

# Electronic Partition Function Paradox

Almost any modern physical chemistry book will give some discussion of statistical thermodynamics in terms of the single-molecule partition function ( $Q$ ):

$$Q = \sum_i g_i e^{-\epsilon_i/kT}$$

where  $g_i$  and  $\epsilon_i$  are the degeneracies and energies of the states of the system. The zero of energy is usually taken to be the lowest energy state of the system, and the sum extends over all energy levels.

In many cases the energy of an atom or molecule can be approximately divided into a sum of electronic, vibrational, rotational, and translational energies. To the extent that this can be done, it is possible to separate the partition function into a product of electronic, vibrational, rotational, and translational partition functions. The electronic partition function is simply the sum over all electronic states,  $j$ :

$$Q_{el} = \sum_j g_j e^{-\epsilon_j/kT} \quad (1)$$

The statement is usually made that for most systems the energies of all electronic states except the ground state are much greater than  $kT$ , so that all of the terms in the sum are negligible except the first. This has energy equal to zero, so  $Q_{el}$  reduces to the degeneracy of the ground state. There are a few cases, (nitric oxide is one), where one or two other states have energies comparable to  $kT$ , and these can be included explicitly in the sum. Most of the electronic states will lie at such high energies as to make negligible contributions to the partition function.

The above statements about the lack of contribution of excited electronic states are usually presented as obvious, since it is easy to check that the exponential term is really extremely small for most excited electronic states at normal temperatures. The purpose of this paper is to point out that the conclusion is not at all obvious, and that the statements represent a considerable oversimplification.

Let us examine a specific case in detail. One for which quantum mechanics has been able to give "exact" solutions for the energy levels is the hydrogen atom. The discrete energy levels are given by the familiar formula:

$$\epsilon_n = \frac{2\pi^2\mu e^4}{h^2} \left(1 - \frac{1}{n^2}\right) = \mathcal{R} \left(1 - \frac{1}{n^2}\right), \quad n = 1, 2, \dots \quad (2)$$

Here  $\mu$  is the reduced mass of the atom,  $e$  is the electronic charge,  $h$  is Planck's constant, and  $n$  is the principal quantum number. The zero of energy is taken to be the ground state of the atom (2).  $\mathcal{R}$  is the Rydberg constant and is equal to about 109,678  $\text{cm}^{-1}$  or 13.60 eV (3). If we neglect spin degeneracy,

each quantum shell has a degeneracy of  $n^2$ , that is, there are  $n^2$  orbitals for the shell with principal quantum number  $n$ , all having the same energy. In addition to the discrete energy levels, there is a continuum of unbound states having energy greater than the ionization potential of the hydrogen atom.

We can now examine the electronic partition function  $Q_{el}$  of the hydrogen atom at 25°C. If we consider only the bound states this is given by:

$$Q_{el} = \sum_{n=1}^{\infty} n^2 e^{-\epsilon_n/kT} \quad (3)$$

Let us first look at the values of the exponential terms. For  $n = 1$ ,  $\epsilon_n$  is zero and the exponential is equal to one. For  $n = 2$ ,  $\epsilon_n = 10.20$  eV. Since  $kT$  at 25°C is  $2.569 \times 10^{-2}$  eV, the exponential term is  $e^{-397}$  or  $10^{-172}$ , surely a negligible number. For higher values of  $n$ , the energies rapidly approach the ionization limit of 13.60 eV and the exponential term approaches  $e^{-529}$  or  $10^{-230}$ . At first sight one would conclude that such terms are entirely negligible. However, the trouble lies in the fact that there are an infinite number of such terms. If one writes down the Schrödinger equation for the hydrogen atom there are an infinite number of solutions which correspond to bound states, and the sum must be extended over all of them. The sum then turns out to be infinity times  $10^{-230}$  which is infinite. To put it another way, a necessary condition for the convergence of an infinite series is that the general term should approach zero, and this is not the case for the series in eqn. (3). The exponential part approaches  $10^{-230}$  which is greater than zero, and there is the additional factor  $n^2$  which actually makes the general term of the series go to infinity as  $n$  gets very large. Thus the value of the electronic partition function calculated by eqn. (3) is infinity.

Suppose we wish to calculate the probability of finding the hydrogen atom in its ground state,  $n = 1$ . This is given by

$$\frac{g_1 e^{-\epsilon_1/kT}}{Q_{el}} = \frac{1}{\infty} = 0$$

i.e., the probability of finding the atom in its ground state is zero.

Now this result is clearly contrary to experience. Hydrogen is a common chemical substance and we always expect to find it in its ground state unless we have extremely high temperatures or some special conditions such as an electric discharge. Yet we have arrived at this conclusion using only the commonly accepted formulas of quantum mechanics and statistical mechanics. It is this contradiction which provides the title for this article, "The Electronic Partition Function Paradox." It suggests that either quantum mechanics

or statistical mechanics must be wrong. This is a problem which receives no mention in most books, and yet a resolution of the paradox is essential if we are to put any faith in these two fields of physical chemistry.

A view of the way out of this contradiction follows, but the reader may wish to think about it himself first. There are one or two objections which might be raised to the previous discussion which do not resolve the contradiction. One is that hydrogen atoms do not usually exist as such in the laboratory, but are found as hydrogen molecules. But this does not get one out of trouble, since it is well known (4) that molecules have "Rydberg states" in which an electron is in an orbital of high principal quantum number, and that these states obey an equation for the energy much like eqn. (2). The details of the energies may be different, but the fact of an infinite number of levels with a finite energy will be just as true for H<sub>2</sub> or for any other atom or molecule as it is for a hydrogen atom. Thus the electronic partition function will diverge for any molecule. Another possible objection is that highly excited atoms can interact strongly with neighboring atoms, and that this will affect the energy levels (5, 6). But again this interaction will not affect the conclusion that there are an infinite number of levels below some finite limiting energy.

The solution to the problem lies in a consideration of the size of the orbital for an electron in a state of large  $n$ . One can get an estimate of the size by taking the radius of the corresponding Bohr orbit for the electron. This radius is given by (3):

$$r = n^2 h^2 / 4\pi^2 \mu e^2 \quad (5)$$

The important thing is that the radius is proportional to  $n^2$ , and the radius of the orbit for  $n = 1$  works out to be about 0.529 Å (10<sup>-8</sup>cm). Using the proportionality to  $n^2$ , we can see that by the time  $n$  reaches a value of 10<sup>5</sup> the orbit will extend out about 50 cm from the nucleus. If the atom is contained in a flask of typical laboratory size, the electron will interact with the wall by the time the principal quantum number reaches about this size. If we assume that the electron stays in the flask, the wave functions would have to change from the hydrogenic functions to some distribution which is confined to the flask. This means that the wave functions for higher quantum numbers will resemble those of a particle in a box, and the energies of the states will be determined essentially by the Schrödinger equation for this case instead of the simple hydrogen atom equation. The energy levels for a particle in an infinite potential well will continue to rise without limit, and there will be only a finite number of levels lying below any finite energy. This means that the exponential term in the electronic partition function will indeed go to zero for this case. The series in eqn. (1) will converge like the translational partition function of a gas which involves the same sort of series.

An idea of the size of  $Q_{el}$  may be obtained in this case by cutting off the sum in eqn. (3) when  $n$  is about 10<sup>5</sup>. The first term is unity and the rest very small. We could get an estimate of the value of the sum by assuming that the exponential term is equal to its limiting value of 10<sup>-230</sup> for all terms but the first, and factoring this value out of the sum. This gives

$$Q_{el} \approx 1 + 10^{-230} \sum_{n=2}^{10^5} n^2 \quad (6)$$

The sum occurring in equation (6) can be shown to be given by

$$\sum_{n=2}^m n^2 = 1/3 m^3 + 1/2 m^2 + 1/6 m - 1$$

Since we need be concerned only with orders of magnitude, this can be taken to be of the order of  $m^3$  for large  $m$ . We can then set the sum in eqn. (6) equal to 10<sup>15</sup> and we obtain

$$Q_{el} = 1 + 10^{-215}$$

which is not significantly different from unity. If we use this value of  $Q_{el}$  in eqn. (4), we find the probability that the atom is in its ground state to be unity.

But, one might ask, suppose the atom is not in a flask but is out in space somewhere where the electron can move at any distance without interference. Would the electron then be expected to be in the lowest state? To investigate this, we can consider the size of the known universe, which is something of the order of 10<sup>28</sup> cm in radius. Applying eqn. (5) we find that the size of the orbit is comparable with the known universe when  $n$  is about 10<sup>18</sup>. Using the approximate evaluation of the partition function with the series terminated at  $n = 10^{18}$  gives  $Q_{el} = 1 + 10^{-176}$  which is still not significantly different from unity. Clearly the exponential factor of 10<sup>-230</sup> allows one to have an immense number of levels without worrying about the divergence of the partition function. Whether the universe is really finite or infinite is a question which may never be answered. Eqn. (1) would appear to diverge for an atom in a truly infinite universe. However, eqn. (4) applies only at equilibrium, and it is clear that the universe is not at equilibrium, so this would not be really contrary to experience.

We now see that the usual procedure of neglecting excited electronic states is, in fact, valid, although it is not obvious that this should be so. The apparent paradox of the divergent partition function can be resolved, and it does not mean that either quantum theory or statistical mechanics are wrong. One just must be careful to apply the theory to the real physical system and not to a hypothetical isolated atom at equilibrium in an infinite volume.

There is little mention of this problem in books on physical chemistry or statistical thermodynamics. Schrödinger does point out that the hydrogen atom should be enclosed in a large but finite box in order to apply the statistical formulas (7). The recent book by Andrews also has an exercise which involves this problem (8). This apparent paradox and its resolution are interesting points which deserve wider attention because they do point out some fundamental aspects of both quantum mechanics and statistical thermodynamics.

I would like to thank Professor S. J. Gill for calling my attention to the last two references.

#### Literature Cited

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