Chapter 9
Time-Dependent Schrödinger Equation

9.1 Introduction

The time-dependent Schrödinger equation is derived from the superposition principle, in the conservative case first, then in the general case. The derivation of the continuity equation follows, leading to the concept of wave packet and density of probability flux. Then, the wave packet for a free particle is investigated in detail, and the concept of group velocity is introduced. The first complement deals with an application of the semiclassical approximation; through it one explains why an electron belonging to a stationary state emits no power, namely, why the radiative decay predicted by the classical model does not occur. The polar form of the time-dependent Schrödinger equation is then shown, that brings about an interesting similarity with the Hamilton–Jacobi equation of Classical Mechanics. The last complement deals with the Hamiltonian operator of a particle subjected to an electromagnetic field, and shows the effect of a gauge transformation on the wave function.

9.2 Superposition Principle

Following De Broglie's line of reasoning (Sect. 7.4.5) one associates the monochromatic wave function $w(\mathbf{r}) \exp(-\mathrm{i}\,\omega\,t)$ to the motion of a particle with definite and constant energy $E = \hbar\,\omega$. The analogy with the electromagnetic case then suggests that a more general type of wave function—still related to the conservative case—can be expressed as a superposition, that is, a linear combination with constant coefficients, of monochromatic wave functions. This possibility is one of the postulates of De Broglie's theory, and is referred to as *Superposition Principle*. To vest it with a mathematical form one must distinguish among the different types of spectrum; for the discrete spectrum, indicating with c_n the complex coefficients of the linear combination, the general wave function reads

$$\psi(\mathbf{r}, t) = \sum_n c_n\, w_n\, \exp(-\mathrm{i}\,\omega_n\, t), \tag{9.1}$$

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with E_n, w_n the eigenvalues and eigenfunctions of the time-independent Schrödinger equation $\mathcal{H} w_n = E_n w_n$, and $\omega_n = E_n/\hbar$. As usual, n stands for a single index or a set of indices. The form of (9.1) is such that the spatial coordinates are separated from the time coordinate; fixing the latter by letting, say, $t = 0$, and remembering that the set of eigenfunctions w_n is complete, yields

$$\psi_{t=0} = \psi(\mathbf{r}, 0) = \sum_n c_n w_n, \qquad c_n = \langle w_n | \psi_{t=0} \rangle. \tag{9.2}$$

The above shows that the coefficients c_n are uniquely determined by the initial condition $\psi_{t=0}$. On the other hand, once the coefficients c_n are known, the whole time evolution of ψ is determined, because the angular frequencies appearing in the time-dependent terms $\exp(-\mathrm{i}\,\omega_n t)$ are also known. In other terms, ψ is determined by the initial condition and by the time-independent Hamiltonian operator whence E_n, w_n derive.

An important aspect of (9.1) is that it allows one to construct a wave function of a given form; for such a construction, in fact, it suffices to determine the coefficients by means of the second relation in (9.2). In particular it is possible to obtain a wave function that is square integrable at all times, even if the eigenfunctions w_n are not square integrable themselves. Thanks to this property the wave function (9.1) is localized in space at each instant of time, hence it is suitable for describing the motion of the particle associated to it. Due to the analogy with the electromagnetic case, were the interference of monochromatic waves provides the localization of the field's intensity, a wave function of the form (9.1) is called *wave packet*. Remembering that the wave function provides the probability density $|\psi|^2$ used to identify the position of the particle, one can assume that the wave packet's normalization holds:

$$\int_\Omega |\psi|^2 \, \mathrm{d}^3 r = \sum_n |c_n|^2 = 1, \tag{9.3}$$

where the second equality derives from Parseval's theorem (8.41). From (9.3) it follows that the coefficients are subjected to the constraint $0 \le |c_n|^2 \le 1$.

As all possible energies E_n appear in the expression (9.1) of ψ, the wave packet does not describe a motion with a definite energy. Now, assume that an energy measurement is carried out on the particle, and let $t = t_E$ be the instant at which the measurement is completed. During the measurement the Hamiltonian operator of (8.46) does not hold because the particle is interacting with the measuring apparatus, hence the forces acting on it are different from those whence the potential energy V of (8.45) derives. Instead, for $t > t_E$ the original Schrödinger equation (8.46) is restored, so the expression of ψ is again given by a linear combination of monochromatic waves; however, the coefficients of the combination are expected to be different from those that existed prior to the measurement, due to the perturbation produced by the latter. In particular, the form of ψ for $t > t_E$ must be compatible with the fact that the energy measurement has found a specific value of the energy; this is possible only if the coefficients are set to zero, with the exception of the one corresponding to the energy that is the outcome of the measurement. The latter must be one of the eigenvalues of (8.46) due to the compatibility requirement; if it is, say, E_m, then the form of the wave function for $t > t_E$ is

$$\psi(\mathbf{r}, t) = w_m \exp[-\mathrm{i}\, E_m\, (t - t_E)/\hbar], \tag{9.4}$$

where the only non-vanishing coefficient, c_m, has provisionally been set to unity.

The reasoning leading to (9.4) can be interpreted as follows: the interaction with the measuring apparatus filters out from (9.1) the term corresponding to E_m; as a consequence, the coefficients c_n whose values were previously set by the original ψ are modified by the measurement and become $c_n = \delta_{nm}$. If the filtered eigenfunction w_m is square integrable, then (9.3) holds, whence $\sum_n |c_n|^2 = |c_m|^2 = 1$, $c_m = \exp(\mathrm{i}\,\Phi)$. As the constant phase Φ does not carry any information, it can be set to zero to yield $c_m = 1$. If w_m is not square integrable, the arbitrariness of the multiplicative constant still allows one to set $c_m = 1$.

As the energy measurement forces the particle to belong to a definite energy state (in the example above, E_m), for $t > t_E$ the particle's wave function keeps the monochromatic form (9.4). If, at a later time, a second energy measurement is carried out, the only possible outcome is E_m; as a consequence, after the second measurement is completed, the form of the wave function is still (9.4), whence $|c_m|^2 = 1$. One notes that the condition $|c_m|^2 = 1$ is associated with the certainty that the outcome of the energy measurement is E_m whereas, when the general superposition (9.1) holds, the coefficients fulfill the relations $\sum_n |c_n|^2 = 1$, $0 \le |c_n|^2 \le 1$, and the measurement's outcome may be any of the eigenvalues. It is then sensible to interpret $|c_n|^2$ as the *probability* that a measurement of energy finds the result E_n. This interpretation, that has been worked out here with reference to energy, is extended to the other dynamical variables (Sect. 10.2).

When the spectrum is continuous the description of the wave packet is

$$\psi(\mathbf{r}, t) = \iiint_{-\infty}^{+\infty} c_{\mathbf{k}}\, w_{\mathbf{k}}\, \exp(-\mathrm{i}\,\omega_{\mathbf{k}}\, t)\, \mathrm{d}^3 k, \tag{9.5}$$

with $E_{\mathbf{k}}$, $w_{\mathbf{k}}$ the eigenvalues and eigenfunctions of $\mathcal{H} w_{\mathbf{k}} = E_{\mathbf{k}}\, w_{\mathbf{k}}$, and $\omega_{\mathbf{k}} = E_{\mathbf{k}}/\hbar$. Such symbols stand for $E_{\mathbf{k}} = E(\mathbf{k})$, $w_{\mathbf{k}} = w(\mathbf{r}, \mathbf{k})$, and so on, with $\mathbf{k}$ a three-dimensional vector whose components are continuous. The relations corresponding to (9.2, 9.3) are

$$\psi_{t=0} = \psi(\mathbf{r}, 0) = \iiint_{-\infty}^{+\infty} c_{\mathbf{k}}\, w_{\mathbf{k}}\, \mathrm{d}^3 k, \qquad c_{\mathbf{k}} = \langle w_{\mathbf{k}} | \psi_{t=0} \rangle, \tag{9.6}$$

$$\int_\Omega |\psi|^2\, \mathrm{d}^3 r = \iiint_{-\infty}^{+\infty} |c_{\mathbf{k}}|^2\, \mathrm{d}^3 k = 1. \tag{9.7}$$

The expression of $\psi_{t=0}$ in (9.6) lends itself to providing an example of a wave function that is square integrable, while the eigenfunctions that build up the superposition are not. Consider, in fact, the relation (C.82) and let $c_k = \sigma \exp(-\sigma^2 k^2/2)$,

$w_k = \exp(\mathrm{i}\, k\, x)/\sqrt{2\pi}$ in it, with σ a length; in this way (C.82) becomes the one-dimensional case of (9.6) and yields $\psi_{t=0} = \exp[-x^2/(2\,\sigma^2)]$, showing that a square-integrable function like the Gaussian one can be expressed as a combination of the non-square-integrable spatial parts of the plane waves.

The extraction of the probabilities in the continuous-spectrum case accounts for the fact the $E(\mathbf{k})$ varies continuously with $\mathbf{k}$. To this purpose one takes the elementary volume d^3k centered on some $\mathbf{k}$ and considers the product $|c_\mathbf{k}|^2\,\mathrm{d}^3k$. Such a product is given the meaning of infinitesimal probability that the outcome of an energy measurement belongs to the range of $E(\mathbf{k})$ values whose domain is d^3k (more comments are made in Sect. 9.7.1).

9.3 Time-Dependent Schrödinger Equation

The Superposition Principle illustrated in Sect. 9.2 prescribes the form of the wave packet in the conservative case. Considering for simplicity a discrete set of eigenfunctions, the time derivative of ψ reads

$$\frac{\partial \psi}{\partial t} = \sum_n c_n\, w_n\, \frac{E_n}{\mathrm{i}\,\hbar}\, \exp(-\mathrm{i} E_n\, t/\hbar). \tag{9.8}$$

Using the time-independent Schrödinger equation $\mathcal{H} w_n = E_n w_n$ transforms the above into

$$\mathrm{i}\,\hbar\,\frac{\partial \psi}{\partial t} = \sum_n c_n\, \mathcal{H} w_n\, \exp(-\mathrm{i}\, E_n\, t/\hbar), \qquad \mathrm{i}\,\hbar\,\frac{\partial \psi}{\partial t} = \mathcal{H}\psi. \tag{9.9}$$

The second relation in (9.9) is a linear, homogeneous partial-differential equation, of the second order with respect to the spatial coordinates and of the first order with respect to time, whose solution is the wave function ψ. It is called *time-dependent Schrödinger equation*; as its coefficients are complex, so is ψ. To solve the equation it is necessary to prescribe the initial condition $\psi(\mathbf{r}, t = 0)$ and the boundary conditions. For the latter the same discussion as in Sect. 8.2 applies, because the spatial behavior of ψ is prescribed by the Hamiltonian operator.

The reasoning leading to the second relation in (9.9) is based on the Superposition Principle, namely, once the form of ψ is given, the equation fulfilled by ψ is readily extracted. Such a reasoning is not applicable in the non-conservative cases, because the time-independent equation $\mathcal{H} w_n = E_n w_n$ does not hold then, so the eigenvalues and eigenfunctions upon which the superposition is based are not available. However, another line of reasoning shows that the time-dependent Schrödinger equation holds also for the non-conservative situations [69]. Although in such cases the wave function ψ is not expressible as a superposition of monochromatic waves, it can still be expanded using an orthonormal set. If the set is discrete, $v_n = v_n(\mathbf{r})$, the expansion reads

$$\psi(\mathbf{r}, t) = \sum_n b_n\, v_n(\mathbf{r}), \qquad b_n(t) = \langle v_n|\psi\rangle, \tag{9.10}$$

whereas for a continuous set $v_{\mathbf{k}} = v(\mathbf{r}, \mathbf{k})$ one finds

$$\psi(\mathbf{r}, t) = \iiint_{-\infty}^{+\infty} b_{\mathbf{k}}\, v_{\mathbf{k}}\, \mathrm{d}^3 k, \qquad b_{\mathbf{k}}(t) = \langle v_{\mathbf{k}} | \psi \rangle. \tag{9.11}$$

9.4 Continuity Equation and Norm Conservation

Remembering that the square modulus of the wave function provides the localization of the particle, it is of interest to investigate the time evolution of $|\psi|^2$, starting from the time derivative of ψ given by the time-dependent Schrödinger equation (9.9). Here it is assumed that the wave function is normalized to unity and that the Hamiltonian operator is real, $\mathcal{H}^* = \mathcal{H} = -\hbar^2/(2\,m)\,\nabla^2 + V$; a case where the operator is complex is examined in Sect. 9.5. Taking the time derivative of $|\psi|^2$ yields

$$\frac{\partial |\psi|^2}{\partial t} = \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} = \psi^* \frac{\mathcal{H}\psi}{\mathrm{i}\,\hbar} - \psi \frac{\mathcal{H}\psi^*}{\mathrm{i}\,\hbar}, \tag{9.12}$$

with $\psi^*\,\mathcal{H}\psi - \psi\,\mathcal{H}\psi^* = -\hbar^2/(2m)\,(\psi^*\,\nabla^2\psi - \psi\,\nabla^2\psi^*)$. Identity (A.17) then yields

$$\frac{\partial |\psi|^2}{\partial t} + \mathrm{div}\mathbf{J}_\psi = 0, \qquad \mathbf{J}_\psi = \frac{\mathrm{i}\,\hbar}{2\,m}\,(\psi\,\mathrm{grad}\psi^* - \psi^*\,\mathrm{grad}\psi). \tag{9.13}$$

The first relation in (9.13) has the form of a continuity equation (compare with (23.3) and (4.23)). As $|\psi|^2$ is the probability density, $\mathbf{J}_\psi$ takes the meaning of *density of the probability flux*;[1] it is a real quantity because the term in parentheses in the second relation of (9.13) is imaginary.

Relations (9.13) provide a physical explanation of the continuity requirements that were discussed from the mathematical standpoint in Sect. 8.2. Such requirements, namely, the continuity of the wave function and of its first derivatives in space, were introduced in Sect. 8.2 with reference to the solutions of the time-independent Schrödinger equation; however, they hold also for the time-dependent one because the spatial behavior of ψ is prescribed by the Hamiltonian operator. Their physical explanation is that they provide the spatial continuity of the probability density and of the probability-flux density. Integrating (9.13) over a volume Ω' whose surface is Σ' yields

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\Omega'} |\psi|^2\,\mathrm{d}\Omega' = -\int_{\Sigma'} \mathbf{J}_\psi \cdot \mathbf{n}\,\mathrm{d}\Sigma', \tag{9.14}$$

with $\mathbf{n}$ the unit vector normal to Σ', oriented in the outward direction. The integral at the left hand side of (9.14) is the probability of localizing the particle within Ω',

[1] Remembering that $[|\psi|^2] = \mathrm{m}^{-3}$, one finds $[\mathbf{J}_\psi] = \mathrm{m}^{-2}\,\mathrm{t}^{-1}$.

that at the right hand side is the probability flux across Σ' in the outward direction; as a consequence, the meaning of (9.14) is that the time variation of the localization probability within Ω' is the negative probability flux across the surface. If $\Omega' \to \infty$ the surface integral vanishes because ψ is square integrable and, as expected,

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_\infty |\psi|^2 \, \mathrm{d}\Omega = 0. \tag{9.15}$$

The above is another form of the normalization condition and is also termed *norm-conservation condition*. Note that the integral in (9.15) does not depend on time although ψ does.

The density of the probability flux can be given a different form that uses the momentum operator $\hat{\mathbf{p}} = -\mathrm{i}\,\hbar\,\mathrm{grad}$ introduced in Sect. 8.5; one finds

$$\mathbf{J}_\psi = \frac{1}{2\,m} \left[\psi\,(\hat{\mathbf{p}}\psi)^* + \psi^*\,\hat{\mathbf{p}}\psi\right] = \frac{1}{m}\,\Re\left(\psi^*\,\hat{\mathbf{p}}\psi\right). \tag{9.16}$$

Although this form is used less frequently than (9.13), it makes the analogy with the classical flux density much more intelligible.

When the wave function is of the monochromatic type (9.4), the time-dependent factors cancel each other in (9.13), to yield

$$\mathrm{div}\mathbf{J}_\psi = 0, \qquad \mathbf{J}_\psi = \frac{\mathrm{i}\,\hbar}{2\,m}\,(w\,\mathrm{grad}w^* - w^*\,\mathrm{grad}w). \tag{9.17}$$

If w is real, then $\mathbf{J}_\psi = 0$.

9.5 Hamiltonian Operator of a Charged Particle

The Hamiltonian function of a particle of mass m and charge e, subjected to an electromagnetic field, is given by (1.35), namely,

$$H = \sum_{i=1}^{3} \frac{1}{2m}\,(p_i - e\,A_i)^2 + e\,\varphi, \tag{9.18}$$

where the scalar potential φ and the components of the vector potential A_i may depend on the spatial coordinates and time. To find the Hamiltonian operator corresponding to H one could apply the same procedure as in (8.48), that consists in replacing p_i with $\hat{p}_i = -\mathrm{i}\,\hbar\,\partial/\partial x_i$. In this case, however, a difficulty arises if A_i depends on the coordinates; in fact, the two equivalent expansions of $(p_i - e\,A_i)^2$, namely, $p_i^2 + e^2\,A_i^2 - 2\,p_i\,e\,A_i$ and $p_i^2 + e^2\,A_i^2 - 2\,e\,A_i\,p_i$ yield two different operators: the first of them contains the summand $\partial(A_i\,\psi)/\partial x_i$, the other one contains $A_i\,\partial\psi/\partial x_i$, and neither one is Hermitean. If, instead, one keeps the order of the factors in the expansion, namely, $(p_i - e\,A_i)^2 = p_i^2 + e^2\,A_i^2 - e\,A_i\,p_i - p_i\,e\,A_i$, the resulting Hamiltonian operator reads $\mathcal{H} = \mathcal{H}_R + \mathrm{i}\,\mathcal{H}_I$, with

$$\mathcal{H}_R = -\frac{\hbar^2}{2\,m}\,\nabla^2 + e\,\varphi + \frac{e^2}{2\,m}\,\mathbf{A}\cdot\mathbf{A}, \qquad \mathcal{H}_I = \frac{\hbar\,e}{2\,m}\sum_{i=1}^{3}\left(A_i\,\frac{\partial}{\partial x_i} + \frac{\partial}{\partial x_i}\,A_i\right), \tag{9.19}$$

and is Hermitean (compare with Sect. 10.2). The particle dynamics is determined by the time-dependent Schrödinger equation $\mathrm{i}\,\hbar\,\partial\psi/\partial t = \mathcal{H}\psi$. The continuity equation fulfilled by ψ is found following the same reasoning as in Sect. 9.4, starting from

$$\frac{\partial|\psi|^2}{\partial t} = \psi^*\,\frac{(\mathcal{H}_R + \mathrm{i}\,\mathcal{H}_I)\psi}{\mathrm{i}\,\hbar} - \psi\,\frac{(\mathcal{H}_R - \mathrm{i}\,\mathcal{H}_I)\psi^*}{\mathrm{i}\,\hbar}. \tag{9.20}$$

The terms related to $\mathcal{H}_R$ yield $-\mathrm{div}\Re(\psi^*\,\hat{\mathbf{p}}\,\psi)/m$ as in Sect. 9.4. Those related to $\mathcal{H}_I$ yield $\mathrm{div}(e\,\mathbf{A}\,|\psi|^2)/m$. In conclusion, the continuity equation for the wave function of a charged particle reads

$$\frac{\partial|\psi|^2}{\partial t} + \mathrm{div}\mathbf{J}_\psi = 0, \qquad \mathbf{J}_\psi = \frac{1}{m}\,\Re\left[\psi^*\,\left(\hat{\mathbf{p}} - e\,\mathbf{A}\right)\,\psi\right]. \tag{9.21}$$

It is worth noting that the transformation from the Hamiltonian function (9.18) to the Hamiltonian operator (9.19) produced by replacing p_i with $\hat{p}_i$ is limited to the dynamics of the particle; the electromagnetic field, instead, is still treated through the scalar and vector potentials, and no transformation similar to that used for the particle is carried out. The resulting Hamiltonian operator (9.19) must then be considered as approximate; the term *semiclassical approximation* is in fact used to indicate the approach based on (9.19), where the electromagnetic field is treated classically whereas Quantum Mechanics is used in the description of the particle's dynamics. The procedure by which the quantum concepts are extended to the electromagnetic field is described in Sect. 12.3.

The semiclassical approximation is useful in several instances, among which there is the calculation of the stationary states of atoms. As shown in Sect. 9.7.2, it explains why the radiative decay predicted in Sect. 5.11.3 using the classical (planetary) model does not actually occur.

9.6 Approximate Form of the Wave Packet for a Free Particle

The energy spectrum of a free particle is continuous, and the wave packet is given by (9.5), with

$$w_{\mathbf{k}}(\mathbf{r}) = \frac{1}{(2\,\pi)^{3/2}}\,\exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r}), \qquad E_{\mathbf{k}} = \frac{\hbar^2}{2\,m}\,\left(k_1^2 + k_2^2 + k_3^2\right) = \hbar\,\omega_{\mathbf{k}}. \tag{9.22}$$

As $-\infty < k_i < +\infty$, here the order of degeneracy of $E_{\mathbf{k}}$ is infinite. Now, remembering that the wave packet is normalized to unity, it follows that $|\psi(\mathbf{r},t)|^2\,\mathrm{d}^3r$ is the infinitesimal probability that at time t the particle is localized within $\mathrm{d}^3 r$; also, from the analysis carried out in Sect. 9.2, the product $|c_\mathbf{k}|^2\,\mathrm{d}^3 k$ is the infinitesimal probability that the outcome of an energy measurement belongs to the range of $E(\mathbf{k})$ values whose domain is $\mathrm{d}^3 k$. Note that $c_\mathbf{k}$ does not depend on time.

Considering the example of a Gaussian wave packet given at the end of Sect. 9.2, one can assume that $|\psi(\mathbf{r},t)|^2$ is localized in the $\mathbf{r}$ space and $|c_\mathbf{k}|^2$ is localized in the $\mathbf{k}$ space. This means that $|\psi(\mathbf{r},t)|^2$ and $|c_\mathbf{k}|^2$ become vanishingly small when $\mathbf{r}$ departs from its average value $\mathbf{r}_0(t)$ and respectively, $\mathbf{k}$ departs from its average value $\mathbf{k}_0$. Such average values are given by[2]

$$\mathbf{r}_0(t) = \iiint_{-\infty}^{+\infty} \mathbf{r}\,|\psi(\mathbf{r},t)|^2\,\mathrm{d}^3 r, \qquad \mathbf{k}_0 = \iiint_{-\infty}^{+\infty} \mathbf{k}\,|c_\mathbf{k}|^2\,\mathrm{d}^3 k. \tag{9.23}$$

An approximate expression of the wave packet is obtained by observing that, due to the normalization condition (9.7), the main contribution to the second integral in (9.7) is given by the values of $\mathbf{k}$ that are in the vicinity of $\mathbf{k}_0$. From the identity $k_i^2 = (k_{0i} - k_{0i} + k_i)^2 = k_{0i}^2 + 2\,k_{0i}\,(k_i - k_{0i}) + (k_i - k_{0i})^2$ it then follows

$$\omega_\mathbf{k} = \frac{\hbar}{2\,m}\,k_0^2 + \frac{\hbar}{m}\,\mathbf{k}_0\cdot(\mathbf{k}-\mathbf{k}_0) + \frac{\hbar}{2\,m}|\mathbf{k}-\mathbf{k}_0|^2 \tag{9.24}$$

where, for $\mathbf{k}$ close to $\mathbf{k}_0$, one neglects the quadratic term to find

$$\omega_\mathbf{k} \simeq \omega_0 + \mathbf{u}\cdot(\mathbf{k}-\mathbf{k}_0), \quad \omega_0 = \frac{\hbar}{2\,m}\,k_0^2, \quad \mathbf{u} = \frac{\hbar}{m}\,\mathbf{k}_0 = \left(\mathrm{grad}_\mathbf{k}\omega_\mathbf{k}\right)_{\mathbf{k}_0}, \tag{9.25}$$

with $\mathbf{u}$ the *group velocity*. The neglect of terms of order higher than the first used to simplify (9.24) could not be applied to $c_\mathbf{k}$; in fact, $c_\mathbf{k}$ has typically a peak for $\mathbf{k} = \mathbf{k}_0$, so its first derivatives would vanish there. Using (9.25) and letting $\Phi_0 = \mathbf{k}_0\cdot\mathbf{r} - \omega_0\,t$ transform (9.5) into $\psi(\mathbf{r},t) \simeq \exp(\mathrm{i}\,\Phi_0)\,A\,(\mathbf{r}-\mathbf{u}\,t\,;\mathbf{k}_0)$, where the *envelope function* A is defined as

$$A\,(\mathbf{r}-\mathbf{u}\,t\,;\mathbf{k}_0) = \iiint_{-\infty}^{+\infty} \frac{c_\mathbf{k}}{(2\,\pi)^{3/2}}\,\exp\left[\mathrm{i}\,(\mathbf{r}-\mathbf{u}\,t)\cdot(\mathbf{k}-\mathbf{k}_0)\right]\mathrm{d}^3 k. \tag{9.26}$$

Within the limit of validity of (9.25), the envelope function contains the whole information about the particle's localization: $|\psi|^2 = |A|^2$. Also, the dependence of A on $\mathbf{r}$ and t is such that, for any two pairs $(\mathbf{r}_1, t_1)$, $(\mathbf{r}_2, t_2)$ fulfilling $\mathbf{r}_2 - \mathbf{u}\,t_2 = \mathbf{r}_1 - \mathbf{u}\,t_1$ the form of $A(\mathbf{r}_2, t_2)$ is the same as that of $A(\mathbf{r}_1, t_1)$. In other terms, A moves without distortion in the direction of $\mathbf{u}$, and its velocity is $(\mathbf{r}_2 - \mathbf{r}_1)/(t_2 - t_1) = \mathbf{u}$. As time evolves, the approximation leading to (9.25) becomes less and less accurate; taking by way of example $t_1 = 0$ as the initial time, and observing that the summands in (9.25) belong to the phase $-\mathrm{i}\,\omega_\mathbf{k}\,t$, the approximation holds as long as $\hbar\,|\mathbf{k}-\mathbf{k}_0|^2\,t/(2\,m) \ll 2\pi$.

[2] Definitions (9.23) provide the correct weighed average of $\mathbf{r}$ and $\mathbf{k}$ thanks to the normalization condition (9.7). A more exhaustive treatment is carried out in Sect. 10.5.

9.7 Complements

9.7.1 About the Units of the Wave Function

Consider the wave function ψ associated to a single particle. When the wave function is square integrable and normalized to unity, its units are $[\psi] = \mathrm{m}^{-3/2}$ due to $\int |\psi|^2 \,\mathrm{d}^3 r = 1$. Then, if the eigenvalues of the Hamiltonian operator are discrete, the second equality in (9.3) shows that $|c_n|^2$, c_n are dimensionless and, finally, (9.2) shows that w_n has the same units as ψ. If the eigenvalues are continuous, the second equality in (9.7) shows that $|c_{\mathbf{k}}|^2$ has the dimensions of a volume of the real space, so that $[c_{\mathbf{k}}] = \mathrm{m}^{3/2}$ and, finally, (9.6) shows that $w_{\mathbf{k}}$ has the same units as ψ.

There are situations, however, where units different from those illustrated above are ascribed to the eigenfunctions. One example is that of the eigenfunctions of the form $w_{\mathbf{k}} = \exp(\mathrm{i}\,\mathbf{k}\cdot\mathbf{r})/(2\,\pi)^{3/2}$, worked out in Sect. 8.2.1, which are dimensionless; another example is that of eigenfunctions of the form (10.7), whose units are $[\delta(\mathbf{r}-\mathbf{r}_0)] = \mathrm{m}^{-3}$. When such eigenfunctions occur, the units of the expansion's coefficients must be modified in order to keep the correct units of ψ (compare with the calculation shown in Sect. 14.6).

The considerations carried out here apply to the single-particle case. When the wave function describes a system of two or more particles, its units change accordingly (Sect. 15.2).

9.7.2 An Application of the Semiclassical Approximation

As indicated in Sect. 9.5 for the case of a particle subjected to an electromagnetic field, the semiclassical approximation consists in using the Hamiltonian operator (9.19), which is derived from the Hamiltonian function (9.18) by replacing p_i with $\hat{p}_i$. The electromagnetic field, instead, is still treated through the scalar and vector potentials. Experiments show that the approximation is applicable in several cases of interest. For instance, consider again the problem of the electromagnetic field generated by a single electron, discussed in classical terms in Sect. 5.11.2. If ψ is the wave function (assumed to be square integrable) associated to the electron in the quantum description, the electron's localization is given by $|\psi|^2$. It is then sensible to describe the charge density and the current density produced by the electron as

$$\rho = -q\,|\psi|^2, \qquad \mathbf{J} = -q\,\mathbf{J}_\psi, \tag{9.27}$$

where q is the elementary charge and $\mathbf{J}_\psi$ is defined in (9.13). If the electron is in a stationary state, namely, $\psi(\mathbf{r}, t) = w(\mathbf{r})\exp(-\mathrm{i}\,\omega\,t)$, then ρ and $\mathbf{J}$ are independent of time. From (4.58, 4.59) it follows that the potentials φ, $\mathbf{A}$ are independent of time as well. As a consequence, the distribution of charge and current density associated to the electron's motion is stationary (compare with (9.17)), which also yields that the acceleration $\dot{u}$ vanishes. From Larmor's formula (5.72) one finally finds that in this situation the electron emits no power; thus, the radiative decay predicted in Sect. 5.11.3 using the classical model does not occur.

9.7.3 Polar Form of the Schrödinger Equation

The time-dependent Schrödinger equation (9.9) is easily split into two real equations by considering the real and imaginary part of ψ. However, in this section the wave function will rather be written in polar form, $\psi = \alpha(\mathbf{r}, t) \exp[\mathrm{i}\, \beta(\mathbf{r}, t)]$, $\alpha \geq 0$, which reminds one of that used to derive the eikonal equation (5.51) of Geometrical Optics. Despite the fact that the resulting relations are non linear, the outcome of this procedure is interesting. Considering a Hamiltonian operator of the type $\mathcal{H} = -\hbar^2 \nabla^2/(2\, m) + V$, replacing the polar expression of ψ in (9.9), and separating the real and imaginary parts, yields two coupled, real equations; the first of them reads

$$\frac{\partial \alpha}{\partial t} = -\frac{\hbar}{2\, m} \left(\alpha\, \nabla^2 \beta + 2 \mathrm{grad}\alpha \cdot \mathrm{grad}\beta \right), \tag{9.28}$$

where the units of α^2 are those of the inverse of a volume. As for the second equation one finds

$$\frac{\partial(\hbar\, \beta)}{\partial t} + \frac{1}{2\, m} |\mathrm{grad}(\hbar \beta)|^2 + V + Q = 0, \qquad Q = -\frac{\hbar^2}{2\, m} \frac{\nabla^2 \alpha}{\alpha}, \tag{9.29}$$

where the units of $\mathrm{grad}(\hbar\, \beta)$ are those of a momentum. Using the short-hand notation

$$P = \alpha^2 = |\psi|^2, \quad S = \hbar\, \beta, \quad \mathbf{v}_e = \frac{\mathrm{grad} S}{m}, \quad H_Q = \frac{1}{2} m v_e^2 + Q + V, \tag{9.30}$$

and multiplying (9.28) by 2α, transforms (9.28, 9.29) into

$$\frac{\partial P}{\partial t} + \mathrm{div}(P\, \mathbf{v}_e) = 0, \qquad \frac{\partial S}{\partial t} + H_Q = 0. \tag{9.31}$$

The wave function is assumed to be square integrable, so that $\int_\Omega P\, \mathrm{d}^3 r = 1$. It is easily found that the first of (9.31) is the continuity equation (9.13): from the expression (9.16) of the current density one finds in fact

$$\mathbf{J}_\psi = \frac{1}{m} \Re \left(\psi^*\, \hat{\mathbf{p}} \psi \right) = \frac{\hbar}{m} \Re \left(\alpha^2\, \mathrm{grad}\beta - \mathrm{i}\, \alpha\, \mathrm{grad}\alpha \right) = P\, \mathbf{v}_e. \tag{9.32}$$

The two differential equations (9.31), whose unknowns are α, β, are coupled with each other. The second of them is similar to the Hamilton–Jacobi equation (1.51) of Classical Mechanics, and becomes equal to it in the limit $\hbar \to 0$, that makes Q to vanish and S to become the Hamilton principal function (Sect. 1.7). Note that the limit $Q \to 0$ decouples (9.31) from each other. In the time-independent case (9.31) reduce to $\mathrm{div}(P\, \mathbf{v}_e) = 0$ and $m\, v_e^2/2 + Q + V = E$, coherently with the fact that in this case Hamilton's principal function becomes $S = W - E\,t$, with W the (time-independent) Hamilton characteristic function. Although $\mathbf{v}_e$ plays the role of an average velocity in the continuity equation of (9.31), determining the expectation value needs a further averaging: in fact, taking definition of (10.13) expectation value and observing that the normalization makes the integral of gradα^2 to vanish, yields

$$m\,\langle \mathbf{v}_e \rangle = \int_\Omega \psi^*\,\hat{\mathbf{p}}\psi\,\mathrm{d}^3 r = \int_\Omega \alpha^2\,\nabla(\hbar\,\beta)\,\mathrm{d}^3 r = m\int_\Omega \alpha^2\,\mathbf{v}_e\,\mathrm{d}^3 r. \tag{9.33}$$

The last relation in (9.30) seems to suggest that Q is a sort of potential energy to be added to V. In fact this is not true, as demonstrated by the calculation of the expectation value of the kinetic energy T,

$$\langle T \rangle = -\frac{\hbar^2}{2m}\int_\Omega \psi^*\nabla^2\psi\,\mathrm{d}^3 r = \int_\Omega \psi^*\left(\frac{1}{2}\,m\,v_e^2 + Q\right)\psi\,\mathrm{d}^3 r, \tag{9.34}$$

showing that Q enters the expectation value of T, not V. To better investigate the meaning of Q it is useful to consider alternative expressions of $\langle Q \rangle$, like

$$\langle Q \rangle = \frac{\hbar^2}{2m}\int_\Omega |\nabla\alpha|^2\,\mathrm{d}^3 r = \frac{1}{2\,m}\,\left(\langle \hat{\mathbf{p}}\cdot\hat{\mathbf{p}} \rangle - \langle p_e^2 \rangle\right), \tag{9.35}$$

where $\hat{\mathbf{p}} = -\mathrm{i}\,\hbar\,\mathrm{grad}$ and $\mathbf{p}_e = m\,\mathbf{v}_e$. The derivation of (9.34, 9.35) follows the same pattern as that of (9.28, 9.29). The first form of (9.35) shows that $\langle Q \rangle$ is positive definite irrespective of the shape of α. The second one is the analogue of the definition of dispersion around the average: the analogy with the treatment used in statistical mechanics (compare with (19.79)) suggests that $p_e^2/(2m)$ provides the analogue of the convective part of the kinetic energy, while Q provides the analogue of the thermal part of it [87].

It is interesting to note that the analogy between the Schrödinger equation and a set of a continuity and a Hamilton–Jacobi-like equations had been noted by de Broglie, who introduced the concept of *pilot wave* in [24]. This cost him severe criticism by Pauli at the Fifth Solvay Conference in 1927. He resumed the idea more than 20 years later, stimulated by the papers by Bohm introducing the concept of *quantum potential*, see, e.g., [8]. The most recent paper by de Broglie on the subject is [25], published when the author was 79 years old.

9.7.4 Effect of a Gauge Transformation on the Wave Function

The Hamiltonian function (1.35) of a particle of mass m and charge e, subjected to an electromagnetic field, has been derived in Sect. 1.5 and reads $H = \sum_{i=1}^{3}(p_i - e\,A_i)^2/(2\,m) + e\,\varphi$, with p_i the ith component of momentum in Cartesian coordinates, φ the electric potential, and A_i the ith component of the magnetic potential. If a gauge transformation (Sect. 4.5) is carried out, leading to the new potentials

$$\varphi \leftarrow \varphi' = \varphi - \frac{\partial\vartheta}{\partial t}, \qquad \mathbf{A} \leftarrow \mathbf{A}' = \mathbf{A} + \mathrm{grad}\vartheta, \tag{9.36}$$

the resulting Hamiltonian function H' differs from the original one. In other terms, the Hamiltonian function is not gauge invariant. However, the Lorentz force $e\,(\mathbf{E} + \dot{\mathbf{r}} \wedge \mathbf{B})$ is invariant, whence the dynamics of the particle is not affected by a gauge transformation.

Also in the quantum case it turns out that the Hamiltonian operator is not gauge invariant, $\mathcal{H}' \neq \mathcal{H}$. As consequence, the solution of the Schrödinger equation is not gauge invariant either: $\psi' \neq \psi$. However, the particle's dynamics cannot be affected by a gauge transformation because the Lorentz force is invariant. It follows that, if the initial condition is the same, $|\psi'|^2_{t=0} = |\psi|^2_{t=0}$, then it is $|\psi'|^2 = |\psi|^2$ at all times; for this to happen, there must exist a real function σ such that

$$\psi' = \psi\, \exp(\mathrm{i}\,\sigma), \qquad \sigma = \sigma(\mathbf{r}, t). \tag{9.37}$$

From the gauge invariance of $|\psi|^2$ at all times it follows $\partial|\psi'|^2/\partial t = \partial|\psi|^2/\partial t$ whence, from the continuity equation (9.21), one obtains $\mathrm{div}\mathbf{J}'_\psi = \mathrm{div}\mathbf{J}_\psi$ with $\mathbf{J}_\psi = \Re[\psi^*(\hat{\mathbf{p}} - e\,\mathbf{A})\psi]/m$. Gauge transforming the quantities in brackets yields $(\psi')^*\,\hat{\mathbf{p}}\,\psi' = \psi^*\,\hat{\mathbf{p}}\,\psi + |\psi|^2\,\hbar\,\mathrm{grad}\sigma$ and $(\psi')^*\,e\,\mathbf{A}'\,\psi' = |\psi|^2\,e\,\mathbf{A} + |\psi|^2\,e\,\mathrm{grad}\vartheta$, whose difference provides

$$\mathbf{J}'_\psi - \mathbf{J}_\psi = \frac{1}{m}\,|\psi|^2\,\mathrm{grad}\,(\hbar\,\sigma - e\,\vartheta)\,. \tag{9.38}$$

In (9.38) it is $|\psi|^2 \neq 0$ and $\mathrm{grad}|\psi|^2 \neq 0$; also, $\hbar\,\sigma - e\,\vartheta$ is independent of ψ. It follows that, for $\mathrm{div}(\mathbf{J}'_\psi - \mathbf{J}_\psi) = 0$ to hold, from (A.17) it must be $\mathrm{grad}\,(\hbar\sigma - e\vartheta) = 0$, namely, $\hbar\sigma - e\vartheta$ is an arbitrary function of time only. Setting the latter to zero finally yields the expression for the exponent in (9.37), that reads[3]

$$\sigma = \frac{e}{\hbar}\,\vartheta. \tag{9.39}$$

Problems

9.1 Using the one-dimensional form of (9.26) determine the envelope function $A(x - u\,t)$ corresponding to $c_k = \sqrt{\sigma/\sqrt{\pi}}\,\exp\,(-\,\sigma^2\,k^2/2)$, with σ a length. Noting that $\int_{-\infty}^{+\infty} |c_k|^2\,\mathrm{d}k = 1$, show that A is normalized to 1 as well.

9.2 Using the envelope function $A(x - u\,t)$ obtained from Prob. 9.1 and the one-dimensional form of definition (9.23), show that $x_0(t) = u\,t$.

[3] The units of ϑ are $[\vartheta] = V\ s$.