## Departure from Boltzmann-Gibbs statistics makes the hydrogen-atom specific heat a computable quantity

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The specific heat of the (nonionized) hydrogen atom in free space cannot be calculated within Boltzmann-Gibbs statistical mechanics essentially because its partition function *diverges*. We show that a recently introduced generalized formalism can overcome this difficulty for q < 1 (the index q characterizes the statistics; Boltzmann-Gibbs corresponds to q = 1).

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Any quantum mechanics introductory textbook should contain the exact solution of five systems, namely, the (nonrelativistic) free particle, the harmonic oscillator, the spin  $\frac{1}{2}$  (in the presence of an external magnetic field), the rigid rotator, and the (nonionized) hydrogen atom in free space. The first four are also present in any textbook on statistical mechanics (for the oblate-prolate rigid rotator see [1]), but very rarely is the hydrogen atom present (a relevant exception to this fact is the early discussion by The reason might be that, within Fowler [2]). Boltzmann-Gibbs (BG) thermostatistics, the partition function diverges, and we are therefore left practically without a prescription for attributing, as a function of the temperature, finite values to an equilibrium quantity such as specific heat. A way out of this is sometimes to change the system, or, more precisely, to consider the hydrogen atom as not in free space but rather within a box (or any other equivalent procedure which essentially consists of "throwing" out of the sums the bothering infinite levels that, in free space, accumulate at the ionization threshold). This type of solution can make sense if the system is thought to be within a limited volume, but becomes hard to accept for hydrogen atoms in free space (say, in interstellar space). For this particular physical situation, the only logical path that is left within BG statistical mechanics is that the hydrogen atom is in its fundamental state if the temperature T is strictly zero and is ionized for any positive temperature (no matter how small T might be).

In other words, that there is no possible thermal equilibrium for a hydrogen atom in free space. This type of approach might not properly accommodate the experimental evidence of photon emission and absorption spectra by atoms and molecules in interstellar space. The direct experimental approach of hydrogen atom thermostatistics is now, unfortunately, inaccessible since the associated energy scale is one Rydberg, which approximately corresponds to a temperature of  $10^5$  K. We must therefore try to discuss the problem on theoretical grounds.

In fact, the difficulties encountered for the hydrogen atom are essentially the same which make the d=3 selfgravitating system untractable within standard statistical mechanics and thermodynamics [3]. More generally speaking, if we consider d-dimensional systems with attractive two-body interactions characterized by a potential energy  $\propto 1/r^{\alpha}$  ( $\alpha > 0$ ;  $r \equiv$  distance), its BG canonical mean value (for the potential) diverges at the long distance limit whenever  $\alpha \leq d$  (quantum effects normally produce a cutoff which avoids mathematical troubles at short distances). Of course, the hydrogen and standard gravitation correspond to ( $\alpha, d$ )=(1,3) and, consequently, they constitute a typical case of untractability. A generalized statistical mechanics and thermodynamics theory is now available [4,5] and addresses precisely this type of difficulty. It consists of the proposal [4] of the following generalized entropy:

$$S_q = k \frac{1 - \sum p_i^q}{q - 1} \quad (q \in \mathbb{R}) , \qquad (1)$$

where k is a positive constant and  $\{p_i\}$  are the probabilities of the microscopic configurations. In the  $q \rightarrow 1$  limit,  $S_q$  becomes the well known Boltzmann-Gibbs-Shannon expression,  $-k_B \sum p_i \ln p_i$ .  $S_q$  is non-negative, extremal for equiprobability (microcanonical ensemble), and is concave (convex) if q > 0 (q < 0), a fact which constitutes an important ingredient for the thermodynamic stability for the system.  $S_q$  satisfies the H theorem [6], i.e.,  $dS_q/dt \ge 0$  ( $\le 0$ ) if q > 0 (q < 0); it is pseudo-additive for two independent systems  $\Sigma$  and  $\Sigma'$ , i.e., if  $\hat{\rho}_{\Sigma \cup \Sigma'} = \hat{\rho}_{\Sigma} \otimes \hat{\rho}_{\Sigma'}$ where  $\hat{\rho}$  denotes the density operator, whose eigenvalues are  $\{p_i\}$ ;  $\hat{\rho}_{\Sigma \cup \Sigma'}$  acts on the tensor product of the Hilbert spaces, respectively, which are associated with  $\Sigma$  and  $\Sigma'$ . In other words it satisfies

$$\frac{S_q^{\Sigma \cup \Sigma'}}{k} = \frac{S_q^{\Sigma}}{k} + \frac{S_q^{\Sigma'}}{k} + (1-q)\frac{S_q^{\Sigma}S_q^{\Sigma'}}{k} .$$
 (2)

Consequently, unless q=1,  $S_q$  is generically nonadditive (nonextensive).

If the system is in thermal equilibrium at temperature  $T \equiv 1/\beta k$ , we must optimize  $S_q$  under the constraints  $\mathrm{Tr}\hat{\rho}=1$  and  $\mathrm{Tr}\hat{\rho}^q\hat{\mathcal{H}} \equiv \langle \hat{\mathcal{H}} \rangle_q = U_q$  [4,5] where  $\hat{\mathcal{H}}$  is the Hamiltonian and  $U_q$  is a *finite* quantity (generalized internal energy). We obtain

6248

## **BRIEF REPORTS**

$$\hat{\rho} = \frac{\left[1 - \beta(1 - q)\hat{\mathcal{H}}\right]^{1/(1 - q)}}{Z_q} \tag{3}$$

with the generalized partition function given by

$$Z_q = \operatorname{Tr}[1 - \beta(1 - q)\widehat{\mathcal{H}}]^{1/(1 - q)} .$$
(4)

In the  $q \rightarrow 1$  limit, these expressions recover the BG distribution  $\hat{\rho} = \exp(-\beta \hat{\mathcal{H}})/Z_1$ . It can be shown [5] for all values of q that

$$\frac{1}{T} = \frac{\partial S_q}{\partial U_q} , \qquad (5)$$

$$U_q = -\frac{\partial}{\partial\beta} \frac{Z_q^{1-q} - 1}{1-q} , \qquad (6)$$

and

$$F_q \equiv U_q - TS_q = -\frac{1}{\beta} \frac{Z_q^{1-q} - 1}{1-q} .$$
 (7)

In addition to the above properties, the present generalized statistics result in the following: (i) the statistics leave form invariant, for all values of q, the Legendretransform structure of thermodynamics [5], the Ehrenfest theorem and the von Neumann equation [7], as well as the Onsager reciprocity theorem [8]; (ii) the statistics satisfy Jaynes information theory duality relations [7], necessary for the associated entropy to be considered as a measure of the (lack of) information; (iii) and they can generalize the Langevin and Fokker-Planck equations [9], the quantum statistics [10], and the fluctuationdissipation theorem [11], among others. This generalized formalism has already been applied in a certain amount of problems: self-gravitating astrophysical problems [12,13], Lévy flights [14,15], correlated anomalous diffusion [16], optimization techniques [17], and a possible connection with quantum groups [18], among others. As mentioned above, we are primarily concerned here with the gravitational case. What has been essentially proved [12] is that many-body d=3 gravitation is consistent with simultaneously finite mass, energy, and entropy if  $q < \frac{7}{9}$  (this threshold has been obtained from [12] by performing the  $q \leftrightarrow 1/q$  transformation which is necessary in order to correct the fact that the authors have used the early version [4] of the generalization rather than the correct one [5]). Another argument which, in our opinion, points to q < 1 for such systems is given by Landsberg in [3]; indeed, there it is demanded for the entropy to be superadditive, which only occurs here [see Eq. (2)] for q < 1. Finally, a third argument which again suggests that q < 1, is that, for two specific many-body astrophysical models, the exact time-dependent solutions of the associated Vlasov equations have been recovered for q = -1 [13]. Since, for these types of problems, the exact  $(\alpha, d)$  dependence of q is still unknown (in contrast with Lévy flights and correlated anomalous diffusion, where it is known [14-16]) we shall address, for the positivetemperature dependence of the specific heat of the hydrogen atom, typical values of q in the range 0,7/9.

The hydrogen-atom spectrum is given by

$$\epsilon_n = R \left[ 1 - \frac{1}{n^2} \right], \quad n = 1, 2, 3, \dots, \tag{8}$$

with the degeneracy

$$g_n = 2n^2 , \qquad (9)$$

where R is the Rydberg constant, and we have chosen the fundamental state to have zero energy. The well known BG prescription for the specific heat is given by

$$\frac{C}{k_B} = \left[\frac{R}{k_B T}\right]^2 \left\{\sum_{n=1}^{\infty} \left[g_n p_n \frac{\epsilon_n^2}{R^2}\right] - \left[\sum_{n=1}^{\infty} g_n p_n \frac{\epsilon_n}{R}\right]^2\right\},$$
(10)

where

$$p_n = \frac{e^{-(\epsilon_n/k_B T)}}{Z_1} \tag{11}$$

and

$$Z_1 = \sum_{m=1}^{\infty} g_m e^{-\epsilon_m / k_B T} . \tag{12}$$

A quick inspection reveals the already mentioned mathematical untractability of this calculation. For q < 1, Eq. (10) is extended into [11,19]



FIG. 1. Temperature dependence of the specific heat: (a) q=0.5 (when the number N of terms in the sum diverge,  $C_q$  vanishes for all kT/R > 0.5); (b) for typical values of q below  $\frac{7}{9}$  (exact results). Whenever kT crosses the hydrogen-atom levels, the specific heat presents divergences if 0 < q < 1/2, cusps if q=1/2, and discontinues in its derivative if 1/2 < q < 1.

$$\frac{C}{k} = \frac{q}{t^2} \left\{ \sum_{n=1}^{\infty} g_n \left[ p_n^q \frac{(\epsilon_n/R)^2}{1 - \frac{1-q}{t} \left[ \frac{\epsilon_n}{R} \right]} \right] - \left[ \sum_{n=1}^{\infty} g_n p_n^q (\epsilon_n/R) \right] \left[ \sum_{n=1}^{\infty} g_n p_n \frac{(\epsilon_n/R)}{1 - \frac{1-q}{t} \left[ \frac{\epsilon_n}{R} \right]} \right] \right\},$$

where

$$t \equiv \frac{kT}{R} \tag{14}$$

and

$$p_n = \begin{cases} \frac{\left[1 - \frac{1 - q}{t} \left[\frac{\epsilon_n}{R}\right]\right]^{1/(1 - q)}}{Z_q}, & \text{if } \frac{1 - q}{t} \left[\frac{\epsilon_n}{R}\right] < 1\\ 0, & \text{otherwise} \end{cases}$$
(15)

with

$$Z_q \equiv \sum_{n=1}^{\infty} \left[ 1 - \frac{1-q}{t} \frac{\epsilon_n}{R} \right]^{1/(1-q)}.$$
 (16)

The sum  $\Sigma'$  is interrupted whenever the argument becomes negative. In practice, all these sums are replaced by  $\lim_{N\to\infty} \sum_{n=1}^{N}$ . The results are indicated in Fig. 1. As illustrated for q=0.5 in Fig. 1(a), anomalies occur at all dimensionless temperatures  $t_n = (1-q)[1-(1/n^2)]$  $(n=2,3,4,\ldots,)$ ; the limit  $N \rightarrow \infty$  has  $C_q$  equal to zero for all dimensionless temperatures t > (1-q). In Fig.

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$$\sum_{n=1}^{\infty} g_n p_n^q(\epsilon_n / R) \left[ \sum_{n=1}^{\infty} g_n p_n \frac{(\epsilon_n / R)}{1 - \frac{1 - q}{t} \left[ \frac{\epsilon_n}{R} \right]} \right] \right], \qquad (13)$$

1(b) we present the exact specific heat associated with three typical values of q below  $\frac{7}{9}$ . In the  $q \rightarrow 1$  limit, the entire function collapses into the physically inacessible T=0 axis.

As mentioned before, it seems to be difficult today for any calorimetric experiment on (highly diluted) nonionized hydrogen atoms for which comparison could be attempted. But, on theoretical grounds, one point has been achieved: within the framework of the recently generalized statistical mechanics, for q < 1, the free space (nonionized) hydrogen-atom specific heat becomes a computable quantity. So, in some sense, we can say that analogous to what happens with the gravitational systems [12,13], the cutoff naturally appearing in the formalism whenever q < 1 regularizes the theory. Further understanding of its physical significance would be very welcome

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