

## Chapter 6

# Quantum Statistics

### 6.1 Introductory Remarks

There are two main differences between *quantum statistics* and *classical statistics*:

1. In quantum statistics the energy levels are nearly always discrete. In classical statistics they are assumed to be continuous. Consider for instance the simple or one-dimensional linear harmonic oscillator. In quantum mechanics its (nondegenerate) energy levels for one element of the system are given by

$$\epsilon_n = h\nu \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \quad (6.1)$$

In classical statistics it has the energy

$$\epsilon = \frac{1}{2m}p^2 + 2\pi^2m\nu^2q^2. \quad (6.2)$$

2. The counting of the number of arrangements of the elements is different in the two types of statistics. A dominant reason for this is the *indistinguishability of the elements in quantum mechanics* (resulting directly from the uncertainty relation). This is by far the most important effect.

The difference between particles in a box in classical mechanics and those in a box in quantum mechanics is illustrated by the difference of Figs. 2.1 and 6.1; in Fig. 6.1 the states (wave functions) of the particles are shown as waves or solutions of the Schrödinger equation.

In this chapter we are concerned with the methods of counting of *arrangements of elements* taking into account the number of elements one can

put into a state, their distinguishability or indistinguishability, and whether their number is conserved or not. These conditions lead to the three different types of statistics, Maxwell–Boltzmann, Fermi–Dirac and Bose–Einstein.

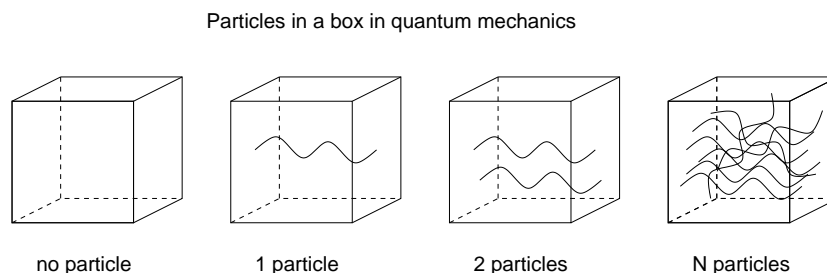


Fig. 6.1 Particles in a box described by the Schrödinger equation.

## 6.2 *A priori* Weighting in Quantum Statistics

We consider first some simple cases exhibiting and explaining the concept of *degeneracy*. Consider an isolated system and suppose the level of energy  $\epsilon_i$  has  $g_i$  degenerate states, *i.e.* it is  $g_i$ -fold degenerate. In other words, we have  $g_i$  different wave functions, *i.e.* solutions of the Schrödinger equation, with the same energy  $\epsilon_i$ . Thus, for instance, for a hydrogen-like atom the spectrum (which is also illustrated in Fig. 6.2) is given by:

$$\epsilon_n = -\left(\frac{e^2}{\hbar c}\right)^2 \frac{mc^2}{2n^2}, \quad n = 1, 2, 3, \dots \infty, \quad (6.3a)$$

where  $n = n_r + l + 1$ ,  $n_r = 0, 1, 2, \dots$ , being the radial quantum number and  $l = 0, 1, 2, \dots$ , that of orbital angular momentum. The degeneracy of the associated quantum states is given by the expression

$$\sum_{l=0}^{n-1} (2l+1) = n(n-1) + n = n^2. \quad (6.3b)$$

Thus\* there are  $n^2$  different weight functions giving the energy  $\epsilon_n$ . Therefore  $g_n = n^2$ . Each of these degenerate levels is equally important. We therefore take the *a priori* probability introduced classically in Sec. 3.2 as proportional to the number of states concerned (this is really the fundamental postulate

---

\*The degeneracy of hydrogen-like states is extensively discussed in H.J.W. Müller–Kirsten [30]. Or see A. Messiah [26], Vol. I, Sec. 11.1.4.

of equal *a priori* probabilities of an isolated system and will become clearer in the context of Sec. 11.2.2). The spectrum of these degenerate states of the hydrogen atom is illustrated in Fig. 6.2; for a consideration of the electronic partition function of the hydrogen atom see Example 6.4 — but note the problem associated with this. Since this is however a one-particle problem, we also recall from quantum mechanics the spectra of higher dimensional isotropic harmonic oscillators. The calculation of the spectra can be found in the treatise of Messiah [26] (there Sec. 12.3.1). Here we are only interested in the results in order to understand the aspect of degeneracy.

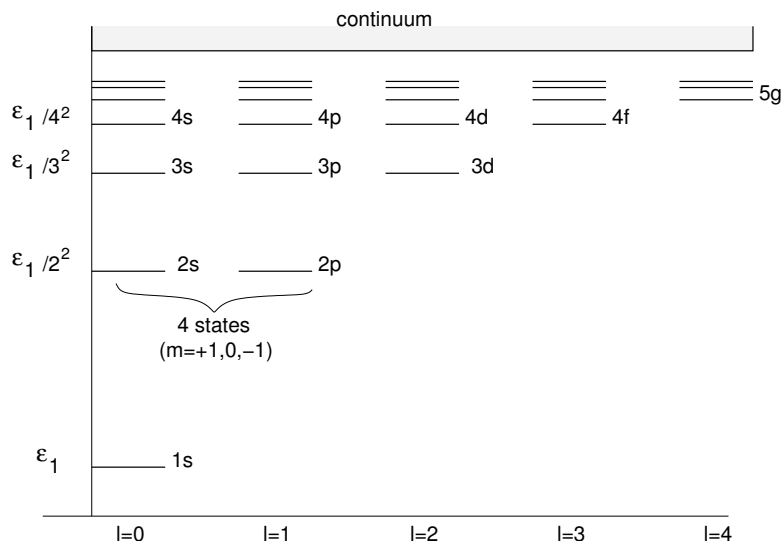


Fig. 6.2 The spectrum of the hydrogen atom.

Thus in the case of a  $p$ -dimensional isotropic harmonic oscillator with Hamiltonian (of  $p$  simple harmonic oscillators)

$$H = \sum_{i=1}^p \frac{1}{2m} (p_i^2 + m^2 \omega^2 q_i^2) \quad (6.4)$$

the eigenvalues  $\epsilon_N$ ,  $N = \sum_{i=1}^p n_i$ ,  $n_1, n_2, n_3, \dots, n_p = 0, 1, 2, \dots$ , are given by

$$\epsilon_N = \left[ N + \frac{1}{2}p \right] \hbar\omega. \quad (6.5)$$

The spectrum of these eigenvalues and the degeneracy of the associated states for  $p = 2$  is shown in Fig. 6.3.

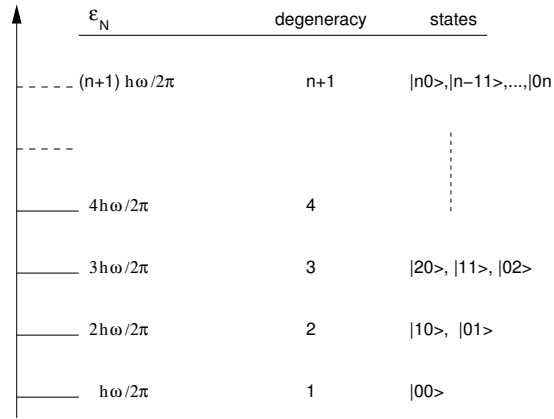


Fig. 6.3 Spectrum of the 2-dimensional isotropic oscillator.

In the special case of the 3-dimensional isotropic harmonic oscillator<sup>†</sup> the eigenvalues  $\epsilon_n$  are given by

$$\epsilon_n = \left( n + \frac{3}{2} \right) \hbar\omega, \quad n = n_x + n_y + n_z, \quad (6.6)$$

with  $n_x, n_y, n_z = 0, 1, 2, \dots$ . The degeneracy of these states (derived later in

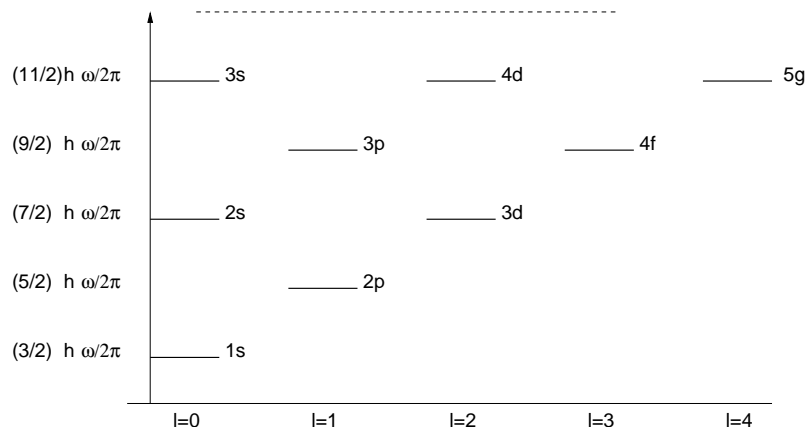


Fig. 6.4 Spectrum of the 3-dimensional isotropic oscillator.

Example 12.1) is given by<sup>‡</sup>

$$\frac{1}{2}(n+1)(n+2). \quad (6.7)$$

<sup>†</sup>A. Messiah [26], Vol. I, Sec. 12.3.3.

<sup>‡</sup>See also A. Messiah [26], Vol. I, Sec. 12.3.3.

The spectrum of this case is shown in Fig. 6.4 and may be compared with that of the hydrogen atom. The result (6.7) will be required in Example 9.3.

### 6.2.1 Approximate calculation of number of states

We recall *Heisenberg's uncertainty principle*. If  $\delta q$  is the error or uncertainty in the spatial coordinate and  $\delta p$  correspondingly the error or uncertainty in the momentum coordinate in the same direction, this principle says

$$\delta q \delta p \geq h \quad (6.8)$$

for each direction. We distinguish between  $\delta q, \delta p$  and some  $\Delta q, \Delta p$ , the latter being  $\delta q, \delta p$  of some cell units in phase space, so that  $\Delta q \Delta p / h$  is a certain number, as *e.g.* 4 in Fig. 6.5. In view of the uncertainty relation we cannot distinguish between these 4 entities, this means we cannot give them labels that permit us to distinguish one from the other. More generally, since the uncertainties  $\delta q, \delta p$  can be anything between zero and infinity, it is not possible to distinguish between particles. In classical mechanics we could do that because there the uncertainties shrink to zero and we can pinpoint a particle exactly and give it a name or label. Therefore the number of *indistinguishable* states for each direction can be taken as  $\Delta q \Delta p / h$ .

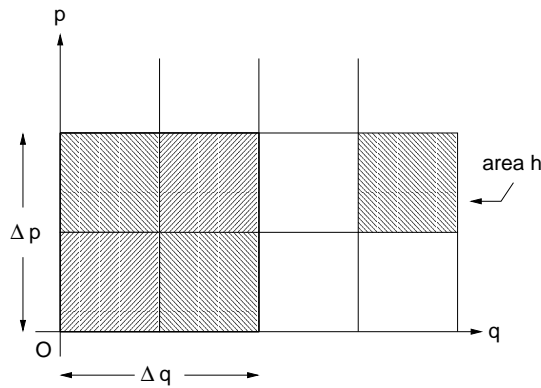


Fig. 6.5 Four states contained in  $\Delta q \Delta p$ .

Consider now, as an example, a *free* particle in three dimensional space. Since the particle is free it has no potential energy, and the number of states is

$$\frac{1}{h^3} \Delta q_x \Delta q_y \Delta q_z \times \Delta p_x \Delta p_y \Delta p_z.$$

Since the potential energy is zero this can be integrated over ordinary space to

give the volume  $V$ . Instead of the Cartesian momentum element  $dp_x dp_y dp_z$  we take the volume of a spherical momentum element as depicted in Fig. 6.6.

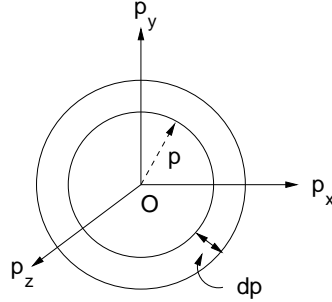


Fig. 6.6 The spherical momentum space element.

This element has volume  $4\pi p^2 dp$ . Hence the number of states in the total momentum range between  $p$  and  $p + dp$  is

$$V \frac{4\pi p^2 dp}{h^3}. \quad (6.9)$$

### 6.2.2 Accurate calculation of number of states

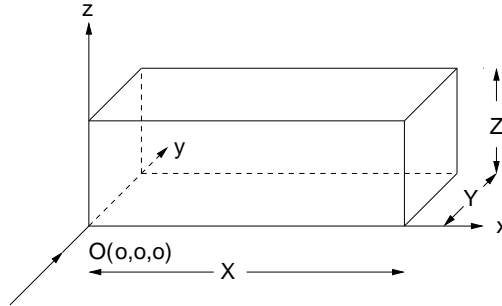


Fig. 6.7 The box-like volume element.

We now consider an accurate evaluation of the number of states per unit momentum range. The problem is to find the number of *normal modes of vibration* in the box of Fig. 6.7.

In 1924 de Broglie postulated: Associated with every particle there is a matter wave. If  $p$  is the momentum of the particle and  $\lambda$  the wavelength of the corresponding matter wave, then, so de Broglie,

$$p = \frac{h}{\lambda}.$$

If  $\psi$  is the amplitude of the matter wave, its Schrödinger wave equation is

$$\nabla^2\psi + \beta^2\psi = 0, \quad \text{where } \beta = \frac{\omega}{c}. \quad (6.10)$$

Here  $\omega$  is the circular frequency  $= 2\pi \times$  ordinary frequency  $\nu$ , and  $c$  is the phase velocity of the wave. Thus with  $c = \nu\lambda$  we have

$$\beta = \frac{2\pi\nu}{c} = \frac{2\pi}{\lambda}.$$

For a Cartesian coordinate system Eq. (6.10) is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \beta^2\psi = 0. \quad (6.11)$$

As solution we take

$$\psi \propto \sin\left(\frac{l\pi x}{X}\right) \sin\left(\frac{m\pi y}{Y}\right) \sin\left(\frac{n\pi z}{Z}\right), \quad (6.12)$$

or with cosines. The expression with sines is more suitable for the analysis to follow. Hence by substitution into Eq. (6.11) we obtain (*cf.* Fig. 6.8)

$$\frac{l^2}{X^2} + \frac{m^2}{Y^2} + \frac{n^2}{Z^2} = \frac{\beta^2}{\pi^2}, \quad (6.13)$$

where  $l, m, n$  are positive integers unequal to zero, to prevent duplication.

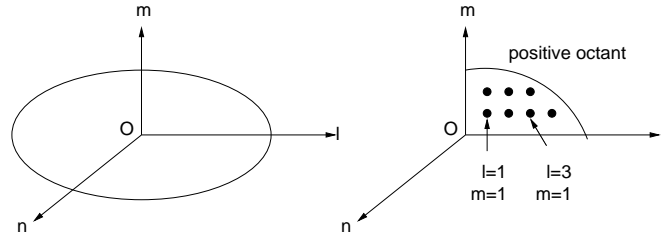


Fig. 6.8 The ellipsoid and its positive octant.

Hence if  $l, m, n$  are integers, the amplitude is zero on all walls of the box (where  $x = X, y = Y, z = Z$ ). The vanishing of the Schrödinger wave function on all walls of the box is the quantum mechanical boundary condition which confines the particle to the inside of the box. Note that here the box is defined by simple 3-dimensional Cartesian coordinates. In the case of a spherical volume the solution (6.12) would involve a spherical Bessel function, and the eigenvalues  $\propto \beta^2$  would be determined by the zeros of this function

(see Examples 6.13 and 7.9). Now consider a range of  $\beta$  corresponding to a range of  $\lambda$ . We want to find the number of solutions for which the inequality

$$\frac{l^2}{X^2} + \frac{m^2}{Y^2} + \frac{n^2}{Z^2} < \frac{\beta^2}{\pi^2} \quad (6.14)$$

is satisfied. We have (note that  $\beta X, \beta Y, \beta Z$  are dimensionless)

$$\frac{l^2}{(\beta X/\pi)^2} + \frac{m^2}{(\beta Y/\pi)^2} + \frac{n^2}{(\beta Z/\pi)^2} < 1. \quad (6.15)$$

This is the equation for the interior of an ellipsoid, *i.e.* for the region within an ellipsoid with semi-axes of lengths  $\beta X/\pi, \beta Y/\pi, \beta Z/\pi$ . We deal only with the positive octant, *i.e.* with positive  $l, m, n$ , as indicated in Fig. 6.8. Since the spacing between the  $l$ 's is unity, and similarly that for the  $m$ 's and  $n$ 's, the size of a unit cell is 1. Hence the number of  $(l, m, n)$  values<sup>§</sup> is approximately equal to the volume of the octant. This is valid only if the number of points within the octant is very large — the case we consider here. The volume of the (non-spatial) octant  $V_{1/8}$ , with  $V = 8V_{1/8}$ , is<sup>¶</sup>

$$\begin{aligned} V_{1/8} &= \frac{1}{8} \frac{4}{3} \pi \left( \frac{\beta X}{\pi} \right) \left( \frac{\beta Y}{\pi} \right) \left( \frac{\beta Z}{\pi} \right) \\ &= XYZ \frac{1}{6} \beta^3 \frac{1}{\pi^2} = V \frac{1}{6} \frac{\beta^3}{\pi^2} \\ &= \text{number of states.} \end{aligned} \quad (6.16)$$

Since  $p = h/\lambda = \beta h/2\pi$ , we have  $\beta = 2\pi p/h$ . Hence the number of states with momentum less than  $p$  is equal to the number  $\mathcal{N}$  of normal modes of vibration of the matter wave in the octant and is

$$\mathcal{N} = \frac{1}{6\pi^2} V \left( \frac{2\pi p}{h} \right)^3 = V \frac{4}{3} \pi \frac{p^3}{h^3}.$$

Hence the *number of states* with momenta between  $p$  and  $p + dp$  in a rectangular box of volume  $V$  is, with energy  $\epsilon = p^2/2m$ ,

$$d\mathcal{N} = V \frac{4\pi p^2 dp}{h^3} = \frac{2\pi V (2m)^{3/2}}{h^3} \epsilon^{1/2} d\epsilon,$$

and this is equal to the value of  $g$  corresponding to a certain momentum range. The result is seen to agree with that in Eq. (6.9), and with the result

<sup>§</sup>This number expressed in terms of the wave number  $\beta$  is called the number of *normal modes*; expressed in terms of momentum it is called the number of *wave-mechanical states*.

<sup>¶</sup>Recall that the area of a circle of radius  $a$  is  $\pi a^2$  and correspondingly the area of an ellipse of semi-major and minor axes  $a$  and  $b$  is  $\pi ab$ . Similarly the volume of a sphere of radius  $a$  is  $4\pi a^3/3$  and that of an ellipsoid of semi-axes  $a, b, c$  is  $4\pi abc/3$ .

(3.9c), the corresponding *a priori* probability. Thus this number of states, the degree of degeneracy, is given by the *a priori* probability as stipulated earlier.

We summarize the above findings in the following statements:

1. We deduce from *Heisenberg's uncertainty principle* that in the approximation in which energy levels are taken to form a continuum, we have

$$\sum_i g_i f(\epsilon_i) = \int \int \cdots \int f(\epsilon) \frac{(dq_1 dq_2 \cdots dq_n)(dp_1 dp_2 \cdots dp_n)}{h^n}, \quad (6.17)$$

where  $\epsilon_i, i = 1, 2, 3, \dots$ , are the possible energy levels of the elements comprising the system,  $n$  is the number of dimensions of the system, and  $gf$  is a distribution function, and  $g$  the *a priori* probability.<sup>||</sup>

2. As an illustration we deduce from Eq. (6.17) that for a free atom in a 3-dimensional volume  $V$ ,

$$\sum_i g_i f(\epsilon_i) = \frac{4\pi V}{h^3} \int f\left(\frac{p^2}{2m}\right) p^2 dp = \frac{2\pi V (2m)^{3/2}}{h^3} \int \epsilon^{1/2} f(\epsilon) d\epsilon. \quad (6.18)$$

This result is confirmed by finding from Schrödinger's equation the energy levels of an atom in a rectangular box and making an approximate evaluation of the number of levels per unit energy range, as we did in the preceding considerations.

### 6.2.3 Examples

#### Example 6.1: Number of quantum states in one dimension

Calculate the approximate number of normal modes with wave numbers between  $\beta$  and  $\beta + d\beta$  associated with the one-dimensional Schrödinger equation

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \beta^2 \psi(x) = 0, \quad \beta = \frac{2\pi}{\lambda}, \quad (6.19)$$

in the domain  $0 < x < L$ . Show that the result could have been obtained by considering the number of half-wavelengths which could be fitted into the length  $L$ . Why would the corresponding number of wave-mechanical states be  $Ldp_x/h$ , and not  $2Ldp_x/h$ , as might appear at first sight?

**Solution:** We have

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \beta^2 \psi(x) = 0, \quad (6.20)$$

---

<sup>||</sup> Recall that in mathematical terms, probability is a *measure* defined for each event, like length, area or volume of a region in one, two or three dimensions. For a non-technical discussion of how the concept of probability is arrived at see A. Ben-Naim [3], pp. 25–30.

and we choose  $\psi(x) \propto \sin(l\pi x/L)$  with  $l$  an integer so that  $\psi(0) = 0$  and  $\psi(L) = 0$ . Then

$$\frac{\partial^2 \psi}{\partial x^2} \propto -\frac{l^2 \pi^2}{L^2} \psi,$$

and therefore

$$\beta^2 = \frac{l^2 \pi^2}{L^2}, \quad \beta = \begin{matrix} (+) \\ (-) \end{matrix} \frac{l\pi}{L}. \quad (6.21)$$

Therefore the integer  $l$  which is equal to the number of normal modes in the domain  $0 < x < L$  is given by

$$l = \frac{L\beta}{\pi}. \quad (6.22)$$

Then

$$dl = \frac{Ld\beta}{\pi}, \quad (6.23)$$

which is the requested number of normal modes. The number of half wavelengths,  $\lambda/2$ , which could be fitted into  $L$  is (since  $\beta = 2\pi/\lambda$ )

$$\frac{L}{\lambda/2} = \frac{2L}{\lambda} = \frac{L\beta}{\pi}. \quad (6.24)$$

Hence as before we obtain  $Ld\beta/\pi$ . Now consider the wave mechanical states with momentum  $p_x$ . Here

$$p_x = \frac{h}{\lambda} = \frac{\beta h}{2\pi}, \quad \beta = \frac{2\pi p_x}{h}. \quad (6.25)$$

Therefore at first sight:

$$\frac{Ld\beta}{\pi} = \frac{L2\pi dp_x}{h\pi} = \frac{2Ldp_x}{h}. \quad (6.26)$$

Here we have to divide by 2 in order to get the number of wave-mechanical states. The reason is that  $p_x$  in Eq. (6.25) can be positive or negative but  $\beta$  is to be positive. This requires  $p_x$  or  $L$  to be divided by 2 here. This is the 1-dimensional reduction of the 2- and 3-dimensional cases of Example 6.2 and Sec. 6.2.2 respectively.

### Example 6.2: Number of quantum states in two dimensions

By considering the solutions of the two-dimensional Schrödinger equation

$$\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} + \beta^2 \psi(x, y) = 0 \quad (6.27)$$

for the rectangular region  $0 < x < X, 0 < y < Y$ , show that the number of normal modes in the wave number domain between  $\beta$  and  $\beta + d\beta$  is approximately  $A\beta d\beta/2\pi$ , where  $A$  is the area  $XY$ . Show that the corresponding number of wave-mechanical states is  $2\pi A p dp/h^2$ .

**Solution:** In this case we have

$$\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} + \beta^2 \psi(x, y) = 0. \quad (6.28)$$

We choose

$$\psi(x, y) \propto \sin\left(\frac{l\pi x}{X}\right) \sin\left(\frac{m\pi y}{Y}\right). \quad (6.29)$$

Inserting this into the wave equation we obtain

$$\frac{l^2}{X^2} + \frac{m^2}{Y^2} = \frac{\beta^2}{\pi^2}. \quad (6.30)$$

The domain within the ellipse shown in Fig. 6.8 is therefore given by the inequality

$$\frac{l^2}{(\beta X/\pi)^2} + \frac{m^2}{(\beta Y/\pi)^2} \leq 1. \quad (6.31)$$

Since the spacing between the  $l$  values is unity and similarly that of the  $m$ 's, the size of a unit cell is 1. Hence the number of  $(l, m)$ -values is approximately equal to the area of a quadrant of the ellipse ( $l, m \geq 0$ ). The area of the quadrant is

$$\frac{1}{4}\pi \frac{\beta^2 XY}{\pi^2} = \frac{1}{4} \frac{\beta^2 A}{\pi}, \quad A = XY. \quad (6.32)$$

This is the number of states. Now

$$p = \frac{h}{\lambda} = \frac{\beta h}{2\pi}, \quad \therefore \beta = \frac{2\pi p}{h}. \quad (6.33)$$

It follows that the number of states with  $\beta$  between  $\beta$  and  $\beta + d\beta$  is

$$\frac{d}{d\beta} \left[ \frac{1}{4} \frac{\beta^2 A}{\pi} \right] d\beta = \frac{1}{2} \frac{A\beta d\beta}{\pi} = \frac{1}{2} A \frac{2\pi p}{h\pi} \frac{2\pi dp}{h} = \frac{2\pi A p dp}{h^2}. \quad (6.34)$$

This result could also have been obtained by multiplying  $\delta x \delta y / h^2 = A/h^2$  by  $\delta p_x \delta p_y = 2\pi p dp$  (this is the 2-dimensional version of the 3-dimensional case of Sec. 6.2.1).

### Example 6.3: Density of states of the harmonic oscillator

Assuming that the number of quantum states in a range  $\delta q \delta p$  for each direction of motion is given, per element, by a factor  $\delta q \delta p / h$ , show that the number of states in the energy range  $d\epsilon$  is for a simple harmonic oscillator of natural frequency  $\nu$  given by  $d\epsilon/h\nu$  as deduced from Eq. (3.12). From elementary quantum mechanics it is known that the energy levels of the simple harmonic oscillator are given by  $\epsilon_n = h\nu(n + 1/2)$ , and are non-degenerate. Calculate approximately the number of states in range  $d\epsilon$  by evaluating  $\partial n / \partial \epsilon = 1/(\partial \epsilon / \partial n)$ .

**Solution:** As given, we have  $g = d\epsilon/\nu = dq dp$ . Hence

$$\frac{dq dp}{h} = \frac{d\epsilon}{h\nu}.$$

The number of states in the range  $d\epsilon$  is  $d\epsilon/h\nu$ . Since  $\epsilon_n = h\nu(n + 1/2)$ , we have  $\partial \epsilon_n / \partial n = h\nu$ , so that

$$\frac{1}{\partial \epsilon / \partial n} = \frac{1}{h\nu} = \frac{\partial n}{\partial \epsilon}, \quad \frac{d\epsilon}{h\nu} = dn. \quad (6.35)$$

### Example 6.4: Number of states of a diatomic molecule in the range $d\epsilon$

Assuming that the number of quantum states in a range  $\delta q \delta p$  for each direction of motion is given, per element, by a factor  $\delta q \delta p / h$ , show that the number of states in the energy range  $d\epsilon$  is  $8\pi^2 I d\epsilon / h^2$  for a rotating diatomic molecule (*cf.* Example 3.6). It is known from wave mechanics that the energy levels of a rotating diatomic molecule are  $\epsilon_J = J(J + 1)h^2/8\pi^2 I$ , each such level being  $(2J + 1)$ -fold degenerate. Calculate approximately the number of states in range  $d\epsilon$  by evaluating  $\partial J / \partial \epsilon = 1/(\partial \epsilon / \partial J)$  and multiplying by the corresponding degeneracy.

**Solution:** From Example 3.6, Eq. (3.25), we know that in the case of the diatomic molecule of moment of inertia  $I$  the *a priori* weighting  $g$  is given by  $g \propto 8\pi^2 I d\epsilon$ . In terms of polar and azimuthal angles  $\theta$  and  $\phi$  we have  $g \propto dq_\theta dq_\phi dp_\theta dp_\phi$ . Here the first two factors are of no importance in view of symmetry conditions. Therefore we have

$$\frac{g}{h^2} = \frac{8\pi^2 I d\epsilon}{h^2}. \quad (6.36)$$

Since

$$\epsilon_J = \frac{J(J+1)h^2}{8\pi^2 I}, \quad \frac{\partial \epsilon_J}{\partial J} = \frac{(2J+1)h^2}{8\pi^2 I}, \quad \frac{\partial J}{\partial \epsilon_J} = \frac{8\pi^2 I}{(2J+1)h^2}, \quad (6.37)$$

we obtain

$$(2J+1) \frac{\partial J}{\partial \epsilon_J} = \frac{8\pi^2 I}{h^2}. \quad (6.38)$$

Therefore the number of states in the range  $d\epsilon$  is approximately  $(2J+1)dJ = 8\pi^2 I d\epsilon/h^2 = g d\epsilon/h^2$ .

### Example 6.5: The partition function for the hydrogen atom

In Sec. 6.2 the hydrogen atom was referred to and its discrete energy eigenvalues were given and the degeneracy  $n^2$  was cited. Establish the electronic partition function (defined in Eq. (5.13)) and consider its sum.

**Solution:** The energy of the  $n$ th energy level of the hydrogen atom, as derived in books on quantum mechanics, is  $\epsilon_n = -R_\infty/n^2$ , where  $R_\infty$  is the constant, known as *Rydberg constant*, given in Eq. (6.3a). The partition function  $Z$  was defined in Eq. (5.13). Measuring the excited energies from the ground state  $n = 1$  upwards, the *electronic partition function* per atom is

$$Z_{\text{el}} = \sum_n n^2 \exp \left[ -\frac{R_\infty}{kT} \left( 1 - \frac{1}{n^2} \right) \right]. \quad (6.39)$$

Here the nondegenerate ground state energy has been subtracted out. We observe that owing to the degeneracy  $g = n^2$ , the sum does not converge, implying that the sum is infinite. This cannot be correct, and may be another one of the divergence problems associated with the Coulomb potential and solved in field theory by vacuum polarization.\*\*

## 6.3 The Allowed Number of Elements in Quantum States

### 6.3.1 One element

Consider one particle (element) 'a'. This particle will be represented by a wave function. The wave function of the matter wave has an amplitude  $\psi(a)$ . The intensity is proportional to the square of the amplitude (assumed real as in the previous section). The probability of finding the element per unit volume is equal to

$$\psi_n^2(a),$$

or, more generally, as in the case when  $\psi$  is complex,  $|\psi_n(a)|^2$ . The quantum number  $n$  designates the energy level in which the element is situated.

### 6.3.2 Two non-interacting elements

We consider non-interacting elements, like *e.g.* the non-interacting atoms or molecules of a perfect gas. Let the particles be 'a' and 'b'. At first sight one

---

\*\*For a simple discussion see R.P.H. Gasser and W.G. Richards [17], p. 45.

would think the wave function of the pair is

$$\Psi_1 = \psi_n(a)\psi_m(b),$$

where  $\Psi_1$  is the total wave function for the system consisting of the two non-interacting elements. However,  $\Psi_1$  is only one solution. There is another solution

$$\Psi_2 = \psi_m(a)\psi_n(b).$$

The energy of the 2-particle state is the same in both cases, but the (identical) elements are interchanged. This solution is therefore just as good as the first ( $m$  and  $n$  being quantum numbers).

What linear combination forms the actual wave function? The condition that the interchange of 'a' and 'b' labels is unobservable is that the observed probability

$$\Psi^2(a, b) \quad \text{or} \quad |\Psi(a, b)|^2$$

is independent of the interchange of 'a' and 'b'. Hence

$$\Psi^2(a, b) = \Psi^2(b, a), \quad (6.40)$$

and therefore

$$\Psi(a, b) = \pm\Psi(b, a). \quad (6.41)$$

Hence the conditions are satisfied only by

$$\Psi(a, b) \rightarrow \Psi_{\pm}(a, b) = \Psi_1 \pm \Psi_2 = \psi_n(a)\psi_m(b) \pm \psi_m(a)\psi_n(b). \quad (6.42)$$

Here the + sign gives a *symmetrical total wave function*, and the - sign an *antisymmetrical total wave function*. The transition probability between wave functions of different symmetry is zero, because

$$\int dV \Psi_+(a, b)\Psi_-(a, b) = \int dV \psi_n^2(a)\psi_m^2(b) - \int dV \psi_m^2(a)\psi_n^2(b) = 0.$$

For practically all basic real elementary particles, *e.g.* electrons, protons *etc.* (but also quarks), the spatial wave functions are antisymmetrical and give rise to *Fermi-Dirac statistics*. Non-real elements, such as photons and phonons, but also mesons (*e.g.* pions) obey the spatially symmetrical *Bose-Einstein statistics*. For Bose-Einstein statistics it is possible to have  $m = n$ , so that

$$\Psi \propto \psi_n(a)\psi_n(b)$$

for any number of elements in the same state. In the case of Fermi-Dirac statistics with the antisymmetrical total wave function, putting  $n = m$  implies

$$\Psi \propto \psi_n(a)\psi_n(b) - \psi_n(a)\psi_n(b) = 0.$$

Thus this number state corresponds to that of the *Pauli exclusion principle*. This says, it is impossible to put more than one element into a given quantum state.

### 6.3.3 More than two elements

In the case of *polyatomic molecules* which contain identical atoms only such states are realizable in nature for which the total wave functions are (a) symmetric if the mass number (*i.e.* number of elementary particles) of the atoms is even, or (b) antisymmetric if this mass number is odd. An even number of particles stuck together obeys Bose–Einstein statistics in spite of the fact that each of them separately obeys Fermi–Dirac statistics. This follows from the fact that an even number of changes of sign in the total wave function produces no change in sign. For example, Helium with atomic weight 4 has four elementary particles contained in its nucleus, *i.e.* an even number of elementary particles in the nucleus. Hence He obeys Bose–Einstein statistics, although the elementary particles of which it is composed obey Fermi–Dirac statistics. Hence Bose–Einstein statistics can also apply to real atoms.

## 6.4 Counting of Number of Arrangements

We now consider the counting of the *number of arrangements* of a number of elements in quantum statistics, *e.g.*  $N$ . We assume

1. The elements are indistinguishable from one another, *i.e.* they have no labels.
2. In the case of Bose–Einstein statistics we can have any number of elements in the same state. In the case of Fermi–Dirac statistics we have either 0 or 1 element in each state.

### 6.4.1 Fermi–Dirac statistics

We begin with Fermi–Dirac statistics. *Temporarily* attach labels to the elements. Let us deal with one energy level of a one-particle system of energy  $\epsilon_i$  by itself. Let the degeneracy of this energy level  $\epsilon_i$  be  $g_i$ , *i.e.*  $g_i$  states all have the same energy  $\epsilon_i$ , as indicated in Fig. 6.9. Suppose there are  $n_i$  elements to be distributed amongst the  $g_i$  states (temporarily with labels attached).

Stick the first element in any one of the  $g_i$  states (since we are considering Fermi–Dirac statistics this one element is the only one we can put into this state),

stick the second element in any one of the other  $(g_i - 1)$  states (again only one element is admissible),

.....

Therefore the number of arrangements is

$$\begin{aligned} &= g_i(g_i - 1)(g_i - 2) \cdots \quad \text{to } n_i \text{ factors} \\ &= g_i(g_i - 1)(g_i - 2) \cdots (g_i - n_i + 1) \\ &= \frac{g_i!}{(g_i - n_i)!}. \end{aligned}$$

To remove the labels attached to these elements we divide this number of arrangements of  $n_i$  particles with labels by the number of arrangements of  $n_i$  elements amongst themselves, *i.e.*  $n_i!$ .

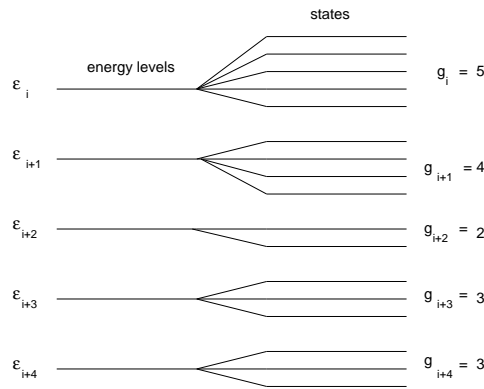


Fig. 6.9 Energy levels with energy  $\epsilon_i$  and degeneracy  $g_i$ .

Therefore the number of arrangements required is:

$$\frac{g_i!}{n_i!(g_i - n_i)!} = g_i C_{n_i} = \binom{g_i}{n_i}. \quad (6.43)$$

Therefore, taking into account *all* the energy levels of the total number of indistinguishable elements  $N = \sum_i n_i$ , the number of arrangements becomes

$$\prod_i \frac{g_i!}{n_i!(g_i - n_i)!} = W_{FD}. \quad (6.44)$$

This expression is referred-to as the *number of arrangements of particles in Fermi–Dirac statistics*.

### 6.4.2 Bose–Einstein statistics

Next we consider Bose–Einstein statistics. *Temporarily* we attach labels to both states and elements. A typical arrangement of elements amongst states is (omitting indices  $i$ ):

$$g^{(4)} n^{(1)} n^{(27)} g^{(2)} n^{(2)} n^{(4)} n^{(5)} g^{(13)} g^{(3)}.$$

Here  $g^{(4)}$  stands for “state labelled ‘4’”, and (note the order of  $g$ ’s and  $n$ ’s)  $n^{(1)}, n^{(27)}$  stand for “elements numbers (1) and (27) put into state  $g^{(4)}$ ”. In the given arrangement there are no elements in state  $g^{(13)}$ ! Hence in describing our arrangements we must always start with a state, *i.e.* with a  $g$ . The remaining  $(g + n - 1)$  quantities can be arranged in any way. Therefore:

$$\text{number of arrangements} = g(g + n - 1)!, \quad (6.45a)$$

where the factor  $g$  on the right gives the number of ways of choosing a  $g$  to be the first quantity.

Now remove the labels on the  $n$ ’s by dividing by  $n!$ . Also remove the labels on the  $g$ ’s by dividing by  $g!$ . Hence if both states and elements are unlabelled, the number of arrangements is

$$\frac{g(g + n - 1)!}{n!g!} = \frac{(g + n - 1)!}{n!(g - 1)!}, \quad (6.45b)$$

and therefore the *number of arrangements of particles in Bose–Einstein statistics* is

$$W_{BE} = \prod_i \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!}. \quad (6.46)$$

Both this and the Fermi–Dirac number of arrangements (6.44) should now be compared with the Maxwell–Boltzmann number of arrangements given by Eq. (4.2), *i.e.*

$$W_{MB} = N! \prod_i \frac{g_i^{n_i}}{n_i!}. \quad (6.47)$$

It is particularly instructive to consider the comparison at high temperatures. This is done in the next section.

## 6.5 Quantum Statistics at High Temperatures

We want to consider the relationships between the  $W$ ’s at high temperatures. At high temperatures plenty of energy is available and the high energy levels are very often occupied ( $\epsilon$  is large). Therefore over all states the dilution is

very great. Plenty of states are effectively available. Therefore the probability of any state being occupied is small. Therefore the maximum occupation of energy level  $\epsilon_i$  is  $g_i$ , *i.e.*  $n_i = g_i$ . Therefore at high temperatures  $n_i$  is normally less than this maximum, *i.e.*:

$$n_i \ll g_i. \quad (6.48)$$

Consider  $W_{FD}$ . In this case

$$\frac{g!}{n!(g-n)!} = \frac{g(g-1)(g-2)\cdots \text{to } n \text{ factors}}{n!} \sim \frac{g^n}{n!}, \quad (6.49)$$

where  $\sim$  means 'of order of magnitude'. Thus at high temperatures

$$W_{FD} \rightarrow \prod_i \frac{g_i^{n_i}}{n_i!}. \quad (6.50)$$

However, at all temperatures:

$$W_{MB} = N! \prod_i \frac{g_i^{n_i}}{n_i!}. \quad (6.51)$$

Similarly at high temperatures:

$$W_{BE} \rightarrow \prod_i \frac{g_i^{n_i}}{n_i!} \quad (6.52)$$

Hence *the classical Maxwell-Boltzmann result is wrong*, even at high temperatures it is wrong by the factor  $N!$ . In classical statistics the elements are erroneously regarded as distinguishable which, of course, is wrong according to the Heisenberg uncertainty principle (*cf.* the extra factor  $N!$  in  $W_{MB}$ ).<sup>††</sup>

We now *consider the removal* of the factor  $N!$  from previous classical results (*e.g.*  $W_{MB}$ ). Then there is no difference in occupation numbers, *i.e.* (*cf.* Eqs. (4.10), (4.14))

$$\begin{aligned} n_i &= g_i e^{-\epsilon_i/kT} && \text{for nonconserved elements,} \\ n_i &= \frac{N g_i e^{-\epsilon_i/kT}}{\sum_i g_i e^{-\epsilon_i/kT}} && \text{for conserved elements.} \end{aligned} \quad (6.53)$$

---

<sup>††</sup>This does not mean that Maxwell-Boltzmann statistics is always wrong — it is wrong only in the case of indistinguishable elements. For a case in which Maxwell-Boltzmann statistics is appropriate see Example 9.2.

However, it does affect the entropy  $S$ . We consider this now. Since  $S_{MB} = k \ln W_{MB}$ , we must subtract  $k \ln N!$  from  $S_{MB}$ . We had (*cf.* Eqs. (5.11), (5.9)) for the Maxwell–Boltzmann entropy

$$S_{MB} = \frac{E}{T} + Nk \ln \sum_i g_i e^{-\epsilon_i/kT}. \quad (6.54)$$

Therefore the high temperature quantum statistics entropy  $S$  is given by:

$$S \simeq S_{MB} - k \ln N! \simeq S_{MB} - kN(\ln N - 1), \quad (6.55)$$

where we used Stirling's theorem  $\ln N! \simeq N(\ln N - 1)$  for  $N$  large. Therefore from Eqs. (5.11), (5.9):

$$S = \frac{E}{T} + Nk \left[ 1 + \ln \left( \frac{\sum_i g_i e^{-\epsilon_i/kT}}{N} \right) \right]. \quad (6.56)$$

From this we obtain the *high temperature* free energy  $F$  as

$$F \stackrel{(5.10)}{=} E - TS = F_{MB} + kT \ln N! = -NkT \left[ 1 + \ln \left( \frac{\sum_i g_i e^{-\epsilon_i/kT}}{N} \right) \right]. \quad (6.57)$$

This is the free energy  $F$  with the factor  $N!$  removed from  $W_{MB}$ . We can now consider applications.

## 6.6 Applications

We apply the above results to *free particles*, *i.e.* here to a monatomic gas, in a volume  $V$ . In this case

$$g = V \frac{4\pi p^2 dp}{h^3}, \quad (6.58)$$

and therefore, using one of the results (2.20),

$$\sum_i g_i e^{-\epsilon_i/kT} = \frac{4\pi V}{h^3} \int_0^\infty e^{-p^2/2mkT} p^2 dp = \frac{V}{h^3} (2\pi mkT)^{3/2}. \quad (6.59)$$

By a corresponding direct evaluation of

$$E = \sum_i n_i \epsilon_i,$$

or by equipartition of energy, we obtain

$$E = \frac{3}{2} NkT. \quad (6.60)$$

The entropy  $S$  of a vapour is therefore given by

$$\begin{aligned}
 S &\stackrel{(6.56)}{=} \frac{E}{T} + Nk \left[ 1 + \ln \left( \frac{\sum_i g_i e^{-\epsilon_i/kT}}{N} \right) \right] \\
 &\stackrel{(6.60)}{=} Nk \left[ 1 + \frac{3}{2} + \ln \left( \frac{\sum_i g_i e^{-\epsilon_i/kT}}{N} \right) \right] \\
 &\stackrel{(6.59)}{=} Nk \left[ \frac{5}{2} + \ln \left\{ \frac{V}{Nh^3} (2\pi mkT)^{3/2} \right\} \right] \\
 &= Nk \left[ \frac{3}{2} \ln T + \ln \frac{V}{N} + \frac{5}{2} + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^3} \right) \right]. \quad (6.61)
 \end{aligned}$$

This formula\* is known as the *Sackur–Tetrode formula*.<sup>†</sup> From this formula, valid at temperatures low enough to permit neglecting the entropy of the condensed states, we can derive below the vapour pressure. We combine this with the expression for the *latent heat*  $L_{\text{vapour}}$  of a vapour. This latent heat is as in Eq. (5.52) defined as the quantity:

$$L_{\text{vapour}} = \frac{1}{T} (S_{\text{vapour}} - S_{\text{liquid}}), \quad (6.62)$$

where  $S_{\text{liquid}}$  is very small and almost constant. With (*cf.* Eq. (5.17))

$$P_{\text{vapour}} = T \left( \frac{\partial S}{\partial V} \right)_E = \left( \frac{N}{V} \right) kT \quad (6.63)$$

the vapour pressure is obtained in terms of  $L_{\text{vapour}}$  and  $T$ .

## 6.7 Summary

We summarize our results for the distributions:

$$W_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{(g_i - 1)! n_i!}, \quad (6.64)$$

$$W_{FD} = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}. \quad (6.65)$$

We observe that in each case: The sum of terms in the numerator = the sum of terms in the denominator.

---

\*Observe that the term  $\ln V$  in the classical (Maxwell–Boltzmann) expression (5.47) (there per atom) is here in the quantum statistical result  $\ln(V/N)$ .

<sup>†</sup>For further discussion see R.P.H. Gasser and W.G. Richards [17], pp. 38–40, E. Schrödinger [39], p. 57.

The results of high temperature quantum statistics are good enough for dilute systems (a system is dilute when its elements are at large distances away from one another), *i.e.* for perfect gases. But this does not apply to solids and liquids. Hence use high temperature results for all gases.

## 6.8 Applications and Examples

### Example 6.6: Estimating errors in high temperature approximations

By employing the methods of Examples 4.1, 4.2, estimate the respective errors incurred in approximating

$$W_{FD} = \prod_i \frac{g_i!}{(g_i - n_i)!n_i!} \quad \text{and} \quad W_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{(g_i - 1)!n_i!} \quad (6.66)$$

by  $\tilde{W} = \prod_i g_i^{n_i}/n_i!$ .

**Solution:** Consider the *Fermi-Dirac distribution*. As argued before Eq. (6.48) high temperatures imply  $g_i \gg n_i$ . In this case we have, with the help of the Stirling formula  $n! \simeq \sqrt{2\pi n} n^{n+1/2} e^{-n}$ ,

$$\frac{g_i!}{(g_i - n_i)!n_i!} \simeq \frac{g_i^{g_i+1/2} e^{-g_i}}{g_i^{g_i-n_i+1/2} e^{-g_i+n_i} n_i!} \simeq \frac{1}{n_i! e^{n_i}} \simeq \frac{g_i^{n_i}}{n_i!}. \quad (6.67)$$

The error incurred by this approximation is  $\Delta = W_{FD} - \tilde{W}$ , *i.e.*

$$\begin{aligned} \Delta &= \prod_i \frac{g_i!}{(g_i - n_i)!n_i!} - \prod_i \frac{g_i^{n_i}}{n_i!} \\ &= \prod_i \frac{g_i^{g_i+1/2} e^{-g_i}}{\sqrt{2\pi}(g_i - n_i)^{g_i-n_i+1/2} e^{-g_i+n_i} n_i^{n_i+1/2} e^{-n_i}} - \prod_i \frac{g_i^{n_i}}{n_i!} \\ &\simeq \prod_i \frac{g_i^{g_i+1/2}}{\sqrt{2\pi} g_i^{g_i-n_i+1/2} (1 - n_i/g_i)^{g_i-n_i+1/2} n_i^{n_i+1/2}} - \prod_i \frac{g_i^{n_i}}{n_i!} \\ &\simeq \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i+1/2}} \left(1 - \frac{n_i}{g_i}\right)^{-g_i+n_i-1/2} - \prod_i \frac{g_i^{n_i}}{n_i!} \\ &\simeq \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i+1/2}} \left(1 - \frac{n_i}{g_i}\right)^{-g_i+n_i-1/2} - \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i+1/2}} e^{n_i}. \end{aligned} \quad (6.68)$$

In this expression

$$\left(1 - \frac{n_i}{g_i}\right)^{-g_i} \left\{ \left(1 - \frac{n_i}{g_i}\right)^{n_i-1/2} \right\}^{g_i \rightarrow \infty} \simeq \frac{1}{e^{-n_i}} \left\{ 1 - \frac{n_i(n_i - 1/2)}{g_i} \right\}, \quad (6.69)$$

where we used a formula of the exponential function given in the literature.\* Hence

$$\Delta \simeq \left( \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i+1/2}} e^{n_i} \right) \prod_i \left\{ 1 - \frac{n_i(n_i - 1/2)}{g_i} \right\} - \left( \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i+1/2}} e^{n_i} \right)$$

\*See *e.g.* R. Courant [8], Vol.I, p. 175:

$$e^N = \lim_{n \rightarrow \infty} \left(1 + \frac{N}{n}\right)^n.$$

$$\simeq \left( \prod_i \frac{g_i^{n_i} e^{n_i}}{\sqrt{2\pi n_i}^{n_i+1/2}} \right) \left( - \sum_i \frac{n_i(n_i-1/2)}{g_i} \right) = - \left( \sum_i \frac{n_i(n_i-1/2)}{g_i} \right) \bar{W}. \quad (6.70)$$

Thus the error is of the order of  $\bar{W}/(\text{degeneracies } g_i)$ , where  $g_i \gg n_i$  for all  $i$ .

In the case of *Bose-Einstein statistics* we arrive at a similar result. We have with the help of Stirling's formula in the form given above:

$$\frac{(n_i + g_i - 1)!}{(g_i - 1)! n_i!} \simeq \frac{(n_i + g_i - 1)^{n_i + g_i - 1/2} e^{-n_i - g_i + 1}}{(g_i - 1)^{g_i - 1/2} e^{-g_i + 1} n_i!} \simeq \frac{g_i^{n_i}}{n_i! e^{n_i}} \stackrel{g_i \gg n_i}{\simeq} \frac{g_i^{n_i}}{n_i!}. \quad (6.71)$$

The error incurred by this approximation is

$$\begin{aligned} \Delta &= \prod_i \frac{(n_i + g_i - 1)!}{(g_i - 1)! n_i!} - \prod_i \frac{g_i^{n_i}}{n_i!} = \prod_i \frac{(n_i + g_i - 1)^{n_i + g_i - 1/2} e^{-n_i - g_i + 1}}{\sqrt{2\pi} (g_i - 1)^{g_i - 1/2} e^{-g_i + 1} n_i^{n_i + 1/2} e^{-n_i}} - \prod_i \frac{g_i^{n_i}}{n_i!} \\ &= \prod_i \frac{g_i^{n_i + g_i - 1/2} [1 + (n_i - 1)/g_i]^{n_i + g_i - 1/2}}{\sqrt{2\pi} g_i^{g_i - 1/2} n_i^{n_i + 1/2} [1 - 1/g_i]^{g_i - 1/2}} - \prod_i \frac{g_i^{n_i}}{n_i!} \\ &= \prod_i \frac{g_i^{n_i} [1 + (n_i - 1)/g_i]^{n_i + g_i - 1/2}}{\sqrt{2\pi} n_i^{n_i + 1/2} [1 - 1/g_i]^{g_i - 1/2}} - \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2} e^{-n_i}} \\ &\simeq \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2}} \left( 1 + \frac{n_i - 1}{g_i} \right)^{n_i + g_i - 1/2} \left( 1 - \frac{1}{g_i} \right)^{1/2 - g_i} - \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2}} e^{n_i} \\ &\simeq \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2}} \left( 1 + \frac{n_i - 1}{g_i} \right)^{g_i} \left( 1 - \frac{1}{g_i} \right)^{1/2 - g_i} \left\{ \left( 1 + \frac{n_i - 1}{g_i} \right)^{n_i - 1/2} \right\} \\ &\quad - \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2}} e^{n_i}. \end{aligned} \quad (6.72)$$

Here

$$\begin{aligned} &\left( 1 + \frac{n_i - 1}{g_i} \right)^{g_i} \left( 1 - \frac{1}{g_i} \right)^{1/2 - g_i} = \left( 1 - \frac{1}{g_i} \right)^{1/2} \left( \frac{1 + (n_i - 1)/g_i}{1 - 1/g_i} \right)^{g_i} \\ &\simeq \left( 1 - \frac{1}{g_i} \right)^{1/2} \left( 1 + \frac{n_i - 1}{g_i} + \frac{1}{g_i} \right)^{g_i} = \left( 1 - \frac{1}{g_i} \right)^{1/2} \left( 1 + \frac{n_i}{g_i} \right)^{g_i}. \end{aligned} \quad (6.73)$$

Then

$$\begin{aligned} \Delta &\simeq \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2}} \underbrace{\left( 1 + \frac{n_i}{g_i} \right)^{g_i}}_{\simeq e^{n_i}} \left\{ 1 + \frac{(n_i - 1)(n_i - 1/2)}{g_i} \right\} \left( 1 - \frac{1}{g_i} \right)^{1/2} \\ &\quad - \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2}} e^{n_i} \\ &\simeq \left( \prod_i \frac{g_i^{n_i}}{\sqrt{2\pi} n_i^{n_i + 1/2}} e^{n_i} \right) \left( \sum_i \frac{n_i(n_i - 3/2)}{g_i} \right) = \bar{W} \sum_i \frac{n_i(n_i - 3/2)}{g_i}. \end{aligned} \quad (6.74)$$

### Example 6.7: Free energy, entropy and latent heat on quantum statistics

Taking the number of states per particle of a perfect gas, in momentum range  $dp$  and volume  $V$ , to be  $4\pi V p^2 dp / h^3$ , show that at "high" temperatures the free energy  $F$  and the entropy  $S$  are given by

$$F \simeq -NkT \left[ 1 + \ln \left\{ \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right\} \right], \quad (6.75)$$

and

$$S \simeq Nk \left[ \frac{3}{2} \ln T + \ln \frac{V}{N} + \frac{5}{2} + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right) \right]. \quad (6.76)$$

Show that this result gives a reasonable expression for the latent heat of evaporation per atom.

**Solution:** We use Eq. (6.57) together with the Stirling approximation, *i.e.*

$$F = F_{MB} + kT \ln N! \simeq F_{MB} + NkT(\ln N - 1), \quad F_{MB} \stackrel{(5.20)}{\equiv} -NkT \ln \sum_i g_i e^{-\epsilon_i/kT}. \quad (6.77)$$

Therefore:

$$\begin{aligned} F &= -NkT \ln \sum_i g_i e^{-\epsilon_i/kT} + NkT(\ln N - 1) = -NkT \left[ 1 + \ln \sum_i g_i e^{-\epsilon_i/kT} - \ln N \right] \\ &= -NkT \left[ 1 + \ln \sum_i \frac{4\pi V p_i^2 dp_i e^{-\epsilon_i/kT}}{h^3 N} \right] \\ &= -NkT \left[ 1 + \ln \frac{4\pi V}{h^3 N} + \ln \int_0^\infty p^2 e^{-p^2/2mkT} dp \right] \\ &\stackrel{(2.20)}{\equiv} -NkT \left[ 1 + \ln \frac{4\pi V}{h^3 N} + \ln \frac{1}{4} \sqrt{2^3 m^3 \pi k^3 T^3} \right] = -NkT \left[ 1 + \ln \frac{V}{h^3 N} + \ln (2mkT\pi)^{3/2} \right] \\ &= -NkT \left[ 1 + \ln \left\{ \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right\} \right]. \end{aligned} \quad (6.78)$$

Correspondingly we have for the entropy:

$$S \stackrel{(6.55)}{\equiv} S_{MB} - k \ln N! \simeq S_{MB} - kN(\ln N - 1), \quad (6.79)$$

and hence with  $E = (3/2)NkT$  (see Eq. (6.60)) the entropy in the high temperature domain is

$$\begin{aligned} S &\stackrel{(6.57)}{\equiv} = \frac{E}{T} - \frac{F}{T} = \frac{E}{T} + Nk \left[ 1 + \ln \left\{ \frac{1}{N} \sum_i g_i e^{-\epsilon_i/kT} \right\} \right] \\ &= Nk \left[ \frac{3}{2} + 1 + \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right) \right] \\ &= Nk \left[ \frac{5}{2} + \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right) \right]. \end{aligned} \quad (6.80)$$

With the relation (6.62) for  $L_{\text{vapour}}$ , the latent heat of evaporation per atom, we now obtain (as compared with the Maxwell-Boltzmann method of Example 5.4, Eq. (5.53)):

$$L_{\text{vapour}} \simeq \frac{S_{\text{vapour}}}{NT} = \frac{k}{T} \left[ \frac{5}{2} + \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right) \right]. \quad (6.81)$$

This expression is reasonable as it now implies a dependence of  $V$  on  $N$ , as one would expect.

### Example 6.8: The rotational partition function of a diatomic molecule

Evaluate the rotational partition function  $Z_{\text{rot}}$  of a diatomic molecule of moment of inertia  $I$  semi-classically.

**Solution:** The partition function  $Z$  of a system of  $N$  particles was defined in Eq. (5.13) as

$$Z = \left( \sum_i g_i e^{-\epsilon_i/kT} \right)^N \equiv z^N. \quad (6.82)$$

For a single molecule of moment of inertia  $I$  the rotational energy is given by quantum mechanics as\*

$$\epsilon_J = \frac{J(J+1)\hbar^2}{8\pi^2 I}, \quad \text{with degeneracy } g_J = 2J+1, \quad (6.83)$$

and the rotational partition function  $z_{\text{rot}}$  is therefore

$$z_{\text{rot}} = \sum_J (2J+1)e^{-J(J+1)\hbar^2/8\pi^2 IkT}. \quad (6.84)$$

Setting

$$x = \frac{\hbar^2}{8\pi^2 IkT} \equiv \frac{\hbar^2}{2IkT}, \quad \epsilon_J = J(J+1)xkT, \quad (6.85)$$

this becomes

$$z_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)e^{-J(J+1)x} = 1 + 3e^{-2x} + 5e^{-6x} + 7e^{-12x} + \dots \quad (6.86)$$

As in the classical result (3.25) of Example 3.6 we have  $d\epsilon = (2J+1)kTxdJ$ , and therefore we can rewrite  $z_{\text{rot}}$  semi-classically as the integral

$$z_{\text{rot}} = \int_0^{\infty} (2J+1)e^{-J(J+1)x}dJ = -\frac{1}{x} \int_0^{\infty} dJ \frac{d}{dJ} \left[ e^{-J(J+1)x} \right] = \frac{1}{x} = \frac{8\pi^2 IkT}{\hbar^2}. \quad (6.87)$$

With the *Euler–Maclaurin summation formula* (4.30) additional higher order terms can be obtained to provide better approximations; thus

$$z_{\text{rot}} = \frac{1}{x} + \frac{1}{3} + \frac{x}{15} - \frac{4x^2}{315} + \dots \quad (6.88)$$

Since the diatomic molecule vibrates along its axis, there is also a vibrational partition function (multiplying  $z_{\text{rot}}$ ), and hence there are corresponding contributions to the thermodynamical functions.†

### Example 6.9: Similar and dissimilar diatomic molecules

The energy  $\epsilon$  of a rotating diatomic molecule,‡ considered as a rigid rotator with a single moment of inertia  $I$ , is  $p_{\varphi}^2/2I$ , where  $p_{\varphi}$  is the angular momentum. By quantizing this angular momentum according to the rules of the *Old Quantum Theory* (*i.e.* that of Bohr), show that

$$\epsilon_J = \frac{J^2\hbar^2}{2I}, \quad \text{where } J = 0, 1, 2, \dots \quad (6.89)$$

According to the proper quantum theory, *i.e.* here the Schrödinger equation, the correct result is

$$\epsilon_J = \frac{J(J+1)\hbar^2}{2I}, \quad \text{where } J = 0, 1, 2, \dots, \quad (6.90)$$

\*Recall the relative Schrödinger equation of the 2-particle system separated in spherical coordinates  $(r, \theta, \varphi)$ :

$$\left[ \frac{p_r^2}{2m_0} + \frac{\mathbf{l}^2}{2m_0 r^2} + V(r) \right] \psi(r, \theta, \varphi) = \epsilon \psi(r, \theta, \varphi),$$

where the reduced mass is  $m_0 = m_1 m_2 / (m_1 + m_2)$ . Here  $\mathbf{l}^2 |\psi\rangle = l_0(l_0 + 1)\hbar^2 |\psi\rangle$ ,  $l_0 \equiv J$ . See H.J.W. Müller–Kirsten [30], pp. 205, 210.

†See D.C. Mattis and R.H. Swendsen [28], pp. 90–94. Both types of contributions are summarized in Appendices 2 and 3 of R.P.H. Gasser and W.G. Richards [17].

‡Diverse aspects of diatomic gases are treated in D.J. Amit and Y. Verbin [1], pp. 352–365.

if the two atoms are dissimilar, and each such energy has a multiplicity  $g_J = 2J + 1$ . Show from the relation (6.57) for the free energy in both Bose–Einstein and Fermi–Dirac statistics at high temperatures, *i.e.*

$$F = -NkT \left[ 1 + \ln \left\{ \frac{1}{N} \sum_j g_j e^{-\epsilon_j/kT} \right\} \right], \quad (6.91)$$

that the rotational contribution to the entropy of a diatomic gas of  $N$  molecules is

$$S_{\text{rot}} = Nk \ln \left( \frac{2IkT}{\hbar^2} \right), \quad (6.92)$$

if the two atoms forming each molecule are dissimilar. (Hint: Replace the sums over  $J$  by integrals). If the two atoms in each molecule are similar, only alternate levels could be occupied. Explain this and show that in this case

$$S_{\text{rot}} = Nk \ln \left( \frac{IkT}{\hbar^2} \right). \quad (6.93)$$

**Solution:** In the Old Quantum Theory

$$\oint p_\varphi d\varphi = n_\varphi h. \quad (6.94)$$

In the present problem  $p_\varphi = \text{const.}$ , and  $n_\varphi \equiv J$ . Therefore

$$p_\varphi \oint d\varphi = 2\pi p_\varphi = Jh, \quad p_\varphi = J\hbar, \quad \hbar = \frac{h}{2\pi}. \quad (6.95)$$

It follows that in this old and incorrect consideration the energy is

$$\epsilon_J = \frac{p_\varphi^2}{2I} = \frac{J^2 \hbar^2}{2I}. \quad (6.96)$$

Next we set  $a = 2Ik/\hbar^2$ , and evaluate the partition function of one molecule with the correct expression of Eq. (6.90):

$$\begin{aligned} \sum_{J=0}^{\infty} g_J e^{-\epsilon_J/kT} &= \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)/aT} \simeq \int_0^{\infty} (2J+1) e^{-J(J+1)/aT} dJ \\ &= \left[ -aT e^{-J(J+1)/aT} \right]_0^{\infty} = aT. \end{aligned} \quad (6.97)$$

Hence the free energy  $F$  is

$$F = -NkT \left[ 1 + \ln \left( \frac{aT}{N} \right) \right] = -NkT - NkT \ln(aT) + NkT \ln(N). \quad (6.98)$$

The entropy  $S$  is therefore given by

$$\begin{aligned} S &= - \left( \frac{\partial F}{\partial T} \right)_V = Nk + Nk \ln(aT) - Nk \ln(N) + \frac{NkT}{aT} a \\ &= 2Nk + Nk \ln(aT) - Nk \ln(N) \\ &= 2Nk + Nk \ln \left( \frac{2IkT}{\hbar^2} \right) - Nk \ln(N). \end{aligned} \quad (6.99)$$

The rotational contribution to the entropy of the gas of  $N$  diatomic dissimilar (*i.e.* distinguishable) molecules is therefore

$$S_{\text{rot}} = Nk \ln \left( \frac{2IkT}{\hbar^2} \right). \quad (6.100)$$

We now consider the case of a “mono-atomic diatomic” molecule, *i.e.* one made of identical elements. In general the total wave function  $\Psi_{\text{tot}}$  of a molecule consists of the product of wave functions describing different properties of the molecule, just as the total energy  $\epsilon_{\text{tot}}$  of the molecule is the sum of the corresponding energy terms, *e.g.*

$$\epsilon_{\text{tot}} = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{el}}, \quad (6.101)$$

which is the sum of the translational energy part, the rotational energy part, the vibrational energy part, and the electronic energy part. The corresponding total wave function is the product

$$\Psi_{\text{tot}} = \psi_{\text{trans}} \times \psi_{\text{rot}} \times \psi_{\text{vib}} \times \psi_{\text{el}}, \quad (6.102)$$

and the overall partition function is a corresponding product. Here we may be thinking of the simpler problem of the hydrogen atom. But in the case of the hydrogen molecule or the deuterium we would also have to take into account nuclear or *isospin* (the difference between neutron and proton), and hence there would be a wave function  $\psi_{\text{ns}}$  taking this nuclear spin into account (which, by multiplication, increases the number of states). As a case that immediately comes to mind consider a diatomic molecule. If the two atoms are dissimilar, the molecule is described as *hetero-atomic*, if they are identical the molecule is described as *mono-atomic* or *homonuclear*. The two cases differ in their symmetries, and this difference is described by a number called the *symmetry number*  $\gamma$ . This symmetry number is the number of indistinguishable positions into which the molecule can be rotated, and must be introduced into the quantitative description in order to avoid double counting.

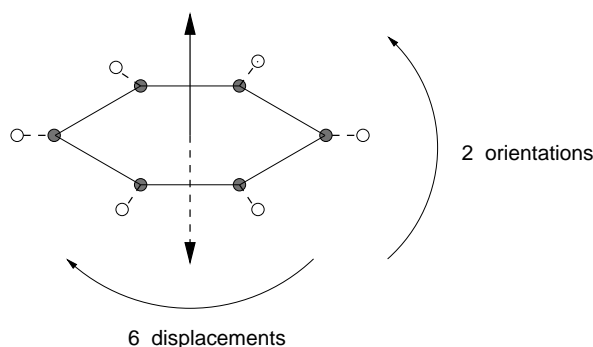


Fig. 6.10 Symmetry of the benzene molecule making the symmetry factor  $\gamma = 2 \times 6 = 12$ .

If one considers the simplest case of zero nuclear spin (isospin), only one nuclear spin function exists for each of the two atoms and consequently also only one for the diatomic molecule, and this single function is symmetric. It follows that a homonuclear molecule in which the nuclei have zero nuclear spin must have a total wave function which is symmetric with respect to interchange of the nuclei or elements. Thus with the symmetric nuclear wave function must be associated a symmetric rotational wave function (implying angular momentum  $J$  even). However, since under these conditions (*i.e.* zero nuclear spin) no antisymmetric nuclear spin function exists, this cannot be multiplied by an antisymmetric rotational wave function. Thus the *complete absence of an antisymmetric wave function* implies the absence of antisymmetrical rotational states ( $J$  odd). Thus no molecules occupy odd rotational levels, and this implies the absence of alternate levels or spectral lines.\* This absence of alternate levels in the sum of Eq. (6.97) implies in the present case

\*For very detailed discussions see in particular J.E. Mayer and M.G. Mayer [29], pp. 175–176, R.P.H. Gasser and W.G. Richards [17], p. 117.

(cf. Example 6.12)

$$\sum_{J=0,2,4,\dots} g_J e^{-\epsilon_J/kT} = \frac{aT}{2} = \frac{IkT}{\hbar^2}, \quad (6.103)$$

and hence

$$S_{\text{rot}} = Nk \ln \left( \frac{IkT}{\hbar^2} \right). \quad (6.104)$$

Thus only the fraction  $1/\gamma$  of adjacent rotational levels have the correct symmetry, where  $\gamma$  is the symmetry number referred to above. This number is the number of ways in which a molecule may be rotated into positions which would be different from the original one if the identical atoms were numbered and distinguishable, but which look identical to the original orientation in view of the identity of the atoms of the same element. For the diatomic molecule  $\gamma = 2$ .<sup>†</sup> Thus correspondingly in the case of the linear molecule  $CO_2$  this number is  $\gamma = 2$ , in the case of tetrahedral methane  $CH_4$  it is 12, as also in the case of planar hexagonal benzene  $C_6H_6$ , as illustrated in Fig. 6.10.<sup>‡</sup>

### Example 6.10: Vibrational and electronic contributions to the entropy

Show that the *additional* contributions to the entropy  $S$  arising from any vibrational and electronic energy levels in a diatomic or polyatomic gas are

$$S_{\text{vib, elect}} = Nk \ln \sum_i g_i e^{-\epsilon_i/kT}, \quad (6.105)$$

where  $g_i$  and  $\epsilon_i$  are respectively the relevant multiplicities (statistical weights) and energy eigenvalues — these would normally have to be determined from spectroscopic knowledge of the vibrational and electronic excitation levels.<sup>§</sup>

**Solution:** The crux of this problem is that energies add but partition functions multiply (their logarithms add), as observed after Eq. (5.13). Therefore in the present case with  $i$ -th level energy  $\epsilon_i$  of an element (molecule),

$$\epsilon_i = \epsilon_i^{\text{rot}} + \epsilon_i^{\text{vib}} + \epsilon_i^{\text{elec}}, \quad (6.106)$$

and degeneracies  $g_i^{\text{rot}}, g_i^{\text{vib}}, g_i^{\text{elec}}$ , the partition function  $Z$  is

$$Z = \prod_i \left( \sum_i g_i e^{-\epsilon_i/kT} \right)^N = Z^{\text{rot}} Z^{\text{vib}} Z^{\text{elec}}, \quad (6.107)$$

and the free energy  $F$  of Bose–Einstein and Fermi–Dirac statistics at high temperature  $T$  is

$$F \stackrel{(6.57)}{=} -NkT \left[ 1 - \ln N + \ln \sum_i g_i^{\text{rot}} e^{-\epsilon_i^{\text{rot}}/kT} + \ln \sum_i g_i^{\text{vib}} e^{-\epsilon_i^{\text{vib}}/kT} + \ln \sum_i g_i^{\text{elec}} e^{-\epsilon_i^{\text{elec}}/kT} \right], \quad (6.108)$$

and the entropy  $S$  is (cf. Eq. (6.53)), showing the additional contributions,

$$\begin{aligned} S &= \frac{E}{T} + k \ln Z = \frac{E}{T} + Nk \left[ 1 - \ln N + \ln \sum_i g_i^{\text{rot}} e^{-\epsilon_i^{\text{rot}}/kT} \right. \\ &\quad \left. + \ln \sum_i g_i^{\text{vib}} e^{-\epsilon_i^{\text{vib}}/kT} + \ln \sum_i g_i^{\text{elec}} e^{-\epsilon_i^{\text{elec}}/kT} \right]. \end{aligned} \quad (6.109)$$

<sup>†</sup>J.E. Mayer and M.G. Mayer [29], p. 136.

<sup>‡</sup>J.E. Mayer and M.G. Mayer [29], p. 195.

<sup>§</sup>To avoid confusion: The contribution proportional to  $N(\ln N - 1) \simeq \ln N!$  contained in the high  $T$  approximation (6.57) of the free energy  $F$  of both Bose–Einstein and Fermi–Dirac statistics is what distinguishes these correct expressions from that of Maxwell–Boltzmann statistics, Eqs. (5.11), (5.12). See comments after Eq. (6.52).

**Example 6.11: The factors responsible for distinguishability**

Show that the difference between the entropies calculated according to Maxwell–Boltzmann statistics in Example 5.4 on the one hand, and Bose–Einstein and Fermi–Dirac statistics at reasonably high temperatures on the other in Example 6.7, lies in the extra factors  $N!/(n_1!)(n_2!)(n_3!)\dots$  introduced into the number of arrangements in the Maxwell–Boltzmann case, *i.e.* in the factor expressing the distinguishability of the elements.

**Solution:** This aspect has effectively already been pointed out in the Examples cited. At fairly high temperatures the probability of occupation of any one energy level is very small, so that  $n_i! \simeq 1$  for all  $i$ . Also,  $\ln N! \sim N \ln N - N$ , since  $N$  is a given large number. Finally, we recall that  $S = k \ln(\text{number of arrangements})$ .

**6.9 Problems without Worked Solutions****Example 6.12: Absence of alternate levels**

Prove the result (6.103), *i.e.* show that

$$\sum_{J=0,2,4,\dots}^{\infty} e^{-J(J+1)/aT} = \frac{1}{2}aT. \quad (6.110)$$

**Example 6.13: Number of states in a spherical volume V**

Consider free nonrelativistic motion of particles in a spherical volume of radius  $R$ . What is the number of states with momentum  $p$  in the interval  $(p, p + dp)$ ?

**Example 6.14: Classical diatomic perfect gas**

Consider a perfect gas consisting of diatomic molecules. Write down the Lagrangian function  $L$  of a single molecule of moment of inertia  $I$ . Let the harmonic vibrations of the two atoms along the axis and about an equilibrium position  $\eta_0$  be described by the coordinate  $x(t) = \eta(t) - \eta_0$ , and the sum of kinetic and potential parts of the vibrations by  $L_{\text{vib}} = (m/2)(\dot{x}^2 - \omega^2 x^2)$ , where  $m_0$  is the reduced mass of the two atoms and  $\omega$  a constant. Write down the Hamilton function and count the number of quadratic terms. Then obtain the specific heat  $C_V$  per particle in this purely classical consideration with the help of the law of equipartition of energy. (Answer:  $C_V = 7k/2$ ).

**Example 6.15: Pressure of a particle in a cube**

Consider a particle of mass  $m$  in a cube of volume  $V = L^3$  and calculate its pressure  $P$  on a wall. [Hint: From the Schrödinger equation (6.10) the energy  $E$  of the particle is given by the eigenvalue relation (6.13) as

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (l^2 + m^2 + n^2). \quad (6.111)$$

In a change  $dL$  of a length  $L$  the particle of energy  $E$  performs work  $dW = -dE$ . Use ( $F$  meaning force)  $dW = FdL$  and  $P = F/L^2$ ]. (Answer:  $P = 2E/3V$ ).