

Nonlocal thermodynamic equilibrium self-consistent average-atom model for plasma physics

G. Faussurier, C. Blancard, and E. Berthier

Commissariat à l'Energie Atomique, 91680 Bruyères-le-Châtel, Boîte Postale 12, France

(Received 26 June 2000; published 12 January 2001)

A time-dependent collisional-radiative average-atom model is presented to study statistical properties of highly charged ion plasmas in off-equilibrium conditions. The time evolution of electron populations and the electron covariance matrix is obtained as approximate solutions of a master equation. Atomic structure is described either with a screened-hydrogenic model including ℓ splitting, or by calculating one-electron states in a self-consistent average-atom potential. Collisional and radiative excitation/deexcitation and ionization/recombination rates, as well as autoionization and dielectronic recombination rates, are formulated within the average-configuration framework. Local thermodynamic equilibrium is obtained as a specific steady-state solution. The influence of atomic structure and the role of autoionization and dielectronic recombination processes are studied by calculating steady-state average ionization and ionization variance of hot plasmas with or without radiation field.

DOI: 10.1103/PhysRevE.63.026401

PACS number(s): 52.25.Kn, 05.70.Ln

I. INTRODUCTION

The properties of hot dense matter are of great importance in astrophysics or laboratory-plasma physics [1]. Their study is often difficult because of the extended range of existing thermodynamic situations. An attractive situation takes place when plasmas can be considered in local thermodynamic equilibrium (LTE). This occurs when collisional processes between ions and electrons are more important than radiation deexcitation and recombination (provided that microreversibility prevails in particle collisions). Matter is thus assumed to be in equilibrium for any pair of temperature densities defined locally in space. Furthermore, the emission and absorption coefficients satisfy an equilibrium-type relation. If at least one of the above assumptions does not hold, the medium is said to be in nonlocal thermodynamic equilibrium (NLTE).

When LTE conditions fail, the problem at hand shows a great complexity. Since no *a priori* expressions are available for the electronic configurations, one must resort to finding the statistical distribution of the different ionic states by solving the relevant rate equation, or master equation, involving ions, free electrons, and photons. Even if the level of detail of the ionic structure does not exceed the configuration description, the number of selected many-electron configurations can be very large. In this situation, known as the detailed configuration accounting (DCA) method, data are often lacking or known only for isolated atoms or ions.

One solution is to group levels in configuration sets called superconfigurations. Bar-Shalom *et al.* [2] have used this kind of statistical approach to take up the NLTE population kinetic problem in high- Z plasmas. They have generalized the LTE supertransition array (STA) approach to calculate collisional and radiative rates connecting superconfigurations [3]. However, the basic STA tools, well-defined to perform statistical sums in LTE, are questionable in NLTE each time ionization temperature is invoked [4].

Another solution is to extend the average-atom model formalism to NLTE situations [5–7]. By taking into account various microscopic processes that can alter the shell occu-

pations of an electronic configuration, this method consists in going from integer to fractional occupation numbers and in calculating all the transition rates of interest affecting the configuration under study. The shell-occupation fractional numbers obey a set of time-dependent nonlinear coupled equations. The system is closed by using the neutrality condition. This method seems very attractive and has been recently proven to be well-defined [8,9]. In short, the master equation is approximately solved by searching a particular solution of the density probability distribution. This density probability is assumed to be a Gaussian distribution centered around a reference configuration. The shell-occupation numbers of this configuration and the symmetric matrix, which defines the Gaussian function, satisfy a set of nonlinear coupled time-dependent equations that must be solved self-consistently. The reference configuration appears to be identical with the heuristic NLTE average-atom configuration [5,6], and the Gaussian distribution allows one to estimate the average value and the standard deviation of any physical quantity that is an explicit function of electron shell populations. Furthermore, the model is shown to match with the LTE formalism by assuming the principle of detailed balance. This kind of method is surely an important step towards improving NLTE atomic-physics models used in-line or off-line in hydrodynamic codes to simulate laser-plasma interaction experiments. However, up to now nothing clear and of practical interest has been done concerning the explicit implementation of dielectronic recombination and autoionization within the average-atom model formalism. The lack of a proper description of these processes has been a major difficulty in a statistical treatment of dielectronic recombination and autoionization [10]. Taking them into account would be a major improvement of models employed in the context of laboratory-plasma physics.

A simple expression has been recently proposed for these rates within the screened-hydrogenic model (SHM) [11,12], but its accuracy is still unknown and nothing clear has been done about the calculation of the electron covariance matrix. Moreover, most of the average-atom models are based on a SHM or use rates calculated by different codes [13]. The

internal consistency is problematic and these methods have to be carefully benchmarked. To this end, a NLTE average-atom model is needed in which one-electron states are computed with self-consistent potential for fractional electron-shell populations, rates are expressed within the average-configuration formalism, and the electron covariance matrix is calculated self-consistently. To our knowledge, the whole problem has never been undertaken.

This paper is organized as follows. In Sec. II, general expressions for the NLTE average atom and the electron covariance matrix, taking into account recombination and auto-ionization processes, are deduced from a master equation written in electronic configuration space. Particular attention is paid to inherent approximations and shortcomings of the method. In this section, which is devoted to NLTE statistical mechanics, no assumption is made concerning the treatment of atomic structure. This is the aim of Sec. III, where the main quantities involved in NLTE kinetics self-consistent-field calculations, such as atomic structure, average-configuration energy, one-electron energies, oscillator strengths and photoionization cross sections, and transition rates are discussed. In Sec. IV, numerical applications are presented and results are discussed. Section V is the conclusion.

II. FORMAL DEVELOPMENTS

A. Collisional-radiative model

The properties of matter are very difficult to study in NLTE conditions because the related formalism is not as strongly settled as in the LTE case. One must resort to using approximate techniques to handle a NLTE medium. A widespread method is to estimate the change of probability of a microscopic state by using the transition rates of the processes that can modify it.

Let us consider a one-component (no mixture) highly charged ion plasma in which the level of detail of the atomic structure is limited to the DCA approach. Z is the nuclear charge of the element and (n_k) are the electron occupancies of the K_{\max} bound orbitals that describe the ion species embedded in the plasma. Each orbital k ($1 \leq k \leq K_{\max}$) has a degeneracy number D_k ($0 \leq n_k \leq D_k$). Then we introduce the probability of an electronic configuration $P[(n_k), t]$ and the transition rate $M[(n_k), (n'_k)]$ between configurations (n_k) and (n'_k) . $P[(n_k), t]$ depends on time and satisfies a master equation,

$$\begin{aligned} \dot{P}[(n_k), t] = & - \sum_{(n'_k) \neq (n_k)} P[(n_k), t] M[(n_k), (n'_k)] \\ & + \sum_{(n'_k) \neq (n_k)} P[(n'_k), t] M[(n'_k), (n_k)], \end{aligned} \quad (1)$$

where the dot denotes a differentiation with respect to time and

$$\sum_{(n_k)} \equiv \sum_{n_1=0}^{D_1} \cdots \sum_{n_{K_{\max}}=0}^{D_{K_{\max}}}.$$

Equation (1) is linear with respect to probabilities but is often intractable due to the large number of configurations and transition rates that have to be considered. Nevertheless, it is possible to write its formal solution. Let us first define the vector $P(t)$,

$$P(t) = \begin{pmatrix} \vdots \\ P[(n_k), t] \\ \vdots \end{pmatrix},$$

and the matrix \tilde{M} ,

$$\tilde{M}[(n_k), (n'_k)] = M[(n'_k), (n_k)],$$

where $(n_k) \neq (n'_k)$. If we assume that

$$\tilde{M}[(n_k), (n_k)] = - \sum_{(n'_k) \neq (n_k)} M[(n_k), (n'_k)]$$

it is easy to rewrite Eq. (1) as $\dot{P}(t) = \tilde{M}P(t)$, which can be integrated to yield $P(t) = e^{\tilde{M}t} P^0$. P^0 involves the initial probabilities at time $t=0$. \tilde{M} is called the Markov matrix. When this latter is irreducible (the transition rates are positive), the zero value is shown to be a nondegenerate eigenvalue and all the other eigenvalues have a negative real part. In plasma physics, this situation arises when collisional ionization and excitation and their inverse processes (collisional recombination and deexcitation) are taken into account. Consequently, $P(t)$ relaxes to the steady-state distribution P^S : $\tilde{M}P^S = 0$. If one needs the Gibbs equilibrium distribution defined as P^{eq} to be a steady-state solution of Eq. (1), it is then sufficient that the elements of the matrix \tilde{M} satisfy the detailed balance principle:

$$\tilde{M}[(n_k), (n'_k)] P^{\text{eq}}[(n'_k)] = \tilde{M}[(n'_k), (n_k)] P^{\text{eq}}[(n_k)],$$

where

$$P^{\text{eq}}[(n_k)] = \left[\prod_{k=1}^{K_{\max}} \binom{D_k}{n_k} \right] e^{-\beta E[(n_k)] + \eta \sum_{k=1}^{K_{\max}} n_k}.$$

Here, $\binom{D_k}{n_k}$ is a binomial coefficient equal to $D_k!/[n_k!(D_k - n_k)!]$, η is related to the chemical potential μ by $\eta = \beta\mu$, and β is defined by $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T the electron temperature. The free electrons are supposed to be in thermal equilibrium. They play the role of a reservoir by allowing exchange of energy and particles between bound and free electrons. The detailed balance principle ensures that each individual process is time-reversible. It can be shown that the detailed balance principle originates from the reversibility of the microscopic equations with respect to time. It can be violated if a current of matter and/or photons is imposed in an open system.

B. Self-consistent average-atom model

Very often, Eq. (1) is too general to be of practical use and several assumptions must be introduced to simplify it.

Major ones consist in considering average-configuration rates [14,15] and in taking into account the radiative and collisional processes that change the charge state by at most two units. This methodology suits any other process, but in this paper we will concentrate on the major improvement of showing how autoionization and dielectronic recombination naturally enter the average-atom equations and electron covariance matrix. Usual NLTE average-atom models [5,6] leave out both autoionization and its inverse process, the dielectronic attachment. This fact is known to be a troublesome limitation for application to low-density high- Z plasmas, causing systematic errors in predicted ionization states and electronic populations. At high enough densities, the highly excited electron resulting from dielectronic attachment is easily removed by collisional ionization and three-body recombination is likely to be dominant in any case. In these conditions, it may be reasonable to ignore the dielec-

tronic process. Furthermore, since these processes are two-electron transitions and induce strong correlations between electron populations, their implementation within the framework of the average-atom model cannot bypass the simultaneous consideration of the electron covariance matrix [10].

The derivation is going to be carefully detailed because the inherent approximations are essential to understanding the shortcomings of the equations obtained in the end. Moreover, we found nothing else, but we mention these approximations to argue that the SCAALP model discussed in this paper, i.e., self-consistent average-atom for laboratory plasmas, belongs to a larger class of mean-field descriptions of NLTE highly charged ion plasmas. This point recalls the state of the art in LTE mean-field description of many-particle systems standing on a saddle-point evaluation of an integral representation of a partition function [16–18]. By doing so, Eq. (1) can be written as

$$\begin{aligned}
\dot{P}[(n_k), t] = & - \sum_{i,j} P[(n_k), t] n_i (D_j - n_j) \tau_{i,j} - \sum_i P[(n_k), t] n_i I_{i,c} - \sum_i P[(n_k), t] R_{c,i} (D_i - n_i) \\
& + \sum_{i,j} P \left[\begin{pmatrix} \vdots \\ n_i - 1 \\ \vdots \\ n_j + 1 \\ \vdots \end{pmatrix}, t \right] (n_j + 1) (D_i - n_i + 1) \bar{\tau}_{j,i} + \sum_i P \left[\begin{pmatrix} \vdots \\ n_i + 1 \\ \vdots \end{pmatrix}, t \right] (n_i + 1) \bar{I}_{i,c} \\
& + \sum_i P \left[\begin{pmatrix} \vdots \\ n_i - 1 \\ \vdots \end{pmatrix}, t \right] (D_i - n_i + 1) \bar{R}_{c,i} - \sum_{i,j,m} P[(n_k), t] n_m (n_i - \delta_{i,m}) (D_j - n_j) A_{i,j}^{m,c} \\
& - \sum_{i,j,m} P[(n_k), t] (D_m - n_m) (D_i - n_i + \delta_{i,m}) n_j R_{j,i}^{c,m} + \sum_{i,j,m} P \left[\begin{pmatrix} \vdots \\ n_i - 1 \\ \vdots \\ n_j + 1 \\ \vdots \\ n_m - 1 \\ \vdots \end{pmatrix}, t \right] (D_m - n_m + 1) \\
& \times (D_i - n_i + 1 + \delta_{i,m}) (n_j + 1) \bar{R}_{j,i}^{c,m} + \sum_{i,j,m} P \left[\begin{pmatrix} \vdots \\ n_i + 1 \\ \vdots \\ n_j - 1 \\ \vdots \\ n_m + 1 \\ \vdots \end{pmatrix}, t \right] (n_m + 1) (n_i + 1 - \delta_{i,m}) (D_j - n_j + 1) \bar{A}_{i,j}^{m,c}. \quad (2)
\end{aligned}$$

Here, $\tau_{i,j}, I_{i,c}, R_{c,i}$, are the one-electron transition rates of excitation (or deexcitation) from subshell i to subshell j , and of ionization and recombination involving subshell i , respectively. These rates may be radiative or collisional. $A_{i,j}^{m,c}$ is the two-electron autoionization rate of the process in which one of the electron makes the transition from subshell i to sub-

shell j while the other electron of subshell m goes to the continuum. $R_{j,i}^{c,m}$ is the rate of the inverse process. With $I_{i,c}$, $R_{c,i}$, $A_{i,j}^{m,c}$, and $R_{j,i}^{c,m}$, each configuration can be related to any other configuration by a sequence of at least one-electron microscopic processes.

The Markov matrix is irreducible and the charge states are

not evolving independently of each others because charge states are not directly coupled by microscopic processes. When only the excitation and deexcitation rates $\tau_{i,j}$ are kept, the Markov matrix becomes reducible. The relaxation towards equilibrium is nontrivial and the uniqueness of the steady-state solution is not guaranteed. An overbar means that the corresponding rate is not calculated by using the occupation numbers of the reference configuration (n_k) but those of the electronic configuration involved in the specific transition. This point of view of writing the master equation is illustrated on the particular example of the $2p \rightarrow 2s$ transition (Fig. 1). The reference configuration (n_k) is $1s2s2p$ and the

deexcitation rate from the configuration $1s2p^2$ is written $\bar{\tau}_{2p,2s}$ because it is calculated by using the electron populations of configuration $1s2p^2$; $\bar{\tau}_{2p,2s}$ is different from $\tau_{2p,2s}$ because the latter is calculated with the electron populations of the configuration $1s2s2p$.

To simplify the developments, fractional occupation numbers are used preferentially to integer values. Orbital relaxation is assumed to play a minor role for the highly charged ion plasmas under study and the ‘‘law of great number’’ is supposed to be valid. Let us notice that the last assumption is questionable when the subshells are nearly occupied or empty [18,19]. Equation (2) becomes

$$\begin{aligned} \dot{P}[(n_k),t] = & - \sum_{i,j} P[(n_k),t] n_i (D_j - n_j) \tau_{i,j} - \sum_i P[(n_k),t] n_i I_{i,c} - \sum_i P[(n_k),t] R_{c,i} (D_i - n_i) \\ & + \sum_{i,j} P \left[\begin{pmatrix} \vdots \\ n_i - 1 \\ \vdots \\ n_j + 1 \\ \vdots \end{pmatrix}, t \right] n_j (D_i - n_i) \tau_{j,i} + \sum_i P \left[\begin{pmatrix} \vdots \\ n_i + 1 \\ \vdots \end{pmatrix}, t \right] n_i I_{i,c} + \sum_i P \left[\begin{pmatrix} \vdots \\ n_i - 1 \\ \vdots \end{pmatrix}, t \right] (D_i - n_i) R_{c,i} \\ & - \sum_{i,j,m} P[(n_k),t] n_m n_i (D_j - n_j) A_{i,j}^{m,c} - \sum_{i,j,m} P[(n_k),t] (D_m - n_m) (D_i - n_i) n_j R_{j,i}^c \\ & + \sum_{i,j,m} P \left[\begin{pmatrix} \vdots \\ n_i - 1 \\ \vdots \\ n_j + 1 \\ \vdots \\ n_m - 1 \\ \vdots \end{pmatrix}, t \right] (D_m - n_m) (D_i - n_i) n_j R_{j,i}^{c,m} + \sum_{i,j,m} P \left[\begin{pmatrix} \vdots \\ n_i + 1 \\ \vdots \\ n_j - 1 \\ \vdots \\ n_m + 1 \\ \vdots \end{pmatrix}, t \right] n_m n_i (D_j - n_j) A_{i,j}^{m,c}. \end{aligned} \quad (3)$$

By writing $P[(n_k),t]$ as $\exp\{-S[(n_k),t]\}$, all terms that involve integer changes with respect to occupation numbers are expressed as a Taylor expansion of $P[(n_k),t]$. Doing so, we just write the master equation, which is a finite-difference equation in the electronic configuration space, as a partial differential equation with respect to shell populations. At the level of approximation retained in this paper, it is sufficient to expand $S[(n_k),t]$ up to first order. This is equivalent to expanding $P[(n_k),t]$ in Taylor series around some reference configuration up to second order by neglecting any second-order differentiation of $S[(n_k),t]$ with respect to occupation numbers. For example, the energy differences of Fig. 1 are $\Delta E_{2s,2p} \approx \Delta \tilde{E}_{2s,2p} \approx \varepsilon_{2p} - \varepsilon_{2s}$, $\Delta E_{2s} \approx \Delta \tilde{E}_{2s} \approx -\varepsilon_{2s}$, and $\Delta E_{2p} \approx \Delta \tilde{E}_{2p} \approx -\varepsilon_{2p}$, respectively. The (ε_k) are the first derivatives of the configuration energy calculated by using the occupation numbers of the reference configuration ($1s2s2p$ in our example) [20]. This point may appear obscure at first sight but is perfectly sound and fruitful because the self-consistent-field equations found in the end depend on the approximate differential equation written at this stage. A

whole family of mean-field description of matter may be obtained. Our method is consistent with existing LTE average-atom models and is easy to implement since the average-atom populations and electron covariance matrix satisfy uncoupled equations, as will be shown later.

Following previous works [19,21–23], we are only looking for a particular solution because the master equation is still difficult to solve exactly, even written as a partial differential equation of first order with respect to time but of second order with respect to shell populations. For practical applications, it appears that a Gaussian ansatz for $P[(n_k),t]$, namely $P[(n_k),t] \approx e^{-(1/2)\sum_{k,l}\Delta n_k(t)U_{kl}(t)\Delta n_l(t)}$, is very well suited. The symmetric matrix $[U_{kl}(t)]$ is time-dependent and gives an estimate of the electron covariance-matrix: $(U^{-1})_{kl}(t) \approx \langle \Delta n_k(t)\Delta n_l(t) \rangle$. $\langle A \rangle$ means the statistical average of the quantity A and $\Delta n_k(t) = n_k - N_k(t)$; $[N_k(t)]$ is a still unknown reference configuration. From now on, if no ambiguity exists, $P[(n_k),t]$, $[N_k(t)]$, and $[U_{kl}(t)]$ are simply written as P , (N_k) , and (U_{kl}) . Moreover, any index repetition means a sum on the index of interest. Starting from Eq. (3), we have $(\partial_i \equiv \partial/\partial n_i)$ and $\partial_{ij} \equiv \partial^2/\partial n_i \partial n_j$

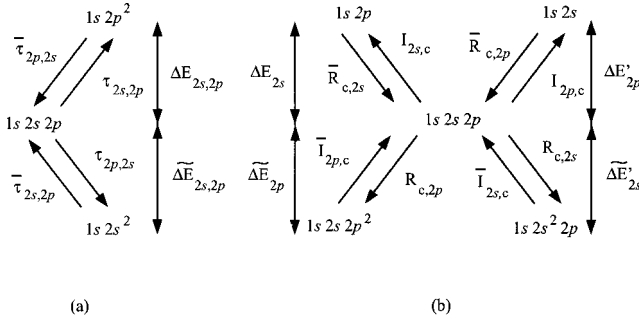


FIG. 1. Example of processes involving subshells 2s and 2p of the reference configuration $1s2s2p$: (a) bound-bound transitions, (b) bound-free transitions. $\tau_{i,j}$ is the one-electron rate of transition $i \rightarrow j$ (excitation or deexcitation). $I_{i,c}$ and $R_{c,i}$ are the one-electron ionization and recombination rates associated with the subshell i , respectively. The overbar means that the corresponding rate is not calculated by using the reference configuration but the configuration involved in the transition of interest ($1s2p$ for $\bar{R}_{c,2s}$). The energy difference with respect to $1s2s2p$ has been mentioned too.

$$\begin{aligned} \dot{P} = & [\partial_j P - \partial_i P + \frac{1}{2} (\partial_{ii}^2 P + \partial_{jj}^2 P - 2\partial_{ij}^2 P)] n_j (D_i - n_i) \tau_{j,i} \\ & + (\partial_i P + \frac{1}{2} \partial_{ii}^2 P) n_i I_{i,c} + (-\partial_i P + \frac{1}{2} \partial_{ii}^2 P) (D_i - n_i) R_{c,i} \\ & + [\partial_i P - \partial_j P + \partial_m P + \frac{1}{2} (\partial_{ii}^2 P + \partial_{jj}^2 P + \partial_{mm}^2 P - 2\partial_{ij}^2 P \\ & + 2\partial_{im}^2 P - 2\partial_{jm}^2 P)] n_m n_i (D_j - n_j) A_{i,j}^{m,c} \\ & + [-\partial_i P + \partial_j P - \partial_m P + \frac{1}{2} (\partial_{ii}^2 P + \partial_{jj}^2 P + \partial_{mm}^2 P - 2\partial_{ij}^2 P \\ & + 2\partial_{im}^2 P - 2\partial_{jm}^2 P)] (D_m - n_m) (D_i - n_i) n_j R_{j,i}^{c,m}. \quad (4) \end{aligned}$$

We then use $\dot{P} = (\dot{N}_i U_{kl} \Delta n_k - \frac{1}{2} \Delta n_k \dot{U}_{kl} \Delta n_l) P$, $\partial_i P = (-\Delta n_k U_{ki}) P$, and $\partial_{ij}^2 P \approx (\Delta n_k U_{ki}) (\Delta n_l U_{lj}) P$. Occupation numbers and rates are developed around (N_k) . After changing the index and symmetrizing the terms in $\Delta n_k \Delta n_l$,

algebraic manipulations show that the linear terms in Δn_k and the quadratic terms in $\Delta n_k \Delta n_l$ give the evolution equations for the (N_k) and the (U_{kl}) , respectively.

As for the evolution equations for the reference configuration (N_k) , we find that

$$\begin{aligned} \dot{N}_i = & N_j (D_i - N_i) \tau_{j,i} - N_i (D_j - N_j) \tau_{i,j} - N_i I_{i,c} + (D_i - N_i) R_{c,i} \\ & - N_m N_i (D_j - N_j) A_{i,j}^{m,c} + N_m N_j (D_i - N_i) A_{j,i}^{m,c} \\ & - N_i N_m (D_j - N_j) A_{m,j}^{i,c} + (D_m - N_m) (D_i - N_i) N_j R_{j,i}^{c,m} \\ & - (D_m - N_m) (D_j - N_j) N_i R_{i,j}^{c,m} \\ & + (D_i - N_i) (D_m - N_m) N_j R_{j,m}^{c,i}, \quad (5) \end{aligned}$$

if the matrix (U_{kl}) is nonsingular. It should be stressed that all rates are calculated with the occupation numbers (N_k) . In other words, the (N_k) satisfy the common NLTE average-atom equations [5,6,8], as long as autoionization and its inverse process are neglected. However, when these processes are taken into account, they easily enter within the framework of the average-atom model, but in a nontrivial way. Our mean-field equations differ from the work of Rozsnyai [7] because we have four additional terms, namely the two first terms in the second and third lines of Eq. (5), which are absent in the heuristic average-atom equations published by him recently. There is no reason to suppress them, even if autoionization may enter with a positive sign and its inverse process with a negative one. Indeed, autoionization involves three subshells. One electron of subshell i may go into the continuum while an electron from subshell m goes into subshell j . This process corresponds to the third term in the second line of Eq. (5). However, the subshell i of interest may also be involved in the deexcitation process, hence the presence of the two other terms in the same line [11,12].

As for the evolution equations for the matrix (U_{kl}) , we obtain the following result:

$$\begin{aligned} -\dot{U}_{kl} = & (U_{ki} - U_{kj}) (U_{li} - U_{lj}) N_j (D_i - N_i) \tau_{j,i} + U_{ki} U_{li} [N_i I_{i,c} + R_{c,i} (D_i - N_i)] + (U_{ki} - U_{kj} + U_{km}) (U_{li} - U_{lj} + U_{lm}) \\ & \times [N_m N_i (D_j - N_j) A_{i,j}^{m,c} + (D_m - N_m) (D_i - N_i) N_j R_{j,i}^{c,m}] + (U_{ki} - U_{kj}) \partial_l [N_j (D_i - N_i) \tau_{j,i}] + (U_{li} - U_{lj}) \partial_k [N_j (D_i \\ & - N_i) \tau_{j,i}] - U_{ki} \partial_l [N_i I_{i,c} - R_{c,i} (D_i - N_i)] - U_{li} \partial_k [N_i I_{i,c} - R_{c,i} (D_i - N_i)] - (U_{ki} - U_{kj} + U_{km}) \partial_l [N_m N_i (D_j - N_j) A_{i,j}^{m,c} \\ & - (D_m - N_m) (D_i - N_i) N_j R_{j,i}^{c,m}] - (U_{li} - U_{lj} + U_{lm}) \partial_k [N_m N_i (D_j - N_j) A_{i,j}^{m,c} - (D_m - N_m) (D_i - N_i) N_j R_{j,i}^{c,m}]. \quad (6) \end{aligned}$$

Equations (5) and (6) are both nonlinear in (N_k) and (U_{kl}) and have to be integrated self-consistently. However, as long as (U_{kl}) is nonsingular, Eq. (5) does not contain any term in (U_{kl}) . They can thus be solved one after the other. In the most general case, evolution equations for (N_k) and (U_{kl}) are highly coupled since (U_{kl}) is present in the equation governing the time evolution of (N_k) .

At this stage, one could think that the problem is solved. In fact, it is known that only the inverse matrix of (U_{kl}) [$C_{kl} = (U^{-1})_{kl}$] has an immediate physical interpretation because it gives an estimate of the electron covariance matrix. Surprisingly, the evolution equations for (C_{kl}) are far more simple since they are linear with respect to (C_{kl}) . These equations are found from Eq. (6) by using the identity matrix $(\dot{M}^{-1} = -M^{-1} \dot{M} M^{-1})$. We get

$$\dot{C}_{\lambda\mu} = B_{\lambda\mu} + C_{\lambda k} \partial_k V_{\mu} + C_{\mu k} \partial_k V_{\lambda}, \quad (7)$$

where

$$\begin{aligned}
V_\mu = & (D_\mu - N_\mu)R_{c,\mu} - N_\mu I_{\mu,c} + \sum_i [N_i(D_\mu - N_\mu)\tau_{i,\mu} - N_\mu(D_i - N_i)\tau_{\mu,i}] + \sum_{i,j} [(D_j - N_j)(D_\mu - N_\mu)N_i R_{i,\mu}^{c,j} \\
& - N_j N_\mu (D_i - N_i)A_{\mu,i}^{j,c}] + \sum_{i,j} [-(D_j - N_j)(D_i - N_i)N_\mu R_{\mu,i}^{c,j} + N_j N_i (D_\mu - N_\mu)A_{i,\mu}^{j,c}] + \sum_{i,j} [(D_\mu - N_\mu) \\
& \times (D_i - N_i)N_j R_{j,i}^{c,\mu} - N_\mu N_i (D_j - N_j)A_{i,j}^{\mu,c}]
\end{aligned} \tag{8}$$

and

$$\begin{aligned}
B_{\lambda\mu} = & -N_\lambda(D_\mu - N_\mu)\tau_{\lambda,\mu} - N_\mu(D_\lambda - N_\lambda)\tau_{\mu,\lambda} + \sum_i [N_\lambda N_\mu (D_i - N_i)A_{\mu,i}^{\lambda,c} + (D_\lambda - N_\lambda)(D_\mu - N_\mu)N_i R_{i,\mu}^{c,\lambda}] \\
& + \sum_i [N_\mu N_\lambda (D_i - N_i)A_{\lambda,i}^{\mu,c} + (D_\mu - N_\mu)(D_\lambda - N_\lambda)N_i R_{i,\lambda}^{c,\mu}] - \sum_i [N_i N_\mu (D_\lambda - N_\lambda)A_{\mu,\lambda}^{i,c} \\
& + (D_i - N_i)(D_\mu - N_\mu)N_\lambda R_{\lambda,\mu}^{c,i}] - \sum_i [N_i N_\lambda (D_\mu - N_\mu)A_{\lambda,\mu}^{i,c} + (D_i - N_i)(D_\lambda - N_\lambda)N_\mu R_{\mu,\lambda}^{c,i}] \\
& - \sum_i [N_\lambda N_i (D_\mu - N_\mu)A_{i,\mu}^{\lambda,c} + (D_\lambda - N_\lambda)(D_i - N_i)N_\mu R_{\mu,i}^{c,\lambda}] - \sum_i [N_\mu N_i (D_\lambda - N_\lambda)A_{i,\lambda}^{\mu,c} + (D_\mu - N_\mu)(D_i - N_i)N_\lambda R_{\lambda,i}^{c,\mu}] \\
& + \delta_{\lambda\mu} \left\{ \begin{aligned} & (D_\mu - N_\mu)R_{c,\mu} + N_\mu I_{\mu,c} + \sum_i [N_i(D_\mu - N_\mu)\tau_{i,\mu} + N_\mu(D_i - N_i)\tau_{\mu,i}] \\ & + \sum_{i,j} [(D_j - N_j)(D_\lambda - N_\lambda)N_i R_{i,\lambda}^{c,i} + N_j N_\lambda (D_i - N_i)A_{\lambda,i}^{j,c}] \\ & + \sum_{i,j} [(D_j - N_j)(D_i - N_i)N_\lambda R_{\lambda,i}^{c,j} + N_j N_i (D_\lambda - N_\lambda)A_{i,\lambda}^{j,c}] \\ & + \sum_{i,j} [(D_\lambda - N_\lambda)(D_i - N_i)N_j R_{j,i}^{c,\lambda} + N_\lambda N_i (D_j - N_j)A_{i,j}^{\lambda,c}] \end{aligned} \right\}.
\end{aligned} \tag{9}$$

In practical applications, only Eqs. (5) and (7)–(9) must be solved starting from given initial conditions. Steady-state solutions are obtained by saying that any term involving a differentiation with respect to time is null. The charge neutrality of the plasma is ensured by the constraint $\sum_{k=1}^{K_{\max}} N_k + \bar{Z}^* = Z$. The average ionization \bar{Z}^* is calculated analytically:

$$\bar{Z}^* = \frac{4}{\sqrt{\pi}} \frac{A}{\rho N_A} \left(\frac{m_e k_B T}{2\pi\hbar^2} \right)^{3/2} F_{1/2}(\eta)$$

with

$$F_\alpha(\eta) = \int_0^\infty dx \frac{x^\alpha}{1 + e^{x-\eta}}.$$

A , ρ , N_A , and m_e are the molar mass, the mass density, the Avogadro number, and the electron mass. Before closing this section, we think it is worthwhile to discuss the following points: the Gaussian ansatz for the density probability distribution P , its normalization, the consistency of those developments with LTE, and the detailed balance.

C. Remarks about the Gaussian ansatz

As mentioned above, the Gaussian ansatz made for P is a natural trick to find an approximate solution of the master equation (4) that is consistent, at least formally, with what can be found in LTE by replacing the original discrete summation in the grand-canonical partition function with a K_{\max} -dimensional integral, using the Stirling formula to approximate the binomial coefficients, and by developing the action around its minimum up to second order [23]. If this Gaussian expression for P is well defined in LTE, it is by no means obvious that the probability distribution may not sometimes have a second maximum in NLTE. There is, therefore, the danger of extrapolating a quadratic approximation far from the reference configuration (N_k). One could integrate the differential equation (4), which looks like a Fokker-Planck equation [8], to test this assumption on some specific examples. One could also run intensive benchmark computations using, for example, the superconfiguration approach [24].

D. Consistency of SCAALP with LTE and detailed balance

The second point we want to clarify concerns the normalization of P . By looking for a solution of the form

$P[(n_k), t] \approx e^{-(1/2)\sum_{k,l}\Delta n_k(t)U_{kl}(t)\Delta n_l(t)}$, Eq. (4) is in fact solved for the non-normalized density probability distribution. The normalization factor is easy to find since it is sufficient to multiply P by $\sqrt{\det(U)/(2\pi)^{K_{\max}}}$ to work with a density probability distribution normalized to unity. We can see that the most general Gaussian ansatz is $P[(n_k), t] \approx A(t)e^{-(1/2)\sum_{k,l}\Delta n_k(t)U_{kl}(t)\Delta n_l(t)}$, where $A(t)$ is some unknown function. If we inject this expression in Eq. (4), we find that $A(t)$ must be time-independent, and if we impose P to be normalized to unity from the beginning, $A(t) = \sqrt{\det(U)/(2\pi)^{K_{\max}}}$, the only allowed ‘‘trajectories’’ in configuration space are those at constant $\det(U)$. This paradox is easily solved by remembering where Eq. (4) comes from. By using fractional occupation numbers, invoking the ‘‘law of great numbers,’’ neglecting orbital relaxation, and transforming a finite-difference equation into a differential equation, we have altered the exactness of the original master equation (2). We are not keeping the configuration space volume constant and we are compelled to normalize P afterwards. This means that $A(t)$ is irrelevant and cannot be determined from Eq. (4). We have already encountered this problem (well known in quantum field theory) in dense plasma physics [18]. This raises automatically the consistency of our developments with LTE. Essentially, are Eqs. (5) and (7)–(9) consistent with LTE and, if yes, with which LTE?

In LTE, (N_k) and (U_{kl}) are known to be given by [23]

$$\begin{aligned} N_k &= D_k f_k, \\ f_k &= \frac{1}{1 + e^{\beta(\varepsilon_k - \mu)}}, \quad g_k = 1 - f_k, \\ \varepsilon_k &= \partial_k E|_{(N_i)}, \quad V_{kl} = \partial_{kl}^2 E|_{(N_i)}, \\ \varpi_k^2 &= D_k f_k g_k, \\ U_{kl} &= \delta_{kl} / \varpi_k^2 + \beta V_{kl}. \end{aligned} \quad (10)$$

When free electrons are supposed to be in LTE among themselves, one-electron rates obey the detailed balance principle,

$$\begin{aligned} e^{-\beta\varepsilon_i} \tau_{i,j} &= e^{-\beta\varepsilon_j} \tau_{j,i}, \\ e^{-\beta(\varepsilon_i - \mu)} I_{i,c} &= R_{c,i}, \\ e^{-\beta(\varepsilon_m + \varepsilon_i - \mu)} A_{i,j}^{m,c} &= e^{-\beta\varepsilon_j} R_{j,i}^{c,m}. \end{aligned} \quad (11)$$

It is thus easy to find that we have a true microreversibility between one-electron processes for the average-atom configuration:

$$\begin{aligned} N_i(D_j - N_j) \tau_{i,j} &= N_j(D_i - N_i) \tau_{j,i}, \\ N_i I_{i,c} &= (D_i - N_i) R_{c,i}, \\ N_i N_m (D_j - N_j) A_{i,j}^{m,c} &= (D_i - N_i)(D_m - N_m) N_j R_{j,i}^{c,m}. \end{aligned} \quad (12)$$

These equations are well known but their derivation is by no means straightforward and many assumptions are often over-

looked. The first one is related to the detailed balance principle. In fact, the average-atom configuration has no physical meaning and the detailed balance principle is valid in the strict sense between configurations. The detailed balance relations obeyed by the one-electron rates calculated within the average-atom formalism are no more than a direct consequence of these general relations. As an example, we are going to derive the one between excitation and deexcitation between configuration (N_k) to configuration $(N_k - \delta_{ik} + \delta_{jk})$ for the transition $i \rightarrow j$. Let us start from the exact relation, as long as the rates are calculated within the average-configuration framework,

$$\begin{aligned} & \left[\prod_{k=1}^{K_{\max}} \binom{D_k}{N_k} \right] e^{-\beta E[(N_k)] + \eta \sum_{k=1}^{K_{\max}} N_k N_i (D_j - N_j) \tau_{i,j}} \\ &= \left[\prod_{k=1}^{K_{\max}} \binom{D_k}{N_k - \delta_{ik} + \delta_{jk}} \right] \\ & \times e^{-\beta E[(N_k - \delta_{ik} + \delta_{jk})] + \eta \sum_{k=1}^{K_{\max}} (N_k - \delta_{ik} + \delta_{jk}) (N_j + 1)} \\ & \times (D_i - N_i + 1) \bar{\tau}_{j,i}, \end{aligned}$$

and neglecting orbital relaxation. We get

$$e^{-\beta E[(N_k)]} \tau_{i,j} = e^{-\beta E[(N_k - \delta_{ik} + \delta_{jk})]} \bar{\tau}_{j,i}.$$

It is clear that if the transition energies are calculated as

$$E[(N_k - \delta_{ik} + \delta_{jk})] - E[(N_k)] \approx \partial_j E|_{(N_k)} - \partial_i E|_{(N_k)} = \varepsilon_j - \varepsilon_i,$$

the standard detailed-balance relations for the average atom are recovered. This explains that the detailed-balance principle and the way we go from a finite-difference master equation to a partial-derivative master equation have to be self-consistently treated. Nothing prevents one from taking into account higher-order terms in the computation of the transition energy. Yet, one must modify the differential equation (4) as a consequence. If all the rates satisfy the detailed-balance principle, the steady state will be a LTE situation in which the average-atom shell occupations will not be given by Fermi-Dirac relations. The LTE so obtained will be in between the common ‘‘Fermi-Dirac-like’’ and the true LTE giving the grand-canonical partition function in configuration space. To end this section, we are going to show now that Eqs. (5) and (7)–(9) are consistent with the LTE equations (10).

If checking the consistency of the NLTE average-atom equations (5) with the LTE ones is straightforward, the task is harder for Eqs. (7)–(9). Instead of taking the LTE solution for (N_k) and (U_{kl}) and injecting them in Eq. (6) or Eqs. (7)–(9), a more elegant method consists in writing the detailed-balance equations for some configuration within the Gaussian ansatz framework, and expanding them around (N_k) . In our NLTE formalism, these equations read

$$\begin{aligned} & e^{-(1/2)\Delta n_k U_{kl} \Delta n_l} N_i (D_j - N_j) \tau_{i,j} \\ &= e^{-(1/2)\Delta \tilde{n}_k U_{kl} \Delta \tilde{n}_l} N_j (D_i - N_i) \tau_{j,i}, \end{aligned}$$

$$e^{-(1/2)\Delta n_k U_{kl} \Delta n_l N_i I_{i,c}} = e^{-(1/2)\Delta \hat{n}_k U_{kl} \Delta \hat{n}_l (D_i - N_i) R_{c,i}}, \quad (13)$$

$$e^{-(1/2)\Delta n_k U_{kl} \Delta n_l N_i N_m (D_j - N_j) A_{i,j}^{m,c}} \\ = e^{-(1/2)\Delta \hat{n}_k U_{kl} \Delta \hat{n}_l N_j (D_m - N_m) (D_i - N_i) A_{j,i}^{c,m}},$$

where $\Delta \tilde{n}_k U_{kl} \Delta \tilde{n}_l \approx \Delta n_k U_{kl} \Delta n_l + 2\Delta n_k (U_{kj} - U_{ki})$ (excitation/deexcitation), $\Delta \hat{n}_k U_{kl} \Delta \hat{n}_l \approx \Delta n_k U_{kl} \Delta n_l - 2\Delta n_k U_{ki}$ (ionization/recombination), and $\Delta \hat{n}_k U_{kl} \Delta \hat{n}_l \approx \Delta n_k U_{kl} \Delta n_l + 2\Delta n_k (U_{kj} - U_{ki} - U_{km})$. When the reference configuration (N_k) is considered, Eq. (13) leads to Eq. (12); by combining it with Eq. (11), the LTE average-atom equations (10) are recovered. Let us now expand each right-hand side and left-hand side terms in Eq. (13) with respect to (Δn_k), and calculate the result for (N_k) at LTE. We obtain first that

$$\ln\left(\frac{\tau_{i,j}}{\tau_{j,i}}\right) + \ln\left[\frac{N_i}{(D_i - N_i)}\right] = -\Delta n_k (U_{kj} - U_{ki}) + \ln\left[\frac{N_j}{(D_j - N_j)}\right], \\ \ln\left(\frac{I_{i,c}}{R_{c,i}}\right) + \ln\left[\frac{N_i}{(D_i - N_i)}\right] = \Delta n_k U_{ki}, \\ \ln\left(\frac{A_{i,j}^{m,c}}{A_{j,i}^{c,m}}\right) + \ln\left[\frac{N_i}{(D_i - N_i)}\right] + \ln\left[\frac{N_m}{(D_m - N_m)}\right] \\ = -\Delta n_k (U_{kj} - U_{ki} - U_{km}) + \ln\left[\frac{N_j}{(D_j - N_j)}\right].$$

Using Eq. (11), we find, as usual, that rates have no meaning and disappear to level space for the one-electron energies and the chemical potential. After differentiation, the only remaining quantities are

$$\beta(V_{ki} - V_{kj})\Delta n_k + \frac{\delta_{ik}}{\varpi_k^2}\Delta n_k = \Delta n_k (U_{ki} - U_{kj}) + \frac{\delta_{jk}}{\varpi_k^2}\Delta n_k,$$

$$\beta V_{ki}\Delta n_k + \frac{\delta_{ik}}{\varpi_k^2}\Delta n_k = \Delta n_k U_{ki},$$

$$\beta(V_{ki} + V_{km} - V_{kj})\Delta n_k + \frac{\delta_{ik}}{\varpi_k^2}\Delta n_k + \frac{\delta_{mk}}{\varpi_k^2}\Delta n_k \\ = \Delta n_k (U_{ki} + U_{km} - U_{kj}) + \frac{\delta_{jk}}{\varpi_k^2}\Delta n_k.$$

Consequently, $U_{kl} = \beta V_{kl} + (\delta_{kl}/\varpi_k^2)$ is the unique solution due to ionization/recombination processes. We find that our NLTE formalism is consistent with LTE for the average-atom populations (N_k) and for the (inverse) electron covariance matrix (U_{kl}). This is the mean-field equilibrium without corrections resulting from fluctuations of the occupation probabilities around it [18].

E. Summary

We have developed a NLTE technique to calculate statistical distributions in time-dependent off-equilibrium atomic

physics by taking into account one- and two-electron processes, namely ionization, excitation, autoionization, and their inverse processes. Starting from a master equation written in the configuration space with average-configuration rates, we found that the average-atom equations and time evolution of two-electron correlation naturally emerge by assuming a Gaussian ansatz for the density probability distribution of the configurations. By carefully underlying all the inherent assumptions, we have discussed with which LTE our method is consistent, when of course external conditions make it possible.

III. ATOMIC PHYSICS AND NUMERICAL METHOD

A. Atomic structure

Two different methods can be used in SCAALP to determine the average-atom populations (N_k) and the matrix (U_{kl}). Atomic structure may be described either with a screened-hydrogenic model including ℓ splitting [25], or with a self-consistent-field approach using the optimized-potential method (OPM) [26]. These models are very similar conceptually. The screening constants have been fitted to reproduce Hartree-Fock ionization potentials and excitation energies, whereas the optimized potential is the best local potential matching Hartree-Fock calculations. In the first case, only semianalytic expressions are available for the oscillator strengths, photoionization cross sections, and transition rates for the radiative and collisional excitation, ionization, and autoionization processes. Since free electrons are assumed to be in LTE, the transition rates of the inverse processes are calculated invoking the detailed balance principle. In the second case, one-electron orbitals are effectively computed and all the rates may be calculated within the average-configuration framework [14]. However, since we focus in this work on the role of atomic structure at given transition rates and statistical mechanics formalism, only semianalytic formulas for the transition rates of interest are considered.

B. Transition rates

The Lotz and Mewe formulas are used for the collisional ionization and excitation [27–29]. The corresponding radiative rates are computed using the knowledge of the photoionization and photoexcitation cross sections and the radiation intensity [13,30]. We assume that the radiation field does not alter significantly over the line profiles that are assumed to be Dirac functions. In practice, the radiation field is supposed to be Planckian at some radiation temperature T_r . However, to allow for a general form for the radiation field, the integrals of interest are evaluated numerically by spectral methods. As usual, the rates are in detailed balance when the radiation temperature is equal to the electron temperature ($T_r = T_e$). Though the energy levels are calculated from the screened-Coulomb approximation by differentiating the configuration energy with respect to shell populations (n_k) for reasons explained in the preceding section, collisional rates, photoexcitation, and photoionization cross sections are not obtained within this approximation. We employ a method

proposed elsewhere to evaluate average-atom bound-bound and bound-free oscillator strengths [31]. This technique ensures that one-electron sum rules and the continuum series are continuously connected. This is a powerful method for studying photoabsorption properties of LTE plasmas but the positive sign of the one-electron photoionization differential oscillator strength was not taken for granted. We then decide to slightly modify it as follows. The expressions of the $\Delta n \neq 0$ oscillator strengths and of the differential oscillator strengths stay unchanged. The $\Delta n = 0$ oscillator strengths $f_{n\ell-1, n\ell}$ are now obtained remembering a simple scaling law for the radial matrix element $R_{n\ell}^{n\ell-1}$ [32]:

$$R_{n\ell}^{n\ell-1} = \frac{3}{2} n \sqrt{n^2 - l^2} / \sqrt{Z_{n\ell} Z_{n\ell-1}},$$

where $Z_{n\ell-1}$ and $Z_{n\ell}$ are the screened nuclear charges of subshells $n\ell-1$ and $n\ell$, respectively. We then assume that the photoionization differential oscillator strength at threshold of the partial wave $n\ell \rightarrow E\ell-1$ is proportional to that of the partial wave $n\ell \rightarrow E\ell+1$. Waiting for more intensive comparisons with sophisticated atomic calculations, the coefficient is simply taken to be equal to the ratio of the geometric factors entering in each partial-wave one-electron sum rule satisfied by oscillator strengths in many-electron atoms in the nonrelativistic regime, namely $-\frac{1}{3}[\ell(2\ell-1)]/(2\ell+1)$ for $n\ell \rightarrow E\ell-1$ and $\frac{1}{3}[(\ell+1)(2\ell+3)]/(2\ell+1)$ for $n\ell \rightarrow E\ell+1$. We thus calculate the $n\ell$ -subshell threshold photoionization amplitude by using the one-electron sum rule obtained by adding the two aforementioned partial-wave sum rules. For safety, the oscillator strength $f_{n\ell-1, n\ell}$ is replaced with $\tanh(f_{n\ell-1, n\ell})$ to manipulate a quantity between zero and unity. In summary, we keep the key idea that consists in connecting the discrete spectrum and the continuum series by continuity while satisfying the one-electron sum rules. We have reduced by two the number of equations to be solved to get the threshold photoionization amplitudes ($df_{k,c}/d\varepsilon$), and as a consequence, all the oscillator strengths ($f_{k,k'}$). Sign problems are not encountered anymore. Moreover, since these threshold photoionization amplitudes satisfy nothing but a linear system, the differentiation with respect to shell populations (n_k) is tedious but straightforward. This means that we can calculate quite easily the gradient of any rate with respect to (n_k) and obtain the matrix (U_{kl}) quickly and with high precision. Fortunately, we can also take into account the autoionization and dielectronic recombination because the autoionization rate $A_{i,j}^{k,c}$ can be expressed as follows:

$$A_{i,j}^{k,c} = \frac{3\pi Ry^2}{2\hbar Z^*2} \left(\frac{\varepsilon_i - \varepsilon_j}{Ry} \right)^2 \frac{f_{i,j}}{D_j^0} \frac{df_{k,c}}{d\varepsilon} g_A,$$

where Ry , g_A , and D_j^0 are the Rydberg constant, a Gaunt factor, and the degeneracy of subshell j without density effects [33]. In practice, g_A is chosen equal to 0.2 [11,12]. As explained above, the dielectronic attachment $R_{j,i}^{c,k}$ is simply deduced from $A_{i,j}^{k,c}$ by detailed balance.

As for the self-consistent-field approach, we prefer to keep the aforementioned rates to examine the role of atomic

structure. The rates used from now on are sufficient to study the shortcomings of the screened hydrogenic model in a systematic way. For reasons easy to grasp, the analytical formulas for the gradients of the rates with respect to (n_k) are very hard to find due to the self-consistency of the mean-field equations. When one population is changed by an infinitesimal amount, complicated reordering occurs within the mean-field quantities, inducing intricate response of the one-electron energies and orbitals. Note that the situation is analytically solvable for a parametric potential. In the present state of the art, the differentiation of the rates with respect to (n_k) is performed numerically. This task is time-consuming but tractable and induces moderate uncertainties about (U_{kl}). It is important to realize that our formalism, like the response matrix method [34,35], is a stringent test of the consistency of a NLTE matter model with LTE. To be complete, a Maxwell distribution for the free electrons is used to get the rates starting from the cross sections of interest. As a consequence, the average ionization and the chemical potential are calculated by considering a nondegenerate free-electron gas. The implementation of free-electron degeneracy, as well as the continuum lowering and screening phenomena, is difficult and beyond the scope of this paper.

C. Numerical method

The average-atom equations (5) are very hard to solve for a wide range of temperature, density, and material for three main reasons. They are nonlinear with respect to shell populations, stiff, and the electroneutrality must always be satisfied. Even at constant rates, they are quadratic without dielectronic recombination and autoionization processes, and cubic when these processes are included. Many attempts have been made to get a robust algorithm while minimizing the number of times the rates are calculated. We finally found two different methods that satisfy such severe constraints.

The first one consists in finding the time evolution of variables (ϕ_k) defined by $\phi_k = \ln[(D_k - N_k)/N_k]$. In other words, $N_k = D_k/(1 + e^{\phi_k}) = D_k f_k$, and in LTE one has the well-known result $\phi_k = \phi_k^{\text{LTE}} = \beta(\varepsilon_k - \mu)$. In NLTE, it is very convenient to choose as unknown the deviation $\Delta\phi_k = \phi_k - \phi_k^{\text{LTE}}$. Let us note that if Eq. (5) is divided by N_i , we get the time evolution of $\ln(N_i)$. Similarly, if we divide by $D_i - N_i$ [$D_i - N_i = D_i/(1 + e^{-\phi_i}) = D_i g_i$], the time evolution of $\ln(D_i - N_i)$ is obtained. One thus realizes that the time evolution of ϕ_i is simply found by combining these equations. The final result reads

$$-\dot{\phi}_i = T_i^{+, \text{ion}} - T_i^{-, \text{ion}} + T_i^{+, \text{rec}} - T_i^{-, \text{rec}}, \quad (14)$$

where

$$\begin{aligned} T_i^{+, \text{ion}} &= D_j g_j \bar{\tau}_{i,j} e^{\Delta\phi_i - \Delta\phi_j} + \tilde{I}_{i,c} e^{\Delta\phi_i} \\ &+ D_m D_j g_m g_j R_{i,j}^{c,m} e^{\Delta\phi_i - \Delta\phi_m - \Delta\phi_j} \\ &+ D_m D_j f_m g_j A_{i,j}^{m,c} e^{\Delta\phi_i + \Delta\phi_m - \Delta\phi_j} \\ &+ D_j D_m f_m g_j A_{m,j}^{i,c} e^{\Delta\phi_i + \Delta\phi_m - \Delta\phi_j}, \end{aligned}$$

$$\begin{aligned}
T_i^{-,\text{ion}} &= D_j g_j \tau_{i,j} + I_{i,c} + D_m D_j g_m g_j R_{i,j}^{c,m} \\
&\quad + D_m D_j f_m g_j A_{j,i}^{m,c} + D_j D_m f_m g_j A_{j,i}^{i,c}, \\
T_i^{+,\text{rec}} &= D_j f_j \tau_{j,i} + R_{c,i} + D_m D_j f_m f_j A_{j,i}^{m,c} \\
&\quad + D_m D_j g_m f_j R_{j,i}^{c,m} + D_j D_m g_m f_j R_{j,i}^{c,i}, \\
\tilde{T}_i^{-,\text{rec}} &= D_j f_j \tilde{\tau}_{j,i} e^{-\Delta\phi_i + \Delta\phi_j} + \tilde{R}_{c,i} e^{-\Delta\phi_i} \\
&\quad + D_m D_j f_m f_j A_{j,i}^{m,c} e^{-\Delta\phi_i + \Delta\phi_m + \Delta\phi_j} \\
&\quad + D_m D_j g_m f_j R_{j,i}^{c,m} e^{-\Delta\phi_i - \Delta\phi_m + \Delta\phi_j} \\
&\quad + D_j D_m g_m f_j R_{j,i}^{c,i} e^{-\Delta\phi_i - \Delta\phi_m + \Delta\phi_j}.
\end{aligned} \tag{15}$$

In LTE, one can see that $T_i^{+,\text{ion}}$ and $T_i^{+,\text{rec}}$ balance, respectively, $T_i^{-,\text{ion}}$ and $T_i^{-,\text{rec}}$. The rates with a tilde are defined from the original rates by imposing detailed balance. They can be understood as dual rates. For collisional rates with a free electron in LTE or radiative rates with the Planck radiation field at electron temperature, these dual rates are simply equal to the usual rates. Equations (14) and (15) are solved by starting from a given initial set (ϕ_k^0) using an implicit scheme. (ϕ_k) are calculated iteratively at fixed rates. New rates are then obtained. To improve the convergence and to avoid oscillatory problems, the relaxation scheme proposed in [36] has been adopted for variables (ϕ_k) . At low temperature, the system is near LTE and it is cautious to choose $\phi_k^0 = \phi_k^{\text{LTE}}$.

The second method consists in dividing Eq. (5) by N_i . The system is then written by choosing the variable $\alpha_k = e^{\phi_k}$. Starting from given (α_k^0) , we are looking for (α_k) of the form $\alpha_k^{n+1} = \alpha_k^n (1 + \varepsilon_k)$, where $n \geq 0$. These (ε_k) satisfy the linear equation $T_{k,k'} \varepsilon_{k'} = S_k$, where

$$\begin{aligned}
S_k &= \frac{1}{\Delta t} \left(\frac{\alpha_k^0 - \alpha_k}{1 + \alpha_k^0} \right) + I_{k,c} - \alpha_k R_{c,k} + \frac{D_{k'}}{1 + \alpha_{k'}} \\
&\quad \times (\alpha_{k'} \tau_{k,k'} - \alpha_k \tau_{k',k}) - \frac{D_{k'}}{1 + \alpha_{k'}} \frac{D_m}{1 + \alpha_m} \\
&\quad \times [\alpha_k A_{k',k}^{m,c} + \alpha_k \alpha_m (R_{k',k}^{c,m} + R_{k',m}^{c,k}) - \alpha_{k'} \alpha_m R_{k,k'}^{c,m} \\
&\quad - \alpha_{k'} (A_{k,k'}^{m,c} + A_{m,k'}^{k,c})], \\
T_{kk'} &= \delta_{kk'} \left\{ \frac{1}{\Delta t} \frac{\alpha_k}{1 + \alpha_k^0} + \alpha_k R_{c,k} + \frac{D_{k''}}{1 + \alpha_{k''}} \alpha_k \tau_{k'',k} + \frac{D_{k''}}{1 + \alpha_{k''}} \right. \\
&\quad \times \left. \frac{D_m}{1 + \alpha_m} [\alpha_k \alpha_m (R_{k'',k}^{c,m} + R_{k'',m}^{c,k}) + \alpha_k A_{k'',k}^{m,c}] \right\} - \frac{D_{k'}}{1 + \alpha_{k'}} \\
&\quad \times \alpha_{k'} \tau_{k,k'} + \frac{D_{k'}}{1 + \alpha_{k'}} \frac{D_m}{1 + \alpha_m} [\alpha_k \alpha_{k'} (R_{m,k}^{c,k'} + R_{m,k'}^{c,k}) \\
&\quad - \alpha_{k'} \alpha_m (R_{k,k'}^{c,m} + R_{k,m}^{c,k'}) - \alpha_{k'} (A_{k,k'}^{m,c} + A_{m,k'}^{k,c})].
\end{aligned}$$

Δt is the time step. The process is iterated until achieving convergence: in that case, $\varepsilon_k = 0$. In every case, from low ($T_e < 10$ eV) to high ($T_e > 100$ eV) electron temperatures,

with or without radiation field, rates are calculated at most 30–50 times. Only stationary NLTE situations are studied in this paper. Nevertheless, both methods can be used to perform time-dependent NLTE calculations. In that case, Eqs. (5) and (7)–(9) must be solved self-consistently, whereas in stationary problems, Eqs. (5) and (7)–(9) can be solved one after the other. Finally, let us note that one needs to differentiate the configuration energy, the one-electron energies, and the transition rates with respect to electron populations to calculate the average-atom populations or the electron-covariance matrix. SHM causes no problem because the whole differentiations can be done exactly. As for OPM, the one-electron energies and the electrostatic interaction matrix element potentials are obtained by differentiating the average energy of the configuration neglecting orbital relaxation, while the transition rates are differentiated numerically.

IV. RESULTS AND DISCUSSION

In order to illustrate the whole methods, we have chosen to consider the case of a NLTE steady-state germanium plasma. From now on, SHM and OPM mean that the atomic structure is calculated by using the screened hydrogenic model with ℓ splitting or the optimized potential method, respectively. SCAALP works in LTE or NLTE with the semianalytic rates presented above. Moreover, woDR (wiDR) means that the calculation of interest has been done without (with) autoionization and dielectronic recombination processes. All the computations have been performed with a maximum principal quantum number n equal to 8 and an orbital quantum number ℓ between 0 and $n-1$. Finally, the two-parameter degeneracy lowering is the only dense-plasma effect currently modeled in SCAALP [23,33].

Figure 2 shows the average ionization \bar{Z}^* of a germanium plasma at 0.0537 g cm^{-3} . Calculations were done using the SHM at three different radiation temperatures: $T_r = 0$, $T_e/2$, and T_e (LTE). As expected, \bar{Z}_{wiDR}^* is generally lower than \bar{Z}_{woDR}^* , in particular between 500 and 2000 eV and beyond 10000 eV, corresponding to the opening of K and L shells respectively. Moreover, we confirm that the presence of a moderate radiation field is sufficient to drastically reduce the role of autoionization and dielectronic recombination processes [12]. Figure 3 presents the ionization variance $\sigma_{Z^*}^2$ of this plasma in the same thermodynamic conditions. The results here are far more interesting. As is well known, $\sigma_{Z^*}^2$ is maximum for a half-filled shell and reaches its minimum value near the closure of a shell. Three important facts must be emphasized. First, without radiation field, large differences are found beyond 800 eV. Second, the convergence of the NLTE $\sigma_{Z^*}^2$ to LTE values at low temperature is slower than \bar{Z}_{wiDR}^* and \bar{Z}_{woDR}^* . This indicates that the mean ionization is not a relevant parameter to test the vicinity to LTE. Since $\sigma_{Z^*}^2$ is of fundamental interest to estimate the dominant charge-stage fractions, one can conclude that the charge-stage distribution is far more sensible to NLTE than the average ionization. Third, one can see in this example that the ionization variance is a key parameter to differentiate

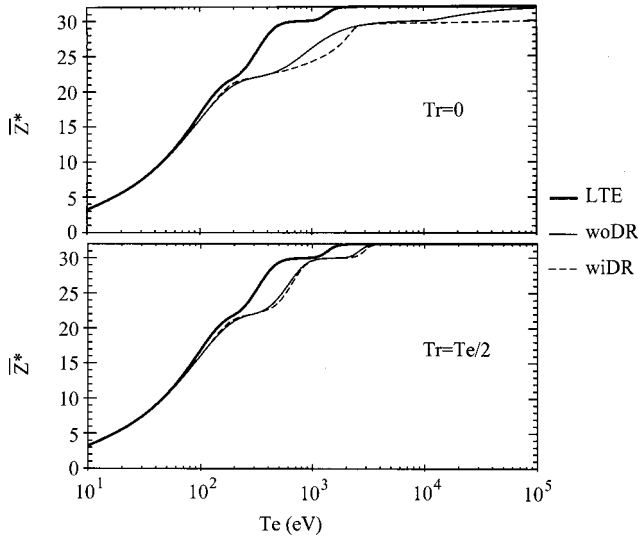


FIG. 2. Average ionization \bar{Z}^* of a NLTE germanium steady-state plasma at 0.0537 g cm^{-3} using a screened hydrogenic model [25]. Electron temperature T_e is between 10 and 10^5 eV. Three radiation temperatures T_r have been chosen: 0, $T_e/2$, and T_e (LTE). Dielectronic recombination and autoionization have been included (wiDR) or suppressed (woDR).

two close situations. In Fig. 2, one could infer that the dielectronic recombination and the autoionization processes have a rather small influence when the radiation field with $T_r = T_e/2$ is present. This remark has to be seriously questioned by inspecting the associated curves of Fig. 3. Indeed, interesting physics is also depicted between 60 and 100 eV. Two small structures can be seen on both curves with dielec-

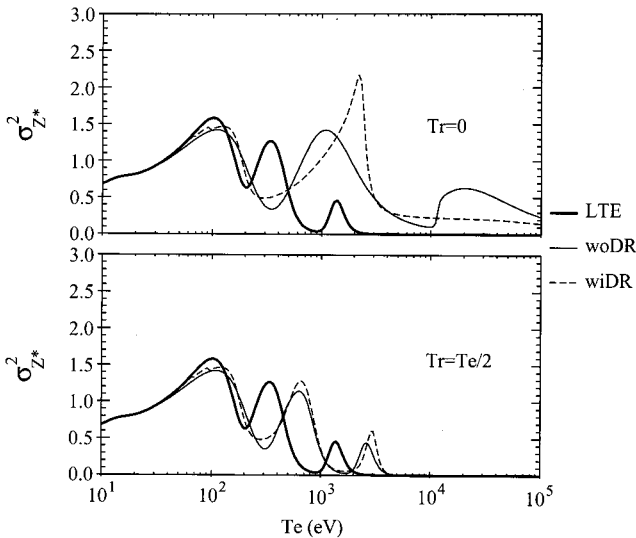


FIG. 3. Ionization variance $\sigma_{Z^*}^2$ of a NLTE germanium steady-state plasma at 0.0537 g cm^{-3} using a screened hydrogenic model [25]. Electron temperature T_e is between 10 and 10^5 eV. Three radiation temperatures T_r have been chosen: 0, $T_e/2$, and T_e (LTE). Dielectronic recombination and autoionization have been included (wiDR) or suppressed (woDR).

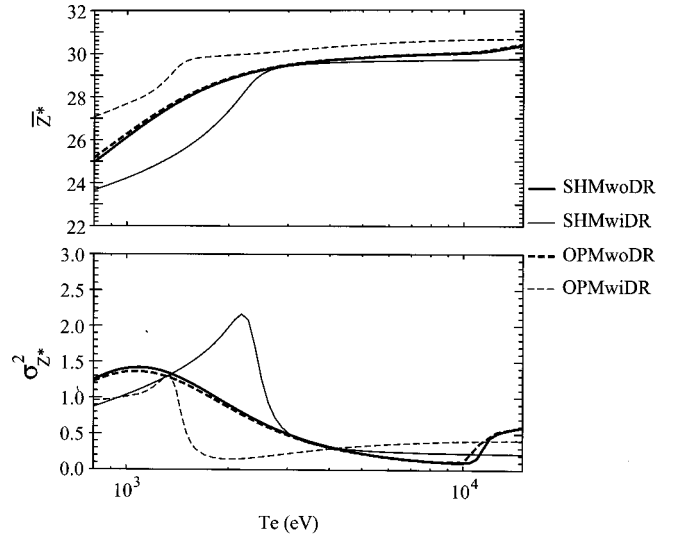


FIG. 4. Average ionization \bar{Z}^* and ionization variance $\sigma_{Z^*}^2$ of a NLTE germanium steady-state plasma at 0.0537 g cm^{-3} using a screened hydrogenic model (SHM) [25] or the optimized potential method (OPM) [26]. Electron temperature T_e is between 800 and 15 000 eV and the radiation temperature T_r is zero. Dielectronic recombination and autoionization have been included (wiDR) or suppressed (woDR).

tronic recombination. They are not calculation artifacts. Each local minimum corresponds to the closure of a subshell, namely $3s$ around 100 eV and $3p$ around 60 eV. This phenomenon is well known in LTE [23]. The closure of a principal shell is far more easy to resolve than the closure of a subshell. Here, it is clear that the presence of dielectronic recombination and autoionization enhances this phenomenon, but only on the ionization-variance curves because nothing noticeable can be detected on the average-ionization curves. In NLTE, there is a subtle coupling between atomic physics and statistical mechanics.

To be complete, we mention that we have compared the aforementioned results with $\sigma_{Z^*}^2$ calculated by extending to NLTE the standard textbook LTE expressions or using the ionization temperature. These two last approximations cannot be derived from general laws of nonequilibrium thermodynamics. As already encountered [9], we confirm that they produce incorrect results.

Let us now study the influence of atomic structure at given transition rates and statistical mechanics formalism. Since the role of dielectronic recombination is more important without radiation field, we have plotted in Fig. 4 the average-ionization and the ionization-variance curves using OPM and SHM with $T_r = 0$, with or without dielectronic recombination and autoionization, for T_e between 800 and 15 000 eV. When these two-electron processes are neglected, both atomic models are in excellent agreement. When these processes are taken into account, there is clearly a strong divergence. It is well known that dielectronic recombination and autoionization processes play a central role around the closure (or the opening) of a shell. This is the case here since the range of electron temperatures has been chosen in order

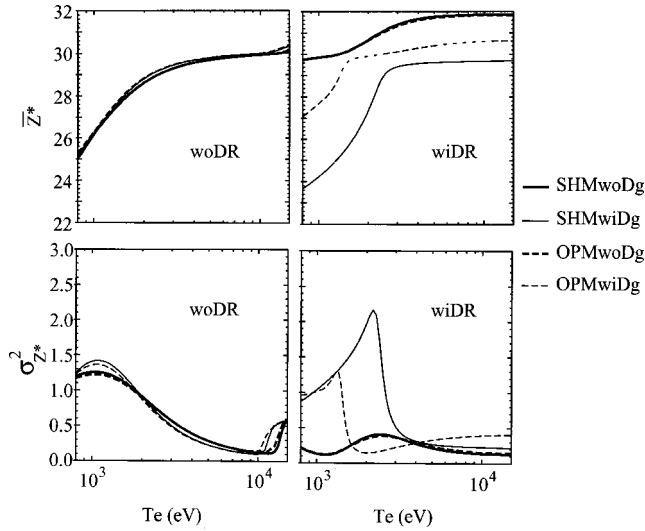


FIG. 5. Average ionization \bar{Z}^* and ionization variance $\sigma_{Z^*}^2$ of a NLTE germanium steady-state plasma at 0.0537 g cm^{-3} using a SHM [25] or the OPM [26]. Electron temperature T_e is between 800 and 15 000 eV and the radiation temperature T_r is zero. Dielectronic recombination and autoionization have been included (wiDR) or suppressed (woDR). Calculations have been made with (wiDR) or without (woDg) degeneracy lowering to simulate density effects.

to see what happens around the opening of the L shell. In order to understand this phenomenon, we have done the same calculations neglecting the degeneracy-lowering model of Zimmerman and More [33] used to simulate density effects. The results are gathered in Fig. 5. One can see that OPM and SHM are in very close agreement, with or without dielectronic recombination and autoionization processes, when the subshell degeneracies are integers. This statement remains true as long as dielectronic recombination and autoionization processes are suppressed when the subshell degeneracies are fractional. This means that the description of atomic structure and statistical mechanics does not depend too much of the atomic model in this example. On the contrary, when dielectronic recombination and autoionization processes and density effects are included, one can conclude from Fig. 5 that the computation of average ionization and ionization variance depends closely on the degeneracy lowering. This can be understood by remembering that the average-configuration autoionization and dielectronic recombination rates involve a triple product of subshell degeneracies. Even at such a moderate density, careful attention should be paid to the treatment of dense plasma effects.

Before closing this section, we are going to confront SCAALP predictions to measurements. To our knowledge, the results published recently in Ref. [37] provide the first accurate determination of the charge-state distribution in a highly ionized high- Z plasma. For a well-characterized Au plasma at an electron density $6 \times 10^{20} \text{ cm}^{-3} \pm 20\%$ and an electron temperature $2200 \text{ eV} \pm 10\%$, the average value of the charge-state distribution is $\bar{Z}^* = 49.3 \pm 0.5$. The superconfiguration-based collisional-radiative code RIGEL predicts $\bar{Z}^* = 49.1$ with dielectronic recombination and autoionization processes [37]. If these two-electron processes are

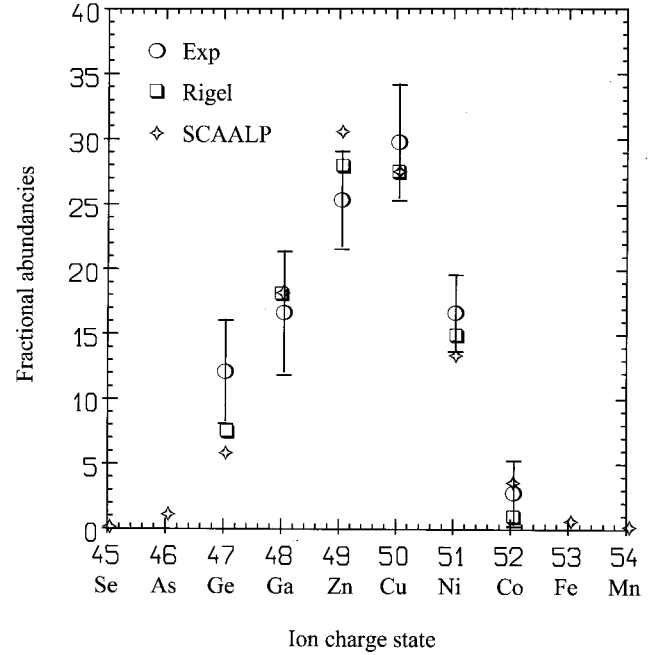


FIG. 6. Charge-state distribution of a NLTE gold steady-state plasma at an electron density $6 \times 10^{20} \text{ cm}^{-3}$, $T_e = 2200 \text{ eV}$, and $T_r = 0 \text{ eV}$. Circles with error bars and squares correspond, respectively, to experimental data and RIGEL code predictions [37]. Stars are SCAALP results using SHM including dielectronic recombination and autoionization processes.

not included, the predicted average charge $\bar{Z}^* = 53.3$, far outside the range of experimental results. With SHM, SCAALP predicts $\bar{Z}_{\text{woDR}}^* = 51.43$ and $\bar{Z}_{\text{wiDR}}^* = 49.33$, whereas OPM predicts $\bar{Z}_{\text{woDR}}^* = 49.32$. Unfortunately, it was not possible to get \bar{Z}_{wiDR}^* with OPM for lack of convergence of the code in this specific example. For completeness, ionic abundancies are shown in Fig. 6. SCAALP data are obtained with SHM including two-electron processes for electron density $6 \times 10^{20} \text{ cm}^{-3}$, $T_e = 2200 \text{ eV}$, and $T_r = 0 \text{ eV}$. They are compared to charge-state distributions derived from the experiment and from the RIGEL code. The peak position and width given by our model agree well with the experimental data.

V. CONCLUSION

A new time-dependent self-consistent average-atom model has been presented. The time evolution of average-atom electron populations and the electron covariance matrix are obtained as approximate solutions of a master equation. Local thermodynamic equilibrium is recovered as a specific steady-state solution. Autoionization and dielectronic recombination enter naturally in the average-atom theory. The atomic structure can be calculated by using a screened hydrogenic model or the optimized potential approach. All the rates of interest are formulated within the average-configuration framework. The model has been used to calculate the mean ionization and the ionization variance of a germanium plasma at moderate density in the LTE and NLTE steady-state situation. It has also been compared both

to measurements and to another theoretical model in the case of a NLTE steady-state highly ionized gold plasma.

The next step consists in using accurate transition rates to study their influence on average ionization and ionization variance. Indeed, all the formulas of interest are well known [14,15]. However, their implementation as robust packages is not trivial and a great attention has to be paid to numerical problems. The free-electron treatment is another important topic. The self-consistent calculation of bound- and free-

electron densities is as crucial as the role of free-electron degeneracy on the rates to insure the consistency of the whole model with LTE as high density.

ACKNOWLEDGMENTS

The authors thank Dr. J. Albritton and Dr. B. Wilson for the approximate autoionization rate formula used in this paper and the helpful comments and explanations.

-
- [1] S. J. Rose, in *Proceedings of the 45th Scottish University Summer School in Physics-Laser Plasma Interactions*, edited by M. B. Hooper (IOP, Bristol, 1995).
- [2] A. Bar-Shalom, J. Oreg, and M. Klapisch, *J. Quant. Spectrosc. Radiat. Transf.* **58**, 427 (1997).
- [3] A. Bar-Shalom, J. Oreg, W. H. Goldstein, D. Shvarts, and A. Zigler, *Phys. Rev. A* **40**, 3183 (1989).
- [4] M. Klapisch and A. Bar-Shalom, *J. Quant. Spectrosc. Radiat. Transf.* **58**, 687 (1997).
- [5] W. A. Lokke and W. H. Grassberger, Report UCRL-52276, Lawrence Livermore Laboratory (Livermore, CA, 1977).
- [6] R. M. More, Report UCRL-84991, Lawrence Livermore National Laboratory (University of California, Livermore, 1981).
- [7] B. F. Rozsnyai, *Phys. Rev. E* **55**, 7507 (1997).
- [8] P. Dallot, G. Faussurier, A. Decoster, and A. Mirone, *Phys. Rev. E* **57**, 1017 (1998).
- [9] A. Mirone, F. Gilleron, J. C. Gauthier, and G. Faussurier, *J. Quant. Spectrosc. Radiat. Transf.* **60**, 551 (1998).
- [10] R. M. More, G. B. Zimmerman, and Z. Zinamon, in *Atomic Processes in Plasmas*, edited by A. Hauer and A. L. Merts, AIP Conf. Proc. No. 168 (AIP, New York, 1988).
- [11] J. Albritton and B. G. Wilson, *Phys. Rev. Lett.* **83**, 1594 (1999).
- [12] J. Albritton and B. G. Wilson, *J. Quant. Spectrosc. Radiat. Transf.* **65**, 1 (2000).
- [13] S. J. Rose, *J. Phys. B* **31**, 2129 (1998).
- [14] M. S. Pindzola, D. C. Griffin, and C. Bottcher, in *Atomic Processes in Electron-Ion and Ion-Ion Collisions*, edited by F. Brouillard, Vol. 145 of NATO Advanced Study Institute Series B: Physics (Plenum, New York, 1986).
- [15] O. Peyrusse, *J. Phys. B* **32**, 683 (1999).
- [16] A. K. Kerman, S. Levit, and T. Troudet, *Ann. Phys. (N.Y.)* **148**, 436 (1983).
- [17] J. H. Negele and H. Orland, *Quantum Many-Particle Systems* (Addison-Wesley, New York, 1988).
- [18] G. Faussurier, *Phys. Rev. E* **59**, 7096 (1999).
- [19] F. Perrot, *Physica A* **150**, 357 (1988).
- [20] J. C. Slatter, in *A Tribute to E. U. Condon*, edited by W. E. Brittin and H. Odabasi (Colorado Associated University Press, Boulder, 1971).
- [21] R. Balian and M. Vénéroni, *Phys. Rev. Lett.* **47**, 1353 (1981); **47**, 1765(E) (1981).
- [22] O. Eboli, R. Jackiw, and S. Y. Pi, *Phys. Rev. D* **37**, 3557 (1988).
- [23] G. Faussurier, C. Blancard, and A. Decoster, *Phys. Rev. E* **56**, 3474 (1997).
- [24] O. Peyrusse, *J. Phys. B* **33**, 4303 (2000).
- [25] G. Faussurier, C. Blancard, and A. Decoster, *J. Quant. Spectrosc. Radiat. Transf.* **58**, 233 (1997).
- [26] J. D. Talman and W. F. Shadwick, *Phys. Rev. A* **14**, 36 (1976); J. D. Talman, *Comput. Phys. Commun.* **54**, 85 (1989).
- [27] W. Lotz, *Z. Phys.* **216**, 241 (1968).
- [28] R. Mewe, *Astron. Astrophys.* **20**, 215 (1972).
- [29] M. Itoh, T. Yabe, and S. Kiyokawa, *Phys. Rev. A* **35**, 233 (1987).
- [30] D. Mihalas, *Stellar Atmospheres* (Freeman, San Francisco, 1978).
- [31] G. Faussurier, C. Blancard, and A. Decoster, *Phys. Rev. E* **56**, 3488 (1997).
- [32] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).
- [33] G. B. Zimmerman and R. M. More, *J. Quant. Spectrosc. Radiat. Transf.* **23**, 517 (1980).
- [34] R. M. More and T. Kato, *Phys. Rev. Lett.* **81**, 814 (1998).
- [35] G. Faussurier and R. M. More, *J. Quant. Spectrosc. Radiat. Transf.* **65**, 387 (2000).
- [36] A. Djaoui, *J. Quant. Spectrosc. Radiat. Transf.* **62**, 303 (1999).
- [37] M. E. Foord, S. H. Glenzer, R. S. Thoe, K. L. Wong, K. B. Fournier, B. G. Wilson, and P. T. Springer, *Phys. Rev. Lett.* **85**, 992 (2000).