

The Electronic Partition Function for Atoms or Ions

Atoms (especially in the plasma) can exist in a number of electronically excited states, in addition to the ground state. Measuring energy now from the ground state, the set of energies is $(0, \epsilon_1, \epsilon_2 \dots)$, and each may contain several identifiable quantum states, so their degeneracies are $(0, g_1, g_2 \dots)$. Typically, ϵ_1 is from $1/2$ to $3/4$ of the ionization energy, and then successive ϵ_j 's tend to cluster ever closer to the ionization energy. So, at least for the lower excited levels, the energies are well separated (compared to kT_e), and we cannot use a continuum approximation as we did for the translational partition function. Instead, we simply write,

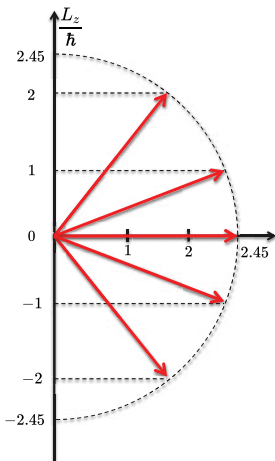
$$Q^{electr.} = g_0 + g_1 e^{-\frac{\epsilon_1}{kT}} + \dots \quad (20)$$

and, since $\epsilon_{j>0} \gg kT$ typically, we truncate the summation early on, most often using only,

$$Q^{electr.} \simeq g_0 \quad (21)$$

i.e., the ground state degeneracy. Only at very high temperatures are other terms significant. This is simple, but the complexity arises in calculating g_0 . For atoms, this is still reasonably simple (it becomes much less so for molecules). The degeneracy of an atomic state arises from the fact that the angular momentum of the electrons may not affect the energy. Specifically, in the absence of very strong \vec{B} fields, the orientation of the overall angular momentum of the atom does not affect the energy. In addition, for light atoms (to about Na) even the magnitude of the overall angular momentum is insensitive. For heavy atoms, there are appreciable spin-orbital interactions, and the magnitude of the total angular momentum does matter. There are two sources of electronic angular momentum: spin and orbital motion. Each of these characterized by a quantum number (s for spin, l for orbit), and their vector sum, the overall angular momentum, is also quantized along any space direction (quantum number J). The magnitude of the angular momentum of each kind is given by

$$\begin{aligned} L_s^2 &= s(s+1)\hbar^2 && \text{(spin)} \\ L_l^2 &= l(l+1)\hbar^2 && \text{(orbit)} \\ L^2 &= J(J+1)\hbar^2 && \text{(overall)} \end{aligned} \quad (22)$$



and for a given magnitude, the component along any given axis can only take some discrete values. For instance, for a total angular momentum quantum number J , J_z can be $(-J, -J+1, \dots, 0, \dots, J-1, J) \times \hbar$. The sketch shows the case with $J = 2$. The magnitude of L is $L = \sqrt{2 \times (2+1)}\hbar = \sqrt{6}\hbar = 2.45\hbar$. The z -components can be $(-2, -1, 0, 1, 2)\hbar$, and if there is no strong B field, this means a degeneracy of 5. More generally, for a given J the electronic degeneracy is,

$$g = 2J + 1 \quad (23)$$

As stated, $\vec{L} = \vec{L}_s + \vec{L}_l$, and the quantum sum rules are such that, when the quantum numbers (s, l) are fixed, the quantum number J can take values $s+l, s+l-1, \dots, |s-l|$. In heavy atoms, each of these would have a different energy, and a degeneracy $2J+1$. In

light atoms, we can lump these states together into one (the energies are very close to each other in this so-called “multiplet”), and its degeneracy is then,

$$g = \sum_{J=|s-l|}^{s+l} (2J + 1) \quad (24)$$

This sum can be evaluated using expressions for arithmetic sequences, but it is fairly clear that the answer is,

$$g = (2s + 1)(2l + 1) \quad (\text{light atoms, multiplet}) \quad (25)$$

i.e., each \vec{L}_s vector can take $2s + 1$ orientations for each of the $2l + 1$ orientations of the \vec{L}_l vector. The required information on s, l, J is contained in the Spectroscopic Notation for the state in question. For the highest occupied principal quantum number n (roughly the size of the electron orbit), the angular momentum situation is summarized by the symbol $^{2s+1}A_J$ where

s =spin quantum number (1/2 the number of unpaired electrons)

A =a letter designating the orbital quantum number:

$A=s$	p	d	f	g	\dots
$l=0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	\dots

J =total angular momentum quantum number

Examples:

$$(1) \quad {}^2S_{1/2} \quad : \quad s = \frac{1}{2} \quad , \quad l = 0 \quad ; \quad J = \frac{1}{2} \quad ; \quad g = 2J + 1 = 2$$

This is for example the ground state of H or of any alkali atom (Na, Cs...), or of an alkaline earth ion (Ca^+ ...). The $g = 2$ is because of the two possible spin orientations (up-down), which are also those of J , since $l = 0$.

$$(2) \quad \left\{ \begin{array}{l} {}^2P_{1/2} \quad : \quad s = \frac{1}{2} \quad , \quad l = 1 \quad ; \quad J = 1 - \frac{1}{2} = \frac{1}{2} \quad ; \quad g = 2J + 1 = 2 \\ {}^2P_{3/2} \quad : \quad s = \frac{1}{2} \quad , \quad l = 1 \quad ; \quad J = 1 + \frac{1}{2} = \frac{3}{2} \quad ; \quad g = 2J + 1 = 4 \end{array} \right.$$

This is the 2P doublet. For H or Li, its total degeneracy is $g = (2s + 1)(2l + 1) = 2 \times 3 = 6$ (or $g = 2 + 4$).

For Na, the two components of the doublet begin to have noticeably different energies, but may still be lumped together for some purposes. For Cs, they need to be considered as different energy states, with $g = 2$ and $g = 4$ respectively.

Note: In a sodium atom (or K, or Cs...), the ground state has $n = 0$ as its principal quantum number, and its configuration is, as noted ${}^2S_{1/2}$ again. The radiative transitions from $n = 1$ to $n = 0$ are forbidden (at least the strong dipole transitions) unless $\Delta l = \pm 1$, so the ${}^2S_{1/2}$

state will not radiate, but the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ will. The two resulting spectral lines are very close to each other, but can be resolved with a reasonable spectrograph. They are the famous D-lines of sodium, very intense in the yellow.

The Vibrational Partiton Function

Molecules (unlike atoms) can vibrate, each atom being elastically restrained by the others. To linear order, these are harmonic vibrations. One can do a classical modal analysis and identify the normal modes and their frequencies ν_i (for a dynamic molecule, only one mode, with frequency $\nu = \sqrt{k/m}$). The vibrational energy for each mode is then quantified according to,

$$\epsilon_n = h\nu \left(n + \frac{1}{2} \right) \quad ; \quad n = 0, 1, 2 \dots \quad (26)$$

(notice the “zero point energy” $\frac{1}{2}h\nu$) and these are singly degenerate states. The vibrational partition function is then,

$$Q^v = \sum_{n=0}^{\infty} e^{-\frac{h\nu(n+\frac{1}{2})}{kT}} \quad (27)$$

Define a characteristic “vibrational temperature”,

$$\theta_v = \frac{h\nu}{k} \quad (28)$$

then

$$Q^v = e^{-\frac{\theta_v}{2T}} \sum_{n=0}^{\infty} e^{-\frac{\theta_v}{T}n} = e^{-\frac{\theta_v}{2T}} \frac{1}{1 - e^{-\frac{\theta_v}{T}}} \quad (29)$$

or $Q^v = \frac{e^{\frac{\theta_v}{2T}}}{e^{\frac{\theta_v}{T}} - 1}$

Following are a few common θ_v values:

Molecule	H_2	N_2	O_2
$\theta_v(K)$	6100	3340	2230

These are fairly high values, so in T ranges where molecules dominate the composition, one can neglect the 1 in (29) and approximate $Q^v \simeq e^{-\frac{\theta_v}{2T}}$.

The Rotational Partition Function

Molecules can also rotate as a solid body. Diatomic molecules have nearly zero moment of inertia about the inter-atomic axis, so they have two independent rotations, with the same moment of inertia I . Polyatomic molecules have in general three distinct moments of inertia, about their three principal directions.

For each rotation,

$$\epsilon = \frac{H^2}{2I}$$

where H , the angular momentum, is quantized as,

$$H^2 = J(J+1)\hbar^2 \quad (J = 0, 1, 2 \dots)$$

Define a “Rotational Temperature”

$$\theta_r = \frac{\hbar^2}{2Ik} \quad (30)$$

Since the \vec{H} vector can take $2J + 1$ orientations, we have $g = 2J + 1$, and,

$$Q^r = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J + 1) e^{-J(J+1)\frac{\theta_r}{T}} \quad (31)$$

The factor σ is 2 for symmetric A-A molecule, and it accounts for the fact that the two atoms are indistinguishable, so a rotation through 180° reproduces the same configuration. For an asymmetric diatomic molecule (A-B), $\sigma = 1$. For a polyatomic molecule σ is the number of rotational coordinate sets that correspond to a single orientation, remembering that atoms of the same species are indistinguishable. Some θ_r 's for diatomic molecules are listed below:

Molecule	H_2	N_2	O_2
$\theta_v(K)$	85.4	2.86	2.07

Thus, except for H_2 possibly, $\frac{\theta_r}{T} \ll 1$ and we can convert the summation in (31) to an integral:

$$\begin{aligned} Q^r &\simeq \frac{1}{\sigma} \int_0^{\infty} (2J + 1) e^{-J(J+1)\frac{\theta_r}{T} dJ} \\ &= \frac{1}{\sigma} \frac{T}{\theta_r} \int_0^{\infty} e^{-t} dt \quad \left(t = J(J + 1) \frac{\theta_r}{T} \right) \end{aligned}$$

$$\boxed{Q_r = \frac{1}{\sigma} \frac{T}{\theta_r}} \quad (\text{diatomic or linear polyatomic}) \quad (32)$$

The calculation for non-linear polyatomic molecules is a little more involved. The result is,

$$Q_r = \frac{1}{\sigma} \left(\frac{\pi T^3}{\theta_{r_1} \theta_{r_2} \theta_{r_3}} \right)^{1/2} \quad (33)$$

Energy for the various cases

We had $E = NkT^2 \frac{\partial \ln Q}{\partial T}$ for the energy of all the particles in a distribution. Since $\ln Q$ is additive, we can apply for this translation, excitation, etc. separately:

(a) Translation

$$Q^{tr} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

$$\boxed{E^{tr} = NkT^2 \frac{3}{2} \frac{1}{T} = \frac{3}{2} NkT} \quad (34)$$

This is an example of the classical “equipartition of energy”. Translation has three quadratic pieces (in velocity), along x, y, z , and each carries an energy $\frac{1}{2}kT$ per particle.

(b) Excitation

$$Q^{exc.} = \sum_{i=0}^{\infty} g_i e^{-\frac{\epsilon_i}{kT}} \simeq g_0$$

$$\boxed{E^{exc.} = 0} \quad (35)$$

Clearly, this is only true when $\epsilon_i \gg kT$; the vast majority of the atoms are then not excited. To the next approximation (high T), $Q^{exc.} \simeq g_0 + g_1 e^{-\frac{\epsilon_1}{kT}}$, and,

$$\frac{\partial \ln Q^{exc.}}{\partial T} = \frac{g_1 \frac{\epsilon_1}{kT^2}}{g_0 + g_1 e^{-\frac{\epsilon_1}{kT}}} \simeq \frac{g_1}{g_0} e^{-\frac{\epsilon_1}{kT}} \frac{\epsilon_1}{kT^2} \text{ and so,}$$

$$E^{exc.} \simeq N \epsilon_1 \frac{g_1}{g_0} e^{-\frac{\epsilon_1}{kT}} \quad (36)$$

(c) Vibration

$$Q^v = \frac{e^{\frac{\theta_v}{2T}}}{e^{\frac{\theta_v}{T}} - 1}$$

$$\boxed{E^v = NkT^2 \left(-\frac{\theta_v}{2T^2} + \frac{e^{\frac{\theta_v}{T}}}{e^{\frac{\theta_v}{T}} - 1} \frac{\theta_v}{T^2} \right) = Nk \frac{\theta_v}{2} \frac{e^{\frac{\theta_v}{T}} + 1}{e^{\frac{\theta_v}{T}} - 1}} \quad (37)$$

which can also be written as,

$$E^v = \frac{Nk\theta_v/2}{\tanh(\frac{\theta_v}{2T})} \quad (38)$$

This is clearly for each vibrational mode. For near-room temperatures, $\frac{\theta_v}{T} \gg 1$, $\tanh \frac{\theta_v}{2T} \simeq 1$, and $E^v \simeq Nk \frac{\theta_v}{2}$. This is a temperature-independent zero-point energy, and the vibrational specific heat is zero. The vibration is said to be “not excited”.

For very high temperatures, such that $\frac{\theta_v}{T} \ll 1$, $\tanh \frac{\theta_v}{2T} \simeq \frac{\theta_v}{2T}$, and (28) gives $E^v \simeq NkT$. This is the “classical” limit (no quantum effects), and it indicates two $\frac{1}{2}kT$ contributions per particle. These come from two quadratic parts of the vibrational energy, one in velocity (kinetic energy) and one in displacement (potential energy).

(d) Rotation

For diatomics or linear polyatomics, $\frac{\partial \ln Q^r}{\partial T} = \frac{1}{T}$, whereas for other molecules, $\frac{\partial \ln Q^r}{\partial T} = \frac{3}{2} \frac{1}{T}$. Hence

$$\boxed{E^{rot} = NkT \text{ (diatomics)} ; E^{rot} = \frac{3}{2} NkT \text{ (polyatomics)}} \quad (39)$$

These are also classical, because we assumed $T \gg \theta_r$. Diatomic molecules have $\frac{1}{2}kT$ contributions, one per axis of rotation. Polyatomics have three $\frac{1}{2}kT$ contributions.

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16.55 Ionized Gases
Fall 2014

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