Chapter 15
Many-Particle Systems

15.1 Introduction

The chapter illustrates the properties of many-particle systems. The quantum-mechanical description of the latter is obtained by solving the time-dependent Schrödinger equation. After commenting the simplifications that occur when the Hamiltonian operator is separable, the important issue of the symmetry or antisymmetry of the wave function is introduced, to the purpose of illustrating the peculiar properties possessed by the systems of identical particles. Then, the concept of spin and the exclusion principle are introduced. After a general discussion, the above concepts are applied to the important case of a conservative system, and further properties related to the separability of the Hamiltonian operator are worked out. The remaining part of the chapter is devoted to the derivation of the equilibrium statistics in the quantum case (Fermi–Dirac and Bose–Einstein statistics). The connection between the microscopic statistical concepts and the macroscopic thermodynamic properties is illustrated in the complements, where two important examples of calculation of the density of states are also given.

15.2 Wave Function of a Many-Particle System

The quantum-mechanical concepts outlined in Parts II and III dealt with wave functions ψ describing a single particle. In such a case, if ψ is normalized to unity, the product $|\psi(\mathbf{r}, t)|^2\, \mathrm{d}^3 r$ is the infinitesimal probability that at time t the particle's position belongs to the elementary volume $\mathrm{d}^3 r = \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z$ centered on $\mathbf{r}$; specifically, the x coordinate belongs to $\mathrm{d}x$, and so on. It is now necessary to extend the treatment to the case of many-particle systems. This is readily accomplished by considering, first, a system made of two particles: the wave function ψ describing such a system depends on two sets of coordinates, $\mathbf{r}_1$, $\mathbf{r}_2$, and time. The first set labels one of the

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particles, the second set labels the other particle. Assume that ψ is normalized to unity,

$$\int |\psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 = 1, \tag{15.1}$$

where $\int$ is a short-hand notation for a six-fold integral over $\mathrm{d}x_1 \dots \mathrm{d}z_2$. Then, the product $|\psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2$ is the infinitesimal probability that, at time t, set $\mathbf{r}_1$ belongs to $\mathrm{d}^3 r_1$ and set $\mathbf{r}_2$ belongs to $\mathrm{d}^3 r_2$. The wave function in (15.1) is the solution of the time-dependent Schrödinger equation

$$\mathrm{i}\hbar \frac{\partial \psi}{\partial t} = \mathcal{H}\psi, \qquad \psi(\mathbf{r}_1,\mathbf{r}_2,0) = \psi_0(\mathbf{r}_1,\mathbf{r}_2), \tag{15.2}$$

where the initial condition ψ_0 is prescribed. In turn, the Hamiltonian operator in (15.2) is derived, following the procedure illustrated in Sect. 10.2, from the Hamiltonian function that describes the two-particle system in the classical case. Considering by way of example a case where the forces acting on the two particles derive from a potential energy $V = V(\mathbf{r}_1,\mathbf{r}_2,t)$, the Hamiltonian function and the Hamiltonian operator read, respectively,

$$H = \frac{p_1^2}{2\,m_1} + \frac{p_2^2}{2\,m_2} + V, \qquad \mathcal{H} = -\frac{\hbar^2}{2\,m_1}\nabla_1^2 - \frac{\hbar^2}{2\,m_2}\nabla_2^2 + V, \tag{15.3}$$

where m_1, m_2 are the particles' masses, while $p_1^2 = p_{x1}^2 + p_{y1}^2 + p_{z1}^2$, $\nabla_1^2 = \partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2$, and the same for label 2.

It may happen that the Hamiltonian operator is separable with respect to the two sets $\mathbf{r}_1$, $\mathbf{r}_2$, namely, $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$ such that $\mathcal{H}_1$ does not contain any component of $\mathbf{r}_2$ and $\mathcal{H}_2$ does not contain any component[1] of $\mathbf{r}_1$. Also, let $\psi_1 = \psi_1(\mathbf{r}_1,t)$, $\psi_2 = \psi_2\big(\mathbf{r}_2,t\big)$ be solutions, respectively, of

$$\mathrm{i}\hbar \frac{\partial \psi_1}{\partial t} = \mathcal{H}_1\psi_1, \qquad \mathrm{i}\hbar \frac{\partial \psi_2}{\partial t} = \mathcal{H}_2\psi_2, \tag{15.4}$$

with the initial conditions $\psi_{10} = \psi_1\big(\mathbf{r}_1,0\big)$, $\psi_{20} = \psi_2\big(\mathbf{r}_2,0\big)$. Letting $\psi = \psi_1\,\psi_2$ and using (15.4) yields

$$\mathrm{i}\hbar \frac{\partial \psi}{\partial t} - \mathcal{H}\psi = \psi_2 \left(\mathrm{i}\hbar \frac{\partial \psi_1}{\partial t} - \mathcal{H}_1\psi_1\right) + \psi_1 \left(\mathrm{i}\hbar \frac{\partial \psi_2}{\partial t} - \mathcal{H}_2\psi_2\right) = 0, \tag{15.5}$$

showing that $\psi_1\,\psi_2$ solves the Schrödinger equation for the particles' system, with $\psi_{10}\,\psi_{20}$ as initial condition. The concepts introduced in this section are readily extended to the case of larger systems. Letting $N > 2$ be the number of particles, and still assuming that the system's wave function is normalized to unity,

$$\int |\psi\big(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N,t\big)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \dots \mathrm{d}^3 r_N = 1, \tag{15.6}$$

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[1] By way of example, (15.3) is separable if $V = V_1\big(\mathbf{r}_1,t\big) + V_2\big(\mathbf{r}_2,t\big)$.

the product $|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \dots \mathrm{d}^3 r_N$ is the infinitesimal probability that, at time t, set $\mathbf{r}_i$ belongs to $\mathrm{d}^3 r_i$, with $i = 1, 2, \dots, N$. If the Hamiltonian operator is separable, the solution of the time-dependent Schrödinger equation of the system has the form $\psi = \psi_1(\mathbf{r}_1, t) \dots \psi_N(\mathbf{r}_N, t)$. From (15.6) one also notes that the units of ψ depend on the number of particles involved; specifically, in (15.6) it is $[\psi] = \mathrm{cm}^{-3N/2}$ (compare with the discussion of Sect. 9.7.1).

15.3 Symmetry of Functions and Operators

The Hamiltonian operator and the wave function describing a many-particle system contain sets of coordinates like $\mathbf{r}_1$, $\mathbf{r}_2$ .... It is important to introduce a number of properties related to the exchange of two such sets within the operator or the wave function. The problem is tackled first in a rather abstract way; the applications to specific cases of interest are shown in Sect. 15.6.

Consider a function $f = f(q_1, q_2, \dots, q_n)$, where q_k represents a group of coordinates.[2] Let $\mathcal{S}_{ij}$ be an operator such that [78, Chap. XIV.3]

$$\mathcal{S}_{ij} f(q_1, \dots, q_i, \dots, q_j, \dots, q_n) = f(q_1, \dots, q_j, \dots, q_i, \dots, q_n), \tag{15.7}$$

namely, $\mathcal{S}_{ij}$ exchanges the names of the ith and jth group, leaving the rest unchanged. From the definition it follows $\mathcal{S}_{ij}^2 = \mathcal{S}_{ij} \, \mathcal{S}_{ij} = \mathcal{I}$. Now, let λ be an eigenvalue of $\mathcal{S}_{ij}$, and w an eigenfunction corresponding to it: $\mathcal{S}_{ij} w = \lambda w$. The following relations hold together:

$$\mathcal{S}_{ij}^2 w = w, \qquad \mathcal{S}_{ij}^2 w = \lambda^2 w, \tag{15.8}$$

the first due to the general property shown before, the second to the definition of λ and w. As a consequence, $\lambda = \pm 1$, namely, $\mathcal{S}_{ij}$ has two eigenvalues. As their modulus equals unity, $\mathcal{S}_{ij}$ is unitary (Sect. 8.6.2), namely, $\mathcal{S}_{ij}^{-1} = \mathcal{S}_{ij}^{\dagger}$.

The properties of the operator's eigenfunctions are found by letting $w^s = \mathcal{S}_{ij} w$, so that w^s is the function that results from exchanging the names of the ith and jth group of coordinates. Depending on the eigenvalue, two cases are possible: the first one is $\lambda = +1$, whence $\mathcal{S}_{ij} w = +1 \times w$ and $\mathcal{S}_{ij} w = w^s$ hold together, so that $w^s = w$; the second case is $\lambda = -1$, whence $\mathcal{S}_{ij} w = -1 \times w$ and $\mathcal{S}_{ij} w = w^s$ hold together, so that $w^s = -w$. A function such that $w^s = w$ is called *symmetric* with respect to indices ij, while a function such that $w^s = -w$ is called *antisymmetric* with respect to indices ij. In conclusion,

- all symmetric functions are eigenfunctions of $\mathcal{S}_{ij}$ belonging to $\lambda = +1$;
- all antisymmetric functions are eigenfunctions of $\mathcal{S}_{ij}$ belonging to $\lambda = -1$.

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[2] A "group" of coordinates may also consist of a single coordinate.

The set of eigenfunctions of $\mathcal{S}_{ij}$ is complete; in fact, for any function f it is

$$f = \frac{1}{2}\left(f + \mathcal{S}_{ij} f\right) + \frac{1}{2}\left(f - \mathcal{S}_{ij} f\right), \tag{15.9}$$

where the first term at the right hand side is symmetric and the second one is antisymmetric, so that both terms at the right hand side are eigenfunctions of $\mathcal{S}_{ij}$. This shows that any function is expressible as a linear combination of eigenfunctions of $\mathcal{S}_{ij}$.

Only a specific pair ij of coordinate group has been considered so far. On the other hand it may happen that a function is symmetric (antisymmetric) with respect to all pairs of indices; in this case it is called *symmetric* (*antisymmetric*) with no further specification.

The definitions above extend to operators. For instance, an operator $\mathcal{A}$ is symmetric with respect to ij if $\mathcal{A}^s = \mathcal{S}_{ij}\mathcal{A} = \mathcal{A}$; it is symmetric without further specification if $\mathcal{A}^s = \mathcal{A}$ for any pair ij. Given a function f and an operator $\mathcal{A}$, and letting $f^s = \mathcal{S}_{ij} f$, it is for all f,

$$(\mathcal{A} f)^s = \mathcal{S}_{ij}\mathcal{A} f = \mathcal{S}_{ij}\mathcal{A}\mathcal{S}_{ij}^{-1}\mathcal{S}_{ij} f = \mathcal{A}^s f^s. \tag{15.10}$$

If $\mathcal{A}$ is symmetric, replacing $\mathcal{A}^s = \mathcal{A}$ in (15.10) shows that $\mathcal{S}_{ij}\mathcal{A} f = \mathcal{A}\mathcal{S}_{ij} f$ namely, $\mathcal{S}_{ij}$ commutes with all symmetric operators.

The operator whose symmetry properties are of interest is typically the Hamiltonian one. Considering for instance a system of N particles interacting with each other through Coulomb interactions *in vacuo*, one has

$$\mathcal{H} = -\sum_{k=1}^{N} \frac{\hbar^2}{2\, m_k}\, \nabla_k^2 + \frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{s=1\\ s\neq k}}^{N} \frac{e_k\, e_s}{4\,\pi\,\varepsilon_0\,|\mathbf{r}_k - \mathbf{r}_s|} \tag{15.11}$$

with ε_0 the vacuum permittivity, $\nabla_k^2 = \partial^2/\partial x_k^2 + \partial^2/\partial y_k^2 + \partial^2/\partial z_k^2$, and m_k, e_k the mass and charge of the kth particle, respectively. In general, this operator has no particular symmetry property; however, it is symmetric with respect to the groups of coordinates x_k, y_k, z_k when the particles are identical to each other $\big(m_1 = m_2 = \ldots = m_N$, $e_1 = e_2 = \ldots = e_N\big)$.

15.4 Conservation of Symmetry in Time

Consider a wave function ψ expanded into a complete set of orthonormal functions w_k. Using as in Sect. 15.3 the symbols q_i for the groups of coordinates, one has

$$\psi\big(q_1, \ldots, q_n, t\big) = \sum_k a_k(t)\, w_k\big(q_1, \ldots, q_n\big). \tag{15.12}$$

The wave function is assumed to be normalized to unity, so that from Parseval theorem (8.41) it follows

$$\langle\psi|\psi\rangle = \sum_k |a_k|^2 = 1 \tag{15.13}$$

at all times. Now assume that ψ is the solution of a Schrödinger equation deriving from a symmetric Hamiltonian operator, and that ψ itself is symmetric at some instant t' with respect to the pair ij. As the functions w_k of (15.12) are linearly independent, the symmetry of ψ entails that of w_k for all k. As a consequence, for the pair ij, w_k is an eigenfunction of the operator $\mathcal{S}_{ij}$ corresponding to $\lambda = 1$. Combining (15.13) with the definition (10.13) of the expectation value of the eigenvalues yields $\langle\lambda\rangle = 1$ at $t = t'$. In turn, due to symmetry, $\mathcal{H}$ commutes with $\mathcal{S}_{ij}$; this yields, for the time derivative (10.27) of the average value of the eigenvalues of $\mathcal{S}_{ij}$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\lambda\rangle = -\mathrm{i}\,\hbar \int \psi^* \left(\mathcal{H}\mathcal{S}_{ij} - \mathcal{S}_{ij}\mathcal{H}\right) \psi \,\mathrm{d}q_1 \ldots \mathrm{d}q_n = 0, \qquad (15.14)$$

namely, $\langle\lambda\rangle$ is conserved in time. The above calculation can be summarized as follows:

- Given a symmetric Hamiltonian $\mathcal{H}$, select a pair of indices ij. Due to commutativity, a complete set of eigenfuctions w_k of $\mathcal{H}$ exists, that belongs also to operator $\mathcal{S}_{ij}$.
- The eigenfunctions w_k of $\mathcal{H}$ can thus be separated into two sets, made of symmetric and antisymmetric functions, respectively.
- Let $\psi(q_1, \ldots, t) = \sum_k a_k(t) w_k\big(q_1, \ldots\big)$ be the wave function of the system described by $\mathcal{H}$, and let ψ be symmetric at some instant t'. It follows that the non vanishing coefficients $a_k\big(t'\big)$ in the expansion of $\psi\big(q_1, \ldots, q_n, t'\big)$ are only those multiplying the symmetric eigenfunctions.

As $\langle\lambda\rangle = \int \psi^* \, \mathcal{S}_{ij} \, \psi \,\mathrm{d}q_1 \ldots q_n = 1$ at all times, the expansion of ψ is made in terms of the symmetric w_ks at all times. Hence, ψ is always symmetric with respect to the groups of coordinates of indices ij. The above reasoning can be repeated for all pairs of indices for which ψ is symmetric. Note that, in order to repeat the reasoning for different pairs of indices, say, ij and jk, one needs not assume that the corresponding operators $\mathcal{S}_{ij}$, $\mathcal{S}_{jk}$ commute with each other (in fact, they typically do not commute). The analysis holds equally for the case where ψ, at time t', is antisymmetric with respect to two indices. In such a case, it remains antisymmetric at all times with respect to them.

15.5 Identical Particles

It is interesting to ascertain whether the mathematical properties related to symmetry or antisymmetry, briefly discussed in Sects. 15.3 and 15.4, correspond to some physical property. This is indeed so, and is especially important when a system of identical particles is considered.

Take for instance a system of two identical particles interacting with each other.[3] In classical terms, the two identical objects that form the system can always be

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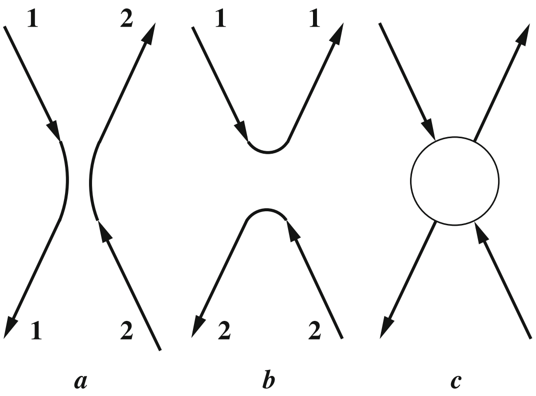
[3] The reasoning outlined here does not apply to systems where the particles are different: they can be distinguished in $|\psi|^2$, e.g., by the mass or electric charge.

Fig. 15.1 Schematic description of a system made of two identical particles



made distinguishable from each other, without disturbing their motion. The typical example is that of two identical billiard balls, that are made distinguishable by a different coloring; although the latter has no influence on the balls' dynamics, it allows one to distinguish them from each other irrespective of the number of collisions they undergo. As a consequence, the conjugate variables describing the motion of each particle (e.g., position and momentum) are exactly known at each instant of time. By way of example consider the collision of two identical, charged particles schematically illustrated in Fig. 15.1: it is assumed that the particles are initially far apart, with equal moduli of the initial velocities; the initial velocity of the particle labeled 1 is described by the upper-left arrow visible in cases *a* and *b* of the figure, while the initial velocity of the particle labeled 2 is described by the lower-right arrow. As they come closer, the particles repel each other due to the Coulomb interaction, and their classical motion is described as in Sects. 3.5–3.8. If the initial velocities were exactly aligned (this case is not shown in the figure), the two particles would bounce back along the same direction; if, however, the initial velocity of particle 1 were slightly misaligned to the left, the collision would yield case *a*, whereas it would yield case *b* for a right misalignment. Even if the misalignment is made as small as we please, either case *a* or *b* occurs, and the two possible outcomes are distinguishable from each other.

In the quantum-mechanical description, instead, it is not possible to track each particle separately, because the dynamical information about the system derives from the wave function; when the particles come closer, the norm of the wave function in (15.1) is significantly different from zero in a finite region of space, which is schematically indicated by the circle of case *c* in Fig. 15.1. Due to the Heisenberg principle (10.22), it is impossible to determine the position and momentum of each particle at the same time with arbitrary precision. It follows that, for identical particles, the collision is described as an event where two particles enter the circle and two particles eventually leave it, without the possibility of distinguishing between cases *a* and *b*: the two cases must in fact be counted as one, and the wave function describing the system must be consistent with it. This requires $|\psi|^2$ be symmetric with respect to the groups $\mathbf{r}_1, \mathbf{r}_2$:

$$|\psi^s|^2 = |\mathcal{S}_{12}\psi|^2 = |\psi|^2, \tag{15.15}$$

which implies $\psi^s = \exp(\mathrm{i}\alpha)\,\psi$ with α a real constant. On the other hand, remembering the first equation in (15.8),

$$\mathcal{S}_{12}^2\psi = \exp(2\,\mathrm{i}\alpha)\,\psi, \qquad \mathcal{S}_{12}^2\psi = \psi, \tag{15.16}$$

whence $\exp(j\alpha) = \pm 1$. In conclusion, when the two particles of the system are indistinguishable from each other, the system's wave function is either symmetric or antisymmetric. One may argue that, when the system is made of more than two identical particles, its wave function could be symmetric with respect to some pairs of indices and antisymmetrical with respect to other pairs. However this is not possible, as the simple case of three identical particles shows [69, Sect. 26]. Assume that ψ is symmetric with respect to $\mathbf{r}_1, \mathbf{r}_2$ and antisymmetric with respect to $\mathbf{r}_1, \mathbf{r}_3$; it follows

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t) = \psi(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3, t) = -\psi(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_1, t) = -\psi(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, t) = \tag{15.17}$$

$$= \psi(\mathbf{r}_3, \mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_1, t) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t), \tag{15.18}$$

that is, a contradiction. In other terms, ψ can either be symmetric with respect to all the identical particles of the system, or antisymmetric with respect to all of them. This result has a far-reaching consequence, namely, the class of all particles is made of two subclasses: the first one collects the types of particles whose systems are described by symmetric wave functions; they are called *Bose particles* or *bosons*. The second subclass collects the types of particles whose systems are described by antisymmetric wave functions; they are called *Fermi particles* or *fermions*. This applies to all known particles, including composite ones (e.g., atoms) and particles describing collective motions (e.g., phonons, photons).[4]

15.5.1 Spin

The properties discussed so far in this section bring about an interesting question: consider a single particle, e.g., an electron. Although electrons are fermions,[5] here the concept of symmetry or antisymmetry does not apply because the wave function of a

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[4] The names "bosons", "fermions" of the two subclasses have this origin: when a system of identical particles is in thermodynamic equilibrium, the particles' energy follows a statistical distribution whose expression is named after Bose and Einstein (Sect. 15.8.2) and, respectively, Fermi and Dirac (Sect. 15.8.1).

[5] It must be noted, however, that in condensed-matter physics two electrons or other fermions may bind together at low temperatures to form a so-called Cooper pair, which turns out to have an integer spin, namely, it is a composite boson [20].

single electron contains only one group of coordinates. Then add a second electron, so that a system of two identical particles is formed: how do these electrons "know" that, when paired, the wave function of their system must be antisymmetric? It is reasonable to assume that each particle in itself must possess a property that makes it to behave like a fermion or a boson within a system of particles identical to it. Such a property, called *spin*, does in fact exist; as its existence can be proven only within the frame of the relativistic quantum theory [31], [32], [99, Sect. 15], which is beyond the scope if this book, only a brief illustration of spin's properties of interest will be given.

In contrast with the other dynamic quantities considered so far, there is no classical counterpart of spin. Therefore, the latter can not be derived from the expression of a dynamic variable by replacing conjugate coordinates with suitable operators. It can be shown that the eigenvalues of spin are derived in a manner similar to that of angular momentum: this leads, like in Sect. 13.5.1, to determining the square modulus of spin, σ^2, and its component along one of the coordinate axes, say, σ_z. Their values are given by expressions similar to (13.46), specifically,

$$S^2 = \hbar^2 \, s \, (s+1), \qquad S_z = \hbar \, s_z. \tag{15.19}$$

The important difference with (13.46) is that s, instead of being a non-negative integer, is a non-negative half integer: $s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$; in turn, s_z can take the $2\,s+1$ values $-s, -s+1, \dots, s-1, s$.

The introduction of spin must be accounted for in the expression of the wave function: the latter, in the case of a single particle, must be indicated with $\psi(\mathbf{r}, s_z, t)$, and its normalization to unity, if existing, is expressed by

$$\sum_{s_z} \int_\Omega |\psi(\mathbf{r}, s_z, t)|^2 \, \mathrm{d}^3 r = 1. \tag{15.20}$$

If (15.20) holds, the product $|\psi(\mathbf{r}, s_z, t)|^2 \, \mathrm{d}^3 r$ is the probability that at time t the particle is in the elementary volume $\mathrm{d}^3 r$ centered on $\mathbf{r}$, and the component of its spin along the z axis is $S_z = \hbar \, s_z$.

The connection between spin and boson-like or fermion-like behavior is the following: the quantum number s is integer for bosons, half integer for fermions [81]. It is then meaningful to use the terms "boson" or "fermion" for an individual particle. All known fermions have $s = 1/2$, whence $2\,s+1 = 2$. It follows that for fermions the z-component of spin has two possible values, $\hbar/2$ (*spin up*) and $-\hbar/2$ (*spin down*). As anticipated above, electrons are fermions. Photons are bosons with $s = 1$.

The similarity between the expressions of the quantum numbers for spin and those of the angular momentum (Eqs. (13.46) cited above) is the origin of the qualitative visualization of spin in classical terms: spin is described as an intrinsic angular momentum of the particle, as if the particle were a sphere spinning on its axis.

15.6 Pauli Exclusion Principle

Consider a system of identical particles, so that its Hamiltonian operator $\mathcal{H}$ is symmetric with respect to each pair of particle labels ij. Its wave function, in turn, is either symmetric or antisymmetric depending on the nature of the particles forming the system. It may happen that, when solving the Schrödinger equation of the system, a solution is found, say φ, that does not possess the necessary symmetry properties. One can then exploit a relation like (15.9) to construct from φ another solution which is either symmetric or antisymmetric. For this, one must remember that φ depends on the groups of coordinates $(\mathbf{r}_1, s_{z1})$, $(\mathbf{r}_2, s_{z2}), \dots$ which, for the sake of conciseness, will be indicated with the symbol $\mathbf{q}_i = (\mathbf{r}_i, s_{zi})$. Remembering from Sect. 15.3 that the Hamiltonian operator, due to its symmetries, commutes with any operator $\mathcal{S}_{ij}$, one finds

$$\mathcal{S}_{ij}\left(\mathcal{H} - \mathrm{i}\,\hbar\,\frac{\partial}{\partial t}\right)\varphi = \left(\mathcal{H} - \mathrm{i}\,\hbar\,\frac{\partial}{\partial t}\right)\varphi^s, \tag{15.21}$$

where $\mathcal{S}_{ij}$ exchanges $\mathbf{q}_i$ with $\mathbf{q}_j$. The parenthesis on the left hand side of (15.21) is zero because φ solves the Schrödinger equation; it follows that φ^s is also a solution. Due to the linearity of the Schrödinger equation, the two functions

$$\varphi + \varphi^s, \qquad \varphi - \varphi^s, \tag{15.22}$$

are solutions of the Schrödinger equation, which are also symmetric and, respectively, antisymmetric with respect to the pair ij. The procedure is easily generalized to obtain a wave function that is symmetric or antisymmetric with respect to all pairs of indices. To this purpose, one considers the $N!$ permutations of the system's N particles; let ν be an index representing the order of each permutation with respect to the fundamental one ($1 \le \nu \le N!$), and $\mathcal{S}_\nu$ the operator that achieves the νth permutation of the particles' coordinates within φ. The functions

$$\psi = a\sum_\nu \mathcal{S}_\nu \varphi, \qquad \psi = b\sum_\nu (-1)^\nu \mathcal{S}_\nu \varphi \tag{15.23}$$

are solutions of the Schrödinger equation, which are also symmetric and, respectively, antisymmetric with respect to all particles' permutations. Symbols a and b denote two constants, that can be used to normalize ψ if φ is normalizable. The above constructions can be worked out at any instant, as the symmetry or antisymmetry of the wave function is conserved in time (Sect. 15.4). The second relation in (15.23) lends itself to an interesting derivation. Considering for simplicity the case $N = 2$ one finds

$$\psi = b\left[\varphi(\mathbf{r}_1, s_{z1}, \mathbf{r}_2, s_{z2}, t) - \varphi(\mathbf{r}_2, s_{z2}, \mathbf{r}_1, s_{z2}, t)\right], \tag{15.24}$$

If it were $\mathbf{r}_2 = \mathbf{r}_1$, $s_{z2} = s_{z1}$, the wave function (15.24) would vanish, which is not acceptable. The same unphysical results is found by letting $\mathbf{r}_j = \mathbf{r}_i$, $s_{zj} = s_{zi}$ in the second expression in (15.23). The conclusion is that in a system of identical fermions, two (or more) particles with the same spin can not occupy the same position; this finding derives solely from the antisymmetry of the wave function for a system of identical fermions, and is called *Pauli principle* or *exclusion principle*.[6] As shown in Sect. 15.7 it can be restated in different forms depending on the system under consideration. No similar restriction applies to system of identical bosons, as the form of the first relation in (15.23) shows.

15.7 Conservative Systems of Particles

An important example of a system of N interacting particles occurs when the forces are conservative. To begin, the general case of non-identical particles is considered. The Hamiltonian function and the corresponding Hamiltonian operator read, respectively:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V, \qquad \mathcal{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2\,m_i} \nabla_i^2 + V, \tag{15.25}$$

where the symbols are the same as in (15.3). Here the potential energy depends only on the spatial coordinates, $V = V\big(\mathbf{r}_1, \dots, \mathbf{r}_N\big)$. If the system is in a state of definite and constant energy E_S, its wave function reads

$$\varphi = W\, \exp(-\,\mathrm{i}\, E_S\, t/\hbar), \qquad W = W\big(\mathbf{q}_1, \dots \mathbf{q}_N\big), \tag{15.26}$$

where E_S is an eigenvalue of $\mathcal{H}W = E\,W$. Extending to this case the definition of Sect. 15.2, the system is separable if $V = \sum_i V_i(\mathbf{r}_i)$, which gives the Hamiltonian operator the form

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i, \qquad \mathcal{H}_i = -\frac{\hbar^2}{2\,m_i} \nabla_i^2 + V_i\big(\mathbf{r}_i\big). \tag{15.27}$$

Assuming that the eigenvalues are discrete, the ith Hamiltonian yields the single-particle equations

$$\mathcal{H}_i w_{n(i)} = E_{n(i)} w_{n(i)}, \tag{15.28}$$

where index $n(i)$ denotes the nth eigenvalue of the ith particle. From the general properties of operators (Sect. 10.3) it follows that each eigenfunction of the whole system is the product of eigenfunctions like $w_{n(i)}$,

$$W = w_{n(1)}\big(\mathbf{q}_1\big)\, w_{n(2)}\big(\mathbf{q}_2\big)\, \dots\, w_{n(N)}\big(\mathbf{q}_N\big), \tag{15.29}$$

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[6] Like the Heisenberg principle illustrated in Sect. 10.6, that of Pauli was originally deduced from heuristic arguments. The analysis of this section shows in fact that it is a theorem rather than a principle.

and the eigenvalue of $\mathcal{H}$ is the sum of eigenvalues like $E_{n(i)}$:

$$E_S = E_{n(1)} + E_{n(2)} + \ldots + E_{n(N)}. \tag{15.30}$$

If the particles are identical, $m_1 = m_2 = \ldots = m_N$, then the single-particle Hamiltonian operators $\mathcal{H}_i$ become identical to each other; as a consequence, each eigenvalue Eq. (15.28) produces the same set of eigenvalues and eigenfunctions. It follows that all $N!$ permutations of the indices $1, 2, \ldots, N$ in (15.30) leave the total energy unchanged. On the other hand, as for any pair of groups $\mathbf{q}_r$, $\mathbf{q}_s$ it is

$$w_{n(r)}\big(\mathbf{q}_r\big)\, w_{n(s)}\big(\mathbf{q}_s\big) \neq w_{n(s)}\big(\mathbf{q}_r\big)\, w_{n(r)}\big(\mathbf{q}_s\big), \tag{15.31}$$

the total eigenfuction is changed by a permutation of the coordinate indices. Thus, to E_S there correspond $N!$ eigenfunctions w, namely, the eigenvalues of $\mathcal{H}W = E\,W$ for a system of identical particles are $N!$-fold degenerate.

As noted in Sect. 15.6, the solution (15.26) of the system's Schrödinger equation is not necessarily symmetric or antisymmetric. A solution with the correct symmetry property is found from (15.23) and has the form

$$\psi = a\, \exp(-\,\mathrm{i}\, E_S\, t/\hbar) \sum_\nu \mathcal{S}_\nu w_{n(1)}\big(\mathbf{q}_1\big) \ldots w_{n(N)}\big(\mathbf{q}_N\big) \tag{15.32}$$

in the symmetric case, and

$$\psi = b\, \exp(-\,\mathrm{i}\, E_S\, t/\hbar) \sum_\nu (-\,1)^\nu\, \mathcal{S}_\nu w_{n(1)}\big(\mathbf{q}_1\big) \ldots w_{n(N)}\big(\mathbf{q}_N\big) \tag{15.33}$$

in the antisymmetric one. It is worth specifying that $\mathcal{S}_\nu$ acts on the coordinate groups $\mathbf{q}_1, \ldots, \mathbf{q}_N$, not on the indices $n(1), \ldots, n(N)$.

When the wave function has the form (15.32) or (15.33), and the eigenfunctions $w_{n(1)}, \ldots, w_{n(N)}$ are normalized to unity, the constants a and b are readily found. Considering the symmetric case with $N = 2$, the wave function reads

$$\psi = a\, \exp(-\,\mathrm{i}\, E_S\, t/\hbar)\, \big[w_{n(1)}(\mathbf{q}_1)\, w_{n(2)}(\mathbf{q}_2) + w_{n(2)}(\mathbf{q}_1)\, w_{n(1)}(\mathbf{q}_2)\big], \tag{15.34}$$

where it is assumed that the single-particle eigenfunctions are normalized to unity:

$$\sum_{s_{z1}} \int |w_{n(i)}(\mathbf{r}_1, s_{z1})|^2\, \mathrm{d}^3 r_1 = 1, \qquad \sum_{s_{z2}} \int |w_{n(i)}(\mathbf{r}_2, s_{z2})|^2\, \mathrm{d}^3 r_2 = 1. \tag{15.35}$$

In (15.35) it is $i = 1, 2$, and the indication of the domain of $\mathbf{r}_1$, $\mathbf{r}_2$ is omitted. As $n(2) \neq n(1)$, the pairs of eigenfunctions with such indices are mutually orthogonal (Sect. 8.4.1), whence

$$\sum_{s_{z1}} \sum_{s_{z2}} \iint |\psi\big(\mathbf{r}_1, s_{z1}, \mathbf{r}_2, s_{z2}\big)|^2\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 = 2\, |a|^2. \tag{15.36}$$

Imposing the normalization of ψ to unity, and observing that the phase factor in a is irrelevant, yields $a = 1/\sqrt{2}$. The treatment of (15.33) is identical and yields the same result for b. By the same token, one finds $a = b = 1/\sqrt{N!}$ in the N-particle case. Still with reference to the antisymmetric wave function (15.33), one notes that its spatial part can be recast as a determinant,

$$\sum_{\nu} (-1)^{\nu} \mathcal{S}_{\nu} w_{n(1)}(\mathbf{q}_1) \ldots w_{n(N)}(\mathbf{q}_N) = \begin{bmatrix} w_{n(1)}(\mathbf{q}_1) & \cdots & w_{n(N)}(\mathbf{q}_1) \\ \vdots & \ddots & \vdots \\ w_{n(1)}(\mathbf{q}_N) & \cdots & w_{n(N)}(\mathbf{q}_N) \end{bmatrix}, \tag{15.37}$$

that is called *Slater determinant*. A transposition of two particles involves the exchange of the corresponding coordinate sets, but not of the eigenfunction indices; this is equivalent to exchanging two rows of the determinant, whence the change of sign. Also, if two or more particles belonged to the same state (including spin), two or more columns of the Slater determinant would be equal to each other and the wave function (15.33) would vanish. This is another form of the proof of Pauli's exclusion principle.

15.8 Equilibrium Statistics in the Quantum Case

This section illustrates the quantum-mechanical treatment of a system of particles in a condition of macroscopic equilibrium. The approach is the same as that outlined in Sect. 6.3 for the classical case; however, the constraints to which the particles are subjected are different. Here the term "particle" is used in a broader meaning, incorporating, e.g., also the case of photons (Sect. 12.3) and phonons (Sect. 16.6). As in Sect. 6.3 one considers a conservative system of identical particles, having a total energy E_S, enclosed in a stationary container of volume Ω. The conservation of the total energy introduces a first constraint, identical to (6.10):

$$F_E(N_1, N_2, \ldots) = 0, \qquad F_E = -E_S + \sum_i N_i\, E_i. \tag{15.38}$$

The constraint identical to (6.9),

$$F_N(N_1, N_2, \ldots) = 0, \qquad F_N = -N + \sum_i N_i, \tag{15.39}$$

describing the conservation of the total number of particles, may, instead, be fulfilled or not depending on the type of particles. For instance, a system of photons does not fulfill it: in fact, a photon may be absorbed by the container's wall and, say, two photons may be emitted by it, such that the energy of the emitted photons equals that of the absorbed one. In this way, constraint (15.38) applies, whereas constraint (15.39) does not. Another difference from the classical treatment is that, as remarked in Sect. 15.5, identical quantum particles belonging to a system are not distinguishable from each other; as a consequence, the method of counting their

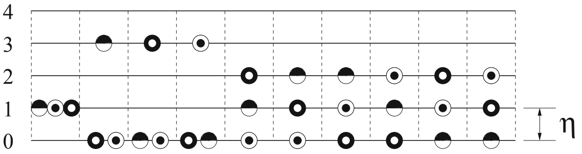

Fig. 15.2 Placement of three identical particles into equally-spaced energy states. The particles' total energy equals three energy units η. Different graphic symbols are used for the particles to make the classical treatment clearer

placement into the cells of the phase space (illustrated in Sect. 6.3 for the classical case), is different here. A further distinction must be made between the cases of systems made of fermions, to which the exclusion principle applies, and systems made of bosons, to which it does not apply. To appreciate the strong differences that are introduced by the constraints due to indistinguishability and exclusion, the example below is of help.

Consider a system made of three identical particles, whose total energy E_S is, in some units η, equal to $3\,\eta$. For simplicity, the particles are considered spinless and, instead of the phase space, a space made of energy cells[7] is used, where the energies of the particles are assumed to be quantized starting from a ground level. As a consequence, the energies allowed to the particles are $0, \eta, 2\,\eta, 3\,\eta, \ldots$; the energy levels are shown in Fig. 15.2, where the particles are drawn with different graphics to make them provisionally distinguishable. If the system is considered as classical, it is easily found that there are ten possible ways of placing the three particles into the available states in such a way as to fulfill the energy constraint $E_S = 3\,\eta$. One way is to place all three particles in the η state. Another choice is to place one particle in the $3\,\eta$ state and the remaining two in the ground state; this provides three different ways, as there are three distinct possibilities to choose the particle to be placed in the $3\,\eta$ state. The last choice is to place one particle in the ground state, another particle in the η state, and the remaining one in the $2\,\eta$ state; this yields 3! ways as shown in the figure. If, instead, the particles are bosons, the three former combinations with energies $(0, 0, 3\eta)$ reduce to a single one because of the particles' indistinguishability; by the same token, the six former combinations with energies $(0, \eta, 2\eta)$ reduce to a single one as well. This gives a total of three ways for bosons, in contrast with the ten ways of the classical particles. Finally, if the particles are fermions, the combinations (η, η, η) and $(0, 0, 3\eta)$ must be excluded because the exclusion principle forbids one or more fermions to occupy the same state; as a consequence, the only way left for fermions is $(0, \eta, 2\eta)$, that fulfills both indistinguishability and exclusion.

Coming back to the general case, consider a system in thermodynamic equilibrium at temperature T, with E_S the system's total energy. As in the classical case outlined in Sect. 6.3, the system is considered dilute, namely such that the mutual interaction

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[7] The use of energy intervals does not entail a loss of generality, as the subsequent treatment of the general case will show.

among the particles, albeit necessary for the existence of the system, is weak enough to assume that the energy of the interaction among the particles is negligible within the Hamiltonian operator. It follows that the latter is separable, and the expressions found in Sect. 15.7 are applicable. As the particles are identical, the single-particle eigenvalues $E_{n(i)}$ and eigenfunctions $w_{n(i)}(\mathbf{q}_i)$ obtained by solving (15.28) are the same for all particles. Also, the indices[8] $n(i)$ are those of an energy, so that the procedure of placing the particles into the available states can be carried out directly in the energy space. To account for spin, states corresponding to the same energy and different spin are to be considered as distinct. The minimum eigenvalue of (15.28) is fixed by the form of the potential energy within the Hamiltonian operator. Given these premises, the energy axis is divided into equal intervals of length ΔE; as in the classical case, the partitioning has the advantage that the set of intervals is countable. The intervals are numbered starting from the one containing the minimum eigenvalue mentioned above, and their size ΔE is such that each of them contains a number of eigenvalues of (15.28). Let g_r be the number of eigenvalues within the rth interval, $r = 1, 2 \ldots$, and N_r the number of particles whose eigenvalues belong to the same interval; if the size ΔE is taken small, one can approximate the energy of the N_r particles with the product $N_r\, E_r$, where E_r is the energy at the interval's center. Following the same procedure as in Sect. 6.4, one then constructs the function

$$F\big(N_1, N_2, \ldots, \alpha, \beta\big) = \log W + \alpha\, F_N + \beta\, F_E, \qquad (15.40)$$

where α, β are the Lagrange multipliers, respectively related to the total number of particles and total energy of the system, and the form of W depends on the type of particles, as shown below. If the constraint on the total number of particles is not applicable, one lets $\alpha = 0$. Using the numbers N_1, $N_2, \ldots$ as continuous variables, taking the derivative of F with respect to N_r and equating it to zero yields

$$\frac{\partial}{\partial N_r} \log W = \alpha + \beta\, E_r. \qquad (15.41)$$

On the other hand it is $W = W_1\, W_2\, \ldots, W_r\, \ldots$, where W_r is the number of ways in which N_r particles can be placed into the g_r states of the rth interval, subjected to the constraints of the type of particles under consideration. As in the left hand side of (15.41) only the rth summand depends on N_r, the relation to be worked out is eventually

$$\frac{\partial}{\partial N_r} \log W_r = \alpha + \beta\, E_r. \qquad (15.42)$$

The expression of W_r depends on the type of particles; it is given in Sect. 15.8.1 for the case of fermions and in Sect. 15.8.2 for that of bosons.

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[8] Here the eigenvalues of the Hamiltonian operator are discrete because the system is enclosed in a container, hence the wave function is normalizable. As usual, the notation $n(i)$ stands for a group of indices.

15.8.1 Fermi–Dirac Statistics

For a system of fermions it is $N_r \le g_r$ due to the exclusion principle. To calculate the number of ways of placing N_r particles into g_r states one provisionally assumes that the particles are distinguishable. There are g_r possibilities to place the first particle; after the latter has been placed, there remain $g_r - 1$ states due to the exclusion principle, hence the different ways of placing the first two (distinct) particles are $g_r\,(g_r - 1)$. The process continues until all N_r particles are used up, this leading to $g_r\,(g_r - 1)\,\dots\,(g_r - N_r + 1)$ ways of placing them. On the other hand the particles are not distinct; as a consequence, after the placement is completed, any of the $N_r!$ permutations of the particles corresponds to the same placement. In conclusion, the product above must be divided by $N_r!$, this leading to

$$W_r = \frac{g_r\,(g_r - 1)\,\dots\,(g_r - N_r + 1)}{N_r!} = \frac{g_r!}{N_r!\,(g_r - N_r)!} = \binom{g_r}{N_r}. \tag{15.43}$$

Using the same procedure as in Sect. 6.4 yields

$$\frac{\mathrm{d}\log W_r}{\mathrm{d}N_r} = \frac{\mathrm{d}\log\left[(g_r - N_r)!\right]}{\mathrm{d}(-N_r)} - \frac{\mathrm{d}\log(N_r!)}{\mathrm{d}N_r} \simeq \log(g_r - N_r) - \log(N_r) \tag{15.44}$$

which, combined with (15.42), provides $N_r = g_r/[\exp(\alpha + \beta E_r) + 1]$. For convenience, the total number of particles is indicated here with N_S instead of N; the constraints then read

$$\sum_{r=1}^{U} \frac{g_r}{\exp(\alpha + \beta\,E_r) + 1} = N_S, \qquad \sum_{r=1}^{U} \frac{g_r E_r}{\exp(\alpha + \beta\,E_r) + 1} = E_S, \tag{15.45}$$

by which the two Lagrange multipliers α and β are determined. The sums are carried out up to a maximum energy E_U; in fact, being the total energy of the system prescribed, there exists a maximum energy that the single particle can not exceed. As outlined in Sect. 15.9.1, a comparison with the findings of Thermodynamics shows that, in full analogy with the classical case treated in Sect. 6.4, it is

$$\beta = \frac{1}{k_B T}, \tag{15.46}$$

where $k_B \simeq 1.38 \times 10^{-23}$ J K^{-1} is Boltzmann's constant and T the system temperature. As a consequence it is $\alpha = \alpha(T)$. Defining the *Fermi energy* or *Fermi level* $E_F(T) = -k_B\,T\,\alpha(T)$, the expression of N_r becomes

$$N_r = \frac{g_r}{\exp\left[(E_r - E_F)\,/\,(k_B\,T)\right] + 1}. \tag{15.47}$$

In general the number of energy levels is large and their separation small so that, instead of using the number g_r of states at energy E_r, one disposes of the index and

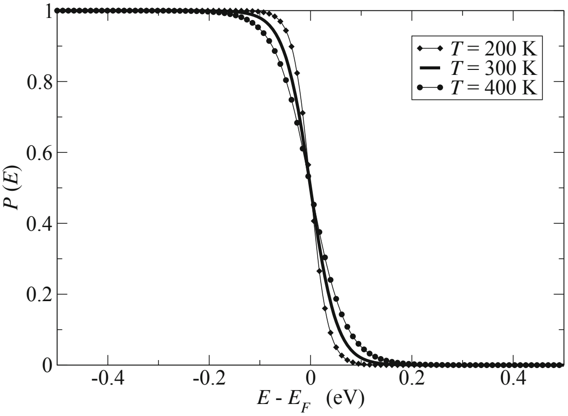

Fig. 15.3 The Fermi–Dirac statistics as a function of energy for different values of the system's temperature. For simplicity the temperature dependence of the Fermi level E_F is not considered

considers the number $g(E)\,\mathrm{d}E$ of states in the infinitesimal interval $\mathrm{d}E$ around E. Thus, $g(E)$ indicates the number of states per unit energy, and is called *density of states in energy* (compare with Sect. B.5). The constraints now read

$$\int_{E_1}^{E_U} \frac{g(E)\,\mathrm{d}E}{\exp\big(\alpha + \beta E\big) + 1} = N_S, \qquad \int_{E_1}^{E_U} \frac{E\,g(E)\,\mathrm{d}E}{\exp\big(\alpha + \beta E\big) + 1} = E_S, \tag{15.48}$$

with $\beta = 1/(k_B T)$. Consistently, N_r is replaced with $N(E)\,\mathrm{d}E$, where $N(E)$ is the number of particles per unit energy.[9] As a consequence, the relation $N(E) = g(E)\,P(E)$ is fulfilled, where function

$$P(E) = \frac{1}{\exp\left[(E - E_F)\,/\,(k_B\,T)\right] + 1} \tag{15.49}$$

is called *Fermi–Dirac statistics*. As $0 < P(E) < 1$, the Fermi–Dirac statistics bears also the meaning of occupation probability of a state at energy E. Its high-energy tail $\big(E - E_F \gg k_B\,T\big)$ identifies with the Maxwell–Boltzmann distribution law (6.14). The dependence of (15.49) on E is shown in Fig. 15.3 at different temperatures. The states whose energy is substantially lower than the Fermi level $\big(E - E_F \ll -k_B\,T\big)$ are mostly filled with particles, those whose energy is substantially higher than the Fermi level are mostly empty. The energy states in the vicinity of the Fermi level have a probability around $1/2$ of being filled. For the sake of simplicity the dependence of E_F on T is not considered in the figure; in fact, it is influenced by the form of $g(E)$ and must therefore be determined on a case-by-case basis. In the limit $T \to 0$ the function becomes discontinuous, specifically it is $P = 1$ for $E < E_F$ and $P = 0$ for $E > E_F$.

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[9] The units are $[g], [N] = \mathrm{J}^{-1}$.

15.8.2 Bose–Einstein Statistics

For a system of Bosons the exclusion principle does not hold, hence it may be $N_r \ge g_r$. Also in this case, to calculate the number of ways of placing N_r particles, not subject to the exclusion principle, into g_r states, one provisionally assumes that the particles are distinguishable. This yields a number of ways equal to $\left(g_r + N_r - 1\right)\left(g_r + N_r - 2\right) \dots g_r$. Then, to account for indistinguishability one divides the result by $N_r!$, to find

$$W_r = \frac{\left(g_r + N_r - 1\right) \dots g_r}{N_r!} = \frac{\left(g_r + N_r - 1\right)!}{N_r!\,\left(g_r - 1\right)!} = \binom{g_r + N_r - 1}{N_r}. \tag{15.50}$$

Using the same procedure as in Sect. 6.4 yields

$$\frac{\mathrm{d}\log W_r}{\mathrm{d}N_r} = \frac{\mathrm{d}\log\left[(g_r + N_r - 1)!\right]}{\mathrm{d}N_r} - \frac{\mathrm{d}\log\left(N_r!\right)}{\mathrm{d}N_r} \simeq \log\left(g_r + N_r - 1\right) - \log N_r \tag{15.51}$$

which, combined with (15.42) after neglecting the unity in $g_r + N_r - 1$, yields $N_r = g_r/\left[\exp(\alpha+\beta E_r)-1\right]$. As in the latter it is $N_r, g_r > 0$, it follows $\alpha+\beta E_r > 0$. Still indicating the number of particles with N_S instead of N, the constraints read

$$\sum_{r=1}^{U} \frac{g_r}{\exp\left(\alpha + \beta\, E_r\right) - 1} = N_S, \qquad \sum_{r=1}^{U} \frac{g_r\, E_r}{\exp\left(\alpha + \beta\, E_r\right) - 1} = E_S, \tag{15.52}$$

by which the two Lagrange multipliers α and β are determined. The explanation of the upper summation limit U in (15.52) is similar to that given in Sect. 15.8.1. As outlined in Sect. 15.9.5, a comparison with the findings of Thermodynamics shows that, in full analogy with the cases of Sects. 6.4 and 15.8.1, β is given by (15.46), whence it is $\alpha = \alpha(T)$. Defining $E_B(T) = -k_B\, T\, \alpha(T)$, the expression of N_r becomes

$$N_r = \frac{g_r}{\exp\left[(E_r - E_B)\,/\,(k_B\, T)\right] - 1}. \tag{15.53}$$

The inequality $\alpha + \beta\, E_r > 0$ found above implies $E_r > E_B$. If the constraint on the number of particles does not hold, one lets $\alpha = 0$ whence $E_B = 0$, $E_r > 0$. In general the number of energy levels is large and their separation small so that, instead of using the number g_r of states at energy E_r, one disposes of the index and considers the number $g(E)\,\mathrm{d}E$ of states in the infinitesimal interval $\mathrm{d}E$ around E. The constraints now read

$$\int_{E_1}^{E_U} \frac{g(E)\,\mathrm{d}E}{\exp(\alpha + \beta\, E) - 1} = N_S, \qquad \int_{E_1}^{E_U} \frac{E\, g(E)\,\mathrm{d}E}{\exp(\alpha + \beta\, E) - 1} = E_S, \tag{15.54}$$

with $\beta = 1/(k_B T)$. Consistently, N_r is replaced with $N(E)\,\mathrm{d}E$, where $N(E)$ is the number of particles per unit energy. As a consequence, the relation $N(E) = g(E)\,P(E)$ is fulfilled, where function

$$P(E) = \frac{1}{\exp\left[(E - E_B)\,/\,(k_B T)\right] - 1} \tag{15.55}$$

is called *Bose–Einstein statistics*. As $P(E)$ may be larger than unity, the Bose–Einstein statistics is not a probability; rather, it represents the occupation number of a state at energy E. Its high-energy tail $\big(E - E_B \gg k_B T\big)$ identifies with the Maxwell–Boltzmann distribution law (6.14).

15.9 Complements

15.9.1 Connection with Thermodynamic Functions

The calculation of the equilibrium distribution carried out in Sects. 6.4, 15.8.1, and 15.8.2 respectively for classical particles, fermions, and bosons, entails the maximization of the function $\log W$, subjected to suitable constraints. On the other hand, from the second principle of Thermodynamics one derives that the equilibrium state of a system corresponds to the condition that the system's entropy S has a maximum. For this reason one expects that a functional dependence $W(S)$ exists; to identify its form one notes that, if W_1 and W_2 indicate the value of W of two independent systems, the value for the composite system is $W_1\,W_2$ due to the definition of W. On the other hand, entropy is additive, so that the functional dependence sought must be such that $S\big(W_1\,W_2\big) = S\big(W_1\big) + S\big(W_2\big)$, namely, of the logarithmic type. In fact it is

$$S = k_B\,\log W, \tag{15.56}$$

with $k_B = 1.38 \times 10^{-23}$ J K^{-1} the Boltzmann constant. The choice of the constant makes (15.56) consistent with the definition $\mathrm{d}S = \mathrm{d}Q/T$ of entropy in Thermodynamics, with $\mathrm{d}Q$ the heat absorbed during an infinitesimal transformation.[10]

Now, consider a system subjected to both constraints (15.38) and (15.39), and assume that the container where the system is placed undergoes an infinitesimal volume change[11] $\mathrm{d}\Omega$ which, in turn, makes all variables N_r and g_r to change; due to (15.41) it is $\partial \log W/\partial N_r = \alpha + \beta\,E_r$ so that [27]

$$\frac{1}{k_B}\,\mathrm{d}S = \mathrm{d}\log W = \sum_{r=1}^{U}\left[(\alpha + \beta\,E_r)\;\mathrm{d}N_r + \frac{\partial \log W}{\partial g_r}\,\mathrm{d}g_r\right]. \tag{15.57}$$

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[10] Compare with the non-equilibrium definition of entropy introduced in Sect. 6.6.3 and the note therein.

[11] The geometrical configuration is kept similar to the original one during the change in volume.

Using the constraints and the relation $\mathrm{d}S = \mathrm{d}Q/T$ transforms (15.57) into

$$\mathrm{d}Q = k_B\, T\, \alpha\, \mathrm{d}N + k_B\, T\, \beta\, \mathrm{d}E_S + k_B\, T \sum_{r=1}^{U} \left(\frac{\partial \log W}{\partial g_r} \frac{\mathrm{d}g_r}{\mathrm{d}\Omega} \right) \mathrm{d}\Omega. \tag{15.58}$$

Assuming that during the change in volume there is no exchange of matter with the environment, one lets $\mathrm{d}N = 0$ in (15.58); the first principle of Thermodynamics shows that for this type of transformation it is $\mathrm{d}Q = \mathrm{d}E_S + P\, \mathrm{d}\Omega$, with P the pressure at the boundary of Ω. A comparison with (15.58) then yields

$$k_B\, T\, \beta = 1, \qquad k_B\, T \sum_{r=1}^{U} \left(\frac{\partial \log W}{\partial g_r} \frac{\mathrm{d}g_r}{\mathrm{d}\Omega} \right) = P. \tag{15.59}$$

The first of (15.59) coincides with (6.26), and provides the expected relation between one of the Lagrange multipliers of (15.45) and a state function of Thermodynamics.

15.9.2 Density of States for a Particle in a Three-Dimensional Box

The density of states $g(E)$ that has been introduced in (15.48) and (15.54) is the number of states per unit energy. Its form depends on the system under consideration. Two examples of the derivation of $g(E)$ are given here (with reference to the problem of an electron in a box) and in Sect. 15.9.4 (with reference to photons).

The problem of the particle confined within a one-dimensional box has been tackled in Sect. 8.2.2. The set of eigenvalues is given by the first relation in (8.6), and the corresponding eigenfunctions are (8.8). For a three-dimensional box whose sides have lengths d_1, d_2, d_3, due to the properties of separable operators (Sect. 10.3), the eigenfunctions are products of one-dimensional eigenfunctions,

$$w_{n_1 n_2 n_3}(\mathbf{r}) = \sqrt{8/V}\, \sin\left(k_{n_1}\, x_1\right)\, \sin\left(k_{n_2}\, x_2\right)\, \sin\left(k_{n_3}\, x_3\right), \tag{15.60}$$

where $V = d_1\, d_2\, d_3$ is the volume of the box. In turn, the eigenvalues are

$$E_{n_1 n_2 n_3} = E_{n_1} + E_{n_2} + E_{n_3}, \qquad E_{n_i} = \frac{\hbar^2\, k_{n_i}^2}{2\, m}, \qquad k_{n_i} = n_i\, \frac{\pi}{d_i}, \tag{15.61}$$

namely,

$$E = \frac{\hbar^2\, k^2}{2\, m}, \qquad \mathbf{k} = n_1\, \frac{\pi}{d_1}\, \mathbf{i}_1 + n_2\, \frac{\pi}{d_2}\, \mathbf{i}_2 + n_3\, \frac{\pi}{d_3}\, \mathbf{i}_3, \qquad n_i = 1, 2, \ldots \tag{15.62}$$

with $\mathbf{i}_1, \ldots$ the unit vectors of the Cartesian axes and $k^2 = \mathbf{k} \cdot \mathbf{k}$. In contrast with the one-dimensional case, the eigenvalues (15.61) are degenerate, because different triads n_1, n_2, n_3 correspond to the same energy.

The density of states could be calculated by the procedure depicted in Sect. (B.5), with the provision that in this case the variables k_{n_i} belong to a discrete set whereas those in Sect. B.5 are continuous. On the other hand, the relations involved here are simple enough to be tackled by a direct calculation. One observes, first, that the distance between two consecutive projections of **k** along the ith axis is π/d_i; as a consequence, one may partition the $k_1 k_2 k_3$ space into equal volumes[12] π^3/V, so that each **k** vector is associated to one and only one volume: this shows that the density of **k** vectors in the $k_1\,k_2\,k_3$ space is $Q_k = V/\pi^3$. Given the electron's energy E, from the geometrical point of view the first relation in (15.62) describes a sphere of radius $(2\,m\,E/\hbar^2)^{1/2}$ in the $k_1\,k_2\,k_3$ space; thus, the total number N_k of π^3/V volumes contained within the sphere is obtained by multiplying the sphere's volume by the density Q_k. Clearly the volumes that are near the boundary produce a ragged surface; the latter is identified with that of the sphere by assuming that the distribution of **k** vectors belonging to the spherical surface is very dense. With this provision one finds

$$N_k = Q_k\,\frac{4}{3}\,\pi\,k^3 = \frac{V}{\pi^3}\,\frac{4}{3}\,\pi\,\left(\frac{2\,m\,E}{\hbar^2}\right)^{3/2} = \frac{V}{\pi^2}\,\frac{8\,\sqrt{2}\,m^{3/2}}{3\,\hbar^3}\,E^{3/2}. \qquad (15.63)$$

As indices n_1, n_2, n_3 take only positive values, the **k** vectors belong to $1/8$ of the sphere only; it follows that their number is $N_k/8$. Each **k** vector is associated to a triad of quantum numbers n_1, n_2, n_3; however, to completely define the state of the electron a fourth quantum number is necessary, related to spin (Sect. 15.5.1). Remembering that electrons have two possible spin states, one finds that the number of electron states within the sphere is twice the number of **k** vectors, namely, $N_k/4$. Finally, the number of states per unit energy is found by differentiating the latter with respect to energy,[13]

$$\mathrm{d}\frac{N_k}{4} = \frac{\sqrt{2}\,V m^{3/2}}{\pi^2 \hbar^3}\,E^{1/2}\,\mathrm{d}E = g(E)\,\mathrm{d}E, \qquad g(E) = \frac{\sqrt{2}\,V\,m^{3/2}}{\pi^2\,\hbar^3}\,E^{1/2}. \qquad (15.64)$$

Apart from the constants involved, this results is consistent with (B.34). Along with the density of state in energy it is useful to define a combined density of states in energy and coordinate space, that is indicated with γ. In the case of the electron within a box one finds, from (15.64),

$$\gamma(E) = \frac{g(E)}{V} = \frac{\sqrt{2}\,m^{3/2}}{\pi^2\,\hbar^3}\,E^{1/2}. \qquad (15.65)$$

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[12] Here the term "volume" is used in a broader meaning; in fact, the units of π^3/V are m^{-3}.

[13] As noted above the **k** vectors, hence the values of energy corresponding to them, are distributed very densely. This makes it possible to treat E as a continuous variable.

15.9.3 Density of States for a Two- or One-Dimensional Box

As observed in Sect. B.5, the functional dependence of g on E is influenced by the number of spatial dimensions: considering by way of example the case of an electron within a two-dimensional box, one must associate to each vector $\mathbf{k}$ an area of the $k_1 k_2$ space equal to $\pi^2/(d_1\, d_2) = \pi^2/A$, where $A = d_1\, d_2$ is the area of the box. The density of the $\mathbf{k}$ vectors in the $k_1 k_2$ space is $Q_k = A/\pi^2$, whence the total number of π^2/A areas in a circle of radius $\left(2\, m\, E/\hbar^2\right)^{1/2}$ is

$$N_k = Q_k\, \pi\, k^2 = \frac{A}{\pi^2}\, \pi\, \frac{2\, m\, E}{\hbar^2}. \tag{15.66}$$

As indices n_1, n_2 take only positive values, the $\mathbf{k}$ vectors belong to $1/4$ of the circle only; it follows that their number is $N_k/4$. Accounting for spin one finds that the number of states within the circle is twice the number of $\mathbf{k}$ vectors, namely, $N_k/2$. Finally, the number of states per unit energy is found by differentiating the latter with respect to energy,

$$g(E) = \frac{\mathrm{d}N_k/2}{\mathrm{d}E} = \frac{A\, m}{\pi\, \hbar^2}. \tag{15.67}$$

When the energy dependence on the k coordinates is quadratic, the density of states of a two-dimensional case is constant (compare with (B.33)).

Finally, considering the case of an electron within a one-dimensional box, one must associate to each vector $\mathbf{k}$ a segment π/d_1 of the k_1 space, to find $Q_k = d_1/\pi$ for the density of the $\mathbf{k}$ vectors. The total number of π/d_1 segments in a domain of length $\left(2\, m\, E/\hbar^2\right)^{1/2}$ is

$$N_k = \frac{d_1}{\pi} \left(\frac{2\, m\, E}{\hbar^2}\right)^{1/2}. \tag{15.68}$$

Accounting for spin one finds that the number of states within the domain is twice the number of $\mathbf{k}$ vectors, namely, $2\, N_k$. Finally, the number of states per unit energy is found by differentiating the latter with respect to energy,

$$g(E) = \frac{\mathrm{d}2\, N_k}{\mathrm{d}E} = \frac{d_1\, (2\, m)^{1/2}}{\pi\, \hbar\, E^{1/2}}, \tag{15.69}$$

to be compared with (B.32). Expression (15.67) is useful, e.g., for treating the problem of a two-dimensional charge layer in the channel of a semiconductor device (Sect. 17.6.7); in turn, expression (15.69) is used with reference to nanowires (Sect. 17.6.7);

15.9.4 Density of States for Photons

Consider the case of the electromagnetic field within a box whose sides d_1, d_2, d_3 are aligned with the coordinate axes and start from the origin. It is assumed that no charge is present within the box, so that the calculation of the modes is the same as that illustrated in Sect. 5.5. The wave vectors have the form

$$\mathbf{k} = n_1 \frac{2\pi}{d_1} \mathbf{i}_1 + n_2 \frac{2\pi}{d_2} \mathbf{i}_2 + n_3 \frac{2\pi}{d_3} \mathbf{i}_3, \qquad n_i = 0, \pm 1, \pm 2, \ldots, \tag{15.70}$$

the angular frequency of the mode corresponding to $\mathbf{k}$ is $\omega = c\,k$, with k the modulus of $\mathbf{k}$, and the energy of each photon of that mode is $E = \hbar\,\omega = \hbar\,c\,k$, with c the speed of light. The calculation of the density of states associated to this case follows the same line as that used in Sect. 15.9.2 for a particle in a three-dimensional box; the differences are that the distance between two consecutive projections of $\mathbf{k}$ along the ith axis is $2\pi/d_i$ instead of π/d_i, the indices n_i are not limited to the positive values, and the $E(\mathbf{k})$ relation is linear instead of being quadratic.

With these premises, and with reference to Fig. 15.4, the volume associated to each $\mathbf{k}$ is $(2\,\pi)^3/(d_1\,d_2\,d_3) = (2\,\pi)^3/V$, where V is the volume of the box, so that the density of the $\mathbf{k}$ vectors in the k space is $Q_k = V/(2\,\pi)^3$; in turn, the total number of $\mathbf{k}$ vectors within a sphere of radius k like that shown in the figure is[14]

$$N_k = Q_k\,\frac{4}{3}\,\pi\,k^3 = \frac{V}{(2\,\pi)^3}\,\frac{4}{3}\,\pi\,\frac{E^3}{\hbar^3\,c^3} = \frac{V}{2\,\pi^2}\,\frac{E^3}{3\,\hbar^3\,c^3}. \tag{15.71}$$

Due to spin, the total number of states is $2N_k$ so that, differentiating with respect to energy,

$$\mathrm{d}2\,N_k = \frac{V}{\pi^2}\,\frac{E^2}{\hbar^3\,c^3}\,\mathrm{d}E = g(E)\,\mathrm{d}E, \qquad g(E) = \frac{V}{\pi^2\,\hbar^3\,c^3}\,E^2. \tag{15.72}$$

The result expressed by (15.72) can be recast in equivalent forms by using another variable proportional to energy; for instance, letting $G(\omega)$ denote the density of states with respect to angular frequency and $\tilde{g}(\nu)$ denote the density of states with respect to frequency, from the relations

$$\tilde{g}(\nu)\,\mathrm{d}\nu = G(\omega)\,\mathrm{d}\omega = g(E)\,\mathrm{d}E, \qquad E = \hbar\,\omega = \hbar\,2\,\pi\,\nu \tag{15.73}$$

one obtains

$$G(\omega) = \frac{V}{\pi^2\,c^3}\,\omega^2, \qquad \tilde{g}(\nu) = 8\,\pi\,\frac{V}{c^3}\,\nu^2. \tag{15.74}$$

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[14] The calculation shown here is equivalent to counting the number of elements of volume $(2\,\pi)^3/\big(d_1\,d_2\,d_3\big)$ that belong to the spherical shell drawn in Fig. 15.4. The result is then multiplied by 2 to account for spin.

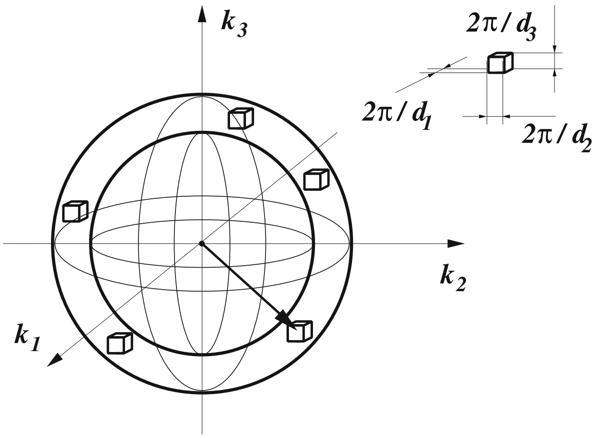

Fig. 15.4 Constant-energy sphere of the **k** space illustrating the procedure for determining the density of states

15.9.5 Derivation of Planck's Law

As illustrated in Sect. 7.4.1, Planck's law provides the black-body's spectral energy density u at equilibrium. From its definition it follows that the product $u\,\mathrm{d}\nu$ is the electromagnetic energy per unit volume in the elementary interval $\mathrm{d}\nu$; using the quantum concepts, the electromagnetic energy in $\mathrm{d}\nu$ may, in turn, be written as the product of the number $\mathrm{d}N_{\mathrm{ph}}$ of photons belonging to $\mathrm{d}\nu$ by the energy $h\,\nu$ of each photon. Considering that photons are bosons, and that the equilibrium case is considered, the number $\mathrm{d}N_{\mathrm{ph}}$ is given in turn by the product $\tilde{g}(\nu)\,\mathrm{d}\nu\,P(E = h\,\nu)$, with P the Bose–Einstein statistics (15.55). In summary, using the second relation in (15.74), one finds

$$u\,\mathrm{d}\nu = \frac{1}{V}\,h\,\nu\,\mathrm{d}N_{\mathrm{ph}} = \frac{h\,\nu}{V}\,\frac{\tilde{g}(\nu)\,\mathrm{d}\nu}{\exp(\beta\,h\,\nu) - 1} = \frac{8\,\pi\,h\,\nu^3/c^3}{\exp(\beta\,h\,\nu) - 1}\,\mathrm{d}\nu. \tag{15.75}$$

The expression of the Bose–Einstein statistic used in (15.75) accounts for the fact that the number of photons is not conserved, so that the only constraint to be considered is that on the total electromagnetic energy within volume V. It follows that the Bose–Einstein statistics has only one Lagrange multiplier, whose value is provisionally left undetermined. From (15.75) one derives Planck's law

$$u(\nu,\beta) = \frac{8\,\pi\,h\,\nu^3/c^3}{\exp(\beta\,h\,\nu) - 1}, \tag{15.76}$$

to be compared with (7.19). Like in Sect. 15.9.1, the undetermined parameter β is obtained by comparing the result of the microscopic derivation carried out above with those of Thermodynamics. Letting $W_{\mathrm{em}}^{\mathrm{eq}}$ be the electromagnetic energy within V at equilibrium, the following relations hold:

$$\frac{W_{\mathrm{em}}^{\mathrm{eq}}}{V} = \int_0^\infty u\,\mathrm{d}\nu, \qquad \frac{W_{\mathrm{em}}^{\mathrm{eq}}}{V} = \frac{4}{c}\,\sigma\,T^4, \tag{15.77}$$

with $\sigma \simeq 5.67\,10^{-12}$ W cm^{-2}K^{-4} the *Stefan–Boltzmann constant*. In fact, the first one derives from the definition of spectral energy density, while the second one (called *Stefan–Boltzmann law*) is found experimentally, On the other hand, using (C.127) one finds

$$\int_0^\infty u\,\mathrm{d}\nu = \frac{8\,\pi\,h}{c^3\,(\beta h)^4}\int_0^\infty \frac{(\beta\,h\,\nu)^3}{\exp(\beta\,h\,\nu)-1}\,\mathrm{d}(\beta\,h\,\nu) = \frac{8\,\pi}{c^3\,h^3\,\beta^4}\,\frac{\pi^4}{15}. \qquad (15.78)$$

Combining (15.78) with (15.77) yields $1/(\beta T)^4 = 15\,c^2\,h^3\,\sigma/(2\,\pi^5)$; replacing the constants at the right hand side of the latter shows that the units and numerical value of it are those of k_B^4; it follows that $1/(\beta T)^4 = k_B^4$ and the expected result $\beta = 1/(k_B\,T)$ is found.

Problems

15.1 Estimate the extension of the energy region where the main variation of the Fermi statistics (15.49) occurs.