Short-time emission of higher-angular-momentum photons by atomic transitions

Meng Lok Lei and Vincent Debierre

Max Planck Institute for Nuclear Physics, Saupfercheckweg 1, 69117 Heidelberg, Germany

E-mail: vincent.debierre@mpi-hd.mpg.de

Received 30 July 2020, revised 2 November 2020
Accepted for publication 27 November 2020
Published 4 January 2021

Abstract

The short-time regime of spontaneous light emission by few-electron ions is examined in detail, with a specific emphasis on the angular momentum of the emitted light. It is found that, in general, photons carrying a higher angular momentum are emitted with important probabilities, at short times, in transitions that are not of the electric dipole type. The probability of emission of such photons is found to be parametrically non-negligible in this time regime, and even numerically dominant for some cases. It is also found that, in all time regimes, the emission of electric $2^{n+1}$-pole fields is typically numerically dominant over the emission of magnetic $2^n$-pole fields by many orders of magnitude. These results refine and deepen our understanding of the emission of angular momentum-carrying light by simple atomic systems.

Keywords: spontaneous emission, short-time regime, photon angular momentum, electromagnetic multipoles

(Some figures may appear in colour only in the online journal)

1. Introduction

Recent decades have seen increased interest in the orbital angular momentum (OAM) of light [1–4], with many different points of emphasis, including the topological properties of light carrying such angular momentum [5–7], conversion from spin to orbital angular momenta [8, 9], the relation of angular momenta to the symmetries of relativistic spacetime [10, 11], generation of twisted electromagnetic beams [12, 13] including at very high frequency [14], propagation of twisted light in media [15–17], sorting of light according to OAM [18, 19], and corresponding applications in telecommunications [20, 21] and quantum information [22, 23]. Others have examined the interaction of twisted light with atomic systems [24–29]. In this work, we reverse the latter situation, and study in detail the angular momentum properties of light emitted by simple atomic systems through the process of spontaneous emission, and exhibit non-trivial results in the regime of emission that precedes the establishment of Fermi’s golden rule. This regime could be accessed experimentally with the help of the stimulated Raman adiabatic passage (STIRAP) technique, as discussed in reference [30]. Through dephasing measurements, this process can indeed ‘freeze’ the dynamics in the short-time regime [31].

In a recent work [30], one of us show (with co-workers) that, for atomic electronic transitions that are not of the electric-dipole ($E1$) type, a strong enhancement of the decay with respect to the golden rule prediction is to be expected up to times that verify $\omega_f t \gg 1$ (a condition which is necessary to ensure the validity of the two-level and rotating-wave approximations made here), with $\omega_f$ the resonant frequency of the transition. In the present work, we highlight, and elaborate on a result that we had partially derived in passing but not focused upon. Namely, for non-$E1$ transitions involving...
no s states, in the time-regime described just above, photons of different angular momenta are emitted with intensities that only differ through non-trivial numerical pre-factors. This is in stark contrast with the usual formulation of the selection rules of atomic physics, which, in their oft-used, approximated version, state that only photons with an angular momentum J that satisfies $J = |l_e - l_g|$ can be emitted for electric transitions, and also $J = |l_e - l_g| + 1$ if $J = |l_e - l_g|$ corresponds to a magnetic transition. Here $l_e$ and $l_g$ are the OAM of the excited (with quantum numbers $n_e$, $l_e$ and $m_e$) and ground states (with quantum numbers $n_g$, $l_g$ and $m_g$) considered. In the specific case where $l_e = l_g$, these approximate selection rules are amended to $J = 1, 2$, where $J = 1$ corresponds to the magnetic dipole channel and $J = 2$ to the electric quadrupole channel, typically considered to have comparable decay rates [32, 33]. As can be anticipated from the rules of addition of angular momenta, and as was confirmed by the work of Moses [34], the exact numbers of different angular momenta are emitted with intensities that all longertimes, the emission of electric 2-pole fields by many orders of magnitude. For non-E1 transitions, there exists a realistically accessible short-time regime in which the emission rates of photons of all allowed momenta have the same parametric dependence on the characteristic frequencies of the system, that is, the resonant transition frequency, the cutoff frequency of the atom–field coupling, and the inverse of the measurement time. However, dramatic differences in numerical pre-factors mean that these emission rates are typically not commensurable. The angular momentum of photons emitted during spontaneous emission could be accessed experimentally by filtering the emitted light according to its OAM, for instance as done in references [18, 19, 35].

The rest of the manuscript is organised as follows. In section 2, the basic equations of the dynamics of atom–light interaction are presented in the two-level approximation. In section 3, the expressions for the rates of emission of photons of specific angular momenta are derived, both in Fermi’s golden rule regime and in the short-time regime that precedes it. Numerical results for specific transitions and ions are presented in section 4, and conclusions are drawn in section 5.

2. Spontaneous emission in the two-level approximation

We consider a two-level atom in free space, consisting of a ground state $|g\rangle$ and an excited state $|e\rangle$ separated by the Bohr energy $\hbar \omega_0$, and prepared in $|e\rangle$ at $t = 0$. The state of the electromagnetic field at $t = 0$ is the vacuum state $|0\rangle$. In what follows, we monitor the emission rates of photons carrying all allowed angular momenta $J$. In the framework of the rotating wave approximation, the state of the system at time $t$ reads

$$|\psi(t)\rangle = c_e(t) e^{-i\omega_0 t}\langle e| 0\rangle + \sum_{J,M} \int d\omega c_{J,M}\langle \omega | e, t\rangle$$

(1)

The single-photon state $|J,M,\omega\rangle$ is labelled by its angular momentum $J$, its angular momentum projection number $M$, its helicity $\lambda$ and its frequency $\omega$, with the corresponding wave function a (vector) spherical wave [34]. The orthogonality relation is $\langle J,M,\omega| J',M',\omega'\rangle = \delta_{JJ'} \delta_{MM'} \delta_{\lambda\lambda'} \delta(\omega - \omega')$. Schrödinger’s equations of motion for the probability amplitudes read [36]

$$\dot{c}_e(t) = \frac{i}{\hbar} \sum_{J,M} \int d\omega G_{J,M}(\omega) c_{J,M}(\omega, t) e^{-i(\omega - \omega_0)t}$$

(2a)

$$\dot{c}_{J,M}(\omega, t) = -\frac{i}{\hbar} G_{J,M}(\omega) c_e(t) e^{i(\omega - \omega_0)t}$$

(2b)

where the atom–field couplings are given by

$$G_{J,M}(\omega) = \langle J,M,| H| e, 0\rangle$$

(3)

with the interaction Hamiltonian

$$\hat{H}_1 = \frac{e}{m_e} \hat{A} (\hat{x}, t = 0) \cdot \hat{p}$$

(4)

The matrix elements (3) have been calculated exactly in non-relativistic hydrogen-like atoms (the relativistic corrections, which we do not consider here, bring contributions of relative order $(Z\alpha)^2$ [37]). The calculation was initiated by Moses [34] and completed by Seke [38] (see appendix A for the explicit expressions of the matrix elements). In the following, we will examine the emission rates

$$\Gamma_J(t) \equiv \frac{1}{\hbar} \sum_{M} \int d\omega |c_{J,M}(\omega, t)|^2$$

(5)

of photons of specific angular momenta $J$. Note that these rates are in general time-dependent [30], which might be counter-intuitive. As is well known, in Fermi’s golden rule regime, the emissions rates are constant. Emission rates, both in this golden rule regime, and in the short-time regime that precedes it, will now be investigated in more detail.

3. Photon emission rates

3.1. General expressions

We write the atomic states as $|g\rangle = |n_e, l_e, m_e\rangle$ and $|e\rangle = |n_e, l_e, m_e\rangle$ where each atomic state is described by three discrete quantum numbers $n_e$, $l_e$ and $m_e$ which are respectively, as indicated above, the principal, angular momentum and magnetic quantum numbers. It is well-known that the transition which we consider here can only
cause the emission of photons with angular momenta $J$ that verify $|l_e - l_g| \leq J \leq l_e + l_g$, and that $J = |l_e - l_g|$, and also $J = |l_e - l_g| + 1$ if $J = |l_e - l_g|$ corresponds to a magnetic transition, is the dominant emission channel(s), as expected by following the approximate selection rules. We will show that there is a certain time regime for which emission of photons of all allowed angular momenta takes place at parametrically similar rates, with the only difference a non-trivial numerical pre-factor. For that purpose, we will use time-dependent perturbation theory, which yields [30, 39] the emission rate [see equation (5)] of photons with angular momentum $J$ as

$$\Gamma_j(t) = 2\pi \int_0^{+\infty} d\omega F_j(\omega - \omega_0) R_j(\omega).$$

(6)

The spectral profile $F_j$ of the atom at time $t$ is given by

$$F_j(\omega - \omega_0) = \frac{I}{2\pi} \sin^2 \left( \frac{\omega - \omega_0}{2} \right).$$

(7)

The form factor for the coupling of the atom to photons of angular momentum $J$ is given by [30, 34, 38] (see also appendix A)

$$R_j(\omega) = \sum_{\mu>\nu=0}^{N_J} \frac{D_J}{\omega_0^{\mu+2\nu}} \frac{\omega_0^{\mu+2\nu}}{1 + \left( \frac{\omega}{\omega_0} \right)^2},$$

(8)

where $\eta_J = 1 + 2J$ for magnetic transitions, and $\eta_J = -1 + 2J$ for electric transitions; $\mu = 2(n_g + n_e - 1)$; the $D_J$ are dimensionless constants involving the Clebsch–Gordan coefficients of the transition under consideration; and $\omega_X \gg \omega_0$ is the non-relativistic cutoff frequency

$$\omega_X = \frac{1}{n_e + n_g} \frac{c}{a_0} Z \alpha,$$

(9)

$$= \left( \frac{2}{\alpha} \right) \left( \frac{n_g n_e}{n_e - n_g} \right) \omega_0,$$

with $a_0$ the Bohr radius and $Z$ the atomic number, and $\alpha \approx 1/137$ the fine-structure constant of electrodynamics. Finally, the index at which the sum is terminated is $N_J = 2(n_g + n_e) - 4 - J - l_e - l_g - \epsilon$ with $\epsilon = 0$ for electric transitions and $\epsilon = 1$ for magnetic transitions. In the present work we focus on transitions for which neither $l_e$ nor $l_g$ is equal to zero, namely, in which no $s$ states are involved. In this case, it is easily seen that several values of $J$ are always allowed.

For a given pair of initial (excited) and final (ground) states, both electric and magnetic transitions are generally allowed. As explained in the appendix A, for given initial and final states, in general, several photon angular momenta $J$ are allowed. If $l_e + l_g + J$ is even, then the corresponding photon is said to be emitted through the electric channel, while, if $l_e + l_g + J$ is odd, it is emitted through the magnetic channel. The transition matrix elements are calculated from the vector potential $\mathbf{A}(\mathbf{k}, t = 0)$ at the position of the electron and, for electric transitions, only the poloidal part of the vector potential contributes, while, for magnetic transitions, only the toroidal part contributes (see appendix A).

### Table 1. Parameters of the atom–field coupling form factor given by equation (8) for the transitions $4F – 2P$, $5F – 4F$, and $3P – 2P$.

| Transitions | $4F – 2P$ | $5F – 4F$ | $3P – 2P$ |
|-------------|-----------|-----------|-----------|
| $J$         | 2 3 4     | 2 3 4 5   | 6 1 2     |
| $\eta$      | 3 7 7 3   | 2 3 7 11  | 11 3 3    |
| $N_J$       | 2 0 0 6   | 2 4 4 2   | 2 2 2     |
| $\mu$       | 10 16     | 10 16 8   | 16 44 4   |
| $Z \times \omega_X/\omega_0$ | 1096.3 | 5481.4 | 1644.4 |

The parameters $J$, $\eta$, $N_J$, $\mu$ and $\omega_X$ corresponding to the transitions $4F – 2P$, $5F – 4F$, and $3P – 2P$, to be investigated in detail in section 4, are given in table 1. These transitions are normally considered electric quadrupole, magnetic dipole and magnetic dipole transitions, respectively, because the $(J = 2, \epsilon = 0)$, $(J = 1, \epsilon = 1)$, and $(J = 1, \epsilon = 1)$ channels, respectively, correspond to the lowest allowed $J$ in each case. However, they are accompanied by the emission of photons of higher $J$ (see table 1). As we will now see, this is not in contradiction with the approximate selection rule $J = |l_e - l_g|$ (or $J = 1$ and $J = 2$ in the case where $l_e = l_g$), except potentially in the short-time regime of emission.

### 3.2. Photon emission in Fermi’s regime

For sufficiently long times, it is known that it is permissible to approximate $F_i(\omega - \omega_0) \rightarrow \delta(\omega - \omega_0)$, so that

$$\Gamma_j(t) = 2\pi \sum_{\nu=0}^{N_J} \frac{D_J}{\omega_0^{\nu+2\nu}} \frac{\omega_0^{\nu+2\nu}}{1 + \left( \frac{\omega}{\omega_0} \right)^2},$$

(10)

where we used the hierarchy $\omega_0/\omega_X \ll 1$ in the last step. That step is valid unless, of course, $D_J$ vanishes, which happens for instance for electric dipole transitions ($\epsilon = 0, J = 1$) between levels sharing the same principal quantum number [30, 38]. However, we do not focus on this special case here. Explicit results for the Fermi decay rates of various transitions are given in tables 2 and 3, and compared with those compiled in the NIST Atomic Spectra Database [40]. We chose, in all cases, to implement the single-electron results in a simple effective nuclear charge framework, for which the valence electron is screened by the core electrons, yielding $Z_{\text{eff}} = Z - (N_e - 1)$, with $N_e$ the number of electrons present in the ion. The good agreement with the NIST database confirms the approximate validity of the single-electron approximation for two- and three-electron systems (such as Be$^{2+}$ or F$^{3+}$). For systems with more electrons, such as Ti$^{11+}$ and Ca$^+$, the results obtained...
Table 2. Decay rates in the Fermi regime for some transitions, as calculated in the present work, and given in the NIST database [40].

| Ion  | Transition | Calc. rate \( (s^{-1}) \) | NIST rate \( (s^{-1}) \) |
|------|------------|---------------------------|---------------------------|
| H    | 2P–1S      | \( 6.25 \times 10^8 \)    | \( 6.26 \times 10^8 \)    |
| H    | 3D–1S      | \( 5.93 \times 10^7 \)    | \( 5.94 \times 10^7 \)    |
| Ca\(^+\) | 3D–4S   | \( 1.31 \times 10^5 \)    | \( 1.3 \times 10^6 \)    |

Table 3. Decay rates in the Fermi regime for the transitions 4F–2P, 5F–4F and 3P–2P, as calculated in the present work, and given in the NIST database [40]. Discrepancies by a factor of 10\(^5\) for the 4F–2P transitions are almost certainly due to a mistake in the NIST database: in reference [44], from which the NIST values are taken, the quadrupole oscillator strengths are given in units of 10\(^{-2}\), which was probably overlooked. Discrepancies by a factor of 10 for the 3P–2P transitions are probably due to a systematic mistake in the NIST database, as we also found a result almost exactly ten times smaller than the database one for He and for Li\(^+\).

Ion  | Transition | Calc. rate \( (s^{-1}) \) | NIST rate \( (s^{-1}) \) |
|------|------------|---------------------------|---------------------------|
| Be\(^{2+}\) | 4F–2P   | \( 4.50 \times 10^4 \)    | \( 4.51 \times 10^4 \)    |
| B\(^{3+}\)  | 4F–2P   | \( 2.53 \times 10^3 \)    | \( 2.53 \times 10^3 \)    |
| O\(^{9+}\)  | 4F–2P   | \( 7.25 \times 10^5 \)    | \( 7.28 \times 10^5 \)    |
| P\(^{2+}\)  | 4F–2P   | \( 5.96 \times 10^5 \)    | \( 7.3 \times 10^6 \)    |
| Ti\(^{11+}\) | 5F–4F | \( 1.90 \times 10^1 \)    | \( 4.08 \times 10^1 \)    |
| Be\(^{2+}\) | 3P–2P   | \( 1.74 \times 10^3 \)    | \( 1.71 \times 10^4 \)    |
| B\(^{3+}\)  | 3P–2P   | \( 9.78 \times 10^3 \)    | \( 9.65 \times 10^3 \)    |
| F\(^{2+}\)  | 3P–2P   | \( 2.81 \times 10^3 \)    | \( 1.5 \times 10^4 \)    |

are within one order of magnitude of the literature data. A more thorough treatment of screening would surely improve our results, but, while effective charges for neutral atoms were investigated in detail in reference [41], we are not aware of any detailed study of effective charges for ions in the literature. The simpler Slater rules [42], improve only moderately, at best, the agreement of our results with the NIST database, therefore, we opted not to pursue the Slater approach. Ultimately, of course, many-electron codes such as Grasp2K [43] yield the most reliable results for this type of problem, but our simpler approach highlights trends and patterns that could then be checked with such methods.

Now, we focus on transitions for which several \( J \) are allowed. In the Fermi regime, we can calculate the ratio of emitted photons of two different angular momenta \( J \) and \( J' \) as

\[
\frac{\Gamma_J(t)}{\Gamma_{J'}(t)} \approx \frac{D_{J0}}{D_{J'0}} \left( \frac{\omega_0}{\omega_X} \right)^{\eta_J - \eta_{J'}}.
\] (11)

Since the cutoff frequency of the transition is much larger than the resonant frequency: \( \omega_0/\omega_X \ll 1 \) [see equation (9)], it is clear from equation (11) that the more intense emission of the two should be expected to be that of the photons with the lower \( \eta_J \). If the lowest \( J \) allowed by the matrix elements, \( J_{\min} \), is such that \( l + l' + J_{\min} \) is even, then the lowest \( \eta_J \) allowed is \(-1 + 2J_{\min}\), which means that the electric channel of lowest allowed multipolar order dominates in the Fermi regime (also see references [32, 33]). If \( l + l' + J_{\min} \) is odd, then both \( J_{\min} \) and \( J_{\max} + 1 \) correspond to the same \( \eta = 1 + 2J_{\min} \), which means that the magnetic channel of the lowest allowed multipolar order, and the electric channel of the next multipolar order, are expected to dominate in the Fermi regime.

We find, however, that the non trivial pre-factors \( D_{J0} \) are such that the electric 2\(^{J+1}\)-pole channels dominate the emission over the magnetic 2\(^J\)-pole channels by many orders of magnitude (here \( n = 1 \) stands for dipole, \( n = 2 \) for quadrupole, \( n = 3 \) for octupole, etc.). For instance, for the 5F–4F transition in Ti\(^{11+}\), the calculated magnetic dipole decay rate is 26 orders of magnitude smaller than the electric quadrupole decay rate given in table 3, and for the 3P–2P transition in Be\(^{2+}\), it is smaller by 13 orders of magnitude.

Despite these hierarchies, we emphasise that all allowed \( J \) contribute to the decay/transition dynamics. As we will now see, photons with all allowed angular momenta are potentially important contributors to the dynamics at short times.

3.3. Photon emission before the onset of Fermi’s regime

As we have previously found (See equation (C2) of reference [30]), there is a time regime \( 1/\omega_0 \ll t \ll 1/(2\pi\omega_0) \left( \omega_X/\omega_0 \right)^{\eta_J-1} \) for which all terms in the sum over \( r \) in (8) have a contribution to the modified emission rate that has an identical parametrical dependence on the characteristic frequencies \( \omega_0, \omega_X \) and \( 1/t \) of the system. For arbitrary \( J \), the photon emission rate is given by

\[
\Gamma_J(t) \approx 2\pi D_{J0} \frac{\omega_0}{\omega_X} \left( \frac{1}{2} \sum_{r=0}^{NJ} D_{Jr} \theta \left( \eta_J + 2r - \frac{3}{2} \right) \right) \times B \left( \frac{1 - \eta_J - 2r}{2} + \mu, -\frac{1 - \eta_J - 2r}{2} \right),
\] (12)

with \( \theta \) the Heaviside step function. This expression is easily seen to reduce to the golden rule value (10) for sufficiently large times \( 1/\omega_0 \ll 1/(2\pi\omega_0) \left( \omega_X/\omega_0 \right)^{\eta_J-1} \ll t \). For shorter times, on the other hand, two different cases appear: for electric dipole fields, \( \eta_J = 1 \), and the condition \( \omega_0 \gg 1 \) guarantees that the first (Fermi) term on the rhs of (12) dominates over the sum over \( r \) at all realistic times. For all other multipolar orders for electric fields, and for all multipolar orders of magnetic fields, though, there is a time regime at which the sum over \( r \) dominates. Namely, in this regime, the emission rate of photons of a specific angular momentum \( J \) is

\[
\Gamma_J(t) \approx \frac{1}{2} \sum_{r=0}^{NJ} D_{Jr} \theta \left( \eta_J + 2r - \frac{3}{2} \right) \times B \left( \frac{1 - \eta_J - 2r}{2} + \mu, -\frac{1 - \eta_J - 2r}{2} \right).
\] (13)

We write \( \eta_{\min} \) the smallest value of \( \eta \) allowed in the \( |e\rangle \rightarrow |g\rangle \) transition, and we focus on transitions for which the electric dipole channel does not contribute: \( \eta_{\min} \neq 1 \). In this case, for all allowed \( J \), equation (13) is valid in a certain time regime. More specifically, for \( 1/\omega_0 \ll t \ll 1/(2\pi\omega_0) \left( \omega_X/\omega_0 \right)^{\eta_{\min}-1} \), the ratio of photon emission rates between two arbitrary allowed angular momenta is

\[
\frac{\Gamma_J(t)}{\Gamma_{J'}(t)} \approx \frac{\sum_{r=0}^{NJ} D_{Jr} B \left( \frac{1 - \eta_J - 2r}{2} + \mu, -\frac{1 - \eta_J - 2r}{2} \right)}{\sum_{r=0}^{NJ} D_{J'r} B \left( \frac{1 - \eta_{J'} - 2r}{2} + \mu, -\frac{1 - \eta_{J'} - 2r}{2} \right)}.
\] (14)
numbers 2. The rates were obtained by averaging over initial magnetic quantum numbers \( m_\ell \), and summing over final magnetic quantum numbers \( m_\ell \). In the lower table, we give the numerical value of the end of the short-time regime [see paragraph before equation (12)].

Here we have sums starting at

\[
\Gamma_{\text{tot}} \equiv \max \left\{ \frac{3}{4} - \frac{\eta_{\min}}{2} \right\},
\]

\[
\Gamma_{\text{tot}}^{P} \equiv \max \left\{ \frac{3}{4} - \frac{\eta_{\min}}{2} \right\},
\]

owing to the Heaviside step function in equation (13). At least parametrically, the ratio (14) is of order unity, as it does not feature the characteristic frequencies of the system, namely, the atomic resonant frequency \( \omega_0 \), the cutoff frequency \( \omega_K \), and the inverse observation time \( 1/\Gamma \). Although, as soon as \( t \sim 1/(2\pi\omega_0) (\omega_K/\omega_0)^{\text{unm}-1} \), photons with \( \eta_{\min} \) start dominating (at least parametrically) the emission, before this Fermi regime takes over, it is therefore seen through equation (14) that there exists a regime in which all allowed angular momenta contribute equally to the decay at the parametric level, with the only difference determined by non-trivial numerical pre-factors. In the next section, we turn to the calculation of these pre-factors, in order to describe emission at short times in terms of the photon angular momentum, in more detail.

### 4. Detailed study of a few specific transitions

Here we inspect three transitions in detail: 4F–2P, 5F–4F, and 3P–2P. The corresponding parameters were given in table 1. Tables 4, 5, and 6 show the branching ratios of emission rates \( \Gamma_j \) of photons of different angular momenta \( J \), in the short-time regime of emission, defined by \( t \ll 1/(2\pi\omega_0) (\omega_K/\omega_0)^{\text{unm}-1} \). Numerical values for the upper limit of this time regime are also given in tables 4, 5, and 6. The results indicated are obtained by averaging over initial magnetic quantum numbers \( m_\ell \), and summing over final magnetic quantum numbers \( m_\ell \) [45]. The branching ratios can be computed using equation (14), with the expressions for the \( D \) coefficients obtained through the expressions for the matrix elements given in appendix A. Our results are illustrated by figure 1, where the evolution of emission rates for photons of all allowed angular momenta is represented, highlighting the transition between the short-time and the Fermi regimes.

For the 4F–2P transition (table 4), it appears that the emission rate of the magnetic octupole channel is entirely negligible even in the short-time regime. On the other hand, the emission rate of the electric hexadecapole channel is not always negligible.

| Ion | \( \Gamma_{\text{tot}} \) | \( \text{Table 4.} \) |
|-----|-----------------|------------------|
| Be\(^{2+}\) | 5.02 \times 10^{-10} | \( \text{Table 6.} \) |
| B\(^{1+}\) | 2.12 \times 10^{-10} | \( \text{Table 5.} \) |
| O\(^{6+}\) | 3.95 \times 10^{-11} |
| P\(^{8+}\) | 3.95 \times 10^{-11} |
Figure 1. Evolution of the photon emission rates for all allowed decay channels as a function of time, for the (a) $4^2F - 2^2P$ ($\omega_0 = 3.49 \times 10^{16} \text{ s}^{-1}$), (b) $5^2F - 4^2F$ ($\omega_0 = 6.70 \times 10^{16} \text{ s}^{-1}$) and (c) $3^2P - 2^2P$ ($\omega_0 = 2.58 \times 10^{16} \text{ s}^{-1}$) transitions. En and Mn refer to the electric and magnetic multipolar channels, respectively. The emission rates are seen to decrease until the establishment of the Fermi regime, in which they become constant.

Figure 2. Evolution of the average photon angular momentum $\langle J \rangle$ of the photon as a function of time, for the (a) $4^2F - 2^2P$ ($\omega_0 = 3.49 \times 10^{16} \text{ s}^{-1}$), (b) $5^2F - 4^2F$ ($\omega_0 = 6.70 \times 10^{16} \text{ s}^{-1}$) and (c) $3^2P - 2^2P$ ($\omega_0 = 2.58 \times 10^{16} \text{ s}^{-1}$) transitions. Notable deviations from the expected result can be noted, which survive until the establishment of the Fermi regime.

The obtained curves illustrate the non-negligible presence, before the establishment of the Fermi regime, of photons of angular momenta different from that of the dominant emission channel. In particular for the $4^2F - 2^2P$ and $5^2F - 4^2F$ transitions, which are both dominated by the electric quadrupole
(\(J = 2\)) in the Fermi regime, large deviations from \(\langle J \rangle(t) = 2\) are observed in the short-time regime, which represents a striking illustration of our results.

It can be envisaged to access the short-time regimes that interest us experimentally, for instance, with the help of the STIRAP technique mentioned at the beginning of the present work. Through dephasing measurements, this process can ‘freeze’ the dynamics in the short-time regime \([31]\). In a different approach, the Zeno dynamics of a driven two-level transition was recently observed \([46]\). Then, the OAM of the emitted light could be analyzed, for instance with techniques discussed in references \([18, 19, 35]\).

\section{Conclusion}

We have studied spontaneous emission by few-electron ions at short times with a focus on the angular momentum of the emitted photons. Our results show the emergence of a pattern whereby, for a given atomic transition, the pre-factors corresponding to the electric \(2^n+1\)-pole emission channels are typically numerically dominant over those of the emission of magnetic \(2^n\)-pole channels by many orders of magnitude. This is true both in the short-time regime of emission \(t \ll 1/(2\pi\omega_0)(\omega_0/\omega_0)^\text{num-1}\), where the photon emission rates are given by equation \((13)\) (only valid for non-\(E1\) transitions), and in the Fermi regime, where they are given by equation \((10)\). Indeed, in the short-time regime, for non-\(E1\) transitions, photons of all allowed angular momenta are emitted with rates that have an identical parametric dependence, and, in the Fermi regime, we established through equation \((11)\) that the emission rates for electric \(2^n+1\)-pole and magnetic \(2^n\)-pole channels have the same parametric dependence on the characteristic frequencies of the system. However, in both cases, non-trivial numerical pre-factors cause the electric \(2^n+1\)-pole channels to dominate the emission process over the magnetic \(2^n\)-pole channels by many orders of magnitude. These results complete, refine, and, to some extent, contradict the standard paradigm in which electric \(2^n+1\)-pole and magnetic \(2^n\)-pole couplings are considered to be mutually commensurate \([32, 33]\).

Moreover, we have also established that, for some transitions, electric \(2^n+1\)-pole channels can compete with electric \(2^n\)-pole channels in the spontaneous emission process at short times, as evidenced for instance in the case of the \(4F-2P\) and \(5F-4F\) transitions (see tables \(4\) and \(6\), as well as figure \(2\)). This causes significant deviations, in the short-time regime, from the average value of the angular momentum of emitted photons that would be expected from the approximate selection rules.

Our results motivate a re-examination of the relative strengths of electric \(2^n+1\)-pole and magnetic \(2^n\)-pole channels in atomic transitions. Given the time-symmetry between emission and absorption, our work also motivates further study into the problem of the interaction between OAM-carrying light and simple atomic systems, with potential relevance for quantum information applications. It would also be relevant to try, in a more detailed way, to extend this study to many-electron systems, for which non-\(E1\) transitions are more easily accessible \([30, 47]\). In this case, the \(D_{J\ell}\) coefficients in the form factor \((8)\) have to be computed numerically.

\section*{Acknowledgments}

We thank Caroline Champenois for helpful discussions and advice on the scientific literature about radiative atomic transitions. We thank Emmanuel Lassalle and Zoltán Harman for their suggestions on the manuscript.

\section*{Appendix A. Transition matrix elements for hydrogen-like ions}

The explicit form of the transition matrix elements \((3)\) is given in reference \([38]\). We recall that, for given excited and ground states with respective angular momenta \(l_e\) and \(l_g\), values of the photon angular momentum \(J\) in the range \(|l_e - l_g| < J < l_e + l_g + 1\) are allowed. Further, the allowed transitions can be split into electric and magnetic transitions. The significance of this classification is understood as follows. The vector potential used for the computation of the matrix elements is taken in the Coulomb gauge: \(\nabla \cdot \mathbf{A} = 0\). As a result, it can be decomposed into a toroidal component \(\mathbf{T}\) and a poloidal component \(\mathbf{P}\), according to \(\mathbf{A} = \mathbf{T} + \mathbf{P}\). These components can be expressed as follows:

\begin{align*}
\mathbf{T} &= \nabla \times (r\Phi), \\
\mathbf{P} &= \nabla \times (\nabla \times (r\Phi)) \quad (A1b)
\end{align*}

where \(\Psi\) and \(\Phi\) are scalar fields. It can be understood that the toroidal component corresponds to the part of \(\mathbf{A}\) that generates the magnetic field. Indeed, \(\mathbf{B} = \nabla \times \mathbf{A}\), and it can be checked that \(\nabla \times \mathbf{P} = 0\), so that \(\mathbf{B} = \nabla \times \mathbf{T}\). For the electric field, contributions are expected from both the toroidal and poloidal components of the vector potential, however, Moses has shown \([34]\) that only the poloidal part contributes to the matrix elements.

Let us come to the explicit form of the matrix elements. Electric transitions, for which only the poloidal part of \(\mathbf{A}\) contributes, are only allowed for \(l_e + l_g + J\) even, and the matrix element is given by

\[
G_{J\ell M}(\omega) = \langle g, 1_J M \rangle \langle H | \mathbf{e}, 0 \rangle
\]

\[
= \alpha^2 (\hbar m_e c^3)^{\frac{1}{2}} \frac{1}{n_e + n_g} \lambda \langle (-1)^{J+M} | J M -l_e - l_g \rangle
\]

\[
\times \sqrt{\frac{(J+1) (2l_e + 1) (2l_g + 1)}{(J+1)}} \left( \begin{array}{cc}
J & l_e \\
M & -l_g
\end{array} \right)
\]

\[
\times \left( \begin{array}{cc}
l_e & l_g \\
0 & 0
\end{array} \right) \sqrt{(n_e - l_e - 1)! (n_e + l_e + 1)!}
\]

\[
\times \sqrt{(n_g - l_g - 1)! (n_g + l_g + 1)!} \frac{2^{l_e + l_g}}{n_{l_e}^2 + n_{l_g}^2}
\]
\[
\times \sum_{\mu=0}^{n_e+n_g-w-2} \left\{ [J (J + 1) + \Delta (w + 1)]
\times \left[ (l_e p_{00} + p_{01}) p_1 F_2 - \frac{1}{n_g} p_{00} p_2 F_1 \right]
+ [-J (J + 1) + \Delta (w + 1)]
\times \left[ (l_e p_{00} + p_{01}) q_1 F_2 - \frac{1}{n_g} p_{00} q_2 F_1 \right]\right\}
\times \left( \frac{2}{n_g} \right)^\mu. \quad (A2)
\]

Magnetic transitions, for which only the toroidal part of the vector potential \( A \) contributes, are only allowed for \( l_e + l_g + J \) and, the matrix element is given by

\[
G_{\lambda M\lambda} (\omega) = \langle g, 1_{JM\lambda} | \hat{H} | e, 0 \rangle
= \alpha^2 (\hbar m_e c^3)^\frac{1}{2} K Y^{l+1}(-1)^l m_0^1
\]

\[
K \equiv \left( \frac{n_e n_g}{n_e + n_g} \right) a_0 Z, \quad Q_\nu \equiv \left( \frac{1}{n_e - l_e - 1 + \nu} \right) (l_e + 1 + \nu)! (l_g + 1 + \nu)! (n_g - l_g - 1 - \mu + \nu)! (2 l_g + 1 + \mu + u)!(n_g n_e)^{1/2} \quad (A4b)
\]

The following notations have been used:

\[
w \equiv l_e + l_g, \quad \Delta \equiv l_e - l_g,
\]

\[
u_{\text{min}} \equiv \max \left(0, \mu - n_g + l_g + 1\right), \quad (A4a)
\]

\[
u_{\text{max}} \equiv \min \left(n_e - l_e - 1, \mu\right);
\]

\[
p_{ab} = \sum_{\nu=\nu_{\text{min}}}^{\nu_{\text{max}}} Q_\nu
\]

\[
q_l = \left( \frac{\nu + \mu + l + s}{\nu + \mu + l + s + 1} \right) \left( 1 + K \right)^{-\nu-\mu+1-l};
\]

\[
F_1 \equiv 2 F_1 \left( \frac{1}{2} J - w - \mu + 1 + s, \right)
\times \left( \frac{1}{2} \left( J - w - \mu + s + 1 \right) \right) ; J + \frac{3}{2} - K^2 \right)
\]

where \( ^2F_1 \) indicates the hypergeometric function.

### ORCID iDs

Vincent Debierre  
https://orcid.org/0000-0001-7120-6792

### References

1. Allen L, Beijersbergen M W, Spreeuw R J C and Woerdman J P 1992 Phys. Rev. A 45 8185
2. Allen L, Barnett S M and Padgett M J 2003 Optical Angular Momentum (Boca Raton, FL: CRC Press)
3. Andrews D L and Babiker M 2012 The Angular Momentum of Light (Cambridge: Cambridge University Press)
4. Molina-Terriza G, Torres J P and Torner L 2007 Nat. Phys. 3 305
5. Coullet P, Gil L and Rocca F 1989 Opt. Commun. 73 403
6. Bliokh K Y 2006 Phys. Rev. Lett. 97 043901
7. Bliokh K Y and Nori F 2012 Phys. Rev. A 86 033824
8. Marrucci L, Manzo C and Paparo D 2006 Phys. Rev. Lett. 96 163905
9. Bouchard F, Leon I D, Schulz S A, Upham J, Karimi E and Boyd R W 2014 Appl. Phys. Lett. 105 305
10. Fernandez-Corbaton I, Zambrana-Puyalto X and Molina-Terriza G 2014 J. Opt. Soc. Am. B 31 2136
11. Debierre V 2019 Commun. Theor. Phys. 71 403
12. Nienhuis G 2006 J. Phys. B: At. Mol. Opt. Phys. 39 S529
13. Naidoo D, Roux F S, Dudley A, Litvin I, Piccirillo B, Marrucci L and Forbes A 2016 Nat. Photon. 10 327
14. Chen Y-Y, Li J-X, Hatsagortsyan K Z and Keitel C H 2018 Phys. Rev. Lett. 121 074801
15. Thakur A and Berakdar J 2010 Opt. Express 18 027691
16. Khamed M and Bahrampour A R 2013 Europhys. Lett. 104 25001
17. Roux F S, Wellens T and Shatokhin V N 2015 Phys. Rev. A 92 012326
18. Berkhout G C G, Lavery M P J, Courtial J, Beijersbergen M W and Padgett M J 2010 Phys. Rev. Lett. 105 153601
19. Wen Y, Chreimmos I, Chen Y, Zhu J, Zhang Y and Yu S 2018 Phys. Rev. Lett. 120 193904
20. Yan Y et al 2014 Nat. Commun. 5 4876
21. Xie Z et al 2018 Light Sci. Appl. 7 18001
22. Deng L-P, Wang H and Wang K 2007 J. Opt. Soc. Am. B 24 2517
[23] Farman F, Toffighi S and Bahrampour A 2018 J. Opt. Soc. Am. B 35 2348
[24] Matula O, Hayrapetyan A G, Serbo V G, Surzhykov A and Fritzsche S 2013 J. Phys. B: At. Mol. Opt. Phys. 46 205002
[25] Scholz-Marggraf H M, Fritzsche S, Serbo V G, Afanasev A and Surzhykov A 2014 Phys. Rev. A 90 013425
[26] Rodrigues J D, Marcassa L G and Mendonça J T 2016 J. Phys. B: At. Mol. Opt. Phys. 49 074007
[27] Afanasev A, Carlson C E and Mukherjee A 2014 J. Opt. Soc. Am. B 31 2721
[28] Babiker M, Andrews D L and Lembessis V E 2018 J. Opt. 21 013001
[29] Solyanik-Gorgone M, Afanasev A, Carlson C E, Schmiegelow C T and Schmidt-Kaler F 2019 J. Opt. Soc. Am. B 36 565
[30] Lassalle E, Champenois C, Stout B, Debierre V and Durt T 2018 Phys. Rev. A 97 062122
[31] Kofman A G and Kurizki G 2000 Nature 405 546
[32] Corney A 1977 Atomic and Laser Spectroscopy (Oxford: Oxford University Press)
[33] Sobelman I I 1992 Atomic Spectra and Radiative Transitions 2nd edn (Berlin: Springer)
[34] Moses H E 1973 Phys. Rev. A 8 1710
[35] Pachava S, Dharmavarapu R, Vijayakumar A, Jayakumar S, Manthalkar A, Dixit A, Viswanathan N K, Srinivasan B and Bhattacharya S 2019 Opt. Eng. 58 041205
[36] Debierre V 2015 La fonction d’onde du photon en principe et en pratique PhD Thesis Ecole centrale de Marseille
[37] Grant I P 1974 J. Phys. B: At. Mol. Phys. 7 1458
[38] Seke J 1994 Physica A 203 269
[39] Cohen-Tannoudji C, Dupont-Roc J and Grynberg G 1989 Photons and Atoms: Introduction to Quantum Electrodynamics (New York: Wiley)
[40] Kramida A,Ralchenko Y, Reader J and N. A. Team 2019 NIST atomic spectra database (version 5.7.1)
[41] Guerra M, Amaro P, Santos J P and Indelicato P 2017 At. Data Nucl. Data Tables 117–118 439
[42] Slater J C 1930 Phys. Rev. 36 57
[43] Jönsson P, Gaigalas G, Bieroni J, Fischer C F and Grant I P 2013 Comput. Phys. Commun. 184 2197
[44] Godefroid M and Verhaegen G 1980 J. Phys. B: At. Mol. Phys. 13 3081
[45] Drake G W F (ed) 2006 Springer Handbooks of Atomic, Molecular, and Optical Physics (Berlin: Springer)
[46] Zhang M-C, Wu W, He L-Z, Xie Y, Wu C-W, Li Q and Chen P-X 2018 Chin. Phys. B 27 090305
[47] Sukachev D et al 2016 Phys. Rev. A 94 022512