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Systems and Subsystems, Multiple Particles

19.1 Introduction

Up to this point, we have considered the state of a quantum system to be described by a unit vector in the corresponding Hilbert space, or more properly, an equivalence class of unit vectors under the equivalence relation $\psi \sim e^{i\theta}\psi$. We will see in this section that this notion of the state of a quantum system is too limited. We will introduce a more general notion of the state of a system, described by a *density matrix*. The special case in which the system can be described by a unit vector will be called a *pure state*.

One way to see the inadequacy of the notion of state as a unit vector is to consider systems and subsystems. We will examine this topic in greater detail in Sect. 19.5, but for now let us consider the example of a system of two spinless "distinguishable" particles moving in $\mathbb{R}^3$. (For now, the reader need not worry about the notion of distinguishable particles; just think of them as being two different types of particles, with, say, different masses or charges.) Let us assume the combined state of the two particles can be described by a unit vector in the corresponding Hilbert space, which is (according to Sect. 3.11) $L^2(\mathbb{R}^6)$. We have, then, a wave function $\psi(\mathbf{x},\mathbf{y})$, where $\mathbf{x}$ is the position of the first particle and $\mathbf{y}$ is the position of the second particle.

Given a wave function $\psi(\mathbf{x},\mathbf{y})$ for the combined system, what is the wave function describing the state of the first particle only? *If* the wave function of the combined system happens to be a product, say, $\psi(\mathbf{x},\mathbf{y}) =$

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$\psi_1(\mathbf{x})\psi_2(\mathbf{y})$, then, naturally, we would say that the state of the first particle is simply ψ_1. Of course, one might object that we could rewrite ψ as $\psi(\mathbf{x},\mathbf{y}) = [c\psi_1(\mathbf{x})][\psi_2(\mathbf{y})/c]$ for any constant c, but this only affects the wave function for the first particle by a constant, which does not affect the physical state.

In general, however, the wave function of the combined system need not be a product. Already when ψ is a linear combination of two products, $\psi(\mathbf{x},\mathbf{y}) = \psi_1(\mathbf{x})\psi_2(\mathbf{y}) + \phi_1(\mathbf{x})\phi_2(\mathbf{y})$, it is unclear what the correct wave function is for the first particle. At first glance, it might seem natural to try $\psi_1(\mathbf{x}) + \phi_1(\mathbf{x})$, but upon closer examination, this is not an unambiguous proposal. After all, we can just as well write $\psi(\mathbf{x},\mathbf{y}) = [c_1\psi_1(\mathbf{x})][\psi_2(\mathbf{y})/c_1] + [c_2\phi_1(\mathbf{x})][\phi_2(\mathbf{y})/c_2]$, but then the resulting wave functions for the first particle, $\psi_1(\mathbf{x}) + \psi_2(\mathbf{x})$ and $c_1\psi_1(\mathbf{x}) + c_2\psi_2(\mathbf{x})$, are not scalar multiples of one another. For a general unit vector ψ in $L^2(\mathbb{R}^6)$, the situation is even worse. The conclusion is this: There does not seem to be any way to associate to ψ a general unit vector ψ' in $L^2(\mathbb{R}^3)$ such that ψ' could sensibly be described as "the state of the first particle."

Although we cannot associate with ψ a wave function ψ' for the first particle, there is no difficulty in taking expectation values of observables related to the first particle. We can make perfect sense of, say, the expected position of the first particle, as

$$\left\langle \psi, X_j^{(1)}\psi \right\rangle = \int_{\mathbb{R}^6} x_j \left|\psi(\mathbf{x},\mathbf{y})\right|^2 \, d\mathbf{x}\, d\mathbf{y}.$$

Here $X_j^{(1)}$ indicates the operator of multiplication by the jth component of the *first* vector in the function $\psi(\cdot,\cdot) : \mathbb{R}^3 \times \mathbb{R}^3 \to \mathbb{C}$. That is to say, the operator X_j acting on $L^2(\mathbb{R}^3)$ can be "promoted" to an operator on $L^2(\mathbb{R}^6)$ by having it act in the first variable only. Similarly, the momentum operator P_j on $L^2(\mathbb{R}^3)$ can be promoted to an operator $P_j^{(1)}$ on $L^2(\mathbb{R}^6)$, by letting it act on the first variable, meaning that $P_j^{(1)}\psi$ is $-i\hbar$ times the partial derivative with respect to the jth component of the first vector in $\psi(\cdot,\cdot)$. In fact, as we will see in Sect. 19.5, given *any* self-adjoint operator on $L^2(\mathbb{R}^3)$, there is a natural way to promote it into an operator on $L^2(\mathbb{R}^6)$, where its expectation value may then be defined.

Thus, although there is no natural way to associate with a unit vector ψ in $L^2(\mathbb{R}^6)$ a unit vector in $L^2(\mathbb{R}^3)$, there *is* a natural way to associate with ψ expectation values of observables on $L^2(\mathbb{R}^3)$. This suggests that we should introduce a more general notion of the "state" of a quantum system, a notion in which with each "reasonable" family of expectation values for the quantum observables there is associated a quantum state. This notion turns out to be that of *density matrices* (positive, self-adjoint operators with trace 1).

In Sect. 19.3, we introduce the notion of a density matrix. Theorem 19.9 in that section will tell us that, given any reasonable assignment ϕ of expectation values to observables, there is a unique density matrix ρ such that $\phi(A) = \operatorname{trace}(\rho A)$ for all observables A. In the special case in which the state of the system is given by a unit vector ψ in the Hilbert space, then ρ will be just the projection onto ψ and $\operatorname{trace}(\rho A)$ will be equal to the familiar expression $\langle \psi, A\psi \rangle$. In Sect. 19.5, we will consider composite quantum systems and introduce a method (the partial trace) of defining a density matrix for a subsystem from a density matrix for the whole system. Finally, in Sect. 19.6, we will consider the important special case of composite systems made up of multiple identical particles.

19.2 Trace-Class and Hilbert–Schmidt Operators

In this section, we explore notions related to the trace of an operator on a Hilbert space. The results of this section are presented without proof; see Chap. VI in Volume I of [34] for proofs and additional information.

Proposition 19.1 *Suppose $A \in \mathcal{B}(\mathbf{H})$ is non-negative and self-adjoint. Then for any two orthonormal bases $\{e_j\}$ and $\{f_j\}$ for $\mathbf{H}$, we have*

$$\sum_j \langle e_j, Ae_j \rangle = \sum_j \langle f_j, Af_j \rangle .$$

Note that since A is non-negative, $\langle e_j, Ae_j \rangle$ and $\langle f_j, Af_j \rangle$ are non-negative real numbers. Thus, the sums are always well defined, but may have the value of $+\infty$.

Definition 19.2 *If $A \in \mathcal{B}(\mathbf{H})$ is non-negative and self-adjoint, the value of $\sum_j \langle e_j, Ae_j \rangle$, for any arbitrarily chosen orthonormal basis, is called the **trace** of A. If $\operatorname{trace}(A) < +\infty$, then we say that A is **trace class**.*

*For a general $A \in \mathcal{B}(\mathbf{H})$, we say that A is **trace class** if the non-negative self-adjoint operator $\sqrt{A^*A}$ is a trace class.*

Note that for any $A \in \mathcal{B}(\mathbf{H})$, A^*A is self-adjoint and non-negative. Thus, the square root of A^*A may be defined by the functional calculus (Definition 7.13 or Proposition 8.4).

Proposition 19.3

1. *If $A \in \mathcal{B}(\mathbf{H})$ is trace class, then for any orthonormal basis $\{e_j\}$, the sum $\sum_j \langle e_j, Ae_j \rangle$ is absolutely convergent. Furthermore, the value of this sum, which we denote as $\operatorname{trace}(A)$, is independent of the choice of orthonormal basis.*

2. *If $A \in \mathcal{B}(\mathbf{H})$ is trace class, then A^* is also trace class and*

$$\operatorname{trace}(A^*) = \overline{\operatorname{trace}(A)}.$$

3. *If* $A \in \mathcal{B}(\mathbf{H})$ *is trace class, then for all* $B \in \mathcal{B}(\mathbf{H})$, *the operators* AB *and* BA *are also trace class, and*

$$\operatorname{trace}(AB) = \operatorname{trace}(BA).$$

Recall that $A \in \mathcal{B}(\mathbf{H})$ is said to be compact if A maps every bounded set in $\mathbf{H}$ to a set with compact closure. If a self-adjoint operator A is trace class, it is necessarily compact and thus has an orthonormal basis $\{e_j\}$ of eigenvectors, for which the associated eigenvalues λ_j are real and tend to zero as j tends to infinity. (See Theorem VI.16 in Volume I of [34]. One can deduce the result from, say, the direct integral form of the spectral theorem for bounded self-adjoint operators by verifying that unless A has point spectrum with eigenvalues tending to zero, the operator of multiplication by λ in the direct integral will not be compact.) Point 1 of Proposition 19.3 then tells us that $\sum_j |\lambda_j| < \infty$ and that $\operatorname{trace}(A) = \sum_j \lambda_j$. Conversely, if A is a self-adjoint operator having an orthonormal basis of eigenvectors for which the associated eigenvalues satisfy $\sum_j |\lambda_j| < \infty$, then A is trace class.

Definition 19.4 *An operator* $A \in \mathcal{B}(\mathbf{H})$ *is said to be* ***Hilbert–Schmidt*** *if* $\operatorname{trace}(A^*A) < \infty$.

Since A^*A is self-adjoint and non-negative, $\operatorname{trace}(A^*A)$ is defined (but possibly infinite) for any $A \in \mathcal{B}(\mathbf{H})$. If A is trace class, then (by definition) the trace of $\sqrt{A^*A}$ is finite, in which case, the trace of $\sqrt{A^*A}\sqrt{A^*A}$ is also finite, by Point 3 of Proposition 19.3. Thus, every trace-class operator is Hilbert–Schmidt (but not vice versa).

Proposition 19.5 *If* $A \in \mathcal{B}(\mathbf{H})$ *is Hilbert–Schmidt, so is* A^*. *If* $A, B \in \mathcal{B}(\mathbf{H})$ *are Hilbert–Schmidt, then* AB *and* BA *are trace class and* $\operatorname{trace}(AB)$ *equals* $\operatorname{trace}(BA)$.

If A and B are Hilbert–Schmidt operators, the *Hilbert–Schmidt inner product* of A and B is $\langle A, B\rangle_{HS} := \operatorname{trace}(A^*B)$ and the *Hilbert–Schmidt norm* of A satisfies $\|A\|_{HS}^2 = \langle A, A\rangle_{HS}$. The space of Hilbert–Schmidt operators is a Hilbert space with respect to $\langle \cdot, \cdot\rangle_{HS}$.

19.3 Density Matrices: The General Notion of the State of a Quantum System

Typically, we think of the quantum observables—the ones with expectations values that we wish to take—as being unbounded self-adjoint operators. But of course we can also take expectation values of bounded self-adjoint operators, and indeed expectations for bounded operators determine those for unbounded operators. After all, suppose A is an unbounded self-adjoint operator and suppose we know the expectation value for $1_E(A)$ for every Borel set $E \subset \mathbb{R}$, where 1_E is the indicator function of E and

$1_E(A)$ is defined by the functional calculus (Definition 7.13). The expectation value for $1_E(A)$ is the probability of obtaining a value in E for a measurement of the observable A. If we know this probability for each E, then we know the full probability distribution of the measurements, and thus we can compute the expectation value of A. Furthermore, we can always introduce expectation values for (bounded) non-self-adjoint operators. Each such operator A is of the form $A = A_1 + iA_2$ with A_1 and A_2 self-adjoint, and so we may reasonably define the expectation value of A to be the expectation value of A_1 plus i times the expectation value of A_2.

We then postulate that the general notion of the "state" of a quantum system should be simply a "list" of expectation values for all bounded operators, satisfying some reasonable hypotheses.

Definition 19.6 *A linear map $\Phi : \mathcal{B}(\mathbf{H}) \to \mathbb{C}$ is a* ***family of expectation values*** *if the following conditions hold.*

1. $\Phi(I) = 1$.
2. $\Phi(A)$ *is real whenever A is self-adjoint.*
3. $\Phi(A) \geq 0$ *whenever A is self-adjoint and non-negative.*
4. *For any sequence A_n in $\mathcal{B}(\mathbf{H})$, if $\|A_n\psi - A\psi\| \to 0$ for all $\psi \in \mathbf{H}$, then $\Phi(A_n) \to \Phi(A)$.*

Point 4 in the definition says that Φ is continuous with respect to the strong (sequential) convergence in $\mathcal{B}(\mathbf{H})$. By Exercise 3, any linear map on $\mathcal{B}(\mathbf{H})$ satisfying Points 1, 2, and 3 is automatically continuous with respect to the operator norm topology, meaning that if $\|A_n - A\| \to 0$ then $\Phi(A_n) \to \Phi(A)$. However, to establish our characterization of families of expectation values in terms of density matrices, we need continuity of Φ under a more general sort of convergence, where we only assume that $\|A_n\psi - A\psi\| \to 0$ for each ψ. This stronger continuity property does not follow from Properties 1–3. Exercise 5 gives an example of a linear functional on $\mathcal{B}(\mathbf{H})$ that satisfies Points 1–3 of Definition 19.6, but not Point 4.

Definition 19.7 *An operator $\rho \in \mathcal{B}(\mathbf{H})$ is a* ***density matrix*** *if ρ is self-adjoint and non-negative and* $\operatorname{trace}(\rho) = 1$.

Of course, since the trace of a density matrix is assumed to be finite, every density matrix is trace class. The next two results give a precise characterization of families of expectation values in terms of density matrices.

Proposition 19.8 *Suppose ρ is a density matrix on $\mathbf{H}$. Then the map $\Phi_\rho : \mathcal{B}(\mathbf{H}) \to \mathbb{C}$ given by*

$$\Phi_\rho(A) = \operatorname{trace}(\rho A) = \operatorname{trace}(A\rho)$$

is a family of expectation values.

Proof. If we define $\Phi_\rho(A) = \operatorname{trace}(\rho A)$, then $\Phi_\rho(I) = \operatorname{trace}(\rho) = 1$. For any $A \in \mathcal{B}(\mathbf{H})$, we have,

$$\operatorname{trace}(\rho A^*) = \operatorname{trace}(A^*\rho) = \operatorname{trace}((\rho A)^*) = \overline{\operatorname{trace}(\rho A)}.$$

It follows that $\operatorname{trace}(\rho A)$ is real when A is self-adjoint. Let $\rho^{1/2}$ be the non-negative self-adjoint square root of ρ. Then $\rho^{1/2}$ and $A\rho^{1/2}$ are Hilbert–Schmidt (in the latter case, by Point 3 of Proposition 19.3). It follows that $\operatorname{trace}(A\rho^{1/2}\rho^{1/2}) = \operatorname{trace}(\rho^{1/2}A\rho^{1/2})$, by Proposition 19.5. Thus, if A is self-adjoint and non-negative,

$$\operatorname{trace}(\rho A) = \operatorname{trace}(\rho^{1/2}\rho^{1/2}A) = \operatorname{trace}(\rho^{1/2}A\rho^{1/2}) \geq 0, \tag{19.1}$$

because $\rho^{1/2}A\rho^{1/2}$ is self-adjoint and non-negative. We have established that Φ_ρ satisfies Points 1, 2, and 3 of Definition 19.6.

Meanwhile, suppose $A_n\psi$ converges in norm to $A\psi$, for each ψ in $\mathbf{H}$. Then $\|A_n\psi\|$ is bounded as a function of n for each fixed ψ. Thus, by the principle of uniform boundedness (Theorem A.40), there is a constant C such that $\|A_n\| \leq C$. Now, if $\{e_j\}$ is an orthonormal basis for $\mathbf{H}$, we have

$$\left|\left\langle e_j, \rho^{1/2}A_n\rho^{1/2}e_j\right\rangle\right| = \left|\left\langle \rho^{1/2}e_j, A_n\rho^{1/2}e_j\right\rangle\right| \leq C\left\|\rho^{1/2}e_j\right\|^2,$$

and,

$$\sum_j \left\|\rho^{1/2}e_j\right\|^2 = \sum_j \left\langle \rho^{1/2}e_j, \rho^{1/2}e_j\right\rangle = \sum_j \langle e_j, \rho e_j\rangle = \operatorname{trace}(\rho) < \infty.$$

Furthermore, since $A_n(\rho^{1/2}e_j)$ converges to $A(\rho^{1/2}e_j)$ for each j, dominated convergence tells us that

$$\begin{aligned}\operatorname{trace}(\rho^{1/2}A\rho^{1/2}) &= \sum_j \left\langle e_j, \rho^{1/2}A\rho^{1/2}e_j\right\rangle \\ &= \lim_{n\to\infty}\sum_j \left\langle e_j, \rho^{1/2}A_n\rho^{1/2}e_j\right\rangle \\ &= \lim_{n\to\infty}\operatorname{trace}(\rho^{1/2}A_n\rho^{1/2}).\end{aligned}$$

As in (19.1), we can shift the second factor of $\rho^{1/2}$ to the front of the trace to obtain Point 4 in Definition 19.6. ∎

Theorem 19.9 *For any family of expectation values* $\Phi : \mathcal{B}(\mathbf{H}) \to \mathbb{C}$, *there is a unique density matrix* ρ *such that* $\Phi(A) = \operatorname{trace}(\rho A)$ *for all* $A \in \mathcal{B}(\mathbf{H})$.

Proof. Recall from Sect. 3.12 the Dirac notation, in which the expression $|\phi\rangle\langle\psi|$ denotes the linear operator taking any vector $\chi \in \mathbf{H}$ to the vector $|\phi\rangle\langle\psi|\chi\rangle$ (in physics notation), that is, the vector $\langle\psi,\chi\rangle\,\phi$ (in math notation). If ρ is trace class, then by Exercise 2,

$$\operatorname{trace}(\rho\,|\phi\rangle\langle\psi|) = \langle\psi, \rho\phi\rangle\,.$$

Thus, if an operator ρ with the desired properties is to exist, we must have

$$\langle \psi, \rho\phi \rangle = \Phi(|\phi\rangle\langle\psi|).$$

Now, by Exercise 3, Φ satisfies $\|\Phi(A)\| \leq \|A\|$. From this, we can see that the map

$$L_\Phi(\phi, \psi) := \Phi(|\phi\rangle\langle\psi|)$$

is a bounded sesquilinear form, so that (by Proposition A.63), there is a unique bounded operator ρ such that $\Phi(|\phi\rangle\langle\psi|) = \langle\psi, \rho\phi\rangle$ for all ϕ and ψ. Since $|\phi\rangle\langle\phi|$ is self-adjoint and non-negative, $L_\Phi(\phi, \phi)$ is real and non-negative, which means that ρ is self-adjoint (by Proposition A.63) and non-negative.

Meanwhile, if $\{e_j\}$ is an orthonormal basis for $\mathbf{H}$, then by Definition 19.2,

$$\begin{aligned}
\operatorname{trace}(\rho) &= \lim_{N\to\infty} \sum_{j=1}^{N} \langle e_j, \rho e_j \rangle \\
&= \lim_{N\to\infty} \Phi\left(|e_1\rangle\langle e_1| + \cdots + |e_N\rangle\langle e_N|\right) \\
&= \Phi(I) = 1.
\end{aligned}$$

In passing from the second line to the third, we have used Point 4 of Definition 19.6. Thus, ρ is a density matrix.

We have now found a density matrix ρ such that $\Phi(|\phi\rangle\langle\psi|)$ agrees with $\operatorname{trace}(\rho\,|\phi\rangle\langle\psi|)$ for all $\phi, \psi \in \mathbf{H}$. By linearity, $\Phi(A) = \operatorname{trace}(\rho A)$ for all finite-rank operators A (see Exercise 4). Now, if $\{e_j\}$ is an orthonormal basis for $\mathbf{H}$, let P_N be the orthogonal projection onto the span of $e_1, \ldots, e_N$. Then for any $A \in \mathcal{B}(\mathbf{H})$, the operator $P_N A$ has finite rank and $P_N A\psi \to A\psi$ for all $\psi \in \mathbf{H}$. Thus, for all $A \in \mathcal{B}(\mathbf{H})$,

$$\Phi(A) = \lim_{N\to\infty} \Phi(P_N A) = \lim_{N\to\infty} \operatorname{trace}(\rho P_N A) = \operatorname{trace}(\rho A),$$

by Proposition 19.8 ■

Our next result shows that our new notion of the state of a system includes our old notion.

Proposition 19.10 *For any unit vector* $\psi \in \mathbf{H}$, *let* $|\psi\rangle\langle\psi|$, *in accordance with Notation 3.29, denote the orthogonal projection onto the span of* ψ. *Then* $|\psi\rangle\langle\psi|$ *is a density matrix and for all* $A \in \mathcal{B}(\mathbf{H})$, *we have*

$$\operatorname{trace}(|\psi\rangle\langle\psi|\, A) = \langle \psi, A\psi \rangle.$$

Note that if $\psi_2 = e^{i\theta}\psi_1$, then $|\psi_1\rangle\langle\psi_1| = |\psi_2\rangle\langle\psi_2|$. Thus, from our new point of view, we may say that the reason ψ_1 and ψ_2 represent the same "physical state" is that they determine the same density matrix.

Proof. Since it is an orthogonal projection, $|\psi\rangle\langle\psi|$ is bounded, self-adjoint, and non-negative. To compute its trace, we choose an orthonormal basis

$\{e_j\}$ for $\mathbf{H}$ with $e_1 = \psi$, which gives $\mathrm{trace}(|\psi\rangle\langle\psi|) = 1$. Using the same orthonormal basis, we compute that, for any $A \in \mathcal{B}(\mathbf{H})$,

$$\mathrm{trace}(|\psi\rangle\langle\psi|\, A) = \sum_j \langle e_j, \psi\rangle\langle\psi, Ae_j\rangle = \langle\psi, A\psi\rangle\,,$$

as desired. ■

Definition 19.11 *A density matrix $\rho \in \mathcal{B}(\mathbf{H})$ is a **pure state** if there exists a unit vector $\psi \in \mathbf{H}$ such that ρ is equal to the orthogonal projection onto the span of ψ. The density matrix ρ is called a **mixed state** if no such unit vector ψ exists.*

An isolated system that is in a pure state initially will remain in a pure state for all later times, since the initial state ψ_0 evolves to the pure state $e^{-i\hat{H}t/\hbar}\psi_0$, where $\hat{H}$ is the Hamiltonian for the system. But if a system is interacting with its environment, then as discussed in Sect. 19.5, the system may move into a mixed state at a later time.

There are several different ways of characterizing the pure states as a subset of the density matrices. First, it is not hard to see (Exercise 6) that a density matrix ρ is a pure state if and only if $\mathrm{trace}(\rho^2) = 1$. Second, the set of density matrices is a convex set, since if ρ_1 and ρ_2 are non-negative and have trace 1, then so is $\lambda\rho_1 + (1-\lambda)\rho_2$, for $0 < \lambda < 1$. According to Exercise 7, the pure states are precisely the extreme points of this set. That is, a density matrix ρ is a pure state if and only if it *cannot* be expressed as $\rho = \lambda\rho_1 + (1-\lambda)\rho_2$ where ρ_1 and ρ_2 are distinct density matrices and λ belongs to $(0,1)$. Third, we may define the *von Neumann entropy* $S(\rho)$ of a density matrix ρ by

$$S(\rho) = \mathrm{trace}(-\rho\log\rho),$$

where $\rho\log\rho$ is defined by the functional calculus. (Since $\lim_{\lambda\to 0^+}\lambda\log\lambda = 0$, we interpret $0\log 0$ as being 0.) Since the eigenvalues of ρ are all between 0 and 1, we see that $-\rho\log\rho$ is a non-negative self-adjoint operator, which has a well-defined trace, which may have the value $+\infty$. According to Exercise 8, a density matrix ρ is a pure state if and only if $S(\rho) = 0$.

Suppose that we have two pure states, coming from unit vectors ψ_1 and ψ_2. Then there are two different senses in which we can take a *superposition,* that is, linear combination, of the corresponding quantum states. If we use our old point of view, in which the states are vectors in $\mathbf{H}$, then we may take the linear combination $c_1\psi_1 + c_2\psi_2$, and then normalize this vector to be a unit vector. If we use our new point of view, in which the states are density matrices, then we may take the linear combination $c_1\,|\psi_1\rangle\langle\psi_1| + c_2\,|\psi_2\rangle\langle\psi_2|\,$, where in this case c_1 and c_2 should be non-negative and should add to 1. These two notions of superposition are different, since

$$C\,|c_1\psi_1 + c_2\psi_2\rangle\langle c_1\psi_1 + c_2\psi_2| \neq c_1\,|\psi_1\rangle\langle\psi_1| + c_2\,|\psi_2\rangle\langle\psi_2|\,, \tag{19.2}$$

no matter how the constant C is chosen. After all, the state on the left-hand side of (19.2) is a pure state, whereas (unless ψ_2 is a multiple of ψ_1), the state on the right-hand side of (19.2) is a mixed state, since the range of this operator is 2-dimensional rather than 1-dimensional.

Physicists call the first sort of superposition (in which we take a linear combination of vectors in $\mathbf{H}$) *coherent superposition* or *quantum superposition*, and they call the second sort of superposition (in which we take a linear combination of the associated density matrices) *incoherent superposition.* The reason for the term "coherent" is that coherent superposition depends on the *phases* of the coefficients. That is, if ψ_1 and ψ_2 are linearly independent, the vector $c_1 e^{i\theta}\psi_1 + c_2 e^{i\phi}\psi_2$ does not represent the same quantum state as $c_1\psi_1 + c_2\psi_2$, unless $e^{i\theta} = e^{i\phi}$. By contrast, the density matrix associated with $e^{i\theta}\psi$ is the same as the density matrix associated with ψ, and so the phases have no effect when taking linear combinations of the density matrices associated to vectors in $\mathbf{H}$. When taking a coherent superposition, there is no simple relationship between the expectation value of an observable in the states ψ_1 and ψ_2 and the expectation value of the same observable in the state $c_1\psi_1 + c_2\psi_2$. On the other hand, when taking an incoherent superposition, expectation values in the new state are just linear combinations of the original expectation values:

$$\operatorname{trace}\left((c_1 \left|\psi_1\right\rangle\!\left\langle\psi_1\right| + c_2 \left|\psi_2\right\rangle\!\left\langle\psi_2\right|)A\right) = c_1 \left\langle \psi_1, A\psi_1\right\rangle + c_2 \left\langle \psi_2, A\psi_2\right\rangle .$$

19.4 Modified Axioms for Quantum Mechanics

We may now modify the axioms of quantum mechanics introduced in Sect. 3.6 to incorporate density matrices, beginning with our revised notion of a state.

Axiom 6 *The state of a quantum system is described by a density matrix* ρ *on an appropriate Hilbert space* $\mathbf{H}$. *If* A *is any bounded operator on* $\mathbf{H}$, *the expectation value of* A *in the state* ρ *is given by the quantity* $\operatorname{trace}(\rho A) = \operatorname{trace}(A\rho)$.

In Axiom 6, we assume that A is bounded, so that $\operatorname{trace}(\rho A)$ and $\operatorname{trace}(A\rho)$ are defined and equal by Proposition 19.3. If A is unbounded and self-adjoint, we can construct a probability measure μ_ρ^A describing the probabilities for measurements of A in the state ρ, by the formula

$$\mu_\rho^A(E) = \operatorname{trace}(\rho 1_E(A)),$$

where $1_E(A)$ is defined by the functional calculus.

We then define the expectation value of A in the state ρ as $\int_{\mathbb{R}} \lambda \; d\mu_\rho^A(\lambda)$, provided the integral is absolutely convergent. If the integral is absolutely convergent, it is reasonable to hope that both ρA and $A\rho$ will be densely defined and bounded, that (the bounded extension to **H** of) these operators will be trace class, and that both trace(ρA) and trace($A\rho$) will coincide with $\int_{\mathbb{R}} \lambda \, d\mu_\rho^A(\lambda)$. We will not, however, enter into an investigation of this issue.

Next, we propose a variant of Axiom 4, describing the "collapse of the wave function."

Axiom 7 *Suppose a quantum system is initially in a state ρ and a measurement of a self-adjoint operator A with point spectrum is performed. If the measurement results in the value λ for A, then immediately after the measurement, the system will be in the state ρ', where*

$$\rho' = \frac{1}{Z} P_\lambda \rho P_\lambda.$$

Here P_λ is the orthogonal projection onto the λ-eigenspace of A and $Z =$ trace$(P_\lambda \rho P_\lambda)$.

Note that if ρ is non-negative, self-adjoint, and trace class, then $P_\lambda \rho P_\lambda$ is also non-negative, self-adjoint, and trace class. Implicit in Axiom 7 is the assumption that the measurement can only result in values λ for which $P_\lambda \rho P_\lambda$ is nonzero. In particular, λ must be an eigenvalue for A.

Finally, we introduce the notion of time-evolution for our new notion of "state."

Axiom 8 *The time evolution of the state of the system is described by the following equation for a time-dependent density matrix $\rho(t)$:*

$$\frac{d\rho}{dt} = -\frac{1}{i\hbar}[\rho, \hat{H}]. \tag{19.3}$$

This equation may be solved, formally, by setting

$$\rho(t) = e^{-it\hat{H}/\hbar} \rho_0 e^{it\hat{H}/\hbar}, \tag{19.4}$$

where ρ_0 is the state of the system at time $t = 0$.

There are some domain issues involved in the interpretation of the equation (19.3). Rather than entering into an examination of those issues here, we will simply take (19.4) as the definition of the time-evolution of a density matrix. Presumably, if ρ_0 is nice enough, then the map $t \mapsto \rho(t)$ will be differentiable as a curve in the Banach space $\mathcal{B}(\mathbf{H})$ and its derivative will be (an extension of) the operator on the right-hand side of (19.3). By comparison, it follows from Stone's theorem and Lemma 10.17 that the family of pure states $\psi(t) := e^{-it\hat{H}/\hbar}\psi_0$ satisfies the Schrödinger equation in the natural Hilbert space sense if and only if ψ_0 belongs to the domain of $\hat{H}$. To see that the time-evolution in (19.4) is consistent with the previously defined time-evolution of pure states, observe that

$$e^{-it\hat{H}/\hbar} \left|\psi_0\right\rangle\!\left\langle\psi_0\right| e^{it\hat{H}/\hbar} = \left|e^{-it\hat{H}/\hbar}\psi_0\right\rangle\!\left\langle e^{-it\hat{H}/\hbar}\psi_0\right| = \left|\psi(t)\right\rangle\!\left\langle\psi(t)\right|,$$

since $(e^{it\hat{H}/\hbar})^* = e^{-it\hat{H}/\hbar}$.

It should be noted that (19.3) differs by a minus sign from the time-evolution in the Heisenberg picture of quantum mechanics (Definition 3.20). Although this difference may seem strange, keep in mind that in Axiom 8, we are *not* adopting the Heisenberg point of view, in which the states are independent of time and the observables evolve in time. Rather, we are adopting a modified version of the Schrödinger picture, in which it is the *states* that evolve in time, but where the states are now certain sorts of operators. Even though both the states and the observables are now operators, the observables (in the Heisenberg picture) and the states (in the Schrödinger picture) must evolve in *opposite directions* in time, in order for the expectation values of the observables to be the same in the two pictures.

19.5 Composite Systems and the Tensor Product

As discussed in Sect. 3.11, the Hilbert space for two (nonidentical, spinless) particles moving in $\mathbb{R}^3$ is $L^2(\mathbb{R}^6)$. Given a unit vector (i.e., a pure state) ψ in $L^2(\mathbb{R}^6)$, the quantity $\left|\psi(\mathbf{x}^1,\mathbf{x}^2)\right|^2$ represents the joint probability distribution for the position $\mathbf{x}^1$ of the first particle and the position $\mathbf{x}^2$ of the second particle. The following result shows that $L^2(\mathbb{R}^6)$ is naturally isomorphic to the Hilbert tensor product of two copies of the Hilbert space for the individual particles, namely $L^2(\mathbb{R}^3)$.

Proposition 19.12 *Suppose that* (X_1,μ_1) *and* (X_2,μ_2) *are* σ*-finite measure spaces. Then there is a unique unitary map*

$$p : L^2(X_1,\mu_1)\hat{\otimes}L^2(X_2,\mu_2) \to L^2(X_1\times X_2,\mu_1\times\mu_2)$$

such that

$$p(\phi\otimes\psi)(x,y) = \phi(x)\psi(y)$$

for all $\phi\in L^2(X_1,\mu_1)$ *and* $\psi\in L^2(X_2,\mu_2)$.

Here $\hat{\otimes}$ denotes the Hilbert tensor product defined in Appendix A.4.5.

Proof. For simplicity of notation, we suppress the dependence of L^2 spaces on the measure, writing, say, $L^2(X_1)$ rather than $L^2(X_1,\mu_1)$. Consider first the algebraic (i.e., uncompleted) tensor product $L^2(X_1)\otimes L^2(X_2)$. Using the universal property of tensor products, we can construct a linear map p of $L^2(X_1)\otimes L^2(X_2)\to L^2(X_1\times X_2)$ determined uniquely by the requirement that

$$p(\phi\otimes\psi)(x,y) = \phi(x)\psi(y).$$

Now, every element of the algebraic tensor product $L^2(X_1)\otimes L^2(X_2)$ can be expressed as a linear combination of elements of the form $\phi_j\otimes\psi_j$, with

$\phi_j \in L^2(X_1)$ and ψ_j in $L^2(X_2)$. By computing on such linear combinations, we can easily verify that p is isometric. Thus, by the bounded linear transformation (BLT) theorem (Theorem A.36), p has a unique isometric extension to a map of the completed tensor product $L^2(X_1)\hat{\otimes}L^2(X_2)$ into $L^2(X_1 \times X_2)$.

It remains only to show that p is surjective. Since both measures are σ-finite, it is a simple exercise to reduce the problem to the case where μ_1 and μ_2 are finite, which we henceforth assume. Suppose $\psi \in L^2(X_1 \times X_2)$ is orthogonal to the image of p. Then ψ is orthogonal to the indicator function of every measurable rectangle, and hence to the indicator function of any finite disjoint union of measurable rectangles. The collection $\mathcal{A}$ of such disjoint unions is an algebra of sets. Let $\mathcal{M}$ denote the collection of measurable subsets E of $X_1 \times X_2$ such that the integral of ψ over E is zero. Then $\mathcal{M}$ is a monotone class containing $\mathcal{A}$. By the monotone class lemma (Theorem A.8), $\mathcal{M}$ contains the σ-algebra generated by $\mathcal{A}$, which is the σ-algebra on which $\mu_1 \times \mu_2$ is defined. Thus, the integral of ψ over every measurable set is zero, which implies that ψ is zero almost everywhere. ■

The preceding example suggests the following general principle.

Axiom 9 *The Hilbert space for a composite system made up of two subsystems is the Hilbert tensor product* $\mathbf{H}_1\hat{\otimes}\mathbf{H}_2$ *of the Hilbert spaces* $\mathbf{H}_1$ *and* $\mathbf{H}_2$ *describing the subsystems.*

If A and B are bounded operators on $\mathbf{H}_1$ and $\mathbf{H}_2$, respectively, then there is a unique bounded operator $A \otimes B$ on $\mathbf{H}_1\hat{\otimes}\mathbf{H}_2$ such that

$$(A \otimes B)(\phi \otimes \psi) = (A\phi) \otimes (B\psi)$$

for all $\phi \in \mathbf{H}_1$ and $\psi \in \mathbf{H}_2$. (See Appendix A.4.5.)

Theorem 19.13 *Suppose that* ρ *is a density matrix on* $\mathbf{H}_1\hat{\otimes}\mathbf{H}_2$. *Then there exists a unique density matrix* $\rho^{(1)}$ *on* $\mathbf{H}_1$ *with the property that*

$$\operatorname{trace}(\rho^{(1)}A) = \operatorname{trace}(\rho(A \otimes I)) \tag{19.5}$$

for all $A \in \mathcal{B}(\mathbf{H}_1)$. *We call* $\rho^{(1)}$ *the partial trace of* ρ *with respect to* $\mathbf{H}_2$. *If* $\{f_k\}$ *is an orthonormal basis for* $\mathbf{H}_2$, *then the operator* $\rho^{(1)}$ *satisfies*

$$\langle \phi, \rho^{(1)}\psi\rangle = \sum_k \langle \phi \otimes f_k, \rho(\psi \otimes f_k)\rangle \tag{19.6}$$

for all $\phi, \psi \in \mathbf{H}_1$. *Similarly, there is a unique density matrix* $\rho^{(2)}$ *on* $\mathbf{H}_2$ *satisfying* $\operatorname{trace}(\rho^{(2)}B) = \operatorname{trace}(\rho(I \otimes B))$ *for all* $B \in \mathcal{B}(\mathbf{H}_2)$. *If* $\{e_j\}$ *is an orthonormal basis for* $\mathbf{H}_1$, *then* $\rho^{(2)}$ *satisfies*

$$\langle \phi, \rho^{(2)}\psi\rangle = \sum_j \langle e_j \otimes \phi, \rho(e_j \otimes \psi)\rangle \tag{19.7}$$

for all $\phi, \psi \in \mathbf{H}_2$.

The motivation for the terminology “partial trace” is provided by (19.6) and (19.7), which are similar to the formula for the trace of an operator, except that the sums range only over a basis for one of the two Hilbert spaces. One special case of Theorem 19.13 is the one in which the density matrix ρ is of the form $\rho = \rho_1 \otimes \rho_2$, where ρ_1 and ρ_2 are density matrices on $\mathbf{H}_1$ and $\mathbf{H}_2$, respectively. (Any operator ρ of this form is a density matrix on $\mathbf{H}_1 \times \mathbf{H}_2$.) In that case, it is not hard to see that $\rho^{(1)} = \rho_1$ and $\rho^{(2)} = \rho_2$. We may describe this case by saying that the state of the first system is “independent” of the state of the second system.

Lemma 19.14 *For any sequence $A_n \in \mathcal{B}(\mathbf{H}_1)$, if $\|A_n\psi - A\psi\| \to 0$ for some $A \in \mathcal{B}(\mathbf{H})$ and all $\psi \in \mathbf{H}_1$, then*

$$\|(A_n \otimes I)\phi - (A \otimes I)\phi\| \to 0$$

for all $\phi \in \mathbf{H}_1 \otimes \mathbf{H}_2$. A similar result holds for operators of the form $I \otimes B_n$.

Proof. See Exercise 9. ∎

Proof of Theorem 19.13. The existence and uniqueness of $\rho^{(1)}$ and $\rho^{(2)}$ follow from Lemma 19.14 and Theorem 19.9. Meanwhile, if $\{e_j\}$ is an orthonormal basis for $\mathbf{H}_1$ and $\{f_k\}$ is an orthonormal basis for $\mathbf{H}_2$, we have

$$\begin{aligned}
\langle \phi, \rho^{(1)}\psi \rangle &= \operatorname{trace}(\rho^{(1)}\, |\psi\rangle\langle\phi|) \\
&= \sum_{j,k} \langle e_j \otimes f_k, \rho(|\psi\rangle\langle\phi| \otimes I)(e_j \otimes f_k)\rangle \\
&= \sum_{j,k} \langle e_j \otimes f_k, \rho(\psi \,\langle \phi, e_j\rangle \otimes f_k)\rangle \\
&= \sum_k \left\langle \left(\sum_j \langle e_j, \phi\rangle\, e_j \right) \otimes f_k, \rho(\psi \otimes f_k) \right\rangle \\
&= \sum_k \langle \phi \otimes f_k, \rho(\psi \otimes f_k)\rangle\,.
\end{aligned}$$

This is the desired formula for $\left\langle \phi, \rho^{(1)}\psi \right\rangle$. Note that because ρ is trace class and $|\psi\rangle\langle\phi| \otimes I$ is bounded, $\rho(|\psi\rangle\langle\phi| \otimes I)$ is trace class, in which case the sum in the second line is absolutely convergent, by Proposition 19.3. Thus, we are allowed to rearrange the sum freely. ∎

Suppose we have two quantum systems with Hilbert spaces $\mathbf{H}_1$ and $\mathbf{H}_2$ and Hamiltonians $\hat{H}_1$ and $\hat{H}_2$. If the two systems do not interact with each other and the composite system is initially in a (pure) state of the form $\phi_0 \otimes \psi_0$, then we expect that at some later time, the composite system will be in the state $\phi(t) \otimes \psi(t)$, where $\phi(t) = e^{-it\hat{H}_1/\hbar}\psi_0$ and $\psi(t) = e^{-it\hat{H}_2/\hbar}$. Ignoring domain considerations, we may compute that

$$\begin{aligned} i\hbar \frac{d}{dt}\left[\phi(t) \otimes \psi(t)\right] &= (\hat{H}_1\phi(t)) \otimes \psi(t) + \phi(t) \otimes (\hat{H}_2\psi(t)) \\ &= (\hat{H}_1 \otimes I + I \otimes \hat{H}_2)(\phi(t) \otimes \psi(t)). \end{aligned}$$

This calculation suggests that the correct Hamiltonian for a noninteracting composite system is the operator $\hat{H}_1 \otimes I + I \otimes \hat{H}_2$.

It is not, however, obvious how to select a domain for $\hat{H}_1 \otimes I + I \otimes \hat{H}_2$ in such a way that this operator will be self-adjoint. (The reader is invited to try to choose such a domain "by hand.") The easiest way to deal with this issue is to use Stone's theorem, as in the following definition.

Definition 19.15 *If A and B are self-adjoint operators on $\mathbf{H}_1$ and $\mathbf{H}_2$, define the operator $A \otimes I + I \otimes B$ to be the infinitesimal generator of the strongly continuous one-parameter unitary group $e^{itA} \otimes e^{itB}$. Thus, by Stone's theorem, $A \otimes I + I \otimes B$ is self-adjoint.*

It is not hard to check that $e^{itA} \otimes e^{itB}$ is indeed strongly continuous. In the case $B = 0$, the operator $A \otimes I$ is defined as the infinitesimal generator of $e^{itA} \otimes I$. If A and B happen to be bounded, then $A \otimes I + I \otimes B$ defined by Definition 19.15 coincides with $A \otimes I + I \otimes B$ defined as the sum of tensor products of bounded operators, as in Sect. A.4.5.

Axiom 10 *Suppose $\mathbf{H}_1$ and $\mathbf{H}_2$ are the Hilbert spaces for two quantum systems, with Hamiltonians $\hat{H}_1$ and $\hat{H}_2$, respectively. Then the Hamiltonian for the noninteracting composite system is $\hat{H}_1 \otimes I + I \otimes \hat{H}_2$, where the domain of $\hat{H}_1 \otimes I + I \otimes \hat{H}_2$ is as in Definition 19.15.*

A physicist would write $\hat{H}_1 \otimes I + I \otimes \hat{H}_2$ simply as $\hat{H}_1 + \hat{H}_2$, with the understanding that $\hat{H}_1$ acts only on the first factor in the tensor product and $\hat{H}_2$ acts only on the second factor.

In general, the two components of a composite system will interact, in which case the Hamiltonian for the composite system is typically of the form

$$\hat{H} = \hat{H}_1 \otimes I + I \otimes \hat{H}_2 + \hat{H}_{\text{int}},$$

where $\hat{H}_{\text{int}}$ is an "interaction term." Often, the interaction term may be considered "small" compared with the other terms in the Hamiltonian. Consider, for example, a system consisting of particles in a box, with a barrier dividing the box in half. Suppose the particles interact by means of a two-particle potential of the form $\sum_{j<k} V(\mathbf{x}^j - \mathbf{x}^k)$ (Sect. 2.3.2) and that $V(\mathbf{x}^j - \mathbf{x}^k)$ is very small unless the two particles are close together. There will typically be far more pairs of nearby particles in which the two particles are on the same side of the box than nearby pairs on opposite sides. Thus, even though the interaction between the two systems may substantially affect the behavior of the composite system over long periods of time, it is

still reasonable to think of $\hat{H}_1 \otimes I$ as "the energy of the first subsystem" and $I \otimes \hat{H}_2$ as "the energy of the second subsystem."

Suppose we start out in a state ρ of the composite system for which the state $\rho^{(1)}$ of the first subsystem is a pure state. If the system is an interacting one, the first subsystem will probably not remain in a pure state at later times. Indeed, suppose that the second subsystem is very large system having temperature T. Then, according to the postulates of quantum statistical mechanics, we are supposed to believe that once the two systems have reached thermal equilibrium, the state of the first subsystem will be given by the following highly mixed state:

$$\rho^{(1)} = \frac{1}{Z(\beta)} e^{-\beta \hat{H}_1}. \tag{19.8}$$

Here $\beta = 1/(k_B T)$, where k_B is Boltzmann's constant, and $Z(\beta)$ is a normalization constant, known as the *partition function* of the theory, given by $Z(\beta) = \mathrm{trace}(e^{-\beta \hat{H}_1})$.

Of course, for this idea to make sense, $e^{-\beta \hat{H}_1}$ must be trace class. This will be the case provided that $\hat{H}_1$ has discrete spectrum with eigenvalues tending to $+\infty$ at some reasonable rate. Thus, in quantum statistical mechanics, the expectation value of some observable A for the first subsystem will be (once equilibrium is reached)

$$\langle A \rangle = \frac{1}{Z} \mathrm{trace}(e^{-\beta \hat{H}_1} A). \tag{19.9}$$

In particular, when $A = \hat{H}_1$, (19.9) provides a natural generalization of Planck's model of blackbody radiation; compare Exercise 2 in Chap. 1.

19.6 Multiple Particles: Bosons and Fermions

As discussed in Sect. 17.8, each type of particle (electron, proton, neutron, etc.) has a *spin* l, where the possible value for l are

$$l = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots.$$

The Hilbert space for a particle moving in $\mathbb{R}^3$ and having spin l is $L^2(\mathbb{R}^3)\hat{\otimes} V_l$, where V_l is a finite-dimensional Hilbert space that carries an irreducible *projective* unitary representation of $\mathsf{SO}(3)$ of dimension $2l+1$. There is a natural unitary identification of $L^2(\mathbb{R}^3)\hat{\otimes} V_l$ with $L^2(\mathbb{R}^3; V_l)$, the space of square-integrable functions on $\mathbb{R}^3$ with values in V_l, in which the element $\psi \otimes v$ of $L^2(\mathbb{R}^3)\hat{\otimes} V_l$ is identified with the function

$$\mathbf{x} \mapsto \psi(\mathbf{x}) v$$

in $L^2(\mathbb{R}^3; V_l)$.

Now, we have already mentioned, in Sect. 3.11, the idea that in quantum mechanics, *identical particles are indistinguishable.* Let us think about this in the case of two identical particles with spin l. Our first guess as to the Hilbert space for such a system is the tensor product of two copies of $L^2(\mathbb{R}^3; V_l)$, which may be identified with

$$L^2(\mathbb{R}^6; V_l \otimes V_l).$$

If ψ is a unit vector in this space, thought of as a pure state, then saying that the two particles are "indistinguishable" means that $\psi(\mathbf{x}^2, \mathbf{x}^1)$ should represent the same physical state as $\psi(\mathbf{x}^1, \mathbf{x}^2)$, that is, $\psi(\mathbf{x}^2, \mathbf{x}^1) = c\psi(\mathbf{x}^1, \mathbf{x}^2)$ for some nonzero constant c. Applying this rule twice shows that c must be either 1 or -1.

A variety of theoretical and experimental considerations suggest the following principle: For particles with integer spin ($l = 0, 1, \ldots$), the constant c in the preceding paragraph is 1, whereas for particles with half-integer spin ($l = 1/2, 3/2, \ldots$) the constant c is -1. Particles with integer spin are called *bosons* and particles with half-integer spin are called *fermions.* We encode the discussion in the two preceding paragraphs in the following axiom.

Axiom 11 *Consider a collection of N identical particles moving in $\mathbb{R}^3$ and having integer spin l. Then the Hilbert space for such a collection is the subspace of $L^2(\mathbb{R}^{3N}; (V_l)^{\otimes N})$ consisting of those square-integrable functions ψ for which*

$$\psi(\mathbf{x}^{\sigma(1)}, \mathbf{x}^{\sigma(2)}, \ldots, \mathbf{x}^{\sigma(N)}) = \psi(\mathbf{x}^1, \mathbf{x}^2, \ldots, \mathbf{x}^N)$$

for every permutation σ. Consider also a collection of N identical particles moving in $\mathbb{R}^3$ and having half-integer spin l. Then the Hilbert space for such a collection is the subspace of $L^2(\mathbb{R}^{3N}; (V_l)^{\otimes N})$ consisting of those square-integrable functions ψ for which

$$\psi(\mathbf{x}^{\sigma(1)}, \mathbf{x}^{\sigma(2)}, \ldots, \mathbf{x}^{\sigma(N)}) = \operatorname{sign}(\sigma)\psi(\mathbf{x}^1, \mathbf{x}^2, \ldots, \mathbf{x}^N)$$

for every permutation σ.

One may well ask *why* Axiom 11 holds. More specifically, one may first ask why it is that identical particles are indistinguishable, and then separately ask why integer-spin particles are bosons and half-integer-spin particles are fermions. Both questions are best answered from the point of view of quantum field theory, to which ordinary nonrelativistic quantum mechanics is an approximation.

In field theory, one starts with a "classical" field theory, meaning a differential equation for functions $\phi(\mathbf{x}, t)$ on $\mathbb{R}^4$ with values in some finite-dimensional vector space. Electromagnetic fields, for example, are—at any one fixed time—functions on $\mathbb{R}^3$ with values in $\mathbb{R}^6$, where $\mathbb{R}^6$ describes the three components of the electric field and the three components of the magnetic field. These functions on $\mathbb{R}^3$ then evolve in time according to Maxwell’s equation. In *quantum* field theory, one regards, say, Maxwell’s equations as a sort of infinite-dimensional dynamical system, which we may quantize in something like the way we quantize Newton’s equation to get ordinary nonrelativistic quantum mechanics. In the quantum version of Maxwell’s equations, the energy in each mode of the fields is “quantized,” meaning that one can only add energy to each mode in multiples of a certain unit (or “quantum”) of energy. This is analogous to the quantum harmonic oscillator, in which the allowed energies differ by integer multiples of the $\hbar\omega$. In quantum field theory, then, a *particle* is one quantum of excitation of a certain field.

For simplicity, let us think of a field theory in which the classical fields take values in $\mathbb{R}$. Then even at the classical level, it is possible to think that we have something like particles, namely localized bumps in the field $\phi(\mathbf{x})$ located at several different points in space. These bumps might, for example, be in the shape of a Gaussian wave-packet, that is, a Gaussian envelope multiplied by a sinusoidally oscillating function. From this point of view, we can gain some understanding of why identical particles are indistinguishable. Suppose we have a Gaussian wave packet near a point $\mathbf{a}$ in $\mathbb{R}^3$ and then an identically shaped Gaussian wave packet near another point $\mathbf{b}$. The state $\phi(\mathbf{x})$ of the field is precisely the same as if we have a packet near $\mathbf{b}$ and then also a packet near $\mathbf{a}$. That is to say, there is no distinct state of the system that corresponds to interchanging the two particles; whichever bump we think of as the “first” particle, we have the same field $\phi(\mathbf{x})$. Even in the quantum version of such a system, there no meaning to asking which is the first particle and which is the second. Thus, even in nonrelativistic quantum mechanics, which is a low-energy approximation to quantum field theory, we expect identical particles to be indistinguishable.

Although the preceding discussion does not explain the distinction between bosons and fermions, that distinction also emerges from quantum field theory, through something called the *spin–statistics theorem* (see, e.g., [38]).

19.7 “Statistics” and the Pauli Exclusion Principle

The spin of an electron is equal to $1/2$ and electrons are, therefore, fermions. The famous *Pauli exclusion principle* is a consequence of the fermionic nature of electrons. Pauli’s principle states that two electrons cannot be in the same state at the same time. This means that if ψ is a square-integrable, $\mathbb{C}^2$-valued function on $\mathbb{R}^3$ (which could describe the state of a single electron), then the function $\Psi : \mathbb{R}^6 \to \mathbb{C}^2 \otimes \mathbb{C}^2$ given by

$$\Psi(\mathbf{x}^1, \mathbf{x}^2) = \psi(\mathbf{x}^1) \otimes \psi(\mathbf{x}^2)$$

is *not* a possible state of a two-electron system, since Ψ does not satisfy Axiom 11. On the other hand, if ψ_1 and ψ_2 are two linearly independent elements of $L^2(\mathbb{R}^3;\mathbb{C}^2)$, then the function $\Phi:\mathbb{R}^6\to\mathbb{C}^2\otimes\mathbb{C}^2$ given by

$$\Phi(\mathbf{x}^1,\mathbf{x}^2)=\psi_1(\mathbf{x}^1)\psi_2(\mathbf{x}^2)-\psi_2(\mathbf{x}^1)\psi_1(\mathbf{x}^2) \tag{19.10}$$

is a possible state of a two-electron system. [If ψ_1 and ψ_2 are independent, then Φ is a nonzero element of $L^2(\mathbb{R}^6;\mathbb{C}^2\otimes\mathbb{C}^2)$, which can then be normalized to be a unit vector. See Exercise 10.]

Let us try to understand the implications of the Pauli exclusion principle for multielectron atoms. Let us model an N-electron atom as having a nucleus with positive charge Nq, where the charge of a single electron is $-q$. Since the nucleus is much more massive than the electrons, we can treat the nucleus as being fixed and the electrons as moving in potential of the form $-Nq/\left|\mathbf{x}\right|$. As a *very* rough approximation to the structure of such an atom, we can ignore the electron–electron interaction and take a Hamiltonian of the form

$$\hat{H}=\sum_{j=1}^{N}\left(-\frac{\hbar^2}{2m}\Delta^j-\frac{Nq^2}{\left|\mathbf{x}^j\right|}\right),$$

where Δ^j is the Laplacian acting on the jth variable. That is, we are taking our Hamiltonian to be simply

$$(\hat{H}\otimes I\otimes I\otimes\cdots\otimes I)+(I\otimes\hat{H}\otimes I\otimes\cdots\otimes I)+(I\otimes I\otimes\hat{H}\otimes\cdots\otimes I)+\cdots,$$

where $\hat{H}$ is the Hamiltonian for a single electron.

If, say, N is even, the lowest-energy state for this Hamiltonian in the antisymmetric subspace of $L^2(\mathbb{R}^{3N};(\mathbb{C}^2)^{\otimes N})$ will be

$$\begin{aligned}&\Psi_0(\mathbf{x}^1,\mathbf{x}^2,\ldots,\mathbf{x}^N)\\&\quad=\mathrm{AS}\left(\psi_0^+(\mathbf{x}^1)\otimes\psi_0^-(\mathbf{x}^2)\otimes\psi_1^+(\mathbf{x}^3)\otimes\cdots\otimes\psi_{N/2}^+(\mathbf{x}^{N-1})\otimes\psi_{N/2}^-(\mathbf{x}^N)\right).\end{aligned} \tag{19.11}$$

If N is odd, the product ends with $\psi^+_{(N+1)/2}(\mathbf{x}^N)$. The notation in (19.11) is as follows. First, AS is the antisymmetrization operator, given by

$$\mathrm{AS}(f)(\mathbf{x}^1,\ldots,\mathbf{x}^N)=\sum_{\sigma\in S^N}\mathrm{sign}(\sigma)f(\mathbf{x}^{\sigma(1)},\mathbf{x}^{\sigma(2)},\cdots,\mathbf{x}^{\sigma(N)}).$$

Second, the functions $\psi_0,\psi_1,\psi_2,\ldots$ are the eigenvectors in $L^2(\mathbb{R}^3)$ for the Hamiltonian of a single particle in $\mathbb{R}^3$ moving in a potential of the form $-Nq^2/\left|\mathbf{x}\right|$, arranged so that the eigenvalues of ψ_j are weakly increasing with j. The ψ_j's are just the states computed in Chap. 18, but with q replaced by $\sqrt{N}q$. Third, $\psi_j^+(\mathbf{x})$ denotes $\psi_j(\mathbf{x})\otimes e_1$ and $\psi_j^-(\mathbf{x})$ denotes $\psi_j(\mathbf{x})\otimes e_2$, where $\{e_1,e_2\}$ is the standard basis for $\mathbb{C}^2$.

What the expression for Ψ_0 means is that, if we ignore (at first) the interaction between the electrons, but retain the Pauli exclusion principle, then we put the first electron into the ground state of the single-electron system, with "spin up" (i.e., tensored with e_1). Then we put the second electron into the ground state with "spin down" (tensored with e_2). Then the third electron goes into the first excited state of the single-electron system with spin up, and so on. Of course, this model of a multielectron atom is very rough, since the interaction between the electrons actually plays a significant role. Nevertheless, this model highlights the critical role played by the exclusion principle, which forces successive electrons to go into higher and higher energy states. In particular, this crude approximation suggests (correctly!) that even for more realistic models of a multielectron atom, the lowest energy level in the antisymmetric subspace of $L^2(\mathbb{R}^{3N}; (\mathbb{C}^2)^{\otimes N})$ is much higher than the lowest energy level of the same Hamiltonian in all of $L^2(\mathbb{R}^{3N}; (\mathbb{C}^2)^{\otimes N})$.

Meanwhile, in quantum statistical mechanics, one considers a large collection of identical particles confined to some finite region of space. If the system is isolated (rather than in thermal equilibrium with its environment), the goal of statistical mechanics is to "count" the number $N(E)$ of quantum states with energy less than E, as a function of E. [That is, $N(E)$ is number of eigenvalues for the Hamiltonian less than E, counted with their multiplicity.] As the preceding discussion of the Pauli exclusion principle suggests, we will get very different answers for $N(E)$ if the particles are fermions than if they are bosons. Bosons are said to follow *Bose–Einstein statistics*, whereas fermions are said to follow *Fermi–Dirac statistics*. The term "statistics" here refers to the different behavior of the two types of particles in quantum statistical mechanics. The spin–statistics theorem in quantum field theory tells us that particles with integer spin have to be bosons (obeying Bose–Einstein statistics) and particles with half-integer spin have to be fermions (obeying Fermi–Dirac statistics).

One fascinating example of quantum statistical mechanics occurs when the particles are bosons and the interaction between particles is negligible. In that case, the lowest energy state will simply be

$$\Psi_0(\mathbf{x}^1, \mathbf{x}^2, \ldots, \mathbf{x}^N) = \psi_0(\mathbf{x}^1) \otimes \psi_0(\mathbf{x}^2) \otimes \cdots \otimes \psi_0(\mathbf{x}^N),$$

where ψ_0 is the ground state of the single-particle system. Now, quantum statistical mechanics tells us that at a given temperature, the state of the system will be an (incoherent) superposition of the ground state and the various excited states. If the temperature is low enough, then the coefficient of the ground state will be close to 1, and thus, "all the particles are in the ground state." A system in such a state is called a *Bose–Einstein condensate*, a state that was predicted on theoretical grounds by Satyendra Nath Bose and Einstein in the 1920s. Bose–Einstein condensates were first observed experimentally in laser-cooled gases in June 1995 by Eric Cornell and Carl Wieman, in work for which they, along with Wolfgang Ketterle, were awarded the 2001 Nobel Prize in physics.

19.8 Exercises

1. Suppose that X is a Hilbert–Schmidt operator on $\mathbf{H}$ and that $\{e_j\}$ is an orthonormal basis for $\mathbf{H}$. Show that

$$\|X\|_{HS}^2 = \sum_{j,k} |\langle e_j, Xe_k\rangle|^2 .$$

2. Given $\phi, \psi \in \mathbf{H}$, let $|\phi\rangle\langle\psi|$ denote the operator defined in Notation 3.28. Show that if $A \in \mathcal{B}(\mathbf{H})$ is trace class, then

$$\operatorname{trace}(A\,|\phi\rangle\langle\psi|) = \langle\psi, A\phi\rangle .$$

Hint: If $\{e_j\}$ is an orthonormal basis for $\mathbf{H}$, then for any $\chi \in \mathbf{H}$, we have $\chi = \sum_j \langle e_j, \chi\rangle\, e_j$.

3. Suppose $\Phi : \mathcal{B}(\mathbf{H}) \to \mathbb{C}$ is a linear functional with the properties (1) that $\Phi(A)$ is real whenever A is self-adjoint and (2) that $\Phi(A)$ is real and non-negative whenever A is self-adjoint and non-negative. Show that if A is self-adjoint, then

$$-\|A\|\,\Phi(I) \leq \Phi(A) \leq \|A\|\,\Phi(I).$$

Conclude that Φ is bounded relative to the operator norm on $\mathcal{B}(\mathbf{H})$.

Hint: Show that if A is self-adjoint, then $\|A\|\,I + A$ and $\|A\|\,I - A$ are non-negative.

4. An operator $A \in \mathcal{B}(\mathbf{H})$ is said to have *finite rank* if range(A) is finite dimensional.

   (a) Show that if $A \in \mathcal{B}(\mathbf{H})$ has finite rank, then so does A^*.

   (b) Given $A \in \mathcal{B}(\mathbf{H})$, show that A has finite rank if and only if there exist vectors $\phi_1, \ldots, \phi_N$ and $\psi_1, \ldots, \psi_N$ such that

$$A = |\phi_1\rangle\langle\psi_1| + \cdots + |\phi_N\rangle\langle\psi_N| .$$

   (c) Let A be any element of $\mathcal{B}(\mathbf{H})$, let $\{e_j\}$ be an orthonormal basis for $\mathbf{H}$, and let P_N be the orthogonal projection onto the span of $e_1, \ldots, e_N$. Show that $P_N A$ has finite rank and that for all $\psi \in \mathbf{H}$, we have

$$\lim_{N\to\infty} \|P_N A\psi - A\psi\| = 0.$$

Note: This result shows that each bounded operator can be expressed as a strong limit of finite-rank operators. By contrast, if $\dim \mathbf{H} = \infty$, then Part (a) of Exercise 5 shows that not every bounded operator can be expressed as an operator-norm limit of finite-rank operators.

5. In this exercise, assume that $\dim \mathbf{H} = \infty$.
   (a) Show that if A has finite rank, then $\|A + cI\| \geq |c|$ for any $c \in \mathbb{C}$. (With $c = -1$, this shows that I is not an operator-norm limit of finite-rank operators.)
   (b) Let $\mathcal{K}(\mathbf{H})$ denote the closure of the finite-rank operators with respect to the operator norm on $\mathcal{B}(\mathbf{H})$. Let V denote the space of operators of the form $B + cI$, with $B \in \mathcal{K}(\mathbf{H})$. Define a linear functional $\Phi : V \to \mathbb{C}$ by $\Phi(B + cI) = c$ for all $B \in \mathcal{K}(\mathbf{H})$. Show that $|\Phi(A)| \leq \|A\|$ for all $A \in V$.

   Note: It can be shown that $\mathcal{K}(\mathbf{H})$ is precisely the space of compact operators on $\mathbf{H}$.
   (c) Let $\Psi_1 : \mathcal{B}(\mathbf{H}) \to \mathbb{C}$ be any linear functional such that $\Psi_1 = \Phi$ on V and such that $|\Psi_1(A)| \leq \|A\|$ for all $A \in \mathcal{B}(\mathbf{H})$. (Such a functional exists by the Hahn–Banach theorem.) Let $\Psi_2 : \mathcal{B}(\mathbf{H}) \to \mathbb{C}$ be defined by

$$\Psi_2(A) = \frac{1}{2}(\Psi_1(A) + \overline{\Psi_1(A^*)}).$$

   Show that Ψ_2 satisfies Properties 1, 2, and 3 of Definition 19.6, but that there does not exist any density matrix ρ such that $\Psi_2(A) = \operatorname{trace}(\rho A)$ for all $A \in \mathcal{B}(\mathbf{H})$. (Thus, in light of Theorem 19.9, Ψ_2 must not satisfy Property 4 of Definition 19.6.)

6. In Exercises 6, 7, and 8, assume that each density matrix ρ is compact, so that ρ has an orthonormal basis $\{e_j\}$ of eigenvectors, for which the associated eigenvalues $\{\lambda_j\}$ are real and tend to zero as j tends to infinity. (Compare Theorem VI.16 in [34].)

   Show that a density matrix ρ is a pure state if and only if $\operatorname{trace}(\rho^2) = 1$.

7. (a) Show that each mixed state ρ is a nontrivial convex combination of other density matrices.
   (b) Show that a pure state cannot be expressed as a nontrivial convex combination of other density matrices.

   Hint: Show that the function $f(\lambda) := \operatorname{trace}\left((\lambda\rho_1 + (1-\lambda)\rho_2)^2\right)$ is a convex function of λ.

8. For any density matrix ρ, show that the von Neumann entropy $S(\rho) := \operatorname{trace}(-\rho \log \rho)$ is zero if and only if ρ is a pure state.

9. Prove Lemma 19.14.

   Hint: First use the principle of uniform boundedness (Theorem A.40) to show that there exists a constant C with $\|A_n\| \leq C$ for all n. Then, if $\{f_j\}$ is an orthonormal basis for $\mathbf{H}_2$, decompose $\mathbf{H}_1 \hat{\otimes} \mathbf{H}_2$ as the Hilbert space direct sum of the subspaces $\mathbf{H}_1 \otimes f_j$, where each of these subspaces is isometrically identified with $\mathbf{H}_1$ in the obvious way.

10. Suppose that ψ_1 and ψ_2 are two linearly independent elements of $L^2(\mathbb{R}^3; \mathbb{C}^2)$. Show that the function Φ in (19.10) is a nonzero element of $L^2(\mathbb{R}^6; \mathbb{C}^2 \otimes \mathbb{C}^2)$.