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 WILEY-VCH

REPRINT

## EXPERT OPINION

## The divergent atomic partition function or how to assign correct statistical weights to bound states

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Soon after the spectrum of the hydrogen atom was understood theoretically, a difficult problem appeared: how to do correct statistical mechanical calculations that include bound states when the internal partition function of the hydrogen atom diverges? According to Bohr, the hydrogen atom has an infinite number of bound states with energies  $E_n = -|E_H|/n^2$  and degeneracies  $g_n = n^2$  ( $E_H \approx -13.6$  eV). Since the terms in the atomic partition function

$$Z_{\text{bound}}(T) = \sum_{n=1}^{\infty} g_n e^{-E_n/kT} = \infty$$

grow asymptotically as  $n^2$ , the series is strongly divergent. Such divergences of the electronic partition function plague actually all internal atomic, ionic and molecular partition functions. The divergence arises from the long-range character of the Coulomb interaction, which allows for an infinite number of bound states.

The paper by Ebeling et al. [1] in the present issue starts with an interesting historical review of this problem and its solution, and then gives a novel quantum statistical mechanical derivation of an equation of state for a reacting hydrogen gas  $H \rightleftharpoons e + p$  that should be reliable in the regime where atomic recombination/dissociation prevails.

The problem with the partition function  $Z_{\text{bound}}(T)$  is that it describes a single hydrogen atom at

## Bound states of hydrogen atom

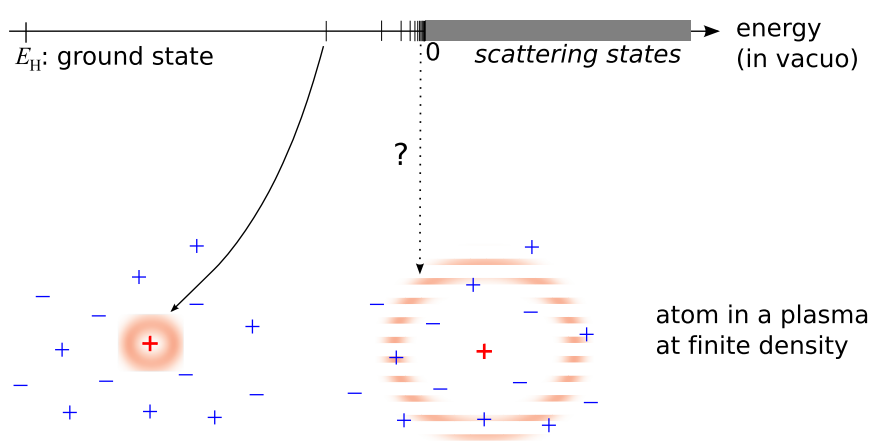


Figure 1 What happens to the Rydberg states of a single hydrogen atom in a plasma at finite density?

finite temperatures with an unlimited accessible volume. In such a situation, Rydberg states with very large  $n$  do exist. There is also an infinite number of scattering states. At thermal equilibrium, the atom will actually always be found in a dissociated state, because entropy wins over energy at low densities.

In a gas at finite density, the atomic partition function is convergent because the space available for bound states is finite (states with large  $n$  cannot exist, see figure). Let us consider, as in [1], a partially ionized hydrogen gas described within the physical picture,

that is as a quantum gas of electrons and protons interacting via the Coulomb potential. The particles feel an effective screened interaction, given at low densities by the Debye formula  $\exp(-\kappa r)/r$ , where  $\kappa = \sqrt{4\pi e^2 \rho_{\text{free}}/kT}$  is the inverse Debye screening length and  $\rho_{\text{free}}$  is the density of ionized particles. Thanks to screening, the number of bound states (which depends now on density and temperature) is finite, and a finite atomic partition function can be built with them. That approach does however not provide a fully satisfying answer to the original problem. For instance, if one tries to compute the deviations at low densities from the ideal gas law caused by the interactions between the particles (with possible formation of bound states), the problem of the diver-

gence of the atomic partition function re-appears since screening effects are evacuated in the low density limit ( $\kappa \rightarrow 0$  as  $\rho \rightarrow 0$ ). Indeterminate products of the form  $\infty \times 0$  arise, which can only be resolved by a better understanding of the subtle interplay between the contributions from bound states, scattering states and screening effects.

As recalled in [1], a complete solution to the problem of the divergence of the atomic partition function has been obtained in the context of asymptotic low-density (virial) expansions. The solution involves as ingredient the so-called Brillouin-Planck-Larkin partition function

$$Z_{\text{BPL}}(T) = \sum_{n=1}^{\infty} g_n \left( e^{-E_n/kT} - 1 + \frac{E_n}{kT} \right),$$

first introduced by Brillouin following a work of Planck (see [1] for the historical perspective). A full understanding of the emergence of the BPL atomic partition function in the virial expansion using methods of many-body quantum statistical mechanics was achieved in the sixties with works of Larkin [2] and Ebeling [3,4]. In those works, screening plays a crucial role to ensure the finiteness of all quantities, giving rise in particular to the subtracted terms in the BPL partition function. As emphasized in Sect. 3 of [1],  $Z_{\text{BPL}}(T)$  is only a part of the second virial coefficient that can be expressed in terms of Ebeling direct and exchange functions  $Q(T)$  and  $E(T)$  [5]. Strictly speaking, it's only the sum of all terms in the second virial coefficient that makes an unambiguous sense, free of any arbitrary definition. However, it turns out that this coefficient is essentially determined by  $Z_{\text{BPL}}(T)$  as long as the temperature is not too high. Other definitions of the partition function for a hydrogen atom are possible, but it is crucial that there is a correct counting of all contributions (as provided

by the full second virial coefficient), without any missing term nor double counting [1].

The virial expansion is obtained from the asymptotic limit  $\rho \rightarrow 0$  at fixed temperature  $T$ , and can hence only describe fully ionized phases (because entropy always wins over energy as  $\rho \rightarrow 0$ ). The contributions of two-body bound states (hydrogen atoms) appear in that expansion inside the second virial coefficient, that is as a small correction of order  $\rho^2$ . Deriving accurate equations, without any double counting of states, for the hydrogen gas in regimes where a substantial fraction of electrons and protons are recombined into hydrogen atoms (or even molecules) is a challenging theoretical task with important practical implications in astrophysics and other fields. Significant progress has been made recently on that topic [1,6–10].

Ebeling et al. [1] derive an equation of state (EOS) for a partially ionized hydrogen gas by performing partial resummations in the virial expansion in such a way that the resulting EOS has a structure compatible not only with the virial expansion, but also with the Saha equation for the ionization/recombination equilibrium of hydrogen atoms (implemented with the BPL partition function). The construction of this EOS involves a suitable inversion of low-fugacity expansions and includes degeneracy effects on the ionized charges at high density. Their analytical EOS compares satisfactorily with known chemical models, though a stringer test would be to compare to accurate quantum Monte Carlo simulation results in the expected validity domain of the theory.

The EOS derived in [1] neglects the possible formation of hydrogen molecules and the effects of atom-atom and atom-charge interactions. We note that the formation in the e-p plasma of any chemi-

cal species ( $H$ ,  $H^-$ ,  $H_2$ ,  $H_2^+$ ,  $H_2^-$ ,  $H_3^+$  ...), and their (screened) interactions with the ionized charges and with other chemical species, can be described fully consistently, without any double counting of states, by the Screened Cluster Representation (SCR) introduced in [6]. Parts of the SCR can be viewed as a formalization of ideas first introduced by Rogers [11]. The statistical weight of any bound entity in the SCR involves a finite internal partition function that depends solely on the fundamental physical constants, and that can be viewed as a generalization of Ebeling's two-body virial functions  $Q$  and  $E$  to a higher number of interacting particles [6]. The SCR has been used to derive the Scaled Low-Temperature (SLT) equation of state [7–9] for a partially ionized hydrogen gas, which is asymptotically exact in a coupled low-density – low-temperature limit. Though it is obtained in the vicinity of a  $T \rightarrow 0$  limit, the SLT EOS reduces, as it should, to the virial expansion when one lets  $\rho \rightarrow 0$  at fixed  $T$ , providing thus a rigorous extension of the validity domain of the usual virial expansion into the partially (or fully) recombined atomic phase.

The work in [1] and [10] contain interesting results for achieving a good description of the effects of bound states from low up to quite high density. The destruction of bound states at high density (Mott transition to full ionization) is studied in [10] for temperature above 10 000 K by introducing dressed atoms (the shift in the atomic levels are determined from an effective wave equation which takes into account Pauli blocking and the Fock self-energy). We note that the aforementioned recent works might serve also as guides for improving the accuracy of current well established chemical models [12, 13]. A full and controlled description, within the

physical picture, of the contributions of bound states in the high density regime, including temperatures below 10 000 K where  $H_2$  molecules dominate and where the famous plasma phase transition might take place, is still an open and challenging problem.

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