1 *Ab initio* calculation of the line-broadening due to fluorescence decay

In the following, I will discuss how core-excited states are broadened due to the coupling to the continuous energy spectrum of the electromagnetic field (fluorescence decay). I will present an *ab initio* description of the broadening in terms of self-energies and briefly derive all relevant equations. Starting from the multipole expansion of the light-matter interaction (see section 1.1), in section 1.2 an expression of the fluorescence self-energy is derived. This document summarizes parts of my PhD thesis (see https://archiv.ub.uni-heidelberg.de/volltextserver/32091/).

1.1 Multipole expansion of the relativistic light-matter interaction

The Hamiltonian describing the (relativistic) interaction of light with matter in the Coulomb gauge is given by

$$H_{e\gamma} = e \int \psi^\dagger(\mathbf{r}) \boldsymbol{\alpha} \cdot \mathbf{A}(\mathbf{r}) \psi(\mathbf{r}) \mathrm{d}^3 r \tag{1.1}$$

where $\psi^\dagger(\mathbf{r})$ and $\psi(\mathbf{r})$ are the four-component Dirac-spinor fields and $\boldsymbol{\alpha}$ the Dirac matrix. $\mathbf{A}(\mathbf{r})$ denotes the vector potential which in its canonical form reads

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k}_\gamma} \sum_{\mu=1}^{2} \frac{1}{\sqrt{2V\omega_\gamma}} \left(\boldsymbol{\epsilon}_\mu(\mathbf{k}_\gamma) a^\dagger_{\mathbf{k}_\gamma,\mu} e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} + \boldsymbol{\epsilon}^*_\mu(\mathbf{k}_\gamma) a_{\mathbf{k}_\gamma,\mu} e^{-i\mathbf{k}_\gamma \cdot \mathbf{r}} \right). \tag{1.2}$$

Here V denotes the quantization volume, which we set to 1. $\boldsymbol{\epsilon}_\nu(\mathbf{k}_\gamma)$ represents the polarization vector and $a^\dagger_{\mathbf{k}_\gamma,\nu}$ and $a_{\mathbf{k}_\gamma,\nu}$ are the creation and annihilation operators of a photon in mode $\{\mathbf{k}_\gamma, \mu\}$, respectively. The kinetic energy of the photons is

given by

$$H_\gamma = \sum_{\mathbf{k}_\gamma} \sum_{\mu=1}^{2} \omega_\gamma a^\dagger_{\mathbf{k}_\gamma,\mu} a_{\mathbf{k}_\gamma,\mu}. \tag{1.3}$$

where $\omega_\gamma = c|\mathbf{k}_\gamma| = k_\mu$ with $c = 1$. Inserting the vector potential (1.2) into (1.1), the light-matter interaction Hamiltonian becomes

$$\begin{aligned} H_{e\gamma} = e \sum_{\mathbf{k}_\gamma} \sum_{\mu=1}^{2} & \frac{1}{\sqrt{2\omega_\gamma}} \\ & \times \int \psi^\dagger(\mathbf{r}) \boldsymbol{\alpha} \cdot \left(\boldsymbol{\epsilon}_\mu(\mathbf{k}_\gamma) a^\dagger_{\mathbf{k}_\gamma,\mu} e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} + \boldsymbol{\epsilon}^*_\mu(\mathbf{k}_\gamma) a_{\mathbf{k}_\gamma,\mu} e^{-i\mathbf{k}_\gamma \cdot \mathbf{r}} \right) \psi(\mathbf{r}) \mathrm{d}^3 r. \end{aligned} \tag{1.4}$$

In order to simplify notation, we introduce the transition operator

$$T_{e\gamma}(\mathbf{k}_\gamma, \mu) = \boldsymbol{\epsilon}_\mu(\mathbf{k}_\gamma) \cdot \int \mathrm{d}^3 r \; \psi^\dagger(\mathbf{r}) \boldsymbol{\alpha} e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} \psi(\mathbf{r}) \tag{1.5}$$

such that $H_{e\gamma}$ takes the compact form

$$H_{e\gamma} = e \sum_{\mathbf{k}_\gamma} \sum_{\mu=1}^{2} \frac{1}{\sqrt{2\omega_\gamma}} \left(a^\dagger_\mu(\mathbf{k}_\gamma) T_{e\gamma}(\mathbf{k}_\gamma, \mu) + a_\mu(\mathbf{k}_\gamma) T^\dagger_{e\gamma}(\mathbf{k}_\gamma, \mu) \right). \tag{1.6}$$

Note that the light-matter interaction involves only a single photon, i.e. $H_{e\gamma}$ can induce transitions from an initial state with n to a final state with $n \pm 1$ photons by absorbing or emitting a photon.

To systematically study the interaction between light and matter, it is convenient to decompose $T_{e\gamma}(\mathbf{k}_\gamma, \mu)$ into its multipoles. For brevity, we first drop the momentum dependence of $\boldsymbol{\epsilon}_\mu(\mathbf{k}_\gamma)$, i.e. $\boldsymbol{\epsilon}_\mu(\mathbf{k}_\gamma) \to \boldsymbol{\epsilon}_\mu$, and then expand $\boldsymbol{\epsilon}_\mu \cdot e^{i\mathbf{k}_\gamma \cdot \mathbf{r}}$ in terms of multipole potentials

$$\boldsymbol{\epsilon}_\mu \cdot e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} = 4\pi \sum_{JM\lambda} i^{J-\lambda} \left(\boldsymbol{\epsilon}_\mu \cdot \mathbf{Y}^{(\lambda)*}_{JM}(\hat{k}_\gamma) \right) \mathbf{a}^{(\lambda)}_{JM}(\mathbf{r}) \tag{1.7}$$

where $\lambda = 0, 1$ and $M = -J, \ldots, J$. As $\boldsymbol{\epsilon}_\nu \cdot e^{i\mathbf{k}_\gamma \cdot \mathbf{r}}$ transforms as a vector under rotations, the multipole potentials $\mathbf{a}^{(\lambda)}_{JM}(\mathbf{r})$ can be expressed as linear combinations of vector spherical harmonics $\mathbf{Y}^{(\lambda)}_{JM}(\hat{r})$

$$\begin{aligned} \mathbf{a}^{(0)}_{JM}(\mathbf{r}) &= j_J(k_\gamma r) \mathbf{Y}^{(0)}_{JM}(\hat{r}) \\ \mathbf{a}^{(1)}_{JM}(\mathbf{r}) &= \left(j'_J(k_\gamma r) + \frac{j_J(k_\gamma r)}{k_\gamma r} \right) \mathbf{Y}^{(1)}_{JM}(\hat{r}) + \sqrt{J(J+1)} \frac{j_J(k_\gamma r)}{k_\gamma r} \mathbf{Y}^{(-1)}_{JM}(\hat{r}). \end{aligned} \tag{1.8}$$

A definition of the vector spherical harmonics $\mathbf{Y}_{JM}^{(\lambda)}(\hat{r})$ can be found in the literature I refer to in my PhD thesis. In the Coulomb gauge plane waves are transverse, therefore their polarization vector $\boldsymbol{\epsilon}_\mu$ is perpendicular to the direction of propagation $\mathbf{k}_\gamma$, i.e. $\boldsymbol{\epsilon}_\mu \cdot \mathbf{k}_\gamma = 0$. Since the vector spherical harmonic $\mathbf{Y}_{JM}^{(-1)}(\hat{k}_\gamma)$ is parallel to $\mathbf{k}_\gamma$, we find that $\boldsymbol{\epsilon}_\mu \cdot \mathbf{Y}_{JM}^{(-1)}(\hat{k}_\gamma) = 0$ and only the multipoles with $\lambda = 0, 1$ contribute to the above expansion. The parts with $\lambda = 0$ are referred to as *magnetic* multipoles, while those with $\lambda = 1$ represent the *electric* multipoles. This labeling will become meaningful as soon as we have derived explicit expressions for the matrix elements later on, when it will turn out that the magnetic and electric multipoles matrix elements satisfy the corresponding selection rules.

Inserting the multipole expansion (1.7) into (1.5), the transition operator decomposed into the individual multipole moments is given by

$$T_{e\gamma}(\mathbf{k}_\gamma, \mu) = 4\pi \sum_{JM\lambda} i^{J-\lambda} \left(\boldsymbol{\epsilon}_\mu \cdot \mathbf{Y}_{JM}^{(\lambda)*}(\hat{k}_\gamma) \right) \int \mathrm{d}^3 r \, \psi^\dagger(\mathbf{r}) \boldsymbol{\alpha} \cdot \mathbf{a}_{JM}^{(\lambda)}(\mathbf{r}) \psi(\mathbf{r}). \tag{1.9}$$

In order to obtain an expression for $T(\mathbf{k}_\gamma, \mu)$ in second quantization, we next expand the four component Dirac-spinor field in terms creation $e_\tau^\dagger$ and annihilation e_τ operators weighted by the single-particle wave functions $\phi_\tau^\dagger(\mathbf{r})$ and $\phi_\tau(\mathbf{r})$, respectively,

$$\psi(\mathbf{r}) = \sum_\tau \phi_\tau(\mathbf{r}) e_\tau \qquad \psi^\dagger(\mathbf{r}) = \sum_\tau \phi_\tau^\dagger(\mathbf{r}) e_\tau^\dagger \tag{1.10}$$

where τ comprises the quantum numbers $\tau = \{n, \kappa, m\}$. Here n denotes the principal, κ the relativistic and m the magnetic quantum number related to the total angular momentum. The single-particle wave functions are given by four-component spinors

$$\phi_\tau(\mathbf{r}) = \begin{pmatrix} G_{n\kappa}(r) \Omega_{\kappa m}(\theta, \phi) \\ \mathrm{i} F_{n\kappa}(r) \Omega_{-\kappa m}(\theta, \phi) \end{pmatrix}. \tag{1.11}$$

Here $G_{n\kappa}(r)$ is the large and $F_{n\kappa}(r)$ the small component of the radial wave function, where $\Omega_{\kappa m}(\theta, \phi)$ represents a spherical spinor. Inserting (1.10) into (1.9) and using (1.11) as the single-particle wave functions, the second quantized form of the transition operator decomposed into a sum over *magnetic* ($\lambda = 0$) and *electric* ($\lambda = 1$) multipoles takes the form:

$$T_{e\gamma}(\mathbf{k}_\gamma, \mu) = \sum_{\lambda=0}^{1} \sum_{\tau_a \tau_b} t_{\tau_b \tau_a}^{(\lambda)}(\mathbf{k}_\gamma, \mu) e_{\tau_b}^\dagger e_{\tau_a} \tag{1.12}$$

The matrix elements $t^{(\lambda)}_{\tau_b\tau_a}(\mathbf{k}_\gamma,\nu)$ are explicitly given by

$$\begin{aligned}
&t^{(0)}_{\tau_b\tau_a}(\mathbf{k}_\gamma,\mu)\\
&= 4\pi\sum_{JM} i^J \left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(0)*}_{JM}(\hat{k}_\gamma)\right)\int \mathrm{d}^3r\;\phi^\dagger_{\tau_b}(\mathbf{r})\boldsymbol{\alpha}\cdot\mathbf{a}^{(0)}_{JM}\phi_{\tau_a}(\mathbf{r})\\
&= 4\pi\sum_{JM} i^{J+1} \left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(0)*}_{JM}(\hat{k}_\gamma)\right)\int \mathrm{d}r\;\Big(g_{n_b\kappa_b}(r)j_J(k_\gamma r)f_{n_a\kappa_a}(r)\\
&\quad\times\langle\Omega_{\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(0)}_{JM}|\Omega_{-\kappa_a m_a}\rangle - f_{n_b\kappa_b}(r)j_J(k_\gamma r)g_{n_a\kappa_a}(r)\langle\Omega_{-\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(0)}_{JM}|\Omega_{\kappa_a m_a}\rangle\Big)
\end{aligned} \tag{1.13}$$

and

$$\begin{aligned}
&t^{(1)}_{\tau_b\tau_a}(\mathbf{k}_\gamma,\mu)\\
&= 4\pi\sum_{JM} i^{J-1} \left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(1)*}_{JM}(\hat{k}_\gamma)\right)\int \mathrm{d}^3r\;\phi^\dagger_{\tau_b}(\mathbf{r})\boldsymbol{\alpha}\cdot\mathbf{a}^{(1)}_{JM}\phi_{\tau_a}(\mathbf{r})\\
&= 4\pi\sum_{JM} i^{J} \left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(1)*}_{JM}(\hat{k}_\gamma)\right)\int \mathrm{d}r\;\Bigg[\left(j'_J(k_\gamma r)+\frac{j_J(k_\gamma r)}{k_\gamma r}\right)\Big(g_{n_b\kappa_b}(r)f_{n_a\kappa_a}(r)\\
&\qquad\times\langle\Omega_{\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(1)}_{JM}|\Omega_{-\kappa_a m_a}\rangle - f_{n_b\kappa_b}g_{n_a\kappa_a}\langle\Omega_{-\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(1)}_{JM}|\Omega_{\kappa_a m_a}\rangle\Big)\\
&\qquad+\sqrt{J(J+1)}\frac{j_J(k_\gamma r)}{k_\gamma r}\Big(g_{n_b\kappa_b}f_{n_a\kappa_a}\langle\Omega_{\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(-1)}_{JM}|\Omega_{-\kappa_a m_a}\rangle\\
&\qquad-f_{n_b\kappa_b}g_{n_a\kappa_a}\langle\Omega_{-\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(-1)}_{JM}|\Omega_{\kappa_a m_a}\rangle\Big)\Bigg]
\end{aligned} \tag{1.14}$$

for the *magnetic* and *electric* multipoles, respectively. Both involve matrix elements of products of the vector of Pauli matrices $\boldsymbol{\sigma}$ and vector spherical harmonics that can be rewritten in terms of matrix elements of ordinary spherical harmonics using the following relations:

$$\begin{aligned}
\langle\Omega_{\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(-1)}_{JM}|\Omega_{\kappa_a m_a}\rangle &= -\langle\Omega_{-\kappa_b m_b}|Y_{JM}|\Omega_{\kappa_a m_a}\rangle\\
\langle\Omega_{\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(0)}_{JM}|\Omega_{\kappa_a m_a}\rangle &= \frac{\kappa_a-\kappa_b}{\sqrt{J(J+1)}}\langle\Omega_{\kappa_b m_b}|Y_{JM}|\Omega_{\kappa_a m_a}\rangle\\
\langle\Omega_{\kappa_b m_b}|\boldsymbol{\sigma}\cdot\mathbf{Y}^{(1)}_{JM}|\Omega_{\kappa_a m_a}\rangle &= \frac{\kappa_a+\kappa_b}{\sqrt{J(J+1)}}\langle\Omega_{-\kappa_b m_b}|Y_{JM}|\Omega_{\kappa_a m_a}\rangle
\end{aligned} \tag{1.15}$$

Hence, the matrix element for magnetic multipoles simplifies to

$$\begin{aligned} t^{(0)}_{\tau_b\tau_a}(\mathbf{k}_\gamma,\mu) &= 4\pi\sum_{JM} i^{J+1}\left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(0)*}_{JM}(\hat{k}_\gamma)\right)\langle\Omega_{\kappa_b m_b}|Y_{JM}|\Omega_{-\kappa_a m_a}\rangle \\ &\qquad\times\frac{-(\kappa_a+\kappa_b)}{\sqrt{J(J+1)}}R^{(0)}_{\tau_b\tau_a}(\omega_\gamma) \\ &\equiv 4\pi\sum_{JM} i^{J+1}\left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(0)*}_{JM}(\hat{k}_\gamma)\right)\left[T^{(0)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a} \end{aligned} \tag{1.16}$$

with radial integral $R^{(0)}_{\tau_b\tau_a}(\omega_\gamma)=\int \mathrm{d}r\, j_J(k_\gamma r)\,(g_{n_b\kappa_b}f_{n_a\kappa_a}+f_{n_b\kappa_b}g_{n_a\kappa_a})$. For the electric multipoles, on the other hand, we obtain matrix elements of the form

$$\begin{aligned} t^{(1)}_{\tau_b\tau_a}(\mathbf{k}_\gamma,\mu) &= 4\pi\sum_{JM} i^{J}\left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(1)*}_{JM}(\hat{k}_\gamma)\right)\langle\Omega_{\kappa_b m_b}|Y_{JM}|\Omega_{\kappa_a m_a}\rangle \\ &\qquad\times\left[\frac{\kappa_b-\kappa_a}{\sqrt{J(J+1)}}R^{(1,1)}_{\tau_b\tau_a}(\omega_\gamma)+\sqrt{J(J+1)}R^{(1,2)}_{\tau_b\tau_a}(\omega_\gamma)\right] \\ &\equiv 4\pi\sum_{JM} i^{J}\left(\boldsymbol{\epsilon}_\mu\cdot\mathbf{Y}^{(1)*}_{JM}(\hat{k}_\gamma)\right)\left[T^{(1)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a} \end{aligned} \tag{1.17}$$

where we have introduced the following abbreviations for the two radial integrals:

$$R^{(1,\alpha)}_{\tau_b\tau_a}(\omega_\gamma)=\begin{cases}\int \mathrm{d}r\,(g_{n_b\kappa_b}f_{n_a\kappa_a}+f_{n_b\kappa_b}g_{n_a\kappa_a})\left(j'_J(k_\gamma r)+\frac{j_J(k_\gamma r)}{k_\gamma r}\right) & \text{for } \alpha=1\\ \int \mathrm{d}r\,(f_{n_b\kappa_b}g_{n_a\kappa_a}-g_{n_b\kappa_b}f_{n_a\kappa_a})\,\frac{j_J(k_\gamma r)}{k_\gamma r} & \text{for } \alpha=2\end{cases} \tag{1.18}$$

Note that the matrix elements $\left[T^{(0)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a}$ and $\left[T^{(1)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a}$ involve only those parts that are independent of the photon's polarization and direction of propagation.

While the radial part must be evaluated numerically, for the angular part there exists an analytical solution. Matrix elements of the form $\langle\Omega_{\kappa_b m_b}|Y_{JM}|\Omega_{\kappa_a m_a}\rangle$ are conveniently evaluated by using the Wigner-Eckart theorem which allows us to write the angular part as

$$\langle\Omega_{\kappa_b m_b}|Y_{JM}|\Omega_{\kappa_a m_a}\rangle=(-1)^{j_b-m_b}\begin{pmatrix} j_b & J & j_a\\ -m_b & M & m_a\end{pmatrix}\langle\Omega_{\kappa_b}||Y_J||\Omega_{\kappa_a}\rangle. \tag{1.19}$$

Here $\langle\Omega_{\kappa_b}||Y_J||\Omega_{\kappa_a}\rangle$ denotes the reduced matrix element and the expression in brackets is the Wigner 3j-symbol. The reduced matrix element vanishes if l_b+

$J + l_a$ is odd and takes the value

$$\langle \Omega_{\kappa_b} || Y_J || \Omega_{\kappa_a} \rangle = (-1)^{j_b+1/2} \sqrt{(2j_b+1)(2j_a+1)(2J+1)/4\pi} \begin{pmatrix} j_b & j_a & J \\ -1/2 & 1/2 & 0 \end{pmatrix} \tag{1.20}$$

if $l_b + J + l_a$ is even. Thus, $\left[T^{(0)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a}$ can be written as

$$\begin{aligned} \left[T^{(0)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a} = (-1)^{2j_b-m_b+3/2} &\begin{pmatrix} j_b & J & j_a \\ -m_b & M & m_a \end{pmatrix} \begin{pmatrix} j_b & j_a & J \\ -1/2 & 1/2 & 0 \end{pmatrix} \\ &\times \sqrt{(2j_b+1)(2j_a+1)(2J+1)/4\pi} \frac{\kappa_a + \kappa_b}{\sqrt{J(J+1)}} R^{(0)}_{\tau_b\tau_a}(\omega_\gamma) \end{aligned} \tag{1.21}$$

if $l_b + J + l_a \pm 1$ is even, whereas $\left[T^{(1)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a}$ becomes

$$\begin{aligned} \left[T^{(1)}_{JM}(\omega_\gamma)\right]_{\tau_b\tau_a} = (-1)^{2j_b-m_b+1/2} &\begin{pmatrix} j_b & J & j_a \\ -m_b & M & m_a \end{pmatrix} \begin{pmatrix} j_b & j_a & J \\ -1/2 & 1/2 & 0 \end{pmatrix} \\ &\times \sqrt{(2j_b+1)(2j_a+1)(2J+1)/4\pi} \left[\frac{\kappa_b - \kappa_a}{\sqrt{J(J+1)}} R^{(1,1)}_{\tau_b\tau_a}(\omega_\gamma) \right. \\ &\left. + \sqrt{J(J+1)} R^{(1,2)}_{\tau_b\tau_a}(\omega_\gamma) \right] \end{aligned} \tag{1.22}$$

if $l_b + J + l_a$ is even. This matrix element without inclusion of $R^{(1,1)}$ and $R^{(1,2)}$ is created by the function 'CreateElectricMultipoleOp()'.

Note that the condition $'l_b + J + l_a \pm 1 = \text{even}'$ for magnetic and $'l_b + J + l_a = \text{even}'$ for electric multipole transitions to be non-vanishing, along with the properties of the Wigner 3j-symbols, reflects what is referred to as 'selection rules'. For electric dipole transitions ($\lambda = 1$, $J = 1$), for example, the selection rule states that a transition is only possible between states with opposite parity and $\Delta j = j_b - j_a = 0, 1$, while a transition between two states with $j_b = j_a = 0$ is forbidden. In addition, the condition $m_b = m_a, m_a \pm 1$ must be fulfilled. This condition is exactly reflected in (1.22). On the other hand, the selection rule for a magnetic dipole transition ($\lambda = 0$, $J = 1$) is identical to the one for the electric dipole with the difference that here the two states must have the same parity. This condition is contained in $'l_b + J + l_a \pm 1 = \text{even}'$.

1.2 Fluorescence self-energy in terms of multipoles

In the following we want to derive an expression for the self-energy due to fluorescence decay employing the derived multipole expansion of the light-matter interaction Hamiltonian. This allows us to systematically study the impact of individual multipoles on the spectral line-shape.

The self-energy can be understood as a matrix on a basis of states before fluorescence decay. This can, for example, be a set of states describing the XAS spectrum. Let ψ_i and ψ_j be two of such resonances, then the corresponding matrix element of the self-energy can be written as:

$$\Sigma_{ij}(\omega) = \langle \psi_i | H_{e\gamma} \frac{1}{\omega + i\eta^+ - H_0 - H_\gamma} H_{e\gamma} | \psi_j \rangle. \tag{1.23}$$

Substituting (1.6) for $H_{e\gamma}$, the self-energy becomes

$$\Sigma_{ij}(\omega) = \frac{e^2}{2} \sum_{\mu=1}^{2} \sum_{\mathbf{k}_\gamma} \frac{1}{\omega_\gamma} \langle \psi_i | T^\dagger_{e\gamma}(\mathbf{k}_\gamma, \mu) \frac{1}{\omega + i\eta^+ - H_0 - H_\gamma} T_{e\gamma}(\mathbf{k}_\gamma, \mu) | \psi_j \rangle. \tag{1.24}$$

The sum over all photon momenta $\mathbf{k}_\gamma$ can be performed by taking the continuum limit as

$$\sum_{\mathbf{k}_\gamma} \to \frac{1}{(2\pi)^3} \int \mathrm{d}^3 k_\gamma = \frac{1}{(2\pi)^3} \int \mathrm{d}\omega_\gamma \omega_\gamma^2 \mathrm{d}\Omega_\gamma \tag{1.25}$$

where spherical coordinates are assumed. Then, the fluorescence self-energy can be written as

$$\begin{aligned} \Sigma_{ij}(\omega) = \frac{e^2}{2(2\pi)^3} \sum_{\mu=1}^{2} \int \langle \psi_i | T^\dagger_{e\gamma}(\mathbf{k}_\gamma, \mu) \frac{1}{\omega + i\eta^+ - H_0 - H_\gamma} T_{e\gamma}(\mathbf{k}_\gamma, \mu) | \psi_j \rangle \\ \times \omega_\gamma \mathrm{d}\omega_\gamma \mathrm{d}\Omega_\gamma. \end{aligned} \tag{1.26}$$

Inserting (1.12) for the transition operator $T_{e\gamma}(\mathbf{k}_\gamma, \mu)$ with matrix elements (1.16) and (1.17) for the magnetic and electric multipoles, respectively, and further using that $H_\gamma a^\dagger_{\mathbf{k}_\gamma,\mu} |\psi_i\rangle = \omega_\gamma a^\dagger_{\mathbf{k}_\gamma,\mu} |\psi_i\rangle$, we finally end up with

$$\begin{aligned} \Sigma_{ij}(\omega) = 4\alpha \sum_{\mu=1}^{2} \int \omega_\gamma \mathrm{d}\omega_\gamma \mathrm{d}\Omega_\gamma \sum_{\tau_a \tau_b \tau'_a \tau'_b} \sum_{JM\lambda} \sum_{J'M'\lambda'} \left(\mathbf{Y}^{(\lambda')}_{J'M'}(\hat{k}_\gamma) \cdot \boldsymbol{\epsilon}^*_\mu \right) \left(\boldsymbol{\epsilon}_\mu \cdot \mathbf{Y}^{(\lambda)*}_{JM}(\hat{k}_\gamma) \right) \\ \times \left[T^{(\lambda')}_{J'M'}(\omega_\gamma) \right]_{\tau'_b \tau'_a} \left[T^{(\lambda)}_{JM}(\omega_\gamma) \right]_{\tau_b \tau_a} \langle \psi_i | e^\dagger_{\tau'_b} e_{\tau'_a} \frac{1}{\omega + i\eta^+ - H_0 - \omega_\gamma} e^\dagger_{\tau_b} e_{\tau_a} | \psi_j \rangle \end{aligned} \tag{1.27}$$

where α denotes the fine-structure constant. As the vector spherical harmonics with $\lambda = 0, 1$ both are orthogonal to $\hat{k}_\gamma$, the sum over the two polarizations can be performed as

$$\sum_{\mu=1}^{2} \left(\mathbf{Y}_{J'M'}^{(\lambda')}(\hat{k}_\gamma) \cdot \boldsymbol{\epsilon}_\mu^* \right) \left(\boldsymbol{\epsilon}_\mu \cdot \mathbf{Y}_{JM}^{(\lambda)*}(\hat{k}_\gamma) \right) = \left(\mathbf{Y}_{J'M'}^{(\lambda')}(\hat{k}_\gamma) \cdot \mathbf{Y}_{JM}^{(\lambda)*}(\hat{k}_\gamma) \right) \tag{1.28}$$

such that the self-energy simplifies to

$$\begin{aligned} \Sigma_{ij}(\omega) = 4\alpha \int \omega_\gamma \sum_{\tau_a \tau_b \tau_a' \tau_b'} \sum_{JM\lambda} \sum_{J'M'\lambda'} \left(\mathbf{Y}_{J'M'}^{(\lambda')}(\hat{k}_\gamma) \cdot \mathbf{Y}_{JM}^{(\lambda)*}(\hat{k}_\gamma) \right) \left[T_{J'M'}^{(\lambda')}(\omega_\gamma) \right]_{\tau_b' \tau_a'} \\ \times \left[T_{JM}^{(\lambda)}(\omega_\gamma) \right]_{\tau_b \tau_a} \left\langle \psi_i \middle| e_{\tau_b'}^\dagger e_{\tau_a'} \frac{1}{\omega + i\eta^+ - H_0 - \omega_\gamma} e_{\tau_b}^\dagger e_{\tau_a} \middle| \psi_j \right\rangle \mathrm{d}\omega_\gamma \mathrm{d}\Omega_\gamma. \end{aligned} \tag{1.29}$$

In the following we integrate over the photon's kinetic energy and all momentum directions. To evaluate the latter integral, we exploit that the vector spherical harmonics obey in analogy to the ordinary ones the orthonormality relation

$$\int \mathrm{d}\Omega_\gamma \, \mathbf{Y}_{J'M'}^{(\lambda')*}(\hat{k}_\gamma) \cdot \mathbf{Y}_{JM}^{(\lambda)}(\hat{k}_\gamma) = \delta_{J'J} \delta_{M'M} \delta_{\lambda'\lambda} \tag{1.30}$$

which enables us to directly integrate over all photon directions

$$\begin{aligned} \Sigma_{ij}(\omega) = 4\alpha \int \sum_{\tau_a \tau_b \tau_a' \tau_b'} \sum_{JM\lambda} \left[T_{JM}^{(\lambda)}(\omega_\gamma) \right]_{\tau_b' \tau_a'} \left[T_{JM}^{(\lambda)}(\omega_\gamma) \right]_{\tau_b \tau_a} \\ \times \left\langle \psi_i \middle| e_{\tau_b'}^\dagger e_{\tau_a'} \frac{1}{\omega + i\eta^+ - H_0 - \omega_\gamma} e_{\tau_b}^\dagger e_{\tau_a} \middle| \psi_j \right\rangle \omega_\gamma \mathrm{d}\omega_\gamma. \end{aligned} \tag{1.31}$$

It is important to note that a direct consequence of the orthonormality relation (1.30) is that different multipoles as well as magnetic and electric parts of the transition operator never interfere.

To evaluate the integral over ω_γ, we replace

$$\frac{1}{\omega + i\eta^+ - H_0 - \omega_\gamma} \longrightarrow \sum_n \frac{|\psi_n\rangle\langle\psi_n|}{\omega + i\eta^+ - E_n - \omega_\gamma}$$

where $|\psi_n\rangle$ are eigenstates of H_0. Then we rewrite $\frac{1}{\omega + i\eta^+ - E_n - \omega_\gamma}$ as

$$\frac{1}{\omega + i\eta^+ - E_n - \omega_\gamma} = \mathcal{P} \frac{1}{\omega - E_n - \omega_\gamma} - i\pi\delta(\omega - E_n - \omega_\gamma) \tag{1.32}$$

where $\mathcal{P}$ represents the Cauchy principal value. Now the self-energy is split into a real and an imaginary part, both involving an integral over ω_γ. For the imaginary part the integration is simple and leads to

$$\begin{aligned}\mathrm{Im}\Sigma_{ij}(\omega) = -4\pi\alpha \sum_{\tau_a\tau_b\tau_a'\tau_b'} \sum_{JM\lambda} \sum_n \left[T_{JM}^{(\lambda)}(\omega - E_n)\right]_{\tau_b'\tau_a'} \left[T_{JM}^{(\lambda)}(\omega - E_n)\right]_{\tau_b\tau_a} \\ \times (\omega - E_n) \left\langle \psi_i \middle| e_{\tau_b'}^\dagger e_{\tau_a'} \middle| \psi_n \right\rangle \left\langle \psi_n \middle| e_{\tau_b}^\dagger e_{\tau_a} \middle| \psi_j \right\rangle \Theta(\omega - E_n). \qquad (1.33)\end{aligned}$$

This matrix element without inclusion of $R^{(1,1)}$ and $R^{(1,2)}$ is created by the function 'CalculateFluorescenceSEmatrix()'. The (radiative) level width which is often referred to in the literature corresponds to the full width at half maximum and therefore can be compared to twice the imaginary part of the fluorescence self-energy evaluated at the resonance energy.