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Departure from Boltzmann-Gibbs Statistics Makes the Hydrogen Atom Specific Heat a Computable Quantity

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Abstract: The specific heat of the (non ionized) Hydrogen atom cannot be calculated within Boltzmann-Gibbs Statistical Mechanics essentially because its partition function **diverges**. We show that the generalized formalism recently introduced by one of us overcomes this difficulty for $q < 1$ (the index q characterizes the statistics; Boltzmann-Gibbs corresponds to $q = 1$).

Key-words: Hydrogen atom; Specific heat; Generalized Statistical Mechanics; Non-extensive entropy.

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Any good Quantum Mechanics introductory textbook contains the exact solution of **five** systems, namely, the (nonrelativistic) free particle, the harmonic oscillator, the spin 1/2 (in the presence of an external magnetic field), the rigid rotator and the (non ionized) Hydrogen atom. The first **four** are also present in any good Statistical Mechanics textbook (for the oblate/prolate rigid rotator see [1]) but **never the Hydrogen atom!** Worse than that, in most of them, not a single word is dedicated to this remarkable absence. The reason is that, within Boltzmann-Gibbs (BG) thermostatistics, the partition function **diverges**; more than that, there is no prescription for attributing, as a function of the temperature, finite values to an equilibrium quantity such as the specific heat. In fact, the difficulties encountered for the Hydrogen atom are essentially the same which make the $d = 3$ self-gravitating systems to be untractable within standard Statistical Mechanics and Thermodynamics [2]. 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 cut-off which avoids mathematical troubles at short distances). Of course, the Hydrogen atom and standard gravitation correspond to $(\alpha, d) = (1, 3)$, consequently they constitute a typical case of untractability. A Generalized Statistical Mechanics and Thermodynamics now available [3,4] addresses precisely this type of difficulty. It consists in the proposal [3] of the following generalized entropy

$$S_q = k\frac{1-\sum_i p_i^q}{q-1} \quad (q \in \mathcal{R}) \tag{1}$$

where k is a conventional positive constant, and $\{p_i\}$ are the probabilities of the microscopic configurations. In the $q \to 1$ limit, S_q becomes the well known Boltzmann-Gibbs-Shannon expression $-k_B \sum_i p_i \ln p_i$. S_q is non-negative, extremal for equiprobability (microcanonical ensemble), concave (convex) if $q > 0$ $(q < 0)$, a fact which guarantees **thermodynamic stability** for the system. S_q satisfies the H-theorem [5], i.e., $dS_q/dt \geq 0$ (≤ 0) if $q > 0$ $(q < 0)$; it is **pseudoadditive** for two **independent** systems Σ and Σ' (i.e., if $\widehat{\rho}_{\Sigma\cup\Sigma'} = \widehat{\rho}_\Sigma \otimes \widehat{\rho}_{\Sigma'}$ where $\widehat{\rho}$ denotes the density operator, whose eigenvalues are the $\{p_i\}$; $\widehat{\rho}_{\Sigma\cup\Sigma'}$ acts on the tensor product of the Hilbert spaces respectively associated with Σ and Σ'), in other words it satisfies

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

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 $Tr\ \widehat{\rho} = 1$ and $Tr\ \widehat{\rho}^q\ \widehat{\mathcal{H}} \equiv < \widehat{\mathcal{H}} >_q = U_q$ [3,4] where $\widehat{\mathcal{H}}$ is the Hamiltonian and U_q is a **finite** quantity (**generalized internal energy**). We then obtain

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

with the **generalized partition function** given by

$$Z_q = Tr[1 - \beta(1-q)\widehat{\mathcal{H}}\,]^{\frac{1}{1-q}} \tag{4}$$

In the $q \to 1$ limit, these expressions recover the BG distribution $\widehat{\rho} = \exp\,(-\beta\widehat{\mathcal{H}}\,)/Z_1$. It can be shown [4] that, for all values of q,

$$\frac{1}{T} = \frac{\partial S_q}{\partial U_q} \tag{5}$$

$$U_q = -\frac{\partial}{\partial\beta}\frac{Z_q^{1-q}-1}{1-q} \tag{6}$$

and

$$F_q \equiv U_q - T\;S_q = -\frac{1}{\beta}\frac{Z_q^{1-q}-1}{1-q} \quad . \tag{7}$$

In addition to the above properties, the present generalized statistics: (i) leaves **form-invariant**, for all values of q, the Legendre-transform structure of Thermodynamics [4], the Ehrenfest theorem and the von Neumann equation [6], as well as the Onsager reciprocity theorem [7]; (ii) satisfies Jaynes Information Theory duality relations [6], necessary for the associated entropy to be considered as a measure of the (lack of) information; (iii) generalizes the Langevin and Fokker-Planck equations [8], the quantum statistics [9], the fluctuation-dissipation theorem [10], among others. This generalized formalism has already been applied in a certain amount of problems: self-gravitating astrophysical systems [11], Lévy flights [12], and others. As mentioned above, we are primarily concerned here with the gravitational case. What has been essentially proved [11] is that $d = 3$ gravitation is consistent with **simultaneously finite** mass, energy and entropy if $q < 7/9$ (this threshold has been obtained from [11] 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 [3] of the generalization rather than the correct one [4]). Another argument which points $q < 1$ for such systems is given in Landsberg 1984 [2]; indeed, it is there demanded for the entropy to be **superadditive**, which only occurs here (see Eq. (2)) for $q < 1$. Since the exact (α, d)-dependence of q is still unknown (in contrast with $d = 1$ Lévy flights, where it is known [12]) we shall address, for the positive-temperature 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

$$\epsilon_n = R\,(1 - \frac{1}{n^2}) \quad (n = 1, 2, 3, ...) \tag{8}$$

with the degeneracy

$$g_n = 2n^2 \tag{9}$$

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

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

where

$$p_n = \frac{e^{-\frac{\epsilon_n}{k_BT}}}{Z_1} \tag{11}$$

with

$$Z_1 = \sum_{m=1}^{\infty} g_m \; e^{-\epsilon_m/k_BT} \tag{12}$$

A quick inspection reveals the already mentioned mathematical untractability of this calculation. For $q < 1$, Eq. (10) is extended into [10,13]

$$\frac{C_q}{k} = \frac{q}{t^2} \left\{ \sum_{n=1}^{\infty} g_n \left[p_n^q \frac{(\epsilon_n/R)^2}{1 - \frac{1-q}{t}\frac{\epsilon_n}{R}} \right] - \left[\sum_{n=1}^{\infty} g_n p_n^q (\epsilon_n/R) \right] \left[\sum_{n=1}^{\infty} g_n p_n \frac{(\epsilon_n/R)}{1 - \frac{1-q}{t}\frac{\epsilon_n}{R}} \right] \right\} \tag{13}$$

where

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

and

$$p_n = \frac{\left[1 - \frac{1-q}{t}\frac{\epsilon_n}{R}\right]^{\frac{1}{1-q}}}{Z_q}, \quad if \;\; \frac{1-q}{t}\frac{\epsilon_n}{R} < 1 \quad (p_n = 0, \; otherwise) \tag{15}$$

with

$$Z_q \equiv \sum_{n=1}^{\infty}{}' \left[1 - \frac{1-q}{t}\frac{\epsilon_n}{R}\right]^{\frac{1}{1-q}} \tag{16}$$

The sum $\sum'$ is interrupted whenever the argument becomes negative. In practice, all these sums are computationally replaced by $\ell im_{N\to\infty} \sum_{n=1}^{N}{}'$. The results are indicated in Fig. 1. As illustrated for $q = 0.5$ in Fig.1(a), anomalies occur at all dimensionless temperatures $t_n = (1-q)(1-1/n^2)$ $(n = 2, 3, 4, ..)$; the limit $N \to \infty$ provides C_q **zero** for all dimensionless temperatures $t > (1-q)$. In Fig.1(b) we present the exact specific heat associated with three typical values of q **below 7/9** . In the $q \to 1$ limit, the entire function collapses into the physically inacessible $T = 0$ axis.

We are unaware of any calorimetric experiment on (highly diluted) **non ionized** Hydrogen atoms with which comparison could be tempted. But, on theoretical grounds, one point has been achieved: the recently generalized Statistical Mechanics makes, for $q < 1$, the Hydrogen atom specific heat a **computable quantity**. So, in some sense we can say that, analogously with what happens with the gravitational systems [11], the cut-off naturally appearing in the formalism whenever $q < 1$, "regularizes the theory".

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Caption for figure

Fig.1 - Temperature dependence of the specific heat: (a) For $q = 0.5$ (when the number N of terms in the sum diverges, C_q vanishes for all $kT/R > 0.5$); (b) For typical values of q below 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 discontinuities in its derivative if $1/2 < q < 1$.

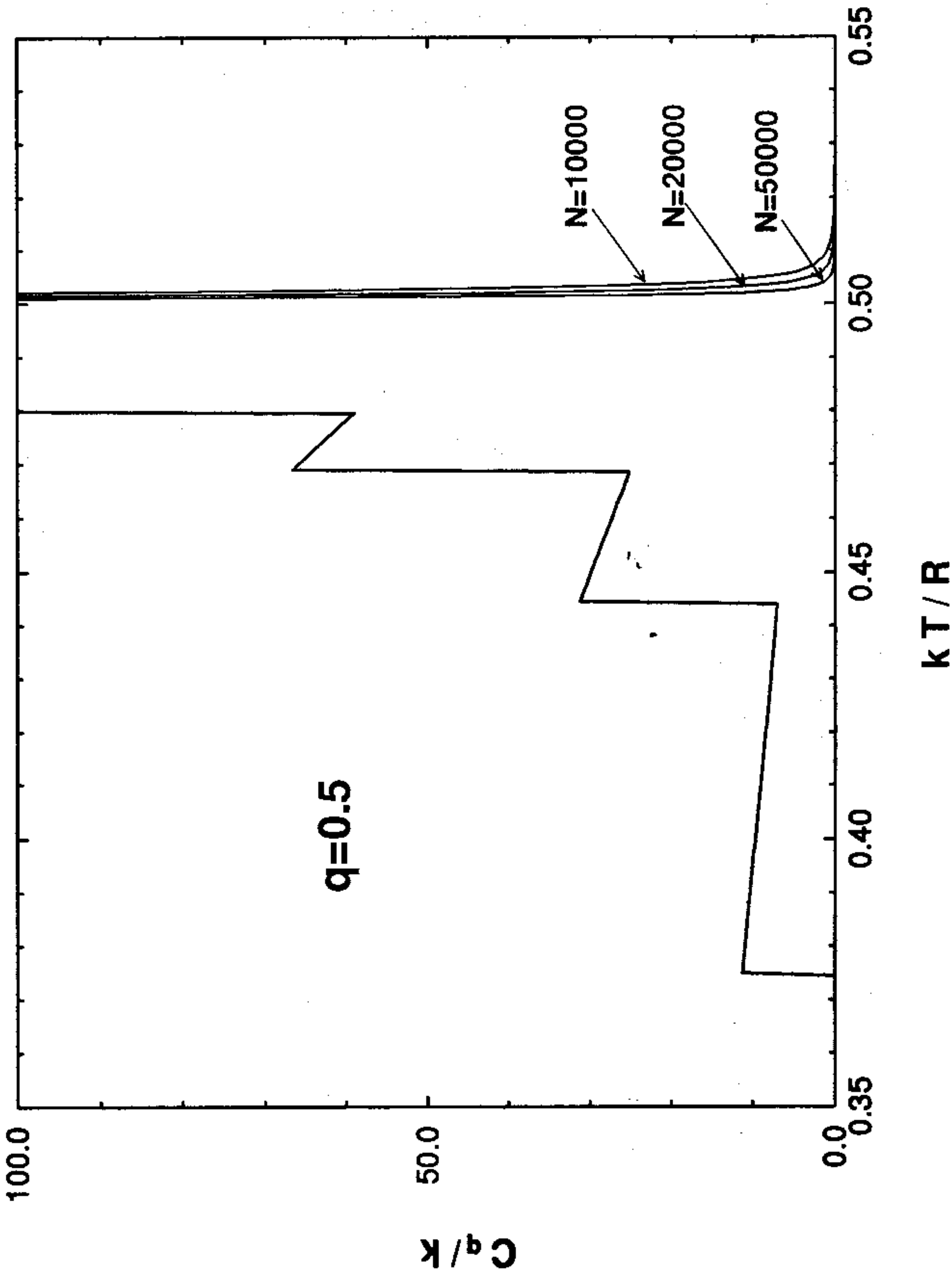
N=10000
N=20000
N=50000
q=0.5
0.35
0.40
0.45
0.50
0.55
k T / R
0.0
50.0
100.0
C q / k

Fig. 1(a)

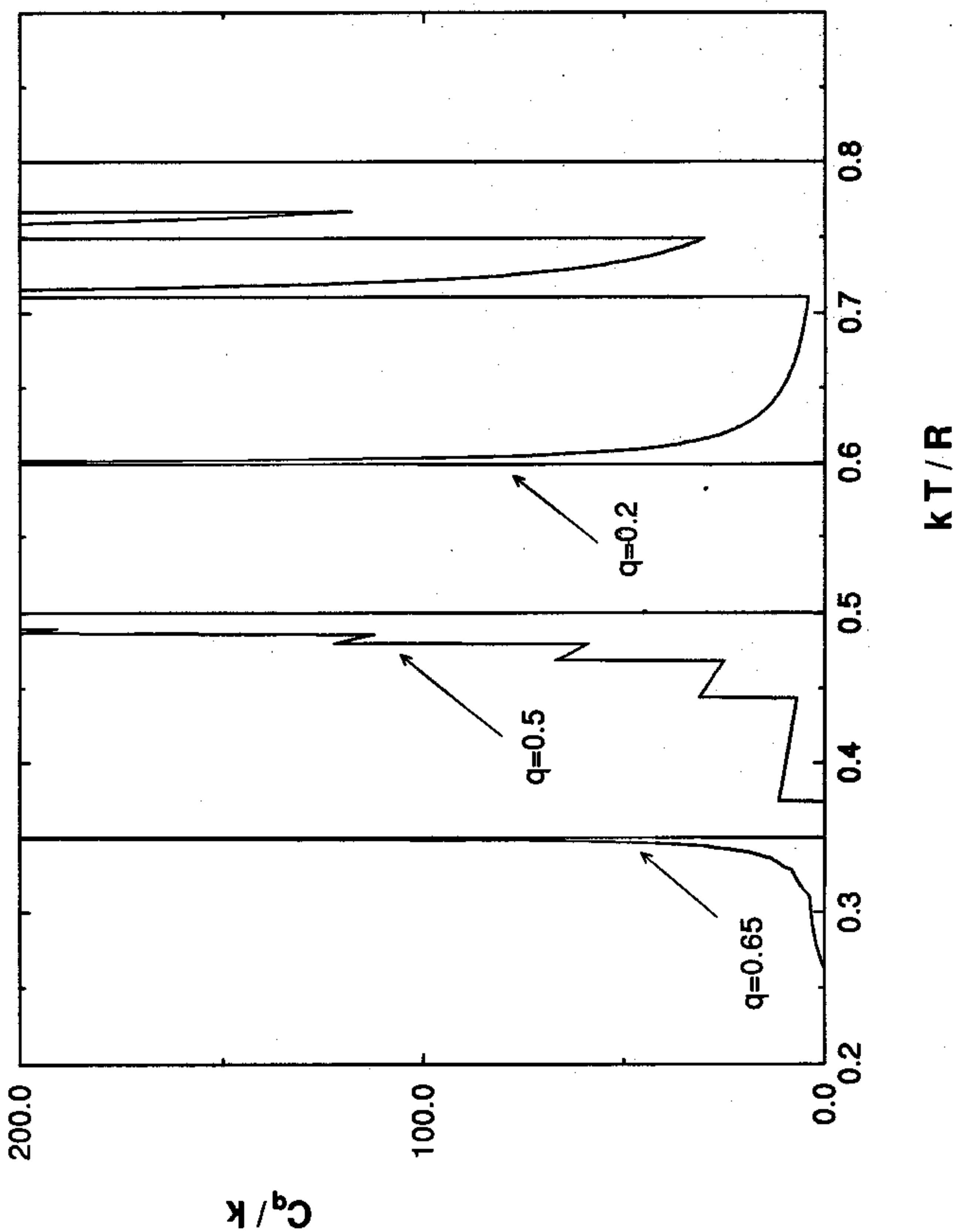

Fig. 1(b)

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