

# Energy levels of atomic hydrogen in a closed box: A natural cutoff criterion of the electronic partition function

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The radial part of the Schrödinger equation for atomic hydrogen in a spherical box of radius  $\delta$  is numerically solved. Two sets of energy levels are obtained, the first one reproduces the unperturbed (bound) levels up to a given principal quantum number while the other one (unbound) describes levels with energy greater than the unperturbed ionization energy of atomic hydrogen  $E_H$ . These last levels asymptotically converge to the corresponding set which can be obtained by the particle in the box model, i.e., levels which increase their energy as  $n^2$  thus ensuring the convergence of the electronic partition function.

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## I. INTRODUCTION

The divergence of electronic partition function of atomic systems is a problem of large interest for plasma and astrophysical communities. In the case of atomic hydrogen we can write

$$f = \sum_n g_n \exp\left[-\frac{E_n}{kT}\right], \quad (1)$$

where  $g_n$  is the statistical weight of the  $n$ th level and  $E_n$  is the corresponding energy. In the case of atomic hydrogen we can express  $g_n$  and  $E_n$  as a function of principal quantum number  $n$  obtaining

$$g_n = 2n^2, \quad (2)$$

$$E_n = -\frac{2\pi\mu e^4}{h^2 n^2} = -\frac{E_H}{n^2}, \quad (3)$$

where  $n$  is the principal quantum number,  $\mu$  and  $e$ , respectively, the reduced mass and the electron charge and  $E_H = 13.5984$  eV is the ionization potential of the unperturbed atomic hydrogen. We obtain infinite bound (negative energies) states in the range

$$E_{n=1} = -E_H \quad E_{n=\infty} = 0. \quad (4)$$

Equation (3) can be also rearranged by taking the ground state as reference level in the form

$$\frac{E_n}{E_H} = \left[1 - \frac{1}{n^2}\right]. \quad (5)$$

In this frame  $n=1$  is the ground state with energy zero while for  $n \rightarrow \infty$   $E_{n=\infty}/E_H=1$ , i.e.,  $E_{n=\infty}=E_H$ . From these simple considerations one can understand the divergence of the partition function due to the divergence of the statistical weight and the convergence of the exponential factor. This is true for all temperatures but also if we consider only the  $s$  states in the atomic hydrogen (this point will appear more clear in the next pages), i.e.,

$$f_r = \sum_{ns} 2 \exp\left[-\frac{E_{ns}}{kT}\right]. \quad (6)$$

We call this a *reduced partition function* obtained by summing only on the  $s$  states.

The problem of the divergence of the partition function is overcome in the literature by cutting the sum to an  $n_{\max}$  which in the case of atomic hydrogen can be written in different ways according to different physical conditions. In this context large use is often made of the following equations:

$$a_0 n_{\max}^2 = [N']^{-1/3}, \quad (7)$$

$$a_0 n_{\max}^2 = D, \quad (8)$$

where  $a_0$  is the Bohr radius,  $N'$  is the particle density ( $\text{cm}^{-3}$ ), and  $D$  is the Debye length. In doing so we consider excited states in the partition function the radius of which does not exceed the interparticle distance  $N^{-1/3}$  (Fermi criterion) [1,2] or Debye length (Griem criterion) [3].

In both cases the unperturbed levels from Eqs. (3) and (5), i.e., coming from the analytical solution of the Schrödinger equation for the atomic hydrogen in the presence of the Coulomb potential, are used in the calculation of partition function. This kind of cutoff criteria are to be considered as *ad-hoc* procedures which in general are applied to low-pressure plasmas.

On the other hand a completely different literature exists on the subject started by Planck [4] and extended by Larkin [5], yielding the famous Planck-Larkin partition function. This approximation has been further improved by taking into account the multiparticle interaction and usually is applied to understand very high-pressure strongly coupled plasmas [6–8].

The aim of this paper is to reconsider the divergence of the partition function by considering not an isolated atom but an atom closed in a spherical box of radius  $\delta$ , i.e., we nu-

merically solve the radial part of the Schrödinger equation  $R(r)$  for atomic hydrogen by considering the following boundary conditions:

$$R(r=0)=0 \quad R(r=\delta)=0. \quad (9)$$

The numerical solution of the Schrödinger equation yields a number of energy levels equal to the number of points considered in the integration grid. In all cases we recover, independently from the integration domain, two sets of energy levels one which reproduces the unperturbed levels from Eq. (1) up to a given principal quantum number, the other one which describes levels with energy greater than the unperturbed ionization energy of atomic hydrogen  $E_H$ . Inspection of the second kind of levels shows that they converge to the corresponding set of levels which can be obtained by the particle in the box system i.e., levels which increase their energy as  $n^2$  thus ensuring the convergence of the partition function.

It is worth noting that the generation of the two types of levels by solving the Schrödinger equation for atomic hydrogen closed in a box is a well known phenomenon studied many years ago by De Groot and Ten Suldan [9] in their attempt to investigate the dependence of hydrogen polarizability on extreme pressure conditions. More recent applications deal with the use of such levels for the calculation of electron atom ionization cross sections [10,11] as well as for multiquantum well heterostructure applications [12]. Note also that very recently a multiauthor book [13] has been published collecting the different contributions on the solution of quantum chemistry problem for confined hydrogen atoms, these results being in agreement with our numerical results.

To our knowledge the results of the quantum approach have been never applied to solve the problem of the divergence of the partition function. Solution, in fact, of the Schrödinger equation for atomic hydrogen in the presence of a Debye potential [14]

$$\varphi(r) = -\frac{e^2}{r} \exp -r/D \quad (10)$$

while affecting the energy levels in a way similar to the present approach does not transform bound levels in unbound ones [15].

Debye length and  $\delta$  introduce a sort of repulsive forces in the Schrödinger equation. To a given extent the essence of our approach, even though completely different, could be recovered by the Planck's paper. Planck starts distinguishing three classes of energy levels: those with energy  $E > 0$  (unbound), those near to the continuum and a class of actual bound levels ( $E < 0$ ). By using an ingenious quantum-classical approach the  $E > 0$  levels bring to the translational partition function for free proton-electron states. The second contribution is neglected in the Planck approach, while the third contribution brings to a convergent partition function. In our approach we self-consistently produce, by solving the Schrödinger equation of hydrogen atom in a box, bound and unbound levels connected by a transition zone, avoiding the division of classical levels performed by Planck. We can also anticipate that bound and unbound levels are affected by the

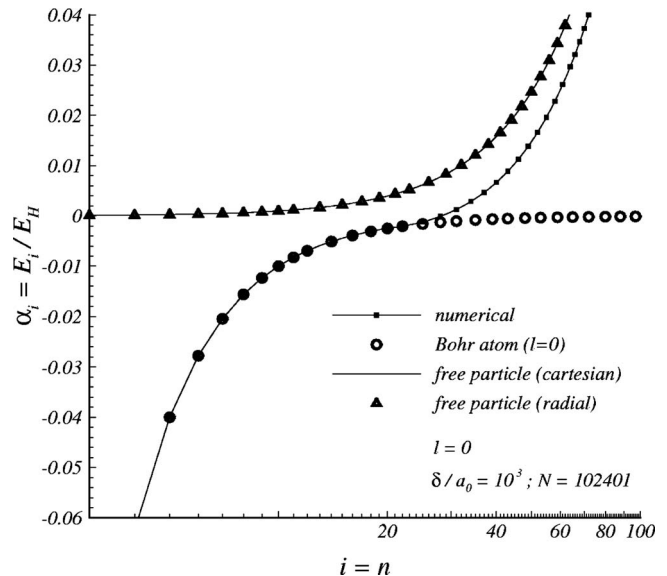


FIG. 1. Reduced energy levels calculated according to numerical ( $\delta/a_0=10^3$ ) and analytical (called Bohr atom) solution of the Schrödinger equation. In the same figure are also reported the particle in the box energy levels calculated numerically and analytically.

dimension of the box, this effect becoming dramatic for very small  $\delta$  values. This last point has been neglected by Planck by using classical and Bohr energy levels.

The outline of the present paper is as follows. In the next section we discuss the energy levels obtained by numerically solving the Schrödinger equation for different  $\delta$  values. Then we report the calculation of the reduced partition function from the obtained levels and a comparison of these results with the partition function obtained by using the Fermi criterion. Finally the last section is dedicated to perspectives and conclusions.

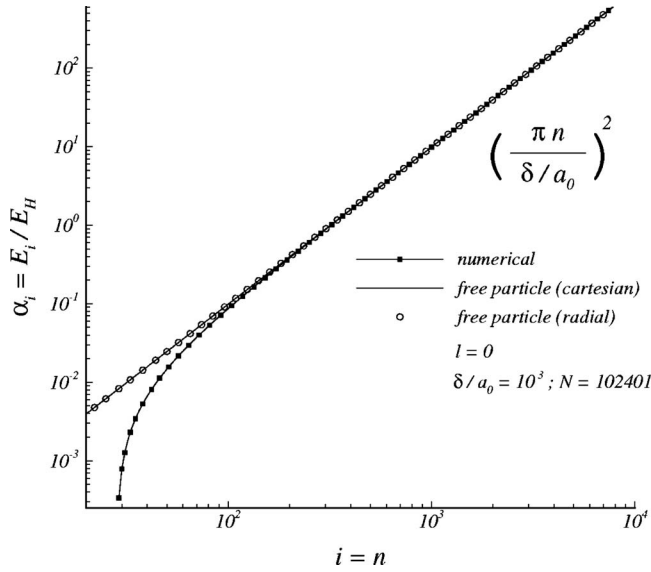
## II. ENERGY LEVELS

We solve the radial part of the Schrödinger equation for atomic hydrogen on a numerical integration grid by imposing the boundary conditions expressed by Eq. (9). The boundary condition  $R(r=\delta)=0$  is completely different from that one appearing in the analytical solution of the Schrödinger equation, i.e.,  $R(r=\infty)=0$ . The bulk of results refers to  $\delta/a_0=10^3$  and  $\delta/a_0=10^4$  values by imposing  $\ell=0$  in the radial part of the Schrödinger equation. In both cases we divide the integration grid in 102 401 points getting an equal number of energy levels (bound and free), which can be identified as  $ns$  levels. Details of the integration procedure will be reported elsewhere.

Figure 1 shows the numerical adimensional energy level values

$$\alpha = \frac{E_n}{E_H} \quad (11)$$

obtained with  $\delta/a_0=10^3$  as a function of the number of grid points which can be identified with the principal quantum

FIG. 2. Extension of results of Fig. 1 to very high  $n$ .

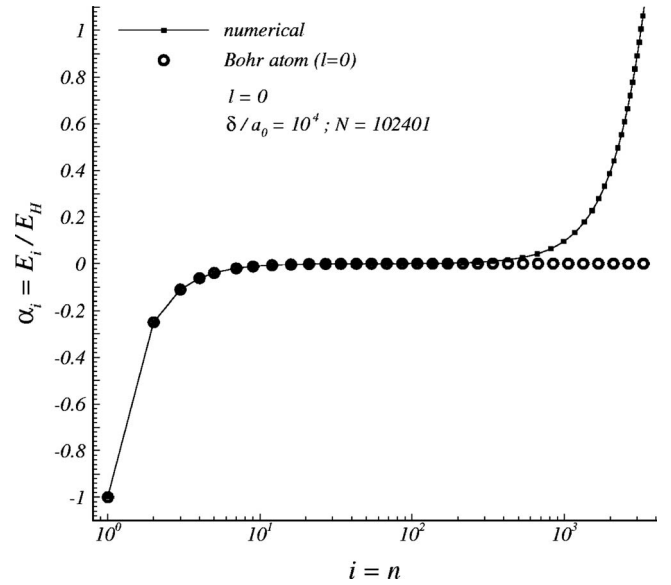
number  $n$ . In the same figure we have also reported the analytical reduced energy levels, i.e.,  $\alpha = -1/n^2$  (also called Bohr), which show the well known asymptotic trend of energy levels to  $\alpha=0$ . The numerical results present values which closely follow the analytical ones up to a given  $n$  suddenly becoming positive from  $n=28$  on. The numerical results clearly show the existence of two types of energy levels, the negative ones which can be assimilated to the bound states and the positive ones which represent the discretized continuum. These last levels strongly increase their energy with  $n$  asymptotically going to the analytical energy levels obtained by the particle in the box model described by the following equations (see for example Ref. [16])

$$E_n = \frac{h^2}{8m_e \delta^2} n^2, \quad (12)$$

$$\alpha_n = \frac{E_n}{E_H} = \left( \frac{\pi n}{\delta/a_0} \right)^2, \quad (13)$$

where  $m_e$  is the electron mass.

This behavior can be understood by comparing numerical values and analytical particle in the box results also reported in Figs. 1 and 2. Note the perfect coincidence of the particle in the box results obtained with the analytical formula (13) as well as by numerical integration of our atomic hydrogen model without Coulomb potential. Finally it is worth noting that the differences between numerical and analytical results (see Fig. 1) become important when the numerical energies become positive. Similar results have been obtained for  $\delta/a_0=10^4$  (see Fig. 3). In this case the numerical results reproduce the analytical ones up to  $n=89$  suddenly becoming positive from  $n>89$ . Again the positive levels asymptotically go toward the corresponding particle in the box values. Comparing the numerical results with  $\delta/a_0=10^3$  and  $\delta/a_0=10^4$  we can see that the increase of  $\delta/a_0$  shifts the onset of positive levels to higher  $n$  thus implying the disappearance of positive levels for  $\delta/a_0 \rightarrow \infty$ . On the other hand we can ex-

FIG. 3. A comparison of numerical and analytical reduced energy levels for  $\delta/a_0=10^4$ .

pect the disappearance of bound states for  $\delta/a_0 \rightarrow 0$ . This last point has been tested in the  $\delta/a_0$  range 2–4 where our values confirm the older observations of De Groot and Ten Seldan, as well as with the very recent calculations of Langhlin [17].

It is interesting to note that the values of  $n$  ( $\ell=0$ ), where there is the sharp transition between the Bohr and the box levels (28 and 89), can be approximated by  $C(\delta/a_0)^{(1/2)}$  with  $C$  close to 0.9. Suggestions to interpolate between the two regimes could be attempted by following the general mathematical approach in Ref. [18].

### III. REDUCED PARTITION FUNCTION

Let us now consider the reduced partition function calculated by inserting the numerical energy levels in Eq. (4) (only  $s$  states) assigning to each level a degeneracy of 2. The energy levels introduced in the partition function are referred to the ground state, i.e., so that all the numerical levels in this case become positive. The increase of energy levels as  $n^2$ , when the levels follow the particle in the box behavior, ensures the convergence of the partition function. Let us define the total reduced partition function  $f_t$  as

$$f_t = f_b + f_f, \quad (14)$$

where  $f_b$  is the contribution due the bound states and  $f_f$  the corresponding one from the discretized continuum.  $f_b$ ,  $f_b$  and  $f_f$ , all calculated from the numerical energies, have been reported as a function of temperature in Fig. 4 ( $10\,000 < T < 100\,000$  K). In the same figure we have also reported  $f_{bF}$  obtained by using the analytical levels up to  $n_{\max}$  given by the Fermi criterion as well as  $f_{fp}$  obtained by the analytical particle in the box model. It should be noted that  $f_{fp}$  is modulated by a factor  $\exp[-E_H/kT]$  and with a statistical weight of 2 to take into account electron spin multiplicity. Before examining the results we want to report how to calculate  $n_{\max}$  according to the Fermi criterion through Eq. (7). First

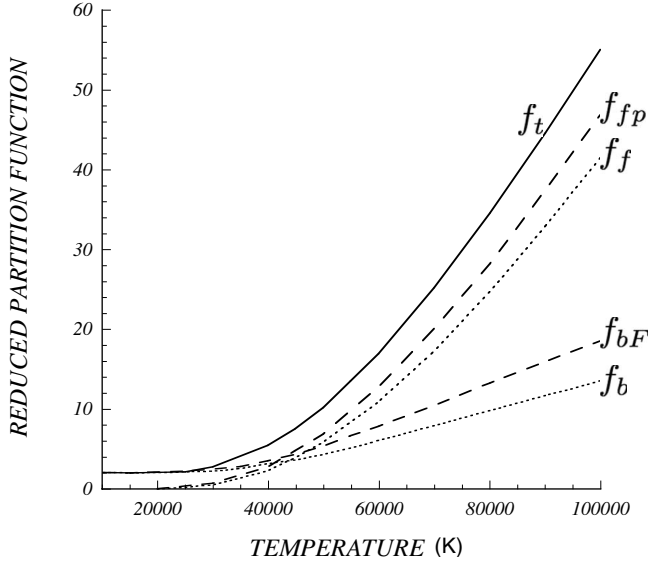


FIG. 4. Reduced partition functions  $f_t$ ,  $f_b$ ,  $f_f$ , and corresponding Fermi's,  $f_{bF}$ , and particle in the box,  $f_{fp}$ , values as a function of temperature.

we calculate the volume relative to the considered  $\delta/a_0$  value as

$$V = \frac{4}{3} \pi \delta^3 a_0^3 \quad (15)$$

so that  $V^{-1}$  represents the particle density  $N'$ . The value of  $n_{\max}$  is therefore given by the following equation:

$$n_{\max} = \left( \frac{4}{3} \pi \right)^{1/6} \delta^{1/2}. \quad (16)$$

We get for the two considered case studies i.e.,  $\delta/a_0=10^3$  and  $\delta/a_0=10^4$   $n_{\max}$  values respectively equal to 40 and 127. On the other hand, as anticipated, the onset of positive energy values from the present calculations occurs respectively at  $n=28$  and  $n=89$ . This means that we should expect  $f_b < f_{bF}$ ; on the other hand our  $f_f$  values should be less than the corresponding ones obtained by the particle in the box model since in this last case we are summing on an infinite number of levels rather than on the finite number of levels i.e., 102, 401. Inspection of the results confirms these qualitative considerations. Note that in any case  $f_b$  and  $f_{bF}$  as well as  $f_f$  and  $f_{fp}$  closely follow the same trend as a function of temperature. Similar results occur for the other  $\delta/a_0=10^4$  case study.

The previous results indicate that a hydrogen atom closed in a box naturally brings to a self-consistent cutoff criterion of the electronic partition function.

Going beyond this approximation can be done by calculating all the energy levels with different  $\ell$  values. Here we report the calculation involving  $\ell \neq 0$  for the  $\delta/a_0=10^3$  case. Figure 5 reports the energy levels as a function of  $(n-\ell)$  at different  $\ell$  in the  $\ell$  range 0–41, while Fig. 6 is a different representation as a function of  $\ell$  for selected  $n$  values. We can see that the quantum number  $\ell$  starts affecting the results

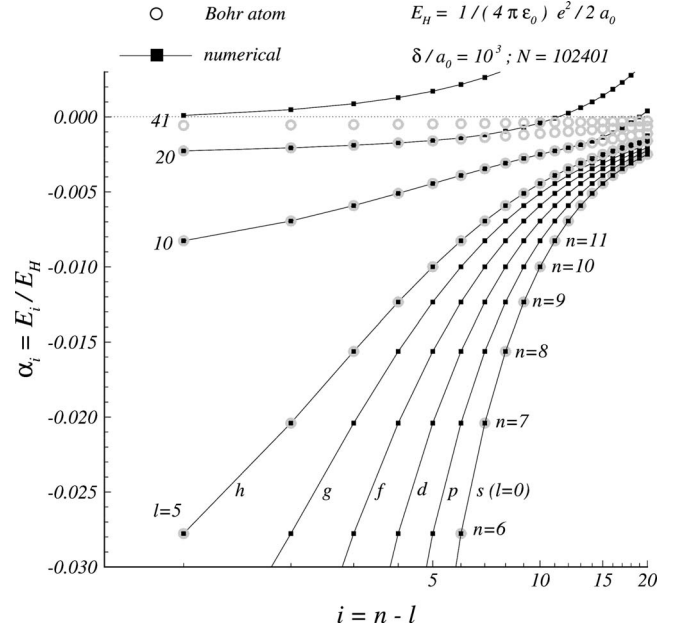


FIG. 5. A comparison of numerical and reduced energy levels for  $\delta/a_0=10^3$  for different  $\ell$  values.

only for  $n > 15$ . On the other hand the dependence on  $\ell$  becomes dramatic when we consider very small  $\delta/a_0$  values [17].

#### IV. PERSPECTIVES AND CONCLUSIONS

We have reported the effect of a closed box on the energy levels of atomic hydrogen. This approach indicates that the levels are split in two classes; the first one reproduces the behavior of the bound states obtained by the analytical solution of the Schrödinger equation, while the second one describes unbound states, which asymptotically go toward the

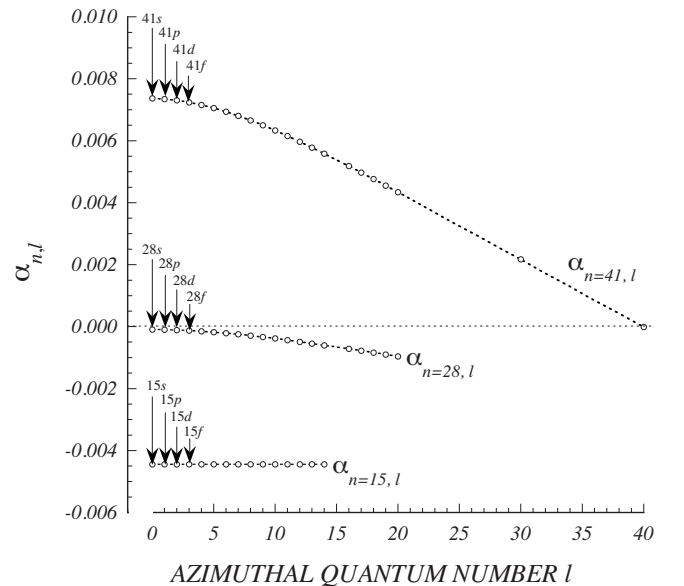
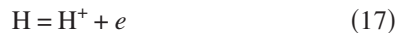


FIG. 6. Reduced energy levels for  $\delta/a_0=10^3$  as a function of  $\ell$ , for different  $n$  values.

levels from the particle in the box model. The results indicate a large dependence of level energy on  $\ell$  which in turn depends on the size of the box. The  $ns$  bound levels have been used to calculate a *reduced electronic partition function* which shows satisfactory agreement with the corresponding one obtained by using the Fermi cutoff criterion. The unbound levels on the other hand reproduce to a first approximation the particle in the box partition function i.e., the translational partition function. We believe that this approach can open interesting perspectives in statistical thermodynamics. First of all we can reformulate the Saha's equation for the ionization equilibrium



by writing it as

$$\text{H}(b) = \text{H}(f), \quad (18)$$

where  $\text{H}(b)$  and  $\text{H}(f)$ , respectively, represent bound and unbound energy levels obtained by solving the Schrödinger equation in the closed box. In this way we treat bound and unbound levels on the same basis avoiding the assumption made in the Saha's equation of treating the bound levels from the analytical Schrödinger equation (atom in the universe) and the unbound levels from the particle in the box model.

According to the "chemical picture" [Eq. (17)] the Saha's equation assumes the well-known form

$$\frac{N_e N_{\text{H}^+}}{N_{\text{H}}} = \frac{(2\pi m_e kT)^{3/2} V}{h^3} \frac{2}{f_{\text{H}}} \exp\left(-\frac{E_{\text{H}}}{kT}\right), \quad (19)$$

where  $N_e$ ,  $N_{\text{H}^+}$ , and  $N_{\text{H}}$  represent in the order the electron, atom and neutral particle numbers and  $f_{\text{H}}$  the internal partition function of atomic hydrogen ( $f_{\text{H}^+}=1$ ). The multiplicity of free electron is given by the factor 2.

Following Eq. (18), i.e., the "physical picture," we can write an equilibrium constant

$$K = \frac{N_f}{N_b} = \frac{f_f}{f_b} = \frac{N_{\text{H}^+} N_e}{N_{\text{H}}}, \quad (20)$$

where we have identified  $N_f = N_{\text{H}^+} N_e$  and  $N_b = N_{\text{H}}$ . Moreover considering

$$f_b \approx f_{\text{H}},$$

$$f_f \approx \frac{(2\pi m_e kT)^{3/2} V}{h^3} 2 \exp\left(-\frac{E_{\text{H}}}{kT}\right)$$

we recover the Saha equation.

Another interesting perspective is to understand some non linear effects in plasma physics by investigating the energy levels from the numerical calculation of Schrödinger equation in the box allowing the presence of a Debye potential [15].

#### ACKNOWLEDGMENTS

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