Generalization of super-transition-array methods to hot dense plasmas by using optimum independent particle reference systems

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The computation of superconfiguration partition functions relies upon independent electron statistics, with electron-electron contributions included as an average first-order correction factor. The decomposition into a first-order correction and reference independent electron system has degrees of freedom not exploited by current methods. We present a derivation for the conventional choice of decomposition and propose a different method for obtaining an optimal decomposition for each superconfiguration. This constitutes an alternative procedure to recomputing self-consistent fields for the refinement of superconfiguration partition functions. Numerical results are presented and discussed.

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I. INTRODUCTION

The super-transition-array (STA) method [1,2] has been shown to be rather powerful for the modeling of hot dense plasmas in local thermodynamic equilibrium (LTE). Central to the method is the computation of ionization distributions by calculating the partition function

$$U_{\Xi}=\sum_{\vec{n}\in\Xi} G_{\vec{n}} \exp[-\beta(E_{\vec{n}}-|\vec{n}|\mu)] \tag{1}$$

over a restricted ensemble of configurations specified by the total number of electrons in groupings of atomic orbitals (supershells), denoted as the superconfiguration Ξ. Here $\beta=1/k_BT$ is the inverse of temperature T, k_B the Boltzmann constant, and μ the chemical potential. The statistical weight for each configuration $\vec{n}$ (denoted as a vector of orbital occupations) within the superconfiguration is given by

$$G_{\vec{n}}=\prod_{\alpha}\binom{g_\alpha}{n_\alpha}. \tag{2}$$

$E_{\vec{n}}$ is the configuration-average total energy and $|\vec{n}|=\Sigma_\alpha n_\alpha$, where n_α is the occupation number of shell α with degeneracy g_α.

Simple closed form evaluations of the partition function, using recursion relations, are available for independent electron systems, that is to say, when configuration-average total energies are linear functions of the occupations

$$E^0_{\vec{n}}=\sum_{\alpha} n_\alpha\theta_\alpha. \tag{3}$$

No such closed form evaluation exist for interacting electron systems where $E_{\vec{n}}$ is a nonlinear function of the shell occupations (n_α). However, $E_{\vec{n}}$ may be well approximated by quadratic functions, written in the general form

$$E_{\vec{n}}=\sum_{\alpha} n_\alpha\epsilon_\alpha+\tfrac{1}{2}\sum_{\alpha,\gamma} n_\alpha(n_\gamma-\delta_{\alpha,\gamma})\Delta_{\alpha\gamma}. \tag{4}$$

In this paper, we show that this form allows us to propose a different and powerful way to calculate partition function combining the standard STA method and the well-known Gibbs-Bogolyubov (or Jensen-Feyrunan) variational approach [3]. This procedure is naturally named the variational STA technique and constitutes an additional degree of freedom in the current STA method. In Sec. II, the standard STA method is considered and the variational STA method is presented in Sec. III. Section IV is devoted to numerical applications and Sec. V summarizes results.

II. THE STA METHOD

The STA method approximates the evaluation of the partition function by adding and subtracting Eq. (3) in the expression for the energy given by Eq. (4),

$$\begin{aligned} e^{-\beta F}\equiv U_{\Xi}&=\sum_{\vec{n}\in\Xi} G_{\vec{n}}\exp\Bigg\{-\beta\Bigg[\sum_{\alpha} n_\alpha(\theta_\alpha-\mu)\\ &\quad+\sum_{\alpha} n_\alpha(\epsilon_\alpha-\theta_\alpha)+\frac{1}{2}\sum\Sigma_{\alpha,\gamma} n_\alpha(n_\gamma-\delta_{\alpha,\gamma})\Delta_{\alpha\gamma}\Bigg]\Bigg\}\\ &\equiv\sum_{\vec{n}\in\Xi} G_{\vec{n}}\exp[-\beta(K^0_{\vec{n}}+V_{\vec{n}})] \end{aligned} \tag{5}$$

and then using the Gibbs-Bogolyubov (or Jensen-Feynman) inequality,

$$F\leqslant F_0+\langle V_{\vec{n}}\rangle_0, \tag{6}$$

where

$$K^0_{\vec{n}}\equiv E^0_{\vec{n}}-|\vec{n}|\mu,$$

$$V_{\vec{n}}\equiv E_{\vec{n}}-E^0_{\vec{n}}=\sum_{\alpha} n_\alpha(\epsilon_\alpha-\theta_\alpha)+\tfrac{1}{2}\sum_{\alpha,\gamma} n_\alpha(n_\gamma-\delta_{\alpha,\gamma})\Delta_{\alpha\gamma}, \tag{7a}$$

$$F_0 \equiv \sum_{\vec{n}\in\Xi} G_{\vec{n}} e^{-\beta K^0_{\vec{n}}}, \quad \langle\{\cdots\}_{\vec{n}}\rangle_0 \equiv \frac{\sum_{\vec{n}\in\Xi} G_{\vec{n}} e^{-\beta K^0_{\vec{n}}}\{\cdots\}_{\vec{n}}}{\sum_{\vec{n}\in\Xi} G_{\vec{n}} e^{-\beta K^0_{\vec{n}}}}, \tag{7b}$$

but with the specific reference system

$$\theta_\alpha = -\epsilon_\alpha^{\text{ion}}, \tag{8}$$

where the average-atom one-electron ionization energy is

$$\epsilon_\alpha^{ion} = -\epsilon_\alpha - \sum_\gamma (\langle n_\gamma\rangle_0 - \delta_{\alpha\gamma})\Delta_{\alpha\gamma} \tag{9}$$

with

$$\langle n_\alpha\rangle_0 = g_\alpha f(\alpha\theta_\alpha),$$

$$f(\theta) = \frac{1}{e^{\beta(\theta-\mu)}+1}. \tag{10}$$

This choice of the reference system is *optimal* for the average atom (i.e., when Ξ encompasses all of configuration space) [4]. In that situation we have the closed form expression

$$F_0 = -k_B T \sum_\gamma g_\gamma \ln[1+e^{-\beta(\theta_\gamma-\mu)}] \tag{11}$$

and

$$\langle V_{\vec{n}}\rangle_0 = \sum_\alpha (\epsilon_\alpha - \theta_\alpha)\langle n_\alpha\rangle_0 + \tfrac{1}{2}\sum_\alpha \sum_\gamma \Delta_{\alpha\gamma}\langle n_\alpha(n_\gamma - \delta_{\alpha\gamma})\rangle$$

$$= \sum_\alpha (\varepsilon_\alpha - \theta_\alpha) g_\alpha f(\theta_\alpha) + \tfrac{1}{2}\sum_\alpha \sum_\gamma \Delta_{\alpha\gamma} g_\alpha (g_\gamma - \delta_{\alpha\gamma}) \times f(\theta_\alpha) f(\theta_\gamma) \tag{12}$$

minimizing the right-hand side of Eq. (6) with respect to the set of variational parameters (θ_α). Using

$$\frac{\partial F_0}{\partial \theta_\alpha} = \langle n_\alpha\rangle_0 \tag{13}$$

yields immediately the choice of Eq. (8).

Although simple to implement, the global use of reference set Eq. (8) implies that one set of ionization energies are used in the construction of superconfiguration population averages, even for those superconfigurations belonging to different ion stages. Current STA models employ Eq. (4) obtained from Hartree-Fock configuration-average total energy calculations from self-consistent fields. These self-consistent field calculations are periodically reperformed, for example, at different ionstages, to optimize the parameters.

However another paradigm exits for STA calculations. One can employ a Taylor series expansion for the total energy about some reference configuration

$$E = E^* + \sum_\alpha a_\alpha (n_\alpha - n_\alpha^*) + \tfrac{1}{2}\sum_\alpha \sum_\gamma (n_\alpha - n_\alpha^*) \times b_{\alpha\gamma}(n_\gamma - n_\gamma^*). \tag{14}$$

This representation is accurate for several ionization stages about the reference configuration, ameliorating the need for reperforming self-consistent field calculations. The physical meaning of the coefficients $\{a_\alpha\}$ and $\{b_{\alpha\gamma}\}$ differs from the one-electron and electrostatic interaction energies, respectively, of Hartree-Fock calculations by containing the full effect of orbital relaxation; this necessitates the reference total energy coefficient E^*. By rearranging Eq. (14) into the form of Eq. (4) the current STA algorithms can still be applied, albeit with an additional constant term arising E^*. In such an implementation, an analog for optimizing parameters in lieu of reperforming self-consistent field calculations must be presented. In Sec. III, we present a method for optimizing the partition for each superconfiguration.

III. GENERALIZATION OF THE STA METHOD

The generalization to obtain the optimum set $\{\theta_\alpha\}$ for a specific superconfiguration is straightforward [5–7]. The analog of Eq. (10) may be constructed from supershell partition functions of Q electrons

$$U_Q[\vec{g}] \equiv \sum_{n_1=0}^{g_1}\sum_{n_2=0}^{g_2}\cdots\sum_{n_n=0}^{g_n}\prod_{\alpha=1}^{n}\binom{g_\alpha}{n_\alpha}\exp[-\beta(\theta_\alpha-\mu)n_\alpha],$$

$$n_1+n_2+\cdots+n_n = Q \tag{15}$$

computed by using the recursion relation

$$X_\alpha U_{Q-1}[\vec{g}-\vec{l}_\alpha] = U_Q[\vec{g}] - U_Q[\vec{g}-\vec{l}_\alpha]. \tag{16}$$

Here

$$X_\alpha \equiv e^{-\beta(\theta_\alpha-\mu)} \tag{17}$$

and the set of orbital degeneracy's (denoted by the vector $\vec{g}$) may be formally reduced in the αth component/orbital as

$$\vec{g}-\vec{l}_\alpha = \{g_1, g_2, \ldots, g_\alpha - 1, \ldots, g_n, \ldots\}. \tag{18}$$

(In general $\vec{i}_\alpha$ will denote a vector with value i in the αth component.) Similarly the analogs of the expectation values appearing in Eq. (12) are found to be

$$\langle n_\alpha\rangle_0 = g_\alpha X_\alpha \frac{U_{Q-1}[\vec{g}-\vec{l}_\alpha]}{U_Q[\vec{g}]} = \frac{g_\alpha X_\alpha}{X_\alpha + r_Q[\vec{g}-\vec{l}_\alpha]} \tag{19}$$

and

$$\langle n_\alpha(n_\gamma-\delta_{\alpha\gamma})\rangle_0 = g_\alpha(g_\gamma-\delta_{\alpha\gamma})X_\alpha X_\gamma \frac{U_{Q-2}[\vec{g}-\vec{l}_\alpha-\vec{l}_\gamma]}{U_Q[\vec{g}]}$$

$$= \langle n_\alpha\rangle_0 \left\{ \frac{(g_\gamma-\delta_{\alpha\gamma})X_\gamma}{X_\gamma + r_{Q-1}[\vec{g}-\vec{l}_\alpha-\vec{l}]} \right\}, \quad (20)$$

where

$$r_Q[\vec{g}] \equiv \frac{U_Q[\vec{g}]}{U_{Q-1}[\vec{g}]} \quad (21)$$

denotes a ratio of partition functions for the supershell (that reduces to unity in an unrestricted or average-atom ensemble).

In contrast to the average-atom example the minimization procedure does not separate into decoupled equations for each orbital parameter. To see this we take the derivative of the right-hand side of Eq. (6) with respect to a parameter $\{\theta_\tau\}$. We find that Eq. (13) still holds, however the correlations

$$\frac{\partial\langle n_\alpha\rangle_0}{\partial\theta_\tau} = \beta(\langle n_\alpha\rangle_0\langle n_\tau\rangle_0 - \langle n_\alpha n_\tau\rangle_0) \quad (22)$$

and

$$\frac{\partial\langle n_\alpha(n_\gamma-\delta_{\alpha\gamma})\rangle_0}{\partial\theta_\tau} = \beta[\langle n_\tau\rangle_0\langle n_\alpha(n_\gamma-\delta_{\alpha\gamma})\rangle_0 - \langle n_\tau n_\alpha(n_\gamma-\delta_{\alpha\gamma})\rangle_0], \quad (23)$$

now, no longer vanishes for τ not equal to α and γ.

The remaining complication arises from the evaluation of Eqs. (19) and (20) and the triple average

$$\langle n_\alpha(n_\gamma-\delta_{\alpha\gamma})(n_\tau-\delta_{\alpha\tau}-\delta_{\gamma\tau})\rangle_0 = g_\alpha(g_\gamma-\delta_{\alpha\gamma})(g_\tau-\delta_{\alpha\tau}-\delta_{\gamma\tau}) \times X_\alpha X_\gamma X_\tau \frac{U_{Q-3}[\vec{g}-\vec{l}_\alpha-\vec{l}_\gamma-\vec{l}_\tau]}{U_Q[\vec{g}]} \quad (24)$$

for use in Eqs. (22) and (23); these must be numerically evaluated from recursion relations for the partition functions of formally reduced occupation and orbital degeneracies. Algebra can be highly simplified by using the notion of integral representation in the complex plane [7].

Once determined the (θ_τ), the superconfiguration partition function U_Ξ is simply found from Eqs. (5), (6), (14), (15), and (25)

$$U_\Xi \approx \exp[-\beta(\Delta E_\Xi + F_0 + \langle V_{\vec{n}}\rangle)],$$

$$\Delta E_\Xi = E^* - \sum_\alpha a_\alpha n^*_\alpha + \tfrac{1}{2}\sum_{\alpha,\gamma} b_{\alpha\gamma} n^*_\alpha n^*_\gamma,$$

$$\epsilon_\alpha = a_\alpha - \sum_\gamma b_{\alpha\gamma}(n^*_\gamma - \delta_{\alpha,\gamma}/2),$$

$$\Delta_{\alpha\gamma} = b_{\alpha\gamma}. \quad (25)$$

Then, the statistical average $\langle O\rangle$ of any quantity O can be determined from the superconfiguration average $\langle O\rangle_\Xi$ by the formula

$$\langle O\rangle = \frac{\sum_\Xi U_\Xi\langle O\rangle_\Xi}{\sum_\Xi U_\Xi}. \quad (26)$$

IV. NUMERICAL APPLICATIONS

Let us illustrate the variational STA method by comparing key plasma statistical averages, such as the average ionization $\overline{Z^*}$ and the variance of ionization $\sigma^2_{\overline{Z^*}}$ obtained from different methods. For clarity, we take the cases studied in Ref. [7], i.e., a LTE germanium plasma ($\rho = 0.05307\ \mathrm{g\,cm^{-3}}$), in a range of temperatures between 1 eV and 250 eV. We want to study what happens when the M shell empties with increasing temperature.

Calculations have been made using a screened-hydrogenic model (SHM) with l splitting with subshells ranging from $1s$ to $5g$. We restrict ourselves to the nonrelativistic regime; moreover, plasma effects on the electron structure are neglected. In the framework of the SHM, $E_{\vec{n}}$ (in atomic units) is given by

$$E_{\vec{n}} = -\sum_\alpha \mathcal{B}_\alpha Z^2_\alpha n_\alpha, \quad Z_\alpha = Z - \sum_\gamma n_\gamma \sigma_{\alpha\gamma}(1-\delta_{\alpha,\delta}/g_\alpha), \quad (27)$$

where $(\sigma_{\alpha\gamma})$ is a set of screening parameters independent of the electronic configuration [8] and Z is the nuclear charge. $\mathcal{B}_\alpha$ is equal to half the inverse of the square of the principal quantum number of subshell α. From Eq. (27), a Taylor expansion is done to obtain Eq. (14). The reference configuration (n^*_α) is the same fictitious average configuration handled by Peyrusse (Eq. (17) in Ref. [9]). Note that we do not compute explicitly Eqs. (22) and (23), to obtain the gradient of the right-hand side of Eq. (6), with respect to the superconfiguration one-electron variational energies (θ_τ). We rather use a very powerful (approximate) conjugate-gradient algorithm to minimize the right-hand side of Eq. (6) with respect to the (θ_τ) [10].

The three methods described in Ref. [7], namely the average-atom model (AAM), the average-atom model with fluctuations around average atom (AAM+FAA), and the STA method are compared to the variational STA method (VSTA). In Ref. [7], we used the abbreviation SCA for super-configuration accounting. Since STA and SCA methods are the same, we have decided in this paper to unify names and abbreviations. Variations of $\overline{Z^*}$ and $\sigma^2_{\overline{Z^*}}$ with respect to temperature for VSTA are plotted on Fig. 1. Results are nearly identical with the STA results of Fig. 2 in Ref. [7]. VSTA data are considered to be the reference ones with respect to which AAM, AAM+FAA, and STA results are compared.

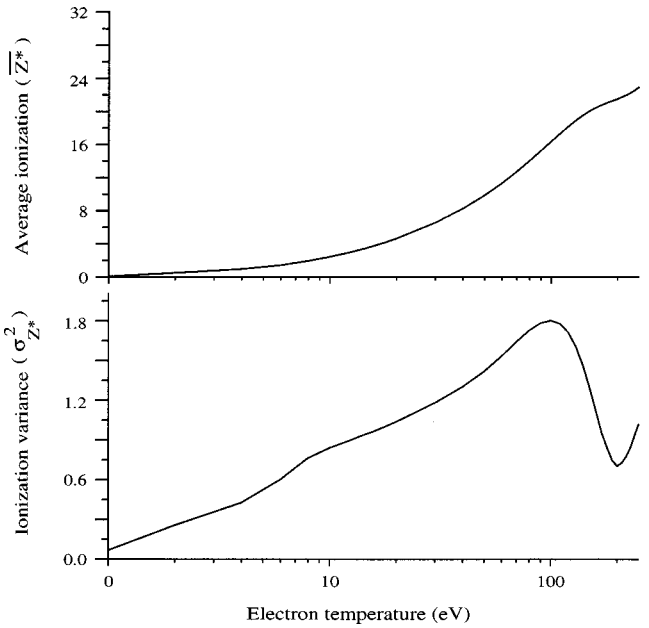

FIG. 1. Average ionization and ionization variance of a LTE germanium plasma ($\rho = 0.053\,07\,\mathrm{g\,cm^{-3}}$) calculated using the variational STA method.

The variation with respect to temperature of the relative error of $\overline{Z^*}$ ($\sigma^2_{\overline{Z^*}}$) calculated with AAM, AAM+FAA, and STA with respect to VSTA is plotted on Fig. 2 (Fig. 3). In each case, we take the absolute value of the relative error to have a positive number. We precise we did not have multiplied this quantity by 100 to convert it in percent. We find

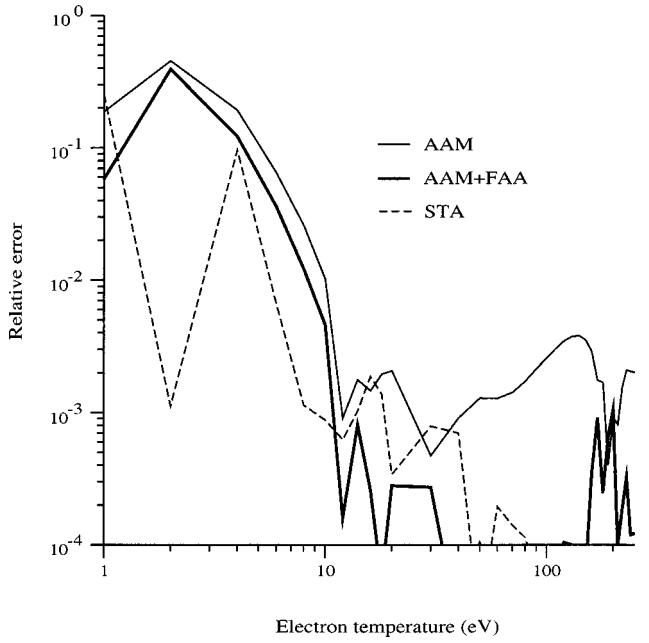

FIG. 2. Relative errors in absolute values of the average ionization, with respect to the reference VSTA values of a LTE germanium plasma ($\rho = 0.053\,07\,\mathrm{g\,cm^{-3}}$), for the average-atom model (AAM), the average-atom model with fluctuations around average-atom (AAM+FAA), and the STA method [7].

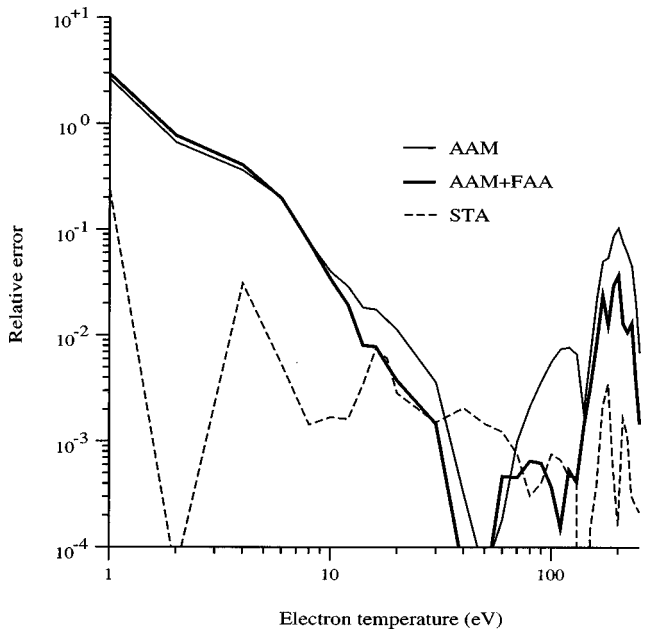

FIG. 3. Relative errors in absolute values of the ionization variance, with respect to the reference VSTA values of a LTE germanium plasma ($\rho = 0.053\,07\,\mathrm{g\,cm^{-3}}$), for the average-atom model (AAM), the average-atom model with fluctuations around average-atom (AAM+FAA), and the STA method [7].

again that the average-atom calculations remain competitive with respect to the superconfiguration accounting results, except towards a principal-shell closure (or emptiness) where the discrepancy may reach a few percents. This discrepancy is enhanced at low temperature where only a limited number of configurations play a significant role. In the case studied here, the fluctuations around average atom are not sufficient to improve the zero-order average-atom data below 10 eV and the statistical meaning of the average atom breaks down.

As for VSTA and STA, they converge to the same values with increasing temperature. On this example, the number of superconfigurations for VSTA is at most equal to a few thousands to converge on the average ionization with a relative error less than 10^{-5}, the number of supershells staying between 3 and 12. However, we realize that we need far less superconfigurations for VSTA when the principal shell is half-closed (or half-open). This is the main result of this paper. We can see this on Fig. 4 where we have plotted one minus the ratio of the number of superconfigurations used in STA by the number of superconfigurations used in VSTA to achieve convergence. As for Figs. 3 and 4, we have taken the absolute value of this quantity without multiplying it by 100 to convert it in percent. Around 100 eV, the *M* shell is half-open and the variance of ionization is maximum. We find that we need between one and two order of magnitude less superconfigurations with VSTA than with STA to converge. This is precisely in that region that many configurations can contribute to the partition function. The price to pay for neglecting the quadratic term in the average-configuration energy is the huge number of superconfigurations to consider with the standard STA in order to reduce, the more as we can, the influence of this quadratic term. VSTA allows one to take into account this quadratic term in the variational one-

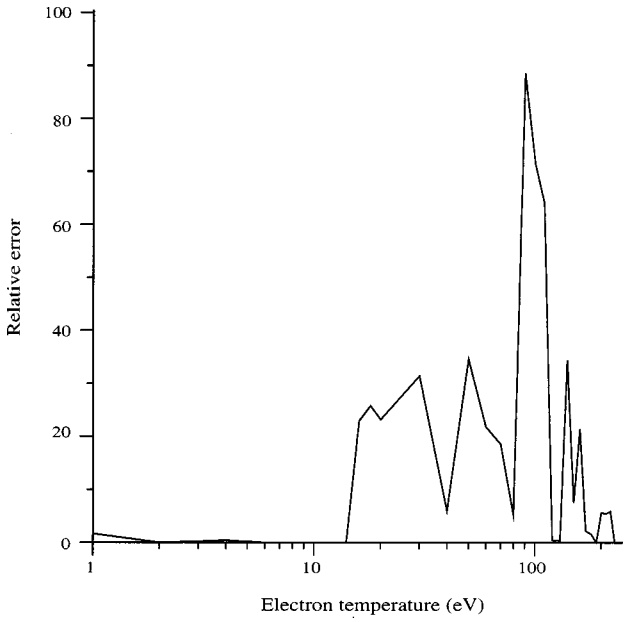

FIG. 4. The relative error is equal to the absolute value of one minus the ratio of the number of superconfigurations used in STA by the number of super-configurations used in VSTA to achieve convergence for a LTE germanium plasma ($\rho = 0.053\,07\ \mathrm{g\,cm^{-3}}$).

electron energies, and this explains why we do not have to partition so much the configuration space into superconfigurations.

At low temperature, the quadratic term cannot be neglected but each superconfiguration reduces to a configuration. Since we have limited the maximum number of supershells to 12 for practical reasons, a slight discrepancy between STA and VSTA persists at low temperature. We have checked that if this number can reach 15, VSTA and STA converges to the same values for temperatures below 10 eV. This indicates that the VSTA procedure (and the convergence) is smoother and more robust than the original STA method.

Before closing this paper, we want to mention a subtle point. Our concern is whether it is advantageous, for computing time reason, to use an optimized reference with fewer superconfigurations (VSTA) or to use a nonoptimized reference with more superconfigurations (STA). This problem should be asked when self-consistent field equations are considered instead of the simple screened hydrogenic model where the average configuration energy in Eq. (14), as well as any partial derivative with respect to shell population, can be given in closed analytic forms. Whether it is advantageous to use the additional degree of freedom in the STA method depends on the particular STA implementation. In this work, we merely report the formalism of the VSTA method, present a concrete example where it has a positive impact, and discuss new physics. We think that STA and VSTA methods should not exclude each other since both methods, for instance, may be used to make sure that calculations have converged in some specific situations.

V. CONCLUSION

The motivation for using one-electron removal energies in lieu of orbital eigenvalues for the Fermi factors used in calculating approximate superconfiguration partition functions has been presented. Optimal improvements to this approximation, which require superconfiguration dependent one-electron parameters, have also been derived. The combination of the super-transition array method and of the Gibbs-Bogolyubov variational method allow one to reduce drastically the number of superconfigurations and to obtain a smoother convergence.

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