Statistics of electric-quadrupole lines in atomic spectra

Jean-Christophe Pain\textsuperscript{1}, Franck Gilleron\textsuperscript{1}, Jacques Bauche\textsuperscript{2} and Claire Bauche-Arnoult\textsuperscript{2}

\textsuperscript{1} CEA, DAM, DIF, F-91297 Arpajon, France
\textsuperscript{2} Laboratoire Aimé Cotton, Bâtiment 505, Campus d’Orsay, 91405 Orsay, France

Received 9 March 2012, in final form 17 April 2012
Published 13 June 2012
Online at stacks.iop.org/JPhysB/45/135006

Abstract
In hot plasmas, a temperature of a few tens of eV is sufficient for producing highly stripped ions where multipole transitions become important. At low density, the transitions from tightly bound inner shells lead to electric-quadrupole (E2) lines which are comparable in strength with electric-dipole ones. In this work, we propose analytical formulas for the estimation of the number of E2 lines in a transition array. Such expressions rely on statistical descriptions of electron states and $J$-levels. A generalized '$J$-file' sum rule for E2 lines and the strength-weighted shift and variance of the line energies of a transition array $n\ell N+1 \rightarrow n\ell n'$ of inter-configuration E2 lines are also presented.

1. Introduction

In atomic spectroscopy, the transition probabilities of electric-quadrupole (E2) lines are low, as compared to electric-dipole (E1) ones. Indeed, the ratio between E2 and E1 transition probabilities is proportional to $(a_0/\lambda Z^*)^2$, where $a_0$ is the Bohr radius, $Z^*$ is the effective charge of the plasma and $\lambda$ is the wavelength \cite{1}. This quantity is very small for most atomic transitions located in the range of UV to IR. However, they are important in astrophysics; for instance, Charro et al performed a careful study of intensities of E2 spectral lines in the ion Mg II along the spectral series \cite{2,3}. In astrophysical plasmas of Nebulae and of the interstellar medium, the density $n_e$ of the free electrons, which are responsible for collisional excitations and de-excitations, is generally very low, and the mean time between collisions is longer than radiative E2 lifetimes, even though these are much longer than for E1 transitions. Consequently, whenever an atom gets excited by a collision onto a level, metastable or not, its only decay channel is by radiative transitions (forbidden or allowed), and forbidden transitions appear with an intensity comparable to the allowed ones \cite{4}. Fournier et al \cite{5} identified by \textit{ab initio} calculations a bright 3d$^8 \rightarrow 3d^44s$ E2 line for Mo XVII. They also studied the ratio of 3d$-4s$ E2 to 3d$-4p$ E1 emission in Mo XVI as a function of density, and noted that the sharp falloff in the values of this ratio for Mo XVI above certain densities provides a plasma diagnostic for planned fusion reactors (high-Z impurities breed the dilution of the fusion ‘fuel’ in reactors and can have a strong impact on spatial current distributions and radiative patterns in the plasma) \cite{6,7}. Atomic data of tungsten are strongly needed for identification of emission lines in future fusion reactors (ITER) where it is used as a plasma-facing material \cite{8}. Then, forbidden lines are of great interest for plasma diagnostics because the associated radiation intensity is very sensitive to density and temperature. Quinet gave a theoretical survey of forbidden transitions (E2 and M1) in the 4p$^5$ and 4d$^6$ ground configurations of ions Rh-like W$^{29+}$ to Ga-like W$^{43+}$ \cite{9}. Recently, Neu et al pointed out a very strong E2 spectral line in the soft x-ray region at a wavelength of 0.793 nm originating from Ni-like tungsten W$^{46+}$ \cite{10}. Clementson et al measured this E2 line together with M3 (magnetic octupole) ground-state transitions in the same ion using high-resolution crystal spectroscopy at the electron-beam ion trap (EBIT) facility in Livermore \cite{11}. An EBIT light source was also used by Ralchenko et al \cite{12,13} to record spectra of Br-like W$^{39+}$ to Co-like W$^{47+}$ in the 12–20 nm region. On the other hand, in most laboratory plasmas, $n_e$ is notably higher. For medium-range $n_e$, the probability for collisional depopulation may be surpassed only by the probability of radiative decay through allowed transitions. In this case, quadrupole transitions are not observed, justifying their name ‘forbidden’. However, they can be important in some circumstances \cite{14–16}. For instance, E2 decays were observed in the spectra of neon-like \cite{17} and nickel-like \cite{18} ions produced by laser irradiation.

As mentioned before, forbidden lines can arise from metastable levels of excited configurations [19]. In highly ionized atoms having ground configurations $3p^m$, the lowest excited configuration is $3p^{m-1}3d$. For $m > 1$, $p^{m-1}d$ has levels with $J'$ greater by two than the largest $J$ of $p^m$, and downwards $E1$ transitions from those levels are therefore forbidden by the dipole selection rule $|\Delta J| \leq 1$. Magnetic-dipole transitions and $E2$ transitions within the configuration $Fe$ IX $3p^33d$ and arising from such metastable levels are responsible for several lines of the solar corona. It is interesting to mention that in Pb I, parity-forbidden transitions for $E1$ radiation $6p^2 \rightarrow 6p7p$ have been observed [19]. In that case, the upper levels are not metastable, because $E1$ transitions to $6p7s$ are possible. In absorption, $E2$ transitions of the type $s \rightarrow d$ have been extensively studied in the alkalis [20, 21].

The effective core charge (or screened nuclear charge) seen by an electron is the net charge $Z$ of the nucleus with the $N_e - 1$ electrons of the ion core $Z_e = Z - N_e + 1$. Along an isolated-electronic sequence, the $E2$ radial matrix elements decrease like $Z^{-2}$, rather than like $Z^{-1}$ as do the $E1$ matrix elements. For inter-configuration transitions with $\Delta n \neq 0$, one has $A_{E2}/A_{E1} \propto Z_a^2$, where $A_{E1}$ and $A_{E2}$ represent the transition probability rates for $E1$ and $E2$ lines, respectively [19, 22]. For inter-configuration transitions with $\Delta n = 0$, the orders of magnitudes of the $E1$ and $E2$ transition probabilities vary in the same way with respect to the effective core charge $Z_e$ [19].

The detailed calculation of all the line energies and strengths in complex atomic spectra is difficult and, in some circumstances, useless. Indeed, when the density is sufficiently high so that the physical broadening mechanisms (e.g. Stark shifts) are important and/or when the number of lines becomes large, the lines coalesce into broad structures. Statistical methods [23–33] are required because, experimentally, some quantities cannot be determined individually, but only as weighted average quantities (for instance, in emission/absorption spectra of highly ionized atoms). Moreover, explicit quantum calculations can be inappropriate, e.g. if the Hamiltonian matrix is huge. In addition, global methods can reveal physical properties hidden in a detailed treatment of levels and lines. For example, they have opened the way to the definition of the generalized $J$-file sum rule [34] and of effective temperatures for the configuration populations [35].

Even for $E1$ lines, there exists no general compact formula for the exact number of lines in a transition array. Using group-theoretical methods, Krasnitz [36, 37] obtained such a compact formula only in the simple case of configurations built with non-equivalent electrons. The statistics of $E1$ lines was studied by Baeche and Baeche-Arnoult [28, 38], but very few results were obtained concerning the statistics of $E2$ lines in complex atomic spectra. The purpose of this work is to provide an analytical formula for the estimation of the number of $E2$ lines in a transition array. Such a quantity is important for opacity codes, for instance, in order to decide whether a transition array can be described statistically [24–27] or requires a detailed-line accounting (DLA) calculation, relying on the diagonalization of the Hamiltonian [39]. Like for the $E1$ case, a statistical description is used, because this problem does not lend itself readily to exact calculations. The first step consists in determining the statistics of the angular quantum number $J$. However, due to the fact that the quantum number $J$ is the eigenvalue of no simple operator, its mathematical study is tedious. Therefore, it is more appropriate to study the distribution of $M$, the eigenvalue (in units of $\hbar$) of the operator $J_y$ (projection along the $z$-axis of operator $\hat{J}$). The $J$ values can be obtained from the $M$ values by means of the method of Condon and Shortley [40]. Any unknown distribution can be characterized by its moments. The $n$th moment of the $M$ distribution reads

$$\mu_n = \frac{1}{g} \sum y JM |J_y y J M|^n,$$

where the sum runs over all the $g$ states of the configuration in intermediate coupling. The distribution $P(M)$ of $M$ being symmetrical, the odd-order moments are zero. In general, it is admitted [41] that the first four moments are sufficient to capture the shape of a distribution.

In section 2, the second- and fourth-order moments of $P(M)$ for a non-relativistic configuration are recalled. Section 3 contains the calculation of the number of $E2$ lines between two configurations in the case of three different modelings of $P(M)$: Gaussian, Gram–Charlier and generalized Gaussian. Section 4 contains the calculation, using the aforementioned three distributions, of the number of $E2$ lines inside a configuration. In section 5, a generalized $J$-file sum rule for $E2$ lines is given, and in section 6 the expressions of the strength-weighted shift and variance of a transition array of inter-configuration $E2$ lines are provided for $nE^{\ell n+1} \rightarrow nE^{\ell n}$. Section 7 is the conclusion.

2. Variance and kurtosis of the projection of the $J$ angular momentum

The variance $\nu$ of the states of configuration $\ell^N$ is given by

$$\nu(\ell^N) = \mu_2(\ell^N) = \frac{N(4\ell + 2 - N)}{4\ell + 1} \nu(\ell),$$

where

$$\nu(\ell) = \frac{4\ell^2 + 4\ell + 3}{12}.$$  

The fourth-order moment of configuration $\ell^N$ reads

$$\mu_4(\ell^N) = N(4\ell + 2 - N)[x(\ell)N(4\ell + 2 - N) + y(\ell)].$$

where

$$x(\ell) = \frac{2\ell - 1}{240(16\ell^2 - 1)} (40\ell^3 + 84\ell^2 + 110\ell + 51),$$

and

$$y(\ell) = \frac{2\ell + 1}{60(16\ell^2 - 1)} (-16\ell^4 - 24\ell^3 - 8\ell^2 + 24\ell + 9).$$

For a configuration with $w$ open subshells $\ell_1^N \ell_2^N \ell_3^N \cdots \ell_w^N$, one has for the total variance

$$\nu(\ell_1^N \ell_2^N \ell_3^N \cdots \ell_w^N) = \sum_{i=1}^w \nu(\ell_i^N),$$
and for the total kurtosis

\[ \mu_4(e_1^N, e_2^N, e_3^N, \ldots, e_w^N) = \sum_{i=1}^{w} \mu_4(e_i^N) + 6 \sum_{i,j=1, i \neq j} \mu_2(e_i^N) \mu_2(e_j^N). \]

where the first sum runs over all subshells \( i \) of interest, and the second sum runs over all pairs \((i, j)\) of subshells. In the following section, we will use the fourth-order-reduced moment

\[ \alpha_4 = \frac{\mu_4}{\nu^4}, \]

which can also be put in the form [42]

\[ \alpha_4 = 3 - \frac{1}{\nu^2} \sum_{i=1}^{w} q_i(a_i + q_i b_i), \]

where

\[ a_i = \frac{(2\ell_i + 1)(16\ell_i^3 + 24\ell_i^3 + 8\ell_i^2 - 24\ell_i - 9)}{60(4\ell_i - 1)}, \]

\[ b_i = \frac{-16\ell_i^2 - 16\ell_i^2 + 80\ell_i^2 + 136\ell_i + 3}{120(4\ell_i - 1)}, \]

and

\[ q_i = \frac{N_i(4\ell_i^2 + 2 - N_i)}{4\ell_i + 1}. \]

3. Number of E2 lines between two different configurations

The initial and final configurations are denoted \( C \) and \( C' \), respectively. The selection rules for E2 transitions in intermediate coupling are \( \Delta J = 0, \pm 1, \pm 2 \) with \( J + J' \geq 2 \), and \( \Delta \ell = 0, \pm 2 \) with \( \ell + \ell' \geq 2 \) (transitions \( \ell \rightarrow \ell' \) are strictly forbidden for isolated atoms, but have been observed by means of Stark-effect-induced mixing of \( n\ell\ell' \) with \( n\ell\ell' \) states [43]). Therefore, the number \( L_{EC}(C - C') \) of E2 lines between two different configurations is given by

\[ L_{EC}(C - C') = \sum_{J=J_{\text{min}}}^{\infty} Q_C(J) Q_{C'}(J) + Q_C(J + 1) + Q_C(J - 1) + Q_C(J + 2) + Q_C(J - 2) + \epsilon(J_{\text{min}}), \]

where \( Q_C(J) \) (respectively \( Q_{C'}(J) \)) is the number of the levels of configuration \( C \) (respectively \( C' \)) with the total angular momentum \( J \) and \( \epsilon(J_{\text{min}}) \) is a small correction, \( J_{\text{min}} \) being the smallest value of \( J \). In many cases, \( J_{\text{min}} = 0 \) or \( 1/2 \) according to the parity of the number of electrons. For configuration sd, \( J_{\text{min}} = 1 \) and for configurations involving orbitals with a large angular momentum \( J \), the value of \( J_{\text{min}} \) can be larger. A continuous representation of equation (14) yields

\[ L_{EC}(C - C') \approx \int_{-1/2}^{\infty} Q_C(J) Q_{C'}(J) + Q_C(J + 1) + Q_C(J - 1) + Q_C(J + 2) + Q_C(J - 2) \, dJ + \epsilon(J_{\text{min}}), \]

where \( \epsilon(J_{\text{min}}) \) is a border correction. In fact, \( \epsilon'(0) = \epsilon'(1/2) = 0 \) are values compatible with the accuracy of the replacement of a discrete sum by an integral (see appendix A). Using the second-order Taylor development

\[ Q(J + k) \approx Q(J) + k \frac{dQ}{dJ} \bigg|_J + \frac{k^2}{2} \frac{d^2Q}{dJ^2} \bigg|_J, \]

one obtains

\[ L_{EC}(C - C') \approx 5 \int_{-1/2}^{\infty} Q_C(J) \left[ \frac{d^2Q_{C'}}{dJ^2} \right] dJ. \]

The method of Condon and Shortley [40] enables one to express \( Q(J) \) as

\[ Q(J) = \sum_{M=J}^{M=J+1} (-1)^{J-M} P(M) = P(J) - P(J + 1), \]

where \( P(M) \) represents the distribution of the angular-momentum projection \( M \). For a configuration \( \ell_1^N, \ell_2^N, \ldots, \ell_w^N \), \( P(M) \) is determined through the relation

\[ P_{N_1, N_2, \ldots, N_w}(M) = (P_{N_1} \otimes P_{N_2} \otimes P_{N_1} \otimes \cdots \otimes P_{N_w})(M), \]

where the distributions are convolved two at a time, which means that

\[ (P_{N_1} \otimes P_{N_2})(M) = \sum_{M=-\infty}^{+\infty} P_{N_1}(M') \times P_{N_2}(M - M'). \]

The total number \( L_{EC}(C - C') \) of E2 lines is invariant under the following transformations.

(i) The configurations \( C \) and \( C' \) can be interchanged.

(ii) In \( C \) and \( C' \), one can replace simultaneously all the subshells by their complementary subshells, e.g., \( \ell_1^N \) by \( \ell_1^{4s+2-N} \). Therefore, the \( C \rightarrow C' \) array, denoted in general \( \ell_1^{N_1+1} \ell_2^{N_2} \rightarrow \ell_1^{N_2} \ell_2^{N_2+1} \) has the same number of E2 lines as its complementary array

\[ \ell_1^{4s+1-N_1} \ell_2^{2s+1-N_2} \rightarrow \ell_1^{4s+1-N_1} \ell_2^{2s+1-N_2}. \]

(iii) The \( C \rightarrow C' \) transition array has also the same number of E2 lines as its two following semi-complementary arrays

\[ \ell_1^{4s+1-N_1} \ell_2^{2s+2-N_2} \rightarrow \ell_1^{4s+1-N_1} \ell_2^{2s+2-N_2}, \]

and

\[ \ell_1^{N_1+1} \ell_2^{2s+2-N_2} \rightarrow \ell_1^{N_1+1} \ell_2^{2s+2-N_2}. \]

The first semi-complementary array is deduced from \( C \rightarrow C' \) as follows: replace the \( \ell_1 \) subshells by their complementaries, and exchange the \( \ell_2 \) subshells. For the second one, replace the \( \ell_2 \) subshells by their complementaries, and exchange the \( \ell_1 \) subshells. Complemenarity ensures that the variances are unchanged, but it is not the case for semi-complemenarity. However, since

\[ v(\ell_1^{N_1+1-N_1}) + v(\ell_2^{N_2+1}) + v(\ell_1^{4s+2-N_2}) + v(\ell_2^{N_2}) \]

\[ = v(\ell_1^{N_1+1}) + v(\ell_2^{N_2}) + v(\ell_1^{4s+1+N_1}) + v(\ell_2^{N_2+1}), \]

semi-complemenarity can be ensured by replacing \( v_C \) and \( v_{C'} \) by their half-sum \( (v_C + v_{C'})/2 \) [38]. However, the kurtosis does not follow a relation similar to equation (24). It can only be ensured that the final formula for \( L_{EC}(C - C') \) be symmetrical.
It was also suggested in [38] to use a fourth-order Gram–Charlair and generalized–Gaussian modellings of $P(M)$ and compared to the exact values. An orbital $\ell$ corresponds to $\ell = 6$.

| Transition array | Exact | Gaussian | Gram–Charlair | Generalized Gaussian |
|------------------|------|---------|--------------|----------------------|
| $d^4 \to d^5 s$  | 887  | 953     | 885          | 839                  |
|                  |      | (+7.44%)| (-0.23%)     | (-5.41%)             |
| $d^4 \to d^5 g$  | 1015 | 1215    | 1092         | 1045                 |
|                  |      | (+19.70%)| (+7.56%)     | (+2.96%)             |
| $p^3 \to p^1 f$  | 110  | 124     | 116          | 81                   |
|                  |      | (+12.73%)| (+5.45%)     | (-27.27%)            |
| $p^4 \to p^1 f$  | 110  | 124     | 116          | 81                   |
|                  |      | (+12.73%)| (+5.45%)     | (-26.36%)            |
| $d^5 \to d^5 g$  | 8299 | 9550    | 8697         | 8415                 |
|                  |      | (+15.07%)| (+4.80%)     | (+0.14%)             |
| $d^4 g^2 \to d^4 g^4$ | 296780266 | 299065925 | 298981701 | 293198984 |
|                  |      | (+0.77%) | (+0.74%)     | (-1.21%)             |
| $d^4 l^1 \to d^4 l^1 l^1$ | 762544 | 897641 | 783942 | 774216 |
|                  |      | (+17.72%)| (+2.81%)     | (+1.54%)             |

Finally, considering the generalized–Gaussian modelling of $P(M)$,

$$P(M) = \frac{g}{\sqrt{2\pi v}} \exp \left( -\frac{M^2}{2v} \right),$$

one obtains

$$Q(J) = \frac{g}{v^{\sqrt{8\pi v}}} (2J + 1) \exp \left( -\frac{(2J + 1)^2}{8v} \right),$$

which yields

$$L_{E_2}(C = C') = \frac{5gcgc(2v - 3)}{16\sqrt{\pi v} v^{5/2}},$$

where $gc$ represents the degeneracy (total number of states) of configuration $C$; for instance, the degeneracy of a configuration $e_{1}^{\ell_1} e_{2}^{\ell_2} e_{3}^{\ell_3} \ldots e_{w}^{\ell_w}$ reads

$$gc = \prod_{i=1}^{w} \left( \ell_i + 2 \right).$$

It was also suggested in [38] to use a fourth-order Gram–Charlair modelling of $P(M)$:

$$P(M) = \frac{g}{\sqrt{2\pi v}} \exp \left( -\frac{M^2}{2v} \right) \times \left[ 1 + \frac{(\alpha_4 - 3)}{24} \left( 3 - 6\frac{M^2}{v} + \frac{M^4}{v^2} \right) \right].$$

In that case, one finds

$$Q(J) = \frac{g}{v^{\sqrt{8\pi v}}} \left[ (2J + 1) + \frac{(\alpha_4 - 3)}{24} \left( 15(2J + 1) - 10\frac{(2J + 1)^3}{4v} + \frac{(2J + 1)^5}{16v^2} \right) \right] \exp \left( -\frac{(2J + 1)^2}{8v} \right),$$

which yields

$$L_{E_2}(C = C') = \frac{1}{16384\sqrt{\pi v} v^{5/2}} \left[ 5gcgc(-6747 + 2018v) + 5\alpha_4(938 - 124v + 21\alpha_4(-11 + 2v))) \right].$$

As can be seen in table 1, the fourth-order Gram–Charlair expansion series provides a better agreement in most of the cases, except for $d^4 l^1 \to d^4 l^1 l^1$ and $d^5 \to d^4 l^4$. This is due to the fact that, when a high-$\ell$ electron is involved, the shape of the distribution $P(M)$ is not quasi–Gaussian anymore, but exhibits a plateau [42], which cannot be modelled by Gram–Charlair expansion. On the other hand, the generalized Gaussian can depict such situations (the ‘door function’ corresponds to an exponent equal to $v = 9/8$). Furthermore, the second-order Taylor series expansion (see equation (16)) is not as precise as in the E1 case, since the selection rules here imply that the maximum value of $k$ is 2 (against 1 in the E1 case).

### 4. Number of E2 lines in the intra-configuration case ($C = C'$)

The number of E2 lines inside a configuration can be estimated as

$$L_{E_2} \approx \int_{-1/2}^{\infty} Q(J) \left[ \frac{1}{2} (Q(J) - 1) + Q(J + 1) + Q(J + 2) \right] dJ.$$
Table 2. Number of E2 lines inside different configurations calculated using Gaussian, fourth-order Gram–Charlier and generalized–Gaussian modellings of P(M) and compared to the exact values. An orbital \( l \) corresponds to \( \ell = 8 \).

| Configuration | Exact | Gaussian | Gram–Charlier | Generalized Gaussian |
|---------------|-------|----------|---------------|---------------------|
| \( d^8 \)     | 358   | 380      | 352           | 365                 |
|               |       | (6.15%)  | (1.68%)       | (6.42%)             |
| \( d^4p^2 \)   | 15383 | 16499    | 15446         | 14967               |
|               |       | (+7.25%) | (+0.41%)      | (+2.70%)            |
| \( p^6f^2 \)   | 353   | 402      | 358           | 322                 |
|               |       | (+13.88%)| (+1.42%)      | (+8.78%)            |
| \( p^6f^3 \)   | 611   | 696      | 622           | 567                 |
|               |       | (+13.91%)| (+1.80%)      | (+7.20%)            |
| \( g^7 \)      | 903622| 968412   | 909329        | 892418              |
|               |       | (+7.17%) | (+0.64%)      | (+1.24%)            |
| \( f^6p^3 \)   | 5437574| 5839649 | 5481760       | 5373233             |
|               |       | (+7.39%) | (+0.81%)      | (+1.18%)            |
| \( f^6d^2 \)   | 40832855| 43429407 | 41104770      | 40379223            |
|               |       | (+6.35%) | (+0.67%)      | (+1.11%)            |
| \( f^7p^4 \)   | 97615 | 107207   | 98683         | 96137               |
|               |       | (+9.83%) | (+1.09%)      | (+1.51%)            |
| \( d^7f \)     | 2376  | 2545     | 2064          | 2365                |
|               |       | (+8.11%) | (+1.33%)      | (+0.46%)            |
| \( p^5l^1 \)   | 616   | 655      | 529           | 581                 |
|               |       | (+6.33%) | (+14.12%)     | (+5.68%)            |

Using the second-order Taylor development presented in equation (16), one finds the approximate expression

\[
L_{E2} \approx \frac{1}{2} \int_{-1/2}^{1/2} Q(J) \left[ 5 \frac{Q(J)}{Q^2(J)} + \frac{6}{Q^3(J)} - 1 \right] dJ. \tag{37}
\]

A Gaussian expression of \( P(M) \) (see equation (26)) leads to

\[
L_{E2} = \frac{g_C}{32 \pi v_C^2} \left[ -8 \sqrt{2} J + 5 g_C (2v_C - 3) \right], \tag{38}
\]

and a fourth-order Gram–Charlier expression of \( P(M) \) (see equation (30)) leads to

\[
L_{E2} = -2048 g_C (4a_{4,4} + 5v_C^2) \left[ \frac{5}{32 \pi v_C^2 \Gamma(1/2)} \right] + 32768 \Gamma(1/2) - 6747 + 2018v_C + 5a_{4,4} (938 - 124v_C + 21a_{4,4} (2v_C - 11))]. \tag{39}
\]

Using a generalized–Gaussian expression of \( P(M) \) (see equation (33)), one obtains

\[
L_{E2} = \frac{5 g_C v^2 \Gamma(\nu)}{128 \lambda^3 \Gamma(3/2) \Gamma(1/2)} \left[ \frac{1}{v^2} \left( \nu - 3 \right) \right] + 4 \Gamma \left( 2 - \frac{1}{\nu} \right) - \frac{v g_C}{4 \lambda \sqrt{\gamma^2 + 1}} \left( \frac{1}{\nu} \right). \tag{40}
\]

Here also the fourth-order Gram–Charlier expansion series provides a better agreement in most of the cases, except for configurations with high-\( \ell \) electrons (see table 2). The results are closer to the exact values in the intra-configuration case than in the inter-configuration case. This is due to the fact that the number of lines in the intra-configuration case is evaluated with the exact variance and the exact kurtosis of the distribution of \( M \) (in the inter-configuration case, they were obtained as the arithmetic average over the initial and final configurations).

It is worth mentioning that global methods were also used for the study of statistical properties of Auger amplitudes and rates [44] and the dispersion of gyromagnetic ratios in complex spectra [45]. In appendix C, we give, following the work of Kyniën et al [44], an approximate expression for the number of Auger amplitudes with three different modellings of \( P(M) \).

5. A generalized J-file sum rule for E2 lines

Using the second quantization technique [46], Bauche et al [34] established a linear relationship between the angular coefficient of the exchange Slater integral \( G^{(1)} (n\ell, n\ell - 1) \) and the \( J \)-file sums of the E1 line strengths defined by Condon and Shortley [40]. In the case of E2 lines, a \( J \)-file sum rule can be also obtained, following the same procedure as for E1 lines. The sum of the strengths of all E2 lines starting from a level \( \gamma J \) of the upper configuration in the \( \ell^N \ell^{N+1} \rightarrow \ell^N \ell^{N+1} \) array is given by

\[
S_{E2}(\ell^N \ell^{N+1} | \ell - \ell^{N+1} \ell' C) = (2J + 1) \times \left[ \frac{(N' + 1)}{(2\ell' + 1)} [\langle |\epsilon^{(2)}(\ell') \rangle^2 + C(G^2; \gamma J)] |I(n\ell, n\ell')|^2, \tag{41}
\]

with

\[
I(n\ell, n\ell') = \int_0^{\infty} R_{n\ell}(r) r^2 R_{n\ell'}(r) dr \tag{42}
\]

and

\[
\langle \epsilon |\epsilon^{(2)}(\ell') \rangle = \left( -1 \right)^{1/2} \sqrt{(2\ell + 1)(2\ell' + 1)} \begin{pmatrix} \ell & 2 & \ell' \\ 0 & 2 & 0 \end{pmatrix}. \tag{43}
\]

The quantity \( C(G^2; \gamma J) \) represents the coefficient of the \( G^2(n\ell, n\ell') \) Slater integral in the electrostatic energy of the level \( \gamma J \). In this case, one has, if \( |\ell' - \ell| = 2 \) and \( \ell > = \max (\ell, \ell') \)

\[
\langle \epsilon |\epsilon^{(2)}(\ell') \rangle^2 = \frac{3 \epsilon_{\ell}(\ell > - 1)}{2(2\ell' + 1)}. \tag{44}
\]

and if \( \ell = \ell' \)

\[
\langle \epsilon |\epsilon^{(2)}(\ell') \rangle^2 = \frac{\ell(\ell + 1)}{2(2\ell + 3)}. \tag{45}
\]

These results remain unchanged if passive subshells are added to both configurations. It is interesting to mention that the total strength of transition array \( C \rightarrow C' \) with \( C = n\ell^{N+1} n\ell'^N n\ell'' \cdots \) and \( C' = n\ell^{N'} n\ell'^{N+1} n\ell'' \cdots \) reads

\[
T(C \rightarrow C') = 2(2\ell + 1)(2\ell + 2) \frac{g_C}{2\ell + 3} \frac{\langle \epsilon |\epsilon^{(2)}(\ell') \rangle^2}{[I(n\ell, n\ell')]^2}, \tag{46}
\]

where \( g_C \) represents the degeneracy of configuration \( C \), i.e.

\[
g_C = \left( \frac{\ell + 2}{N + 1} \right) \left( \frac{\ell' + 2}{N'} \right) \left( \frac{\ell'' + 2}{N''} \right) \cdots. \tag{47}
\]
6. Shift and variance of a transition array \( n\ell n'\ell' \rightarrow n\ell n'\ell' \) of E2 lines

To our knowledge [47], Harrison and Johnson [48] were the first to introduce the term ‘transition array’ for the entire bunch of lines resulting from transitions between two configurations. The first experimental spectrum showing transition arrays was published by Edlén in 1947 [49]: it concerned transition elements in the XUV range and the spectra were generated by low-inductance discharge lamps. Since then, such arrays have been observed in a very large variety of spectra (see for instance [50–54]). Although in tokamak applications, E2 lines usually appear as isolated (only a few distinct lines are visible), it is also possible to estimate the global properties (strength-weighted moments) of a transition array of E2 lines. In this section, we consider the case of inter-configuration E2 lines for the specific transition array \( n\ell n'\ell' \rightarrow n\ell n'\ell' \) with \( \ell' - \ell = 0, \pm 2 \) and \( \ell + \ell' \geq 2 \). The moments of the distribution of the line energies can be written as

\[
M_n = \sum_{a,b} \left[ \langle a | H | b \rangle - \langle a | \Sigma a | a \rangle \right] P \left( \langle a | Q | b \rangle \right)^2, \tag{48}
\]

where \( a \) and \( b \) run over all the exact eigenstates of the Hamiltonian in configurations \( C \) and \( C' \), respectively, and \( Q \) is the \( z \) component of the quadrupole transition operator. The first two moments were calculated by Bauche-Arnoult et al [24] using the second quantization techniques of Judd [46]. The most useful quantities are the mean energy \( M_1 \) and the variance \( M_2 - M_1^2 \), related to the spectral width of the UTA. For the mean energy of the array, it was found in [24] that

\[
M_1 = E_C - E_{C'} + \delta E, \tag{49}
\]

where \( E_C \) and \( E_{C'} \) are the average energies of the initial and final configurations, respectively. There exists a shift between the weighted average energy of a transition array and the difference of the average energies of the initial and final configurations. The shift \( \delta E \) stems from the weighting factor \( \langle a | Q | b \rangle \) and is non-zero for transition arrays \( n\ell n'\ell' \rightarrow n\ell n'\ell' \). It was shown in [24] that \( \sigma^2 \) can be written as

\[
\sigma^2 = \sum_i c_i \left[ \sum_{k,k'} d_i(k, k', \ell, \ell', \ldots) \times e_i(n\ell, n'\ell', \ldots) \right], \tag{50}
\]

where \( c_i \) are numerical coefficients depending on the number of equivalent electrons \( N, d_i(k, k', \ell, \ell', \ldots) \) are combinations of \( 3n_j (n = 1, 2 \) and \( 3) \) symbols independent of \( N \) and \( e_i(n\ell, n'\ell', \ldots) \) are products of Slater integrals of ranks \( k \) and \( k' \). In the following, \( F_{kC}^k \) and \( F_{kC'}^k \) represent the direct Slater integrals in configurations \( C \) and \( C' \), respectively, and \( G_{kC}^k \) represents the exchange Slater integral of \( C \). As in [24], we define the quantities as follows:

\[
x = N(N + 1)(4\ell - N)(4\ell' - N + 1) = (N + 1)(4\ell - N)w, \]
\[
y = N(N + 1)(4\ell - N + 1)(4\ell' - N + 2) \]
\[
z = N(N + 1)(4\ell - N)(4\ell' - N + 1) = (N - 1)(4\ell - N)w, \]
\[
u = N(4\ell - N)(4\ell' - N + 1) = (4\ell - N)w, \]
\[
w = N(4\ell - N + 1). \tag{51}
\]

In the following, in agreement with the convention of [24], indices \( n \) and \( n' \) are omitted in the Slater integrals. The shift is given by

\[
\delta E = N \left( \frac{(2\ell + 1)(2\ell' + 1)}{4\ell + 1} \right) \times \left( \sum_{k' \neq 0} f_k F_{kC}^k(\ell\ell') + \sum_k g_k G_{kC}^k(\ell\ell') \right), \tag{52}
\]

with

\[
f_k = \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & 0 & \ell' \\ 0 & 0 & 2 \end{pmatrix} \tag{53}
\]

and

\[
g_k = \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k & \ell' \end{pmatrix} \begin{pmatrix} 2 & \delta_{k,2} - \frac{1}{2(2\ell + 1)(2\ell' + 1)} \end{pmatrix}, \tag{54}
\]

where \( \delta_{ij} \) represents a Kronecker symbol. The variance can be written as

\[
\sigma^2 = \sum_{i=1}^\gamma H_i. \tag{55}
\]

As compared to [24], the term \( H_1 \) remains unchanged:

\[
H_1 = \sum_{k \neq 0} \sum_{k' \neq 0} \left( \frac{2\delta_{k,k'}}{(2k + 1)} - \frac{1}{(2\ell + 1)(4\ell + 1)} \right) \times \left( \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k' & \ell' \\ 0 & 0 & 0 \end{pmatrix} \right) \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 2 & \delta_{k,2} - \frac{1}{2(2\ell + 1)(2\ell' + 1)} \end{pmatrix} \right)^2, \tag{56}
\]

and one has

\[
H_2 = \sum_{k \neq 0} \sum_{k' \neq 0} \left( \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k' & \ell' \\ 0 & 0 & 0 \end{pmatrix} \right) \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 2 & \delta_{k,2} - \frac{1}{2(2\ell + 1)(2\ell' + 1)} \end{pmatrix} \right)^2, \tag{57}
\]

and

\[
H_3 = \sum_{k \neq 0} \sum_{k'} \left( \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k' & \ell' \\ 0 & 0 & 0 \end{pmatrix} \right) \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 2 & \delta_{k,2} - \frac{1}{2(2\ell + 1)(2\ell' + 1)} \end{pmatrix} \right)^2, \tag{58}
\]
The range of energy of the levels of the upper configuration \( C' \) responsible for the preferential emission constitutes an ‘emissive zone’ [34]. In the same way as for an E1 UTA, the shift and width of the emissive zone of an E2 UTA are deduced from those of the complete UTA by restricting them to the radial parameters related to the upper configuration of the array.

### 7. Conclusion

We propose analytical expressions for the number of electric-quadrupole (E2) lines both in the inter- and intra-configuration cases. The resulting formulas are based on three different modellings of the distribution of the angular-momentum projection \( M \) (Gaussian, fourth-order Gram–Charlier and generalized Gaussian). The Gram–Charlier modelling gives satisfactory results but, for high-\( \ell \) electrons, the generalized–Gaussian distribution is more accurate (as for E1 lines, see [42]). The results are better in the intra- than in the inter-configuration case, which can be explained by the fact that the number of lines between two different configurations is evaluated with averaged parameters (variance and kurtosis of the distribution of the angular-momentum projection \( M \)). We also provide the expression of the generalized \( J \)-file sum rule giving the total strength of the lines arising from a given level of the upper configuration, together with the formula for the average strength-weighted position and variance of E2 lines. The next step will consist in investigating the statistics of the amplitudes and strengths of E2 lines.

### Appendix A. Boundary effect on the number of lines of an array

At very small values of \( J \), we can linearize the exponential in equation (27), i.e.

\[
Q_C(J) = K_C \times (2J + 1) \quad (A.1)
\]

and

\[
Q_C(J) = K'_C \times (2J + 1), \quad (A.2)
\]

where \( K_C \) and \( K'_C \) do not depend on \( J \).

- **(i) Intra-configuration case.** In the intra-configuration case, the error committed in considering that \( \epsilon' (\frac{1}{2}) = 0 \) in equation (15) is equal to

\[
\Delta \epsilon_{\text{intra}} = 5 \int_{-1/2}^{0} Q_C(J)Q_C(-J) dJ. \quad (A.3)
\]

Using the linearized expressions (A.1) and (A.2), one obtains

\[
\Delta \epsilon_{\text{intra}} \approx \frac{1}{2} (K_C + K'_C). \quad (A.4)
\]

- **(ii) Intra-configuration case.** In the intra-configuration case, the error committed in considering that \( \epsilon' (\frac{1}{2}) = 0 \) in equation (15) is equal to

\[
\Delta \epsilon_{\text{intra}} = 3 \int_{-1/2}^{0} Q_C(J)Q_C(-J) dJ. \quad (A.5)
\]

Using the linearized expressions (A.1) and (A.2), one obtains

\[
\Delta \epsilon_{\text{intra}} \approx \frac{K_C + K'_C}{2}. \quad (A.6)
\]
Appendix B. Estimation of $J_{\text{min}}$

Usually, $J_{\text{min}}$ is equal to 0 (for integer values) or to 1/2 (for half-integer values). However, in some circumstances [42] (for instance in the case of configurations containing an electron in an orbital with a high angular momentum $\ell$), the distribution $P(M)$ exhibits a plateau, for which we showed that the generalized Gaussian is a good approximation [42]. In that case, $J_{\text{min}}$ differs from 0 and 1/2. An estimation of $J_{\text{min}}$ can be obtained through the relation

$$Q(J) \geq \frac{1}{2}, \quad \text{B.1}$$

Using the expression of $Q(J)$ given in equation (34), we find

$$J_{\text{min}} \approx \sqrt[4]{2} \ln \left( \frac{1 - v}{v} \right) \left[ \frac{v}{1 - v} \right]^{\frac{1}{4}} - \frac{1}{2}, \quad \text{B.2}$$

with

$$\Lambda = \frac{\lambda^2 v_c}{v^2 g_c} \left( \frac{1}{v} \right), \quad \text{B.3}$$

and $x \mapsto W[x]$ represents Lambert’s function, solution of the equation $xe^x = y$. The function $W$ can be expanded as [59–62]

$$W(x) = \ln x - \ln(\ln x) + \sum_{k=0}^{\infty} \sum_{m=1}^{\infty} c_{km} \left( \frac{\ln(\ln x)}{\ln x} \right)^m,$$

where

$$c_{km} = \frac{(-1)^{k+1}}{m!} S[k + m, k + 1], \quad \text{B.5}$$

with $S[p, q]$ being the Stirling number of the first kind [63, 64], also denoted $S(q)^{p}$, $s(p, q)$ or $\left[ \begin{array}{c} p \\ q \end{array} \right]$. Stirling numbers can be obtained by recursion relations [60], and an explicit expression was provided by Karanicoloff [65]. However, since we are only interested in an approximate formula, the first two terms $\ln x - \ln(\ln x)$ are sufficient.

Appendix C. Number of Auger amplitudes

Auto-ionization from a state that involves a hole in an inner subshell of the core is known as the Auger [66] effect, and the ejected electron is called an Auger electron. The term ‘auto-ionization’ (applied to levels produced by excitation of loosely bound electrons) was coined by Shenstone [67]. In the non-relativistic approximation, the amplitude of Auger transitions is equal to the reduced matrix element of the Coulomb interaction operator $H_c$:

$$\langle C^J | H_c | C' y' J' \epsilon \ell J \rangle = \sqrt{\gamma J + 1} \langle C^J | H_c | C' y' J' \epsilon \ell J \rangle,$$

where $C$ is the configuration of an atom, $J$ is the quantum number of total angular momentum, $y$ denotes all the additional quantum numbers and $\epsilon$ is the energy of the Auger electron. In intermediate coupling, the number of Auger amplitudes for a given channel $\epsilon \ell$ or $\epsilon \ell J$ can be obtained as the number of reduced matrix elements of the scalar operator acting between two configurations:

$$N_{\text{Auger}}(C - C') \approx \int_0^\infty Q_c(J)Q_{c'}(J) \, dJ, \quad \text{C.2}$$

where $C'$ denotes $C' \epsilon \ell$ and $C'$ is the final configuration of the ion. In the configuration $C''$, the contribution of the Auger electron to the variance and kurtosis of the distribution $P(M)$ is equal to the one of an electron of the discrete spectrum $v(\epsilon \ell) = v(\ell)$, where $v(\ell)$ is defined in equation (3) and

$$\mu_4(v(\ell)) = \frac{1}{320}(2\ell + 1)(48\ell^4 + 96\ell^3 + 152\ell^2 + 104\ell + 15). \quad \text{C.3}$$

It was shown by Kynienė et al [44] that the Auger transition $\ell_1^{\ell_1+1}N_2^N \ell_3 \rightarrow \ell_1^{\ell_1+2}N_2^{N-1} \ell_3$ does not change under the replacements $N_2 \rightarrow 4\ell_2 + 4 - N_2$ and $N_3 \rightarrow 4\ell_3 + 4 - N_3$. In the same way, the transition $\ell_1^{\ell_1+1}N_2^N \rightarrow \ell_1^{\ell_1+2}N_2^{N-2} \ell_3$ does not change under the replacement $N_2 \rightarrow 4\ell_2 + 4 - N_2$. This is a consequence of complementarity, and can be explained by the fact that the recoupling does not change the number of matrix elements [44]. Here also, since

$$v(\ell_1^{\ell_1+1}) + v(\ell_1^{\ell_1+2}) + v(\ell_2^{N-2}) + v(\ell_1^{\ell_1+2}) + v(\ell_2^{\ell_2+4-N_2}) + v(\ell_1^{\ell_1+2})$$

we set $v = (v(\ell_1^{\ell_1+1}) + v(\ell_1^{\ell_1+2}) + v(\ell_2^{N-2}) + v(\ell_1^{\ell_1+2}) + v(\ell_2^{\ell_2+4-N_2}) + v(\ell_1^{\ell_1+2}))$.\quad \text{C.6}

The Gram–Charlier modelling of $P(M)$ (see equation (26)), Kynienė et al obtained [44]

$$N_{\text{Auger}}(C - C') \approx \frac{g_c g_c}{8\sqrt{v^3/2}}, \quad \text{C.7}$$

The Gram–Charlier modelling of $P(M)$ (see equation (30)) leads to

$$N_{\text{Auger}}(C - C') \approx \frac{g_c g_c}{8192\sqrt{v^{3/2}}} = \frac{1009 + 5\alpha_4(46 + 21\ell_4)}{8192\sqrt{v^{3/2}}}, \quad \text{C.8}$$

and using a generalized–Gaussian approximation of $P(M)$, we find

$$N_{\text{Auger}}(C - C') \approx \frac{g_c g_c}{2^{2+1/\alpha_4} \lambda \Gamma \left(1 + \frac{1}{\alpha_4}\right)/\sqrt{v}}. \quad \text{C.9}$$

References

[1] Sobelman I I 1972 Introduction to the Theory of Atomic Spectra (New York: Pergamon).
[2] Charro E and Martín I 2003 Astrophys. J. 585 1191
[3] Charro E, López-Ferrero S and Martín I 2001 Astron. Astrophys. 406 741
[4] Klapisch M, Schwob J L, Finkenthal M, Fraenkel B S, Egert S, Bar-Shalom A, Breton C, DeMichelis C and Mattioli M 1978 Phys. Rev. Lett. 41 403
[5] Fourrier K B, Goldstein W H, May M and Finkenthal M 1996 Phys. Rev. A 53 709
[6] Isler C R 1984 Nucl. Fusion 24 1599
[7] Cummings J, Cohen S, Hulse R, Post D, Redi M and Perkins J 1990 J. Nucl. Mater 176–177 916
[8] Fourrier K B 1998 At. Data Nucl. Data Tables 68 1
[9] Quinet P 2012 J. Phys. B: At. Mol. Opt. Phys. 45 025003
[10] Neu R et al (the ASDEX Upgrade Team) 2005 Nucl. Fusion 45 209
[11] Clementson J, Beiersdorfer P and Gu M F 2010 Phys. Rev. A 81 012505
[12] Rachenko Yu, Tan J N, Gillaspy J D, Pomeroy J M and Silver E 2006 Phys. Rev. A 74 042514
