

CALCULATION OF IONIZATION EQUILIBRIUM FOR DENSE PLASMAS

MASSACRIER GERARD

DARC – UPR176, Observatoire de Paris–Meudon, 92195 Meudon Cedex, France

ABSTRACT We propose a new approach to calculate the populations of the different ionic states and ionization stages that may exist in a plasma in thermodynamic equilibrium. A self-consistent scheme is solved for each ionization stage, which couples the local density of free electrons and the atomic structure of this stage.

INTRODUCTION

The calculation of equilibrium populations of the various species in a plasma is a necessary step to study opacities, radiation transfer or thermodynamic quantities. When the density is so high that the mean ionic volume is of the order of a few Bohr radii, Saha equation breaks down and models must be refined to take into account density effects like pressure ionization. Current models include free energy minimization (Graboske *et al.* 1969, Däppen 1980, Däppen *et al.* 1987) and average–atom approaches (Rozsnyai 1975, Feng *et al.* 1981, Davis and Blaha 1982). The first one leaves the bound states essentially unperturbed. Though very useful for a quick analysis of the equilibrium of such complicated systems, the average–atom approach leads to a fictitious ion with a non-integer number of bound electrons and to a one-electron energy spectra not relevant to the actual one. To proceed up to the individual populations of the different ionization stages is further hazardous. The model presented in this paper treats separately each degree of ionization. It has the advantage to lead at the same time to the equilibrium populations and to spectroscopic energies.

A MODEL PARTICULARIZING THE IONIZATION STAGES

The equilibrium of a pure plasma of a given element with nuclear charge Z is completely defined by two thermodynamic parameters, e.g. its temperature T and its total electron number density N_{elec} . We use instead of N_{elec} its associated intensive parameter μ , the electronic chemical potential.

The free electron number density N_{free} is a bad thermodynamic parameter for dense plasmas. It is indeed impossible to assign to all the electrons in these plasmas a definite bound or free character, because of those electrons delocalized on a few ionic sites (the hopping electrons, Dharma-Wardana and Perrot 1992). However, looking at a given nucleus, one might find bound ionic structures with N electrons strongly localized around this nucleus. These N -electronic states are similar to those of the isolated ion. The Coulombic interaction between them is very strong and

must be solved through a Hamiltonian. On the contrary, their interaction with the other free (delocalized) electrons is weaker and might be treated through an averaged spherically symmetric potential (energy) V_{free}^N . We hence obtain for each ionization stage with N bound electrons the energies $E_{N\alpha}$ and the antisymmetrical N -electronic wavefunctions $\Psi_{N\alpha}$ by solving (in a.u. here and after):

$$H_N \Psi_{N\alpha} = \left[\sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + V_{\text{free}}^N(r_i) \right) + \sum_{i<j}^N \frac{1}{r_{ij}} \right] \Psi_{N\alpha} = E_{N\alpha} \Psi_{N\alpha} \quad (1)$$

From the states $\Psi_{N\alpha}$, we get the mean bound electron density n_{bound}^N for this ionization stage by:

$$n_{\text{bound}}^N(\mathbf{r}) = \sum_{\alpha} \frac{e^{-E_{N\alpha}/T}}{Z_N} \sum_{i=1}^N \int |\Psi_{N\alpha}(\mathbf{r}_1 \dots \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1} \dots \mathbf{r}_N)|^2 d\mathbf{R}_i \quad (2)$$

where $d\mathbf{R}_i = d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N$ and $Z_N = \sum_{\alpha} e^{-E_{N\alpha}/T}$ is the partition function. Boltzmann statistics has to be used because we consider a system with a given (small) integer number N of particles. The mean potential due to these bound electrons V_{bound}^N is obtained from Poisson equation: $\Delta V_{\text{bound}}^N = -4\pi n_{\text{bound}}^N$.

V_{free}^N is in the same way connected to the mean free electron density n_{free}^N around the ion by the Poisson equation: $\Delta V_{\text{free}}^N = -4\pi n_{\text{free}}^N$. A free electron is in this region in the potential due to the nucleus, to the bound electrons and to the other free electrons V_{free}^N . We should normally use different bound potentials, one for each bound state $\Psi_{N\alpha}$. We instead use their thermal average V_{bound}^N due to computational constraint. We calculate the density of free electrons through:

$$\left(-\frac{\nabla^2}{2} - \frac{Z}{r} + V_{\text{bound}}^N + V_{\text{free}}^N \right) \psi_{Ni} = \epsilon_{Ni} \psi_{Ni} \quad (3)$$

$$n_{\text{free}}^N(\mathbf{r}) = \int_0^{\infty} d\epsilon \frac{1}{1 + e^{-\beta(\epsilon - \mu)}} \sum_i \delta(\epsilon - \epsilon_{Ni}) |\psi_{Ni}(\mathbf{r})|^2 \quad (4)$$

We use here Fermi-Dirac statistics because the free electron gas is an open system of assumed independent particles. An improvement would be to add exchange and correlation potentials (Dharma-Wardana and Perrot 1982).

This set of equations is solved self-consistently for each ionization stage. From the total potentials $V_{\text{tot}}^N = -Z/r + V_{\text{bound}}^N + V_{\text{free}}^N$ we get the radii of neutrality R_N by $dV_{\text{tot}}^N/dr(R_N) = 0$. This null gradient condition allows to match the different ionization stages potentials and spheres in the whole plasma volume. The chemical potential μ defines the reference energy from which $V_{\text{tot}}^N(R_N)$ is positioned (see (3) and (4)). The probability p_N of a given ionization stage is given by:

$$p_N = e^{\mu N/T} Z_N / \Xi \quad \text{where} \quad \Xi = \sum_N e^{\mu N/T} Z_N \quad (5)$$

from which all quantities may be deduced: mean volume, ionic density, mean ionization charge, "free" electronic density...

PRACTICAL PROBLEMS AND PHYSICAL DISCUSSION

As written this set of equations is numerically unsolvable because of the great number of levels involved in the bound structure. It can however be shown that the majority of the N -electron wavefunctions $\Psi_{N\alpha}$ solution of H_N are quite unperturbed, so that their energies need not be computed at each step but are simply shifted by the amount $\langle \Psi_{N\alpha} | V_{\text{free}}^N | \Psi_{N\alpha} \rangle$. Moreover the $\Psi_{N\alpha}$ are built using a LS-coupling multiconfigurational scheme from one-electron bound wavefunctions $\varphi_{Ni}(\mathbf{r}) = P_{nl}^N(r)Y_l^m(\vartheta, \varphi)/r$ in such a way that configuration interaction is for most states negligible (Massacrier and Dubau 1990, 1991). As a consequence (2) is summed in a straighter way as a sum of one-electron wave-functions. Concerning Z_N , precise energies are needed in the lower part of the spectrum. This contribution is directly summed retaining the term splitting. The highest states contribute mainly through their huge number. They are totally summed with energies estimated from the one-electron spectrum.

A word must be said on the external boundary conditions imposed on the bound wavefunctions. Tightly bound states are not sensitive to them. The situation becomes much more confuse for the higher states which tend to extend on neighbouring ions. Our simplified point of view consists in solving the Schrödinger equation for φ_{Ni} with two boundary conditions: $P_{nl}^N(R_N) = 0$ and $r dP_{nl}^N/dr(R_N) = P_{nl}^N(R_N)$. We interpret the resulting two energies as the lower and upper bounds of an energy band (Rozsnyai 1972). It gives an idea of the sharpness of bound states and becomes noticeable only for those states close to the ionization limit. For bands sitting astride the limit, we decrease the degeneracy of this state by the amount of this band energy still in the bound part of the energy spectrum. Though crude this approach has the further advantage to avoid step-like behaviours of the partition functions, an important problem lengthily studied (Hummer and Mihalas 1988).

CONCLUSION

Our model totally takes into account the strong interaction of bound electrons in each ionization stage and gives in a coherent way the populations and the energies of bound states. Its flexibility allows to easily adapt it to treat mixtures or examine given levels. Improvements might be sought to the calculation of the free electron density and effects due to neighbouring ions included in V_{free}^N . Detailed results will be presented in a further paper.

REFERENCES

- Däppen, W. 1980, *Astr. Ap.*, **91**, 212
 Däppen, W. Anderson, L. and Mihalas, D. 1987, *Ap. J.*, **319**, 195
 Davis, J. and Blaha, M. 1982, *J. Quant. Spectros. Radiat. Transfer.*, **27**, 307
 Dharma-wardana, M. W. C. and Perrot, F. 1982, *Phys. Rev. A*, **26**, 2096
 Dharma-wardana, M. W. C. and Perrot, F. 1992, *Phys. Rev. A*, **45**, 5883
 Feng, I. J. Zakowicz, W. and Pratt, R. H. 1981, *Phys. Rev. A*, **23**, 883,
 Graboske, H. C. Jr., Harwood, D. J. and Rogers, F. J. 1969, *Phys. Rev.*, **186**, 210
 Hummer, D. G. and Mihalas, D. 1988, *Ap. J.*, **331**, 794
 Massacrier, G. and Dubau, J. 1991, in *Proc. 4th Int. Workshop on Radiative Properties of Hot Dense Matter*, Sarasota, 1990, Ed. W Goldstein, p. 130
 Massacrier, G. and Dubau, J. 1990, *J. Phys. B*, **23**, 2459S
 Rozsnyai, B. F. 1972, *Phys. Rev.*, **145**, 1137
 Rozsnyai, B. F. 1975, *J. Quant. Spectros. Radiat. Transfer*, **15**, 695