quad (4.8)$$

$$J_{\pm}|j, m\rangle = \hbar\sqrt{(j \mp m)(j \pm m + 1)}|j, m \pm 1\rangle \quad (4.9)$$

Let us consider a commutator of J_{\pm} with spherical harmonic:

$$\begin{aligned} [J_{\pm}, Y_j^m]\psi &= J_{\pm}Y_j^m\psi - Y_j^mJ_{\pm}\psi = (\psi J_{\pm}Y_j^m + Y_j^mJ_{\pm}\psi) - Y_j^mJ_{\pm}\psi = \\ &= \hbar\sqrt{(j \mp m)(j \pm m + 1)}Y_j^{m \pm 1}\psi \end{aligned} \quad (4.10)$$

Here we used the property of the derivative of a product.

Note that from hereon we use atomic units, where $\hbar = 1$.

5 Irreducible tensor operators and Wigner–Eckart theorem

An irreducible tensor operator of rank k is defined as an operator $T^{(k)}$, which has $2k + 1$ components. These components $T_q^{(k)}$ ($q = -k, \dots, k$) are transformed under rotation of the coordinate system in the same way as do the spherical harmonic operators. Equivalently, they satisfy the same commutation rule with respect to the angular momentum J as the spherical harmonics, that is

$$[J_{\pm}, T_q^{(k)}] = \sqrt{(k \mp q)(k \pm q + 1)}T_{q \pm 1}^{(k)}, \quad (5.1)$$

$$[J_z, T_q^{(k)}] = qT_q^{(k)}. \quad (5.2)$$

Examples of irreducible tensor operators are spherical tensor operators, which components are defined as renormalized spherical harmonics

$$C_q^{(k)} \equiv \sqrt{\frac{4\pi}{2k+1}}Y_k^q$$

The spherical functions with $k = 0, 1$ are

$$\begin{aligned} Y_0^0 &= \frac{1}{2}\sqrt{\frac{1}{\pi}}, & Y_1^{-1} &= \frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-i\phi} \\ Y_1^0 &= \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta, & Y_1^1 &= \frac{-1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}. \end{aligned}$$

Now let us consider the operators x , y and z . As known,

$$x = r \sin\theta \cos\phi, \quad y = r \sin\theta \sin\phi, \quad z = r \cos\theta$$

And obviously, they can be expanded in renormalized spherical tensor operators as

$$x = \frac{C_{-1}^{(1)} - C_1^{(1)}}{\sqrt{2}}r, \quad y = i\frac{C_{-1}^{(1)} + C_1^{(1)}}{\sqrt{2}}r, \quad z = C_0^{(1)}r$$

where

$$C_q^{(1)} = \sqrt{\frac{4\pi}{3}} Y_1^q$$

are rank-1 spherical tensor operators, because Y_l^m are spherical tensors of rank l .

Similarly, any vector \vec{V} can be written as an rank-1 irreducible tensor operator with three components

$$\left\{ \frac{V_x - iV_y}{\sqrt{2}}, V_z, -\frac{V_x + iV_y}{\sqrt{2}} \right\}$$

Thus, for irreducible tensor operators we see that

$$T_{\pm 1}^{(1)} = \frac{\mp 1}{\sqrt{2}}(T_x \pm iT_y), \quad T_0^{(1)} = T_z \quad (5.3)$$

It can be shown that $J_{\pm 1}^{(1)}$ is a tensor operator of rank 1 with components $\{J_-/\sqrt{2}, J_z, -J_+/\sqrt{2}\}$. Thus, this irreducible tensor operator is similar to the shift operator J_{\pm} , but differs in sign and normalization!

The Wigner-Eckart theorem states that matrix elements of irreducible tensor operators in the basis of angular momentum eigenstates can be expressed as the product of two factors, one of which is independent of angular momentum orientation, and the other is a Clebsch–Gordan coefficient:

$$\langle j' m'_j | T_q^{(k)} | j m_j \rangle = \frac{(-1)^{2k}}{\Pi_{j'}} C_{j m_j k q}^{j' m'_j} \langle j' || T^{(k)} || j \rangle \quad (5.4)$$

where k is the tensor rank, $\langle j' || T^{(k)} || j \rangle$ is a so-called reduced matrix element, and

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

Note that there are different conventions for reduced matrix elements (normalization and phase factors may differ). Here, we use the same convention as used by Racah, Wigner, Wybourne and Cowan.

It can be shown that for any rank k the reduced matrix element of spherical tensor operator in the basis of spherical functions is

$$\langle l' || \mathbf{C}^{(k)} || l \rangle = (-1)^k \Pi_{l'} C_{l'0k0}^{l0} = \Pi_l C_{l0k0}^{l'0} \quad (5.5)$$

For $k = 1$, this matrix element is nonzero only for $\Delta l = \pm 1$.

Let us find the reduced matrix elements for the angular momentum operators. For the operator J_z we may write (see 4.7)

$$m_j \delta_{\alpha j m_j, \alpha' j' m'_j} = \langle \alpha j m_j | J_z | \alpha' j' m'_j \rangle = \langle \alpha j m_j | J_0^{(1)} | \alpha' j' m'_j \rangle = \frac{1}{\Pi_j} C_{j' m'_j 10}^{j m_j} \langle j || J_0^{(1)} || j' \rangle \quad (5.6)$$

from which we find that

$$\langle j || J_0^{(1)} || j' \rangle = m_j \delta_{j,j'} \sqrt{2j+1} \left(C_{j m_j, 10}^{j m_j} \right)^{-1} \quad (5.7)$$

Using

$$C_{jm_j,10}^{jm_j} = \frac{m_j}{\sqrt{j(j+1)}}$$

we obtain the reduced matrix element

$$\langle j || J_0^{(1)} || j' \rangle = \delta_{j,j'} \sqrt{j(j+1)(2j+1)} \quad (5.8)$$

Similarly,

$$\langle j || J_{\pm} || j' \rangle = \mp \sqrt{2} \delta_{j,j'} \sqrt{j(j+1)(2j+1)} \quad (5.9)$$

Thus, for any q

$$\langle j || J_q^{(1)} || j' \rangle = \delta_{j,j'} \sqrt{j(j+1)(2j+1)} \quad (5.10)$$

and

$$\langle l || l_q^{(1)} || l' \rangle = \delta_{l,l'} \sqrt{l(l+1)(2l+1)} \quad (5.11)$$

and

$$\langle s || s_q^{(1)} || s' \rangle = \delta_{s,s'} \sqrt{s(s+1)(2s+1)} = \delta_{s,s'} \sqrt{\frac{3}{2}} \quad (5.12)$$

Let us consider the electric dipole transition operator regarding vectors \vec{r} and $\vec{\varepsilon}$ as the rank 1 irreducible tensor operators

$$\vec{\varepsilon} \cdot \vec{r} = r(\varepsilon_x \sin \theta \cos \phi + \varepsilon_y \sin \theta \sin \phi + \varepsilon_z \cos \theta) = \sqrt{\frac{4\pi}{3}} r \left(\frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_1^{-1} + \varepsilon_z Y_1^0 + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_1^1 \right) \quad (5.13)$$

Thus, we have

$$\vec{\varepsilon} \cdot \vec{r} = r \sum_{q=-1}^1 \varepsilon_q C_q^{(1)}$$

Then, for the matrix element of one-electron transition from $|jm_j\rangle$ to $|j'm'_j\rangle$ we have

$$\langle j'm'_j | \vec{\varepsilon} \cdot \vec{r} | jm_j \rangle = \frac{1}{\Pi_{jj'}} \langle j' || r \mathbf{C}^{(1)} || j \rangle \sum_q \varepsilon_q C_{jm_j 1q}^{j'm'_j}$$

Thus, for linear polarization $\Delta m = 0$, while for circular $\Delta m = \pm 1$ depending on left or right polarization. The cross section averaged over the ground states m_j (nonmagnetic case) and summed over the final states m'_j is

$$\begin{aligned} \sigma(j', j) &= \frac{1}{\Pi_j^2} \sum_{m_j m'_j} |\langle j'm'_j | \vec{\varepsilon} \cdot \vec{r} | jm_j \rangle|^2 = \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{jj'}^2} \sum_{m_j m'_j} \left| \sum_q \varepsilon_q C_{jm_j 1q}^{j'm'_j} \right|^2 = \\ &= \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{jj'}^2} \sum_{m_j m'_j q} |\varepsilon_q|^2 \left(C_{jm_j 1q}^{j'm'_j} \right)^2 = \frac{1}{\Pi_{1j}^2} |\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2 \quad (5.14) \end{aligned}$$

For a one-electron transition between the states $|l\rangle$ and $|l'\rangle$, the cross section averaged over m is

$$\sigma(l', l) = \frac{1}{\Pi_{ll'}^2} |\langle l' || r \mathbf{C}^{(1)} || l \rangle|^2 = \left(C_{l0 10}^{l'0} \right)^2 \frac{1}{3} R^2(l', l) \quad (5.15)$$

where $R(l', l)$ is a radial matrix element of the position operator r

$$R(l', l) = \int_0^\infty r R_{n'l'} R_{nl} dr.$$

6 Matrix elements for angular momentum eigenstates

For an type-F operator ($F = \sum f_i$, e.g. dipole operator), the matrix element is related to one-electron matrix element as (Eq. 2-74 in [5])

$$\langle l^N; wLS || F || l^{N-1}(w'L'S')l'; \psi \rangle = \sqrt{N}Q(wLS|w'L'S')\langle l^{N-1}l_N; wLS || f_N || l^{N-1}(w'L'S')l'_N; \psi \rangle$$

The matrix elements of the scalar product of spherical tensor operators is given by (Eq. 11.47 in [6])

$$\begin{aligned} \langle \alpha_1 j_1 \alpha_2 j_2; jm | \mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)} | \alpha'_1 j'_1 \alpha'_2 j'_2; j' m' \rangle = \\ = \delta_{jm, j' m'} (-1)^{j'_1 + j_2 + j} \left\{ \begin{matrix} j_1 & j_2 & j \\ j'_2 & j'_1 & k \end{matrix} \right\} \langle \alpha_1 j_1 || \mathbf{T}^{(k)} || \alpha'_1 j'_1 \rangle \langle \alpha_2 j_2 || \mathbf{U}^{(k)} || \alpha'_2 j'_2 \rangle \end{aligned} \quad (6.1)$$

For tensor operator $\mathbf{T}^{(k)}$ operating only on part 1 of the system, the matrix element is given by (Eq. 2-48 in [5], and Eq. 11.38 in [6])

$$\langle \alpha_1 j_1 \alpha_2 j_2; j || \mathbf{T}^{(k)} || \alpha'_1 j'_1 \alpha'_2 j'_2; j' \rangle = \delta_{\alpha_2 j_2, \alpha'_2 j'_2} (-1)^{j_1 + j_2 + j' + k} \Pi_{jj'} \langle \alpha_1 j_1 || \mathbf{T}^{(k)} || \alpha'_1 j'_1 \rangle \left\{ \begin{matrix} j & j' & k \\ j'_1 & j_1 & j_2 \end{matrix} \right\} \quad (6.2)$$

For tensor operator $\mathbf{U}^{(k)}$ operating only on part 2 of the system, the matrix element is given by (Eq. 2-49 in [5], and Eq. 11.39 in [6])

$$\langle \alpha_1 j_1 \alpha_2 j_2; j || \mathbf{U}^{(k)} || \alpha'_1 j'_1 \alpha'_2 j'_2; j' \rangle = \delta_{\alpha_1 j_1, \alpha'_1 j'_1} (-1)^{j_1 + j'_2 + j + k} \Pi_{jj'} \langle \alpha_2 j_2 || \mathbf{U}^{(k)} || \alpha'_2 j'_2 \rangle \left\{ \begin{matrix} j & j' & k \\ j'_2 & j_2 & j_1 \end{matrix} \right\} \quad (6.3)$$

Scalar product of two tensor operators is defined as

$$\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)} \equiv \sum_q (-1)^q \mathbf{T}_q^{(k)} \mathbf{U}_{-q}^{(k)}.$$

In the particular case when $\mathbf{T}^{(k)}$ and $\mathbf{U}^{(k)}$ operate only on $\alpha_1 j_1 m_1$ and $\alpha_2 j_2 m_2$, respectively, the matrix element of the scalar product is (Eq. 11.47 in [6])

$$\begin{aligned} \langle \alpha_1 j_1 \alpha_2 j_2; jm | \mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)} | \alpha'_1 j'_1 \alpha'_2 j'_2; j' m' \rangle = \\ = \delta_{jm, j' m'} (-1)^{j'_1 + j_2 + j} \left\{ \begin{matrix} j_1 & j_2 & j \\ j'_2 & j'_1 & k \end{matrix} \right\} \langle \alpha_1 j_1 || \mathbf{T}^{(k)} || \alpha'_1 j'_1 \rangle \langle \alpha_2 j_2 || \mathbf{U}^{(k)} || \alpha'_2 j'_2 \rangle \end{aligned} \quad (6.4)$$

Fractional parentage coefficients and Wigner symbols (3-j, 6-j and 9-j) can be calculated e.g. with the help of Mapple libraries RACAH and JUCYS [7]. However, there are mistakes in Table 1 of Ref. [7] and the calculated fractional parentage coefficients for more than half-filled shell may have wrong sign. To calculate correct coefficients for l^q configurations with $q > 2l + 2$ one can use the following relation (Eq. 2-22 in [5]):

$$Q(l^{4l+2-q} wLS | l^{4l+1-q} w'L'S') = (-1)^{L'+S'+L+S-l-s} \sqrt{\frac{q+1}{4l+2-q}} \frac{\Pi_{L'S'}}{\Pi_{LS}} Q(l^{q+1} w'L'S' | l^q wLS)$$

For $q = 2l + 2$ (e.g. for f^8) this equation must be preceded by a factor $(-1)^{(\nu'-1)/2}$, where ν is a seniority number.

7 Matrix elements of electrostatic interaction in LS basis

Coulomb interaction can be expanded in the following series:

$$V_{ij} = \frac{e^2}{r_{ij}} = e^2 \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \gamma_{ij}).$$

Using spherical harmonics addition theorem the Legendre polynomials can be written as

$$P_k(\cos \gamma_{ij}) = \frac{4\pi}{2k+1} \sum_q Y_k^{q*}(\theta_i, \phi_i) Y_k^q(\theta_j, \phi_j) = \sum_q (-1)^q (\mathbf{C}_{-q}^{(k)})_i (\mathbf{C}_q^{(k)})_j = \mathbf{C}_i^{(k)} \cdot \mathbf{C}_j^{(k)}$$

Consider two electrons in possibly different shells nl , which form a two-electron state LS . Since the wave function must be antisymmetric, we have

$$|n_a l_a, n_b l_b; LS\rangle = 2^{-1/2} (|n_{a1} l_{a1}, n_{b2} l_{b2}; LS\rangle - |n_{a2} l_{a2}, n_{b1} l_{b1}; LS\rangle)$$

where 1 and 2 refer to the coordinates of two electrons and the spin quantum numbers are omitted for brevity. Let us exchange the coupling sequence:

$$\begin{aligned} |n_{a2} l_{a2}, n_{b1} l_{b1}; LS\rangle &= \sum_{MM_S} C_{l_a m_a, l_b m_b}^{LM} C_{s_a m_{sa}, s_b m_{sb}}^{SM_S} |n_{a2} l_{a2}\rangle |n_{b1} l_{b1}\rangle = \\ &(-1)^{l_a + l_b - L + s_a + s_b - S} \sum_{MM_S} C_{l_b m_b, l_a m_a}^{LM} C_{s_b m_{sb}, s_a m_{sa}}^{SM_S} |n_{b1} l_{b1}\rangle |n_{a2} l_{a2}\rangle = \\ &(-1)^{l_a + l_b - L + s_a + s_b - S} |n_{b1} l_{b1}, n_{a2} l_{a2}; LS\rangle = -(-1)^{l_a + l_b + L + S} |n_{b1} l_{b1}, n_{a2} l_{a2}; LS\rangle \end{aligned} \quad (7.1)$$

Thus,

$$|n_a l_a, n_b l_b; LS\rangle = 2^{-1/2} (|n_{a1} l_{a1}, n_{b2} l_{b2}; LS\rangle + (-1)^{l_a + l_b + L + S} |n_{b1} l_{b1}, n_{a2} l_{a2}; LS\rangle)$$

Because Coulomb operator commutes with angular momentum operators, its matrix elements are diagonal in LS . Consider another state with same LS :

$$|n_c l_c, n_d l_d; LS\rangle = 2^{-1/2} (|n_{c1} l_{c1}, n_{d2} l_{d2}; LS\rangle + (-1)^{l_c + l_d + L + S} |n_{d1} l_{d1}, n_{c2} l_{c2}; LS\rangle)$$

Consider Coulomb matrix element of two-particle operator $V_{12} = e^2/r_{12}$. Taking into account symmetry in regard to exchange of 1 and 2, we get

$$\begin{aligned} \langle n_a l_a, n_b l_b; LS | V_{12} | n_c l_c, n_d l_d; LS\rangle &= \langle n_{a1} l_{a1}, n_{b2} l_{b2}; LS | V_{12} | n_{c1} l_{c1}, n_{d2} l_{d2}; LS\rangle + \\ &+ (-1)^{l_c + l_d + L + S} \langle n_{a1} l_{a1}, n_{b2} l_{b2}; LS | V_{12} | n_{d1} l_{d1}, n_{c2} l_{c2}; LS\rangle \end{aligned} \quad (7.2)$$

Expanding the Coulomb potential in spherical tensor operators, we get

$$\begin{aligned} \langle n_a l_a, n_b l_b; LS | V_{12} | n_c l_c, n_d l_d; LS\rangle &= \\ &e^2 \sum_k \langle n_{a1} l_{a1}, n_{b2} l_{b2}; LS | \frac{r_{<}^k}{r_{>}^{k+1}} \mathbf{C}_1^{(k)} \cdot \mathbf{C}_2^{(k)} | n_{c1} l_{c1}, n_{d2} l_{d2}; LS\rangle + \\ &+ (-1)^{l_c + l_d + L + S} \langle n_{a1} l_{a1}, n_{b2} l_{b2}; LS | \frac{r_{<}^k}{r_{>}^{k+1}} \mathbf{C}_1^{(k)} \cdot \mathbf{C}_2^{(k)} | n_{d1} l_{d1}, n_{c2} l_{c2}; LS\rangle = \\ &\sum_k [f_k(l_a, l_b; l_c, l_d) R^k(n_a l_a, n_b l_b; n_c l_c, n_d l_d) + g_k(l_a, l_b; l_d, l_c) R^k(n_a l_a, n_b l_b; n_d l_d, n_c l_c)] \end{aligned} \quad (7.3)$$

where R^k are radial integrals, f_k and g_k are obtained from 6.4

$$f_k(l_a, l_b; l_c, l_d) = (-1)^{l_b+l_c+L} \langle l_a || \mathbf{C}^{(k)} || l_c \rangle \langle l_b || \mathbf{C}^{(k)} || l_d \rangle \left\{ \begin{matrix} l_a & l_b & L \\ l_d & l_c & k \end{matrix} \right\}$$

$$g_k(l_a, l_b; l_d, l_c) = (-1)^S \langle l_a || \mathbf{C}^{(k)} || l_d \rangle \langle l_b || \mathbf{C}^{(k)} || l_c \rangle \left\{ \begin{matrix} l_a & l_b & L \\ l_c & l_d & k \end{matrix} \right\}$$

The two terms are the so-called direct and exchange terms. Note that the exchange term is spin-dependent. For triplet state ($S = 1$) with parallel spins g_k is negative and the energy is lower than for the singlet state ($S = 0$) with antiparallel spins. This is the origin of exchange interaction.

From the triangle rule for 6-j symbol components it is obvious that for $l_a = l_b = l_c = l_d = 3$ the coefficients f_k and g_k are nonzero only for $k = 0, 2, 4, 6$.

Matrix elements for more complex configurations with more electrons can be reduced to the two-electron matrix elements using recoupling and fractional parentage coefficients. All matrix elements for the f^n configurations are given in [1].

8 Matrix elements of spin-orbit interaction in LSJ basis

In LSJ basis, spin-orbit matrix elements for $q \leq 2l + 1$ are (Eq. 12.42 in [6] and Eq. 2.106 in [5])

$$\begin{aligned} \langle l^q w L S J M_J | \xi_{nl} \sum_i \mathbf{s}_i \cdot \mathbf{l}_i | l^q w' L' S' J M_J \rangle = \\ = \xi_{nl} (-1)^{J+L'+S} \left\{ \begin{matrix} L & L' & 1 \\ S' & S & J \end{matrix} \right\} \sqrt{l(l+1)(2l+1)} \langle l^q w L S || V^{11} || l^q w' L' S' \rangle \end{aligned} \quad (8.1)$$

where (Eq. 11.68 in [6])

$$\begin{aligned} \langle l^q w L S || V^{11} || l^q w' L' S' \rangle = q \sqrt{\frac{3}{2}} \Pi_{LSL'S'} \sum_{w'' L'' S''} Q(w L S | w'' L'' S'') Q(w' L' S' | w'' L'' S'') \\ \times (-1)^{L''+S''+L+S+l+1/2} \left\{ \begin{matrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & S'' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & 1 \\ l & l & L'' \end{matrix} \right\} \end{aligned} \quad (8.2)$$

For $q > 2l + 1$, the SO matrix differ only in sign (for f^8 its absolute values are equal to the f^6 case). Note that the phase factor is different from the case of SL coupling (used by Wybourne [5]). Also it is worth noting that

$$\langle w' L' S' || V^{11} || w L S \rangle = (-1)^{L'-L+S'-S} \langle w L S || V^{11} || w' L' S' \rangle$$

SO interaction leads to mixing of LS states (intermediate coupling). Good quantum numbers are only $J M_J$.

9 Configuration interaction

In the LS basis the matrix elements of the Hamiltonian

$$\hat{H}_{CI} = \alpha \hat{L}^2 + \beta \hat{G}(G_2) + \gamma \hat{G}(R_7)$$

can be calculated from a set of quantum numbers L , $U = \{u_1, u_2\}$ and $W = \{w_1, w_2, w_3\}$ as [8]

$$H_{CI} = \alpha L(L+1) + \frac{\beta}{12}(u_1^2 + u_1 u_2 + u_2^2 + 5u_1 + 4u_2) + \frac{\gamma}{10}(w_1(w_1+5) + w_2(w_2+3) + w_3(w_3+1))$$

These matrix elements are diagonal in all quantum numbers.

10 Crystal electric field splitting

CEF potential can be expanded in spherical tensors as

$$V_{CEF} = \sum_{k,q} B_q^k \mathbf{C}_q^{(k)} \frac{r^k}{\langle r^k \rangle}$$

The equivalent CEF Hamiltonian is

$$H_{CEF} = \sum_{k,q,i} B_q^k (\mathbf{C}_q^{(k)})_i$$

where the summation over i is over all electrons of the ion. Due to symmetry,

$$B_{-q}^k = (-1)^q B_q^{k*}$$

The potential does not act on spin. Therefore, the matrix elements in LSJ coupling are

$$\langle l^N w L S J M_J | H_{CEF} | l^N w' L' S J' M_J' \rangle = \sum_{k,q} B_q^k \langle l^N w L S J M_J | \mathbf{U}_q^{(k)} | l^N w' L' S J' M_J' \rangle \langle l || \mathbf{C}^{(k)} || l \rangle$$

The matrix element on the right side can be reduced (using Eq. 5.4 and 6.2) as

$$\begin{aligned} \langle l^N w L S J M_J | \mathbf{U}_q^{(k)} | l^N w' L' S J' M_J' \rangle &= \frac{1}{\Pi_J} C_{J'M_J' kq}^{JM_J} \langle l^N w L S J || \mathbf{U}^{(k)} || l^N w' L' S J' \rangle = \\ &= (-1)^{L+S+J'+k} \Pi_{J'} C_{J'M_J' kq}^{JM_J} \left\{ \begin{matrix} J & J' & k \\ L' & L & S \end{matrix} \right\} \langle l^N w L S || \mathbf{U}^{(k)} || l^N w' L' S \rangle \quad (10.1) \end{aligned}$$

(Note the wrong phase in Eq. 6.5 of Wybourne [5].) Hence, using Eq. 5.5 we obtain

$$\begin{aligned} \langle l^N w L S J M_J | H_{CEF} | l^N w' L' S J' M_J' \rangle &= \\ &= \sum_{k,q} B_q^k C_{J'M_J' kq}^{JM_J} (-1)^{L+S+J'+k} \Pi_{LJ'} C_{l0 k0}^{l0} \left\{ \begin{matrix} J & J' & k \\ L' & L & S \end{matrix} \right\} \langle l^N w L S || \mathbf{U}^{(k)} || l^N w' L' S \rangle \quad (10.2) \end{aligned}$$

Due to C_{l0k0}^{l0} , terms with odd k vanish. The reduced matrix elements of the tensor $\mathbf{U}^{(k)}$ can be taken from the tables of Nielson and Koster [1], or calculated as (Eq. 11.53 in [6])

$$\begin{aligned} \langle l^N wLS || \mathbf{U}^{(k)} || l^N w'L'S' \rangle = \\ = \delta_{SS'} N \Pi_{LL'} \sum_{w''L''S''} Q(wLS | w''L''S'') Q(w'L'S' | w''L''S'') (-1)^{L''+L+l+k} \left\{ \begin{matrix} L & L' & k \\ l & l & L'' \end{matrix} \right\} \end{aligned} \quad (10.3)$$

for $N \leq 2l + 1$. For conjugate shell l^{4l+2-N} the reduced matrix elements of $\mathbf{U}^{(k)}$ differ by the factor of $(-1)^{k+1}$. Note that

$$\langle w'L'S' || \mathbf{U}^{(k)} || wLS \rangle = (-1)^{L'-L} \langle wLS || \mathbf{U}^{(k)} || w'L'S' \rangle$$

For the f shell, k may take values 0, 2, 4, 6. J and M_J cease to be good quantum numbers. For intermediate coupling we may write

$$\langle l^N JM_J | H_{CEF} | l^N J'M'_J \rangle = \sum_{\substack{wLS \\ w'L'S'}} \delta_{SS'} C_{wLS}^J C_{w'L'S'}^{J'} \langle l^N wLS JM_J | H_{CEF} | l^N w'L'SJ'M'_J \rangle \quad (10.4)$$

As a simplest approximation we may assume LSJ coupling and $J' = J$, and consider only mixing of M_J states.

For $J' = 0$ (e.g. Eu^{3+}) the state cannot be split. In the particular case of spherically symmetric shell with $L' = 0$ (e.g. Eu^{2+}), we have

$$\langle l^N wLS JM_J | H_{CEF} | l^N w'L'SJ'M'_J \rangle \propto \left\{ \begin{matrix} J & J' & k \\ L' & L & S \end{matrix} \right\} \propto \delta_{L,k} \quad (10.5)$$

Thus, $L = k \geq 2$. The matrix element is zero because there is no term with $L > 0$ and $S = 7/2$ for the f^7 configuration. However, intermediate coupling may result in appearance of small CEF splitting due to admixture of states with $L > 0$.

For tetragonal symmetry (including D_{4h} and C_{4v}) the non-vanishing terms for f -shells are (Tab. 1.7 in [9])

$$H_i = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + (C_{-4}^{(4)} + C_4^{(4)}) \text{Re} B_4^4 + B_0^6 C_0^{(6)} + (C_{-4}^{(6)} + C_4^{(6)}) \text{Re} B_4^6$$

Old alternative form of CEF Hamiltonian is

$$H_{CEF} = \sum_{k,q,i} \theta_k A_k^q \langle r^k \rangle (O_k^q)_i$$

where O_k^q are Stevens operators. The coefficients θ_k are functions of J : $\theta_2 = \alpha_J$, $\theta_4 = \beta_J$ and

$\theta_6 = \gamma_J$ (their values are given in [10]). The relations between the parameters are [9]

$$\begin{aligned}
B_0^2 &= 2A_2^0 \langle r^2 \rangle & B_0^6 &= 16A_6^0 \langle r^6 \rangle \\
B_2^2 &= \frac{\sqrt{6}}{3} A_2^2 \langle r^2 \rangle & B_2^6 &= \frac{16\sqrt{105}}{105} A_6^2 \langle r^6 \rangle \\
B_0^4 &= 8A_4^0 \langle r^4 \rangle & B_3^6 &= -\frac{8\sqrt{105}}{105} A_6^3 \langle r^6 \rangle \\
B_2^4 &= \frac{2\sqrt{10}}{5} A_4^2 \langle r^4 \rangle & B_4^6 &= \frac{8\sqrt{14}}{21} A_6^4 \langle r^6 \rangle \\
B_3^4 &= -\frac{2\sqrt{35}}{35} A_4^3 \langle r^4 \rangle & B_6^6 &= \frac{16\sqrt{231}}{231} A_6^6 \langle r^6 \rangle \\
B_4^4 &= \frac{4\sqrt{70}}{35} A_4^4 \langle r^4 \rangle & &
\end{aligned} \tag{10.6}$$

To extract CEF parameters from (one-electron) DFT calculations, let us consider one-electron CEF matrix elements:

$$\langle lm | H_{CEF} | lm' \rangle = \sum_{k,q} B_q^k \langle lm | \mathbf{C}^{(k)} | lm' \rangle = \frac{1}{\Pi_l} \sum_{k,q} B_q^k C_{lm' k q}^{lm} \langle l || \mathbf{C}^{(k)} || l \rangle = \sum_{k,q} B_q^k C_{l0 k 0}^{l0} C_{lm' k q}^{lm} \tag{10.7}$$

Consider the following “vectors” with components numbered by mm'

$$A_{mm'}^{kq} = C_{l0 k 0}^{l0} C_{lm' k q}^{lm}.$$

Let us check that these “vectors” are orthogonal

$$\vec{A}^{kq} \cdot \vec{A}^{k'q'} = \sum_{mm'} A_{mm'}^{kq} A_{mm'}^{k'q'} = C_{l0 k 0}^{l0} C_{l0 k' 0}^{l0} \sum_{mm'} C_{lm' k q}^{lm} C_{lm' k' q'}^{lm} = (C_{l0 k 0}^{l0})^2 \frac{\Pi_l^2}{\Pi_k^2} \delta_{kq, k'q'}$$

Hence, to determine CEF parameters from DFT-calculated one-electron matrix elements we use

$$\vec{H}_{CEF} \cdot \vec{A}^{kq} = B_q^k \vec{A}^{kq} \cdot \vec{A}^{kq} = B_q^k (C_{l0 k 0}^{l0})^2 \frac{\Pi_l^2}{\Pi_k^2}$$

If we know the crystal-field potential, we may directly obtain parameters by expanding the potential in spherical harmonics as

$$B_q^k = \sqrt{\frac{2k+1}{4\pi}} \int V_{CEF}(\vec{r}) Y_k^{q*}(\theta, \phi) (R(r)/r)^2 d^3r$$

where $R(r)$ is a radial wave function. However, there is a problem of taking into account hybridization.

11 Zeeman effect (field along \mathbf{Z})

Let us consider an external magnetic field oriented along z axis. Then

$$H_{mag}^z = -\vec{\mu} \cdot \vec{B} = B_z \mu_B (L^{(1)} + g_s S^{(1)}) = B_z \mu_B (J_0^{(1)} + (g_s - 1) S_0^{(1)})$$

where $g_s \approx 2.0023192$ is the anomalous gyromagnetic ratio. The matrix elements in LSJ coupling (in atomic units) is

$$\begin{aligned}
& \frac{1}{B_z \mu_B} \langle wLSJM_J | H_{mag}^z | w'L'S'J'M'_J \rangle = \\
& = M_J \delta_{wLSJM_J, w'L'S'J'M'_J} + \frac{g_s - 1}{\Pi_J} C_{J'M'_J}^{JM_J} \langle wLSJ || S_0^{(1)} || w'L'S'J' \rangle = \\
& = M_J \delta_{wLSJM_J, w'L'S'J'M'_J} + (g_s - 1) \Pi_{J'} C_{J'M'_J}^{JM_J} \delta_{wL, w'L'} (-1)^{L+S'+J+1} \left\{ \begin{matrix} J & J' & 1 \\ S' & S & L \end{matrix} \right\} \langle S || S_0^{(1)} || S' \rangle = \\
& = M_J \delta_{wLSJM_J, w'L'S'J'M'_J} + \\
& + (g_s - 1) \Pi_{J'} C_{J'M'_J}^{JM_J} \delta_{wL, w'L'} (-1)^{L+S'+J+1} \left\{ \begin{matrix} J & J' & 1 \\ S & S & L \end{matrix} \right\} \sqrt{S(S+1)(2S+1)} \quad (11.1)
\end{aligned}$$

This matrix element is diagonal in all quantum numbers except of J. For diagonal elements it can be evaluated analytically as

$$\frac{1}{B_z \mu_B} \langle wLSJM_J | H_{mag}^z | wLSJM_J \rangle = M_J g_J$$

where

$$g_J = 1 + (g_s - 1) \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

is a Landé factor. In the particular case of $L = 0$ we have $g_J = g_s$

In the absence of CEF, for the ground state we have $M_J = -J$ and magnetic moment of atom is aligned along Z . Thus, for magnetic moment we have

$$\mu = -\frac{E}{B_z} = J g_J \mu_B \quad (11.2)$$

It is different from the effective magnetic moment, which appears in the expression for magnetic susceptibility (Getzlaf, 2.134)

$$\mu_{eff} = g_J \mu_B \sqrt{J(J+1)} \quad (11.3)$$

Let us calculate spin projection on the z axis for the diagonal states:

$$\begin{aligned}
\langle wLSJM_J | S_z | wLSJM_J \rangle &= \langle wLSJM_J | S_0^{(1)} | wLSJM_J \rangle = \\
&= \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} M_J \approx (g_J - 1) M_J \quad (11.4)
\end{aligned}$$

Thus, the effective spin moment is proportional to the effective total moment as

$$S_{eff} \propto (g_J - 1) \sqrt{J(J+1)} \quad (11.5)$$

12 Zeeman effect (field in XY plane)

The Hamiltonian is

$$H_{mag} = -\vec{\mu} \cdot \vec{B} = \mu_B \sum_q B_q (J_q^{(1)} + (g_s - 1) S_q^{(1)})$$

where (similarly to Eq. 5.13)

$$B_{\pm 1} = \frac{\mp B_x + iB_y}{\sqrt{2}}, \quad B_0 = B_z, \quad J_{\pm 1} = \frac{\mp 1}{\sqrt{2}}(J_x \pm iJ_y)$$

For step-up and step-down operators J_{\pm}

$$J_{\pm} |j, m_j\rangle = \sqrt{(j \mp m_j)(j \pm m_j + 1)} |j, m_j \pm 1\rangle = \sqrt{j(j+1) - m_j(m_j \pm 1)} |j, m_j \pm 1\rangle$$

$$J_{\pm 1} |j, m_j\rangle = \frac{\mp 1}{\sqrt{2}} \sqrt{(j \mp m_j)(j \pm m_j + 1)} |j, m_j \pm 1\rangle$$

The nonzero xy matrix elements in LSJ coupling are

$$\frac{1}{B_{\pm 1}\mu_B} \langle wLSJM_J | H_{mag}^{\pm} | w'L'S'J'M'_J \rangle = \frac{\mp 1}{\sqrt{2}} \sqrt{(J \mp M'_J)(J \pm M'_J + 1)} \delta_{wLSJ, w'L'S'J'} \delta_{M_J, M'_J \pm 1} +$$

$$+ (g_s - 1) \Pi_{J'} C_{J'M'_J}^{JM_J} \delta_{wLS, w'L'S'} (-1)^{L+S+J+1} \left\{ \begin{matrix} J & J' & 1 \\ S & S & L \end{matrix} \right\} \sqrt{S(S+1)(2S+1)} \quad (12.1)$$

Note that the second term differs from the H_{mag}^z case only in Clebsch-Gordan coefficient. For elements diagonal in LSJ we obtain

$$\frac{1}{B_{\pm 1}\mu_B} \langle wLSJM_J | H_{mag}^{\pm} | wLSJM'_J \rangle = \mp \frac{g_J}{\sqrt{2}} \sqrt{(J \mp M'_J)(J \pm M'_J + 1)}$$

For field along x we get $B_{+1} = -B_x/\sqrt{2}$, $B_{-1} = B_x/\sqrt{2}$ and for elements diagonal in LSJ we obtain

$$\frac{1}{B_x\mu_B} \langle wLSJM_J | H_{mag}^x | wLSJM_J \pm 1 \rangle = \frac{g_J}{2} \sqrt{(J \mp M_J)(J \pm M_J + 1)}$$

For intermediate coupling, we may write

$$\langle l^N JM_J | H_{mag} | l^N J'M'_J \rangle = \sum_{wLS} C_{wLS}^J C_{wLS}^{J'} \langle l^N wLSJM_J | H_{mag} | l^N wLSJ'M'_J \rangle \quad (12.2)$$

13 Magnetic ordering (molecular field theory)

Zero CEF.

In the absence of CEF, magnetic field splits the energy level J in $2J+1$ sublevels. In this case photoemission cross section is given by summation over all M_J :

$$\frac{d\sigma_{J'}}{d\Omega} = \sum_{M_J} u_{M_J} \frac{d\sigma_{J'M_J}}{d\Omega}$$

where u_{M_J} is the occupation of the level M_J . In the absence of CEF, it is given by the Boltzmann distribution [11]

$$u_{M_J} = \frac{1}{Z} \exp \left(-y \frac{M_J}{J} \right),$$

where (Eq. 2.97 in [11])

$$y = \frac{Jg_J\mu_B B(T)}{kT} = \frac{B}{B_S} \frac{Jg_J\mu_B B_S}{kT}.$$

From Eq. 5.14 or 5.16 [11], the saturation field is

$$B_S = \frac{3kT_C^0}{(J+1)g_J\mu_B}.$$

Thus,

$$y = \frac{B}{B_S} \frac{3JT_C^0}{(J+1)T}.$$

The field (or magnetization) can be found from the Eq. 5.19 [11]:

$$\frac{B}{B_S} = B_J \left(\frac{3J}{J+1} \frac{B}{B_S} \frac{T_C^0}{T} \right),$$

or

$$B_J(y) = y \frac{(J+1)T}{3JT_C^0} \quad (13.1)$$

Here, the Brillouin function is given by Eq. 2.109 [11]

$$B(y) = \frac{2J+1}{2J} \coth \left(\frac{2J+1}{2J} y \right) - \frac{1}{2J} \coth \left(\frac{y}{2J} \right)$$

From Eq. 2.95 [11]

$$Z = \frac{\sinh \left(\frac{2J+1}{2J} y \right)}{\sinh \left(\frac{y}{2J} \right)}$$

Energy difference between neighboring M_J levels at saturation ($T=0$) can be estimated as

$$\Delta E = \frac{ykT}{J} = \frac{3kT_C}{J+1}$$

For $T_C = 48$ K and $J = 7/2$ (EuIr₂Si₂ case) $\Delta E = 2.8$ meV.

It is useful to calculate thermally averaged J_Z moment

$$\langle J_Z \rangle = \langle M_J \rangle = \sum_{M_J} M_J u_{M_J} = \frac{J}{Z} \frac{dZ}{dy} = \frac{1}{2} \left[(2J+1) \coth \left(\frac{2J+1}{2J} y \right) - \coth \left(\frac{y}{2J} \right) \right]$$

and

$$\begin{aligned} \langle M_J^2 \rangle &= \frac{J^2}{Z} \frac{d^2 Z}{dy^2} = J(J+1) - \frac{\coth \left(\frac{y}{2J} \right)}{2} \left((2J+1) \coth \left(\frac{2J+1}{2J} y \right) - \coth \left(\frac{y}{2J} \right) \right) = \\ &= J(J+1) - \langle M_J \rangle \coth \left(\frac{y}{2J} \right) \end{aligned} \quad (13.2)$$

Nonzero CEF.

In the case of CEF-split states in presence of magnetic field, if we neglect mixing of different J , we have the wave function of the form

$$|J\nu\rangle = \sum_{M_J} A_{M_J}^\nu |JM_J\rangle$$

Then, the thermally averaged J_Z moment will be

$$\langle J_Z \rangle = \sum_{\nu} \langle J\nu | J_Z | J\nu \rangle u_{\nu} = \sum_{M_J} M_J \sum_{\nu} |A_{M_J}^\nu|^2 u_{\nu} \quad (13.3)$$

The moments along X and Y will be

$$\langle J_{\pm 1} \rangle = \sum_{\nu} \langle J\nu | J_{\pm 1} | J\nu \rangle u_{\nu} = \mp \frac{1}{\sqrt{2}} \sum_{M_J} \sqrt{J(J+1) - M_J(M_J \pm 1)} \sum_{\nu} A_{M_J \pm 1}^{\nu*} A_{M_J}^\nu u_{\nu} \quad (13.4)$$

$$\langle J_X \rangle = \frac{1}{\sqrt{2}} \sum_{\nu} \langle J\nu | J_{-1} - J_{+1} | J\nu \rangle u_{\nu} = \sum_{M_J, \pm} \frac{\sqrt{J(J+1) - M_J(M_J \pm 1)}}{2} \sum_{\nu} A_{M_J \pm 1}^{\nu*} A_{M_J}^\nu u_{\nu} \quad (13.5)$$

$$\langle J_Y \rangle = \frac{1}{i\sqrt{2}} \sum_{\nu} \langle J\nu | J_{-1} + J_{+1} | J\nu \rangle u_{\nu} = \sum_{M_J, \pm} \mp \frac{\sqrt{J(J+1) - M_J(M_J \pm 1)}}{2} \sum_{\nu} A_{M_J \pm 1}^{\nu*} A_{M_J}^\nu u_{\nu} \quad (13.6)$$

The averaged magnetic moment can be obtained as

$$\langle \vec{\mu} \rangle = -g_J \mu_B \langle \vec{J} \rangle$$

The magnetic field is

$$\vec{B} = \lambda \vec{M} = \lambda n \langle \vec{\mu} \rangle$$

where n is the concentration and λ is the molecular field constant, which is related to Curie (Néel) temperature T_C^0 in the absence of CEF as (5.15 in [11])

$$\lambda = \frac{3kT_C^0}{n\mu_{eff}^2}$$

Hence, the magnetic field is

$$\vec{B} = \frac{3kT_C^0}{\mu_{eff}^2} \langle \vec{\mu} \rangle = -\frac{3kT_C^0}{g_J \mu_B J(J+1)} \langle \vec{J} \rangle$$

The effective Zeeman Hamiltonian can be written (supposing no mixing of different J)

$$H_{mag} = -\vec{\mu} \cdot \vec{B} = -\frac{3kT_C^0}{J(J+1)} \vec{J} \cdot \langle \vec{J} \rangle$$

Matrix elements of this Hamiltonian must be determined self-consistently. We start from a given $\langle \vec{J} \rangle$, find the eigenstates and calculate new $\langle \vec{J} \rangle$ from them. This procedure is repeated until convergence is reached.

This type of Hamiltonian is able to describe a temperature-dependent canting of magnetic moments, which can be determined as [12]

$$\tan \theta = \frac{\langle J_X \rangle}{\langle J_Z \rangle}$$

The value of T_C^0 can be roughly estimated using a so-called de Gennes scaling for compounds that differ only by the type of rare-earth atom [13]

$$T_C^0 = (g_J - 1)^2 J(J + 1) \frac{T_C^{Gd}}{J_{Gd}(J_{Gd} + 1)},$$

where T_C^{Gd} is a Curie temperature of Gd compound (no CEF). This relation comes from Eq. 11.5 and from the fact that the exchange interaction is proportional to the spin moments of interacting atoms (not to their magnetic moments).

0.2 Photoemission

1 Photoemission matrix element for determinantal basis states

The final state is an antisymmetrized and normalized product of the states of ion and photoelectron:

$$|f\rangle = \{\chi_s, k'_1, k'_2, \dots, k'_{N-1}\}.$$

The initial state is

$$|i\rangle = \{k_1, k_2, \dots, k_N\}.$$

The dipole transition operator is an F-type operator

$$D = \sum_i \vec{\varepsilon} \cdot \vec{r}_i$$

The matrix element for an F-type operator is (see [4], p. 17)

$$\begin{aligned} \langle f | D | i \rangle &= \langle \{\chi_s, k'_1, k'_2, \dots, k'_{N-1}\} | D | \{k_1, k_2, \dots, k_n \dots k_N\} \rangle = \\ &= (-1)^{n-1} \langle \{\chi_s, k'_1, k'_2, \dots, k'_{N-1}\} | D | \{k_n, k_1, k_2, \dots, k_{N-1}\} \rangle = \\ &= (-1)^{n-1} \delta_{\{k'_1, k'_2, \dots, k'_{N-1}\}, \{k_1, k_2, \dots, k_{N-1}\}} \langle \chi_s | \vec{\varepsilon} \cdot \vec{r} | k_n \rangle \quad (1.1) \end{aligned}$$

where $(n - 1)$ is a number of permutations needed to place the function k_n , which is absent in the final state, to the first position.

In general, eigenfunctions of the Hamiltonian are linear combinations of the basis states $|b\rangle$

$$|f^q\rangle = \sum_b C_b |b\rangle, \quad |f^{q-1}\rangle = \sum_{b'} C_{b'} |b'\rangle,$$

where the coefficients C_b can be calculated, e.g. with the LANTHANIDE program [3]. Then the photoemission matrix element is

$$\langle f | D | i \rangle = \sum_{bb'} C_b^* C_{b'} \langle \{\chi, b'\} | D | b \rangle \quad (1.2)$$

Thus, matrix element calculation is very simple in this basis. The main disadvantage is a large number of basis states.

2 Photoemission intensity for LSJ states

The state of atom polarized by magnetic field in the LSJ coupling scheme is described by the magnetic quantum number M_J . Consider the transformation of the wave functions from LS- to LSJ- coupling [14]. In the LSJ coupling scheme, the initial state is

$$|i\rangle = |wLSJM_J\rangle_{l^q} = \sum_{MM_S} C_{LM,SM_S}^{JM_J} |wLSMM_S\rangle_{l^q}$$

The $|wLSMM_S\rangle_{l^q}$ state can be expressed as a combination of states produced by adding one electron to one of the possible ionized states $|L'S'\rangle_{l^{q-1}}$:

$$|wLSMM_S\rangle_{l^q} = \sum_{w'L'S'} Q(wLS, w'L'S') |(w'L'S')wLSMM_S\rangle$$

where Q are coefficients of fractional parentage. Addition of one electron to the ion is described by

$$|(w'L'S')wLSMM_S\rangle = \sum_{M'M'_S mm_s} C_{S'M'_S, \frac{1}{2}m_s}^{SM_S} C_{L'M', lm}^{LM} |w'L'S'M'M'_S\rangle_{l^{q-1}} |lmm_s\rangle$$

The final state is an antisymmetrized product of the states of ion and photoelectron:

$$|f\rangle = \hat{A} |(w'L'S'J'M'_J) \chi\rangle$$

Antisymmetrization can be removed from the matrix element because the matrix element is the same for any electron occupying the continuum state χ

$$\langle f | \vec{\varepsilon} \cdot \vec{r} | i \rangle = \sqrt{q} \langle (w'L'S'J'M'_J) \chi | \vec{\varepsilon} \cdot \vec{r} | i \rangle$$

Writing

$$|w'L'S'J'M'_J\rangle_{l^{q-1}} = \sum_{M'M'_S} C_{L'M', S'M'_S}^{J'M'_J} |w'L'S'M'M'_S\rangle_{l^{q-1}}$$

and taking into account that the ionized states are orthogonal, we obtain for the matrix element

$$\langle f | \vec{\varepsilon} \cdot \vec{r} | i \rangle = \sqrt{q} Q(wLS, w'L'S') \sum_{m, m_s} U(LSJM_J | L'S'J'M'_J l m m_s) \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle. \quad (2.1)$$

The transformation matrix U is given by

$$U(LSJM_J | L'S'J'M'_J l m m_s) = \sum_{M, M', M_S, M'_S} C_{L'M', lm}^{LM} C_{S'M'_S, \frac{1}{2}m_s}^{SM_S} C_{LM, SM_S}^{JM_J} C_{L'M', S'M'_S}^{J'M'_J}$$

The sum of the product of the four Clebsch-Gordan coefficients is given by (Eq. 8.7.20, [15])

$$\begin{aligned} \sum_{\beta\gamma\varepsilon\varphi} C_{b\beta c\gamma}^{a\alpha} C_{e\varepsilon f\varphi}^{d\delta} C_{e\varepsilon b\beta}^{g\eta} C_{f\varphi c\gamma}^{j\mu} &= \\ &= (-1)^{a-b+c+d+e-f} \sum_{k\kappa} \Pi_{kkag} C_{a\alpha k\kappa}^{j\mu} C_{g\eta k\kappa}^{d\delta} \begin{Bmatrix} b & c & a \\ j & k & f \end{Bmatrix} \begin{Bmatrix} b & e & g \\ d & k & f \end{Bmatrix} = \\ &= \Pi_{adgj} \sum_{k\kappa} C_{g\eta j\mu}^{k\kappa} C_{d\delta a\alpha}^{k\kappa} \begin{Bmatrix} c & b & a \\ f & e & d \\ j & g & k \end{Bmatrix} \end{aligned} \quad (2.2)$$

Let

$$a\alpha = JM_J, \quad b\beta = LM, \quad c\gamma = SM_S, \quad e\varepsilon = L'M', \quad f\varphi = S'M'_S, \quad g\eta = lm, \quad j\mu = \frac{1}{2}m_s, \quad d\delta = J'M'_J.$$

Then,

$$\begin{aligned} & \sum_{M, M_S, M', M'_S} C_{LM SM_S}^{JM_J} C_{L' M' S' M'_S}^{J' M'_J} C_{L' M' LM}^{lm} C_{S' M'_S SM_S}^{\frac{1}{2}m_s} = (-1)^{J-L+S+J'+L'-S'} \\ & \times \sum_{k\kappa} \Pi_{kkJl} C_{JM_J k\kappa}^{\frac{1}{2}m_s} C_{lm k\kappa}^{J' M'_J} \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\} \end{aligned} \quad (2.3)$$

We use the following relations (Eq. 8.4.10, [15]):

$$\begin{aligned} C_{L' M' LM}^{lm} &= (-1)^{L'-M'} \frac{\Pi_l}{\Pi_L} C_{L' M' l-m}^{L-M} = (-1)^{L'-M'-l} \frac{\Pi_l}{\Pi_L} C_{L'-M' lm}^{LM} \\ C_{S' M'_S SM_S}^{\frac{1}{2}m_s} &= (-1)^{S'-M'_S} \frac{\Pi_{\frac{1}{2}}}{\Pi_S} C_{S' M'_S \frac{1}{2}-m_s}^{S-M_S} = (-1)^{S-M'_S-1/2} \frac{\Pi_{\frac{1}{2}}}{\Pi_S} C_{S'-M'_S \frac{1}{2}m_s}^{SM_S} \\ C_{L' M' S' M'_S}^{J' M'_J} &= (-1)^{L'+S'-J'} C_{L'-M' S'-M'_S}^{J'-M'_J} \end{aligned}$$

Then

$$\begin{aligned} & \frac{\Pi_{\frac{1}{2}l}}{\Pi_{SL}} \sum_{M, M_S, M', M'_S} (-1)^{L'-M'-l+S-M'_S-1/2+L'+S'-J'} C_{L'-M' lm}^{LM} C_{S'-M'_S \frac{1}{2}m_s}^{SM_S} C_{LM SM_S}^{JM_J} C_{L'-M' S'-M'_S}^{J'-M'_J} \\ &= (-1)^{J-L+S+J'+L'-S'} \sum_{k\kappa} \Pi_{kkJl} C_{JM_J k\kappa}^{\frac{1}{2}m_s} C_{lm k\kappa}^{J' M'_J} \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\} \end{aligned} \quad (2.4)$$

Taking into account that $M' + M'_S = M'_J$, and using following replacement of variables

$$M' \rightarrow -M', \quad M'_S \rightarrow -M'_S, \quad M'_J \rightarrow -M'_J$$

we obtain

$$\begin{aligned} & \frac{\Pi_{\frac{1}{2}l}}{\Pi_{SL}} \sum_{M, M_S, M', M'_S} C_{L' M' lm}^{LM} C_{S' M'_S \frac{1}{2}m_s}^{SM_S} C_{LM SM_S}^{JM_J} C_{L' M' S' M'_S}^{J' M'_J} \\ &= (-1)^{J+l+1/2-M'_J} \sum_{k\kappa} \Pi_{kkJl} C_{JM_J k\kappa}^{\frac{1}{2}m_s} C_{lm k\kappa}^{J'-M'_J} \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\}. \end{aligned} \quad (2.5)$$

Then

$$U = (-1)^{J+l+1/2-M'_J} \sum_{k\kappa} \frac{\Pi_{kkLSJ}}{\Pi_{\frac{1}{2}}} C_{JM_J k\kappa}^{\frac{1}{2}m_s} C_{lm k\kappa}^{J'-M'_J} \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\}. \quad (2.6)$$

or

$$U = (-1)^{J-M_J+J'-M'_J+l+m} \Pi_{JJ'LS} \sum_{k\kappa} C_{J-M_J \frac{1}{2}m_s}^{k\kappa} C_{l-m J'-M'_J}^{k\kappa} \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\}. \quad (2.7)$$

For U^2 we have

$$U^2 = \left[\sum_{k\kappa} \Pi_{kkLS} C_{\frac{1}{2}m_s k\kappa}^{JM_J} C_{lm k-\kappa}^{J'-M'_J} \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\} \right]^2. \quad (2.8)$$

Alternatively,

$$\begin{aligned} U &= (-1)^{L+S-l-1/2+L'+S'-J'+M'_J} \Pi_{JJ'LS} \sum_{k\kappa} C_{lm \frac{1}{2}m_s}^{k\kappa} C_{J'-M'_J JM_J}^{k\kappa} \left\{ \begin{matrix} S & L & J \\ S' & L' & J' \\ \frac{1}{2} & l & k \end{matrix} \right\} = \\ &= \Pi_{JJ'LS} \sum_{k\kappa} (-1)^{J+1+k+M'_J} C_{lm \frac{1}{2}m_s}^{k\kappa} C_{J'-M'_J JM_J}^{k\kappa} \left\{ \begin{matrix} L & S & J \\ L' & S' & J' \\ l & \frac{1}{2} & k \end{matrix} \right\}, \quad (2.9) \end{aligned}$$

where, $k = l \pm \frac{1}{2}$ and $m + m_s = \kappa = M_J - M'_J$.

Assuming conservation of m_s upon photoemission, the cross section is

$$\frac{d\sigma_{M_J J' M'_J}}{d\Omega} = qQ^2 \sum_{m_s} \left| \sum_m U(LSJM_J | L'S'J'M'_J l m m_s) \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m \rangle \right|^2, \quad (2.10)$$

The inner sum contains **only one term** with $m = M_J - M'_J - m_s$, therefore we can write

$$\frac{d\sigma_{M_J J' M'_J}}{d\Omega} = qQ^2 \sum_{mm_s} U^2(LSJM_J | L'S'J'M'_J l m m_s) \frac{d\sigma_m}{d\Omega}. \quad (2.11)$$

To calculate photoemission intensity, the matrix element must be squared, summed over M'_J and averaged over M_J .

For nonmagnetic case we obtain.

$$\frac{d\sigma_{w'J'}}{d\Omega} = \frac{qQ^2}{\Pi_J^2} \sum_{mm_s M_J M'_J} U^2(LSJM_J | L'S'J'M'_J l m m_s) \frac{d\sigma_m}{d\Omega}.$$

Let $W(k)$ be the $9j$ symbol and $k_{\pm} = l \pm 1/2$. Then

$$\frac{d\sigma_{w'J'}}{d\Omega} = \frac{qQ^2}{\Pi_J^2} \sum_{mm_s M_J M'_J} \left(\sum_{\kappa} C_{lm \frac{1}{2}m_s}^{k_+\kappa} C_{J'M'_J JM_J}^{k_+\kappa} W(k_+) + \sum_{\kappa'} C_{lm \frac{1}{2}m_s}^{k_-\kappa'} C_{J'M'_J JM_J}^{k_-\kappa'} W(k_-) \right)^2 \frac{d\sigma_m}{d\Omega}.$$

Taking into account Eq. 8.7.4 and 8.7.5 (p. 219 in [15]), for the terms in the sum we have

$$\sum_{M_J M'_J} C_{J'M'_J JM_J}^{k_+\kappa} C_{J'M'_J JM_J}^{k_-\kappa'} = 0$$

and

$$\sum_{mm_s M_J M'_J} \left(\sum_{\kappa} C_{J'M'_J JM_J}^{k\kappa} C_{lm \frac{1}{2}m_s}^{k\kappa} \right)^2 \frac{d\sigma_m}{d\Omega} = \sum_m \frac{d\sigma_m}{d\Omega} \sum_{\kappa m_s} \left(C_{lm \frac{1}{2}m_s}^{k\kappa} \right)^2 = \frac{\Pi_{kk}}{\Pi_{ll}} \sum_m \frac{d\sigma_m}{d\Omega} = \Pi_{kk} \frac{d\sigma^{(one)}}{d\Omega}.$$

Thus, we get

$$\frac{d\sigma_{w'J'}}{d\Omega} = qQ^2(wLS, w'L'S') \frac{d\sigma^{(one)}}{d\Omega} \Pi_{J'LS}^2 \sum_{k=l\pm\frac{1}{2}} \Pi_k^2 \left\{ \begin{matrix} L & S & J \\ L' & S' & J' \\ l & \frac{1}{2} & k \end{matrix} \right\}^2. \quad (2.12)$$

This formula can be found in Ref. [14]. It is valid for transitions between the states with given wLS . Alternatively,

$$\frac{d\sigma_{w'J'}}{d\Omega} = qQ^2(wLS, w'S'L') \frac{d\sigma^{(one)}}{d\Omega} \sum_{k=J\pm\frac{1}{2}} \left[\Pi_{kJ'LS} \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\} \right]^2 \quad (2.13)$$

3 A special case of $L=0$

For $L = 0$ 6j-symbols are given by

$$\left\{ \begin{matrix} 0 & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} = \delta_{S,J} \delta_{k,S'} \frac{(-1)^{k+S+1/2}}{\Pi_{kS}}, \quad \left\{ \begin{matrix} 0 & L' & l \\ J' & k & S' \end{matrix} \right\} = \delta_{l,L'} \delta_{k,S'} \frac{(-1)^{k+L'+J'}}{\Pi_{kL'}}.$$

Then, using $\varkappa = -M'_S$,

$$U(L=0 S J M_J | L' S' J' M'_J l m m_s) = (-1)^{2J+1-M'_J+J'+2S'} \sum_{M'_S} \frac{\Pi_J}{\Pi_{\frac{1}{2}l}} C_{J M_J S' - M'_S}^{\frac{1}{2}m_s} C_{l m S' - M'_S}^{J' - M'_J} \quad (3.1)$$

where $M'_S = M_J - m_s = M'_J + m$.

4 A closed shell

We have initial state term 1S_0 and final state with $J' = l \pm \frac{1}{2}$. Thus,

$$L = 0, J = 0, S = 0, M_J = 0, L' = l, S' = \frac{1}{2}.$$

Also, $M'_S = -m_s = M'_J + m$, and we get

$$U = \frac{(-1)^{J'-M'_J}}{\Pi_{\frac{1}{2}l}} C_{l m \frac{1}{2}m_s}^{J'-M'_J} = \frac{(-1)^{J'+m+m_s}}{\Pi_{\frac{1}{2}l}} C_{l m \frac{1}{2}m_s}^{J'(m+m_s)} \quad (4.1)$$

Taking into account that $Q = 1$ and that m_s should be equal to the that of photoelectron, we obtain

$$\frac{d\sigma_{J'}}{d\Omega} = \frac{q}{2(2l+1)} \sum_{m, m_s} \left(C_{l m \frac{1}{2}m_s}^{J'(m+m_s)} \right)^2 \frac{d\sigma_m}{d\Omega}$$

In particular, for $J' = l + \frac{1}{2}$ we obtain $C^2 = \frac{l+1\pm m}{2l+1}$ for $m_s = \pm \frac{1}{2}$. For $J' = l - \frac{1}{2}$ we obtain $C^2 = \frac{l\mp m}{2l+1}$ for $m_s = \pm \frac{1}{2}$ (Eq. 3, p. 210). Hence,

$$\frac{d\sigma_{J'}}{d\Omega} = q \frac{J' + 1/2}{(2l+1)^2} \sum_m \frac{d\sigma_m}{d\Omega} = 2 \frac{J' + 1/2}{2l+1} \sum_m \frac{d\sigma_m}{d\Omega}$$

As one could expect, the total cross section is

$$\frac{d\sigma_{nl}}{d\Omega} = 2 \sum_m \frac{d\sigma_m}{d\Omega}.$$

Thus, in the case of a closed shell, the cross section is a sum of one-electron cross sections.

5 Example of Eu^{2+} in magnetic field along Z

Consider the initial configuration f^7 and initial term $^8S_{7/2}$ and final term $^7F_{J'}$, where $J' = 0, 1, 2, 3, 4, 5, 6$. Only $m_s = -\frac{1}{2}$ is allowed (because $M'_S = M_J - m_s$). Then

$$l = 3, \quad q = 7, \quad L = 0, \quad S = 7/2, \quad J = 7/2, \quad M_J = -7/2, \quad L' = 3, \quad S' = 3, \quad M'_S = -3.$$

In this case for “coefficient of fractional parentage” we obtain

$$Q(S', S') = 1$$

and, using $M'_S = M'_J + m$, we get

$$U = (-1)^{J'-M'_J} \frac{\Pi_{7/2}}{\Pi_{\frac{1}{2}3}} C_{\frac{7}{2}-\frac{7}{2}33}^{\frac{1}{2}-\frac{1}{2}} C_{3m33}^{J'(m+3)}.$$

Using

$$C_{\frac{7}{2}-\frac{7}{2}33}^{\frac{1}{2}-\frac{1}{2}} = \frac{1}{2}$$

we obtain

$$U = (-1)^{J'-M'_J} \frac{1}{\sqrt{7}} C_{3m33}^{J'(m+3)}$$

and

$$(qU)^2 = \left(C_{3m33}^{J'(3+m)} \right)^2.$$

Then, the squared expression must be summed over all components M'_J of the final state (related to m). The photoemission intensity is

$$\frac{d\sigma_{J'}}{d\Omega} = \sum_m \left(C_{3m33}^{J'(3+m)} \right)^2 \frac{d\sigma_m}{d\Omega}$$

General expression for any M_J is

$$\frac{d\sigma_{M_J J'}}{d\Omega} = \sum_{mm_s(M'_J M'_S)} \frac{d\sigma_m}{d\Omega} \left(C_{\frac{1}{2}m_s S' M'_S}^{J M_J} C_{lm S' - M'_S}^{J' M'_J} \right)^2$$

The total intensity of the multiplet is given by summation over $J'(M'_J)$ (using Eq. 8.8, p.202 in [15]):

$$\frac{d\sigma_{M_J}}{d\Omega} = \sum_{mm_s(M'_S)} \frac{d\sigma_m}{d\Omega} \left(C_{\frac{1}{2}m_s S' M'_S}^{J M_J} \right)^2 = \sum_m \frac{d\sigma_m}{d\Omega}$$

6 Rotation of magnetization direction (quantization axis)

In the case of zero CEF, we can avoid the Zeeman term in the Hamiltonian and use the Brillouin function to describe magnetization. In this case the direction of magnetic field can be taken into account in the following way.

The one-electron cross section is given by

$$\frac{d\sigma_m}{d\Omega} \propto |\langle \chi | \vec{\varepsilon} \cdot \vec{r} | lm \rangle|^2, \quad (6.1)$$

where $|\chi\rangle$ is the continuum final state of the photoelectron and the quantum number m describes the orbital momentum projection on the magnetization direction. Thus, the cross section depends on the photon polarization and magnetization direction. For calculation of one-electron photoemission matrix elements, one can use the EDAC code [16], where the quantization axis is fixed along the Z axis, which is along the surface normal. To rotate the quantization axis to the desired direction, one can use the complex conjugate of the Wigner D-matrix $D^*(\alpha, \beta, \gamma)$:

$$\langle \chi | \vec{\varepsilon} \cdot \vec{r} | lm \rangle = \sum_{m'} D_{mm'}^{l*}(\alpha, \beta, \gamma) \langle \chi | \vec{\varepsilon} \cdot \vec{r} | lm' \rangle, \quad (6.2)$$

where (α, β, γ) is a set of Euler angles, describing the axis rotation. The matrix elements in the right part can be directly calculated with EDAC.

The D-matrix is given by

$$D_{mm'}^j(\alpha, \beta, \gamma) \equiv e^{-im\alpha} d_{mm'}^j(\beta) e^{-im'\gamma}$$

where $d_{mm'}^j(\beta)$ is a small d-matrix (Eq. 4.3.5 in [15])

$$d_{mm'}^j(\beta) = [(j+m')!(j-m')!(j+m)!(j-m)!]^{\frac{1}{2}} \times \sum_s \left[\frac{(-1)^{m-m'+s} \left(\cos \frac{\beta}{2}\right)^{2j+m'-m-2s} \left(\sin \frac{\beta}{2}\right)^{m-m'+2s}}{(j+m'-s)!s!(m-m'+s)!(j-m-s)!} \right] \quad (6.3)$$

The sum over s is over such values that the factorials are nonnegative. For the Euler angles, z-x-z convention is used.

An example of this approach is given in [17].

7 Example of Eu^{3+}

Consider the initial configuration f^6 and initial term 7F_0 and final term ${}^6L'_{J'}$, where $L' = 3, 5$ and $J' = \frac{5}{2}, \frac{7}{2}$. Then

$$l = 3, \quad q = 6, \quad L = 3, \quad S = 3, \quad J = 0, \quad M_J = 0, \quad S' = \frac{5}{2}.$$

Due to Clebsch-Gordan coefficients in Eq. 2.6, we have

$$k = \frac{1}{2}, \quad \varkappa = m_s, \quad m + m_s = -M'_J.$$

Then

$$U = (-1)^{m+m_s-\frac{1}{2}} \Pi_3 C_{lm\frac{1}{2}m_s}^{J'(m+m_s)} \left\{ \begin{matrix} 3 & L' & 3 \\ J' & \frac{1}{2} & \frac{5}{2} \end{matrix} \right\}. \quad (7.1)$$

Similarly to the case of closed shell, we obtain

$$\frac{d\sigma_{L'J'}}{d\Omega} = q Q_{L'}(J' + 1/2) \left\{ \begin{matrix} 3 & L' & 3 \\ J' & \frac{1}{2} & \frac{5}{2} \end{matrix} \right\} \sum_m \frac{d\sigma_m}{d\Omega}.$$

8 Intermediate coupling

Spin-orbit interaction leads to mixing of states with different LS and same J , which results in deviation from the LS coupling scheme. Therefore, we use an intermediate coupling when the state is considered as a combination of basis states obtained in well-defined coupling scheme (in our case LS coupling):

$$|JM_J\rangle = \sum_{wLS} C_{wLS}^J |wLSJM_J\rangle$$

Then for the matrix element we obtain

$$\langle f | \vec{\epsilon} \cdot \vec{r} | i \rangle = \sqrt{q} \sum_{m, m_s} \sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M_J' l m m_s) \langle \chi | \vec{\epsilon} \cdot \vec{r} | l m m_s \rangle. \quad (8.1)$$

Similarly to Eq. 2.11, we obtain for the cross section

$$\frac{d\sigma_{M_J J' M_J'}}{d\Omega} = q \sum_{m m_s} \frac{d\sigma_m}{d\Omega} \left[\sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M_J' l m m_s) \right]^2. \quad (8.2)$$

For nonmagnetic case the photoemission intensity is

$$\frac{d\sigma_{J'}}{d\Omega} = q \frac{d\sigma^{(one)}}{d\Omega} \sum_{k=l\pm\frac{1}{2}} \left[\Pi_{kJ'} \sum_{\substack{wLS \\ w'L'S'}} \Pi_{LS} C_{wLS}^J C_{w'L'S'}^{J'} Q(wLS, w'S'L') \left\{ \begin{matrix} l & \frac{1}{2} & k \\ L & S & J \\ L' & S' & J' \end{matrix} \right\} \right]^2 \quad (8.3)$$

or

$$\frac{d\sigma_{J'}}{d\Omega} = q \frac{d\sigma^{(one)}}{d\Omega} \sum_{k=J\pm\frac{1}{2}} \left[\Pi_{kJ'} \sum_{\substack{wLS \\ w'L'S'}} \Pi_{LS} C_{wLS}^J C_{w'L'S'}^{J'} Q(wLS, w'S'L') \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\} \right]^2 \quad (8.4)$$

For magnetic case from Eq. 2.9 and 2.11 we obtain similarly to 2.12

$$\frac{d\sigma_{J'M_J}}{d\Omega} = q \sum_{\substack{mm_s \\ (M_J')}} \frac{d\sigma_m}{d\Omega} \left[\Pi_{JJ'} \sum_{\substack{k=l\pm\frac{1}{2} \\ (\neq)}} (-1)^{k+\frac{1}{2}} C_{lm\frac{1}{2}m_s}^{k\neq} C_{J'-M_J'JM_J}^{k\neq} \sum_{\substack{wLS \\ w'L'S'}} \Pi_{LS} C_{wLS}^J C_{w'L'S'}^{J'} Q(wLS|w'S'L') \left\{ \begin{matrix} l & \frac{1}{2} & k \\ L & S & J \\ L' & S' & J' \end{matrix} \right\} \right]^2 \quad (8.5)$$

or

$$\frac{d\sigma_{J'M_J}}{d\Omega} = q \sum_{mm_s} \frac{d\sigma_m}{d\Omega} \left[\Pi_{JJ'} \sum_{k=J\pm\frac{1}{2}} C_{J-M_J, \frac{1}{2}m_s}^{k(m_s-M_J)} C_{l-m, J'(m_s+m-M_J)}^{k(m_s-M_J)} \times \sum_{\substack{wLS \\ w'L'S'}} \Pi_{LS} C_{wLS}^J C_{w'L'S'}^{J'} Q(wLS, w'S'L') \left\{ \begin{matrix} L & S & J \\ \frac{1}{2} & k & S' \end{matrix} \right\} \left\{ \begin{matrix} L & L' & l \\ J' & k & S' \end{matrix} \right\} \right]^2 \quad (8.6)$$

9 Photoemission from CEF-split and/or Zeeman-split states

In presence of CEF and/or magnetic field, J is not a good quantum number. However, in order to simplify and speed up calculations, we considerably truncate the basis, considering only a single J term in the ground state. This approximation is acceptable when the admixture of other basis states to the ground state is negligible for the purpose of calculation. The possibility of such truncation is the main reason for using the LSJ basis. Otherwise, it would be much more easy to calculate photoemission using determinantal product states.

Let us assume that the ground and excited states are formed as linear combinations of states with same J and different M_J (we neglect mixing of different J in CEF and magnetic field):

$$|\nu J\rangle = \sum_{M_J} A_{M_J}^\nu |JM_J\rangle = \sum_{wLSM_J} A_{M_J}^\nu C_{wLS}^J |wLSJM_J\rangle$$

where ν distinguishes different states with same J . Then for the matrix element we obtain

$$\langle f | \vec{\varepsilon} \cdot \vec{r} | i \rangle = \sqrt{q} \sum_{m, m_s} \sum_{\substack{wLSM_J \\ w'L'S'M_J'}} Q(wLS, w'L'S') A_{M_J}^\nu A_{M_J'}^{\nu'*} C_{wLS}^J C_{w'L'S'}^{J'} \times U(LSJM_J | L'S'J'M_J' l m m_s) \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle. \quad (9.1)$$

We obtain for the cross section

$$\frac{d\sigma_{J'\nu'\nu}}{d\Omega} = q \sum_{m_s} \left| \sum_m \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle \sum_{M_J M'_J} A_{M_J}^\nu A_{M'_J}^{\nu'*} \sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M'_J l m m_s) \right|^2. \quad (9.2)$$

In the particular case, when we can neglect CEF/Zeeaman splitting in the final state, we sum over degenerate final states and get

$$\begin{aligned} \frac{d\sigma_{J'\nu}}{d\Omega} &= q \sum_{m_s M'_J} \left| \sum_m \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle \sum_{M_J} A_{M_J}^\nu \sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M'_J l m m_s) \right|^2 = \\ &= q \sum_{m_s M'_J} \left| \sum_m \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle \sum_{(M_J)} A_{M_J}^\nu \sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M'_J l m m_s) \right|^2 = \\ &= \Pi_{JJ'} \sum_{k(\varkappa)} (-1)^{k+\frac{1}{2}} C_{lm\frac{1}{2}m_s}^{k\varkappa} C_{J'-M'_J JM_J}^{k\varkappa} \sum_{\substack{wLS \\ w'L'S'}} \Pi_{LS} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} \left\{ \begin{matrix} L & S & J \\ L' & S' & J' \\ l & \frac{1}{2} & k \end{matrix} \right\} \Big|^2. \end{aligned} \quad (9.3)$$

Taking into account temperature-dependent occupation of levels ν we get

$$\begin{aligned} \frac{d\sigma_{J'}}{d\Omega} &= q \sum_{\nu m_s M'_J} u_\nu(T) \left| \sum_m \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle \sum_{M_J} A_{M_J}^\nu \sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M'_J l m m_s) \right|^2 = \\ &= q \sum_{\nu m_s M'_J} u_\nu(T) \left| \sum_m \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle \sum_{(M_J)} A_{M_J}^\nu \sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M'_J l m m_s) \right|^2 = \\ &= \Pi_{JJ'} \sum_{k(\varkappa)} (-1)^{k+\frac{1}{2}} C_{lm\frac{1}{2}m_s}^{k\varkappa} C_{J'-M'_J JM_J}^{k\varkappa} \sum_{\substack{wLS \\ w'L'S'}} \Pi_{LS} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} \left\{ \begin{matrix} L & S & J \\ L' & S' & J' \\ l & \frac{1}{2} & k \end{matrix} \right\} \Big|^2. \end{aligned} \quad (9.4)$$

In the particular case when only one M_J is present in the single initial state ν , we have

$$\begin{aligned}
\frac{d\sigma_{J'\nu M_J}}{d\Omega} &= q \sum_{m_s M'_J} \left| \sum_m \langle \chi | \vec{\varepsilon} \cdot \vec{r} | l m m_s \rangle \right. \\
&\quad \left. \sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M'_J l m m_s) \right|^2 = \\
&= q \sum_{\substack{m m_s \\ (M'_J)}} \frac{d\sigma_m}{d\Omega} \left[\sum_{\substack{wLS \\ w'L'S'}} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} U(LSJM_J | L'S'J'M'_J l m m_s) \right]^2 = \\
&= q \sum_{\substack{m m_s \\ (M'_J)}} \frac{d\sigma_m}{d\Omega} \left[\Pi_{JJ'} \sum_{k(\kappa)} (-1)^{k+\frac{1}{2}} C_{lm \frac{1}{2}m_s}^{k\kappa} C_{J'-M'_J JM_J}^{k\kappa} \times \right. \\
&\quad \left. \times \sum_{\substack{wLS \\ w'L'S'}} \Pi_{LS} Q(wLS, w'L'S') C_{wLS}^J C_{w'L'S'}^{J'} \left\{ \begin{matrix} L & S & J \\ L' & S' & J' \\ l & \frac{1}{2} & k \end{matrix} \right\} \right]^2. \quad (9.5)
\end{aligned}$$

10 Example of paramagnetic Yb compound: CEF in the final state

Consider Yb^{2+} with initial configuration f^{14} (closed shell). There is no CEF splitting in the ground state since $J = M_J = 0$. We analyze CEF in the final state. In this case, using Eq. 4.1, we get

$$\begin{aligned}
\frac{d\sigma_{J'}}{d\Omega} &= q \sum_{m m_s \nu'} \frac{d\sigma_m}{d\Omega} \left[\sum_{(M'_J)} A_{M'_J}^{\nu'} U(LSJM_J | L'S'J'M'_J l m m_s) \right]^2 = \\
&= q \sum_{m m_s \nu'} \frac{d\sigma_m}{d\Omega} \left[\sum_{(M'_J)} A_{M'_J}^{\nu'} \frac{(-1)^{J'-M'_J}}{\Pi_{\frac{1}{2}l}} C_{lm \frac{1}{2}m_s}^{J'-M'_J} \right]^2 = \sum_{m m_s \nu'} \frac{d\sigma_m}{d\Omega} \sum_{(M'_J)} (A_{M'_J}^{\nu'})^2 \left[C_{lm \frac{1}{2}m_s}^{J'-M'_J} \right]^2 \quad (10.1)
\end{aligned}$$

where $A_{M'_J}$ are wave function amplitudes for CEF-split final states. The inner sum contains only one term with $M'_J = -m - m_s$. For Kramers doublets we need a sum over two ν' with $\pm M'_J$. We have $|A_{M'_J}| = |A_{-M'_J}|$. Thus

$$\frac{d\sigma_{J'}}{d\Omega} = \sum_{M'_J(m)m_s} A_{M'_J}^2 \frac{d\sigma_m}{d\Omega} \left(\left[C_{lm \frac{1}{2}m_s}^{J'M'_J} \right]^2 + \left[C_{lm \frac{1}{2}m_s}^{J'-M'_J} \right]^2 \right)$$

For $J' = 7/2$ we take into account that

$$\left[C_{lm \frac{1}{2} \pm \frac{1}{2}}^{J'M'_J} \right]^2 = \frac{l+1 \pm m}{2l+1} = \frac{4 \pm m}{7}$$

and obtain

	Basis	Photoemission cross section
Γ_{t6}^-	$ \pm 7/2\rangle, \pm 1/2\rangle$	$(\sigma_{-3} + \sigma_3)A_{7/2}^2 + \left[\frac{3}{7}(\sigma_{-1} + \sigma_1) + \frac{8}{7}\sigma_0\right]A_{1/2}^2$
Γ_{t7}^-	$ \pm 3/2\rangle, \pm 5/2\rangle$	$\left[\frac{5}{7}(\sigma_{-1} + \sigma_1) + \frac{2}{7}(\sigma_{-2} + \sigma_2)\right]A_{3/2}^2 + \left[\frac{6}{7}(\sigma_{-2} + \sigma_2) + \frac{1}{7}(\sigma_{-3} + \sigma_3)\right]A_{5/2}^2$

11 One-electron photoemission matrix element

The wave function of electron in a free space is

$$\chi_{free} = e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(kr) Y_l^{m*}(\mathbf{k}) Y_l^m(\mathbf{r})$$

where j_l are spherical Bessel functions and complex conjugation $*$ can be interchanged between the two spherical harmonics due to symmetry. Wave function in central potential must have asymptotics

$$e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta) \frac{e^{ikr}}{r}$$

such wave function expanded in spherical harmonics is (§123,136 in [18])

$$\chi(\mathbf{k}, \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l e^{i\delta_l} R_{kl}(kr) Y_l^{m*}(\mathbf{k}) Y_l^m(\mathbf{r})$$

The one-electron wave function is

$$\phi_{nlm} = R_{nl}(r) Y_l^m(\mathbf{r})$$

The one-electron photoemission matrix element is

$$\begin{aligned} \langle \chi | \vec{\varepsilon} \cdot \vec{r} | \phi_{nlm} \rangle &= \sum_{l'm'} \langle \chi_{l'm'}(\mathbf{k}) | \vec{\varepsilon} \cdot \vec{r} | \phi_{nlm} \rangle = \sum_{l'm'} \frac{1}{\Pi_{l'}} \langle \mathbf{k}l' || r \mathbf{C}^{(1)} || nl \rangle \sum_q \varepsilon_q C_{lm1q}^{l'm'} = \\ &= \sum_{l'm'} \frac{i^{l'}}{\Pi_{l'}} Y_{l'}^{m'}(\mathbf{k}) \langle l' || \mathbf{C}^{(1)} || l \rangle \sum_q \varepsilon_q C_{lm1q}^{l'm'} (-i)^{l'} e^{-i\delta_{l'}} \int r^3 R_{kl'}^*(kr) R_{nl}(r) dr = \\ &= \sum_{l'} \frac{(-i)^{l'} e^{-i\delta_{l'}}}{\Pi_{l'}} R(kl', nl) \langle l' || \mathbf{C}^{(1)} || l \rangle \sum_{qm'} \varepsilon_q C_{lm1q}^{l'm'} Y_{l'}^{m'}(\mathbf{k}) \quad (11.1) \end{aligned}$$

where $R(kl', nl)$ is a radial matrix element.

Consider linear polarization $\vec{\varepsilon} = (0, 0, 1)$. Let $R_{\pm} = R(k(l \pm 1), nl)$ Then, differential cross section is

$$\begin{aligned} \sigma_z(\theta) &= \frac{1}{\Pi_l^2} \sum_m |\langle \chi | z | \phi_{nlm} \rangle|^2 = \sum_m \left| \sum_{l'} \frac{(-i)^{l'} e^{-i\delta_{l'}}}{\Pi_{l'}} R(kl', nl) C_{l010}^{l'0} C_{lm10}^{l'm} Y_{l'}^m(\mathbf{k}) \right|^2 = \\ &= \frac{R_-^2}{\Pi_{(l-1)}^2} \sum_m \left| C_{l010}^{(l-1)0} C_{lm10}^{(l-1)m} Y_{l-1}^m(\mathbf{k}) \right|^2 + \frac{R_+^2}{\Pi_{(l+1)}^2} \sum_m \left| C_{l010}^{(l+1)0} C_{lm10}^{(l+1)m} Y_{l+1}^m(\mathbf{k}) \right|^2 - \\ &\quad - 2\text{Re} \frac{R_+ R_-^* e^{i(\delta_{l+1} - \delta_{l-1})}}{\Pi_{(l+1)(l-1)}} \sum_m C_{l010}^{(l+1)0} C_{l010}^{(l-1)0} C_{lm10}^{(l+1)m} C_{lm10}^{(l-1)m} Y_{(l+1)}^m(\mathbf{k}) Y_{(l-1)}^{m*}(\mathbf{k}) \quad (11.2) \end{aligned}$$

Further one can use the relations

$$\begin{aligned}
C_{lm10}^{(l+1)m} &= \sqrt{\frac{(l+1)^2 - m^2}{(l+1)(2l+1)}}, & C_{lm10}^{(l-1)m} &= -\sqrt{\frac{l^2 - m^2}{l(2l+1)}} \\
C_{l010}^{(l+1)0} C_{lm10}^{(l+1)m} &= \frac{\sqrt{(l+1)^2 - m^2}}{(2l+1)}, & C_{l010}^{(l-1)0} C_{lm10}^{(l-1)m} &= \frac{\sqrt{l^2 - m^2}}{(2l+1)} \\
\sum_m |Y_l^m|^2 &= \frac{2l+1}{4\pi}, & \sum_m m^2 |Y_l^m|^2 &= \frac{l(l+1)(2l+1)}{8\pi} \sin^2 \theta \\
\sum_{m=-l}^l \sqrt{((l+1)^2 - m^2)(l^2 - m^2)} Y_{(l-1)}^m Y_{l+1}^{m*} &= \frac{l(l+1)}{8\pi} \sqrt{(2l-1)(2l+3)} (3 \cos^2 \theta - 1) \\
P_2(\cos \theta) &= \frac{3 \cos^2 \theta - 1}{2}
\end{aligned}$$

to get

$$\begin{aligned}
\sigma_z(\theta) &= \frac{|R_-|^2}{\Pi_{(l-1)}^2} \sum_m \frac{l^2 - m^2}{(2l+1)^2} |Y_{l-1}^m(\mathbf{k})|^2 + \frac{|R_+|^2}{\Pi_{(l+1)}^2} \sum_{m=-l}^l \frac{(l+1)^2 - m^2}{(2l+1)^2} |Y_{l+1}^m(\mathbf{k})|^2 - \\
&\quad - 2 \operatorname{Re} \frac{R_+ R_-^* e^{i(\delta_{l+1} - \delta_{l-1})}}{\Pi_{(l+1)(l-1)}} \sum_m \frac{\sqrt{((l+1)^2 - m^2)(l^2 - m^2)}}{(2l+1)^2} Y_{(l+1)}^m(\mathbf{k}) Y_{(l-1)}^{m*}(\mathbf{k}) = \\
&= \frac{l|R_-|^2}{8\pi\Pi_l^4} (l+1 + (l-1) \cos^2 \theta) + \frac{(l+1)|R_+|^2}{8\pi\Pi_l^4} (l + (l+2) \cos^2 \theta) - \\
&\quad - 4 \frac{\operatorname{Re} R_+ R_-^* e^{i(\delta_{l+1} - \delta_{l-1})}}{8\pi\Pi_l^4} l(l+1) P_2(\cos \theta) = \frac{1/3}{4\pi\Pi_l^4} [l(2l+1)|R_-|^2 + (2l+1)(l+1)|R_+|^2 + \\
&\quad + \{l(l-1)|R_-|^2 + (l+1)(l+2)|R_+|^2 - 6l(l+1) \operatorname{Re} R_+ R_-^* e^{i(\delta_{l+1} - \delta_{l-1})}\} P_2(\cos \theta)] = \\
&= \frac{\sigma_{nl}}{4\pi} (1 + \beta_{nl} P_2(\cos \theta)) \quad (11.3)
\end{aligned}$$

where

$$\begin{aligned}
\sigma_{nl} &= \frac{l|R_-|^2 + (l+1)|R_+|^2}{3(2l+1)} \\
\beta_{nl} &= \frac{l(l-1)|R_-|^2 + (l+1)(l+2)|R_+|^2 - 6l(l+1) \operatorname{Re}\{R_+ R_-^* e^{i(\delta_{l+1} - \delta_{l-1})}\}}{(2l+1)(l|R_-|^2 + (l+1)|R_+|^2)}
\end{aligned} \quad (11.4)$$

The radial matrix elements R_{\pm} and phase shifts $\delta_{l\pm 1}$ must be calculated numerically as functions of the photon energy.

More general formula valid also for circular polarization (in XY plane) has the form (Eq. 3.15 in [19])

$$\sigma_q = \frac{\sigma_{nl}}{4\pi} (1 + (-2)^{-|q|} \beta_{nl} P_2(\cos \theta))$$

This formula is also valid for unpolarized light, which can be modeled as an average of two opposite circular polarizations.

Let us consider angle-integrated one-electron photoemission cross section:

$$\sigma_{nlm} = \int_{\Omega} \left| \sum_{l'} \frac{(-i)^{l'}}{\Pi_{l'}} e^{-i\delta_{l'}} R(kl', nl) \langle l' || \mathbf{C}^{(1)} || l \rangle \sum_{qm'} \varepsilon_q C_{lm'1q}^{l'm'} Y_{l'}^{m'}(\mathbf{k}) \right|^2 d\Omega \quad (11.5)$$

Due to orthonormality of spherical harmonics, i.e. $\int Y_l^m Y_{l'}^{m'*} d\Omega = \delta_{ll'} \delta_{mm'}$, we may write

$$\sigma_{nlm} = \sum_{l'm'} \left| \frac{\Pi_l}{\Pi_{l'}} R(kl', nl) C_{l010}^{l'0} \sum_q \varepsilon_q C_{lm'1q}^{l'm'} \right|^2 \quad (11.6)$$

So the total angle-integrated cross section is a sum of partial cross sections. In the particular case of linear polarization along z , we get

$$\sigma_{nlm,z} = \sum_{l'm'} \left| \frac{\Pi_l}{\Pi_{l'}} R(kl', nl) C_{l010}^{l'0} C_{lm'10}^{l'm'} \right|^2 = \frac{(l+1)^2 - m^2}{\Pi_{l,l+1}^2} R_+^2 - \frac{(l^2 - m^2)}{\Pi_{l,l-1}^2} R_-^2 \quad (11.7)$$

So the angle-integrated cross section is m -dependent and polarization-dependent.

For unpolarized initial state of atom (nonmagnetic case) we should average the cross section over m . Then

$$\begin{aligned} \sigma_{nl} &= \frac{1}{\Pi_l^2} \sum_{m,l'm'} \left| \frac{\Pi_l}{\Pi_{l'}} R(kl', nl) C_{l010}^{l'0} \sum_q \varepsilon_q C_{lm'1q}^{l'm'} \right|^2 = \\ &= \sum_{l'm'm} \frac{R^2(kl', nl)}{\Pi_{l'}^2} (C_{l010}^{l'0})^2 \sum_{qq'} \varepsilon_q \varepsilon_{q'}^* C_{lm'1q}^{l'm'} C_{lm'1q'}^{l'm'} = \sum_{l'} \frac{R^2(kl', nl)}{\Pi_{l'}^2} (C_{l010}^{l'0})^2 \sum_q |\varepsilon_q|^2 \frac{\Pi_{l'}^2}{\Pi_1^2} = \\ &= \sum_{l'} \frac{R^2(kl', nl)}{3} (C_{l010}^{l'0})^2 = \frac{(l+1)R_+^2 + lR_-^2}{3(2l+1)} \quad (11.8) \end{aligned}$$

which is identical to 11.4, as expected. Thus, σ_{nl} is the average one-electron cross section. Also we can see that the average cross-section σ_{nl} could be readily obtained from 5.15 as a sum $\sigma(l-1, l) + \sigma(l+1, l)$.

12 Magnetic circular dichroism (MCD) in angle-integrated photoemission

Consider an atom (no CEF) in magnetic field. The partial cross section is

$$\begin{aligned} \sigma(j', j) &= \sum_{m_j m'_j} |\langle j' m'_j | \vec{\varepsilon} \cdot \vec{r} | j m_j \rangle|^2 u_{m_j} = \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{j'}^2} \sum_{m_j m'_j} \left| \sum_q \varepsilon_q C_{jm_j 1q}^{j' m'_j} \right|^2 u_{m_j} = \\ &= \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{j'}^2} \sum_{m_j m'_j q} |\varepsilon_q|^2 \left(C_{jm_j 1q}^{j' m'_j} \right)^2 u_{m_j} \quad (12.1) \end{aligned}$$

We assume circular polarization with either $\varepsilon = \{1, 0, 0\}$ ($q = -1$) or $\varepsilon = \{0, 0, 1\}$ ($q = 1$). Then, the partial angle-integrated cross section for a given polarization is

$$\sigma_q(j', j) = \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{j'}^2} \sum_{m_j m'_j} \left(C_{jm_j 1q}^{j' m'_j} \right)^2 u_{m_j} \quad (12.2)$$

The total angle-integrated cross section is

$$\sigma_q(j) = \sum_{j'} \sigma_q(j', j) = \sum_{j'} \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{j'}^2} \sum_{m_j m'_j} \left(C_{jm_j 1q}^{j' m'_j} \right)^2 u_{m_j} \quad (12.3)$$

The difference between two intensities at different polarizations is (using Eq. 8.6.5 in [15])

$$\begin{aligned} \sigma_1(j) - \sigma_{-1}(j) &= \sum_{j' m_j m'_j} \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{j'}^2} \left[\left(C_{jm_j 11}^{j' m'_j} \right)^2 - \left(C_{jm_j 1-1}^{j' m'_j} \right)^2 \right] u_{m_j} = \\ &= \sum_{j' m_j} \frac{|\langle j' || r \mathbf{C}^{(1)} || j \rangle|^2}{\Pi_{j'}^2} u_{m_j} \left[\left(C_{jm_j 11}^{j'(m_j+1)} \right)^2 - \left(C_{jm_j 1-1}^{j'(m_j-1)} \right)^2 \right] \end{aligned} \quad (12.4)$$

The values of coefficients are given in Tab. 1.

	$q = \pm 1$	$q = 0$	$\frac{1}{\Pi_{j'}^2} \left[\left(C_{jm 11}^{j'(m+1)} \right)^2 - \left(C_{jm 1-1}^{j'(m-1)} \right)^2 \right]$
$j' = j - 1$	$\frac{j(j-1) \mp (2j-1)m + m^2}{2j(2j+1)}$	$\frac{j^2 - m^2}{j(2j+1)}$	$\frac{-m}{j(2j+1)}$
$j' = j$	$\frac{j(j+1) \mp m - m^2}{2j(j+1)}$	$\frac{m^2}{j(j+1)}$	$\frac{-m}{j(j+1)(2j+1)}$
$j' = j + 1$	$\frac{(j+1)(j+2) \pm (2j+3)m + m^2}{2(j+1)(2j+1)}$	$\frac{(j+1)^2 - m^2}{(j+1)(2j+1)}$	$\frac{m}{(j+1)(2j+1)}$

Table 1: Values of coefficients $\left(C_{jm 1q}^{j'(m+q)} \right)^2$.

Hence,

$$\begin{aligned} \sigma_1(j) - \sigma_{-1}(j) &= \\ &= \frac{1}{\Pi_j^2} \left[\frac{|\langle j+1 || D || j \rangle|^2}{(j+1)} - \frac{|\langle j-1 || D || j \rangle|^2}{j} - \frac{|\langle j || D || j \rangle|^2}{j(j+1)} \right] \sum_{m_j} m_j u_{m_j} = \\ &= \frac{\langle m_j \rangle}{\Pi_j^2} \left[\frac{|\langle j+1 || D || j \rangle|^2}{(j+1)} - \frac{|\langle j-1 || D || j \rangle|^2}{j} - \frac{|\langle j || D || j \rangle|^2}{j(j+1)} \right] \end{aligned} \quad (12.5)$$

where $\langle m_j \rangle$ is the angular magnetic moment. Thus, MCD signal is proportional to the angular magnetic moment. Note that this result is valid in the absence of CEF splitting and for the case when the ground state is well-separated in energy from the other states.

13 Magnetic linear dichroism (MLD) in angle-integrated photoemission

Consider two polarizations: parallel to magnetization ($\varepsilon_z = 1$) and perpendicular to magnetization ($\varepsilon_x = 1$). We readily obtain the angle-integrated cross section as

$$\sigma_z(j', j) - \sigma_x(j', j) = \frac{|\langle j' || D || j \rangle|^2}{\Pi_{j'}^2} \sum_{m_j} u_{m_j} \left[\left(C_{jm_j 10}^{j' m_j} \right)^2 - \frac{1}{2} \left(C_{jm_j 1-1}^{j'(m_j-1)} \right)^2 - \frac{1}{2} \left(C_{jm_j 1+1}^{j'(m_j+1)} \right)^2 \right] \quad (13.1)$$

	$\left(C_{jm\ 10}^{j'm}\right)^2 - \frac{1}{2} \left(C_{jm\ 1-1}^{j'(m-1)}\right)^2 - \frac{1}{2} \left(C_{jm\ 1+1}^{j'(m+1)}\right)^2$
$j' = j - 1$	$\frac{j(j+1)-3m^2}{2j(2j+1)}$
$j' = j$	$-\frac{j(j+1)-3m^2}{2j(j+1)}$
$j' = j + 1$	$\frac{j(j+1)-3m^2}{2(j+1)(2j+1)}$

Table 2: Values of coefficient.

The values are given in Tab. 2.

Thus, we obtain (using Eq. 13.2)

$$\begin{aligned}
\sigma_z(j) - \sigma_x(j) &= \sum_{j'} \sigma_z(j', j) - \sigma_x(j', j) = \\
&= \left[\frac{|\langle j-1 || D || j \rangle|^2}{(2j-1)j} - \frac{|\langle j || D || j \rangle|^2}{j(j+1)} + \frac{|\langle j+1 || D || j \rangle|^2}{(2j+3)(j+1)} \right] \sum_{m_j} u_{m_j} \frac{3j(j+1) - 3m_j^2}{2(2j+1)} = \\
&= \left[\frac{|\langle j-1 || D || j \rangle|^2}{(2j-1)j} - \frac{|\langle j || D || j \rangle|^2}{j(j+1)} + \frac{|\langle j+1 || D || j \rangle|^2}{(2j+3)(j+1)} \right] \frac{3}{2(2j+1)} [j(j+1) - \langle m_j^2 \rangle] = \\
&= \left[\frac{|\langle j-1 || D || j \rangle|^2}{(2j-1)j} - \frac{|\langle j || D || j \rangle|^2}{j(j+1)} + \frac{|\langle j+1 || D || j \rangle|^2}{(2j+3)(j+1)} \right] \frac{3}{2(2j+1)} \langle m_j \rangle \coth \left(\frac{y}{2j} \right) \quad (13.2)
\end{aligned}$$

where y is a function of temperature, which can be found from Eq. 13.1. At $T = 0$ we have $y \rightarrow \infty$ and $\coth = 1$, therefore, the MLD signal is proportional to the moment. This result is valid in the absence of CEF splitting and for the case when the ground state is well-separated in energy from the other states.

14 Transition between two shells $l_1^n l_2^{k-1} \leftrightarrow l_1^{n-1} l_2^k$ in LSJ coupling

The reduced matrix element is

$$\begin{aligned}
D_{LS} &\equiv \langle (w_1 L_1 S_1, w_2 L_2 S_2) LS, J || D || (w'_1 L'_1 S'_1, w'_2 L'_2 S'_2) L' S', J' \rangle = \\
&= \delta_{S,S'} (-1)^{L+S+J'+1} \Pi_{JJ'} \left\{ \begin{matrix} J & J' & 1 \\ L' & L & S \end{matrix} \right\} \langle (w_1 L_1 S_1, w_2 L_2 S_2) LS || D || (w'_1 L'_1 S'_1, w'_2 L'_2 S'_2) L' S' \rangle \quad (14.1)
\end{aligned}$$

Now we decouple one electron from l_1^n and one electron from l_2^k

$$\begin{aligned}
&\langle (w'_1 L'_1 S'_1, l_1 s_{1(N)}) w_1 L_1 S_1, w_2 L_2 S_2; LS || D_N || w'_1 L'_1 S'_1, (w_2 L_2 S_2, l_2 s_{2(N)}) w'_2 L'_2 S'_2; L' S' \rangle \times \\
&\quad \times \sqrt{n k} Q(w_1 L_1 S_1 | w'_1 L'_1 S'_1) Q(w'_2 L'_2 S'_2 | w_2 L_2 S_2) \quad (14.2)
\end{aligned}$$

Then, we recouple $l_1 s_1$ (Eq. 9.1.7 twice)

$$\begin{aligned} & \langle (w'_1 L'_1 S'_1, l_1 s_{1(N)}) w_1 L_1 S_1, w_2 L_2 S_2; LS || D_N || w'_1 L'_1 S'_1, (w_2 L_2 S_2, l_2 s_{2(N)}) w'_2 L'_2 S'_2; L' S' \rangle = \\ & = \sum_{L_R S_R} (-1)^{L'_1 + L + L_R + S'_1 + S + S_R} \Pi_{L_1 L_R S_1 S_R} \left\{ \begin{matrix} L'_1 & l_1 & L_1 \\ L_2 & L & L_R \end{matrix} \right\} \left\{ \begin{matrix} S'_1 & s & S_1 \\ S_2 & S & S_R \end{matrix} \right\} \times \\ & \times \langle L'_1, (L_2, l_{1(N)}) L_R; L || D_N || L'_1, (L_2, l_{2(N)}) L'_2; L' \rangle \delta_{S_R, S'_2} \quad (14.3) \end{aligned}$$

Then, we use Eq. 6.3

$$\begin{aligned} & \langle L'_1, (L_2, l_{1(N)}) L_R; L || D_N || L'_1, (L_2, l_{2(N)}) L'_2; L' \rangle = \\ & = (-1)^{L'_1 + L'_2 + L + 1} \Pi_{LL'} \left\{ \begin{matrix} L & L' & 1 \\ L'_2 & L_R & L'_1 \end{matrix} \right\} \langle (L_2, l_{1(N)}) L_R || D_N || (L_2, l_{2(N)}) L'_2 \rangle \quad (14.4) \end{aligned}$$

and once more we use Eq. 6.3

$$\langle (L_2, l_{1(N)}) L_R || D_N || (L_2, l_{2(N)}) L'_2 \rangle = (-1)^{L_2 + l_2 + L_R + 1} \Pi_{L_R L'_2} \left\{ \begin{matrix} L_R & L'_2 & 1 \\ l_2 & l_1 & L_2 \end{matrix} \right\} \langle l_1 || D || l_2 \rangle \quad (14.5)$$

Now consider all terms with L_R and Eq. 10.2.20 in [15]:

$$\sum_{L_R} (-1)^{2L_R} \Pi_{L_R}^2 \left\{ \begin{matrix} L_2 & L & L_1 \\ L'_1 & l_1 & L_R \end{matrix} \right\} \left\{ \begin{matrix} L'_2 & L' & L'_1 \\ L & L_R & 1 \end{matrix} \right\} \left\{ \begin{matrix} l_2 & 1 & l_1 \\ L_R & L_2 & L'_2 \end{matrix} \right\} = \left\{ \begin{matrix} L_2 & L & L_1 \\ L'_2 & L' & L'_1 \\ l_2 & 1 & l_1 \end{matrix} \right\} \quad (14.6)$$

Finally, for the total matrix element we obtain

$$\begin{aligned} D_{LS} &= \delta_{S, S'} (-1)^{1 + S'_1 + S'_2 + L'_2 + L + L_2 + l_2 - J'} \Pi_{JJ' S_1 S'_2 LL' L_1 L'_2} \left\{ \begin{matrix} L & S & J \\ J' & 1 & L' \end{matrix} \right\} \left\{ \begin{matrix} S_1 & S_2 & S \\ S'_2 & S'_1 & s \end{matrix} \right\} \times \\ & \times \left\{ \begin{matrix} L_1 & L_2 & L \\ L'_1 & L'_2 & L' \\ l_1 & l_2 & 1 \end{matrix} \right\} \sqrt{nk} Q(w_1 L_1 S_1 | w'_1 L'_1 S'_1) Q(w'_2 L'_2 S'_2 | w_2 L_2 S_2) \langle l_1 || D || l_2 \rangle \quad (14.7) \end{aligned}$$

This result is similar to Cowan's Eq. 14.88 [6].

In the particular case of transition from a closed to an open shell $l_1^n l_2^{4l_2+1} \leftarrow l_1^{n-1} l_2^{4l_2+2}$ we have $L'_2 = S'_2 = 0$ and the result is simplified to

$$\begin{aligned} D_{LS}^{closed} &= \delta_{S, S'} \delta_{S'_1, S'_1} \delta_{S_2, \frac{1}{2}} \delta_{l_2, L_2} \delta_{L', L'_1} (-1)^{L - J' - S_1 + \frac{1}{2}} \frac{\Pi_{JJ' S_1 LL_1}}{\Pi_S} \left\{ \begin{matrix} L & S & J \\ J' & 1 & L'_1 \end{matrix} \right\} \times \\ & \times \left\{ \begin{matrix} 1 & l_1 & l_2 \\ L_1 & L & L'_1 \end{matrix} \right\} \sqrt{n} Q(w_1 L_1 S_1 | w'_1 L'_1 S'_1) \langle l_1 || D || l_2 \rangle \quad (14.8) \end{aligned}$$

In the particular case of $\text{Eu}^{2+} 4f^8 4d^9 \leftarrow 4f^7 4d^{10}$ transition we have $S'_1 = 7/2$, $L'_1 = L'_2 = S'_2 = 0$ and the result is further simplified to

$$D_{LS}^{Eu^{2+}} = \delta_{\frac{7}{2}, S, S'} \delta_{S'_1, S'_1} \delta_{S_2, \frac{1}{2}} \delta_{l_2, L_2} \delta_{L', 0} \delta_{L_1, 1} \delta_{L_1, 3} (-1)^{J - S_1 + \frac{1}{2}} \frac{\Pi_{J3}}{\Pi_1} Q(w_1 L_1 S_1 | w'_1 L'_1 S'_1) \langle l_1 || D || l_2 \rangle \quad (14.9)$$

Due to 6j-symbol, $S_1 = 3$. Initial state term is $4f^7(^8S)4d^{10}(^1S)(^8S_{\frac{7}{2}})$. Final state term is $4f^8(^7F)4d^9(^2D)(^8P_J)$ with three J values. $Q^2 = \frac{1}{7}$. Total cross section is

$$\sigma_{LS}^{Eu^{2+}} = \sum_J \frac{\Pi_{J3,2}^2}{\Pi_{1,\frac{7}{2}}^2} \sigma(f, d) Q^2 (f^8(^7F) | f^7(^8S)) = \frac{1}{7} \sigma(f, d) \frac{7 \cdot 5}{3 \cdot 8} \sum_J \Pi_J^2 = 5 \sigma(f, d)$$

which is rather obvious because only five d electrons can be excited into the half-filled f -shell.

15 Resonant photoemission

The matrix element in resonance is

$$\langle f | T | i \rangle \approx \langle f | \vec{\varepsilon} \cdot \vec{r} | i \rangle + \sum_t \frac{\langle f | V | t \rangle \langle t | \vec{\varepsilon} \cdot \vec{r} | i \rangle}{E_t - E_i - E - i\Gamma_t}$$

where $|t\rangle$ are intermediate states, V is a Coulomb operator

$$V = \sum_{i>j} \frac{e^2}{r_{ij}}$$

For $d \rightarrow f$ resonance, we have

$$\begin{aligned} |i\rangle &= |d^{10}, f^q\rangle \\ |t\rangle &= |d^9, f^{q+1}\rangle \\ |f\rangle &= |d^{10}, f^{q-1}, \chi\rangle \end{aligned}$$

To be continued ...

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