Atomic phenomena are described mainly on the basis of non-relativistic quantum mechanics. Relativistic effects can generally be accounted for in a satisfactory way with perturbative methods. In recent years it has become increasingly apparent that a better understanding of the classical dynamics of an atomic system can lead to a deeper appreciation of various features in its observable quantum mechanical properties, see e.g. [FE97] and Sect. 5.3. This does not, however, invalidate the generally accepted point of view that quantum mechanics is the relevant theory for atomic physics.

This chapter gives a brief review of quantum mechanics as it is needed for use in later chapters. Although the reader is expected to have some experience in the subject already, the presentation starts at the beginning and is self-contained so that it should, at least in principle, be understandable without previous knowledge of quantum mechanics. A more thorough introduction can be found in numerous textbooks, e.g. [Sch68, Bay69, Gas74, Mes70, Sch92].

1.1 Wave Functions and Equations of Motion

1.1.1 States and Wave Functions

Non-relativistic quantum mechanics describes the state of a physical system at a given time $t$ with a complex-valued wave function $\psi(X; t)$. The wave function $\psi$ depends on the parameter $t$ and a complete set of variables summarized as $X$. As an example let us think of a system of $N$ electrons, which plays a central role in atomic physics. Then $X$ can stand for the $N$ spatial coordinates $r_1, \ldots, r_N$ and the $N$ spin coordinates $m_{s_1}, \ldots, m_{s_N}$ of the electrons. The spatial coordinates $r_i$ are ordinary (real) vectors in three-dimensional space; the spin coordinates $m_{si}$ can each assume only two values, $m_{si} = \pm 1/2$.

The set of wave functions describing a given system is closed with respect to linear superposition. This means that all multiples and sums of possible wave functions are again possible wave functions. Mathematically, the possible wave functions of a system form a vector space. The scalar product of two wave functions $\psi(X; t), \phi(X; t')$ in this vector space is defined as
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\[ \langle \psi(t) | \phi(t') \rangle = \int \psi^*(X; t) \phi(X; t') \, dX \quad . \tag{1.1} \]

The integral in (1.1) stands for integration over the continuous variables and summation over the discrete variables. In the above-mentioned example of an \( N \)-electron system we have

\[ \int dX = \int d^3r_1 \cdots \int d^3r_N \sum_{m_{z_1} = -1/2}^{1/2} \cdots \sum_{m_{z_N} = -1/2}^{1/2} \quad . \]

The scalar product (1.1) is linear,

\[ \langle \psi | \phi_1 + c \phi_2 \rangle = \langle \psi | \phi_1 \rangle + c \langle \psi | \phi_2 \rangle \quad , \tag{1.2} \]

and it is replaced by its complex conjugate if we interchange the wave functions,

\[ \langle \phi | \psi \rangle = \langle \psi | \phi \rangle^* \quad . \tag{1.3} \]

Two wave functions \( \psi \) and \( \phi \) are orthogonal if the scalar product \( \langle \psi | \phi \rangle \) vanishes. The scalar product \( \langle \psi | \psi \rangle \) is a non-negative real number, and its square root is the norm of the wave function \( \psi \). Square integrable wave functions, i.e. wave functions \( \psi(X; t) \) with the property

\[ \langle \psi | \psi \rangle = \int |\psi(X; t)|^2 \, dX < \infty \quad , \tag{1.4} \]

are normalizable. This means that they become wave functions of norm unity,

\[ \langle \psi | \psi \rangle = \int |\psi(X; t)|^2 \, dX = 1 \quad , \tag{1.5} \]

when multiplied by an appropriate constant. The non-negative function \( |\psi(X; t)|^2 \) is a probability density. If, at time \( t \), a physical state is described by the wave function \( \psi(X; t) \) (which is normalized to unity, \( \langle \psi | \psi \rangle = 1 \)), then the integral

\[ \int_{\delta V} |\psi(X; t)|^2 \, dX \]

over a part \( \delta V \) of the full space of values of the variable \( X \) gives the probability that a measurement of the variable \( X \) (at time \( t \)) will yield values within \( \delta V \). The concept of probability densities can also be applied to wave functions which are not normalizable, as long as we only study relative probabilities.

The square integrable functions (1.4) form a subspace of the space of all wave functions. This subspace has the properties of a Hilbert space. In particular it is complete, meaning that the limit of each convergent sequence of wave functions in the Hilbert space is again a wave function in the Hilbert space. It also has a denumerable basis, i.e. there exists a sequence \( \phi_1(X), \phi_2(X), \ldots \), of linearly independent square integrable functions such that any square integrable function \( \psi(X) \) can be written as a linear combination