1

Second Quantization

In this chapter we revisit the quantum mechanical description of one-particle systems and many-particle systems. We highlight the differences between distinguishable and indistinguishable, or identical, particles and bring to the front the mathematical complications that arise when dealing with identical particles. We then introduce the second quantization formalism and show how to overcome these complications. The main actors of the second quantization formalism are the field operators, which can be used to represent states and quantum observables in the Hilbert space of identical particles.

1.1 Quantum Mechanics of One Particle

In quantum mechanics the physical state of a particle is described in terms of a *ket* $|\Psi\rangle$. This ket belongs to a *Hilbert space*, which is nothing but a vector space endowed with an inner product. The dimension of the Hilbert space is essentially fixed by our physical intuition; it is us who decide which kets are relevant to the description of the particle. For instance, if we want to describe how a laser works we can choose those energy eigenkets that get populated and depopulated, and discard the rest. This selection of states leads to the well-known description of a laser in terms of a three-level system, four-level system, etc. A fundamental property following from the vector nature of the Hilbert space is that any linear superposition of kets is another ket in the Hilbert space. In other words, we can make a linear superposition of physical states and the result is another physical state. In quantum mechanics, however, it is only the "direction" of the ket that matters, so $|\Psi\rangle$ and $C|\Psi\rangle$ represent the same physical state for all complex numbers C. This redundancy prompts us to work with *normalized* kets. What do we mean by that? We said before that there is an inner product in the Hilbert space. Let us denote by $\langle\Phi|\Psi\rangle = \langle\Psi|\Phi\rangle^*$ the inner product between two kets $|\Psi\rangle$ and $|\Phi\rangle$ of the Hilbert space. Then every ket has a real positive inner product with itself,

$$0 < \langle\Psi|\Psi\rangle < \infty.$$

A ket is said to be normalized if the inner product with itself is 1. Throughout this book we always assume that a ket is normalized unless otherwise stated. Every ket can be normalized by choosing the complex constant $C = e^{i\alpha}/\sqrt{\langle\Psi|\Psi\rangle}$ with α an arbitrary real number. Thus, the normalization fixes the ket of a physical state only modulo a phase factor. As we see in Section 1.3, this freedom is the basis of a fundamental property about the nature

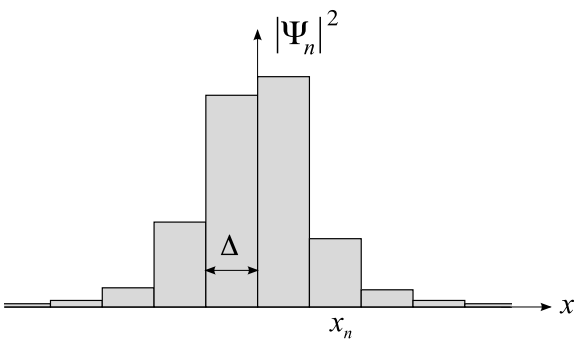

Figure 1.1 Histogram of the normalized number of clicks of the detector in $x_n = n\Delta$. The height of the bars corresponds to the probabilities $|\Psi_n|^2$.

of elementary particles. The notion of inner product also allows us to define the *dual space* as the vector space of linear operators $\langle\Phi|$, which deliver the complex number $\langle\Phi|\Psi\rangle$ when acting on the ket $|\Psi\rangle$. The elements of the dual space are called *bra*, and we can think of the inner product as the action of a bra on a ket. The formulation of quantum mechanics in terms of bras and kets is due to Dirac [1, 2] and turns out to be extremely useful.

According to the basic principles of quantum mechanics [2],

- With every physical observable is associated a Hermitian operator whose eigenvalues λ represent the outcome of an experimental measurement of the observable.
- If the particle is described by the ket $|\Psi\rangle$, then the probability of measuring λ is given by
$$P(\lambda) = |\langle\lambda|\Psi\rangle|^2,$$
where $|\lambda\rangle$ is the eigenket of the operator with eigenvalue λ.
- The experimental measurement is so invasive that just after measurement the particle *collapses* in the ket $|\lambda\rangle$.

Let us discuss the implications of these principles with an example.

Discrete formulation Suppose that we want to measure the position of a particle living in a one-dimensional world. We can construct a detector with the property that it clicks whenever the particle is no further away than, say, $\Delta/2$ from the position of the detector. We distribute these detectors on a uniform grid $x_n = n\Delta$, with n integers, so as to cover the entire one-dimensional world. The experiment consists in preparing the particle in a state $|\Psi\rangle$ and in taking note of which detector clicks. After the click, we know for sure that the particle is in the interval $x_n \pm \Delta/2$, where x_n is the position of the detector that clicked. Repeating the experiment $N \gg 1$ times, counting the number of times that a given detector clicks, and dividing the result by N, we obtain the probability that the particle is in the interval $x_n \pm \Delta/2$, see histogram in Fig. 1.1. Quantum mechanics tells us that this probability is
$$P(n) = |\langle n|\Psi\rangle|^2,$$

where $|n\rangle$ is the ket describing the particle in the interval $x_n \pm \Delta/2$. The experimental setup does not allow us to say where exactly the particle is within this interval. In fact, it does not make sense to speak about the exact position of the particle since it cannot be measured. From the experimental output we could even argue that the one-dimensional world is discrete! What we want to say is that in our experiment the "exact position" of the particle is a mere speculative concept, like the gender, color, or happiness of the particle. These degrees of freedom may also exist, but if they cannot be measured then we should not include them in the description of the physical world. As scientists we can only assign a ket $|n\rangle$ to the state of the particle just after measurement, and we can interpret this ket as describing the particle in some discrete position. The probability of finding the particle in $|n'\rangle$ just after the nth detector has clicked is zero for all $n' \neq n$ and unity for $n' = n$, and hence,

$$\langle n'|n\rangle = \delta_{n'n}. \tag{1.1}$$

The kets $|n\rangle$ are orthonormal and it is easy to show that they form a basis of our Hilbert space. Suppose by absurdum that there exists another ket $|\chi\rangle$ orthogonal to all the $|n\rangle$. If the particle is described by this ket then the probability that the nth detector clicks is $|\langle n|\chi\rangle|^2 = 0$ for all n. This cannot be the case unless the particle is somewhere outside the one-dimensional world – that is, in a state not included in our original description.

Let us continue to elaborate on the example of the particle in a one-dimensional world. We said before, that the kets $|n\rangle$ form a basis. Therefore, any ket $|\Psi\rangle$ can be expanded as

$$|\Psi\rangle = \sum_n \Psi_n |n\rangle. \tag{1.2}$$

Since the basis is orthonormal, the coefficient Ψ_n is simply

$$\Psi_n = \langle n|\Psi\rangle, \tag{1.3}$$

and its square modulus is exactly the probability $P(n)$:

$$|\Psi_n|^2 = \begin{pmatrix} \text{probability of finding the particle in} \\ \text{volume element } \Delta \text{ around } x_n \end{pmatrix}.$$

It is important to appreciate the advantage of working with normalized kets. Since $\langle\Psi|\Psi\rangle = 1$, then

$$\sum_n |\Psi_n|^2 = 1, \tag{1.4}$$

according to which the probability of finding the particle anywhere is unity. The interpretation of the $|\Psi_n|^2$ as probabilities would not be possible if $|\Psi\rangle$ and $|n\rangle$ were not normalized.

Given an orthonormal basis, the inner product of a normalized ket $|\Psi\rangle$ with a basis ket gives the probability amplitude of having the particle in that ket.

Inserting (1.3) back into (1.2), we find the interesting relation

$$|\Psi\rangle = \sum_n \langle n|\Psi\rangle\, |n\rangle = \sum_n |n\rangle\langle n|\Psi\rangle.$$

This relation is interesting because it is true for all $|\Psi\rangle$ and hence

$$\sum_n |n\rangle\langle n| = \hat{\mathbb{1}}, \tag{1.5}$$

with $\hat{\mathbb{1}}$ the identity operator. Equation (1.5) is known as the *completeness relation* and expresses the fact that the set $\{|n\rangle\}$ is an orthonormal basis. Vice versa, any orthonormal basis satisfies the completeness relation.

Continuum formulation We now assume that we can construct more and more precise detectors and hence reduce the range Δ. Then we can also refine the description of our particle by putting the detectors closer and closer. In the limit $\Delta \to 0$, the probability $|\Psi_n|^2$ approaches zero and it makes more sense to reason in terms of the *probability density* $|\Psi_n|^2/\Delta$ of finding the particle in x_n. Let us rewrite (1.2) as

$$|\Psi\rangle = \Delta \sum_n \frac{\Psi_n}{\sqrt{\Delta}} \frac{|n\rangle}{\sqrt{\Delta}}. \tag{1.6}$$

We now define the continuous function $\Psi(x_n)$ and the continuous ket $|x_n\rangle$ as

$$\Psi(x_n) \equiv \lim_{\Delta\to 0} \frac{\Psi_n}{\sqrt{\Delta}}, \qquad |x_n\rangle = \lim_{\Delta\to 0} \frac{|n\rangle}{\sqrt{\Delta}}.$$

In this definition the limiting function $\Psi(x_n)$ is well defined, while the limiting ket $|x_n\rangle$ makes *mathematical sense* only under an integral sign since the norm $\langle x_n|x_n\rangle = \infty$. However, we can still give to $|x_n\rangle$ a precise *physical meaning* since in quantum mechanics only the "direction" of a ket matters.[1] With these definitions (1.6) can be seen as the Riemann sum of $\Psi(x_n)|x_n\rangle$. In the limit $\Delta \to 0$ the sum becomes an integral over x, and we can write

$$|\Psi\rangle = \int dx\ \Psi(x)|x\rangle.$$

The function $\Psi(x)$ is usually called the *wavefunction* or the *probability amplitude*, and its square modulus $|\Psi(x)|^2$ is the probability density of finding the particle in x, or equivalently

$$|\Psi(x)|^2\, dx\ = \begin{pmatrix} \text{probability of finding the particle} \\ \text{in volume element } dx \text{ around } x \end{pmatrix}.$$

In the continuum formulation the orthonormality relation (1.1) becomes

$$\langle x_{n'}|x_n\rangle = \lim_{\Delta\to 0} \frac{\delta_{n'n}}{\Delta} = \delta(x_{n'} - x_n),$$

where $\delta(x)$ is the Dirac δ-function, see Appendix A. Similarly, the completeness relation becomes

$$\int dx\ |x\rangle\langle x| = \hat{\mathbb{1}}.$$

[1] The formulation of quantum mechanics using nonnormalizable states requires the extension of Hilbert spaces to *rigged Hilbert spaces*. Readers interested in the mathematical foundations of this extension can consult, for example, Ref. [3]. Here we simply note that in a rigged Hilbert space everything works as in the more familiar Hilbert space. We simply have to keep in mind that every divergent quantity comes from some continuous limit and that in all physical quantities the divergency is canceled by an infinitesimally small quantity.

The entire discussion can easily be generalized to particles with spin in three (or any other) dimension. Let us denote by $\mathbf{x} = (\mathbf{r}\sigma)$ the collective index for the position $\mathbf{r}$ and the spin projection (say along the z axis) σ of the particle. If in every point of space we put a spin-polarized detector which clicks only if the particle has spin σ then $|\mathbf{x}\rangle$ is the state of the particle just after the spin-polarized detector in $\mathbf{r}$ has clicked. The *position–spin kets* $|\mathbf{x}\rangle$ are orthonormal

$$\langle \mathbf{x}'|\mathbf{x}\rangle = \delta_{\sigma'\sigma}\delta(\mathbf{r}'-\mathbf{r}) \equiv \delta(\mathbf{x}'-\mathbf{x}), \tag{1.7}$$

and form a basis. Hence they satisfy the completeness relation, which in this case reads

$$\boxed{\int d\mathbf{x}\, |\mathbf{x}\rangle\langle\mathbf{x}| = \hat{\mathbb{1}}} \tag{1.8}$$

Here and in the remainder of the book we use the symbol

$$\int d\mathbf{x} \equiv \sum_{\sigma} \int d\mathbf{r}$$

to signify a sum over spin and an integral over space. The expansion of a ket in this continuous Hilbert space follows directly from the completeness relation

$$|\Psi\rangle = \hat{\mathbb{1}}|\Psi\rangle = \int d\mathbf{x}\, |\mathbf{x}\rangle\langle\mathbf{x}|\Psi\rangle,$$

and the square modulus of the wavefunction $\Psi(\mathbf{x}) \equiv \langle\mathbf{x}|\Psi\rangle$ is the probability density of finding the particle in $\mathbf{x} = (\mathbf{r}\sigma)$:

$$|\Psi(\mathbf{x})|^2\, d\mathbf{r} \;=\; \left(\begin{array}{c}\text{probability of finding the particle with spin } \sigma \\ \text{in volume element } d\mathbf{r} \text{ around } \mathbf{r}\end{array}\right).$$

Operators So far we have only discussed the possible states of the particle, and the physical interpretation of the expansion coefficients. To say something about the dynamics of the particle, we must know the Hamiltonian operator $\hat{h}$. The knowledge of the Hamiltonian in quantum mechanics is analogous to knowledge of the forces in Newtonian mechanics. In Newtonian mechanics the dynamics of the particle is completely determined by the position and velocity at a certain time and by the forces. In quantum mechanics the dynamics of the wavefunction is completely determined by the wavefunction at a certain time and by $\hat{h}$. The Hamiltonian operator $\hat{h} \equiv h(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}, \hat{\boldsymbol{\mathcal{S}}})$ does, in general, depend on the position operator $\hat{\boldsymbol{r}}$, the momentum operator $\hat{\boldsymbol{p}}$, and the spin operator $\hat{\boldsymbol{\mathcal{S}}}$. An example is the Hamiltonian for a particle of mass m, charge q, and gyromagnetic ratio g moving in an external scalar potential ϕ, vector potential $\mathbf{A}$, and whose spin is coupled to the magnetic field $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$:

$$\hat{h} = \frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{q}{c}\mathbf{A}(\hat{\boldsymbol{r}})\right)^2 + q\phi(\hat{\boldsymbol{r}}) - g\mu_{\rm B}\mathbf{B}(\hat{\boldsymbol{r}})\cdot\hat{\boldsymbol{\mathcal{S}}}, \tag{1.9}$$

with c the speed of light and $\mu_{\rm B}$ the Bohr magneton.[2] Unless otherwise stated in this book we use atomic units, so $\hbar = 1$, $c \sim 137$, electron charge $e = -1$, and electron mass

[2] Other relativistic corrections like the spin–orbit interaction can be incorporated without any conceptual complication.

$m_e = 1$. Thus, in (I.9) the Bohr magneton $\mu_{\rm B} = \frac{e\hbar}{2m_e c} \sim 3.649\times 10^{-3}$, and charge and mass of the particles are measured in units of e and m_e, respectively. To distinguish operators from scalar or matrix quantities we always put the symbol " ˆ " (read "hat") on them. The position–spin kets are eigenstates of the position operator and of the z-component of the spin operator:

$$\hat{\boldsymbol{r}}|\mathbf{x}\rangle = \mathbf{r}|\mathbf{x}\rangle, \qquad \hat{\mathcal{S}}_z|\mathbf{x}\rangle = \sigma|\mathbf{x}\rangle,$$

with $\sigma = -S, -S+1, \ldots, S-1, S$ for spin S particles. The eigenstates of the momentum operator are instead the *momentum–spin kets* $|\mathbf{p}\sigma\rangle$:

$$\hat{\boldsymbol{p}}|\mathbf{p}\sigma\rangle = \mathbf{p}|\mathbf{p}\sigma\rangle.$$

These kets are also eigenstates of $\hat{\mathcal{S}}_z$ with eigenvalue σ. The momentum–spin kets form an orthonormal basis like the position–spin kets. The inner product between $|\mathbf{x}\rangle = |\mathbf{r}\sigma\rangle$ and $|\mathbf{p}\sigma'\rangle$ is proportional to $\delta_{\sigma\sigma'}$ times the plane wave $e^{\mathrm{i}\mathbf{p}\cdot\mathbf{r}}$. In this book we choose the constant of proportionality to be unity, so that

$$\boxed{\langle \mathbf{x}|\mathbf{p}\sigma'\rangle = \delta_{\sigma\sigma'}\langle \mathbf{r}|\mathbf{p}\rangle \qquad \text{with} \qquad \langle \mathbf{r}|\mathbf{p}\rangle = e^{\mathrm{i}\mathbf{p}\cdot\mathbf{r}}} \tag{I.10}$$

This inner product fixes uniquely the form of the completeness relation for the kets $|\mathbf{p}\sigma\rangle$. We have

$$\begin{aligned}\langle \mathbf{p}'\sigma'|\mathbf{p}\sigma\rangle &= \delta_{\sigma'\sigma}\langle \mathbf{p}'|\mathbf{p}\rangle = \delta_{\sigma'\sigma}\int d\mathbf{r}\,\langle \mathbf{p}'|\mathbf{r}\rangle\langle \mathbf{r}|\mathbf{p}\rangle = \delta_{\sigma'\sigma}\int d\mathbf{r}\, e^{\mathrm{i}(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}} \\ &= (2\pi)^3\delta_{\sigma'\sigma}\delta(\mathbf{p}'-\mathbf{p}),\end{aligned}$$

and therefore

$$\boxed{\sum_\sigma \int \frac{d\mathbf{p}}{(2\pi)^3}|\mathbf{p}\sigma\rangle\langle \mathbf{p}\sigma| = \hat{\mathbb{1}}} \tag{I.11}$$

as can easily be verified by acting with (I.11) on the ket $|\mathbf{p}'\sigma'\rangle$ or on the bra $\langle \mathbf{p}'\sigma'|$.

Before moving to the quantum mechanical description of many particles, let us briefly recall how to calculate the matrix elements of the Hamiltonian $\hat{h}$ in the position–spin basis. If $|\Psi\rangle$ is the ket of the particle, then

$$\langle \mathbf{x}|\hat{\boldsymbol{p}}|\Psi\rangle = -\mathrm{i}\boldsymbol{\nabla}\langle \mathbf{x}|\Psi\rangle \quad \Rightarrow \quad \langle \Psi|\hat{\boldsymbol{p}}|\mathbf{x}\rangle = \mathrm{i}\langle \Psi|\mathbf{x}\rangle\overleftarrow{\boldsymbol{\nabla}},$$

where the arrow over the gradient specifies that $\boldsymbol{\nabla}$ acts on the quantity to its left. It follows from these identities that

$$\langle \mathbf{x}|\hat{\boldsymbol{p}}|\mathbf{x}'\rangle = -\mathrm{i}\delta_{\sigma\sigma'}\boldsymbol{\nabla}\delta(\mathbf{r}-\mathbf{r}') = \mathrm{i}\delta_{\sigma\sigma'}\delta(\mathbf{r}-\mathbf{r}')\overleftarrow{\boldsymbol{\nabla}}', \tag{I.12}$$

where $\boldsymbol{\nabla}'$ means that the gradient acts on the primed variable. Therefore, the matrix element $\langle \mathbf{x}|\hat{h}|\mathbf{x}'\rangle$ with $\hat{h} = h(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}, \hat{\boldsymbol{\mathcal{S}}})$ can be written as

$$\boxed{\langle \mathbf{x}|\hat{h}|\mathbf{x}'\rangle = h_{\sigma\sigma'}(\mathbf{r}, -\mathrm{i}\boldsymbol{\nabla}, \mathbf{S})\delta(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')h_{\sigma\sigma'}(\mathbf{r}', \mathrm{i}\overleftarrow{\boldsymbol{\nabla}}', \mathbf{S})} \tag{I.13}$$

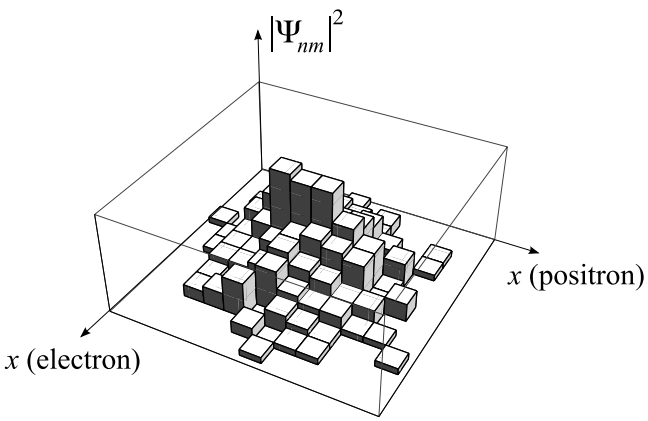

Figure 1.2 Histogram of the normalized number of simultaneous clicks of the electron and positron detectors in $x_n = n\Delta$ and $x_m = m\Delta$, respectively. The height of the parallelepipeds corresponds to the probabilities $|\Psi_{nm}|^2$.

where $\mathbf{S}$ is the matrix of the spin operator with elements $\langle\sigma|\hat{\boldsymbol{\mathcal{S}}}|\sigma'\rangle = \mathbf{S}_{\sigma\sigma'}$. For example, for the one-particle Hamiltonian in (1.9) we have

$$h_{\sigma\sigma'}(\mathbf{r}, -\mathrm{i}\boldsymbol{\nabla}, \mathbf{S}) = \frac{\delta_{\sigma\sigma'}}{2m}\left(-\mathrm{i}\boldsymbol{\nabla} - \frac{q}{c}\mathbf{A}(\mathbf{r})\right)^2 + \delta_{\sigma\sigma'} q\phi(\mathbf{r}) - g\mu_{\mathrm{B}}\mathbf{B}(\mathbf{r})\cdot\mathbf{S}_{\sigma\sigma'}.$$

We use (1.13) over and over in the following chapters to recognize the matrix structure of several equations.

1.2 Quantum Mechanics of Many Particles

We want to generalize the concepts of the previous section to many particles. Let us first discuss the case of *distinguishable particles*. Particles are called distinguishable if one or more of their properties, such as mass, charge, spin, etc., are different. Let us consider, for instance, an electron and a positron in one dimension. These particles are distinguishable since the charge of the positron is opposite to the charge of the electron.

Discrete formulation for two particles To measure the position of the electron and the position of the positron at a certain time, we put an electron detector and a positron detector at every point $x_n = n\Delta$ of the real axis and perform a *coincidence experiment*. This means that we take note of the position of the electron detector and of the positron detector only if they click *at the same time*. The result of the experiment is the pair of points (x_n, x_m), where x_n refers to the electron and x_m refers to the positron. Performing the experiment $N \gg 1$ times, counting the number of times that the pair (x_n, x_m) is measured and dividing the result by N, we obtain the probability that the electron is in x_n and the positron in x_m, see the histogram in Fig. 1.2. According to quantum mechanics, the electron–positron pair collapses in the ket $|n\rangle|m\rangle$ just after measurement. This ket

describes an electron in the interval $x_n \pm \Delta/2$ and a positron in the interval $x_m \pm \Delta/2$. Therefore, the probability of finding the electron–positron pair in $|n'\rangle|m'\rangle$ is zero unless $n' = n$ and $m' = m$; that is,

$$(\langle n'|\langle m'|) (|n\rangle|m\rangle) = \delta_{n'n}\delta_{m'm}.$$

The kets $|n\rangle|m\rangle$ are orthonormal and form a basis since if there was a ket $|\chi\rangle$ orthogonal to all of them then the electron–positron pair described by $|\chi\rangle$ would not be on the real axis. The orthonormality of the basis is expressed by the completeness relation

$$\sum_{nm} (|n\rangle|m\rangle) (\langle n|\langle m|) = \hat{\mathbb{1}}.$$

This relation can be used to expand any ket as

$$|\Psi\rangle = \hat{\mathbb{1}}|\Psi\rangle = \sum_{nm} (|n\rangle|m\rangle) (\langle n|\langle m|) |\Psi\rangle,$$

and if $|\Psi\rangle$ is normalized then the square modulus of the coefficients $\Psi_{nm} \equiv (\langle n|\langle m|) |\Psi\rangle$ is the probability represented in the histogram.

Continuum formulation for two particles As in the previous section, we could refine the experiment by putting the detectors closer and closer. We could also rethink the entire experiment in three (or any other) dimensions and use spin-polarized detectors. We then arrive at the position–spin kets $|\mathbf{x}_1\rangle|\mathbf{x}_2\rangle$ for the electron–positron pair with inner product

$$(\langle \mathbf{x}_1'|\langle \mathbf{x}_2'|) (|\mathbf{x}_1\rangle|\mathbf{x}_2\rangle) = \delta(\mathbf{x}_1' - \mathbf{x}_1)\delta(\mathbf{x}_2' - \mathbf{x}_2),$$

from which we deduce the completeness relation

$$\int d\mathbf{x}_1 d\mathbf{x}_2 (|\mathbf{x}_1\rangle|\mathbf{x}_2\rangle) (\langle \mathbf{x}_1|\langle \mathbf{x}_2|) = \hat{\mathbb{1}}.$$

The expansion of a generic ket is

$$|\Psi\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 (|\mathbf{x}_1\rangle|\mathbf{x}_2\rangle) (\langle \mathbf{x}_1|\langle \mathbf{x}_2|) |\Psi\rangle,$$

and if $|\Psi\rangle$ is normalized then the square modulus of the wavefunction $\Psi(\mathbf{x}_1, \mathbf{x}_2) \equiv (\langle \mathbf{x}_1|\langle \mathbf{x}_2|) |\Psi\rangle$ yields the probability density of finding the electron in $\mathbf{x}_1 = (\mathbf{r}_1\sigma_1)$ and the positron in $\mathbf{x}_2 = (\mathbf{r}_2\sigma_2)$:

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \, d\mathbf{r}_1 d\mathbf{r}_2 = \left(\begin{array}{c} \text{probability of finding the electron with spin } \sigma_1 \\ \text{in volume element } d\mathbf{r}_1 \text{ around } \mathbf{r}_1 \text{ and the positron} \\ \text{with spin } \sigma_2 \text{ in volume element } d\mathbf{r}_2 \text{ around } \mathbf{r}_2 \end{array} \right).$$

Continuum formulation for N particles The generalization to N distinguishable particles is straightforward. The position–spin ket $|\mathbf{x}_1\rangle \dots |\mathbf{x}_N\rangle$ describes the physical state in which the first particle is in $\mathbf{x}_1$, the second particle is in $|\mathbf{x}_2\rangle$, etc. These kets form an orthonormal basis with inner product

$$(\langle \mathbf{x}_1'| \dots \langle \mathbf{x}_N'|) (|\mathbf{x}_1\rangle \dots |\mathbf{x}_N\rangle) = \delta(\mathbf{x}_1' - \mathbf{x}_1) \dots \delta(\mathbf{x}_N' - \mathbf{x}_N), \tag{1.14}$$

and therefore the completeness relation reads

$$\int d\mathbf{x}_1 \dots d\mathbf{x}_N \; (\; |\mathbf{x}_1\rangle \dots |\mathbf{x}_N\rangle \;) \; (\; \langle \mathbf{x}_1| \dots \langle \mathbf{x}_N| \;) = \hat{\mathbb{1}}.$$

Operators Having discussed the Hilbert space for N distinguishable particles, we now consider the operators acting on the N-particle kets. We start with an example and consider again the electron–positron pair. Suppose that there is an electric field $\mathbf{E}(\mathbf{r}) = -\boldsymbol{\nabla}\phi(\mathbf{r})$ extending across all of space and that we are interested in measuring the total potential energy. This is an observable quantity and, hence, associated with it there exists an operator $\hat{\mathcal{H}}_{\rm pot}$. By definition the eigenstates of this operator are the position–spin kets $|\mathbf{x}_1\rangle|\mathbf{x}_2\rangle$ and the corresponding eigenvalues are $-\phi(\mathbf{r}_1)+\phi(\mathbf{r}_2)$, independent of the spin of the particles (in atomic units the charge of the electron is $q=-1$ and hence the charge of the positron is $q=+1$). The operator $\hat{\mathcal{H}}_{\rm pot}$ is then the sum of the electrostatic potential operator acting on the first particle and doing nothing to the second particle and the electrostatic potential operator acting on the second particle and doing nothing to the first particle:

$$\hat{\mathcal{H}}_{\rm pot} = -\phi(\hat{\boldsymbol{r}}) \otimes \hat{\mathbb{1}} + \hat{\mathbb{1}} \otimes \phi(\hat{\boldsymbol{r}}). \tag{1.15}$$

The symbol $\otimes$ denotes the *tensor product* of operators acting on different particles:

$$\hat{\mathcal{H}}_{\rm pot}|\mathbf{x}_1\rangle|\mathbf{x}_2\rangle = -\phi(\hat{\boldsymbol{r}})|\mathbf{x}_1\rangle\hat{\mathbb{1}}|\mathbf{x}_2\rangle + \hat{\mathbb{1}}|\mathbf{x}_1\rangle\phi(\hat{\boldsymbol{r}})|\mathbf{x}_2\rangle = \big[-\phi(\mathbf{r}_1)+\phi(\mathbf{r}_2)\big]|\mathbf{x}_1\rangle|\mathbf{x}_2\rangle.$$

The generalization of the potential energy operator to N particles of charge $q_1,\dots,q_N$ is rather voluminous

$$\hat{\mathcal{H}}_{\rm pot} = q_1\phi(\hat{\boldsymbol{r}})\otimes\underbrace{\hat{\mathbb{1}}\otimes\dots\otimes\hat{\mathbb{1}}}_{N-1 \text{ times}} + q_2\hat{\mathbb{1}}\otimes\phi(\hat{\boldsymbol{r}})\otimes\underbrace{\dots\otimes\hat{\mathbb{1}}}_{N-2 \text{ times}} + \dots + q_N\underbrace{\hat{\mathbb{1}}\otimes\hat{\mathbb{1}}\otimes\dots}_{N-1 \text{ times}}\otimes\phi(\hat{\boldsymbol{r}}), \tag{1.16}$$

and it is typically shortened to

$$\hat{\mathcal{H}}_{\rm pot} = \sum_{j=1}^{N} q_j\phi(\hat{\boldsymbol{r}}_j),$$

where $\hat{\boldsymbol{r}}_j$ is the position operator acting on the jth particle and doing nothing to the other particles. Similarly, the noninteracting part of the Hamiltonian of N particles is typically written as

$$\hat{\mathcal{H}}_0 = \sum_{j=1}^{N}\hat{h}_j = \sum_{j=1}^{N} h(\hat{\boldsymbol{r}}_j,\hat{\boldsymbol{p}}_j,\hat{\boldsymbol{\mathcal{S}}}_j), \tag{1.17}$$

while the interaction part is written as

$$\hat{\mathcal{H}}_{\rm int} = \frac{1}{2}\sum_{i\neq j}^{N} v(\hat{\boldsymbol{r}}_i,\hat{\boldsymbol{r}}_j), \tag{1.18}$$

with $v(\mathbf{r}_1,\mathbf{r}_2)$ the interparticle interaction. We observe that these operators depend explicitly on the number of particles and are therefore difficult to manipulate in problems where the

number of particles can fluctuate, such as in systems at finite temperature. As we see later in this chapter, another disadvantage is that the evaluation of their action on kets describing *identical* particles is very lengthy. Fortunately, an incredible simplification occurs for identical particles and the expressions for operators and kets become much lighter and easier to manipulate. To appreciate this simplification, however, we first have to understand how the quantum-mechanical formulation changes when the particles are identical.

1.3 Quantum Mechanics of Many Identical Particles

Two particles are called *identical particles* or *indistinguishable particles* if they have the same internal properties (i.e., the same mass, charge, spin etc.). For example, two electrons are two identical particles. To understand the qualitative difference between distinguishable and identical particles, let us perform the coincidence experiment of the previous section for two electrons both with spin projection $1/2$ and again in one dimension.

Discrete formulation for two particles At every point $x_n = n\Delta$ we put a spin-polarized electron detector and since the particles are identical we need only one kind of detector. If the detectors in x_n and x_m click at the same time, then we can be sure that just after this time there is one electron around x_n and another electron around x_m. Let us denote by $|nm\rangle$ with $n \geq m$ the ket describing the physical state in which the two electrons collapse after measurement. For mathematical convenience we also define the ket $|nm\rangle$ with $n \leq m$ as the ket describing the *same physical state* as $|mn\rangle$. Notice the different notation with respect to the previous section, where we have used the ket $|n\rangle|m\rangle$ to describe the first particle around x_n and the second particle around x_m. In the case of the electron–positron pair we could make the positron-click louder than the electron-click and hence distinguish the state $|n\rangle|m\rangle$ from the state $|m\rangle|n\rangle$. However, in this case we only have electron detectors and it is impossible to distinguish which electron has made a given detector click.

In Section 1.1 we observed that the normalized ket of a physical state is uniquely defined up to a phase factor. For our mathematical description to make sense, we then must impose that

$$|nm\rangle = e^{\mathrm{i}\alpha}|mn\rangle \qquad \text{for all } n,\, m.$$

Using the above relation twice, we find that $e^{2\mathrm{i}\alpha} = 1$, or equivalently $e^{\mathrm{i}\alpha} = \pm 1$. Consequently, the ket

$$|nm\rangle = \pm|mn\rangle \tag{1.19}$$

is either symmetric or antisymmetric under the interchange of the electron positions. This is a fundamental property of nature: All particles can be grouped in two main classes. Particles described by a symmetric ket are called *bosons*, while those described by an antisymmetric ket are called *fermions*. The electrons of our example are fermions. Here and in the rest of the book the upper sign always refers to bosons and the lower sign to fermions. In the case of fermions (1.19) implies $|nn\rangle = -|nn\rangle$ and hence $|nn\rangle$ must be the *null ket* $|\emptyset\rangle$ – that is, it is not possible to create two fermions in the same position and with the same spin. This peculiarity of fermions is known as the *Pauli exclusion principle*.