

Stable method for the calculation of partition functions in the superconfiguration approach

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A general method for the calculation of the partition function of a canonical ensemble of noninteracting bound electrons is presented. It consists in a doubly recursive procedure with respect to the number of electrons and the number of orbitals. Contrary to existing approaches, this recursion relation contains no alternate summation of positive and negative numbers, which was the main source of numerical uncertainties. It is accompanied with a normalization of partition function through the determination of a free parameter consistent with the zeroth-order saddle-point approximation. The recursion relation allows one to calculate accurately partition functions for ions with a large number of orbitals, and is therefore important for calculations relying on the superconfiguration approximation.

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I. INTRODUCTION

In hot and dense plasmas of intermediate or high- Z element, atomic-physics calculations using a detailed-configuration-accounting method may become computationally prohibitive due to the huge number of configurations to be taken into account. The supertransition-array (STA) method is a rather powerful approach [1] that permits to model these situations in a statistical framework by gathering the numerous configurations into a reduced number of superconfigurations. A superconfiguration consists of supershells, i.e., groups of ordinary orbitals ($n\ell$ subshells), which are populated in all possible ways consistent with the Pauli exclusion principle. Average atomic variables (such as energy and width of the transition arrays, shell occupation, etc.) can be deduced from the computation of the partition functions of the supershells.

In the STA method, partition functions are calculated using recursion relations which can involve alternate summation of large negative and positive numbers. In case of large supershells, this results in a strong numerical instability that can severely limit the range of applicability of the STA model, in particular, in the low temperature regime. An improvement consisting of a recursion relation on ratios of partition functions has been proposed recently [2], but it still contains alternate summations. In Ref. [2] an approximate treatment based on a saddle-point technique is proposed when the numerical instabilities occur.

We propose a stable method to calculate partition functions of superconfigurations without any restriction on thermodynamic conditions and on the dimension of the supershell. Our method represents a considerable progress for applications of the STA theory, since it allows one to perform fast and precise calculations in any case, even for large supershells. The method, based on recursion relations with respect to the number of electrons and the number of orbitals, is free of the numerical problems encountered with the pre-

vious recursion relations originally proposed. The formalism introduces a normalization factor in the calculation of partition functions, and a translation of the energies of orbitals inside a supershell that arise from a variational principle in a grand-canonical ensemble.

In Sec. II, the standard methods of calculation of ionic partition functions are recalled and analyzed. In Sec. III, the doubly recursive approach is presented, as well as the variational choice for the scaling of energies and of the normalization factor, which is shown to be consistent with the zeroth-order saddle-point evaluation of the integral representation of the partition function.

In Sec. IV, numerical limitations of existing approaches and of our method are tested by calculating ratios of partition functions for a large supershell. Examples are shown for a supershell representing an ion charge. Average populations of orbitals are also presented and compared with approximate values.

II. THE PARTITION FUNCTION OF A Q -ELECTRON SYSTEM

Throughout this paper, emphasis is put on the evaluation of average ionic variables (such as average population of orbitals and their variances in each ion), which can be obtained from the partition functions of *isolated* ions.

A. Definitions

The partition function \mathcal{Z}_Q of a canonical Q -electron ensemble may be written in the general form as

$$\mathcal{Z}_Q = \text{Tr} e^{-\beta H} = \sum_{\alpha(Q)} \langle \alpha | e^{-\beta H} | \alpha \rangle = \sum_{\alpha(Q)} e^{-\beta E_\alpha}, \quad (1)$$

where α runs over all possible Q -electron quantum states of total energy E_α , H is the Hamiltonian of the system taking into account all relevant interaction processes, and $\beta = 1/(k_B T)$ where k_B is the Boltzmann constant and T the electron temperature. For numerical reasons due to the evaluation of exponential terms, it is necessary to introduce a free parameter λ in order to scale the energies. Therefore, the

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partition function which is effectively calculated is

$$\mathcal{U}_Q = \sum_{\alpha(Q)} e^{-\beta(E_\alpha - \lambda Q)} = e^{\beta\lambda Q} \mathcal{Z}_Q, \quad (2)$$

which is simply proportional to \mathcal{Z}_Q . The introduction of λ is a Legendre transformation which is similar to the change from canonical to grand-canonical ensemble, but one has to keep in mind that the number of electrons in the system is fixed and therefore the parameter λ is not a *real* chemical potential with physical meanings.

The simplest approach for atomic-physics calculations of a many-electron system is the nonrelativistic central-field model [3]. Any given electron moves independently of the others in a central potential that represents the electrostatic field of the nucleus and the spherically averaged mutual Coulomb repulsions of the other electrons. This zeroth-order Hamiltonian allows one to construct Q -electron wave functions $|\alpha\rangle$ from the one-electron spin orbitals $|n_i \ell_i m_{\ell_i} m_{s_i}\rangle$ in the form of determinantal functions, whereas E_α is simply the sum of the energies of each electron which do not depend on magnetic quantum numbers m_{ℓ_i} and m_{s_i} . Therefore, quantum states of the system having the energy E_α can be represented by groups of degenerated *electron configuration* that are noted,

$$(n_1 \ell_1)^{p_1} (n_2 \ell_2)^{p_2} \dots (n_N \ell_N)^{p_N} \quad \text{with} \quad \sum_{i=1}^N p_i = Q. \quad (3)$$

A spin orbital with a given $n\ell$ value is simply called *orbital*, p_i is the *population* of the i th orbital allowed by the Pauli exclusion principle and varies from 0 to $g_i = 2(2\ell_i + 1)$, and N is the number of orbitals. A configuration is completely defined by the set \vec{p} of populations of the N given orbitals. Now, the partition function in Eq. (2) can be expressed as a sum over configurational states,

$$\mathcal{U}_Q = \sum_{|\vec{p}|=Q} e^{-\beta\Omega(\vec{p})}, \quad (4)$$

where the sum runs over all \vec{p} configurations containing Q electrons; this constraint is noted $|\vec{p}| = \sum_{i=1}^N p_i = Q$. The function $\Omega(\vec{p})$ is the thermodynamic potential associated to the electron configuration \vec{p} and reads

$$\Omega(\vec{p}) = E^{(0)}(\vec{p}) - TS(\vec{p}) - \lambda Q. \quad (5)$$

The total energy of the configuration is defined, in the zeroth-order central-field approximation, by

$$E^{(0)}(\vec{p}) = \sum_{i=1}^N p_i \epsilon_i, \quad (6)$$

where ϵ_i is the energy of orbital i . The entropy term $S(\vec{p})$ is linked to the total degeneracy $W(\vec{p})$ of the configuration by the formula

$$S(\vec{p}) = k_B \ln W(\vec{p}), \quad (7)$$

with

$$W(\vec{p}) = \prod_{i=1}^N \binom{g_i}{p_i}, \quad (8)$$

where $\binom{g_i}{p_i} = g_i! / p_i! (g_i - p_i)!$ is the binomial coefficient.

The mean Hartree-Fock energy of a configuration can be obtained by evaluating the nonspherical part of the Hamiltonian. The energy of a configuration is then given by

$$E(\vec{p}) = \sum_{i=1}^N p_i \langle i \rangle + \frac{1}{2} \sum_{i=1}^N \sum_{i'=1}^N p_i (p_{i'} - \delta_{i,i'}) \langle i, i' \rangle, \quad (9)$$

where $\langle i \rangle$ and $\langle i, i' \rangle$ are the one- and two-electron energies evaluated with basis functions of the central-field Hamiltonian. It is possible to calculate \mathcal{U}_Q with the expression of the energy of a configuration given by Eq. (9). However, the quadratic terms with respect to the populations prevent any factorization of the partition functions, as it will be shown in the following section.

B. Closed form evaluation using recursion relations

Despite its apparent simplicity, the direct use of Eq. (4), with or without corrections to the energies due to electrostatic interactions, is often intractable due to the huge number of configurations to be summed up. As an example, the number of configurations with 20 electrons distributed among orbitals 1s to 5g is roughly equal to 0.38×10^9 (see Sec. III D).

Avoiding a direct calculation of the partition function of a many-particle system is a classical problem of statistical physics. The key point is the ability to provide an exact generating function from which one can derive simple recursion relations. Such closed form formula can be found, usually, only in noninteracting systems. Indeed, the factorization of Eq. (4) requires that the energy of a configuration be a linear function of the populations, as in Eq. (6). We will adopt this approximation from now. However, it can be noted that quadratic terms with respect to the populations in Eq. (9) can be averaged following the procedure described by Bar-Shalom *et al.* in Ref. [1]. This allows one to take into account, approximately, the interaction effects between electrons.

Using classical results from the independent-electron model [4,5], partition function \mathcal{U}_Q can be recursively built from

$$\mathcal{U}_Q(\beta) = \frac{1}{Q} \sum_{k=1}^Q (-1)^{k+1} \mathcal{U}_1(k\beta) \mathcal{U}_{Q-k}(\beta), \quad (10)$$

where $\mathcal{U}_1(\beta)$ is the single-electron partition function defined by

$$\mathcal{U}_1(\beta) = \sum_{i=1}^N g_i e^{-\beta(\epsilon_i - \lambda)}. \quad (11)$$

This recursion relation is the central point of the STA approach, published by Bar-Shalom *et al.* in Ref. [1], which allows us to calculate all average variables of the system. The strength of Eq. (10) stems from the fact that only Q

recursive steps are required in order to evaluate the partition function of a Q -electron ion, starting from $\mathcal{U}_0 \equiv 1$ and propagating up to \mathcal{U}_Q . However, an algorithm based on Eqs. (10) and (11) is usually numerically unstable without special care for the exponential terms. Indeed the evaluation of Eq. (11) may in some cases exceed the precision of the processor (“overflow”) or rapidly decrease to zero (“underflow”), resulting in a dramatic loss of precision. The situation may get worse if one has in Eq. (10) an alternate summation of large positive and negative terms. These problems can be avoided by requiring that the maximum value of the argument of exponential terms be of the order of unity,

$$|\epsilon_i - \lambda|Q \leq k_B T \quad \forall i \in [1, N]. \quad (12)$$

This set of inequalities defines, roughly, the domain of stability of Eq. (10). Therefore, we see that the introduction of the free parameter λ is essential since it can be adjusted in order to reach a numerical stability. As will be shown further, an optimal value of the parameter λ can be chosen according to a simple variational principle. Moreover, the stability of relation (10) can be severely limited if the number of electrons Q in the system is too high.

Blenski *et al.* have proposed in Ref. [6] to apply Eq. (10) for the “holes” (complement of the electrons) when the number of electrons is bigger than $G/2$, G being the total degeneracy of a supershell (summation of degeneracies of all orbitals). The use of *electron-hole* formalism presents two main advantages. First of all, numerical instabilities are considerably reduced, because when values of \mathcal{U}_{Q-k} become huge (i.e., when k is close to $G/2$), one prefers reasoning on holes rather than electrons which allows us to deal with reasonably large numbers. The second advantage of this method is that it allows a reduction in calculation time. This can be explained by the fact that calculation time grows with k and becomes particularly important near $k=G/2$.

Wilson and Chen proposed recently [2] to reformulate Eq. (10) into a recursion relation over ratios of consecutive partition functions

$$\frac{Q\mathcal{R}_Q(\beta)}{\mathcal{R}_1(\beta)} = 1 + \sum_{i=2}^Q (-1)^{i-1} \prod_{k=1}^{i-1} \frac{\mathcal{R}_1((k+1)\beta)}{\mathcal{R}_1(k\beta)} \frac{1}{\mathcal{R}_{Q-k}(\beta)}, \quad (13)$$

where $\mathcal{R}_Q(\beta)$ is defined by

$$\mathcal{R}_Q(\beta) = \frac{\mathcal{U}_Q(\beta)}{\mathcal{U}_{Q-1}(\beta)}, \quad (14)$$

and is initialized with the condition $\mathcal{R}_1 = \mathcal{U}_1$ [see Eq. (11)]. There are many good reasons to calculate ratios of partition functions. First, this latter quantity appears explicitly in the expression of average variables (see Sec. IV B for the average level population). Then, it is a way to compensate the large values of the partition functions, and to handle more “reasonable” numbers. Although recursion relation (13) is a little more robust than relation (10), it does not solve the problem of alternate sums.

One of the consequences of criterion (12) is the impossibility to perform statistical calculations on a set of orbitals for which energies are spread out on a scale larger than $\sim k_B T$. Moreover, the condition becomes extremely severe as the temperature decreases, and this explains the difficulties to perform STA calculations at low temperatures. In the following section, we present an approach allowing to encompass these limitations.

III. A DIRECT AND STABLE APPROACH TO CALCULATE THE PARTITION FUNCTION

A. Derivation of a recursion relation

Numerical errors due to the summation of alternate-sign numbers is one of the major source of instability in the recursion relations (10) and (13). These problems appear when the consecutive terms in the recursion relation become comparable to round-off errors. A good way to eliminate this problem is to derive a recursion relation that consists in adding only positive numbers. For that purpose, we have derived a recursion relation with respect to the number of electrons and orbitals in the system. The derivation of this recursion relation is now detailed.

The constraint $|\vec{p}|=Q$ in Eq. (4) can be removed if, at the same time, the following identity [8] is inserted in the relation

$$\delta_{0,L} = \frac{1}{2i\pi} \int_{-i\pi+\alpha_0}^{i\pi+\alpha_0} dt e^{tL}, \quad (15)$$

where $L=Q-|\vec{p}|$ and α_0 is an arbitrary real parameter. This allows us to factorize Eq. (4) in the form

$$\mathcal{U}_Q = \frac{1}{2i\pi} \int_{-i\pi+\alpha_0}^{i\pi+\alpha_0} dt e^{tQ} \prod_{s=1}^N \sum_{p_s=0}^{g_s} \binom{g_s}{p_s} (X_s e^{-t})^{p_s}, \quad (16)$$

using the notation $X_s = e^{-\beta(\epsilon_s - \lambda)}$. By setting $z = e^{-t}$, the integration in the complex plane is performed around a closed circle of radius $e^{-\alpha_0}$, surrounding the pole at $z=0$. The last expression becomes

$$\mathcal{U}_Q = \frac{1}{2i\pi} \oint dz \frac{\mathcal{F}(z)}{z^{Q+1}}, \quad (17)$$

where $\mathcal{F}(z)$ is defined by

$$\mathcal{F}(z) = \prod_{s=1}^N \sum_{p_s=0}^{g_s} \binom{g_s}{p_s} (zX_s)^{p_s} \quad (18)$$

$$= \prod_{s=1}^N (1 + zX_s)^{g_s}. \quad (19)$$

Expression (17) is calculated using the Cauchy formula, by evaluating the residue of the function $\mathcal{F}(z)/z^{Q+1}$ at the pole $z=0$ of order $Q+1$,

$$U_Q = \text{Res} \left[\frac{\mathcal{F}(z)}{z^{Q+1}}; 0 \right] = \lim_{z \rightarrow 0} \left[\frac{1}{Q!} \frac{\partial^Q}{\partial z^Q} \mathcal{F}(z) \right]. \quad (20)$$

The partition function U_Q of a non-interacting Q -electron system is thus obtained by successive derivations of the function $z \mapsto \mathcal{F}(z)$, which is called the *generating function*. A recursion relation can be found by searching relationships between two consecutive derivatives of the function $\mathcal{F}(z)$. A recursive formula over the number of electrons Q of the system has already been established [1] and presented in Sec. II B.

The speciality, here, consists in the derivation of a recursion relation over the number of electrons Q and over the number of orbitals N of the system. This can be done starting from the usual generating function $\mathcal{F}(z)$ of the system, and considering it as an explicit function of the number of orbitals. Therefore, we define one generating function $\mathcal{F}_N(z)$ for each possible value of the number of orbitals, and we introduce the notation $U_{Q;N}$ which refers to the partition function of Q electrons distributed among N given orbitals. Using the multiple derivative formula of Leibnitz,

$$\frac{\partial^Q}{\partial z^Q} [AB] = \sum_{i=0}^Q \binom{Q}{i} \left[\frac{\partial^{Q-i}}{\partial z^{Q-i}} A \right] \left[\frac{\partial^i}{\partial z^i} B \right], \quad (21)$$

we can write

$$\begin{aligned} U_{Q;N} &= \lim_{z \rightarrow 0} \frac{1}{Q!} \frac{\partial^Q}{\partial z^Q} [\mathcal{F}_{N-1}(z)(1 + zX_N)^{g_N}] \\ &= \sum_{i=0}^Q \binom{Q}{i} \frac{(Q-i)!}{Q!} U_{Q-i;N-1} \lim_{z \rightarrow 0} \left[\frac{\partial^i}{\partial z^i} (1 + zX_N)^{g_N} \right]. \end{aligned} \quad (22)$$

The derivative of the polynomial function in the square brackets can be easily calculated by

$$\frac{\partial^i}{\partial z^i} (1 + zX_N)^{g_N} = X_N^i (1 + zX_N)^{g_N-i} \frac{g_N!}{(g_N-i)!} \Theta(g_N-i). \quad (23)$$

The Heaviside function $\Theta(g_N-i)$ ensures that the i th derivative is null in the case where i is greater than the order g_N of the polynomial. Evaluation of the last expression in the limit $z \rightarrow 0$, and the substitution of the result in Eq. (22) leads to

$$U_{Q;N} = \sum_{i=0}^Q \binom{Q}{i} \frac{(Q-i)!}{Q!} U_{Q-i;N-1} X_N^i \frac{g_N!}{(g_N-i)!} \Theta(g_N-i). \quad (24)$$

The factorial numbers can be simplified and arranged in a single-binomial coefficient. Thus, the final expression for the recursion relation over the number of electrons and over the number of orbitals of the system reads

$$U_{Q;N} = \sum_{i=0}^Q U_{Q-i;N-1} X_N^i \binom{g_N}{i} \Theta(g_N-i), \quad (25)$$

and is initialized with $U_{Q;0} = \delta_{Q;0}$.

Generalizing this result, the partition function $U_{t;k}$ of t electrons distributed among k orbitals can be obtained from a recursion formula which reads, in compact form,

$$U_{t;k} = \sum_{p_k=0}^{\min(t,g_k)} U_{t-p_k;k-1} e^{-\beta \Omega_k(p_k)}, \quad (26)$$

where we define

$$\Omega_k(p_k) = p_k(\epsilon_k - \lambda) - \frac{1}{\beta} \ln \binom{g_k}{p_k}. \quad (27)$$

One may note that in Eq. (26) the terms have been gathered in the argument of a single-exponential term in order to prevent numerical imprecisions due to multiplication of a large binomial coefficient by a small exponential term. The procedure used to calculate the partition function of Q electrons in an N -orbitals system is as follows. Starting with $U_{t;0} = \delta_{t;0}$, Eq. (26) is applied in order to determine the Q possible values of the partition functions $U_{t;1}$ ($1 \leq t \leq Q$) for a chosen orbital. The results are used to build the next Q values $U_{t;2}$ that take into account one additional orbital, and so on. The expected value $U_{Q;N}$ is obtained at iteration N , i.e., when all orbitals have been taken into account. Therefore, the partition function is obtained in a maximum of NQ steps, i.e., N times more than the recursion relations (10) and (13). This additional numerical cost remains very reasonable compared to the enhanced precision of the method. The most interesting property of this recursion relation is that the contribution of each orbital to the total partition function has been separated from the others in successive steps. This becomes more evident if the relation is compared to the direct expression of the partition functions given by Eq. (4), and noting that

$$\Omega(\vec{p}) = \sum_{k=1}^N \Omega_k(p_k). \quad (28)$$

The recursion relation given by Eq. (26) can be considered as a *direct* approach to calculate the partition function because the $\Omega_k(p_k)$ functions are components of the thermodynamic potential $\Omega(\vec{p})$, whereas the entropy term apparent in Eq. (27) is hidden by mathematical complexity in Eqs. (10) and (13). This particularity can be used to introduce a shift to the thermodynamic potential and thus normalize the partition functions, as we will see in the following section. In the practical implementation, the precision of the relation (26) depends critically on the choice of the free parameter λ whose role is to *minimize* the values of $\Omega_k(p_k)$ in order to prevent numerical problems due to the evaluation of exponential terms. Thus, we see that an optimal value of λ can be found from a variational principle applied to the potential $\Omega(\vec{p})$. This point will be also detailed in the following section.

B. Normalization of partition functions by variational considerations

When the orbitals of the system have too different energies (separated by more than $k_B T$), the $\Omega_k(p_k)$ functions can take significant values, whatever the choice of λ may be. In that situation, numerical problems of overflow or underflow of exponentials appear inevitably in Eq. (26). A way to avoid these problems consists in *normalizing* the partition function \mathcal{U}_Q . The basic idea is to factorize the dominant exponential term in Eq. (4), this term being associated to a particular configuration \vec{p}^* of the system, and to evaluate the normalized partition function \mathcal{V}_Q with

$$\mathcal{V}_{Q:N} = \frac{\mathcal{U}_{Q:N}}{e^{-\beta\Omega(\vec{p}^*)}} = \sum_{|\vec{p}|=Q} e^{-\beta[\Omega(\vec{p}) - \Omega(\vec{p}^*)]}. \quad (29)$$

Configuration \vec{p}^* , which represents the most probable electronic configuration of the system, can be obtained through variational considerations. The search for extrema leads one to impose the condition

$$\vec{\nabla} \Omega(\vec{p}^*) = \vec{0} \quad \Rightarrow \quad \frac{\partial \Omega_k}{\partial p_k}(p_k^*) = 0 \quad \forall k \in [1, N]. \quad (30)$$

The resolution of the system of Eq. (30) is performed by approximating binomial coefficients with Stirling formula. As a result, \vec{p}^* involves the well-known Fermi-Dirac distribution,

$$p_k^* = \frac{g_k}{1 + e^{\beta(\epsilon_k - \lambda_Q)}} \quad \forall k \in [1, N], \quad (31)$$

where Lagrange multiplier λ_Q is adjusted in order to ensure preservation of the number of electrons in the system,

$$\sum_{k=1}^N p_k^* = Q. \quad (32)$$

In this way, we find the optimal value $\lambda \equiv \lambda_Q$, which has been introduced as a free parameter in this paper. It is interesting to mention that Blenski *et al.* in Ref. [7] used the same Eq. (31) in their superconfiguration code in order to calculate the average populations of the orbitals inside a supershell made of Q electrons.

The introduction of the normalization factor into the recursion relation (26) can be done by using Eq. (28) for \vec{p}^* . The recursion relation can be therefore written as

$$\tilde{\mathcal{V}}_{t,k} = \sum_{p_k=0}^{\min(t, g_k)} \tilde{\mathcal{V}}_{t-p_k, k-1} e^{-\beta \Delta \tilde{\Omega}_k(p_k)}, \quad (33)$$

with

$$\begin{aligned} \Delta \tilde{\Omega}_k(p_k) &= \tilde{\Omega}_k(p_k) - \tilde{\Omega}_k(p_k^*) \\ &= (\epsilon_k - \lambda_Q)(p_k - p_k^*) - \frac{1}{\beta} \left[\ln \binom{g_k}{p_k} - \ln \binom{g_k}{p_k^*} \right]. \end{aligned} \quad (34)$$

The symbol $\tilde{}$ reminds one that the corresponding variable is

implicitly evaluated by taking $\lambda = \lambda_Q$. The numerical stability and accuracy of Eq. (33) relies on the property $\Delta \tilde{\Omega}_k(p_k) > 0 \quad \forall k$, which eliminates overflow problems in the evaluation of exponential terms, and, at the same time, allows one to take correctly into account numerical underflow of exponentials corresponding to configurations with a very low probability. Moreover, the fact that the partition functions are normalized, i.e., $\tilde{\mathcal{V}}_{Q:N} \approx 1$, allows one to calculate ratios of the form $\tilde{\mathcal{V}}_{Q:N} / \tilde{\mathcal{V}}_{Q-1:N}$ with a high accuracy.

We note that the resolution of Eq. (30) provides a configuration \vec{p}^* with fractional populations. However, an accurate value of $\Omega(\vec{p}^*)$ is not necessary since it is used only in order to prevent the divergence of exponential terms. Therefore, it is possible to retain the closest integer populations to this solution for the practical implementation. Nevertheless, the advantage in using the fractional populations is the consistency with the zeroth-order saddle-point evaluation of the integral representation of the partition function. This point is discussed in the following section.

C. Equivalence between variational normalization coefficient and saddle-point approximation

It has been shown that the partition function $Z_{Q:N}$ of a noninteracting Q -electron system with N orbitals can be evaluated more easily with the change of variables,

$$\mathcal{Z}_{Q:N} = \tilde{\mathcal{U}}_{Q:N} e^{-\beta \lambda_Q Q} = \tilde{\mathcal{V}}_{Q:N} e^{-\beta[\Omega(\vec{p}^*) + \lambda_Q Q]}, \quad (35)$$

where $\tilde{\mathcal{V}}_{Q:N}$ is evaluated from recursive Equation (33), $\Omega(\vec{p}^*)$ is the normalization coefficient, and λ_Q is the translation of energies obtained from a variational principle. It is interesting to stress the link between this change of variables and the continuous representation of the partition function [8], which can be expressed, using Eqs. (16) and (35),

$$\mathcal{Z}_{Q:N} = \frac{\beta}{2i\pi} \int_{i\pi/\beta + \alpha'_0}^{i\pi/\beta + \alpha'_0 + \beta} e^{-\beta \zeta(u)} du, \quad (36)$$

with

$$\zeta(u) = -\frac{1}{\beta} \sum_{i=1}^N g_i \ln[1 + Y_i e^{\beta u}] + uQ, \quad (37)$$

where $Y_i = e^{-\beta \epsilon_i}$ and α'_0 is an arbitrary real parameter. The saddle point ν is obtained by a minimization of the function $u \mapsto \zeta(u)$ on the real axis,

$$\left. \frac{d\zeta(u)}{du} \right|_{\nu} = 0 = -\sum_{i=1}^N g_i \frac{Y_i e^{\beta \nu}}{1 + Y_i e^{\beta \nu}} + Q. \quad (38)$$

Therefore, ν is the root of

$$\sum_{i=1}^N \tilde{p}_i = Q \quad \text{with} \quad \tilde{p}_i = g_i \frac{Y_i e^{\beta \nu}}{1 + Y_i e^{\beta \nu}} = \frac{g_i}{1 + e^{\beta(\epsilon_i - \nu)}}, \quad (39)$$

which implies, comparing Eq. (39) with Eq. (31), that $\nu = \lambda_Q$ and that $\tilde{\vec{p}} = \vec{p}^*$. Moreover, it can be proven that

$$\begin{aligned}
 -\beta\zeta(\nu) &= \sum_{i=1}^N (g_i \ln[1 + Y_i e^{\beta\nu}] - \beta\nu\tilde{p}_i) = \sum_{i=1}^N \ln \left[\binom{g_i}{p_i^*} Y_i^{p_i^*} \right] \\
 &= -\beta[\Omega(\vec{p}) + \lambda_Q Q], \tag{40}
 \end{aligned}$$

assuming Stirling approximation for the binomial coefficient. Since the partition function is equal, in the zeroth-order approximation, to $\mathcal{Z}_{Q:N}^{(0)} = e^{-\beta\zeta(\nu)}$, we can write

$$\mathcal{Z}_{Q:N}^{(0)} = e^{-\beta\zeta(\nu)} = \prod_{i=1}^N \binom{g_i}{p_i^*} Y_i^{p_i^*} = e^{-\beta[\Omega(\vec{p}^*) + \lambda_Q Q]}. \tag{41}$$

The comparison of Eqs. (41) and (35) shows that the normalization factor, introduced by variational considerations in the preceding section, is strictly equal to the zeroth-order saddle-point evaluation of the integral representation of the partition function. The change of variable can be rewritten as

$$\mathcal{Z}_{Q:N} = \mathcal{Z}_{Q:N}^{(0)} \tilde{\mathcal{V}}_{Q:N}. \tag{42}$$

This means that the normalized partition function $\tilde{\mathcal{V}}_{Q:N}$ represents the exact value of the neglected terms (order ≥ 2) in the development of the continuous representation of the partition function. The first-order correction being equal to zero [Eq. (38)], $\tilde{\mathcal{V}}_{Q:N}$ can be estimated in the second-order approximation by

$$\tilde{\mathcal{V}}_{Q:N} = \frac{1}{\Gamma} \int_0^\Gamma e^{-t^2} dt + o(\lambda_Q^3), \tag{43}$$

where $\Gamma = \pi\sqrt{-\xi''(\lambda_Q)/2\beta}$. The consistency of the recursion relation on normalized partition functions with the approximate saddle-point approach is interesting since it allows us to develop a fast optimized algorithm that selects the appropriate method, according to the number of electrons in the system. Indeed, the second-order saddle-point approximation appears to be accurate for highly degenerated and half-filled system. We note that a similar hybrid algorithm, between exact and approximate calculations, has also been proposed by Wilson and Chen in Ref. [2].

D. Applications to statistical counting

An additional possibility of the recursion relation is to provide, with slight modifications, a fast and exact method to count the number of configurations and nondegenerated states (number of basis functions of the Hamiltonian) in a given ion.

The number of nondegenerated states of the system can be formally evaluated from the expression

$$\mathcal{W}_{Q:N} = \sum_{|\vec{p}|=Q} W(\vec{p}) = \sum_{|\vec{p}|=Q} \prod_{k=1}^N \binom{g_k}{p_k}. \tag{44}$$

It appears that $\mathcal{W}_{Q:N}$ is the high temperature limit $\beta \rightarrow 0$ of the partition function of the system. Therefore, it is easy to show that the relevant generating function $z \mapsto \mathcal{G}_N(z)$ is equal to

TABLE I. Number of configurations and number of nondegenerated states calculated with Eqs. (49) and (46) for different values of the number of electrons distributed in orbitals 1s to 5g.

Q	\mathcal{N}_Q	\mathcal{W}_Q
1	15	110
5	11028	0.12239152×10^9
10	1407606	$0.46897637 \times 10^{14}$
15	35997772	$0.11757598 \times 10^{19}$
20	0.37700611×10^9	$0.43939715 \times 10^{22}$
25	$0.21997138 \times 10^{10}$	$0.36347042 \times 10^{25}$
30	$0.84076570 \times 10^{10}$	$0.83662309 \times 10^{27}$
35	$0.23135515 \times 10^{11}$	$0.61954559 \times 10^{29}$

$$\mathcal{G}_N(z) = \prod_{s=1}^N (1+z)^{g_s}, \tag{45}$$

from which is derived

$$\mathcal{W}_{Q:N} = \sum_{i=0}^{\min(Q, g_N)} \binom{g_N}{i} \mathcal{W}_{Q-i; N-1}, \quad (\mathcal{W}_{Q;0} = \delta_{Q;0}). \tag{46}$$

The exact number of possibilities to distribute Q electrons in N orbitals (i.e., the number of configurations if all orbitals are gathered in one single supershell) reads

$$\mathcal{N}_{Q:N} = \sum_{|\vec{p}|=Q} 1. \tag{47}$$

From a derivation similar to the one presented in Sec. III A, it can be shown that the relevant generating function $z \mapsto \mathcal{H}_N(z)$ is

$$\mathcal{H}_N(z) = \prod_{s=1}^N \frac{1-z^{g_s+1}}{1-z}, \tag{48}$$

leading to the recursion relation

$$\mathcal{N}_{Q:N} = \sum_{i=0}^{\min(Q, g_N)} \mathcal{N}_{Q-i; N-1}, \quad (\mathcal{N}_{Q;0} = \delta_{Q;0}). \tag{49}$$

This formula can be applied, more generally, when the orbitals are gathered in more than one supershell, and therefore when each ion can be represented by many superconfigurations. For example, considering a superconfiguration Ξ composed of many supershells σ containing Q_σ electrons and N_σ orbitals, the total number of configurations is given by $\mathcal{N}_\Xi = \prod_\sigma \mathcal{N}_{Q_\sigma; N_\sigma}$, and the total number of nondegenerated states is simply $\mathcal{W}_\Xi = \prod_\sigma \mathcal{W}_{Q_\sigma; N_\sigma}$.

A numerical example, in which the number of configurations and the number of nondegenerated states are calculated exactly through Eqs. (46) and (49), is presented in Table I versus the number of electrons distributed in one single supershell containing orbitals from 1s to 5g.

Another interesting quantity that can be easily and precisely obtained from our approach is the number of pairs of configurations connected by a given one-electron transition

between two superconfigurations. Considering two orbitals α and β for an ion containing Q electrons and N orbitals, the number of transitions $\alpha \rightarrow \beta$ is given by [8]

$$\mathcal{T}_{Q:N}^{\alpha \rightarrow \beta} = \mathcal{N}_{Q-1;N^{(\alpha\beta)}}, \quad (50)$$

where notation $N^{(\alpha\beta\gamma\delta\dots)}$ [1] represents a set of N orbitals where degeneracies of orbitals $\alpha, \beta, \gamma, \delta, \dots$ are equal to $g_\alpha - 1, g_\beta - 1, g_\gamma - 1, g_\delta - 1$, etc. Indeed, the transition will be possible only if there is a vacancy (or hole) in orbital β , and the electron involved in the transition will leave a vacancy in orbital α . Thus, the number of transitions is equal to the number of configurations of $Q-1$ electrons among N orbitals, degeneracies of both involved orbitals being diminished by one. In the superconfiguration approximation, if α belongs to supershell 1 having Q_1 electrons and N_1 orbitals and β to supershell 2 having Q_2 electrons and N_2 orbitals, the number of transitions $\alpha \rightarrow \beta$ is given by

$$\mathcal{T}_{Q:N}^{\alpha \rightarrow \beta} = \mathcal{N}_{Q_1-1;N_1^{(\alpha)}} \mathcal{N}_{Q_2-1;N_2^{(\beta)}}, \quad (51)$$

where $N = N_1 + N_2$ and $Q = Q_1 + Q_2$.

IV. NUMERICAL RESULTS

A. Ratios of partition functions

In Sec. II B, it was shown that the accuracy of Eqs. (10) and (13), called here standard approaches for the calculations of partition functions, are considerably limited by the summation of alternate-sign numbers. This can be emphasized by comparing the results from these numerical methods with results from our recursion relation (26) with respect to the number of electrons and orbitals of a supershell. The study is limited to one supershell made of six orbitals ($4p4d4f5s5p5d$), with a number of electrons varying from 0 to the total degeneracy 48. For numerical convenience (the purpose is only to check the stability of the recursion relations), the energies of the orbitals for all possible configurations are ‘‘frozen’’ to the average-atom values calculated from a screened hydrogenic model with nl -splitting [9]. The example corresponds to a gold plasma at a temperature of 100 eV and a density of 0.01 g/cc, the energies of the orbitals being specified in Table II. According to the qualitative criterion defined by Eq. (12), this case is numerically unstable for standard approaches since the difference of energy between orbitals $4p$ and $5d$ is much greater than the temperature: $|\epsilon_{4p} - \epsilon_{5d}| = 8.37k_B T$.

This can be checked in Figs. 1 and 2, where ratios of consecutive partition functions, i.e., $\mathcal{U}_{Q:N}/\mathcal{U}_{Q-1:N}$, are plotted versus the number of electrons in the supershell. Results from standard approaches are compared with results obtained with the recursion relation in the simplest formulation [Eq. (26)] that does not take into account the normalization of the partition functions. In Fig. 1, partition functions are calculated separately from the recursion relation of Bar-Shalom *et al.* in Ref. [1], i.e., by using Eq. (10) in electron counting and its equivalent expression in hole counting [6]; the ratios are obtained thereafter. The ratios in Fig. 2 are calculated directly from the recursion relation of Wilson and Chen in Ref. [2], expressed by Eq. (13) in electron counting, and a similar

TABLE II. Screened hydrogenic average-atom energies [9] of orbitals $1s$ to $6h$ for a gold plasma, $T=100$ eV, $\rho=0.01$ g/cc, and $Z^*=26.02(\mu=-32.833$ a.u.).

Orbital	Degeneracy	Energy (a.u.)
$1s$	2	-0.274051×10^4
$2s$	2	-0.484283×10^3
$2p$	6	-0.473351×10^3
$3s$	2	-0.137963×10^3
$3p$	6	-0.132304×10^3
$3d$	10	-0.120587×10^3
$4s$	2	-0.542832×10^2
$4p$	6	-0.500120×10^2
$4d$	10	-0.425647×10^2
$4f$	14	-0.320102×10^2
$5s$	2	-0.240696×10^2
$5p$	6	-0.231469×10^2
$5d$	10	-0.192439×10^2
$5f$	14	-0.152350×10^2
$5g$	18	-0.148924×10^2
$6s$	2	-0.105012×10^2
$6p$	6	-0.103823×10^2
$6d$	10	-0.984352×10^1
$6f$	14	-0.964902×10^1
$6g$	18	-0.956894×10^1
$6h$	22	-0.954993×10^1

expression in hole counting. All calculations were performed by setting the parameter λ equal to -32.833 . Standard calculations are known to be correct for a small number of electrons or holes and to show a breakdown in accuracy near half occupancy of the supershell (which prevents the use of the recursion relations for a large number of electrons or holes). This can be observed in Figs. 1 and 2, where ratios of partition functions for $20 \leq Q \leq 23$ are not accurately reproduced by these approaches, neither in electron counting nor in hole counting. Indeed, near half-filled supershells contain configurations with a high degeneracy. Therefore, the calculation of the partition function involves an alternate summation of large numbers, which leads to cancellation errors as explained in Sec. III A. These numerical problems can be fixed by a multiprecision arithmetic calculation [2], but the numerical cost is definitely prohibitive. On the contrary, the recursion relation (26) is applied with single-precision arithmetic and provides correct ratios of partition functions for all Q in electron counting, as well as in hole counting. This demonstrates that the summation of alternate-sign numbers, intrinsic property of the standard recursion relations, can have a dramatic impact on the accuracy of partition functions, and that the resulting error cannot be everywhere compensated by hole counting.

B. Average populations and their variances

We have shown that the recursion relation (26) can be improved, with a proper normalization of the partition func-

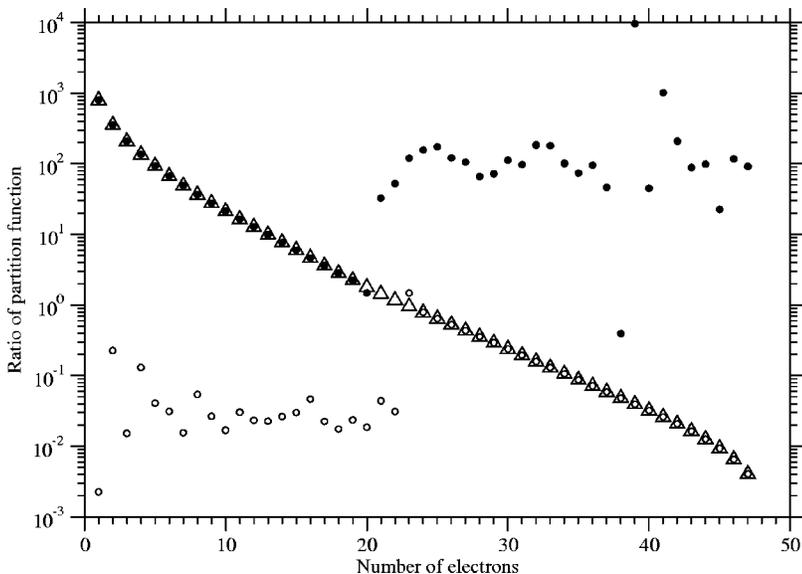


FIG. 1. Ratios of partition function $U_{Q;N}/U_{Q-1;N}$, vs number of electrons in the super-shell ($4p4d4f5s5p5d$). The case is specified in Table II. Results obtained from the recursion relation of Bar-Shalom *et al.* in Ref. [1] applied in electron counting (●) and in hole counting (○) [6] are compared to the results obtained with the recursion relation (26) applied in electron counting only (△).

tion, in order to treat arbitrarily defined supershells without any limitations on the number of orbitals and on the values of their energies. This allows one to perform very accurate statistical calculations on large thermodynamic ensembles. To illustrate this possibility, the formalism was applied to the evaluation of average properties of ions where all the electrons are distributed in a single supershell containing all the orbitals of Table II. The difficulty of this case is apparent since the difference of energy between orbitals $1s$ and $6h$ is $|\epsilon_{1s} - \epsilon_{6h}| = 743.14k_B T$, which is enormous in terms of temperature. We put the focus on the evaluation of the average population of orbitals and their standard deviation.

The average population of orbital k in the Q -electron ion, noted $\langle p_k \rangle_Q$, can be expressed in the form of a generalized Fermi-Dirac distribution [2,6]

$$\langle p_k \rangle_Q = \frac{g_k}{1 + \frac{Z_{Q;N^{(k)}}}{Z_{Q-1;N^{(k)}}} e^{\beta \epsilon_k}} = \frac{g_k}{1 + \frac{\tilde{V}_{Q;N^{(k)}}}{\tilde{V}_{Q-1;N^{(k)}}} e^{\beta(\epsilon_k - \lambda_Q)}}. \quad (52)$$

We note that the restriction of averaging the populations over Q -electron configurations introduces an additional factor in the usual Fermi-Dirac expression, which is the ratio of the partition functions corresponding to two ions of consecutive charges, evaluated for degeneracy of the involved orbital diminished by one unit. This change of degeneracy, applied to the orbital k , is symbolized by the notation $N^{(k)}$. If this restriction is removed, which means that the average is performed over all Q -electron configurations, the average population is given by Eq. (31). It is important to mention that the

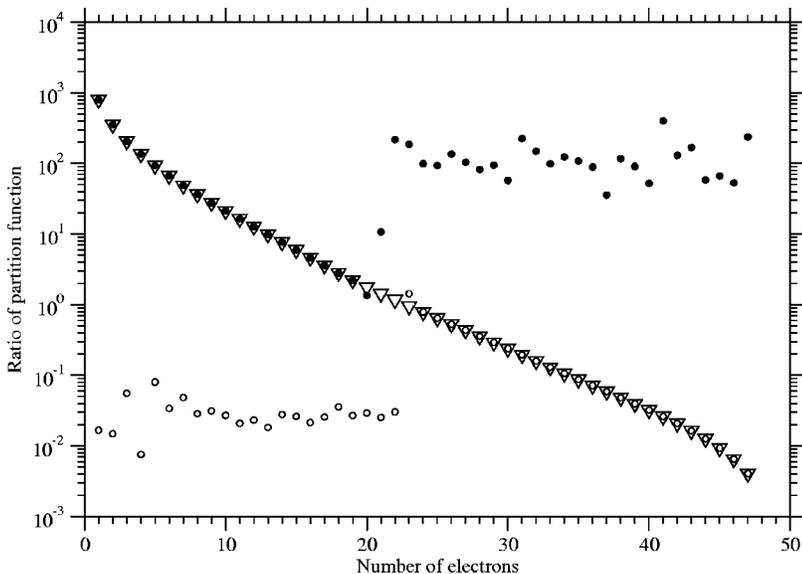


FIG. 2. Same as Fig. 1. Results obtained from the recursion relation of Wilson and Chen in Ref. [2] applied in electron counting (●) and in hole counting (○) are compared to the calculations performed with the recursion relation (26) applied in hole counting only (▽).

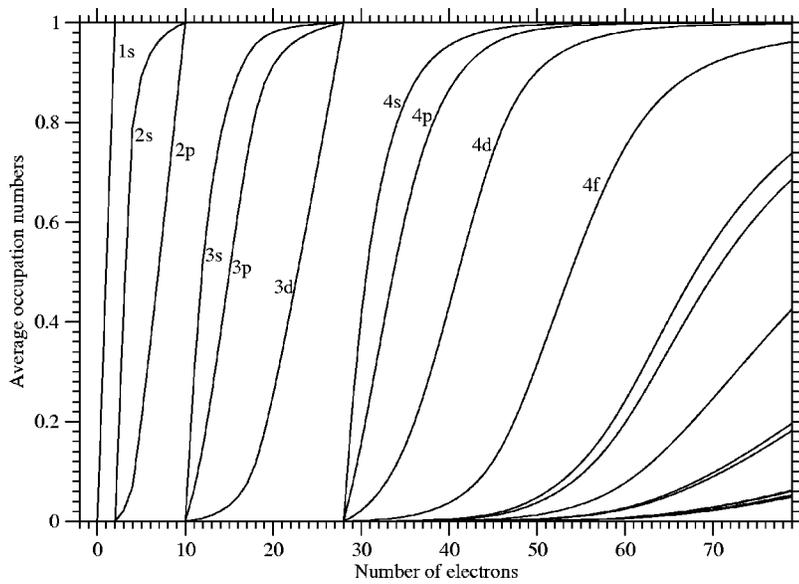


FIG. 3. Each ion is represented by one super-configuration made of one supershell containing all $n\ell$ orbitals of Table II. The recursion relation on normalized partition functions (33) is used to calculate the average occupation number (population divided by degeneracy) of these orbitals in each ion.

average population determined by Eq. (52) is independent of λ_Q , because ratios of normalized partition functions $\tilde{V}_{Q;N^{(k)}}/\tilde{V}_{Q-1;N^{(k)}}$ are proportional to $e^{\beta\lambda_Q}$ by construction [see Eq. (35)].

The average occupation numbers (the population divided by its degeneracy) of several orbitals are displayed in Fig. 3 as a function of the number of electrons in the supershell. The values were obtained by using the following procedure. For a given value of Q , the populations p^* and the Lagrange multiplier λ_Q associated to the conservation of the number of bound electrons of the ion are evaluated through Eq. (31). These quantities are part of the normalization coefficient of the approach. Then, for each orbital k , we apply the recursion relation [Eq. (33)], taking into account the change of degen-

eracy of the involved orbital, to calculate the normalized partition functions $\tilde{V}_{Q;N^{(k)}}$ and $\tilde{V}_{Q-1;N^{(k)}}$. The ratio of both values are then used in Eq. (52) to determine the average population of the orbital k in the Q -electron ion.

It is interesting to see the difference between average populations of a Q -electron ion, $\langle p_k \rangle_Q$, and the values p_k^* (31) used by Blenski *et al.* in Ref. [7].

The relative difference, $p_k^* - \langle p_k \rangle_Q / \langle p_k \rangle_Q$, is plotted in Fig. 4 for several orbitals. The difference was considered to be zero in the case where $|p_k^* - \langle p_k \rangle_Q| / \langle p_k \rangle_Q \leq 10^{-6}$. Significant discrepancies between both averaging methods are observed in some range of supershell population. As we can see, performing the average with Eq. (31) leads to an overestimate of the $2p$ population up to 50% and the $3d$ orbital around 20%.

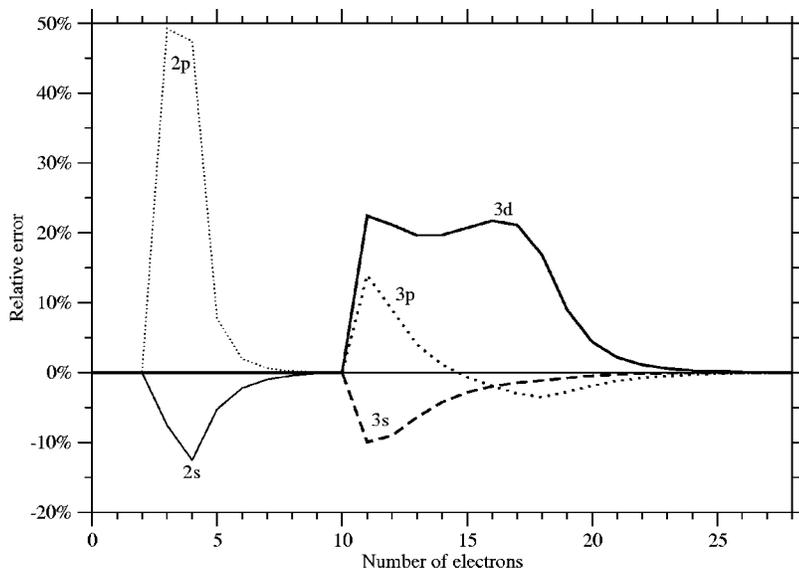


FIG. 4. For the case from Table II, the relative error of two methods of calculating the average occupation numbers of orbitals [Eqs. (52) and (31)] is estimated vs the number of electrons.

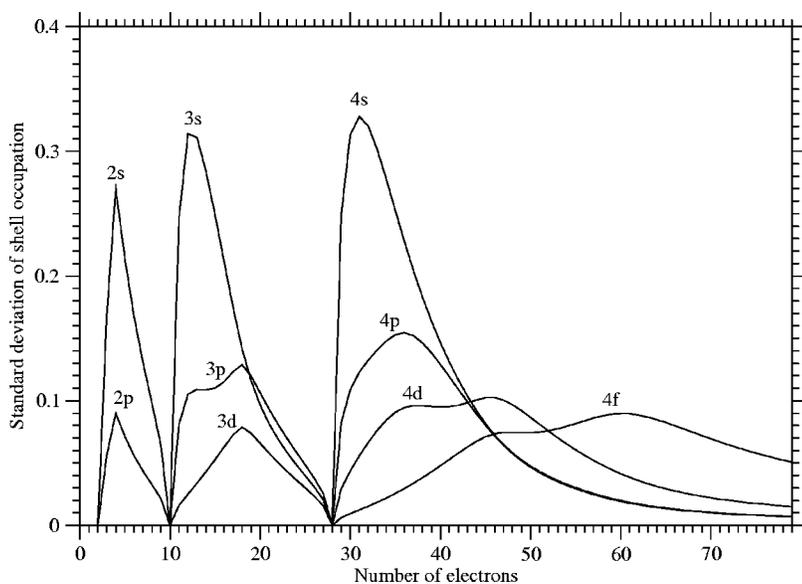


FIG. 5. The standard deviation of orbital occupation is calculated with the model as a function of the number of electrons in each ion. The case is specified in Table II.

The differences observed for the other orbitals are close to 10%, and become negligible when the number of electrons becomes large.

The other interesting quantity that can be studied is the second-order moment

$$\langle p_k^2 \rangle_Q = \langle p_k \rangle_Q \left[1 + \frac{g_k - 1}{1 + \frac{\tilde{V}_{Q;N^{(kk)}}}{\tilde{V}_{Q-1;N^{(kk)}}} e^{\beta(\epsilon_k - \lambda_Q)}} \right]. \quad (53)$$

The ratio of partition functions of two consecutive ions, which appears in the last formula, must be evaluated by reducing the degeneracy of the orbital k of interest by two; this is noted $N^{(kk)}$. The variance of population inside the Q -electron ion is therefore defined by $\sigma_{k,Q}^2 = \langle p_k^2 \rangle_Q - \langle p_k \rangle_Q^2$, where $\sigma_{k,Q}$ is the standard deviation of the population. The variation of this last quantity is displayed in Fig. 5 as a function of supershell population for orbitals 2s to 4f. An

estimation of the variance can be obtained by the standard formula

$$\sigma_k^2 = p_k^* \left(1 - \frac{p_k^*}{g_k} \right). \quad (54)$$

It can be derived by substituting the ratios of partition functions by one in Eqs. (52) and (53), which leads to the change $\langle p_k \rangle_Q \rightarrow p_k^*$ and $\sigma_{k,Q} \rightarrow \sigma_k$. Numerical results of Eq. (54) for the same case is presented in Fig. 6. Strong discrepancies are observed between both averaging methods.

V. CONCLUSION

A numerical method for the calculation of partition functions of Q -electron ions and their average thermodynamic quantities was presented. It consists of a recursion relation with respect to both the number of electrons and the number of orbitals. This recursion relation does not contain any al-

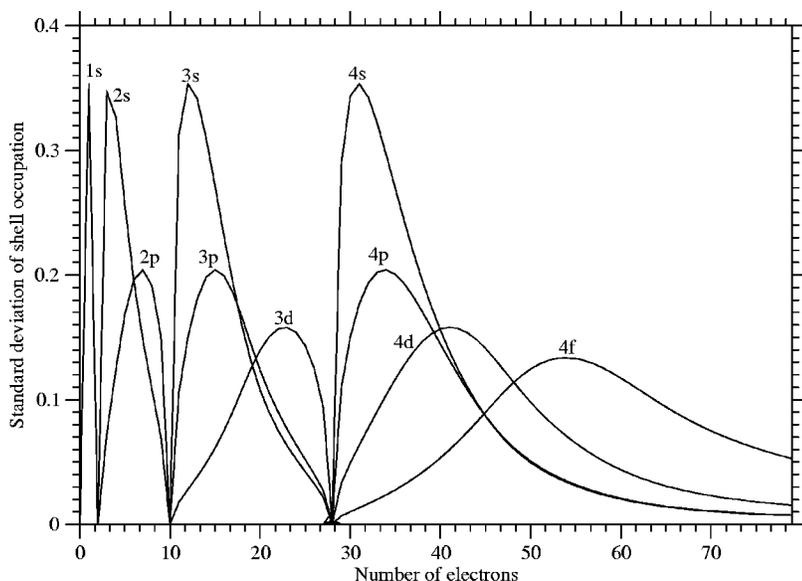


FIG. 6. Same as Fig. 5, but the standard deviation of orbital occupation is evaluated through Eq. (54).

ternate summation, which permits one to avoid numerical difficulties due to the subtraction of large numbers that may appear in the formula of Bar-Shalom *et al.* in Ref. [1].

The precision and stability of the method is considerably improved by the introduction of a translation of the energies for the orbitals inside a supershell and of a normalization of partition functions consistent with the continuous zeroth-order saddle-point approximation.

This method brings a considerable improvement to the STA method, since it allows accurate calculations of partition functions, even in the case of large supershells. Indeed, it permits to initialize the superconfiguration calculations with a single superconfiguration for each ion charge state, preparing further refinement of the supershell dimensions. Moreover, it is important to mention that calculation time remains reasonable.

Thus, this numerical method is interesting for all codes relying on the superconfiguration approximation in local thermodynamic equilibrium (LTE) [1,6] as well as non-LTE conditions [10–12], provided in the latter case that local thermodynamic equilibrium is approached inside a supershell. Furthermore, this method can also be generalized to the case where one deals with holes rather than with electrons. However, contrary to existing approaches, such a procedure is not

necessary in the recursion relation, but still allows one to divide calculation time by a factor close to 2.

Furthermore, this recursion relation can be adapted in order to obtain a recursion relation for different statistical quantities (such as the total number of nondegenerated states, the number of configurations gathered in a superconfiguration, or the number of transitions between two superconfigurations). It is important to mention that the approximation of a partition function by an integral evaluated through the saddle-point technique appears to be precise in the case where the number of electrons is close to half the degeneracy. One can therefore establish a criterion that would allow one to determine the best method for the calculation of partition functions, in order to find the best compromise between precision and calculation time. It is important to have a strong and fast method of calculation because the number of quantities to be determined in a photoabsorption cross-section calculation code can be tremendous.

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