Electronic Partition Function

Contrary to other contributions to the molecular partition function, the electronic part shows no simple and predictable structure and no small gap between different electronic levels. This is simultaneously an advantage and a disadvantage. The only systems that show a relatively well-structured spectra of energies are atoms, for which we can use the Bohr model

$$E_n = -\frac{13.6Z^2}{n^2} \tag{1}$$

Molecules show no such structured energy levels. However, due to the huge gap between the ground electronic state and any excited state, one includes typically only the ground electronic state (at most the first few electronic states) in the calculation of electronic partition functions to cover most of the molecular cases in most typical situations. Consequently there is also no need to rewrite the partition function in any particular way.

$$q^{el} = \sum\nolimits_i g_i e^{-\frac{E_i}{k_B T}} \tag{2}$$

Note however that the degeneracy g_i plays in the electronic partition function a significant role, since many molecules and atoms might be in non-singlet electronic states. For convenience however, we rewrite the electronic partition function as

$$q^{el} = e^{-\frac{E_0}{k_B T}} \sum\nolimits_i g_i e^{-\frac{(E_i - E_0)}{k_B T}} \tag{3}$$

As already mentioned, the sum over i includes only a few of the first electronic states. From here it is straightforward to obtain

$$log\left(q^{el}\right) = -\frac{E_0}{k_B T} + log\left(\sum\nolimits_i g_i e^{-\frac{[E_i - E_0]}{k_B T}}\right) \tag{4}$$

and the derivatives

$$\frac{\partial}{\partial V} log\left(q^{el}\right) = 0 \tag{5}$$

$$\frac{\partial}{\partial T} log\left(q^{el}\right) = \frac{E_0}{k_B T^2} + \frac{\sum_i \frac{(E_i - E_0)}{k_B T^2} g_i e^{-\frac{(E_i - E_0)}{k_B T}}}{\sum_i g_i e^{-\frac{(E_i - E_0)}{k_B T}}} \tag{6}$$

$$\begin{aligned} \frac{\partial^2}{\partial^2 T} log\left(q^{el}\right) = -\frac{2E_0}{k_B T^3} - \frac{2}{k_B T^3} \frac{\sum_i (E_i - E_0) g_i e^{-\frac{(E_i - E_0)}{k_B T}}}{\sum_i g_i e^{-\frac{(E_i - E_0)}{k_B T}}} \\ + \frac{1}{(k_B T^2)^2} \frac{\sum_i (E_i - E_0)^2 g_i e^{-\frac{(E_i - E_0)}{k_B T}}}{\sum_i g_i e^{-\frac{(E_i - E_0)}{k_B T}}} - \frac{1}{(k_B T)^2} \left(\frac{\sum_i (E_i - E_0) g_i e^{-\frac{(E_i - E_0)}{k_B T}}}{\sum_i g_i e^{-\frac{(E_i - E_0)}{k_B T}}} \right)^2 \end{aligned} \tag{7}$$

Despite their simplicity, electronic partition functions carry a sour complication whenever electronic excited states must be considered: different molecular electronic states are characterized by different rovibrational spectra. To see this, consider the excitation of a single electron in a molecule. In the process of exciting the electron from one level into another, it will either leave bonding or non-bonding orbitals in order to occupy non-bonding or antibonding orbitals. This excitation goes then along a weakening or even the breaking of chemical bonds in extreme cases. Consequently, force constants between bonds are different and equilibrium geometries as well. Because different electronic states are characterized by distinct potential energy surfaces, the distribution of rotational and vibrational energy levels is necessarily different and different electronic states are coupled to different rovibrational partition functions. It is however an acceptable approximation (if high accuracy is not required) to consider that all low-lying electronic states couple to the same (or very similar) rovibrational partition function, which immensely simplifies the calculations.

Bibliography