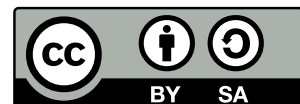


Quantum-, Molecular-, and Solid State Physics

<https://www.github.com/Lauchmelder23/quantumphysics>
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Chapter 1

Fundamentals of Quantum Physics

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Due to the uncertainty principle, location and impulse of an atomic particle cannot be both stated with arbitrary precision. The classic trajectory, represented in the model of mass points by a well-defined curve in space $\mathbf{r}(t)$, is replaced by the probability

$$W(x, y, z, t) dv = |\psi(x, y, z, t)|^2 dV \quad (1.1)$$

to find the particle in the volume element $dV = dx dy dz$ at the time t . This probability depends on the absolute square of the matter wave function $\psi(x, y, z, t)$.

In this chapter we want to show how this wave function can be calculated for simple examples. These examples will also demonstrate the physical fundamentals of quantum mechanics and its differences to classical particle mechanics, elaborate on the concept of *quantum numbers* and show under which conditions quantum mechanical results can be transitioned into classical physics. This is supposed to clarify that classic (i.e. pre-quantum) mechanics are contained in quantum mechanics as a limiting case for very small de Broglie wavelengths $\lambda_{dB} \rightarrow 0$.

These examples should also demonstrate that almost all insights of quantum mechanics are already known in classic wave optics. This means: the actual novel concepts in quantum mechanics is the description of classic particles with matter waves. The deterministic description of the temporal development of location and impulse of a particle is thus replaced with a statistical treatment, by which we can only discuss probabilities of the results of a measurement. A fundamental uncertainty occurs when we observe location and impulse at the same time.

1.1 The Schrödinger Equation

In this section we will outline the fundamental equation of quantum mechanics, which was established by *Erwin Schrödinger* (1887–1961) in 1926. The solutions of this equation are the desired wave functions $\psi(x, y, z, t)$. However, these solutions can only be derived in analytical form for a few very simple physical problems. Very fast computers are usually able to numerically compute solutions for complex problems.

First, we will consider the mathematically simplest case. A free particle of mass m which moves at a constant velocity \mathbf{v} in direction x . With $\mathbf{p} = \hbar\mathbf{k}$ and $E = \hbar\omega = E_{\text{kin}}$ (because $E_{\text{pot}} = 0$), we know the wave function must be of the form

$$\psi(x, t) = Ae^{i(kx - \omega t)} = Ae^{(i/\hbar)(px - E_{\text{kin}}t)} \quad (1.2)$$

Here we use the fact that $E_{\text{kin}} = p^2/2m$, which is the kinetic energy of the particle. Since the mathematical representation is absolutely identical to that of an electromagnetic wave, it makes sense to start with the wave equation

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{u^2} \frac{\partial^2 \psi}{\partial t^2} \quad (1.3)$$

for waves propagating with phase velocity u in direction x . For *stationary* problems where \mathbf{p} and E are time-independent the wave function can be split into a strictly location-dependent

factor $\psi(x) = Ae^{ikx}$, and a strictly time-dependent phase factor $e^{-i\omega t}$. Thus we can write

$$\psi(x, t) = \psi(x) \cdot e^{-i\omega t} = Ae^{ikx} \cdot e^{-i\omega t} \quad (1.4)$$

If we use the ansatz (1.4) in the wave equation (1.3), and the fact that $k^2 = p^2/\hbar^2 = 2mE_{\text{kin}}/\hbar^2$, we get the equations

$$\begin{aligned} \frac{\partial^2 \psi}{\partial x^2} &= -k^2 \psi = -\frac{2m}{\hbar^2} \cdot E_{\text{kin}} \cdot \psi \\ \frac{\partial^2 \psi}{\partial t^2} &= -\omega^2 \psi \end{aligned} \quad (1.5)$$

Comparison with (1.3) gives us

$$u^2 = \frac{\omega^2}{k^2} \implies u = \frac{\omega}{k}$$

Note that the particle velocity $v_p = v$

$$v = \frac{p}{m} = \frac{\hbar k}{m} = \frac{\partial \omega}{\partial k}$$

is different from the phase velocity $u = v_{\text{ph}} = \omega/k$.

In the general case the particle can move in a force field. If it is conservative then we can assign each point a potential energy, with the condition that the total energy $E = E_{\text{kin}} + E_{\text{pot}}$ remains constant. Using $E_{\text{kin}} = E - E_{\text{pot}}$ and (1.5) we then receive the one-dimensional stationary Schrödinger equation

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + E_{\text{pot}} \psi = E \psi \quad (1.6)$$

For the general case where the particle is moving freely in three-dimensional space we can use the three-dimensional wave equation

$$\Delta \psi = \frac{1}{u^2} \frac{\partial^2 \psi}{\partial t^2}$$

and the ansatz $\psi(x, y, z, t) = \psi(x, y, z) \cdot e^{-i\omega t}$, we can establish the three-dimensional stationary Schrödinger equation

$$\frac{-\hbar^2}{2m} \Delta \psi = E_{\text{pot}} \psi = E \psi \quad (1.7)$$

If we differentiate (1.2) partially for time we receive

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} E_{\text{kin}} \cdot \psi$$

and with (1.5) we can find the time-dependent equation for a free particle with $E_{\text{pot}} = 0$ (i.e. $E_{\text{kin}} = \text{const}$)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (1.8)$$

The three-dimensional representation is then

$$-\frac{\hbar^2}{2m} \Delta \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad (1.9)$$

There are some remarks to be made:

- In this “derivation” we have used the de Broglie-relationship $\mathbf{p} = \hbar \mathbf{k}$, which is only supported by experiments and has no mathematical justification.
- The law of conservation of energy of quantum mechanics is $E\psi = E_{\text{kin}}\psi + E_{\text{pot}}\psi$. Like in classical mechanics, there is no derivation for this law, and is accepted as truth from experience.
- While electromagnetic waves have a linear dispersion relation $\omega(k) = kc$, the matter wave $\psi(\mathbf{r}, t)$ of a free particle has a *quadratic* dispersion relation $\omega(k) = (\hbar/2m) \cdot k^2$. This results from $E = \hbar\omega = p^2/2m$.
- The Schrödinger equations are a *linear* homogeneous differential equation. Because of this, different solutions of the equation can be superpositioned. This means, if ψ_1 and ψ_2 are solutions to the equation, then $\psi_3 = a \cdot \psi_1 + b \cdot \psi_2$ is also a solution.
- Since the time-dependent Schrödinger equation is a complex equation, the wave functions ψ may also be complex. The absolute square $|\psi|^2$ however, which represents the probability of the presence of a particle, is always real.

For non-stationary problems (i.e. $E = E(t)$ and $p = p(t)$), the dispersion relation $\omega(t)$ also becomes time-dependent. This means that $\partial^2 \psi / \partial t^2$ can no longer be written as $-\omega^2 \psi$, and cannot be derived from the wave equation for matter waves of particles.

Schrödinger postulated (!), that even for time-dependent potential energy $E_{\text{pot}}(\mathbf{r}, t)$ the equation

$$\frac{-\hbar^2}{2m} \Delta \psi(\mathbf{r}, t) + E_{\text{pot}}(\mathbf{r}, t) \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad (1.10)$$

holds. The general time-dependent Schrödinger equation has since been verified in numerous experiments, and is generally considered correct, even if no mathematical justification exists. This equation is the fundamental equation of quantum mechanics.

For stationary problems we can separate $\psi(\mathbf{r}, t)$ into $\psi(\mathbf{r}, t) = \psi(\mathbf{r}) \cdot e^{-i(E/\hbar) \cdot t}$. Inserting this into (1.10) yields the stationary Schrödinger equation (1.7) for $\psi(\mathbf{r})$.

1.2 Examples of the Stationary Schrödinger Equation

We now want to solve the Schrödinger equation

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + E_{\text{pot}}\psi = E\psi$$

for a few simple, one-dimensional problems. These examples will illustrate the description of classical particles as waves and the following physical consequences.

1.2.1 The Free Particle

A particle is said to be free, if it is moving in a constant potential ϕ_0 , because then $\mathbf{F} = -\nabla E_{\text{pot}}$ means that no forces are acting on the particle. Through a suitable choice of the zero point energy we can set $\phi_0 = 0$, i.e. $E_{\text{pot}} = 0$, and thus get the Schrödinger equation for a free particle

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (1.11)$$

The total energy $E = E_{\text{kin}} + E_{\text{pot}}$ is because of E_{pot} now

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

Thus (1.11) gets reduced to

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

which has the general solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (1.12)$$

The time-dependent wave function

$$\psi(x, t) = \psi(x) \cdot e^{-i\omega t} = Ae^{i(kx - \omega t)} + Be^{-i(kx + \omega t)} \quad (1.13)$$

represents the superposition of a planar wave travelling in the $+x$ and $-x$ direction.

The coefficients A and B are the amplitudes of those waves, which are determined by the boundary conditions. For example, the wave function of electrons which are emitted from a cathode in $+x$ direction towards a detector, will have $B = 0$, since there are no particles moving in $-x$. From this experimental setup we know that the electrons are found along the length L of the path between cathode and detector. This means their wave function can only be different from zero in this region of space. Using the normalization condition we get

$$\int_0^L |\psi(x)|^2 dx = 1 \\ \implies A^2 \cdot L = 1 \implies A = \frac{1}{\sqrt{L}}$$

To determine the location of a particle at time t more accurately, we will have to construct *wave packets* in place of planar waves (1.12)

$$\psi(x, t) = \int_{k_0 - \Delta k/2}^{k_0 + \Delta k/2} A(k) e^{i(kx - \omega t)} dk \quad (1.14)$$

The location uncertainty of this packet at $t = 0$ is

$$\Delta x \geq \frac{\hbar}{2\Delta p_x} = \frac{1}{2\Delta k}$$

and depends on the pulse width $\Delta p_x = \hbar\Delta k$. The larger k is, the more certainly $\Delta x(t = 0)$ can be determined, but the faster the wave packet spreads.

Experimentally, this can be illustrated as follows: If we apply a short voltage pulse to the cathode at time $t = 0$, then electrons can start travelling towards the detector at this instance. The emitted electrons have a velocity distribution Δv , such that electrons with differing velocities v will not necessarily be in the same location x at a later point in time t . Instead they are spread over the interval $\Delta x(t) = t \cdot \Delta v$. The velocity distribution is described by $\Delta v \propto \Delta k$ of the wave packet, such that the location uncertainty Δx

$$\frac{d(\Delta x(t))}{dt} = \Delta v(t = 0) = \frac{\hbar}{m} \Delta k(t = 0)$$

changes proportionally to the initial impulse uncertainty.