

A new formula for the statistical weight for a sequence of Rydberg levels in an atom or ion

M Eriksson and H Lennerstad

Blekinge Institute of Technology, Department of mathematics and natural sciences, 371 79 Karlskrona, Sweden

E-mail: meo@bth.se

Abstract. We present a new formula for the total statistical weight of all Rydberg levels $G^{ion}(n_l, n_h)$ for which the principal quantum number n is between higher, n_h , and a lower, n_l , limits. This formula can be used for all atoms in the periodic table and for all corresponding ions.

1. Introduction

The statistical weight g of a set of quantum states defined by a set of quantum numbers describing a system is the total number of states possible with this set of quantum numbers. If all the states corresponding to the same set have a negligible energy difference, this set of states is often called one state and its statistical weight is called its degeneracy. In atomic physics the energy difference between different m_j states is negligible, as long as the states are not in a strong magnetic or electric field. Atomic states are mostly described by terms that describe how the spin and angular momenta of the valence electrons have coupled and the resulting final angular momentum J . Those states have the statistical weight $2J + 1$, which correspond to the number of possible m_j states for a given J .

A Rydberg level is a level for which the remaining ion after removing the valence electron is in the ground level. This means that the number of Rydberg levels in the theoretical limit of no perturbation is unlimited. But in all real cases there is a non-zero perturbation, that is why the number of Rydberg levels are limited by a highest possible principal quantum number n_h . In this work we have obtained a formula for the total statistical weight $G^{ion}(n_l, n_h)$ for all Rydberg levels for which $n_l \leq n \leq n_h$. It turns out that the statistical weight for all $n_l \leq n \leq n_h$ Rydberg levels is a function of the orbital and spin angular momenta of the ground state of the mother ion, L_p and S_p , respectively. That is why we write $G^{ion}(n_l, n_h) = G(L_p, S_p, n_l, n_h)$.

When calculating the population distribution between states, the statistical weights are crucial. For atoms and ions, the population of different ionization stages depends on the partition function of each corresponding ion, which in turn is a weighted sum of the statistical weight of each bound J state. A major part of those partition functions are from the Rydberg series, that is why those are usually given extra attention when calculating partition functions [2]. In the case of low perturbation the number of Rydberg levels contributing to the partition function are very high, in which case our formula can be very useful.

We present the formula in Section 2 followed by the proof of the formula in Section 3. In Section 4 we discuss how our formula could be used for atomic and ionic partition functions.



2. The formula for statistical weight of a Rydberg sequence

For a specific ion there is a total statistical weight, $G^{ion}(n_l, n_h)$ for all $n_l \leq n \leq n_h$ Rydberg levels. This number is a function of the chosen n_l and n_h and of the orbital and angular momenta L_p and S_p of the ground state of the corresponding mother ion. In atomic physics this is called the parent term of the mother ion. The formula reads

$$G^{ion}(n_l, n_h) = G(L_p, S_p, n_l, n_h) = \frac{1}{3}(2L_p + 1)(2S_p + 1)(N_f - N_{break}), \quad (1)$$

in which $N_f = n_f(n_f + 1)(2n_f + 1)$ and $N_{break} = n_{break}(n_{break} + 1)(2n_{break} + 1)$.

3. Derivation of a formula for the statistical weight of a Rydberg sequence

Let $G(L_p, S_p, n)$ be the statistical weight of all levels for which the principal quantum number is n . We now prove the following theorem.

Theorem: The total statistical weight G of the levels for which the parent term spin and orbital angular momentum quantum numbers are S_p and L_p and the principal quantum number of the valence electron is n . Using the selection rules in atomic physics, we show that

$$G(L_p, S_p, n) = \sum_{l=0}^{n-1} \sum_{L_2=|L_p-l|}^{L_p+l} \sum_{S_2=|S_p-\frac{1}{2}|}^{S_p+\frac{1}{2}} \sum_{J=|L_2-S_2|}^{L_2+S_2} (2J+1) = 2(2S_p+1)(2L_p+1)n^2. \quad (2)$$

In some of these sums, indicies may be half-integers. The summation indicies however run in unit steps.

Proof: The proof uses the elementary summation rule

$$\sum_{k=m}^n k = \frac{1}{2}(n(n+1) - m(m-1)), \quad (3)$$

many times. First, we evaluate the two innermost sums

$$\sum_{S_2=|S_p-\frac{1}{2}|}^{S_p+\frac{1}{2}} \sum_{J=|L_2-S_2|}^{L_2+S_2} (2J+1). \quad (4)$$

The substitution $J' = J + \frac{1}{2}$ and $S'_2 = S_2 + \frac{1}{2}$ provides integer arguments in the sums, namely

$$\sum_{S_2=|S_p-\frac{1}{2}|}^{S_p+\frac{1}{2}} \sum_{J=|L_2-S_2|}^{L_2+S_2} (2J+1) = 2 \sum_{S'_2=S_p}^{S_p+1} \sum_{J'=|L_2-S'_2+\frac{1}{2}|+\frac{1}{2}}^{L_2+S'_2} J'. \quad (5)$$

Furthermore we can observe that the sum over S'_2 has only two terms, namely

$$\sum_{S'_2=S_p}^{S_p+1} \sum_{J'=|L_2-S'_2+\frac{1}{2}|+\frac{1}{2}}^{L_2+S'_2} J' = \sum_{J'=|L_2-S_p+\frac{1}{2}|+\frac{1}{2}}^{L_2+S_p} J' + \sum_{J'=|L_2-S_p-\frac{1}{2}|+\frac{1}{2}}^{L_2+S_p+1} J'. \quad (6)$$

Now considering the first term, if $L_2 \geq S_p$ it follows that $|L_2 - S_p + \frac{1}{2}| + \frac{1}{2} = L_2 - S_p + 1$, while from $L_2 \leq S_p$ we get $|L_2 - S_p + \frac{1}{2}| + \frac{1}{2} = S_p - L_2$.

For the second term, $L_2 \geq S_p + 1$ implies $|L_2 - S_p - \frac{1}{2}| + \frac{1}{2} = L_2 - S_p$, while $L_2 \leq S_p + 1$ gives $|L_2 - S_p - \frac{1}{2}| + \frac{1}{2} = S_p - L_2 + 1$. Remarkably, all three cases give the same expression by the elementary summation rule, or

$$L_2 \geq S_p + 1 \Rightarrow \sum_{J'=L_2-S_p+1}^{L_2+S_p} J' + \sum_{J'=L_2-S_p}^{L_2+S_p+1} J' = 2L_2 + 2S_p + 4L_2S_p + 1, \quad (7)$$

$$L_2 = S_p \Rightarrow \sum_{J'=L_2-S_p+1}^{L_2+S_p} J' + \sum_{J'=S_1-L_2+1}^{L_2+S_p+1} J' = 2L_2 + 2S_p + 4L_2S_p + 1, \quad (8)$$

$$L_2 \leq S_p - 1 \Rightarrow \sum_{J'=S_p-L_2}^{L_2+S_p} J' + \sum_{J'=S_p-L_2+1}^{L_2+S_p+1} J' = 2L_2 + 2S_p + 4L_2S_p + 1. \quad (9)$$

Thus we obtain

$$\sum_{S_2=|S_p-\frac{1}{2}|}^{S_p+\frac{1}{2}} \sum_{J=|L_2-S_2|}^{L_2+S_2} (2J+1) = 2(2S_p+1)(2L_2+1). \quad (10)$$

Hence, if $S_p > L_p + n - 1$, it remains to calculate

$$G(L_p, S_p, n) = 2(2S_p+1) \sum_{l=0}^{n-1} \sum_{L_2=|L_p-l|}^{L_p+l} (2L_2+1). \quad (11)$$

Dividing the summation over l , to avoid the absolute value, provides

$$\sum_{l=0}^{n-1} \sum_{L_2=|L_p-l|}^{L_p+l} (2L_2+1) = \sum_{l=0}^{L_p} \sum_{L_2=L_p-l}^{L_p+l} (2L_2+1) + \sum_{l=L_p+1}^{n-1} \sum_{L_2=l-L_p}^{L_p+l} (2L_2+1), \quad (12)$$

from which the summation rule gives

$$\begin{aligned} G(L_p, S_p, n) &= (L_p+1)^2 (2L_p+1) + (n^2 (2L_p+1) - (L_p+1)^2 (2L_p+1)), \\ &= 2(2S_p+1)(2L_p+1)n^2, \end{aligned} \quad (13)$$

which is the theorem. Now it follows from the sum of quadratic numbers that

$$\begin{aligned} G(L_p, S_p, n_l, n_h) &= \sum_{n=n_l}^{n_h} G(L_p, S_p, n) = 2(2S_p+1)(2L_p+1) \sum_{n=n_l}^{n_h} n^2, \\ &= \frac{1}{3}(2L_p+1)(2S_p+1)(N_f - N_{break}). \end{aligned} \quad (14)$$

4. Statistical weights and partition functions

For using either the Saha equation or free energy minimization methods [1, 4] to calculate the ionization balance of a plasma, the partition functions of all the involved ions in the plasma are needed. A partition function Q is defined as

$$Q = \sum_{i=0}^{\rho} e^{-\frac{E_i}{k_B T}}, \quad (15)$$

where E_i is the energy of the state i . The state i is characterized by its configuration, term, quantum number for its total orbital momentum j and quantum number of the z-projection of its orbital momentum m_j . The number of bound m_j states for the ion is ρ . For almost all practical cases the energy splitting due to external electric or magnetic fields is very small compared to the $k_B T$ factor, that is why the energy is considered degenerate with respect to orientation of the angular momentum. Because of this degeneracy, the following simplified form for the partition function is used in astrophysics

$$Q = \sum_{i=0}^{\mu} g_i e^{-\frac{E_i}{k_B T}} = \sum_{i=0}^{\mu} (2J_i + 1) e^{-\frac{E_i}{k_B T}}, \quad (16)$$

where the states i now are characterized only by configuration, term and the quantum number J . The number of bound i states are now μ and g_i is the number of possible projections of the total orbital momentum and is called the statistical weight of the state i . The observed levels are mostly tiny fractions of all bound levels when calculating the partition functions, that is why computational atomic codes, such as the Cowan code [5], are needed to obtain the energies to calculate the partition function. Following is a four-step description of how the formula for the statistical weights can be used to estimate partition functions. (1) Determine the highest value of n for the bound Rydberg states, n_h . There are some methods for determining n_h in the literature [3]. (2) Determine the lowest value of n , n_l , for which the excitation energy of the corresponding levels differ negligibly from the excitation energies of the n_h levels. (3) Make a list of the set of bound levels which are not Rydberg levels or Rydberg levels with $n < n_l$, ψ_i^{oth} . (4) Calculate the partition function from

$$Q = \sum_{i=1}^{|\Psi_{oth}|} g_i^{oth} \cdot e^{-\frac{E_i^{oth}}{k_B T}} + G(L_p, S_p, n_l, n_h) \cdot e^{-\frac{E_R}{k_B T}}, \quad (17)$$

where $|\Psi_{oth}|$ is the cardinality of the set of bound states ψ_i^{oth} , and g_i^{oth} and E_i^{oth} are the corresponding statistical weights and energies. The energy E_R is the energy of the highest excited bound Rydberg levels.

5. Summary

This paper presented a formula for the total statistical weight of all Rydberg levels defined by $n_l \leq n \leq n_h$, see equation (1). It is shown to be a function of the ground parent term of the mother ion. This formula can be used in calculations of population distributions in atomic physics. One example of future possible utility is for calculation of partition functions.

References

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