# Chapter 23
# Identical Particles

The fact that there are identical quantum objects has far-reaching consequences, e.g. the Pauli principle. We also take a closer look at the spectrum of the helium atom and make the acquaintance of another approximation method, namely Ritz's method.

We have thus far always tacitly assumed that the quantum objects we are dealing with are distinguishable. This is familiar from classical physics, where it is always possible to distinguish between two particles (for example by coloring them differently), without changing their measurable properties. Quantum mechanics is different: Here, identical quantum objects are not distinguishable *in principle*.[1] This fact leads, among other things, to the Pauli principle and to the exchange energy in helium.

A note on nomenclature: Whenever possible, we have consistently avoided speaking of 'particles', and have instead used the term 'quantum objects'. This is intended to emphasize that we are usually dealing not with a particle or a wave, but with something new and peculiar to quantum mechanics. In the everyday parlance of physics, however, the term 'particle' is well established in many contexts (which in part is for historical reasons, and partly is due to the convenience of language and physics folklore). This is the case here also, where the expression 'identical particles' does not point up the particle nature of the objects in question, but rather it parallels the term 'identical quantum objects'. However, since 'identical particles' is an established standard term, we will continue to use it in the following sections.[2]

Finally, a remark on notation. In Chap. 20, using the notation $|nm\rangle$ or the like, we described the situation that quantum object 1 is in the state $|n\rangle$ and quantum object 2 in the state $|m\rangle$. In this chapter, the situation is more complicated in that quantum objects can exchange their states, which means that we must ideally number both

---

[1] Some authors express this fact explicitly as a postulate of quantum mechanics, see Appendix R, Vol. 1.

[2] Similar nomenclature problems exist in other disciplines. For example, Egon Friedell writes about the transcriptions of Oriental proper names in the Bible: "Almost all the other names are mangled in a similar way, but since they were adopted by Luther in his Bible translation and are therefore now naturalized as fixed terms, it would be pure harassment and learned affectation to try to correct them." (*Cultural History of Egypt and the Ancient Orient*, p. 1082).

J. Pade, *Quantum Mechanics for Pedestrians 2*, Undergraduate Lecture Notes in Physics, https://doi.org/10.1007/978-3-030-00467-5_23

the objects and their states independently of each other. In addition, we consider in general not just two objects, but a larger number $N$. In the literature there are various notations for this purpose. We choose in the following $|1:\alpha_1, 2:\alpha_2, \ldots\rangle$ for the situation that object 1 is in state $\alpha_1$ and so on. The $\alpha_i$'s signify all the quantum numbers that are necessary for the unique description of the $i$th state. An exchange of the $i$th and $j$th state (i.e. object $i$ is in state $\alpha_j$, object $j$ is in state $\alpha_i$) is then written as

$$\left|1:\alpha_1, \ldots, i:\alpha_i, \ldots, j:\alpha_j, \ldots\right\rangle \rightarrow \left|1:\alpha_1, \ldots, i:\alpha_j, \ldots, j:\alpha_i, \ldots\right\rangle. \tag{23.1}$$

## 23.1 Distinguishable Particles

For this case, we have provided the necessary ingredients in Chap. 20. We link the Hilbert spaces $\mathcal{H}_i$ of the $N$ individual quantum objects[3] to give the product space[4]:

$$\mathcal{H}_{(N)} = \mathcal{H}_{1(1)} \otimes \mathcal{H}_{2(1)} \otimes \cdots \otimes \mathcal{H}_{N(1)}. \tag{23.2}$$

In each Hilbert space $\mathcal{H}_{i(1)}$, there is a CONS $\{|i:a_i\rangle\}$, from which the $N$-particle product states

$$|1:\alpha_1, 2:\alpha_2, \ldots, N:\alpha_N\rangle = |1:\alpha_1\rangle\, |2:\alpha_2\rangle \ldots |N:\alpha_N\rangle \tag{23.3}$$

may be generated. The states (23.3) form a CONS in $\mathcal{H}_{(N)}$, in terms of which any of the $N$ particles can be expanded:

$$|\psi_N\rangle = \sum\!\!\!\!\!\!\int_{\alpha_1\ldots\alpha_N} c_{\alpha_1\ldots\alpha_N}\, |1:\alpha_1, 2:\alpha_2, \ldots, N:\alpha_N\rangle\,. \tag{23.4}$$

Scalar products refer to the same space:

$$\begin{aligned}&\langle 1:\beta_1, 2:\beta_2, \ldots, N:\beta_N\, |1:\alpha_1, 2:\alpha_2, \ldots, N:\alpha_N\rangle \\ &\quad = \langle 1:\beta_1\, |1:\alpha_1\rangle\, \langle 2:\beta_2\, |2:\alpha_2\rangle \ldots \langle N:\beta_N\, |N:\alpha_N\rangle\,.\end{aligned} \tag{23.5}$$

---

[3] We denote the particle number $n$ by a subscript, the number $m$ of particles (if necessary) by a bracketed subscript and the dimension $d$ by a superscript, i.e. $\mathcal{H}^d_{n(m)}$.

[4] Or more compactly, $\mathcal{H}_{(N)} = \bigotimes_{n=1}^{N} \mathcal{H}_{n(1)}$.

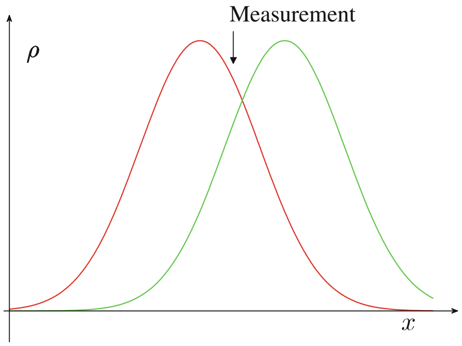

**Fig. 23.1** By a measurement as shown (arrow position), it is not possible to conclude unambiguously which electron was observed

## 23.2 Identical Particles

We assume that we have two free electrons. Their probability densities are given by Gaussian curves (see Chap. 5, Vol. 1) which overlap as in Fig. 23.1. This means that if we detect an electrona somewhere, we do not know which one of the two we have observed—unless the two differ in their spin orientations, and we measure them as well. Thus, we assume that identical quantum objects agree in *all* their properties, even if we do not observe these in detail. In contrast to classical mechanics, identical quantum objects are *indistinguishable*—there is no way (no matter how sophisticated) to distinguish them.

Now we *must* perform a particle numbering in the formal description, so to speak for accounting purposes. How are we to number indistinguishable quantum objects? In any case, this must be done in such a way that experimentally-detectable quantities do *not* depend on the method of numbering.

### 23.2.1 A Simple Example

We consider the simplest example, namely a two-particle product state $|1:\alpha_1\rangle$ $|2:\alpha_2\rangle = |1:\alpha_1; 2:\alpha_2\rangle$. If we interchange the two particles, we obtain the state $|1:\alpha_2; 2:\alpha_1\rangle$. From these two states, we can now construct total states for which, as intended, the physics does not depend on the method of numbering. These are (this is intuitively obvious, but is treated explicitly in an exercise):

$$|\psi_\pm\rangle = \frac{|1:\alpha_1, 2:\alpha_2\rangle \pm |1:\alpha_2, 2:\alpha_1\rangle}{\sqrt{2}} \text{ for } \alpha_1 \neq \alpha_2 \tag{23.6}$$

and

$$|\psi\rangle = |1:\alpha_1, 2:\alpha_2\rangle \text{ for } \alpha_1 = \alpha_2. \tag{23.7}$$

Interchanging the two particles, we have $|\psi_+\rangle \to |\psi_+\rangle$ (symmetric state) and $|\psi_-\rangle \to -|\psi_-\rangle$ (antisymmetric state). We recall that a global phase (e.g. here the factor $-1$) is not observable. The two states (23.6) are clearly entangled, and consequently, the two particles do not have individual features, as we emphasized in Chap. 20.

We illustrate this by means of two electrons. For electron $i$, we denote the state 'spin up' by $\left|i : \frac{1}{2}\right\rangle$ and 'spin down' by $\left|i : -\frac{1}{2}\right\rangle$.[5] Two spins of $\frac{1}{2}$ can be added to give a total spin of $S = 1$ or 0. The corresponding spin states $|S, m_S\rangle$ for total spin $S = 1$ form a triplet $|1, m_S\rangle$ (symmetric), with $m_S = -1, 0, 1$, i.e.

$$\begin{aligned} |1,1\rangle &= \left|1 : \frac{1}{2}, 2 : \frac{1}{2}\right\rangle \\ |1,0\rangle &= \frac{\left|1 : \frac{1}{2}, 2 : -\frac{1}{2}\right\rangle + \left|1 : -\frac{1}{2}, 2 : \frac{1}{2}\right\rangle}{\sqrt{2}} \\ |1,-1\rangle &= \left|1 : -\frac{1}{2}, 2 : -\frac{1}{2}\right\rangle; \end{aligned} \tag{23.8}$$

and for total spin $S = 0$, a singlet $|0, 0\rangle$ (antisymmetric):

$$|0,0\rangle = \frac{\left|1 : \frac{1}{2}, 2 : -\frac{1}{2}\right\rangle - \left|1 : -\frac{1}{2}, 2 : \frac{1}{2}\right\rangle}{\sqrt{2}}. \tag{23.9}$$

### 23.2.2 The General Case

For systems of more than two particles, it is convenient to use *permutations*. A permutation changes the order within am $n$-tuple; for instance, $(1, 4, 3, 2)$ is a permutation of $(1, 2, 3, 4)$. Every permutation can be written as the product of *transpositions*, i.e. permutations which interchange just two positions, such as in $(1, 2, 3, 4) \to (1, 3, 2, 4)$.

The transposition operator $P_{ij}$ interchanges the $i$th and the $j$th position[6]:

$$P_{ij} \left|\ldots, i : \alpha_i, \ldots, j : \alpha_j, \ldots\right\rangle = \left|\ldots, i : \alpha_j, \ldots, j : \alpha_i, \ldots\right\rangle. \tag{23.10}$$

In words: Particle $i$ now has the quantum numbers $\alpha_j$ and particle $j$ the quantum numbers $\alpha_i$. The transpositions are unitary in $\mathcal{H}_{(N)}$ and Hermitian, because of $P_{ij}^2 = 1$:

$$P_{ij}^{-1} = P_{ij}^{\dagger} = P_{ij}. \tag{23.11}$$

---

[5] Since the spin of both quantum objects is $\frac{1}{2}$, we omit it below and write for short $\left|i : \pm\frac{1}{2}\right\rangle$ instead of $\left|i : \frac{1}{2}, \pm\frac{1}{2}\right\rangle$, and similarly for the total state, $\left|1 : \frac{1}{2}; 2 : -\frac{1}{2}\right\rangle$ instead of $\left|1 : \frac{1}{2}, \frac{1}{2}; 2 : \frac{1}{2}, -\frac{1}{2}\right\rangle$.

[6] We note that $P_{ij}$ is not a projection operator. The letter $P$ is derived from 'permutation'.

We stated above that experimentally measurable quantities must not depend on the method of numbering. For matrix elements of an observable $A_N$ with an allowed state $|\varphi\rangle$, this requirement can be formulated as follows:

$$\langle\varphi| A_N |\varphi\rangle \overset{!}{=} \left\langle P_{ij}\varphi\right| A_N \left|P_{ij}\varphi\right\rangle = \langle\varphi| P_{ij}^{\dagger} A_N P_{ij} |\varphi\rangle \text{ for all pairs } i, j, \tag{23.12}$$

which implies[7] that:

$$A_N = P_{ij}^{\dagger} A_N P_{ij} \quad \text{or} \quad \left[A_N, P_{ij}\right] = 0 \text{ for all pairs } i, j. \tag{23.13}$$

In particular, of course, this must apply to the Hamiltonian $H_N$ (otherwise we would have found a tool to distinguish the particles after all):

$$\left[H_N, P_{ij}\right] = 0 \text{ for all pairs } i, j. \tag{23.14}$$

We now ask for the eigenvalues $\eta_{ij}$ of $P_{ij}$:

$$P_{ij} |\psi\rangle = \eta_{ij} |\psi\rangle . \tag{23.15}$$

Because of $P_{ij}^2 = 1$, we have $\eta_{ij}^2 = 1$; thus there are two possible eigenvalues $\eta_{ij} = \pm 1$. Now, if $|\psi\rangle$ is an eigenvector of *all* transpositions,[8] then the eigenvalues $\eta_{ij}$ are the same for all pairs $i, j$. This holds because due to e.g. $P_{ni}P_{mj}P_{nm}P_{ni}P_{mj} = P_{ij}$ (see exercises), the equation $\eta_{ij} = \eta_{ni}^2\eta_{mj}^2\eta_{nm} = \eta_{nm} = \eta$ applies for all pairs $i, j$ and all pairs $n, m$. Generalizing (23.6), we can therefore distinguish two cases:

$$\begin{aligned} \eta = +1 &: \text{ totally symmetric state } \left|\psi_N^{(+)}\right\rangle \leftrightarrow P_{ij}\left|\psi_N^{(+)}\right\rangle = \left|\psi_N^{(+)}\right\rangle \; \forall \; (i, j) \\ \eta = -1 &: \text{ totally antisymmetric state } \left|\psi_N^{(-)}\right\rangle \leftrightarrow P_{ij}\left|\psi_N^{(-)}\right\rangle = -\left|\psi_N^{(-)}\right\rangle \; \forall \; (i, j) . \end{aligned} \tag{23.16}$$

Hence, the states of a quantum system of identical objects are either symmetric or antisymmetric with regard to the interchange of two indices. Other possibilities do not exist.

This means, *inter alia*, that identical particles do not populate the whole Hilbert space $\mathcal{H}_{(N)}$, but only the subspaces $\mathcal{H}_{(N)}^{(+)}$ (symmetric states) and $\mathcal{H}_{(N)}^{(-)}$ (antisymmetric states). These two subspaces are mutually orthogonal:

$$\left\langle\psi_N^{(+)} \middle| \psi_N^{(-)}\right\rangle = \left\langle\psi_N^{(+)}\right| P_{ij}^{\dagger} P_{ij} \left|\psi_N^{(-)}\right\rangle = -\left\langle\psi_N^{(+)} \middle| \psi_N^{(-)}\right\rangle = 0, \tag{23.17}$$

---

[7] In general, transpositions do not commute, $P_{23}P_{12} \neq P_{12}P_{23}$.

[8] The $N$-particle states (23.3) do not satisfy this condition; we still have to construct the said eigenvectors.

and, due to (23.13), there is no observable $A_N$ which mediates between the two spaces:

$$\left\langle \psi_N^{(+)} \right| A_N \left| \psi_N^{(-)} \right\rangle = \left\langle \psi_N^{(+)} \right| P_{ij}^{\dagger} A_N P_{ij} \left| \psi_N^{(-)} \right\rangle = - \left\langle \psi_N^{(+)} \right| A_N \left| \psi_N^{(-)} \right\rangle = 0. \quad (23.18)$$

Thus, the two subspaces $\mathcal{H}_{(N)}^{(+)}$ and $\mathcal{H}_{(N)}^{(-)}$ are strictly separated.[9]

Now what are the allowed states? We start from the $N$-particle product states (23.3) that are *not* totally symmetric or antisymmetric. We can construct symmetric or antisymmetric states from them by suitable superpositions. For this purpose, we introduce two new operators, namely the *symmetrization operator* $S_N^{(+)}$ and the *antisymmetrization* operator $S_N^{(-)}$:

$$S_N^{(\pm)} = \frac{1}{N!} \sum_P (\pm 1)^p \, P \quad (23.19)$$

where the sum runs over all the $N!$ permutations $P$ of the $N$-tuple.[10] The number $p$ denotes the number of transpositions from which $P$ is constructed.[11] The states

$$\left| \varphi_N^{(\pm)} \right\rangle = |1 : \alpha_1, 2 : \alpha_2, \ldots N : \alpha_N\rangle^{(\pm)} = S_N^{(\pm)} \, |1 : \alpha_1, 2 : \alpha_2, \ldots N : \alpha_N\rangle \quad (23.20)$$

are elements of $\mathcal{H}_{(N)}^{(\pm)}$, and it holds that

$$P_{ij} \left| \varphi_N^{(\pm)} \right\rangle = \pm \left| \varphi_N^{(\pm)} \right\rangle ; \; P \left| \varphi_N^{(\pm)} \right\rangle = (\pm 1)^p \left| \varphi_N^{(\pm)} \right\rangle . \quad (23.21)$$

This leads immediately to

$$S_N^{(\pm)} \left| \varphi_N^{(\pm)} \right\rangle = \frac{1}{N!} \sum_P (\pm 1)^p \, P \left| \varphi_N^{(\pm)} \right\rangle = \left| \varphi_N^{(\pm)} \right\rangle . \quad (23.22)$$

It follows that the (anti)symmetrized product states $\left| \varphi_N^{(\pm)} \right\rangle$ form an orthogonal basis of their subspaces $\mathcal{H}_{(N)}^{(+)}$ and $\mathcal{H}_{(N)}^{(-)}$. However, they are not normalized. The normalized states are

$$|1 : \alpha_1, 2 : \alpha_2, \ldots N : \alpha_N\rangle_{norm}^{(-)} = \frac{1}{\sqrt{N!}} \sum_P (-1)^p \, P \, |1 : \alpha_1, 2 : \alpha_2, \ldots N : \alpha_N\rangle \quad (23.23)$$

---

[9] This illustrates with an example the remark of Chap. 14, Vol. 1 that not every vector in the Hilbert space necessarily corresponds to a physically realizable state (i.e. that a superselection rule exits).

[10] Example for a 3-tuple: (1, 2, 3), (1, 3, 2), (2, 1, 3), (2, 3, 1), (3, 1, 2), (3, 2, 1).

[11] $p$ is even for a cyclic permutation and odd for a non-cyclic one.

and

$$|1:\alpha_1,2:\alpha_2,\ldots N:\alpha_N\rangle^{(+)}_{norm}=\sqrt{\frac{N_1!N_2!\ldots}{N!}}\sum_{P'}P'\,|1:\alpha_1,2:\alpha_2,\ldots N:\alpha_N\rangle\,, \tag{23.24}$$

where $N_i$ is the multiplicity of $\alpha_i$ and the sum extends only over those permutations $P'$ which lead to different states (whose number is $\frac{N!}{N_1!N_2!\ldots}$). The completeness relation then reads:

$$\sum\!\!\!\!\!\!\!\int_{\alpha_1\ldots\alpha_N}|1:\alpha_1,2:\alpha_2,\ldots N:\alpha_N\rangle^{(\pm)}_{norm}\,\langle 1:\alpha_1,2:\alpha_2,\ldots N:\alpha_N|^{(\pm)}_{norm}=1. \tag{23.25}$$

By the way, we see that the states $|1:\alpha_1,2:\alpha_2,\ldots N:\alpha_N\rangle^{(\pm)}$ do not factorize—they are entangled. This means that the individual identical quantum objects do not have individually assignable properties, which is just the basic requirement of this section.[12]

## 23.3 The Pauli Exclusion Principle

If one looks closely at the state $|1:\alpha_1,2:\alpha_2,\ldots N:\alpha_N\rangle^{(-)}$, it can be seen that it vanishes if two sets of quantum numbers are equal, i.e. $\alpha_k=\alpha_l$ with $k\neq l$. Thus we have found the *Pauli (exclusion) principle*; it states that two identical particles cannot agree on all their quantum numbers in a totally antisymmetric state. This is shown perhaps even more clearly in the equivalent notation

$$|1:\alpha_1,2:\alpha_2,\ldots N:\alpha_N\rangle^{(-)}_{norm}=\frac{1}{\sqrt{N!}}\begin{vmatrix}|1:\alpha_1\rangle & |2:\alpha_1\rangle & \ldots & |N:\alpha_1\rangle\\ |1:\alpha_2\rangle & |2:\alpha_2\rangle & \ldots & |N:\alpha_2\rangle\\ \vdots & \vdots & \vdots & \vdots\\ |1:\alpha_N\rangle & |2:\alpha_N\rangle & \ldots & |N:\alpha_N\rangle\end{vmatrix}. \tag{23.26}$$

This determinant, formed of single-particle states, is called the *Slater determinant*. We see directly that for $\alpha_k=\alpha_l$ with $k\neq l$, two rows of this determinant are equal and therefore it is zero.

The particles which are described by a totally antisymmetric state are called *fermions*; they have half-integer spins and obey Fermi-Dirac statistics. In contrast, *bosons* are described by totally symmetric states; they have integer spins and obey Bose-Einstein statistics. Unlike fermions, bosons are *not* subject to the Pauli prin-

---

[12] Another way to formulate states of many quantum objects is provided by the so-called second quantization, see Appendix W, Vol. 2. This method works with creation and annihilation operators, and in this regard is somewhat similar to the algebraic treatment of the angular momentum or the harmonic oscillator.

ciple, which means that bosons can agree in all quantum numbers, i.e. more than one can occupy precisely the same state. As already mentioned in Chap. 16, all the elementary particles belong to one of these two particle classes.[13] Incidentally, this connection between spin and statistics cannot be derived from what we have said here, but it follows from the so-called *spin-statistics theorem*.

The Pauli principle is of fundamental importance for the structure of matter, since it ensures that atoms cannot collapse: Each state $(n, l, m_l)$ can be occupied by only two electrons, which differ by their spin orientations. If there are more electrons, they must populate higher levels, i.e. outer shells; as is well known, the periodic table is based on this principle. Similarly, in astronomy, the Pauli principle explains why old stars (with the exception of black holes) do not collapse under the weight of their own gravity: The fermions must occupy different states, thus creating a back pressure which prevents further collapse.

## 23.4 The Helium Atom

The helium atom is a prime example of the application of the ideas discussed in this chapter. The problem cannot be solved exactly, so that we have to introduce some approximations, but we will see that even with this approximate method, the indistinguishability of the two electrons leads to classically inexplicable effects (summarized under the term *exchange energy*).

We neglect the motion of the nucleus,[14] which is about 8000 times heavier than the electrons, and place our coordinate origin in the nucleus, which has the atomic number $Z = 2$. In addition, we neglect spin-dependent interactions, in contrast to our treatment of the hydrogen atom in Chap. 19. The spin will be considered later, but only for the classification of the electrons. Thus, the single-particle states can be represented as $|n_1 l_1 m_1\rangle$.

The total Hamiltonian reads

$$H = H_1 + H_2 + V_{1,2} \tag{23.27}$$

with

$$H_i = \frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_i}\ ;\ V_{1,2} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{23.28}$$

$Ze$ is the nuclear charge, with $Z = 2$ for helium. The interaction $V_{1,2}$ describes the electron-electron interaction, i.e. the mutual electrostatic repulsion of the two electrons.

---

[13] In theoretical solid-state physics, one considers so-called anyons (not to be confused with anions). These are quasiparticles in two dimensions which are neither bosons nor fermions.

[14] In the equations, therefore, the mass of the electrons and not the reduced mass appears.

We treat the problem as follows: We consider $V_{1,2}$ as a ‘small’ perturbation potential in the sense of the perturbation theory of Chap. 19. Accordingly, we neglect $V_{1,2}$ in the first step and look for the states which the (identical) electrons can occupy generally. Then we take $V_{1,2}$ into account and calculate the first energy correction as a perturbation.

### 23.4.1 Spectrum Without $V_{1,2}$

If we ‘turn off’ the electron-electron interaction as a start, then each electron can occupy the hydrogen eigenstates, as discussed in Chap. 17. We call them position states in the following (which is somewhat imprecise, since we write them in the abstract representation), in order to distinguish them readily from the spin states. The single-particle product states are given by

$$|1:\alpha_1\rangle\,|2:\alpha_2\rangle\,;\;\; \alpha_i = n_i l_i m_i \tag{23.29}$$

and the total state reads[15]:

$$|1:\alpha_1\rangle\,|2:\alpha_2\rangle \equiv |1:n_1l_1m_1, 2:n_2l_2m_2\rangle\,. \tag{23.30}$$

For the unperturbed energies, we have

$$E^{(0)}_{n_1n_2} = -Z^2R_\infty\frac{1}{n_1^2} - Z^2R_\infty\frac{1}{n_2^2}, \tag{23.31}$$

with[16]

$$R_\infty = \frac{me^4}{2\hbar^2\left(4\pi\varepsilon_0\right)^2\,.} \tag{23.32}$$

In accordance with these considerations, the ground state of helium is given by $E^{(0)}_{11} = -8\cdot 13.6\,\mathrm{eV} = -108.8\,\mathrm{eV}$. But since the experimental value is $-78.975\,\mathrm{eV}$, we obviously have to improve our method. This is done below by means of perturbation theory.

---

[15] Since we have only two particles, we could use the shorter notation, familiar from Chap. 20, in which the state of the first or second particle is listed in first or second place, i.e. $|1:\alpha_1\rangle\,|2:\alpha_2\rangle \equiv |n_1l_1m_1, n_2l_2m_2\rangle$. Nevertheless, we choose the slightly more cumbersome version, since it is unambiguous.

[16] The mass effect could be taken into account here by

$$R_{He} = R_\infty\left(1+\frac{m}{m_{He}}\right)^{-1}.$$

But first, we want to get an overview of the states, whereby we consider the symmetrization postulate for identical particles. The (anti)symmetrized position states are

$$|n_1 l_1 m_1, n_2 l_2 m_2\rangle^{(\pm)} = C\left\{|1 : n_1 l_1 m_1, 2 : n_2 l_2 m_2\rangle \pm |1 : n_2 l_2 m_2, 2 : n_1 l_1 m_1;\rangle\right\} \tag{23.33}$$

with the normalization constant

$$C = \begin{cases} \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{cases} \text{for} \begin{cases} (n_1 l_1 m_1) \neq (n_2 l_2 m_2) \\ (n_1 l_1 m_1) = (n_2 l_2 m_2) \end{cases} \tag{23.34}$$

In the next step, we take into account also the spins of the two electrons. Two spins of $\frac{1}{2}$ can be added to give a total spin of $S = 1$ or $S = 0$; in (23.8) and (23.9), we have written down the corresponding spin states $|S, m_S\rangle$. For a total spin $S = 1$, they form a triplet $|1, m_S\rangle$; for $S = 0$, a singlet $|0, 0\rangle$. For historical reasons, these are called *orthohelium* (triplet) and *parahelium* (singlet). The spin part in orthohelium is symmetric, so that the position state must be antisymmetric according to the Pauli principle, and *vice versa* for parahelium. With (23.33), the possible states for orthohelium are:

$$\begin{aligned} &|n_1 l_1 m_1, n_2 l_2 m_2\rangle^{(-)} |1, 1\rangle \\ &|n_1 l_1 m_1, n_2 l_2 m_2\rangle^{(-)} |1, 0\rangle \\ &|n_1 l_1 m_1, n_2 l_2 m_2\rangle^{(-)} |1, -1\rangle ; \end{aligned} \tag{23.35}$$

and for parahelium, they are:

$$|n_1 l_1 m_1, n_2 l_2 m_2\rangle^{(+)} |0, 0\rangle . \tag{23.36}$$

We see that for orthohelium, it must hold that $(n_1 l_1 m_1) \neq (n_2 l_2 m_2)$, while for parahelium, the spin states must be different. This means that the undisturbed ground state $|1 : n_1 l_1 m_1, 2 : n_2 l_2 m_2\rangle = |1 : 1, 0, 0; 2 : 1, 0, 0\rangle$ can be occupied only by parahelium. Neglecting the terms caused by $V_{1,2}$, the helium spectrum has the structure shown in Fig. 23.2. In this spectrum, the boundary to the continuum is a limiting point for the bound energy levels; this is only implied in the figure.

Obviously, there are discrete levels in the continuum. This is due to the following: To raise both electrons from the ground state into the first excited state, we need $81.6\,\text{eV} = (108.8 - 68) \cdot 2\,\text{eV}$ of energy. On the other hand, the ionization energy (one of the electrons is transferred into the continuum) is $54.4\,\text{eV} = \frac{1}{2} \cdot 108.8\,\text{eV}$. The doubly-excited state therefore does not necessarily decay to the ground state or another bound state, but can also lead to a state of a singly-ionized helium plus a free electron (*autoionization*). It follows that in *all* the discrete states below the ionization limit, one electron is in the one-particle ground state.

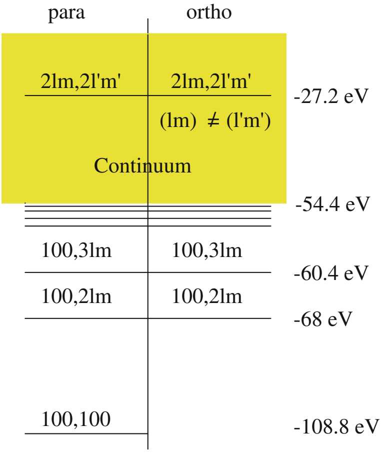

**Fig. 23.2** Helium spectrum without electron-electron interaction (not to scale). The yellow part indicates the continous spectrum

## 23.4.2 Spectrum with $V_{1,2}$ (Perturbation Theory)

Having established the 'rough' helium spectrum, we calculate by means of the tools of Chap. 19 the corrections due to the electron-electron interaction $V_{1,2}$, i.e. in first-order perturbation theory. We have for the ground state:

$$\begin{aligned} E^{(1)}_{100;100} &= \langle 1,0,0;1,0,0|^{(+)}\ V_{1,2}\,|1,0,0;1,0,0\rangle^{(+)} \\ &= \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1 d^3r_2\,\left|\psi_{1,0,0}(\mathbf{r}_1)\right|^2\left|\psi_{1,0,0}(\mathbf{r}_2)\right|^2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \end{aligned} \tag{23.37}$$

with the position functions[17]

$$\psi_{1,0,0}(\mathbf{r}) = \frac{1}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}. \tag{23.38}$$

After some computations, the result reads

$$E^{(1)}_{1,0,0;1,0,0} = \frac{5}{4}ZR_\infty. \tag{23.39}$$

For $Z = 2$, it follows that $E^{(1)}_{1,0,0;1,0,0} \approx \frac{5}{2}\cdot 13.6\,\text{eV} = 34\,\text{eV}$, so that we obtain the result for the ground state energy $E_{1,0,0;1,0,0}$:

$$E_{1,0,0;1,0,0} \approx E^{(0)}_{11} + E^{(1)}_{1,0,0;1,0,0} = -108.8\text{eV} + 34\text{eV} = -74.8\text{eV}, \tag{23.40}$$

---

[17] cf. Chap. 17 and Appendix B, Vol. 2.

and thus we have finally obtained a value which is after all in the neighborhood of the experimentally-measured energy of $-78.975\,\mathrm{eV}$.

Next, let us look at the perturbative correction for states with $n_1 = 1$ and $n_2 = n \geq 2$. Since one electron must be in the state $|1,0,0\rangle$ (one-particle ground state), we have (see exercises)

$$\begin{aligned} E^{(1)}_{1,0,0;nlm} &= \langle 1,0,0;nlm|^{(\pm)}\ V_{1,2}\,|1,0,0;nlm\rangle^{(\pm)} \\ &= \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1 d^3r_2 \frac{\left|\psi_{1,0,0}(\mathbf{r}_1)\,\psi_{nlm}(\mathbf{r}_2) \pm \psi_{nlm}(\mathbf{r}_1)\,\psi_{1,0,0}(\mathbf{r}_2)\right|^2}{2\,|\mathbf{r}_1-\mathbf{r}_2|} \\ &= C_{nl} \pm A_{nl}, \end{aligned} \tag{23.41}$$

with the *Coulomb energy*

$$C_{nl} = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1 d^3r_2 \frac{\left|\psi_{1,0,0}(\mathbf{r}_1)\,\psi_{nlm}(\mathbf{r}_2)\right|^2}{|\mathbf{r}_1-\mathbf{r}_2|} \tag{23.42}$$

and the *exchange energy*

$$A_{nl} = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1 d^3r_2 \frac{\psi_{1,0,0}(\mathbf{r}_1)\,\psi_{nlm}(\mathbf{r}_2)\,\psi^*_{nlm}(\mathbf{r}_1)\,\psi^*_{1,0,0}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}. \tag{23.43}$$

The exchange energy is due to the Pauli principle and is a purely quantum-mechanical effect, which is not explainable classically.[18] The corrections to the energy are given by

$$E_{12} = E^{(0)}_{12} + C_{2l} \pm A_{2l};\ +\text{ parahelium},\ -\text{ orthohelium}. \tag{23.44}$$

$C_{nl}$ is positive, which can be seen directly; $A_{nl}$ is also positive, as the calculation shows. The detailed calculations can be found in Appendix N, Vol. 2. The result now reads

$$\begin{aligned} C_{20} &= \frac{e^2}{4\pi\varepsilon_0}\frac{17}{81}\frac{Z}{a_0};\quad C_{21} = \frac{e^2}{4\pi\varepsilon_0}\frac{59}{243}\frac{Z}{a_0} \\ A_{20} &= \frac{e^2}{4\pi\varepsilon_0}\frac{16}{729}\frac{Z}{a_0};\quad A_{21} = \frac{e^2}{4\pi\varepsilon_0}\frac{112}{6561}\frac{Z}{a_0}. \end{aligned} \tag{23.45}$$

Numerically,[19] we have for $Z = 2$

---

[18] The Coulomb energy would also have the same form for non-identical particles.

[19] In some textbooks, a few incorrect values for $C_{2l}$ and $A_{2l}$ are quoted. We mention this here not in order to find fault with other textbooks; in fact, there are always some mistakes in any longer text (in this one as well), in spite of the most careful editing. The remark is aimed rather at making it clear that learning is a process for which each individual is responsible for his or her own progress. A certain critical distance should be maintained towards every textbook; no single one is absolutely correct. Thus, look not only into *one* book as an aid to learning, but always use several!

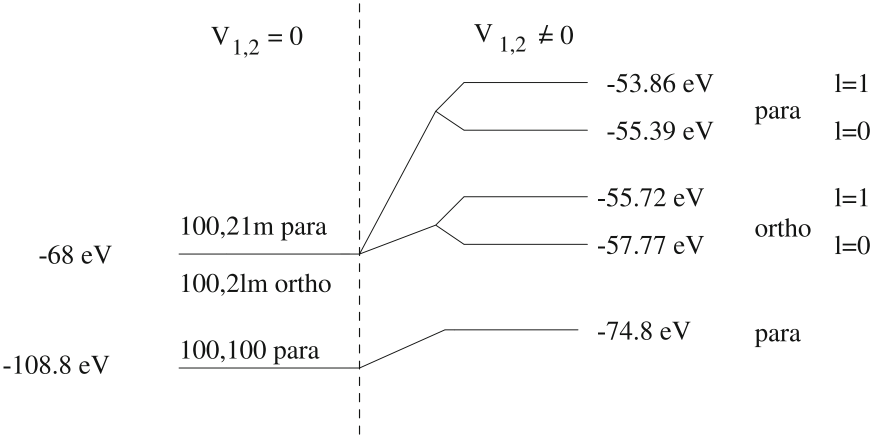

**Fig. 23.3** The lowest discrete levels of the helium spectrum with and without electron-electron interactions (not to scale)

$$\begin{aligned} E_{12}^{(0)} &\approx -68.0\text{ eV}\ ;\ C_{20} \approx 11.42\text{ eV};\ C_{21} \approx 13.21\text{ eV} \\ A_{20} &\approx 1.19\text{ eV};\ A_{21} \approx 0.93\text{ eV}. \end{aligned} \tag{23.46}$$

With these values, the energy levels of parahelium are found to be $-55.39\,\text{eV}$ and $-53.86\,\text{eV}$; and those of orthohelium are $-57.77\,\text{eV}$ and $-55.72\,\text{eV}$. Figure 23.3 illustrates the situation. We see that the degeneracy is removed (strictly speaking, only partially, because the $m$-degeneracy remains).

## 23.5 The Ritz Method

The (Rayleigh-) Ritz method is a general,[20] very simple, elegant and—properly applied—very effective method of approximation for the energy of the ground state.

We have a Hamiltonian with

$$H\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle. \tag{23.47}$$

An arbitrary state $|\psi\rangle$ (not necessarily normalized) can be expanded in terms of a CONS $\{|\varphi_n\rangle\}$

$$|\psi\rangle = \sum_n c_n\left|\varphi_n\right\rangle. \tag{23.48}$$

---

[20] i.e. not limited to identical quantum objects.

It follows that

$$\langle\psi| H |\psi\rangle = \sum_{n,m} c_n^* c_m \langle\varphi_n| H |\varphi_m\rangle = \sum_n |c_n|^2 E_n. \tag{23.49}$$

We now perform an estimation. On the one hand, we have

$$\langle\psi |\psi\rangle = \sum_n |c_n|^2 , \tag{23.50}$$

and on the other hand

$$E_n \geq E_0 \ \text{ for } n > 0 \tag{23.51}$$

where $E_0$ is the ground-state energy. This leads to

$$\langle\psi| H |\psi\rangle = \sum\nolimits_n |c_n|^2 E_n \geq \sum\nolimits_n |c_n|^2 E_0 = E_0 \langle\psi |\psi\rangle , \tag{23.52}$$

or[21]

$$E_0 = \inf_{\psi} \frac{\langle\psi| H |\psi\rangle}{\langle\psi |\psi\rangle}. \tag{23.53}$$

This means that we have to choose reasonable states with one or several parameters and vary them so that the right side is a minimum. If we find values that are lower than the experimental value, this is not a failure of the variational principle, but rather evidence that the Hamiltonian chosen does not correctly describe the problem and needs to be improved. The method can thus provide important information even if it does not ‘work’.

As an example, we consider the helium atom. We assume the following trial function:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\frac{\zeta}{a_0} r_1} e^{-\frac{\zeta}{a_0} r_2}. \tag{23.54}$$

It is the product of single-particle functions as found in Chap. 17. A relatively unimportant difference is the lack of normalization,[22] but an essential difference is the use of $\zeta$ instead of $Z$; this parameter is chosen in such a way that our value in (23.53) becomes minimal. With $H = H_1 + H_2 + V_{1,2}$, we find after some calculations

$$\frac{\langle\psi| H_1 + H_2 |\psi\rangle}{\langle\psi |\psi\rangle} = R_\infty \left(2\zeta^2 - 8\zeta\right), \tag{23.55}$$

and (see also (23.39))

$$\frac{\langle\psi| V_{1,2} |\psi\rangle}{\langle\psi |\psi\rangle} = R_\infty \frac{5}{4} \zeta. \tag{23.56}$$

---

[21] inf means *infimum*, the greatest lower bound.

[22] This shortcoming is cured by the process itself, as stated above.

This leads to

$$\frac{\langle\psi|\, H\, |\psi\rangle}{\langle\psi\ |\psi\rangle} = R_\infty\left(2\zeta^2 - \frac{27}{4}\zeta\right). \tag{23.57}$$

The right-hand side shows a minimum with respect to $\zeta$ at $\zeta = \frac{27}{16} = 2 - \frac{5}{16}$. One interprets this equation to mean that the two electrons shield each other to some extent from the nuclear charge, and accordingly experience a smaller charge. The quantity $\zeta$ is called the *effective charge number*. The numerical value for the ground-state energy is

$$E_0 \le -R_\infty\frac{(27)^2}{128} \approx -77.5\ \text{eV}. \tag{23.58}$$

This value is already relatively close to the experimental value of $E_0 = -78.975\,\text{eV}$.

## 23.6 How Far does the Pauli Principle Reach?

In this section, we consider the question of whether we always have to apply the symmetrization postulate. Does the Pauli principle not include *all* identical particles in the universe? Why can we consider the properties of a system that consists of only one or a few quantum objects? Obviously, we need not take into account all identical quantum properties of our universe in most of our considerations.

We consider two electrons in two spatial regions, region $A$ with $|\Phi\rangle$, and region $B$ with $|\Psi\rangle$, where the regions are so far apart that there is virtually no overlap of the two wavefunctions; see Fig. 23.4. This condition, which will apply in the following, is the salient point of our discussion. We can write it as $|\langle\Phi\ |\Psi\rangle| = \varepsilon \ll 1$. In addition, we want to measure a two-particle observable, which has eigenfunctions in $A$ with $|\varphi_n\rangle$ and in $B$ with $|\psi_m\rangle$, where it holds that $|\langle\varphi_n\ |\psi_m\rangle| = \eta \ll 1$. These eigenfunctions each form a CONS.

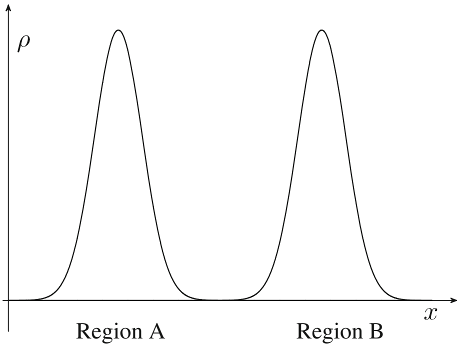

**Fig. 23.4** Probability density for two electrons in two separate spatial regions, $A$ and $B$

To keep the following considerations clear, we consider only the limiting case of $\varepsilon, \eta \to 0$. Thus we can assume for simplicity that all the scalar products of states in $A$ with states in $B$ vanish, e.g.

$$\langle \Phi \,|\Psi \rangle \approx 0;\ \langle \varphi_n \,|\psi_m \rangle \approx 0. \tag{23.59}$$

### 23.6.1 Distinguishable Quantum Objects

Let us first assume that the electrons are *distinguishable*. The product state reads

$$|\Phi\Psi\rangle := |1:\Phi\rangle\,|2:\Psi\rangle\,. \tag{23.60}$$

We want to measure

$$|\varphi_n\psi_m\rangle := |1:\varphi_n\rangle\,|2:\psi_m\rangle\,. \tag{23.61}$$

We have

$$\langle \varphi_n\psi_m \,|\Phi\Psi\rangle = \langle 1:\varphi_n \,|1:\Phi\rangle\,\langle 2:\psi_m \,|2:\Psi\rangle\,. \tag{23.62}$$

The probability $w_{nm}$ to find this state in a measurement is given as usual by the squared value

$$w_{nm} = |\langle \varphi_n\psi_m \,|\Phi\Psi\rangle|^2\,. \tag{23.63}$$

If we are interested only in electron 1, we can average over the variables of electron 2. Then the probability $w_n$ of measuring the state $|\varphi_n\rangle$ is given by

$$\begin{aligned} w_n &= \sum_m |\langle \varphi_n\psi_m \,|\Phi\Psi\rangle|^2 = \sum_m |\langle 1:\varphi_n \,|1:\Phi\rangle\,\langle 2:\psi_m \,|2:\Psi\rangle|^2 \\ &= |\langle 1:\varphi_n \,|1:\Phi\rangle|^2 \sum_m |\langle 2:\psi_m \,|2:\Psi\rangle|^2 = |\langle 1:\varphi_n \,|1:\Phi\rangle|^2\,, \end{aligned} \tag{23.64}$$

where the last equation follows because of

$$\sum_m |\langle 2:\psi_m \,|2:\Psi\rangle|^2 = \sum_m \langle 2:\Psi \,|2:\psi_m\rangle\,\langle 2:\psi_m \,|2:\Psi\rangle = 1. \tag{23.65}$$

### 23.6.2 Identical Quantum Objects

Let us now assume that the electrons are *indistinguishable*. Then we have to start from the antisymmetric states

$$|\Phi\Psi\rangle^{(-)} := \frac{|1:\Phi\rangle\,|2:\Psi\rangle - |1:\Phi\rangle\,|2:\Psi\rangle}{\sqrt{2}} \tag{23.66}$$

and

$$|\varphi_n\psi_m\rangle^{(-)} := \frac{|1:\varphi_n\rangle\,|2:\psi_m\rangle - |1:\psi_m\rangle\,|2:\varphi_n\rangle}{\sqrt{2}}. \tag{23.67}$$

This leads to

$$^{(-)}\langle\varphi_n\psi_m\;|\Phi\Psi\rangle^{(-)} \approx \frac{\langle 1:\varphi_n|\,1:\Phi\rangle\,\langle 2:\psi_m|\,2:\Psi\rangle + \langle 2:\varphi_n|\,2:\Phi\rangle\,\langle 1:\psi_m|\,1:\Psi\rangle}{2} \tag{23.68}$$

where we have assumed, following our above assumptions about the spatial distribution of the two electrons, that 'mixed terms' according to (23.59) do not have to be taken into account, i.e.

$$\langle 1:\varphi_n|\,1:\Psi\rangle\,,\;\; \langle 2:\psi_m|\,2:\Phi\rangle\,,\;\; \langle 2:\varphi_n|\,2:\Psi\rangle\,,\;\; \langle 1:\psi_m|\,1:\Phi\rangle \approx 0. \tag{23.69}$$

With this, it follows that

$$w_{nm} = \left|^{(-)}\langle\varphi_n\psi_m\;|\Phi\Psi\rangle^{(-)}\right|^2. \tag{23.70}$$

If we are interested only in the electron in region 1, we can average over region 2 and obtain (see the exercises):

$$\begin{aligned} w_n &= \sum_m \left|^{(-)}\langle\varphi_n\psi_m\;|\Phi\Psi\rangle^{(-)}\right|^2 \\ &= |\langle 1:\varphi_n|\,1:\Phi\rangle|^2 = |\langle 2:\varphi_n|\,2:\Phi\rangle|^2 = |\langle\varphi_n|\,\Phi\rangle|^2. \end{aligned} \tag{23.71}$$

In other words, under the assumptions made above, the measurement result for 1 is independent of 2—we need not worry about 2 or the Pauli principle.

## 23.7 Exercises

1. Two identical quantum objects are in the states $|\alpha_1\rangle$ and $|\alpha_2\rangle$. Show that the total state must be symmetric or antisymmetric,

$$|\psi_\pm\rangle = \frac{|1:\alpha_1, 2:\alpha_2\rangle \pm |1:\alpha_2, 2:\alpha_1\rangle}{\sqrt{2}}. \tag{23.72}$$

2. Two identical particles are in the states $|a\rangle$ and $|b\rangle$. What is the correct expression for the total state $|\psi\rangle$?
3. Let $|\varphi\rangle = |1:\alpha_1, 2:\alpha_2, 3:\alpha_3\rangle$. Determine $P_{12}P_{23}\,|\varphi\rangle$ and $P_{23}P_{12}\,|\varphi\rangle$. Under what conditions do $P_{12}$ and $P_{23}$ commute?
4. Write down explicitly the normalized states $|1:\alpha_1, 2:\alpha_2, \ldots, N:\alpha_N\rangle^{(\pm)}_{\text{norm}}$ for 2 and 3 particles.

5. Given 3 identical particles; to save paperwork, we denote the product states simply by $|1,2,3\rangle$ instead of by $|1:\alpha_1, 2:\alpha_2, 3:\alpha_3\rangle$; $|1:\alpha_2, 2:\alpha_1, 3:\alpha_3\rangle$ is then $|2,1,3\rangle$, etc.

   (a) Write down all 6 product states.
   (b) Show explicitly that for the total (anti)symmetrical state, $P_{12}|\psi\rangle^{\pm} = \eta_{12}|\psi\rangle^{\pm}$. Determine $\eta_{12}$.
   (c) Given the state $|\varphi\rangle = |1,2,3\rangle - |1,3,2\rangle + |2,1,3\rangle - |2,3,1\rangle + |3,1,2\rangle - |3,2,1\rangle$, show explicitly that $P_{12}|\varphi\rangle$ cannot be written as $c|\varphi\rangle$.

6. Show explicitly that $P_{ni}P_{mj}P_{nm}P_{ni}P_{mj} = P_{ij}$.
7. Show that

$$E^{(1)}_{100;nlm} = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1 d^3r_2 \frac{|\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \pm \psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)|^2}{2|\mathbf{r}_1 - \mathbf{r}_2|} = C_{nl} \pm A_{nl}. \tag{23.73}$$

8. Prove (23.71), i.e.

$$w_n = \sum_m \left|{}^{(-)}\langle\varphi_n\psi_m\,|\Phi\Psi\rangle^{(-)}\right|^2 = |\langle\varphi_n|\,\Phi\rangle|^2. \tag{23.74}$$