9

Wave mechanics

In this chapter we shall study a particular realization of quantum mechanics of great practical importance, namely *wave mechanics*, used to describe the motion of one[1] quantum particle in three-dimensional space $\mathbb{R}^3$. It is this realization which serves as the introduction to the fundamentals of quantum mechanics in most textbooks. It amounts to taking the "eigenvectors"[2] $|\vec{r}\,\rangle$ of the position operator $\vec{R}$ as the basis in $\mathcal{H}$, or, in other words, choosing a basis in which the position operator is diagonal. In wave mechanics a state vector can be identified with an element $\varphi(\vec{r})$ of the Hilbert space $L^2_{\vec{r}}(\mathbb{R}^3)$ of functions which are square-integrable in three-dimensional space $\mathbb{R}^3$. This state vector is called the *wave function*, and we shall see that it is identified with the probability amplitude $\langle \vec{r}\,|\varphi\rangle$ for finding the particle in the state $|\varphi\rangle$ localized at position $\vec{r}$. The wave function is normalized by the integrability condition (7.10)

$$\int_{-\infty}^{\infty} \mathrm{d}^3 r\, |\varphi(\vec{r})|^2 = 1. \tag{9.1}$$

Owing to the symmetric roles played by the position and momentum operators, it is also possible to use eigenvectors of $\vec{P}$ and "momentum-space wave functions" $\tilde{\varphi}(\vec{p}) = \langle \vec{p}\,|\varphi\rangle$, which we shall see are the Fourier transforms of the $\varphi(\vec{r})$. After examining the principal properties of the wave functions, we shall study some applications: bound states, scattering, tunneling, and the periodic potential. These applications will first be treated in the simplest case of one dimension. The generalization to three dimensions will permit us to discuss the important notion of the density of states and its use in Fermi's Golden Rule.

9.1 Diagonalization of X and P and wave functions

9.1.1 Diagonalization of X

We wish to study the motion of a quantum particle, and for the time being we restrict this motion to the real line $\mathbb{R}$, on which the particle moves between $-\infty$ and $+\infty$. The relevant

[1] Or more; see the generalization in Section 9.9.3 and Chapter 13.

[2] As we have seen in Section 7.3.1, these objects are not vectors of the Hilbert space, which we have stressed by using quotation marks. However, since we shall make intensive use of these "vectors" in what follows, we shall drop the quotation marks in order to simplify the notation.

physical properties are a priori the position and momentum of the particle, represented mathematically by the operators X and P whose properties we have established in Section 8.3. We shall study the eigenvectors of X starting from the canonical commutation relation between X and P in the form (8.40):

$$\exp\Big(\mathrm{i}\frac{Pa}{\hbar}\Big)\, X\, \exp\Big(-\mathrm{i}\frac{Pa}{\hbar}\Big) = X + aI. \tag{9.2}$$

Let us first of all show that the spectrum of X is continuous. We take $|x\rangle$ to be an eigenvector of X

$$X|x\rangle = x|x\rangle, \tag{9.3}$$

and examine the action of X on the vector $\exp(-\mathrm{i}Pa/\hbar)|x\rangle$:

$$\begin{aligned} X\Big[\exp\Big(-\mathrm{i}\frac{Pa}{\hbar}\Big)|x\rangle\Big] &= \exp\Big(-\mathrm{i}\frac{Pa}{\hbar}\Big)(X + aI)|x\rangle \\ &= (x+a)\Big[\exp\Big(-\mathrm{i}\frac{Pa}{\hbar}\Big)|x\rangle\Big]. \end{aligned} \tag{9.4}$$

We have used the commutation relation (9.2) and the definition (9.3) of the eigenvector $|x\rangle$. The vector $\exp(-\mathrm{i}Pa/\hbar)|x\rangle$ is an eigenvector of X with eigenvalue $(x+a)$, and since a is arbitrary, this shows that all real values of x between $-\infty$ and $+\infty$ are eigenvalues of X. This also proves that the spectrum of x is continuous, and consequently the normalization must be written as in (7.34) using Dirac delta functions:

$$\langle x'|x\rangle = \delta(x - x'). \tag{9.5}$$

In view of the arguments of Section 8.3.1, the result (9.4), which can be written as

$$\exp\Big(-\mathrm{i}\frac{Pa}{\hbar}\Big)|x\rangle = |x+a\rangle,$$

is not surprising, since $\exp(-\mathrm{i}Pa/\hbar)$ is the operator for translation by a which transforms the state $|x\rangle$ exactly localized at x into the state $|x+a\rangle$ exactly localized at $(x+a)$: P is the infinitesimal generator of translations. The vector $|x+a\rangle$ satisfies a normalization condition analogous to (9.5) because the operator $\exp(-\mathrm{i}Pa/\hbar)$ is unitary. If we wish, we can fix the phase of the basis vectors $|x\rangle$ by the condition

$$|x\rangle = \exp\Big(-\mathrm{i}\frac{Px}{\hbar}\Big)|x = 0\rangle. \tag{9.6}$$

Let us return to the physical interpretation. What exactly does the vector $|x\rangle$ represent? According to the postulates of Chapter 4, $|x\rangle$ represents a state in which the position of the particle is known with absolute precision: the particle is localized exactly at the point x on the real line. However, in quantum mechanics it is impossible to realize such a state physically. As we shall soon see, such a state has all possible momenta between $p = -\infty$ and $p = +\infty$ with equal probabilities. The mathematical property "$|x\rangle$ is not an element of the Hilbert space" corresponds to the physical property "$|x\rangle$ is not a realizable physical state." Physically realizable states are always represented by "true" vectors of $\mathcal{H}$, that is, normalizable vectors.

We have implicitly assumed that the eigenvalues x of X are nondegenerate. Of course, this is not necessarily the case; for example, the particle can have spin 1/2, in which case it is necessary to specify whether the particle is in a state with spin up $|+\rangle$ or one with spin down $|-\rangle$, and every eigenvalue of X will be doubly degenerate. Under these conditions, the Hilbert space of states will be the tensor product $L^{(2)}_x(\mathbb{R}) \otimes \mathcal{H}_2$ of the space of position states $L^{(2)}_x(\mathbb{R})$ and the two-dimensional space of spin states $\mathcal{H}_2$. A basis in this space might, for example, be constructed from the states $|x \otimes +\rangle$ and $|x \otimes -\rangle$ with

$$(X \otimes \sigma_z)|x \otimes \pm\rangle = \pm x|x \otimes \pm\rangle.$$

Even though the use of eigenvectors that are not true elements of $\mathcal{H}$ is mathematically questionable, it is extremely convenient and we shall do it often in what follows without any particular precautions. We shall also generalize the notion of a matrix element. Since the operator X is diagonal in the basis $|x\rangle$, we can write down the "matrix elements" of X:

$$\langle x'|X|x\rangle = x\langle x'|x\rangle = x\,\delta(x-x'), \tag{9.7}$$

and more generally those of a function $F(X)$:

$$\langle x'|F(X)|x\rangle = F(x)\langle x'|x\rangle = F(x)\,\delta(x-x'). \tag{9.8}$$

The completeness relation (7.37) is written as

$$\int_{-\infty}^{\infty} |x\rangle\,\mathrm{d}x\,\langle x| = I. \tag{9.9}$$

The projector $\mathcal{P}[a,b]$ onto the subspace of eigenvalues of X in the interval $[a,b]$ is obtained by restricting the integration over x to this interval:

$$\mathcal{P}[a,b] = \int_a^b |x\rangle\,\mathrm{d}x\,\langle x|. \tag{9.10}$$

This expression generalizes that for a finite-dimensional space. If Δ is the subspace of a set of eigenvalues of a Hermitian operator A, the projector $\mathcal{P}(\Delta)$ onto this subspace is

$$\mathcal{P}(\Delta) = \sum_{n\in\Delta} |n\rangle\langle n|.$$

9.1.2 Realization in $L^{(2)}_x(\mathbb{R})$

Now let us make the connection between the Dirac formalism which we have just made explicit in the basis in which X is diagonal and the realization given in Section 8.3.2 of the operators X and P as operators acting in the space $L^{(2)}(\mathbb{R})$ of square-integrable functions on $\mathbb{R}$. Let $|\varphi\rangle$ be a normalized vector of $\mathcal{H}$ representing a physical state. Using the completeness relation (9.9), we can decompose $|\varphi\rangle$ in the basis $|x\rangle$,

$$|\varphi\rangle = \int_{-\infty}^{\infty} |x\rangle\,\mathrm{d}x\,\langle x|\varphi\rangle, \tag{9.11}$$

where $\langle x|\varphi\rangle$ is thus a component of $|\varphi\rangle$ in the basis $|x\rangle$, or, in physical terms, the probability amplitude of finding the particle localized at point x. Let us examine the matrix elements of the operators X and $\exp(-\mathrm{i}Pa/\hbar)$:

$$\langle x|\big[X|\varphi\rangle\big] = \langle Xx|\varphi\rangle = x\,\langle x|\varphi\rangle = x\,\varphi(x), \tag{9.12}$$

$$\langle x\Big|\Big[\exp\Big(-\mathrm{i}\frac{Pa}{\hbar}\Big)\Big|\varphi\rangle\Big] = \langle x-a|\varphi\rangle = \varphi(x-a). \tag{9.13}$$

These equations show that $\langle x|\varphi\rangle$ can be identified with a function $\varphi(x)$ of $L^{(2)}_x(\mathbb{R})$ such that the action of the operators X and P will be given by (8.44). The equation (9.12) then is

$$\boxed{\big[X\varphi\big](x) = x\varphi(x)}\,, \tag{9.14}$$

and (9.13) is written as

$$\Big[\exp\Big(-\mathrm{i}\frac{Pa}{\hbar}\Big)\varphi\Big](x) = \varphi(x-a). \tag{9.15}$$

Expanding to first order in a, we have

$$\boxed{\big[P\varphi\big](x) = -\mathrm{i}\hbar\,\frac{\partial\varphi}{\partial x}}\,. \tag{9.16}$$

We recover the action of the operators X and P as defined in Section 8.3.2. Let us check that the scalar product is correctly given by (7.11) using the completeness relation (9.9):

$$\langle\chi|\varphi\rangle = \int_{-\infty}^{\infty}\mathrm{d}x\,\langle\chi|x\rangle\langle x|\varphi\rangle = \int_{-\infty}^{\infty}\mathrm{d}x\,\chi^*(x)\varphi(x). \tag{9.17}$$

The function $\varphi(x-a)$ in (9.15) is just the function $\varphi(x)$ translated by $+a$, and not by $-a$. If, for example, $\varphi(x)$ has a maximum at $x=x_0$, then $\varphi(x-a)$ has a maximum at $x-a=x_0$, that is, at $x=x_0+a$ (Fig. 9.1). We emphasize the fact that the choice $\varphi_a(x)=\varphi(x-a)$ for the translated wave function is the simplest one, but it is not unique. The function

$$\varphi'_a(x) = \mathrm{e}^{\mathrm{i}\theta(x)}\varphi(x-a)$$

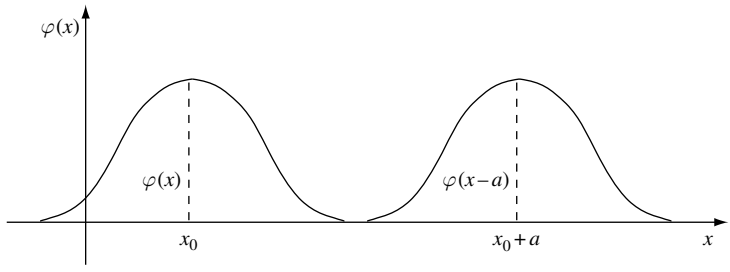

Fig. 9.1. Translation by a of a particle localized in the neighborhood of x_0.

is derived from $\varphi(x-a)$ by a local gauge transformation (8.65). The choice $\varphi(x-a)$ is related to that of the infinitesimal translation generator, and the phase transformation $\varphi_a(x) \to \varphi'_a(x)$ will correspond to using an infinitesimal translation generator derived from (9.16) by the local gauge transformation

$$P' = \mathrm{e}^{-\mathrm{i}\theta(x)} \left(\mathrm{i}\hbar \frac{\partial}{\partial x} \right) \mathrm{e}^{\mathrm{i}\theta(x)}.$$

In summary, the physical state of a particle moving on the x axis is described by a normalized wave function $\varphi(x)$ belonging to $L^{(2)}_x(\mathbb{R})$:

$$\int_{-\infty}^{\infty} \mathrm{d}x \, |\varphi(x)|^2 = 1, \tag{9.18}$$

which is interpreted physically as the probability amplitude $\langle x|\varphi\rangle$ of finding the particle localized at the point x. The action of the position and momentum operators X and P on $\varphi(x)$ is given by (9.14) and (9.16). The squared modulus

$$|\varphi(x)|^2 = |\langle x|\varphi\rangle|^2$$

is called the *probability for the particle to be found* at a point x; it is actually a *probability density*, in this case a probability per unit length. According to (9.10), the probability $\mathsf{p}([a,b])$ of finding the particle localized in the interval $[a,b]$ is

$$\mathsf{p}([a,b]) = \langle \varphi|\mathcal{P}[a,b]|\varphi\rangle = \int_a^b \mathrm{d}x \, |\varphi(x)|^2. \tag{9.19}$$

This probability is normalized to unity by construction since $\langle\varphi|\varphi\rangle = 1$, which is the same as (9.18). If we take the interval $[x, x+\mathrm{d}x]$ to be infinitesimal, $|\varphi(x)|^2 \mathrm{d}x$ is the probability of finding the particle in this interval.

When the particle possesses extra degrees of freedom, for example, a spin 1/2, its quantum state can be described using the wave functions $\varphi_\pm(x)$:

$$\varphi_+(x) = \langle x \otimes +|\varphi\rangle, \quad \varphi_-(x) = \langle x \otimes -|\varphi\rangle.$$

We have just defined what is customarily called "wave mechanics in the x representation," as we have chosen to start from the basis $|x\rangle$ in which the position operator is diagonal. Since X and P play symmetric roles, we could have just as well started from the basis in which P is diagonal; that is, we could have defined "wave mechanics in the p representation." The following subsection is devoted to this representation and its relation to the x representation.

9.1.3 Realization in $L^{(2)}_p(\mathbb{R})$

Let $|p\rangle$ be an eigenvector of P:

$$P|p\rangle = p|p\rangle. \tag{9.20}$$

First we shall determine the corresponding wave functions

$$\chi_p(x) = \langle x|p\rangle \tag{9.21}$$

in the x representation:

$$\begin{aligned}\langle x|\big[P|p\rangle\big] &= p\langle x|p\rangle = p\,\chi_p(x)\\ &= -\mathrm{i}\hbar\,\frac{\partial}{\partial x}\,\chi_p(x).\end{aligned}$$

We have used (9.16) to obtain the second line of the preceding equation. For any p in the interval $[-\infty, +\infty]$, the differential equation

$$-\mathrm{i}\hbar\,\frac{\partial}{\partial x}\,\chi_p(x) = p\,\chi_p(x)$$

has the solution

$$\chi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\,\mathrm{e}^{\mathrm{i}px/\hbar}, \tag{9.22}$$

which shows that the spectrum of P is continuous, like that of x. The normalization factor $(2\pi\hbar)^{-1/2}$ in (9.22) was chosen such that $\chi_p(x)$ is normalized to a Dirac delta function:

$$\int_{-\infty}^{\infty}\mathrm{d}x\,\chi^*_{p'}(x)\chi_p(x) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\mathrm{d}x\,\exp\Big[\mathrm{i}\,\frac{(p-p')x}{\hbar}\Big] = \delta(p-p'), \tag{9.23}$$

and the completeness relation is written as

$$\int_{-\infty}^{\infty}\mathrm{d}p\,\chi_p(x)\chi^*_p(x') = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\mathrm{d}p\,\exp\Big[\mathrm{i}\,\frac{p(x-x')}{\hbar}\Big] = \delta(x-x'). \tag{9.24}$$

We could equally well have started from the completeness relation in the form

$$\int_{-\infty}^{\infty}|p\rangle\,\mathrm{d}p\,\langle p| = I \tag{9.25}$$

and written

$$\int_{-\infty}^{\infty}\langle x'|p\rangle\,\mathrm{d}p\,\langle p|x\rangle = \langle x'|I|x\rangle = \delta(x-x'),$$

which also leads to (9.24).

If $|\varphi\rangle$ is the state vector of a particle, the "wave function in the p representation" will be $\tilde{\varphi}(p) = \langle p|\varphi\rangle$. This wave function in the p representation is just the Fourier transform of the wave function $\varphi(x) = \langle x|\varphi\rangle$ in the x representation. Since $|\langle x|p\rangle|^2$ is a constant, the $|x\rangle$ and $|p\rangle$ bases are complementary according to a slight generalization of the definition in Section 3.1.2. Using the completeness relation (9.9) as well as (9.21) and (9.22), we find

$$\boxed{\tilde{\varphi}(p) = \langle p|\varphi\rangle = \int_{-\infty}^{\infty}\langle p|x\rangle\,\mathrm{d}x\,\langle x|\varphi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\mathrm{d}x\,\mathrm{e}^{-\mathrm{i}px/\hbar}\,\varphi(x)}\,, \tag{9.26}$$

and conversely

$$\boxed{\varphi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}p\, \mathrm{e}^{\mathrm{i}px/\hbar}\, \tilde{\varphi}(p)} \,. \tag{9.27}$$

The action of the operators X and P in the p representation is easily obtained:

$$\big[X\tilde{\varphi}\big](p) = \mathrm{i}\hbar \frac{\partial}{\partial p}\, \tilde{\varphi}(p), \tag{9.28}$$

$$\big[P\tilde{\varphi}\big](p) = p\, \tilde{\varphi}(p). \tag{9.29}$$

An expression analogous to (9.19) holds in momentum space: the probability $\mathsf{p}([k, q])$ for the particle to have momentum in the interval $[k, q]$ is

$$\mathsf{p}([k, q]) = \int_k^q \mathrm{d}p\, |\tilde{\varphi}(p)|^2, \tag{9.30}$$

where $|\tilde{\varphi}(p)|^2$ is a probability density in momentum space.

9.1.4 Evolution of a free wave packet

Let us start from the Fourier representation (9.27) of the wave function $\varphi(x)$ of a physical state. The Fourier transform $\tilde{\varphi}(p)$, like $\varphi(x)$, satisfies the normalization condition

$$\int_{-\infty}^{\infty} \mathrm{d}p\, |\tilde{\varphi}(p)|^2 = 1. \tag{9.31}$$

Such a physical state is often called a *wave packet*, because according to (9.27) it is a superposition of plane waves. The expectation values of position $\langle X\rangle$ and momentum $\langle P\rangle$ are calculated by inserting the completeness relations (9.9) and (9.25) twice:[3]

$$\langle X\rangle = \langle\varphi|X|\varphi\rangle = \int \mathrm{d}x\, \mathrm{d}x' \langle\varphi|x\rangle\langle x|X|x'\rangle\langle x'|\varphi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, x|\varphi(x)|^2, \tag{9.32}$$

$$\langle P\rangle = \langle\varphi|P|\varphi\rangle = \int \mathrm{d}p\, \mathrm{d}p' \langle\varphi|p\rangle\langle p|P|p'\rangle\langle p'|\varphi\rangle = \int_{-\infty}^{\infty} \mathrm{d}p\, p|\tilde{\varphi}(p)|^2. \tag{9.33}$$

We have also used (9.7) and an analogous equation in momentum space. The dispersions ΔX and ΔP are given by a similar calculation:

$$(\Delta X)^2 = \langle\varphi|(X - \langle X\rangle)^2|\varphi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, (x - \langle X\rangle)^2 |\varphi(x)|^2, \tag{9.34}$$

$$(\Delta P)^2 = \langle\varphi|(P - \langle P\rangle)^2|\varphi\rangle = \int_{-\infty}^{\infty} \mathrm{d}p\, (p - \langle P\rangle)^2 |\tilde{\varphi}(p)|^2. \tag{9.35}$$

[3] The explicit notation would be $\langle X\rangle_\varphi$ and $\langle P\rangle_\varphi$; we have suppressed the index φ to simplify the notation.

According to the general argument of Section 4.1.3, these dispersions satisfy the Heisenberg inequality:

$$\boxed{\Delta x\,\Delta p \geq \frac{1}{2}\hbar}\,, \tag{9.36}$$

where we have used the usual notation $\Delta x\,\Delta p$ instead of $\Delta X\,\Delta P$. A direct demonstration of (9.36) is proposed in Exercise 9.7.1.

Let us introduce a time dependence in the state vector: the state vector is $|\varphi(0)\rangle \equiv |\varphi\rangle$ at time $t = 0$ and $|\varphi(t)\rangle$ at time t. The wave function $\varphi(x, t)$ at time t then is $\varphi(x, t) = \langle x|\varphi(t)\rangle$. To obtain $|\varphi(t)\rangle$ as a function of $|\varphi(0)\rangle$, we need the evolution equation (4.11) and also the Hamiltonian H. Until the end of this section, we shall restrict ourselves to the case where the potential energy is zero and the Hamiltonian reduces to the kinetic energy term K (8.66):

$$H = K = \frac{P^2}{2m}. \tag{9.37}$$

Since K and P commute, the eigenstates of H can be chosen among those of P:

$$P|p\rangle = p|p\rangle \quad H|p\rangle = \frac{P^2}{2m}|p\rangle = \frac{p^2}{2m}|p\rangle = E(p)|p\rangle, \tag{9.38}$$

and consequently

$$\exp\Big[-\mathrm{i}\frac{Ht}{\hbar}\Big]|p\rangle = \exp\Big[-\mathrm{i}\frac{E(p)t}{\hbar}\Big]|p\rangle. \tag{9.39}$$

Then it is natural to express $\langle x|\varphi(t)\rangle$ as a function of the components of $|\varphi(t)\rangle$ in the basis $|p\rangle$:

$$\begin{aligned}\langle x|\varphi(t)\rangle &= \langle x|\exp\Big(-\mathrm{i}\frac{Ht}{\hbar}\Big)|\varphi(0)\rangle = \int \mathrm{d}p\,\langle x|p\rangle\langle p|\exp\Big(-\mathrm{i}\frac{Ht}{\hbar}\Big)|\varphi\rangle \\ &= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\mathrm{d}p\,\exp\Big(\mathrm{i}\,\frac{px}{\hbar} - \mathrm{i}\,\frac{E(p)t}{\hbar}\Big)\tilde{\varphi}(p).\end{aligned} \tag{9.40}$$

In order to eliminate the factors of $\hbar$, we introduce the wave vector $k = p/\hbar$ and the frequency $\omega(k)$:

$$k = \frac{p}{\hbar}, \quad \omega(k) = \frac{E(\hbar k)}{\hbar} = \frac{\hbar k^2}{2m}, \quad A(k) = \sqrt{\hbar}\,\tilde{\varphi}(\hbar k)$$

so that $\varphi(x, t)$ can be written as

$$\varphi(x, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\mathrm{d}k A(k)\exp\Big(\mathrm{i}kx - \mathrm{i}\omega(k)t\Big). \tag{9.41}$$

The qualitative behavior of $|A(k)|^2$ and $|\varphi(x, 0)|^2$ is shown in Fig. 9.2. The function $|A(k)|^2$ is centered at $k \simeq \overline{k}$ and has width Δk. The Heisenberg inequality (9.36) becomes

$$\Delta x\,\Delta k \geq \frac{1}{2}. \tag{9.42}$$

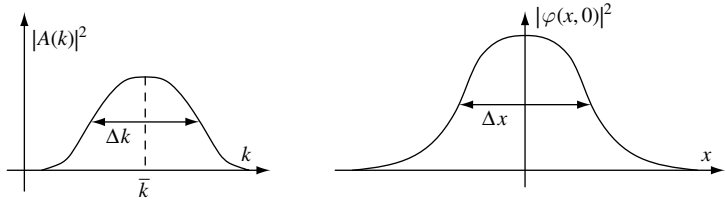

Fig. 9.2. Spread of a wave packet in k and in x.

The limiting cases are

- A particle of sharply defined wave vector (or momentum), which is a plane wave:

$$A(k) = \delta(k - \bar{k}), \quad \varphi(x,0) = \frac{1}{\sqrt{2\pi}} e^{i\bar{k}x}. \tag{9.43}$$

- A particle localized exactly at $x = x_0$:

$$A(k) = \frac{1}{\sqrt{2\pi}} e^{-ikx_0}, \quad \varphi(x,0) = \delta(x - x_0). \tag{9.44}$$

We recall that neither a plane wave (9.43) nor a perfectly localized state (9.44) corresponds to a physically realizable state. In the case (9.44) of a localized particle, the probability $|A(k)|^2$ of observing momentum $\hbar k$ is independent of k, and so the probability distribution cannot be normalized. Similarly, for the case (9.43) of fixed momentum we have $|\varphi(x)|^2 =$ const. and the probability density is uniform on the x axis, so that again the probability distribution cannot be normalized. According to (9.31), for a state to be physically realizable we must have

$$\int_{-\infty}^{\infty} dk\, |A(k)|^2 < \infty.$$

Let us now study the time evolution of a wave packet. We shall use the stationary phase approximation to evaluate (9.41). Defining $A(k) = |A(k)| \exp[i\phi(k)]$, the phase $\theta(k)$ of the exponential in (9.41) becomes

$$\theta(k) = kx - \omega(k)t + \phi(k).$$

We obtain the leading contribution to the integral (9.41) if the phase $\theta(k)$ is stationary in the region $k \simeq \bar{k}$ where $|A(k)|$ has a maximum; if $\theta(k)$ is not stationary, the exponential oscillates rapidly and the contribution to the integral (9.41) averages to zero. We then must have

$$\frac{d\theta}{dk}\Big|_{k=\bar{k}} = x - t\frac{d\omega}{dk}\Big|_{k=\bar{k}} + \frac{d\phi}{dk}\Big|_{k=\bar{k}} = 0.$$

The center of the wave packet will move according to the law

$$x = v_g(t - \tau), \tag{9.45}$$

where v_g is the group velocity, which is just the average velocity $\overline{v}$ of the particle:

$$v_g = \overline{v} = \frac{d\omega}{dk}\Big|_{k=\overline{k}} = \frac{d}{dk}\frac{\hbar k^2}{2m}\Big|_{k=\overline{k}} = \frac{\hbar\overline{k}}{m} = \frac{\overline{p}}{m}. \tag{9.46}$$

The time τ determining the $t=0$ position $x_0 = -v_g\tau$ of the center of the wave packet is

$$\tau = \frac{1}{v_g}\frac{d\phi}{dk}\Big|_{k=\overline{k}} = \hbar\frac{d\phi}{dE}\Big|_{k=\overline{k}}. \tag{9.47}$$

In order to obtain a more precise result, we can rewrite the phase by expanding $\omega(k)$ in the neighborhood of $k=\overline{k}$:

$$\begin{aligned}\theta(k) &= kx - \omega(\overline{k})t - (k-\overline{k})v_g t - \frac{1}{2}(k-\overline{k})^2\frac{\hbar}{m}t + \phi(k)\\ &= \omega(\overline{k})t + k(x-v_g t) - \frac{1}{2}(k-\overline{k})^2\frac{\hbar}{m}t + \phi(k).\end{aligned}$$

We obtain a very simple form for $\varphi(x,t)$ if it is possible to neglect the quadratic term in $(k-\overline{k})^2$:

$$\begin{aligned}\varphi(x,t) &= \frac{1}{\sqrt{2\pi}}\exp[i\omega(\overline{k})t]\int dk A(k)\exp[ik(x-v_g t)]\\ &= \exp[i\omega(\overline{k})t]\varphi(x-v_g t,0).\end{aligned} \tag{9.48}$$

This equation shows that aside from the phase factor $\exp[i\omega(\overline{k})t]$, the wave function at time t is obtained from that at time $t=0$ by the substitution $x \to x - v_g t$, that is, if $v_g > 0$ the wave packet propagates without deformation in the direction of positive x with velocity v_g. However, this result is only approximate since we have neglected the quadratic term in $(k-\overline{k})^2$. This term gives a contribution to the phase

$$-\frac{1}{2}(k-\overline{k})^2\frac{\hbar}{m}t$$

which must remain $\ll 1$ in the domain where $|A(k)|$ is sizable if we want to remain within the linear approximation. The contribution of this term can be neglected if

$$\frac{1}{2}(k-\overline{k})^2\frac{\hbar t}{m} \ll 1$$

in a region of extent Δk about $\overline{k}$. For the deformation of the wave packet to be small, we must have

$$t \ll \frac{2m}{\hbar(\Delta k)^2} = \frac{2m\hbar}{(\Delta p)^2}. \tag{9.49}$$

If this condition is not satisfied, the wave packet is deformed and broadens, with its center continuing to move at speed v_g. This phenomenon is called *wave-packet spreading*.

Let us conclude this section by showing how the Heisenberg inequality (9.36) can be used as a heuristic tool to estimate the energy of the ground state of the hydrogen atom

(see Section 1.5.2). If the electron describes a circular orbit of radius r with momentum $p = mv$, its classical energy will be

$$E = \frac{p^2}{2m} - \frac{e^2}{r}. \tag{9.50}$$

In classical physics, the orbital radius of the electron tends to zero (it is said that the "electron falls into the nucleus") with the emission of electromagnetic radiation. In fact, in classical physics the energy of a circular orbit $E = -e^2/(2r)$ is not bounded below and nothing prevents the orbit radius from becoming arbitrarily small. The decrease in the energy of the orbit is compensated for by the emission of energy in the form of electromagnetic radiation, which ensures energy conservation. However, in an orbit of radius r the spread Δx of the position on the x axis is of order r, which makes the momentum spread at least $\sim \hbar/\Delta x = \hbar/r$. We find $rp \sim \hbar$, and the expression for the energy (9.50) becomes

$$E \sim \frac{\hbar^2}{2mr^2} - \frac{e^2}{r}.$$

Let us seek the minimum of E:

$$\frac{\mathrm{d}E}{\mathrm{d}r} \sim -\frac{\hbar^2}{mr^3} + \frac{e^2}{r^2} = 0,$$

so that a minimum occurs at

$$r = a_0 = \frac{\hbar^2}{me^2}, \tag{9.51}$$

which is just the Bohr radius (1.34) of the hydrogen atom. Naturally, the fact that we obtain exactly a_0 in this order-of-magnitude calculation is a happy coincidence. It leads to the ground-state energy (1.35):

$$E_0 = -\frac{e^2}{2a_0} = -\frac{me^4}{2\hbar^2}. \tag{9.52}$$

While this calculation can give only the order of magnitude, the accompanying physics explains the deep reason for the stability of the atom: owing to the Heisenberg inequalities, the electron cannot exist in an orbit of very small radius without acquiring a large momentum, which makes its kinetic energy high. The energy of the ground state is obtained by finding the best possible compromise between the kinetic and potential energy so as to obtain the minimum total energy.

9.2 The Schrödinger equation

9.2.1 The Hamiltonian of the Schrödinger equation

We have seen in Section 8.4.1 that the most general time-independent Hamiltonian compatible with Galilean invariance in dimension $d = 1$ is given by (8.68):

$$H = \frac{P^2}{2m} + V(X), \tag{9.53}$$

where $K = P^2/2m$ is the kinetic energy operator and $V(X)$ is the potential energy operator, or briefly the *potential*. We also recall the evolution equation (4.11):

$$\mathrm{i}\hbar \frac{\mathrm{d}|\varphi(t)\rangle}{\mathrm{d}t} = H|\varphi(t)\rangle. \tag{9.54}$$

We multiply both sides of this equation on the left by the bra $\langle x|$ taking (9.53) as the Hamiltonian:

$$\begin{aligned}
\mathrm{i}\hbar \frac{\mathrm{d}}{\mathrm{d}t} \langle x|\varphi(t)\rangle &= \mathrm{i}\hbar \frac{\partial}{\partial t}\varphi(x,t), \\
\langle x|P^2|\varphi(t)\rangle &= (P^2\varphi)(x,t) = \left(-\mathrm{i}\hbar \frac{\partial}{\partial x}\right)^2 \varphi(x,t) = -\hbar^2 \frac{\partial^2 \varphi(x,t)}{\partial x^2}, \\
\langle x|V(X)|\varphi(t)\rangle &= V(x)\varphi(x,t),
\end{aligned}$$

where we have used (9.8) and (9.16). We thus obtain the time-dependent Schrödinger equation:

$$\boxed{\mathrm{i}\hbar \frac{\partial \varphi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \varphi(x,t)}{\partial x^2} + V(x)\varphi(x,t)}, \tag{9.55}$$

which is a wave equation for the wave function $\varphi(x,t)$.

Since the potential $V(X)$ is independent of time, we know that there exist stationary solutions of (9.54):

$$|\varphi(t)\rangle = \exp\left(-\mathrm{i}\frac{Et}{\hbar}\right)|\varphi(0)\rangle, \quad H|\varphi(0)\rangle = E|\varphi(0)\rangle. \tag{9.56}$$

Multiplying on the left by the bra $\langle x|$, the equation $H|\varphi\rangle = E|\varphi\rangle$ becomes the time-independent Schrödinger equation:

$$\boxed{\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)\right]\varphi(x) = E\varphi(x)}. \tag{9.57}$$

Equation (9.55) can be generalized in two ways. While remaining compatible with Galilean invariance, it is possible to add a time dependence to the potential: $V(x) \to V(x,t)$. It is also possible to use velocity-dependent potentials, for example to approximate relativistic effects. In this case the Galilean invariance is lost, and moreover ambiguities may be introduced when it is necessary to choose the ordering of a product of position and momentum operators.

9.2.2 The probability density and the probability current density

With the probability density $|\varphi(x,t)|^2$ we can associate a current density $j(x,t)$ by analogy with hydrodynamics or electrodynamics. Let us recall the example of hydrodynamics to see how this works. Let $\rho(\vec{r},t)$ be the mass density of a compressible fluid of total mass M

flowing with local velocity $\vec{v}(\vec{r},t)$.[4] The *current density* (or simply current) $\vec{j}(\vec{r},t)$ is defined as

$$\vec{j}(\vec{r},t) = \rho(\vec{r},t)\,\vec{v}(\vec{r},t). \tag{9.58}$$

We consider a surface $\mathcal{S}$ surrounding the volume $\mathcal{V}$, which contains a mass $M(\mathcal{V})$ of fluid (Fig. 9.3). The mass $\mathrm{d}M(\mathcal{V})/\mathrm{d}t$ of fluid leaving $\mathcal{V}$ per unit time is equal to the flux of current through $\mathcal{S}$:

$$\frac{\mathrm{d}M(\mathcal{V})}{\mathrm{d}t} = \int_{\mathcal{S}} \vec{j}\cdot\mathrm{d}\vec{\mathcal{S}} = \int_{\mathcal{V}} (\vec{\nabla}\cdot\vec{j})\;\mathrm{d}^3 r,$$

where we have used Green's theorem. This fluid mass is also equal to minus the time derivative of the integral of the density over $\mathcal{V}$:

$$\frac{\mathrm{d}M(\mathcal{V})}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}} \mathrm{d}^3 r\,\rho(\vec{r},t) = -\int_{\mathcal{V}} \mathrm{d}^3 r\,\frac{\partial\rho(\vec{r},t)}{\partial t}.$$

The two expressions for $\mathrm{d}M(\mathcal{V})/\mathrm{d}t$ must be equal for any volume $\mathcal{V}$, which implies that the integrands must be equal. This leads to the *continuity equation*:

$$\boxed{\frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot\vec{j} = 0}\;. \tag{9.59}$$

In electrodynamics ρ is the charge density and $\vec{j}$ is the current density, which also satisfy a continuity equation of the type (9.59) expressing the local conservation of electric charge. Returning to dimension $d = 1$,

$$\frac{\partial\rho}{\partial t} + \frac{\partial j}{\partial x} = 0. \tag{9.60}$$

In quantum mechanics we expect to find a continuity equation of the type (9.59), or (9.60) in one dimension. If

$$\int_a^b \mathrm{d}x\,|\varphi(x,t)|^2$$

is the probability of finding the particle at time t in the interval $[a,b]$, this probability will in general depend on the time. If, for example, this probability decreases, this indicates

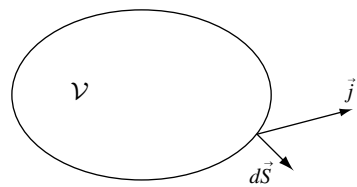

Fig. 9.3. Current and flux leaving a volume $\mathcal{V}$.

[4] We temporarily revert to the dimension $d = 3$.

that the probability of finding the particle in the union of the two intervals $[-\infty, a]$ and $[b, +\infty]$ must increase, because for any t the integral

$$\int_{-\infty}^{\infty} \mathrm{d}x\, |\varphi(x,t)|^2$$

is constant and equal to unity. Similarly, the integral of the fluid density over all space remains constant and equal to the total mass M, whereas in electrodynamics the integral of the charge density over all space remains constant and equal to the total charge Q. The analog of the density in quantum mechanics is $\rho(x,t) = |\varphi(x,t)|^2$; however, this is a probability density and not an actual density. We shall seek a current $j(x,t)$ satisfying (9.60); this also will be a probability current and not an actual current. The form of this current is suggested by the following argument. In hydrodynamics, the average velocity $\langle v(t)\rangle$ of a fluid (or the velocity of the center of mass) is given by

$$\langle v(t)\rangle = \frac{1}{M}\int \rho(x,t)v(x,t)\mathrm{d}x = \frac{1}{M}\int j(x,t)\mathrm{d}x. \tag{9.61}$$

In quantum mechanics, the velocity operator according to (8.61) is

$$\dot{X} = \frac{\mathrm{i}}{\hbar}[H, X] = \frac{P}{m},$$

and its expectation value is

$$\langle \dot{X}\rangle(t) = \langle \varphi(t)\Big|\frac{P}{m}\Big|\varphi(t)\rangle = \int \mathrm{d}x\, \varphi^*(x,t)\frac{\hbar}{\mathrm{i}m}\frac{\partial\varphi(x,t)}{\partial x},$$

where we have used (9.9) and (9.16). The integrand in this equation is in general complex and is not suitable for the current density. Integration by parts allows us to construct a current which is a real function of x:

$$\langle \dot{X}\rangle(t) = \frac{\hbar}{2\mathrm{i}m}\int \mathrm{d}x \left(\varphi^*(x,t)\frac{\partial\varphi(x,t)}{\partial x} - \varphi(x,t)\frac{\partial\varphi^*(x,t)}{\partial x}\right). \tag{9.62}$$

Comparison of (9.61) for $M = 1$ with (9.62) suggests the following form for the current $j(x,t)$:

$$\boxed{j = \frac{\hbar}{2\mathrm{i}m}\left(\varphi^*(x,t)\frac{\partial\varphi(x,t)}{\partial x} - \varphi(x,t)\frac{\partial\varphi^*(x,t)}{\partial x}\right) = \mathrm{Re}\left(\frac{\hbar}{\mathrm{i}m}\,\varphi^*(x,t)\frac{\partial\varphi(x,t)}{\partial x}\right)}. \tag{9.63}$$

In order to familiarize ourselves with this rather unintuitive expression, let us examine the case of a plane wave:

$$\varphi(x) = A\,\mathrm{e}^{\mathrm{i}px/\hbar}.$$

The density is $\rho(x) = |A|^2$. The current becomes

$$j(x) = \mathrm{Re}\left(\frac{\hbar}{\mathrm{i}m}\,A^*\,\mathrm{e}^{-\mathrm{i}px/\hbar}\left[\frac{\mathrm{i}p}{\hbar}\right]A\,\mathrm{e}^{\mathrm{i}px/\hbar}\right) = |A|^2\,\frac{p}{m} \tag{9.64}$$

and is interpreted as current = density × velocity. The current points to the right if $p > 0$ and to the left if $p < 0$. When the wave function is independent of time, as in the case of a plane wave, the current is necessarily independent of x since $\partial\rho/\partial t = 0 \Rightarrow \partial j/\partial x = 0$. We still need to check that the current (9.63) is actually the current that satisfies the continuity equation (9.60). On the one hand

$$\frac{\partial j}{\partial x} = \frac{\hbar}{2\mathrm{i}m}\left[\varphi^*\frac{\partial^2\varphi}{\partial x^2} - \varphi\frac{\partial^2\varphi^*}{\partial x^2}\right] = \frac{\mathrm{i}}{\hbar}\left[\varphi^*(H\varphi) - \varphi(H\varphi)^*\right],$$

where we have used

$$\frac{\hbar}{2\mathrm{i}m}\frac{\partial^2\varphi}{\partial x^2} = \frac{\mathrm{i}}{\hbar}\left[(H-V)\varphi\right]$$

and the fact that V is a real function of x and t. On the other hand

$$\frac{\partial}{\partial t}|\varphi(x,t)|^2 = \varphi^*\frac{\partial\varphi}{\partial t} + \varphi\frac{\partial\varphi^*}{\partial t} = \frac{1}{\mathrm{i}\hbar}\left[\varphi^*(H\varphi) - (H\varphi)\varphi^*\right],$$

which shows that

$$\frac{\partial}{\partial t}|\varphi(x,t)|^2 + \frac{\partial}{\partial x}j(x,t) = 0. \tag{9.65}$$

9.3 Solution of the time-independent Schrödinger equation

9.3.1 Generalities

The sections 9.3 to 9.5 will be devoted to finding the solutions of the time-independent Schrödinger equation (9.57), that is, the eigenvalues E and the corresponding eigenfunctions $\varphi(x)$. We start with the simplest case where the potential $V(x) = 0$. The equation (9.57) becomes

$$\left(\frac{\partial^2}{\partial x^2} + \frac{2mE}{\hbar^2}\right)\varphi(x) = 0. \tag{9.66}$$

The general solution of this equation is a combination of plane waves with $p = \sqrt{2mE} > 0$,

$$\varphi(x) = A\,\mathrm{e}^{\mathrm{i}px/\hbar} + B\,\mathrm{e}^{-\mathrm{i}px/\hbar} \tag{9.67}$$

propagating toward the positive x direction with amplitude A and the negative x direction with amplitude B. Since the solution (9.67) is independent of time, it generates a stationary current,[5] which according to (9.64) consists of a term $|A|^2p/m$ pointing to positive x and a term $-|B|^2p/m$ pointing to negative x. To the time-independent solutions $\exp(\pm\mathrm{i}px/\hbar)$ there correspond time-dependent solutions of (9.55), namely, $\exp[\mathrm{i}(\pm px - E(p)t)/\hbar]$, which are traveling waves propagating in the positive or negative x direction. The traveling waves $\exp[\mathrm{i}(+px - E(p)t)/\hbar]$ can be combined to form wave packets propagating in the positive x direction, and we say that these wave packets originate from a *source* of particles at $x = -\infty$. From the traveling waves $\exp[\mathrm{i}(-px - E(p)t)/\hbar]$ we can construct

[5] An example of a stationary current is the d.c. electric current.

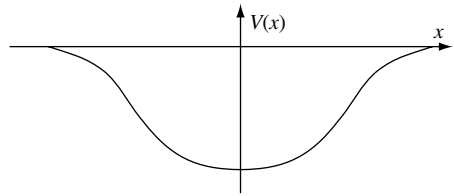

Fig. 9.4. A potential well.

wave packets propagating in the negative x direction, corresponding to a source of particles at $x = +\infty$.

Let us consider the case $V(x) \neq 0$ and, to be specific, assume that $V(x)$ has the form in Fig. 9.4, that of a "potential well" with $V(x) \to 0$ if $x \to \pm\infty$. In classical mechanics, from the discussion of Section 1.5.1, this potential has bound states if $E < 0$ and scattering states if $E > 0$. For $E < 0$ the classical particle remains confined in a finite range of the x axis, and for $E > 0$ it travels to infinity. The range of the x axis allowed for the classical particle is that for which $E > V(x)$ and the momentum $p(x)$ is real:

$$p(x) = \pm\sqrt{2m(E - V(x))}, \tag{9.68}$$

while the region $E < V(x)$ where the momentum is imaginary,

$$p(x) = \pm \mathrm{i}\sqrt{2m(V(x) - E)}, \tag{9.69}$$

is forbidden. We shall see that this classical behavior is reflected in the quantum behavior: the form of the solutions of (9.57) will differ depending on whether $p(x)$ is real or imaginary. For $\varphi(x)$ to be an acceptable solution, it is not sufficient that it formally satisfies (9.57); $\varphi(x)$ must also be normalizable:

$$\int_{-\infty}^{\infty} \mathrm{d}x\, |\varphi(x)|^2 < \infty.$$

It is this condition which we shall use to obtain the bound states. However, it is too strong for the scattering states. We have seen that for $V(x) = 0$ the solutions of (9.57) are non-normalizable plane waves. For $x \to \pm\infty$ we expect the solutions of (9.57) to have plane-wave behavior because the potential vanishes at infinity. For the scattering states $E > 0$ of the potential in Fig. 9.4 we shall demand only plane-wave behavior at infinity: one should not require more from the solution in the presence of the potential than in its absence!

9.3.2 Reflection and transmission by a potential step

In the rest of this section we shall be interested in the case where the potential is piecewise-constant, that is, $V(x)$ is constant in some range and then jumps abruptly to another constant value at certain points (Fig. 9.5). This type of potential represents a good approximation of an actual potential in certain cases and can be used to approximate

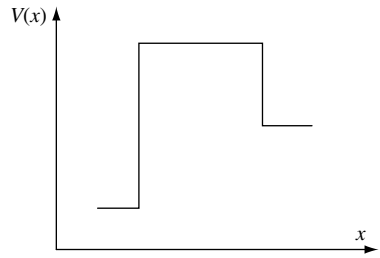

Fig. 9.5. A piecewise-constant potential.

a potential which varies continuously in other cases (Fig. 9.6). Since the potential has discontinuities, it is necessary to examine the behavior of the wave function in the neighborhood of one. We shall show that the wave function $\varphi(x)$ and its derivative $\varphi'(x)$ are continuous if the potential has a *finite* discontinuity V_0 at the point $x = x_0$ (Fig 9.7). Since $|\varphi(x)|^2$ must be integrable at x_0, $|\varphi(x)|$ must be also. It will be convenient to rewrite the time-independent Schrödinger equation (9.57) as

$$\left(\frac{\partial^2}{\partial x^2} + \frac{2m(E - V(x))}{\hbar^2}\right)\varphi(x) = 0. \tag{9.70}$$

We can find the behavior of $\varphi'(x)$ in the neighborhood of the discontinuity using

$$\varphi'(x_0 + \varepsilon) - \varphi'(x_0 - \varepsilon) = \int_{x_0-\varepsilon}^{x_0+\varepsilon} \frac{\partial^2 \varphi(x)}{\partial x^2}\, \mathrm{d}x = \int_{x_0-\varepsilon}^{x_0+\varepsilon} \left[\frac{2m(V(x) - E)}{\hbar^2}\right]\varphi(x).$$

The second integral is well defined because $\varphi(x)$ is integrable. This integral must tend to zero with ε, which shows that $\varphi'(x)$ and *a fortiori* $\varphi(x)$ are continuous as long as the discontinuity V_0 is finite.

Instead of writing down the continuity equations for $\varphi(x)$ and $\varphi'(x)$, it is often convenient to write them down for $\varphi(x)$ and its logarithmic derivative $\varphi'(x)/\varphi(x)$. An immediate consequence of these conditions is that the current $j(x)$ is equal to the same

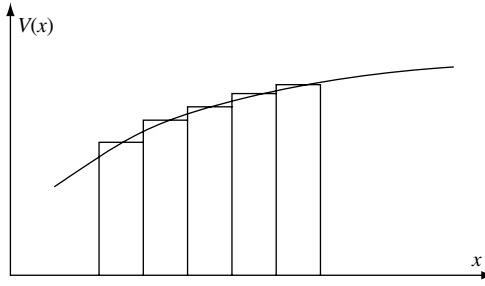

Fig. 9.6. Approximation of a potential by a sequence of steps.

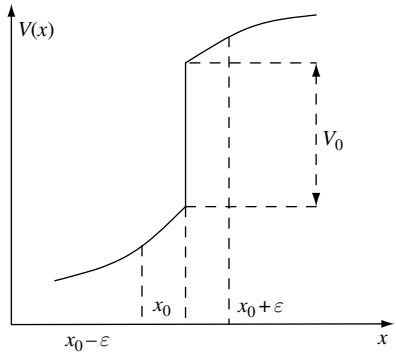

Fig. 9.7. A discontinuity in the potential.

constant on both sides of x_0. As an application of these continuity conditions, we take the case of a "step potential" (Fig. 9.8):

$$\begin{aligned} &\text{region I}: V(x) = 0 \quad &&\text{for} \quad x < 0, \\ &\text{region II}: V(x) = V_0 \quad &&\text{for} \quad x > 0. \end{aligned}$$

To be specific we first choose $0 < E < V_0$. If we define k and κ as

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}, \tag{9.71}$$

the solutions of (9.70) are written in regions I and II as

$$\text{I}: \varphi(x) = A\,\mathrm{e}^{\mathrm{i}kx} + B\,\mathrm{e}^{-\mathrm{i}kx}, \tag{9.72}$$

$$\text{II}: \varphi(x) = C\,\mathrm{e}^{-\kappa x} + D\,\mathrm{e}^{\kappa x}. \tag{9.73}$$

If $V(x)$ remains equal to V_0 for all $x > 0$, the behavior (9.73) of the wave function remains unchanged for any $x > 0$. It is then necessary that $D = 0$, because otherwise the function $|\varphi(x)|^2$ behaves as $\exp(2\kappa x)$ for $x \to \infty$. Behavior of constant modulus like that of a

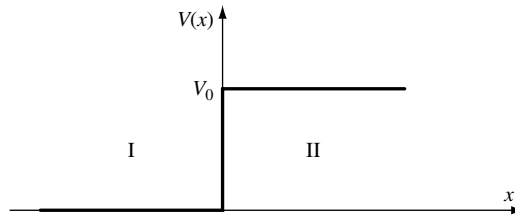

Fig. 9.8. A step potential.

plane wave is acceptable, but behavior this divergent is not. Under these conditions, the continuity of φ and its logarithmic derivative at $x = 0$ is written as

$$\varphi : C = A + B, \quad \frac{\varphi'}{\varphi} : -\kappa = \frac{\mathrm{i}k(A-B)}{A+B}.$$

The coefficients A and B are a priori defined up to a multiplicative constant since we have not made any hypotheses about the region $x > 0$. We can arbitrarily set $A = 1$, and then the solution for the other two coefficients becomes

$$B = -\frac{\kappa + \mathrm{i}k}{\kappa - \mathrm{i}k}, \quad C = -\frac{2\mathrm{i}k}{\kappa - \mathrm{i}k}. \tag{9.74}$$

Since $C \neq 0$, we see that the region $x > 0$, in which the particle momentum is imaginary (see (9.69)), is not strictly forbidden to the quantum particle. From these expressions we can derive the limiting case of $V_0 \to \infty$, which corresponds to a barrier insurmountable by a classical particle no matter what its energy – that is an infinite potential barrier. Equation (9.71) then shows that $\kappa \to \infty$ and (9.74) that $B \to -1$ and $C \to 0$. The wave function vanishes in region II and remains continuous at the point $x = 0$. However, its derivative $\varphi'(x)$ is discontinuous at this point.

Let us now discuss the physical interpretation of these results. We assume that at $x = -\infty$ we have a source of particles of unit amplitude: $A = 1$. The corresponding incident wave will be partly reflected and partly transmitted by the potential step. If we take as above the case $0 < E < V_0$, we expect that the quantum particle will be reflected with 100% probability, since the corresponding classical particle cannot cross the potential step. On the other hand, in the case $E > V_0$ we can show that the solution of the quantum problem corresponds to partial reflection and partial transmission, whereas a classical particle is 100% transmitted. Let us compare these two cases.

The potential step: total reflection

We have as above $E < V_0$. The wave functions in regions I and II are

$$\mathrm{I} : \varphi(x) = \mathrm{e}^{\mathrm{i}kx} + B\,\mathrm{e}^{-\mathrm{i}kx},$$

$$\mathrm{II} : \varphi(x) = C\,\mathrm{e}^{-\kappa x}.$$

The values of B and C are given by (9.74). We note that $|B| = 1$, and so B is a phase factor, $B = \exp(-\mathrm{i}\phi)$. This shows that the reflected wave

$$B\mathrm{e}^{-\mathrm{i}kx} = \mathrm{e}^{-\mathrm{i}kx - \mathrm{i}\phi}$$

has intensity equal to that of the incident wave, so that there is total reflection at the potential discontinuity. A classical particle arriving at the potential discontinuity will also be reflected. However, the quantum motion presents two important differences compared to the classical motion.

- The probability density is nonzero in region II, which is strictly inaccessible to the classical particle: the depth of penetration into the classically forbidden region is $\ell = 1/\kappa$. This phenomenon parallels that of an evanescent wave in optics.

- If we construct an incident wave packet, the particle will be reflected with a delay τ given by (9.47):

$$\tau = -\hbar \frac{\mathrm{d}\phi}{\mathrm{d}E},$$

whereas the reflection of the classical particle is instantaneous.

The potential step: reflection and transmission

Now we turn to the case $E > V_0$, assuming as before that the particles are incident from the left and arrive at the potential step, so that in region II the particles can travel only to the right:[6] there is no source of particles at $x = +\infty$, only at $x = -\infty$. We define

$$k' = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}.$$

The wave functions in regions I and II are now

$$\mathrm{I} : \varphi(x) = \mathrm{e}^{\mathrm{i}kx} + B\,\mathrm{e}^{-\mathrm{i}kx},$$
$$\mathrm{II} : \varphi(x) = C\,\mathrm{e}^{\mathrm{i}k'x}.$$

The continuity conditions are

$$1 + B = C, \quad \mathrm{i}k' = \frac{\mathrm{i}k(1 - B)}{1 + B},$$

so that

$$B = \frac{k - k'}{k + k'}, \quad C = \frac{2k}{k + k'}. \tag{9.75}$$

A classical particle will always cross the potential step (and in the process lose kinetic energy), but in quantum mechanics there exists a reflection probability $|B|^2 \neq 0$, so that $|B|^2 = R$ is the reflection coefficient and $T = 1 - R$ is the transmission coefficient:

$$R = \left(\frac{k - k'}{k + k'}\right)^2, \quad T = 1 - R = \frac{4kk'}{(k + k')^2}. \tag{9.76}$$

It is important to note that $T \neq |C|^2$. In fact, it is not the probability density which must be conserved, but the particle current (or flux). In Fig. 9.9 the particle flux entering the hatched area must be equal to the flux leaving it, or

$$\frac{\hbar k}{m} = \frac{\hbar k}{m}|B|^2 + \frac{\hbar k'}{m}|C|^2, \tag{9.77}$$

which is satisfied for the values (9.75) of B and C. The transmission coefficient is not $|C|^2$, but

$$T = \frac{k'}{k}|C|^2.$$

[6] As we have already emphasized, to be completely rigorous it is necessary to construct wave packets from superpositions of plane waves in order to have a truly time-dependent problem describing the motion of a quantum particle.

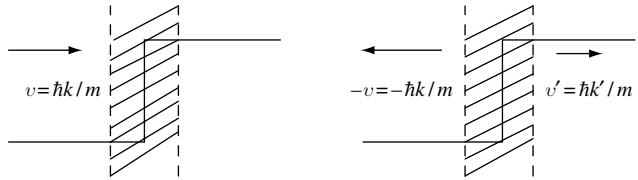

Fig. 9.9. Conservation of the current in crossing a potential step.

It takes into account the change of velocity in crossing the potential step: $v'/v = k'/k$. The loss of kinetic energy is of course the same as in classical mechanics.

9.3.3 The bound states of the square well

As the first example of bound states, let us study those of the infinite square well (Fig. 9.10):

$$V(x) = 0, \qquad 0 \le x \le a,$$
$$V(x) = +\infty, \quad x < 0 \ \text{ or } \ x > a.$$

The potential barriers at $x = 0$ and $x = a$ are infinite: a classical particle is confined to the region $0 \le x \le a$ for any energy. According to the preceding discussion, the wave function of a quantum particle vanishes outside the range $[0, a]$ and so the quantum particle is also strictly confined to the interval $[0, a]$; its probability density is zero outside the range $[0, a]$. Since the wave function vanishes at $x = 0$, the solutions of (9.70) have the form

$$\varphi(x) = A \sin(kx), \quad k = \sqrt{\frac{2mE}{\hbar^2}},$$

and they must also vanish at $x = a$. The values of k then are

$$k = k_n = \frac{\pi(n+1)}{a}, \quad n = 0, 1, 2, 3, \ldots \tag{9.78}$$

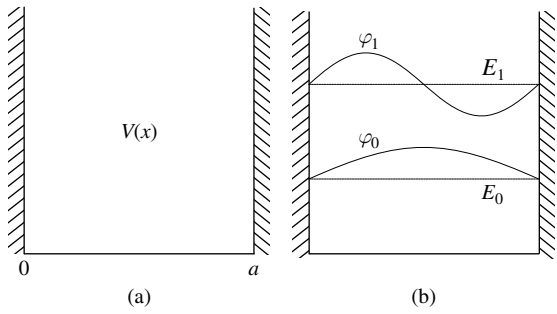

Fig. 9.10. The infinite square well and the wave functions of its first two levels.

We see that the energy takes discrete values labeled by a positive integer n:[7]

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 (n+1)^2, \quad n = 0, 1, 2, 3, \ldots} \,. \tag{9.79}$$

In other words, we have just shown that the energy levels of the infinite well are *quantized*, and this is the first example in which we have explicitly demonstrated this quantization. The correctly normalized wave function corresponding to the level E_n is

$$\varphi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi(n+1)x}{a}. \tag{9.80}$$

It is easy to check that two wave functions $\varphi_n(x)$ and $\varphi_m(x)$ are orthogonal for $n \neq m$. The values k_n and $-k_n$ correspond to the same physical state, because the substitution $k_n \to -k_n$ leads to a simple change of sign of the wave function, and a minus sign is a phase factor. This is why we have not included negative values of n in (9.78). We also note that the wave function $\varphi_n(x)$ vanishes n times in the interval $[0, a]$: it is said that the wave function has n *nodes* in this interval. The number of nodes gives a classification of the levels according to increasing energy: the higher the energy, the more nodes there are in the wave function. This is a general result when the potential $V(x)$ is sufficiently regular, which we always assume is the case: if E_n is the energy of the nth level, the corresponding wave function will have n nodes. The ground state wave function E_0 does not vanish. Another remark is that the Heisenberg inequality can be used to find the order of magnitude of the ground-state energy. It gives $p \sim \hbar/x \sim \hbar/a$, from which we find

$$E = \frac{p^2}{2m} \sim \frac{\hbar^2}{2ma^2},$$

in agreement with (9.79) for $n = 0$ up to a factor of π^2. In contrast to the case of the hydrogen atom, the heuristic result differs from the exact result by a factor of ~ 10. This originates in the strong variation of the potential at $x = 0$ and $x = a$ which makes the wave function vanish abruptly, resulting in a large kinetic energy. The expectation value of the kinetic energy in the state φ is

$$\langle K \rangle_\varphi = \langle \varphi | K | \varphi \rangle = -\frac{\hbar^2}{2m} \int \mathrm{d}x\, \varphi^*(x) \frac{\mathrm{d}^2 \varphi(x)}{\mathrm{d}x^2},$$

and it is larger the larger the second derivative of $\varphi(x)$.

Let us now find the energy levels of the finite square well (Fig. 9.11):

$$V(x) = 0, \qquad |x| > a/2,$$
$$V(x) = -V_0, \quad |x| < a/2.$$

[7] Our convention is that $n = 0$ corresponds to the ground state, so as to conform with the usual convention: in general, the ground-state energy is denoted E_0.

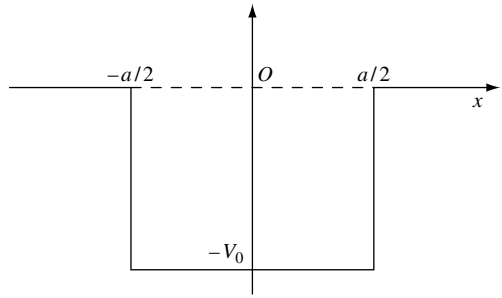

Fig. 9.11. The finite square well.

We seek the bound states, and so we must choose the energy to lie in the range $[-V_0, 0]$. We define k and κ as

$$\kappa = \sqrt{-\frac{2mE}{\hbar^2}}, \quad k = \sqrt{\frac{2m(V_0+E)}{\hbar^2}}, \quad 0 \le \kappa^2 \le \frac{2mV_0}{\hbar^2}. \tag{9.81}$$

The potential $V(x)$ is invariant under the parity operation Π: $x \to -x$, as $V(x)$ is an even function of x, $V(-x) = V(x)$, and so the Hamiltonian is also parity-invariant: $H(-x) = H(x)$. Following the discussion of Section 8.3.3, we can seek the eigenvectors $|\varphi_\pm\rangle$ of H which are even or odd under the parity operation:

$$\Pi|\varphi_\pm\rangle = \pm|\varphi_\pm\rangle.$$

In terms of the wave function, if $\langle x|\varphi_\pm\rangle = \varphi_\pm(x)$, then

$$\varphi_+(-x) = \varphi(x), \quad \varphi_-(-x) = -\varphi_-(x)$$

where we have used $\Pi|x\rangle = |-x\rangle$:

$$\begin{aligned}\langle x|\Pi|\varphi_\pm\rangle &= \langle -x|\varphi_\pm\rangle = \varphi_\pm(-x)\\ &= \pm\langle x|\varphi_\pm\rangle = \pm\varphi_\pm(x).\end{aligned}$$

The solutions of the Schrödinger equation (9.57) split up into even and odd ones. In the following display we give these solutions for region I where $x < -a/2$, region II where $|x| < a/2$, and region III where $x > a/2$. The middle column gives the wave functions of the even solutions, and the right-hand column gives the wave functions of the odd ones:

$$\begin{aligned}\text{I}: &\ A\,\mathrm{e}^{-\kappa|x|} && -A'\mathrm{e}^{-\kappa|x|}\\ \text{II}: &\ B\cos(kx) && B'\sin(kx)\\ \text{III}: &\ A\,\mathrm{e}^{-\kappa x} && A'\mathrm{e}^{-\kappa x}.\end{aligned}$$

The continuity conditions on φ'/φ at the point $x = a/2$ give

$$\kappa = k\tan(ka/2) \quad \text{for even solutions,} \tag{9.82}$$

$$\kappa = -k\cot(ka/2) \quad \text{for odd solutions.} \tag{9.83}$$

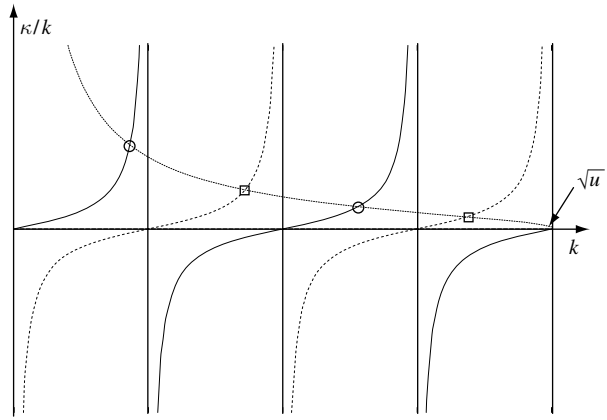

Fig. 9.12. Graphical solution for the bound states of the finite square well, located at points where the curves $\tan ka/2$ (solid line) and $-\cot ka/2$ (dotted line) intersect the curve $\sqrt{U-k^2}/k$, with $U = 2mV_0/\hbar^2$.

The graphical solution of these equations is shown in Fig. 9.12. We see that the number of bound states is finite, and there always exists at least one.

9.4 Potential scattering

9.4.1 The transmission matrix

Now that we have studied bound states, let us turn to scattering states. We shall study the behavior of a particle when it passes over a square well (Fig. 9.11) or a square barrier (Fig. 9.13) using explicit expressions based on the continuity of the wave function and its derivative at a discontinuity of the potential. In the course of our discussion, we shall also be able to derive results which are general as they are independent of the shape of

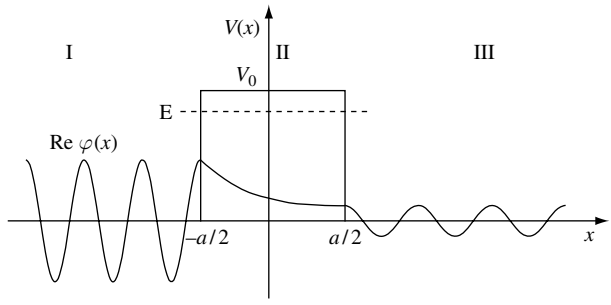

Fig. 9.13. Behavior of the real part of the wave function in the presence of the tunnel effect.

the potential. Let us start with the square well of Fig. 9.11. In Section 9.3.3 we found its bound states $E < 0$, and now we are interested in the scattering states $E > 0$. Defining

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad k' = \sqrt{\frac{2m(V_0 + E)}{\hbar^2}}, \tag{9.84}$$

the wave functions in the three regions become

$$\mathrm{I}: x < -\frac{a}{2}, \qquad \varphi(x) = A\,\mathrm{e}^{\mathrm{i}kx} + B\,\mathrm{e}^{-\mathrm{i}kx}, \tag{9.85}$$

$$\mathrm{II}: -\frac{a}{2} \le x \le \frac{a}{2}, \quad \varphi(x) = C\,\mathrm{e}^{\mathrm{i}k'x} + D\,\mathrm{e}^{-\mathrm{i}k'x}, \tag{9.86}$$

$$\mathrm{III}: x > \frac{a}{2}, \qquad \varphi(x) = F\,\mathrm{e}^{\mathrm{i}kx} + G\,\mathrm{e}^{-\mathrm{i}kx}. \tag{9.87}$$

Let us first study the passage from region I to region II, that is, the point $x = -a/2$. Since the Schrödinger equation is linear, A and B are linearly related to C and D, which we can write in matrix form:[8]

$$\begin{pmatrix} A \\ B \end{pmatrix} = R \begin{pmatrix} C \\ D \end{pmatrix}, \tag{9.88}$$

where R is a 2×2 matrix. The properties of R can be determined without explicitly writing down the continuity conditions. A first observation is that if $\varphi(x)$ is a time-independent solution of the Schrödinger equation (9.70), then the complex conjugate $\varphi^*(x)$ is also a solution of this equation because the potential $V(x)$ is real. This property is related to the invariance under time reversal; see Section 9.4.3 and Appendix A. The function $\varphi^*(x)$ in regions I and II is

$$\mathrm{I}: \varphi^*(x) = A^*\mathrm{e}^{-\mathrm{i}kx} + B^*\mathrm{e}^{\mathrm{i}kx}, \tag{9.89}$$

$$\mathrm{II}: \varphi^*(x) = C^*\mathrm{e}^{-\mathrm{i}k'x} + D^*\mathrm{e}^{\mathrm{i}k'x}. \tag{9.90}$$

Comparing the coefficients of $\exp(\pm \mathrm{i}kx)$ and $\exp(\pm \mathrm{i}k'x)$ with those of (9.85) and (9.86), from (9.88) we find that

$$\begin{pmatrix} B^* \\ A^* \end{pmatrix} = R \begin{pmatrix} D^* \\ C^* \end{pmatrix},$$

or

$$R_{11}^* = R_{22}, \quad R_{12}^* = R_{21}.$$

We can then write the matrix R as a function of two complex numbers α and β:

$$R = \sqrt{\frac{k'}{k}} \begin{pmatrix} \alpha & \beta \\ \beta^* & \alpha^* \end{pmatrix}. \tag{9.91}$$

[8] One can also observe that the continuity conditions linearly relate (A, B) to (C, D).

The reason for the introduction of the a priori arbitrary factor $\sqrt{k'/k}$ will become apparent shortly. The current conservation in regions I and II is expressed as (cf. (9.77))

$$k(|A|^2 - |B|^2) = k'(|C|^2 - |D|^2).$$

Let us calculate the current in region I, writing A and B as functions of C and D:

$$\begin{aligned} k(|A|^2 - |B|^2) &= k\frac{k'}{k}\left(|\alpha C + \beta D|^2 - |\beta^* C + \alpha^* D|^2\right) \\ &= k'\left(|\alpha|^2 - |\beta|^2\right)\left(|C|^2 - |D|^2\right), \end{aligned}$$

which implies that $|\alpha|^2 - |\beta|^2 = 1$: the matrix $\sqrt{k/k'}\,R$ has unit determinant. We see why the coefficient $\sqrt{k'/k}$ in (9.91) is of interest: owing to the variation of the velocity between regions I and II, it is the matrix $\sqrt{k/k'}\,R$ which possesses the simplest properties.

Let us now return to the explicit calculation of the continuity conditions in order to find the parameters α and β of the matrix R. It is convenient to choose $C = 1$ and $D = 0$, which corresponds to the situation where there is no source of particles at $x = +\infty$ (see Footnote 6). The continuity conditions then become

$$\begin{aligned} \mathrm{e}^{-\mathrm{i}k'a/2} &= A\,\mathrm{e}^{-\mathrm{i}ka/2} + B\,\mathrm{e}^{\mathrm{i}ka/2}, \\ k'\,\mathrm{e}^{-\mathrm{i}k'a/2} &= kA\,\mathrm{e}^{-\mathrm{i}ka/2} - kB\,\mathrm{e}^{\mathrm{i}ka/2}. \end{aligned}$$

Multiplying the first equation by k' and then adding and subtracting the two equations, we immediately obtain A and B:

$$\alpha = \sqrt{\frac{k}{k'}}\,A = \frac{k+k'}{2\sqrt{kk'}}\,\mathrm{e}^{\mathrm{i}(k-k')a/2}, \tag{9.92}$$

$$\beta = \sqrt{\frac{k}{k'}}\,B^* = \frac{k-k'}{2\sqrt{kk'}}\,\mathrm{e}^{\mathrm{i}(k+k')a/2}. \tag{9.93}$$

These values of α and β satisfy $|\alpha|^2 - |\beta|^2 = 1$. The continuity equations for $x = a/2$ are obtained by the substitutions $a \to -a$ and $k \leftrightarrow k'$. The matrix $\tilde{R}$ satisfying

$$\begin{pmatrix} C \\ D \end{pmatrix} = \tilde{R}\begin{pmatrix} F \\ G \end{pmatrix}$$

is written as

$$\tilde{R} = \sqrt{\frac{k}{k'}}\begin{pmatrix} \tilde{\alpha} & \tilde{\beta} \\ \tilde{\beta}^* & \tilde{\alpha}^* \end{pmatrix}$$

with

$$\begin{aligned} \tilde{\alpha} &= \frac{k+k'}{2\sqrt{kk'}}\,\mathrm{e}^{\mathrm{i}(k-k')a/2} = \alpha, \\ \tilde{\beta} &= -\frac{k-k'}{2\sqrt{kk'}}\,\mathrm{e}^{-\mathrm{i}(k+k')a/2} = -\beta^*. \end{aligned}$$

The transmission matrix M for regions I and III relates the coefficients A and B to the coefficients F and G:

$$\begin{pmatrix} A \\ B \end{pmatrix} = R \begin{pmatrix} C \\ D \end{pmatrix} = R\tilde{R} \begin{pmatrix} F \\ G \end{pmatrix} = M \begin{pmatrix} F \\ G \end{pmatrix}, \tag{9.94}$$

and so we have $M = R\tilde{R}$. The arguments used above immediately give two properties of M.

(i) Since $\varphi^*(x)$ is a solution of (9.57) (invariance under time reversal), we find relations identical to those for R:

$$M_{11} = M_{22}^*, \quad M_{12} = M_{21}^*.$$

(ii) Current conservation implies that $\det M = 1$. There is no factor $\sqrt{k'/k}$ because the velocity is the same in regions I and III.

The general form of M is therefore

$$M = \begin{pmatrix} \gamma & \delta \\ \delta^* & \gamma^* \end{pmatrix}, \quad |\gamma|^2 - |\delta|^2 = 1. \tag{9.95}$$

This expression for M is independent of the form of the potential provided that the latter vanishes sufficiently rapidly for $x \to \pm\infty$; for example, it is valid for the potential of Fig. 9.4. Let us explicitly calculate M for the potential well of Fig. 9.11 using the results obtained for the matrices R and $\tilde{R}$:

$$\begin{aligned} M_{11} = \gamma = \alpha^2 - \beta^2 &= \frac{\mathrm{e}^{\mathrm{i}ka}}{4kk'} \left[(k+k')^2 \mathrm{e}^{-\mathrm{i}k'a} - (k-k')^2 \mathrm{e}^{\mathrm{i}k'a} \right] \\ &= \mathrm{e}^{\mathrm{i}ka} \left[\cos k'a - \mathrm{i} \frac{k^2 + k'^2}{2kk'} \sin k'a \right], \end{aligned} \tag{9.96}$$

$$M_{12} = \delta = -\alpha\beta^* + \alpha^*\beta = \mathrm{i} \frac{k'^2 - k^2}{2kk'} \sin k'a. \tag{9.97}$$

It is instructive to check, using (9.95), that the expressions (9.96) and (9.97) satisfy $|\gamma|^2 - |\delta|^2 = 1$.

There is a general property of M which we have not yet used. When the potential is parity-invariant, $V(x) = V(-x)$, the parity operation $x \to -x$ exchanges regions I and III. If $\varphi(x)$ is the initial solution and $\chi(x) = \varphi(-x)$, we have

$$\begin{aligned} \mathrm{I} : \chi(x) &= F\,\mathrm{e}^{-\mathrm{i}kx} + G\,\mathrm{e}^{\mathrm{i}kx}, \\ \mathrm{III} : \chi(x) &= A\,\mathrm{e}^{-\mathrm{i}kx} + B\,\mathrm{e}^{\mathrm{i}kx}, \end{aligned}$$

and the relation between the various coefficients is now

$$\begin{pmatrix} G \\ F \end{pmatrix} = M \begin{pmatrix} B \\ A \end{pmatrix}$$

or

$$\begin{pmatrix} B \\ A \end{pmatrix} = M^{-1} \begin{pmatrix} G \\ F \end{pmatrix} = \begin{pmatrix} M_{22} & -M_{12} \\ -M_{21} & M_{11} \end{pmatrix} \begin{pmatrix} G \\ F \end{pmatrix}.$$

We have used $\det M = 1$. Comparing with (9.94), we find that M is an antisymmetric matrix, $M_{12} = -M_{21}$, which together with $M_{12}^* = M_{21}$ implies that δ is purely imaginary, $\delta = \mathrm{i}\eta$, with η real. This property is satisfied by (9.97). The general form of M for an even potential $[V(x) = V(-x)]$ then is

$$M = \begin{pmatrix} \gamma & \mathrm{i}\eta \\ -\mathrm{i}\eta & \gamma^* \end{pmatrix} \quad |\gamma|^2 - \eta^2 = 1, \tag{9.98}$$

with γ complex and η real.

All of these results can be used to calculate the reflection and transmission coefficients for the potential well of Fig. 9.11 and to understand their behavior. We shall return to this subject in Exercise 9.7.8. Now we go directly to the case of a potential barrier, which will lead to discussion of the tunnel effect.

9.4.2 The tunnel effect

Let us consider the potential barrier of Fig. 9.13:

$$\begin{aligned} V(x) &= V_0, \quad |x| \le \frac{a}{2}, \\ V(x) &= 0, \quad |x| > \frac{a}{2}, \end{aligned} \tag{9.99}$$

for energy $E < V_0$ (the case $E > V_0$ is solved immediately using the results of the preceding subsection). The quantity k' then is purely imaginary:

$$k' = \mathrm{i}\kappa, \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}, \tag{9.100}$$

and the wave function in region II, $|x| \le a/2$, is

$$\varphi(x) = C\,\mathrm{e}^{-\kappa x} + D\,\mathrm{e}^{\kappa x}. \tag{9.101}$$

The element M_{11} of the transmission matrix is obtained without calculation by replacing k' by $\mathrm{i}\kappa$ in (9.96); this gives, for example,

$$\sin k'a = \frac{1}{2\mathrm{i}} \left(\mathrm{e}^{\mathrm{i}k'a} - \mathrm{e}^{-\mathrm{i}k'a}\right) \to \frac{1}{2\mathrm{i}} \left(\mathrm{e}^{-\kappa a} - \mathrm{e}^{\kappa a}\right) = \mathrm{i} \sinh \kappa a$$

and similarly $\cos k'a \to \cosh \kappa a$. The result for M_{11} then is

$$M_{11} = \mathrm{e}^{\mathrm{i}ka} \left[\cosh \kappa a + \mathrm{i}\,\frac{\kappa^2 - k^2}{2\kappa k} \sinh \kappa a\right]. \tag{9.102}$$

We assume that the particle source is located at $x = -\infty$ and we adopt the normalization $A = 1$. Since there is no particle source at $x = +\infty$, we must have $G = 0$, which gives

$$\begin{pmatrix} 1 \\ B \end{pmatrix} = M \begin{pmatrix} F \\ 0 \end{pmatrix} = \begin{pmatrix} M_{11} F \\ M_{21} F \end{pmatrix}$$

or $F = 1/M_{11}$:

$$F = \frac{\mathrm{e}^{-\mathrm{i}ka}}{\cosh \kappa a + \mathrm{i} \dfrac{\kappa^2 - k^2}{2\kappa k} \sinh \kappa a}. \tag{9.103}$$

This leads to an important physical result, namely, the transmission coefficient $T = |F|^2$:

$$\boxed{T = |F|^2 = \frac{1}{1 + \dfrac{q^4}{4k^2\kappa^2} \sinh^2 \kappa a}}, \tag{9.104}$$

where we have defined $q^2 = k^2 + \kappa^2 = 2mV_0/\hbar^2$. The essential point is that $T \neq 0$. Whereas region III is inaccessible to a classical particle incident from $x = -\infty$ with an energy $E < V_0$, a quantum particle has a nonzero probability of passing through the potential barrier. This is called the *tunnel effect*. The origin of this effect is easy to understand: the wave function does not vanish in the region $|x| \leq a/2$ and it can be matched to a plane wave in the region $x > a/2$ (Fig. 9.13).

An approximate expression for T can be obtained in the commonly encountered case $\kappa a \gg 1$:

$$T \simeq \frac{16k^2\kappa^2}{q^4} \mathrm{e}^{-2\kappa a}. \tag{9.105}$$

The dominant factor in this equation is the exponential $\exp(-2\kappa a)$. It is possible to derive heuristically a widely used approximation for a potential barrier of any shape when $E < \mathrm{Max}\, V(x)$. Approximating the barrier as a sequence of steps of length Δx as in Fig. 9.6, we can calculate the transmission factor in the range $[x_i, x_i + \Delta x]$:

$$T(x_i) \simeq \mathrm{e}^{-2\kappa(x_i)\Delta x}, \quad \kappa(x_i) = \sqrt{\frac{2m(V(x_i) - E)}{\hbar^2}},$$

and for the total transmission factor we find

$$T \simeq \prod_i \mathrm{e}^{-2\kappa(x_i)\Delta x} = \exp\left(-2\Delta x \sum_i \kappa(x_i)\right).$$

We recognize this as a Riemann sum, and in the limit $\Delta x \to 0$

$$\boxed{T \simeq \exp\left(-2\int_{x_1}^{x_2} \sqrt{\frac{2m(V(x) - E)}{\hbar^2}}\, \mathrm{d}x\right)}. \tag{9.106}$$

The points x_1 and x_2 are defined by $V(x_1) = V(x_2) = E$. The demonstration we have just given is not rigorous, because the treatment of the turning points x_1 and x_2 is actually rather delicate. An important observation is that the exponential dependence in (9.106) makes the transmission coefficient T extremely sensitive to the height of the barrier and the value of the energy.

The tunnel effect has numerous applications in quantum physics. Here we shall consider only two, α-radioactivity and tunneling microscopy. Alpha-radioactivity is the decay of a heavy nucleus with the emission of an α-particle, that is, a ^{4}He nucleus. Using Z and N to denote the numbers of protons and neutrons in the initial nucleus ($A = Z + N$) (in general, $Z \gtrsim 80$), the nuclear α-decay reaction can be written as

$$(Z, N) \rightarrow (Z-2, N-2) + {}^4\mathrm{He}. \tag{9.107}$$

An example is the decay of polonium into lead:

$${}^{214}_{84}\mathrm{Po} \rightarrow {}^{210}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He} + 7.8\ \mathrm{MeV}. \tag{9.108}$$

In an approximate theory of α radioactivity, it is assumed that the α-particle pre-exists inside the initial nucleus and for simplicity the problem is assumed to be one-dimensional. If $R \simeq 1.2 \times A^{1/3} \simeq 7\,\mathrm{fm}$ is the nuclear radius, the α-particle will be subjected to the nuclear potential and the repulsive Coulomb potential between the ^{4}He nucleus of charge 2 (in units of the proton charge) and the final nucleus of charge $(Z-2)$ assuming that the charge distribution is spherically symmetric. If r is the distance between the helium nucleus and the final nucleus, for $r > R$ we will have

$$V_{\mathrm{Coul}}(r) = \frac{2(Z-2)e^2}{r^2}.$$

When $r < R$ the attractive nuclear forces dominate the Coulomb forces and the latter can be neglected. The result is the potential shown schematically in Fig. 9.14. It has a potential barrier which would prevent the α-particle from leaving the nucleus if its motion were governed by classical physics. It is the tunnel effect that allows the α-particle to

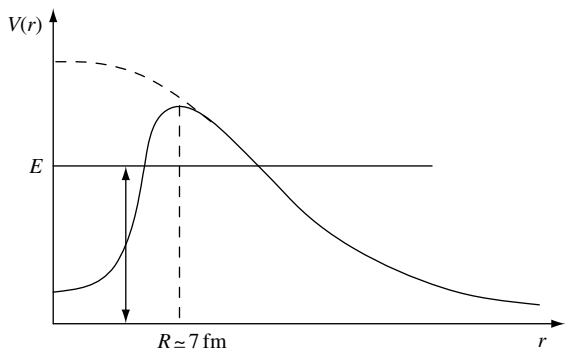

Fig. 9.14. Potential barrier of α-radioactivity.

leave the nucleus. This argument can be used to obtain a theoretical estimate of the lifetime of the initial nucleus, but the approximations we have made are crude and the tunnel effect is very sensitive to the details. While the underlying physics is undoubtedly correct, we cannot expect to obtain results in quantitative agreement with experiment. The reverse of radioactive decay is the fusion reaction; an example is the reaction mentioned in Section 1.1.2:

$$^2\mathrm{H} + ^3\mathrm{H} \rightarrow ^4\mathrm{He} + \mathrm{n} + 17.6\ \mathrm{MeV},$$

which also involves the tunnel effect and is studied in Exercise 12.5.1.

A very important application of the tunnel effect is scanning tunneling microscopy (STM). In such a microscope a very fine tip is moved over the surface of the conducting sample very close to it (Fig. 9.15). Owing to the tunnel effect, electrons can pass from the tip to the sample, thus producing a macroscopic current that depends very sensitively on the distance between the tip and the sample (the dependence (9.105) is exponential). This allows a very precise mapping of the surface of the sample with a resolution of about 0.01 nm. An extension of this technique can be used to manipulate atoms and molecules deposited on a substrate (Fig. 9.16).

9.4.3 The S matrix

In Chapter 12 we shall study the theory of scattering in three-dimensional space. We shall see that an important tool in this theory is the S matrix, which we introduce here in the simplest case of one dimension. We assume a potential of arbitrary shape which vanishes in the region $|x| > L$.[9] Particle sources at $x = -\infty$ and $x = +\infty$ generate plane waves

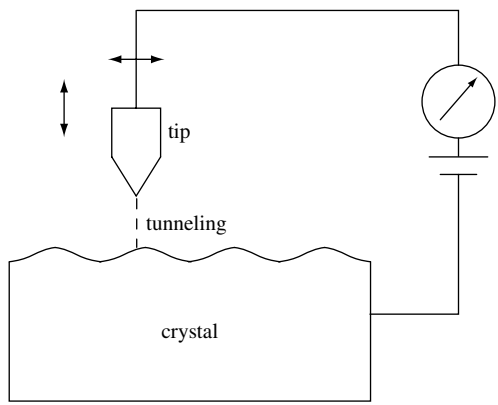

Fig. 9.15. The principle of the scanning tunneling microscope (STM). A fine tip is moved near the surface of a crystal and the distance is adjusted such that the current is constant. This gives a map of the electron distribution on the surface.

[9] We can generalize to the case of a potential which vanishes sufficiently rapidly for $x \rightarrow \pm\infty$.

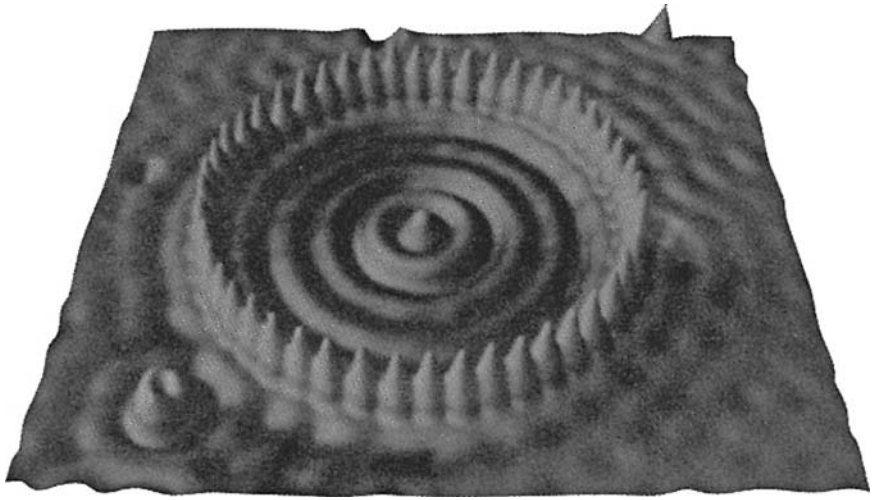

Fig. 9.16. Deposition of atoms by scanning tunneling microscopy. Iron atoms (peaks) are deposited in a circle on a copper substrate and form resonant electron states (waves) on the copper surface. Copyright: IBM.

$\exp(\mathrm{i}kx)$ and $\exp(-\mathrm{i}kx)$ in the regions $x < -L$ and $x > L$, respectively; we call these the *incoming waves*. These incoming waves can be reflected or transmitted, resulting in outgoing waves $\exp(-\mathrm{i}kx)$ in the region $x < -L$ and $\exp(\mathrm{i}kx)$ in the region $x > L$. By definition, the S matrix relates the coefficients B and F of the outgoing waves to the coefficients A and G of the incoming waves (cf. (9.85) and (9.87)):

$$\begin{pmatrix} B \\ F \end{pmatrix} = S \begin{pmatrix} A \\ G \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A \\ G \end{pmatrix}. \tag{9.109}$$

The S matrix can be expressed as a function of M. However, before deriving the expressions for going from M to S, it is instructive to repeat the arguments that led us to the general properties of M.

(i) Current conservation:

$$|A|^2 - |B|^2 = |F|^2 - |G|^2 \Longrightarrow |A|^2 + |G|^2 = |B^2| + |F|^2.$$

This equation shows that the norm of S is conserved and so S is unitary.[10]

(ii) $\varphi^*(x)$ is a solution of the Schrödinger equation, so that

$$\begin{pmatrix} A^* \\ G^* \end{pmatrix} = S \begin{pmatrix} B^* \\ F^* \end{pmatrix} \Longrightarrow \begin{pmatrix} B \\ F \end{pmatrix} = (S^*)^{-1} \begin{pmatrix} A \\ G \end{pmatrix},$$

[10] This argument is valid only for finite dimension: we have proved only that S is an isometry, which is sufficient to make it a unitary operator in finite dimension. It turns out that S is unitary also in infinite dimension, but the proof of this requires additional arguments.

from which we find

$$S = (S^*)^{-1} = (S^{-1})^* = (S^\dagger)^* = S^T.$$

The S matrix is symmetric: $S_{12} = S_{21}$. The operation of complex conjugation exchanges the incoming and outgoing waves, which corresponds to time reversal. The symmetry property $S_{12} = S_{21}$ is therefore related to invariance under time reversal.

Now let us relate S and M in the form (9.95) by calculating the coefficient B:

$$\begin{aligned} B &= S_{11}A + S_{12}G = S_{11}(\gamma F + \delta G) + S_{12}G \\ &= S_{11}\gamma F + (S_{11}\delta + S_{12})G. \end{aligned}$$

We identify

(a) $S_{11}\gamma = \delta^*, \quad S_{11} = \dfrac{\delta^*}{\gamma}$;

(b) $S_{12} + S_{11}\delta = \gamma^*, \quad S_{12} = \gamma^* - S_{11}\delta = \dfrac{1}{\gamma}$,

or

$$S = \frac{1}{\gamma}\begin{pmatrix} \delta^* & 1 \\ 1 & -\delta \end{pmatrix}. \tag{9.110}$$

If the potential is even $V(x) = V(-x)$, $\delta = \mathrm{i}\eta$ with η real and S becomes

$$S = \frac{1}{\gamma}\begin{pmatrix} -\mathrm{i}\eta & 1 \\ 1 & -\mathrm{i}\eta \end{pmatrix}. \tag{9.111}$$

To write S in the most transparent form possible, we set

$$\gamma = |\gamma|\mathrm{e}^{-\mathrm{i}\phi}, \quad \frac{\eta}{|\gamma|} = \cos\theta, \quad \frac{1}{|\gamma|} = \sin\theta.$$

The S matrix becomes

$$S = -\mathrm{i}\mathrm{e}^{\mathrm{i}\phi}\begin{pmatrix} \cos\theta & \mathrm{i}\sin\theta \\ \mathrm{i}\sin\theta & \cos\theta \end{pmatrix}. \tag{9.112}$$

However, we cannot have $\theta = 0$, as this would correspond to $|\gamma| \to \infty$. On the other hand, it is possible to have $\theta = \pm\pi/2$ if $\eta = 0$.

An interesting aspect of the S matrix is that it can be used to relate scattering to bound states and, more generally, to resonances (Exercise 12.5.4). Taking a potential well of arbitrary shape (but such that $V(x) = 0$ outside some finite range in order to simplify the discussion), we choose $E < 0$ with $\kappa = -\mathrm{i}k$ given by (9.81). The wave functions in regions I and III are

$$\begin{aligned} \mathrm{I} &: \varphi(x) = A\,\mathrm{e}^{-\kappa x} + B\,\mathrm{e}^{\kappa x}, \\ \mathrm{III} &: \varphi(x) = F\,\mathrm{e}^{-\kappa x} + G\,\mathrm{e}^{\kappa x}. \end{aligned}$$

We must have $A = G = 0$ in order for $\varphi(x)$ to be normalizable. Using the relation (9.109), if we want to have $(B, F) \neq 0$, S must have a pole[11] at $k = \mathrm{i}\kappa$. This property is general and can be verified for the square well of Fig. 9.11. According to (9.96),

$$\gamma(\mathrm{i}\kappa) = \mathrm{e}^{-\kappa a}\left[\cos k'a - \frac{k'^2 - \kappa^2}{2\kappa k'}\sin k'a\right].$$

Since S contains an overall factor of $1/\gamma$ (cf. (9.111)), γ must vanish for a bound state. Setting $v = \tan(k'a/2)$, the equation $\gamma = 0$ is equivalent to

$$\kappa k' v^2 + v(k'^2 - \kappa^2) - \kappa k' = 0,$$

whose solutions are $v = \kappa/k'$ and $v = -k'/\kappa$, that is, precisely the relations (9.82) and (9.83) found directly for the finite square well.

9.5 The periodic potential

9.5.1 The Bloch theorem

As a final example of the one-dimensional Schrödinger equation, let us take the case of a periodic potential of spatial period l:

$$V(x) = V(x + l). \tag{9.113}$$

The results that we shall obtain are of great importance in solid-state physics, as an electron in a crystal is subjected to a periodic potential due to its interactions with the ions of the crystal lattice. That case is, of course, three-dimensional, but the results obtained for one dimension generalize to three. The periodicity of the potential leads to the existence of energy bands which, in combination with the Pauli principle, form the basis of our understanding of electrical conductivity. If the potential has the form (9.113), the problem is invariant under any translation $x \to x + l$, and according to the Wigner theorem there exists a unitary operator T_l acting in the Hilbert space of states, here the space of wave functions $L_x^{(2)}(\mathbb{R})$, such that

$$(T_l\varphi)(x) = \varphi(x - l), \quad T_l^\dagger = T_l^{-1}. \tag{9.114}$$

We recall that the function obtained from $\varphi(x)$ by translation by l is $\varphi(x - l)$. Since the operator T_l is unitary, its eigenvalues t_l have unit modulus and can be written as a function of a parameter q as

$$t_l(q) = \mathrm{e}^{-\mathrm{i}ql}. \tag{9.115}$$

The parameter q is defined up to an integer multiple of $2\pi/l$; if

$$q \to q' = q + \frac{2\pi p}{l}, \quad p = 0, \pm 1, \pm 2, \ldots, \tag{9.116}$$

[11] Or, more generally, a singularity, but it can be shown that bound states and resonances correspond to poles.

the value of t_l is unchanged. Since T_l commutes with the Hamiltonian owing to the periodicity (9.113) of the potential, T_l and H can be diagonalized simultaneously. Let $\varphi_q(x)$ be the common eigenfunctions of T_l and H:

$$T_l\varphi_q(x) = t_l(q)\varphi_q(x) = \mathrm{e}^{-\mathrm{i}ql}\,\varphi_q(x),$$
$$H\varphi_q(x) = E_q\varphi_q(x). \tag{9.117}$$

The first of these equations shows that

$$\varphi_q(x-l) = \mathrm{e}^{-\mathrm{i}ql}\,\varphi_q(x),$$

and we derive the *Bloch theorem*,[12] which states that the stationary states in a periodic potential (9.113) have the form

$$\varphi_q(x) = \mathrm{e}^{\mathrm{i}qx}\,u_{sq}(x), \quad u_{sq}(x) = u_{sq}(x+l), \tag{9.118}$$

where $u_{sq}(x)$ is a periodic function with period l. The index s is needed because several possible solutions correspond to each value of q; we shall see below that s labels the energy bands. It is easy to write down the differential equation satisfied by $u_{sq}(x)$. Since $P = -\mathrm{i}\hbar\mathrm{d}/\mathrm{d}x$, we have

$$P\mathrm{e}^{\mathrm{i}qx} = \hbar q\,\mathrm{e}^{\mathrm{i}qx},$$
$$P\varphi_q(x) = \mathrm{e}^{\mathrm{i}qx}\,(P+\hbar q)u_{sq}(x),$$
$$P^2\varphi_q(x) = \mathrm{e}^{\mathrm{i}qx}\,(P+\hbar q)^2u_{sq}(x),$$

from which

$$H\varphi_q(x) = \mathrm{e}^{\mathrm{i}qx}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \mathrm{i}\frac{\hbar^2q}{m}\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\hbar^2q^2}{2m} + V(x)\right]u_{sq}(x) = E_{sq}\mathrm{e}^{\mathrm{i}qx}\,u_{sq}(x),$$

or, dividing by $\exp(\mathrm{i}qx)$,

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \mathrm{i}\frac{\hbar^2q}{m}\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\hbar^2q^2}{2m} + V(x)\right]u_{sq}(x) = E_{sq}u_{sq}(x). \tag{9.119}$$

The wave function in a periodic potential is obtained by solving (9.119) in, for example, the range $[0, l]$ with the boundary condition $u_{sq}(0) = u_{sq}(l)$. The quantity $\hbar q$ has the dimensions of momentum and is in some ways analogous to a momentum. However, it is not a true momentum, because according to (9.116) q is not unique; $\hbar q$ is therefore called a *quasi-momentum*. Finally, we note that if the potential is even, $V(x) = V(-x)$, then (9.119) is unchanged under the simultaneous transformations $x \to -x$, $q \to -q$; $u_{s,-q}(x)$ is therefore a solution of (9.119) with the same value of the energy, $E_{sq} = E_{s,-q}$, and all levels are doubly degenerate.

[12] This theorem is also known as the Floquet theorem in the case of periodicity in time.

9.5.2 Energy bands

Let us now examine the properties of the solutions of the Schrödinger equation (9.119) for the periodic potential of Fig. 9.17. Here $V(x)$ is a series of potential barriers and $V(x)$ is nonzero in intervals centered on $x = pl$, $p = \ldots, -2, -1, 0, 1, 2 \ldots$ and vanishes in the intervals[13]

$$\left(p - \frac{1}{2}\right) l - \Delta x \leq x \leq \left(p - \frac{1}{2}\right) l + \Delta x. \tag{9.120}$$

In the intervals where $V(x)$ vanishes a solution $\varphi(x)$ of the Schrödinger equation is a superposition of plane waves with wave vector $\pm k$, $k = (2mE/\hbar^2)^{1/2}$. To the left of the nth barrier and in the interval (9.120) for $p = n$, $\varphi(x)$ is written as

$$\varphi(x) = A_n e^{ikx} + B_n e^{-ikx},$$

and to the right of this barrier, in the interval (9.120) with $p = n + 1$,

$$\varphi(x) = A_{n+1} e^{ikx} + B_{n+1} e^{-ikx}.$$

The coefficients (A_n, B_n) are related to the coefficients (A_{n+1}, B_{n+1}) as in (9.94) by the transmission matrix M (9.95) corresponding to a barrier $V(x)$:

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} \gamma & \delta \\ \delta^* & \gamma^* \end{pmatrix} \begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix}. \tag{9.121}$$

However, using the Bloch theorem (9.118) we find

$$\varphi(x + l) = e^{iql} \varphi(x),$$

so that

$$A_{n+1} e^{ikl} e^{ikx} + B_{n+1} e^{-ikl} e^{-ikx} = e^{iql} \left(A_n e^{ikx} + B_n e^{-ikx}\right)$$

or

$$e^{iql} \begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} e^{ikl} A_{n+1} \\ e^{-ikl} B_{n+1} \end{pmatrix} = D \begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = DM^{-1} \begin{pmatrix} A_n \\ B_n \end{pmatrix}. \tag{9.122}$$

Here D is a diagonal matrix with elements $D_{11} = \exp(ikl)$, $D_{22} = \exp(-ikl)$ and

$$DM^{-1} = \begin{pmatrix} \gamma^* e^{ikl} & -\delta e^{ikl} \\ -\delta^* e^{-ikl} & \gamma e^{-ikl} \end{pmatrix}. \tag{9.123}$$

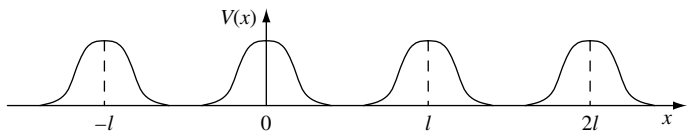

Fig. 9.17. A periodic potential of period l in one dimension.

[13] In fact, it is not necessary to assume this vanishing to obtain the following results, but it simplifies the discussion.

Equation (9.122) implies that (A_n, B_n) is an eigenvector of the matrix $\tilde{M} = DM^{-1}$ with eigenvalue $\exp(\mathrm{i}ql)$, which has unit modulus. The eigenvalues λ of the matrix $\tilde{M}$ are given by ($\det \tilde{M} = 1$)

$$\lambda^2 - 2\lambda \mathrm{Re}\,(\gamma^* \mathrm{e}^{\mathrm{i}kl}) + 1 = 0,$$

and setting $x = \mathrm{Re}\,[\gamma^* \exp(\mathrm{i}kl)]$ the eigenvalues $\lambda_\pm$ become

$$\lambda_\pm = x \pm \sqrt{x^2 - 1}, \quad |x| > 1,$$
$$\lambda_\pm = x \pm \mathrm{i}\sqrt{1 - x^2}, \quad |x| \leq 1.$$

The case $|x| > 1$ is excluded because the roots cannot have unit modulus as their product is equal to unity and they are real. However, the two complex roots have unit modulus for $|x| \leq 1$; they are nondegenerate if $|x| < 1$ and degenerate if $|x| = 1$.

To study the energy eigenvalues we could use the example of the rectangular barrier $V(x)$ (9.99) of Fig. 9.13. In order to simplify the calculations as much as possible, we shall study a limiting case of (9.99) where the barrier becomes a delta function. Our results can be qualitatively generalized to any periodic potential. The periodic potential (9.113) then is

$$V(x) = \sum_{p=-\infty}^{\infty} \frac{\hbar^2 g}{2m}\, \delta(x - lp). \tag{9.124}$$

The delta-function potential is obtained by taking the limit $a \to 0$ of the barrier (9.99) while keeping the product $V_0 a$ constant:

$$V_0 a = \frac{\hbar^2 g}{2m}.$$

The arbitrary factor $\hbar^2/2m$ is chosen so as to simplify the expressions which follow. Taking $V_0 \gg E$, we find that κ (9.100) has the limit

$$\kappa \to \sqrt{\frac{2mV_0}{\hbar^2}} = \sqrt{\frac{g}{a}},$$

which gives

$$\frac{\kappa^2 - k^2}{2\kappa k} \to \frac{\kappa}{2k} = \frac{\sqrt{g/a}}{2k},$$

while $\gamma = M_{11}$ in (9.102) becomes (see also Exercise 9.7.7)

$$\gamma \to 1 + \mathrm{i}\,\frac{\sqrt{g/a}}{2k}\sqrt{ga} = 1 + \mathrm{i}\,\frac{g}{2k}. \tag{9.125}$$

We then find

$$x = \mathrm{Re}\,(\gamma^* \mathrm{e}^{\mathrm{i}kl}) = \cos kl + \frac{g}{2k}\sin kl,$$

and the eigenvalue equation is written as

$$x = \cos ql = \cos kl + \frac{g}{2k}\sin kl. \tag{9.126}$$

It should be noted that q is not fixed uniquely by (9.126), as $q' = q + 2\pi p/l$ with integer p also satisfies (9.126). This equation shows that certain ranges of k, and therefore certain energy ranges owing to $E = \hbar^2 k^2/2m$, are excluded because the right-hand side of (9.126) can have modulus greater than unity. These ranges are called *forbidden bands*. Let us demonstrate this explicitly in the region $k \simeq 0$. We set $y = kl$ and

$$f(y) = \cos y + \frac{gl}{2y}\sin y.$$

Since $f(0) = 1 + gl/2$, we see that the range $0 \le y < y_0$ or $0 \le k < k_0$ is forbidden. Assuming that $gl \ll 1$ in order to make an analytic estimate, we find

$$y_0 \simeq \sqrt{gl} \quad \text{or} \quad k_0 \simeq \sqrt{g/l}.$$

Other forbidden bands exist; in fact, if

$$y = n\pi + \varepsilon, \quad |\varepsilon| \ll 1,$$

then

$$|f(y)| \simeq 1 + \frac{gl}{2y}\varepsilon,$$

and we see that there is a forbidden region where $|f(y)| > 1$ for $0 < \varepsilon \ll 1$. These remarks allow us to qualitatively sketch the curve $f(y)$ in Fig. 9.18. We adopt the convention where E is a function of q (recalling that $\hbar q$ is the quasi-momentum), which gives Fig. 9.19, in which the allowed bands labeled by s are displayed. Using (9.116), q can be restricted to the range $[0, 2\pi/l]$, or, equivalently, the range $[-\pi/l, \pi/l]$, which is called the *first Brillouin zone*. In certain regions E can be expressed simply as a function of q. For example, let us examine the region $k \simeq k_0$. Since $\cos ql = 1$ for $k = k_0$, (9.126) becomes, taking $f(k_0 l) = 1$,

$$-\frac{1}{2}q^2 l^2 \simeq (k - k_0) l f'(k_0 l).$$

This allows us to estimate $(E - E_0)$:

$$E - E_0 = \frac{\hbar^2}{2m}(k^2 - k_0^2) \simeq \frac{\hbar^2 k_0 (k - k_0)}{m},$$

or

$$E - E_0 = \frac{\hbar^2 l k_0}{2m|f'(k_0 l)|}q^2 = \frac{\hbar^2}{2m^*}q^2. \tag{9.127}$$

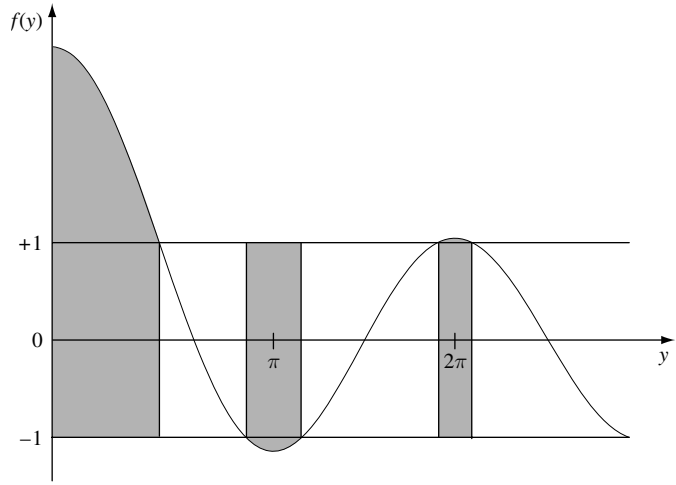

Fig. 9.18. Solutions of (9.126).

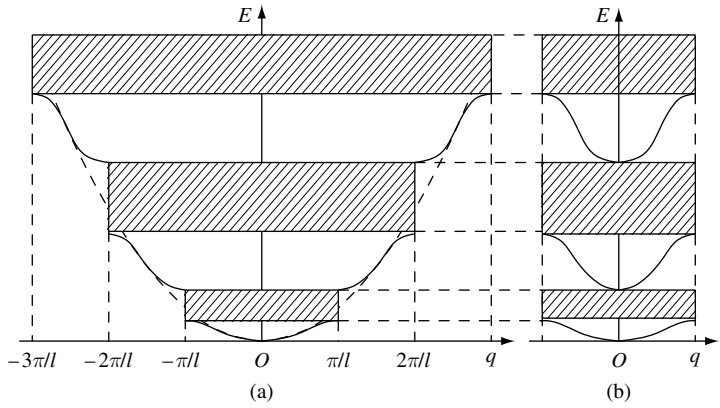

Fig. 9.19. Energy bands. (a) q varies without restrictions; (b) q is limited to the first Brillouin zone. The hatched regions correspond to forbidden bands.

In the neighborhood of $k = k_0$ the behavior of the energy is that of a particle of effective mass m^*:

$$m^* = \frac{m|f'(k_0 l)|}{lk_0}. \tag{9.128}$$

This effective mass plays an important role in the theory of electrical conductivity. To a first approximation the effect of the crystal lattice amounts to a simple change of the mass.

9.6 Wave mechanics in dimension $d = 3$

9.6.1 Generalities

Let $\vec{R}$ and $\vec{P}$ be the position and momentum operators in three-dimensional space with components X_j and P_j, $j = x, y, z$.[14] We recall the canonical commutation relations (8.45):

$$[X_j, P_k] = \mathrm{i}\hbar\,\delta_{jk}\,I. \tag{9.129}$$

The components of $\vec{R}$ and $\vec{P}$ commute if $j \neq k$. We can then construct the space of states as the tensor product of the spaces $L^{(2)}_x(\mathbb{R})$, $L^{(2)}_y(\mathbb{R})$, and $L^{(2)}_z(\mathbb{R})$:

$$L^{(2)}_{\vec{r}}(\mathbb{R}^3) = L^{(2)}_x(\mathbb{R}) \otimes L^{(2)}_y(\mathbb{R}) \otimes L^{(2)}_z(\mathbb{R}). \tag{9.130}$$

In this space the X component of $\vec{R}$ will be the operator

$$X \otimes I_y \otimes I_z.$$

If $\varphi_n(x)$ is an orthonormal basis of $L^{(2)}_x(\mathbb{R})$, we can construct a basis $\varphi_{nlm}(x, y, z)$ of $L^{(2)}_{\vec{r}}(\mathbb{R}^3)$ by taking the products[15]

$$\varphi_{nlm}(x, y, z) = \varphi_n(x)\varphi_m(y)\varphi_l(z). \tag{9.131}$$

The construction of the space of states and the orthonormal basis is strictly parallel to that of the space of states of two spins 1/2. In Section 6.2.3 we observed that the most general state vector of the space of states of two spins 1/2 is not in general a tensor product $|\varphi_1 \otimes \varphi_2\rangle$ of two state vectors of the individual spins. Similarly, a function $\psi(x, y, z)$ of $L^{(2)}_{\vec{r}}(\mathbb{R}^3)$ is not in general a product $\varphi(x)\chi(y)\eta(z)$, but $\psi(x, y, z)$ can be decomposed on the basis (9.131):

$$\psi(x, y, z) = \sum_{n,m,l} c_{nml}\,\varphi_n(x)\varphi_m(y)\varphi_l(z), \tag{9.132}$$

$$c_{nlm} = \int \mathrm{d}^3 r\,\varphi^*_n(x)\varphi^*_m(y)\varphi^*_l(z)\psi(x, y, z). \tag{9.133}$$

We can immediately write down the three-dimensional generalization of the equations in Section 9.1. We shall just give a few examples, leaving it to the reader to derive the other expressions.

- The eigenstates $|\vec{r}\rangle$ of $\vec{R}$ (cf. (9.3)):

$$\vec{R}\,|\vec{r}\rangle = \vec{r}\,|\vec{r}\rangle. \tag{9.134}$$

- The completeness relation (cf. (9.9)):

$$\int \mathrm{d}^3 r\,|\vec{r}\rangle\langle\vec{r}| = I. \tag{9.135}$$

[14] The components of $\vec{R}$ will also be denoted as (X, Y, Z) and those of $\vec{r}$ will be denoted as (x, y, z).

[15] To simplify the notation, we have taken the same basis functions in the (x, y, z) spaces, but we could of course have chosen three different bases.

- The probability amplitude $\varphi(\vec{r})$ for finding a particle in the state $|\varphi\rangle$ at the point $\vec{r}$, that is, the wave function of the particle:

$$\varphi(\vec{r}) = \langle \vec{r}|\varphi\rangle. \tag{9.136}$$

- The probability density: $|\varphi(\vec{r})|^2 \mathrm{d}^3 r$ is the probability of finding the particle in the volume $\mathrm{d}^3 r$ about the point $\vec{r}$.
- The action of the operators $\vec{R}$ and $\vec{P}$ on $\varphi(\vec{r})$ [cf. (9.14) and (9.16)]:

$$\boxed{\left(\vec{R}\varphi\right)(\vec{r}) = \vec{r}\varphi(\vec{r}), \quad \left(\vec{P}\varphi\right)(\vec{r}) = -\mathrm{i}\hbar\vec{\nabla}\varphi(\vec{r})}\ . \tag{9.137}$$

- The Fourier transform (cf. (9.26)):

$$\boxed{\tilde{\varphi}(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int \mathrm{d}^3 r\, \varphi(\vec{r})\, \mathrm{e}^{-\mathrm{i}\vec{p}\cdot\vec{r}/\hbar}}\ . \tag{9.138}$$

  The factor $(2\pi\hbar)^{-1/2}$ for each space dimension should be noted.

In Section 8.4.2 we determined the general form of the Hamiltonian in dimension $d = 3$. In the rest of this section we assume that $\vec{A}$ is a gradient: $\vec{A} = \vec{\nabla}\Lambda(\vec{r})$. Physically, this means that there is no magnetic field; the case of nonzero magnetic field will be studied in Section 11.3. The Hamiltonian (8.74) is simply

$$H = \frac{\vec{P}^2}{2m} + V(\vec{R}). \tag{9.139}$$

The time-independent Schrödinger equation[16] generalizing (9.57) to three dimensions is

$$\boxed{\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right)\varphi(\vec{r}) = E\varphi(\vec{r})}\ . \tag{9.140}$$

The generalization of the probability current (9.63) is

$$\boxed{\vec{j}(\vec{r}, t) = \mathrm{Re}\left[\frac{\hbar}{\mathrm{i}m}\,\varphi^*(\vec{r}, t)\vec{\nabla}\varphi(\vec{r}, t)\right]}\ , \tag{9.141}$$

which satisfies the continuity equation (Exercise 9.7.10)

$$\frac{\partial|\varphi(\vec{r}, t)|^2}{\partial t} + \vec{\nabla}\cdot\vec{j}(\vec{r}, t) = 0. \tag{9.142}$$

[16] We leave to the reader the task of writing down the time-dependent Schrödinger equation that generalizes (9.55) to three dimensions.

9.6.2 The phase space and level density

In many problems it is necessary to know how to count the number of energy levels in a certain region of space $(\vec{r}, \vec{p})$; this space is called the *phase space*. Let us return to the infinite well of Section 9.3.3 and use L_x to denote the width of the well. The energy levels are labeled by a positive integer n, and we shall consider the case where $n \gg 1$ and L_x is large. Then the energy levels (9.79) are very closely spaced and the sums over n can be replaced by integrals. Let us take a wave vector (9.78) with $k_n = \pi(n+1)/L_x$. We shall calculate the number of energy levels in a range of k: $[k_n, k_n + \Delta k]$. According to (9.78) for $a \to L_x$, the number of levels Δn $(1 \ll \Delta n \ll n)$ in the range $[k, k + \Delta k]$ is

$$\Delta n = \frac{L_x}{\pi} \Delta k. \tag{9.143}$$

Instead of vanishing boundary conditions for the wave function at the points $x = 0$ and $x = L_x$, it is often more convenient to choose *periodic boundary conditions*, $\varphi(0) = \varphi(L_x)$, leading to the wave functions[17]

$$\varphi_n(x) = \frac{1}{\sqrt{L_x}} \mathrm{e}^{\mathrm{i}k_n x}, \quad k_n = \frac{2\pi n}{L_x}, \quad n = \ldots, -2, -1, 0, 1, 2, \ldots, \tag{9.144}$$

and therefore

$$\Delta n = \frac{L_x}{2\pi} \Delta k. \tag{9.145}$$

At first sight (9.145) differs from (9.143) by a factor of 1/2.[18] However, we have already observed that for the wave functions (9.78) the values k_n and $-k_n$ correspond to the same physical state because the substitution $k_n \to -k_n$ leads to a simple change of sign of the wave function. By contrast, the substitution $k_n \to -k_n$ in (9.144) leads to a different physical state; thus the division by two in (9.145) is compensated for by doubling the number of possible values of k_n. Periodic and vanishing boundary conditions are equivalent for counting the energy levels (see also Footnote 19).

Let us now turn to the infinite square well in dimension $d = 3$. The wave functions vanish outside the ranges where $V(\vec{x}) = 0$, i.e., outside

$$0 \le x \le L_x, \quad 0 \le y \le L_y, \quad 0 \le z \le L_z. \tag{9.146}$$

The wave functions inside the well take the form

$$\varphi_{[n_x,n_y,n_z]}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{\pi(n_x+1)x}{L_x}\right) \sin\left(\frac{\pi(n_y+1)y}{L_y}\right) \sin\left(\frac{\pi(n_z+1)z}{L_z}\right) \tag{9.147}$$

[17] This choice of wave function is sometimes called "quantization in a box." It makes it possible to avoid working with plane waves of the continuum, since the "plane waves" of (9.144) are normalizable. However, the Fourier integrals of the continuum case then are replaced by Fourier sums, making the calculations more cumbersome.

[18] Since $n \gg 1$, no distinction is made between n and $(n+1)$.

with $(n_x, n_y, n_z) = 0, 1, 2, \ldots$. The corresponding energies are

$$E(n_x, n_y, n_z) = \frac{\hbar^2\pi^2}{2m}\left(\frac{(n_x+1)^2}{L_x^2} + \frac{(n_y+1)^2}{L_y^2} + \frac{(n_z+1)^2}{L_z^2}\right). \tag{9.148}$$

When $L_x = L_y = L_z = L$, these eigenvalues are in general degenerate (Exercise 9.7.9). Let us count the levels in three dimensions. It will be convenient to use periodic boundary conditions:

$$\varphi(x, y, z) = \varphi(x + L_x, y + L_y, z + L_z). \tag{9.149}$$

Let $\Delta\mathcal{K}$ be the volume element $\Delta k_x \Delta k_y \Delta k_z$ of $\vec{k}$ space such that the tip of the wave vector $\vec{k}$ lies in $\Delta\mathcal{K}$. The (x, y, z) components of this vector lie in the ranges

$$[k_x, k_x + \Delta k_x],\ [k_y, k_y + \Delta k_y],\ [k_z, k_z + \Delta k_z].$$

The number of energy levels in $\Delta\mathcal{K}$ is found by generalizing (9.145):

$$\Delta n = \left(\frac{L_x}{2\pi}\right)\Delta k_x \left(\frac{L_y}{2\pi}\right)\Delta k_y \left(\frac{L_z}{2\pi}\right)\Delta k_z = \frac{L_x L_y L_z}{(2\pi)^3}\Delta\mathcal{K}. \tag{9.150}$$

Taking $\Delta\mathcal{K}$ to be infinitesimal, $\Delta\mathcal{K} = \mathrm{d}^3k$, we define the *level density* (or *density of states*) $\mathcal{D}(\vec{k})$ in $\vec{k}$ space as follows: $\mathcal{D}(\vec{k})\mathrm{d}^3k$ is the number of levels in the volume d^3k centered on $\vec{k}$. According to (9.150),

$$\boxed{\mathcal{D}(\vec{k})\mathrm{d}^3k = \frac{\mathcal{V}}{(2\pi)^3}\,\mathrm{d}^3k}\,, \tag{9.151}$$

where $\mathcal{V} = L_x L_y L_z$ is the volume of the box with sides (L_x, L_y, L_z).[19] Using $\vec{p} = \hbar\vec{k}$, for the level density[20] in $\vec{p}$ space we find

$$\boxed{\mathcal{D}(\vec{p}) = \frac{\mathcal{V}}{(2\pi\hbar)^3} = \frac{\mathcal{V}}{h^3}}\,. \tag{9.152}$$

This is a very often used result. Now let us find the level density per unit energy.[21] Since $\mathcal{D}(\vec{p})$ depends only on $p = |\vec{p}|$, we have

$$\mathcal{D}(p) = \frac{4\pi\mathcal{V}}{(2\pi\hbar)^3}\,p^2 = \frac{\mathcal{V}}{2\pi^2\hbar^3}\,p^2. \tag{9.153}$$

[19] This result is also valid for a box which is not a parallelepiped. The correction terms are powers of $(kL)^{-1}$, where L is the typical scale of the box. The first correction represents a surface term. The difference between periodic and vanishing boundary conditions, which is a surface effect, is also included by this type of correction. Such corrections are negligible in a sufficiently large box.

[20] To be rigorous we should use different notation for the various level densities; however, we use the same letter $\mathcal{D}$ everywhere so as to reduce the amount of notation.

[21] When vanishing boundary conditions on the wave function are used, a factor of 1/8 is introduced in (9.151) to take into account the fact that the components of $\vec{k}$ are positive. The final result will in any case be the same, because of the factor of 1/2 difference between (9.143) and (9.145): $(1/2)^3 = 1/8$.

The level density per unit energy $\mathcal{D}(E)$ is

$$\mathcal{D}(E) = \frac{\mathcal{V}}{2\pi^2\hbar^3}\, p^2 \frac{\mathrm{d}p}{\mathrm{d}E} = \frac{\mathcal{V}}{2\pi^2\hbar^3}\, mp$$

or

$$\boxed{\mathcal{D}(E) = \frac{\mathcal{V}m}{2\pi^2\hbar^3}(2mE)^{1/2}} \,. \tag{9.154}$$

The number of levels in $[E, E + \mathrm{d}E]$ is $\mathcal{D}(E)\mathrm{d}E$. It is also possible to calculate $\mathcal{D}(E)$ starting from $\Phi(E)$, which is the number of energy levels below E: $\mathcal{D}(E) = \Phi'(E)$ (Exercise 9.7.11). The quantity $\mathcal{D}/\mathcal{V}$ is the level density per unit volume and is independent of the volume.

Noting that $\mathcal{V} = \int_{\mathcal{V}} \mathrm{d}^3 r$, from (9.152) we find that the number of levels in $\mathrm{d}^3 r\, \mathrm{d}^3 p$ is

$$\boxed{\mathrm{d}N = \frac{\mathrm{d}^3 r\, \mathrm{d}^3 p}{(2\pi\hbar)^3} = \frac{\mathrm{d}^3 r\, \mathrm{d}^3 p}{h^3}} \,, \tag{9.155}$$

where $\mathrm{d}^3 r\, \mathrm{d}^3 p$ is an infinitesimal volume in phase space $(\vec{r}, \vec{p})$. Equation (9.155) can be interpreted as follows: h^3 is the volume of an elementary cell in phase space, and one can assign one energy level to each elementary cell. The Heisenberg inequality explains this: if a particle is confined within a range Δx, its momentum satisfies $p \sim h/\Delta x$, and then (9.155) can be expressed more pictorially as follows. Whereas a classical particle whose state is defined by its position $\vec{r}$ and its momentum $\vec{p}$ occupies a point $(\vec{r}, \vec{p})$ in phase space, a quantum particle must occupy at least a volume $\sim h^3$.

The results (9.153) or (9.154) are very important in quantum statistical mechanics: the probability that a system in thermal equilibrium has energy E (see (1.12) and Footnote 16 of Chapter 1) is

$$\mathsf{p}(E) = \mathcal{N}\, \mathcal{D}(E)\, \mathrm{e}^{-\beta E},$$

where $\mathcal{N}$ is a normalization constant fixed by

$$\int \mathrm{d}E\, \mathsf{p}(E) = 1.$$

9.6.3 The Fermi Golden Rule

The concept of level density will be used in the proof of one of the most important formulas of quantum physics, the *Fermi Golden Rule*, which allows us to calculate the probabilities of transition to scattering states. These are also called continuum states because they belong to the continuous spectrum of the Hamiltonian, which in the present case is $H^{(0)}$ (9.156). Let us consider a physical system governed by a time-dependent Hamiltonian $H(t)$:

$$H(t) = H^{(0)} + W(t), \tag{9.156}$$

where $H^{(0)}$ is time-independent and has known spectrum with eigenvalues E_n and eigenvectors $|n\rangle$:

$$H^{(0)}|n\rangle = E_n|n\rangle. \tag{9.157}$$

We wish to solve the following problem. At time $t = 0$ the system is in the initial state $|\psi(0)\rangle = |i\rangle$, an eigenstate of $H^{(0)}$ with energy E_i, and we want to calculate the probability $\mathsf{p}_{i\to f}(t)$ of finding it at time t in the eigenstate $|f\rangle$ of $H^{(0)}$ with energy E_f. For this we must find the state vector $|\psi(t)\rangle$ of the system at time t, because

$$\mathsf{p}_{i\to f}(t) = |\langle f|\psi(t)\rangle|^2 \quad \text{with} \quad |\psi(t=0)\rangle = |i\rangle. \tag{9.158}$$

We have already encountered this problem in a simple case. In Chapter 5 we calculated the probability of transition from one level to another for an ammonia molecule in an oscillating electromagnetic field. The Hamiltonian (9.156) generalizes (5.52), with $H^{(0)}$ being the analog of (5.43). We follow the method of Section 5.3.2 adapted to any number of levels. Generalizing (5.53), we decompose the state vector $|\psi(t)\rangle$ on the basis $|l\rangle$ of eigenstates of $H^{(0)}$:

$$|\psi(t)\rangle = \sum_l c_l(t)\,|l\rangle. \tag{9.159}$$

Multiplying (9.159) on the left by the bra $\langle n|H^{(0)}$, we obtain

$$\begin{aligned}\langle n|H^{(0)}|\psi(t)\rangle &= \sum_l \langle n|H^{(0)}|l\rangle\,\langle l|\psi(t)\rangle = \sum_l H^{(0)}_{nl}\,c_l(t)\\ &= E_n\langle n|\psi(t)\rangle = c_n(t)E_n.\end{aligned} \tag{9.160}$$

The system of differential equations obeyed by the coefficients $c_n(t)$ is, according to (4.13),

$$\mathrm{i}\hbar\dot{c}_n(t) = \sum_l \left(H^{(0)}_{nl} + W_{nl}(t)\right) c_l(t). \tag{9.161}$$

Still following the method of Section 5.3.2, we eliminate the trivial dependence on t, the factor $\exp(-\mathrm{i}E_n t/\hbar)$ in $c_n(t)$ arising from the time evolution due to $H^{(0)}$, by setting

$$c_n(t) = \mathrm{e}^{-\mathrm{i}E_n t/\hbar}\,\gamma_n(t), \tag{9.162}$$

which transforms (9.161) into

$$\mathrm{i}\hbar\dot{\gamma}_n(t)\mathrm{e}^{-\mathrm{i}E_n t/\hbar} + E_n c_n(t) = \sum_l H^{(0)}_{nl}\,c_l(t) + \sum_l W_{nl}(t)\,\gamma_l(t)\mathrm{e}^{-\mathrm{i}E_l t/\hbar}.$$

Using (9.160), this equation simplifies to become

$$\mathrm{i}\hbar\dot{\gamma}_n(t) = \sum_l W_{nl}\mathrm{e}^{\mathrm{i}\omega_{nl}t}\,\gamma_l(t), \quad \omega_{nl} = \frac{E_n - E_l}{\hbar}. \tag{9.163}$$

The system of differential equations (9.163) generalizes (5.55). The equations are exact, but they are not solvable analytically, except in special cases, and approximations must be made. We shall use the method called *time-dependent perturbation theory*. It is

convenient to introduce a real parameter λ, $0 \leq \lambda \leq 1$, multiplying the perturbation W. Then $W \to \lambda W$, which allows the strength of the perturbation to be varied by hand.[22] Perturbation theory amounts to obtaining an approximate solution of the Schrödinger equation in the form of a series in powers of λ and taking $\lambda = 1$ at the end of the calculation. In what follows we shall limit ourselves to first order in λ.[23] At time $t = 0$ the system is assumed to be in the state $|i\rangle$:

$$\gamma_n(0) = \delta_{ni},$$

and we write

$$\gamma_n(t) = \delta_{ni} + \gamma_n^{(1)}(t).$$

When t is sufficiently small, $|\gamma_n^{(1)}(t)| \ll 1$ because the system does not have time to evolve appreciably. Upon introduction of the parameter λ, (9.163) becomes

$$\mathrm{i}\hbar \frac{\mathrm{d}}{\mathrm{d}t}\left(\delta_{ni} + \gamma_n^{(1)}(t)\right) = \sum_l \lambda W_{nl}(t)\left[\delta_{li} + \gamma_l^{(1)}(t)\right]\mathrm{e}^{\mathrm{i}\omega_{ni}t}.$$

We observe that $\gamma_l^{(1)}(t)$ is of order λ, and that the term $\sum_l \lambda W_{nl}(t)\gamma_l^{(1)}(t)$ will therefore be of order λ^2. This term is negligible to first order in λ, and taking $\lambda = 1$ we find

$$\mathrm{i}\hbar\dot{\gamma}_n^{(1)}(t) \simeq W_{ni}(t)\,\mathrm{e}^{\mathrm{i}\omega_{ni}t}. \tag{9.164}$$

An important special case is that of an oscillating potential:

$$W(t) = A\,\mathrm{e}^{-\mathrm{i}\omega t} + A^\dagger \mathrm{e}^{\mathrm{i}\omega t}, \tag{9.165}$$

where A is an operator. It is this type of potential that describes, for example, the interaction of an atom with an oscillating electromagnetic field:

$$\mathcal{E}(t) = \mathcal{E}_0\,\mathrm{e}^{-\mathrm{i}\omega t} + \mathcal{E}_0^*\,\mathrm{e}^{\mathrm{i}\omega t}.$$

If as in Chapter 5 we are interested in a transition $i \to f$ to a well-defined final level $|f\rangle$, the probability amplitude $\langle f|\psi(t)\rangle$ is given up to a phase by $\gamma_f(t) \simeq \gamma_f^{(1)}(t)$, which is the solution of the differential equation (9.164),

$$\mathrm{i}\hbar\dot{\gamma}_f^{(1)}(t) = A_{fi}\,\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t} + A_{if}^*\,\mathrm{e}^{\mathrm{i}(\omega+\omega_0)t}, \tag{9.166}$$

with $\omega_0 = \omega_{fi} = (E_f - E_i)/\hbar$. This differential equation can be integrated immediately because the coefficients $A_{fi} = \langle f|A|i\rangle$ are independent of time:

$$\gamma_f^{(1)}(t) = \frac{1}{\hbar}\left[A_{fi}\frac{\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t} - 1}{\omega - \omega_0} - A_{if}^*\frac{\mathrm{e}^{\mathrm{i}(\omega+\omega_0)t} - 1}{\omega + \omega_0}\right]. \tag{9.167}$$

This probability amplitude will be important if $\omega \simeq \pm\omega_0$, that is, as in Chapter 5, at resonance. For $\omega \simeq \omega_0$ we have

$$E_f \simeq E_i + \hbar\omega,$$

[22] If the perturbation is due to an interaction with an external field, it can be varied by varying the field.
[23] The complexity of the expressions grows rapidly with increasing powers of λ.

and the system absorbs an energy $\hbar\omega$. If we consider the situation of interaction with an electromagnetic wave, the system absorbs a photon of energy $\hbar\omega$. In the case $\omega \simeq -\omega_0$

$$E_f \simeq E_i - \hbar\omega,$$

and the system gives up an energy $\hbar\omega$, for example, by emitting a photon of energy $\hbar\omega$. To clarify these ideas let us study the first case. The transition probability $\mathsf{p}_{i\to f}(t)$ will be

$$\mathsf{p}_{i\to f}(t) = |\gamma_f^{(1)}(t)|^2 = \frac{1}{\hbar^2}\,|A_{fi}|^2 t^2 f(\omega-\omega_0;\, t), \tag{9.168}$$

where the function f was defined in (5.63):

$$f(\omega-\omega_0;\, t) = \frac{\sin^2[(\omega-\omega_0)t/2]}{[(\omega-\omega_0)t/2]^2} \simeq \frac{2\pi}{t}\,\delta(\omega-\omega_0). \tag{9.169}$$

We recover the results of Section 5.3.3 in a more general case. Within our approximations, a necessary condition for (9.168) to be valid is that $\mathsf{p}_{i\to f}(t) \ll 1$.

However, it is in general impossible to isolate a transition to any particular final state f, and so we are usually interested in a transition to a set of final states close in energy:

$$\Gamma = \sum_f \Gamma_{i\to f}.$$

The summation over f is equivalent to integration over energy if we include the level density $\mathcal{D}(E)$:

$$\sum_f \to \int \mathrm{d}E\, \mathcal{D}(E).$$

For example, if the final state corresponds to that of a free particle and if $|A_{fi}|^2$ is isotropic, the level density will be given by (9.154). If $|A_{fi}|^2$ is not isotropic but depends, for example, on the direction of the momentum $\vec{p}$ of the final particle, we will use

$$\mathcal{D}(E) = \frac{\mathcal{V} m}{2\pi^2\hbar^3}(2mE)^{1/2}\,\frac{\mathrm{d}\Omega}{4\pi},$$

where $\Omega = (\theta, \phi)$ defines the direction of $\vec{p}$. Using (9.168) and (9.169), we obtain a *transition probability per unit time* Γ

$$\begin{aligned}\Gamma &= \frac{1}{\hbar^2}\int \mathrm{d}E\,|A_{fi}|^2\,\mathcal{D}(E)\,t\,\frac{\sin^2[(\omega-\omega_0)t/2]}{[(\omega-\omega_0)t/2]^2} \\ &\simeq \frac{1}{\hbar}\int \mathrm{d}E\,|A_{fi}|^2\,\mathcal{D}(E)\,2\pi\,\delta[E-(E_i+\hbar\omega)].\end{aligned}$$

Performing the integration, we obtain the Fermi Golden Rule with energy absorption:

$$\boxed{\Gamma = \frac{2\pi}{\hbar} |A_{fi}|^2 \, \mathcal{D}(E_f), \quad E_f = E_i + \hbar\omega} \, . \tag{9.170}$$

This equation holds also in the case of energy emission if we take $E_f = E_i - \hbar\omega$, and for a constant potential $V(t)$ if $E_f = E_i$ (Exercise 9.7.12). The calculation is valid under the following conditions.

- The probability of finding the system in the initial state (i) must be close to unity, or

$$\sum_{f \neq i} \mathsf{p}_{i\to f}(t) \ll 1 \;\text{ or, in terms of } \Gamma_{i\to f}, \; \left(\sum_{f\neq i} \Gamma_{i\to f}\right) t \ll 1,$$

  which implies that t must be sufficiently short: $t \ll \tau_2$.
- In the integral over energy E the quantity $f(\omega - (E - E_i)/\hbar; t)$ may be replaced by a delta function:

$$\int \mathrm{d}E \, g(E) f\left(\omega - \frac{E - E_i}{\hbar}; t\right) \to \int \mathrm{d}\omega \, g(E) \, \frac{2\pi}{t} \, \delta(E - \hbar\omega_0) = \frac{2\pi}{t} \, g(E_f).$$

  If ΔE_1 is the characteristic range of variation of $g(E) = |A_{fi}|^2 \, \mathcal{D}(E)$, $\tau_1 = \hbar/\Delta E_1$ must be small compared to t: $t \gg \tau_1$.

In summary, t must lie in the range $\tau_1 \ll t \ll \tau_2$. When the condition $t \ll \tau_2$ is not satisfied, it is sometimes possible to use the resonance approximation to reduce the problem to one of two levels, for which an exact solution exists (Exercise 9.7.12).

An important application of the Fermi Golden Rule is to the decay of an unstable state i (an excited state of an atom or a nucleus, an unstable particle, and so on) to a continuum of states f. The perturbation is then time-independent and $E_f \simeq E_i$ in (9.170). For sufficiently short times the probability of finding the system in the initial unstable state i (survival probability) is

$$\mathsf{p}_{ii}(t) = 1 - \Gamma t \simeq \mathrm{e}^{-\Gamma t}, \quad t \ll \tau_2, \tag{9.171}$$

and it is tempting to identify Γ as the inverse of the lifetime τ: $\Gamma = \hbar/\tau$. The calculation we have just done does not permit us to make this identification, because it is not a priori valid for any t. However, the exponential decay law (9.171) can be generalized to long times using a method due to Wigner and Weisskopf described in Appendix C. This method shows that the spread ΔE of the energy E_f of the final states is $\Delta E = \hbar/\tau = \hbar\Gamma/2$.

9.7 Exercises

9.7.1 The Heisenberg inequalities

1. Let $\varphi(x)$ be a square-integrable function normalized to unity and $I(\alpha)$ the non-negative quantity:

$$I(\alpha) = \int_{-\infty}^{\infty} \mathrm{d}x \left| x\varphi(x) + \alpha \frac{\mathrm{d}\varphi}{\mathrm{d}x} \right|^2 \geq 0,$$

with α a real number. Integrating by parts, show that

$$I(\alpha) = \langle X^2 \rangle - \alpha + \alpha^2 \langle K^2 \rangle,$$

where $K = -\mathrm{i}\mathrm{d}/\mathrm{d}x$ and

$$\langle X^2 \rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, x^2 |\varphi(x)|^2, \quad \langle K^2 \rangle = -\int_{-\infty}^{\infty} \mathrm{d}x\, \varphi^*(x) \frac{\mathrm{d}^2 \varphi}{\mathrm{d}x^2}.$$

Derive the expression

$$\langle X^2 \rangle \langle K^2 \rangle \geq \frac{1}{4}.$$

2. How should the argument of the preceding question be modified to obtain the Heisenberg inequality

$$\Delta x\, \Delta k \geq \frac{1}{2} \ ?$$

Show that $\Delta x\, \Delta k = 1/2$ implies that $\varphi(x)$ is a Gaussian:

$$\varphi(x) \propto \exp\left(-\frac{1}{2}\sigma^2 x^2\right).$$

9.7.2 Wave-packet spreading

1. Show that $[P^2, X] = -2\mathrm{i}\hbar P$.
2. Let $\langle X^2 \rangle(t)$ be the mean square position in the state $|\varphi(t)\rangle$:

$$\langle X^2 \rangle(t) = \langle \varphi(t) | X^2 | \varphi(t) \rangle.$$

Show that

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle X^2 \rangle(t) = \frac{1}{m} \langle PX + XP \rangle$$
$$= \frac{\mathrm{i}\hbar}{m} \int_{-\infty}^{\infty} \mathrm{d}x\, x \left[\varphi \frac{\partial \varphi^*}{\partial x} - \varphi^* \frac{\partial \varphi}{\partial x} \right].$$

Are these results valid if the potential $V(x) \neq 0$?

3. Show that if the particle is free ($V(x) = 0$), then

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2} \langle X^2 \rangle(t) = \frac{2}{m^2} \langle P^2 \rangle = 2v_1^2 = \text{const.}$$

4. Use these results to derive

$$\langle X^2 \rangle(t) = \langle X^2 \rangle(t=0) + \xi_0 t + v_1^2 t^2, \quad \xi_0 = \left. \frac{\mathrm{d}\langle X^2 \rangle}{\mathrm{d}t} \right|_{t=0},$$

as well as the expression for $(\Delta x(t))^2$:

$$(\Delta x(t))^2 = (\Delta x(t=0))^2 + [\xi_0 - 2v_0 \langle X \rangle(t=0)]t + (v_1^2 - v_0^2)t^2$$

with $v_0 = \langle P/m \rangle = \text{const.}$

9.7.3 A Gaussian wave packet

1. We assume that the function $A(k)$ in (9.41) is a Gaussian:

$$A(k) = \frac{1}{(\pi\sigma^2)^{1/4}} \exp\left[-\frac{(k-\bar{k})^2}{2\sigma^2}\right].$$

Show that

$$\int |A(k)|^2 \mathrm{d}k = 1, \quad \Delta k = \frac{1}{\sqrt{2}}\,\sigma,$$

and that the wave function $\varphi(x, t=0)$ is

$$\varphi(x, t=0) = \frac{\sigma^{1/2}}{\pi^{1/4}} \exp\left[\mathrm{i}\bar{k}x - \frac{1}{2}\,\sigma^2 x^2\right].$$

Sketch the curve of $|\varphi(x, t=0)|^2$. What is the width of this curve? Identify the dispersion Δx and show that $\Delta x\,\Delta k = 1/2$.

2. Calculate $\varphi(x, t)$. Show that if $\hbar\sigma^2 t/m \ll 1$ we have

$$\varphi(x, t) = \exp\left(\frac{\mathrm{i}\hbar\bar{k}^2}{2m}\,t\right) \varphi(x - v_g t, 0), \quad v_g = \frac{\hbar\bar{k}}{m}.$$

3. Calculate $\varphi(x, t)$ exactly:

$$\varphi(x, t) = \left(\frac{1}{\pi\sigma^2}\right)^{1/4} \sigma' \exp\left[\mathrm{i}\bar{k}x - \mathrm{i}\omega(\bar{k})t - \frac{1}{2}\,\sigma'^2 (x - v_g t)^2\right]$$

with

$$\frac{1}{\sigma'^2} = \frac{1}{\sigma^2} + \frac{\mathrm{i}\hbar t}{m}$$

and find $|\varphi(x, t)|^2$. Show that

$$\Delta x^2(t) = \frac{1}{2\sigma^2}\left(1 + \frac{\hbar^2\sigma^4 t^2}{m^2}\right).$$

Interpret this result physically.

4. A neutron leaves a nuclear reactor with a wavelength of 0.1 nm. We assume that the wave function at $t = 0$ is a Gaussian wave packet of width $\Delta x = 1$ nm. How long does it take for the width to double? What distance does the neutron travel during this time?

9.7.4 Heuristic estimates using the Heisenberg inequality

1. If the electron emitted in neutron β decay

$$\mathrm{n} \to \mathrm{p} + \mathrm{e}^- + \overline{\nu}_\mathrm{e}$$

were initially confined inside the neutron with radius of about 0.8 fm, what would its kinetic energy be? What conclusion can be drawn?

2. A quantum particle of mass m moves on the x axis in the harmonic potential

$$V(x) = \frac{1}{2} m\omega^2 x^2.$$

Use the Heisenberg inequality to estimate the energy of its ground state.

9.7.5 The Lennard–Jones potential for helium

1. The potential energy of two atoms separated by a distance r is often well represented by the Lennard–Jones potential:

$$V(r) = \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - 2 \left(\frac{\sigma}{r} \right)^{6} \right],$$

where ε and σ are parameters with the dimensions of energy and length, respectively. Calculate the position r_0 of the potential minimum and sketch $V(r)$ qualitatively. Show that near $r = r_0$

$$V(r) \simeq -\varepsilon \left[1 - 36 \left(\frac{r - r_0}{r_0} \right)^2 \right] = \frac{1}{2} m\omega^2 (r - r_0)^2 + V_0.$$

2. In the case of helium, $\varepsilon \simeq 10^{-3}$ eV and $r_0 \simeq 0.3$ nm. Calculate the vibration frequency ω and the energy $\hbar\omega/2$ of the ground state. Why does helium remain a liquid even if the temperature $T \to 0$? Does the reasoning hold for the two isotopes ^{3}He and ^{4}He?
3. For hydrogen, $\varepsilon \simeq 4$ eV. Why does hydrogen become a solid at low temperature? What about the rare gases (argon, neon, etc.)?

9.7.6 Reflection delay

1. The equation (9.74) gives the coefficient B of the reflected wave when an incident wave $\exp(\mathrm{i}kx)$ of energy $E = \hbar^2 k^2/2m < V_0$ arrives at a potential step, where V_0 is the step height. Show that $|B| = 1$ and B can be written as $B = \exp(-\mathrm{i}\phi)$. Find ϕ and $\mathrm{d}\phi/\mathrm{d}E$.
2. We assume that the incident wave is a wave packet of the type (9.41),

$$\varphi(x, t) = \int \frac{\mathrm{d}k}{\sqrt{2\pi}} A(k) \exp[\mathrm{i}kx - \mathrm{i}\omega(k)t].$$

What will the reflected wave packet be? Show that the reflection occurs with a delay

$$\tau = -\hbar \frac{\mathrm{d}\phi}{\mathrm{d}E} > 0.$$

9.7.7 A delta-function potential

We consider a one-dimensional potential of the form

$$V(x) = \frac{\hbar^2 g}{2m} \delta(x),$$

where m is the mass of the particle subject to the potential. This potential sometimes can be used as a convenient approximation. For example, it can represent a potential barrier

of width a and height V_0 in the limit $a \to 0$ and $V_0 \to \infty$ with $V_0 a$ constant and equal to $\hbar^2 g/2m$. In the case of a barrier (a repulsive potential) $g > 0$, but we can also model a well (an attractive potential), in which case $g < 0$.

1. Show that g has the dimensions of an inverse length.
2. The function $\varphi(x)$ obeys the Schrödinger equation

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}x^2} + g\,\delta(x)\right]\varphi(x) = \frac{2mE}{\hbar^2}\,\varphi(x).$$

Show that the derivative of $\varphi(x)$ satisfies the following equation near $x = 0$:

$$\varphi'(0^+) - \varphi'(0^-) = g\,\varphi(0), \quad \varphi(0^\pm) = \lim_{\varepsilon \to 0^\pm} \varphi(\varepsilon).$$

Assuming $g < 0$, show that there exists one and only one bound state. Determine its energy and the corresponding wave function. Show that we recover these results by taking the limit of a square well with $V_0 a \to \hbar^2 |g|/2m$ and $a \to 0$.

3. *Model of a diatomic molecule.* Assuming always that $g < 0$, we can very crudely model the potential felt by an electron of a diatomic molecule as

$$V(x) = \frac{\hbar^2 g}{2m}\Big[\delta(x+l) + \delta(x-l)\Big].$$

The nuclear axis is taken as the x axis, and the two nuclei are located at $x = -l$ and $x = +l$. Show that the solutions of the Schrödinger equation can be classified as even and odd. If the wave function is even, show that there exists a single bound state given by

$$\kappa = \frac{|g|}{2}\,(1 + \mathrm{e}^{-2\kappa l}), \quad \kappa = \sqrt{\frac{2m|E|}{\hbar^2}}.$$

Draw a qualitative sketch of its wave function.

If the wave function is odd, find the equation giving the energy of the bound state:

$$\kappa = \frac{|g|}{2}\,(1 - \mathrm{e}^{-2\kappa l}).$$

Is there always a bound state? If not, what condition must be obeyed for there to be one? Qualitatively sketch the wave function when there is a bound state.

4. *The double well and the tunnel effect.* Let us consider the preceding question assuming that $\kappa l \gg 1$. Show that the two bound states form a two-level system whose Hamiltonian is

$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix},$$

and relate A to $\sqrt{T}$, where T is the transmission coefficient due to tunneling between the two wells.

5. *The potential barrier.* Now we are interested in the case $g > 0$, which models a potential barrier. Directly calculate the transmission matrix and show that it is the limit of that in the case of a square barrier if $V_0 a \to g$ and $a \to 0$. Give the expression for the transmission coefficient.

6. *A periodic potential.* An electron moves in a one-dimensional crystal in a periodic potential of period l modeled as

$$V(x) = \sum_{n=-\infty}^{\infty} \frac{\hbar^2 g}{2m} \delta(x - nl).$$

For convenience we take $g > 0$. Show that the periodicity of the potential implies that the wave function, labeled by q, has the form

$$\varphi_q(x - l) = \mathrm{e}^{-\mathrm{i}ql} \varphi_q(x).$$

Hint: examine the action of the operator T_l which translates by l. It is therefore possible to limit ourselves to study of the range $[-l/2, l/2]$. Outside the point $x = 0$ the wave functions are complex exponentials:

$$-\frac{l}{2} \le x < 0: \quad \varphi_q(x) = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx},$$

$$0 < x \le \frac{l}{2}: \quad \varphi_q(x) = F\mathrm{e}^{\mathrm{i}kx} + G\mathrm{e}^{-\mathrm{i}kx}.$$

Use the conditions on $\varphi'(x)$ to obtain

$$\cos ql = \cos kl + \frac{g}{2k} \sin kl.$$

Show that there exist forbidden regions of energy. Qualitatively sketch the energy E_q as a function of q.

9.7.8 Transmission by a well

1. Show that the transmission coefficient T for the square well of Fig. 9.11 is

$$T = \frac{1}{1 + \left(\dfrac{q^2}{4kk'}\right)^2 \sin^2 k'a}, \quad q^2 = \frac{2mV_0}{\hbar^2}.$$

   Show that T passes through a maximum if the de Broglie wavelength in the well $\lambda' = 2\pi/k'$ is of the form $2a/n$, n integer.
2. Qualitatively sketch the curves giving T and the reflection coefficient $1 - T$. This behavior explains, among other things, the Ramsauer–Townsend effect.[24]

9.7.9 Energy levels of an infinite cubic well in dimension $d = 3$

Find the energies of the first six energy levels of the infinite cubic well as a function of the length L of a side of the cube along with their degeneracies.

[24] Cf. Lévy-Leblond and Balibar [1990], page 314.

9.7.10 The probability current in three dimensions

Show that the continuity equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0, \quad \rho = |\varphi(\vec{r}, t)|^2$$

holds for the current (9.141).

9.7.11 The level density

1. Calculate the energy level density $\mathcal{D}(E)$ in dimension $d = 2$. Show that it is independent of E.
2. Calculate directly the number of levels $\Phi(E)$ of energy lower than E by counting the number of possible levels in a sphere of radius $|p| = \sqrt{2mE}$ in momentum space and taking into account the boundary conditions. Recover the expression (9.154) for $\mathcal{D}(E)$:

$$\mathcal{D}(E) = \frac{\mathrm{d}\Phi(E)}{\mathrm{d}E}.$$

3. Calculate the energy level density $\mathcal{D}(E)$ for an ultrarelativistic particle of energy $E = cp$. Generalize to the case $E = (p^2c^2 + m^2c^4)^{1/2}$. Show that d^3p/E is a Lorentz invariant. Owing to this invariance, this expression is often taken as the level density.

9.7.12 The Fermi Golden Rule

1. *Comparison with the Rabi formula*. In a two-level system, the Rabi formula (5.40) gives the exact transition probability between the two levels in the presence of a harmonic perturbation, for example,

$$\mathsf{p}_{+\to -}(t) = \frac{\omega_1^2}{\Omega^2} \sin^2 \frac{\Omega t}{2}, \quad \Omega^2 = \left[(\omega - \omega_0)^2 + \omega_1^2\right]^{1/2}.$$

   Show that the approximate expression (9.168) is obtained as the limit of the Rabi formula if

   - $|\omega - \omega_0| \gg \omega_1$, that is, far from resonance, or
   - $\omega_1 t \ll 1$, that is, for sufficiently short times.

2. *A constant potential.* Give the expression for the amplitude (9.167) $\gamma^{(1)}(t)$ and the transition probability per unit time Γ when the potential $W(t)$ of (9.165) is time-independent.

9.7.13 Study of the Stern–Gerlach experiment

1. *Classical study*. We use the notation of Section 3.2.2. The trajectory of the silver atoms (Fig. 3.8) is assumed to lie in the symmetry plane yOz and along the y axis. Show that $\partial B_z/\partial x|_{x=0} = 0$ and $\partial B_z/\partial y = 0$ if edge effects are neglected. Show that an approximate form of the magnetic field satisfying the Maxwell equations between the magnet poles near $x = 0$ and $z = 0$ is

$$\vec{B} = B_0\hat{z} + b(z\hat{z} - x\hat{x}),$$

   where $b = \partial B_z/\partial z|_{z=0}$. The classical expression for the force is $\vec{F} = -\vec{\nabla}(\vec{\mu} \cdot \vec{B})$. Find the components F_x, F_y, and F_z. Show that under the influence of B_0 the magnetic moment $\vec{\mu}$ precesses

about the z axis with frequency $\omega = |\gamma B_0|$, where γ is the gyromagnetic ratio, and that if $1/\omega$ is very small compared with the time for the atom to travel between the magnet poles, then the component μ_x gives a vanishing average force. Therefore, it is as though the magnetic moment were subject to an effective force $\vec{F} = b\mu_z \hat{z}$.

2. *Numerical data.* Silver atoms of mass $m = 1.8 \times 10^{-27}$ kg leave an oven with a speed $v \simeq 500\,\mathrm{m\,s^{-1}}$ and a velocity spread $\Delta v \sim 10\,\mathrm{m\,s^{-1}}$. The collimating slits have height $\Delta z = 10^{-4}$ m, the length of the gap is $L = 5 \times 10^{-2}$ m, the magnetic field is $B_0 = 1$ T, and $b = 10^4\,\mathrm{T\,m^{-1}}$. Show that at the exit from the magnet poles the spacing δ between the two trajectories corresponding to $S_z = \hbar/2$ and $S_z = -\hbar/2$ is

$$\delta = \frac{\mu b}{m}\left(\frac{L}{v}\right)^2.$$

Evaluate δ numerically. Calculate the product $\Delta z \Delta p_z$ and show that $\Delta z \Delta p_z \gg \hbar$. The atomic trajectories can therefore be treated classically.

3. *The quantum description.* Let $\varphi_\pm(\vec{r}, t)$ be the wave function of an atom with spin in the state $|\pm\rangle$. Show that $\varphi_\pm$ satisfies the Schrödinger equation

$$\mathrm{i}\hbar \frac{\partial \varphi_\pm}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 \mp \mu B\right)\varphi_\pm.$$

We define the average position $\langle \vec{r}_\pm \rangle(t)$ and the average momentum $\langle \vec{p}_\pm \rangle(t)$ of the wave packets $\varphi_\pm(\vec{r}, t)$ as

$$\langle \vec{r}_\pm \rangle(t) = \int \mathrm{d}^3 r\, \vec{r}\, |\varphi_\pm(\vec{r}, t)|^2,$$

$$\langle \vec{p}_\pm \rangle(t) = \int \mathrm{d}^3 r\, \varphi_\pm^*(\vec{r}, t)\left[-\mathrm{i}\hbar\vec{\nabla}\varphi_\pm(\vec{r}, t)\right].$$

Write down the evolution equations for these average values by calculating $\mathrm{d}\langle \vec{r}_\pm \rangle(t)/\mathrm{d}t$ and $\mathrm{d}\langle \vec{p}_\pm \rangle(t)/\mathrm{d}t$ using the Ehrenfest theorem (4.26). Show that the spacing δ between the centers of the two wave packets is the same as that calculated in question 2 for classical trajectories.

4. *Parity invariance.* In an experimental configuration for analyzing a spin pointing in the z direction using a Stern–Gerlach apparatus such that $\vec{B} \parallel Ox$, we assume that the spin is deflected preferentially in the direction $x > 0$, for example, $\langle S_x \rangle > 0$. By examining the image of the experiment in a mirror located in the xOy plane, show that such a preferred deflection is excluded if the relevant interactions in the experiment are invariant under parity (which is indeed the case).

9.7.14 The von Neumann model of measurement

1. In the model of quantum measurement imagined by von Neumann, a physical property A of a quantum system S is measured by allowing the system to interact with a (quantum) particle Π whose momentum operator is P. For simplicity we consider the case of one spatial dimension. The interaction Hamiltonian is assumed to be of the form

$$H = g(t)AP,$$

where $g(t)$ is a positive function with a sharp peak of width τ at $t = 0$ and

$$g = \int_{-\infty}^{\infty} g(t)\mathrm{d}t \simeq \int_{-\tau/2}^{\tau/2} g(t)\mathrm{d}t.$$

We assume that the evolution of S and Π can be neglected during the very short time τ of the interaction between S and Π, which occurs between times t_i and t_f: $t_i \simeq -\tau/2$ and $t_f \simeq \tau/2$. Find the evolution operator (4.14):

$$U(t_f, t_i) \simeq \mathrm{e}^{-\mathrm{i}gAP/\hbar}.$$

2. We assume that the $S + \Pi$ initial state is

$$|\psi(t_i)\rangle = |n \otimes \varphi\rangle,$$

where $|n\rangle$ is an eigenvector of A with, for simplicity, nondegenerate spectrum, $A|n\rangle = a_n|n\rangle$, and $|\varphi\rangle$ is a state of the particle localized near the point $x = x_0$ with dispersion Δx. Show that the final state is

$$|\psi(t_f)\rangle = |n \otimes \varphi_n\rangle \quad \text{with} \quad |\varphi_n\rangle = \mathrm{e}^{-\mathrm{i}gAP/\hbar}\,|\varphi\rangle.$$

Let $\varphi_n(x) = \langle x|\varphi_n\rangle$ be the final wave function of the particle. Show that

$$\varphi_n(x) = \varphi(x - ga_n).$$

The function $\varphi_n(x)$ then is localized near the point $x_0 - ga_n$, and if $g|a_n - a_m| \gg \Delta x$ for any $n \neq m$, the position of the particle allows one to deduce the value a_n of A so that a measurement of A is obtained. The final state of the particle is perfectly correlated with the value of A and the final state of S because the states $|\varphi_n\rangle$ and $|\varphi_m\rangle$ are orthogonal for $n \neq m$: $\langle\varphi_n|\varphi_m\rangle = \delta_{nm}$.

3. What is the final state of Π if the initial state of S is the linear superposition

$$|\chi\rangle = \sum_n c_n|n\rangle?$$

Show that the probability of observing S in the final state $|n\rangle$ is $|c_n|^2$. The measurement is ideal because it does not modify the probabilities $|c_n|^2$.

9.7.15 The Galilean transformation

Let us consider a classical plane wave, for example a sound wave, propagating along the x axis:

$$f(x, t) = A\cos(kx - \omega t)$$

and a Galilean transformation of velocity v:

$$x' = x + vt, \quad t' = t.$$

1. Show that for a classical wave the transformed amplitude $f'(x', t')$ satisfies

$$f'(x', t') = f(x, t),$$

from which we extract the transformation law of the wave vectors and frequencies:

$$k' = k, \quad \omega' = \omega + vk.$$

What is the physical interpretation of the frequency transformation law? Now let us assume that we are dealing with the de Broglie wave of a particle of mass m. Are the preceding relations compatible with the momentum and energy transformation laws

$$p' = p + mv, \quad E' = E + pv + \frac{1}{2}mv^2?$$

2. Show that for a de Broglie wave we should not require

$$\varphi'(x', t') = \varphi(x, t)$$

but rather

$$\varphi'(x', t') = \exp\left[\frac{\mathrm{i}f(x, t)}{\hbar}\right]\varphi(x, t).$$

Using the relations (prove them)

$$\frac{\partial}{\partial t'} = \frac{\partial}{\partial t} - v\frac{\partial}{\partial x},$$
$$\frac{\partial}{\partial x'} = \frac{\partial}{\partial x},$$

determine the form of the function $f(x, t)$ by requiring that if $\varphi(x, t)$ obeys the Schrödinger equation, $\varphi'(x', t')$ must also.

9.8 Further reading

The results of this chapter are classic and can be found in similar form in most texts on quantum mechanics. One of the clearest expositions is that of Merzbacher [1970], Chapter 6. Lévy-Leblond and Balibar [1990], Chapter 6, also give a very complete discussion with many illustrative examples. See also Messiah [1999], Chapter III; Cohen-Tannoudji *et al*. [1977], Chapter I; or Basdevant and Dalibard [2002], Chapter 2; this last reference comes with a CD made by M. Joffre which allows the motion of wave packets to be visualized. For the Fermi Golden Rule the reader can consult Messiah [1999], Chapter XVII, or Cohen-Tannoudji *et al*. [1977], Chapter XIII.