

Chapter 2

Two and Three Level Systems: Toward the Understanding of the Thermodynamics of Multilevel Systems

In this chapter, we will introduce few level systems to analyze the contribution of excited states on thermodynamic properties of atomic species, using elementary concepts of statistical thermodynamics. The present formulation will be applied to enthalpy and energy, as well as to the specific heats.

Describing the properties of two- or three-level systems gives a general overview of the contribution of atomic internal states on the thermodynamic functions (Colonna and Capitelli 2009; D'Ammando et al. 2010; Maczek 1998). Nevertheless, the few-level approach goes over the simple qualitative description of the internal contribution, because level lumping in two or three groups approximates with a good accuracy the contribution of the whole ladder of electronic states for many systems.

2.1 Two-Level Systems

Let us model an atom as a two-level system, the ground state and one excited level having, respectively, degeneracies g_1 and g_2 and molar energies of $\varepsilon_1 = 0$ and $\varepsilon_2 > 0$. Denoting with n_1 , n_2 and n , respectively, the ground state, excited level and total number of moles, we can write the following balance equation

$$n_1 + n_2 = n. \quad (2.1)$$

The population n_1 and n_2 are linked by the Boltzmann distribution

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\frac{\theta_2}{T}} \quad (2.2)$$

$$\theta_2 = \frac{\varepsilon_2}{k}. \quad (2.3)$$

Solving the system of equations for n_1 and n_2 , we get the moles of atom in each state as

$$\begin{aligned} n_1 &= n \frac{g_1}{g_1 + g_2 e^{-\frac{\theta_2}{T}}} \\ n_2 &= n \frac{g_2 e^{-\frac{\theta_2}{RT}}}{g_1 + g_2 e^{-\frac{\theta_2}{T}}}. \end{aligned} \quad (2.4)$$

The denominator of the above expressions

$$Q = g_1 + g_2 e^{-\frac{\theta_2}{T}} \quad (2.5)$$

is the partition function of the two-level system.

The populations in the low and high temperature limits are given by

$$\begin{aligned} T \ll \theta_2 &\Rightarrow n_1 = n & n_2 = 0 \\ T \gg \theta_2 &\Rightarrow n_1 = n \frac{g_1}{g_1 + g_2} & n_2 = n \frac{g_2}{g_1 + g_2} \end{aligned} \quad (2.6)$$

i.e., at low temperature, only the ground state is populated while at high temperature both levels are populated proportionally to the respective statistical weight.

The molar internal energy is given by

$$\bar{U}^{\text{int}} = \frac{R}{n} (\theta_2 n_1 + \theta_2 n_2) = R \theta_2 \frac{n_2}{n} = R \theta_2 \frac{g_2 e^{-\frac{\theta_2}{T}}}{g_1 + g_2 e^{-\frac{\theta_2}{T}}}, \quad (2.7)$$

where $\theta_1 = \varepsilon_1/k = 0$. The corresponding limiting values are

$$\begin{aligned} T \ll \theta_2 &\Rightarrow \bar{U}^{\text{int}} = 0 \\ T \gg \theta_2 &\Rightarrow \bar{U}^{\text{int}} = R \theta_2 \frac{g_2}{g_1 + g_2}. \end{aligned} \quad (2.8)$$

As a general behavior, we have $g_2 \gg g_1$ and $\theta_2 \approx I/k$, I being the ionization potential. As a consequence, at high temperature we have $\bar{U}^{\text{int}} \approx N_d I$. Finally, the internal specific heat \bar{C}^{int} is given by

$$\bar{C}^{\text{int}} = \frac{d\bar{U}^{\text{int}}}{dT} = \frac{R \theta_2}{n} \frac{dn_2}{dT} = R \left(\frac{\theta_2}{T} \right)^2 \frac{g_1 g_2 e^{-\frac{\theta_2}{T}}}{\left(g_1 + g_2 e^{-\frac{\theta_2}{T}} \right)^2}, \quad (2.9)$$

which goes to zero in both high temperature and low temperature limits.

Table 2.1 Degeneracy (g^*) and characteristic temperature (θ^*) for atomic hydrogen considered as a two-level system, for different values of the maximum principal quantum number included in the upper lumped level

$n = 1$	g^*	θ^* [K]
	2	0
n_{\max}		
5	108	146,187
10	768	154,181
25	11,048	157,196
50	85,848	157,701
75	286,898	157,800
100	676,698	157,835

As case study, let us consider atomic hydrogen which levels have energy and multiplicity given by

$$g_{H,n} = 2n^2$$

$$\varepsilon_{H,n} = I_H \left(1 - \frac{1}{n^2} \right), \quad (2.10)$$

where n is the principal quantum number and I_H is the ionization potential of the hydrogen atom. We reduce the multiplicity of electronically excited states of the atomic hydrogen to a two-level system¹:

1. The ground state characterized by energy $\varepsilon_{H,1}^* = 0$, degeneracy $g_{H,1}^* = 2$.
2. One excited level having the degeneracy equal to the sum of degeneracies and the energy equal to the mean energy of all excited states from $n = 2$ up to a fixed n_{\max} .

$$g_{H,2}^* = \sum_{n=2}^{n_{\max}} g_{H,n} \quad (2.11)$$

$$\theta_{H,2}^* = \frac{1}{k g_{H,2}^*} \sum_{n=2}^{n_{\max}} g_{H,n} \varepsilon_{H,n}. \quad (2.12)$$

The energy of the excited state and its characteristic temperature, as well as the statistical weight depend on n_{\max} , as shown in Table 2.1, where total degeneracy and characteristic temperature are reported for some values of n_{\max} .

Inspection of the table shows the strong dependence of the upper level degeneracy on the number of states inserted in the lumped level, while its energy rapidly converges to I_H , spreading around 10,000 K passing from $n_{\max} = 5$ to $n_{\max} = 100$.

¹For the sake of clarity, the symbols of the reduced levels are distinguished by those of the real level by the superscript*.

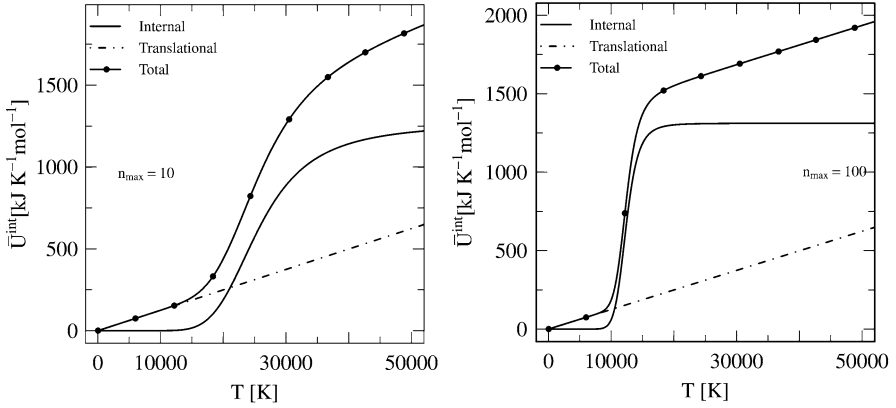


Fig. 2.1 Atomic hydrogen translational, internal and total molar energy as a function of the temperature for (a) $n_{\max} = 10$ and (b) $n_{\max} = 100$

In Fig. 2.1, one can observe the sensitivity of the molar internal energy on n_{\max} . For $n_{\max} = 100$, the internal energy grows rapidly with the temperature, reaching an asymptotic value equal to the ionization potential, while for $n_{\max} = 10$ the growth is much slower, and up to $T = 50,000$ K the asymptotic value of 1,282 kJ/mole has not been reached yet. The upper limit of the internal energy can be obtained from (2.7), considering that, in any case (see Table 2.1), $g_{H,2}^* \gg g_{H,1}^*$ and therefore in the denominator of (2.8) $g_{H,1}^* + g_{H,2}^* \approx g_{H,2}^*$ thus giving $\bar{U}_H^{\text{int}} \approx R\theta_2$. In both cases, the internal energy becomes much higher than the translational one if the temperature is sufficiently high.

Figure 2.2 shows the dimensionless constant volume specific heat for the same cases discussed in Fig. 2.1. The internal specific heat presents a maximum value, which is shifted at lower temperature as n_{\max} increases. It should be also noted that the internal specific heat, negligible at low and high temperatures, overcomes the translational contribution ($\frac{3}{2}$) for intermediate temperatures, as reported in Fig. 2.2.

2.2 Three-Level Systems

Many-electron atoms often possess low lying energy states corresponding to rearrangement of angular and spin momenta of the valence electrons. In this case, the two-level approximation must be improved introducing a new level which describes the low-lying excited states. To this end, we consider a three-level system composed by the ground state and two excited states, characterized by

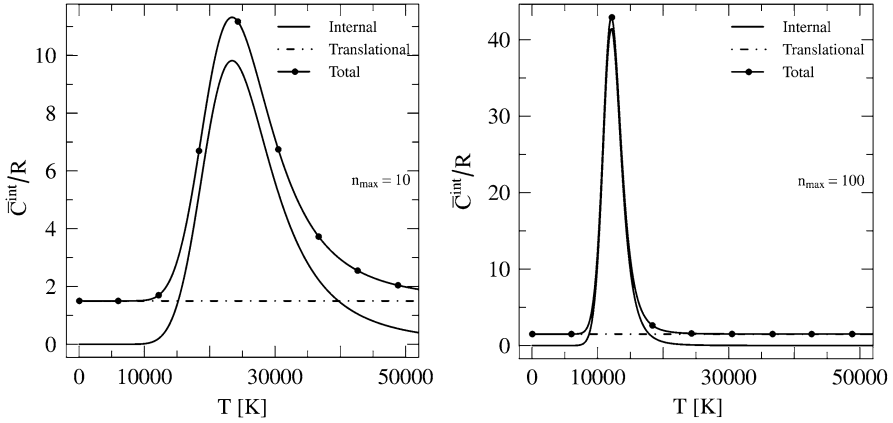


Fig. 2.2 Atomic hydrogen translational, internal and total reduced molar specific heat for (a) $n_{\max} = 10$ and (b) $n_{\max} = 100$

level degeneracies g_1 , g_2 , g_3 and energies $\varepsilon_1 = 0$ and $\varepsilon_1 < \varepsilon_2 \ll \varepsilon_3$. The balance equations read

$$\begin{aligned}
 n_1 + n_2 + n_3 &= n \\
 \frac{n_2}{n_1} &= \frac{g_2}{g_1} e^{-\frac{\theta_2}{T}} \\
 \frac{n_3}{n_1} &= \frac{g_3}{g_1} e^{-\frac{\theta_3}{T}},
 \end{aligned} \tag{2.13}$$

where the θ 's are the energies expressed in K as in (2.3). Solution of the above system leads to the following expressions for the molar fractions of levels

$$\begin{aligned}
 \frac{n_1}{n} &= \frac{g_1}{g_1 + g_2 e^{-\frac{\theta_2}{T}} + g_3 e^{-\frac{\theta_3}{T}}} \\
 \frac{n_2}{n} &= \frac{g_2 e^{-\frac{\theta_2}{T}}}{g_1 + g_2 e^{-\frac{\theta_2}{T}} + g_3 e^{-\frac{\theta_3}{T}}} \\
 \frac{n_3}{n} &= \frac{g_3 e^{-\frac{\theta_3}{T}}}{g_1 + g_2 e^{-\frac{\theta_2}{T}} + g_3 e^{-\frac{\theta_3}{T}}}.
 \end{aligned} \tag{2.14}$$

Likewise the two-level case, the denominator of the above expressions is the partition function of our three-level system

$$Q = g_1 + g_2 e^{-\frac{\theta_2}{T}} + g_3 e^{-\frac{\theta_3}{T}} \tag{2.15}$$

Let us consider a temperature such that $\theta_2 \ll T \ll \theta_3$. In this case, we can drop the contribution of the last level and, being the first exponential very close to one, we have

$$\begin{aligned}\frac{n_1}{n} &\approx \frac{g_1}{g_1 + g_2} \\ \frac{n_2}{n} &\approx \frac{g_2}{g_1 + g_2} \\ \frac{n_3}{n} &\approx \frac{g_3 e^{-\frac{\theta_3}{T}}}{g_1 + g_2} \approx 0\end{aligned}\quad (2.16)$$

reproducing the same situation as a two level system. At very high temperature ($\theta_2 \ll \theta_3 \ll T$), the following asymptotic behavior is obtained

$$\begin{aligned}\frac{n_1}{n} &= \frac{g_1}{g_1 + g_2 + g_3} \\ \frac{n_2}{n} &= \frac{g_2}{g_1 + g_2 + g_3} \\ \frac{n_3}{n} &= \frac{g_3}{g_1 + g_2 + g_3}.\end{aligned}\quad (2.17)$$

The internal energy can be written as

$$\begin{aligned}\bar{U}^{\text{int}} &= \frac{R}{n} (\cancel{\theta_1 n_1} + \theta_2 n_2 + \theta_3 n_3) \\ &= R \frac{g_2 \theta_2 e^{-\frac{\theta_2}{T}} + g_3 \theta_3 e^{-\frac{\theta_3}{T}}}{g_1 + g_2 e^{-\frac{\theta_2}{T}} + g_3 e^{-\frac{\theta_3}{T}}}\end{aligned}\quad (2.18)$$

and the internal specific heat as²

$$\begin{aligned}\bar{C}^{\text{int}} &= \frac{\ll U^2 \gg - (\bar{U}^{\text{int}})^2}{RT^2} \\ \ll U^2 \gg &= R^2 \frac{g_2 \theta_2^2 e^{-\frac{\theta_2}{T}} + g_3 \theta_3^2 e^{-\frac{\theta_3}{RT}}}{g_1 + g_2 e^{-\frac{\theta_2}{RT}} + g_3 e^{-\frac{\theta_3}{RT}}}.\end{aligned}\quad (2.19)$$

²See Sect. 3.2 for a general definition of $\ll U^2 \gg$.

Table 2.2 Statistical weight and energy of low lying states of nitrogen atom

Configuration	g	ε [eV]
$^2D_{5/2,3/2}$	10	2.3838
$^2P_{3/2,1/2}$	6	3.5757

Table 2.3 Degeneracy and characteristic temperature for atomic nitrogen considered as a three-level system, ground state, low lying level and upper lumped level, in hydrogen-like approximation, for different values of the maximum principal quantum number

	g^*	θ^* [K]
Ground	4	0
Low lying	16	32849
n_{\max}		
5	900	158702
10	6840	165282
25	99360	168125
50	772560	168647
75	2582010	168752
100	6090210	168787

As a case study for the three-level system, let us consider the atomic nitrogen. The ground state configuration is $^4S_{3/2}$ having statistical weight $g_{N,1}^* = g_{N,1} = 4$. There are other two low-lying levels resulting from $2s^22p^3$ electronic configuration, one corresponding to $^2D_{5/2,3/2}$ and one to $^2P_{3/2,1/2}$ whose energy and statistical weight are reported in Table 2.2. These two levels are grouped together to give a single low lying state which statistical weight, given by

$$g_2^* = g(^2D) + g(^2P)$$

and characteristic temperature, calculated as

$$\theta^* = \frac{g(^2D)\varepsilon(^2D) + g(^2P)\varepsilon(^2P)}{k g_2^*}$$

are reported in Table 2.3.

The energy of the other levels are calculated by using an hydrogen-like approximation

$$\varepsilon_n = I_N - \frac{I_H}{n^2} \quad (2.20)$$

(I_N and I_H are, respectively, the ionization potential of nitrogen and hydrogen atoms) and a statistical weight

$$g_n = 2n^2 g_{\text{core}} \quad (2.21)$$

($g_{\text{core}} = 9$ represents the statistical weight of the ground state of the more stable nitrogen core (3P)). They are then grouped to form the third lumped level (see Table 2.3), limited to the maximum number n_{\max} . A more accurate approach to calculate electronically excited state energies consists in extending available (experimental or theoretical) data following the Ritz–Rydberg series (see Appendix A).

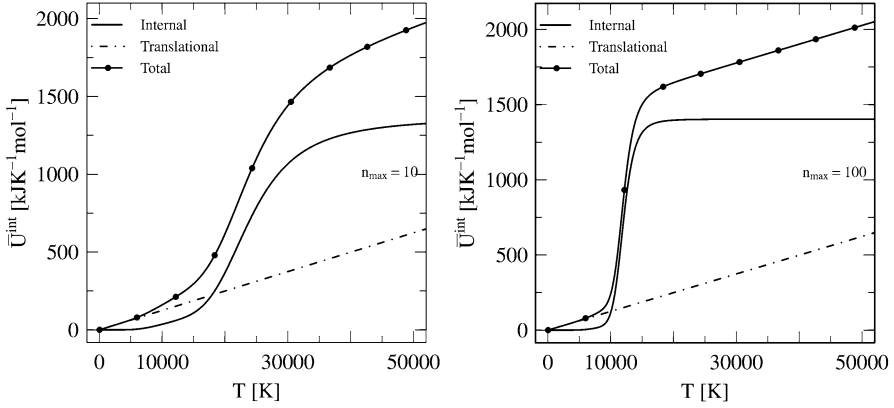


Fig. 2.3 Atomic nitrogen translational, internally and total molar energy as a function of the temperature for (a) $n_{\max} = 10$ and (b) $n_{\max} = 100$

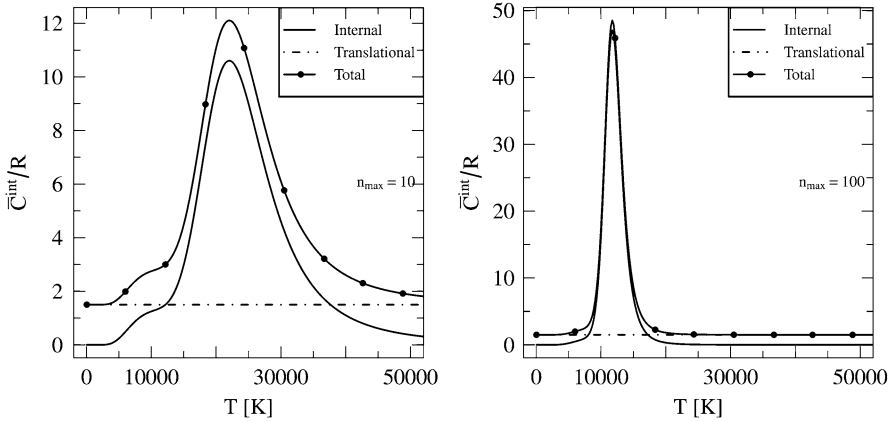
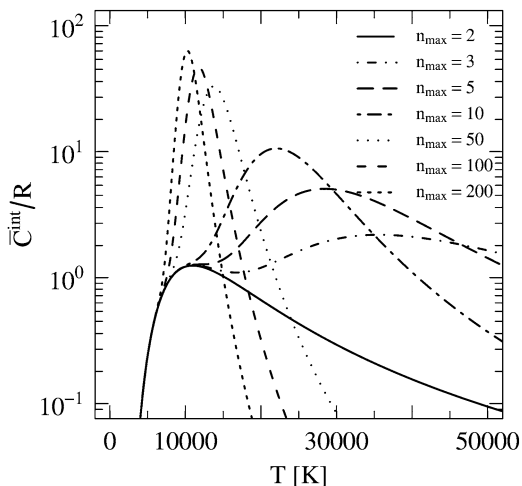


Fig. 2.4 Atomic nitrogen translational, internal and total reduced molar specific heat as a function of the temperature for (a) $n_{\max} = 10$ and (b) $n_{\max} = 100$

In Fig. 2.3, we report the internal energy of atomic nitrogen considered as a three level system. Inspection of this figure shows that, similar to the hydrogen atom case (see Fig. 2.1), the internal energy of the atomic nitrogen strongly increases with the temperature as well as with the number of excited states considered. In both cases, the internal energy is much higher than the translational one. This behavior is reflected on the specific heat (Fig. 2.4) showing similar behavior as the Hydrogen atom. It should be noted, for $n_{\max} = 10$, the presence of a shoulder in the internal contribution around $T = 10000$ K due to the low lying states. However, this effect disappears for $n_{\max} = 100$ hidden by highest lumped level. This point is evident in Fig. 2.5 where we report different \bar{C}^{int} curves corresponding to different n_{\max} values.

Fig. 2.5 Reduced internal specific heat of atomic nitrogen as a function of the temperature for different values of n_{\max} . Note that the case $n_{\max} = 2$ considers only the low-lying state



In particular, the curve labeled with $n_{\max} = 2$ does not consider the third level: in this case, the first maximum is well evident, disappearing as the degeneracy of the lumped level grows up.

The results reported in the different figures refers to atomic systems when the high level energies are lumped allowing their dependence on the principal quantum number.

2.3 Few-Level Model Accuracy

In previous sections, we have observed that a simplified atomic model, considering only two or three representative levels, gives a good qualitative description of the internal contribution to thermodynamic functions of atomic species. In a recent paper (Colonna and Capitelli 2009), it has been demonstrated that the few-level approach has a mathematical foundation, showing under what conditions the results obtained by detailed calculations are reproduced with good accuracy. The demonstration is based on the Taylor series expansion of the exponential function around the mean energy

$$\bar{\varepsilon} = \frac{1}{G} \sum_{n=2}^{n_{\max}} g_n \varepsilon_n$$

$$G = \sum_{n=2}^{n_{\max}} g_n \quad (2.22)$$

of the excited states, i.e.

$$\begin{aligned}
 Q^{\text{exact}} &= \sum_{n=1}^{n_{\text{max}}} g_n e^{-\frac{\varepsilon_n}{kT}} = g_1 + e^{-\frac{\bar{\varepsilon}}{kT}} \sum_{n=2}^{n_{\text{max}}} g_n e^{-\frac{\varepsilon_n - \bar{\varepsilon}}{kT}} = \\
 &= g_1 + e^{-\frac{\bar{\varepsilon}}{kT}} \sum_{n=2}^{n_{\text{max}}} g_n \left[1 - \left(\frac{\varepsilon_n - \bar{\varepsilon}}{kT} \right) + \frac{1}{2} \left(\frac{\varepsilon_n - \bar{\varepsilon}}{kT} \right)^2 + \dots \right] \\
 &= g_1 + G e^{-\frac{\bar{\varepsilon}}{kT}} + e^{-\frac{\bar{\varepsilon}}{kT}} \sum_{n=2}^{n_{\text{max}}} \frac{g_n}{2} \left(\frac{\varepsilon_n - \bar{\varepsilon}}{kT} \right)^2 + \dots \quad (2.23)
 \end{aligned}$$

(2.5), (2.15) are obtained in the first order approximation³ i.e.

$$Q^1 = g_1 + G e^{-\frac{\bar{\varepsilon}}{kT}}. \quad (2.24)$$

This approximation is obviously better as narrower the distribution of excited states around their mean value. To improve the results, higher order corrections can be used (see (Colonna and Capitelli 2009) for details) without losing the advantages of having coefficients that do not depend on the temperature. For example, the second order approximation is given by

$$Q^2 = g_1 + G e^{-\frac{\bar{\varepsilon}}{kT}} + e^{-\frac{\bar{\varepsilon}}{kT}} \sum_{n=2}^{n_{\text{max}}} \frac{g_n}{2} \left(\frac{\varepsilon_n - \bar{\varepsilon}}{kT} \right)^2 = Q^1 + \delta Q^*. \quad (2.25)$$

Moreover, it is possible to estimate the error calculating the successive term in expansion series. As an example, the first order approximate error (see Fig. 2.6 for atomic hydrogen) is given by the sum of the square terms in (2.23), i.e. the term δQ^* in (2.25). This value should be compared with the exact errors defined as the relative difference between the state-to-state calculation and the two-level value obtained in the i -th order approximation, i.e. retaining the i terms in the expansion. In our case we have as exact first order error $\delta Q^1 = Q^{\text{exact}} - Q^1$ and exact second order error $\delta Q^2 = Q^{\text{exact}} - Q^2$.

As an example, the hydrogen atom shows a good agreement between the two-level approximation and the exact calculation (see Fig. 2.6). The error is below 2% for the partition function and 3% for the specific heat when just 5 levels are considered, decreasing below 1% for 20 levels. It should be noted that the exact and approximate errors are quite similar and that the second order correction reduces the error below 0.5%.

To apply this model to nitrogen and oxygen atoms, we should consider the three-level approach, due to the presence of low-lying states. The results have been reported in Fig. 2.7 for a cutoff $\Delta I = 500 \text{ cm}^{-1}$, i.e. by considering levels with

³It should be noted that the first order term in (2.23) gives a null contribution.

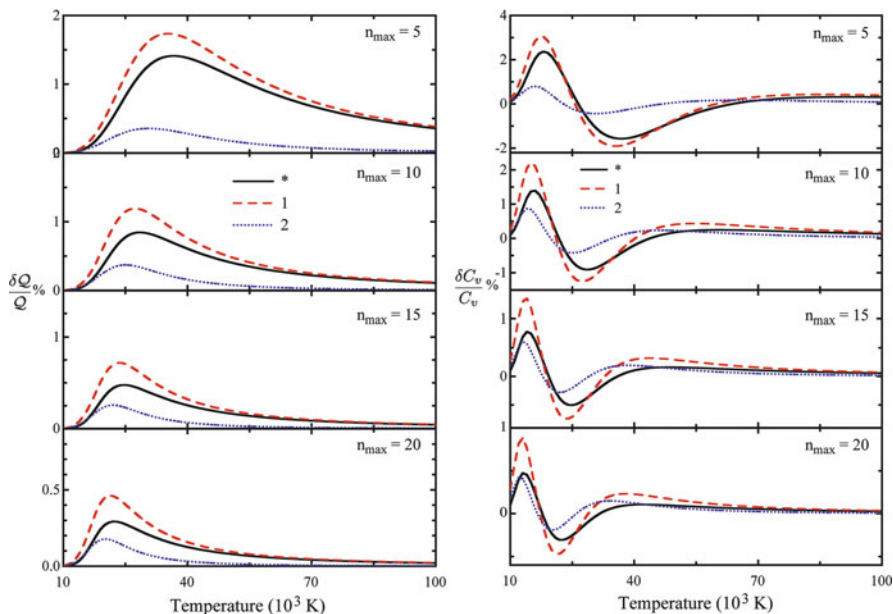


Fig. 2.6 Approximate first-order error (\star) and exact first (1) and second (2) order errors for the hydrogen atom partition function and total constant volume specific heat (internal plus translational) for different number of levels included in the calculation

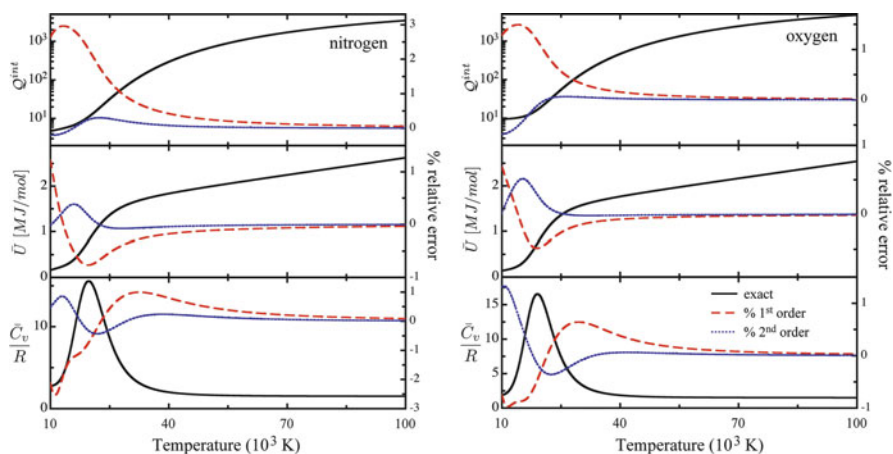


Fig. 2.7 Exact values and relative percentage errors (first and second order) of the partition function, internal energy (translational plus internal) and total constant volume specific heat (translational plus internal) of nitrogen and oxygen atom in the three-level approximation for cutoff $\Delta I = 500 \text{ cm}^{-1}$

energy lower than $I - \Delta I$ in the electronic partition function (see Chap. 8). Also in this case the first-order error is lower than 2% and the second order error is below 0.5% in the whole temperature range.



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