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Quantum mechanical model for the study of pressure ionization in the superconfiguration approach

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Abstract

The knowledge of plasma equation of state and photoabsorption requires suitable and realistic models for the description of ions. The number of relevant electronic configurations of ions in hot dense plasmas can be immense (increasing with atomic number Z). In such cases, calculations relying on the superconfiguration approximation appear to be among the best statistical approaches to photoabsorption in plasmas. The superconfiguration approximation enables one to perform rapid calculation of averages over all possible configurations representing excited states of bound electrons. We present a thermodynamically consistent model involving detailed screened ions (described by superconfigurations) in plasmas. The density effects are introduced via the ion-sphere model. In the usual approaches, bound electrons are treated quantum mechanically while free electrons are described within the framework of semi-classical Thomas–Fermi theory. Such a hybrid treatment can lead to discontinuities in the thermodynamic quantities when pressure ionization occurs. We propose a model in which all electrons (bound and free) are treated quantum mechanically. Furthermore, resonances are carefully taken into account in the self-consistent calculation of the electronic structure of each superconfiguration. The model provides the contribution of electrons to the main thermodynamic quantities, together with a treatment of pressure ionization, and gives a better insight into the electronic properties of hot dense plasmas.

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1. Introduction

Electronic properties of hot dense plasmas are important for the study of equation of state and radiative transfer. They play a major role in inertial confinement fusion, in astrophysics

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(for the understanding of stellar structure and evolution), and in the simulation of laser-driven experiments (for spectroscopic diagnostics for instance). It is worth mentioning that future big lasers will allow experiments at much higher densities than in present-day experiments, which will enable one to study density effects in a more accurate way. Moreover, electronic properties of hot dense plasmas are of great interest in warm dense matter. In order to model the various atomic processes, we need to describe plasma ions in their ground and excited states. The superconfiguration (SC) method [1] appears to be a powerful statistical approach for the treatment of real ionic species (i.e. associated with an integer number of bound electrons). Such a method generally leads to a good agreement between theory and transmission experiments involving plasmas of medium Z elements, due to the possible inclusion of a large number of electronic configurations and states. The present work constitutes an attempt to improve the SC calculations in order to take plasma density effects into account in a more detailed way. The main objectives are the extension of our previous approaches [2–4] to high density regimes (of the order of solid density and more), and the simultaneous calculation of equation of state and photoabsorption (from the same formalism and therefore from the same code). Such a model is now tractable numerically, since the SC approach allows one to evaluate efficiently averages over excited states. However, in the best formulation, which would be variational, all the electrons should be treated quantum mechanically and the confinement of ionic species in a spherical cell should be abandoned. In this work, we propose a quantum treatment of all electrons in the self-consistent-field (SCF) calculation of the SCs, but the spherical cell is still used. In that sense the present model is different from the one proposed by Liberman [5]. We consider strongly coupled plasmas, i.e. plasmas for which the ionic Coulomb interaction energy is greater than the thermal kinetic energy. This situation corresponds, in atomic units, to $\Gamma = \frac{Z_{\rm eff}^2}{r_{\rm ws} k_B T} > 1$, T being the temperature, $r_{\rm ws}$ the Wigner–Seitz radius (radius of the average ionic spherical cell) and $Z_{\rm eff}$ the effective charge of the plasma.

2. Theoretical features of the model

2.1. Superconfiguration description of ionic species

The entire plasma is represented by an imaginary atom, characterized by the Wigner–Seitz sphere, containing bound and free electrons. The well-known average-atom model enables one to calculate the average electronic configuration of the plasma. Such a model gives fractional populations of the orbitals and the average ionization state of the plasma. On the basis of these results, the relevant 'real' configurations of the plasma can be obtained. Unfortunately, the number of electronic configurations can be tremendous, especially when the atomic number Z increases. Therefore, it is suitable to group together ordinary subshells (orbitals) whose average-atom energies are close to each other. Such an ensemble is called a supershell. A superconfiguration [1] consists of supershells populated in all possible ways, consistently with the Pauli exclusion principle. For instance, $(1s2s2p)^3(3s)^2(3p3d)^2(4s4p4d4f)^3$ is a superconfiguration made of four supershells associated respectively with 3, 2, 2 and 3 electrons. A configuration is a particular case of SC in which each supershell contains only one shell. Moreover, a reasonable number of SCs (typically a few hundred for medium Z elements) can contain a tremendous number of ordinary configurations. Therefore, the precision for spectral photoabsorption can be improved by refinement of the SCs (i.e. subdivision of the supershells), and it is possible to calculate macroscopic thermodynamic variables (pressure, internal energy, Helmholtz free energy), by averaging over a reduced number of SCs made of large supershells [6]. Assuming local thermodynamic equilibrium for all the configurations

described by a SC Ξ enables one to write the probability of a configuration c containing Q electrons using Boltzmann's law:

$$P_c^{(\Xi)} = \frac{G_c\, \mathrm{e}^{-(E_c-\mu Q)/T}}{U_Q^{(\Xi)}}, \tag{1}$$

where G_c and E_c are the degeneracy and energy of the Q-electron configuration and $U_Q^{(\Xi)}$ is the partition function of the SC. The value of a thermodynamic quantity A_Ξ for SC Ξ is obtained by averaging this quantity A_c over all the configurations of the SC:

$$A_\Xi = \sum_{c\in\Xi} A_c P_c^{(\Xi)}. \tag{2}$$

Furthermore, it is important to mention that the main feature of the SC approximation consists in a linearization of the energy of a configuration with respect to orbital populations $\{q_s\}$:

$$E_c \approx E_c^{(0)} + \overline{\Delta E} \qquad \text{with} \quad E_c^{(0)} = \sum_{s\in c} q_s \epsilon_s \quad \text{and} \quad \overline{\Delta E} = \left\langle E_c - E_c^{(0)} \right\rangle_\Xi. \tag{3}$$

Expressions (3) enable one to 'factorize' the partition function of a SC and therefore to evaluate it using recurrence relations [1, 2, 6]. The calculation of the electronic structure of a SC is similar to the traditional average-atom calculation, except that each SC has an integer number of bound electrons. The equations required for the calculation of SCs are obtained from the stationarity of the ion-cell free energy with imposed integer populations for the defined supershells. The exchange-correlation effects are taken into account in the local density approximation (LDA) using the formulae of Iyetomi and Ichimaru [7].

2.2. *Quantum mechanical description of the electrons*

In the previous approaches [2–4], bound electrons were treated quantum mechanically, and free electrons were described within the semi-classical Thomas–Fermi approximation [8]. In the present work, all electrons are treated quantum mechanically. The electron density reads therefore:

$$n(r) = \sum_{n,l} f(\epsilon_{nl}, \mu) \frac{2(2l+1)}{4\pi} \frac{y_{nl}^2(r)}{r^2} + \int_0^\infty \mathrm{d}\epsilon\, f(\epsilon, \mu) \sum_{l=0}^{\infty} \frac{2(2l+1)}{4\pi} \frac{y_{\epsilon l}^2(r)}{r^2}, \tag{4}$$

bound- and free-electron wavefunctions being normalized in the whole space. f is the Fermi–Dirac factor, μ is the free-electron chemical potential, y_{nl} is the radial part of the bound-electron wavefunction multiplied by r and $y_{\epsilon l}$ the radial part of the free-electron wavefunction multiplied by r.

2.3. *Calculation of average thermodynamic quantities*

The value of thermodynamic quantity A is obtained by averaging A_Ξ over all the SCs:

$$A = \sum_\Xi W_\Xi A_\Xi \qquad \text{with} \quad W_\Xi \propto \mathrm{e}^{-\frac{F_\Xi}{T}}, \tag{5}$$

where F_Ξ is the free energy of SC Ξ. The quantum pressure of SC Ξ is calculated using the

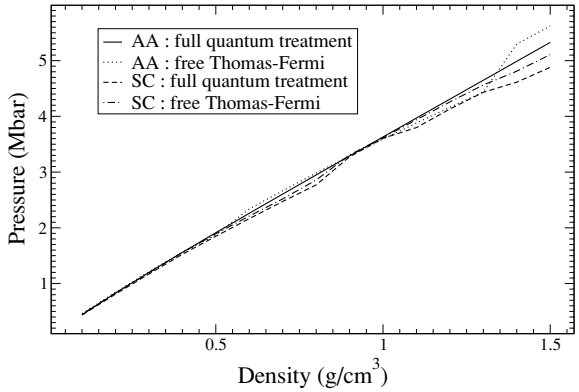

Figure 1. Pressure versus density for an aluminium plasma at $T = 30$ g cm^{-3}.

stress-tensor formula:

$$P_{\Xi} = \sum_{n,l} \frac{(2l+1)\, f(\epsilon_{nl}, \mu_{\Xi})}{4\pi r_{\Xi}^2 \left(1 + \frac{\epsilon_{nl}}{2E_0}\right)} \left[\left(\left. \frac{\mathrm{d}y_{nl}}{\mathrm{d}r} \right|_{r_{\Xi}} \right)^2 + \left(2\epsilon_{nl} \left(1 + \frac{\epsilon_{nl}}{2E_0} \right) - \frac{l^2 + l + 1}{r_{\Xi}^2} \right) y_{nl}^2(r_{\Xi}) \right]$$
$$+ \int_0^{\infty} \frac{(2l+1)\, f(\epsilon, \mu_{\Xi})}{4\pi r_{\Xi}^2 \left(1 + \frac{\epsilon}{2E_0}\right)} \left[\left(\left. \frac{\mathrm{d}y_{\epsilon l}}{\mathrm{d}r} \right|_{r_{\Xi}} \right)^2 + \left(2\epsilon \left(1 + \frac{\epsilon}{2E_0} \right) - \frac{l^2 + l + 1}{r_{\Xi}^2} \right) y_{\epsilon l}^2(r_{\Xi}) \right] + P_{xc}, \tag{6}$$

where E_0 is the rest mass of the electron, r_{Ξ} is the Wigner–Seitz radius of SC Ξ and P_{xc} is the exchange-correlation pressure. It is important to mention that in a more elaborate model, pressure should be evaluated as a derivative of the Helmholtz free energy with respect to volume. Figure 1 shows that the discontinuity of the average-atom pressure in the hybrid model does not exist in the full quantum model. However, it is also important to note that the superconfiguration pressure, even in the hybrid model, is smoother than the average-atom pressure in the hybrid model. This can be explained by the fact that pressure ionization occurs only in one SC and can be smeared out by the presence of other SCs.

3. Shape resonances

3.1. Definition and consequences

When the matter density increases, some bound states can disappear into the continuum. Such a phenomenon, named pressure ionization [9, 10], leads, in the hybrid description of electrons, to discontinuities in the thermodynamic functions. For instance, the main discontinuity in figure 1 around 1.3 g cm^{-3} is due to pressure ionization of 3p orbital. Such discontinuities are nonphysical [11], since normally there should be a smooth change of a discrete bound state into a narrow shape resonance (peak in the density of free states). A shape resonance close to the continuum boundary is narrow, especially for large values of orbital momentum l. Higher energy resonances are broader and become indistinguishable from the continuum. Shape resonances may affect calculation of many plasma properties, such as equation of state, x-ray opacities, electrical conductivity and bremsstrahlung emission. Inclusion of shape resonances may give a better insight into the meaning of the ionization state of the plasma.

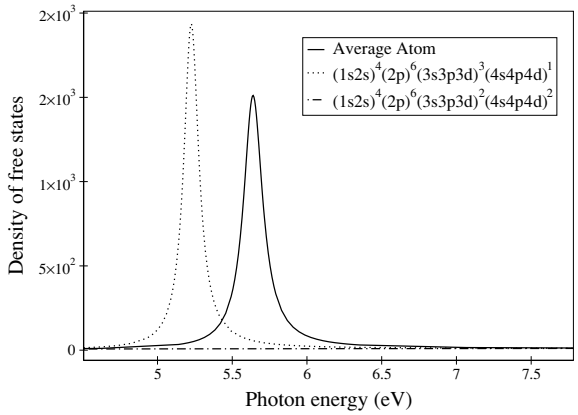

Figure 2. Density of free states for an iron plasma at $T = 120$ eV and $\rho = 3.6$ g cm^{-3} for two different SCs, compared to the one resulting from an average-atom calculation.

3.2. Mathematical characterization

The free-electron wavefunctions can be expressed as

$$y_{\epsilon l}(r) = \sqrt{\frac{2\sqrt{2\epsilon}}{\pi}} r[\cos(\delta_l(\epsilon))\, j_l(\sqrt{2\epsilon}r) - \sin(\delta_l(\epsilon)) n_l(\sqrt{2\epsilon}r)], \tag{7}$$

where δ_l is the well-known phase shift. j_l and n_l are Bessel functions. The search for shape resonances has been implemented so that one cannot miss any of them. The derivative of the phase shift with respect to energy $\frac{\mathrm{d}\delta_l}{\mathrm{d}\epsilon}(\epsilon)$ is calculated numerically, and when it becomes larger than a fixed threshold value, the corresponding energy interval is refined to a smaller mesh using a larger number of points, and so on. In that way, shape resonances are taken into account through an iterative process of refinement of the energy grid. The density of free states is given by

$$g(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}[\mathrm{Tr}(\hat{G})], \qquad \text{with} \quad \hat{G} = \hat{G}_0 + \hat{G}_0 \hat{T} \hat{G}_0 \quad \text{and} \quad \hat{G}_0 = \frac{1}{\epsilon - \hat{H}_0}, \tag{8}$$

where $\hat{H}_0 = -\frac{1}{2}\vec{\nabla}^2$. Using the expression of the $\hat{T}$-scattering matrix $T_l \propto \frac{\mathrm{e}^{\mathrm{i}\delta_l(\epsilon)}}{\sqrt{2\epsilon}} \sin[\delta_l(\epsilon)]$, one gets

$$g(\epsilon) = \frac{\sqrt{2}}{\pi^2} V \sqrt{\epsilon} + \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \frac{\mathrm{d}\delta_l}{\mathrm{d}\epsilon}(\epsilon), \tag{9}$$

V being the ion-sphere volume. Figures 2 and 3 represent respectively the density of free states and the phase shift for $l = 3$, for two superconfigurations and for an average-atom calculation in the case of an iron plasma at $T = 120$ eV and $\rho = 3.6$ g cm^{-3}. The jump of π in the phase shift $\delta_3(\epsilon)$ indicates that a f orbital has been pressure ionized. Taking the shape resonances into account during the iterations, the sudden increase of the free-electron number (figure 4) due to pressure ionization of the 3p bound level of potassium at 3 eV is absorbed by an increase of continuum density of states. The abrupt change of the bound-electron pressure is compensated by an abrupt change of the free-electron pressure, leading to a continuous total pressure.

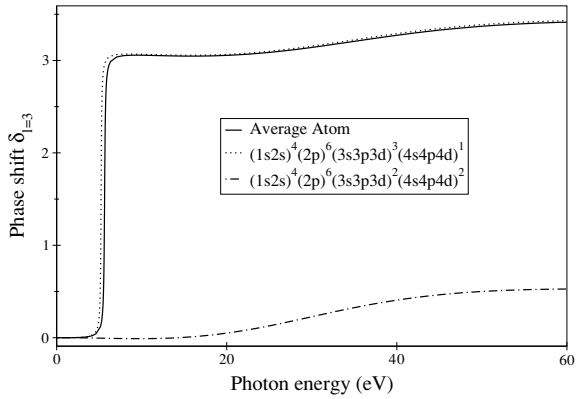

Figure 3. Phase shift δ_3 for an iron plasma at $T = 120$ eV and $\rho = 3.6$ g cm^{-3} for two different SCs, compared to the one resulting from an average-atom calculation.

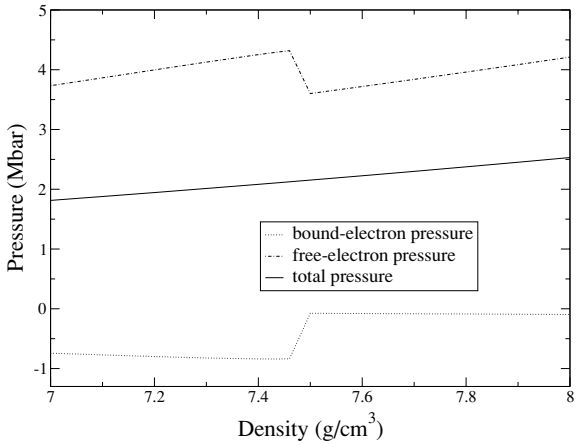

Figure 4. Bound-electron pressure, free-electron pressure and total pressure for a potassium (K) plasma at $T = 3$ eV and different values of density.

4. Comparisons with neutral-pseudo-atom (NPA) model

The NPA model [12–14] relies on a density-functional theory of the ion distribution coupled to a homogeneous electron fluid. Kohn–Sham–Mermin equations are solved for a 'pseudo-atom' embedded in a jellium of negative charges with a cavity. The ionic fluid is described by classical theory of liquids (classical DFT for ions). Pressure is then obtained from the virial theorem. Figure 5 shows that the results obtained from our model are very close to the results from the NPA model.

5. Impact on photoabsorption spectra

Figure 6 illustrates the fact that the strong enhancement (corresponding to pressure ionization of the 4f orbital) in the spectrum of iron at $T = 120$ eV and $\rho = 3.6$ g cm^{-3} obtained in the hybrid model does not exist in the new full quantum model. This is due to the better treatment of pressure ionization resulting from our new approach.

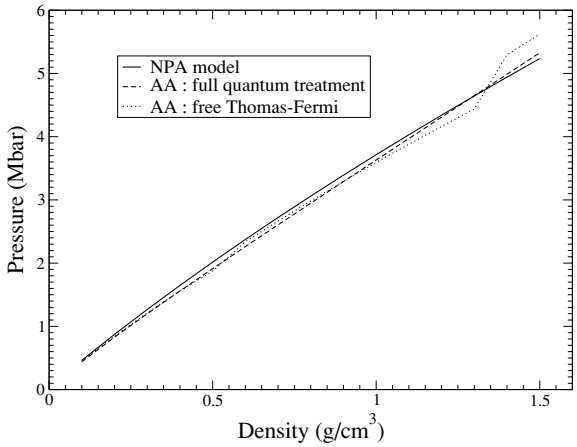

Figure 5. Comparison with NPA model for an aluminium plasma at $T = 30$ eV.

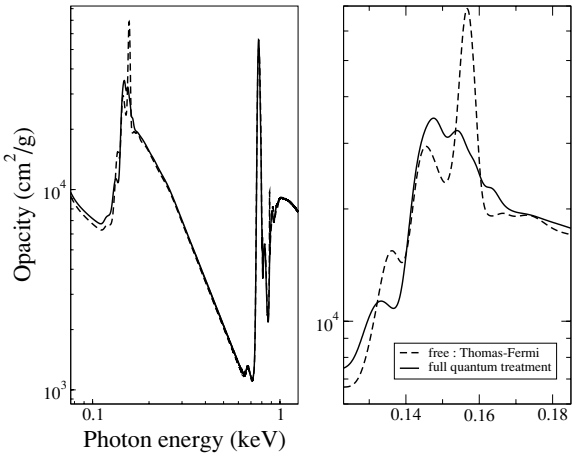

Figure 6. Photoabsorption spectrum for an iron plasma at $T = 120$ eV and $\rho = 3.6$ g cm^{-3}.

6. Conclusion and perspectives

The model enables one to perform simultaneous calculations of photoabsorption and equation of state, in the superconfiguration approximation. At present, the ions are still confined in the spherical cell, but all the electrons are described quantum mechanically. The calculation of shape resonances and the statistics of the superconfigurations provide a better treatment of pressure ionization. The corresponding numerical code enables one to calculate the thermodynamic functions over a wide range of densities and temperatures, and, thanks to the superconfiguration averaging process, for mid-Z elements. In the future, it would be interesting to calculate the ionic structure factor and therefore to evaluate electrical static resistivities, using the extended Ziman formula.

Acknowledgments

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References

[1] Bar-Shalom A, Oreg J, Goldstein W H, Shvarts D and Zigler A 1989 *Phys. Rev.* A **40** 3183
[2] Blenski T, Grimaldi A and Perrot F 1997 *Phys. Rev.* E **55** R4889
[3] Blenski T, Grimaldi A and Perrot F 2000 *J. Quant. Spectrosc. Radiat. Transfer* **65** 91
[4] Pain J C and Blenski T 2003 *J. Quant. Spectrosc. Radiat. Transfer* **81** 355
[5] Liberman D A 1979 *Phys. Rev.* B **20** 4981
[6] Gilleron F and Pain J C 2004 *Phys. Rev.* E **69** 056117
[7] Iyetomi H and Ichimaru S 1986 *Phys. Rev.* A **34** 433
[8] Feynman R P, Metropolis N and Teller E 1949 *Phys. Rev.* **75** 1561
[9] More R M 1985 *Adv. At. Mol. Phys.* **21** 305
[10] Blenski T and Ishikawa K 1995 *Phys. Rev.* E **51** 4869
[11] Kohn W and Majundar C 1965 *Phys. Rev.* **138** A1617
[12] Dagens L 1973 *J. Phys. (Paris)* **34** 879
[13] Perrot F and Dharma-Wardana M W C 1995 *Phys. Rev.* E **52** 5352
[14] Perrot F, Dharma-Wardana M W C and Benage J 2002 *Phys. Rev.* E **65** 046414