

**Notation:** I am using  $n_{r,m}$ 's for level populations;  $r$  identified the ion and  $m$  the level.  $m = 0$  means the ground state.  $n_e$  is always the *actual* electron density at the place in question.

$N_r$ 's are ion populations;  $N_r = \sum_m n_{r,m}$ . I have slightly departed from Nick's notation for self-consistency here. I am using lower case  $\phi$  for the Saha factor when defined with statistical weights ( $g_{r,m}$ -values) and upper case  $\Phi$  for when defined with partition functions ( $Z_r$ -values).

### Discussion

The question is if (and how) it matters whether we formulate ionization balances as e.g. something like (Nick's equation 1.4):

$$\frac{n_{r+1,0}n_e}{n_{r,0}} = W\phi_0^*(T_R)\sqrt{T_e/T_R} \quad (1)$$

where (Nick's equation 1.3)

$$\phi_0^*(T) = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{g_{r+1,0}g_e}{g_{r,0}} \exp(-\chi_r/kT) \quad (2)$$

OR

$$\frac{N_{r+1}n_e}{N_r} = W\Phi_0^*(T_R)\sqrt{T_e/T_R} \quad (3)$$

where

$$\Phi_0^*(T) = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{Z_{r+1}g_e}{Z_r} \exp(-\chi_r/kT) \quad (4)$$

I think the answer is that it doesn't matter, provided that one uses the correct partition functions ( $Z_r$ -values). I agree that this is not properly pointed out in the papers (including my own - sorry!) but I believe it is handles correctly in both the Lucy & Abbott code and in my code. We should check whether Python does this correctly or not.

The point is that one must adopt a self-consistent definition of the partition function and *not* use the LTE partition function – I agree that this is confusing when we have been claiming that  $*$  means “to be evaluated in LTE”...but the partition functions must actually always be consistent with the excitation formula, which (for us) means it's usually not LTE.

To try and explain, the partition function can be defined (in terms of an excitation formula – i.e. an expression for  $\frac{n_{r,m}}{n_{r,0}}$ ) by

$$n_{r,m} = \frac{1}{Z_r} N_r g_{r,0} \frac{n_{r,m}}{n_{r,0}} \quad (5)$$

i.e. the partition function is the normalisation factor required so that the sum of all the level populations gives the ion population. You can explicitly verify this by summing the above equation over  $m$ . It reduces to the thermal-equilibrium case if one adopts the Boltzmann formula for excitation: i.e. if

$$\frac{n_{r,m}}{n_{r,0}} = \frac{g_{r,m}}{g_{r,0}} \exp(-\epsilon_{r,m}/kT) \quad (6)$$

(where  $\epsilon_{r,m}$  is the excitation energy of level  $m$ ), then the above equation becomes

$$n_{r,m} = \frac{1}{Z_r^{LTE}} N_r g_{r,m} \exp(-\epsilon_{r,m}/kT) \quad (7)$$

Summing this over  $m$ , using the definition of  $N_r = \sum_m n_{r,m}$  and inverting this gives the familiar

$$Z_r^{LTE} = \sum_m g_{r,m} \exp(-\epsilon_{r,m}/kT) . \quad (8)$$

However, this was only true if the *excitation* was in LTE which it is (generally) not in our approximations. For a general excitation formula, the partition function follows from equation 5 and is

$$Z_r = \sum_m g_{r,0} \frac{n_{r,m}}{n_{r,0}} \quad (9)$$

With this definition (i.e. consistent with the excitation formula), it is then true (particular case of equation 5) that

$$n_{r,0} = \frac{1}{Z_r} N_r g_{r,0} \quad (10)$$

such that

$$\frac{n_{r,0}}{g_{r,0}} = \frac{N_r}{Z_r} \quad (11)$$

...but the thing to notice is that this *is only true of the partition function is defined self-consistently with the excitation formula*...if one used the LTE partition function it would not be true (unless one happened to have adopted the Boltzman excitation formula).

Provided that equation 11 is true then it is easy to see that my pair of equations (1 and 2) are equivalent to my second pair (3 and 4) since

$$\frac{n_{r,0}}{n_{r+1,0}} \frac{g_{r+1,0}}{g_{r,0}} = \frac{N_r}{N_{r+1}} \frac{Z_{r+1}}{Z_r} \quad (12)$$

So, my view is that which formulation one uses doesn't matter *provided* that the partition function is correctly defined in terms of the excitation formula. I agree with you that this highlights that using the \* notation around the whole term and calling it "LTE" is a bad choice (or perhaps just plain wrong) since it buries this subtle point (by implying that the partition functions should be evaluated in LTE). I am pretty sure, however, that this is correctly done in Leon's code (I have seen that code, at some point and do remember puzzling over the partition function calculation) and I also use partition functions that are derived from my excitation formula (although this is a mute point in my current code version since I'm using the Boltzmann excitation formula anyway).

I see no problem in formulating the whole thing in terms of the level populations as you have done - this avoids the need to worry about the partition functions and should give the same result.