3. Probability Waves of Matter

3.1 de Broglie Waves

In Section 2.7 we learned that through the probability interpretation photons can be described by waves. We have made explicit use of the simple relation $E = c|\mathbf{p}|$ between energy and momentum of the photon, which holds only for particles moving with the velocity c of light. For particles with a finite rest mass m, which move with velocities v slow compared to the velocity of light, the corresponding nonrelativistic relation between energy and momentum is

$$E = \frac{p^2}{2m} \quad , \qquad p = mv \quad .$$

Plane waves that are of the same type as those for photons, which were discussed at the end of Chapter 2, but have the nonrelativistic relation just given,

$$\begin{aligned} \psi_p(x,t) &= \frac{1}{(2\pi\hbar)^{1/2}} \exp\left[-\frac{\mathrm{i}}{\hbar}(Et - px)\right] \\ &= \frac{1}{(2\pi\hbar)^{1/2}} \exp\left[-\frac{\mathrm{i}}{\hbar}\left(\frac{p^2}{2m}t - px\right)\right] \quad , \end{aligned}$$

are called *de Broglie waves* of matter. The factor in front of the exponential is chosen for convenience. The *phase velocity* of these de Broglie waves is

$$v_\mathrm{p} = \frac{E}{p} = \frac{p}{2m}$$

and is thus different from the particle velocity $v = p/m$.

3.2 Wave Packet, Dispersion

The harmonic de Broglie waves, like the harmonic electric waves, are not localized in space and therefore are not suited to describing a particle. To

localize a particle in space, we again have to superimpose harmonic waves to form a wave packet. To keep things simple, we first restrict ourselves to discussing a one-dimensional wave packet.

For the spectral function we again choose a Gaussian function,[1]

$$f(p) = \frac{1}{(2\pi)^{1/4}\sqrt{\sigma_p}} \exp\left[-\frac{(p-p_0)^2}{4\sigma_p^2}\right] \quad .$$

The corresponding de Broglie wave packet is then

$$\psi(x,t) = \int_{-\infty}^{+\infty} f(p)\psi_p(x - x_0, t)\,\mathrm{d}p \quad .$$

For the de Broglie wave packet, as for the light wave packet, we first approximate the integral by a sum,

$$\psi(x,t) \approx \sum_{n=-N}^{N} \psi_n(x,t) \quad ,$$

where the $\psi_n(x,t)$ are harmonic waves for different values $p_n = p_0 + n\Delta p$ multiplied by the spectral weight $f(p_n)\Delta p$,

$$\psi_n(x,t) = f(p_n)\psi(x - x_0, t)\Delta p \quad .$$

Figure 3.1a shows the real parts $\mathrm{Re}\,\psi_n(x,t)$ of the harmonic waves $\psi_n(x,t)$ as well as their sum being equal to the real part $\mathrm{Re}\,\psi(x,t)$ of the wave function $\psi(x,t)$ for the wave packet at time $t = t_0 = 0$. The point $x = x_0$ is marked on each harmonic wave. In Figure 3.1b the real parts $\mathrm{Re}\,\psi_n(x,t)$ and their sum $\mathrm{Re}\,\psi(x,t)$ are shown at later time $t = t_1$. Because of their different phase velocities, the partial waves have moved by different distances $\Delta x_n = v_n(t_1 - t_0)$ where $v_n = p_n/(2m)$ is the phase velocity of the harmonic wave of momentum p_n. This effect broadens the extension of the wave packet.

The integration over p can be carried out so that the explicit expression for the wave packet has the form

$$\psi(x,t) = M(x,t)\mathrm{e}^{\mathrm{i}\phi(x,t)} \quad .$$

Here the exponential function represents the carrier wave with a *phase* ϕ varying rapidly in space and time. The bell-shaped amplitude function

[1]We have chosen this spectral function to correspond to the square root of the spectral function that was used in Section 2.4 to construct a wave packet of light. Since the area under the spectral function $f(k)$ of Section 2.4 was equal to one, the area under $[f(p)]^2$ is now equal to one. This guarantees that the normalization condition of the wave function ψ in the next section will be fulfilled.

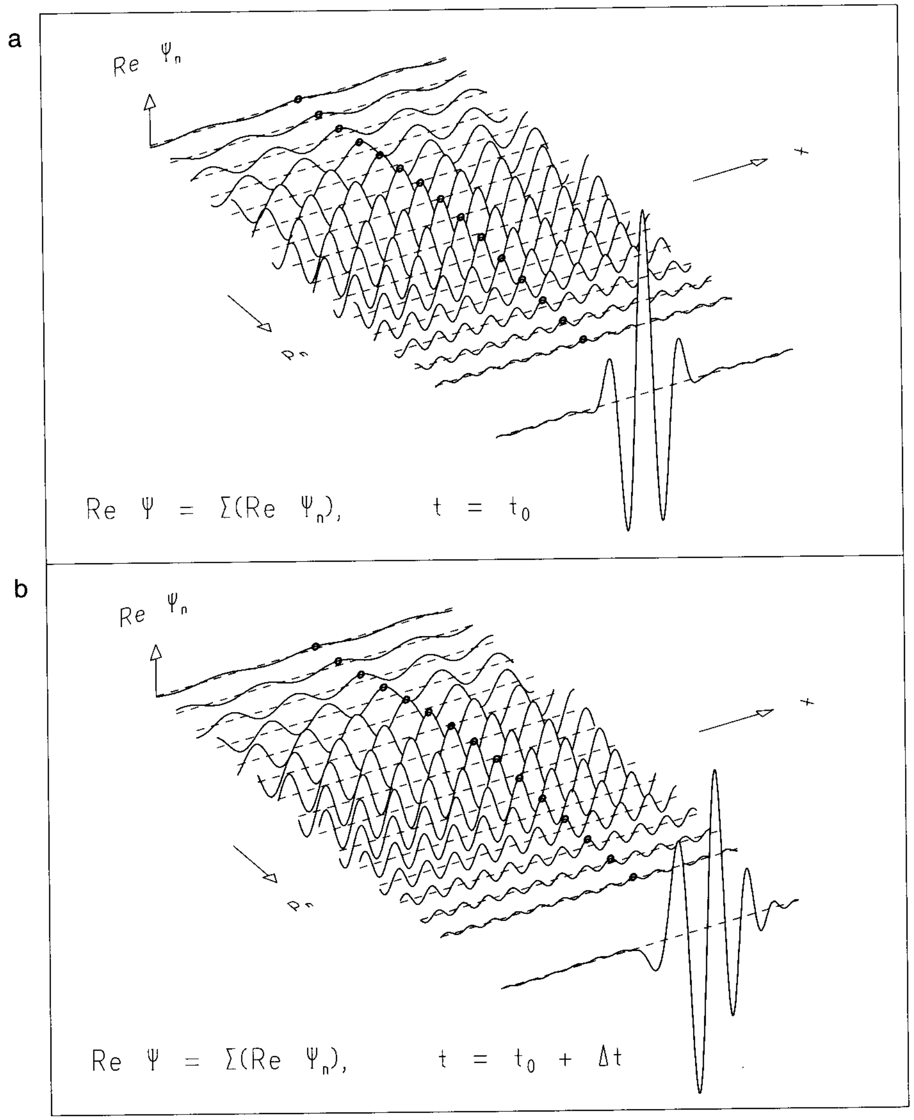

Fig. 3.1. **Construction of a wave packet as a sum of harmonic waves ψ_n of different momenta and consequently of different wavelengths. Plotted are the real parts of the wave functions. The terms of different momenta and different amplitudes begin with the one of longest wavelength in the background. In the foreground is the wave packet resulting from the summation. (a) The situation for time $t = t_0$. All partial waves are marked by a circle at point $x = x_0$. (b) The same wave packet and its partial waves at time $t_1 > t_0$. The partial waves have moved different distances $\Delta x_n = v_n(t_1 - t_0)$ because of their different phase velocities v_n, as indicated by the circular marks which have kept their phase with respect to those in part a. Because of the different phase velocities, the wave packet has changed its form and width.**

$$M(x,t) = \frac{1}{(2\pi)^{1/4}\sqrt{\sigma_x}} \exp\left[-\frac{(x - x_0 - v_0 t)^2}{4\sigma_x^2}\right]$$

travels in x direction with the *group velocity*

$$v_0 = \frac{p_0}{m} \quad .$$

The group velocity is indeed the particle velocity and different from the phase velocity. The localization in space is given by

$$\sigma_x^2 = \frac{\hbar^2}{4\sigma_p^2}\left(1 + \frac{4\sigma_p^4}{\hbar^2}\frac{t^2}{m^2}\right) \quad .$$

This formula shows that the spatial extension σ_x of the wave packet increases with time. This phenomenon is called *dispersion*. Figure 3.2 shows the time developments of the real and imaginary parts of two wave packets with different group velocities and widths. We easily observe the dispersion of the wave packets in time. The fact that a wave packet comprises a whole range of momenta is the physical reason why it disperses. Its components move with different velocities, thus spreading the packet in space.

The function $\phi(x,t)$ determines the phase of the carrier wave. It has the form

$$\phi(x,t) = \frac{1}{\hbar}\left[p_0 + \frac{\sigma_p^2}{\sigma_x^2}\frac{v_0 t}{2p_0}(x - x_0 - v_0 t)\right](x - x_0 - v_0 t) + \frac{p_0}{2\hbar}v_0 t - \frac{\alpha}{2}$$

with

$$\tan\alpha = \frac{2\,\sigma_p^2}{\hbar\;m}\,t \quad .$$

For fixed time t it represents the phase of a harmonic wave modulated in wave number. The effective wave number k_{eff} is the factor in front of $x - x_0 - v_0 t$ and is given by

$$k_{\mathrm{eff}}(x) = \frac{1}{\hbar}\left[p_0 + \frac{\sigma_p^2}{\sigma_x^2}\frac{v_0 t}{2p_0}(x - x_0 - v_0 t)\right] \quad .$$

At the value $x = \langle x\rangle$ corresponding to the maximum value of the bell-shaped amplitude modulation $M(x,t)$, that is, its position average

$$\langle x\rangle = x_0 + v_0 t \quad ,$$

the effective wave number is simply equal to the wave number that corresponds to the average momentum p_0 of the spectral function,

$$k_0 = \frac{1}{\hbar}p_0 = \frac{1}{\hbar}m v_0 \quad .$$

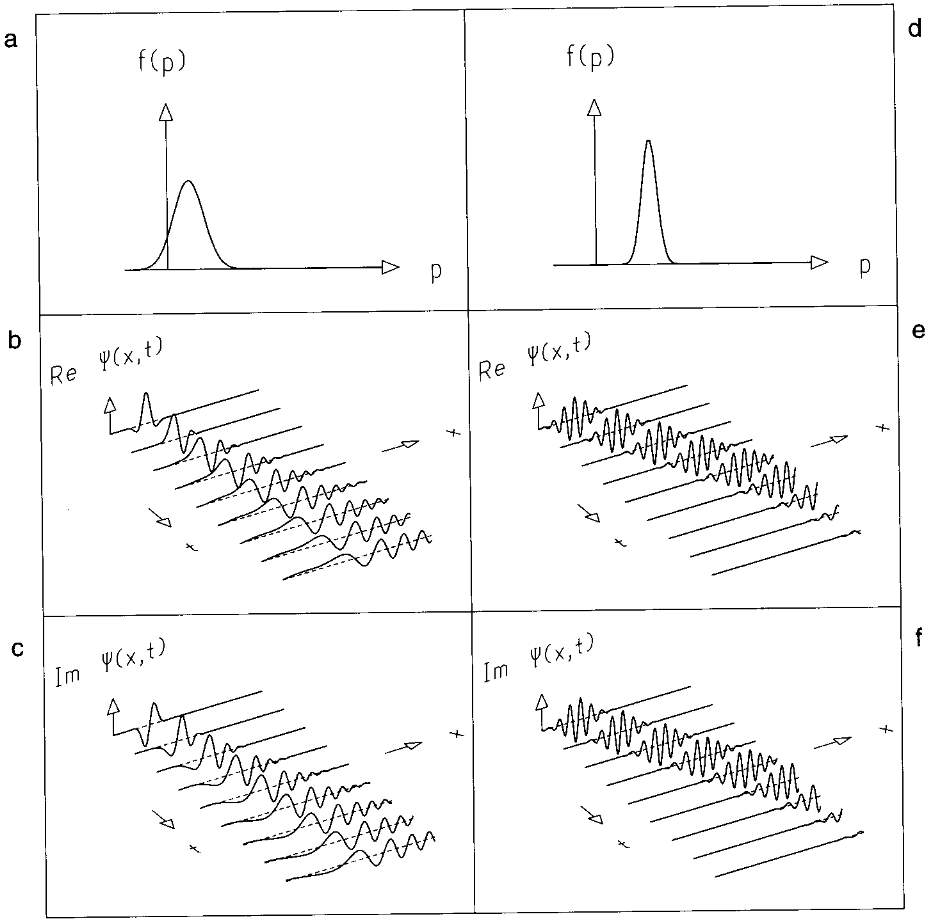

Fig. 3.2. **(a, d) Spectral functions and time developments of (b, e) the real parts and (c, f) the imaginary parts of the wave functions for two different wave packets. The two packets have different group velocities and different widths and spread differently with time.**

For values $x > x_0 + v_0 t$, that is, in front of the average position $\langle x \rangle$ of the moving wave packet, the effective wave number increases,

$$k_{\text{eff}}(x > x_0 + v_0 t) > k_0 \quad ,$$

so that the local wavelength

$$\lambda_{\text{eff}}(x) = \frac{2\pi}{|k_{\text{eff}}(x)|}$$

decreases.

For values $x < x_0 + v_0 t$, that is, behind the average position $\langle x \rangle$, the effective wave number decreases,

$$k_{\text{eff}}(x < x_0 + v_0 t) < k_0 \quad .$$

This decrease leads to negative values of k_{eff} of large absolute value, which, far behind the average position, makes the wavelengths $\lambda_{\text{eff}}(x)$ short again. This wave number modulation can easily be verified in Figures 3.1 and 3.2. For a wave packet at rest, that is, $p_0 = 0$, $v_0 = p_0/m = 0$, the effective wave number

$$k_{\text{eff}}(x) = \frac{1}{\hbar}\frac{\sigma_p^2}{\sigma_x^2}\frac{t}{2m}(x - x_0)$$

has the same absolute value to the left and to the right of the average position x_0. This implies a decrease of the effective wavelength that is symmetric on both sides of x_0. Figure 3.4 corroborates this statement.

3.3 Probability Interpretation, Uncertainty Principle

Following Max Born (1926), we interpret the wave function $\psi(x, t)$ as follows. Its absolute square

$$\rho(x, t) = |\psi(x, t)|^2 = M^2(x, t)$$

is identified with the *probability density* for observing the particle at position x and time t, that is, the probability of observing the particle at a given time t in the space region between x and $x + \Delta x$ is $\Delta P = \rho(x, t)\Delta x$. This is plausible since $\rho(x, t)$ is positive everywhere. Furthermore, its integral over all space is equal to one for every moment in time so that the *normalization condition*

$$\int_{-\infty}^{+\infty} |\psi(x, t)|^2 \,\mathrm{d}x = \int_{-\infty}^{+\infty} \psi^*(x, t)\psi(x, t)\,\mathrm{d}x = 1$$

holds.

Notice, that there is a strong formal similarity between the average energy density $w(x, t) = \varepsilon_0 |E_c(x, t)|^2/2$ of a light wave and the probability density $\rho(x, t)$. Because of the probability character, the wave function $\psi(x, t)$ is not a field strength, since the effect of a field strength must be measurable wherever the field is not zero. A probability density, however, determines the probability that a particle, which can be point-like, will be observed at a given position. This probability interpretation is, however, restricted to normalized wave functions. Since the integral over the absolute square of a harmonic plane wave is

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}\exp\left[\frac{\mathrm{i}}{\hbar}(Et-px)\right]\exp\left[-\frac{\mathrm{i}}{\hbar}(Et-px)\right]\mathrm{d}x=\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}\mathrm{d}x$$

and diverges, the absolute square $|\psi(x,t)|^2$ of a harmonic plane wave cannot be considered a probability density. We shall call the absolute square of a wave function that cannot be normalized its *intensity*. Even though wave functions that cannot be normalized have no immediate physical significance, they are of great importance for the solution of problems. We have already seen that normalizable wave packets can be composed of these wave functions. This situation is similar to the one in classical electrodynamics in which the plane electromagnetic wave is indispensable for the solution of many problems. Nevertheless, a harmonic plane wave cannot exist physically, for it would fill all of space and consequently have infinite energy.

Figure 3.3 shows the time developments of the probability densities of the two Gaussian wave packets given in Figure 3.2. Underneath the two time developments the motion of a classical particle with the same velocity is presented. We see that the center of the Gaussian wave packet moves in the exact same way as the classical particle. But whereas the classical particle at every instant in time occupies a well-defined position in space, the quantum-mechanical wave packet has a finite width σ_x. It is a measure for the size of the region in space surrounding the classical position in which the particle will be found. The fact that the wave packet disperses in time means that the location of the particle becomes more and more uncertain with time.

The dispersion of a wave packet with zero group velocity is particularly striking. Without changing position it becomes wider and wider as time goes by (Figure 3.4a).

It is interesting to study the behavior of the real and imaginary parts of the wave packet at rest. Their time developments are shown in Figures 3.4b and 3.4c. Starting from a wave packet that at initial time $t=0$ was chosen to be a real Gaussian packet, waves travel in both positive and negative x directions. Obviously, the harmonic waves with the highest phase velocities, those whose wiggles escape the most quickly from the original position $x=0$, possess the shortest wavelengths. The spreading of the wave packet can be explained in another way. Because the original wave packet at $t=0$ contains spectral components with positive and negative momenta, it spreads in space as time elapses.

The probability interpretation of the wave function now suggests that we use standard concepts of probability calculus, in particular the expectation value and variance. The *expectation value* or *average value of the position* of a particle described by a wave function $\psi(x,t)$ is

$$\langle x\rangle=\int_{-\infty}^{+\infty}x\rho(x,t)\,\mathrm{d}x=\int_{-\infty}^{+\infty}\psi^*(x,t)x\psi(x,t)\,\mathrm{d}x\quad,$$

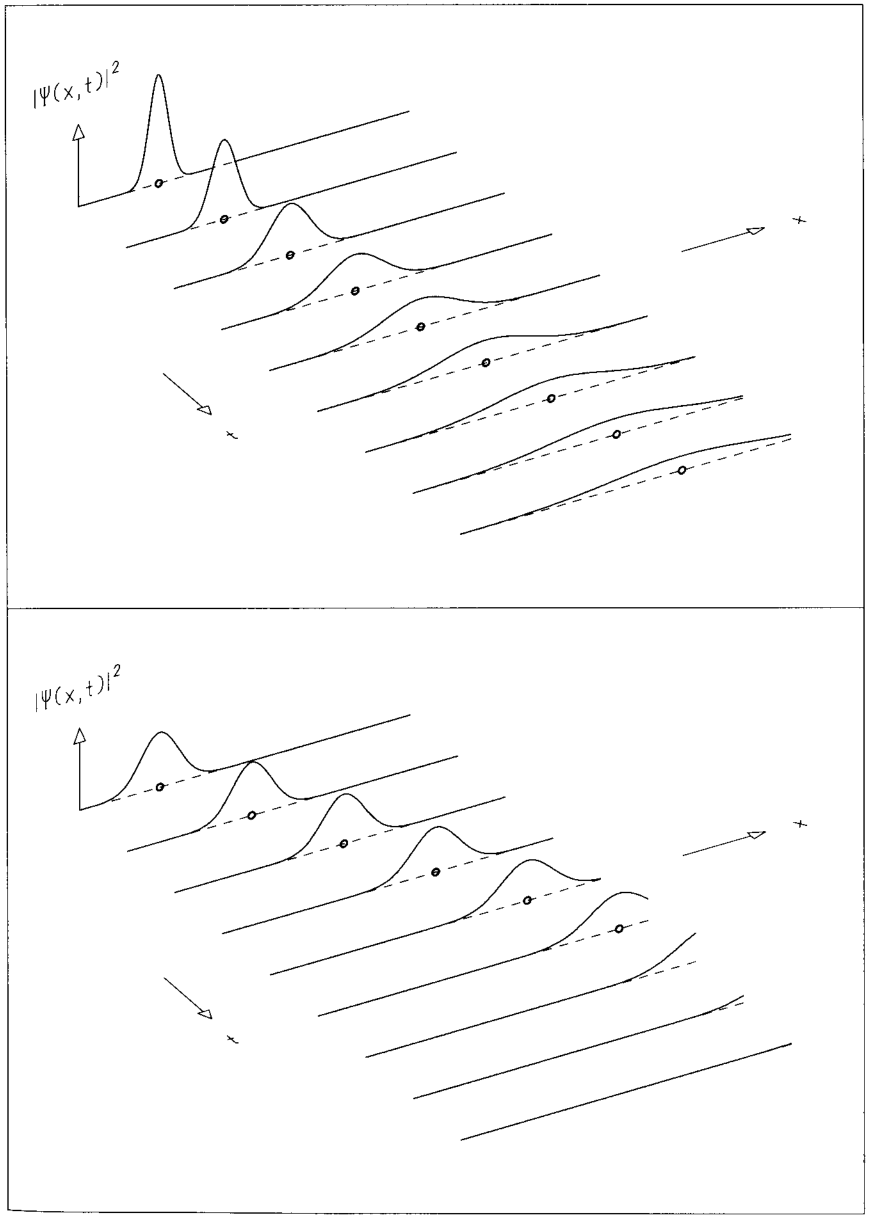

Fig. 3.3. Time developments of the probability densities for the two wave packets of Figure 3.2. The two packets have different group velocities and different widths. Also shown, by the small circles, is the position of a classical particle moving with a velocity equal to the group velocity of the packet.

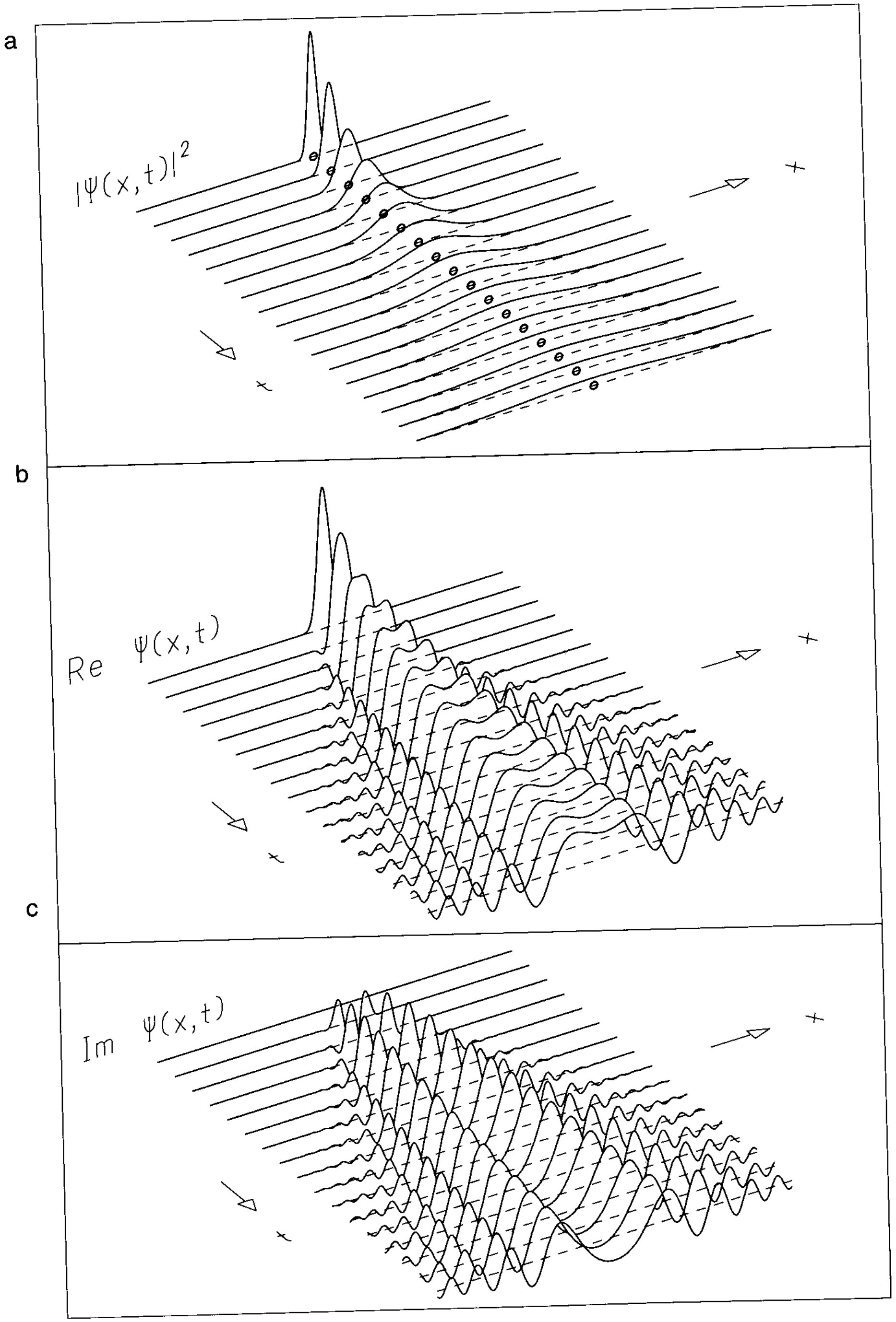

Fig. 3.4. **Time developments of the probability density for a wave packet at rest and of the real part and the imaginary part of its wave function.**

which, in general, remains a function of time. For a Gaussian wave packet the integration indeed yields

$$\langle x\rangle = x_0 + v_0 t \quad , \qquad v_0 = \frac{p_0}{m} \quad ,$$

corresponding to the trajectory of classical unaccelerated motion. We shall therefore interpret the Gaussian wave packet of de Broglie waves as a quantum-mechanical description of the unaccelerated *motion of a particle*, that is, a particle moving with constant velocity. Actually, the Gaussian form of the spectral function $f(k)$ allows the explicit calculation of the wave packet. With this particular spectral function, the wave function $\psi(x,t)$ can be given in closed form.

The *variance of the position* is the expectation value of the square of the difference between the position and its expectation:

$$\begin{aligned}\mathrm{var}(x) &= \left\langle (x - \langle x\rangle)^2\right\rangle \\ &= \int_{-\infty}^{+\infty} \psi^*(x,t)(x-\langle x\rangle)^2\psi(x,t)\,\mathrm{d}x \quad .\end{aligned}$$

Again, for the Gaussian wave packet the integral can be carried out to give

$$\mathrm{var}(x) = \sigma_x^2 = \frac{\hbar^2}{4\sigma_p^2}\left(1 + \frac{4\sigma_p^4}{\hbar^2}\frac{t^2}{m^2}\right) \quad ,$$

which agrees with the formula quoted in Section 3.2.

Calculation of the expectation value of the momentum of a wave packet

$$\psi(x,t) = \int_{-\infty}^{+\infty} f(p)\psi_p(x - x_0, t)\,\mathrm{d}p$$

is carried out with the direct help of the spectral function $f(p)$, that is,

$$\langle p\rangle = \int_{-\infty}^{+\infty} p|f(p)|^2\,\mathrm{d}p \quad .$$

For the spectral function $f(p)$ of the Gaussian wave packet given at the beginning of Section 3.2, we find

$$\langle p\rangle = \int_{-\infty}^{+\infty} p\frac{1}{\sqrt{2\pi}\sigma_p}\exp\left[-\frac{(p-p_0)^2}{2\sigma_p^2}\right]\mathrm{d}p \quad .$$

We replace the factor p by the identity

$$p = p_0 + (p - p_0) \quad .$$

Since the exponential in the integral above is an even function in the variable $p - p_0$, the integral

$$\int_{-\infty}^{+\infty} (p - p_0) \frac{1}{\sqrt{2\pi}\sigma_p} \exp\left[-\frac{(p-p_0)^2}{2\sigma_p^2}\right] \mathrm{d}p = 0$$

vanishes, for the contributions in the intervals $-\infty < p < p_0$ and $p_0 < p < \infty$ cancel. The remaining term is the product of the constant p_0 and the normalization integral,

$$\int_{-\infty}^{+\infty} |f(p)|^2 \,\mathrm{d}p = 1 \quad ,$$

so that we find

$$\langle p \rangle = p_0 \quad .$$

This result is not surprising, for the Gaussian spectral function gives the largest weight to momentum p_0 and decreases symmetrically to the left and right of this value. At the end of Section 3.2, we found $v_0 = p_0/m$ as the group velocity of the wave packet. Putting the two findings together, we have discovered that the momentum expectation value of a free, unaccelerated Gaussian wave packet is the same as the momentum of a free, unaccelerated particle of mass m and velocity v_0 in classical mechanics:

$$\langle p \rangle = p_0 = m v_0 \quad .$$

The expectation value of momentum can also be calculated directly from the wave function $\psi(x,t)$. We have the simple relation

$$\begin{aligned} \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\psi_p(x - x_0, t) &= \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\left\{\frac{1}{(2\pi\hbar)^{1/2}}\exp\left[-\frac{\mathrm{i}}{\hbar}(Et - px)\right]\right\} \\ &= p\psi_p(x - x_0, t) \quad . \end{aligned}$$

This relation translates the momentum variable p into the *momentum operator*

$$p \to \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x} \quad .$$

The momentum operator allows us to calculate the expectation value of momentum from the following formula:

$$\langle p \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\psi(x,t)\,\mathrm{d}x \quad .$$

It is completely analogous to the formula for the expectation value of position given earlier. We point out that the operator appears between the functions $\psi^*(x,t)$ and $\psi(x,t)$, thus acting on the second factor only. To verify this formula, we replace the wave function $\psi(x,t)$ by its representation in terms of the spectral function:

$$\begin{aligned} \langle p \rangle &= \int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\int_{-\infty}^{+\infty} f(p)\psi_p(x - x_0, t)\,\mathrm{d}p\,\mathrm{d}x \\ &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \psi^*(x,t)\psi_p(x - x_0,t)\,\mathrm{d}x\, pf(p)\,\mathrm{d}p \quad . \end{aligned}$$

The inner integral

$$\begin{aligned} &\int_{-\infty}^{+\infty} \psi^*(x,t)\psi_p(x - x_0,t)\,\mathrm{d}x \\ &\quad = \int_{-\infty}^{+\infty} \psi^*(x,t)\frac{1}{(2\pi\hbar)^{1/2}}\exp\left\{-\frac{\mathrm{i}}{\hbar}[Et - p(x - x_0)]\right\}\mathrm{d}x \end{aligned}$$

is by Fourier's theorem the inverse of the representation

$$\begin{aligned} \psi^*(x,t) &= \int_{-\infty}^{+\infty} f^*(p)\psi_p^*(x - x_0,t)\,\mathrm{d}p \\ &= \frac{1}{(2\pi\hbar)^{1/2}}\int_{-\infty}^{+\infty} f^*(p)\exp\left\{\frac{\mathrm{i}}{\hbar}[Et - p(x - x_0)]\right\}\mathrm{d}p \end{aligned}$$

of the complex conjugate of the wave packet $\psi(x,t)$. Thus we have

$$\int_{-\infty}^{+\infty} \psi^*(x,t)\psi_p(x - x_0,t)\,\mathrm{d}x = f^*(p) \quad .$$

Substituting this result for the inner integral of the expression for $\langle p \rangle$, we rediscover the expectation value of momentum in the form

$$\langle p \rangle = \int_{-\infty}^{+\infty} f^*(p)pf(p)\,\mathrm{d}p = \int_{-\infty}^{+\infty} p|f(p)|^2\,\mathrm{d}p \quad .$$

This equation justifies the identification of momentum p with the operator $(\hbar/\mathrm{i})(\partial/\partial x)$ acting on the wave function. The *variance of the momentum* for a wave packet is

$$\mathrm{var}(p) = \langle (p - \langle p \rangle)^2 \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t)\left(\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x} - p_0\right)^2 \psi(x,t)\,\mathrm{d}x \quad .$$

For our Gaussian packet we have

$$\mathrm{var}(p) = \sigma_p^2$$

again independent of time because momentum is conserved.

The square root of the variance of the position,

$$\Delta x = \sqrt{\mathrm{var}(x)} = \sigma_x \quad ,$$

determines the width of the wave packet in the position variable x and therefore is a measure of the *uncertainty* about where the particle is located. By the same token, the corresponding uncertainty about the momentum of the particle is

$$\Delta p = \sqrt{\mathrm{var}(p)} = \sigma_p \quad .$$

For our Gaussian wave packet we found the relation

$$\sigma_x = \frac{\hbar}{2\sigma_p}\left(1 + \frac{4\sigma_p^4}{\hbar^2}\frac{t^2}{m^2}\right)^{1/2} \quad .$$

For time $t = 0$ this relation reads

$$\sigma_x \sigma_p = \frac{\hbar}{2} \quad .$$

For later moments in time, the product becomes even larger so that, in general,

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2} \quad .$$

This relation expresses the fact that the product of uncertainties in position and momentum cannot be smaller than the fundamental Planck's constant h divided by 4π.

We have just stated the *uncertainty principle*, which is valid for wave packets of all forms. It was formulated by Werner Heisenberg in 1927. This relation says, in effect, that a small uncertainty in localization can only be achieved at the expense of a large uncertainty in momentum and vice versa. Figure 3.5 illustrates this principle by comparing the time development of the probability density $\rho(x,t)$ and the square of the spectral function $f^2(p)$. The latter, in fact, is the probability density in momentum. Looking at the spreading of the wave packets with time, we see that the initially narrow wave packet (Figure 3.5, top right) becomes quickly wide in space, whereas the initially wide wave packet (Figure 3.5, bottom right) spreads much more slowly. Actually, this behavior is to be expected. The spatially narrow wave packet requires a wide spectral function in momentum space. Thus it comprises components with a wide range of velocities. They, in turn, cause a quick dispersion of the packet in space compared to the initially wider packet with a narrower spectral function (Figures 3.5, bottom left and bottom right).

At its initial time $t = 0$ the Gaussian wave packet discussed at the beginning of Section 3.2 has the smallest spread in space and momentum because Heisenberg's uncertainty principle is fulfilled in the equality form $\sigma_x \cdot \sigma_p = \hbar/2$. The wave function at $t = 0$ takes the simple form

$$\begin{aligned}\psi(x,0) &= \frac{1}{(2\pi)^{1/4}\sqrt{\sigma_x}} \exp\left[-\frac{(x-x_0)^2}{4\sigma_x^2}\right] \exp\left[\frac{\mathrm{i}}{\hbar} p_0 (x - x_0)\right] \\ &= M(x,0) \exp\left[\mathrm{i}\phi(x,0)\right] \quad .\end{aligned}$$

The bell-shaped amplitude function $M(x,0)$ is centered around the position x_0 with the width σ_x; ϕ is the phase of the wave function at $t = 0$ and has the simple linear dependence

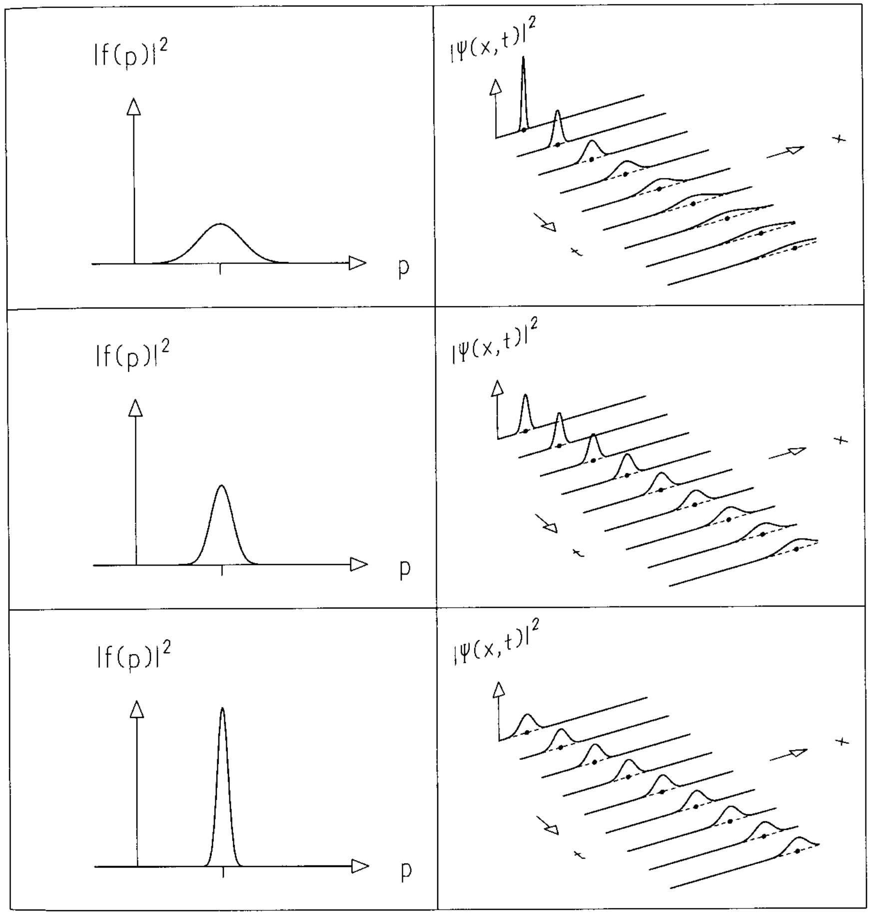

Fig. 3.5. **Heisenberg's uncertainty principle. For three different Gaussian wave packets the square $f^2(p)$ of the spectral function is shown on the left, the time development of the probability density in space on the right. All three packets have the same group velocity but different widths σ_p in momentum. At $t = 0$ the widths σ_x in space and σ_p in momentum fulfill the equality $\sigma_x\sigma_p = \hbar/2$. For later moments in time the wave packets spread in space so that $\sigma_x\sigma_p > \hbar/2$.**

$$\phi(x,0) = \frac{1}{\hbar} p_0 (x - x_0) \quad .$$

This phase ensures that the wave packet at $t = 0$ stands for a particle with an average momentum p_0. We shall use this observation when we have to prepare wave functions for the initial state of a particle with the initial conditions $\langle x \rangle = x_0$, $\langle p \rangle = p_0$ at the initial moment of time $t = t_0$.

3.4 The Schrödinger Equation

Now that we have introduced the wave description of particle mechanics, we look for a *wave equation*, the solutions of which are the de Broglie waves. Starting from the harmonic wave

$$\psi_p(x,t) = \frac{1}{(2\pi\hbar)^{1/2}} \exp\left[-\frac{\mathrm{i}}{\hbar}(Et - px)\right] \quad , \qquad E = \frac{p^2}{2m} \quad ,$$

we compare the two expressions

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi_p(x,t) = E\psi_p(x,t)$$

and

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_p(x,t) = \frac{p^2}{2m}\psi_p(x,t) = E\psi_p(x,t) \quad .$$

Equating the two left-hand sides, we obtain the *Schrödinger equation* for a free particle,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi_p(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_p(x,t) \quad .$$

It was formulated by Erwin Schrödinger in 1926.

Since the solution ψ_p occurs linearly in this equation, an arbitrary linear superposition of solutions, that is, any wave packet, is also a solution of Schrödinger's equation. Thus this Schrödinger equation is the *equation of motion* for any free particle represented by an arbitrary wave packet $\psi(x,t)$:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) \quad .$$

In the spirit of representing physical quantities by differential operators, as we did for momentum, we can now represent kinetic energy T, which is equal to the total energy of the free particle $T = p^2/(2m)$, by

$$T \rightarrow \frac{1}{2m}\left(\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\right)\left(\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\right) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \quad .$$

The equation can be generalized to describe the motion of a particle in a force field represented by a potential energy $V(x)$. This is done by replacing the kinetic energy T with the total energy,

$$E = T + V \rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \quad .$$

With this substitution we obtain the *Schrödinger equation for the motion of a particle in a potential* $V(x)$:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x)\psi(x,t) \quad .$$

We now denote the operator of total energy by the symbol

$$H = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x} + V(x) \quad .$$

In analogy to the Hamilton function of classical mechanics, operator H is called the *Hamilton operator* or *Hamiltonian*. With its help the Schrödinger equation for the motion of a particle under the influence of a potential takes the form

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t) \quad .$$

At this stage we should point out that the Schrödinger equation, generalized to three spatial dimensions and many particles, is the fundamental law of nature for all of nonrelativistic particle physics and chemistry. The rest of this book will be dedicated to the pictorial study of the simple phenomena described by the Schrödinger equation.

3.5 Bivariate Gaussian Probability Density

To facilitate the physics discussion in the next section we now introduce a *Gaussian probability density of two variables* x_1 and x_2 and demonstrate its properties. The bivariate Gaussian probability density is defined by

$$\begin{aligned}\rho(x_1,x_2) &= A\exp\left\{-\frac{1}{2(1-c^2)}\left[\frac{(x_1-\langle x_1\rangle)^2}{\sigma_1^2}\right.\right.\\ &\qquad \left.\left. - 2c\frac{(x_1-\langle x_1\rangle)}{\sigma_1}\frac{(x_2-\langle x_2\rangle)}{\sigma_2} + \frac{(x_2-\langle x_2\rangle)^2}{\sigma_2^2}\right]\right\} \quad .\end{aligned}$$

The normalization constant

$$A = \frac{1}{2\pi\sigma_1\sigma_2\sqrt{1-c^2}}$$

ensures that the probability density is properly normalized:

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho(x_1,x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2 = 1 \quad .$$

The bivariate Gaussian is completely described by five parameters. They are the *expectation values* $\langle x_1\rangle$ and $\langle x_2\rangle$, the *widths* σ_1 and σ_2, and the *correlation coefficient* c. The *marginal distributions* defined by

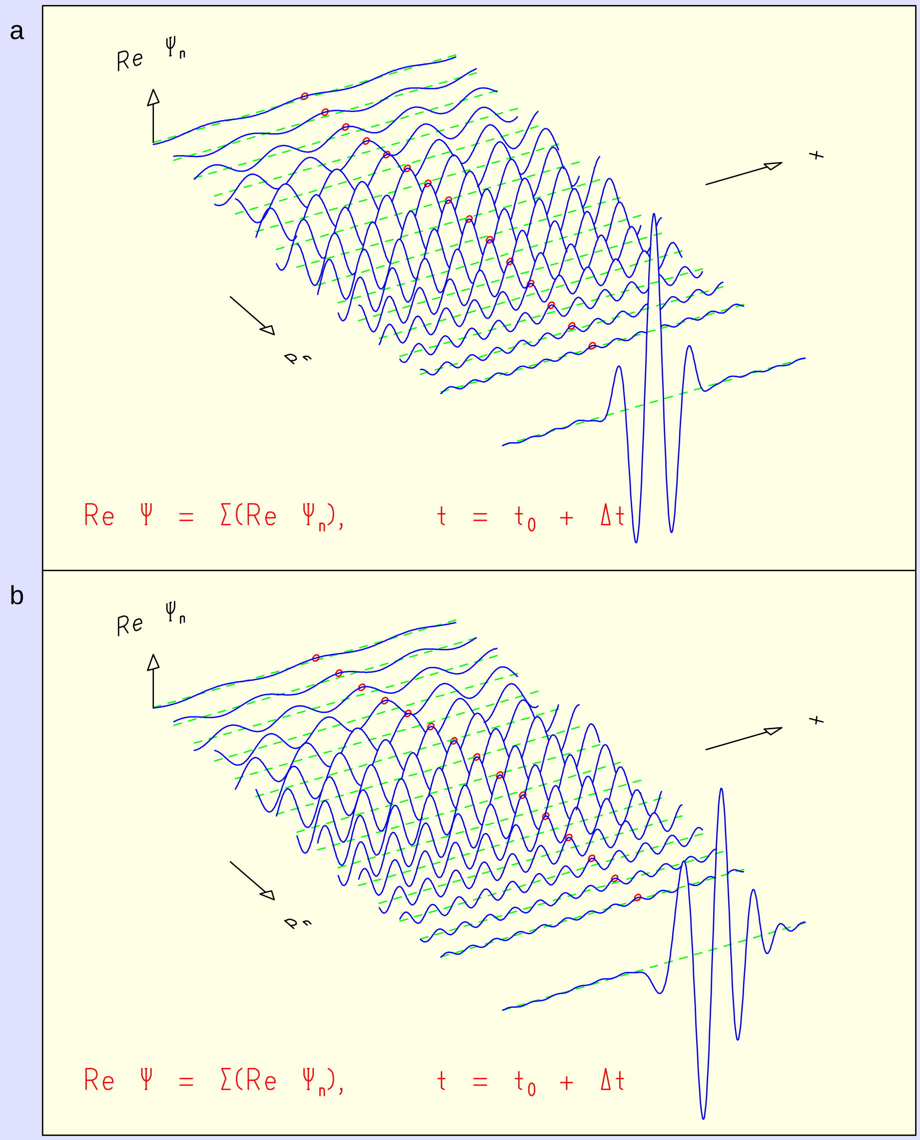

Fig. 3.1. Construction of a wave packet as a sum of harmonic waves ψ_n of different momenta and consequently of different wavelengths. Plotted are the real parts of the wave functions. The terms of different momenta and different amplitudes begin with the one of longest wavelength in the background. In the foreground is the wave packet resulting from the summation. (a) The situation for time $t = t_0$. All partial waves are marked by a circle at point $x = x_0$. (b) The same wave packet and its partial waves at time $t_1 > t_0$. The partial waves have moved different distances $\Delta x_n = v_n(t_1 - t_0)$ because of their different phase velocities v_n, as indicated by the circular marks which have kept their phase with respect to those in part a. Because of the different phase velocities, the wave packet has changed its form and width.

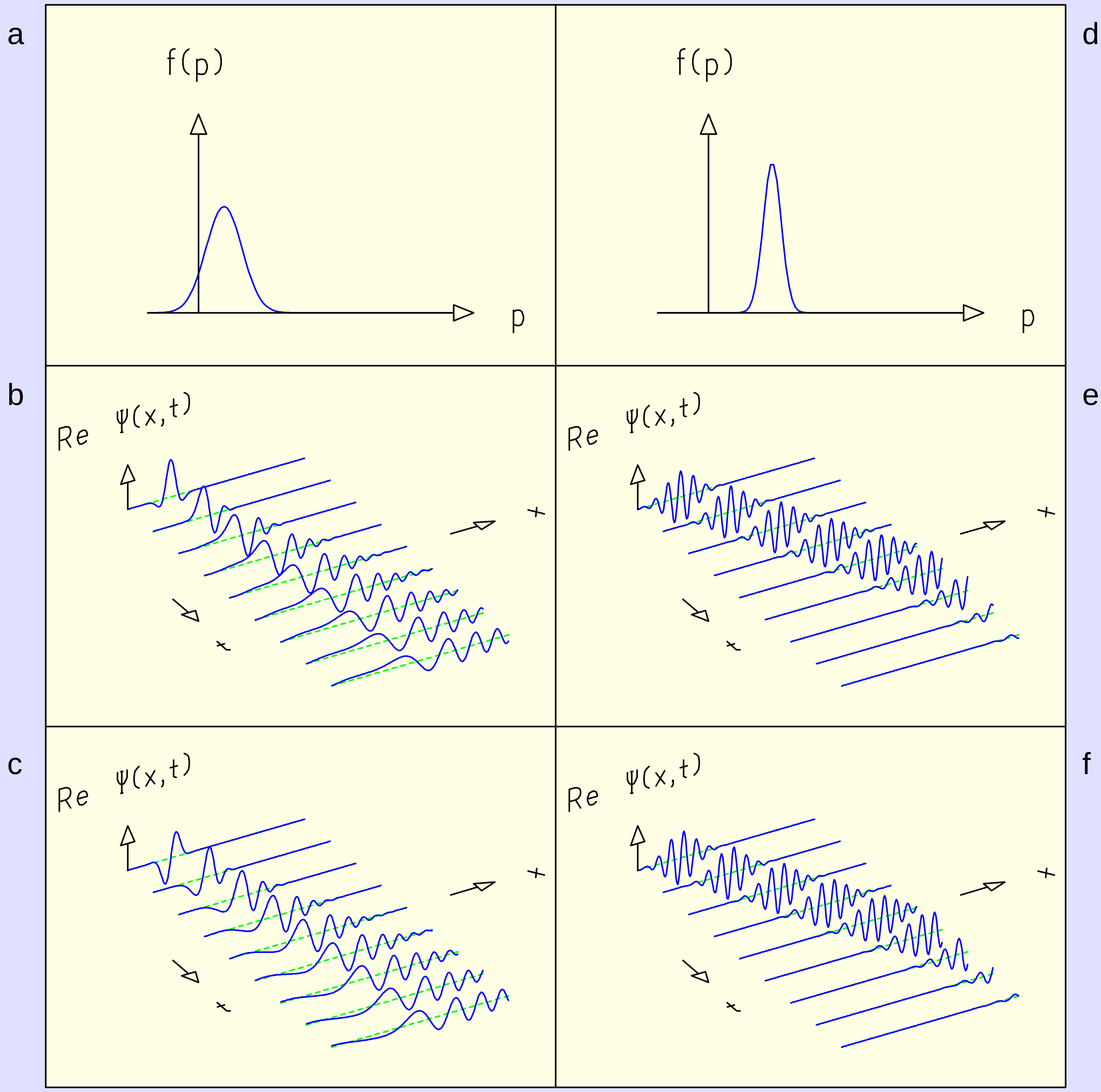

Fig. 3.2. **(a, d) Spectral functions and time developments of (b, e) the real parts and (c, f) the imaginary parts of the wave functions for two different wave packets. The two packets have different group velocities and different widths and spread differently with time.**

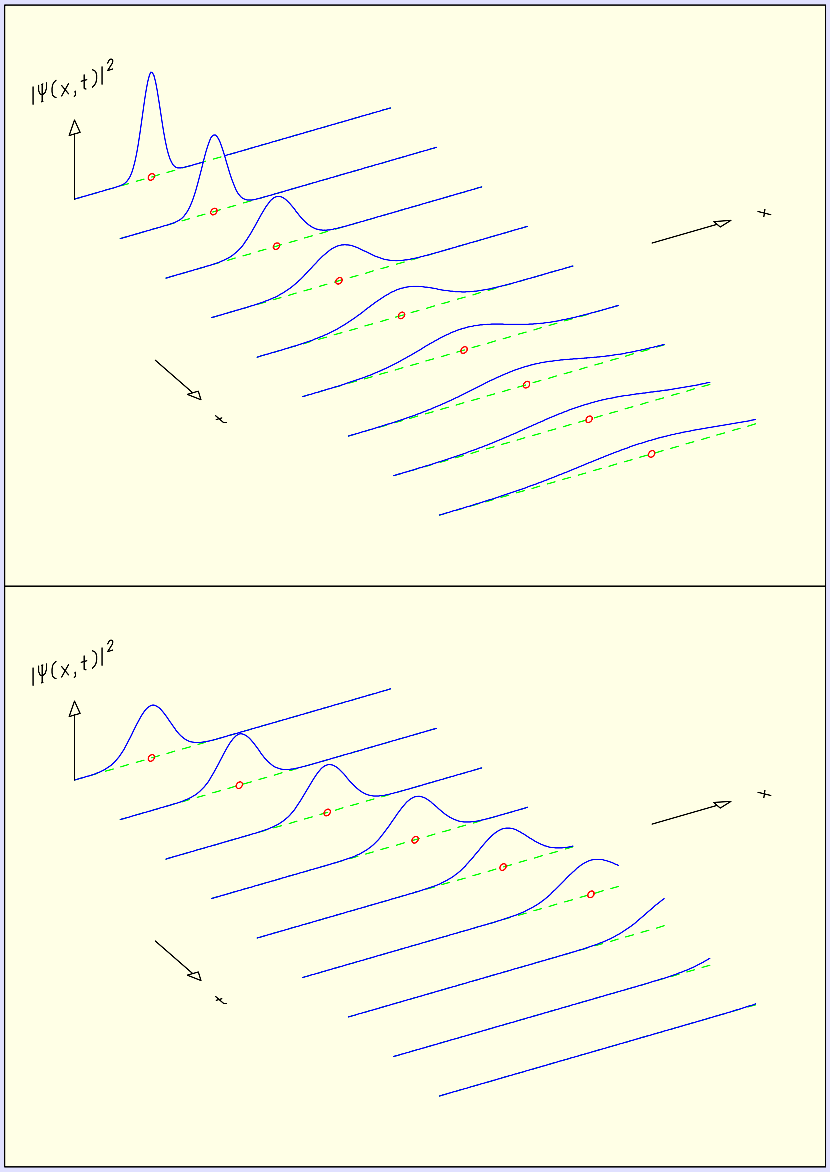

Fig. 3.3. Time developments of the probability densities for the two wave packets of Figure 3.2. The two packets have different group velocities and different widths. Also shown, by the small circles, is the position of a classical particle moving with a velocity equal to the group velocity of the packet.

a

b

c

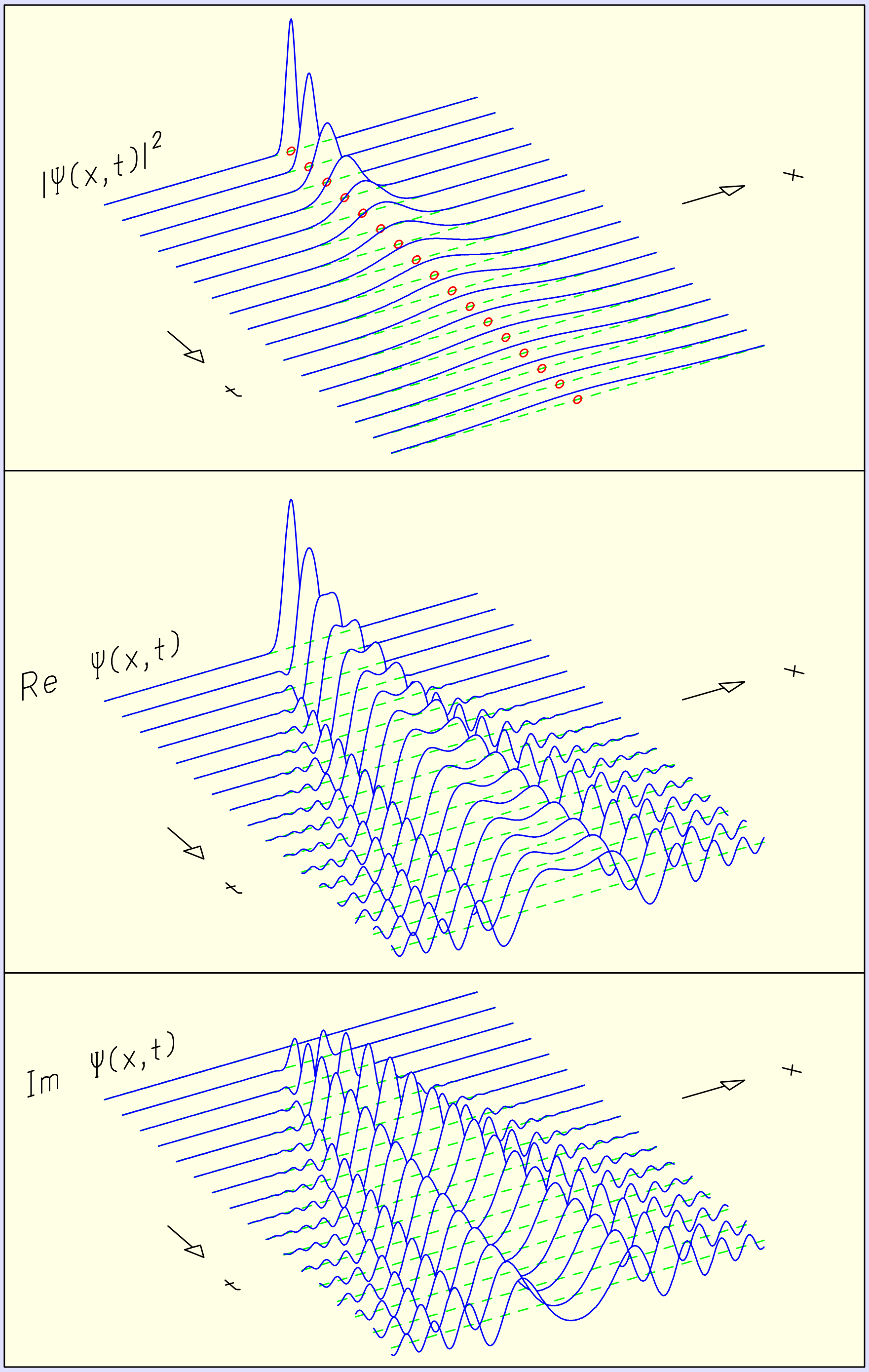

Fig. 3.4. Time developments of the probability density for a wave packet at rest and of the real part and the imaginary part of its wave function.

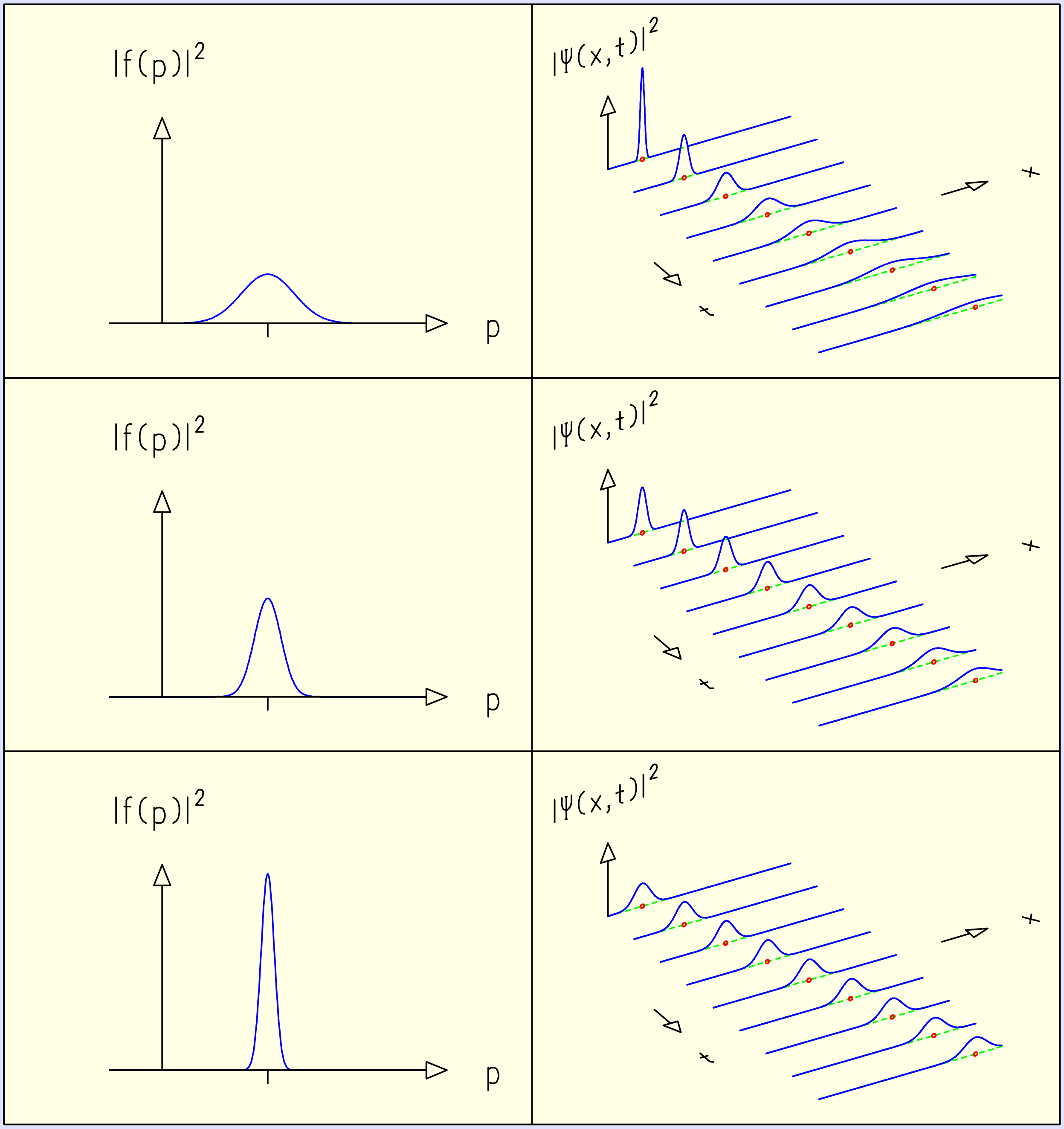

Fig. 3.5. Heisenberg's uncertainty principle. For three different Gaussian wave packets the square $f^2(p)$ of the spectral function is shown on the left, the time development of the probability density in space on the right. All three packets have the same group velocity but different widths σ_p in momentum. At $t = 0$ the widths σ_x in space and σ_p in momentum fulfill the equality $\sigma_x\sigma_p = \hbar/2$. For later moments in time the wave packets spread in space so that $\sigma_x\sigma_p > \hbar/2$.