

Calculation of the maximum number of vibrational and rotational energy states for diatomic molecules

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Recibido el 9 de agosto de 2011; aceptado el 1 de marzo de 2012

A procedure for finding the maximum number of energy states for a diatomic molecule is presented. We consider the background energy of a gaseous thermodynamic system containing atoms, diatomic molecules and their ions, together with the spacing of adjacent energy states in the molecules. Using similitude and dimensional analysis techniques and defining linear energy densities of the molecular and thermodynamic systems we obtain expressions for the maximum levels that a molecule can attain. These results are relevant for the correct evaluation of the partition function.

Keywords: Equation of state; diatomic molecules; plasma: diagnostics.

Se presenta un método para obtener el máximo número de estados energéticos de una molécula diatómica. Se considera la energía del sustrato del sistema termodinámico gaseoso el cual está constituido por átomos, moléculas y sus respectivos iones, así como el espaciamiento entre niveles adyacentes de energía de las moléculas. Usando técnicas de similitud y análisis dimensional y definiendo las densidades lineales de energía de la molécula y del sistema termodinámico, se obtienen las expresiones de los niveles energéticos máximos que la molécula puede alcanzar. Estos resultados son relevantes para la correcta evaluación de la función de partición.

Descriptores: Ecuación de estado; moléculas diatómicas; plasma: diagnóstico.

PACS: 51.30.+i; 31.15.vn; 52.70.-m

1. Introduction

The maximum number of vibrational and rotational states of a partially ionized and dissociated perfect gas consisting of diatomic molecules is important for evaluating the vibrational and rotational partition function which is fundamental to calculate the equation of state for plasmas and stellar atmospheres. It is important to note that neither a plasma nor a stellar atmosphere is in global thermodynamic equilibrium however it is possible to make an analysis of the system by considering regions with local thermodynamic equilibrium, therefore without loss of generality we will consider that the gas is in thermal equilibrium. When the partition function of such a system is evaluated, in most of the cases, the number of energy levels is considered as infinite and everything is evaluated under this assumption [3]. However the physical conditions of a thermodynamic system impose restrictions in the number of energy levels through the mean internal energy [4]. In the present paper, we calculate the maximum number of vibrational and rotational states of a perfect gas consisting of diatomic molecules, atoms and their ions. This calculation is based, on the one hand, on the relationship between the energy equipartition principle per degree of freedom and the internal energy; and on the other hand on basic concepts of molecular structure: the internal energy of the molecules together with similitude and dimensional analysis techniques [1].

The outline of the paper is as follows: In Sec. 2, based on quantum mechanical considerations the vibrational and rotational energy states of a diatomic molecule are introduced. Sec. 3 includes the procedure to obtain a relation between the

dissociation energy and the last discrete energy levels firstly, from a geometric point of view and later on with a physical approach. In Sec. 4, one discusses some numerical results for hydrogen chloride (HCl) and finally in Sec.6, some conclusions are presented.

2. Energy States of Diatomic Molecules

As it is well known, the energy states of a molecule are the result of its electronic configuration, the relative vibrations of its atoms and the rotation of the molecule as a whole.

We consider a diatomic gas for which $k_B T$ is small compared with the energy of dissociation E_{diss} ; for different molecules this amounts to the condition, $T \ll E_{\text{diss}}/k_B \approx 10^4 - 10^5$ K. At these temperatures the number of dissociated molecules in the gas would be quite insignificant. At the same time, in most cases, there would be practically no molecules in the excited states as well, for the separation of any of these states from the ground state of the molecule is in general comparable to the dissociation energy itself. Accordingly, in what follows we take into account only the lowest electronic state of the molecule. Hence, in the developments presented in this work, we consider only the vibrational and rotational states of the diatomic molecules.

2.1. Vibrational States

According to quantum mechanics the vibrational energy states of a diatomic molecule correspond to the eigenvalues of the internuclear potential energy. For the lowest energy levels this potential can be approximated by the potential of

a harmonic oscillator whose eigenvalues, in terms of the intrinsic oscillator frequency ν_0 , are given by the following expression

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0, \quad (1)$$

for $v = 0, 1, 2, \dots$, the vibrational quantum number, where h is the Planck constant. The oscillator intrinsic frequency is given by

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \quad (2)$$

with k the force constant of the oscillator and μ the reduced mass of the diatomic molecule [5,6]. It is probable that some vibrational states of the diatomic molecule may not be well described by the harmonic oscillator potential however a detailed treatment of them is beyond the scope of this work.

2.2. Rotational States

The lowest rotational energy states of a diatomic molecule, derived from quantum mechanics, can be approximated by the energy levels of a rigid quantum rotor which for the moment of inertia I are expressed by

$$E_K = \frac{K(K+1)h^2}{8\pi^2 I}, \quad (3)$$

for $K = 0, 1, 2, \dots$, the rotational quantum number [7]. As in the previous case, some rotational states may not be adequately described by this approximation but we leave their analysis for future work.

3. Thermodynamics of a gaseous system composed of diatomic molecules

The main variables that describe a gaseous system in thermodynamic equilibrium are connected functionally by the equation of state. By definition in a perfect gas the particles interact only through collisions. In such a gas, the particles are immersed in a medium with finite temperature and therefore are governed by the internal energy. The equation of state of a weakly ionized gas, composed by atoms, diatomic molecules and their ions, relates the temperature T , the pressure P and the total number density of particles N by the equation

$$P = Nk_B T \quad (4)$$

where k_B is the Boltzmann constant. The imperfect nature manifests itself only at very high densities and it is not the case in the astrophysical scenarios where the contents of the present work can be applied [2]. The mean internal energy per particle of the system is given by thermodynamics and statistical mechanics as

$$U = \frac{3}{2} k_B T \quad (5)$$

and is one of the most important parameters for characterizing a thermodynamic system in equilibrium [8,9].

3.1. Procedure for Obtaining the Number of Levels in Diatomic Molecules

There are no restrictions in the number of energy states available for an isolated molecule before dissociation. But a molecule in a thermodynamic system is subjected to the interaction with other molecules through collisions and with the background energy that permeate the system making the number of energy states available dependent on the physical conditions of the system. The techniques of similitude and dimensional analysis are used in developing the procedures for deriving the maximum number of states in a diatomic molecule given the physical conditions in the system under study. For this purpose one defines linear densities of the energy of the diatomic molecules and of the mean energy per particle of the thermodynamic system through a procedure similar to the one used in the atomic case [4]. We consider two approaches for obtaining the number of states for the different vibrational and rotational states. On the one hand, the geometric formulation, where one considers only the size of the box that each particle occupies in the thermodynamic system as a measure of the size of the molecule. On the other hand, the physical approach where one considers one of the most important variables of a thermodynamic system the mean energy per particle as the governing agent in setting the size of the molecules.

3.2. Geometric formulation

In a thermodynamic system with total number density of particles N the volume occupied by each particle is given by

$$L^3 = \frac{1}{N}, \quad (6)$$

considering that the volume occupied by the particle is cubic and of side L . This imposes a maximum size that the molecule may have without invading the space of other molecules and therefore the number of states becomes finite, hence this condition is called geometric, because the energy states of the molecules are a function of the radial distance from the center of mass, among other quantum mechanical variables.

3.2.1. Vibrational states

The diatomic molecules behave as a harmonic oscillator for small displacements of the atoms from the center of mass. In this part we develop the procedure for obtaining the maximum vibrational state that remains in the molecule just after the dissociation energy. The total energy of a harmonic oscillator is given by

$$E_v = \frac{1}{2} k X^2, \quad (7)$$

where X is the maximum displacement or amplitude of the oscillator from the center of mass and k is the force constant of the oscillator. Making the assumption

$$L = 2X \quad (8)$$

and using Eq. (1), Eq. (6), Eq. (7), and Eq. (8) one obtains

$$v_g^* = \frac{k}{8h\nu_0 N^{\frac{2}{3}}} - \frac{1}{2}, \quad (9)$$

for the maximum vibrational level v_g^* of the diatomic molecule whose derivative with respect to N is

$$\frac{dv_g^*}{dN} = -\frac{kN^{\frac{1}{3}}}{12h\nu_0}, \quad (10)$$

that is necessary for some applications on the partition function.

3.2.2. Rotational States

The diatomic molecule rotates around the center of mass as if the two atoms were a single particle with mass equal to the reduced mass. In this part of the paper, for the rotational states we develop a procedure, similar to the one for the vibrational states, to obtain the maximum rotational state that remains in the molecules. From the results of Leighton [5] and Herzberg [7] the size of the rotating molecules is given by

$$r_K \approx \frac{K(K+1)h^2}{4\pi^2 r_K k I}, \quad (11)$$

here r_K is the internuclear distance, and r_e is the equilibrium position of the molecule. Making

$$L = 2r_K \quad (12)$$

and from Eq. (6) and Eq. (11), one obtains

$$K(K+1) = b \quad (13)$$

with

$$b = \frac{\pi^2 k I}{h^2 N^{\frac{2}{3}}} \quad (14)$$

and solving for K_g^* , the maximum possible rotational state of the molecule, yields

$$K_g^* = \frac{-1 \pm \sqrt{1+4b}}{2} \quad (15)$$

where distances are measured from the equilibrium position. The derivative of K_g^* with respect to N is

$$\frac{dK_g^*}{dN} = -\frac{2\pi k I N^{\frac{1}{3}}}{3h^2 \sqrt{1+4b}} \quad (16)$$

necessary for some applications on the partition function as well.

3.3. Physical Approach

The number of energy states of the molecules is delimited by the interactions with the rest of the system since the energy state above the last one becomes dissociated by the mean background thermal energy of the system under study.

3.3.1. Vibrational States

For the vibrational states the linear energy density is obtained from the mean energy of the system per degree of freedom divided by the size of the side of the cubic volume occupied by each particle.

$$\frac{U}{3L} = \frac{\frac{1}{2}k_B T}{L} = \frac{1}{2}k_B T N^{\frac{1}{3}} \quad (17)$$

Otherwise, the difference in energy between the two last adjacent vibrational states of the molecule is given by

$$E_{v+1} - E_v \approx h\nu_0 \left(v + \frac{3}{2} \right) - h\nu_0 \left(v + \frac{1}{2} \right) = h\nu_0 = \frac{E_{v+1}}{\left(v + \frac{3}{2} \right)} \quad (18)$$

so that, by setting

$$E_{v+1} = \frac{1}{2}k_B T, \quad (19)$$

that means that the molecule is dissociated for the state $v+1$, one obtains

$$\frac{E_v}{\frac{1}{2}k_B T} = \frac{\left(v + \frac{1}{2} \right)}{\left(v + \frac{3}{2} \right)}. \quad (20)$$

Additionally, making the two linear energy densities equal to each other, Eq. (17) and Eq. (20), the following result is obtained

$$\frac{\left(v + \frac{1}{2} \right)}{\left(v + \frac{3}{2} \right)} = 2XN^{\frac{1}{3}} \quad (21)$$

and using Eqs. (1) and (7) the solution for X gives

$$X = \sqrt{\frac{2\left(v + \frac{1}{2} \right)h\nu_0}{k}} \quad (22)$$

so that together with Eq. (20) and after some algebra (21) yields

$$v^2 - (3-c)v + \frac{9}{4} - \frac{1}{2}c = 0 \quad (23)$$

with

$$c = \frac{k}{8h\nu_0 N^{\frac{2}{3}}}. \quad (24)$$

Solving the quadratic equation for v , one gets

$$v_p^* = \frac{(c-3) + \sqrt{c^2 - 4c}}{2}. \quad (25)$$

for the maximum vibrational state v_p^* of the diatomic molecule, *i.e.* the last discrete energy state. Hence, the derivative with respect to N is given by

$$\frac{dv_p^*}{dN} = -\frac{kN^{\frac{1}{3}}}{24h\nu_0} \left[1 + \frac{c-4}{\sqrt{c^2-4c}} \right] \quad (26)$$

for some application on the partition function.

3.3.2. Rotational States

For the rotational states of the diatomic molecules, one defines the linear energy density similarly to the case of the vibrational states using the size of the orbit that the reduced mass makes around the center of mass. With the aid of (17), one gets

$$\frac{E_K}{2\pi r_K} = \frac{U}{3L} = \frac{1}{2}k_B T N^{\frac{1}{3}} \tag{27}$$

or

$$\frac{E_K}{\frac{1}{2}k_B T} = 2\pi r_K N^{\frac{1}{3}} \tag{28}$$

According to Eq. (3), the energy difference between the last two adjacent rotational energy states of the rigid rotator is given by

$$E_{K+1} - E_K = \frac{2E_{K+1}}{K+2} \tag{29}$$

making

$$E_{K+1} = \frac{1}{2}k_B T \tag{30}$$

the dissociation energy for state $K + 1$. Now from Eqs. (11), (28), (29), and (30), one obtains

$$\frac{K^2}{(K+2)^2} = \frac{K(K+1)h^2}{kI} N^{\frac{2}{3}} \tag{31}$$

or

$$\frac{dK}{(K+2)^2} = K(K+1) \tag{32}$$

with

$$d = \frac{kI}{h^2 N^{\frac{2}{3}}} \tag{33}$$

consequently, one obtains the following equation,

$$K^3 + 5K^2 + (8-d)K + 4 = 0 \tag{34}$$

that is a normal form of a cubic equation for K with real coefficients. The number of real solutions depends on the sign of the discriminant $D = R^2 - Q^3$ where

$$Q \equiv \frac{25 - 3(8-d)}{9} \tag{35}$$

and

$$R \equiv \frac{250 - 45(8-d) + 108}{54} \tag{36}$$

When $R^2 < Q^3$ the cubic equation has three real roots. Setting

$$\theta = \arccos\left(\frac{R}{\sqrt{Q^3}}\right), \tag{37}$$

the positive root useful in our work is

$$x = -2\sqrt{Q} \cos\left(\frac{\theta + 2\pi}{3}\right) - \frac{5}{3}, \tag{38}$$

so the maximum rotational state of the molecule is given by

$$K_p^* = x. \tag{39}$$

The derivative of K_p^* with respect to N is obtained using Eqs. (33) (35), (36) and (38), producing

$$\frac{dK_p^*}{dN} = -\frac{2kIN^{\frac{1}{3}}}{9h^2\sqrt{Q}} \left[\frac{Q^7 \sin\left(\frac{\theta+2\pi}{3}\right)}{R^2\sqrt{Q^3-R^2}} - \cos\left(\frac{\theta+2\pi}{3}\right) \right] \tag{40}$$

When $R^2 > Q^3$ there are not valid roots for our purpose.

In the following, other useful results are presented to complete the set of equations for the number of states in diatomic molecules. Whereas the energy spacing between vibrational levels in the quantum harmonic oscillator is constant and given by $h\nu_0$ near the equilibrium position only [5], the energy between adjacent levels decreases with increasing ν in the anharmonic oscillator approximation, so that the last discrete vibrational state before dissociation is given by

$$v_D = \frac{4D_e}{h\nu_0} - \frac{1}{2}. \tag{41}$$

This expression has been derived from the Morse potential function, where D_e is the dissociation energy of the molecule. This condition means that one can not surpass this natural maximum limit in the vibrational states imposed by the molecular dissociation. Indeed, the above derived expressions for the maximum of energy states apply below this limit. For the rotational energy states there are not results reported that give an upper bound for the number of energy states imposed by the physical conditions in the gas as for the case of the vibrational states. The energy spacing between rotational levels in the quantum rigid rotator is constant, the energy between adjacent levels decreases with increasing K for a nonrigid rotator. The energy formula for a nonrigid rotator for the state K is given by [7]

$$E_K = BK(K+1) - DK^2(K+1)^2. \tag{42}$$

Making Eq. (42) equal to zero one gets the maximum rotational number,

$$K_D = \frac{-1 \pm \sqrt{1 + 4\frac{B}{D}}}{2}, \tag{43}$$

where

$$\frac{B}{D} = \frac{4\pi r_e^2 k l}{h^2}. \tag{44}$$

This maximum rotational number corresponds to the last rotational state before dissociation consequently, it imposes a natural maximum limit on the number of the rotational states that only depends on the dissociation energy of the molecule. Therefore, the number of rotational energy states is finite and just below this maximum rotational number the above derived equations apply.

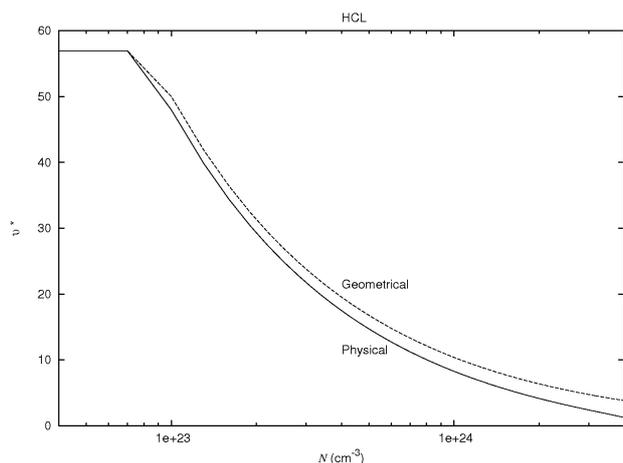


FIGURE 1. Maximum vibrational states of a diatomic molecule as a function of the total number density of particles

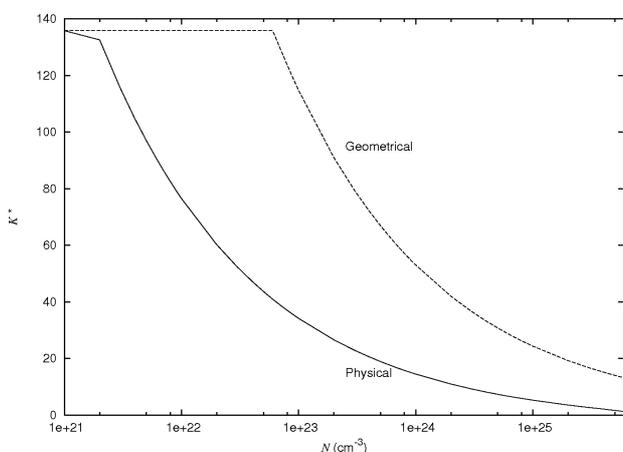


FIGURE 2. Maximum possible rotational states of a diatomic molecule as a function of the total number density of particles

4. Numerical Results for the Number of States for Some Diatomic Molecules

In this section numerical results from the derived equations for the maximum number of states in diatomic molecules as a function of the total number density of particles [Eqs. (25), (39)] are shown. Figure 1 shows the behavior of the vibrational states and Fig. 2 shows the same but for the rotational states of the hydrogen chloride (HCl) molecule

by considering the geometrical and the physical constraints. The data for other molecules can be found in different publications [10,6,11]. In these figures one can observe that the physical constraints are more restrictive than the geometrical ones. In general for the low density regions the maximum number of states is controlled by the dissociation energy given by Eqs. (41) and (43) respectively. At high densities, *i.e.* at number densities of the order of 10^{22} cm^{-3} , the effects of the interactions of the crowded particles with the background energy begin to dominate the maximum number of states in the molecules. For higher densities the number of states decays faster for the physical constraints that are the most representative of physical conditions of the system.

5. Conclusions

When one takes into account the interaction of the molecules with the medium in a gaseous system the available number of vibrational and rotational energy states becomes finite. By defining linear densities of the molecular and thermodynamic energies with respect to their natural dimensions one can compare those linear densities to obtain expressions for the maximum states that the molecules can reach under the prevailing physical conditions of the thermodynamic system under study. These expressions depend on the number density of particles in the given system and become very useful for the calculation of the equation of state in plasmas and stellar atmospheres.

One has restricted the application of our method to the hydrogen chloride molecule because of its relevance from the astrophysical point of view. Hydrogen chloride has been detected at high densities in Orion Nebula [14]. HCL is also present in molecular clouds [13,15], dense interstellar clouds [16], interstellar medium [17], diffuse clouds [12] and in the sun [18,19]. Another application of the method proposed in the present paper is the theoretical calculation of partitions functions associated to stellar atmospheres [20-24].

Acknowledgments

The authors thank the referee for the critical comments, constructive remarks and valuable suggestions. We would like also to thank Dr. A L. Gelover-Santiago for useful discussions and G. Hernández, V. Cortés, T. Gallegos and A. López for computer support.

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