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Self-consistent average-atom scheme for electronic structure of hot and dense plasmas of mixture

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An average-atom model is proposed to treat the electronic structures of hot and dense plasmas of mixture. It is assumed that the electron density consists of two parts. The first one is a uniform distribution with a constant value, which is equal to the electron density at the boundaries between the atoms. The second one is the total electron density minus the first constant distribution. The volume of each kind of atom is proportional to the sum of the charges of the second electron part and of the nucleus within each atomic sphere. By this way, one can make sure that electrical neutrality is satisfied within each atomic sphere. Because the integration of the electron charge within each atom needs the size of that atom in advance, the calculation is carried out in a usual self-consistent way. The occupation numbers of electron on the orbitals of each kind of atom are determined by the Fermi-Dirac distribution with the same chemical potential for all kinds of atoms. The wave functions and the orbital energies are calculated with the Dirac-Slater equations. As examples, the electronic structures of the mixture of Au and Cd, water (H_2O), and CO_2 at a few temperatures and densities are presented.

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The average-atom model is applied to calculate the electronic structure of atoms and ions in hot and dense plasmas based on the statistical average over the details of the populations and occupations of the ions and electrons [1,2]. The average-atom model is easy to use in conjunction with a variety of treatments of electron orbitals in atoms. A widely used scheme of the average-atom calculation is to use a full self-consistent Dirac-Slater model to obtain the electron orbitals [1,3]. With such a proper treatment of the interactions between electrons and between electron and nucleus, the average-atom model can produce reasonable results for stellar opacities and equation of states.

Although the average-atom model is a significant simplified treatment to the detailed occupations of the electron orbitals and atomic energy levels, it is still quite inconvenient to apply the method to a mixture. The main problem is how to determine the size of the average-atom (or the density) of each kind of element in the mixture. One of the most widely used approach to treat mixtures is the so-called ideal gas mixing procedure [4]. In this kind of method [5,6], the electronic structure of each element is calculated separately and a mixture is obtained by simply including all the individual elements at fixed temperature and chemical potential with their abundances. The density of the resulting mixture is determined by the ideal gas law of additive volumes. Generally, if the free electron density can be calculated in the Thomas-Fermi (TF) or Thomas-Fermi-Dirac approximation, it depends only on the temperature, the chemical potential, and the potential field in which the electrons move [1]. If the difference between the potential fields of any two kinds of atom in the mixture is small at the boundary, one can assume approximately the same free electron density at the boundary when mixing the elements at fixed temperature and chemical potential. However, for a mixture at a fixed temperature and density, it is not easy to find the common chemical potential. Therefore, application of the above mixing approach usually needs interpolations on density or chemical potential [6]. Quite early, a method was proposed to treat a specific kind of mixture [7], in which a TF atom consists of electrons and light nuclei in the field of a heavy nucleus. More recently, it was proposed to determine the size of the average-atom by means of solving a set of TF equations [8]. There also are other ways to treat mixtures beyond the statistical model, including the widely used Saha-Boltzmann equation at low densities [9] and the so-called grand cannonical many-body activity expansion in the OPAL approach [10]. The details of these methods are beyond the present study. Within the average-atom scheme, here we present a much simple way of determining the size of atoms and ions in the mixture. As examples, the electronic structures of the mixture of Au and Cd, water (H_2O), and CO_2 at a few thermodynamic conditions are presented.

The influence of the environment on the atom is assumed to have spherical symmetry in average. The movement of an electron under the interactions of nucleus and other electrons is approximated by a central field, which is determined with the standard self-consistent calculation. In the central field, the radial part of the Dirac equation has the form

$$\frac{dP_{n\kappa}(r)}{dr}+\frac{\kappa}{r}P_{n\kappa}(r)=\frac{1}{c}[\epsilon_{n\kappa}+c^2-V(r)]Q_{n\kappa}(r),$$

$$\frac{dQ_{n\kappa}(r)}{dr}-\frac{\kappa}{r}Q_{n\kappa}(r)=-\frac{1}{c}[\epsilon_{n\kappa}-c^2-V(r)]P_{n\kappa}(r), \tag{1}$$

where $P(r)$ and $Q(r)$ are, respectively, the large and small components of the wave function, c is the light speed, and $V(r)$ is the self-consistent potential, which consists of three parts

$$V_{scf}(r)=V_s(r)+V_{ex}(r)+V_{corr}(r). \tag{2}$$

$V_s(r)$, $V_{ex}(r)$, and $V_{corr}(r)$ are, respectively, the so-called static, exchange, and correlation potentials. $V_s(r)$ is calculated from the charge distributions in the atom, while $V_{ex}(r)$, and $V_{corr}(r)$ take the approximate temperature-dependent

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forms of Dharma-Wardana and Taylor [11]. For bound states, we have the boundary conditions satisfied by the radial wave functions

$$P_{n\kappa}(r)\xrightarrow{r\to 0} ar^{l+1},$$
$$P_{n\kappa}(R_b)=0, \tag{3}$$

where R_b is the radius of the atom. The electron distribution is calculated separately for the bound and free electron parts. The bound electron density is obtained according to

$$\rho_b(r)=\frac{1}{4\pi r^2}\sum_j b_j[P_j^2(r)+Q_j^2(r)], \tag{4}$$

where b_j is the occupation number of the state j. In the average-atom model, the occupation number b_j is determined by the Fermi-Dirac distribution

$$b_j=\frac{2|\kappa_j|}{\exp[(\epsilon_j-\mu)/T]+1}. \tag{5}$$

The free electrons are considered much more simply with an assumption of the TF treatment, and the local free electron density is calculated with a Fermi-Dirac distribution of the local free electrons in the plane wave momentum k space, which can be written as

$$\rho_f(r)=\frac{1}{\pi^2}\int_{k_0(r)}^{\infty}\frac{k^2dk}{e^{[\sqrt{k^2c^2+c^4}-c^2-V(r)-\mu]/T}+1}, \tag{6}$$

where $k_0(r)=[2V(r)c^2+V(r)^2]^{1/2}/c$ and μ is the so-called chemical potential. The total electron density is the sum of $\rho_b(r)$ and $\rho_f(r)$,

$$\rho_i(r)=\rho_b^i(r)+\rho_f^i(r). \tag{7}$$

The chemical potential μ is determined so that the electrical neutrality is satisfied

$$\sum_i n_i\int_0^{R_b^i}4\pi r^2\rho_i(r)dr=\sum_i n_iZ_i, \tag{8}$$

where n_i is the number of the ith kind of atom, and Z_i the nuclear charge. The summation runs over all kinds of atom. In hot and dense plasmas, the size effects on the electronic structures of atoms and ions are considerable. For pure matter the average atomic size is taken to be

$$R_b=\left(\frac{3\Omega_0}{4\pi}\right)^{1/3}, \tag{9}$$

where Ω_0 is the average atomic volume. For mixtures, there is not a simple analytical way to determine the atomic size of each kind of atom strictly. A few requirements should be satisfied, i.e., all kinds of atom must have the same temperature, the same electronic pressure, and the same chemical potential. If we choose the potential at the boundary as the common reference point for all kinds of atom, we will have the same free electron density at the boundary for all atoms from Eq. (6). From the TF theory [12], the electronic pressure is determined by the density of the free electrons, therefore we will have the same electronic pressure at the boundary. With these considerations, we separate the electron density into two parts. The first part is a uniform distribution over the whole space with a value of the free electron density at the boundary between the atoms. The second part, which is the total electron density minus the first constant distribution, is used to determine the size of the atom. The general criterion for calculating the atomic size is that the volume of each atom kind is proportional to the net positive charge, which is the sum of the second part of the electron charge and the nuclear charge within each atomic sphere. Because the integration of the second part of the electron density within an atomic sphere needs the atomic size in advance, the calculation is carried out in a self-consistent way. By this way, we ensure the electrical neutrality of each atom species naturally. It will be shown that for a quite large range of temperature and density the electrical neutrality is satisfied accurately for all kinds of atom.

For a mixture with the elements of $A_1, A_2, A_3, \ldots,$ where A_i represents the atomic weight, if the mass percentage of the elements are respectively $W_1, W_2, W_3, \ldots,$ the relative numbers $n_1, n_2, n_2, \ldots$ of the atoms for the different elements should be given by

$$n_i=(W_i/A_i)\Big/\sum_j (W_j/A_j). \tag{10}$$

According to the relative numbers given above, a mixture molecule, consisting of all elements in the mixture, has the weight of

$$A=\sum_j n_jA_j. \tag{11}$$

With a density D of the mixture, the volume occupied by one mixture molecule is

$$V_0=11.22\frac{A}{D}. \tag{12}$$

The constant, 11.22, is coming from the use of atomic unit for V_0, g/cm^3 for D, and a unit of $A^{carbon}=12.011$ for A. According to the separation of the electron density mentioned above, the second part of the electron density is

$$\rho_i^{2nd}(r)=\rho_i(r)-\rho_f^i(R_b^i), \tag{13}$$

where R_b^i is the radius of the ith atom. The net charge, which is the sum of the second electron part and the nucleus within an atom, is given by

$$Z_i^{net}=Z_i-\int_0^{R_b^i}4\pi r^2\rho_i^{2nd}(r)dr. \tag{14}$$

The volume of one atom of the ith kind element is

$$V_i=V_0\frac{Z_i^{net}}{\sum_j n_jZ_j^{net}} \tag{15}$$

TABLE I. The calculated atomic radius R, total (Z_t^{elec}), and bound (Z_b^{elec}) electron charge in each atomic sphere, and the chemical potential μ for the Au-Gd mixture with the mass ratios of Au (70%) and Gd (30%) and density of 100 g/cm^3.

T (eV)		R	Z_t^{elec}	Z_b^{elec}	μ
100	Au	1.70230	79.0000	57.6578	0.499
	Gd	1.69282	64.0000	43.1651	0.499
	Au [a]	1.710			
	Gd [a]	1.667			
	Au [b]	1.74087	79.0000	59.2368	−0.155
	Gd [b]	1.61497	64.0000	43.1077	1.164
400	Au	1.71939	79.0000	46.4735	−24.409
	Gd	1.65964	64.0000	35.0587	−24.409
	Au [a]	1.720			
	Gd [a]	1.660			
	Au [b]	1.74087	79.0000	46.3866	−24.928
	Gd [b]	1.61497	64.0000	35.2352	−23.265
800	Au	1.71628	79.0000	37.7024	−71.828
	Gd	1.66583	64.0000	26.4722	−71.828
	Au [a]	1.720			
	Gd [a]	1.657			
	Au [b]	1.74087	79.0000	37.6411	−73.041
	Gd [b]	1.61497	64.0000	26.8143	−69.352
1600	Au	1.72663	79.0000	24.6219	−188.743
	Gd	1.64497	64.0000	17.3126	−188.743
	Au [a]	1.720			
	Gd [a]	1.650			
	Au [b]	1.74087	79.0000	24.7474	−190.315
	Gd [b]	1.61497	64.0000	17.5435	−185.803
3000	Au	1.72634	79.0000	14.6997	−437.644
	Gd	1.64556	64.0000	8.5978	−437.644
	Au [a]	1.730			
	Gd [a]	1.640			
	Au [b]	1.74087	79.0000	14.5884	−440.201
	Gd [b]	1.61497	64.0000	8.7192	−431.724

[a] From Meng *et al.* [8].

[b] Pure matter.

with a radius of

$$R_b^i = \left[\frac{3V_i}{4\pi}\right]^{1/3}. \tag{16}$$

The average ionization degree and the chemical potential μ are solved self-consistently along with the atomic self-consistent potentials and the one-electron orbital energies of every kind of element by a self-consistent-field (SCF) calculation. For a mixture, the chemical potential μ at each step of the SCF calculation is determined by satisfying that

$$\begin{cases} \rho_i(r) = \rho_b^i(r) + \rho_f^i(r), \\ \sum_i n_i \int_0^{R_b^i} 4\pi r^2 \rho_i(r)\,dr = \sum_i n_i Z_i\,. \end{cases} \tag{17}$$

TABLE II. As in Table I, but for water (H_2O) with density of 3 g/cm^3.

T (eV)		R	Z_t^{elec}	Z_b^{elec}	μ
10	H	1.43460	1.0000	0.0000	0.632
	O	2.16734	8.0000	3.9015	0.632
50	H	1.41058	1.0000	0.0000	−2.388
	O	2.18784	8.0000	3.8945	−2.388
100	H	1.33259	1.0000	0.0000	−8.050
	O	2.24751	8.0000	2.8781	−8.050
500	H	1.18971	1.0000	0.0000	−78.428
	O	2.33420	8.0000	0.2416	−78.428
1000	H	1.17904	1.0000	0.0000	−194.059
	O	2.33968	8.0000	0.0649	−194.059

In TF theory, the electron pressure on the atomic boundary depends only on the free electron density at the atomic surface. From Eq. (6), one can find that because we set the potential at the boundary as the common reference point for all atoms, i.e., the same value [for an example, at the boundary $V(r)$ is set to be zero for all atoms], with the same chemical potential the free electron density at the boundary is the same for all kinds of atom. Therefore, the equality of the electron pressure at the atomic boundary is satisfied naturally by having the same chemical potential.

As examples, we present the calculated results for a mixture of Au and Gd with a mass ratio of Au (70%) and Gd (30%) and a density of 100 g/cm^3, water (H_2O) with a density of 3 g/cm^3, and CO_2 with a density of 0.1 g/cm^3. In Table I, we give the atomic radius, the total and bound electron charges, and the chemical potentials of the mixture of Au and Gd at a few different temperatures along with the calculated results of Meng *et al.* [8] by using a different method for the determination of the atomic size. From Table I, one can find that for each atom the electrical neutrality has been satisfied very accurately. The chemical potential of the mixture always falls between the chemical potentials of the pure Au and Gd at the same temperature and density. The present atomic radius is slightly different from that of Meng *et al.* [8] obtained by applying the TF theory. The variation of the atomic radius with the temperature shows also differences from the corresponding TF result. The present result shows that the atomic radius does not monotonously increase or decrease with the temperature, but slightly oscillates to reflect the shell structure effects on the ionization of the bound electrons. The number of the bound electrons of the atoms in the mixture has small difference from that of the atoms in the pure matter. However, this small change of the bound electron with respect to the pure matter is also temperature dependent and also oscillates slightly with the temperature. This oscillation comes also from the shell structure effects and is opposite for these two atoms. Because the binding energy of a orbital is generally different for different kinds of atom, the ionization of the electrons at the orbital must occurs at different temperatures for different atoms. The competition between the ionization from different atoms results in the oscillations mentioned above. The TF result [8], however, does not show the shell structure effects.

TABLE III. As in Table I, but for CO_2 with density of 0.1 g/cm^3.

T (eV)		R	Z_t^{elec}	Z_b^{elec}	μ
5	C	7.48830	6.0000	4.9031	−0.539
	O	7.23968	8.0000	7.0218	−0.539
10	C	7.36656	6.0000	3.9456	−1.200
	O	7.30319	8.0000	6.0037	−1.200
50	C	6.83224	6.0000	2.0838	−8.716
	O	7.54750	8.0000	2.6655	−8.716
100	C	7.12042	6.0000	0.6162	−20.477
	O	7.42231	8.0000	1.8808	−20.477
500	C	6.85701	6.0000	0.0145	−142.201
	O	7.53730	8.0000	0.0325	−142.201

In Table II, we present an example of a large size difference between the two kinds of atom in a hot and dense plasma, where the result for the plasma of water with a density of 3 g/cm^3 is provided at a few temperatures. At this density, the hydrogen atom has been completely ionized due to the pressure. Therefore, there is no longer any ionization competition between hydrogen and oxygen. The atomic radius changes monotonously with the temperature, when more and more electrons are ionized continuously from oxygen.

In Table III, results for the plasma of CO_2 with density of 0.1 g/cm^3 are presented. As in the previous tables, the results are provided for only a few temperatures in Table III. However, much more details of the variations of the atomic radii of carbon and oxygen are plotted in Fig. 1 at much more temperature points. From Fig. 1, the competition between the ionization of the two kinds of atom can be seen very clearly. One can find that there are two main structures starting from 6 and 50 eV, respectively. The first increase of the carbon radius from 6 eV is due to the ionization of $2s$ and $2p$ orbitals, and arrives at the maximum value at 7 eV. After 7 eV, as the increased ionization of the 2s and 2p orbitals of oxygen, which occurs later due to the more bounding energies compared with those of carbon, the radius of carbon goes down and the radius of oxygen goes up. For the same reason, the carbon radius increase again at 50 eV due to the ionization of the $1s$ orbital.

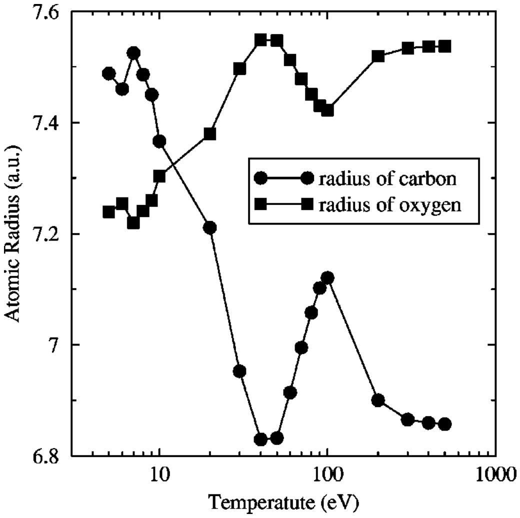

FIG. 1. The competition between the atomic radii of carbon and oxygen in the plasma of CO_2 with the temperature.

In conclusion, a simple self-consistent field average atom approach is proposed for the calculation of electronic structure of hot and dense plasmas of mixture. The essential criterion of the approach is that by using the SCF calculation the size of each kind of atom in the plasma is determined such that the electrical neutrality within each atomic sphere is satisfied, that electron density at the boundaries between the atoms is a constant and the electronic pressure at the boundaries has the same value for all atom species, and that the chemical potential has the same value for all atom species. Results for a few samples show that the approach works smoothly and predicts some interesting features in the variations of the radii or ionization with the temperature that was not shown by a TF model calculation. These features are attributed to the so-called shell structure effects.

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