SOME REMARKS ON AN ALTERNATIVE APPROACH FOR BOLTZMANN DISTRIBUTION OF HYDROGEN ATOMS

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ABSTRACT

We propose an alternative approach to Boltzmann distribution concerning the hydrogen atom and compare our results to previous formalism for some observables.

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THE PROBLEM

The probability P_n for the Boltzmann distribution is given by

$$P_n = \frac{\exp -(\beta E_n)}{\sum_n \exp -(\beta E_n)} \ . \tag{1}$$

It gives the probabilty that a system in equilibrium with a heat reservoir is found in the energy level n. Here $\beta = 1/(k_B T)$, the inverse of the temperature, while E_n are the various energy states the system could have. Of particular interest is the partition function

$$Z = \sum_n \exp -(\beta E_n) \ , \tag{2}$$

from which it is possible to extract all the relevant thermodinamical quantities.

The hydrogen atom obeys to an attractive potential given by

$$V(r) = -\frac{e^2}{r} \ , \tag{3}$$

and when solved the two–body quantum mechanical problem gives us the binding energy levels

$$E_n = -\frac{R}{n^2}, \tag{4}$$

where R has the value of 1 Rydberg, 13.6 eV, the ionization energy of hydrogen atom, equivalent to a temperature of about 1.58×10^5 Kelvin.

Because of the symmetry of the Coulombic potential (3), apart from the angular momentum **L** there exists another conserved vector, the Laplace–Runge–Lenz vector given by

$$\mathbf{A} = \mathbf{p} \times \mathbf{L} - e^2 m_e \frac{\mathbf{r}}{r} \ . \tag{5}$$

That is due to a supplementary $SO(4)$ symmetry of the system Fock (1935); Bargmann (1936) besides the usual rotational invariance $SO(3)$ that gives the n^2 degeneracy to energy levels in (4).

Computing the partition function for the hydrogen atom and considering the degeneracy one obtains

$$Z = \sum_{n=1}^{+\infty} n^2 \exp \left(\frac{\beta R}{n^2}\right) \geq \sum_{n=1}^{+\infty} n^2 \ , \tag{6}$$

which contrary to some other known cases, like the quantum harmonic oscillator, is clearly a divergent quantity. This makes impossible to extract any meaningful thermodinamical quantity out of (6) for an otherwise well-defined problem with sound results for energy levels, fine structure, relativistic effects and so on.

A possible solution to this problem was proposed by Tsallis et al.(see Lucena et al. (1995) and references therein). Essentially it consists on deforming the exponential measure by means of a continuous parameter q

$$\exp_q(x) = \begin{cases} [1 + (1 - q)x]^{\frac{1}{1-q}} & \text{for } 1 + (1 - q)x > 0 \text{ and } q \neq 1 \\ \exp(x) & \text{for } q = 1 \\ 0 & \text{else} \end{cases} \tag{7}$$

The idea of the so–called q-deformation was first introduced by Box & Cox (1964) for statistical distributions. In this approach equation (6) becomes

$$Z = \sum_{n=1}^{+\infty} n^2 \left[1 + (1 - q)\frac{\beta R}{n^2}\right]^{\frac{1}{1-q}} \ . \tag{8}$$

Setting $m = 1/(1 - q)$ so that for $m = +\infty$ one recovers the usual Boltzmann distribution, and $t = \beta R$, one could write the Tsallis partition function as

$$Z_{Ts} := \sum_{n=1}^{+\infty} n^2 \left(1 + \frac{t}{mn^2}\right)^m \ . \tag{9}$$

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A DIFFERENT APPROACH

As we have seen in eq. (6) this partition function diverges. Rewriting the expression in a different way one obtains

$$Z = \sum_{n=1}^{+\infty} n^2 \exp\left(\frac{\beta R}{n^2}\right) = \sum_{n=1}^{+\infty} n^2 \sum_{k=0}^{+\infty} \frac{(\beta R)^k}{n^{2k}} \frac{1}{k!} = \sum_{k=0}^{+\infty} \frac{(\beta R)^k}{k!} \sum_{n=1}^{+\infty} \frac{1}{n^{2k-2}}$$

$$= \sum_{k=0}^{+\infty} \frac{(\beta R)^k}{k!} \zeta(2k-2) = \sum_{k=0}^{+\infty} \frac{t^k}{k!} \zeta(2k-2) =: Z_\zeta . \quad (10)$$

With this definition, owing to the fact that $\zeta(-2) = 0, \zeta(0) = -1/2, \zeta(2) = \pi^2/6$ and $\zeta(2k-2) < 2$ for $k > 1$, the partition function Z_ζ converges and is well defined.

Rearranging eq. (9) in the same way as done with eq. (10) one obtains

$$Z_{Ts} = \sum_{n=1}^{+\infty} n^2 \left(1 + \frac{\beta R}{mn^2}\right)^m = \sum_{n=1}^{+\infty} n^2 \sum_{k=0}^{m} \left(\frac{\beta R}{mn^2}\right)^k \binom{m}{k} =$$

$$\sum_{k=0}^{m} \left(\frac{\beta R}{m}\right)^k \binom{m}{k} \sum_{n=1}^{+\infty} \frac{1}{n^{2k-2}} = \sum_{k=0}^{m} \left(\frac{t}{m}\right)^k \binom{m}{k} \zeta(2k-2) . \quad (11)$$

The ζ function regularization allows to make sense of both partition functions Z_{Ts} and Z_ζ (the former, at least for finite m). However there is no way to obtain a closed form for either partition function. Therefore we shall compare the two results only for some special cases.

LOW TEMPERATURE EXPANSION

Starting from the partition function Z it is possible to extract the internal energy

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \quad (12)$$

along with the variation of energy

$$\langle E^2 - \langle E \rangle^2 \rangle = \left(-\frac{\partial}{\partial \beta}\right)^2 \ln Z \quad (13)$$

and its fluctuation

$$\frac{\langle E^2 - \langle E \rangle^2 \rangle}{\langle E \rangle^2} . \quad (14)$$

Comparing Z_{Ts} and Z_ζ at low temperature translates to keep only the highest β terms in the series, respectively

$$Z_{Ts} = \frac{(\beta R)^m}{m^m} \zeta(2m-2) + \frac{(\beta R)^{m-1}}{m^{m-2}} \zeta(2m-4) +$$

$$\frac{(\beta R)^{m-2}}{m^{m-3}} \left(\frac{m-1}{2}\right) \zeta(2m-6) + \dots , \quad (15)$$

and

$$Z_\zeta = \frac{(\beta R)^m}{m!} \zeta(2m-2) + \frac{(\beta R)^{m-1}}{(m-1)!} \zeta(2m-4) + \frac{(\beta R)^{m-2}}{(m-2)!} \zeta(2m-6) + \dots , \quad (16)$$

eventually letting $m \to +\infty$.

We will start with results given by Z_{Ts}:

$$\langle E \rangle = -mk_BT + \frac{m^2 \zeta(2m-4)}{\zeta(2m-2)} \frac{k_B^2 T^2}{R} +$$

$$\frac{\left[(m^4 - m^3)\zeta(2m-6)\zeta(2m-2) - m^4\zeta(2m-4)^2\right] k_B^3 T^3}{\zeta(2m-2)^2} \frac{k_B^3 T^3}{R^2} + \dots =$$

$$-mk_BT + m^2 \frac{k_B^2 T^2}{R} - m^3 \frac{k_B^3 T^3}{R^2} + \dots , \quad (17)$$

and the result for the internal energy is always consistently negative even before taking the limit $m \to +\infty$.

$$\langle E^2 - \langle E \rangle^2 \rangle = -mk_B^2 T^2 + \frac{2m^2 \zeta(2m-4)}{\zeta(2m-2)} \frac{k_B^3 T^3}{R} + \dots =$$

$$-mk_B^2 T^2 + 2m^2 \frac{k_B^3 T^3}{R} + \dots , \quad (18)$$

the energy variation is also negative irrespective of the value for m, and behaves like T^2 as expected.

$$\frac{\langle E^2 - \langle E \rangle^2 \rangle}{\langle E \rangle^2} = -\frac{1}{m} + \left[\frac{m^2\zeta(2m-6)}{\zeta(2m-2)} + \frac{m\zeta(2m-4)^2}{\zeta(2m-2)^2} - \right.$$

$$\left. \frac{m\zeta(2m-6)}{\zeta(2m-2)} - \frac{m^2\zeta(2m-4)^2}{\zeta(2m-2)^2}\right] \frac{k_B^2 T^2}{R^2} + \left[\frac{2m^4\zeta(2m-4)^3}{\zeta(2m-2)^3} + \right.$$

$$\frac{7m^3\zeta(2m-4)\zeta(2m-6)}{\zeta(2m-2)^2} + \frac{2m^2\zeta(2m-4)^3}{\zeta(2m-2)^3} -$$

$$\frac{4m^2\zeta(2m-4)\zeta(2m-6)}{\zeta(2m-2)^2} - \frac{4m^3\zeta(2m-4)^3}{\zeta(2m-2)^3} -$$

$$\left. \frac{3m^4\zeta(2m-4)\zeta(2m-6)}{\zeta(2m-2)^2}\right] \frac{k_B^3 T^3}{R^3} + \dots = -\frac{1}{m} -$$

$$m^2(m^2 - 3m + 2)\frac{k_B^3 T^3}{R^3} + \dots = -\frac{1}{m} - m^4 \frac{k_B^3 T^3}{R^3} + \dots , \quad (19)$$

the first term shows that the energy fluctuation goes to zero with increasing m independently from the temperature. Adding further terms in T in the expression above appears to cancel out, that is the energy fluctuation seems to be independent from the temperature at least for several terms in the expansion.

The ζ function regularized partition function Z_ζ furnishes us with the following results:

$$\langle E \rangle = -mk_BT + \frac{m!\zeta(2m-4)}{(m-1)!\zeta(2m-2)} \frac{k_B^2 T^2}{R} +$$

$$\frac{\left[2((m-1)!)^2 m!\zeta(2m-6)\zeta(2m-2) - (m-2)!(m!)^2\zeta(2m-4)^2\right]}{(m-2)!((m-1)!)^2\zeta(2m-2)^2} \times$$

$$\frac{k_B^3 T^3}{R^2} + \dots = -mk_BT + m\frac{k_B^2 T^2}{R} + m(m-2)\frac{k_B^3 T^3}{R^2} + \dots , \quad (20)$$

in this case also the internal energy turns out to be negative even before considering large m values, consistently with the previous case.

$$\langle E^2 - \langle E \rangle^2 \rangle = -mk_B^2 T^2 + \frac{2m!\zeta(2m-4)}{(m-1)!\zeta(2m-2)} \frac{k_B^3 T^3}{R} + \dots =$$

$$-mk_B^2 T^2 + 2m\frac{k_B^3 T^3}{R} + \dots , \quad (21)$$

and like in the previous case the energy variation turns out to be negative in the low temperature limit considered.

$$\frac{\langle E^2 - \langle E \rangle^2 \rangle}{\langle E \rangle^2} = -\frac{1}{m} +$$

$$\left[\frac{2\zeta(2m-6)}{\zeta(2m-2)} + \frac{\zeta(2m-4)^2}{m\zeta(2m-2)^2} - \frac{\zeta(2m-4)^2}{\zeta(2m-2)^2} - \frac{2\zeta(2m-6)}{m\zeta(2m-2)} \right] \frac{k_B^2 T^2}{R^2} +$$

$$\left[\frac{14\zeta(2m-4)\zeta(2m-6)}{\zeta(2m-2)^2} + \frac{2m\zeta(2m-4)^3}{\zeta(2m-2)^3} + \frac{2\zeta(2m-4)^3}{m\zeta(2m-2)^3} - \right.$$

$$\left. \frac{8\zeta(2m-4)\zeta(2m-6)}{m\zeta(2m-2)^2} - \frac{6m\zeta(2m-4)\zeta(2m-6)}{\zeta(2m-2)^2} - \frac{4\zeta(2m-4)^3}{\zeta(2m-2)^3} \right] \times$$

$$\frac{k_B^3 T^3}{R^3} + \cdots = -\frac{1}{m} + \left(\frac{m-1}{m} \right) \frac{k_B^2 T^2}{R^2} + \left(\frac{10m - 4m^2 - 6}{m} \right) \frac{k_B^3 T^3}{R^3} +$$

$$\cdots = -\frac{1}{m} + \frac{k_B^2 T^2}{R^2} - 4m \frac{k_B^3 T^3}{R^3} + \cdots , \qquad (22)$$

the energy fluctuation approaches zero from below in the relevant limit, irrispective of the temperature. The only difference with the previous case is an additional term proportional to T^2 and independent from m, again not influent in the low temperature limit.

HIGH TEMPERATURE EXPANSION

We shall now discuss some results obtained in the high temperature limit. It is understood that whith this expression we mean a high value of T (that is, $\beta \to 0$) such that $k_B T < R$ in order that the discrete spectrum of eq. (4) is still valid, being below the ionization level.

In this regime the two partition functions are given by

$$Z_{Ts} = -\frac{m}{2}\beta R + \frac{\pi^2}{12} \frac{m-1}{2m} (\beta R)^2 \qquad (23)$$

and

$$Z_\zeta = -\frac{1}{2}\beta R + \frac{\pi^2}{12} (\beta R)^2 . \qquad (24)$$

The results from Z_{Ts} are the following:

$$\langle E \rangle = -\frac{1}{\beta} + \frac{\pi^2}{12} \frac{(m-1)}{m^2} R + \frac{\pi^4}{144} \frac{(m-1)^2}{m^4} R^2 \beta + \dots , \qquad (25)$$

the internal energy approaches a negative value limited by the cut-off R as previously discussed. In the Boltzmann limit $m \to +\infty$ all other terms disappear irrispective of the temperature.

$$\langle E^2 - \langle E \rangle^2 \rangle = -\frac{1}{\beta^2} - \frac{\pi^4}{144} \frac{(m-1)^2}{m^4} R^2 - \frac{\pi^6}{864} \frac{(m-1)^3}{m^6} R^3 \beta + \dots , \qquad (26)$$

the energy variation behaves just like the internal energy discussed above, assuming a negative value.

$$\frac{\langle E^2 - \langle E \rangle^2 \rangle}{\langle E \rangle^2} = -1 - \frac{\pi^2}{6} \frac{(m-1)}{m^2} R\beta + \dots , \qquad (27)$$

the energy fluctuation approaches the constant value -1 when either one of the limits $\beta \to 0$ or $m \to +\infty$ is considered.

The results given by the regularized Z_ζ are:

$$\langle E \rangle = -\frac{1}{\beta} + \frac{\pi^2}{6} R + \frac{\pi^4}{36} R^2 \beta + \dots , \qquad (28)$$

as in the previous case, the internal energy is negative. The presence of a constant term independent from the temperature cannot change its sign as we have that $k_B T < R$ by hypothesis.

$$\langle E^2 - \langle E \rangle^2 \rangle = -\frac{1}{\beta^2} - \frac{\pi^4}{36} R^2 - \frac{\pi^6}{108} R^3 \beta + \dots , \qquad (29)$$

even the energy variation has the same behaviour of internal energy as a function of temperature. The presence of a negative constant term does not change the result. Notice that an analogous term is present in Z_{Ts} for finite m.

$$\frac{\langle E^2 - \langle E \rangle^2 \rangle}{\langle E \rangle^2} = -1 - \frac{\pi^2}{3} R\beta + \dots , \qquad (30)$$

the energy fluctuation assumes a constant negative value -1 for small β, in agreement with the previous model.

CONCLUSIONS

We have considered the problem of the thermodinamics for hydrogen atom in the canonical ensemble. We have compared the results given by an alternative distribution to the Boltzmann one with our approach of a ζ function regularization of the partition function. Comparing some thermodinamical quantities in the limits of low and high temperature we have shown that the results given by our approach are sound, do not contradict results of quantum mechanical bound states and are consistent with the continuosly deformed exponential measure.

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