A paradox in the electronic partition function or how to be cautious with mathematics

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Abstract
When the electronic partition functions of atoms or molecules are evaluated in textbooks, only the contribution of the ground state is considered. The excited states' contribution is argued to be negligible. However, a closer look shows that the partition function diverges if such states are taken into account. This paper shows that the blind use of mathematics is the reason behind this odd behaviour.

When teaching a course on Statistical Mechanics or Chemical Physics, one is faced with the evaluation of the electronic contribution to the partition function of atoms and molecules. Such contribution can be written as

$$Z_{\text{elec}} = \sum_j g_j \, e^{-E_j/kT}. \tag{1}$$

The symbols have their usual meanings: E_j is the energy of level j, g_j is the degeneracy of that level, k is the Boltzmann constant and T is the temperature. Usually it is said that the only contribution to (1) comes from the ground state because the energies of the excited states are large compared with kT, and the contributions of those states are irrelevant. The aim of this paper is to show that the previous statement is true, but for a more subtle reason, and textbooks oversimplify the problem when dealing with it.

Let us analyse one particular case, that of the hydrogen atom, in detail. The motive for this choice is clear: there is an exact formula for the energy of its excited states. It is well known [1] that the energy of a state with principal quantum number n is given by

$$E_n = \frac{\mu e^4}{8\varepsilon_0^2 h^2}\left(1 - \frac{1}{n^2}\right) = R\left(1 - \frac{1}{n^2}\right). \tag{2}$$

As usual, μ is the reduced mass of the atom and e is the electric charge of the electron; R is the Rydberg constant with a value of 13.6 eV. We have taken the ground state, i.e. $n = 1$, as a reference level for the energy. Since n can take any positive value, there is an infinite number

of excited states. If electron spin is not considered, the degeneracy of each level is simply n^2, i.e. there are n^2 states with the energy given by (2).

Let us now evaluate the electronic partition function of the hydrogen atom. According to our previous considerations, it is given by

$$Z_{elec} = \sum_{n=1}^{\infty} n^2 \, e^{-E_n/kT}. \tag{3}$$

We want to calculate the contribution of each term to (3). For $n = 1$, from (2) we have $E_1 = 0$; the ground-state contribution is a 1 to the sum. The first excited state ($n = 2$) has an energy $E_2 = 10.20$ eV. Let us assume that the working temperature is $T = 298$ K (i.e. 25 °C); then, $kT = 2.569 \times 10^{-2}$ eV. The second term exponential is insignificant $e^{-397} \sim 10^{-172}$. For higher levels, the energy goes quickly to the ionization energy, i.e. 13.6 eV, and the exponential goes to $e^{-529} \sim 10^{-230}$. These values are so small that the usual explanation seems to be correct: their contributions to the partition function are negligible and they can be disregarded. However, a problem arises because there is an infinite number of terms in the series (3). Let us assume that the exponential value is e^{-529} except for the first term. Therefore, the following inequality can be written:

$$Z_{elec} > 1 + e^{-529} \sum_{n=2}^{\infty} n^2. \tag{4}$$

The generic term of the series on the right-hand side does not go to zero, i.e. the necessary condition for the convergence of a series is not fulfilled. It is not hard to prove that (4) diverges. It is known [2] that

$$\sum_{n=1}^{m} n^2 = \frac{1}{3}m^3 + \frac{1}{2}m^2 + \frac{1}{6}m. \tag{5}$$

Therefore, even if all terms in (3)—except the first one—are multiplied by 10^{-230}, the total sum diverges as m^3 when $m \to \infty$. We reach the paradoxical conclusion that the probability of finding a hydrogen atom in its ground state is zero! (Remember that such probability is $1/Z_{elec}$). Obviously this is a nonsense, and something should be wrong with the series (3).

This is not the only example in physics where a diverging series gives non-sensical results. Usually, the justification for using diverging series or integrals requires complex techniques— the renormalization of a field theory is a good example—; however, in the present case a bit of good physical sense solves the problem.

To solve the paradox, let us consider the size of the electronic orbital, and consider that it is well approximated by its Bohr radius. This quantity is given by [1]

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi \mu e^2}. \tag{6}$$

If $n = 1$, the orbital has a decent size ($\approx 0.5 \times 10^{-10}$ m); however, if $n = 10^5$, the resulting size is macroscopic (≈ 0.5 m)! This means that the electron wavefunction interacts with the vessel that contains the atom; therefore the wavefunction cannot be hydrogen-like. On the contrary, the electron will be better described by the wavefunctions of a particle in a box with infinite walls. And it is well known the energy of the excited levels in this situation grows as n^2 (i.e. $E_n \propto n^2$). Consequently, the exponential factor in the partition function decreases very rapidly and the generic term in the series goes very quickly to zero (for $n > 10^5$, it is $a_n \propto n^2 \, e^{-n^2}$).

We can estimate the contribution of the excited levels taking into account the cut-off introduced above. Suppose that the sum has only 10^5 terms, and all of them—except the

first one—are multiplied by 10^{-230}, i.e. the limiting value of the exponential factor. Using formula (5) to evaluate the sum:

$$Z_{elec} \cong 1 + 10^{-230} \sum_{n=2}^{10^5} n^2 \cong 1 + 10^{-230} \left(\frac{1}{3}(10^5)^3 + \cdots \right) \cong 1 + 10^{-215} \cong 1. \tag{7}$$

The only relevant contribution to the partition function comes from the ground state; therefore, the probability of finding the atom in such state is one.

Someone interested in astrophysics may ask what happens with a hydrogen atom in the outer space, not bounded by a vessel or laboratory walls. The present conclusion does not change. Let us assume a weird size for the electron orbital, and suppose it is as large as the Universe radius ($\approx 1.5 \times 10^{10}$ light-years $\cong 1 \times 10^{26}$ m). For this value, the quantum number would be $n \approx 10^{18}$, and repeating the estimation in (6) one gets $Z_{elec} \cong 1 + 10^{-230}(10^{18})^3 \cong 1 + 10^{-176} \cong 1$. Even in this case, the hydrogen atom is in its ground state; and notice that the temperature used for the calculation (298 K) is absurdly high for an atom in interstellar space.

In conclusion, the statement made by statistical mechanics textbooks is right; however, the given reason is wrong. $Z_{elec} = 1$ because there is a cut-off in the series motivated by physical considerations, and not because $kT \ll E_n$ for $n > 1$ as it is usually stated. It is true that the contribution due to an excited state is minuscule, but there are an infinite number of such states.

From this exercise in elementary Statistical Physics we profit in two ways: we understand why the contribution of excited states to the electronic partition function may be neglected; and we learn not to blindly trust in mathematics. A correct outcome from a formal point of view may lead to an absurd physical result, and a good student should use his/her physical intuition to check what he/she gets from mathematical manipulations.

Acknowledgment

References

[1] Alonso M and Finn E J 1992 *Physics* (London: Addison-Wesley Longman)
[2] Gradshteyn I S and Ryzhik I M 1980 *Table of Integrals, Series and Products* (New York: Academic)