Chapter 3

The Schrödinger Equation

3.1 Derivation of the Schrödinger Equation

We will consider now the propagation of a wave function $\psi(\vec{r}, t)$ by an infinitesimal time step ϵ. It holds then according to (2.5)

$$\psi(\vec{r}, t + \epsilon) \;=\; \int_\Omega d^3r_0 \, \phi(\vec{r}, t + \epsilon|\vec{r}_0, t) \, \psi(\vec{r}_0, t) \; . \tag{3.1}$$

We will expand the l.h.s. and the r.h.s. of this equation in terms of powers of ϵ and we will demonstrate that the terms of order ϵ require that $\psi(\vec{r}, t)$ satisfies a partial differential equation, namely the Schrödinger equation. For many situations, but by no means all, the Schrödinger equation provides the simpler avenue towards describing quantum systems than the path ingral formulation of Section 2. Notable exceptions are non-stationary systems involving time-dependent linear and quadratic Lagrangians.
The propagator in (3.1) can be expressed through the discretization scheme (2.20, 2.21). In the limit of very small ϵ it is sufficient to employ a single discretization interval in (2.20) to evaluate the propagator. Generalizing (2.20) to $\mathbb{R}^3$ one obtains then for small ϵ

$$\phi(\vec{r}, t + \epsilon|\vec{r}_0, t) \;=\; \left[\frac{m}{2\pi i\hbar\epsilon}\right]^{\frac{3}{2}} \exp\left\{ \frac{i}{\hbar} \left[\frac{m}{2} \frac{(\vec{r} - \vec{r}_0)^2}{\epsilon} \;-\; \epsilon \, U(\vec{r}, t) \right] \right\} \; . \tag{3.2}$$

From this follows

$$\psi(\vec{r}, t + \epsilon) \;=\; \int_\Omega d^3r_0 \, \left[\frac{m}{2\pi i\hbar\epsilon}\right]^{\frac{3}{2}} \exp\left\{ \frac{i}{\hbar} \left[\frac{m}{2} \frac{(\vec{r} - \vec{r}_0)^2}{\epsilon} \;-\; \epsilon \, U(\vec{r}, t) \right] \right\} \psi(\vec{r}_0, t) \; . \tag{3.3}$$

In order to carry out the integration we set $\vec{r}_0 = \vec{r} + \vec{s}$ and use $\vec{s}$ as the new integration variable. We will denote the components of $\vec{s}$ by $(x_1, x_2, x_3)^T$. This yields

$$\begin{aligned} \psi(\vec{r}, t + \epsilon) \;=\; & \textstyle\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \int_{-\infty}^{+\infty} dx_3 \, \left[\frac{m}{2\pi i\hbar\epsilon}\right]^{\frac{3}{2}} \times \\ & \times \underbrace{\exp\left(\frac{i}{\hbar} \frac{m}{2} \frac{x_1^2 + x_2^2 + x_3^2}{\epsilon} \;-\; \epsilon \, U(\vec{r}, t) \right)}_{\text{even in } x_1, x_2, , x_3} \psi(\vec{r} + \vec{s}, t) \; . \end{aligned} \tag{3.4}$$

It is important to note that the integration is **not** over $\vec{r}$, but over $\vec{s} = (x_1, x_2, x_3)^T$, e.g. $U(\vec{r}, t)$ is a constant with respect to this integration. The integration involves only the wave function $\psi(\vec{r}+\vec{s}, t)$ and the kinetic energy term. Since the latter contributes to (3.4) only for small $x_1^2 + x_2^2 + x_3^2$ values we expand

$$\psi(\vec{r}+\vec{s}, t) \;=\; \psi(\vec{r}, t) \;+\; \sum_{j=1}^{3} x_j \frac{\partial}{\partial x_j} \psi(\vec{r}, t) \;+\; \frac{1}{2} \sum_{j,k=1}^{3} x_j x_k \frac{\partial^2}{\partial x_j \partial x_k} \psi(\vec{r}, t) \;+\; \ldots \tag{3.5}$$

assuming that only the leading terms contribute, a supposition which will be examined below. Since the kinetic energy contribution in (3.4) is even in all three coordinates x_1, x_2, x_3, only terms of the expansion (3.5) which are even separately in all three coordinates yield non-vanishing contributions. It is then sufficient to consider the terms

$$\begin{array}{c} \psi(\vec{r}, t) \quad ; \quad \frac{1}{2} \sum_{j=1}^{3} x_j^2 \frac{\partial^2}{\partial x_j^2} \psi(\vec{r}, t) \quad ; \quad \frac{1}{4} \sum_{j,k=1}^{3} x_j^2 x_k^2 \frac{\partial^4}{\partial x_j^2 \partial x_k^2} \psi(\vec{r}, t) \quad ; \\ \frac{1}{12} \sum_{j=1}^{3} x_j^4 \frac{\partial^4}{\partial x_j^4} \psi(\vec{r}, t) \quad ; \ldots \end{array} \tag{3.6}$$

of the expansion of $\psi(\vec{r}+\vec{s}, t)$.
Obviously, we need then to evaluate integrals of the type

$$I_n(a) \;=\; \int_{-\infty}^{+\infty} dx\, x^{2n} \exp\left(i\, a\, x^2\right) \;, \quad n \;=\; 0, 1, 2 \tag{3.7}$$

According to (2.36) holds

$$I_0(a) \;=\; \sqrt{\frac{i\pi}{a}} \tag{3.8}$$

Inspection of (3.7) shows

$$I_{n+1}(a) \;=\; \frac{1}{i} \frac{\partial}{\partial a} I_n(a). \tag{3.9}$$

Starting from (3.8) one can evaluate recursively all integrals $I_n(a)$. It holds

$$I_1(a) \;=\; \frac{i}{2a} \sqrt{\frac{i\pi}{a}} \;; \quad I_2(a) \;=\; -\frac{3}{4a^2} \sqrt{\frac{i\pi}{a}} \;, \ldots \tag{3.10}$$

It is now important to note that in case of integral (3.4) one identifies

$$\frac{1}{a} \;=\; \frac{2\,\epsilon\,\hbar}{m} \;=\; \mathcal{O}(\epsilon) \tag{3.11}$$

and, consequently, the terms collected in (3.6) make contributions of the order

$$\mathcal{O}(\epsilon^{\frac{3}{2}}) \;,\; \mathcal{O}(\epsilon^{\frac{5}{2}}) \;,\; \mathcal{O}(\epsilon^{\frac{7}{2}}) \;,\; \mathcal{O}(\epsilon^{\frac{7}{2}}) \;. \tag{3.12}$$

Here one needs to note that we are actually dealing with a three-fold integral. According to (3.11) holds

$$\left[\frac{m}{2\pi i \hbar \epsilon}\right]^{\frac{3}{2}} \times \left[\frac{i\,\pi}{a}\right]^{\frac{3}{2}} \;=\; 1 \tag{3.13}$$

and one can conclude, using (3.10),

$$\psi(\vec{r}, t+\epsilon) \;=\; \exp\left[-\frac{i\epsilon}{\hbar}\, U(\vec{r},t) \right] \left[\psi(\vec{r},t) \;+\; \frac{1}{4}\, \frac{2i\epsilon\hbar}{m}\, \nabla^2 \psi(\vec{r},t) \;+\; \mathcal{O}(\epsilon^2) \right] . \tag{3.14}$$

This expansion in terms of powers of ϵ suggests that we also expand

$$\psi(\vec{r}, t+\epsilon) \;=\; \psi(\vec{r},t) \;+\; \epsilon \frac{\partial}{\partial t} \psi(\vec{r},t) \;+\; \mathcal{O}(\epsilon^2) \tag{3.15}$$

and

$$\exp\left[-\frac{i\epsilon}{\hbar}\, U(\vec{r},t) \right] \;=\; 1 \;-\; \frac{i\epsilon}{\hbar}\, U(\vec{r},t) \;+\; \mathcal{O}(\epsilon^2) \,. \tag{3.16}$$

Inserting this into (3.14) results in

$$\begin{aligned} \psi(\vec{r},t) \;+\; \epsilon \tfrac{\partial}{\partial t} \psi(\vec{r},t) \;&=\; \psi(\vec{r},t) \;-\; \frac{i\epsilon}{\hbar}\, U(\vec{r},t) \psi(\vec{r},t) \\ &\quad+\; \frac{i\epsilon}{\hbar}\, \frac{\hbar^2}{2m}\, \nabla^2 \psi(\vec{r},t) \;+\; \mathcal{O}(\epsilon^2) \,. \end{aligned} \tag{3.17}$$

Obviously, this equation is trivially satisfied to order $\mathcal{O}(\epsilon^0)$. In order $\mathcal{O}(\epsilon)$ the equation reads

$$i\hbar \frac{\partial}{\partial t}\, \psi(\vec{r},t) \;=\; \left[-\frac{\hbar^2}{2m}\, \nabla^2 \;+\; U(\vec{r},t) \right] \psi(\vec{r},t) \,. \tag{3.18}$$

This is the celebrated *time-dependent Schrödinger equation*. This equation is often written in the form

$$i\hbar \frac{\partial}{\partial t}\, \psi(\vec{r},t) \;=\; \hat{H}\, \psi(\vec{r},t) \tag{3.19}$$

where

$$\hat{H} \;=\; -\frac{\hbar^2}{2m}\, \nabla^2 \;+\; U(\vec{r},t) \,. \tag{3.20}$$

3.2 Boundary Conditions

The time-dependent Schrödinger equation is a partial differential equation, 1st order in time, 2nd order in the spatial variables and linear in the solution $\psi(\vec{r},t)$. The following general remarks can be made about the solution.

Due to its linear character any linear combination of solutions of the time-dependent Schrödinger equation is also a solution.

The 1st order time derivative requires that for any solution a single temporal condition needs to be specified, e.g., $\psi(\vec{r},t_1) \;=\; f(\vec{r})$. Usually, one specifies the so-called initial condition, i.e., a solution is thought for $t \geq t_0$ and the solution is specified at the intial time t_0.

The 2nd order spatial derivatives require that one specifies also properties of the solution on a closed boundary $\partial\Omega$ surrounding the volume Ω in which a solution is to be determined. We will derive briefly the type of boundary conditions encountered. As we will discuss in Chapter 5 below the solutions of the Schrödinger equation are restricted to particular Hilbert spaces $\mathbb{H}$ which are linear vector spaces of functions $f(\vec{r})$ in which a scalar product between two elements $f, g \in \mathbb{H}$ is defined as follows

$$\langle f|g\rangle_\Omega = \int_\Omega d^3r f^*(\vec{r}) g(\vec{r}) \tag{3.21}$$

This leads one to consider the integral

$$\langle f|\, H \,|g\rangle_\Omega = \int_\Omega d^3r f^*(\vec{r})\, \hat{H}\, g(\vec{r}) \tag{3.22}$$

where $\hat{H}$ is defined in (3.20). Interchanging $f^*(\vec{r})$ and $g(\vec{r})$ results in

$$\overline{\langle g|\, H \,|f\rangle_\Omega} = \int_\Omega d^3r\, g(\vec{r})\, \hat{H} f^*(\vec{r})\ . \tag{3.23}$$

Since $\hat{H}$ is a differential operator the expressions (3.22) and (3.23), in principle, differ from each other. The difference between the integrals is

$$\begin{aligned} \langle g|\, H \,|f\rangle_\Omega &= - \overline{\langle g|\, H \,|f\rangle_\Omega} \\ &= \int_\Omega d^3r f^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) g(\vec{r}) \ - \ \int_\Omega d^3r g(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) f^*(\vec{r}) \\ &\quad + \int_\Omega d^3r f^*(\vec{r})\, U(\vec{r},t)\, g(\vec{r}) \ - \ \int_\Omega d^3r g(\vec{r})\, U(\vec{r},t), f^*(\vec{r}) \\ &= -\frac{\hbar^2}{2m} \int_\Omega d^3r f^*(\vec{r}) \left(\nabla^2 \right) g(\vec{r}) \ - \ \int_\Omega d^3r g(\vec{r}) \left(\nabla^2 \right) f^*(\vec{r}) \end{aligned} \tag{3.24}$$

Using Green's theorem[1]

$$\begin{aligned} &\int_\Omega d^3r \left(f^*(\vec{r})\, \nabla^2 g(\vec{r}) \ - \ g(\vec{r})\, \nabla^2 f^*(\vec{r}) \right) \\ &= \int_{\partial\Omega} d\vec{a} \cdot \left(f^*(\vec{r}) \nabla g(\vec{r}) \ - \ g(\vec{r}) \nabla f^*(\vec{r}) \right) \end{aligned} \tag{3.25}$$

one obtains the identity

$$\langle f|\, \hat{H} \,|g\rangle_\Omega = \overline{\langle g|\, \hat{H} \,|f\rangle_\Omega} + \int_{\partial\Omega} d\vec{a} \cdot \vec{P}(f^*, g|\vec{r}) \tag{3.26}$$

where $\int_{\partial\Omega} d\vec{a} \cdot \vec{A}(\vec{r})$ denotes an integral over the surface $\partial\Omega$ of the volume Ω, the surface elements $d\vec{a}$ pointing out of the surface in a direction normal to the surface and the vector–valued function $\vec{A}(\vec{r})$ is taken at points $\vec{r} \in \partial\Omega$. In (3.26) the vector–valued function $\vec{P}(f^*, g|\vec{r})$ is called the *concomitant* of $\hat{H}$ and is

$$\vec{P}(f^*, g|\vec{r}) = -\frac{\hbar^2}{2m} \left(f^*(\vec{r})\, \nabla g(\vec{r}) \ - \ g(\vec{r})\, \nabla f^*(\vec{r}) \right) \tag{3.27}$$

We will postulate below that $\hat{H}$ is an operator in $\mathbb{H}$ which represents energy. Since energy is a real quantity one needs to require that the eigenvalues of the operator $\hat{H}$ are real and, hence, that $\hat{H}$ is hermitian[2]. The hermitian property, however, implies

$$\langle f|\, \hat{H} \,|g\rangle_\Omega = \overline{\langle g|\, \hat{H} \,|f\rangle_\Omega} \tag{3.28}$$

[1] See, for example, *Calssical Electrodynamics, 2nd Ed.*, J. D. Jackson, (John Wiley, New York, 1975), Chapter 1.

[2] The reader is advised to consult a reference text on 'Linear Algebra' to follow this argument.

and, therefore, we can only allow functions which make the differential $d\vec{a} \cdot \vec{P}(f^*, g|\vec{r})$ vanish on $\partial\Omega$. It must hold then for all $f \in \mathbb{H}$

$$f(\vec{r}) \;=\; 0 \quad \forall \vec{r},\, \vec{r} \in \partial\Omega \tag{3.29}$$

or

$$d\vec{a} \cdot \nabla f(\vec{r}) \;=\; 0 \quad \forall \vec{r},\, \vec{r} \in \partial\Omega \tag{3.30}$$

Note that these boundary conditions are linear in f, i.e., if f and g satisfy these conditions than also does any linear combination $\alpha f + \beta g$. Often the closed surface of a volume $\partial\Omega$ is the union of disconnected surfaces[3] $\partial\Omega_j$, i.e., $\partial\Omega = \partial\Omega_1 \cap \partial\Omega_2 \cap \partial\Omega_3 \cap \ldots$ In this case one can postulate both conditions (3.29, 3.30) each condition holding on an entire surface $\partial\Omega_j$. However, to avoid discontinuities in $\psi(\vec{r}, t)$ on a single connected surface $\partial\Omega_j$ only either one of the conditions (3.29, 3.30) can be postulated.
A most common boundary condition is encountered for the volume $\Omega = \vec{R}^3$ in which case one postulates

$$\lim_{|\vec{r}| \to \infty} f(\vec{r}) \;=\; 0 \quad \text{“natural boundary condition”} \,. \tag{3.31}$$

In fact, in this case also all derivatives of $f(\vec{r})$ vanish at infinity. The latter property stems from the fact that the boundary condition (3.31) usually arises when a particle existing in a bound state is described. In this case one can expect that the particle density is localized in the area where the energy of the particle exceeds the potential eenrgy, and that the density decays rapidly when one moves away from that area. Since the total probability of finding the particle anywhere in space is

$$\int d^3r |f(\vec{r})|^2 \;=\; 1 \tag{3.32}$$

the wave function must decay for $|\vec{r}| \to \infty$ rapidly enough to be *square integrable*, i.e., obey (3.32), e.g., like $\exp(-\kappa r)$, $\kappa > 0$ or like $r^{-\alpha}$, $\alpha > 2$. In either case does $f(\vec{r})$ and all of its derivatives vanish asymptotically.

3.3 Particle Flux and Schrödinger Equation

The solution of the Schrödinger equation is the wave function $\psi(\vec{r}, t)$ which describes the state of a particle moving in the potential $U(\vec{r}, t)$. The observable directly linked to the wave function is the probability to find the particle at position $\vec{r}$ at time t, namely, $|\psi(\vec{r}, t)|^2$. The probability to observe the particle anywhere in the subvolume $\omega \subset \Omega$ is

$$p(\omega, t) \;=\; \int_\omega d^3r \, |\psi(\vec{r}, t)|^2 \,. \tag{3.33}$$

The time derivative of $p(\omega, t)$ is

$$\partial_t p(\omega, t) \;=\; \int_\omega d^3r \; [\, \psi^*(\vec{r}, t) \partial_t \psi(\vec{r}, t) \;+\; \psi(\vec{r}, t) \partial_t \psi^*(\vec{r}, t) \,] \;. \tag{3.34}$$

[3]An example is a volume between two concentric spheres, in which case $\partial\Omega_1$ is the inner sphere and $\partial\Omega_2$ is the outer sphere.

Using (3.19) and its conjugate complex[4]

$$- i\hbar \frac{\partial}{\partial t} \psi^*(\vec{r}, t) \;=\; \hat{H}\, \psi^*(\vec{r}, t) \tag{3.35}$$

yields

$$i\hbar\partial_t p(\omega, t) \;=\; \int_\omega d^3r \left[\psi^*(\vec{r}, t)\, \hat{H}\, \psi(\vec{r}, t) \;-\; \psi(\vec{r}, t)\, \hat{H}\, \psi^*(\vec{r}, t) \right] . \tag{3.36}$$

According to (3.26, 3.27) this can be written

$$i\hbar\partial_t p(\omega, t) \;=\; \int_{\partial\omega} d\vec{a} \cdot \vec{P}(\psi^*(\vec{r}, t), \psi(\vec{r}, t)\vec{r}, t) \; . \tag{3.37}$$

If one applies this identity to $\omega \,=\, \Omega$ one obtains according to (3.29, 3.30) $\partial_t p(\Omega, t) \,=\, 0$. Accordingly the probability to observe the particle anywhere in the total volume Ω is constant. A natural choice for this constant is 1. One can multiply the solution of (3.18) by any complex number and accordingly one can define $\psi(\vec{r}, t)$ such that

$$\int_\Omega d^3r |\psi(\vec{r}, t)|^2 \;=\; 1 \tag{3.38}$$

holds. One refers to such solution as *normalized*. We will assume in the remainder of this Section that the solutions discussed are normalized. Note that for a normalized wave function the quantity

$$\rho(\vec{r}, t) \;=\; |\psi(\vec{r}, t)|^2 \tag{3.39}$$

is a probability density with units 1/volume.
The surface integral (3.37) can be expressed through a volume integral according to

$$\int_{\partial\omega} d\vec{a} \cdot \vec{A}(\vec{r}) \;=\; \int_\omega d^3r\, \nabla \cdot \vec{A}(\vec{r}) \tag{3.40}$$

One can rewrite then (3.37)

$$\int_\omega d^3r \left(\partial_t \rho(\vec{r}, t) \;+\; \nabla \cdot \vec{j}(\vec{r}, t) \right) \;=\; 0 \tag{3.41}$$

where

$$\vec{j}(\vec{r}, t) \;=\; \vec{P}(\psi^*, \psi | \vec{r}, t) \; . \tag{3.42}$$

Using (3.27) one can express this

$$\vec{j}(\vec{r}, t) \;=\; \frac{\hbar}{2mi} \left[\psi(\vec{r}, t)\, \nabla\psi^*(\vec{r}, t) \;-\; \psi^*(\vec{r}, t)\, \nabla\psi(\vec{r}, t) \right] . \tag{3.43}$$

Since (3.41) holds for any volume $\omega \subset \Omega$ one can conclude

$$\partial_t \rho(\vec{r}, t) \;+\; \nabla \cdot \vec{j}(\vec{r}, t) \;=\; 0 \; . \tag{3.44}$$

[4]Note that the Hamiltonian $\hat{H}$ involves only real terms.

The interpretation of $\vec{j}(\vec{r},t)$ is that of density flux. This follows directly from an inspection of Eq. (3.41) written in the form

$$\partial_t \int_\omega d^3r\, \rho(\vec{r},t) \;=\; - \int_{\partial\omega} d\vec{a} \cdot \vec{j}(\vec{r},t)\;. \tag{3.45}$$

Obviously, $\vec{j}(\vec{r},t)$ gives rise to a descrease of the total probability in volume ω due to the disappearence of probability density at the surface $\partial\omega$. Note that $\vec{j}(\vec{r},t)$ points in the direction *to the outside* of volume ω.

It is of interest to note from (3.43) that any real wave function $\psi(\vec{r},t)$ has vanishing flux anywhere. One often encounters wave functions of the type

$$\phi(\vec{r}) \;=\; f(\vec{r})\, e^{i\,\vec{k}\cdot\vec{r}} \quad , \qquad \text{for } f(\vec{r}) \in \mathbb{R}. \tag{3.46}$$

The corresponding flux is

$$\vec{j}(\vec{r}) \;=\; \frac{\hbar\vec{k}}{m}\, f^2(\vec{r})\;, \tag{3.47}$$

i.e., arises solely from the complex factor $\exp(i\,\vec{k}\cdot\vec{r})$. Such case arose in Sect. 2 for a free particle [c.f. (2.48, 2.71)], and for particles moving in a linear [c.f. (2.105, 2.125)] and in a quadratic [c.f. (2.148, 2.167)] potential. In Sect. 2 we had demonstrated that a factor $\exp(ip_o x_o/\hbar)$ induces a motion of 1-dimensional wave packets such that p_o/m corresponds to the initial velocity. This finding is consistent with the present evaluation of the particle flux: a factor $\exp(ip_o x_o/\hbar)$ gives rise to a flux p_o/m, i.e., equal to the velocity of the particle. The generalization to three dimenisons implies then that the factor $\exp(i\,\vec{k}\cdot\vec{r})$ corresponds to an intial velocit $\hbar\vec{k}/m$ and a flux of the same magnitude.

3.4 Solution of the Free Particle Schrödinger Equation

We want to consider now solutions of the Schrödinger equation (3.18) in $\Omega_\infty \;=\; \mathbb{R}^{\not\models}$ in the case $U(\vec{r},t) \;=\; 0$

$$i\hbar\frac{\partial}{\partial t}\,\psi(\vec{r},t) \;=\; -\frac{\hbar^2}{2m}\,\nabla^2\,\psi(\vec{r},t) \tag{3.48}$$

which describes the motion of free particles. One can readily show by insertion into (3.48) that the general solution is of the form

$$\psi(\vec{r},t) \;=\; [2\pi]^{-\frac{3}{2}} \int_{\Omega_\infty} d^3k\;\tilde{\phi}(\vec{k})\exp\Big(i(\vec{k}\cdot\vec{r} \,-\, \omega t)\Big) \tag{3.49}$$

where the dispersion relationship holds

$$\omega \;=\; \frac{\hbar k^2}{2m}\;. \tag{3.50}$$

Obviously, the initial condition at $\psi(\vec{r},t_0)$ determines $\tilde{\phi}(\vec{k})$. Equation (3.49) reads at $t \;=\; t_0$

$$\psi(\vec{r},t_0) \;=\; [2\pi]^{-\frac{3}{2}} \int_{\Omega_\infty} d^3k\;\tilde{\phi}(\vec{k})\exp\Big(i(\vec{k}\cdot\vec{r} - \omega t_0)\Big)\;. \tag{3.51}$$

The inverse Fourier transform yields

$$\tilde{\phi}(\vec{k}) \;=\; [2\pi]^{-\frac{3}{2}} \int_{\Omega_\infty} d^3r_0 \exp(-i\vec{k}\cdot\vec{r}_0)\,\psi(\vec{r}_0, t_0)\;. \tag{3.52}$$

We have not specified the spatial boundary condition in case of (3.49). The solution as stated is defined in the infinte space $\Omega_\infty = \mathbb{R}^{\not\Vdash}$. If one chooses the initial state $f(\vec{r})$ defined in (3.51) to be square integrable it follows according to the properties of the Fourier–transform that $\psi(\vec{r}, t)$ as given by (3.49) is square integrable at all subsequent times and, hence, that the "natural boundary condition" (3.31) applies. The ensuing solutions are called wave packets.

Comparision with Path Integral Formulation

One can write solution (3.49, 3.51, 3.52) above

$$\psi(\vec{r}, t) \;=\; \int_{\Omega_\infty} d^3r_0\, \phi(\vec{r}, t|\vec{r}_0, t_0)\,\psi(\vec{r}_0, t_0) \tag{3.53}$$

where

$$\phi(\vec{r}, t|\vec{r}_0, t_0) \;=\; \left[\frac{1}{2\pi}\right]^3 \int_{\Omega_\infty} d^3k \,\exp\left(i\vec{k}\cdot(\vec{r} - \vec{r}_0) \;-\; \frac{i}{\hbar}\,\frac{\hbar^2 k^2}{2m}\,(t - t_0) \right)\;. \tag{3.54}$$

This expression obviously has the same form as postulated in the path integral formulation of Quantum Mechanics introduced above, i.e., in (2.5). We have identified then with (3.54) an alternative representation of the propagator (2.47). In fact, evaluating the integral in (3.54) yields (2.47). To show this one needs to note

$$\begin{aligned} &\frac{1}{2\pi}\int_{-\infty}^{+\infty} dk_1 \,\exp\left(i\vec{k}_1(x - x_0) \;-\; \frac{i}{\hbar}\,\frac{\hbar^2 k_1^2}{2m}\,(t - t_0) \right) \\ &= \left[\frac{m}{2\pi i\hbar(t-t_0)}\right]^{\frac{1}{2}} \exp\left[\frac{im}{2\hbar}\,\frac{(x-x_0)^2}{t-t_0}\right]\;. \end{aligned} \tag{3.55}$$

This follows from completion of the square

$$\begin{aligned} &i\vec{k}_1(x - x_0) \;-\; \frac{i}{\hbar}\,\frac{\hbar^2 k_1^2}{2m}\,(t - t_0) \\ &= -i\,\frac{\hbar(t-t_o)}{2m}\left[k_1 \;-\; \frac{m}{\hbar}\,\frac{x-x_o}{t-t_o}\right]^2 \;+\; \frac{i}{\hbar}\,\frac{m}{2}\,\frac{(x-x_o)^2}{t-t_o} \end{aligned} \tag{3.56}$$

and using (2.247).

Below we will generalize the propagator (3.54) to the case of non-vanishing potentials $U(\vec{r})$, i.e., derive an expression similar to (3.54) valid for this case. The general form for this propagator involves an expansion in terms of a complete set of eigenfunctions as in (3.114) and (4.70) derived below for a particle in a box and the harmonic oscillator, respectively. In case of the harmonoc oscillator the expansion can be stated in a closed form given in (4.81)

Free Particle at Rest

We want to apply solution (3.49, 3.52) to the case that the initial state of a 1-dimensional free particle $\psi(x_0, t)$ is given by (**??**). The 1-dimensional version of (3.53, 3.54) is

$$\psi(x,t) \ = \ \int_{-\infty}^{+\infty} dx_0 \, \phi(x,t|x_0,t_0) \, \psi(x_0,t) \tag{3.57}$$

where

$$\phi(x,t|x_0,t_0) \ = \ \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk \, \exp\left(ik\,(x \ - \ x_0) \ - \frac{i}{\hbar}\,\frac{\hbar^2 k^2}{2m}\,(t \ - \ t_0) \right) \ . \tag{3.58}$$

Integration over x_0 leads to the integral

$$\int_{-\infty}^{+\infty} dx_0 \exp\left(-ikx_0 \ + \ \frac{i}{\hbar}\,p_o x_0 \ - \ \frac{x_0^2}{2\delta^2} \right) \ = \ \sqrt{2\pi\delta^2}\,\exp\left(-\frac{(k - \frac{p_o}{\hbar})^2\delta^2}{2} \right) \tag{3.59}$$

which is solved through completion of the square in the exponent [c.f. (3.55, (3.56)]. The remaining integration over k leads to the integral

$$\int_{-\infty}^{+\infty} dk \, \exp\left[ikx \ - \ \tfrac{1}{2}\,(k - \tfrac{p_o}{\hbar})^2\,\delta^2 \ - \ i\,\tfrac{\hbar k^2}{m}(t - t_0) \right] \\ = ???? \tag{3.60}$$

Combining (3.57–3.60) yields with $t_0 \ = \ 0$

$$\psi(x,t) \quad = \quad \left[\frac{1 \ - \ i\frac{\hbar t}{m\delta^2}}{1 \ + \ i\frac{\hbar t}{m\delta^2}} \right]^{\frac{1}{4}} \left[\frac{1}{\pi\delta^2\,(1 \ + \ \frac{\hbar^2 t^2}{m^2\delta^4})} \right]^{\frac{1}{4}} \times \tag{3.61}$$
$$\times \ \exp\left[-\frac{(x \ - \ \frac{p_o}{m}\,t)^2}{2\delta^2(1 \ + \ \frac{\hbar^2 t^2}{m^2\delta^4})}(1 \ - \ i\frac{\hbar t}{m\delta^2}) \ + \ i\frac{p_o}{\hbar}x \ - \ \frac{i}{\hbar}\frac{p_o^2}{2m}t \right] \ .$$

a result which is identical to the expression (**??**) obtained by means of the path integral propagator (2.46). We have demonstrated then in this case that the Schrödinger formulation of Quantum Mechanics is equivalent to the Feynman path integral formulation.

Stationary States

We consider now solutions of the time-dependent Schrödinger equation (3.19, 3.20) which are of the form

$$\psi(\vec{r},t) \ = \ f(t)\,\phi(\vec{r}) \ . \tag{3.62}$$

We will restrict the space of allowed solutions to a volume Ω such that the functions also make the concomitant (3.27) vanish on the surface $\partial\Omega$ of Ω, i.e., the functions obey boundary conditions of the type (3.29, 3.30). Accordingly, the boundary conditions are

$$\phi(\vec{r}) \ = \ 0 \quad \forall \vec{r}, \, \vec{r} \in \partial\Omega \tag{3.63}$$

or

$$d\vec{a} \cdot \nabla\phi(\vec{r}) \ = \ 0 \quad \forall \vec{r}, \, \vec{r} \in \partial\Omega \tag{3.64}$$

and affect only the spatial wave function $\phi(\vec{r})$. As pointed out above, a common case is $\Omega = \Omega_\infty$ and the 'natural boundary condition' (3.31). We will demonstrate that solutions of the type (3.62) do exist and we will characterize the two factors of the solution $f(t)$ and $\phi(\vec{r})$. We may note in passing that solutions of the type (3.62) which consist of two factors, one factor depending only on the time variable and the other only on the space variables are called *separable in space and time.* It is important to realize that the separable solutions (3.62) are special solutions of the time-dependent Schrödinger equation, by no means all solutions are of this type. In fact, the solutions (3.62) have the particular property that the associated probability distributions are independent of time. We want to demonstrate this property now. It follows from the observation that for the solution space considered (3.27) holds and, hence, according to (3.42) the flux $\vec{j}(\vec{r},t)$ vanishes on the surface of $\partial\Omega$. It follows then from (3.45) that the total probability

$$\int_\Omega d^3r\, \rho(\vec{r},t) \;=\; \int_\Omega d^3r\, |\psi(\vec{r},t)|^2 \;=\; |f(t)|^2 \int_\Omega d^3r\, |\phi(\vec{r})|^2 \tag{3.65}$$

is constant. This can hold only if $|f(t)|$ is time-independent, i.e., if

$$f(t) \;=\; e^{i\alpha},\ \alpha \in \mathbb{R}\ . \tag{3.66}$$

One can conclude that the probability density for the state (3.62) is

$$|\psi(\vec{r},t)|^2 \;=\; |\phi(\vec{r})|^2\ , \tag{3.67}$$

i.e., is time-independent. One calls such states *stationary states.*
In order to further characterize the solution (3.62) we insert it into (3.19). This yields an expression

$$g_1(t)\, h_1(\vec{r}) \;=\; g_2(t)\, h_2(\vec{r}) \tag{3.68}$$

where $g_1(t) = i\hbar\partial_t f(t)$, $g_2(t) = f(t)$, $h_1(\vec{r}) = \phi(\vec{r})$, and $h_2(\vec{r}) = \hat{H}\,\phi(\vec{r})$. The identity (3.68) can hold only for all t and all $\vec{r}$ if $g_1(t) = E\, g_2(t)$ and $E\, h_1(\vec{r}) = h_2(\vec{r})$ for some $E \in \mathbb{C}$. We must postulate therefore

$$\begin{aligned} \partial_t\, f(t) \quad &= \; E\, f(t) \\ \hat{H}\,\phi(\vec{r}) \quad &= \; E\,\phi(\vec{r})\ . \end{aligned} \tag{3.69}$$

If these two equations can be solved simultaneously a solution of the type (3.62) exists.
It turns out that a solution for $f(t)$ can be found for any E, namely

$$f(t) \;=\; f(0)\exp\left(-\frac{i}{\hbar}\,E\,t\right)\ . \tag{3.70}$$

The task of finding solutions $\phi(\vec{r})$ which solve (3.69) is called an eigenvalue problem. We will encounter many such problems in the subsequent Sections. At this point we state without proof that, in general, for the eigenvalue problems in the confined function space, i.e., for functions required to obey boundary conditions (3.63, 3.64), solutions exist only for a set of discrete E values, the eigenvalues of the operator $\hat{H}$. At this point we will accept that solutions $\phi(\vec{r})$ of the type (3.69) exist, however, often only for a discrete set of values E_n, $n = 1, 2, \ldots$ We denote the corresponding solution by $\phi_E(\vec{r})$. We have then shown that

$$\psi(\vec{r},t) \;=\; f(0)\exp\left(-\frac{i}{\hbar}\,E\right)\phi_E(\vec{r}) \quad \text{where} \quad \hat{H}\,\phi_E(\vec{r}) \;=\; E\,\phi_E(\vec{r})\ . \tag{3.71}$$

is a solution of the time-dependent Schrödinger equation (3.19, 3.20).
According to (3.66) E must be real. We want to prove now that the eigenvalues E which arise in the eigenvalue problem (3.71) are, in fact, real. We start our proof using the property (3.28) for the special case that f and g in (3.28) both represent the state $\phi_E(\vec{r})$, i.e.,

$$\int_\Omega d^3r\, \phi_E^*(\vec{r})\, \hat{H}\, \phi_E(\vec{r}) \;=\; \overline{\int_\Omega d^3r\, \phi_E(\vec{r})\, \hat{H}\, \phi_E^*(\vec{r})}\;. \tag{3.72}$$

According to (3.71) this yields

$$E \int_\Omega d^3r\, \phi_E^*(\vec{r})\, \phi_E(\vec{r}) \;=\; E^* \overline{\int_\Omega d^3r\, \phi_E(\vec{r})\, \phi_E^*(\vec{r})}\;. \tag{3.73}$$

from which follows $E = E^*$ and, hence, $E \in \mathbb{R}$. We will show in Section 5 that E can be interprerted as the total energy of a stationary state.

Stationary State of a Free Particle

We consider now the stationary state of a free particle described by

$$\psi(\vec{r},t) \;=\; \exp\left(-\frac{i}{\hbar}\,E\,t\right)\,\phi_E(\vec{r}) \quad , \quad -\frac{\hbar^2}{2m}\,\nabla^2\,\phi(\vec{r}) \;=\; E\,\phi(\vec{r})\;. \tag{3.74}$$

The classical free particle with constant energy $E > 0$ moves without bounds in the space Ω_∞. As a result we cannot postulate in the present case that wave functions are localized and normalizable. We will wave this assumption as we always need to do later whenever we deal with unbound particles, e.g. particles scattered of a potential.
The solution $\phi_E(\vec{r})$ corresponding to the eigenvalue problem posed by (3.74) is actually best labelled by an index $\vec{k}$, $\vec{k} \in \mathbb{R}^{\not\Bbbk}$

$$\phi_{\vec{k}}(\vec{r}) \;=\; N\exp\left(i\,\vec{k}\cdot\vec{r}\right)\;, \quad \frac{\hbar^2 k^2}{2m} \;=\; E\;. \tag{3.75}$$

One can ascertain this statement by inserting the expression for $\phi_{\vec{k}}(\vec{r})$ into the eigenvalue problem posed in (3.74) using $\nabla\exp\left(i\,\vec{k}\cdot\vec{r}\right) = i\vec{k}\exp\left(i\,\vec{k}\cdot\vec{r}\right)$. The resulting total energy values E are positive, a property which is to be expected since the energy is purely kinetic energy which, of course, should be positive.
The corresponding stationary solution

$$\psi(\vec{r},t) \;=\; \exp\left(-\frac{i}{\hbar}\,\frac{\hbar^2k^2}{2m}\,t\right)\,\exp\left(i\,\vec{k}\cdot\vec{r}\right) \tag{3.76}$$

has kinetic energy $\hbar^2k^2/2m$. Obviously, one can interpret then $\hbar k$ as the magnitude of the momentum of the particle. The flux corresponding to (3.76) according to (3.43) is

$$\vec{j}(\vec{r},t) \;=\; |N|^2\,\frac{\hbar\vec{k}}{m}\;. \tag{3.77}$$

Noting that $\hbar k$ can be interpreted as the magnitude of the momentum of the particle the flux is equal to the velocity of the particle $\vec{v} = \hbar\vec{k}/m$ multiplied by $|N|^2$.

3.5 Particle in One-Dimensional Box

As an example of a situation in which only bound states exist in a quantum system we consider the stationary states of a particle confined to a one-dimensional interval $[-a, a] \subset \mathbb{R}$ assuming that the potential outside of this interval is infinite. We will refer to this as a particle in a one-dimensional 'box'.

Setting up the Space $\mathcal{F}_1$ of Proper Spatial Functions

The presence of the infinite energy wall is accounted for by restricting the spatial dependence of the solutions to functions $f(x)$ defined in the domain $\Omega_1 = [-a, a] \subset \mathbb{R}$ which vanish on the surface $\partial\Omega_1 = \{-a, a\}$, i.e.,

$$f \in \mathcal{F}_1 = \{f : [-a, a] \subset \mathbb{R} \rightarrow \mathbb{R}, f \text{ continuous}, \mho(\pm\partial) = \nvdash\} \tag{3.78}$$

Solutions of the Schrödinger Equation in $\mathcal{F}_1$

The time–dependent solutions satisfy

$$i\hbar\partial_t\psi(x,t) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x,t) . \tag{3.79}$$

The stationary solutions have the form $\psi(x,t) = \exp(-iEt/\hbar)\phi_E(x)$ where $\phi_E(x)$ is determined by

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi_E(x) = E\,\phi_E(x) , \quad \phi(\pm a) = 0 . \tag{3.80}$$

We note that the box is symmetric with respect to the origin. We can expect, hence, that the solutions obey this symmetry as well. We assume, therefore, two types of solutions, so-called *even* solutions obeying $\phi(x) = \phi(-x)$

$$\phi_E^{(e)}(x) = A\cos kx , \quad \frac{\hbar^2 k^2}{2m} = E \tag{3.81}$$

and so-called *odd* solutions obeying $\phi(x) = -\phi(-x)$

$$\phi_E^{(o)}(x) = A\sin kx; , \quad \frac{\hbar^2 k^2}{2m} = E . \tag{3.82}$$

One can readily verify that (3.81, 3.82) satisfy the differential equation in (3.80).
The boundary conditions which according to (3.80) need to be satisfied are

$$\phi_E^{(e,o)}(a) = 0 \text{ and } \phi_E^{(e,o)}(-a) = 0 \tag{3.83}$$

The solutions (3.81, 3.82) have the property that either both boundary conditions are satisfied or none. Hence, we have to consider only one boundary condition, let say the one at $x = a$. It turns out that this boundary condition can only be satisfied for a discrete set of k–values $k_n, n \in \mathbb{N}$. In case of the even solutions (3.81) they are

$$k_n = \frac{n\pi}{2a} , \quad n = 1, 3, 5 \ldots \tag{3.84}$$

since for such k_n

$$\cos(k_n a) \;=\; \cos\left(\frac{n\pi a}{2a}\right) \;=\; \cos\left(\frac{n\pi}{2}\right) \;=\; 0\,. \tag{3.85}$$

In case of the odd solutions (3.82) only the k_n–values

$$k_n \;=\; \frac{n\pi}{2a}\,, \quad n \;=\; 2,4,6\ldots \tag{3.86}$$

satisfy the boundary condition since for such k_n

$$\sin(k_n a) \;=\; \sin\left(\frac{n\pi a}{2a}\right) \;=\; \sin\left(\frac{n\pi}{2}\right) \;=\; 0\,. \tag{3.87}$$

(Note that, according to (3.86), n is assumed to be even.)

The Energy Spectrum and Stationary State Wave Functions

The energy values corresponding to the k_n–values in (3.84, 3.86), according to the dispersion relationships given in (3.81, 3.82), are

$$E_n \;=\; \frac{\hbar^2\pi^2}{8ma^2}\,n^2\,, \quad n \;=\; 1,2,3\ldots \tag{3.88}$$

where the energies for odd (even) n–values correspond to the even (odd) solutions given in (3.81) and (3.82), respectively, i.e.,

$$\phi_n^{(e)}(a;x) \;=\; A_n \cos\frac{n\pi x}{2a}\,, \quad n \;=\; 1,3,5\ldots \tag{3.89}$$

and

$$\phi_n^{(o)}(a;x) \;=\; A_n \sin\frac{n\pi x}{2a}\,, \quad n \;=\; 2,4,6\ldots\,. \tag{3.90}$$

The wave functions represent stationary states of the particle in a one-dimensional box. The wave functions for the five lowest energies E_n are presented in Fig. (3.1). Notice that the number of nodes of the wave functions increase by one in going from one state to the state with the next higher energy E_n. By counting the number of their nodes one can determine the energy ordering of the wave functions.
It is desirable to normalize the wave functions such that

$$\int_{-a}^{+a} dx\,|\phi_n^{(e,o)}(a;x)|^2 \;=\; 1 \tag{3.91}$$

holds. This condition implies for the even states

$$|A_n|^2 \int_{-a}^{+a} dx\cos^2\frac{n\pi x}{2a} \;=\; |A_n|^2\,a \;=\; 1\,, \quad n \;=\; 1,3,5\ldots \tag{3.92}$$

and for the odd states

$$|A_n|^2 \int_{-a}^{+a} dx\sin^2\frac{n\pi x}{2a} \;=\; |A_n|^2\,a \;=\; 1\,, \quad n \;=\; 2,4,6\ldots \tag{3.93}$$

The normalization constants are then

$$A_n \;=\; \sqrt{\frac{1}{a}}\,. \tag{3.94}$$

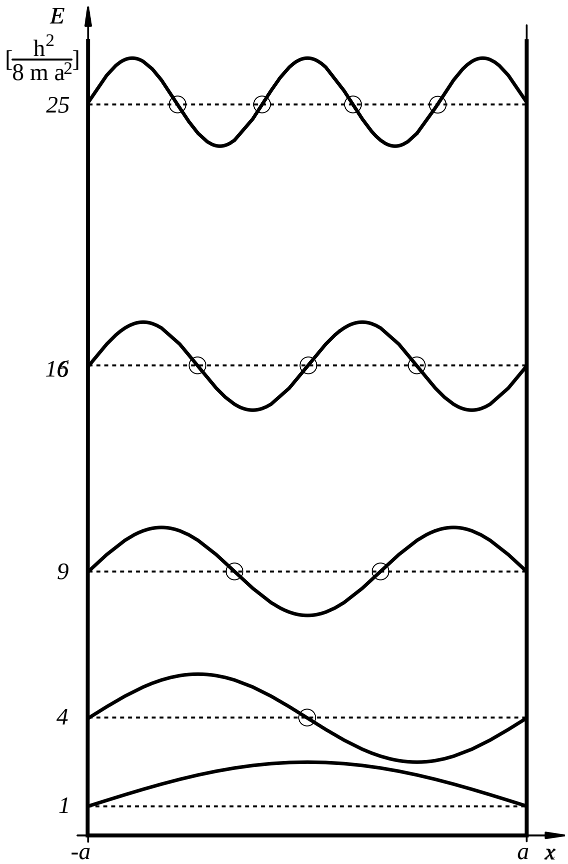

Figure 3.1: Eigenvalues E_n and eigenfunctions $\phi_n^{(e,o)}(a;x)$ for $n = 1, 2, 3, 4, 5$ of particle in a box.

The Stationary States form a Complete Orthonormal Basis of $\mathcal{F}_1$

We want to demonstrate now that the set of solutions (3.89, 3.90, 3.94)

$$\mathcal{B}_1 \;=\; \{\phi_n(a;x)\,,\; n \;=\; 1,2,3,\ldots\} \tag{3.95}$$

where

$$\phi_n(a;x) \;=\; \sqrt{\frac{1}{a}}\left\{\begin{array}{ll}\cos\frac{n\pi x}{2a} & \text{for } n \;=\; 1,3,5\ldots\\ \sin\frac{n\pi x}{2a} & \text{for } n \;=\; 2,4,6\ldots\end{array}\right. \tag{3.96}$$

together with the scalar product[5]

$$\langle f|g\rangle_{\Omega_1} \;=\; \int_{-a}^{+a} dx f(x)\, g(x)\;, \quad f,\, g \,\in\, \mathcal{F}_1 \tag{3.97}$$

form an *orthonormal basis* set, i.e., it holds

$$\langle \phi_n|\phi_m\rangle_{\Omega_1} \;=\; \delta_{n\,m}\;. \tag{3.98}$$

The latter property is obviously true for $n \;=\; m$. In case of $n \;\neq\; m$ we have to consider three cases, (i) n,m both odd, (ii) n,m both even, and (iii) the mixed case. The latter case leads to integrals

$$\langle \phi_n|\phi_m\rangle_{\Omega_1} \;=\; \frac{1}{a}\int_{-a}^{+a} dx \cos\frac{n\pi x}{2a}\sin\frac{m\pi x}{2a}\;. \tag{3.99}$$

Since in this case the integrand is a product of an even and of an odd function, i.e., the integrand is odd, the integral vanishes. Hence we need to consider only the first two cases. In case of n,m odd, $n \neq m$, the integral arises

$$\begin{aligned}\langle \phi_n|\phi_m\rangle_{\Omega_1} \;&=\; \tfrac{1}{a}\textstyle\int_{-a}^{+a} dx \cos\frac{n\pi x}{2a}\cos\frac{m\pi x}{2a} \;=\\ &\tfrac{1}{a}\textstyle\int_{-a}^{+a} dx \left[\cos\frac{(n-m)\pi x}{2a} \;+\; \cos\frac{(n+m)\pi x}{2a}\right]\end{aligned} \tag{3.100}$$

The periods of the two cos-functions in the interval $[-a,a]$ are N, $N \geq 1$. Obviously, the integrals vanish. Similarly, one obtains for n,m even

$$\begin{aligned}\langle \phi_n|\phi_m\rangle_{\Omega_1} \;&=\; \tfrac{1}{a}\textstyle\int_{-a}^{+a} dx \sin\frac{n\pi x}{2a}\sin\frac{m\pi x}{2a} \;=\\ &\tfrac{1}{a}\textstyle\int_{-a}^{+a} dx \left[\cos\frac{(n-m)\pi x}{2a} \;-\; \cos\frac{(n+m)\pi x}{2a}\right]\end{aligned} \tag{3.101}$$

and, hence, this integral vanishes, too.
Because of the property (3.98) the elements of $\mathcal{B}_1$ must be linearly independent. In fact, for

$$f(x) \;=\; \sum_{n=1}^{\infty} d_n\, \phi_n(a;x) \tag{3.102}$$

holds according to (3.98)

$$\langle f|f\rangle_{\Omega_1} \;=\; \sum_{n=1}^{\infty} d_n^2\;. \tag{3.103}$$

[5]We will show in Section 5 that the property of a scalar product do indeed apply. In particular, it holds: $\langle f|f\rangle_{\Omega_1} \;=\; 0 \;\rightarrow\; f(x) \;\equiv\; 0$.

$f(x) \equiv 0$ implies $\langle f|f\rangle_{\Omega_1} = 0$ which in turn implies $d_n = 0$ since $d_n^2 \geq 0$. It follows that $\mathcal{B}_1$ defined in (3.95) is an orthonormal basis.
We like to show finally that the basis (3.95) is also *complete*, i.e., any element of the function space $\mathcal{F}_1$ defined in (3.78) can be expressed as a linear combination of the elements of $\mathcal{B}_1$ defined in (3.95, 3.96). Demonstration of completeness is a formidable task. In the present case, however, such demonstration can be based on the theory of Fourier series. For this purpose we extend the definition of the elements of $\mathcal{F}_1$ to the whole real axis through

$$\tilde{f} : \mathbb{R} \to \mathbb{R}\,; \quad \tilde{f}(x) \;=\; f([x+a]_{2a} - a) \tag{3.104}$$

where $[y]_a = y \bmod 2a$. The functions $\tilde{f}$ are periodic with period $2a$. Hence, they can be expanded in terms of a Fourier series, i.e., there exist real constants $\{a_n,\, n = 0, 1, 2, \ldots\}$ and $\{b_n,\, n = 1, 2, \ldots\}$ such that

$$\tilde{f} \;=\; \sum_{n=0}^{\infty} a_n \cos\frac{n\pi x}{2a} \;+\; \sum_{n=1}^{\infty} a_n \sin\frac{n\pi x}{2a} \tag{3.105}$$

The functions $\tilde{f}$ corresponding to the functions in the space $\mathcal{F}_1$ have zeros at $x = \pm m\, a$, $m = 1, 3, 5 \ldots$ Accordingly, the coefficients a_n, $n = 2, 4, \ldots$ and b_n, $n = 1, 3, \ldots$ in (3.105) must vanish. This implies that only the trigonometric functions which are elements of $\mathcal{B}_1$ enter into the Fourier series. We have then shown that any $\tilde{f}$ corresponding to elements of $\mathcal{F}_1$ can be expanded in terms of elements in $\mathcal{B}_1$. Restricting the expansion (3.105) to the interval $[-a, a]$ yields then also an expansion for any element in $\mathcal{F}_1$ and $\mathcal{B}_1$ is a complete basis for $\mathcal{F}_1$.

Evaluating the Propagator

We can now use the expansion of any initial wave function $\psi(x, t_0)$ in terms of eigenfunctions $\phi_n(a; x)$ to obtain an expression for $\psi(x, t)$ at times $t > t_0$. For this purpose we expand

$$\psi(x, t_0) \;=\; \sum_{n=1}^{\infty} d_n\, \phi_n(a; x)\;. \tag{3.106}$$

Using the orthonormality property (3.98) one obtains

$$\int_{-a}^{+a} dx_0 \phi_m(a; x_0)\, \psi(x_0, t_0) \;=\; d_m\;. \tag{3.107}$$

Inserting this into (3.106) and generalizing to $t \geq t_0$ one can write

$$\psi(x, t) \;=\; \sum_{n=1}^{\infty} \phi_n(a; x)\, c_n(t) \int_{-a}^{+a} dx_0 \phi_n(a; x_0)\, \psi(x_0, t_0) \tag{3.108}$$

where the functions $c_n(t)$ are to be determined from the Schrödinger equation (3.79) requiring the initial condition

$$c_n(t_0) \;=\; 1\;. \tag{3.109}$$

Insertion of (3.108) into the Schrödinger equation yields

$$\begin{aligned} &\textstyle\sum_{n=1}^{\infty} \phi_n(a; x)\, \partial_t c_n(t) \int_{-a}^{+a} dx_0 \phi_n(a; x_0)\, \psi(x_0, t_0) \;= \\ &\textstyle\sum_{n=1}^{\infty} \left(-\frac{i}{\hbar} E_n\right) \phi_n(a; x)\, c_n(t) \int_{-a}^{+a} dx_0 \phi_n(a; x_0)\, \psi(x_0, t_0) \quad . \end{aligned} \tag{3.110}$$

Multiplying both sides by $\phi_m(a;x)$ and integrating over $[-a,a]$ yields, according to (3.98),

$$\partial_t \, c_m(t) \;=\; -\frac{i}{\hbar}\, E_m \, c_m(t) \;, \quad c_m(t_0) \;=\; 1 \;. \tag{3.111}$$

The solutions of these equations which satisfy (3.109) are

$$c_m(t) \;=\; \exp\left(-\frac{i}{\hbar}\, E_m \,(t \,-\, t_0) \right) \;. \tag{3.112}$$

Equations (3.108, 3.112) determine now $\psi(x,t)$ for any initial condition $\psi(x,t_0)$. This solution can be written

$$\psi(x,t) \;=\; \int_{-a}^{+a} dx_0 \, \phi(x,t|x_0,t_0)\, \psi(x_0,t_0) \tag{3.113}$$

where

$$\phi(x,t|x_0,t_0) \;=\; \sum_{n=1}^{\infty} \phi_n(a;x) \exp\left(-\frac{i}{\hbar}\, E_n \,(t \,-\, t_0) \right) \phi_n(a;x_0) \;. \tag{3.114}$$

This expression has the same form as postulated in the path integral formulation of Quantum Mechanics introduced above, i.e., in (2.5). We have identified then with (3.114) the representation of the propagator for a particle in a box with infinite walls.

It is of interest to note that $\phi(x,t|x_0,t_0)$ itself is a solution of the time-dependent Schrödinger equation (3.79) which lies in the proper function space (3.78). The respective initial condition is $\phi(x,t_0|x_0,t_0) \;=\; \delta(x \,-\, x_0)$ as can be readily verified using (3.113). Often the propagator $\phi(x,t|x_0,t_0)$ is also referred to as a *Greens function.* In the present system which is composed solely of bound states the propagator is given by a sum, rather than by an integral (3.54) as in the case of the free particle system which does not exhibit any bound states.

Note that the propagator has been evaluated in terms of elements of a particular function space $\mathcal{F}_1$, the elements of which satisfy the appropriate boundary conditions. In case that different boundary conditions hold the propagator will be different as well.

Example of a Non-Stationary State

As an illustration of a non-stationary state we consider a particle in an initial state

$$\psi(x_0,t_0) \;=\; \left[\frac{1}{2\pi\sigma^2}\right]^{\frac{1}{4}} \exp\left(-\frac{x_0^2}{2\sigma^2} \;+\; i\, k_0 \, x_0 \right) \;, \quad \sigma \;=\; \frac{a}{4}\,,\; k_0 \;=\; \frac{15}{a} \;. \tag{3.115}$$

This initial state corresponds to the particle being localized initially near $x_0 \;=\; 0$ with a velocity $v_0 \;=\; 15\hbar/m\,a$ in the direction of the positive x-axis. Figure 3.2 presents the probability distribution of the particle at subsequent times. One can recognize that the particle moves first to the left and that near the right wall of the box interference effects develop. The particle moves then to the left, being reflected at the right wall. The interference pattern begins to 'smear out' first, but the collision with the left wall leads to new interference effects. The last frame shows the wave front reaching again the right wall and the onset of new interference.

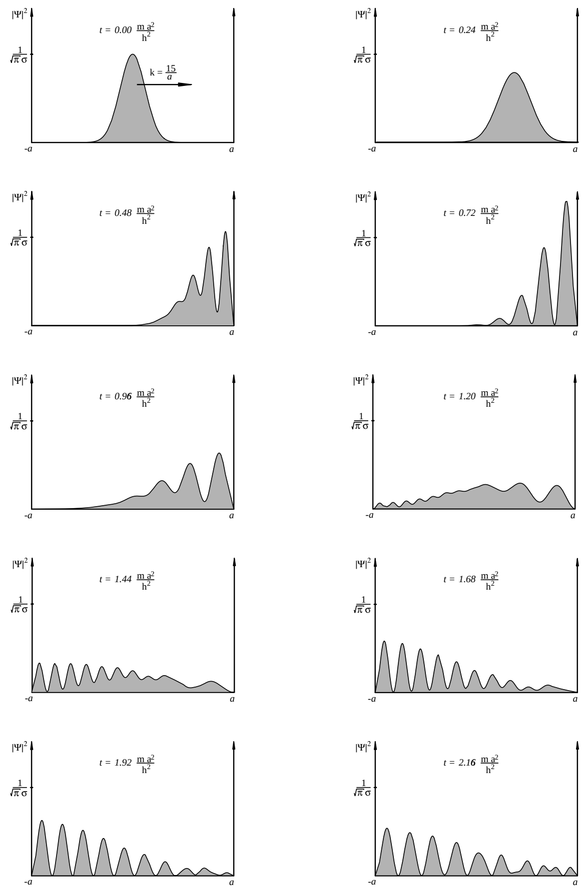

Figure 3.2: Stroboscopic views of the probability distribution $|\psi(x,t)|^2$ for a particle in a box starting in a Gaussian distribution with momentum $15\hbar/a$.

Summary: Particle in One-Dimensional Box

We like to summarize our description of the particle in the one-dimensional box from a point of view which will be elaborated further in Section 5. The description employed a space of functions $\mathcal{F}_1$ defined in (3.78). A complete basis of $\mathcal{F}_1$ is given by the infinite set $\mathcal{B}_1$ (3.95). An important property of this basis and, hence, of the space $\mathcal{F}_1$ is that the elements of the basis set can be enumerated by integer numbers, i.e., can be counted. We have defined in the space $\mathcal{F}_1$ a scalar product (3.97) with respect to which the eigenfunctions are orthonormal. This property allowed us to evaluate the propagator (3.114) in terms of which the solutions for all initial conditions can be expressed.

3.6 Particle in Three-Dimensional Box

We consider now a particle moving in a three-dimensional rectangular box with side lengths $2a_1$, $2a_2$, $2a_3$. Placing the origin at the center and aligning the x_1, x_2, x_3–axes with the edges of the box yields spatial boundary conditions which are obeyed by the elements of the function space

$$\mathcal{F}_3 = \{ f : \Omega \to \mathbb{R},\ f \text{ continuous},\ f(x_1,x_2,x_3) = 0\ \forall\ (x_1,x_2,x_3)^T \in \partial\Omega \} . \qquad (3.116)$$

where Ω is the interior of the box and $\partial\Omega$ its surface

$$\begin{aligned} \Omega &= [-a_1,a_1] \otimes [-a_2,a_2] \otimes [-a_3,a_3] \subset \mathbb{R}^3 \\ \partial\Omega &= \{(x_1,x_2,x_3)^T \in \Omega,\ x_1 = \pm a_1\} \cup \{(x_1,x_2,x_3)^T \in \Omega,\ x_2 = \pm a_2\} \\ &\quad \cup \{(x_1,x_2,x_3)^T \in \Omega,\ x_3 = \pm a_3\} . \end{aligned} \qquad (3.117)$$

We seek then solutions of the time-dependent Schrödinger equation

$$i\hbar\partial_t\psi(x,t) = \hat{H}\,\psi(x_1,x_2,x_3,t) , \quad \hat{H} = -\frac{\hbar^2}{2m}\left(\partial_1^2 + \partial_2^2 + \partial_3^2\right) \qquad (3.118)$$

which are stationary states. The corresponding solutions have the form

$$\psi(x_1,x_2,x_3,t) = \exp\left(-\frac{i}{\hbar}E\,t\right)\phi_E(x_1,x_2,x_3) \qquad (3.119)$$

where $\phi_E(x_1,x_2,x_3)$ is an element of the function space $\mathcal{F}_3$ defined in (3.116) and obeys the partial differential equation

$$\hat{H}\,\phi_E(x_1,x_2,x_3) = E\,\phi_E(x_1,x_2,x_3) . \qquad (3.120)$$

Since the Hamiltonian $\hat{H}$ is a sum of operators $O(x_j)$ each dependent only on a single variable, i.e., $\hat{H} = O(x_1) + O(x_2) + O(x_3)$, one can express

$$\phi(x_1,x_2,x_3) = \prod_{j=1}^{3}\phi^{(j)}(x_j) \qquad (3.121)$$

where

$$-\frac{\hbar^2}{2m}\partial_j^2\,\phi^{(j)}(x_j) = E_j\,\phi^{(j)}(x_j) , \quad \phi^{(j)}(\pm a_j) = 0 , \quad j = 1,2,3 \qquad (3.122)$$

and $E_1 + E_2 + E_3 = E$. Comparing (3.122) with (3.80) shows that the solutions of (3.122) are given by (3.96) and, hence, the solutions of (3.120) can be written

$$\begin{aligned} \phi_{(n_1,n_2,n_3)}(a_1,a_2,a_3;x_1,x_2,x_3) &= \phi_{n_1}(a_1;x_1)\,\phi_{n_2}(a_2;x_2)\,\phi_{n_3}(a_3;x_3) \\ n_1,n_2,n_3 &= 1,2,3,\ldots \end{aligned} \tag{3.123}$$

and

$$E_{(n_1,n_2,n_3)} = \frac{\hbar^2\pi^2}{8m}\left(\frac{n_1^2}{a_1^2}+\frac{n_2^2}{a_2^2}+\frac{n_3^2}{a_3^2}\right), n_1,n_2,n_3 = 1,2,3,\ldots \tag{3.124}$$

The same considerations as in the one-dimensional case allow one to show that

$$\mathcal{B}_3 = \{\phi_{(n_1,n_2,n_3)}(a_1,a_2,a_3;x_1,x_2,x_3)\,,\, n_1,n_2,n_3 = 1,2,3,\ldots\} \tag{3.125}$$

is a complete orthonormal basis of $\mathcal{F}_3$ and that the propagator for the three-dimensional box is

$$\begin{aligned} \phi(\vec{r},t|\vec{r}_0,t_0) = & \sum_{n_1,n_2,n_3=1}^{\infty} \phi_{(n_1,n_2,n_3)}(a_1,a_2,a_3;\vec{r}) \\ & \exp\left(-\frac{i}{\hbar}E_{(n_1n_2n_3)}(t-t_0)\right)\phi_{(n_1,n_2,n_3)}(a_1,a_2,a_3;\vec{r}_0)\,. \end{aligned} \tag{3.126}$$

Symmetries

The three-dimensional box confining a particle allows three symmetry operations that leave the box unchanged, namely rotation by π around the x_1, x_2, x_3–axes. This symmetry has been exploited in deriving the stationary states. If two or all three orthogonal sides of the box have the same length further symmetry operations leave the system unaltered. For example, if all three lengths a_1, a_2, a_3 are identical, i.e., $a_1 = a_2 = a_3 = a$ then rotation around the x_1, x_2, x_3–axes by $\pi/2$ also leaves the system unaltered. This additional symmetry is also reflected by degeneracies in the energy levels. The energies and corresponding degeneracies of the particle in the three-dimensional box with all side lengths equal to $2a$ are given in the following Table:

n_1	n_2	n_3	$E/[\hbar^2\pi^2/8ma^2]$	degeneracy
1	1	1	3	single
1	1	2	6	three-fold
1	2	2	9	three-fold
1	1	3	11	three-fold
2	2	2	12	single
1	2	3	14	six-fold
2	2	3	17	three-fold
1	1	4	18	three-fold
2	3	3	22	three-fold
3	3	3	27	single
1	1	5	27	three-fold

One can readily verify that the symmetry of the box leads to three-fold and six-fold degeneracies. Such degeneracies are always a signature of an underlying symmetry. Actually, in the present case

'accidental' degeneracies also occur, e.g., for $(n_1, n_2, n_3) = (3,3,3)\,(1,1,5)$ as shown in the Table above. The origin of this degeneracy is, however, the identity $3^2 + 3^2 + 3^2 = 1^2 + 1^2 + 5^2$.
One particular aspect of the degeneracies illustrated in the Table above is worth mentioning. We consider the degeneracy of the energy E_{122} which is due to the identity $E_{122} = E_{212} = E_{221}$. Any linear combination of wave functions

$$\tilde{\phi}(\vec{r}) \;=\; \alpha\,\phi_{(1,2,2)}(a,a,a;\vec{r}) \;+\; \beta\,\phi_{(2,1,2)}(a,a,a;\vec{r}) \;+\; \gamma\,\phi_{(2,2,1)}(a,a,a;\vec{r}) \tag{3.127}$$

obeys the stationary Schrödinger equation $\hat{H}\,\tilde{\phi}(\vec{r}) = E_{122}\,\tilde{\phi}(\vec{r})$. However, this linear combination is not necessarily orthogonal to other degeneraste states, for example, $\phi_{(1,2,2)}(a,a,a;\vec{r})$. Hence, in case of degenerate states one cannot necessarily expect that stationary states are orthogonal. However, in case of an n–fold degeneracy it is always possible, due to the hermitian character of $\hat{H}$, to construct n orthogonal stationary states[6].

[6]This is a result of linear algebra which the reader may find in a respective textbook.