

# A simple model to describe the low-temperature behaviour of some atoms and molecules: an application to the hydrogen atom

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Received 22 December 2006, in final form 28 March 2007

Published 18 May 2007

Online at [stacks.iop.org/JPhysB/40/1975](http://stacks.iop.org/JPhysB/40/1975)

## Abstract

A simple model to describe the low-temperature behaviour of some atoms and molecules is proposed and applied to the hydrogen atom. To this end, the low-temperature dynamics of the approach to equilibrium of the hydrogen atom is analysed by means of a standard Monte Carlo simulation. It is shown that, before approaching ionization, the atom may live for a long time in a quasi-equilibrium state whose duration increases exponentially for decreasing temperatures. Essentially, this effect is directly related to the low probability associated with the transition between the ground- and first-excited states, which demands an enormous amount of energy (75% of the whole energy spectrum). Therefore, for low temperatures, the atom may take a long time to overcome such an energy barrier. It is argued that the dynamical behaviour associated with the approach to equilibrium of some composite particles, characterized by an energy spectrum presenting an upper bound, preceded by the accumulation of an infinite number of levels—for which the hydrogen atom represents a prototype—can be described, at low temperatures, by a special class of  $q$ -oscillators. By suitably adjusting the deformation parameter  $q$ , characteristic of these  $q$ -oscillator systems, one obtains a dynamical behaviour at low temperatures which resembles that associated with the composite particle of interest. In order to reproduce the results of the hydrogen atom, the central idea is that this parameter may be set to a value, in such a way that the energy gap between the ground- and first-excited states coincide in the two systems. The method is illustrated by choosing  $q = 1/4$ , in which case one gets a remarkable agreement, from both qualitative and quantitative points of view, with the dynamical behaviour of the hydrogen atom. The conditions of applicability of the method are discussed.

## 1. Introduction

Many composite particles are characterized by an energy spectrum that presents an upper bound—usually known as the ionization (or dissociation) energy—preceded by the accumulation of an infinite number of levels. An analysis of the equilibrium properties of these systems, through standard statistical mechanics, runs into difficulties, since the corresponding canonical partition function diverges. Roughly speaking, this happens because each of the levels in the quasi-continuum yields a small contribution to the partition function; the divergence arises since there are, in principle, an infinite number of these levels. Essentially, such an effect is associated with the fact that these particles always ionize at any temperature; they only exist as metastable states, and could not exist in a true thermodynamic equilibrium. In this sense, one may understand the fact that such systems are scarcely discussed in standard equilibrium statistical-mechanics textbooks (for an exception to this, see [1]).

The most elementary composite particle and, consequently, the prototype of such particles is the hydrogen atom, characterized by a well-known energy spectrum. The impossibility of calculating the canonical partition function of a simple system, such as the hydrogen atom is somewhat frustrating. Although defined only as metastable states, the presence of long-living nonionized hydrogen atoms in galaxy peripheries and in intergalactic media, at low temperatures, is undeniable. Certainly, their density must be very low in such a medium, in order to avoid the combination  $H + H \rightarrow H_2$ , and, in this way, they should spend a long time in their nonionized state, before reaching ionization. Through an analytical approach, we succeed in calculating a regularized (finite) partition function for the hydrogen atom, which is expected to work as a good approximation for low temperatures. Below, we describe briefly the procedure used to achieve this end.

- (i) We investigate the dynamical behaviour related to the approach to equilibrium of the hydrogen atom by applying a standard Monte Carlo method, in which the probability for jumping between states is based on the Boltzmann weight. As expected, for any finite temperature, the simulation always leads the system towards ionization, after some time. However, it is shown that the system may live in a quasi-equilibrium state, characterized by a slowly varying value of its average energy, before approaching its upper bound energy. We verify that the system remains in such a quasi-equilibrium state for a time which increases as temperatures are lowered.
- (ii) We propose a modified dynamics that prevents the system from reaching ionization and whose results coincide, during some time (essentially when the system lies in its low-temperature quasi-equilibrium state), with those of the standard dynamics. Therefore, for low temperatures, depending on the time scale involved, this modified dynamics may reflect the correct dynamical behaviour of the system.
- (iii) The statistical weight associated with the modified dynamics leads to a *finite* canonical partition function. Thus, it is possible to obtain a regularized partition function, in which the divergence of the standard partition function is removed. This method provides an elegant way of introducing a cutoff in the partition function of the hydrogen atom.
- (iv) Obviously, the above procedure is expected to work well only for low temperatures and fails when temperatures are increased. It is important to mention that what we mean by ‘low temperatures’ may reach values as high as  $10^4$  K, which corresponds to about 6% of the ionization temperature of the hydrogen atom (one should recall that this ionization temperature is nearly  $1.6 \times 10^5$  K).

In order to study composite particles in a simple way, we shall use the energy spectrum of  $q$ -oscillators, for  $0 < q < 1$ . These oscillators are deformations of the Heisenberg algebra,

by means of a real parameter  $q$ , recovering this well-known algebra when  $q \rightarrow 1$  [2–5]. Some  $q$ -oscillator systems, for values of the deformation parameter within the range  $0 < q < 1$ , present an energy spectrum characterized by an upper bound, preceded by the accumulation of an infinite number of levels, leading to a divergent canonical partition function, similarly to what happens to some composite particles. Moreover, at sufficiently low temperatures, these systems may also present a long-living quasi-equilibrium state, before approaching its upper bound energy level [6]. Herein, we argue that this simple theoretical model may be used appropriately to describe the dynamical behaviour of some composite particles at low temperatures; we show how this can be done by considering its correspondence with the hydrogen atom.

In the next section, we investigate the dynamical behaviour associated with the approach to equilibrium of the hydrogen atom within a standard Monte Carlo framework; we also introduce a modified dynamics, appropriate only for low temperatures, which is related to a finite regularized canonical partition function, through its statistical weight. In section 3, we repeat the same procedure for the simple model we are proposing (a particular  $q$ -oscillator), comparing our results with those of the hydrogen atom. Finally, in section 4, we present our conclusions.

## 2. Dynamics of the approach to equilibrium of the hydrogen atom

Before introducing a simple model for describing the low-temperature behaviour of atoms, we shall discuss some properties of the hydrogen atom. Let us then consider a hydrogen atom in free space, for which its energy spectrum is given by the well-known formula

$$E_n = R \left( 1 - \frac{1}{n^2} \right) \quad (n = 1, 2, \dots), \quad (1)$$

where  $R$  is the Rydberg constant ( $R = 13.6058$  eV, or  $R = 2.18 \times 10^{-18}$  J, which corresponds to a temperature  $(R/k_B) = 1.579 \times 10^5$  K), and we have chosen the ground state to have zero energy. For large values of  $n$ , one has a quasi-continuum of energy levels, and in the limit  $n \rightarrow \infty$  the atom ionizes, i.e., dissociates (with an ionization energy  $E^* = R$ ), in such a way that the whole energy spectrum is restricted to a range  $[0, R]$ . The dynamical evolution of the hydrogen atom is equivalent to a diffusion process among the energy levels, taking into account temperature effects. A transition between the ground- and first-excited states costs most of the total energy of the spectrum, i.e.,  $3R/4$ , and should happen with a very small probability, at low temperatures. Once this high-energy jump occurs, all further jumps take place in the energy range  $R/4$ , with somewhat higher probabilities. Therefore, for low temperatures, the hydrogen atom is expected to remain for a long time in its lowest energy states (mostly in the ground state). However, as the quantum number  $n$  increases, the energy cost for jumps between nearest-neighbour levels decreases. Therefore, once the system has reached a state characterized by a large quantum number  $n$ , transitions to higher energy levels cost very little energy, in such a way that after a long time, the hydrogen atom will approach its upper bound energy level and dissociation will occur. Such an ionization process will always happen, for any finite temperature; however, a very pertinent question concerns *how long* the system remains in the quasi-equilibrium state (characterized by an average energy close to the ground-state energy) [7].

Before introducing the dynamical numerical procedure to study the hydrogen atom, we discuss and justify some simplifications used in the present approach.

- (a) It is important to recall that the energy spectrum of the hydrogen atom is degenerate, with a given energy level  $E_n$  presenting a total degeneracy  $g_n = n^2$ . Therefore, a precise

analysis of this problem should take into account the degeneracy of the energy levels, as well as of the spins. However, as will be seen later on, only the lowest energy levels will contribute significantly, in such a way that the effects of the degeneracy will not change qualitatively our results. Consequently, we will consider herein,  $g_n = 1$  ( $\forall n$ ), for simplicity.

- (b) We shall neglect any dependence of the environment radiation on the spectral properties of the hydrogen atom. For a typical physical situation where the present study could be applied, e.g., intergalactic media, the radiation field is very weak, leading to very small variations in the energy levels. For this reason, we will consider a hydrogen atom in free space, neglecting the effects of the radiation field; these effects should not change qualitatively the present results.
- (c) We will use Boltzmann weights when dealing with out-of-equilibrium regimes, since one is always interested in the correct approach to the equilibrium state, in the limit of very long times. This is a procedure employed in standard Monte Carlo simulations, e.g., in magnetic models (in both cases of uniform or random interactions among spins), in such a way that the system is driven towards its equilibrium state after starting with an out-of-equilibrium configuration.

Let us then investigate the dynamical behaviour of the hydrogen atom [7] through a standard Monte Carlo procedure [8]. The probabilities  $P(n+1 \rightarrow n)$  and  $P(n \rightarrow n+1)$ , associated with transitions between the states characterized by quantum numbers  $n$  and  $n+1$ , satisfying the detailed-balance condition, and constructed by using the Boltzmann weight, are given by

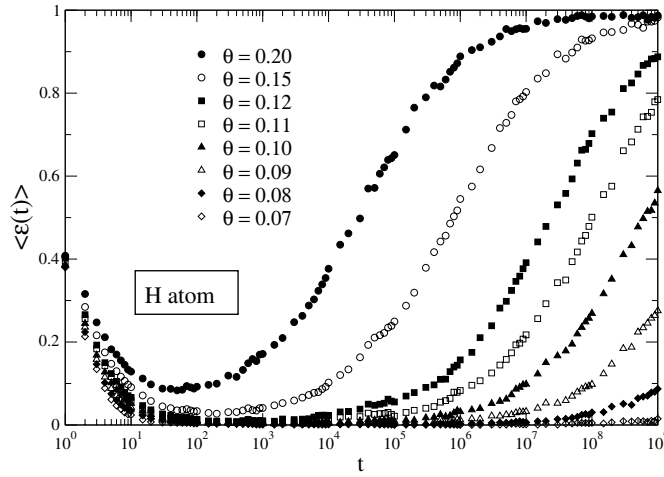
$$P(n+1 \rightarrow n) = c, \quad P(n \rightarrow n+1) = c \exp[-\beta(E_{n+1} - E_n)], \quad (2)$$

where  $\beta = (k_B T)^{-1}$  and  $c$  is an arbitrary constant ( $0 < c \leq 1/2$ ). In order to carry out the dynamical evolution, a uniform random number  $z$  ( $z \in [0, 1]$ ) must be generated at each Monte Carlo step (which will be adopted herein as our unit of time). For a system in a state characterized by the quantum number  $n$  at time  $t$ , transitions between states are performed (or not), depending on the value of  $z(t)$ , according to the following rules:

- (i) if  $z(t) \leq P(n \rightarrow n+1)$ , perform the jump  $n \rightarrow n+1$ ;
- (ii) if  $P(n \rightarrow n+1) < z(t) \leq [P(n \rightarrow n+1) + P(n \rightarrow n-1)]$ , perform the jump  $n \rightarrow n-1$ ;
- (iii) else, remain on level  $n$ .

One may conclude easily that the constant  $c$  is proportional to the probability for no jumps (rule (iii)). In the following results we have used  $c = 1/2$ , although we have verified that other choices for this constant ( $0 < c < 1/2$ ) did not change qualitatively our results. Below,  $\langle \rangle$  corresponds to averages over  $N_s$  distinct samples, i.e., different sequences of random numbers. In all simulations presented herein, we have considered the same initial condition: all samples starting in their corresponding first-excited states. As long as one starts the system in a state characterized by a small quantum number, e.g.,  $n \leq 5$ , different initial conditions only differ from one another, in the transient regimes, before the system reaches the quasi-equilibrium state; after such a state is attained, the particular choice of initial conditions becomes irrelevant.

In figure 1, we present the time evolution of the average dimensionless energy,  $\langle \varepsilon(t) \rangle$  ( $\varepsilon_n = E_n/R$ ), for different values of the dimensionless-temperature variable,  $\theta = (k_B T)/R$ . Our simulations were carried up to a maximum time  $t_{\max} = 10^9$ , whereas for the averages we have considered  $N_s = 2000$  samples. One observes a general tendency for increasing the average energy, towards the ionization energy, after some time. This reflects the fact that the hydrogen atom always ionize for any finite temperature. However, the interesting effect noticed herein is the presence of a quasi-equilibrium state, characterized by a slowly varying



**Figure 1.** Time evolution of the average dimensionless energy (energy in units of the Rydberg constant), for the hydrogen atom, represented for several relative temperatures ( $\theta = k_B T / R$ ). Time is measured in Monte Carlo steps.

average energy, before the approach to ionization. Such a quasi-equilibrium state may present a long duration for low values of  $\theta$ , as shown in figure 1.

An interesting point concerns the persistence of this quasi-equilibrium state for initial conditions very different from those mentioned above, e.g., starting the simulations from a high initial quantum number. In order to investigate this point, we have carried simulations by starting the system with  $n = 300$ . The most significant difference with respect to the simulations starting from low quantum numbers (e.g.,  $n = 2$ , as shown in figure 1) is that, in the former case, the average dimensionless energy  $\langle \varepsilon(t) \rangle$  remains, at first, for a few decades with a value very close to 1; after that, one observes a decay in this quantity, whose behaviour depends on the value of temperature considered: (i) for temperatures  $\theta \geq 0.10$  one gets that  $\langle \varepsilon(t) \rangle$  may decay a little, but not to near zero, and then slowly increase again towards ionization. It is important to mention that a similar behaviour may be observed also for higher values of  $\theta$  (e.g.,  $\theta > 0.20$ ) in the simulations starting with low quantum numbers; (ii) for lower temperatures, e.g.,  $\theta < 0.05$ , the quantity  $\langle \varepsilon(t) \rangle$  decays down to zero and stays around this value for some time, before increasing again towards ionization. This is similar to what happens with the simulations starting from small initial quantum numbers, but now the decay process is characterized by a much larger time scale. These results suggest that, apart from the longer time required for the decay of  $\langle \varepsilon(t) \rangle$ , the other effects may also be present, for sufficiently low temperatures—including the quasi-equilibrium state investigated in this paper—although they are not so easily observed, as in the case of the simulations starting with small quantum numbers.

We have also considered the evolution of the hydrogen atom under a modified dynamics [6, 7], which satisfies detailed balance, but prevents the approach to ionization. The essential motivation for introducing such a dynamical procedure comes from the following facts: (i) for sufficiently low temperatures, the results obtained from the standard and modified dynamics coincide along the quasi-equilibrium state; (ii) the partition function calculated from the weight associated with the later dynamics is finite. Let us define the jumping probabilities of the modified dynamics as

$$P(n+1 \rightarrow n) = c, \quad P(n \rightarrow n+1) = c \frac{\exp(-\beta E_{n+1}) - \exp(-\beta E^*)}{\exp(-\beta E_n) - \exp(-\beta E^*)}, \quad (3)$$

where, as mentioned before,  $E^* = R$  for the hydrogen atom. It is important to mention that, in the present case, the detailed-balance condition applies to the modified weight,  $[\exp(-\beta E_n) - \exp(-\beta E^*)]$ . We have verified an agreement between the two dynamical procedures persisting for a time (essentially within the quasi-equilibrium state) that increases for lowering values of the temperature [7]. Within the modified dynamics, which was constructed in such a way to avoid the system from reaching ionization, the system remains on a quasi-equilibrium state forever; the energy of this state fluctuates slightly around an average value, denoted herein by  $\varepsilon_{\text{mod}}(\theta)$ .

Let us now define the duration of the quasi-equilibrium state,  $t_{\text{QES}}(\theta)$ , as the time during which the system remains on such a state, within the standard dynamics, by keeping the absolute value of the difference between the average dimensionless energies computed from the standard and modified dynamics less than a given value  $\delta$ , i.e.,  $[(\langle \varepsilon(t) \rangle - \varepsilon_{\text{mod}}(\theta)) / \varepsilon_{\text{mod}}(\theta)] \leq \delta$ .

Although the choice of  $\delta$  may be arbitrary, one expects the corresponding law followed by  $t_{\text{QES}}(\theta)$  to be independent of this particular choice. In the present analysis we estimated  $t_{\text{QES}}(\theta)$  by considering several values of  $\theta$  from 0.08 up to 0.12, by imposing that  $\delta$  does not exceed 0.05. Our data fit well the exponential law,

$$t_{\text{QES}}(\theta) \sim \exp(b/\theta) = \exp[bR/(k_B T)] \quad (b = 1.95 \pm 0.06), \quad (4)$$

which implies  $t_{\text{QES}}(\theta) \rightarrow \infty$  when  $T \rightarrow 0$ . Essentially, the duration of the quasi-equilibrium state follows an Arrhenius law, typical of the Kramers' escape problem in chemical reactions [9, 10]. In such cases, the system may remain for a long time in a quasi-stationary state, before overcoming the potential barrier associated with the reaction. A similar picture seems to hold for the low-temperature dynamics of the hydrogen atom.

As mentioned above, for very low temperatures and depending on time scale of interest, the modified dynamics may reflect the correct dynamical behaviour of the system. Let us now show that the corresponding partition function, associated with the statistical weight that generated equation (3), is finite—contrary to that related to the standard dynamics—and may be calculated exactly. Let us address this point by considering in detail the divergence of the partition function associated with the energy spectrum of equation (1),

$$Z = \sum_{n=1}^{\infty} \exp(-\beta E_n) = \exp(-\beta R) \sum_{n=1}^{\infty} \exp[\beta R/(n^2)], \quad (5)$$

which may still be written as

$$Z = \exp(-\beta R) \lim_{n^* \rightarrow \infty} \sum_{n=1}^{n^*} \exp[\beta R/(n^2)], \quad (6)$$

where  $n^*$  represents a convenient cutoff in the quantum number, that will be taken to infinite later on.

It should be mentioned that in a real system, e.g., a gas of noninteracting hydrogen atoms in thermal equilibrium, the mean radius of such atoms cannot become larger than the mean distance between them. This allows the introduction of a cutoff in the partition function above, and one could use this mean distance as an effective cutoff for the hydrogen atom. Such a procedure represents a possible way for avoiding the divergence of the partition function and it has been used frequently in the literature (see, e.g., [11, 12]). In what follows we propose an alternative and more elegant approach for dealing with this difficulty, which has already been used successfully on analogous problems.



One has that

$$\begin{aligned} \exp(\beta R)Z &= \lim_{n^* \rightarrow \infty} \sum_{n=1}^{n^*} \sum_{m=0}^{\infty} \frac{(\beta R)^m}{m!} \frac{1}{n^{2m}} = \lim_{n^* \rightarrow \infty} \sum_{n=1}^{n^*} \left[ 1 + \sum_{m=1}^{\infty} \frac{(\beta R)^m}{m!} \frac{1}{n^{2m}} \right] \\ &= \lim_{n^* \rightarrow \infty} \left[ n^* + \sum_{m=1}^{\infty} H_{n^*, 2m} \frac{(\beta R)^m}{m!} \right], \end{aligned} \quad (7)$$

where  $H_{n^*, 2m} = \sum_{n=1}^{n^*} 1/n^{2m}$  are the harmonic numbers of order  $2m$  [13]. The limits  $n^* \rightarrow \infty$  of the harmonic numbers lead to well-defined, finite coefficients,  $B_{2m} = \lim_{n^* \rightarrow \infty} H_{n^*, 2m}$ . One has, for the lowest order coefficients,  $B_2 = \pi^2/6 = 1.64493\dots$ ,  $B_4 = \pi^4/90 = 1.08232\dots$ , and  $B_6 = \pi^6/945 = 1.01734\dots$ . One notices that  $B_{2m}$  converges to unit for increasing values of  $m$ , e.g.,  $B_{16} = 1.00002\dots$ . Therefore, one obtains

$$Z = \exp(-\beta R) \left[ \lim_{n^* \rightarrow \infty} (n^*) + \sum_{m=1}^{\infty} B_{2m} \frac{(\beta R)^m}{m!} \right], \quad (8)$$

which shows a linear divergence in the quantum number. The interesting point is that the divergent contribution of the partition function comes from a *single* term in the sum over  $m$  of equation (8) (term  $m = 0$ ). Let us now introduce the ‘modified regularized partition function’

$$Z' = Z - \exp(-\beta R) \lim_{n^* \rightarrow \infty} (n^*) = \exp(-\beta R) \sum_{m=1}^{\infty} B_{2m} \frac{(\beta R)^m}{m!}, \quad (9)$$

which is finite. The regularized partition function defined above may be written also as

$$Z' = \sum_{n=1}^{\infty} \exp(-\beta E_n) - \sum_{n=1}^{\infty} \exp(-\beta R) = \sum_{n=1}^{\infty} [\exp(-\beta E_n) - \exp(-\beta R)], \quad (10)$$

where one identifies the statistical weight related to the jumping probabilities of the modified dynamics in equation (3).

It is important to mention that the partition functions above,  $Z$  and  $Z'$ , are very distinct from one another (actually, the difference between them diverges). However, taking into account the fact that, for a sufficiently low temperature, the hydrogen atom remains for a long time in its low-energy state, one may consider the corresponding quasi-equilibrium state as an effective equilibrium within such a time scale, for which the divergent term is not relevant. In fact, the duration of this state has been estimated for some physical realizations, in such a way that for temperatures around room temperature, it may be as long as the age of the universe [7]. Therefore, it seems reasonable that one uses  $Z'$  in order to calculate thermodynamic properties as approximations. As an example, one may calculate a quantity  $u'$ , which should be related to the internal energy at low temperatures,

$$u' = -R \frac{\partial \ln Z'}{\partial (\beta R)} = -R \left\{ -1 + \frac{\sum_{m=1}^{\infty} m (B_{2m}/m!) (\beta R)^{m-1}}{\sum_{m=1}^{\infty} (B_{2m}/m!) (\beta R)^m} \right\}. \quad (11)$$

The energy  $u'$  may be compared with an average energy associated with the quasi-equilibrium state, computed from the numerical simulations. We have verified a very good agreement between the two approaches up to temperatures  $10^4$  K. In fact, the relative discrepancy between the energies computed from these two procedures gets larger for increasing temperatures, yielding the typical values of 0.004, for  $\theta = 0.05$  ( $T \approx 7895$  K) and 0.282, for  $\theta = 0.06$  ( $T \approx 9474$  K).

In the next section, we show that a conveniently chosen  $q$ -oscillator model may reproduce, accurately, all the results presented above.

### 3. Analysis of the energy spectrum of a special $q$ -oscillator

In this section, we will define a simple theoretical model that can be very useful in the analysis of the low-temperature behaviour of some composite particles; in particular, we will be interested in the special case of a correspondence with the hydrogen atom. This simple model is based on the energy spectrum of a special  $q$ -oscillator, which corresponds to a deformation of the Heisenberg algebra, by means of a real parameter  $q$ . In principle, there are many possible Hamiltonians associated with a specific  $q$ -oscillator algebra [14]. Herein, we shall consider the following Hamiltonian

$$H = \hbar\omega a^\dagger a = \hbar\omega [N]_q, \quad \left([N]_q = \frac{q^N - 1}{q - 1}\right), \quad (12)$$

and its associated deformed Heisenberg algebra

$$aa^\dagger - qa^\dagger a = 1, \quad [N, a] = -a, \quad [N, a^\dagger] = a^\dagger, \quad (13)$$

where  $q$  is a real parameter,  $a^\dagger$ ,  $a$  and  $N$  are, respectively, the creation, annihilation and number operators. The model defined above is widely known in the literature as a  $q$ -oscillator; its energy spectrum is given by

$$E_n = \frac{q^n - 1}{q - 1} \hbar\omega \quad (n = 0, 1, 2, \dots). \quad (14)$$

It is easy to see that the above algebra recovers, in the limit  $q \rightarrow 1$ , the well-known Heisenberg algebra for the simple harmonic oscillator. It should be noticed that the deformation parameter  $q$ , defined in such quantum-group oscillators, should not be confused with the widely used entropic index of nonextensive statistical mechanics (see, e.g., [15–19]).

For deformation parameters within the range  $0 < q < 1$ , the energy spectrum in equation (14) is limited, presenting an upper bound  $E^*$ , when  $n \rightarrow \infty$ ,

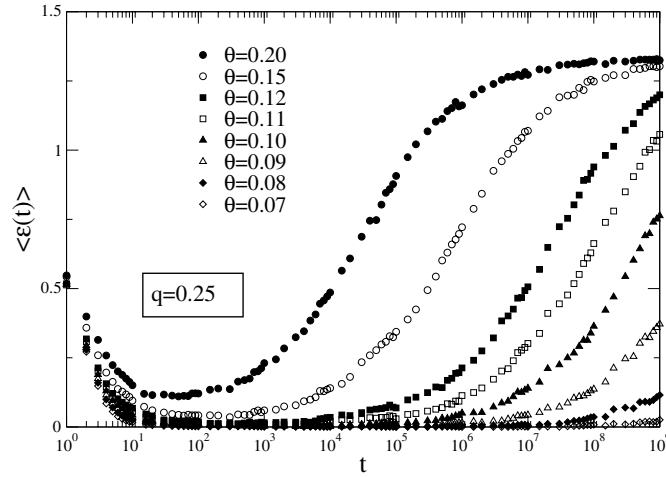
$$E_n = (1 - q^n)E^*, \quad E^* = \frac{1}{1 - q} \hbar\omega, \quad (15)$$

similar to what happens in some composite-particle systems. Due to this close analogy, we shall refer, sometimes, to the upper bound energy  $E^*$  of equation (15), as the ionization energy. The energies of the ground- and the first-excited states are given, respectively, by  $E_0 = 0$  and  $E_1 = (1 - q)E^*$ .

In order to define a special  $q$ -oscillator model that is able to present a dynamical behaviour similar to that of the hydrogen atom, we shall take into consideration the following points:

- (i) For the hydrogen atom, the energy gap separating the two lower energy states is given by  $3R/4$ , corresponding to 75% of its total energy spectrum. Let us then define the dimensionless quantity,  $r_{\text{hydrogen}} = (E_2 - E_1)/(E_\infty - E_1)$ , that, using equation (1), yields  $r_{\text{hydrogen}} = 3/4$ .
- (ii) This large energy gap, which leads to a small transition probability for jumps between these two states, at low temperatures, is essentially responsible for the long-living quasi-equilibrium states of the hydrogen atom, discussed above.
- (iii) Therefore, we choose a particular value of  $q$  in such a way as to impose the energy gap between the ground- and first-excited states (in each case, this gap is measured in units of the respective dissociation energy), to be the same on both systems. In other words, we define for the present  $q$ -oscillator model a quantity analogous to the one introduced in item (i),  $r_q = (E_1 - E_0)/(E_\infty - E_0)$  (i.e.,  $r_q = 1 - q$ ), and set  $r_q = r_{\text{hydrogen}}$ . One expects this condition to be sufficient to ensure that the corresponding  $q$ -oscillator will present a low-temperature dynamical behaviour, before the approach to equilibrium, similar to the



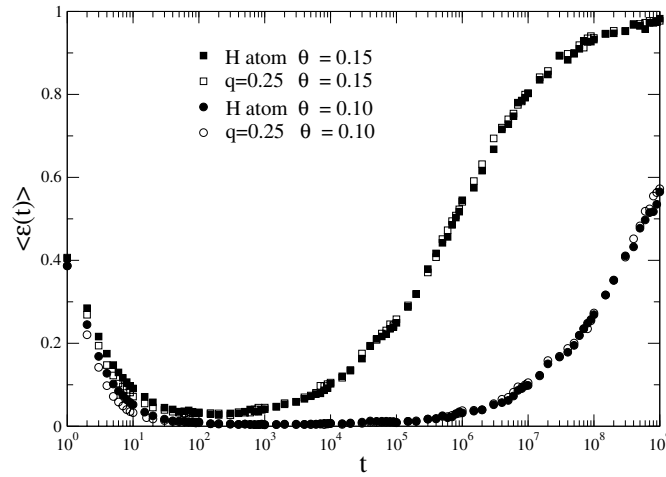


**Figure 2.** The time evolution of the average dimensionless energy (energy in units of  $\hbar\omega$ ), for a  $q$ -oscillator with  $q = 1/4$ , is represented for several relative temperatures ( $\theta = k_B T / E^*$ ).

one of the hydrogen atom. Due to the reasons stated in item (ii) above, we are assuming herein, that the possible differences that may occur on the higher energy levels of these two systems, should not be relevant in this case; the validity of this hypothesis will be verified later on.

Based on these arguments, one finds the  $q$ -oscillator with  $q = 1/4$ , as the candidate for describing the dynamical behaviour of the hydrogen atom. We apply the same standard Monte Carlo procedure defined in equation (2), to the energy spectrum of equation (14) [6], and compute the corresponding average energy as a function of time. In figure 2, we present the time evolution of the average dimensionless energy,  $\langle \varepsilon(t) \rangle$  [ $\varepsilon_n = E_n / (\hbar\omega)$ ], for several values of the relative-temperature variable,  $\theta = (k_B T) / E^*$ , i.e., the ratio of the temperature with respect to the ionization energy  $E^*$  [ $E^* = 4(\hbar\omega)/3$ ]. Similarly to what was done for the hydrogen atom, our simulations were carried up to a maximum time  $t_{\max} = 10^9$ , whereas the averages were considered over  $N_s = 2000$  samples, all of them starting in their first-excited states ( $n = 1$ ). Again, for any temperature, one verifies that the average energy always increases towards the ionization energy, reflecting the real situation, for composite particles, of the approach to dissociation. The long-living quasi-equilibrium states are also present at low temperatures. By introducing the modified dynamics (cf equation (3)) for this system, and using the definition of the previous section for the duration of the quasi-equilibrium state,  $t_{\text{QES}}(\theta)$ , one finds the same exponential law as before (cf equation (4)), with  $b = 2.06 \pm 0.06$ , which agrees with the one of the hydrogen atom, within the error bars.

In order to have a better comparison of the data presented in figures 1 and 2, we will represent the energy in each case scaled by their respective ionization energies, i.e.,  $E^* = R$ , for the hydrogen atom and  $E^* = 4(\hbar\omega)/3$ , for the  $q = 1/4$  quantum-group oscillator. These data are shown in figure 3 for two typical values of  $\theta = (k_B T) / E^*$ . One observes an impeccable agreement between these two sets of data, confirming the validity of the hypothesis stated on the item (iii) above. Therefore, this low-temperature dynamics of the hydrogen atom and the  $q = 1/4$  quantum-group oscillator are essentially identical. The most important common ingredient in these two systems consists in the same energy gap (in units of their respective



**Figure 3.** Time evolution of the average dimensionless energy (energy in units of the ionization energy  $E^*$ ) for the hydrogen atom (full symbols) and the  $q$ -oscillator with  $q = 1/4$  (empty symbols), with two different relative temperatures ( $\theta = k_B T / E^*$ ). For the hydrogen atom one has  $E^* = R$ , whereas for the  $q$ -oscillator,  $E^* = 4(\hbar\omega)/3$ .

dissociation energies) separating the ground- and first-excited states; for this particular case, the possible differences in higher energy levels appear to be irrelevant.

Let us now calculate the regularized canonical partition function for the  $q$  oscillators, and show its close analogy with that of the hydrogen atom. Following the same steps of the previous section,

$$Z = \sum_{n=0}^{\infty} \exp(-\beta E_n) = \sum_{n=0}^{\infty} \exp[-\beta(1 - q^n)E^*] = \exp(-\beta E^*) \sum_{n=0}^{\infty} \exp(\beta E^* q^n). \quad (16)$$

Introducing a cutoff in the quantum number,

$$Z = \exp(-\beta E^*) \lim_{n^* \rightarrow \infty} \sum_{n=0}^{n^*} \exp(\beta E^* q^n) = \exp(-\beta E^*) \lim_{n^* \rightarrow \infty} \sum_{n=0}^{n^*} \sum_{m=0}^{\infty} \frac{(\beta E^* q^n)^m}{m!}, \quad (17)$$

and treating separately the term  $m = 0$  in the second sum,

$$Z = \exp(-\beta E^*) \lim_{n^* \rightarrow \infty} \sum_{n=0}^{n^*} \left[ 1 + \sum_{m=1}^{\infty} \frac{(\beta E^* q^n)^m}{m!} \right], \quad (18)$$

which leads to

$$Z = \exp(-\beta E^*) \left[ \lim_{n^* \rightarrow \infty} (n^*) + \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{(\beta E^* q^n)^m}{m!} \right]. \quad (19)$$

Since the second term in the rhs of equation (19) is finite, we can interchange the order of the summations,

$$Z = \exp(-\beta E^*) \left[ \lim_{n^* \rightarrow \infty} (n^*) + \sum_{m=1}^{\infty} \frac{(\beta E^*)^m}{m!} \sum_{n=0}^{\infty} (q^m)^n \right], \quad (20)$$

where one identifies readily, for  $0 < q < 1$ , a convergent infinite geometric series in the summation over  $n$ . One obtains

$$Z = \exp(-\beta E^*) \left[ \lim_{n^* \rightarrow \infty} (n^*) + \sum_{m=1}^{\infty} \frac{1}{1 - q^m} \frac{(\beta E^*)^m}{m!} \right], \quad (21)$$

where the  $q$ -dependent coefficients,  $(1 - q^m)^{-1}$ , approach unit for increasing values of  $m$ . Similarly to what happens for the hydrogen atom, the divergence in the partition function above appears also linearly in the quantum number; this result holds for any  $q$ -oscillator with  $0 < q < 1$ . For the particular case  $q = 1/4$ , one may write

$$Z = \exp(-\beta E^*) \left[ \lim_{n^* \rightarrow \infty} (n^*) + \sum_{m=1}^{\infty} A_{2m} \frac{(\beta E^*)^m}{m!} \right], \quad A_{2m} = \frac{1}{1 - 2^{-2m}}, \quad (22)$$

where one finds the close analogy with the partition function of the hydrogen atom (cf equation (8)). In a similar way, the coefficients  $A_{2m}$  converge rapidly to unit, for increasing values of  $m$ , and may be compared with those of the hydrogen atom ( $B_{2m}$ ), e.g.,  $A_2 = 4/3 = 1.333 \dots$ ,  $A_4 = 16/15 = 1.066 \dots$ , and  $A_6 = 64/63 = 1.01587 \dots$ . Apart from a relative discrepancy of about 20% in the lowest order coefficients  $A_2$  and  $B_2$ , all higher order coefficients  $A_{2m}$  and  $B_{2m}$  ( $m = 2, 3, \dots$ ) are very close, ensuring that the finite parts of the partition functions of equations (8) and (22) are approximately the same.

Let us now introduce the regularized partition function for the  $q$ -oscillators

$$Z' = Z - \exp(-\beta E^*) \lim_{n^* \rightarrow \infty} (n^*) = \exp(-\beta E^*) \sum_{m=1}^{\infty} \frac{1}{1 - q^m} \frac{(\beta E^*)^m}{m!}, \quad (23)$$

which is finite, and may also be expressed in terms of the statistical weights of the modified dynamics (cf equation (3)),

$$Z' = \sum_{n=0}^{\infty} \exp(-\beta E_n) - \sum_{n=0}^{\infty} \exp(-\beta E^*) = \sum_{n=0}^{\infty} [\exp(-\beta E_n) - \exp(-\beta E^*)]. \quad (24)$$

Due to the strong similarity between the  $q = 1/4$  quantum-group oscillator and the hydrogen atom, verified above, the regularized partition function of equation (23) should also be a good approximation for low temperatures, from which one may calculate appropriate thermodynamic functions for the hydrogen atom. As an illustration, one may compute approximate expressions for the internal energy and specific heat of the  $q = 1/4$  quantum-group oscillator,

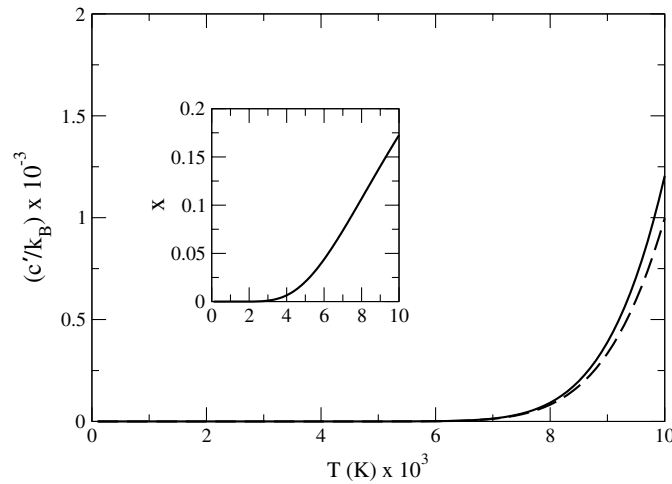
$$u' = -E^* \frac{\partial \ln Z'}{\partial (\beta E^*)} = -E^* \left\{ -1 + \frac{\sum_{m=1}^{\infty} m (A_{2m}/m!) (\beta E^*)^{m-1}}{\sum_{m=1}^{\infty} (A_{2m}/m!) (\beta E^*)^m} \right\}, \quad (25a)$$

$$\frac{c'}{k_B} = (\beta E^*)^2 \frac{\partial^2 \ln Z'}{\partial (\beta E^*)^2} = (\beta E^*)^2 \left\{ \frac{\sum_{m=1}^{\infty} m(m-1) (A_{2m}/m!) (\beta E^*)^{m-2}}{\sum_{m=1}^{\infty} (A_{2m}/m!) (\beta E^*)^m} - \frac{[\sum_{m=1}^{\infty} m (A_{2m}/m!) (\beta E^*)^{m-1}]^2}{[\sum_{m=1}^{\infty} (A_{2m}/m!) (\beta E^*)^m]^2} \right\}, \quad (25b)$$

where the prime notations mean that these quantities were calculated from a regularized partition function. An analogous expression for the specific heat of the hydrogen atom may be obtained from the regularized partition function in equation (9),

$$\frac{c'}{k_B} = (\beta R)^2 \frac{\partial^2 \ln Z'}{\partial (\beta R)^2} = (\beta R)^2 \left\{ \frac{\sum_{m=1}^{\infty} m(m-1) (B_{2m}/m!) (\beta R)^{m-2}}{\sum_{m=1}^{\infty} (B_{2m}/m!) (\beta R)^m} - \frac{[\sum_{m=1}^{\infty} m (B_{2m}/m!) (\beta R)^{m-1}]^2}{[\sum_{m=1}^{\infty} (B_{2m}/m!) (\beta R)^m]^2} \right\}. \quad (26)$$

In figure 4, we compare the specific heat of the  $q = 1/4$  quantum-group oscillator (obtained from equation (25b)) with the one of the hydrogen atom (obtained from equation (26)) up



**Figure 4.** The specific heat (in units of the Boltzmann constant  $k_B$ ) of the hydrogen atom (full line) is compared to that of the  $q = 1/4$  quantum-group oscillator (dashed line) for temperatures up to  $T = 10\,000$  K. In the inset we show the dimensionless relative discrepancy  $x$  between these two quantities, in the same temperature range.

to a temperature  $T = 10\,000$  K. The relative discrepancy between these two quantities,  $x = [c'(\text{hydrogen}) - c'(\text{oscillator})]/c'(\text{hydrogen})$ , is exhibited in the inset, for the whole temperature range considered. As expected, the discrepancy between these two quantities gets larger for increasing temperatures, although for ranges much higher than room temperature, the quantum-group oscillator considered herein works as a very good approximation for describing the hydrogen atom. In fact, one observes that around  $T = 8\,000$  K the relative discrepancy between these two quantities is still small, getting around 10%.

Recently, a generalization of the Heisenberg algebra was constructed [20, 21], which contains the  $q$ -oscillator algebra as a particular case. This generalized Heisenberg algebra can be used also as a simple model for describing phenomenologically the energy spectrum of more complicated composite particles (for an application of such an approach to the CO molecule, see [22]).

#### 4. Conclusions

We have proposed a simple model appropriate to describe phenomenologically the low-temperature behaviour of some atoms and molecules (i.e., composite particles), and have applied it to the hydrogen atom. By analysing the low-temperature dynamical behaviour of the hydrogen atom through a Monte Carlo simulation, we have shown that before approaching ionization, the hydrogen atom can live in a quasi-equilibrium state, whose duration increases exponentially with decreasing temperatures. This result certainly holds for a time measured in Monte Carlo steps, and one is mostly interested in whether such an effect could also occur in real time. Although a connection between these two different measures of time may be possible, under certain idealized conditions [7], to make this connection represents a difficult task in general. However, any monotonic function that may, in some way, relate Monte Carlo steps with real time, should lead to a low-temperature divergence in the duration of this quasi-equilibrium state in real time as well. As another possible alternative for the

connection with real time, one could implement a Monte Carlo method similar to that defined in equation (2), with the constant  $c$  determined by the Fermi golden rule for the transitions between two given states. Although this later procedure would require a larger computational effort, this could in principle capture the order of magnitude of the real time scale involved in this problem. Although a definite answer to this point requires careful and non-trivial experiments, the presence of long-living nonionized hydrogen atoms in galaxy peripheries and in intergalactic media, at low temperatures, is certainly unquestionable. We believe that this effect is essentially related to the low probability of the transition from the ground- to the first-excited state, at low temperatures; jumps involving higher energy levels would not be so important in this case.

Two possible physical realizations in which the above-mentioned long-living quasi-equilibrium state may take place have been discussed already in [7]: (i) in the first case, one should mention the case of hydrogen atoms interacting with a photon bath, which consists of a typical situation currently found in intergalactic media, where hydrogen atoms exist in very low concentrations and at very low temperatures (around 3 K); (ii) In the second example, we propose a gas of hydrogen atoms that is experimentally feasible under well-known appropriated techniques for avoiding the combinations  $H + H \rightarrow H_2$ . The important aspect in both cases is that the duration of this quasi-equilibrium state increases exponentially like  $\exp[bR/(k_B T)]$  where  $b$  is number that changes slightly from one example to another, with  $b \cong 2$  in both physical realizations considered. It should be stressed that this behaviour is in agreement with that found in the present numerical simulations (including the estimates of the factor  $b$ , that yield  $b \cong 2$  in both hydrogen-atom and  $q = 1/4$  oscillator numerical simulations), leading to a duration time that diverges exponentially as one lowers the temperature. We have estimated these duration times in both examples, for typical values of the physical parameters involved in each case, and we have obtained times of the order of the age of universe, for temperatures around room temperature. These results support the computation of thermodynamic properties using such a transient state.

The model we have proposed to describe phenomenologically such a low-temperature behaviour is based on a special  $q$ -oscillator, characterized by a single deformation parameter  $q$ . For  $0 < q < 1$ , the energy spectrum of these  $q$ -oscillators presents an upper bound, preceded by a quasi-continuum of states, similar to what happens with some composite particles, such as the hydrogen atom. We have chosen a particular value of  $q$  ( $q = 1/4$ ), in such a way as to make the energy gap separating the ground- and first-excited states of this system coincide, with that of the hydrogen atom (in each case, this gap is measured in units of the respective dissociation energy). We have shown that the low-temperature dynamical behaviour of the hydrogen atom and the  $q$ -oscillator with  $q = 1/4$  are essentially the same. Furthermore, we have calculated finite regularized canonical partition functions in both cases, showing that these two quantities are approximately the same, presenting small discrepancies. The procedure used for removing the divergence of these partition functions consists in an alternative technique, inspired in quantum-field-theory regularization approaches, which is commonly used in the literature on similar problems, and it turns up to be more elegant and less arbitrary than a simple cutoff in the number of states. Such regularized partition functions are appropriate only for low temperatures—when compared with the corresponding ionization temperature—typically up to 6% of the ionization temperature, corresponding, e.g., in the case of the hydrogen atom, to temperatures up to  $10^4$  K. For this reason, we do not estimate the continuum contributions of these partition functions, contrary to what is done in [11, 12], since they are not relevant for the present low-temperature quasi-equilibrium state study. We approach this quasi-equilibrium state by starting the system with a low quantum number, in such a way that for low temperatures the atom gets restricted for a long time to a small

region of phase space, characterized by a set of discrete states close to the ground state. Since this represents a low-temperature out-of-equilibrium—but quasi-stationary—regime, there is no need to include the continuous part of the partition function, which would certainly be relevant for the calculation of thermodynamic quantities in a true equilibrium. These results open up the possibility of treating systems of composite particles, such as the hydrogen atom, for temperature ranges well above room temperature, through standard statistical-mechanics methods. It should be mentioned that an alternative theoretical proposal for treating such systems consists in the application of non-extensive statistical mechanics formalism [23].

For the sake of simplicity of the numerical simulations, we did not consider the degeneracy of energy levels in the present approach. However, this effect can be also incorporated in the corresponding  $q$ -oscillator model, for a more realistic description of the desired system of composite particles. The inclusion of degeneracy should not change qualitatively the present results, and it is expected to produce [7]: (i) a simple shift (by a constant value) in the computed internal energy; (ii) a reduction in the temperature range of the quasi-equilibrium state.

The present work suggests that the special  $q$ -oscillator model we have analysed is a suitable simple system for investigating composite particles at low temperatures. We believe that the close agreement between the present  $q$ -oscillator model with  $q = 1/4$  and the hydrogen atom, determined by a simple imposition for the same gap separating the ground- and first-excited states on both systems (measured in units of their respective dissociation energies), could not work in general. In the present case, this agreement is due to the fact that such a gap represents 75% of the whole energy spectrum of the hydrogen atom; all further energy levels (actually, an infinite number of them) are restricted to 25% of the energy spectrum. We expect that for any physical system presenting the same order of magnitude for such an energy gap, the corresponding  $q$ -oscillator model will certainly be an appropriate system for studying the dynamics of its approach to equilibrium at low temperatures accurately. Therefore, one may consider  $q$  as a phenomenological parameter that can be adjusted in order to investigate certain physical systems, allowing one to obtain an approximation for their corresponding energy spectra. As an example, one may study the helium gas, for which an analytical expression of its energy spectrum is not known, although the numerical values of the energies of its lower levels are reported in standard textbooks. It seems likely that some additional conditions may be required, in cases of composite particles characterized by respectively smaller lowest energy gaps, in order to be properly described by an adequate  $q$ -oscillator model.

## Acknowledgments

The partial financial support from CNPq and Pronex/MCT (Brazilian agencies) is acknowledged.

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