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Distribution of angular momenta M_L and M_S in non-relativistic configurations: statistical analysis using cumulants and Gram-Charlier series

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The distributions $P(M_L, M_S)$ of the total magnetic quantum numbers M_L and M_S for N electrons of angular momentum ℓ , as well as the enumeration of LS spectroscopic terms and spectral lines, are crucial for the calculation of atomic structure and spectra, in particular for the modeling of emission or absorption properties of hot plasmas. However, no explicit formula for $P(M_L, M_S)$ is known yet. In the present work, we show that the generating function for the cumulants, which characterize the distribution, obeys a recurrence relation, similar to the Newton-Girard identities relating elementary symmetric polynomials to power sums. This enables us to provide an explicit formula for the generating function. We also analyze the possibility of representing the $P(M_L, M_S)$ distribution by a bi-variate Gram-Charlier series, which coefficients are obtained from the knowledge of the exact moments of $P(M_L, M_S)$. It is shown that a simple approximation is obtained by truncating this series to the first few terms, though it is not convergent.

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I. INTRODUCTION

In the non-relativistic case, electrons are characterized by uncoupled moments ℓ, s , where s is the one-half spin and ℓ the orbital quantum number. The magnetic quantum numbers M_L and M_S are respectively the sums of the individual numbers m_ℓ, m_s for each electron. The enumeration of the spectroscopic LS terms arising in a given non-relativistic configuration made of ℓ^N subshells, N being the number of electrons, was addressed by different methods, such as the so-called vector model [1], recurrence relations [2] or group theory [3–7]. The knowledge of LS terms, of the distribution $Q(L, S)$ of angular momenta L and S , as well as of the distribution $P(M_L, M_S)$ of their projections (M_L and M_S), is a prerequisite for the determination of the lines between two configurations, which plays a major role in the study of emission or absorption spectral properties of hot plasmas [8], encountered for instance in stellar physics [9], inertial-confinement fusion [10], or laser-plasma experiments [11]. The latter applications imply taking into account complex ions, i.e., multi-electron configurations with several open subshells [12]. The properties (regularities, trends) of $Q(L, S)$ and $P(M_L, M_S)$, are also worth investigating [13], from a fundamental point of view but also in order to develop approximate models [14]. The statistics of electric-dipole (E1) lines was studied by Moszkowski [15], Bancewicz [16], Bauche and Bauche-Arnoult [2, 17], Kucas [18, 19], Gilleron and Pain [20] and by us in a previous article [21]. Such a quantity is important for opacity codes, for instance, in order to decide whether a transition array can be described statistically or requires a detailed-line accounting calculation, relying on the diagonalization of the Hamiltonian [22]. In the same spirit, the statistics of electric quadrupole (E2) lines was also investigated [23]. We recently published explicit and recurrence formulas for magnetic quantum number M_J , projection of the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ on the z axis [24], together with a statistical analysis through the computation of cumulants. Recurrence relations obtained within this formalism lead to analytical expressions for the number of states of a given value of total magnetic number M and number of fermions N . Explicit formulas have been given for this distribution for the values of N up to 4 [25] and then obtained up to $N = 6$ together with a general algorithm for any number of fermions [26]. This formalism also allows one to obtain closed-form expressions for the distribution of the total angular momentum J [21]. Worth noticing is the expression of the total number of levels given by a piecewise polynomial, derived in the above quoted papers [25] and [26] for $N = 3, 4, 5$ and 6 in the so-called “relativistic configuration” framework, i.e., when the electrons are characterized by their total angular momentum j . A particular

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case of fluctuation, the odd-even staggering (i.e., the fact that, in an electronic configuration, the number of odd values of J can differ from the number of even values of J), was also studied [21, 27].

The object of this work is to show that similar considerations apply to the distribution of the magnetic quantum numbers M_L and M_S . Up to our knowledge, there exists no compact analytical expression for the quantum magnetic number distribution, which motivates the present investigations.

The paper is organized as follows. In section II, the recursive determination of $P(M_L, M_S)$ is outlined. The latter method is a generalization of the one described in Ref. [20] (which was limited to (J, M_J)). In section III, we introduce the two-variable generating functions for the cumulants of the (M_L, M_S) joint distribution. A recurrence relation for that function is derived. Based on an analogy with the Newton-Girard identities for elementary symmetric polynomials, an explicit formula is provided for the cumulant generating function. Expressions of the first moments for small values of ℓ and of the number of fermions N are provided in section IV, and the corresponding expressions for the cumulants are given in section V. In section VI, the exact expressions for the magnetic quantum number distribution are compared to simple analytical formulas based on the Gram-Charlier expansion.

It is worth noting that, with minor changes, the present work also concerns nuclear physics, where nucleons in a given shell are characterized by a total angular momentum j and isospin $1/2$ [28–30].

II. NUMERICAL DETERMINATION OF (L, S) STATISTICS USING A RECURSION RELATION FOR $P(M_L, M_S)$

The number $Q(L, S)$ of LS terms of a configuration ℓ^N can be obtained from the relation

$$\begin{aligned} Q(L, S) &= \sum_{M_L=L}^{L+1} \sum_{M_S=S}^{S+1} (-1)^{L-M_L+S-M_S} P(M_L, M_S) \\ &= P(L, S) - P(L+1, S) - P(L, S+1) + P(L+1, S+1), \end{aligned} \quad (1)$$

where $P(M_L, M_S)$ is the number of states with total orbital magnetic number M_L and spin magnetic number M_S . For a N -electron configuration $\ell_1^{N_1} \ell_2^{N_2} \ell_3^{N_3} \dots \ell_w^{N_w}$, $P(M_L, M_S)$ is determined through the standard convolution formula

$$P(M_L, M_S) = (P_1 \otimes P_2 \otimes \dots \otimes P_w)(M_L, M_S), \quad (2)$$

P_i being the (M_L, M_S) distribution for the i -th subshell $\ell_i^{N_i}$. The distributions are convoluted two at a time, namely

$$(P_i \otimes P_j)(M_L, M_S) = \sum_{M'_L} \sum_{M'_S} P_i(M'_L, M'_S) P_j(M_L - M'_L, M_S - M'_S). \quad (3)$$

The individual-subshell distributions $P_i(M_L, M_S)$ can be obtained by an efficient algorithm proposed in Ref. [20], adapted to the present situation, where (M_L, M_S) are considered separately, instead of their sum $M_L + M_S$. The idea is to consider the $g = 4\ell + 2$ one-electron states (or micro-states) of ℓ^N . Each of them is characterized by the projection $m_i = m_{\ell,i} + m_{s,i}$, with the spin projection $m_{s,i} = (-1)^i/2$ and the orbital-angular-momentum projection $m_{\ell,i} = [2i - 4\ell - 3 - (-1)^i]/4$. One has therefore $m_i = [2i - 4\ell - 3 + (-1)^i]/4$. The index i varies from 1 to $4\ell + 2$. $P(M_L, M_S)$ is the number of N -electron states such as $m_{\ell,1} + \dots + m_{\ell,N} = M_L$ and $m_{s,1} + \dots + m_{s,N} = M_S$. If the last state (corresponding, in the previous ordering, to $i = 4\ell + 2$) is occupied by one electron (having therefore projections $m_{\ell,4\ell+2} = \ell$ and $m_{s,4\ell+2} = 1/2$), then the $N - 1$ remaining electrons must be distributed in the $4\ell + 1$ remaining one-electron states, their total projections being then $M_L - m_{\ell,4\ell+2} = M_L - \ell$ and $M_S - m_{s,4\ell+2} = M_S - 1/2$. This reads

$$P_{N,4\ell+2}(M_L, M_S) = P_{N-1,4\ell+1}(M_L - \ell, M_S - 1/2) + P_{N,4\ell+1}(M_L, M_S). \quad (4)$$

Such a reasoning applies for any subset of k one-electron states, and one obtains the recurrence relation

$$P_{n,k}(M_L, M_S) = P_{n-1,k-1}(M_L - m_{\ell,k}, M_S - m_{s,k}) + P_{n,k-1}(M_L, M_S), \quad (5)$$

where $P_{n,k}(M)$ represents the number of states with n electrons populating k one-electron states, and giving projections M_L and M_S . The recurrence is initialized with $P_{0,k}(M_L, M_S) = \delta_{M_L,0} \delta_{M_S,0}$ where $\delta_{i,j}$ is the Kronecker symbol and k is varied from 1 to $g = 4\ell + 2$ (total number of one-electron states), n from 1 to N , M_S from $-M_{S,\max}$ to $M_{S,\max}$ and M_L from $-M_{L,\max}$ to $M_{L,\max}$.

We have

$$M_{S,\max} = \begin{cases} N/2 & \text{if } N \leq 2\ell + 1, \\ (4\ell + 2 - N)/2 & \text{if } N \geq 2\ell + 1, \end{cases} \quad (6)$$

and

$$M_{L,\max} = [(-1)^N - 1 + 2N(4\ell + 2 - N)] / 8. \quad (7)$$

L	0	1	2	3	4	5	6	7	8	9	10	11	12
$Q(L, 1/2)$	8	26	37	46	46	44	36	28	19	12	6	3	1
$Q(L, 3/2)$	7	18	28	32	33	29	24	17	11	6	3	1	0
$Q(L, 5/2)$	1	5	5	8	6	6	4	3	1	1	0	0	0

TABLE I. Value of the number of LS spectroscopic terms $Q(L, S)$ for the configuration d^2f^3 and three values of S : $1/2$, $3/2$, and $5/2$. The total degeneracy of d^2f^3 is $\binom{10}{2}\binom{14}{3} = 16380$, the maximum orbital angular momentum is $L_{\max}=12$ and the maximum spin $S_{\max}=5/2$. The correctness of the results can be checked using $\sum_{M_L, M_S} P(M_L, M_S) = 16380$ and $\sum_{L, S} (2L + 1)(2S + 1)Q(L, S) = 16380$. The total number of LS spectroscopic terms is $\sum_{L, S} Q(L, S) = 561$.

Table I provides values of $Q(L, S)$ for the d^2f^3 configuration and $S=1/2, 3/2$ and $5/2$. For fixed S , $Q(L, S)$ has a truncated bell shape.

We may estimate the number of operations needed to obtain the whole set of $P(M_L, M_S)$ values in a ℓ^N subshell. The brute-force technique consists in evaluating all the

$$N_{\text{bf}} = \binom{4\ell + 2}{N} \quad (8)$$

N -tuple elements and compute the sums $\sum_{i=1}^N m_{\ell, i}$ and $\sum_{i=1}^N m_{s, i}$ for each of them. The much better alternative provided by the recurrence (5) amounts to perform roughly

$$N_{\text{Eq.(5)}} = N(4\ell + 2)(2M_{L,\max} + 1)(2M_{S,\max} + 1) \quad (9)$$

operations: (number of one-electron states) \times (number of electrons) \times (number of values of M_L) \times (number of values of M_S). Thus, if $N \leq 2\ell + 1$:

$$N_{\text{Eq.(5)}} = N(N + 1)(4\ell + 2) \left[\frac{(-1)^N + 3 + 2N(4\ell + 2 - N)}{4} \right] \quad (10)$$

and if $N \geq 2\ell + 1$

$$N_{\text{Eq.(5)}} = N(4\ell + 3 - N)(4\ell + 2) \left[\frac{(-1)^N + 3 + 2N(4\ell + 2 - N)}{4} \right]. \quad (11)$$

For a half-filled subshell, one has

$$N_{\text{Eq.(5)}} = 4(\ell + 1)(2\ell + 1)^2 [2\ell(\ell + 1) + 1]. \quad (12)$$

ℓ	0	1	2	3	4	5	6	7	8
$N_{\text{Eq.(5)}}$	4	360	3900	19600	66420	177144	402220	813600	1508580
N_{bf}	2	20	252	3432	48620	705432	10400600	155117520	2333606220

TABLE II. Number of operations needed to obtain the $P(M_L, M_S)$ distribution for the ℓ^N configuration with $N = 2\ell + 1$, using a brute-force technique or recurrence relation (5).

Table II shows the number of operations needed to obtain the $P(M_L, M_S)$ distribution for the ℓ^N configuration with $N = 2\ell + 1$, using a brute-force technique or recurrence relation (5). We can see that for $\ell > 4$, the recurrence relation becomes much more efficient than the direct calculation.

III. THE TWO-VARIABLE GENERATING FUNCTION FOR THE CUMULANTS OF THE (M_L, M_S) JOINT DISTRIBUTION

A. Definition

As stated in statistical treatises [31], the whole information about the distribution $P(M_L, M_S)$ of magnetic quantum number is contained in the exponential of the cumulant generating function defined as

$$\exp(K(u, v)) = \langle \exp(uM_L + vM_S) \rangle = \sum_{M_L, M_S} P(M_L, M_S) e^{uM_L + vM_S} \Big/ \sum_{M_L, M_S} P(M_L, M_S). \quad (13)$$

From the Pauli exclusion principle this normalization factor is given by the binomial coefficient

$$\sum_{M_L, M_S} P(M_L, M_S) = \binom{4\ell + 2}{N}. \quad (14)$$

The numerator of the cumulant generating function of the distribution $P(M_L, M_S)$ reads

$$s(N, \ell, u, v) = \sum_{M_L, M_S} P(M_L, M_S) e^{uM_L} e^{vM_S} = \binom{4\ell + 2}{N} \exp(K(u, v)), \quad (15)$$

and will be, for simplicity, referred to as the “generating function” in the following.

B. Cumulant generating function for the first values of N

The $N = 1$ value is given by

$$s(1, \ell, u, v) = \sum_{m_\ell = -\ell}^{\ell} \sum_{m_s = -1/2}^{1/2} e^{m_\ell u} e^{m_s v} = 2 \frac{\sinh[(2\ell + 1)u/2]}{\sinh(u/2)} \cosh(v/2). \quad (16)$$

The generating function in the case of two fermions reads

$$\begin{aligned} s(2, \ell, u, v) &= \frac{1}{2} \left[\sum_{k=1}^g e^{m_{\ell, k} u} e^{m_{s, k} v} \sum_{i=1, i \neq k}^g e^{m_{\ell, i} u} e^{m_{s, i} v} \right] = \frac{1}{2} \left[\sum_{k=1}^g e^{m_{\ell, k} u} e^{m_{s, k} v} \left(\sum_{i=1}^g e^{m_{\ell, i} u} e^{m_{s, i} v} - e^{m_{\ell, k} u} e^{m_{s, k} v} \right) \right] \\ &= \frac{1}{2} \left[\left(\sum_{k=1}^g e^{m_{\ell, k} u} e^{m_{s, k} v} \right)^2 - \sum_{k=1}^g e^{2m_{\ell, k} u} e^{2m_{s, k} v} \right] = \frac{1}{2} \left[\left(\sum_{k=1}^g e^{m_{\ell, k} u + m_{s, k} v} \right)^2 - \sum_{k=1}^g e^{2m_{\ell, k} u + 2m_{s, k} v} \right]. \end{aligned} \quad (17)$$

Let us set

$$\mathcal{S}_p = \sum_{k=1}^g e^{p(m_{\ell, k} u + m_{s, k} v)} = 2 \frac{\sinh[(2\ell + 1)pu/2]}{\sinh(pu/2)} \cosh(pv/2). \quad (18)$$

By comparison with Eq. (16), one can check that $\mathcal{S}_p = s(1, \ell, pu, pv)$. We have also

$$s(2, \ell, u, v) = \frac{1}{2} (\mathcal{S}_1^2 - \mathcal{S}_2), \quad (19)$$

and a similar calculation for $N = 3$ gives

$$s(3, \ell, u, v) = \frac{1}{6} (\mathcal{S}_1^3 - 3\mathcal{S}_1\mathcal{S}_2 + 2\mathcal{S}_3). \quad (20)$$

In the case of four fermions, a similar direct calculation yields

$$s(4, \ell, u, v) = \frac{1}{24} (\mathcal{S}_1^4 - 6\mathcal{S}_1^2\mathcal{S}_2 + 3\mathcal{S}_2^2 + 8\mathcal{S}_1\mathcal{S}_3 - 6\mathcal{S}_4). \quad (21)$$

C. Recurrence over the number of fermions for the cumulant generating function

The generating function can be expressed as a multiple summation over one-electron states

$$s(N, \ell, u, v) = \sum_{M_L, M_S} \sum_{p_1=0}^1 \sum_{p_2=0}^1 \cdots \sum_{p_g=0}^1 \delta \left(M_L - \sum_{k=1}^g p_k m_{\ell, k} \right) \delta \left(M_S - \sum_{k=1}^g p_k m_{s, k} \right) \delta \left(N - \sum_{k=1}^g p_k \right) e^{M_L u} e^{M_S v}, \quad (22)$$

where the sum over M_L and M_S may be eliminated

$$s(N, \ell, u, v) = \sum_{p_1=0}^1 \sum_{p_2=0}^1 \cdots \sum_{p_g=0}^1 \delta \left(N - \sum_{k=1}^g p_k \right) \exp \left(\sum_{k=1}^g p_k m_{\ell, k} u \right) \exp \left(\sum_{k=1}^g p_k m_{s, k} v \right). \quad (23)$$

In the above equations, for the sake of readability $\delta(Q)$ stands for the Kronecker symbol $\delta_{Q,0}$. Isolating in this multiple sum the contributions of the p_g index and then the p_1 index, repeating exactly the procedure used in Eq. (2.14) of [24], one gets the recurrence property on the generating function

$$s(N, \ell, u, v) = s(N, \ell - 1, u, v) + 2 \cosh(\ell u + v/2) s(N - 1, \ell - 1, u, v) + s(N - 2, \ell - 1, u, v). \quad (24)$$

The recurrence (24) is the same as for a single moment, *i.e.* (5.5) of Ref. [24]. Thus, in the present case, the recurrence over the number of fermions only is, *mutatis mutandis*,

$$s(N, \ell, u, v) = \frac{1}{N} \sum_{p=1}^N (-1)^{p+1} s(1, \ell, pu, pv) s(N - p, \ell, u, v), \quad (25)$$

with $s(0, \ell, u, v) = 1$. The case of a general spin (non necessarily 1/2), *i.e.*, the generalization to a pair of arbitrary angular momenta, is discussed in appendix A.

D. General expression of the generating function

Let x_1, \dots, x_n be variables and denote for $k \geq 1$ by $p_k(x_1, \dots, x_n)$ the k -th power sum:

$$p_k(x_1, \dots, x_n) = \sum_{i=1}^n x_i^k = x_1^k + \cdots + x_n^k, \quad (26)$$

and for $k \geq 0$ denote by $e_k(x_1, \dots, x_n)$ the elementary symmetric polynomial (that is, the sum of all distinct products of k distinct variables). One has

$$e_k(x_1, \dots, x_n) = \sum_{1 \leq i_1 < i_2 < \cdots < i_k \leq n} x_{i_1} x_{i_2} \cdots x_{i_k}, \quad (27)$$

and $e_0 = 1, e_k = 0$ if $k > n$. The Newton-Girard identities can be stated as (see for instance Refs. [32–34]):

$$k e_k(x_1, \dots, x_n) = \sum_{i=1}^k (-1)^{i-1} e_{k-i}(x_1, \dots, x_n) p_i(x_1, \dots, x_n), \quad (28)$$

valid for all $n \geq 1$ and $n \geq k \geq 1$. It can be shown that

$$e_n = (-1)^n \sum_{\substack{m_1+2m_2+\cdots+nm_n=n \\ m_1 \geq 0, \dots, m_n \geq 0}} \prod_{i=1}^n \frac{(-p_i)^{m_i}}{m_i! i^{m_i}}. \quad (29)$$

Our recurrence relation over the number of fermions (25) is the same as Eq. (28), making the replacements $e_N \rightarrow s(N, \ell, u, v)$ and $p_i \rightarrow \mathcal{S}_i$. For the N -fermion case, we have therefore, *mutatis mutandis*, the general expression

$$s(N, \ell, u, v) = (-1)^N \sum_{\vec{q}/q_1+2q_2+\dots+Nq_N=N} \prod_{p=1}^N \frac{1}{q_p!} \left(-\frac{\mathcal{S}_p}{p} \right)^{q_p}, \quad (30)$$

where \vec{q} stands for the N -fold set (q_1, q_2, \dots, q_N) and with

$$\mathcal{S}_p = 2 \frac{\sinh[(2\ell + 1)pu/2]}{\sinh(pu/2)} \cosh(pv/2). \quad (31)$$

A more detailed proof is provided in appendix B. The numerical implementation of Eq. (30) requires the numerical determination of partitions of an integer.

In addition, the cumulant generating function $s(N, \ell, u, v)$ itself can be expressed in terms of incomplete Bell polynomials $B_{n,k}$. One has

$$s(N, \ell, u, v) = \frac{1}{N!} \sum_{k=1}^N B_{N,k}(\mathcal{S}_1, -\mathcal{S}_2, \dots, (-1)^{p-1}(p-1)!\mathcal{S}_p, \dots, (-1)^{N-k}(N-k)!\mathcal{S}_{N-k+1}) \quad (32)$$

where

$$B_{n,k}(x_1, x_2, \dots, x_{n-k+1}) = \sum \frac{n!}{j_1!j_2!\dots j_{n-k+1}!} \left(\frac{x_1}{1!} \right)^{j_1} \left(\frac{x_2}{2!} \right)^{j_2} \dots \left(\frac{x_{n-k+1}}{(n-k+1)!} \right)^{j_{n-k+1}}, \quad (33)$$

the sum running over all ensembles of integers $j_1, j_2, \dots, j_{n-k+1}$ such that $j_1 + j_2 + \dots + j_{n-k+1} = k$ and $j_1 + 2j_2 + 3j_3 + \dots + (n-k+1)j_{n-k+1} = n$.

IV. DETERMINATION OF THE FIRST MOMENTS FOR 2 AND 3 FERMIONS

The expansion of $s(N, \ell, u, v)/\binom{4\ell+2}{N}$ at $(u=0, v=0)$ provides the moments $\mu_{m,n}$. The moments $\mu_{m,n}$ are defined by the expansion

$$M(u, v) = e^{K(u,v)} = \sum_{m,n=0}^{\infty} \mu_{m,n} \frac{u^m v^n}{m!n!}, \quad (34)$$

where $M(u, v)$ is proportional to the generating function defined by Eq. (15). The formulas of the moments can be obtained easily using a computer algebra system, such as Mathematica.

A. Moments for $N = 2$

For $N = 2$, one has

$$s(2, \ell, u, v) = \frac{\sinh[(2\ell + 1)u/2]}{\sinh(u/2) \sinh u} \{ (1 + 2 \cosh v) \sinh(\ell u) + \sinh[(\ell + 1)u] \}. \quad (35)$$

The expressions of the moments as functions of ℓ for $N = 2$ and $m = 0, 2$, are given in Table III.

For $m = 4$, one has, t being any positive integer,

$$\mu_{4,0}(\ell^2) = \frac{4\ell(\ell + 1)(16\ell^3 + 12\ell^2 - 6\ell + 3)}{15(4\ell + 1)}, \quad (36a)$$

$$\mu_{4,2t}(\ell^2) = \frac{2\ell(\ell + 1)(2\ell - 1)(8\ell^2 + 4\ell - 7)}{15(4\ell + 1)}. \quad (36b)$$

m	$n = 0$	$n = 2t$
0	1	$\frac{2\ell}{(4\ell + 1)}$
2	$\frac{8\ell^2(\ell + 1)}{3(4\ell + 1)}$	$\frac{2\ell(\ell + 1)(2\ell - 1)}{3(4\ell + 1)}$

TABLE III. Expressions of the moments $\mu_{m,n}$ for $N = 2$, $m = 0, 2$ and $n = 2t$ with $t > 0$. The moments $\mu_{n,2t}$ are independent of t if $t > 0$.

It is easy to show that $\mu_{2s,2t}$ is independent of $t > 0$ in the two-electron case. Indeed, one has then $S = 0$ or 1 , so that $M_S = 0, \pm 1$ and $M_S^{2t} = M_S^2$ does not depend on t , the same property being valid for $\mu_{4,2t}$. For $n = 6$, t being again any positive integer, one gets

$$\mu_{6,0}(\ell^2) = \frac{4\ell(\ell + 1)(48\ell^5 + 72\ell^4 - 20\ell^3 - 6\ell^2 + 40\ell - 15)}{21(4\ell + 1)}, \quad (37a)$$

$$\mu_{6,2t}(\ell^2) = \frac{2\ell(\ell + 1)(2\ell - 1)(24\ell^4 + 24\ell^3 - 46\ell^2 - 26\ell + 31)}{21(4\ell + 1)}, \quad (37b)$$

and $\mu_{m,n}(\ell^2) = 0$ if n is odd.

B. Moments for $N = 3$

The general expressions of moments for $N = 3$ are more cumbersome. One has

$$s(3, \ell, u, v) = \frac{\sinh(\ell u) \sinh[(2\ell + 1)u/2] \sinh((\ell + 1)u)}{\sinh(u/2) \sinh(u) \sinh(3u/2)} U_1(\cosh(u/2)) U_1(\cosh(v/2)) \\ + \frac{\sinh((2\ell - 1)u/2) \sinh(\ell u) \sinh[(2\ell + 1)u/2]}{\sinh(u/2) \sinh(u) \sinh(3u/2)} U_3(\cosh(v/2)), \quad (38)$$

where U_n is the Chebyshev polynomial of the second kind of order n . Explicitly, one has $U_1(X) = 2X$, $U_3(X) = 8X^3 - 4X$. The expressions of the moments as functions of ℓ for $N = 3$, $m = 0, 2$ and $n = 0, 2, 4$ are given in Table IV.

m	$n = 0$	$n = 2$	$n = 4$
0	1	$\frac{3(4\ell - 1)}{4(4\ell + 1)}$	$\frac{3(28\ell - 13)}{16(4\ell + 1)}$
2	$\frac{\ell(\ell + 1)(4\ell - 1)}{(4\ell + 1)}$	$\frac{(\ell + 1)(12\ell^2 - 13\ell + 4)}{4(4\ell + 1)}$	$\frac{(\ell + 1)(84\ell^2 - 121\ell + 40)}{16(4\ell + 1)}$

TABLE IV. Expressions of the moments $\mu_{m,n}$ for $N = 3$, $m = 0, 2$ and n varying from 0 to 4. The moments are zero if m or n is odd.

For $m = 4$, one has

$$\mu_{4,0}(\ell^3) = \frac{(\ell + 1)(52\ell^4 + 13\ell^3 - 35\ell^2 + 21\ell - 6)}{5(4\ell + 1)}, \quad (39a)$$

$$\mu_{4,2}(\ell^3) = \frac{(\ell + 1)(156\ell^4 - 143\ell^3 - 135\ell^2 + 249\ell - 82)}{20(4\ell + 1)}, \quad (39b)$$

$$\mu_{4,4}(\ell^3) = \frac{(\ell + 1)(1092\ell^4 - 1547\ell^3 - 1035\ell^2 + 2301\ell - 766)}{80(4\ell + 1)}, \quad (39c)$$

and $\mu_{m,n}(\ell^3) = 0$ if n is odd.

V. EXPRESSIONS OF THE FIRST CUMULANTS IN THE TWO- AND THREE-FERMION CASES

The cumulants $\kappa_{m,n}$ are obtained by expanding $\log(s(N, \ell, u, v)/\binom{4\ell+2}{N})$ at $(u = 0, v = 0)$.

A. Cumulants for $N = 2$

The expressions of the cumulants as functions of ℓ for $N = 2$, are given in Table V for $m = 0, 2$ and $n = 0, 2$ and 4.

m	$n = 0$	$n = 2$	$n = 4$
0	0	$\frac{2\ell}{4\ell + 1}$	$-\frac{2\ell(2\ell - 1)}{(4\ell + 1)^2}$
2	$\frac{8\ell^2(\ell + 1)}{3(4\ell + 1)}$	$-\frac{2\ell(\ell + 1)(2\ell + 1)}{3(4\ell + 1)^2}$	$\frac{2\ell(\ell + 1)(2\ell + 1)(8\ell - 1)}{3(4\ell + 1)^3}$

TABLE V. Expressions of the cumulants $\kappa_{m,n}$ for $N = 2$, $m = 0, 2$ and n varying from 0 to 4.

For $m = 4$, one has

$$\kappa_{4,0}(\ell^2) = -\frac{4\ell(\ell + 1)(2\ell - 1)(8\ell^3 + 12\ell^2 + 12\ell + 3)}{15(4\ell + 1)^2}, \quad (40a)$$

$$\kappa_{4,2}(\ell^2) = \frac{2\ell(\ell + 1)(2\ell + 1)(16\ell^3 + 12\ell + 7)}{15(4\ell + 1)^3}, \quad (40b)$$

$$\kappa_{4,4}(\ell^2) = -\frac{2\ell(\ell + 1)(2\ell + 1)(128\ell^4 + 104\ell^3 + 276\ell^2 + 104\ell - 7)}{15(4\ell + 1)^4}, \quad (40c)$$

and $\kappa_{m,n}(\ell^2) = 0$ if n is odd.

B. Cumulants for $N = 3$

The expressions of the cumulants as functions of ℓ for $N = 3$, are given in Table VI.

m	$n = 0$	$n = 2$	$n = 4$
0	0	$\frac{3(4\ell - 1)}{4(4\ell + 1)}$	$-\frac{3(16\ell^2 - 24\ell + 11)}{8(4\ell + 1)^2}$
2	$\frac{\ell(\ell + 1)(4\ell - 1)}{(4\ell + 1)}$	$-\frac{(\ell + 1)(4\ell^2 - 1)}{(4\ell + 1)^2}$	$\frac{(\ell + 1)(4\ell^2 - 1)(8\ell - 7)}{(4\ell + 1)^3}$

TABLE VI. Expressions of the cumulants $\kappa_{m,n}$ for $N = 3$, $m = 0, 2$ and n equal to 0, 2 and 4. The cumulants are zero if m or n is odd.

For $m = 4$, one has

$$\kappa_{4,0}(\ell^3) = -\frac{(\ell + 1)(32\ell^5 + 16\ell^4 + 22\ell^3 - 34\ell^2 + 3\ell + 6)}{5(4\ell + 1)^2}, \quad (41a)$$

$$\kappa_{4,2}(\ell^3) = \frac{(\ell + 1)(4\ell^2 - 1)(16\ell^3 + 8\ell^2 + 56\ell + 25)}{5(4\ell + 1)^3}, \quad (41b)$$

$$\kappa_{4,4}(\ell^3) = -\frac{(\ell + 1)(4\ell^2 - 1)(128\ell^4 + 312\ell^3 + 752\ell^2 - 282\ell - 265)}{5(4\ell + 1)^4}, \quad (41c)$$

and $\kappa_{m,n}(\ell^3) = 0$ if n is odd.

C. Relation between cumulants and moments for the first orders

The cumulants $\kappa_{m,n}$ are obtained from the expansion

$$K(u, v) = \sum_{m,n} \kappa_{m,n} \frac{u^m v^n}{m!n!}, \quad (42)$$

with $M(u, v) = \exp(K(u, v))$ (see Eq. (34)). For the M_L, M_S distribution the function K contains only even-order terms.

The relations between moments and cumulants in the bi-variate case can be obtained by the formal method devised by Kendall [35] and used by Cook [36] who provided tables. For $m + n \leq 6$ one gets

$$\kappa_{2,0} = \mu_{2,0}, \quad (43a)$$

$$\kappa_{4,0} = \mu_{4,0} - 3\mu_{2,0}^2, \quad (43b)$$

$$\kappa_{2,2} = \mu_{2,2} - \mu_{2,0}\mu_{0,2}, \quad (43c)$$

$$\kappa_{6,0} = \mu_{6,0} - 15\mu_{2,0}\mu_{4,0} + 30\mu_{2,0}^3, \quad (43d)$$

$$\kappa_{4,2} = \mu_{4,2} - \mu_{4,0}\mu_{0,2} - 6\mu_{2,0}\mu_{2,2} + 6\mu_{2,0}^2\mu_{0,2}. \quad (43e)$$

These relations are completed using the symmetry $m \leftrightarrow n$, e.g., $\kappa_{0,4} = \mu_{0,4} - 3\mu_{0,2}^2$, etc.

One can also express the moments $\mu_{m,n}$ as a function of cumulants

$$\mu_{4,0} = \kappa_{4,0} + 3\kappa_{2,0}^2, \quad (44a)$$

$$\mu_{2,2} = \kappa_{2,2} + \kappa_{2,0}\kappa_{0,2}, \quad (44b)$$

$$\mu_{6,0} = \kappa_{6,0} + 15\kappa_{2,0}\kappa_{4,0} + 15\kappa_{2,0}^3, \quad (44c)$$

$$\mu_{4,2} = \kappa_{4,2} + \kappa_{4,0}\kappa_{0,2} + 6\kappa_{2,0}\kappa_{2,2} + 3\kappa_{2,0}^2\kappa_{0,2}. \quad (44d)$$

VI. STATISTICAL MODELING OF THE $P(M_L, M_S)$ DISTRIBUTION USING GRAM-CHARLIER EXPANSION SERIES

A. Bi-variate Gram-Charlier series

The Gram-Charlier expansion was derived in an attempt to express non-Gaussian distributions as infinite series using the moments as input terms [37]. The one-dimensional Gram-Charlier series has been widely used in different fields of physics. For instance, it was successfully applied to the statistical modeling of transition arrays of absorption or emission lines in hot-plasma complex spectra, or of the distribution of angular momentum M_J in atomic configurations. The two-variable (or bi-variate) Gram-Charlier series are much less frequent in the literature. However, Kampé de Fériet [38] has provided formulas relevant for this case. If the two variables are uncorrelated (indeed we have here $\langle M_L M_S \rangle = 0$), these expressions become much simpler, and one has

$$\mathcal{G}_T(u, v) = \frac{e^{-u^2/2\sigma^2 - v^2/2\tau^2}}{2\pi\sigma\tau} \left[1 + \sum_{n=2}^T \sum_{j=0}^n c_{2n-2j, 2j} He_{2n-2j} \left(\frac{u}{\sigma} \right) He_{2j} \left(\frac{v}{\tau} \right) \right] \quad (45a)$$

$$\text{where } u = M_L, v = M_S. \quad (45b)$$

In the above equations, T is an arbitrary integer — hereafter called “half truncation order” — and $He_n(X)$ is the Hermite polynomial of order n [39]. The approximation $\mathcal{P}_T(u, v)$ for $P(M_L, M_S)$ is obtained by multiplying the function $\mathcal{G}_T(u, v)$ by the configuration degeneracy

$$\mathcal{P}_T(u, v) = \mathcal{N} \mathcal{G}_T(u, v) \quad \text{with } \mathcal{N} = \prod_{i=1}^w \binom{4\ell_i + 2}{p_i} \quad (46)$$

assuming that the configuration is made of w subshells of orbital momentum ℓ_i and population p_i . The two variances entering Eq. (45a) are given by $\sigma^2 = \kappa_{2,0}$ and $\tau^2 = \kappa_{0,2}$. In the present case, all the odd moments are zero

$$\langle u^{2p+1} \rangle = 0, \quad \langle v^{2q+1} \rangle = 0, \quad (47)$$

as well as $\langle u^{2p+1}v^n \rangle = 0$, $\langle u^m v^{2q+1} \rangle = 0$.

The global error on all M_L, M_S values may be characterized by the averages

$$\Delta_{\text{abs}}(T) = \left(\sum_{M_L, M_S} (\mathcal{P}_T(M_L, M_S) - P(M_L, M_S))^2 / (2L_{\text{max}} + 1)(2S_{\text{max}} + 1) \right)^{1/2}, \quad (48)$$

$$\Delta_{\text{rel}}(T) = \left(\sum'_{M_L, M_S} (\mathcal{P}_T(M_L, M_S)/P(M_L, M_S))^2 / N_{\text{pos}} \right)^{1/2}, \quad (49)$$

where the prime means that the sum is restricted to elements (M_L, M_S) for which $P(M_L, M_S) > 0$ and N_{pos} is the number of such elements. In the following discussion, we have chosen to compute both $\Delta_{\text{abs}}(T)$ and $\Delta_{\text{rel}}(T)$ since they convey different information. The absolute error is more sensitive to the differences where $P(M_L, M_S)$ is maximum, namely for M_L, M_S close to 0, while the relative error favors regions where $P(M_L, M_S)$ is small, namely $|M_L|$ and/or $|M_S|$ close to their maximum value. In the following, for simplicity reasons, the first data point in plots for such errors is at $T = 1$ which is identical to $T = 0$. As seen in Eq.(45a), if $T < 2$ the sum over n is absent and the Gram-Charlier approximation simplifies into the Gaussian expression.

B. Moments expressed as functions of Gram-Charlier coefficients

With the above expression (45a), one may express the various moments $\langle u^{2s}v^{2t} \rangle = \mu_{2s,2t}$ as a function of the Gram-Charlier coefficients $c_{2i,2j}$

$$\langle u^2 \rangle = \sigma^2, \quad (50a)$$

$$\langle u^2 v^2 \rangle = \sigma^2 \tau^2 (1 + 4c_{2,2}), \quad (50b)$$

$$\langle u^4 \rangle = 3\sigma^4 (1 + 8c_{4,0}), \quad (50c)$$

$$\langle u^4 v^2 \rangle = 3\sigma^4 \tau^2 (1 + 8c_{2,2} + 8c_{4,0} + 16c_{4,2}), \quad (50d)$$

$$\langle u^6 \rangle = 15\sigma^6 (1 + 24c_{4,0} + 48c_{6,0}), \quad (50e)$$

$$\langle u^4 v^4 \rangle = 9\sigma^4 \tau^4 (1 + 8c_{4,0} + 16c_{2,2} + 8c_{0,4} + 32c_{4,2} + 32c_{2,4} + 64c_{4,4}), \quad (50f)$$

$$\langle u^6 v^2 \rangle = 15\sigma^6 \tau^2 (1 + 12c_{2,2} + 24c_{4,0} + 48c_{4,2} + 48c_{6,0} + 96c_{6,2}), \quad (50g)$$

$$\langle u^8 \rangle = 105\sigma^8 (1 + 48c_{4,0} + 192c_{6,0} + 384c_{8,0}), \quad (50h)$$

together with expressions obtained by changing $u \leftrightarrow v$. Such formulas assume that T is sufficiently large, for instance if $T = 6$, the terms $c_{6,2}$, $c_{4,4}$ and $c_{8,0}$ are absent from the three above formulas.

It is possible to provide a general form of the moments from properties of the Hermite polynomials. We use the expansion (45a) and calculate the integral $\langle u^p v^q \rangle = \int_{-\infty}^{+\infty} du dv u^p v^q \mathcal{P}_T(u, v)$. Noting that

$$H e_n(x) = n! \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} \frac{(-1)^m}{m!(n-2m)!} \frac{x^{n-2m}}{2^m}, \quad (51)$$

where $\lfloor x \rfloor$ is the integer part of x , the calculation of the average of $u^p v^q$ boils down to the evaluation of simple integrals of the kind

$$\chi_p(\sigma) = \int_{-\infty}^{+\infty} du u^p e^{-u^2/2\sigma^2}. \quad (52)$$

If p is odd, one has $\chi_p(\sigma) = 0$. For $p = 2j$ one gets after basic algebra

$$\chi_{2j}(\sigma) = \sqrt{2\pi} \sigma^{2j+1} \frac{(2j)!}{2^j j!} \quad \text{if } p = 2j \text{ is even.} \quad (53)$$

From the distribution \mathcal{G}_T (45a), the expansion (51) and the above definition of χ , we get the average

$$\langle u^p v^q \rangle = \frac{1}{2\pi\sigma\tau} \left[\chi_p(\sigma)\chi_q(\tau) + \sum_{n=2}^T \sum_{j=0}^n c_{2n-2j,2j} \mathcal{Y}_{p,2n-2j}(\sigma) \mathcal{Y}_{q,2j}(\tau) \right] \quad (54)$$

with

$$\mathcal{V}_{m,n}(\sigma) = \int_{-\infty}^{+\infty} du u^m e^{-u^2/2\sigma^2} H e_n(u/\sigma). \quad (55)$$

Obviously $\mathcal{V}_{m,n}(\sigma) = 0$ if $m + n$ is odd. After basic algebraic manipulations, one gets $\mathcal{V}_{2s,2t}(\sigma) = 0$ if $s < t$, and

$$\mathcal{V}_{2s,2t}(\sigma) = \frac{(2\pi)^{1/2}(2s)!}{2^{s-t}(s-t)!} \sigma^{2s+1} \quad \text{if } s \geq t. \quad (56)$$

C. Gram-Charlier coefficients expressed in terms of averages

Using the orthogonality relation

$$\int_{-\infty}^{\infty} H e_m(x) H e_n(x) e^{-x^2/2} dx = \sqrt{2\pi} n! \delta_{n,m}, \quad (57)$$

we get, after multiplying Eq. (45a) by $H e_{2n-2j}(u/\sigma) H e_{2j}(v/\tau)$ and integrating over u, v ,

$$c_{2n-2j,2j} = \sum_{k=0}^{n-j} \sum_{r=0}^j \frac{(-1)^{k+r} \sigma^{2k-2n+2j} \tau^{2r-2j}}{2^{k+r} k! r! (2n-2j-2k)! (2j-2r)!} \langle u^{2n-2j-2k} v^{2j-2r} \rangle \quad (58)$$

or simplifying the notations

$$c_{2s,2t} = \sum_{m=0}^s \sum_{n=0}^t \frac{(-1)^{m+n} \sigma^{2m-2s} \tau^{2n-2t}}{2^{m+n} m! n! (2s-2m)! (2t-2n)!} \langle u^{2s-2m} v^{2t-2n} \rangle. \quad (59)$$

D. Test of the accuracy of the Gram-Charlier expansion in a single-subshell configuration

The Gram-Charlier expansion $\mathcal{P}_T(M_L, M_S)$ is first tested in the f^3 case in Fig. 1(a). The errors Δ_{abs} (48) and Δ_{rel} (49) are plotted as a function of the half truncation order T in Fig. 1(b). In what follows, the ‘‘Gaussian’’ approximation is provided by the factor before the brackets in Eq. (45a) multiplied by the configuration degeneracy, which is $\mathcal{N} = 364$ in the f^3 case. Using the Gaussian approximation amounts to set $T = 0$ or 1 in this formula, which cancels the sum over n .

We can see that the Gaussian distribution overestimates $P(M_L, M_S = 1/2)$ for small values of $|M_L|$, and that a fairly accurate description is obtained for $T = 2$ or 3 for all values of M_L . With $T = 6$, the agreement is comparable to the $T = 3$ case, which is confirmed by the occurrence of a plateau in the absolute and relative errors. Then the series starts to diverge (see the $T = 9$ case for instance), tending asymptotically (at least in the considered range of T values) to a relative error between 100 and 200 %. The absolute error may be scaled by noticing that the maximum value for the distribution P is reached if $M_L = 0, M_S = 1/2$, for which one has $P(0, 1/2) = 17$.

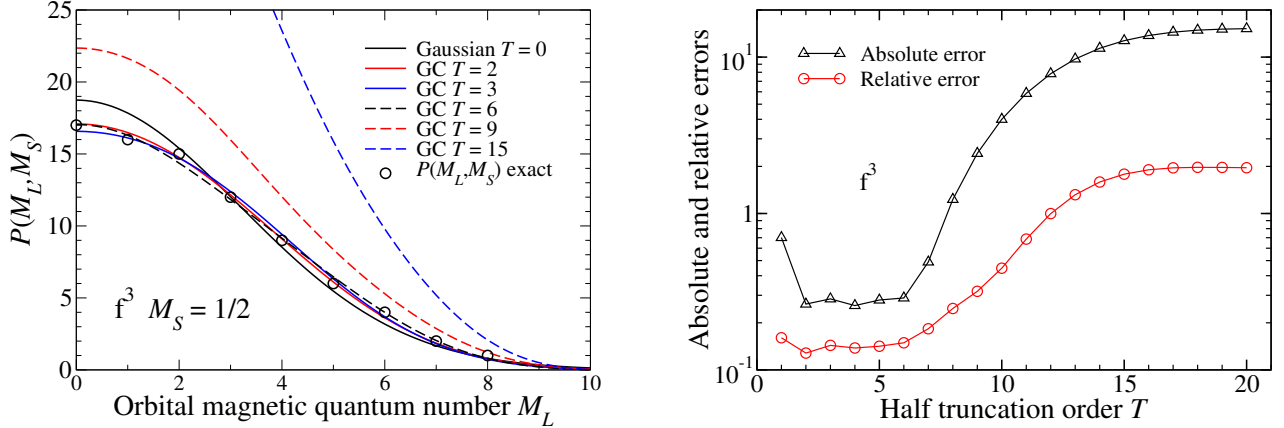
In addition to the errors $\Delta_{\text{abs}}(T), \Delta_{\text{rel}}(T)$, the accuracy of the Gram-Charlier representation at a given order can also be quantified by comparing the area of the latter expansion series to the quantity $\sum_{M_L} P(M_L, M_S)$. Let N_+ be the number of fermions with spin $m_s = 1/2$ and N_- the number of fermions with spin $m_s = -1/2$. We have $N_+ = N/2 + M_S$ and $N_- = N/2 - M_S$. Therefore, one obtains

$$G_{\ell,N}(M_S) \equiv \sum_{M_L} P(M_L, M_S) = \binom{2\ell+1}{N_+} \binom{2\ell+1}{N_-} = \binom{2\ell+1}{N/2+M_S} \binom{2\ell+1}{N/2-M_S}. \quad (60)$$

By simple algebraic manipulations, for instance using the generating-function formalism, we recover the Weyl-Paldus formula for the degeneracy at fixed spin S [40]:

$$G_{\ell,N}(S) - G_{\ell,N}(S+1) = \frac{2S+1}{2\ell+2} \binom{2\ell+2}{N/2-S} \binom{2\ell+2}{N/2+S+1}. \quad (61)$$

As an example, in the f^3 case, we have $s_{1/2} = \sum_{M_L} P(M_L, 1/2) = 147$ and $s_{3/2} = \sum_{M_L} P(M_L, 3/2) = 35$ and since $\sum_{M_L} P(M_L, M_S) = \sum_{M_L} P(M_L, -M_S)$, we recover the proper total degeneracy of configuration f^3 , namely



(a) Distribution $P(M_L, M_S = 1/2)$ as a function of M_L . The lines represent the Gram-Charlier expansion for $T=0, 2, 3, 6$ and $9, 15$, $2T$ being the order of the truncated series. Exact values exist only for integer values of M_L , $M_L \leq 8$.

(b) Absolute and relative errors — defined by Eqs. (48), (49) — on the distribution $P(M_L, M_S)$. In this plot and all the following error plots, the $T = 1$ data points correspond to the Gaussian approximation.

FIG. 1. Gram-Charlier analysis for the configuration f^3 .

$2(s_{1/2} + s_{3/2}) = 364 = \binom{4 \times 3 + 2}{3}$. The quantity (60) must be compared to the area of the statistical modeling by truncated Gram-Charlier expansion series (resulting from the orthogonality and normalization of Hermite polynomials):

$$\int_{-\infty}^{\infty} \mathcal{G}_T(u, v) du = \frac{e^{-v^2/2\tau^2}}{\sqrt{2\pi\tau}} \left[1 + \sum_{n=2}^T c_{0,2n} H e_{2n}(v/\tau) \right], \quad (62)$$

with

$$c_{0,2n} = \sum_{k=0}^n (-1)^k \frac{\tau^{2k-2n}}{2^k k! (2n-2k)!} \langle v^{2n-2k} \rangle. \quad (63)$$

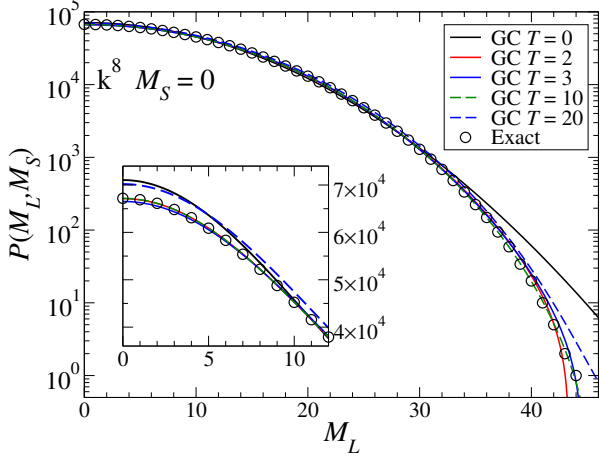
Table VII displays the area of the Gram-Charlier series (integrated between $M_L = -\infty$ and ∞) for different orders $2T$ in the cases $M_S = 1/2$ and $M_S = 3/2$. The right-hand side of Eq. (62) is multiplied by the total degeneracy $\binom{14}{3} = 364$.

$2T$	2	4	6	8	10	12	14	16
$M_S = 1/2$	149.697	147.439	147.485	146.606	145.466	147.342	155.585	172.071
$M_S = 3/2$	30.9650	34.3295	34.3410	35.3613	36.5085	35.1317	31.5573	29.0911

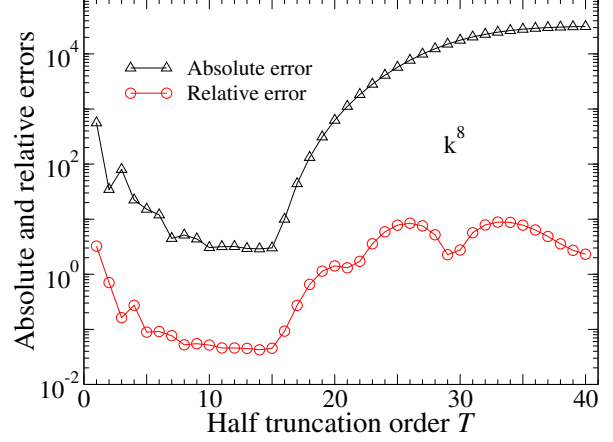
TABLE VII. Area of the Gram-Charlier series (integrated between $M_L = -\infty$ and ∞) in the case of the f^3 configuration for different orders $2T$ and $M_S = 1/2$ (second line) as well as $M_S = 3/2$ (third line). The values are obtained taking the right-hand side of Eq. (62) multiplied by the total degeneracy of f^3 , which is equal to 364. The exact value of $\sum_{M_L} P(M_L, 1/2)$ is 147 and the exact value of $\sum_{M_L} P(M_L, 3/2)$ is 35.

In order to demonstrate how the approximation improves for a greater number of electrons, we have plotted in Figs. 2(a) and 2(b) the corresponding Gram-Charlier data for the configuration k^8 ($\ell = 7$). Looking at the $M_S = 0$ data in Fig. 2(a), we notice that the lowest order $T = 0$, i.e., the simple Gaussian factor in Eq. (45a), provides an acceptable approximation only if $10 < M_L < 35$. The $T = 2$ approximation is correct over the whole range, except for $M_L \geq 43$. The $T = 3$ approximation performs quite well over the whole M_L range (though being one per-cent too low for $M_L = 0$, while $T = 2$ and 4 are then accurate at the per-thousand level). When T increases up to 15, the distribution is almost T -independent: the $T = 10$ and 15 data would be indistinguishable at Fig. 2(a) drawing accuracy. For greater T values the approximation quality deteriorates for any M_L value as seen on the $T = 20$ curve.

Looking into more detail, the absolute and relative errors plotted in Fig. 2(b) significantly decrease for $T < 10$, while the relative error was almost constant for $1 < T < 6$ in the f^3 case. For $T > 15$, as seen on Fig. 2(b), the series begins to diverge, and including more terms may result in a poorer approximation. This observation is similar to the one made for single-variable Gram-Charlier series [24].



(a) Gram-Charlier approximation and exact values of $P(M_L, M_S = 0)$ in semi-log coordinates. The inset shows an enlarged view of the $M_L \leq 12$ region, in linear coordinates. In this region the curves labeled $T = 2$ and 10 are indistinguishable at the drawing accuracy.



(b) Error defined by Eq. (48,49) on the distribution $P(M_L, M_S)$. The absolute error (48) may be scaled by the maximum value $P(M_L = 0, M_S = 0) = 67189$. As above the $T = 1$ value is by convention the Gaussian approximation.

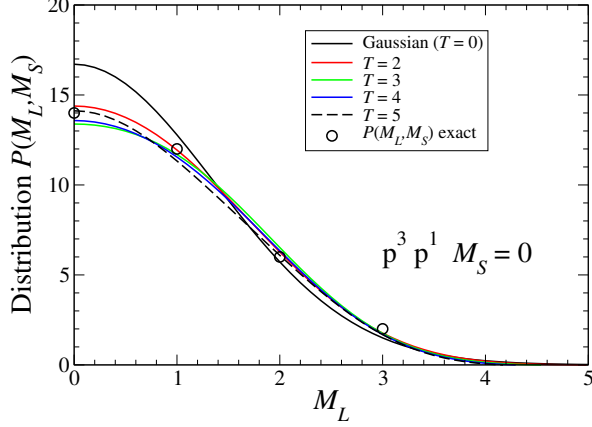
FIG. 2. Gram-Charlier analysis for the configuration k^8 .

E. Accuracy of the Gram-Charlier expansion in a multiple-subshell configuration

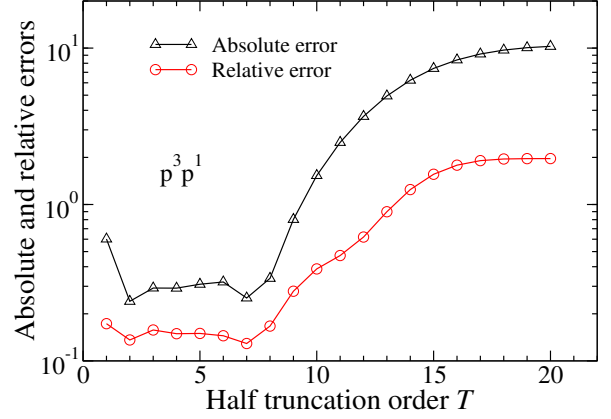
As is well known the interest of cumulants is that they are additive, e.g., the cumulants of the configuration p^2d^3 are the sums of the cumulants of p^2 and d^3 configurations. One may then use the above mentioned values of single-subshell cumulants.

As a first example of multiple-subshell configuration, we present on Fig. 3(a) the Gram-Charlier approximation of $P(M_L, M_S = 0)$ in the case of the configuration p^3p^1 , i.e., containing 3 equivalent p electrons and another p electron on a distinct subshell, as in $2p^33p$. The curve labeled as $T = 0$ corresponds to the plain Gaussian bi-variate function, as given by Eq. (46) where \mathcal{G}_T is replaced by the factor in front of the brackets in Eq. (45a). The curves labeled as $T = 2, 3, 4, 5$ correspond to the various corrections appearing in the series. In this case, we note that the $T = 2$ correction improves the quality of the distribution, while taking into account higher orders does not bring significant changes. This plot displays clear similarities with the f^3 case (Fig. 1(a)). Comparing the absolute errors in Figs. 1(b) and 3(b), we note that in the both cases the plateau $T = 2-7$ is about 3 times below the $T = 1$ (Gaussian) value. The relative error levels off at about 0.15 for $T < 8$ values, while it increases up to $\Delta_{\text{rel}} \simeq 2$ for large T .

Since it is useful to consider configurations with a greater number of electrons we show on Fig. 4(a) the Gram-Charlier analysis in the 5-subshell case $sp^3d^5f^7g^9$. One observes that for this 25-electron configuration, the Gram-Charlier series performs more efficiently than in the 4-electron case p^3p^1 considered above. Noticeably, the $T = 3$ (respectively 4) truncation provides a poor approximation of $P(M_L, M_S)$ if $M_L \geq 33$ (respectively 34) while greater T -values lead to a more acceptable representation. For instance the $T = 10$ and 15 curves are almost superimposed at the drawing accuracy, but the latter approximation is better for the maximum value $M_L = 40$. One has then $P(40, 1/2) = 10$, to be compared to 32.94, 12.46, and 10.16 for $T = 10, 15,$ and 20 respectively. Looking at absolute and relative errors in Fig. 4(b), we observe that increasing T from 1 to 15 results in an improvement in the Gram-Charlier approximation by 4 orders of magnitude. This is even better than in the k^8 case (Fig. 2(b)) where the error was only lowered by a factor of ~ 100 . As mentioned in the caption, when assessing the quality of the present approximation, one must compare the absolute error with a plateau at about 600 to the maximum value $P(M_L, M_S) < 1.83 \times 10^{10}$. In the present case for $T > 32$ the series begins to diverge, though we did not explore



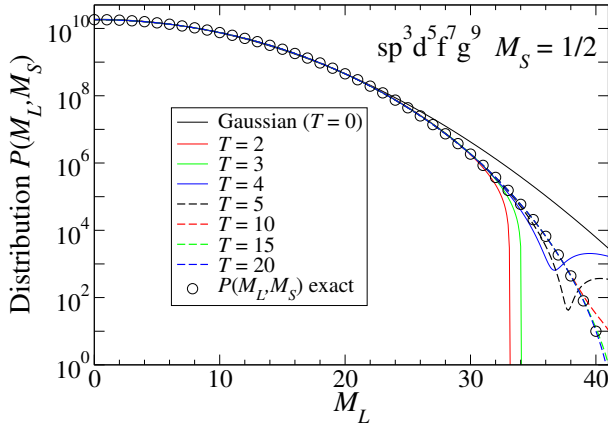
(a) Gram-Charlier approximations (solid lines) and exact values (circles) of the distribution $P(M_L, M_S = 0)$.



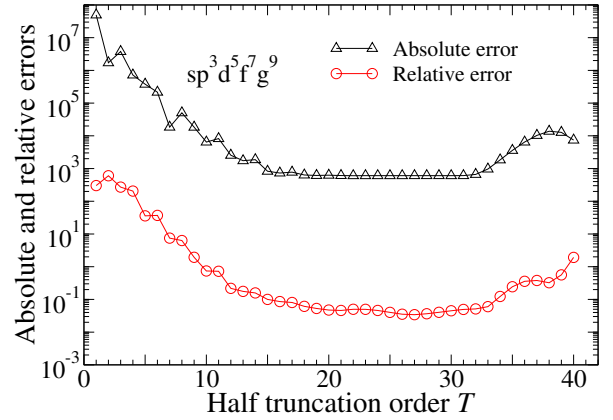
(b) Error defined by Eqs. (48), (49) on the distribution $P(M_L, M_S = 0)$. The absolute error (48) may be scaled knowing that $P(M_L = 0, M_S = 0) = 14$. The $T = 1$ data correspond to the Gaussian case.

FIG. 3. Gram-Charlier analysis for the 2-subshell configuration $p^3 p^1$.

its behavior for very large T . Finally one may notice that one has $\Delta_{\text{rel}}(T) > 0.03$ even in the most favorable case $T \sim 20$, which is due to the approximation for $P(M_L = 40, M_S)$ which is of moderate quality.



(a) Gram-Charlier approximations (lines) and exact values (circles) of the distribution $P(M_L, M_S = 1/2)$. The various curves correspond to various half truncation orders T in the Gram-Charlier series.

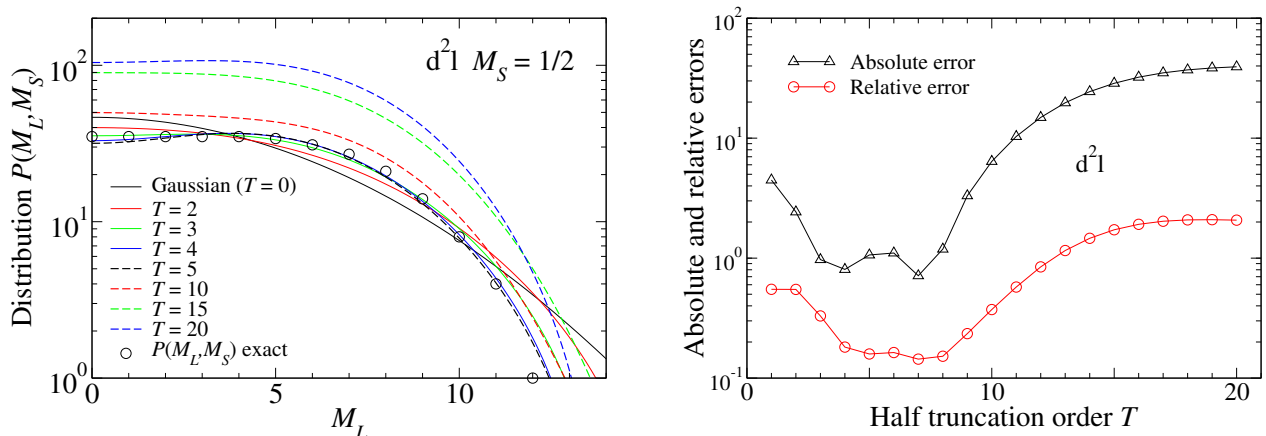


(b) Absolute and relative errors defined by Eqs. (48), (49) of the distribution $P(M_L, M_S = 1/2)$. The absolute error may be scaled noting that $P(M_L = 0, M_S = 1/2) = 1.8297912590 \times 10^{10}$.

FIG. 4. Gram-Charlier analysis for the configuration $sp^3 d^5 f^7 g^9$.

As a last example, we may analyze the two-subshell case $d^2 1$, i.e., with two $\ell = 2$ electrons and a single $\ell = 8$ electron. As noticed before [20], when a configuration contains several low- ℓ electrons together with a large- ℓ electron, the momentum distribution exhibits a wide plateau in its center. This case is analyzed in Figs. 5(a) and 5(b). As expected, one observes that the Gaussian approximation $T = 1$ is a poor representation of the exact $P(M_L, M_S = 1/2)$ distribution. Nevertheless higher-order values such as $T \simeq 5$ provide an acceptable approximation of the whole-range distribution. Looking at the absolute and relative errors in Fig. 5(b), we notice that, as in the previous cases with few electrons (f^3 , $p^3 p^1$), the $T \simeq 5$ expansion improves the simple Gaussian value by less than an order of magnitude. However in the present case, increasing T from 1 to 5 results in a decrease of Δ_{rel} by a factor greater than 3, while

the improvement was mostly negligible in the the f^3 case or in the p^3p^1 case, as seen on Fig. 1(b) or Fig. 3(b)).



(a) Gram-Charlier approximations (lines) and exact values (circles) of the distribution $P(M_L, M_S = 1/2)$. (b) Absolute and relative errors defined by Eqs. (48), (49) on the distribution $P(M_L, M_S)$. The absolute error may be scaled noting that $P(M_L, M_S = 1/2) = 35$ if $|M_L| \leq 4$.

FIG. 5. Gram-Charlier analysis for the configuration $d^2 1$ (two electrons $\ell = 2$, one electron $\ell = 8$).

VII. CONCLUSION

In this paper we have shown that the distribution of (M_L, M_S) magnetic quantum numbers, from which the number of LS spectroscopic terms $Q(L, S)$ is deduced, can be obtained numerically using an efficient recurrence relation generalizing the one described in Ref. [20] for J and M_J . A recurrence relation for the two-variable generating function of the cumulants of the (M_L, M_S) joint distribution was derived, together with an explicit form involving simple partitions. The relation was also extended to the case where the second angular momentum (spin in atomic physics, isospin in nuclear physics) is not necessarily equal to $1/2$ (i.e., for two arbitrary angular momenta). Based on an analogy with the Newton-Girard identities for elementary symmetric polynomials, an explicit formula for the cumulant generating function was also provided. A bi-variate Gram-Charlier expansion has been proposed to provide an analytical approximation for the $P(M_L, M_S)$ distribution. It has been checked that such expansion with few terms included is particularly efficient for configurations with a large number of electrons. Such series with less than a dozen terms may even represent the momentum distribution even for configuration with few electrons in an acceptable way, even in special cases where the $P(M_L, M_S)$ distribution exhibits a wide plateau. Nevertheless as for the single-variable $P(M_J)$ case studied in previous works, it turns out that the Gram-Charlier series diverges, with an onset of this divergence for a number of terms increasing with the total number of electrons in the configuration. The Gram-Charlier-series modeling of $P(M_L, M_S)$ makes it possible to estimate quite accurately the number of lines between two non-relativistic configurations. Such a number is important for the computation of hot-plasma radiative opacity, in particular when combining statistical methods [8] and fine-structure calculations.

Appendix A: Recurrence over the number of fermions for the cumulant generating function: case of a general spin

The recurrence relation for generating functions can be rewritten with minor changes in the case where the fermions are characterized by two moments j_u, j_v , the case of the present work corresponding to $j_u = \ell$ and $j_v = 1/2$. This seems rather formal in an atomic-physics framework, but enables one to deal with the $3/2$ isospin case, relevant in particle physics (see for instance Ref. [41]). Indeed for any “orbital momentum” j_u and “spin momentum” j_v , the *single-particle* generating function for arguments (u, v) is easy to obtain, as shown in this Appendix.

To each fermion is attributed a pair of indices (μ_i, ν_i) where μ_i is the “orbital” (respectively spin-orbital) magnetic quantum number and ν_i the “generalized-spin” magnetic quantum number (respectively the isospin projection) of

fermion i in the atomic-physics (respectively nuclear-physics) case. The composite index becomes

$$\xi_i = (2j_v + 1)\mu_i + \nu_i + 2j_u j_v + j_u + j_v + 1 \text{ with } -j_u \leq \mu_i \leq j_u \text{ and } -j_v \leq \nu_i \leq j_v, \quad (\text{A1})$$

where j_u denotes the ‘‘orbital momentum’’ and j_v the ‘‘spin’’. The index ξ_i varies from 1 to $(2j_u + 1)(2j_v + 1)$. The proof is similar to the $1/2$ -spin case. Because of the Pauli exclusion principle, all the ξ_i coefficients of fermions of a configuration (respectively subshell) are distinct.

The two-variable generating function $s(N, j_u, j_v, u, v)$ — we add an additional argument to the s function considered in Sec. III since two moments are involved now — can be put in a compact form relating the $N = 1$ case to the $N > 1$ case. This can be derived in a similar way as Eq. (25). One obtains

$$s(N, j_u, j_v, u, v) = \frac{1}{N} \sum_{p=1}^N (-1)^{p+1} s(N-p, j_u, j_v, u, v) s(1, j_u, j_v, pu, pv). \quad (\text{A2})$$

The one-fermion generating function can be obtained from the generalization of Eq. (16):

$$s(1, j_u, j_v, u, v) = \sum_{|\mu_1| \leq j_u, |\nu_1| \leq j_v} e^{\mu_1 u + \nu_1 v} = \sum_{\mu_1} e^{\mu_1 u} \sum_{\nu_1} e^{\nu_1 v} = \frac{\sinh[(j_u + 1/2)u]}{\sinh(u/2)} \cdot \frac{\sinh[(j_v + 1/2)v]}{\sinh(v/2)} \quad (\text{A3})$$

and the second factor of Eq. (A3) is, as expected, equal to $2 \cosh(v/2)$ if $j_v = 1/2$.

The single-momentum case is recovered setting $j_v = 0$ which shows that the formula remains valid for a single momentum $j = j_u$.

Appendix B: Newton-Girard identities and explicit formula for the cumulant generating function

The cumulant generating function reads

$$s(k, \ell, u, v) = \sum_{1 \leq i_1 < i_2 < \dots < i_k \leq N} X_{i_1} X_{i_2} \dots X_{i_k}, \quad (\text{B1})$$

with $X_i = e^{(m_{\ell, i} u + m_{s, i} v)}$ and $s(0, \ell, u, v) = 1$. Let us calculate the generating function

$$\Xi = \sum_{0 \leq k \leq \infty} s(k, \ell, u, v) t^k, \quad (\text{B2})$$

noting that in fact the latter summation is finite, since $s(k, \ell, u, v) = 0$ if $k > n$. One has, identifying the coefficients of the t^k terms:

$$\Xi = \prod_{1 \leq i \leq N} (1 + X_i t). \quad (\text{B3})$$

Indeed, in the products of the N factors above, the t^k term is the sum of the $\binom{N}{k}$ products of k factors $X_{i_1} X_{i_2} \dots X_{i_k}$, with $1 \leq i_1 < i_2 < \dots < i_k \leq N$. Let us rewrite (B3) in the form

$$\Xi = \prod_{1 \leq i \leq N} \exp[\log(1 + X_i t)] = \exp \left[\sum_{1 \leq i \leq N} \log(1 + X_i t) \right]. \quad (\text{B4})$$

With the expansion $\log(1+x) = x - x^2/2 + x^3/3 + \dots$ convergent if $|x| < 1$, one gets, if $|\max(X_i)t| < 1$ (for analyticity reasons, the expansion remains actually valid whatever the modulus of t),

$$\Xi = \exp \left(\sum_{1 \leq i \leq n} \sum_{s=1}^{\infty} \frac{(-1)^{s-1}}{s} X_i^s t^s \right) = \exp \left(\sum_{s=1}^{\infty} (-1)^{s-1} \frac{\mathcal{S}_s}{s} t^s \right) = \sum_{m=0}^{\infty} \frac{1}{m!} \left(\sum_{s=1}^{\infty} (-1)^{s-1} \frac{\mathcal{S}_s}{s} t^s \right)^m, \quad (\text{B5})$$

with

$$\mathcal{S}_k = \sum_{1 \leq i \leq N} X_i^k. \quad (\text{B6})$$

The m -th power in the sum may be computed with the identity used in our previous work [42] (see also section 24.1.2 in Ref. [39]):

$$\frac{1}{m!} \left(\sum_{N=1}^{\infty} x_n \frac{t^N}{N!} \right)^m = \sum_{N=m}^{\infty} t^N \sum_{a_1, a_2, \dots, a_N} \prod_{1 \leq j \leq N} \frac{(x_j/j!)^{a_j}}{a_j!} \quad (\text{B7})$$

involving the partition number $\mathcal{P}(N; a_1, \dots, a_N)$, and where integer indices a_1, a_2, \dots, a_N are constrained by

$$\begin{aligned} a_1 + a_2 + \dots + a_N &= m \\ a_1 + 2a_2 + \dots + Na_N &= N. \end{aligned} \quad (\text{B8})$$

With the substitution $x_j/j! \rightarrow (-1)^{j-1} \mathcal{S}_j/j$, the new expression of the expansion of the generating function Ξ (see Eq. (B5)) reads

$$\Xi = \sum_{m=0}^{\infty} \sum_{N=m}^{\infty} t^N \sum_{a_1, a_2, \dots} a_N \prod_{j=1}^N \frac{[(-1)^{j-1} \mathcal{S}_j/j]^{a_j}}{a_j!} \quad (\text{B9})$$

where the a_i satisfy the constraints (B8). In the above expression, the double sum over m, N can be replaced by a single sum over N , and it remains

$$\Xi = \sum_{N=0}^{\infty} (-1)^N t^N \sum_{a_1, a_2, \dots, a_N} \prod_{j=1}^N \frac{(-\mathcal{S}_j/j)^{a_j}}{a_j!}, \quad (\text{B10})$$

where because of constraint (B8), we replaced the product of factors $(-1)^{ja_j}$ by $(-1)^N$. This gives

$$s(N, \ell, u, v) = (-1)^N \sum_{\substack{a_1, a_2, \dots, a_N \\ a_1 + 2a_2 + \dots + Na_N = N}} \prod_{j=1}^N \frac{(-\mathcal{S}_j/j)^{a_j}}{a_j!}. \quad (\text{B11})$$

A similar proof was given by Richter [43]. Setting

$$f(t) = \sum_{k=0}^N s(k, \ell, u, v) t^k, \quad g(t) = \sum_{k=0}^{\infty} \mathcal{S}_k t^k, \quad \text{with } f(0) = N, \quad g(0) = \mathcal{S}_0 = N, \quad (\text{B12})$$

one can check easily that $g(t) = N - tf'(t)/f(t)$. Indeed, as we have seen, $f(t) = \prod_{j=1}^N (1 + X_j t)$, and thus the logarithmic derivative can be reformulated with the Taylor expansion of $1/(1 + X)$,

$$\frac{f'(t)}{f(t)} = \sum_j \frac{X_j}{1 + X_j t} = \sum_{j=1}^N X_j \sum_{k=0}^{\infty} (-1)^k X_j^k t^k = -\frac{1}{t} \sum_{k=0}^{\infty} (-1)^{k+1} \mathcal{S}_{k+1} t^{k+1} = -\frac{g(t) - N}{t} \quad (\text{B13})$$

which, by integration, yields Eq. (B5). The proof ends up as above by expanding the exponential.

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