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PART I

SECOND QUANTIZATION

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1 Elementary quantum mechanics

We assume that the reader is already acquainted with elementary quantum mechanics. An introductory course in quantum mechanics usually addresses most if not all concepts discussed in this chapter. However, there are many ways to teach and learn these subjects. By including this chapter, we can make sure that we understand the basics in the same way. We advise students to read the first six sections (those on classical mechanics, the Schrödinger equation, the Dirac formulation, and perturbation theory) before going on to the advanced subjects of the next chapters, since these concepts will be needed immediately. While the other sections of this chapter address fundamentals of quantum mechanics as well, they do not have to be read right away and are referred to in the corresponding places of the following chapters. The text of this chapter is meant to be concise, so we do not supply rigorous proofs or lengthy explanations. The basics of quantum mechanics should be mastered at an operational level: please also check Table 1.1 and the exercises at the end of the chapter.

1.1 Classical mechanics

Let us start by considering a single particle of mass m, which is moving in a coordinate-dependent potential $V(\mathbf{r})$. In classical physics, the state of this particle at a given moment of time is fully characterized by two vectors, its coordinate $\mathbf{r}(t)$ and its momentum $\mathbf{p}(t)$. Since classical mechanics is a completely deterministic theory, the state of the particle in the future – its position and momentum – can be unambiguously predicted once the initial state of the particle is known. The time evolution of the state is given by Newton's well-known equations

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} = -\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}} \quad \text{and} \quad \frac{d\mathbf{r}}{dt} = \mathbf{v} = \frac{\mathbf{p}}{m}. \tag{1.1}$$

Here the force $\mathbf{F}$ acting on the particle is given by the derivative of the potential $V(\mathbf{r})$, and momentum and velocity are related by $\mathbf{p} = m\mathbf{v}$.

Classical mechanics can be formulated in a variety of equivalent ways. A commonly used alternative to Newton's laws are Hamilton's equations of motion

$$\frac{d\mathbf{p}}{dt} = -\frac{\partial H}{\partial \mathbf{r}} \quad \text{and} \quad \frac{d\mathbf{r}}{dt} = \frac{\partial H}{\partial \mathbf{p}}, \tag{1.2}$$

where the Hamiltonian function $H(\mathbf{r}, \mathbf{p})$ of a particle is defined as the total of its kinetic and potential energy,

$$H = \frac{p^2}{2m} + V(\mathbf{r}). \tag{1.3}$$

One advantage of this formalism is a clear link to the quantum mechanical description of the particle we present below.

An important property of Hamilton's equations of motion is that the Hamiltonian H itself is a constant of motion, i.e. $dH/dt = 0$ in the course of motion.

Control question. Can you prove that $dH/dt = 0$ directly follows from the equations of motion (1.2)?

This is natural since it represents the total energy of the particle, and energy is conserved. This conservation of energy does not hold for Hamiltonians that explicitly depend on time. For instance, an external time-dependent force $\mathbf{F}_{\text{ext}}$ gives an addition $-\mathbf{F}_{\text{ext}} \cdot \mathbf{r}$ to the Hamiltonian. By changing the force, we can manipulate the particle and change its energy.

1.2 Schrödinger equation

The quantum mechanical description of the same particle does not include any new parameters, except for a universal constant $\hbar$. The dynamics of the particle are still determined by its mass m and the external potential $V(\mathbf{r})$. The difference is now that the state of the particle is no longer characterized by just two vectors $\mathbf{r}(t)$ and $\mathbf{p}(t)$, but rather by a continuous function of coordinate $\psi(\mathbf{r}, t)$ which is called the *wave function* of the particle. The interpretation of this wave function is probabilistic: its modulus square $|\psi(\mathbf{r}, t)|^2$ gives the probability density to find the particle at time t at the point $\mathbf{r}$. For this interpretation to make sense, the wave function must obey the normalization condition

$$\int d\mathbf{r}\, |\psi(\mathbf{r}, t)|^2 = 1, \tag{1.4}$$

i.e. the total probability to find the particle anywhere is 1, or in other words, the particle must be *somewhere* at any moment of time.

Since this is a probabilistic description, we never know exactly where the particle is. If the particle is at some time t_0 in a definite state $\psi(\mathbf{r}, t_0)$, then it is generally still impossible to predict at which point in space we will find the particle if we look for it at another time t. However, despite its intrinsically probabilistic nature, quantum mechanics is a deterministic theory. Starting from the state $\psi(\mathbf{r}, t_0)$, the state $\psi(\mathbf{r}, t)$ at any future time t is completely determined by an evolution equation, the time-dependent *Schrödinger equation*

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi = \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V(\mathbf{r}) \right\} \psi. \tag{1.5}$$

Erwin Schrödinger (1887–1961)
Shared the Nobel Prize in 1933 with Paul Dirac for "the discovery of new productive forms of atomic theory."

Before 1925, quantum mechanics was an inconsistent collection of results describing several otherwise unexplained observations. In 1925–1926 two different general theories of quantum mechanics were presented: Heisenberg proposed a matrix mechanics of non-commuting observables, explaining discrete energy levels and quantum jumps, while Schrödinger put forward wave mechanics, attributing a function of coordinates to a particle and a wave-like equation governing its evolution. Schrödinger's theory seemed (and seems) less abstract. Besides, it provided a clear mathematical description of the wave–particle duality, a concept actively advocated by Einstein. Therefore, many people favored his theory over Heisenberg's. As we explain in this chapter, both theories are equivalent. However, for many the Schrödinger equation remains the core of quantum mechanics.

Erwin Schrödinger had a life with several restless periods in it. He was born and educated in Vienna, where he stayed till 1920, only interrupted by taking up his duty at the Italian front in the first world war. In the years 1920–1921 he successively accepted positions in Jena, Stuttgart, Breslau, and finally Zurich, where he remained for several years. The intense concentration that allowed him to develop his quantum theory he achieved during a Christmas stay in 1925 in a sanatorium in Arosa. But in 1927 he moved again, this time to Berlin. When the Nazis came to power in 1933 he decided to leave the Reich, and so he became itinerant again: Oxford, Edinburgh, Graz, Rome, Ghent . . . In 1940 he finally took a position in Dublin where he stayed till his retirement in 1956.

In this notation, $\hat{H}$ is an *operator*: it acts on the function ψ and it returns another function, the time derivative of ψ. This operator $\hat{H}$ is called the Hamiltonian operator, since it represents the total energy of the particle. This is best seen if we rewrite $\hat{H}$ in terms of the momentum operator $\hat{\mathbf{p}} \equiv -i\hbar\partial_{\mathbf{r}}$ and position operator $\hat{\mathbf{r}} \equiv \mathbf{r}$. We then see that $\hat{H}$ is identical to (1.3) but with the vectors $\mathbf{r}$ and $\mathbf{p}$ replaced by their operator analogues.

Not only momentum and position, but any physical property can be expressed in terms of operators. For an arbitrary observable A, we can find the corresponding quantum mechanical operator $\hat{A}$. The average value of this observable, sometimes called expectation value, in a given quantum state reads

$$\langle A \rangle = \int d\mathbf{r}\, \psi^*(\hat{A}\psi), \tag{1.6}$$

ψ^* being the complex conjugate of ψ.

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Control question. Can you write the integral in (1.6) for $\langle x^2 \rangle$? And for $\langle p_x^2 \rangle$?

If a state is known to have a definite value of A, let us say A_0, then the wave function of this state must be an eigenfunction of $\hat{A}$, i.e. $\hat{A}\psi = A_0\psi$. We indeed see from (1.6) that this would result in $\langle A \rangle = A_0$. To prove that not only the expectation value of A is A_0, but also that A_0 is actually the *only* value which can be found for A, we use the definition in (1.6) and compute the fluctuations in the observable A,

$$\langle A^2 \rangle - \langle A \rangle^2 = \int d\mathbf{r}\, \psi^*(\hat{A}\hat{A}\psi) - \left(\int d\mathbf{r}\, \psi^*(\hat{A}\psi) \right)^2. \tag{1.7}$$

If ψ in the above formula is an eigenfunction of the operator $\hat{A}$, the two terms cancel each other and the fluctuations in A become zero. This proves the above statement: any eigenstate of the operator $\hat{A}$ has a well-defined value for the observable A.

As we have already mentioned, the Hamiltonian operator represents the total energy of the particle. Therefore, a state with a definite energy E must obey the eigenvalue equation

$$\hat{H}\psi = E\psi. \tag{1.8}$$

We see that the Schrödinger equation predicts a simple time dependence for such a state,

$$\psi(\mathbf{r}, t) = \exp\{-iEt/\hbar\}\psi(\mathbf{r}). \tag{1.9}$$

These states are called stationary states, and the eigenvalue equation (1.8) is called the stationary Schrödinger equation.

Control question. Why are these states called stationary, while they retain time dependence? *Hint*. Consider (1.6).

Let us now consider the simple case of a free particle ("free" means here "subject to no forces") in an infinite space. This corresponds to setting the potential $V(\mathbf{r})$ to zero or to a constant value everywhere. In this case the solutions of the Schrödinger equation take the form of plane waves

$$\psi_{\mathbf{p}}(\mathbf{r}, t) = \frac{1}{\sqrt{\mathcal{V}}} \exp\{-iEt/\hbar\} \exp\{i\mathbf{p} \cdot \mathbf{r}/\hbar\}, \tag{1.10}$$

where the energy of the particle is purely kinetic, $E = p^2/2m$. The factor $1/\sqrt{\mathcal{V}}$ results from the normalization condition (1.4), where we assumed that the particle dwells in a large but finite volume $\mathcal{V}$. For a free particle, this is of course artificial. To describe an actually infinite space, we have to take the limit $\mathcal{V} \to \infty$. The assumption of a finite $\mathcal{V}$, however, is extremely constructive and we use it throughout the book.

We see that the plane wave states (1.10) are eigenfunctions of the momentum operator, $\hat{\mathbf{p}}\psi_{\mathbf{p}} = \mathbf{p}\psi_{\mathbf{p}}$, and therefore all carry a definite momentum $\mathbf{p}$. In a finite volume, however, only a discrete subset of all momentum states is allowed. To find this set, we have to take into account the boundary conditions at the edges of the volume. Having the volume $\mathcal{V}$ is artificial anyway, so we can choose these conditions at will. An easy and straightforward choice is to take a block volume with dimensions $L_x \times L_y \times L_z$ and assume *periodic boundary conditions* over the dimensions of the block. This gives the conditions

$\psi_{\mathbf{p}}(x+L_x,y,z,t) = \psi_{\mathbf{p}}(x,y+L_y,z,t) = \psi_{\mathbf{p}}(x,y,z+L_z,t) = \psi_{\mathbf{p}}(x,y,z,t)$, resulting in a set of quantized momentum states

$$\mathbf{p} = 2\pi\hbar\left(\frac{n_x}{L_x},\frac{n_y}{L_y},\frac{n_z}{L_z}\right), \tag{1.11}$$

where n_x, n_y, and n_z are integers.

Control question. Can you derive (1.11) from the periodic boundary conditions and (1.10) yourself?

As we see from (1.11), there is a single allowed value of $\mathbf{p}$ per volume $(2\pi\hbar)^3/\mathcal{V}$ in momentum space, and therefore the density of momentum states increases with increasing size of the system, $D(\mathbf{p}) = \mathcal{V}/(2\pi\hbar)^3$. Going toward the limit $\mathcal{V} \to \infty$ makes the spacing between the discrete momentum values smaller and smaller, and finally results in a continuous spectrum of $\mathbf{p}$.

The above plane wave function is one of the simplest solutions of the Schrödinger equation and describes a free particle spread over a volume $\mathcal{V}$. In reality, however, wave functions are usually more complex, and they also can have many components. For example, if the plane wave in (1.10) describes a single electron, we have to take the *spin* degree of freedom of the electron into account (see Section 1.7). Since an electron can be in a "spin up" or "spin down" state (or in any superposition of the two), we generally have to use a two-component wave function

$$\psi_{\mathbf{p}}(\mathbf{r},t) = \begin{pmatrix} \psi_{\mathbf{p},\uparrow}(\mathbf{r},t) \\ \psi_{\mathbf{p},\downarrow}(\mathbf{r},t) \end{pmatrix}, \tag{1.12}$$

where the moduli squared of the two components give the relative probabilities to find the electron in the spin up or spin down state as a function of position and time.

1.3 Dirac formulation

In the early days of quantum mechanics, the wave function had been thought of as an actual function of space and time coordinates. In this form, it looks very similar to a *classical field*, i.e. a (multi-component) quantity which is present in every point of coordinate space, such as an electric field $\mathbf{E}(\mathbf{r},t)$ or a pressure field $p(\mathbf{r},t)$. However, it appeared to be very restrictive to regard a wave function merely as a function of coordinates, as the Schrödinger formalism implies. In his Ph.D. thesis, Paul Dirac proposed to treat wave functions rather as elements of a multi-dimensional linear vector space, a Hilbert space. Dirac's formulation of quantum mechanics enabled a reconciliation of competing approaches to quantum problems and revolutionized the field.

In Dirac's approach, every wave function is represented by a vector, which can be put as a "ket" $|\psi\rangle$ or "bra" $\langle\psi|$. Operators acting on the wave functions, such as the momentum and position operator, make a vector out of a vector and can therefore be seen as matrices in this vector space. For instance, a Hamiltonian $\hat{H}$ in general produces

$$\hat{H}|\psi\rangle = |\chi\rangle. \tag{1.13}$$

An eigenstate of an observable $\hat{A}$ in this picture can be seen as an eigenvector of the corresponding matrix. For any real physical quantity, this matrix is Hermitian, that is $\hat{A}^\dagger = \hat{A}$. As we know, an eigenstate of the operator $\hat{A}$ has a definite value of A, which now simply is the corresponding eigenvalue of the matrix. By diagonalizing the matrix of an observable one retrieves all possible values which can be found when measuring this observable, and the hermiticity of the matrix guarantees that all these eigenvalues are real.

One of the definitions of a Hilbert space is that the inner product of two vectors in the space, $\langle\psi|\chi\rangle = (\langle\chi|\psi\rangle)^*$, exists. Let us try to make a connection with the Schrödinger approach. In the Hilbert space of functions of three coordinates $\mathbf{r}$, the Dirac notation implies the correspondence $|\psi\rangle \leftrightarrow \psi(\mathbf{r})$ and $\langle\psi| \leftrightarrow \psi^*(\mathbf{r})$, and the inner product of two vectors is defined as

$$\langle\psi|\chi\rangle = \int d\mathbf{r}\, \psi^*(\mathbf{r})\chi(\mathbf{r}). \tag{1.14}$$

We see that the normalization condition (1.4) in this notation reads $|\,\langle\psi|\psi\rangle\,|^2 = 1$, and the expectation value of an operator $\hat{A}$ in a state ψ is given by $\langle\psi|\hat{A}|\psi\rangle$.

The dimensionality of the Hilbert space is generally infinite. To give a simple example, let us consider a single spinless particle trapped in a potential well, meaning that $V(\mathbf{r}) \to \infty$ when $|\mathbf{r}| \to \infty$. If one solves the Schrödinger equation for this situation, one finds a set of stationary states, or levels, with a discrete energy spectrum

$$\psi_n(\mathbf{r}, t) = \exp\{-iE_n t/\hbar\}\psi_n(\mathbf{r}), \tag{1.15}$$

where n labels the levels. The wave functions $\psi_n(\mathbf{r})$ depend on the potential landscape of the well, and can be quite complicated. This set of eigenstates of the Hamiltonian can be used as a *basis* of the infinite dimensional Hilbert space. This means that, if we denote the basis vectors by $|n\rangle \equiv \psi_n(\mathbf{r}, t)$, we can write any arbitrary vector in this Hilbert space as

$$|\psi\rangle = \sum_n c_n|n\rangle, \tag{1.16}$$

where the sum in principle runs over all integers.

Control question. Can you write the “bra”-version $\langle\psi|$ of (1.16)?

We note that the basis thus introduced possesses a special handy property: it is *orthonormal*, that is, any two basis states satisfy

$$\langle m|n\rangle = \delta_{mn}. \tag{1.17}$$

Conveniently, the normalized eigenfunctions of any Hermitian operator with non-degenerate (all different) eigenvalues form a proper basis. Making use of orthonormality, we can write any linear operator as

$$\hat{A} = \sum_{nm} a_{nm}\, |n\rangle\langle m|\,, \tag{1.18}$$

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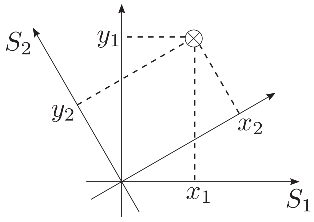

Fig. 1.1 Projections of a vector on the orthogonal axes of a coordinate system. The same point in this two-dimensional space is represented by different vectors in different coordinate systems. The representation (x_1, y_1) in coordinate system S_1 transforms to (x_2, y_2) in coordinate system S_2.

where the complex numbers a_{nm} denote the *matrix elements* of the operator $\hat{A}$, which are defined as $a_{nm} = \langle n|\hat{A}|m\rangle$.

The convenience of the Dirac formulation is the freedom we have in choosing the basis. As is the case with "real" vectors, the basis you choose can be seen as a Cartesian coordinate system, but now in Hilbert space. Let us consider the analogy with usual vectors in two-dimensional space. Any vector then has two components, which are given by the projections of the vector on the orthogonal axes of the coordinate system chosen. When this vector is represented in a different coordinate system, the projections are generally different (see Fig. 1.1). The vector, however, is still the same! Similarly, an arbitrary wave function is defined by a set of its components c_n, which are the projections of the wave function on a certain set of basis vectors. In the case of a discrete set of basis states $|n\rangle$, an arbitrary quantum state $|\psi\rangle$ is written as in (1.16). The projections c_n can then be found from

$$c_n = \langle n|\psi\rangle \,. \tag{1.19}$$

If we were to choose a different set of basis vectors $|n'\rangle$, the components $c_{n'}$ we would find would be different, but still represent the *same* wave function.

The same picture holds for systems with a continuous spectrum, since, as explained above, a continuous spectrum can be approximated by a discrete spectrum with infinitesimally small spacing. Wave functions in the Schrödinger equation are written in a *coordinate* representation. A wave function $\psi(\mathbf{r})$ can be seen as the projection of the state $|\psi\rangle$ on the continuous set of basis vectors $|\mathbf{r}\rangle$, which are the eigenfunctions of the coordinate operator $\hat{\mathbf{r}}$. The same wave function can of course also be expressed in the basis of plane waves given in (1.10). In the space spanned by these plane waves $|\mathbf{p}\rangle$, we write

$$|\psi\rangle = \sum_{\mathbf{p}} c_{\mathbf{p}}|\mathbf{p}\rangle, \tag{1.20}$$

where the components $c_{\mathbf{p}}$ are given by

$$c_{\mathbf{p}} = \langle \mathbf{p}|\psi\rangle = \int \frac{d\mathbf{r}}{\sqrt{\mathcal{V}}}\, e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\psi(\mathbf{r}). \tag{1.21}$$

These components $c_{\mathbf{p}}$ can be seen as a different representation of the same wave function, in this case the *momentum* representation.

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Going over to the continuous limit corresponds to letting $\mathcal{V} \to \infty$. In this limit, the sum in (1.20) can be replaced by an integral provided that the density of states $D(\mathbf{p})$ is included in the integrand and that the components $c_\mathbf{p}$ converge to a smooth function $c(\mathbf{p})$ of $\mathbf{p}$. This is the case when the wave functions are concentrated in a finite region of coordinate space. In this case, the artificial large volume $\mathcal{V}$ is redundant and to get rid of it, it is common to rescale $c_\mathbf{p} \to c(\mathbf{p})/\sqrt{\mathcal{V}}$ such that $c(\mathbf{p})$ does not depend on $\mathcal{V}$. With this rescaling the relations (1.21) and $\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle$ become the expressions of the standard Fourier transforms, forward and reverse respectively,

$$c(\mathbf{p}) = \int d\mathbf{r}\, e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\psi(\mathbf{r}) \quad \text{and} \quad \psi(\mathbf{r}) = \int \frac{d\mathbf{p}}{(2\pi\hbar)^3}\, e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} c(\mathbf{p}). \tag{1.22}$$

Control question. Do you see how the relations (1.22) follow from (1.20) and (1.21), using the rescaling $c_\mathbf{p} \to c(\mathbf{p})/\sqrt{\mathcal{V}}$?

So, what are the advantages of the Dirac formulation? First, it brings us from separate quantum particles to the notion of a quantum *system*. A system can be a single particle, or 10^{26} particles interacting with each other, or an electric circuit, or a vacuum – all these examples are considered in this book. In the Dirac formulation they can be described uniformly, since all their quantum states are elements of a Hilbert space. The case of a system consisting of many particles is considered in detail. In the Schrödinger picture, the wave function of such a system becomes a function of all coordinates of all, say 10^{26}, particles, whereas in the Dirac formulation all allowed quantum states are still simply represented by a vector. Of course, for a many-particle problem more states in the Hilbert space are relevant. However, this does not alter the complexity of the representation: a vector remains a vector irrespective of the number of its components.

Second, the Dirac formulation establishes a "democracy" in quantum mechanics. Given a system, it does not matter which basis is used for a description of a wave function. All bases are equal, and the choice of basis is determined by the personal taste of the descriptor rather than by any characteristic of the system.

Third, the formulation is practically important. It converts any quantum problem for any quantum system to a linear algebra exercise. Since wave functions are now represented by vectors and operators by matrices, finding the eigenstates and eigenvalues of any observable reduces to diagonalizing the corresponding operator matrix.

Let us finish by considering the Dirac formulation for a complex system which is obtained by combining two separate systems. Suppose we have systems A and B which are both described by their own wave functions. We assume that the quantum states of system A are vectors in an M_A-dimensional Hilbert space, spanned by a basis $\{|n_A\rangle\} \equiv \{|1_A\rangle, |2_A\rangle, \ldots, |M_A\rangle\}$, while the states of system B are vectors in an M_B-dimensional space with basis $\{|n_B\rangle\} \equiv \{|1_B\rangle, |2_B\rangle, \ldots, |M_B\rangle\}$. If we combine the two systems and create one large system $A + B$, we find that the states of this combined system can be described in a Hilbert space spanned by the *direct product* of the two separate bases, $\{|n_A\rangle\} \otimes \{|n_B\rangle\} \equiv \{|1_A 1_B\rangle, |1_A 2_B\rangle, |2_A 1_B\rangle, |1_A 3_B\rangle, \ldots\}$, which forms a $(M_A M_B)$-dimensional basis.