Supplementary Information
Interference between multipolar two-photon transitions in quantum emitters near plasmonic nanostructures

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I. CONTRIBUTION OF MULTIPOLAR EMISSION CHANNELS AND INTERFERENCE EFFECTS TO THE TPSE PROCESS

In this section we present the derivation of the multipolar decay channels and of the interference terms for the two-photon spontaneous emission (TPSE) process. We begin with a reminder of the second-order Fermi's golden rule used to calculate transition rates via a perturbative approach and of the Hamiltonian that describes the interaction between the emitter and the electromagnetic field. Then, we derive the expression of the total TPSE rate as well as the contribution to this rate of the two-electric dipole (2ED), the two-electric quadrupole (2EQ) transitions and the interference term between these two multipolar decay channels. Next, the interference term is expressed as a function of the dyadic Green's function and the link with the Purcell factors of the one-photon spontaneous emission process is established. The 2ED and 2EQ transition rates were previously derived in Ref. [1], as well as their link to the one-photon Purcell factors.

A. Fermi's golden rule

The probability per unit time that a system carries out a second-order transition by emitting two quanta from an initial state $|i\rangle$ to a final state $|f\rangle$, upon an interaction described by the Hamiltonian H_{int}, is given by Fermi's golden rule [2, 3]

$$\Gamma^{(2)}_{i\to f} = \frac{2\pi}{\hbar}|M^{(2)}_{fi}|^2\delta(E_f - E_i), \tag{I.1}$$

with the second-order matrix element

$$M^{(2)}_{fi} = \sum_l \frac{\langle f| H_{\text{int}} |l\rangle \langle l| H_{\text{int}} |i\rangle}{E_i - E_l}, \tag{I.2}$$

where the summation runs over all possible virtual intermediate states $|l\rangle$ of the system. In these equations, $\hbar$ is the reduced Planck constant, E_a stands for the energy of the system in the state $|a\rangle$ with $a = i, l, f$, and the superscript (2) indicates that this is a second-order transition, in contrast with first-order transitions. Furthermore, as depicted in Figure I.1, this second-order transition can be seen as two successive transitions in which each one emits a quantum.

Regarding the states in this second-order process [2], the initial one is characterized by the emitter in an excited state $|e\rangle$ and the field in the vacuum state $|\text{vac}\rangle$, while in the final one the emitter is in a lower energy state $|g\rangle$ and the field is in a two-quanta state $|1_\alpha, 1_{\alpha'}\rangle$ where α and α' stand for the modes of the two emitted quanta. Thus, they are respectively written as

$$|i\rangle = |e; \text{vac}\rangle \tag{I.3a}$$

$$\text{and as } |f\rangle = |g; 1_\alpha, 1_{\alpha'}\rangle. \tag{I.3b}$$

In the intermediate states that connect these two states, the emitter is in an intermediate energy state $|m\rangle$ and the field is in a one-quantum state. Depending on in which mode is the emitted quantum, the intermediate states are written as

$$|l\rangle = |m; 1_\alpha\rangle \tag{I.4a}$$

$$\text{or as } |l\rangle = |m; 1_{\alpha'}\rangle. \tag{I.4b}$$

Further on, the energy of the emitter in the state $|a\rangle$ will be denoted as ε_a with $a = e, m, g$.

B. Interaction Hamiltonian

Consider the interaction Hamiltonian, as presented in the main text, involving the electric dipole plus the electric quadrupole interactions. The electric field operator present in its expression can be written as a function of the normal modes $\mathbf{A}_\alpha(\mathbf{r})$ of the vector potential [4, 5]:

$$\mathbf{E}(\mathbf{r}, t) = i\sum_\alpha \sqrt{\frac{\hbar\omega_\alpha}{2\varepsilon_0}} \left\{a_\alpha(t)\mathbf{A}_\alpha(\mathbf{r}) - a^\dagger_\alpha(t)\mathbf{A}^*_\alpha(\mathbf{r})\right\}. \tag{I.5}$$

In these equations, ε_0 is the vacuum electric permittivity, whereas $a_\alpha(t)$ and $a^\dagger_\alpha(t)$ are the annihilation and creation operators of a photon in the mode α of energy $\hbar\omega_\alpha$. Note that the modes $\mathbf{A}_\alpha(\mathbf{r})$ are normalized and form a complete set of solutions of the Helmholtz equation, subject to the boundary conditions imposed by the photonic environment.
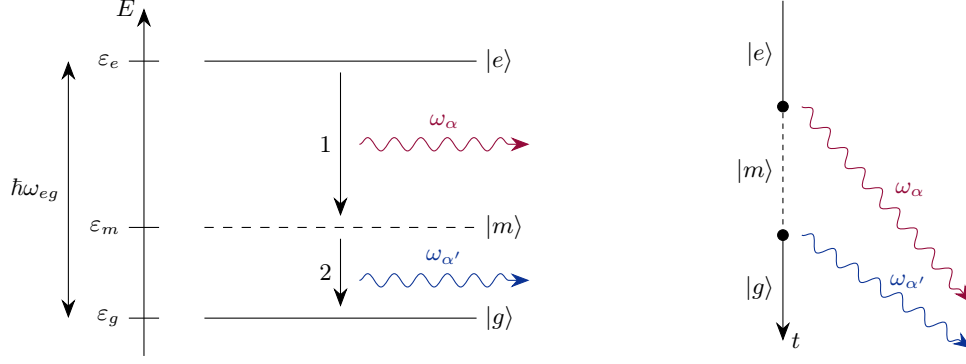
FIG. I.1. Energy and time representations of a second-order transition. The emitter carries-out a first transition from its excited state $|e\rangle$ to a virtual intermediate state $|m\rangle$ by emitting a photon in the mode α. Then, a second transition is carried out to the ground state $|g\rangle$ of lower energy by emitting a photon in the mode α'. The transition energy is given by $\hbar\omega_{eg} := \varepsilon_e - \varepsilon_g$. These representations only consider the intermediate state of the system $|l\rangle = |m; 1_\alpha\rangle$ where the first photon is emitted in the mode α, but similar representations can be sketched by inverting the role of the two emitted quanta.

C.   Derivation of the total TPSE rate

Now that Fermi's golden rule and all the states involved in the second-order transition and the interaction Hamiltonian have been introduced, let us derive the total TPSE rate, which includes the contributions of the 2ED and 2EQ transitions and of the term describing the interference between these two channels. Given that the initial and the final energies of the system are, respectively, $E_i = \varepsilon_e$ and $E_f = \varepsilon_g + \hbar\omega_\alpha + \hbar\omega_{\alpha'}$, the Dirac delta distribution in Fermi's golden rule in equation (I.1) can be rewritten as

$$\delta(E_f - E_i) = \frac{1}{\hbar}\delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}), \tag{I.6}$$

where we define $\hbar\omega_{ab} := \varepsilon_a - \varepsilon_b$ with $a, b = e, m, g$.

Then, given that there are two kinds of intermediate states [Eqs. (I.4)], the summation over them in the expression of the second-order matrix element $M_{fi}^{(2)}$ is split in two:

$$M_{fi}^{(2)} = \sum_{|m\rangle} \frac{\langle 1_\alpha, 1_{\alpha'}| \langle g| H_{\text{int}} |m\rangle |1_\alpha\rangle \langle 1_\alpha| \langle m| H_{\text{int}} |e\rangle |\text{vac}\rangle}{\hbar(\omega_{em} - \omega_\alpha)}$$
$$+ \sum_{|m\rangle} \frac{\langle 1_\alpha, 1_{\alpha'}| \langle g| H_{\text{int}} |m\rangle |1_{\alpha'}\rangle \langle 1_{\alpha'}| \langle m| H_{\text{int}} |e\rangle |\text{vac}\rangle}{\hbar(\omega_{em} - \omega_{\alpha'})}, \tag{I.7}$$

where the first summation corresponds to the representations sketched in Figure I.1.

Let us first calculate the factor $\langle 1_\alpha, 1_{\alpha'}| \langle g| H_{\text{int}} |m\rangle |1_\alpha\rangle$ with the interaction Hamiltonian given in the main text and with the electric field operator given in the equation (I.5). As we are interested in emission processes, only the part of $\mathbf{E}$ involving creation operators, noted as $\mathbf{E}^{(-)}$, is kept in the calculation:

$$\langle 1_\alpha, 1_{\alpha'}| \langle g| H_{\text{int}} |m\rangle |1_\alpha\rangle = \langle 1_\alpha, 1_{\alpha'}| \langle g| -\mathbf{d}\cdot\mathbf{E}(\mathbf{R}) - \mathbf{Q}:[\nabla\mathbf{E}(\mathbf{R})] |m\rangle |1_\alpha\rangle \tag{I.8a}$$

$$= -\langle g| \mathbf{d} |m\rangle \cdot \langle 1_\alpha, 1_{\alpha'}| \mathbf{E}^{(-)}(\mathbf{R}) |1_\alpha\rangle - \langle g| \mathbf{Q} |m\rangle : \left[\nabla \langle 1_\alpha, 1_{\alpha'}| \mathbf{E}^{(-)}(\mathbf{R}) |1_\alpha\rangle\right] \tag{I.8b}$$

$$= -\mathbf{d}^{gm} \cdot \langle 1_\alpha, 1_{\alpha'}| -i\sum_\beta \sqrt{\frac{\hbar\omega_\beta}{2\varepsilon_0}} a_\beta^\dagger \mathbf{A}_\beta^*(\mathbf{R}) |1_\alpha\rangle$$

$$- \mathbf{Q}^{gm} : \left[\nabla \langle 1_\alpha, 1_{\alpha'}| -i\sum_\beta \sqrt{\frac{\hbar\omega_\beta}{2\varepsilon_0}} a_\beta^\dagger \mathbf{A}_\beta^*(\mathbf{R}) |1_\alpha\rangle\right], \tag{I.8c}$$

where $\mathbf{d}^{ab} := \langle a|\mathbf{d}|b\rangle$ and $\mathbf{Q}^{ab} := \langle a|\mathbf{Q}|b\rangle$ stand, respectively, for the transition electric dipole and quadrupole moments (i.e., the first-order matrix element of the operators $\mathbf{d}$ and $\mathbf{Q}$) that describe the emitter's transition from the state $|b\rangle$ to the state $|a\rangle$ ($a, b = e, m, g$). In the previous equation, only the term involving the creation operator that creates

a photon in the mode $\beta = \alpha'$ leads to a non-zero term because the field states form an orthonormal basis[1]. Thus, we get

$$\langle 1_\alpha, 1_{\alpha'} | \langle g | H_{\text{int}} | m \rangle | 1_\alpha \rangle = i \sqrt{\frac{\hbar\omega_{\alpha'}}{2\varepsilon_0}} \left\{ \mathbf{d}^{gm} \cdot \mathbf{A}^*_{\alpha'}(\mathbf{R}) + \mathbf{Q}^{gm} : [\nabla \mathbf{A}^*_{\alpha'}(\mathbf{R})] \right\} \underbrace{\langle 1_\alpha, 1_{\alpha'} | a^\dagger_{\alpha'} | 1_\alpha \rangle}_{\langle 1_\alpha, 1_{\alpha'} | 1_\alpha, 1_{\alpha'} \rangle = 1} \tag{I.9a}$$

$$= i \sqrt{\frac{\hbar\omega_{\alpha'}}{2\varepsilon_0}} \left\{ \mathbf{d}^{gm} \cdot \mathbf{A}^*_{\alpha'}(\mathbf{R}) + \mathbf{Q}^{gm} : [\nabla \mathbf{A}^*_{\alpha'}(\mathbf{R})] \right\}. \tag{I.9b}$$

Similar developments for the second factor in the first summation of equation (I.7) lead to

$$\langle 1_\alpha | \langle m | H_{\text{int}} | e \rangle | \text{vac} \rangle = i \sqrt{\frac{\hbar\omega_\alpha}{2\varepsilon_0}} \left\{ \mathbf{d}^{me} \cdot \mathbf{A}^*_\alpha(\mathbf{R}) + \mathbf{Q}^{me} : [\nabla \mathbf{A}^*_\alpha(\mathbf{R})] \right\}. \tag{I.10}$$

Therefore, the first summation in the equation (I.7) is rewritten as

$$-\frac{\sqrt{\omega_\alpha \omega_{\alpha'}}}{2\varepsilon_0} \sum_{|m\rangle} \frac{(\mathbf{d}^{gm} \cdot \mathbf{A}^*_{\alpha'}(\mathbf{R}) + \mathbf{Q}^{gm} : [\nabla \mathbf{A}^*_{\alpha'}(\mathbf{R})]) (\mathbf{d}^{me} \cdot \mathbf{A}^*_\alpha(\mathbf{R}) + \mathbf{Q}^{me} : [\nabla \mathbf{A}^*_\alpha(\mathbf{R})])}{\omega_{em} - \omega_\alpha}. \tag{I.11}$$

Concerning the second summation presents in the equation (I.7), the result can be obtained by inverting the role of α and α' in the last obtained equation. Thus, the second-order matrix element $M^{(2)}_{fi}$ is rewritten as

$$M^{(2)}_{fi} = -\frac{\sqrt{\omega_\alpha \omega_{\alpha'}}}{2\varepsilon_0} \sum_{|m\rangle} \left\{ \frac{\mathbf{d}^{gm} \cdot \mathbf{A}^*_{\alpha'} \, \mathbf{d}^{me} \cdot \mathbf{A}^*_\alpha}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{d}^{gm} \cdot \mathbf{A}^*_\alpha \, \mathbf{d}^{me} \cdot \mathbf{A}^*_{\alpha'}}{\omega_{em} - \omega_{\alpha'}} \right.$$
$$+ \frac{\mathbf{Q}^{gm} : [\nabla \mathbf{A}^*_{\alpha'}] \, \mathbf{Q}^{me} : [\nabla \mathbf{A}^*_\alpha]}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{Q}^{gm} : [\nabla \mathbf{A}^*_\alpha] \, \mathbf{Q}^{me} : [\nabla \mathbf{A}^*_{\alpha'}]}{\omega_{em} - \omega_{\alpha'}}$$
$$+ \frac{\mathbf{Q}^{gm} : [\nabla \mathbf{A}^*_{\alpha'}] \, \mathbf{d}^{me} \cdot \mathbf{A}^*_\alpha}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{Q}^{gm} : [\nabla \mathbf{A}^*_\alpha] \, \mathbf{d}^{me} \cdot \mathbf{A}^*_{\alpha'}}{\omega_{em} - \omega_{\alpha'}}$$
$$\left. + \frac{\mathbf{d}^{gm} \cdot \mathbf{A}^*_{\alpha'} \, \mathbf{Q}^{me} : [\nabla \mathbf{A}^*_\alpha]}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{d}^{gm} \cdot \mathbf{A}^*_\alpha \, \mathbf{Q}^{me} : [\nabla \mathbf{A}^*_{\alpha'}]}{\omega_{em} - \omega_{\alpha'}} \right\}, \tag{I.12}$$

where the spatial dependency has been omitted. This quantity can be split into four contributions:

$$M^{(2)}_{fi} = M^{2\text{ED}}_{fi} + M^{2\text{EQ}}_{fi} + M^{\text{ED}-\text{EQ}}_{fi} + M^{\text{EQ}-\text{ED}}_{fi}, \tag{I.13}$$

where the first one corresponds to the first two terms in the summation over $|m\rangle$ in the equation (I.12), the second to the next two, and so on. The contributions $M^{2\text{ED}}_{fi}$ and $M^{2\text{EQ}}_{fi}$ are, respectively, obtained when only the electric dipole or the electric quadrupole interaction is taken into account. Thus, by considering these contributions separately, we find the formulas derived for the 2ED and 2EQ transitions [1]. When both electric dipole and quadrupole interactions are present in the interaction Hamiltonian, these first two contributions appear simultaneously as well as two new contributions $M^{\text{ED}-\text{EQ}}_{fi}$ and $M^{\text{ED}-\text{EQ}}_{fi}$ describing mixed transitions. In the following, the contribution of mixed transitions to the second-order matrix element is discarded, because they are not involved in the second-order transition studied in the application in the main text, i.e., between two states of an hydrogen atom that have the same azimuthal quantum numbers [6, 7].

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[1] An orthonormal basis satisfies $\langle 1_\alpha | 1_\beta \rangle = \delta_{\alpha\beta}$ and $\langle 1_\alpha, 1_{\alpha'} | 1_\beta, 1_{\beta'} \rangle = \langle 1_\alpha | 1_\beta \rangle \langle 1_{\alpha'} | 1_{\beta'} \rangle = \delta_{\alpha\beta} \, \delta_{\alpha'\beta'}$.

Using the commutation property of the scalar and double dot products, one obtains

$$M_{fi}^{(2)} = M_{fi}^{2\text{ED}} + M_{fi}^{2\text{EQ}} = -\frac{\sqrt{\omega_\alpha \omega_{\alpha'}}}{2\varepsilon_0} \sum_{|m\rangle} \left\{ \frac{\mathbf{A}_\alpha^* \cdot \mathbf{d}^{me}\, \mathbf{d}^{gm} \cdot \mathbf{A}_{\alpha'}^*}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{A}_\alpha^* \cdot \mathbf{d}^{gm}\, \mathbf{d}^{me} \cdot \mathbf{A}_{\alpha'}^*}{\omega_{em} - \omega_{\alpha'}} \right.$$

$$\left. + \frac{[\nabla \mathbf{A}_\alpha^*] : \mathbf{Q}^{me}\, \mathbf{Q}^{gm} : [\nabla \mathbf{A}_{\alpha'}^*]}{\omega_{em} - \omega_\alpha} + \frac{[\nabla \mathbf{A}_\alpha^*] : \mathbf{Q}^{gm}\, \mathbf{Q}^{me} : [\nabla \mathbf{A}_{\alpha'}^*]}{\omega_{em} - \omega_{\alpha'}} \right\} \quad \text{(I.14a)}$$

$$= -\frac{\sqrt{\omega_\alpha \omega_{\alpha'}}}{2\varepsilon_0} \left(\mathbf{A}_\alpha^* \cdot \sum_{|m\rangle} \left\{ \frac{\mathbf{d}^{me}\mathbf{d}^{gm}}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{d}^{gm}\mathbf{d}^{me}}{\omega_{em} - \omega_{\alpha'}} \right\} \cdot \mathbf{A}_{\alpha'}^* \right.$$

$$\left. + [\nabla \mathbf{A}_\alpha^*] : \sum_{|m\rangle} \left\{ \frac{\mathbf{Q}^{me}\mathbf{Q}^{gm}}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{Q}^{gm}\mathbf{Q}^{me}}{\omega_{em} - \omega_{\alpha'}} \right\} : [\nabla \mathbf{A}_{\alpha'}^*] \right). \quad \text{(I.14b)}$$

Let us take the complex conjugate[2] of $M_{fi}^{(2)}$:

$$\left(M_{fi}^{(2)} \right)^* = -\frac{\sqrt{\omega_\alpha \omega_{\alpha'}}}{2\varepsilon_0} \left(\mathbf{A}_\alpha \cdot \sum_{|m\rangle} \left\{ \frac{\mathbf{d}^{em}\mathbf{d}^{mg}}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{d}^{mg}\mathbf{d}^{em}}{\omega_{em} - \omega_{\alpha'}} \right\} \cdot \mathbf{A}_{\alpha'} \right.$$

$$\left. + [\nabla \mathbf{A}_\alpha] : \sum_{|m\rangle} \left\{ \frac{\mathbf{Q}^{em}\mathbf{Q}^{mg}}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{Q}^{mg}\mathbf{Q}^{em}}{\omega_{em} - \omega_{\alpha'}} \right\} : [\nabla \mathbf{A}_{\alpha'}] \right) \quad \text{(I.15a)}$$

$$= -\frac{\sqrt{\omega_\alpha \omega_{\alpha'}}}{2\varepsilon_0} \left(\mathbf{A}_\alpha \cdot \boldsymbol{\mathcal{D}}^{eg} \cdot \mathbf{A}_{\alpha'} + [\nabla \mathbf{A}_\alpha] : \boldsymbol{\mathcal{Q}}^{eg} : [\nabla \mathbf{A}_{\alpha'}] \right), \quad \text{(I.15b)}$$

where we define two tensors, the first one of rank two and the second one of rank four, as

$$\boldsymbol{\mathcal{D}}^{eg}(\omega_\alpha, \omega_{\alpha'}) := \sum_{|m\rangle} \left(\frac{\mathbf{d}^{em}\, \mathbf{d}^{mg}}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{d}^{mg}\, \mathbf{d}^{em}}{\omega_{em} - \omega_{\alpha'}} \right), \quad \text{(I.16a)}$$

$$\boldsymbol{\mathcal{Q}}^{eg}(\omega_\alpha, \omega_{\alpha'}) := \sum_{|m\rangle} \left(\frac{\mathbf{Q}^{em}\, \mathbf{Q}^{mg}}{\omega_{em} - \omega_\alpha} + \frac{\mathbf{Q}^{mg}\, \mathbf{Q}^{em}}{\omega_{em} - \omega_{\alpha'}} \right), \quad \text{(I.16b)}$$

where the outer product is implied. The components of the tensor that come from the outer product of two tensors $\mathbf{U}$ and $\mathbf{V}$ are $(\mathbf{UV})_{i_1,i_2,\ldots,i_n,j_1,j_2,\ldots,j_n} := U_{i_1,i_2,\ldots,i_n} V_{j_1,j_2,\ldots,j_n}$. These tensors describe the two successive electric dipole and quadrupole transitions of the emitter between the states $|e\rangle$ and $|g\rangle$ of the emitter. Subsequently, we will refer to them as the second-order transition electric dipole and quadrupole moments. Note that since $\mathbf{Q}$ is symmetric, the fourth rank tensor $\boldsymbol{\mathcal{Q}}^{eg}$ is also symmetric:

$$\begin{cases} \mathcal{Q}_{ijkl}^{eg} = \mathcal{Q}_{jikl}^{eg} & \forall i, j, k, l = 1, 2, 3 \quad \text{(I.17a)} \\ \mathcal{Q}_{ijkl}^{eg} = \mathcal{Q}_{ijlk}^{eg} & \forall i, j, k, l = 1, 2, 3. \quad \text{(I.17b)} \end{cases}$$

Moreover, since $\mathbf{Q}$ can be taken traceless [8, 9], given the definition of $\boldsymbol{\mathcal{Q}}^{eg}$, it satisfies the two following properties:

$$\begin{cases} \displaystyle\sum_{i=1}^3 \mathcal{Q}_{iikl}^{eg} = 0 & \forall k, l = 1, 2, 3 \quad \text{(I.18a)} \\[2mm] \displaystyle\sum_{k=1}^3 \mathcal{Q}_{ijkk}^{eg} = 0 & \forall i, j = 1, 2, 3. \quad \text{(I.18b)} \end{cases}$$

Let us now take the square modulus of $M_{fi}^{(2)}$:

$$\left| M_{fi}^{(2)} \right|^2 = \left| \left(M_{fi}^{(2)} \right)^* \right|^2 = \frac{\omega_\alpha \omega_{\alpha'}}{4\varepsilon_0^2} \left| \mathbf{A}_\alpha \cdot \boldsymbol{\mathcal{D}}^{eg} \cdot \mathbf{A}_{\alpha'} + [\nabla \mathbf{A}_\alpha] : \boldsymbol{\mathcal{Q}}^{eg} : [\nabla \mathbf{A}_{\alpha'}] \right|^2, \quad \text{(I.19)}$$

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[2] For an Hermitian operator: $\left(\mathbf{A}^{ab}\right)^* = (\langle a|\mathbf{A}|b\rangle)^* = \langle b|\mathbf{A}^\dagger|a\rangle = \langle b|\mathbf{A}|a\rangle = \mathbf{A}^{ba}$ where the dagger denotes the operation of taking the transpose and the complex conjugate.

that can be directly injected, together with the equation (I.6), in Fermi's golden rule given in the equation (I.1):

$$\Gamma^{(2)}_{2ED+2EQ}(\mathbf{R}) = \frac{2\pi}{\hbar^2} \frac{\omega_\alpha \omega_{\alpha'}}{4\varepsilon_0^2} \left| \mathbf{A}_\alpha \cdot \boldsymbol{\mathcal{D}}^{eg} \cdot \mathbf{A}_{\alpha'} + [\nabla \mathbf{A}_\alpha] : \boldsymbol{\mathcal{Q}}^{eg} : [\nabla \mathbf{A}_{\alpha'}] \right|^2 \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}). \tag{I.20}$$

As a final step, we take the summation over all possible modes for the two emitted quanta. However, since the energy of one photon ranges from 0 to $\hbar\omega_{eg}$, we must take into account a factor $1/2$ to avoid double counting. We finally get the total two-photon spontaneous emission rate:

$$\boxed{\Gamma^{(2)}_{2ED+2EQ}(\mathbf{R}) = \frac{\pi}{4\varepsilon_0^2 \hbar^2} \sum_{\alpha,\alpha'} \omega_\alpha \omega_{\alpha'} \left| \mathbf{A}_\alpha \cdot \boldsymbol{\mathcal{D}}^{eg} \cdot \mathbf{A}_{\alpha'} + [\nabla \mathbf{A}_\alpha] : \boldsymbol{\mathcal{Q}}^{eg} : [\nabla \mathbf{A}_{\alpha'}] \right|^2 \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}),} \tag{I.21}$$

where the spatial dependency of the field modes and the frequency dependency of the second-order multipolar transition moments have been omitted.

D. Multipolar emission channel contributions to the total TPSE rate

As discussed in the main text, the total TPSE rate is decomposed into three distinct contributions:

$$\Gamma^{(2)}_{\text{tot}}(\mathbf{R}) \approx \Gamma^{(2)}_{2ED+2EQ}(\mathbf{R}) = \Gamma^{(2)}_{2ED}(\mathbf{R}) + \Gamma^{(2)}_{2EQ}(\mathbf{R}) + \gamma^{(2)}_{2ED \cap 2EQ}(\mathbf{R}), \tag{I.22}$$

which are sketched in Figure I.2, where we have neglected the magnetic interaction, discarded the mixed transitions, and introduced $\Gamma^{(2)}_{2ED \cap 2EQ}$ as the term representing the interference between the 2ED and 2EQ transitions. This interference term can be either positive or negative, potentially resulting in an increase or decrease of the overall TPSE rate.

By developing the square modulus in equation (I.21), we find the three rate contributions:

$$\Gamma^{(2)}_{2ED}(\mathbf{R}) = \frac{\pi}{4\varepsilon_0^2 \hbar^2} \sum_{\alpha,\alpha'} \omega_\alpha \omega_{\alpha'} \left| \mathbf{A}_\alpha(\mathbf{R}) \cdot \boldsymbol{\mathcal{D}}^{eg}(\omega_\alpha, \omega_{\alpha'}) \cdot \mathbf{A}_{\alpha'}(\mathbf{R}) \right|^2 \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}), \tag{I.23a}$$

$$\Gamma^{(2)}_{2EQ}(\mathbf{R}) = \frac{\pi}{4\varepsilon_0^2 \hbar^2} \sum_{\alpha,\alpha'} \omega_\alpha \omega_{\alpha'} \left| [\nabla \mathbf{A}_\alpha(\mathbf{R})] : \boldsymbol{\mathcal{Q}}^{eg}(\omega_\alpha, \omega_{\alpha'}) : [\nabla \mathbf{A}_{\alpha'}(\mathbf{R})] \right|^2 \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}), \tag{I.23b}$$

$$\Gamma^{(2)}_{2ED \cap 2EQ}(\mathbf{R}) = 2\,\text{Re}\left(\frac{\pi}{4\varepsilon_0^2 \hbar^2} \sum_{\alpha,\alpha'} \omega_\alpha \omega_{\alpha'} \left(\mathbf{A}_\alpha(\mathbf{R}) \cdot \boldsymbol{\mathcal{D}}^{eg}(\omega_\alpha, \omega_{\alpha'}) \cdot \mathbf{A}_{\alpha'}(\mathbf{R}) \right) \right.$$

$$\left. \times \left(\nabla \mathbf{A}_\alpha(\mathbf{R}) : \boldsymbol{\mathcal{Q}}^{eg}(\omega_\alpha, \omega_{\alpha'}) : \nabla \mathbf{A}_{\alpha'}(\mathbf{R}) \right)^* \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}) \right), \tag{I.23c}$$

where the 2ED and 2EQ contributions have been derived in Ref. [1]. For the interference term, Re stands for the real part and the factor 2 is due to cross terms, with one that is the complex conjugate of the other. Hereafter, we will
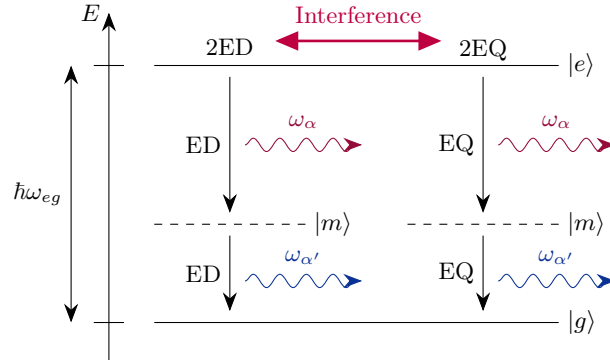

FIG. I.2. Energy representation of the three multipolar contributions to the TPSE process. The emitter performs a 2ED or 2EQ transition which are mediated by different intermediate states, where they can interfere. The transition energy is denoted as $\hbar\omega_{eg}$. A similar representation can be sketched by inverting the role of the two emitted quanta.

omit the real part for clarity purpose. Furthermore, these equations for the electric multipolar contributions to the TPSE rate, including the interference term, are valid regardless of the emitter and its environment. In vacuum, the 2ED and 2EQ transition rates are provided in Ref. [1] while we can show that the interference term vanishes. Indeed, in free-space, there is no interference between different multipolar sources because each type of emitter generates its unique field distribution that remains decoupled from other multipolar sources at the same location [2].

E. Expression of the interference term as a function of the dyadic Green's function

To derive an expression that relies on one-photon Purcell factors, the preliminary step is to express the interference term as a function of the dyadic Green's function and to normalize it with the 2ED and 2EQ transition rates in vacuum, whose expressions are in Ref. [1]. We also introduce and use a modified version of the Voigt notation and use some properties to simplify the equations. Concerning the Green's function, its imaginary part admits a spectral representation that can be expanded in terms of the normal modes $\mathbf{A}_\alpha$ of the electromagnetic field [10]:

$$\text{Im}\mathbf{G}(\omega; \mathbf{r}, \mathbf{r}') = \frac{\pi c^2}{2\omega} \sum_\alpha \mathbf{A}_\alpha(\mathbf{r}) \mathbf{A}_\alpha^*(\mathbf{r}') \, \delta(\omega - \omega_\alpha), \tag{I.24}$$

where c denotes the vacuum speed of light.

Let us start the developments by calculating the scalar and the double dot products:

$$\Gamma_{\text{2ED} \cap \text{2EQ}}^{(2)} = 2\frac{\pi}{4\varepsilon_0^2 \hbar^2} \sum_{\alpha,\alpha'} \omega_\alpha \omega_{\alpha'} \left(A_{\alpha,i} \, \mathcal{D}_{ia}(\omega_\alpha, \omega_{\alpha'}) \, A_{\alpha',a} \right) \left(\partial_k A_{\alpha,j} \, \mathcal{Q}_{jkbc}(\omega_\alpha, \omega_{\alpha'}) \, \partial_c A_{\alpha',b} \right)^* \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}), \tag{I.25a}$$

where the Einstein summation convention is used, where the eg subscript and the spatial dependency have been omitted, and where the components $A_{\alpha,i}$ are these of the vector $\mathbf{A}_\alpha$. Let us now rearrange the equation to reveal the Green's function relative to the photon emitted at frequency $\omega_{\alpha'} = \omega_{eg} - \omega_\alpha$:

$$\Gamma_{\text{2ED} \cap \text{2EQ}}^{(2)} = 2\frac{\pi}{4\varepsilon_0^2 \hbar^2} \sum_\alpha \omega_\alpha(\omega_{eg} - \omega_\alpha) \, \mathcal{D}_{ia}(\omega_\alpha, \omega_{eg} - \omega_\alpha) \, \mathcal{Q}_{jkbc}^*(\omega_\alpha, \omega_{eg} - \omega_\alpha) \, A_{\alpha,i} \, \partial_k A_{\alpha,j}^*$$
$$\times \sum_{\alpha'} A_{\alpha',a} \, \partial_c A_{\alpha',b}^* \, \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}) \tag{I.25b}$$

$$= 2\frac{\pi}{4\varepsilon_0^2 \hbar^2} \sum_\alpha \omega_\alpha(\omega_{eg} - \omega_\alpha) \, \mathcal{D}_{ia}(\omega_\alpha, \omega_{eg} - \omega_\alpha) \, \mathcal{Q}_{jkbc}^*(\omega_\alpha, \omega_{eg} - \omega_\alpha) \, A_{\alpha,i} \, \partial_k A_{\alpha,j}^*$$
$$\times \left\{ \partial_{c'} \sum_{\alpha'} A_{\alpha',a}(\mathbf{r}) A_{\alpha',b}^*(\mathbf{r}') \, \delta(\omega_{eg} - \omega_\alpha - \omega_{\alpha'}) \right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}} \tag{I.25c}$$

$$= 2\frac{1}{2\varepsilon_0^2 \hbar^2 c^2} \sum_\alpha \omega_\alpha(\omega_{eg} - \omega_\alpha)^2 \, \mathcal{D}_{ia}(\omega_\alpha, \omega_{eg} - \omega_\alpha) \, \mathcal{Q}_{jkbc}^*(\omega_\alpha, \omega_{eg} - \omega_\alpha) \, A_{\alpha,i} \, \partial_k A_{\alpha,j}^*$$
$$\times \left\{ \partial_{c'} \text{Im} G_{ab}(\omega_{eg} - \omega_\alpha; \mathbf{r}, \mathbf{r}') \right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}}, \tag{I.25d}$$

where $\partial_{c'}$ means derivatives with respect to the coordinates $\mathbf{r}'$. By using the property $f(\omega_\alpha) = \int_{-\infty}^\infty f(\omega) \, \delta(\omega - \omega_\alpha) \, d\omega$, we obtain

$$\Gamma_{\text{2ED} \cap \text{2EQ}}^{(2)} = 2\frac{1}{2\varepsilon_0^2 \hbar^2 c^2} \int_{-\infty}^\infty \omega(\omega_{eg} - \omega)^2 \, \mathcal{D}_{ia}(\omega, \omega_{eg} - \omega) \, \mathcal{Q}_{jkbc}^*(\omega, \omega_{eg} - \omega)$$
$$\times \sum_\alpha A_{\alpha,i} \, \partial_k A_{\alpha,j}^* \, \delta(\omega - \omega_\alpha) \left\{ \partial_{c'} \text{Im} G_{ab}(\omega_{eg} - \omega; \mathbf{r}, \mathbf{r}') \right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}} \, d\omega \tag{I.26a}$$

$$= 2\frac{1}{\pi \varepsilon_0^2 \hbar^2 c^4} \int_0^{\omega_{eg}} \omega^2(\omega_{eg} - \omega)^2 \, \mathcal{D}_{ia}(\omega, \omega_{eg} - \omega) \, \mathcal{Q}_{jkbc}^*(\omega, \omega_{eg} - \omega)$$
$$\times \left\{ \partial_{k'} \text{Im} G_{ij}(\omega; \mathbf{r}, \mathbf{r}') \right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}} \left\{ \partial_{c'} \text{Im} G_{ab}(\omega_{eg} - \omega; \mathbf{r}, \mathbf{r}') \right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}} \, d\omega, \tag{I.26b}$$

where the Green's function relative to the photon emitted at the frequency ω appears and where the integration limits have been adapted since the frequency of a photon ranges from 0 to ω_{eg}.

Let us normalize the obtained spectral distribution $\gamma^{(2)}_{2ED\cap2EQ}(\omega;\mathbf{R})$, i.e., the integrand of the last equation, by the square root of the product of the vacuum emission rates of the 2ED and 2EQ transitions [1]. We get

$$\frac{\gamma^{(2)}_{2ED\cap2EQ}(\omega;\mathbf{R})}{\sqrt{\gamma^{(2)}_{2ED,0}(\omega)\,\gamma^{(2)}_{2EQ,0}(\omega)}} = 2\,\hat{\mathcal{D}}^{eg}_{ia}(\omega,\omega_{eg}-\omega)\left(\hat{\mathcal{Q}}^{eg}_{jkbc}(\omega,\omega_{eg}-\omega)\right)^{*}T_{ijk}(\omega;\mathbf{R})\,T_{abc}(\omega_{eg}-\omega;\mathbf{R}), \tag{I.27}$$

where the caret indicates normalized tensors (i.e., for an nth rank tensor $\mathbf{U}$ with $n \in \mathbb{N}_0$, $\hat{\mathbf{U}} := \mathbf{U}/\|\mathbf{U}\|$ with $\|\mathbf{U}\|^2 := \sum_{i_1,i_2,\ldots,i_n}|U_{i_1,i_2,\ldots,i_n}|^2$.) and where we define the third rank tensor $\mathbf{T}$ as a function of the imaginary part of the Green's function:

$$T_{ijk}(\omega;\mathbf{R}) := \frac{2\sqrt{30}\pi c^2}{\omega^2}\left\{\partial_{k'}\text{Im}G_{ij}(\omega;\mathbf{r},\mathbf{r}')\right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}}. \tag{I.28}$$

Note that the first tensor $\mathbf{T}$ within the equation (I.27) is related to the quanta emitted at the frequency ω, while the second one concerns the quanta emitted at the complementary frequency $\omega_{eg}-\omega$.

Simplification

The derived equation contains 3^6 terms, but, fortunately, we can leverage the properties of the tensor $\mathcal{Q}^{eg}$ derived from the symmetric and traceless properties of electric quadrupole moments written by the equations (I.17) and (I.18) to eliminate redundant terms. Using the symmetry property provides an expression involving $3^2 \times 6^2$ terms instead of 3^6:

$$\frac{\gamma^{(2)}_{2ED\cap2EQ}(\omega;\mathbf{R})}{\sqrt{\gamma^{(2)}_{2ED,0}(\omega)\,\gamma^{(2)}_{2EQ,0}(\omega)}} = 2\sum_{i,a=1}^{3}\sum_{\mu,\alpha=1}^{6}\hat{\mathcal{D}}^{eg}_{ia}(\omega,\omega_{eg}-\omega)\left(\hat{\mathcal{Q}}^{eg}_{\mu\alpha}(\omega,\omega_{eg}-\omega)\right)^{*}U_{i\mu}(\omega;\mathbf{R})\,U_{a\alpha}(\omega_{eg}-\omega;\mathbf{R}), \tag{I.29}$$

with

$$\forall i = 1,2,3, \quad U_{i\mu} := \begin{cases} T_{i\mu} & \forall\mu = 1,2,3 \\ T_{i\mu} + T_{i\bar{\mu}} & \forall\mu = 4,5,6. \end{cases} \tag{I.30}$$

To derive this equation, we used the Voigt notation. This mathematical convention exploits the symmetry property of a tensor, by removing its redundant components, to represent it by a lower rank tensor defined in a higher dimensional space. In this way the second-order transition electric quadrupole moment, which is a fourth rank tensor in three dimensions, is represented as a second rank tensor in six dimensions:

$$(\mathcal{Q}_{jkbc})_{3\times3\times3\times3} \rightarrow \begin{pmatrix} \mathcal{Q}_{1111} & \mathcal{Q}_{1122} & \mathcal{Q}_{1133} & \mathcal{Q}_{1123} & \mathcal{Q}_{1113} & \mathcal{Q}_{1112} \\ \mathcal{Q}_{2211} & \mathcal{Q}_{2222} & \mathcal{Q}_{2233} & \mathcal{Q}_{2223} & \mathcal{Q}_{2213} & \mathcal{Q}_{2212} \\ \mathcal{Q}_{3311} & \mathcal{Q}_{3322} & \mathcal{Q}_{3333} & \mathcal{Q}_{3323} & \mathcal{Q}_{3313} & \mathcal{Q}_{3312} \\ \mathcal{Q}_{2311} & \mathcal{Q}_{2322} & \mathcal{Q}_{2333} & \mathcal{Q}_{2323} & \mathcal{Q}_{2313} & \mathcal{Q}_{2312} \\ \mathcal{Q}_{1311} & \mathcal{Q}_{1322} & \mathcal{Q}_{1333} & \mathcal{Q}_{1323} & \mathcal{Q}_{1313} & \mathcal{Q}_{1312} \\ \mathcal{Q}_{1211} & \mathcal{Q}_{1222} & \mathcal{Q}_{1233} & \mathcal{Q}_{1223} & \mathcal{Q}_{1213} & \mathcal{Q}_{1212} \end{pmatrix} \rightarrow (\mathcal{Q}_{\mu\alpha})_{6\times6}. \tag{I.31}$$

The Table I.1 establishes the correspondence between the new indices and the ones of the represented tensor. Furthermore, in the equation (I.30), the dependencies have been omitted and the bar over a pair of indices means taking the related symmetric one (e.g., $T_{2\bar{6}} = T_{2\overline{12}} = T_{221}$).

(i,j)	$(1,1)$	$(2,2)$	$(3,3)$	$(2,3)$	$(1,3)$	$(1,2)$
μ	1	2	3	4	5	6

TABLE I.1. Voigt notation: correspondence between the pair of indices (i,j) of a symmetric tensor in three dimensions and the indices μ in six dimensions. The indices $\mu = 1,2,3$ correspond to the diagonal components of a second rank tensor, while the indices $\mu = 3,4,5$ correspond to its three independent off-diagonal components. By convention the indices of this notation are denoted with Greek letters.

Then, using the second property linked to the traceless property, we obtain a formula involving $3^2 \times 5^2$ terms:

$$\frac{\gamma^{(2)}_{2ED\cap2EQ}(\omega;\mathbf{R})}{\sqrt{\gamma^{(2)}_{2ED,0}(\omega)\,\gamma^{(2)}_{2EQ,0}(\omega)}} = 2\sum_{i,a=1}^{3}\sum_{\substack{\mu,\alpha=1 \\ \mu,\alpha\neq3}}^{6}\hat{\mathcal{D}}^{eg}_{ia}(\omega,\omega_{eg}-\omega)\left(\hat{\mathcal{Q}}^{eg}_{\mu\alpha}(\omega,\omega_{eg}-\omega)\right)^{*}F^{ED\cap EQ}_{i\mu}(\omega;\mathbf{R})\,F^{ED\cap EQ}_{a\alpha}(\omega_{eg}-\omega;\mathbf{R}), \tag{I.32}$$

with

$$\forall i = 1, 2, 3, \quad F_{i\mu}^{\text{ED}\cap\text{EQ}} := \begin{cases} U_{i\mu} - U_{i3} & \forall \mu = 1, 2 \\ U_{i\mu} & \forall \mu = 4, 5, 6. \end{cases} \tag{I.33}$$

Using the equation (I.30), the tensor $\mathbf{F}^{\text{ED}\cap\text{EQ}}$ can be rewritten as a function of the tensor $\mathbf{T}$:

$$\forall i = 1, 2, 3, \quad F_{i\mu}^{\text{ED}\cap\text{EQ}} := \begin{cases} T_{i\mu} - T_{i3} & \forall \mu = 1, 2 \\ T_{i\mu} + T_{i\bar{\mu}} & \forall \mu = 4, 5, 6, \end{cases} \tag{I.34}$$

and, given the equation (I.28), as a function of the first derivatives of the imaginary part of the dyadic Green's function.

Finally, by changing indices and modifying the Voigt notation to skip the last diagonal element of second-order tensors[3], we get

$$\boxed{\frac{\gamma_{2\text{ED}\cap2\text{EQ}}^{(2)}(\omega; \mathbf{R})}{\sqrt{\gamma_{2\text{ED},0}^{(2)}(\omega)\gamma_{2\text{EQ},0}^{(2)}(\omega)}} = 2 \sum_{i,j=1}^{3} \sum_{\mu,\nu=1}^{5} \text{Re}\left(\hat{\mathcal{D}}_{ij}^{eg}(\omega, \omega_{eg} - \omega)\left(\hat{\mathcal{Q}}_{\mu\nu}^{eg}(\omega, \omega_{eg} - \omega)\right)^*\right) F_{i\mu}^{\text{ED}\cap\text{EQ}}(\omega; \mathbf{R}) F_{j\nu}^{\text{ED}\cap\text{EQ}}(\omega_{eg} - \omega; \mathbf{R}).}$$

$$\tag{I.35}$$

Note that the first tensor $\mathbf{F}^{\text{ED}\cap\text{EQ}}$ is related to the quanta emitted at the frequency ω, while the second one concerns the quanta emitted at the complementary frequency $\omega_{eg} - \omega$. In the next subsection, the relation between the tensor $\mathbf{F}^{\text{ED}\cap\text{EQ}}$, i.e., the first derivatives of the imaginary part of the Green's function, and the one-photon Purcell factors related to the superposition of an electric dipole and quadrupole is established.

F. Expression of the interference term as a function of the one-photon Purcell factors

In the weak-coupling regime, the Purcell factor is defined as the ratio between the one-photon transition rate of a quantum emitter in a given photonic environment and in vacuum: $P := \Gamma^{(1)}/\Gamma_0^{(1)}$ and can be calculated by considering classical radiating point sources [10]. In the case where multiple multipolar emission channels contribute to the transition rate, the classical source is described by the superposition of multipolar point sources, with multipolar moments identical to the multipolar transition moments of the emitter. In the TPSE process, we know from previous works [1, 11] that the two-photon Purcell effect of multipolar transitions (e.g. 2ED and 2EQ transitions) can be written as a weighted summation of the product between the one-photon Purcell factors of the two emitted quanta, where the summation runs over different source orientations. As for the interference term given by the equation (I.35) there is also a decoupling with regard to the environment between the two emitted quanta through the product $\mathbf{F}^{\text{ED}\cap\text{EQ}}(\omega)\,\mathbf{F}^{\text{ED}\cap\text{EQ}}(\omega_{eg} - \omega)$, the link between the two-photon Purcell effect and the one-photon Purcell factors remains valid when several two-photon multipolar transitions contribute simultaneously to the TPSE process. Therefore, we can write:

$$\frac{\gamma_{2\text{ED}+2\text{EQ}}^{(2)}(\omega; \mathbf{R})}{x^2(\omega)} = \sum w\, P^{\text{ED}+\text{EQ}}(\mathbf{R})\, P'^{\text{ED}+\text{EQ}}(\mathbf{R}), \tag{I.36}$$

where $\gamma_{2\text{ED}+2\text{EQ}}^{(2)}(\omega; \mathbf{R})$ is the spectral distribution of the emitted quanta of the total integrated TPSE rate given by the equation (I.22) and where $x^2(\omega)$ represents a function of the two-photon multipolar vacuum transition rates $\gamma_{2\text{ED},0}^{(2)}$ and $\gamma_{2\text{EQ},0}^{(2)}$. Moreover, $P^{\text{ED}+\text{EQ}}$ denotes the Purcell factor related to the superposition of an electric dipole and quadrupole and the summation runs over different source orientations with w the weights. For clarity purpose, we have adopted the following notation: when the prime symbol is not used, it denotes an evaluation at the frequency ω, whereas when it is used, it denotes the evaluation at the complementary frequency $\omega_{eg} - \omega$.

The total spectral TPSE rate in the previous equation is split into three contributions [Eq. (I.22)]:

$$\gamma_{2\text{ED}+2\text{EQ}}^{(2)}(\omega; \mathbf{R}) = \gamma_{2\text{ED}}^{(2)} + \gamma_{2\text{EQ}}^{(2)} + \gamma_{2\text{ED}\cap2\text{EQ}}^{(2)}, \tag{I.37}$$

---

[3] Thus, the third row and column have been removed in equation (I.31) as well as the third column in Table I.1 ($\mu = 3, 4, 5$ now corresponds to $(i, j) = (2, 3), (1, 3), (1, 2)$).

where the 2ED and 2EQ contributions have been written as function of one-photon Purcell factors in Ref. [1] and where the interference term that we want to establish an expression as a function of the Purcell factors is given by the equation (I.35).

To make the link between the Purcell factors $P^{\mathrm{ED+EQ}}$ and the tensor $\mathbf{F}^{\mathrm{ED\cap EQ}}$ involved in the interference term, the idea is to assume specific directions for the first-order multipolar transition moments involved in the definition of the second-order multipolar transitions moments [Eq. (I.16)]. Since general electric dipole and quadrupole moments involve, respectively, up to three and five independent components, they can be expanded with an orthonormal basis of 3 dipoles and 5 quadrupoles. For the dipolar moments, these are the three basis vectors, while for the quadrupolar ones, the basis is built from two different types of plane quadrupoles [1]. Type I ($\hat{\mathbf{Q}}_{yz}$, $\hat{\mathbf{Q}}_{xz}$, and $\hat{\mathbf{Q}}_{xy}$) involve solely off-diagonal components while Type II ($\hat{\mathbf{Q}}_{xx}$ and $\hat{\mathbf{Q}}_{yy}$) involves only diagonal components and differs from type I by an in-plane rotation of $45°$ [1]. In our adapted Voigt notation, these quadrupoles are represented by a five dimensional vector in which only the μ-th component is non-zero and equals to $1/\sqrt{2}$ [4].

As mentioned in the main text and in the next section, the interference term expressed as a function of the first derivatives of the imaginary part of the Green's function is related to the power emitted by an electric point dipole and an electric point quadrupole at the same position. Thus, there are 3×5 possible combinations of the basis vectors of these two sources. Let us take the two first-order electric dipole transition moments aligned along one basis vector, i.e., $\hat{\mathbf{d}}^{em} = \hat{\mathbf{d}}^{mg} = \hat{\mathbf{e}}_i$ with $i = 1, 2, 3$, and the two first-order electric quadrupole transition moments aligned along one basis vector, i.e., $\hat{\mathbf{Q}}^{em} = \hat{\mathbf{Q}}^{mg} = \hat{\mathbf{e}}_\mu/\sqrt{2}$ with $\mu = 1, \ldots, 5$. In this case, using equations (I.16), the normalized second-order multipolar transition moments are given by

$$\hat{\boldsymbol{\mathcal{D}}}^{eg} = \hat{\mathbf{e}}_i \hat{\mathbf{e}}_i, \tag{I.38a}$$

$$\hat{\boldsymbol{\mathcal{Q}}}^{eg} = \frac{1}{2}\, \hat{\mathbf{e}}_\mu \hat{\mathbf{e}}_\mu. \tag{I.38b}$$

Therefore, using the equations in Ref. [1] for the 2ED and 2EQ terms, the equation (I.35) for the interference term, and the equations (I.38) for the multipolar moments, the total transition rate given by the equation (I.37) is rewritten as

$$\gamma_{\mathrm{2ED+2EQ}}^{(2)} = \gamma_{\mathrm{2ED},0}^{(2)}\, P_i^{\mathrm{ED}} P_i'^{\mathrm{ED}} + \gamma_{\mathrm{2EQ},0}^{(2)}\, P_\mu^{\mathrm{EQ}} P_\mu'^{\mathrm{EQ}} + 2\sqrt{\gamma_{\mathrm{2ED},0}^{(2)}\gamma_{\mathrm{2EQ},0}^{(2)}}\, \frac{1}{2}\, F_{i\mu}^{\mathrm{ED\cap EQ}} F_{i\mu}'^{\mathrm{ED\cap EQ}}, \tag{I.39}$$

where the dependencies have been omitted. In this equation, P_i^{ED} and P_μ^{EQ} correspond, respectively, to the Purcell factors related to an electric dipole aligned along $\hat{\mathbf{e}}_i$ and to an electric quadrupole aligned along $\hat{\mathbf{e}}_\mu$ [1].

As the second-order multipolar moments given by the equations (I.38) involve only one component, there is only one possible direction for the dipole ($\hat{\mathbf{e}}_i$) and for the quadrupole ($\hat{\mathbf{e}}_\mu$) and thereby the summation over the source orientations in the equation (I.36) is reduced to a single term:

$$\gamma_{\mathrm{2ED+2EQ}}^{(2)} = x^2 P_{i\mu}^{\mathrm{ED+EQ}}\, P_{i\mu}'^{\mathrm{ED+EQ}}, \tag{I.40}$$

where the dependencies have been omitted and where $P_{i\mu}^{\mathrm{ED+EQ}}$ is the Purcell factor related to a superposition of an electric dipole aligned along $\hat{\mathbf{e}}_i$ and of an electric quadrupole aligned along $\hat{\mathbf{e}}_\mu$.

Combining the two last equations establishes the link between Purcell factors and the tensors $\mathbf{F}^{\mathrm{ED\cap EQ}}$:

$$x^2 P_{i\mu}^{\mathrm{ED+EQ}}\, P_{i\mu}'^{\mathrm{ED+EQ}} = \gamma_{\mathrm{2ED},0}^{(2)}\, P_i^{\mathrm{ED}}\, P_i'^{\mathrm{ED}} + \gamma_{\mathrm{2EQ},0}^{(2)}\, P_\mu^{\mathrm{EQ}} P_\mu'^{\mathrm{EQ}} + \sqrt{\gamma_{\mathrm{2ED},0}^{(2)}\gamma_{\mathrm{2EQ},0}^{(2)}}\, F_{i\mu}^{\mathrm{ED\cap EQ}} F_{i\mu}'^{\mathrm{ED\cap EQ}}, \tag{I.41}$$

where the Purcell factors can be calculated via the power emitted by classical point sources [10]:

$$P_i^{\mathrm{ED}} = \frac{W_i^{\mathrm{ED}}}{W_0^{\mathrm{ED}}}, \tag{I.42a}$$

$$P_\mu^{\mathrm{EQ}} = \frac{W_\mu^{\mathrm{EQ}}}{W_0^{\mathrm{EQ}}}, \tag{I.42b}$$

$$P_{i\mu}^{\mathrm{ED+EQ}} = \frac{W_{i\mu}^{\mathrm{ED+EQ}}}{W_0^{\mathrm{ED}} + W_0^{\mathrm{EQ}}} = \frac{W_i^{\mathrm{ED}} + W_\mu^{\mathrm{EQ}} + W_{i\mu}^{\mathrm{ED\cap EQ}}}{W_0^{\mathrm{ED}} + W_0^{\mathrm{EQ}}}. \tag{I.42c}$$

---

[4] The factor $1/\sqrt{2}$ for the quadrupoles is the normalization factor for quadrupoles that are described by two equal components in absolute value.

In these equations, the subscript 0 indicates quantities that refer to vacuum whereas W_i^{ED}, W_μ^{EQ}, and $W_{i\mu}^{\mathrm{ED+EQ}}$ denote the powers emitted by a classical dipole aligned along $\hat{\mathbf{e}}_i$, by a classical quadrupole aligned along $\hat{\mathbf{e}}_\mu$, and by the superposition of both sources, respectively. Furthermore, $W_{i\mu}^{\mathrm{ED+EQ}}$ is decomposed into three contributions where $W_{i\mu}^{\mathrm{ED}\cap\mathrm{EQ}}$ represents the interference term between the two classical sources. As a reminder, there is no interference in vacuum.

Replacing the Purcell factor expressions into the equation (I.41) gives a left-hand side composed of nine terms, but a right-hand side consisting of only three terms. This is because in our developments based on Fermi's golden rule we discarded mixed transitions, which are consequently not included in the right-hand side. In the left-hand side, the terms involving the products $W_i^{\mathrm{ED}} W_i'^{\mathrm{ED}}$, $W_\mu^{\mathrm{EQ}} W_\mu'^{\mathrm{EQ}}$, and, $W_{i\mu}^{\mathrm{ED}\cap\mathrm{EQ}} W_{i\mu}'^{\mathrm{ED}\cap\mathrm{EQ}}$ correspond, respectively, to the 2ED, 2EQ, and interference contributions in the right-hand side. The 6 other terms in the left-hand side are related to mixed transitions, as for example the one that involves the product $W_i^{\mathrm{ED}} W_\mu'^{\mathrm{EQ}}$ describing an ED–EQ transition. Furthermore, the interference term in the left-hand side describes simultaneously the interference between the 2ED and 2EQ transitions but also between the mixed transitions ED–EQ and EQ–ED. Indeed, as depicted in Figure I.3, both situations are identical from an interference point of view since it is always a question of an interaction between an ED and EQ emission channels, leading to the same tensor $\mathbf{F}^{\mathrm{ED}\cap\mathrm{EQ}}$ and to the same interference term. It is therefore necessary to take only the half of the interference term in the left-hand side in order to equal it with the one on the right-hand side. Hence, by removing the terms related to mixed transitions in the left-hand side and by matching the remaining terms on either side of the equation, we obtain a system of three equations:

$$\begin{cases} x^2 \dfrac{W_i^{\mathrm{ED}}}{W_0^{\mathrm{ED}} + W_0^{\mathrm{EQ}}} \dfrac{W_i'^{\mathrm{ED}}}{W_0'^{\mathrm{ED}} + W_0'^{\mathrm{EQ}}} = \gamma_{2\mathrm{ED},0}^{(2)} \dfrac{W_i^{\mathrm{ED}}}{W_0^{\mathrm{ED}}} \dfrac{W_i'^{\mathrm{ED}}}{W_0'^{\mathrm{ED}}} & \text{(I.43a)} \\[3mm] x^2 \dfrac{W_\mu^{\mathrm{EQ}}}{W_0^{\mathrm{ED}} + W_0^{\mathrm{EQ}}} \dfrac{W_\mu'^{\mathrm{EQ}}}{W_0'^{\mathrm{ED}} + W_0'^{\mathrm{EQ}}} = \gamma_{2\mathrm{EQ},0}^{(2)} \dfrac{W_\mu^{\mathrm{EQ}}}{W_0^{\mathrm{EQ}}} \dfrac{W_\mu'^{\mathrm{EQ}}}{W_0'^{\mathrm{EQ}}} & \text{(I.43b)} \\[3mm] \dfrac{1}{2} x^2 \dfrac{W_{i\mu}^{\mathrm{ED}\cap\mathrm{EQ}}}{W_0^{\mathrm{ED}} + W_0^{\mathrm{EQ}}} \dfrac{W_{i\mu}'^{\mathrm{ED}\cap\mathrm{EQ}}}{W_0'^{\mathrm{ED}} + W_0'^{\mathrm{EQ}}} = \sqrt{\gamma_{2\mathrm{EQ},0}^{(2)} \gamma_{2\mathrm{EQ},0}^{(2)}}\, F_{i\mu}^{\mathrm{ED}\cap\mathrm{EQ}} F_{i\mu}'^{\mathrm{ED}\cap\mathrm{EQ}}. & \text{(I.43c)} \end{cases}$$
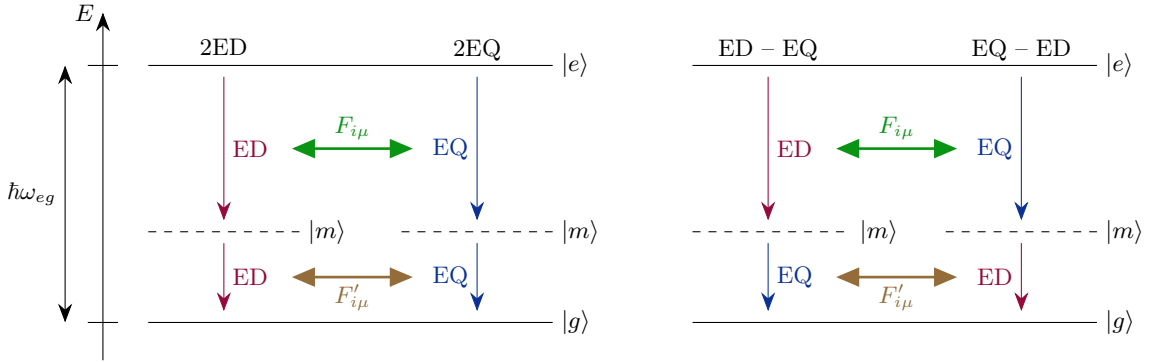

FIG. I.3. Ilustration of the interference between the 2ED and 2EQ transitions (left) and between the mixed transitions ED–EQ and EQ–ED (right). Both situations are identical from an interference point of view since it is always a question of an interaction between an ED and EQ emission channels, leading to the same tensor $\mathbf{F}^{\mathrm{ED}\cap\mathrm{EQ}}$ and to the same interference term.

The two first equations form a system of two equations with two unknowns: x a function of the vacuum TPSE rates and the ratio between the powers emitted in vacuum by the classical ED and EQ sources. Indeed, the power emitted by the classical multipolar sources representing the multipolar transition moments of the emitter need to be set according to the two-photon multipolar transition rates in vacuum. Solving this system by using the symmetry propriety of TPSE rates with respect to $\omega_{eg}/2$ gives:

$$x = x' = \sqrt{\gamma_{2\mathrm{ED},0}^{(2)}} + \sqrt{\gamma_{2\mathrm{EQ},0}^{(2)}}, \tag{I.44a}$$

$$\frac{W_0^{\mathrm{EQ}}}{W_0^{\mathrm{ED}}} = \frac{W_0'^{\mathrm{EQ}}}{W_0'^{\mathrm{ED}}} = \sqrt{\frac{\gamma_{2\mathrm{EQ},0}^{(2)}}{\gamma_{2\mathrm{ED},0}^{(2)}}}. \tag{I.44b}$$

Now, by using the third equation of the system together with the last two, we obtain an expression for the $\mathbf{F}^{\text{ED}\cap\text{EQ}}$ tensor:

$$F_{i\mu}^{\text{ED}\cap\text{EQ}}(\omega;\mathbf{R}) = \frac{W_{i\mu}^{\text{ED}\cap\text{EQ}}(\omega;\mathbf{R})}{\sqrt{2\,W_0^{\text{ED}}(\omega)\,W_0^{\text{EQ}}(\omega)}}, \tag{I.45}$$

which can be written, using the equations (I.42) and (I.44), as a function of the Purcell factors:

$$\left(\gamma_{2\text{ED},0}^{(2)}\,\gamma_{2\text{EQ},0}^{(2)}\right)^{1/4} F_{i\mu}^{\text{ED}\cap\text{EQ}} = \frac{1}{\sqrt{2}}\left[\left(\sqrt{\gamma_{2\text{ED},0}^{(2)}} + \sqrt{\gamma_{2\text{EQ},0}^{(2)}}\right) P_{i\mu}^{\text{ED+EQ}} - \sqrt{\gamma_{2\text{ED},0}^{(2)}}\,P_i^{\text{ED}} - \sqrt{\gamma_{2\text{EQ},0}^{(2)}}\,P_\mu^{\text{EQ}}\right], \tag{I.46}$$

where the dependencies have been omitted, and where the Purcell factors can be calculated via the equations (I.42). Note that in vacuum, all Purcell factors tend towards one and the tensor $\mathbf{F}^{\text{ED}\cap\text{EQ}}$ tends, as expected, towards 0 and leads to an interference term [Eq. (I.35)] equals to zero.

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II.   POWER EMITTED BY CLASSICAL POINT SOURCES

In this section, we briefly look at the power emitted by classical point sources that we express as a function of the dyadic Green's function. Let us consider a linear, isotropic, non-magnetic and homogeneous medium with a dielectric constant equal to 1 in which there is a source contained in a finite volume V. The source is described by a current density $\mathbf{j}$ and we assume a time harmonic dependence $e^{-i\omega t}$, with ω the source oscillation frequency. Thereby, the electric field at a position $\mathbf{r}$ produced by the source can be calculated trough an integral of the dyadic Green's function $\mathbf{G}$ [1]:

$$\mathbf{E}(\mathbf{r}) = i\mu_0 \, \omega \int_V \mathbf{G}(\omega; \mathbf{r}, \mathbf{r}') \, \mathbf{j}(\mathbf{r}') \, \mathrm{d}V'. \tag{II.1}$$

Since the source has a time harmonic dependence, this is also the case for the electromagnetic field. Moreover, the power emitted by the source is given by Poynting's theorem [1]:

$$W = -\frac{1}{2} \int_V \mathrm{Re} \left\{ \mathbf{j}^*(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) \right\} \mathrm{d}V, \tag{II.2}$$

where Re stands for the real part. Then, the use of the two introduced equations allows to write the power emitted by a source as a function of the Green's function and of the source current density:

$$W = \frac{\mu_0 \, \omega}{2} \int_V \int_V \mathrm{Im} \left\{ \mathbf{j}^*(\mathbf{r}) \cdot \mathbf{G}(\omega; \mathbf{r}, \mathbf{r}') \cdot \mathbf{j}(\mathbf{r}') \right\} \mathrm{d}V' \, \mathrm{d}V, \tag{II.3}$$

where Im denotes taking the imaginary part and the obtained expression involves twice the source current density.

Now, let us consider the case where the source is an electric point dipole and an electric point quadrupole at the same location $\mathbf{R}$. Thereby, the source current density is given by [1–3]:

$$\mathbf{j}_{\mathrm{ED+EQ}}(\mathbf{r}) = -i\omega \left(\mathbf{d} - \mathbf{Q}\nabla \right) \delta(\mathbf{r} - \mathbf{R}), \tag{II.4}$$

where $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})^T$ is a column vector with T denoting the transpose and with $\mathbf{d}$ and $\mathbf{Q}$ being the electric dipole and quadrupole moments of the source[1]:

$$\mathbf{d} = \int_V \rho(\mathbf{r}) \, \mathbf{r} \, \mathrm{d}V, \tag{II.5a}$$

$$\mathbf{Q} = \frac{1}{2} \int_V \rho(\mathbf{r}) \left(\mathbf{rr} - \frac{r^2 \mathbb{1}}{3} \right) \mathrm{d}V, \tag{II.5b}$$

with ρ the volume charge density[2] and $\mathbb{1}$ the identity matrix. Injecting the source current density in the equation (II.3) leads to the three following contributions to the emitted power:

$$W_{\mathrm{ED+EQ}} = W_{\mathrm{ED}} + W_{\mathrm{EQ}} + W_{\mathrm{ED} \cap \mathrm{EQ}}, \tag{II.6}$$

where

$$W_{\mathrm{ED}} = \frac{\mu_0 \, \omega^3}{2} \|\mathbf{d}\|^2 \left\{ \hat{\mathbf{d}} \cdot \mathrm{Im} \, \mathbf{G}(\omega; \mathbf{R}, \mathbf{R}) \cdot \hat{\mathbf{d}} \right\}, \tag{II.7a}$$

$$W_{\mathrm{EQ}} = \frac{\mu_0 \, \omega^3}{2} \|\mathbf{Q}\|^2 \left\{ \hat{\mathbf{Q}}\nabla \cdot \mathrm{Im} \, \mathbf{G}(\omega; \mathbf{r}, \mathbf{r}') \cdot \hat{\mathbf{Q}}\nabla' \right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}}, \tag{II.7b}$$

$$W_{\mathrm{ED} \cap \mathrm{EQ}} = 2\frac{\mu_0 \, \omega^3}{2} \|\mathbf{d}\| \, \|\mathbf{Q}\| \left\{ \hat{\mathbf{d}} \cdot \mathrm{Im} \, \mathbf{G}(\omega; \mathbf{R}, \mathbf{r}') \cdot \hat{\mathbf{Q}}\nabla' \right\}_{\mathbf{r}'=\mathbf{R}}, \tag{II.7c}$$

where we defined the squared norm of a rank-n tensor $\mathbf{U}$ with $n \geq 1$ as $\|\mathbf{U}\|^2 := \sum_{i_1, i_2, \ldots, i_n} |U_{i_1, i_2, \ldots, i_n}|^2$, where ∇' means derivatives with respect to the coordinates $\mathbf{r}'$, and where the caret denotes normalized vectors and tensors. All of these equations involve the imaginary part of the Green's function evaluated the emitter's position, which

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[1] The quadrupole moment is sometimes defined with a factor 3 instead of the factor $1/2$. However, it is important to define the quadrupole moment as we did in order to have a correspondence with the electric quadrupole operator $\mathbf{Q} = -e\,\mathbf{rr}/2$ in quantum mechanics. In addition, $\mathbf{Q}$ can be taken traceless in source-free regions ($\int_V \rho(\mathbf{r}) \, \mathrm{d}V = 0$) since $\nabla \cdot \mathbf{E} = 0$ [4–6].

[2] Note that $\int_V \rho(\mathbf{r}) \, \mathrm{d}V = 0$.

is a symmetric tensor. For the electric quadrupole, the equation involves double derivatives of the imaginary part of the Green's function while the interference term $W_{\mathrm{ED}\cap\mathrm{EQ}}$ involves single derivatives. These equations involve, respectively, twice the electric dipole moment $\mathbf{d}$, twice the electric quadrupole moment $\mathbf{Q}$, and once the electric dipole and quadrupole moments for the interference term. Moreover, the Green's function is the result of the field produced by the source alone plus the field scattered by the environment, which explains how the power is modified by the environment of the emitter.

In vacuum the equations reduce to:

$$W_{\mathrm{ED},0} = \frac{\mu_0\,\omega^4}{12\pi c}\,\|\mathbf{d}\|^2\,, \tag{II.8a}$$

$$W_{\mathrm{EQ},0} = \frac{\mu_0\,\omega^6}{40\pi c^3}\,\|\mathbf{Q}\|^2\,, \tag{II.8b}$$

where the interference is zero. In addition, the vacuum normalized powers are written as follows:

$$\frac{W_{\mathrm{ED}}}{W_{\mathrm{ED},0}} = \frac{6\pi c}{\omega}\left\{\hat{\mathbf{d}}\cdot\operatorname{Im}\mathbf{G}(\omega;\mathbf{R},\mathbf{R})\cdot\hat{\mathbf{d}}\right\}, \tag{II.9a}$$

$$\frac{W_{\mathrm{EQ}}}{W_{\mathrm{EQ},0}} = \frac{20\pi c^3}{\omega^3}\left\{\hat{\mathbf{Q}}\nabla\cdot\operatorname{Im}\mathbf{G}(\omega;\mathbf{r},\mathbf{r}')\cdot\hat{\mathbf{Q}}\nabla'\right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}}, \tag{II.9b}$$

$$\frac{W_{\mathrm{ED}\cap\mathrm{EQ}}}{\sqrt{W_{\mathrm{ED},0}\,W_{\mathrm{EQ},0}}} = 2\,\frac{2\sqrt{30}\pi c^2}{\omega^2}\left\{\hat{\mathbf{d}}\cdot\operatorname{Im}\mathbf{G}(\omega;\mathbf{r},\mathbf{r}')\cdot\hat{\mathbf{Q}}\nabla'\right\}_{\mathbf{r}=\mathbf{r}'=\mathbf{R}}. \tag{II.9c}$$

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III. CALCULATION OF THE TWO-ELECTRIC DIPOLE AND THE TWO-ELECTRIC QUADRUPOLE TRANSITION RATES IN VACUUM BETWEEN TWO s STATES OF THE HYDROGEN ATOM

In this section, we calculate the two-electric dipole (2ED) and the two-electric quadrupole (2EQ) vacuum transition rates between the $5s$ and $3s$ states of the hydrogen atom. As in our framework we have obtained expressions for the multipolar contributions which are normalized by the rates in vacuum, it is necessary to know them in order to be able to sum up all the contributions to retrieve the overall TPSE rate. Moreover, they are required to define the power emitted by the classical ED and EQ sources used to calculate the Purcell factors associated with the superposition of these two sources when calculating the tensor $F^{\mathrm{ED} \cap \mathrm{EQ}}$ that describes the interference between the ED and EQ single-photon transitions and which is involved in calculating the interference between the 2ED and 2EQ channels.

Historically, the first estimate of a two-photon spontaneous emission rate was carried out in 1940 by Breit and Teller for the 2s state of hydrogen, for which this is the main process responsible for its mean lifetime [1]. One decade later, Spitzer and Greenstein realized a refinement and found a value of $8.23~\mathrm{s}^{-1}$ for the integrated two-electric dipole transition rate, i.e., the main multipolar contribution to this process [2]. In 1981, Goldman and Drake made the first calculations, relativistic, that include the first multipolar contributions to the TPSE process [3]. They found that the integrated 2ED and 2EQ transition rates are $8.229~\mathrm{s}^{-1}$ and $4.907 \times 10^{-12}~\mathrm{s}^{-1}$, respectively. More recently in 2007, Chluba and Sunyaev studied the two-photon process for the $ns \to 1s$ and $nd \to 1s$ 2ED transitions in hydrogen and up to large n, where they provide analytical fittings of the spectra [4].

In conclusion, the only data available in the literature concerning vacuum 2ED and 2EQ transition rates for hydrogen are, on the one hand, spectra involving the $1s$ state as the final state for the 2ED transition [4] and, on the other hand, the integrated rate between the $2s$ and $1s$ states for the 2EQ transition [3]. Nevertheless, Matsumoto derived in 1991 analytical expressions for the multipole matrix elements for the hydrogen atom [5]. Thus, we can use the method presented in Refs. [4, 6] for their calculation of 2ED transition rates as well as the expressions of the multipole matrix elements in Ref. [5] to calculate the 2ED and 2EQ transition rates between two s states of the hydrogen atom.

The document starts in Section III A with a reminder concerning the expressions of the 2ED and 2EQ transition rates in vacuum and about the multipolar second-order moments relative to a transition between two spherically symmetric states. Then, we derive in Section III B the 2ED and 2EQ decay profiles and we discuss the two contributions to the summation over the virtual intermediate states. In Section III C, we give the expressions of the multipole matrix elements, which are radial integrals over the radial eigenfunctions of the hydrogen atom. Finally, our method and results are presented in Section III D.

A. Reminder

In Ref. [7], we showed that for each multipolar operator $\mathrm{MO} \in \{\mathrm{ED},~\mathrm{EQ}\}$ the vacuum TPSE rate is given by

$$\Gamma^{(2)}_{2\mathrm{MO},0} = \int_0^{\omega_{eg}} \gamma^{(2)}_{2\mathrm{MO},0}(\omega)\,\mathrm{d}\omega, \tag{III.1}$$

where the multipolar contributions $\gamma^{(2)}_{2\mathrm{MO},0}(\omega)$ to the spectral distribution of the emitted quanta are given by

$$\gamma^{(2)}_{2\mathrm{ED},0}(\omega) = \frac{\omega^3(\omega_{eg}-\omega)^3}{36\pi^3\varepsilon_0^2\hbar^2 c^6}\,\left\|\boldsymbol{\mathcal{D}}^{eg}(\omega,\omega_{eg}-\omega)\right\|^2, \tag{III.2a}$$

$$\gamma^{(2)}_{2\mathrm{EQ},0}(\omega) = \frac{\omega^5(\omega_{eg}-\omega)^5}{400\pi^3\varepsilon_0^2\hbar^2 c^{10}}\,\left\|\boldsymbol{\mathcal{Q}}^{eg}(\omega,\omega_{eg}-\omega)\right\|^2, \tag{III.2b}$$

where ω and $\omega_{eg}-\omega$ are the frequencies of the two emitted quanta of complementary energy. In these equations, ε_0 is the vacuum electric permittivity, $\hbar\omega_{eg}$ represents the transition energy with $\hbar$ the reduced Planck constant, and c denotes the speed of light in vacuum. Moreover, the squared norm of an nth rank tensor $\mathbf{U}$ with $n \in \mathbb{N}_0$ is defined as $\|\mathbf{U}\|^2 := \sum_{i_1,i_2,\ldots,i_n} |U_{i_1,i_2,\ldots,i_n}|^2$.

These expressions involve the squared norm of the second-order multipolar transition moments that are defined as:

$$\boldsymbol{\mathcal{D}}^{eg}(\omega,\omega_{eg}-\omega) := \sum_{|m\rangle}\left(\frac{\mathbf{d}^{em}\mathbf{d}^{mg}}{\omega_{em}-\omega} + \frac{\mathbf{d}^{mg}\mathbf{d}^{em}}{\omega_{em}-(\omega_{eg}-\omega)}\right), \tag{III.3a}$$

$$\boldsymbol{\mathcal{Q}}^{eg}(\omega,\omega_{eg}-\omega) := \sum_{|m\rangle}\left(\frac{\mathbf{Q}^{em}\,\mathbf{Q}^{mg}}{\omega_{em}-\omega} + \frac{\mathbf{Q}^{mg}\,\mathbf{Q}^{em}}{\omega_{em}-(\omega_{eg}-\omega)}\right), \tag{III.3b}$$

where $\hbar\omega_{ab} := E_a - E_b$ with E_a denoting the energy of the atom in the state $|a\rangle$ and where the outer product is implied. The components of the tensor that derive from the outer product of two tensors $\mathbf{U}$ and $\mathbf{V}$ are $(\mathbf{UV})_{i_1,i_2,\ldots,i_n,j_1,j_2,\ldots,j_n} := U_{i_1,i_2,\ldots,i_n} V_{j_1,j_2,\ldots,j_n}$. In these definitions, the summation runs over all possible emitter's virtual intermediate states $|m\rangle$. Furthermore, $\mathbf{d}^{ab} := \langle a|\mathbf{d}|b\rangle$ and $\mathbf{Q}^{ab} := \langle a|\mathbf{Q}|b\rangle$, with $\mathbf{d}$ and $\mathbf{Q}$ the electric dipole and quadrupole operators, stand for the electric dipole and electric quadrupole transition moments, respectively, which describe the emitter's transition from the state $|b\rangle$ to the state $|a\rangle$ (a, $b = e$, m, g). Thus, the tensors $\boldsymbol{\mathcal{D}}^{eg}$ and $\boldsymbol{\mathcal{Q}}^{eg}$ describe the two successive electric dipole and quadrupole transitions, respectively, between the excited $|e\rangle$ state and the ground state $|g\rangle$ of the emitter.

<center>*s → s transition*</center>

In the case of a transition between two spherically symmetric states, the second-order electric dipole transition moment is given by [8]:

$$\boldsymbol{\mathcal{D}}^{eg}(\omega, \omega_{eg} - \omega) = \sum_n d^{em} d^{mg} \left(\frac{1}{\omega_{em} - \omega} + \frac{1}{\omega_{em} - (\omega_{eg} - \omega)} \right) \mathbb{1}_3, \tag{III.4}$$

where there is a summation over the principal quantum number n of the intermediate states $|m\rangle$, where $\mathbb{1}_3$ is the identity matrix in three dimensions and where d^{em} and d^{mg} are the electric dipole radial matrix elements:

$$d^{em} := -\frac{e\,a_0}{\sqrt{3}} \langle R_{n_e,l-1}|r|R_{n,l}\rangle, \tag{III.5a}$$

$$d^{mg} := -\frac{e\,a_0}{\sqrt{3}} \langle R_{n,l}|r|R_{n_g,l-1}\rangle. \tag{III.5b}$$

In the previous equations, e is the elementary charge, a_0 represents the Bohr radius, r is the position operator, and $R_{n,l}(r)$ denotes the radial component of the wavefunction of the hydrogen atom. Moreover, l denotes the azimuthal quantum number of the intermediate state whereas n_e and n_g are the principal quantum numbers of the excited and ground states of the emitter, respectively. For consistency of notation, we retain the ground state label for the final state, even though it is not necessarily the ground state. The radial integrals present in these expressions are dimensionless and will be discussed in Section III C.

Concerning the 2EQ transition, for a $s \to s$ transition, the second-order electric quadrupole transition moment is given by [7]:

$$\boldsymbol{\mathcal{Q}}^{eg}(\omega, \omega_{eg} - \omega) = 4\sqrt{5} \sum_n q^{em} q^{mg} \left(\frac{1}{\omega_{em} - \omega} + \frac{1}{\omega_{em} - (\omega_{eg} - \omega)} \right) \hat{\boldsymbol{\mathcal{Q}}}^{eg}, \tag{III.6}$$

where the elements of the normalized tensor are given by

$$\hat{\mathcal{Q}}_{ijkl}^{eg} := \frac{\mathcal{Q}_{ijkl}^{eg}(\omega, \omega_{eg} - \omega)}{\|\boldsymbol{\mathcal{Q}}^{eg}(\omega, \omega_{eg} - \omega)\|} = \frac{1}{\sqrt{20}} \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3} \delta_{ij}\delta_{kl} \right), \tag{III.7}$$

and where q^{em} and q^{mg} are the electric quadrupole radial matrix elements:

$$q^{em} := -\frac{e\,a_0^2}{2\sqrt{30}} \langle R_{n_e,l-2}|r^2|R_{n,l}\rangle, \tag{III.8a}$$

$$q^{mg} := -\frac{e\,a_0^2}{2\sqrt{30}} \langle R_{n,l}|r^2|R_{n_g,l-2}\rangle. \tag{III.8b}$$

B. Vacuum decay profiles for a transition between two isotropic states

To calculate TPSE rates in vacuum, let us rewrite the equations by introducing the dimensionless frequency $y := \omega/\omega_{eg}$ comprised between 0 and 1. By doing so, the equation (III.1) of the integrated transition rate is rewritten as follows [4]:

$$\Gamma_{2\text{MO},0}^{(2)} = \int_0^{\omega_{eg}} \gamma_{2\text{MO},0}^{(2)}(\omega)\,\mathrm{d}\omega = \frac{1}{2} \int_0^1 \phi_{2\text{MO},0}^{(2)}(y)\,\mathrm{d}y = \int_0^{1/2} \phi_{2\text{MO},0}^{(2)}(y)\,\mathrm{d}y, \tag{III.9}$$

with

$$\phi^{(2)}_{2\text{MO},0}(y) = 2\,\omega_{eg}\,\gamma^{(2)}_{2\text{MO},0}(\omega), \tag{III.10}$$

where $\phi^{(2)}_{2\text{MO},0}(y)\,\mathrm{d}y$ denotes the number of photons emitted per second in the frequency interval between y and $y + \mathrm{d}y$. The latter spectrum encompasses the photons emitted simultaneously during this second-order process at complementary frequencies, thus necessitating integration over only half of the spectrum[1]. Note that the probability to emit a photon at the frequency ω is equal to the probability to emit a photon at the complementary energy $\omega_{eg} - \omega$, leading to symmetric profiles with respect to $\omega_{eg}/2$.

Now, let us obtain the expression of the decay profiles for the 2ED and 2EQ transitions in vacuum. Then, we discuss the different contributions to the sum over the virtual intermediate states.

1. Two-electric dipole decay profile

Let us start by rewriting the equations of the spectral transition rate and of the second-order transition moment, given by the equations (III.2a) and (III.4), by introducing the dimensionless frequency $y := \omega/\omega_{eg}$ and by using the new definition of the spectrum given by the equation (III.10):

$$\phi^{(2)}_{2\text{ED},0}(y) = \frac{\omega_{eg}^7}{18\pi^3\varepsilon_0^2\hbar^2 c^6}\,y^3(1-y)^3\,\|\boldsymbol{\mathcal{D}}^{eg}(y,1-y)\|^2, \tag{III.11a}$$

$$\boldsymbol{\mathcal{D}}^{eg}(y,1-y) = \frac{1}{\omega_{eg}}\sum_n d^{em}d^{mg}f_n(y)\,\mathbb{1}_3, \tag{III.11b}$$

where the function $f_n(y)$ has been defined as

$$f_n(y) := \left(\frac{1}{y_{em} - y} + \frac{1}{y_{em} - (1-y)}\right), \tag{III.12}$$

with

$$y_{em} := \frac{\omega_{em}}{\omega_{eg}} := \frac{E_e - E_m}{E_e - E_g} = \frac{n_g^2(n_e^2 - n^2)}{n^2(n_e^2 - n_g^2)}. \tag{III.13}$$

Thus, the function $f_n(y)$ depends only on the principal quantum number n of the intermediate state (these of the initial and final ones are fixed). In the last equation, we used the expression of the eigenvalues, i.e., $E_n = -E_i/n^2$ with $E_i \approx 13.6$ eV the ionization energy of the hydrogen atom.

Using the expressions of the electric dipole radial matrix elements given by the equations (III.5), the squared norm of the second-order transition moment is rewritten as

$$\|\boldsymbol{\mathcal{D}}^{eg}(y,1-y)\|^2 = \frac{e^4 a_0^4}{3\,\omega_{eg}^2}\underbrace{\left|\sum_n \langle R_{n_e,l-1}|r|R_{n,l}\rangle\,\langle R_{n,l}|r|R_{n_g,l-1}\rangle\,f_n(y)\right|^2}_{\left|M^{eg}_{2\text{ED}}(y)\right|^2}. \tag{III.14}$$

Finally, by injecting the last equation in the expression of the 2ED vacuum transition rate [Eq. (III.11a)], we get the expression obtained in Ref. [4] for the 2ED decay profile:

$$\boxed{\phi^{(2)}_{2\text{ED},0}(y) = G^{eg}_{2\text{ED}}\,y^3(1-y)^3\,|M^{eg}_{2\text{ED}}(y)|^2, \quad G^{eg}_{2\text{ED}} := \left(\frac{2}{3}\right)^3\frac{\omega_{eg}^5 a_0^4\alpha^2}{\pi c^4},} \tag{III.15}$$

where $\alpha = e^2/4\pi\varepsilon_0\hbar c$ is the fine-structure constant. Note that this expression is only valid for a $s \to s$ transition. For a $2s \to 1s$ transition, $\omega_{eg} = 3E_i/4\hbar$ and $G^{2s\,1s}_{2\text{ED}} \approx 4.37$ s^{-1}, while for a $5s \to 3s$ transition, $\omega_{eg} = (4/15)^2 E_i/\hbar$ and $G^{5s\,3s}_{2\text{ED}} \approx 3.35 \times 10^{-5}$ s^{-1}.

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[1] The definition of $\gamma^{(2)}_{2\text{MO},0}(\omega)$ doesn't count the quanta emitted simultaneously at complementary frequencies, which explains the factor 2 difference with the definition of $\phi^{(2)}_{2\text{MO},0}(y)$.

2. Two-electric quadrupole decay profile

Now, let us do the same developments for the spectral transition rate and for the second-order transition moment of the 2EQ transition, respectively given by the equations (III.2a) and (III.4):

$$\phi_{2\text{EQ},0}^{(2)}(y) = \frac{\omega_{eg}^{11}}{200\pi^3\varepsilon_0^2\hbar^2 c^{10}} \, y^5(1-y)^5 \, \|\boldsymbol{\mathcal{Q}}^{eg}(y,1-y)\|^2 \,, \tag{III.16a}$$

$$\boldsymbol{\mathcal{Q}}^{eg}(y,1-y) = \frac{4\sqrt{5}}{\omega_{eg}} \sum_n q^{em} q^{mg} f_n(y) \, \hat{\boldsymbol{\mathcal{Q}}}^{eg}. \tag{III.16b}$$

Using the expressions of the electric quadrupole radial matrix elements given by the equations (III.8), the squared norm of the second-order transition moment is rewritten as

$$\|\boldsymbol{\mathcal{Q}}^{eg}(y,1-y)\|^2 = \frac{e^4 a_0^8}{180\,\omega_{eg}^2} \underbrace{\left|\sum_n \langle R_{n_e,l-2}|r^2|R_{n,l}\rangle \langle R_{n,l}|r^2|R_{n_g,l-2}\rangle f_n(y)\right|^2}_{\left|M_{2\text{EQ}}^{eg}(y)\right|^2}. \tag{III.17}$$

Finally, by injecting the last equation in the expression of the 2EQ vacuum transition rate given by the equation (III.16a), we get the 2EQ decay profile:

$$\boxed{\phi_{2\text{EQ},0}^{(2)}(y) = G_{2\text{EQ}}^{eg} \, y^5(1-y)^5 \left|M_{2\text{EQ}}^{eg}(y)\right|^2, \quad G_{2\text{EQ}}^{eg} := \frac{\omega_{eg}^9 a_0^8 \alpha^2}{2250\pi c^8}.} \tag{III.18}$$

Note that this expression is only valid for a $s \to s$ transition. For a $2s \to 1s$ transition, $\omega_{eg} = 3E_i/4\hbar$ and $G_{2\text{EQ}}^{2s\,1s} \approx 3.67 \times 10^{-13}$ s^{-1}, while for a $5s \to 3s$ transition, $\omega_{eg} = (4/15)^2 E_i/\hbar$ and $G_{2\text{EQ}}^{5s\,3s} \approx 2.27 \times 10^{-22}$ s^{-1}.

3. Summation over intermediate states

To calculate the decay profiles $\phi_{2\text{ED},0}^{(2)}(y)$ and $\phi_{2\text{ED},0}^{(2)}(y)$, we need to calculate the quantities $M_{2\text{ED}}^{eg}(y)$ and $M_{2\text{EQ}}^{eg}(y)$ [Eqs. (III.14) and (III.17)] that involve a summation over the principal quantum number of the virtual intermediate states. This one starts from $n = n_e$ and extends to infinity. Indeed, the summation for $n_g < n < n_e$ denotes a summation over real states and thus describes a cascade of two single-photon emissions and not a TPSE process [4]. Moreover, there are two contributions to the summation over $n \geq n_e$:

$$\sum_n = \sum_{n=n_e}^{\infty} + \int_0^{\infty} \mathrm{d}x. \tag{III.19}$$

The first one is a summation over the discrete set of bound states ($E_n = -E_i/n^2 < 0, n \in \mathbb{N}_0$) while the second one is an integral over the continuum of free states ($E_x = x^2 E_i \geq 0, x \in \mathbb{R}^+$) [4].

Now all that is left to do is calculate, in the next section, the multipole matrix elements involved in the calculation of $M_{2\text{ED}}^{eg}(y)$ and $M_{2\text{EQ}}^{eg}(y)$ [Eqs. (III.14) and (III.17)].

C. Calculation of multipole matrix elements

For the radial component of the hydrogen atom's wavefunction, the eigenfunctions can be written, in atomic unit of length, as follows [5, 6]:

$$R_{n,l}(r) = N_{n,l} \, e^{-r/n} \, r^l \, {}_1F_1\left(-n_r; 2l+2; 2\frac{r}{n}\right), \tag{III.20}$$

where n, l, and $n_r := n - l - 1$ are respectively the principal, azimuthal, and radial quantum numbers. Moreover, $N_{n,l}$ is a normalization constant and ${}_1F_1(a;b;z)$ denotes the confluent hypergeometric function defined as [9, 10]:

$$_1F_1(a,b;z) := \sum_{n=0}^{\infty} \frac{(a)_n}{(b)_n} \frac{z^n}{n!} = \frac{\Gamma(b)}{\Gamma(a)\Gamma(b-a)} \int_0^1 e^{zt} \, t^{a-1}(1-t)^{b-a-1} \, \mathrm{d}t, \tag{III.21}$$

where $(\,\cdot\,)_m$ is the Pochhammer symbol defined as

$$(x)_m := \frac{\Gamma(x+m)}{\Gamma(x)} = x(x+1)(x+2)\dots(z+m-1), \tag{III.22}$$

with $\Gamma(x)$ the gamma function.

For the discrete set of bound states ($E < 0$), the eigenvalues E_n and the normalization constant are given by

$$E_n = -\frac{E_i}{n^2} \qquad \text{with } n \in \mathbb{N}_0, \tag{III.23a}$$

$$N_{n,l} = \frac{2^{l+1}}{(2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}}\, n^{-l-2}. \tag{III.23b}$$

For the continuum of unbound states ($E \geq 0$), the principal quantum number $n = -i/x$ is imaginary. In this case, the eigenvalues and the normalization constant, now denoted $C_{x,l}$, are given by[2]

$$E = -\frac{E_i}{n^2} = x^2 E_i \qquad \text{with } x \in \mathbb{R}^+, \tag{III.24a}$$

$$C_{x,l} = \frac{2^{l+1}}{(2l+1)!} \frac{x^{l+\frac{1}{2}}}{\sqrt{1-e^{-\frac{2\pi}{x}}}} \prod_{s=1}^{l} \left(s^2 + x^{-2}\right). \tag{III.24b}$$

Note that even though n may be complex, the radial eigenfunctions remain real.

The expressions obtained for the 2ED and 2EQ vacuum TPSE rates involve, in M_{2ED}^{eg} and M_{2EQ}^{eg} [Eqs. (III.14) and (III.17)], the multipole matrix elements of the radial eigenfunctions that describe the transition from the state characterized by the quantum numbers (m, j) to the state characterized by the quantum numbers (n, l). These are calculated through a radial integral [5, 6]:

$$\langle R_{n,l}|r^a|R_{m,j}\rangle := \frac{1}{a_0} \int_0^\infty R_{n,l}(r)\, r^{a+2}\, R_{m,j}(r)\, \mathrm{d}r, \tag{III.25}$$

where r is the position operator and where the integral is dimensionless due to the division by the atomic unit of length, i.e., the Bohr radius a_0. Moreover, a is equal to 1 for an electric dipole transition and to 2 for an electric quadrupole transition. In the previous equation, (n, l) are the quantum numbers associated to the intermediate state, which can be a bound or a free state, while (m, j) are the ones of the initial or final states, which are always bound states ($m \in \mathbb{N}_0$). We therefore refer to bound-bound and bound-free radial integrals. In addition, as the radial wavefunctions of the hydrogen atom are real and as the position operator r is Hermitian, the following relation is satisfied:

$$\langle R_{n,l}|r^a|R_{m,j}\rangle = \langle R_{m,j}|r^a|R_{n,l}\rangle^* = \langle R_{m,j}|r^a|R_{n,l}\rangle. \tag{III.26}$$

For an ED transition ($a = 1$ and $j = l - 1$), one can show that [5, 6]:

$$\forall n \neq m, \quad \langle R_{n,l}|r|R_{m,l-1}\rangle = N_{n,l}\, N_{m,l-1}\, (-1)^{m-l}\, \frac{(2l+1)!}{2}\, n(nm)^{2l+2}\, \frac{(n-m)^{n+m-2l-2}}{(n+m)^{n+m}}$$

$$\times \left[F(-n_r, -m_r; c; z) - \left(\frac{n-m}{n+m}\right)^2 F(-n_r - 2, -m_r; c; z) \right], \tag{III.27a}$$

$$\langle R_{n,l}|r|R_{n,l-1}\rangle = \frac{3}{2} n \sqrt{n^2 - l^2}, \tag{III.27b}$$

where $c = 2l$, $z = -4nm/(n-m)^2$, and where F is the hypergeometric function ${}_2F_1(a, b; c; z)$ defined as [9, 10]:

$$_2F_1(a, b; c; z) := \sum_{n=0}^{\infty} \frac{(a)_n(b)_n}{(c)_n} \frac{z^n}{n!} = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_0^1 \frac{t^{b-1}(1-t)^{c-b-1}}{(1-tz)^a}\, \mathrm{d}t. \tag{III.28}$$

_____

[2] The normalization constant depends on the scale chosen to integrate over the continuum [6]. A normalization in the energy-scale lead to a normalization constant $C_{E,l} = C_{x,l}/\sqrt{x}$ with $C_{x,l}$ the normalization constant in the x-scale. As we wrote the integral over the continuum in the equation (III.19) as a function of the variable x, we need to take the normalization constant $C_{x,l}$.

For an EQ transition ($a = 2$ and $j = l, l-2$), one can show that[3] [5]:

$$\forall n \neq m, \ \langle R_{n,l}|r^2|R_{m,l-2}\rangle = N_{n,l} N_{m,l-2} (-1)^{m-l+1} \frac{(2l+1)!}{4} n^3 (nm)^{2l} \frac{(n-m)^{n+m-2l-1}}{(n+m)^{n+m-1}}$$

$$\times \left[F(-n_r, -m_r; c-2; z) - 2\left(\frac{n-m}{n+m}\right) F(-n_r-1, -m_r; c-2; z) \right.$$

$$\left. +2\left(\frac{n-m}{n+m}\right)^3 F(-n_r-3, -m_r; c-2; z) - \left(\frac{n-m}{n+m}\right)^4 F(-n_r-4, -m_r; c-2; z) \right], \quad \text{(III.29a)}$$

$$\forall n \neq m, \ \langle R_{n,l}|r^2|R_{m,l}\rangle = 8 N_{n,l} N_{m,l} (-1)^{m-l} (2l+1)! (nm)^{2l+6} \frac{(n-m)^{n+m-2l-4}}{(n+m)^{n+m+2}} F(-n_r, -m_r; c-2; z).$$

$$\text{(III.29b)}$$

Note that the EQ transition is forbidden between two s states ($l = j = 0$) [11] and that the case where $n = m$ has not been derived for an EQ transition. Consequently, we use the definition of the radial eigenfunctions (III.20) and of the multipole radial matrix elements (III.25) to calculate this case. Also the equations (III.27) and (III.29) are valid for the bound-free radial integrals, by replacing $N_{n,l}$ by $C_{x,l}$ with $x = -i/n \in \mathbb{R}^+$.

D. Method and results

To calculate the 2ED and 2EQ vacuum decay profiles $\phi^{(2)}_{2ED,0}(y)$ and $\phi^{(2)}_{2EQ,0}(y)$ given by the equations (III.15) and (III.18), one needs to calculate the two contributions arising from the bound-bound and from the bound-free radial integrals to the summation over the virtual intermediate states given by the equation (III.19) when calculating $M^{eg}_{2ED}(y)$ and $M^{eg}_{2EQ}(y)$ given by the equations (III.14) and (III.17). Moreover, the calculation of $M^{eg}_{2ED}(y)$ and $M^{eg}_{2EQ}(y)$ involves the function $f_n(y)$ defined at the equations (III.12) and (III.13) as well as the bound-bound and bound-free radial integrals given by the equations (III.27) for an ED transition and given by the equations (III.29) for an EQ transition. Then, the integrated rates can be calculated via the integration over half of the spectrum of the decay profiles [Eq. (III.9)].

To compute the profiles, we use the *mpmath* Python library [12] for the confluent hypergeometric function ${}_1F_1(a; b; z)$ and for the hypergeometric function ${}_2F_1(a, b; c; z)$, and we use the *integrate.quad* function of the *SciPy* Python library [13] to integrate. In addition, the discrete summation over the principal quantum number of the virtual intermediate states [Eq. (III.19)] is truncated at the first 200 terms [4]. The computed data for the 2ED and 2EQ transitions between the states $2s \to 1s$ and between the states $5s \to 3s$ are given in Table III.1 and the corresponding profiles are sketched in Figure III.1.

The relative difference between our computed values of $\phi^{(2)}_{2ED,0}(y = 0.5)$ for the transitions $n_e s \to 1s$ with n_e ranging from 1 to 10 and those in Ref. [4] is less than 0.02%. Also, the relative difference is less than 0.01% between our computed values of $\Gamma^{(2)}_{2ED,0}$ and $\Gamma^{(2)}_{2EQ,0}$ for the $2s \to 1s$ transition and those in Ref. [3]. Furthermore, as there is only one 2EQ transition rate datum in vacuum, we checked that we can find the EQ transition rate value[4] for $n_e d \to n_g s$ single-photon transitions with a relative error less than 0.1% [14]. Note that our Python script and the data, for n_g ranging from 1 to 9 and for n_e ranging from $n_g + 1$ to 10, are available upon request.

Transition	$n_e s \to n_g s$	ΔE_{eg} [eV]	ω_{eg} [rad/s]	λ_{eg} [μm]	$\Gamma^{(2)}_{2MO,0}$ [s^{-1}]	$\phi^{(2)}_{2MO,0}(y = 0.5)$ [s^{-1}]
2ED	$2s \to 1s$	10.2	1.55×10^{16}	0.122	8.23	21.3
2ED	$5s \to 3s$	0.968	1.47×10^{15}	1.28	1.18×10^{-2}	3.24×10^{-2}
2EQ	$2s \to 1s$	10.2	1.55×10^{16}	0.122	4.91×10^{-12}	2.40×10^{-11}
2EQ	$5s \to 3s$	0.968	1.47×10^{15}	1.28	1.43×10^{-15}	5.96×10^{-15}

TABLE III.1. Computed data for 2ED and 2EQ transitions between the states $2s \to 1s$ and $5s \to 3s$, with $\Delta E_{eg} = \hbar \omega_{eg} = hc/\lambda_{eg}$.

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[3] There are several typographical errors in the formula provided in the reference [5].

[4] For an $n_e d \to n_g s$ transition, we can show that $\Gamma^{(1)}_{EQ,0} = \frac{\omega_{eg}^5 \alpha a_0}{75 c^4} \langle R_{n_g,0}|r^2|R_{n_e,2}\rangle$.
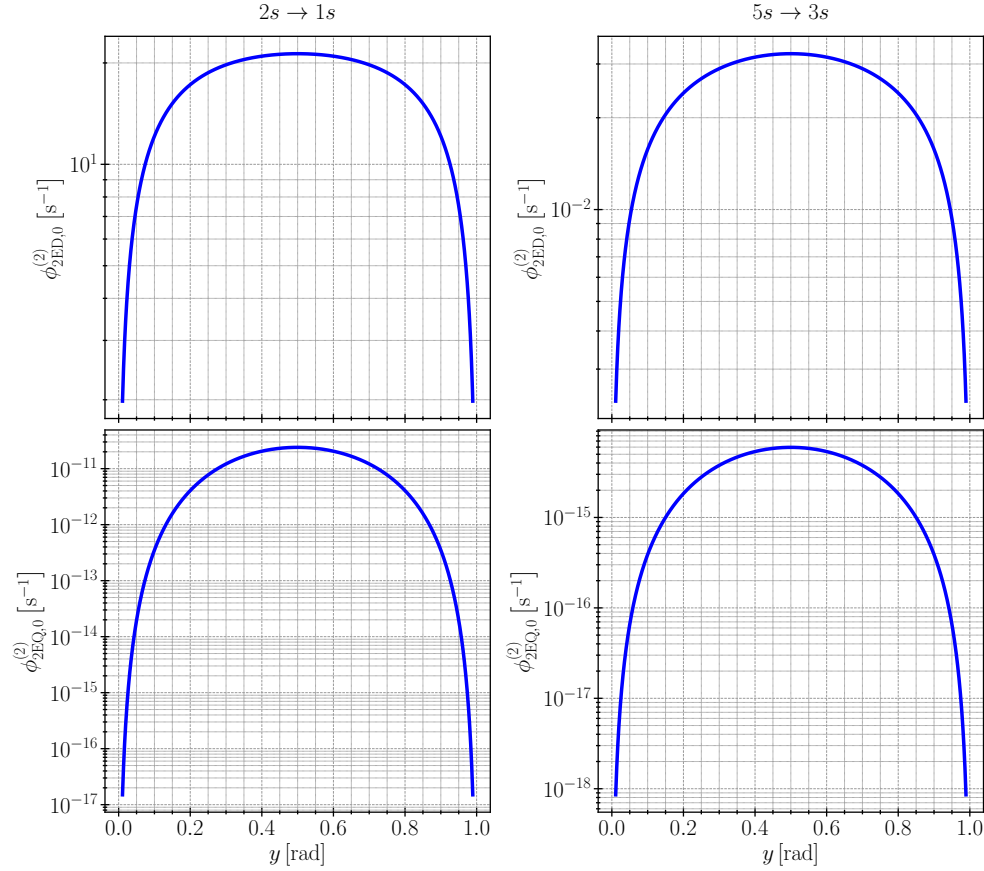
FIG. III.1. Profiles for 2ED (top) and 2EQ (bottom) transitions between the states $2s \to 1s$ (left) and $5s \to 3s$ (right).

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IV. GRAPHENE OPTICAL RESPONSE

The optical response of graphene is characterized by its two-dimensional surface conductivity that is given, as in Ref. [1] in their study of strong multipolar transition enhancement with graphene nanoislands, by two contributions coming from the intraband and interband electronic transitions [2, 3]:

$$\sigma = \sigma_{\text{intra}} + \sigma_{\text{inter}}, \tag{IV.1a}$$

$$\sigma_{\text{intra}} = \frac{2ie^2 k_B T}{\pi \hbar^2 (\omega + i/\tau)} \ln \left[2 \cosh \left(\frac{E_F}{2k_B T} \right) \right], \tag{IV.1b}$$

$$\sigma_{\text{inter}} = \frac{e^2}{4\hbar} \left[\frac{1}{2} + \frac{1}{\pi} \arctan \left(\frac{\hbar\omega - 2E_F}{2k_B T} \right) \right.$$
$$\left. - \frac{i}{2\pi} \ln \left(\frac{(\hbar\omega + 2E_F)^2}{(\hbar\omega - 2E_F)^2 + (2k_B T)^2} \right) \right], \tag{IV.1c}$$

where e represents the electron charge, k_B is the Boltzmann constant, $T = 300$ K denotes the temperature, and E_F stands for the Fermi energy, i.e., the doping level of graphene. Moreover, the scattering lifetime of electrons in graphene is given by $\tau = \mu E_F / e v_F^2$, with $\mu \approx 10^4$ cm^2 V^{-1}s^{-1} the impurity-limited DC conductivity and $v_F = 10^6$ m/s the graphene Fermi velocity [4, 5]. Fig. IV.1 shows the graphene permittivity as a function of its Fermi energy.
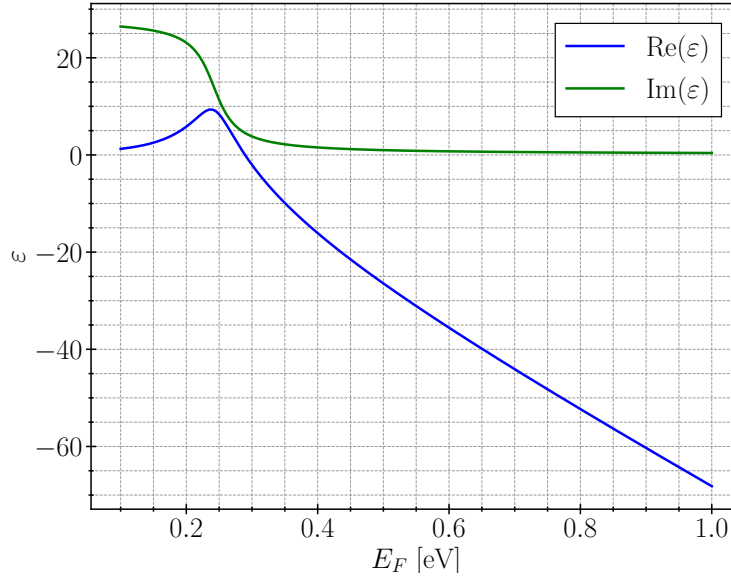

FIG. IV.1. Real and imaginary part of the graphene permittivity as a function of its Fermi energy for an effective thickness of 0.335 nm [6] and a frequency $\hbar\omega = \hbar\omega_{eg}/2 = 0.48$ eV. Below $E_F = 0.29$ eV, graphene assumes a dielectric behavior. The imaginary part of the dielectric constant increases when the Fermi energy decreases and approaches half of the photon energy ($\hbar\omega = 2E_F$) due to interband transitions [7].

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