

High temperature partition function and pressure ionization of confined hydrogen atom

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Partition function of confined atomic hydrogen in different configurations has been investigated as prototype for non-ideal plasmas. The picture of confined atomic systems suggests different criteria for the truncation of the atomic internal partition function, avoiding the well-known problem of divergence affecting the isolated atom picture. The results are then used to discuss the pressure ionization phenomenon for a confined atom.

1. Introduction

The thermodynamics of high-density plasmas [1][2] has attracted large attention, due to the necessity of properly accounting for the effects of the multi-body interaction and in principle requiring the reformulation of the statistical mechanics in terms of a global Hamiltonian for the whole gas, instead of the usual separable form of non-interacting chemical species characterized through internal and translational partition functions. The complexity of the rigorous approach led to the development of simplified models, able to include the neighbour-effects on the isolated system though remaining consistent with the traditional thermodynamic approach, as the confined atom model or the atom under screened Coulomb potential.

A rich literature exists on the treatment of confined atomic hydrogen and helium by different forms of external potentials, i.e. rectangular, spherical or ellipsoidal potential well, with infinite or soft barriers and with special interest in those potentials allowing an analytical solutions of the corresponding eigenvalue problem [3]-[7].

Nowadays the development of new technologies and experimental techniques has triggered intensive theoretical studies on modelling spatially confined quantum systems. In fact the simple model of a confined atom could be used to investigate systems of large interest also in technological applications, i.e. quantum dots [8],[9], trapped atoms in fullerene cages [10],[11] and extreme high-pressure plasmas [12] like in stellar envelopes [13].

In this study, the confined model for atomic hydrogen is considered for the investigation on alternative criteria in the internal partition function truncation and on the phenomenon of the pressure

ionization, being in progress also the study of a confined atom under Debye screened potential.

2. Partition function of confined atomic hydrogen

The calculation of the thermodynamic properties of atomic hydrogen, confined in a box of size δ , has been recently reconsidered [14] in the perspective of naturally avoiding the divergence of the atomic internal partition function, Q_H . This problem is traditionally solved by introducing an external *cutoff*, which allows to write the partition function including all levels (n, ℓ) up to n_{max}

$$Q_H = \sum_n^{n_{max}} \sum_{\ell} (2\ell + 1) \exp(-E^{n,\ell}/k_B T) \quad (1)$$

Note that Eq.(1) does not include the spin degeneracy.

The spectrum of electronic levels characterizing the hydrogen atom in different confining configurations has been derived, implementing both finite difference and finite element algorithms in the solution of the eigenvalue problem, estimating also accuracy and efficiency in the perspective of problems with increasing dimensionality. In particular the spectrum for a 2D square domain has been considered [15], with the atom fixed in the centre or displaced to the boundary of the domain, parametrically varying the length of the square side. The more general case is the centre-fixed confinement of the atom in a spherical box, with the box radius ranging from 1000 to few bohrs.

The system of bound (negative) energy levels is significantly perturbed in strongly confined conditions, the ℓ -degeneracy being destroyed and the levels being progressively pushed into the region of positive values, i.e. the *pseudo-continuum*, as the

box-size is reduced, up to the limiting case where no bound states still exist.

In the case of spherical box three different criteria to determine the maximum value of the quantum numbers have been considered

- *external cutoff* or *Fermi criterion*, this criterion is applied to the unperturbed atom and, considering the volume effectively available by the atom, relates the maximum value of the principal quantum number to the mean interatomic distance δ through

$$n_{max} = \left[\frac{4\pi}{3} \right]^{1/6} \sqrt{\delta} \quad (2)$$

- *natural cutoff 1*, the existence of the infinite barrier, as already pointed out, determines the transition of bound levels to the positive-energy region, thus offering a natural truncation with the inclusion in the sum in Eq. (1) only of negative levels
- *natural cutoff 2*, this last criterion is based on the convergence of the partition function with the inclusion of levels in the pseudo-continuum, i.e. with positive energies.

In Fig.1 the maximum allowed value of the principal quantum number obtained in the three approaches is displayed as a function of the box radius. It is evident that the *external-Fermi* criterion converges to the first *natural* one, differently from what observed in Ref. [14] where only *s* states were actually considered. For small box sizes the curves depart, being the spectrum of bound states reduced to the ground level, while Eq. (2) predicts a smooth behaviour. It is worth to note that the *natural cutoff 2*, with values of n_{max} largely higher than for other criteria, depicts a proton-electron system that is no longer related to independently characterized

chemical species, i.e. the atom and its ion, but a chemical species allowed to electronic states with transition from negative to positive i.e. it includes to a given extent the particle-in-a-box levels. This opens debate on the definition of the ionization and of the equilibrium constant for the ionization process. This point requires a deeper insight in the theory and the use of partition function, obtained with the last criterion, for the derivation thermodynamic properties should be considered in the frame of a physical *picture*, this idea being to some extent discussed in Ref. [14].

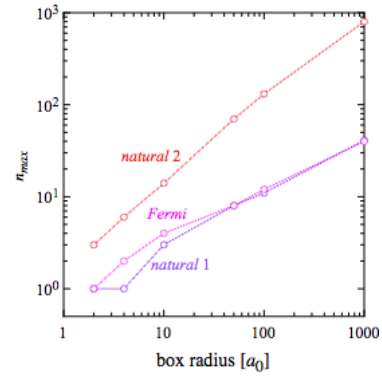


Fig. 1 Maximum value of the principal quantum number as a function of spherical box size obtained using different *cutoff* criteria (for the self-consistent criterion n_{max} has been determined at $T=40\,000$ K)

Figs. 2 (a) and (b) display the partition function as resulting from different choices of the *cutoff* criterion.

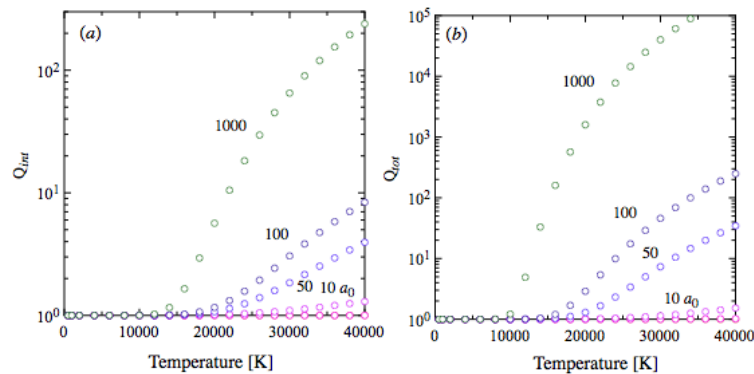


Fig. 2 Partition function for confined atomic hydrogen for different sizes of the spherical box, obtained with different *cutoff* criteria. (a) the *natural cutoff 1* (b) the *natural cutoff 2*

3. Equilibrium composition: pressure ionization

In the frame of the statistical mechanics and adopting the *natural cutoff* 1, the equilibrium constant for the ionization process could be estimated with the Saha equation, including the non-ideal quantum effects due to confinement [14],[16],[17]

$$\frac{N_{H+}N_e}{N_H} = \frac{(2\pi m_e \kappa_B T)^{3/2}}{h^3} \frac{2}{Q_H} e^{-I_H / \kappa_B T} \quad (3)$$

where I_H is the actual ionization potential equal by definition to $-E_{1s}$. The energy of the ground level seems to be unaffected by the confinement up to values of δ lower than 10 bohr, where a sharp fall off takes place as displayed in Fig. 3.

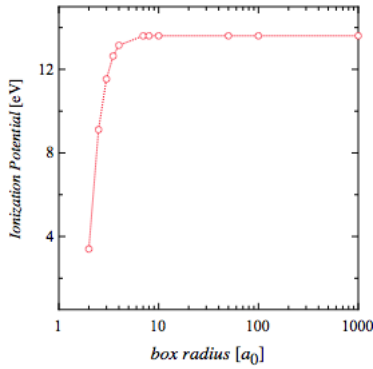


Fig. 3 Ionization potential, i.e. $-E_{1s}$, as a function of spherical box size

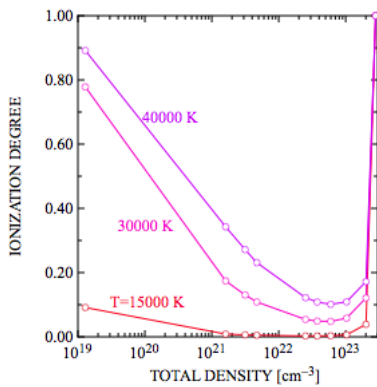


Fig. 4 Ionization degree for confined atomic hydrogen as a function of total (*bound+free*) electron density, for different temperatures

Calculations have been performed, at each confining configuration, keeping constant the total electron density, i.e. electrons *bound* in atomic system plus *free* electrons formed in ionization, over the explored temperature. In Fig. 4 the ionization degree, $\alpha = N_e / (N_e + N_H)$, as a function of the total electron density is displayed, for selected values of

the temperature. Increasing the density, thus decreasing the radius of the spherical box confining the hydrogen atom, the curves exhibit the phenomenon of *pressure ionization* [1].

In low- to medium-density conditions, the increase of pressure in the plasma is usually connected to a temperature shift of the ionization equilibrium, however in very high-pressure regimes quantum effects act moving the levels to the continuum edge (*Mott effect*), reducing the number of terms in the internal partition function of the atomic hydrogen, and, which is the more relevant aspect, decreasing the ionization potential. As evident from Eq. (3), both effects favour the onset of ionization equilibrium, though the pressure ionization is governed by the actual I_H value. This phenomenon results from the interaction of each atom with the neighbors, that is accounted in this model including the confining potential, that perturbs the ensemble of internal energy levels of the atomic species, still allowing the treatment of the plasma system as separable. For confining radii of the order of the bohr radius, all the levels fall in the pseudo-continuum and the ionization degree attained rapidly the unitary value, following the rapid transition to the non-ideal behaviour of the energy levels already observed [16].

The pressure ionization has been deeply investigated in literature as resulting from the non-ideal Debye-Hückel corrections [1]. The simultaneous effects of confinement and Debye screening are in progress, not only deriving the spectra for different configurations, as already done in literature [18], but also calculating the corresponding thermodynamic properties, in view of a synergy between confinement [18] and Debye-Hückel corrections [19]. The approach is self-consistent, ensuring in the whole temperature range the self-consistency of the ensemble of levels corresponding to the Debye screening length due to the plasma and the actual electron density generated by the ionization process.

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