

Analytic partition function for plasmas

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Recibido el 18 de octubre de 2004; aceptado el 12 de septiembre de 2005

The partition function for atoms in a gas with partial ionization is obtained by assuming that the internal and atomic linear energy densities are equal, and considering that the kinetic energy per degree of freedom is sufficient to ionize the upper levels of the atoms, and, at the same time, approximating the sum by an integral, which we solve using the mean value theorem for integrals. The resulting function reproduces the behavior of the partition function in the region of validity of perfect gases; it is also analytic and compact.

Keywords: Partition function; plasmas; equation of state; stellar atmospheres.

La función de partición para átomos en un gas con ionización parcial se obtiene suponiendo que las densidades lineales de energía interna y atómica son iguales, y considerando que la energía cinética por grado de libertad es suficiente para ionizar los niveles superiores de los átomos y al mismo tiempo, aproximando la suma por una intergral, la cual resolvemos usando el teorema del valor medio para integrales. La función resultante reproduce el comportamiento de la función de partición en la región de validez de los gases perfectos, además es analítica y compacta.

Descriptores: Función de partición; plasmas; ecuación de estado; atmósferas estelares.

PACS: 05.70.Ce; 52.25.Kn; 97.10.Ex

1. Introduction

The partition function, called the sum over the states or grand sum (Zustandsumme) by Boltzmann, is the sum of the products of the statistical weights of the energy states of an atom multiplied by the Boltzmann factors, Eq. (1) below. This sum diverges for an isolated atom due to the existence of an infinite number of energy levels where the Boltzmann factors remain practically constant and the statistical weights grow with the increase in energy of the levels. We are interested in evaluating the partition function of the atoms and ions in a partially ionized perfect gas in thermodynamic equilibrium. To carry out this evaluation, it is necessary to find the last internal level an atom or ion can have under the temperature and pressure conditions in the gas. Therefore, we want to find the maximum level that the atoms can attain. Furthermore, once the maximum level is known, one should attempt to find a way of evaluating the sum, developing a fast, efficient method to calculate the partition function many times, for a great number of chemical elements in different states of ionization, in the iterative processes necessary to evaluate the state equation for plasmas and stellar atmospheres. This will be achieved, on the one hand, by considering one of the funda-

mental concepts of statistical mechanics and of the thermodynamics of a perfect gas, the internal energy, and on the other hand, from the basic physical concepts of atomic structure, the internal energy of the atom. In the calculation of the thermodynamic properties of a gaseous system, it is necessary to know the partition function for each chemical species in its different states of ionization in order to determine the populations in plasmas, planetary and stellar atmospheres. From the partition function, one can obtain the Helmholtz free energy and from this the other thermodynamic variables. In all these applications, it is necessary to evaluate repetitively the partition function for each ion of all the chemical elements of the mixture in the gas. Most of the previous methods introduce the electrical interactions among the atoms to explain the absence of high energy levels. When the gas is very dilute and at a low temperature, there are few ionizations and, therefore, there are few charged particles, and consequently the atom would behave as the theoretical atom with an infinite number of levels. The perfect gas by definition does not allow interactions among the particles. In the gas, the particles are immersed in a medium with a finite temperature and therefore governed by the internal energy of the gas. On

the other hand, traditionally, the sum that defines the partition function is evaluated, taking into account very few terms of the power series expansion of the exponentials, and furthermore, this does not produce compact analytical solutions necessary for the repetitive calculations that we mentioned before, where one must pay attention to the numerical behavior of the processes. In what follows, we present in Sec. 2 the physical model and the principal assumptions made to find the maximum level that could exist in an atom or ion with respect to the main variables of the system. The assumptions and mathematical development to find the approximate partition function are derived in Sec. 3, as well as the derivatives of the partition function with respect to the temperature and pressure in the gas. The results of the calculations are presented in Sec. 4, where we show the behavior of our model with respect to other models as well as the comparison with the exact partition function for hydrogen. Finally, in Sec. 5, some conclusions are presented.

2. Model

The partition function is of vital importance in statistical mechanics, since through the Helmholtz free energy one can evaluate the remaining important variables of thermodynamics. The partition function is defined as

$$u_{jk} = \sum_{i=1}^{\infty} g_{ijk} e^{-\frac{E_{ijk}}{k_B T}} \quad (1)$$

where g_{ijk} is the statistic weight of level i and E_{ijk} is the excitation energy of the level with respect to the ground state of the atom or ion j of the element k , and k_B is the Boltzmann constant. We consider an atom in a perfect gas at temperature T with a total number of particles N per unit volume or the pressure from the perfect gas equation $P = Nk_B T$. One of the most important variables of a perfect gas is, as we have said before, the internal energy that defines the state of motion of the gas particles and is proportional to the temperature of the system. From the equipartition theorem of the energy, one can obtain the energy per degree of freedom and per particle. Each particle in the gas has a natural volume, which we take as cubic. In the cube, the energy density per degree of freedom is obtained by dividing this energy by the side of the cube. Now, the linear energy density in the atom is equal to the energy of the level divided by the size of the orbit of the electron in that level. One of the two main assumptions in this work is that these two linear energy densities are equal. The other assumption is that the kinetic energy of the atoms must be capable of ionizing the electrons that lie above a certain level that we will call the maximum level in the atom. To find the mathematical solution of the problem, following Unsöld [1], we divide the sum (1) into two parts, a sum that takes into account the lowest levels of the atom and the other that considers the rest of the levels. The simplest and oldest model, with purely geometric suppositions, considers that the atom cannot have orbits outside its corre-

sponding volume in the gas [2,3,4]. There have been different physical models that consider the disturbances of the most external levels of the atom by the electrical forces produced by the charged particles in the surrounding medium. Robertson and Dewey [5], Lanczos [6], Pannekoek [7], and Inglis and Teller [8] studied the problem of the merging of the hydrogen lines; Unsöld [1], de Jager and Neven [9], Rogers, Graboske and Harwood [10], Fischel and Sparks [11], and Hummer and Mihalas [12] solved the problem for the equation of state calculations. From the internal energy of a perfect gas, together with the free energy that is proportional to the logarithm of the partition function, one can obtain the entropy, the enthalpy, the specific heats, as well as the rest of the most important parameters of thermodynamics. With the linear energy density within the volume for each particle, we take into account the properties of the medium and with the atomic linear energy density we consider the atomic properties. Also, we consider, the ambient energy is capable of ionizing the electrons that are above a certain level in the atom. These physical assumptions are sufficient to obtain the solution to the problem of the maximum level, in a simple form, as a function of the temperature and of the total pressure of the gas. For problems where the pressure is obtained from the hydrostatic equation, this solution is important and also when the pressure is the main variable of the system. The results are consistent with the given physical assumptions.

3. Mathematical formulation

The volume occupied by each particle in the gas is taken as cubic and of side L , and so is defined by

$$L^3 = \frac{1}{N} = \frac{k_B T}{P} \quad (2)$$

The energy, in absolute value, of a hydrogen atom in state n is given by

$$E_n = \frac{e^2 z^2}{2a_0 n^2} \quad (3)$$

where e is the charge of the electron, z is the charge of the nucleus of the atom under study, a_0 is the Bohr radius and n is the principal quantum number of the energy level. The internal energy in the gas per particle and per degree of freedom is

$$\frac{1}{2} k_B T \quad (4)$$

Then, by our first assumption, we equate the energy densities to obtain the following expression:

$$\frac{\frac{1}{2} k_B T}{L} = \frac{E_n}{2\pi r_n}, \quad (5)$$

where r_n is the radius of the orbit for state n . Since

$$r_n = \frac{n^2 a_0}{z}, \quad (6)$$

we have

$$n^2 = \frac{E_n}{\frac{1}{2} k_B T} \frac{zL}{2\pi a_0}. \quad (7)$$

Now, using the difference in energies between the maximum level in the atom and the last one which is ionized, and by our other assumption, $E_{n+1} = (1/2)k_B T$, we obtain

$$\frac{E_n}{\frac{1}{2}k_B T} = 1 + \frac{2n+1}{n^2} = \frac{(n+1)^2}{n^2} \tag{8}$$

Hence, from (7) and (8) we get

$$n^2 = \frac{(n+1)^2}{n^2} \frac{zL}{2\pi a_0} \tag{9}$$

Manipulating this expression produces the second degree equation

$$n^2 - \sqrt{\frac{zL}{2\pi a_0}}(n+1) = 0, \tag{10}$$

whose solution is

$$n^* = \frac{q}{2} \left[1 + \sqrt{1 + \frac{4}{q}} \right] \tag{11}$$

with

$$q = \sqrt{\frac{zL}{2\pi a_0}} = \sqrt{\frac{zk^{\frac{1}{3}}}{2\pi a_0}} \left(\frac{T}{P}\right)^{\frac{1}{6}}. \tag{12}$$

Equation (11) gives us the maximum number of levels that the hydrogenic atom can have for temperature T and pressure P of the gas. The hydrogenic equation (11) is valid for the conditions of the perfect gas; furthermore, the formulas for the hydrogenic atoms are exact. For the other atoms and ions, the expressions change due to the fact that the remaining internal electrons of the atom shield the nucleus, as we shall see below. As is to be supposed, this equation (11) is not valid for large densities where the gas ceases to be perfect. In the problem of evaluating the sum, following Unsöld, expression (1) for the partition function is split into two parts. The first, as mentioned before, considers a reduced number of low levels of the atom and the second takes into account the range from the last level of the previous sum until the maximum level found in (11). That is,

$$u_{jk} = \sum_{i=1}^{n'} g_{ijk} e^{-\frac{E_{ijk}}{k_B T}} + \sum_{i=n'}^{n^*} g_{ijk} e^{-\frac{E_{ijk}}{k_B T}} = u + u' \tag{13}$$

The excitation energy of level $i = n$ in the atom is represented by

$$E_{ijk} = \chi_{jk} - \frac{Rhc z^2}{n^2}, \tag{14}$$

where χ_{jk} is the ionization potential of the ion j of the chemical element k , and Rhc is the energy of one Rydberg. The second sum can be approximated by an integral, since the higher levels are close together so that they appear to be a continuum; furthermore, using the statistical weights $g_{njk} = 2n^2$ for a hydrogenic atom and the second part of (13), one finds the following integral:

$$u' = 2e^{-\frac{\chi_{jk}}{k_B T}} \int_{n'}^{n^*} n^2 e^{-\frac{Rhc z^2}{n^2 k_B T}} dn. \tag{15}$$

This integral can be solved approximately, using the mean value theorem for integrals, that is,

$$\begin{aligned} \int_{n'}^{n^*} n^2 e^{-\frac{Rhc z^2}{n^2 k_B T}} dn &= e^{-\frac{Rhc z^2}{\xi^2 k_B T}} \int_{n'}^{n^*} n^2 dn \\ &= \frac{2}{3} e^{-\frac{Rhc z^2}{\xi^2 k_B T}} (n^*{}^3 - n'^3) \end{aligned} \tag{16}$$

with ($n' \leq \xi \leq n^*$). By numerical tests comparing our result with the second sum of (13), we propose that $\xi = n^*$; therefore,

$$u' = \frac{2}{3} e^{-\left(\frac{\chi_{jk}}{k_B T} - \frac{Rhc z^2}{n^*{}^2 k_B T}\right)} (n^*{}^3 - n'^3) \tag{17}$$

Using (14), we obtain finally

$$u' = \frac{2}{3} e^{-\frac{E_{n^*jk}}{k_B T}} (n^*{}^3 - n'^3). \tag{18}$$

For the hydrogenic atoms, one can take $n' = 2$, and then equation (13) is converted into

$$u_{jk} = g_{1jk} + g_{2jk} e^{-\frac{E_{2jk}}{k_B T}} + \frac{2}{3} e^{-\frac{E_{n^*jk}}{k_B T}} (n^*{}^3 - 8), \tag{19}$$

where E_{2jk} and E_{n^*jk} are the excitation energies of level 2 and of level n^* , respectively. For the hydrogenic atoms, one can begin the integral (15) from any level above 2, since the formulas for the hydrogenic atoms are exact, except that to go from the sum to the integral one supposes that n is large; however, from comparisons with the exact formulas, the errors are not large as we shall see in the results. For the other atoms and ions, the sum should start from levels higher than level 2. The derivatives of the partition function with respect to T and P are obtained from the first part of (13) and from (18), producing the following expressions:

$$\begin{aligned} \frac{du_{jk}}{dT} &= \sum_{i=2}^{n'} \frac{E_{ijk}}{k_B T^2} g_{ijk} e^{-\frac{E_{ijk}}{k_B T}} + \frac{2}{3} e^{-\frac{E_{n^*jk}}{k_B T}} \\ &\times \left[\frac{E_{n^*jk}}{k_B T^2} (n^*{}^3 - n'^3) + \left(3n^*{}^2 - \frac{Rhc z^2}{n^*{}^3 k_B T}\right) \frac{dn^*}{dT} \right], \end{aligned} \tag{20}$$

where we have

$$\frac{dn^*}{dT} = \frac{1}{2} \frac{dq}{dT} \left[\left(1 + \sqrt{1 + \frac{4}{q}}\right) - \frac{4}{q\sqrt{1 + \frac{4}{q}}} \right] \tag{21}$$

and

$$\frac{dq}{dT} = \frac{q}{6T} \tag{22}$$

together with

$$\begin{aligned} \frac{du_{jk}}{dP} &= \frac{2}{3} e^{-\frac{E_{n^*jk}}{k_B T}} \\ &\times \left[3n^*{}^2 - (n^*{}^3 - n'^3) \frac{Rhc z^2}{n^*{}^3 k_B T} \right] \frac{dn^*}{dP}, \end{aligned} \tag{23}$$

where

$$\frac{dn^*}{dP} = \frac{1}{2} \frac{dq}{dP} \left[\left(1 + \sqrt{1 + \frac{4}{q}} \right) - \frac{4}{q\sqrt{1 + \frac{4}{q}}} \right] \quad (24)$$

and

$$\frac{dq}{dP} = -\frac{Pq}{6}. \quad (25)$$

Following Fischel and Sparks [11] for the non-hydrogenic atoms, one can take the hydrogenic approximation for the statistical weights $g_{njk} = m_{jk}n^2$, where m_{jk} is a numerical factor that depends on the atomic structure of each ion j of the element k , for example $m_{02} = 4$ for neutral helium. In Eqs. (15) to (19) and in (20) and (23), the factor 2 should be replaced by m_{jk} and for the effective charge we take $z^* = z - S$, where S is the screening parameter that takes into account the effect of the electrons that surround the nucleus with charge z . For the case of very high levels that are close to hydrogenic, we have $z^* = j + 1$ ($j = 0$, for neutrals). Then, in all the previous equations, one should substitute z by z^* to take into account all types of neutral and ionized atoms. In this case, it is necessary to emphasize that all the expressions are valid for $n \gg 1$. The higher levels of the atoms are spaced very close to each other, which has permitted us to transform the second sum of (13) to the integral (15). This integral should be solved in order to obtain the partition function. Unsöld [1] was one of the first to evaluate the integral (17) approximately, expanding the exponentials in the powers series and integrating the resulting series term by term. The first term of his development, his equation (6), is similar to our equation (17) except that his formula does not contain the exponential term that appears in our formula. He also takes into account other terms in the expansion, but without changing the results much. Also, Fischel and Sparks [11] make a similar development but with more terms. These approximations do not guarantee more precision and, furthermore, they are not compact, and it is not known if one must evaluate as many terms as those of the original sum. Sum (1) can be solved directly, since the maximum level has been found above. When we have many levels, one can have problems of precision from numerical errors due to rounding. Furthermore, when one has to evaluate the partition functions of many ions in the iterative processes for the calculations of the equation of state in the various applications, it is necessary to have efficient analytical methods, where one could know the contribution of each term at each stage of the calculation. In many calculations only the first term of the equation (1) has been used; for certain cases this was thought to be necessary, above all, if the structure of the atom is not known, but as a rule it is not correct to do so because is a very rough approximation. When one obtains the sum (1) directly for very many levels, the process is not as efficient as our approximation of the partition function, especially for the non-hydrogenic atoms, because we do not know the numerical behavior of the statistical weights.

4. Results of the calculation

The Expression (17) is quite general for hydrogenic atoms and it can be applied without restrictions, except where the gas does not behave as a perfect gas. For the non-hydrogenic atoms, in addition to the conditions of the validity of the perfect gas assumptions, the integral u' must begin from higher levels, let us say 5 or 6, so that the levels are close to hydrogenic. The compact analytical formulas found for the maximum level that can exist in an atom under the temperature and pressure conditions in a gas are quite general for the hydrogenic atoms, since there are no approximations whatsoever. For the other atoms and ions, it is approximated and it is valid only for very high levels in the atom. The transformation of the sum to an integral is an approximation valid when the levels are very close to each other, as we have said above. These results are attractive for calculations of the equation of state because they are a function of the temperature and of the total pressure only, usually the main variables of interest in the gas. Our expression for the maximum number of levels is similar to that of the geometric model in which it is function of T and P , though the latter has a different functional form and is obtained from geometric suppositions; as we shall see below in the numerical results, its behavior is different. The models that use the perturbation by charged particles are a function of the number of electrons, *e.g.* Hummer and Mihalas, and Unsöld; and of the number of electrons and ions, as in Inglis and Teller, de Jager and Neven, and in Fischel and Sparks. Where one could make a real comparison among all these models, is at low densities, where the differences are more significant among all the models as we will see in what follows in this section.

Our numerical results of the maximum number of levels is presented in Figs. 1, 2, and 3, for the temperatures 2×10^3 , 10^4 , and 10^7 °K respectively, and vary with the logarithm of the electronic pressure P_e .

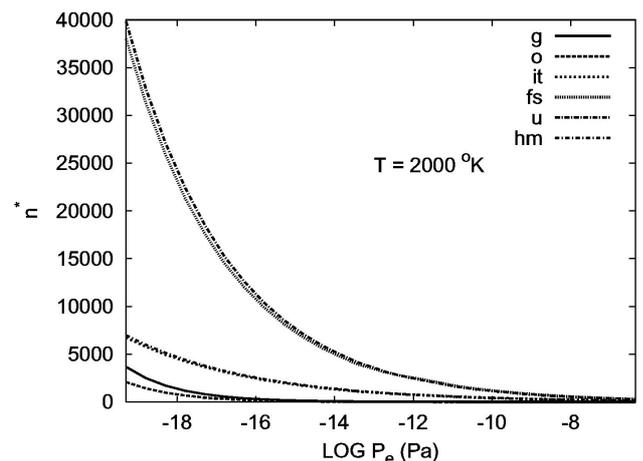


FIGURE 1. The maximum level n^* that an atom can have as a function of the logarithm of the electronic pressure P_e (Pa), for temperature $T = 2000$ °K for different models: geometric (g), our model (o), Inglis and Teller (it), Fischel and Sparks (fs), Unsöld (u), and Hummer and Mihalas (hm).

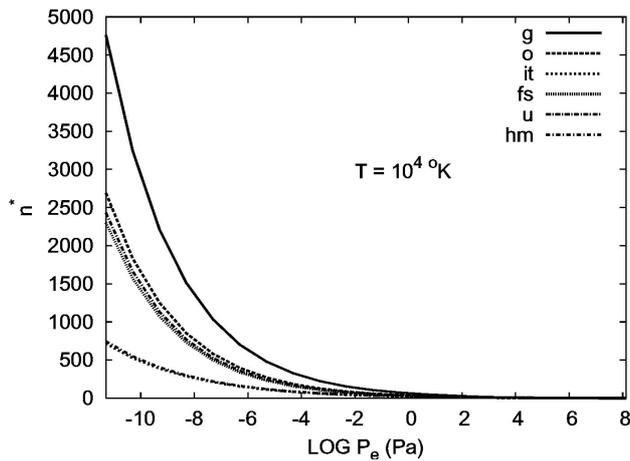


FIGURE 2. Same as Fig. 1, for temperature $T = 10^4$ K.

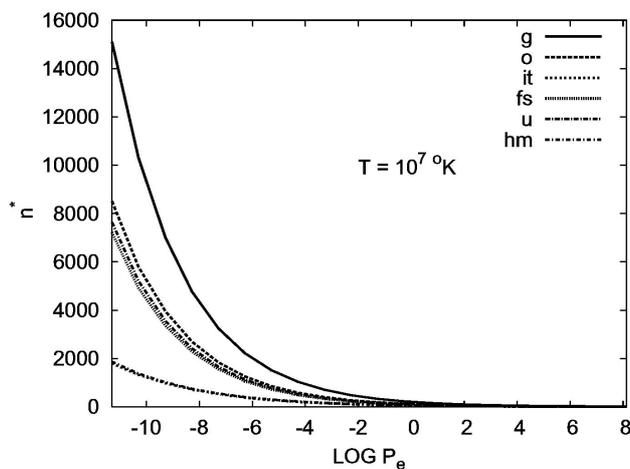


FIGURE 3. Same as Fig. 1, for temperature $T = 10^7$ K.

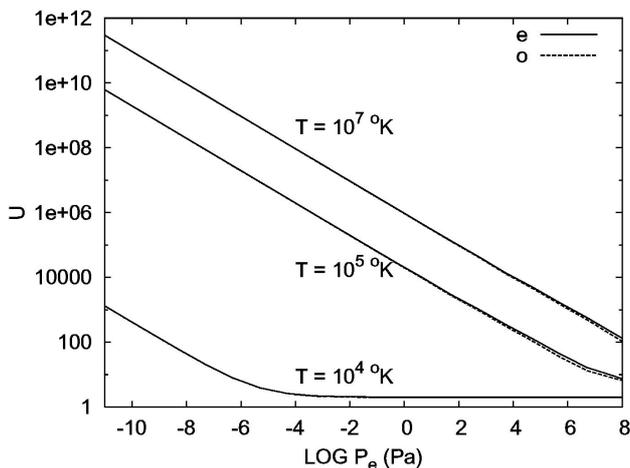


FIGURE 4. The partition function for the exact evaluation of equation (1) (e) and our formula (18) (o), with respect to the logarithm of the electronic pressure P_e (Pa), for temperatures $T = 10^4, 10^5,$ and 10^7 K.

These figures were calculated for total pressures P that go from 10^{-11} to 10^{21} Pa for a solar mixture of the chemical el-

ements. These calculations show the behavior of our model with respect to the models of Inglis and Teller, Unsöld, Fischel and Sparks, and Hummer and Mihalas. For this case, the results of de Jager and Neven are similar to those of Fischel and Sparks. As one can appreciate, on the graphs for low temperatures our results produce few levels compared with the other model, except the geometric one, due to the fact that the number of electrons and of ions is low, and, therefore, the disturbances do not exist and the atoms tend to behave as if they were isolated. Our results are physically correct, since the atom is always immersed in the gas where there is a finite temperature. For higher temperatures and low densities, our results are similar to those of Unsöld, and for very high pressures they look like those of Hummer and Mihalas. The agreement with the model of Unsöld for low density is due to the type of interaction used by him, which is good for low densities (Hummer *et al.*, [12]). For very high densities, the models of Inglis and Teller and of Hummer and Mihalas use a form of interaction valid for high pressures. The assumptions made to obtain our results are simple, physically correct and sufficient to describe the phenomenon. As can be seen, the results are robust and represent the state of an atom in a gaseous medium for any temperature and pressure within the limits of validity of the perfect gas. In Fig. 4, we have drawn the partition function, for the same mixture of the elements as above, as a function of the electronic pressure for total pressures that go from 10^{-11} to 10^{16} Pa for hydrogen using the exact sum (1) directly and our approximation (18).

These results show that the approximation is good especially for low temperatures as in Fig. 4, where the results are indistinguishable from one another for the temperature $T = 10^4$ K and for low pressures. For high pressures, they change behavior due to the small number of levels in the atoms and our approximation fails. The approximation can be improved taking into account more terms in the first sum of (13). Also all, the comparisons with the other methods show that the model is sufficiently good to describe the behavior of the partition function. With this simple formulation, one succeeds in representing the partition function analytically in a compact form, something that is very important in calculating planetary and stellar atmospheric models, and is also the case in different types of plasmas. The agreement for our n^* with some models is not good, but neither is it good among some of them, nor for models with similar derivations as those of de Jager and Neven and of Fischel and Sparks, also between Inglis and Teller, and Hummer and Mihalas. Nevertheless, for each pair of those mentioned above, the behavior is similar but not equal. Our equations are not applicable to very high densities, but even so the results are comparable with the results of other models, particularly those of Hummer and Mihalas. The suppositions made in order to transform sum (1) to the integral (15) are for very close levels, which is only achieved for high principal quantum numbers. The solution of the integral using the mean value theorem for the integral gives good results, as we have seen in the figure, with the advantage that it produces a compact analytical ex-

pression. The same happens with the approximations made for the non-hydrogenic atoms. The interactions between the particles that compose the gas were omitted because, by definition, in a perfect gas the thermodynamic effects dominate. The comparison with the direct evaluation of the sum shows that the disagreements are very small, less than 1%, as mentioned before. It would be conveniente to seek observational results on the number of lines observed at low temperatures in the interstellar material using radioastronomical techniques, in order to make a more general comparison with the other methods. In the absence of observational data, we made the comparisons with the direct evaluation of the sum; we believe that this is the only real comparison that one can make.

5. Conclusions

With two simple fundamental physical assumptions, we have been able to obtain the maximum level that a hydrogenic atom can reach in an ionizing gas, a result that is exact and valid for the perfect gas conditions. For the non-hydrogen atoms, the results are valid when one considers high lying levels in order to use the approximate effective charge and

hydrogenic statistical weights. The partition function that we have found has two parts; the first one is the exact sum of the lower few levels, the second one is our Eq. (18). This Eq. (18) is the result of two approximations; the first one is to transform the sum into an integral, and the second one is the result of applying the mean value theorem for integrals, given a lower bound to the integral. Therefore, we have obtained an approximate partition function for atoms in an ionizing gas in a compact analytic form. Our model and the resulting equations are important for the calculation of the equation of state of partially ionized gases, in plasmas and stellar atmospheres, because they permit the evaluation of the thermodynamic properties of these systems, monitoring the behavior of each one of the variables considered. Also, it is possible to find analytically the derivatives with respect to the temperature and pressure.

Acknowledgments

We acknowledge partial support from CONACYT to project 34564-E.

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