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# Model for atomic species in a dense plasma: Description and applications

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We propose a model describing the various atomic species existing in a dense plasma; a species is a neutral atom with a given frozen configuration in the bound spectrum, surrounded by a screening cloud of free electrons in thermal equilibrium. First, a prescription is given to calculate these atomic species (bound spectrum, electron density, energy). A second part is concerned with the study of bound-bound electronic transitions; the transition energy is determined in terms of "modified effective one-particle energies" for the final and initial bound states. Some numerical applications are presented, proving that the model may be useful in calculating properties relative to various nonequilibrium situations. Finally, turning back to total thermal equilibrium, we define "average atomic species" for any ionization state $Z^*$ and calculate their respective weight; we also compute the average value of $Z^{*n}$ and its fluctuations.

## I. INTRODUCTION

Experimental study of dense plasmas have stimulated research in the field of atomic physics for materials under extreme conditions of pressure or (and) temperature. A more detailed description of these materials is needed for the understanding of their radiative properties.[1] Thermodynamic quantities, such as the equation of state, are generally obtained with acceptable accuracy within the framework of "average-atom" (AA) models. However, quantities related to radiation (spectra for diagnostics, line opacities, etc.) require a more detailed analysis of the electronic distributions

In a dilute plasma, the Saha theory allows a statistical study of the various atoms and ions; in a dense plasma, this theory fails and the study is much more difficult.[2] In the latter case, it is impossible to treat one ion independently of the surrounding electron cloud. The free electrons pile up around a positive ion and tend to form a neutral atom. When an electron jumps from a bound state to another, without changing the net charge of the ion, there is a relaxation of the free electrons and, as a consequence, a self-consistent modification of the whole spectrum. A detailed analysis of the phenomenon requires the knowledge of the atomic configuration, i.e., the occupation numbers in the whole spectrum, bound $(n_i)$ and free $(n_l)$: $\{ \cdots n_i \cdots \mid \cdots n_l \cdots \}$. In a dense plasma, there is a *finite* number of bound states, but the free spectrum includes an *infinite* number of levels. From a practical point of view, it is obviously impossible to take into account any of these total configurations individually. Thus, one must treat the free electrons statistically. This has important consequences regarding the type of models which can be used. We shall discuss these consequences in the following. In Sec. II, the definition of a species will be given and the calculation of the related quantities (electronic charge density, spectrum, and total energy) will be described. Section III will mainly treat the problem of bound-bound transitions: the transition energy will be calculated in terms of modified effective one-electron energies, and the change in a given transition with respect to the ionic configuration will be discussed as an application. In Sec. IV the above model will be applied to show that, in the case of complete thermal equilibrium, it is possible to define an "average atomic species," representative of all the species having a given bound charge, and to calculate its statistical weight. Applications will be suggested; among them are the effects of ionization fluctuations.

## II. ATOMIC SPECIES IN A DENSE PLASMA

### A. Definition of a species

Let us focus attention on an ionic configuration with a given number $Z_b$ of bound electrons. These electrons are distributed among the bound levels with occupation numbers $n_i$ which are 0 or 1. As mentioned in the Introduction, the ion cannot be treated independently of the free electrons. So, in the following, we shall only consider neutral atomic species. A species is a (fictitious) pseudoatom made of a given number of bound electrons in an assumed configuration together with the neutralizing cloud which results from the plasma free-electron polarization.

The free-electron charge density $\rho_l(r)$ is self-consistently determined under the assumption of local thermal equilibrium (LTE) in the continuum. Thus, a species may be understood as the result of averaging on the LTE continuum all the electron charge densities of real atoms having the fixed configuration $\{ \cdots n_i \cdots \}$ in the bound spectrum.

The assumption of LTE for the free electrons is common to all the models dealing with non-LTE ionic populations.[3–6] Actually, this partial equilibrium is maintained by the collisional excitations and deexcitations of the free electrons. The collision rate increasing like the square of the free-electron density, free-electron LTE prevails in dense plasmas. In most of these plasmas where NLTE bound populations do exist, the photon mean free path is larger than the dimensions of the plasma, so that radiation can escape without stimulating transitions which could perturb the continuum LTE. This assumption may thus be considered as sound and not restrictive. Once it has been done, a species is entirely determined by the specified bound configuration.

### B. Total energy and occupation numbers

Since the early work of Slater on the self-consistent central field for atomic structure calculations,[7] followed by the "density-functional theory" (DFT) of Kohn, Sham, and Mermin,[8,9] it is well known that the first-order variation of the total energy of a system when its configuration changes is

$$\delta E(\ldots n_j \ldots) = \sum_j \varepsilon_j \delta n_j \ . \tag{1}$$

This variational expression holds only if the exchange and correlation effects are treated by means of a *local* functional of the density $E_{\mathrm{XC}}(\rho)$. The ε's are thus eigenvalues of a one-particle effective Schrödinger equation. Equation (1) has the considerable advantage of taking the orbital relaxation into account; when the configuration changes, the electron density

$$\rho(\mathbf{r}) = \sum_j n_j \varphi_j^*(\mathbf{r}) \varphi_j(\mathbf{r})$$

is modified through both the variations of the $n_j$'s and $\varphi_j$'s. But the total energy being stationary with respect to the $\varphi_j$'s, the $\delta n_j$'s alone contribute to $\delta E$. Such a property has no equivalence in the Hartree-Fock (HF) theory. In the HF theory, Koopmans theorem, which gives an approximation of the total energy variation due to an occupation number variation,

$$E(\ldots n_j = 1 \ldots) - E(\ldots n_j = 0 \ldots) = \varepsilon_j \ , \tag{2}$$

assumes that the one-electron orbitals are frozen, i.e., no relaxation. (This we feel is a serious shortcoming.) Along with the much greater simplicity in practical calculations, this strongly supports the use of the statistical exchange and correlation formulation instead of the HF model even for the bound electrons. For the free electrons, it is known that the HF model has serious shortcomings in particular for dense materials which are the main interest of this work.

### C. Description of the free spectrum

Let us consider an atom of atomic number $Z$ embedded in an electron gas of uniform density $\bar{\rho}$. The electrical neutrality is preserved by means of a positive-charge background simulating the plasma ions. These we think of as a classical fluid. A model for the ionic charge profile around the embedded atom has been described elsewhere.[10] In this work we mainly focus on the electronic transitions; we shall neither treat this ionic charge profile in detail nor investigate the possible influence of ionic relaxation on electronic transitions. Except in the case of light ions and very high temperature, the ionic relaxation times are much greater than the bound levels lifetimes. Here, we shall restrict ourselves to the most simple approximation of the ionic profile, which is a spherical cavity in the uniform background,

$$\rho_+(r) = \begin{cases} 0 & \text{if } r < R_c \\ -\bar{\rho} & \text{if } r > R_c \end{cases} \tag{3}$$

(we chose the positive sign for electron densities). The cavity radius is such that the corresponding charge $Z_c$ is exactly that of the ion, as calculated in the LTE AA model,

$$4/3\pi R_c^3 \bar{\rho} = Z_c = Z^*_{\mathrm{AA}} \ . \tag{4}$$

In the following, this radius will be held fixed for given free-electron temperature and density, in agreement with the assumption of no ionic relaxation.

Around the immersed ion of fixed charge $Z - \sum_i n_i$, the free electrons polarize to form a neutral atom. The free charge coming from the continuum states is $\rho_l(r)$. As this charge is in LTE at a temperature $T$, $\rho_l$ satisfies the Kohn-Sham-Mermin equations,[8,9]

$$F_l[\rho_l] = F_0[\rho_l] + \langle \rho_l v_l \rangle + \tfrac{1}{2}\left\langle \rho_l \frac{1}{r} \circ \rho_l \right\rangle + F^T_{\mathrm{XC}}[\rho_l] \ , \tag{5}$$

$$\frac{\delta F_l[\rho_l]}{\delta \rho_l(r)} = \mu \ . \tag{6}$$

$F_l$ is the total free energy for the continuum electrons. It includes the noninteracting free energy $F_0[\rho_l]$, the energy of the electrons in the external field $v_l$, the electron-electron Coulomb energy, and the exchange and correlation free energy $F^T_{\mathrm{XC}}[\rho_l]$. The standard notations

$$\langle fg \rangle = \int f(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}$$

and

$$f \circ g = \int f(\mathbf{r}') g(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' \quad \text{(convolution product)}$$

have been used. In this model, the chemical potential $\mu$ depends on the uniform density $\bar{\rho}$ and temperature $T$ only. The density $\rho_l$ is determined by the stationarity condition Eq. (6), for fixed $T$ and $\mu$ (grand-canonical ensemble). Equations (5) and (6) are exact, but they cannot be solved without an approximate form for the functional $F^T_{\mathrm{XC}}[\rho_l]$. The common approximation is the local-density approximation: $F^T_{\mathrm{XC}}[\rho_l] \rightarrow F^T_{\mathrm{XC}}(\rho_l)$, which states that $F^T_{\mathrm{XC}}$ is, at any point in space, a function of the density $\rho_l$ only. Such an approximation neglects any nonlocal effect (dependence on gradient $\nabla \rho_l$ for instance). It is thought to be satisfying for dense materials and is frequently applied in solid-state physics.[11] In our calculations, we used a numerical fit of the results of Rajagopal and Gupta,[12] and Perrot and Dharma-Wardana[13] for the homogeneous electron gas.

With this treatment of exchange and correlation (XC) effects for free electrons, Eq. (6) is equivalent to the system

$$(-1/2\nabla^2 + U_l)\varphi_m = \varepsilon_m \varphi_m \ , \tag{7}$$

$$U_l = v_l + \frac{1}{r} \circ \rho_l + \frac{dF^T_{\mathrm{XC}}(\rho_l)}{d\rho_l} \ , \tag{8}$$

$$\rho_l=\sum_{\text{free}} f(\varepsilon_m)\varphi_m^*\varphi_m \ , \tag{9}$$

$$f(\varepsilon_m)=\{1+\exp[\beta(\varepsilon_m-\mu)]\}^{-1} \ . \tag{10}$$

The system of interacting electrons has been replaced by a system of noninteracting pseudoparticles in an effective potential $U_l$, which has to be self-consistently determined. The density $\rho_l$ is built using the eigenfunctions $\varphi_m$ and the Fermi-Dirac *average* occupation numbers $f(\varepsilon_m)$ (10).

Now, the content of the external potential $v_l$ has to be made explicit. This potential includes (i) the Coulomb potential of the ions $[-Z/r+(1/r)\circ(\rho_b+\rho_+)]$; (ii) a contribution due to XC effects between bound and free electrons, which will be described in Sec. II E.

### D. Description of the fixed bound configuration

For the $Z_b$ bound electrons there is no notion of temperature or of entropy since the configuration is frozen. The bound electron subsystem, that is the ion in its ground state or more generally in an excited state, feels the external potential $v_b$ created by the free electrons, the nucleus, and $\rho_+$. We assume that the total energy of this subsystem is

$$E_b[\rho_b]=K[\rho_b]+\langle\rho_b v_b\rangle+\tfrac{1}{2}\left\langle\rho_b\frac{1}{r}\circ\rho_b\right\rangle+E^0_{\text{XC}}(\rho_b) \ , \tag{11}$$

where $\rho_b$ is the bound density and $K[\rho_b]$ the bound kinetic energy. Equation (11) is correct for an ion in its ground state; as demonstrated by DFT theory, the energy $E_b$ is a functional of the ground-state density, and $E^0_{\text{XC}}(\rho_b)$ is the XC energy (approximated within the local-density approximation). The subscript 0 indicates that the functional is the one relevant to zero temperature. For excited states, Eq. (11) has no rigorous justification. There have been attempts to extend the DFT to excited states;[14] these studies show that the energy is, in that case, a functional of a linear combination of the densities of all the states lower in energy than the state of interest. The theory becomes so complex that its practical use seems out of reach. In the present work, we keep Eq. (11) for all excited states. The bound density is thus

$$\rho_b=\sum_{\text{bound}} n_i\varphi_i^*\varphi_i \ . \tag{12}$$

The eigenfunctions are the solutions of the one-particle equations

$$(-1/2\nabla^2+U_b)\varphi_i=\varepsilon_i\varphi_i \ , \tag{13}$$

$$U_b=v_b+\frac{1}{r}\circ\rho_b+\frac{dE^0_{\text{XC}}(\rho_b)}{d\rho_b} \ . \tag{14}$$

The bound spectrum of Eq. (13) is only relevant for describing the ion. $U_b$ is the total effective potential acting on the bound electrons. The external contribution $v_b$ to $U_b$ includes the bare nuclei potential $[-Z/r+(1/r)\circ\rho_+]$, the Coulomb potential of the free electrons $[(1/r)\circ\rho_l]$, and the effect of XC between bound and free electrons, discussed in the following paragraph.

### E. Exchange and correlation effects between bound and free electrons

In Eq. (11) we use for $E^0_{\text{XC}}$ the Wigner functional

$$E^0_{\text{XC}}(\rho)=\int d\mathbf{r}\rho\left[c\rho^{1/3}+\gamma\frac{\rho^{1/3}}{\nu+\rho^{1/3}}\right] \tag{15}$$

with $c=-3(3/\pi)^{1/3}/4$, $\gamma=-0.05641$, and $\nu=0.07953$ (in atomic units). The bound-free XC contribution is defined as the difference between the total XC energy and the sum of the XC energies, for the bound and free electrons taken separately,

$$E^{ba}_{\text{XC}}(\rho_b,\rho_\alpha)=E_{\text{XC}}(\rho_b+\rho_\alpha)-E_{\text{XC}}(\rho_b)-E_{\text{XC}}(\rho_\alpha) \ . \tag{16}$$

In this formula $\rho_\alpha$ is the density for a given real configuration (with integer occupation numbers) of the free spectrum, before any thermodynamic averaging. Inserting the functional defined by Eq. (15) into the right-hand side of Eq. (16), we can write

$$E^{b\alpha}_{\text{XC}}(\rho_b,\rho_\alpha)=\langle\rho_b\rho_\alpha[G(\rho_b,\rho_\alpha)+G(\rho_\alpha,\rho_b)]\rangle \tag{17}$$

with

$$G(x,y)=[(x+y)^{2/3}+(x+y)^{1/3}x^{1/3}+x^{2/3}]^{-1} \times\{c+\gamma\nu[\nu+(x+y)^{1/3}]^{-1}(\nu+x^{1/3})^{-1}\} \ . \tag{18}$$

Now we have to average $E^{b\alpha}_{\text{XC}}$ over all the possible configurations in the free spectrum, keeping $\rho_b$ fixed. To get an approximate solution, we proceed as follows. We note that, inside the ion, $\rho_\alpha$ is much smaller than $\rho_b$, while outside the ionic volume, $\rho_b$ is very small and $\rho_\alpha$ is close to the mean free electron density $\bar{\rho}$. Thus it is appropriate to substitute $\bar{\rho}$ for $\rho_\alpha$ in the functions $G$ of Eq. (17), where the dependence on $\rho_\alpha$ is not too strong. Once this has been done, $E^{b\alpha}_{\text{XC}}$ is linear in $\rho_\alpha$ and the average is obtained through the substitution $\rho_\alpha\to\rho_l$. We get

$$E^{bl}_{\text{XC}}=\langle\rho_b\rho_l[G(\rho_b,\bar{\rho})+G(\bar{\rho},\rho_b)]\rangle \ . \tag{19}$$

The bound-free XC contribution to the external potential $v_l$ for the free electrons is derived straightforwardly,

$$W_{\text{XC}l}=\frac{\partial E^{bl}_{\text{XC}}}{\partial\rho_l} \tag{20}$$

and its counterpart for the bound electrons,

$$W_{\text{XC}b}=\frac{\partial E^{bl}_{\text{XC}}}{\partial\rho_b} \ ,$$

can be calculated without difficulty.

We conclude by observing that the approximation of $\rho_\alpha$ by $\bar{\rho}$ leads to $W_{\text{XC}l}$ [Eq. (20)] which is independent of the density of the free electrons $\rho_l$. When this form is included in the external potential $v_l$ of Eq. (5) it truly behaves as an external potential independent of $\rho_l$ in accordance with the Kohn-Sham formulation; Eq. (11) is thus justified within this approximation. Finally, we note that such a constant term will not add to the entropy functional of the free electrons.

### F. Solving the equations

The numerical technique for solving Eqs. (7)—(10) for the free spectrum is well known. It has been presented in detail elsewhere.[15] Here we shall summarize the main points. One has to calculate the free states associated with the effective potential $U_l$ [Eq. (8)], which may be written

$$U_l = -\frac{Z}{r} + \frac{1}{r} \circ (\rho_l + \rho_b + \rho_+) + V_{\mathrm{XC}}^T(\rho_l) + W_{\mathrm{XC}l}(\rho_b, \bar{\rho}) , \tag{21}$$

where $\rho_+$ is the ionic profile [Eq. (3)], $V_{\mathrm{XC}}^T$ the free-free XC potential (the derivative of $F_{\mathrm{XC}}^T$ with respect to $\rho_l$) and $W_{\mathrm{XC}l}$ the bound-free XC potential [Eq. (20)]. $U_l$ is the potential for an atomic species with $Z_b$ bound electrons. When the self-consistent solution is obtained, the central ion is totally screened by the charge $\rho_l + \rho_b + \rho_+$, so that

$$Z = \int (\rho_l + \rho_b + \rho_+) d\mathbf{r} = Z_b + Z_c + \int (\rho_l - \bar{\rho}) d\mathbf{r} . \tag{22}$$

The Coulomb part of $U_l$ is thus short ranged. Far away from the central ion, $U_l$ goes to a constant which is $U_{l0} = V_{\mathrm{XC}}^T(\bar{\rho}) + W_{\mathrm{XC}l}(0, \bar{\rho})$. The eigenvalues and eigenfunctions of Eq. (7) are

$$\begin{aligned} \varepsilon_l &= \varepsilon_k = 1/2k^2 + U_{l0} , \\ \varphi_l(\mathbf{r}) &= \varphi_{kLM}(\mathbf{r}) = A_{kL} \varphi_{kL}(r) Y_{LM}(\mathbf{r}) . \end{aligned} \tag{23}$$

The asymptotic behavior of the radial part for large $r$ is

$$\varphi_{kL}(r) \to r^{-1} \sin \left[ kr - L\frac{\pi}{2} + \eta_L(k) \right] .$$

After normalization, and taking the density of states into account, the electron density for the free spectrum is

$$\rho_l(r) = \bar{\rho} + \frac{1}{\pi^2} \int_0^\infty f_k dk \sum_L (2L+1)[\varphi_{kL}^2(r) - k^2 j_L^2(kr)] \tag{24}$$

with $j_L$ the spherical Bessel function of order $L$. The density of states per unit $k$ is

$$N(k) = N_0(k) + \frac{2}{\pi} \sum_L (2L+1) \frac{d\eta_L}{dk} , \tag{25}$$

where $N_0(k)$ is the density of states for the unperturbed electron gas at density $\bar{\rho}$. Let us also recall the sum rule, with $f_k = f(\varepsilon_k)$,

$$Z - Z_b - Z_c = \beta \frac{2}{\pi} \int_0^\infty k\, dk f_k (1 - f_k) \sum_L (2L+1) \eta_L(k) \tag{26}$$

($\beta$ is the inverse temperature); Eq. (16) is a direct consequence of charge neutrality [Eq. (22)].

To calculate the bound charge $\rho_b$, one has to solve Eqs. (13) and (14), that is, to find the bound spectrum of the Schrödinger equation for potential $U_b$ (different from $U_l$),

$$U_b = -\frac{Z}{r} + \frac{1}{r} \circ (\rho_l + \rho_b + \rho_+) + V_{\mathrm{XC}}^0(\rho_b) + W_{\mathrm{XC}b}(\rho_b, \bar{\rho}) . \tag{27}$$

No particular difficulty is encountered in solving these equations. The self-consistent calculation of $\rho_l$ and $\rho_b$ is performed simultaneously since the equations are coupled by the Coulomb potential. We shall not give here more details on the iterative procedure which is now standard.

### G. Total energy for an atomic species

We next present the form for the total energy of the atomic species defined by a configuration of the bound spectrum and a screening charge of free electrons in LTE. Both electron populations are coupled by electrostatic and XC potentials. As in the previous section, the *fixed* integer occupation numbers of the bound electrons are noted by $n_i$, while the *fractional* average occupation numbers of the free-electrons are noted by $f_k$. The eigenvalues $\varepsilon_j$ (bound and free) are measured with respect to the uniform potential $U_{l0}$. The chemical potential for the free electrons with respect to the same origin is $\bar{\mu} = \mu - U_{l0}$. The total energy considered here is that of embedding the atom in the plasma,

$$\Delta E(\ldots n_i \ldots) = E(\ldots n_i \ldots) - \bar{E}[\bar{\rho}] \tag{28}$$

with $\bar{E}[\bar{\rho}]$ the unperturbed electron gas energy (at the temperature and density of the free electrons). Starting from (5) and (11), one gets easily

$$\begin{aligned} \Delta E(\ldots n_i \ldots) = {} & \tfrac{1}{2} \sum_i n_i \langle \nabla \varphi_i^* \nabla \varphi_i \rangle + E_0[\rho_l] - E_0[\bar{\rho}] + \left\langle \left[ -\frac{Z}{r} + \frac{1}{r} \circ \rho_+ \right] (\rho_b + \rho_l) \right\rangle \\ & + \tfrac{1}{2} \left\langle (\rho_b + \rho_l) \frac{1}{r} \circ (\rho_b + \rho_l) \right\rangle + E_{\mathrm{XC}}^0(\rho_b) + E_{\mathrm{XC}}^T(\rho_l) + E_{\mathrm{XC}}^{bl} - E_{\mathrm{XC}}^T(\bar{\rho}) + \left\langle \frac{Z}{r} \rho_+ \right\rangle + \tfrac{1}{2} \left\langle \rho_+ \frac{1}{r} \circ \rho_+ \right\rangle . \end{aligned} \tag{29}$$

The first three terms give the kinetic energies [$E_0$ corresponds to the $F_0$ in Eq. (5)], the next two terms give the electron-ion and electron-electron Coulomb energies. The terms with the subscripts XC give the XC contributions and the last two terms the ion-ion interaction energy. This formal expression can be rewritten

$$\Delta E(\ldots n_i \ldots)=\sum_i n_i\varepsilon_i+\frac{2}{\pi}\sum_L(2L+1)\int_0^\infty f_k\frac{d\eta_L}{dk}\frac{k^2}{2}dk+\langle\bar{\rho}2\pi r^2(\rho_b+\rho_l-\bar{\rho})\rangle$$
$$-\tfrac{1}{2}\left\langle(\rho_b+\rho_l-\bar{\rho})\frac{1}{r}\circ(\rho_b+\rho_l-\bar{\rho})\right\rangle+E^0_{\mathrm{XC}}(\rho_b)-\langle\rho_b[V^0_{\mathrm{XC}}(\rho_b)+W_{\mathrm{XC}b}(\rho_b,\bar{\rho})]\rangle$$
$$+E^T_{\mathrm{XC}}(\rho_l)-E^T_{\mathrm{XC}}(\bar{\rho})-\langle\rho_l V^T_{\mathrm{XC}}(\rho_l)\rangle-\langle(\rho_b+\rho_l)V^T_{\mathrm{XC}}(\bar{\rho})\rangle-\frac{3}{2}\frac{Z_c}{R_c}\left[Z-\frac{3}{5}Z_c\right]. \tag{30}$$

In Eq. (30), $E^T_{\mathrm{XC}}(\rho)$ is the XC energy related to the free-energy $F^T_{\mathrm{XC}}(\rho)$ of Eq. (5) by the thermodynamic relation $F^T_{\mathrm{XC}}=E^T_{\mathrm{XC}}-TS^T_{\mathrm{XC}}$. The statistical weight of a species is $\exp S[\rho_l]$, with $S[\rho_l]$ the total entropy for the electrons in the free spectrum which is, after subtracting the unperturbed electron gas contribution,

$$\Delta S[\rho_l]=-\frac{2}{\pi}\sum_L(2L+1)\int_0^\infty\frac{d\eta_L}{dk}dk[f_k\ln f_k+(1-f_k)\ln(1-f_k)]+S^T_{\mathrm{XC}}(\rho_l)-S^T_{\mathrm{XC}}(\bar{\rho}). \tag{31}$$

The computation of the total energy for a given species can thus be done using Eq. (30). This model is particularly well suited for the study of bound-bound transitions, as will be seen in Sec. III.

## III. DESCRIPTION OF BOUND-BOUND ELECTRONIC TRANSITIONS

### A. Total energy difference in a transition

We next consider the transition of an electron from initial state $i$ to final state $j$ in the bound spectrum. The change in the total energy of the species associated with that transition is

$$\delta E_{Z^*}(i\to j)=\Delta E(\ldots n_i=0,\ldots,n_j=1,\ldots)$$
$$-\Delta E(\ldots n_i=1,\ldots,n_j=0,\ldots). \tag{32}$$

The label $Z^*$ refers to the ionization degree of the species. Energies in the right-hand side of Eq. (32) are defined by Eq. (30) (the constant unperturbed electron gas energy cancels in the difference). The calculation of Eq. (32) is approached in the same spirit as the "transition-state" theory of Slater.[7] Up to now, the bound-levels occupation numbers were integers with the values 0 or 1, but they can be considered, for mathematical convenience, as continuous variables in the interval [0,1], because all the equations of the model (due to the use of a statistical XC functional) maintain their meaning for any value of the $n_i$'s. For a zero-temperature system (atom or solid) the energy change in a bound-bound transition is, according to Eq. (1), $\delta E=\varepsilon_j-\varepsilon_i+O(\delta n^2)$. Because of the stationarity, the states (bound or free) different from $i$ and $j$ do not appear in $\delta E$ to first order (although they relax) since their occupation number is kept fixed. The situation is different in the model presented here; since the free-spectrum occupation numbers obey Fermi-Dirac (FD) statistics, they change with any relaxation of the system, and consequently the internal energy does change, even in first order. When a bound state $n_i$ changes, the potential acting on the continuum electrons changes, the energy levels and occupation numbers of these change, too. In such a relaxation, the stationary quantity is the free-energy $F_l[\rho_l]$ [see Eq. (5)] not the internal energy $E_l[\rho_l]$. Let us assume that $n_i,n_j$ change by $\delta n_i,\delta n_j$. Then the corresponding change of the species energy is

$$\delta E_{Z^*}(i,j)=\varepsilon_i\delta n_i+\varepsilon_j\delta n_j+\left\langle\frac{\delta\Delta E_{Z^*}}{\delta\rho_l}\delta\rho_l\right\rangle+O(\delta n^2). \tag{33}$$

The first contribution to $\delta E_{Z^*}$ comes from the bound states [$\varepsilon_i,\varepsilon_j$ given by Eq. (13)], the second one from the continuum relaxation. But

$$\frac{\delta\Delta E_{Z^*}}{\delta\rho_l}=\frac{\delta\Delta F_l[\rho_l]}{\delta\rho_l}+T\frac{\delta\Delta S[\rho_l]}{\delta\rho_l}.$$

The right-hand side first term is the chemical potential $\mu$; in the transition, the total free charge does not change, so that

$$\delta E_{Z^*}(i,j)=\varepsilon_i\delta n_i+\varepsilon_j\delta n_j+T\left\langle\frac{\delta\Delta S[\rho_l]}{\delta\rho_l}\delta\rho_l\right\rangle+O(\delta n^2). \tag{34}$$

Now the entropy includes a noninteracting contribution and an XC contribution [Eq. (31)]. The first one is easily related to the FD occupation-numbers variation, so that

$$\delta E_{Z^*}(i,j)=\varepsilon_i\delta n_i+\varepsilon_j\delta n_j+\sum_m\varepsilon_m\delta f_m$$
$$+T\left\langle\frac{\delta S^T_{\mathrm{XC}}(\rho_l)}{\delta\rho_l}\delta\rho_l\right\rangle+O(\delta n^2). \tag{35}$$

Assuming that the free density deviation $\rho_l(r)-\bar{\rho}$ is small, we can neglect the XC entropy term in Eq. (35) since the integrated charge $\langle\delta\rho_l\rangle=0$. Then, to first order in the free-states energy change,

$$\delta\varepsilon_m=\langle\varphi^*_m\delta U_l\varphi_m\rangle, \tag{36}$$

we obtain

$$\delta E_{Z^*}(i,j)=\varepsilon_i\delta n_i+\varepsilon_j\delta n_j$$
$$-\sum_m\beta\varepsilon_m f_m(1-f_m)\langle\varphi^*_m\delta U_l\varphi_m\rangle+O(\delta n^2). \tag{37}$$

$\delta U_l$ is the variation of the total potential acting on the continuum states. Linearizing its XC contribution with respect to the bound charge variation $\delta\rho_b = \rho_i \delta n_i + \rho_j \delta n_j$ we can write $\delta U_l = U_{li} \circ \rho_i \delta n_i + U_{lj} \circ \rho_j \delta n_j$ $(\rho_i = \varphi_i^* \varphi_i)$. The potential $U_{li}$ $(U_{lj})$ includes the Coulomb part due to the charge $\rho_i \delta n_i$ $(\rho_j \delta n_j)$ screened by the free electrons, and an XC potential associated with $\rho_i$ $(\rho_j)$. We have used the Thomas-Fermi linearized theory to screen the Coulomb potential; details of this screening calculation are given in the Appendix. Finally, we can write

$$U_{li} \circ \rho_i \delta n_i = \delta n_i \int [K(\mathbf{r},\mathbf{r}') + \frac{\delta^2 E_{\mathrm{XC}}^{bl}}{\delta \rho_i^2} \delta(\mathbf{r}-\mathbf{r}')] \rho_i(\mathbf{r}') d\mathbf{r}' \ , \tag{38}$$

where $K(\mathbf{r},\mathbf{r}')$ is the screened Coulomb interaction. Combining Eqs. (37) and (39) we obtain, with $\rho_m = \varphi_m^* \varphi_m$,

$$\begin{gathered} \delta E_{Z^*}(i,j) = \varepsilon_i^* \delta n_i + \varepsilon_j^* \delta n_j + O(\delta n^2) \ , \\ \varepsilon_i^* = \varepsilon_i - \beta \sum_m \varepsilon_m f_m (1-f_m) \langle \rho_m U_{li} \circ \rho_i \rangle \ . \end{gathered} \tag{39}$$

Equation (39) is the main result of the present work. It shows that, in the plasma, the total energy variation due to a change in the bound-state configuration is described, to first order, by one-particle *modified effective energies* $\varepsilon^*$ (MEE) which take into account the continuum relaxation.

To improve the accuracy of the bound-bound transition energy, one can use the transition-state technique,[7] that is, calculate the $\varepsilon^*$ in the intermediate configuration of the ion, $\{\ldots n_i - \frac{1}{2}, \ldots, n_j + \frac{1}{2} \ldots\}$. One knows that this technique makes the quadratic terms $O(\delta n^2)$ in the expansion of $\delta E$ vanish, so that the transition energy is

$$\delta E_{Z^*}(i \to j) = \varepsilon_j^* - \varepsilon_i^* + O(\delta n^3) \tag{40}$$

for $\varepsilon_i^*, \varepsilon_j^*$ calculated in the transition state. The numerical accuracy of Eq. (40) will be examined in Sec. III B.

### B. Numerical results

We present a numerical test of Eqs. (39) and (40) for iron at a free-electron temperature of 100 eV and an electron density $\bar{\rho} = 0.1148$ a.u. (or $7.75 \times 10^{23} e\ \mathrm{cm}^{-3}$). The corresponding material density is 6.52 $\mathrm{g\,cm}^{-3}$. We first performed a full LTE AA calculation, which gave an average ionization $Z_{\mathrm{AA}}^* = 11.025$, so that the ionic cavity radius is $R_c = 2.8407$ a.u. [Eq. (4)]. The total AA energy was $\Delta E_{\mathrm{AA}} = E_{\mathrm{AA}} - \bar{E}[\bar{\rho}] = -2472.752$ Ry, with a free-electron gas energy $\bar{E}[\bar{\rho}] = 117.399$ Ry. The AA configuration was $1s^2 2s^2 2p^{5.98} 3s^{0.77} 3p^{1.87} 3d^{2.10} 4s^{0.25}$. Then, keeping the same value of $R_c$, we calculated several ionic species around the average configuration, with the aim of comparing the "exact" total energy differences [Eq. (30)] with those estimated using the MEE [Eqs. (39) and (40)]. In each case, we made three calculations: one for the initial, one for the final, and one for the transition configurations. The results are shown in Table I. One sees that the MEE estimate with $\varepsilon^*$ is always closer to the exact result (difference of the total energies) than the estimate with the uncorrected $\varepsilon$. For the high-energy transitions, the correction is not very important in relative value (cases 1,2,5). In absolute magnitude, it is significant when the initial and final states have very different localizations in space. This can be understood in the light of the following argument. The Coulomb potential created by the displaced bound charge is $(1/r) \circ (\varphi_j^* \varphi_j - \varphi_i^* \varphi_i)$, the average value of which is proportional to $\langle \varphi_j | r^2 | \varphi_j \rangle - \langle \varphi_i | r^2 | \varphi_i \rangle$; the correction to $\varepsilon_i$ is mainly governed by the average value of $r^2$ in state $i$. In case 4 of Table I, $\langle r^2 \rangle_{4s} = 2.92$ and $\langle r^2 \rangle_{3p} = 0.58$; in case 7, $\langle r^2 \rangle_{4p} = 3.49$ and $\langle r^2 \rangle_{3s} = 0.58$; in case 9, $\langle r^2 \rangle_{4p} = 3.48$ and $\langle r^2 \rangle_{3d} = 0.52$. This explains the importance of the correction in these three cases. On the other hand, in case 3, the correction is negligible because $\langle r^2 \rangle_{3s} = \langle r^2 \rangle_{3p} = 0.59$.

### C. Study of some particular transitions

The atomic species model is well suited for studying the effect of ionic configuration on a transition. One assumes that the transition probability is constant with time. The description which takes into account the free-electron relaxation in LTE is correct if $1/\nu_p \leq t$, where $\nu_p$ is the plasma frequency and $t$ the initial-state lifetime. This condition is generally met.

TABLE I. Comparison between total energy differences calculations. Iron; free-electrons temperature $T = 100$ eV; free-electrons density $\bar{\rho} = 7.75 \times 10^{23} e\ \mathrm{cm}^{-3}$. $\Delta\varepsilon$ is the difference of the noncorrected one-particle eigenvalues $\varepsilon$ in the transition state. $\Delta\varepsilon^*$: idem with the corrected eigenvalues. The exact result is given in the third column. The average-atom values also shown for comparison. All energies in rydbergs.

| Configuration | $n^0$ | $\Delta\varepsilon$ (Ry) | $\Delta\varepsilon^*$ (Ry) | Total energy difference (Ry) | $\Delta\varepsilon_{\mathrm{AA}}$ (Average atom) (Ry) |
|---|---|---|---|---|---|
| $(2s^2 2p^6 3s^1 3d^1) 1s^2 3p^1 \to 1s^1 3p^2$ | 1 | 519.6681 | 520.4465 | 520.6245 | 508.3053 |
| $(1s^2 2p^6 3s^1 3d^1) 2s^2 3p^1 \to 2s^1 3p^2$ | 2 | 59.7797 | 60.3795 | 60.5647 | 57.8289 |
| $(1s^2 2s^2 2p^6 3d^1) 3s^1 3p^1 \to 3s^0 3p^2$ | 3 | 2.4322 | 2.4308 | 2.4278 | 2.4359 |
| $(1s^2 2s^2 2p^6 3s^1 3d^1) 4s^0 3p^1 \to 4s^1 3p^0$ | 4 | 10.7363 | 12.2137 | 12.3402 | 8.7931 |
| $(2s^2 2p^6 3s^1 3p^1 3d^1) 1s^2 4p^0 \to 1s^1 4p^1$ | 5 | 532.0793 | 534.4856 | 534.7541 | state $4p$ does not exist |
| $(1s^2 2p^6 3s^1 3p^1 3d^1) 2s^2 4p^0 \to 2s^1 4p^1$ | 6 | 71.8901 | 73.9666 | 74.4144 | |
| $(1s^2 2s^2 2p^6 3p^1 3d^1) 3s^1 4p^0 \to 3s^0 4p^1$ | 7 | 13.9768 | 15.6237 | 15.7133 | |
| $(1s^2 2s^2 2p^6 3s^1) 3p^1 3d^1 \to 3p^2 3d^0$ | 8 | $-3.8173$ | $-3.7541$ | $-3.7277$ | $-3.9314$ |
| $(1s^2 2s^2 2p^6 3s^1 3p^1) 4p^0 3d^1 \to 4p^1 3d^0$ | 9 | 7.7950 | 9.5194 | 9.6490 | |

TABLE II. Study of optical transitions in iron, at $T=100$ eV and $\bar{\rho}=7.75\times10^{23}e\,\text{cm}^{-3}$. All the configurations have the ion $1s^22s^22p^6$ in common. The energies are calculated in the transition state. Rydberg units.

| | Configuration | $Z^*$ | $\Delta\varepsilon$ (Ry) | $\Delta\varepsilon^*$ (Ry) | $\lvert\langle i\,\lvert r\rvert\, j\rangle\rvert$ | $f_{ij}=\Delta\varepsilon^*\lvert\langle i\,\lvert r\rvert\, j\rangle\rvert^2$ |
|---|---|---|---|---|---|---|
| Transition | $3s^03d^1$ | 14 | 11.7100 | 13.2323 | 0.2031 | 0.5458 |
| $3p^14s^0\rightarrow3p^04s^1$ | $3s^13d^1$ | 13 | 10.7363 | 12.2137 | 0.2061 | 0.5189 |
| | $3s^23d^1$ | 12 | 9.9619 | 11.7451 | 0.2096 | 0.5160 |
| | $3s^03d^2$ | 13 | 10.7837 | 12.3988 | 0.2082 | 0.5375 |
| | $3s^13d^2$ | 12 | 9.9105 | 11.6779 | 0.2105 | 0.5176 |
| | $3s^23d^2$ | 11 | 9.0009 | 10.9754 | 0.2069 | 0.4697 |
| Transition | $3s^03d^1$ | 13 | 10.8393 | 12.4648 | 0.2074 | 0.5360 |
| $3p^24s^0\rightarrow3p^14s^1$ | $3s^13d^1$ | 12 | 9.9557 | 11.7327 | 0.2098 | 0.5165 |
| | $3s^23d^1$ | 11 | 9.0355 | 11.0193 | 0.2064 | 0.4693 |
| | $3s^03d^2$ | 12 | 9.9046 | 11.6664 | 0.2107 | 0.5181 |
| | $3s^13d^2$ | 11 | 8.9991 | 10.9687 | 0.2070 | 0.4702 |
| | $3s^23d^2$ | | | 4s state does not exist | | |

As an illustration, we give in Table II some results relative to the transition $3p^14s^0\rightarrow3p^04s^1$ and $3p^24s^0\rightarrow3p^14s^1$ in iron, at $T=100$ eV and $\bar{\rho}=7.75\times10^{23}$ $e\,\text{cm}^{-3}$. We kept the simple approximation of a spherically symmetric potential $U_b$ [Eq. (13)], with no attempt to remove angular momentum projection or spin degeneracies. All the configurations presented have the ion $1s^22s^22p^6$ in common, as suggested by the AA calculation. The populations which are changed are those of the $3s$ and $3d$ shells. The ionization degree of the various species range from 11 to 14. We first note the importance of the correction $\varepsilon\rightarrow\varepsilon^*$ in that case; it can be as big as 22%. The transition energy dispersion is also very important; from 10.97 to 13.23 Ry, or $\approx$20%. The matrix element $\langle 3p\,|\,r\,|\,4s\rangle$ is much less sensitive to the configuration, about 4%. Finally, the variation on the oscillator strength tabulated in the last column of Table II is 16%.

As shown by this example, one can easily calculate the radiative transition characteristics for any kind of ion in the plasma. This possibility may be of interest for generating data needed in the study of nonequilibrium situations.

## IV. ATOMIC SPECIES STATISTICS

So far, we derived the model of atomic species with the aim of improving on the AA model for generating data adapted to nonequilibrium situations. However, Eq. (39) may have applications in the case of LTE also. This equation expresses the *total energy* variation of a species in terms of MEE for the bound states only. In other words, it achieves decoupling between the ion and the free electrons provided the number of bound electrons, i.e., the ionization degree, is fixed. This enables us to define an average for all the atomic species with a given ionization degree, as shown in the next paragraph.

### A. Average species with a given ionization degree

We now consider a plasma in which bound and free electrons are all in thermal equilibrium. Let us focus our attention on the species with a given ionization degree $Z^*$, and particularly on the most abundant one. We chose the energy of this one, which has the configuration $\langle\ldots n_{i0}\ldots\rangle$ as a reference. Now, a straightforward generalization of Eq. (39) gives the total energy of another species with same value of $Z^*$ but a different configuration $\{\ldots n_i\ldots\}$,

$$\Delta E_{Z^*}(\ldots n_i\ldots)=\Delta E_{Z^*}(\ldots n_{i0}\ldots)+\sum_i\varepsilon^*_{iZ^*}\Delta n_i+O(\Delta n^2)\,, \tag{41}$$

where the $\varepsilon_{iZ^*}$ are the MEE of the reference species, provided that

$$\sum_{\text{bound}}\Delta n_i=\sum_{\text{bound}}(n_i-n_{i0})=0\,. \tag{42}$$

It follows from Eq. (41) that the total energy of a $Z^*$ species can be interpreted as that of a system of $Z_b$ *independent pseudoparticles,* distributed among states of energy $\varepsilon^*_{iZ^*}$. Let us recall that all relaxation effects are accounted for in Eq. (41). The only limitation is the neglect of quadratic terms $(\Delta n^2)$. Since the effective system is now noninteracting, the average occupation numbers for the species will be given by FD statistics,

$$\bar{n}_i=\{1+\exp[\beta(\varepsilon^*_{iZ^*}-\mu_{Z^*})]\}^{-1}\,. \tag{43}$$

In the case of complete LTE for bound and free electrons, $\beta$ in Eq. (43) is the same as that of Eq. (10). But one could also consider situations where the bound-electron temperature would be different from the free-electron temperature. For instance, if there is very little energy transfer between the ions and the free electrons, the bound-electron temperature has to be determined by a condition of constant energy of the ionic subsystem. This would lead to a two-temperature model. In Eq. (43), $\mu_{Z^*}$ is understood as an effective chemical potential for the bound pseudoparticles, to be determined by the condition

TABLE III. Results of the average-atom calculation at $T=100$ eV and $\bar{\rho}=4.77\times10^{23}e\ \mathrm{cm}^{-3}$ in Al. The origin of energies is the exchange and correlation potential for free electron gas $U_{l0}$. Their absolute position is obtained by adding $-0.516\,96$ Ry. All energies in Rydbergs. $\langle r \rangle$ is the average radius of the shell.

| Level | $\varepsilon_{\mathrm{AA}}$ (Ry) | $\bar{n}_{\mathrm{AA}}$ | $\langle r \rangle$ |
|---|---|---|---|
| 1$s$ | $-122.607\,71$ | 0.999 99 | 0.120 27 |
| 2$s$ | $-14.785\,44$ | 0.378 01 | 0.543 51 |
| 2$p$ | $-12.703\,47$ | 0.314 04 | 0.480 16 |
| 3$s$ | $-0.934\,39$ | 0.084 52 | 1.557 56 |
| 3$p$ | $-0.335\,71$ | 0.078 43 | 1.644 24 |
| $Z_b$ | 5.279 88 | | |
| $R_c$ | 2.869 40 | | |
| $\Delta E$ | $-431.673\,5$ | | |
| $T\Delta S$ | 53.575 7 | | |
| $E[\rho]$ | 74.760 7 | | |
| $TS[\rho]$ | 258.430 5 | | |

$$\sum_i \bar{n}_i = Z - Z^* \ . \qquad (44)$$

Equations (43) and (44) entirely define the *average* species for the ionization degree $Z^*$. The probability of this ionization degree can now be calculated. The number of possible states of the species with the given ionic configuration $\{\ldots n_i \ldots\}$ is (see Sec. II G) $\Omega_l=\exp(S[\rho_l])$, corresponding to all possible arrangements of the free spectrum. The number of bound configurations giving ionization state $Z^*$ is

$$\Omega_b = \exp(S_{Z^*})$$

with $S_{Z^*}$ the entropy of the independent bound pseudoparticles,

$$S_{Z^*} = -k_B \sum_i [\bar{n}_i \ln \bar{n}_i + (1-\bar{n}_i)\ln(1-\bar{n}_i)] \ , \qquad (45)$$

so that the total number of $Z^*$ species is

$$\Omega_Z = \exp(S_{Z^*} + S[\rho_l]) \ . \qquad (46)$$

Finally, the total probability of a $Z^*$ species is

$$P_{Z^*} = A \exp(-\beta F_{Z^*}) \qquad (47)$$

with

$$F_{Z^*} = \Delta E_{Z^*}(\ldots \bar{n}_i \ldots) - TS_{Z^*} - T\Delta S[\rho_l] \ . \qquad (48)$$

$A$ is a normalization constant such that $\sum p_{Z^*}=1$, the summation running over all integer ionization states. $F_{Z^*}$ is an effective free-energy including the entropy contributions and the average total energy of the $Z^*$ species, the expression of which is given by Eq. (30), but now with the average occupation numbers $\bar{n}_i$ instead of the integer $n_i$.

### B. Practical aspects of the average species calculation

This calculation starts with the choice of a reference $Z^*$ species $\{\ldots n_{i0} \ldots\}$. As this one is only a mathematical tool around which the energy is linearized with respect to $\Delta n_i$ [see Eq. (41)], it can be chosen with fractional occupation numbers. So we proceed as follows. We perform an AA calculation which provides average levels $\varepsilon_{\mathrm{AA}}$. These are used to determine the reference $Z^*$ species occupation numbers $n_{i0}$ (FD) under the condition

$$\sum_i n_{i0} = \sum_i \{1+\exp[\beta(\varepsilon_{\mathrm{AA}}-\nu)]\}^{-1} = Z - Z^* \ .$$

With these fixed $n_{i0}$, we make the complete self-consistent calculation of the reference $Z^*$ species, as indicated in Sec. III. The corresponding MEE $\varepsilon^*_{iZ^*}$, the reference energy $\Delta E(\ldots n_{i0} \ldots)$, and entropy $\Delta S[\rho_l]$ are simultaneously computed. Then, using Eqs. (43), the average $\bar{n}_i$'s are calculated, and also the free-energy $F_{Z^*}$ by means of Eqs. (45)—(48). This sequence of calculations has to be repeated for every integer value of $Z^*$ between 0 and $Z$. One can imagine that negative ions do exist, however, for fixed conditions of temperature and density, such ionization states are very improbable and may be deleted, as we shall see in the numerical example below. Once all the significant species are treated, the probabilities $p_{Z^*}$ are normalized.

### C. Applications

In some studies, it is useful to know the average values of $Z^{*n}$. For $n=1$, the AA model gives the answer. But for transport phenomena, for instance, one needs $\langle Z^{*2} \rangle$ (electronic conductivity), and similarly for the bremsstrahlung cross section. When fluctuations are important, $\langle Z^{*n} \rangle$ may be rather different from $\langle Z^* \rangle^n$. The model of average atomic species yields these averages.

TABLE IV. The various average atomic species in aluminum at $T=100$ eV and $\bar{\rho}=4.77\times10^{23}e\ \mathrm{cm}^{-3}$. For each of them, the average occupation numbers $\bar{n}_i$ [Eq. (43)] are shown. The 3$d$ shell exists for large ionizations only.

| $Z^*$ | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1$s$ | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 0.999 1 | 0.5000 |
| 2$s$ | 1.0000 | 0.9027 | 0.7971 | 0.6824 | 0.5205 | 0.3573 | 0.2193 | 0.1157 | 0.000 23 | 0. |
| 2$p$ | 1.0000 | 0.8658 | 0.7343 | 0.6059 | 0.4439 | 0.2973 | 0.1796 | 0.0952 | 0.000 19 | 0. |
| 3$s$ | | | | | 0.1477 | 0.0666 | 0.0299 | 0.0120 | 0.000 18 | 0. |
| 3$p$ | | | | | | 0.0614 | 0.0278 | 0.0112 | 0.000 17 | 0. |
| 3$d$ | | | | | | | 0.0257 | 0.0106 | 0.000 16 | 0. |

TABLE V. Probability $P_{Z^*}$ of the various atomic species in aluminum at $T=100$ eV and $\bar{\rho}=4.77\times10^{23} e\,\mathrm{cm}^{-3}$. Rydberg units.

| $Z^*$ | $\Delta E_{Z^*}(\ldots n_i \ldots)$ | $TS_{Z^*}$ | $T\Delta S[\rho_l]$ | $F_{Z^*}$ | $P_{Z^*}$ |
|---|---|---|---|---|---|
| 3 | −533.1474 | 0. | −141.2545 | −391.8929 | $1.225\times10^{-6}$ |
| 4 | −517.8026 | 22.0827 | −110.9560 | −428.9294 | $1.892\times10^{-4}$ |
| 5 | −500.3762 | 32.9470 | −80.7413 | −452.5819 | 0.004 73 |
| 6 | −480.5893 | 38.7614 | −50.5880 | −468.7628 | 0.042 71 |
| 7 | −454.8157 | 46.6236 | −20.4398 | −480.9995 | 0.225 71 |
| 8 | −426.1120 | 50.1989 | 9.6812 | −485.9921 | 0.445 19 |
| 9 | −397.1376 | 44.8554 | 39.7446 | −481.7376 | 0.249 55 |
| 10 | −369.3399 | 27.1241 | 70.0151 | −466.4791 | 0.031 30 |
| 11 | −337.0107 | 0.2485 | 100.4267 | −437.6859 | $6.228\times10^{-4}$ |
| 12 | −179.3595 | 10.1897 | 130.9460 | −320.4952 | $7.413\times10^{-11}$ |
| 13 | −8.4255 | 0 | 161.5394 | −169.9619 | $9.456\times10^{-20}$ |
| $\langle Z^* \rangle$ | 7.988 | | | | |
| $\langle Z^{*2} \rangle$ | 64.630 | | | | |

The model has been applied to the calculation of the probabilities $P_{Z^*}$ in aluminum, at $T=100$ eV and $\bar{\rho}=4.77\times10^{23}$ $e\,\mathrm{cm}^{-3}$ (i.e., material density is 3.06 g $\mathrm{cm}^{-3}$). The AA results are presented in Table III. Let us recall that the AA average ionization is $Z^*_{\mathrm{AA}}=7.720$. We also give the AA total energy ($\Delta E$), the entropy ($T\Delta S$) and the quantities relative to the unperturbed electron gas.

Table IV represents the occupation numbers $\bar{n}_i$ versus $Z^*$. The states $Z^*=0,1,2$ do not exist in the model because only the one-particle levels $1s$, $2s$, and $2p$ exist when the bound charge is important, and these levels can contain ten electrons at most. For smaller bound charges new levels appear which are quasi unpopulated for $Z^* \geq 11$.

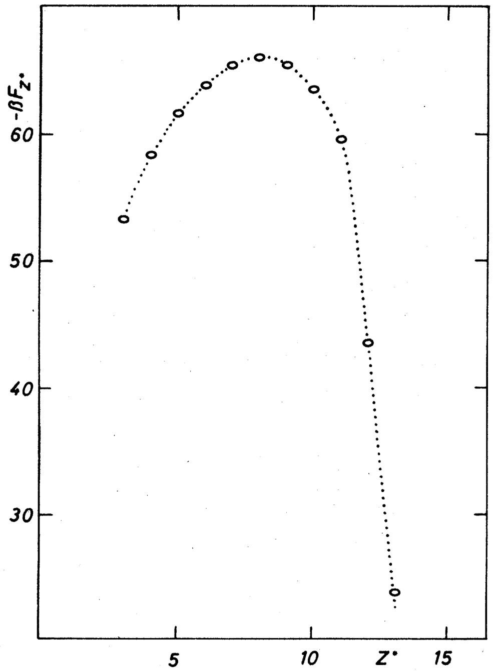

FIG. 1. Variation of the effective free-energy of the average atomic species of ionization degree $Z^*$, with respect to $Z^*$. The quantity $-\beta F_{Z^*}$ ($\beta$ is the inverse temperature) is, except for a constant shift, the logarithm of the statistical weight of the average species.

The total thermodynamic quantities, together with the statistical weights, are given in Table V and plotted in Fig. 1. The calculation of $\langle Z^* \rangle$ gives $\langle Z^* \rangle=7.988$, a value close to $Z^*_{\mathrm{AA}}=7.720$. The deviation can be explained mainly by the differences in the treatment of XC effects. In the AA model bound and free electrons are treated with the same functional $F^T_{\mathrm{XC}}[\rho]$. In the present model $F^T_{\mathrm{XC}}[\rho]$ is still used for the free electrons, but the XC effects among bound electrons are treated phenomenologically, their energy being calculated with the zero-temperature ground-state functional $E^0_{\mathrm{XC}}[\rho]$. The calculation of the free-spectrum relaxation (modification to the ε's) by means of a correction linear in $\delta U_l$ may also contribute to the difference between $\langle Z^* \rangle$ and $Z^*_{\mathrm{AA}}$.

For the average $\langle Z^{*2} \rangle$, we found a value of 64.630, from which we get $\sigma=\langle Z^{*2} \rangle-\langle Z^* \rangle^2=0.822$, a measure of the importance of fluctuations. These mainly originate in the $2s$ and $2p$ shells whose populations vary in the ratio of 1 to 2 among the three most probable species $Z^*=7$, 8, and 9. The effect of the fluctuations on the radiative properties may also be appreciated in the following way. Assuming that the dipolar matrix element $\langle 2s \mid r \mid 2p \rangle$ does not vary significantly, the $2s \rightarrow 2p$ transition probability is proportional to $B=n_{2s}(1-n_{2p})\nu_{2s,2p'}$, where $\nu$ is the transition frequency. The average $\langle B_{Z^*} \rangle$ can be computed and compared to $B_{\mathrm{AA}}$. We find $\langle B_{Z^*} \rangle / B_{\mathrm{AA}}=0.91$, a result which seems to indicate a rather small effect, but hides a large dispersion; $B_{Z^*}$ varies from 3.33 for $Z^*=7$ to 1.10 for $Z^*=9$. The model described here allows a detailed study of the fluctuations which may affect significantly the radiative properties of the plasmas.[16]

## V. CONCLUSION

We have presented a static model describing in some detail the various atomic species in a dense plasma. The XC effects have been treated in the spirit of density-functional theory. The main approximation made is to extrapolate (with no rigorous justification) the theory from the ground state to higher excited states. This treatment has the very important advantage of including all the relaxation effects related to configuration changes straightforwardly. We have shown that the variation of the total energy between two species with the same ionization degree, but different ionic configurations, is easily obtained as the difference of two modified effective one-particle energies, taking into account the free-spectrum relaxation. Generalizing this property to any variation of the occupation numbers of the bound levels, under the constraint of ionic-charge conservation, we defined the average atomic species for any given ionization. We also presented a calculation of the statistical weight of any ionization state. Among the possible applications of the model are the detailed study of radiative transitions in any nonequilibrium configuration and the investigation of fluctuations in equilibrium plasmas. A possible extension of this work could be the study of dynamical effects involved in the electronic transitions.

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## APPENDIX: EFFECT OF SCREENING ON THE FREE SPECTRUM RELAXATION

The change in bound density $\delta\rho_i = \rho_i \delta n_i$ produces a change $\delta U_l$ of the total potential acting on the electrons in the continuum. Let $\delta V_l$ be the Coulomb part of $\delta U_l$. The Poisson equation reads

$$\Delta(\delta V_l) = -4\pi(\delta\rho_i + \delta\rho_l) \,, \tag{A1}$$

where $\delta\rho_l$ is the "free-density" relaxation. In order to solve (A1), $\delta\rho_l$ is calculated in a Thomas-Fermi-like approximation, applied to the free spectrum only. We assume that the variation of $\delta\rho_l$ is well reproduced by the variation of

$$\tilde{\rho}_e = \frac{\sqrt{2}}{\pi^2}\beta^{-3/2}\int_{\sqrt{-\beta U_l}}^{\infty} \frac{\sqrt{y}}{1+e^{y-\beta(\mu-U_l)}}dy \,,$$

that is, neglecting the variation of the XC potential included in $U_l$,

$$\delta\rho_l = \delta\tilde{\rho}_l = -\frac{\sqrt{2}}{\pi^2}\beta^{-1/2}\delta V_l \int_{\sqrt{-\beta U_l}}^{\infty} \frac{\sqrt{y}}{1+e^{y-\beta(\mu-U_l)}}dy \,, \tag{A2}$$

which is written

$$\delta\rho_l = -\frac{1}{4\pi} f_l(r)\delta V_l \,. \tag{A3}$$

With the notations $Y = r\delta V_l$ and $g = -4\pi r \delta\rho_i$, one gets from Eq. (A1) the differential equation

$$\frac{d^2 Y}{dr^2} = fY + g \,. \tag{A4}$$

The boundary conditions on $Y$ are (i) $Y$ behaves like $r$ close to the origin, and (ii) $Y$ decays exponentially for large $r$. The numerical solution of Eq. (A4) presents no particular difficulty. The relation with Eq. (38) is

$$\delta n_i \int K(\mathbf{r},\mathbf{r}')\rho_i(\mathbf{r}')d\mathbf{r}' = \delta V_l(r) \,.$$

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