6.6: Electronic Partition Function

Atoms and molecules can also store energy by populating excited electronic states. For the hydrogen atom or any system that contains only a single electron, the energy levels can be given in closed form, based on the Bohr model,

$$\epsilon_{\mathrm{el},n} = -\frac{z_q^2 R_\mathrm{E}}{n^2} \,, \tag{6.6.1}$$

where $n = 0 \ldots \infty$ is the principal quantum number, z_q the nuclear charge, and R_E the Rydberg constant. However, this is an exception. For molecules and all other neutral atoms closed expressions for the energy levels cannot be found.

In most cases, the problem can be reduced to considering either only the electronic ground state with energy $\epsilon_{\mathrm{el},0}$ or to considering only excitation to the first excited state with energy $\epsilon_{\mathrm{el},1}$. If we use an energy shift to redefine $\epsilon_{\mathrm{el},0} = 0$, we can define a characteristic electronic temperature

$$\Theta_\mathrm{el} = \frac{\epsilon_{\mathrm{el},1}}{k_\mathrm{B}} \,. \tag{6.6.2}$$

Characteristic electronic temperatures are usually of the order of several thousand Kelvin. Hence, in most cases, $\Theta_\mathrm{el} \gg T$ applies, only the electronic ground state is accessible, and thus

$$Z_\mathrm{el} = g_{\mathrm{el},0} \,, \tag{6.6.3}$$

where $g_{\mathrm{el},0}$ is the degeneracy of the electronic ground state. We note that spatial degeneracy of the electronic ground state cannot exist in non-linear molecules, according to the *Jahn-Teller theorem*. However, a spatially non-degenerate ground state can still be spin-degenerate.

In molecules, total orbital angular momentum is usually quenched ($\Lambda = 0$, Σ ground state). In that case

$$Z_\mathrm{el}^{\{\Sigma\}} = 2S+1 \,, \tag{6.6.4}$$

where S is the electron spin quantum number. For the singlet ground state of a closed-shell molecule ($S = 0$) we have $Z_\mathrm{el}^{\{\Sigma\}} = 1$, which means that the electronic contribution to the partition function is negligible. The contribution to internal energy and heat capacity is generally negligible for $\Theta_\mathrm{el} \gg T$. The electronic contribution to molar entropy,

$$S_\mathrm{el}^{\{\Sigma\}} = R \ln(2S+1) \,, \tag{6.6.5}$$

is not negligible for open-shell molecules or atoms with $S > 0$. At high magnetic fields and low temperatures, e.g. at $T < 4.2$ K and $B_0 = 3.5$ T, where the high-temperature approximation for electron spin states does no longer apply, the electronic partition function and corresponding energy contribution are smaller than given in Equation 6.6.4). For a doublet ground state ($S = 1/2$) the problem can be solved with the treatment that we have given in Section [subsection_doublet]. For $S > 1/2$ the spin substates of the electronic ground state are not strictly degenerate even at zero magnetic field, but split by the zero-field splitting, which may exceed thermal energy in some cases. In that case Equation 6.6.4) does not apply and the electronic contribution to the partition function depends on temperature. Accordingly, there is a contribution to internal energy and to heat capacity.

For a $\Lambda > 0$ species with term symbol ${}^{2S+1}\Lambda_\Omega$, each Ω component is doubly degenerate. For instance, for NO with a Π ground state ($\Lambda = 1$), both the ${}^2\Pi_{1/2}$ and the ${}^2\Pi_{3/2}$ state are doubly degenerate. As the ${}^2\Pi_{3/2}$ state is only 125 cm^{-1} above the ground state, the characteristic temperature for electronic excitation is $\Theta_\mathrm{el} = 178$ K. In this situation, Equation 6.6.3) does not apply at ambient temperature. The energy gap to the next excited state, on the other hand, is very large. Thus, we have

$$Z_\mathrm{el} = g_{\mathrm{el},0} + g_{\mathrm{el},1} e^{-\Theta_\mathrm{el}/T} \,. \tag{6.6.6}$$

This equation is fairly general, higher excited states rarely need to be considered. The electronic contribution to the heat capacity of NO derived from Equation 6.6.6) is in good agreement with experimental data from Eucken and d'Or .