

## Chapter 2

# Simple Examples

In this chapter we present a few simple examples. Examples how to make use of the conceptual and mathematical framework sketched in Chap. 1 on Basics.

One of the most simple systems concerns the ground state of the ammonia molecule  $\text{NH}_3$ . There is a unilateral triangle of hydrogen ions and a nitrogen ion on the central axis either below or above. Thus, there are two equivalent configurations, up or down, with rather interesting implications. We can explain the ground state level splitting giving rise to the microwave frequency standard. An external electric field may further shift the energy levels, a phenomenon which goes under the name of Stark effect. It is possible to separate a beam into ground state and excited molecules such that extremely weak microwave signals may be amplified (maser).

Another simple example for quantum theoretic reasoning is the Hopping model. It explains the origins of electronic band structure, the nature of quasi-particles and the scattering and trapping of quasi-electrons on an impurity.

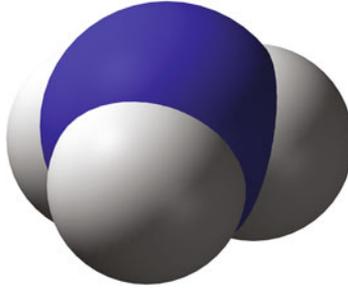
We then turn to neutron scattering. Even if the target consist of randomly oriented molecules, its arrangement of nuclei can be reconstructed from the differential cross section.

The example of a free particle which we will study next is helpful in two respects. It turns out that it moves just like a free particle in classical mechanics, with the expectation value of the location observable replacing the position coordinate. In addition, the particle spreads out more and more in the course of time.

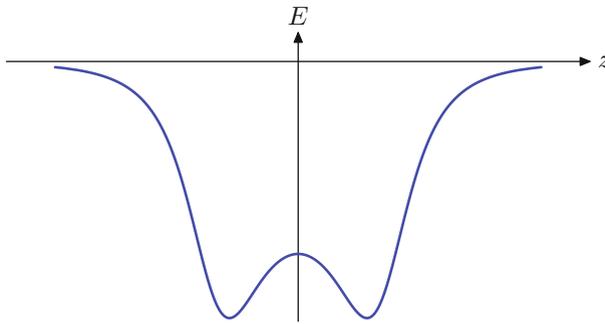
Small oscillations about the equilibrium configuration are quantized, so another simple example. The excited states have discrete, equidistant energies.

### 2.1 Ammonia Molecule

Ammonia, or azan, is a colorless gas with a pungent odor. It is synthesized in large quantities mainly as raw material of fertilizers. Ammonia is the common English name for  $\text{NH}_3$ . There is also a completely different  $\text{NH}_4^-$  ion which in English is



**Fig. 2.1** Sketch of an ammonia molecule. There is an equilateral *triangle* of protons (*smaller spheres*) *above* or *below* the nitrogen ion (*larger sphere*). The ground state is a symmetric superposition of this and the mirror-reflected one



**Fig. 2.2** Ammonia molecule potential energy. The potential energy  $E$  of an ammonia molecule is plotted versus displacement  $z$ . The protons form a unilateral triangle, and an axis through its center and perpendicular to the proton plane is a natural site for the  $N^{3-}$  ion.  $z$  denotes the deviation from an in-plane position

called ammonium. The latter ion (see Fig. 2.1) consists of a tetrahedron of protons with a nitrogen ion at its center, a highly symmetric and firmly bound ion. Here we discuss the ammonia molecule because it is not so symmetric, a fact which gives rise to interesting effects.

There is an  $N^{3-}$  ion, three protons, or  $H^+$ , and three shared electrons which bind this to a molecule. One might think at first that the three protons form an equilateral triangle with the nitrogen ion at its center. Calculations and neutron diffraction experiments however result in another configuration. The three protons which repel each other form a unilateral triangle in fact. The nitrogen ion is located at an axis perpendicular to the hydrogen triangle passing through its center, as expected. But the nitrogen ion is displaced. It is either above or below the hydrogen ions plane. See Fig. 2.2 for a sketch of the potential energy. We disregard here all other possible configurations and concentrate only on this up-down degree of freedom.

### 2.1.1 Hilbert Space and Energy Observable

Let us construct a mathematical model. The two base vectors

$$f_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } f_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (2.1)$$

shall describe the up- and down configuration of the molecule. They span the Hilbert space  $\mathbb{C}^2$  of two-component vectors of complex numbers. For  $f, g \in \mathbb{C}^2$  the scalar product is

$$(g, f) = g_1^* f_1 + g_2^* f_2. \quad (2.2)$$

Evidently, the up- and down vectors are normalized and orthogonal.

Observables are represented by self-adjoint complex  $2 \times 2$  matrices. For the Hamiltonian in particular we may write

$$H = \begin{pmatrix} E & -V \\ -V & E \end{pmatrix}. \quad (2.3)$$

The two diagonal elements must be equal because the up and down configurations are equivalent. One of the off-diagonal elements should be the complex conjugate of the other. By tuning the phase between the base states, they can be chosen equal and real, even positive. The minus sign is there for convenience.

The time-independent Schrödinger equation  $H f = \epsilon f$  is solved by

$$f_{\text{lo}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ with } \epsilon_{\text{lo}} = E - V \quad (2.4)$$

and by

$$f_{\text{hi}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ with } \epsilon_{\text{hi}} = E + V. \quad (2.5)$$

The eigenvectors  $f_{\text{lo}}$  and  $f_{\text{hi}}$  correspond to the orthogonal projectors

$$\Pi_{\text{lo}} = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \text{ and } \Pi_{\text{hi}} = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \quad (2.6)$$

By construction, the energy observable is

$$H = \epsilon_{\text{lo}} \Pi_{\text{lo}} + \epsilon_{\text{hi}} \Pi_{\text{hi}}. \quad (2.7)$$

There are two stationary energy states, one an even, the other an odd superposition of the up and down configurations  $f_{\uparrow}$  and  $f_{\downarrow}$ .

If ammonia molecules are exposed to microwave radiation, photons of energy

$$\hbar\omega_0 = \epsilon_{\text{hi}} - \epsilon_{\text{lo}} = 2V \quad (2.8)$$

will be absorbed. They cause transitions from the ground state  $\Pi_{\text{lo}}$  to the excited state  $\Pi_{\text{hi}}$ . We will study the mechanism for this effect later. Equation (2.8) defines the microwave standard of  $f = 23.87012$  GHz. This frequency corresponds to a vacuum wave length of  $\lambda = 1.255932$  cm.

### 2.1.2 Ammonia Molecule in an External Electric Field

The electric charge of an ammonia molecule vanishes, but not its dipole moment. If the molecule has the  $\uparrow$  configuration, its dipole moment is  $d = ae$ , where  $e$  denotes the unit charge, that of a proton. The length  $a = 0.019$  nm is the average displacement of charges. Hence the electric dipole moment operator is

$$D = \begin{pmatrix} d & 0 \\ 0 & -d \end{pmatrix}. \quad (2.9)$$

In an external constant electric field  $\mathcal{E}$ , the energy contribution of an electric dipole  $D$  is  $-D \cdot \mathcal{E}$ . In our case this reads

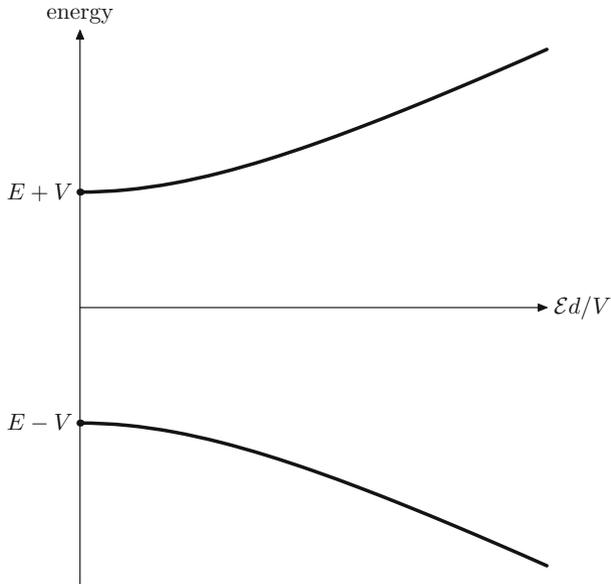
$$H = \begin{pmatrix} E - d\mathcal{E} & -V \\ -V & E + d\mathcal{E} \end{pmatrix}. \quad (2.10)$$

$\mathcal{E} = \mathcal{E}_z$  is the electric field strength along the axis of orientation of the ammonia molecule. Its eigenvalues are

$$\epsilon_{\text{lo}}(\mathcal{E}) = E - \sqrt{V^2 + d^2\mathcal{E}^2} \quad \text{and} \quad \epsilon_{\text{hi}}(\mathcal{E}) = E + \sqrt{V^2 + d^2\mathcal{E}^2}. \quad (2.11)$$

A plausible result. For  $\mathcal{E} = 0$  it reduces to  $\epsilon_{\text{lo}} = E - V$  and  $\epsilon_{\text{hi}} = E + V$ , as discussed above. For  $V = 0$  we obtain  $\epsilon_{\text{lo}}(\mathcal{E}) = E - |d\mathcal{E}|$  and  $\epsilon_{\text{hi}}(\mathcal{E}) = E + |d\mathcal{E}|$  which becomes obvious by inspecting (2.10). See Fig. 2.2 for a visualization (Fig. 2.3).

We have just explained the Stark effect. All kinds of spectral lines are affected if a probe of atoms or molecules is exposed to an external electric field. Atomic, molecular or solid state physics is governed by the motion of electrons due to Coulomb forces. Therefore, Planck's constant  $\hbar$ , the elementary charge  $e$ , the electron mass  $m$  and the factor  $4\pi\epsilon_0$  come into play. We will later discuss the atomic system of units based on these four constants of nature. While the dipole moment  $d$  of an ammonia molecule is 0.40 in atomic units, the atomic unit for electric field strength is  $E_* = 5.151 \times 10^{11}$  V m<sup>-1</sup>. Laboratory field strengths are typically a few kilovolts per centimeter, i.e. very much smaller than  $\mathcal{E}_*$ . Therefore,  $d\mathcal{E}$  is small and we may



**Fig. 2.3** Stark effect of the ammonia molecule. The molecule with dipole moment  $d$  is exposed to an external electric field strength  $\mathcal{E}$ . The energy difference between excited and ground state varies quadratically for small field strengths and linearly for large values

safely assume that the Stark effect is quadratic in the external electric field strength. Only if  $V$  vanishes or is exceptionally small, the linear Stark effect can be observed.

### 2.1.3 Dipole Moment Expectation Value

Let us work out the eigenstates of the ammonia molecule in the presence of an electric field. We know the solution for  $\mathcal{E} = 0$ , namely  $\varrho_{lo} = \Pi_{lo}$  and  $\varrho_{hi}$  of (2.9). We rotate these states by an angle  $\alpha$ ,

$$\Pi_{lo,hi}(\mathcal{E}) = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix} \Pi_{lo,hi} \begin{pmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{pmatrix}, \quad (2.12)$$

which results in

$$\Pi_{lo,hi}(\mathcal{E}) = \frac{1}{2} \begin{pmatrix} 1 \mp \sin 2\alpha & \pm \cos 2\alpha \\ \pm \cos 2\alpha & 1 \pm \sin 2\alpha \end{pmatrix}. \quad (2.13)$$

The negative sign refers to the ground state (lo), the plus to the excited state (hi). The trace (sum of eigenvalues) of both matrices is one, their determinants (product of eigenvalues) vanish. Hence, both  $\Pi_{lo}$  and  $\Pi_{hi}$  are projectors, and by construction,

they are orthogonal. The angle  $\alpha$  should be such that

$$H = \begin{pmatrix} E - d\mathcal{E} & -V \\ -V & E + d\mathcal{E} \end{pmatrix} = \epsilon_{\text{lo}}\Pi_{\text{lo}} + \epsilon_{\text{hi}}\Pi_{\text{hi}} \quad (2.14)$$

holds true, where the energy eigenvalues  $\epsilon_{\text{lo,hi}}(\mathcal{E})$  are (2.10). The solution is

$$\sin 2\alpha = \frac{d\mathcal{E}}{\sqrt{V^2 + d^2\mathcal{E}^2}}. \quad (2.15)$$

In fact a plausible result. If there is no external electric field, the previous situation is recovered. If the field is sufficiently weak, the approximation

$$\sin \alpha \approx \frac{d\mathcal{E}}{2V} \quad (2.16)$$

applies which says that the energy eigenstates  $\varrho_{\text{lo,hi}}(\mathcal{E})$  deviate but little from  $\varrho_{\text{lo,hi}}$  without a field.

We are now ready to calculate the dipole moment expectation value. The observable  $D$  is defined by (2.12), the energy eigenstates are given by (2.12). Here is the result:

$$d_{\text{lo}} = \text{Tr} \varrho_{\text{lo}}(\mathcal{E})D = -\frac{d^2\mathcal{E}}{\sqrt{V^2 + d^2\mathcal{E}^2}}, \quad (2.17)$$

and a similar expression for  $d_{\text{hi}}$  (opposite sign).

For  $V \ll d\mathcal{E}$ , i.e. a large electric field, the dipole moments coincide with  $\mp d$ . In the realistic case  $d\mathcal{E} \ll V$  the dipole moment expectation value is proportional to the electric field strength.  $\alpha = d^2/V$  is the polarizability of a single molecule.

### 2.1.4 Ammonium Maser

MASER stands for Microwave Amplification by Stimulated Emission of Radiation. Its counterpart is LASER, Light Amplification by Stimulated Emission of Radiation. Both methods to generate radiation have in common that there is

- a system with at least two energy levels,
- a mechanism for preferring the excited energy level (pumping),
- a triggering causing, with a small amount of energy, a phase-synchronized transition from the high to the low energy level.

We shall discuss the latter effect in section Sect.4.1 on Forced transitions. Normally, in thermal equilibrium, the low energy level is populated with a higher probability than the high energy level, and stimulation will have no effect. Let us here concentrate on the pumping mechanism: a way to create a situation where the

high energy level is populated with a higher probability than the low energy level. For lasers, pumping is usually achieved by forcing transitions to excited states which decay to long lived intermediate states. The ammonia maser is technically rather complicated, but more straightforward to understand.

A beam of ammonia molecules passes through a spatially inhomogeneous electric field. Initially, their polarization is random, because for reasonable temperatures the difference between  $\epsilon_{\text{hi}}$  and  $\epsilon_{\text{lo}}$  is small as compared with  $k_B T$ . However, the energies  $\epsilon_{\text{lo}}(\mathcal{E}(\mathbf{x}))$  and  $\epsilon_{\text{hi}}(\mathcal{E}(\mathbf{x}))$  differ and depend on location. In an inhomogeneous external electric field there are forces

$$\mathbf{F}_{\text{lo,hi}} = -\nabla_x \epsilon_{\text{lo,hi}}(\mathcal{E}(\mathbf{x})) \quad (2.18)$$

which will deflect molecules with different dipole moment in different directions. With this mechanism it is possible to select a beam of excited molecules. When entering a resonator cavity without electric field, practically all ammonia molecules are in the excited  $\varrho_{\text{hi}}$  state. A feeble microwave field with just the right frequency will stimulate phase-synchronized transitions to the  $\varrho_{\text{lo}}$  state and thereby generate a large and coherent output signal.

The 1964 Nobel prize in physics was awarded to Charles Hard Townes, Nicolay Gennadiyevich Basov and Aleksandr Mikhailovich Prokhorov ‘for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle’.

### 2.1.5 Summary

The ammonia molecule comes in two configurations, one being the mirror of the other. The Hilbert space of this system is  $\mathbb{C}^2$  and the associated  $C^*$  algebra consists of complex  $2 \times 2$  matrices.

The Hamiltonian is set up and diagonalized. The eigenstates correspond to superpositions of the two basic configurations, and there is an energy difference between the ground state and the excited state. This energy difference corresponds to a transition frequency of about 24 GHz and a wave length of 1.26 cm.

An external electric field affects the energy eigenvalues of a molecule with intrinsic electric dipole moment, such as the ammonia molecule. This Stark effect, the shift of spectral lines, is normally small and depends quadratically on the electric field strength unless there is a degeneracy which produces a linear effect. We have calculated the net electric dipole moment of polarized molecules.

A beam of randomly polarized ammonia molecules splits, in an inhomogeneous electric field, into two beams. One is made up of molecules in the ground state, the other consists of excited molecules. The excited molecules are injected into a resonance cavity where a tiny signal may cause the coordinated, in-phase transition to the ground state. This is, in a nutshell, the principle of microwave amplification by the stimulated emission of radiation, or MASER.

## 2.2 Quasi-Particles

We will discuss a very much simplified model for the behavior of electrons or holes in a crystal. This model crystal is a regular one-dimensional chain of identical ions plus a charge which can hop from one site to its next neighbors. The charge may be a loosely bound electron or a missing electron, a hole. As we shall see, such charges will move freely in the model crystal. However, their energy-momentum relation depends on the interaction with the surrounding, and the same is true for velocity and mass. The latter, the effective mass, is not a constant property of the particle!

There are two approaches. One may model the crystal by a finite, periodic ring of  $n$  sites and, in the end, send  $n$  to infinity. But it is also possible to describe the infinite crystal straightaway. In the latter case we have to cope with unbounded operators and continuously distributed quasi-eigenvalues. In this context we will discuss wave packets.

Electrons or holes moving in the crystal are quasi-particles because their energy-momentum relation differs from  $\epsilon = p^2/2m$  of non-relativistic free particles. The dispersion relation  $\epsilon = \epsilon(p)$  or  $\omega = \omega(k)$  is determined by the interaction of the particle with its surrounding.

### 2.2.1 Hilbert Spaces $\mathbb{C}^n$ and $\ell^2$

Denote by  $u_r$  the configuration that the electron is located at site  $r$ . An arbitrary configuration will be described by  $c = \sum c_r u_r$  where  $r$  is an integer index.

We describe a periodic structure by  $r = -m, -m + 1, \dots, m - 1, m$ . There are  $n = 2m + 1$  sites. The structure becomes periodic if  $u_{m+1}$  and  $u_{-m}$  are considered to be identical. In this case the crystal lattice has no boundary which is essential for an infinite lattice. The  $n$ -tuples  $\{c_r\}_{r=-m, \dots, m}$  of complex numbers form a linear space  $\mathbb{C}^n$ . Addition and multiplication by scalars is defined componentwise. With the scalar product

$$(d, c) = \sum_{r=-m}^m d_r^* c_r \quad (2.19)$$

$\mathbb{C}^n$  becomes a Hilbert space. The squared vector norm is  $\|c\|^2 = (c, c)$ .

Sending  $n \rightarrow \infty$  gives the linear space  $\mathbb{C}^\infty$  of complex sequences  $\{c_r\}_{r \in \mathbb{Z}}$ . Again, addition and multiplication by scalars is defined componentwise. However, the usual scalar product can only be defined if

$$\|c\|^2 = \sum_{r \in \mathbb{Z}} |c_r|^2 < \infty. \quad (2.20)$$

Then,

$$(d, c) = \sum_{r \in \mathbb{Z}} d_r^* c_r \quad (2.21)$$

converges for all admissible sequences  $c$  and  $d$  because of the Cauchy–Schwarz inequality

$$|(d, c)| \leq \|c\| \|d\|. \quad (2.22)$$

The corresponding Hilbert space is

$$\ell^2 = \{c \in \mathbb{C}^\infty \mid \|c\|^2 < \infty\}, \quad (2.23)$$

the scalar product being (2.21).

Linear mappings  $\mathbb{C}^n \rightarrow \mathbb{C}^n$  are represented by  $n \times n$  matrices of complex numbers. For an arbitrary unit vector  $c \in \mathbb{C}^n$  and a matrix  $A$  we estimate

$$\|Ac\|^2 = \sum_r \left| \sum_s A_{rs} c_s \right|^2 \leq \sum_r \sum_s |A_{rs}|^2 |c_s|^2 \leq n^2 A_{\max}^2. \quad (2.24)$$

We have estimated the matrix elements  $|A_{rs}|^2$  by their maximal value and  $|c_s|^2$  by 1. Equation (2.24) says that the matrix  $A$  is bounded. Addition and multiplication with scalars is componentwise. Multiplication of matrices is matrix multiplication: first  $A$  then  $B$  defines  $BA$ . There is an operator norm  $A \rightarrow \|A\|$  because all matrices are bounded. Adjoining  $A_{rs} \rightarrow A_{rs}^* = A_{sr}^*$  has all properties of a star operation. The set of complex  $n \times n$  matrices is a  $C^*$  algebra.

Let us now turn to the linear mappings  $\ell^2 \rightarrow \ell^2$ .

The bounded operators form a  $C^*$  algebra, with standard addition, multiplication, operator norm and the adjoint as star operation. Unfortunately, however, we also have to do with observables which are unbounded, such as the location operator  $X$ . It cannot be defined on the entire Hilbert space, but only on a linear subspace, its domain of definition.

With  $\mathcal{L} = \mathbb{C}^\infty$  as the initial linear space,  $\mathcal{H} = \ell^2$  as Hilbert space and  $\mathcal{D}$  as domain of definition we have

$$\mathcal{D} \subset \mathcal{H} \subset \mathcal{L}. \quad (2.25)$$

The linear operator  $X : \mathcal{L} \rightarrow \mathcal{L}$  is initially defined by  $(Xc)_r = arc_r$  where  $a$  denotes the distance between adjacent sites. Restricting it to the Hilbert space results in a mapping  $X : \mathcal{H} \rightarrow \mathcal{L}$ . Images  $Xc$  of Hilbert space vectors will not have a finite norm, in general. We therefore restrict  $X$  further to a linear subspace  $\mathcal{D}$  which is defined by

$$\mathcal{D} = \{c \in \mathcal{H} \mid \|Xc\| < \infty\}. \quad (2.26)$$

$X$  now is a linear operator  $X : \mathcal{D} \rightarrow \mathcal{H}$ . What about its adjoint?

Chose  $c \in \mathcal{D}$  and  $d \in \mathcal{H}$ . Then

$$(d, Xc) = a \sum_r d_r^* (rc_r) = a \sum_r (rd_r)^* c_r = (b, c) \quad (2.27)$$

converges. Per definition,  $b = X^*d$  is the adjoint of  $X$ .  $X^*$  is defined on  $\mathcal{D}$  just as  $X$  and does there the same as  $X$ . We conclude  $X = X^*$ . The location observable, although unbounded, is self-adjoint.

### 2.2.2 Hopping Model

Back to physics. We want to describe a loosely localized electron which may hop to its next neighbor to the left or to the right. We describe this by the energy observable

$$H = E I - V(R + L). \quad (2.28)$$

$E$  is the energy level at which the electron is loosely bound.  $R$  and  $L$  are right and left shifts, respectively:

$$Ru_r = u_{r+1} \text{ and } Lu_r = u_{r-1}. \quad (2.29)$$

The hopping amplitude is  $V$ . As we shall see,  $V > 0$  is a sensible choice. Note  $RL = LR = I$ . Right and left shift commute,  $R^{-1} = L$  and  $L^{-1} = R$ . From

$$(d, Rc) = \sum_r d_r^* c_{r-1} = \sum_s d_{s+1}^* c_s = (Ld, c) \quad (2.30)$$

we learn  $R^* = L$  and  $L^* = R$ . Consequently the operators  $R$  and  $L$  are unitary, hence bounded.

What are the energy eigenvectors and eigenvalues? Because of translational symmetry we try a kind of plane waves:

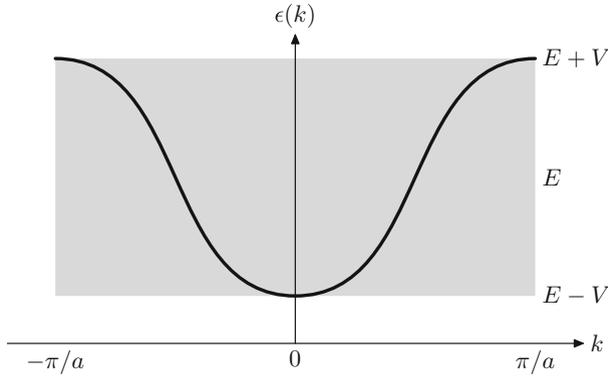
$$w_r \propto e^{ikar}. \quad (2.31)$$

This vector is in fact an eigenvector of  $H$  with eigenvalue

$$\epsilon(k) = \hbar\omega(k) = E - 2V \cos ka. \quad (2.32)$$

For the finite periodic ring, sites  $u_{m+1}$  and  $u_{-m}$  should be considered the same. Therefore, the phase  $kan$  must be an integer multiple of  $2\pi$ . We conclude

$$k_s = \frac{2\pi s}{na} \text{ for } s = -m, -m+1, \dots, m-1, m. \quad (2.33)$$



**Fig. 2.4** Dispersion function of the nearest neighbor hopping model. The function  $E(k) = \hbar\omega(k)$  is plotted versus the wave number  $k$  in the Brillouin zone. The  $n$ -fold degenerate level  $E$  for a localized electron splits into an energy band (*shaded*). In a crystalline solid there is one band for each energy level

There are  $n = 2m + 1$  equally distributed wave numbers  $k_s$  in the interval  $k \in [-\frac{\pi}{a}, +\frac{\pi}{a}]$ . This is the Brillouin zone (Fig. 2.4).

### 2.2.3 Wave Packets

Our arguments for the infinite model crystal remain the same. The difference is that wave numbers are not quantized, but continuously distributed within the Brillouin zone. The dispersion function is a real valued function of a real argument.

We require another modification. The eigenvectors (2.31) belong to  $\mathcal{L} = C^\infty$ , but not to  $\mathcal{H} = \ell^2$ . They cannot be normalized, they are quasi-eigenvectors.

In order to construct normalizable vectors we have to superimpose quasi-eigenvectors by

$$c_r = a \int_{\text{BZ}} \frac{dk}{2\pi} \hat{c}(k) e^{i a k r}, \quad (2.34)$$

where BZ stands for the Brillouin zone. We calculate

$$\sum_r |c_r|^2 = \int_{\text{BZ}} \frac{adq}{2\pi} \int_{\text{BZ}} \frac{adk}{2\pi} \sum_r \hat{c}^*(q) \hat{c}(k) e^{i(k-q)ar}. \quad (2.35)$$

Because of

$$\sum_r e^{i(q-k)ar} = \frac{2\pi}{a} \delta(q-k) \quad (2.36)$$

one obtains

$$\|c\|^2 = a \int_{\text{BZ}} \frac{dk}{2\pi} |\hat{c}(k)|^2 = \|\hat{c}\|^2. \quad (2.37)$$

$\|\hat{c}\|$  is the vector norm of the Hilbert space  $\mathcal{L}_2$  for a finite interval which we shall discuss at a later occasion. With a normalized amplitude  $\hat{c}$  we obtain a normalized wave package.

The energy expectation value for a normalized wave packet—a pure state—is

$$\langle H \rangle = (c, Hc) = a \int_{\text{BZ}} \frac{dk}{2\pi} |\hat{c}(k)|^2 \hbar\omega(k), \quad (2.38)$$

with the dispersion function (2.32). If  $\hat{c} = \hat{c}(k)$  is sharply peaked at  $k = \bar{k}$ , we have realized a wave packet with average energy  $E \approx E(\bar{k})$ . However, this is not an eigenvector.

### 2.2.4 Group Velocity and Effective Mass

Recall that  $R$  and  $L$  commute and note  $[R, X] = -aR$  and  $[L, X] = aL$ .

The quasi-particle's velocity is the observable

$$\dot{X} = \{H, X\} = -\frac{i}{\hbar} \frac{V}{2} [R + L, X] = -\frac{i}{\hbar} \frac{Va}{2} (R - L), \quad (2.39)$$

which, if applied to the wave package (2.34), gives

$$\langle \dot{X} \rangle = a \int_{\text{BZ}} \frac{dk}{2\pi} |\hat{c}(k)|^2 v_{\text{gr}}(k), \quad (2.40)$$

where

$$v_{\text{gr}}(k) = \frac{Va}{\hbar} \sin ka = \omega'(k). \quad (2.41)$$

You should convince yourself that  $Va/\hbar$  is a velocity. We speak of normal dispersion because velocity and wave vector point in the same direction.

And what about the acceleration? Now, for  $H = EI - V(R + L)$  we calculate

$$\ddot{X} = \{H, \dot{X}\} = 0, \quad (2.42)$$

because  $R$  and  $L$  commute. This explains why the mobile electrons in a solid are called quasi-free: they are quasi-particles because their dispersion function is deter-

mined by the surrounding, and they move as free particles, i.e. unaccelerated. How do they respond to an external force?

If an electric field  $\mathcal{E}$  is applied the potential energy  $-q\mathcal{E}X$  has to be added.  $q$  is the particle's charge:  $-e$  for electrons,  $+e$  for holes. The following considerations refer to electrons.

We now have to do deal with the energy

$$H(\mathcal{E}) = EI - V(R + L) + e\mathcal{E}X. \quad (2.43)$$

The expression for the velocity remains the same because the location observable  $X$  commutes with the potential energy. The acceleration is given by

$$\ddot{X} = -\frac{Va^2}{\hbar^2}e\mathcal{E}(L + R). \quad (2.44)$$

For a wave packet (2.34) we find

$$m_{\text{eff}} \langle \ddot{X} \rangle = -e\mathcal{E} \text{ where } \frac{1}{m_{\text{eff}}} = a \int_{\text{BZ}} \frac{dk}{2\pi} |\hat{c}(k)|^2 \frac{1}{\hbar} \omega''(k). \quad (2.45)$$

The effective mass  $m_{\text{eff}}$  is a constant only if energy depends on momentum quadratically which is the case for free particles. Quasi-electrons sufficiently close to the bottom of the energy band have a positive effective mass. The true electron mass  $m_e$  does show up only indirectly if the hopping amplitude  $V$  is calculated within a more basic theory of solids.

By the way, our model can be extended by the possibility to hop directly not only to the next neighbor, but also to next but one, and so on. The dispersion curve then becomes a Fourier series  $V_1 \cos ka + V_2 \cos 2ka + \dots$ . The expressions for the group velocity and effective mass, however, remain unchanged if expressed as derivatives of the dispersion curve.

### 2.2.5 Scattering at Defects

Crystal properties, like conductivity, are determined to a large extent by the interaction of mobile quasi-free electrons with imperfections such as lattice vibrations, dislocations, interstitials, vacancies, or impurities. This is not the right place to discuss imperfections because our crude one-dimensional model cannot describe most of them. We here concentrate on a defect caused by an impurity. At site  $r = 0$  the ordinary ion is replaced by a different one. The energy level of it will differ from  $E$  as well as the hopping amplitude  $V$ . We concentrate on the essential and leave the hopping amplitude untouched.

The following energy observable models the situation:

$$(Hc)_r = E_r c_r - V(c_{r+1} + c_{r-1}) \text{ with } E_r = E - \Delta \delta_{r,0}. \quad (2.46)$$

For the moment we do not bother whether  $\{c_r\}_{r \in \mathbb{Z}}$  is normalizable or not. The energy shift  $\Delta$  may be positive or negative.

A single plane wave will not do because the problem lacks translational symmetry. Guided by intuition we try an incoming plane wave plus an outgoing spherical wavelindexWave!spherical. For one dimension this reads

$$w_r = e^{i kar} + f e^{i ka|r|} \text{ with } k > 0. \quad (2.47)$$

$f = f(k)$  is the scattering amplitude. We have to solve

$$(Hw)_0 = (E - \Delta)w_0 - V(w_1 + w_{-1}) = E(k)w_0 \quad (2.48)$$

and

$$(Hw)_r = E - V(w_{r+1} + w_{r-1}) = E(k)w_r \text{ for } r \neq 0. \quad (2.49)$$

Equation (2.49) is satisfied by (2.47) if  $E(k) = E - V \cos ka$  is chosen, the eigenvalue from the preceding discussion. From (2.48) one obtains

$$f(k) = -\frac{\Delta}{\Delta + 2iV \sin ka}. \quad (2.50)$$

What does this mean?

Our *ansatz* (2.47) describes an incoming wave (amplitude 1), a reflected wave (amplitude  $f$ ) and a transmitted wave (amplitude  $1 + f$ ). Hence, the quasi-electron is reflected with probability  $R$  and transmitted with probability  $T$ ; these are given by

$$R = |f(k)|^2 = \frac{\Delta^2}{\Delta^2 + 4V^2 \sin^2 ka} \quad (2.51)$$

and

$$T = |1 + f(k)|^2 = \frac{4V^2 \sin^2 ka}{\Delta^2 + 4V^2 \sin^2 ka}. \quad (2.52)$$

We list some properties of the scattering amplitude:

- The restriction  $k > 0$  may be dropped. Our results are valid for plane waves running from left to right or from right to left.
- $R + T = 1$ ; no particle gets lost and none is created.
- With  $\Delta \rightarrow 0$  we find  $R \rightarrow 0$  and  $T \rightarrow 1$ . No defect, no scattering.

- Very slow quasi-particles, i.e. with  $k \approx 0$ , will not be transmitted.
- Surprisingly, reflectivity  $R$  and transmittivity  $T$  do not depend on the sign of the energy level difference  $\Delta$ . As we shall see, a defect with positive  $\Delta$  may trap a quasi-electron.  $\Delta < 0$  means repulsion. Attractive and repulsive impurities scatter alike.

### 2.2.6 Trapping by Defects

We rewrite (2.47) as

$$w_r \propto \frac{1}{f(k)} e^{i kar} + e^{i ka|r|} \quad \text{with } k > 0. \quad (2.53)$$

We look for a pole of  $k \rightarrow f(k)$ , which is analytic in the complex  $k$ -plane. If such a pole exists with  $\text{Im } k > 0$ , (2.53) describes a bound state. Now, with  $k = i\kappa$ , there is a pole  $1/f(k) = 0$  if

$$\sinh \kappa a = \frac{\Delta}{2V} \quad (2.54)$$

holds true.  $\text{Im } k > 0$  requires  $\kappa > 0$ , and there is always a solution provided the energy difference  $\Delta$  is positive. The energy level of the defective ion must be lower than the one of the bulk ion. In this case the otherwise mobile quasi-electron is trapped, or immobilized.

Although trapped, it still may be found in its vicinity. It is not difficult to normalize the bound state solution (2.53):

$$w_r = \frac{e^{-\kappa a|r|}}{\sqrt{\tanh \kappa a}}. \quad (2.55)$$

The probability to find the trapped quasi-electron at site  $|r|$  is

$$p_r = |w_r|^2 = \frac{e^{-2\kappa a|r|}}{\tanh \kappa}. \quad (2.56)$$

Small  $\Delta$  means small  $\kappa a$ . Consequently, the extension of the bound state is large. There is a smooth transition from not bound at all to weakly bound to strongly localized.

### 2.2.7 Summary

We have discussed the motion of an electron (or whole) in a one-dimensional model crystal. An electron is loosely localized at an ion and may hop to its next neighbors. We contrast two approaches.

The crystal has finitely many lattice sites and is periodic. This avoids ends, the surface, which would spoil translational symmetry. All linear operators of the corresponding finite-dimensional Hilbert space  $\mathbb{C}^n$  are bounded. More realistic results are obtained if at the end of a calculation  $n$  is sent to infinity

It is also possible to discuss the infinite chain right from the beginning. However, not all vectors of  $\mathbb{C}^\infty$  are normalizable. The subset  $\ell_2$  of normalizable sequences of complex numbers may be equipped with a scalar product to become a Hilbert space. Then, however, we have to deal with unbounded observables, like location  $X$ .

In the case of infinitely many lattice sites, the eigenvector of the energy observable are not normalizable, and one must form normalized wave packets.

The energy eigenvalues, as a function  $\hbar\omega(k)$  of wave number  $k$ , is known as the dispersion function. The dispersion function differs from that of free particles, one therefore speaks of quasi-particles. The electron moves with group velocity  $v_{\text{gr}}$  which is the first derivative of the dispersion function. If an external electric field is applied, the charged quasi-electron reacts with an acceleration. The proportionality factor is the effective mass  $m_{\text{eff}}$  which is not a constant. In fact, it is produced by the electron's interaction with the environment.

Our model even allows to take a crystal defect into account. A normal ion may be replaced by an impurity the energy level of which is  $E - \Delta$  instead of  $E$ . We encounter scattering: an incoming plane wave excites an outgoing spherical wave. The probability  $T$  to be transmitted and the probability  $R$  to be reflected are calculated; they add up to 1.

If the energy level of the impurity is lower than normal ( $\Delta > 0$ ) the otherwise mobile quasi-electron is trapped. There is a smooth transition from not bound at all to loosely bound to strongly bound.

It is generally true that poles of the scattering amplitude in the complex plane indicate bound states.

## 2.3 Neutron Scattering on Molecules

Neutrons are responsive to nucleons only, i.e. protons and neutrons. They are blind to electrons. The shared electrons of two or more nuclei will bind these nuclei to a compound, a molecule. Such a molecule or a molecule ion is seen by neutrons as a rigid configuration of nuclei. The shared electrons are required to glue that configuration, but a neutron will not see them. In this subsection we want to study the scattering on simple and more complex molecules and on a crystal which is nothing else but a giant molecule.

We do so in a formulation which goes back to Richard Feynman.

### 2.3.1 Feynman's Approach

In his famous lectures<sup>1</sup> Feynman postulates three simple rules:

1. The probability of an event in an ideal experiment is given by the square of the absolute value of a complex number  $\phi$  which is called the probability amplitude:

$$\begin{aligned} P &= \text{probability} \\ \phi &= \text{probability amplitude} \\ P &= |\phi|^2 \end{aligned} \tag{2.57}$$

2. When an event can occur in several alternative ways, the probability amplitude for the event is the sum of the probability amplitudes for each way considered separately. There is interference:

$$\begin{aligned} \phi &= \phi_1 + \phi_2 \\ P &= |\phi_1 + \phi_2|^2 \end{aligned} \tag{2.58}$$

3. If an experiment is performed which is capable of determining whether one or another alternative is actually taken, the probability of the event is the sum of the probabilities for each alternative. Interference is lost:

$$P = P_1 + P_2 \tag{2.59}$$

There is no Hilbert space, no observable, and no state, just probabilities, probability amplitudes, and rules for combining them. Feynman got rather far with this concept, but failed to describe something so basic as the hydrogen atom.

The Hilbert space comes into play through the back door. "If an event can occur in several alternative ways" is rather vague. It means that several intermediate mutually orthogonal states are involved. Two states (in the sense of projection on a Hilbert space vector) are either parallel, orthogonal or something in-between. Parallel means they are the same, alternative is associated with orthogonal, and the general case "finding  $g$  in  $f$ " has a probability amplitude  $\phi = (g, f) / \|g\| \|f\|$ .

Let us see how far we will get with the amplitude approach.

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<sup>1</sup><http://www.feynmanlectures.caltech.edu/>.

### 2.3.2 Spherical and Plain Waves

The event “a neutron with wave number  $k$  is emitted at the source  $\mathbf{x}_S$  and detected at location  $\mathbf{x}$ ” has a probability amplitude  $\phi(\mathbf{x}_S, \mathbf{x}, k)$ . No direction is mentioned, so we assume spherical symmetry. Translational invariance—the same amplitude for  $\mathbf{x}_S, \mathbf{x}$  and  $\mathbf{x}_S + \mathbf{a}, \mathbf{x} + \mathbf{a}$ —requires a dependency on both arguments via  $r=|\mathbf{x}_S - \mathbf{x}|$ . The probability to be at any place on a sphere around the source does not depend on its radius. All this amounts to

$$\phi(\mathbf{x}_S, \mathbf{x}, k) = \frac{1}{\sqrt{4\pi}} \frac{e^{ikr}}{r}. \quad (2.60)$$

Indeed, the integral

$$\int_{|\mathbf{x}-\mathbf{x}_S|=R} d\Omega |\phi(\mathbf{x}_S, \mathbf{x}, k)|^2 = 1 \quad (2.61)$$

does not depend on  $R$ .

Let us write  $\mathbf{x} = \mathbf{x}_S + R\mathbf{n} + \boldsymbol{\xi}$  where  $\mathbf{n}$  is a unit vector pointing from the source in direction  $\mathbf{x}$ . The local coordinates with origin  $\mathbf{x}$  are called  $\boldsymbol{\xi}$ . For  $|\boldsymbol{\xi}| \ll R$  the spherical wave is described as

$$\phi(\mathbf{x}_S, \mathbf{x} + \boldsymbol{\xi}, k) \approx \frac{1}{\sqrt{4\pi}} \frac{e^{ikR}}{R} e^{ik\mathbf{n} \cdot \boldsymbol{\xi}}. \quad (2.62)$$

We have approximated

$$r = |R\mathbf{n} + \boldsymbol{\xi}| = \sqrt{R^2 + 2R\mathbf{n} \cdot \boldsymbol{\xi} + \dots} = R + \mathbf{n} \cdot \boldsymbol{\xi} + \dots \quad (2.63)$$

Equation (2.62) says that far away from the source in a restricted area the spherical wavelooks like a plane wave with wave vector  $\mathbf{k} = k\mathbf{n}$ .

### 2.3.3 Neutron Scattering on a Diatomic Molecule

To keep things as simple as possible, we talk about a diatomic molecule with equal nuclei, say  $N_2$ . If the distance between the molecules is  $a$  we write  $\boldsymbol{\xi}_{1,2} = \pm\mathbf{a}/2$  for their locations.

We put a neutron detector at  $\mathbf{x}_D$ . The events are

- a neutron is emitted at  $\mathbf{x}_S$ ,
- it is absorbed and re-emitted by a nucleus a  $\boldsymbol{\xi}_j$ ,
- and is detected  $\mathbf{x}_D$ .

The probability amplitude for this is

$$\phi(\mathbf{x}_S \rightarrow \xi_j \rightarrow \mathbf{x}_D) = \frac{e^{i k R_S}}{\sqrt{4\pi R_S}} e^{i \mathbf{k}_{in} \cdot \mathbf{a}/2} f_j \frac{e^{i k R_D}}{\sqrt{4\pi R_D}} e^{-i \mathbf{k}_{out} \cdot \mathbf{a}/2}. \quad (2.64)$$

$f_j$  is the scattering amplitude for nucleus  $j$ ; here we set  $f_j = f$  because the nuclei are identical. It does not depend on direction because the neutrons we discuss here are slow. More about this in a subsequent chapter.

According to (2.58) we have to sum over  $\mathbf{x}_1$  and  $\mathbf{x}_2$ . The result is

$$\phi(\mathbf{x}_S \rightarrow \mathbf{x}_D) = \frac{2f}{4\pi R_S R_D} \cos \frac{\Delta \cdot \mathbf{a}}{2}. \quad (2.65)$$

$\Delta = \mathbf{k}_{out} - \mathbf{k}_{in}$  is the wave vector transfer from the inbound neutron to the outbound neutron. The probability for a neutron to be scattered by the molecule—the absolute square of (2.65)—

- falls off as  $1/4\pi R_S^2$  with the distance between source and molecule;
- falls off as  $1/4\pi R_D^2$  with the distance between molecule and detector;
- is proportional to  $|f|^2$ , the absolute square of the amplitude for neutron–nitrogen nucleus scattering; and
- depends on the wave vector transfer  $\Delta$  and the molecule orientation  $\mathbf{a}$ .

Before we discuss our result, we rephrase it as an expression for the scattering cross section, and we will also average over the molecule's orientation.

### 2.3.4 Cross Section

A particle which hits an obstacle may ignore it or will be deflected. One speaks of diffraction if the deflected particles run in certain well defined directions only, as is the case if the target is a large enough crystal. If the target is not a crystal, but a gas, liquid or amorphous solid, the deflected particles show a smooth angular distribution, and we speak of scattering.

Denote by  $I = I(x)$  the current density of incident particles.<sup>2</sup> Because of scattering, it depends on the distance  $x$  which the particles have traveled through the target which we assume to be homogeneous. In a thin layer  $dx$  there are  $n dx$  obstacles encountered, per unit area. The number of particles which are removed from the incident beam is proportional to the number of the uncorrelated obstacles, and we write

$$dI = -\sigma n dx, \quad (2.66)$$

<sup>2</sup>Particles per unit time per unit area.

with  $\sigma$  as a proportionality constant. It is an area, a cross section. In classical thinking, if a particle hits it, it will be deflected and removed from the incident beam. Equation (2.66) may be integrated to

$$I(x) = I(0) e^{-\sigma n x}. \quad (2.67)$$

The simplest case is that particles are removed from the incident beam because they are merely deflected by an angle  $\vartheta$ . Unless they are polarized, the azimuth angle  $\varphi$  does not enter. We therefore may write

$$\sigma = \int d\Omega \sigma_d(k, \vartheta). \quad (2.68)$$

The integral over the solid angle is described by

$$\int d\Omega = \int_0^\pi d\vartheta \sin \vartheta \int_0^{2\pi} d\varphi = 4\pi. \quad (2.69)$$

The differential cross section  $\sigma_d = \sigma_d(k, \vartheta)$  normally depends on the wave number of the incident particles and on the deflection angle.

### 2.3.5 Orientation Averaged Cross Section

The differential cross section for neutron–atom scattering is

$$\sigma_d^A = |f|^2, \quad (2.70)$$

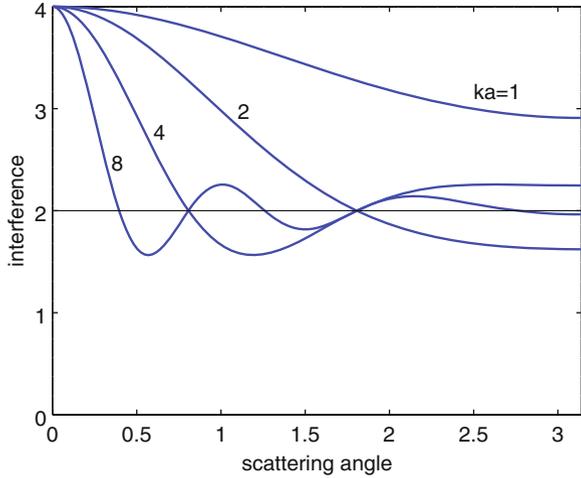
as we will discuss in detail in a later section. Therefore, the differential cross section for neutron–molecule scattering is

$$\sigma_d^M = \left\{ 4 \cos^2 \frac{\Delta \cdot \mathbf{a}}{2} \right\} \sigma_d^A. \quad (2.71)$$

Before discussing this result we should average over the molecule's orientation. Diatomic molecule with equal nuclei, like  $\text{N}_2$ , cannot have an electric dipole moment which is required for at least partially orienting them in an external electric field. So the target—a gas or liquid—is unpolarized, and we obtain

$$\sigma_d^M = 2 \left\{ 1 + \frac{\sin \Delta a}{\Delta a} \right\} \sigma_d^A \quad (2.72)$$

**Fig. 2.5** Differential neutron-nitrogen molecule cross section. The interference factor  $\sigma_d^M/\sigma_d^A$  is plotted versus the scattering angle  $\vartheta$  for  $ka = 1, 2, 4, 8$  in decreasing order. Values above 2 mean constructive interference while values below 2 signify destructive interference



This result is truly remarkable (Fig. 2.5).

Recall that  $a$  is the distance between the two nitrogen nuclei.  $\Delta$  stands for the wave number transfer from the incoming to the outgoing neutron. It is given by

$$\Delta = 2k \sin \frac{\vartheta}{2}. \tag{2.73}$$

$\Delta a$  is dimensionless. A very small value indicates slow neutrons or a small scattering angle. We obtain

$$\sigma^M = 4\sigma^A \text{ for } \Delta a \ll 1. \tag{2.74}$$

For large wave vector transfer, however, the result is

$$\sigma^M = 2\sigma^A \text{ for } \Delta a \gg 1. \tag{2.75}$$

Equation (2.74) means maximal constructive interference. The amplitude doubles, the cross section becomes four times as large. Equation (2.75) says that there is no interference. The cross section for two nitrogen atoms, although bound to a molecule, is simply twice the cross section for a single nucleus. This is the view of classical mechanics. However, the region in between,  $\Delta a \approx 1$ , is interesting. The measured differential cross section  $\sigma_d^M = \sigma_d^M(k, \vartheta)$  may be fitted to (2.72). In this way the structure of the target particle—being diatomic with nucleus distance  $a$ —may be determined even though the molecules are oriented at random.

The example shows why one needs bigger and bigger accelerators to unveil the structure of ever tinier elementary particles. Only with head-on collisions of energetic particles a high momentum transfer  $\hbar\Delta$  may be achieved. By high-energy electron nucleon scattering, for example, it could be proven that protons and neutron are composite particles of three quarks.

### 2.3.6 Neutron Diffraction

In the introductory chapter we have mentioned the impact of electron diffraction experiments. It was clear at this time that electrons are particles and X-rays are waves, electromagnetic waves. However, such particles produced the same diffraction pattern as X-rays. Likewise, the electromagnetic wave comes in lumps, so called photons.

In order to substantiate the viewpoint of particle waves we will discuss neutron-crystal scattering which, as it turns out, is diffraction.

We simply replace the nitrogen molecule by a crystal. To keep things simple, we assume a crystal of one species of ions only. We say ions, because part of the electrons is localized around the nuclei, the remainder is shared and glues the crystal together. Neutrons do not see them.

There are three vectors  $\mathbf{a}^{(1)}$ ,  $\mathbf{a}^{(2)}$ , and  $\mathbf{a}^{(3)}$  which translate copies of the unit cell at the origin. The most general unit cell is situated at

$$\boldsymbol{\xi}_j = \boldsymbol{\xi}_{j_1 j_2 j_3} = j_1 \mathbf{a}^{(1)} + j_2 \mathbf{a}^{(2)} + j_3 \mathbf{a}^{(3)}, \quad (2.76)$$

where the indexes are integer numbers.  $j_1$  runs in  $[-N_1, N_1]$ ,  $j_2$  and  $j_3$  likewise. There are altogether  $(2N_1 + 1)(2N_2 + 1)(2N_3 + 1)$  unit cells which form our crystal.

We generalize (2.64) by replacing  $\pm \mathbf{a}/2$  with  $\boldsymbol{\xi}_j$  and sum over all index triples:

$$I(\boldsymbol{\Delta}) = \left| \sum_j f_j e^{i \boldsymbol{\Delta} \cdot \boldsymbol{\xi}_j} \right|^2. \quad (2.77)$$

$I = I(\boldsymbol{\Delta})$  is the intensity dependency on wave vector transfer. In our example—one species of nuclei only—all scattering amplitudes  $f_j$  are equal. The sum extends over  $j = (j_1, j_2, j_3)$  as in (2.76). One finds

$$I(\boldsymbol{\Delta}) = |f|^2 S_1 S_2 S_3 \quad (2.78)$$

where the factors  $S$  stands for

$$S_1 = \frac{\sin^2 N_1 \boldsymbol{\Delta} \cdot \mathbf{a}^{(1)}/2}{\sin^2 \boldsymbol{\Delta} \cdot \mathbf{a}^{(1)}/2}, \quad (2.79)$$

with similar expressions for  $S_2$  and  $S_3$ . Their order of magnitude is 1 unless the denominator vanishes:

$$\boldsymbol{\Delta} \cdot \mathbf{a}^{(r)} = 2\pi\nu_r \text{ with } \nu_1, \nu_2, \nu_3 \in \mathbb{Z}. \quad (2.80)$$

If these three Laue conditions<sup>3</sup> are satisfied simultaneously, a narrow pencil of diffracted neutrons is observed; otherwise there is just a feeble background.

The same conditions apply to X ray diffraction experiments. The incident wave then is a spherical wave which is emitted by the anode of an X ray tube. The crystal ions  $j$  get polarized periodically, and the oscillating dipole moment emits secondary spherical waves the power of which is registered at the detector. The emitters are excited by one and the same wave, so they oscillate in phase. By the superposition principle of electromagnetism, the fields of the emitters  $j$  sum up and yield an expression (2.77). Instead of the scattering amplitude, the ion's polarizability shows up. No wonder X ray, electron or neutron diffraction are alike.

### 2.3.7 Summary

We have learned that three simple rules for probability amplitudes suffice to describe, for example, the interaction of particles with composite structures. Probabilities  $P$  are absolute squares of probability amplitudes  $\phi$ . If there are alternative intermediate stages and if the particular alternative is not registered, amplitudes add up and the sum must then be squared. In contrast, if the alternative leaves a foot-print, then amplitudes must first be squared to probabilities which are to be summed.

We explain how to describe the scattering process by a differential cross section. It depends on the wave number of the incoming neutrons and on the scattering angle.

The scattering of slow neutrons by diatomic molecules with the same nucleus is the simplest possible case. Even if the molecules are randomly oriented, the differential cross section exhibits a characteristic dependency on the wave number of the incoming neutrons and on the scattering angle. There is maximal constructive interference in forward direction or for slow neutrons. The faster the incoming neutrons, the less interference is observed. In the intermediate region there is even destructive interference. By fitting the data to a model, the molecular structure can be elucidated: number of nuclei, whether they are identical, and their distance.

## 2.4 Free Particles

In this section we consider a single freely moving particle. To simplify even more, we consider one spatial dimension only. The generalization to three dimensions is straightforward although we did not yet discuss angular momentum.

Throughout in this chapter we argue along Schrödinger's line: states change with time, observables remain fixed. We also confine the discussion to pure states to be described by normalized vectors.

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<sup>3</sup>They are equivalent to the Bragg conditions.

The Hilbert space of square-integrable wave function is presented with a digression on test functions. The most interesting linear operators are not bounded, in particular location, linear momentum and energy. Suitable domains of definition have to be introduced. Although self-adjoint, these operators have continuously distributed quasi-eigenvalues with quasi-eigenfunctions which are not in the Hilbert space.

We derive the well-known explicit expression for the linear momentum observable and the canonical commutation relation.

Only then we focus on freely moving particles. We show that the average location moves with constant speed and that the particle's localization deteriorates in the course of time. We conclude with a remark on the classical limit.

### 2.4.1 Square Integrable Functions

Think of a particle that has been prepared in some pure state. As we know, such states are described by one-dimensional projections. They project on a linear subspace which is spanned by a normalized vector.

We refer to the probability amplitude  $f = f(x)$  for the event that the particle is found at location  $x$ . More precisely, the probability  $dw$  to find the particle in the small interval  $[x - dx/2, x + dx/2]$  is proportional to the probability amplitude squared,

$$dw = dx |f(x)|^2. \quad (2.81)$$

The probability that the particle is found anywhere is one,

$$\int dw = \int dx |f(x)|^2 = 1. \quad (2.82)$$

This says that  $f$  describes a state, since it is normalized.

The Hilbert space under discussion therefore is the linear space of square normalizable functions,

$$\mathcal{H} = \mathcal{L}_2(\mathbb{R}) = \{f : \mathbb{R} \rightarrow \mathbb{C} \mid \int dx |f(x)|^2 < \infty\}. \quad (2.83)$$

The natural choice for a scalar product is

$$(g, f) = \int dx g^*(x) f(x). \quad (2.84)$$

It is finite for all  $g, f \in \mathcal{H}$  because of the Cauchy–Schwarz inequality.  $\mathcal{L}_2(\mathbb{R})$  denotes the Lebesgue square-integrable functions living on  $\mathbb{R}$ . Complex valued is silently understood. More on the Lebesgue integral can be found in the chapter on Mathematical Aspects.

### 2.4.2 Location

Let us investigate the location observable  $X$  declared by  $(Xf)(x) = xf(x)$ , i.e. multiplication of the function with its argument.  $X$  is not bounded and therefore not defined for all wave-functions  $f \in \mathcal{H}$ . Just take the sequence  $f_1, f_2, \dots$  where  $f_j(x) = 1$  in the interval  $j \leq x \leq j+1$  and vanishes outside. The  $f_j$  are normalized, and we estimate  $\|Xf_j\| \geq j$ . It follows that  $X$  is unbounded. However, the location operator can be defined on the following domain of definition:

$$\mathcal{D}_X = \{f \in \mathcal{H} \mid \int dx |xf(x)|^2 < \infty\}. \quad (2.85)$$

Note that  $X^*$  does the same as  $X$  and is also defined on  $\mathcal{D}_X$ . Therefore, the location operator is self-adjoint.

There is another way how to cope with physically important, but unbounded operators.

A test function  $t : \mathbb{R} \rightarrow \mathbb{C}$  is infinitely often continuously differentiable and vanishes at  $|x| \rightarrow \infty$ , even after it has been multiplied by an arbitrary polynomial. We denote the linear subspace of test functions by  $\mathcal{S}$ . This test function space  $\mathcal{S}$  is dense in  $\mathcal{H}$  which we will not prove here. Any Hilbert space vector can be approximated arbitrarily well by test functions. Hence, studying  $X$  on the linear space of test functions is nearly the same as studying it on the entire Hilbert space. Clearly, if  $t$  is a test function, the image  $Xt$  is a test function as well.

Let us summarize these considerations by  $X\mathcal{S} \subset \mathcal{S}$  and  $X\mathcal{D}_X \subset \mathcal{H}$ .

### 2.4.3 Linear Momentum

As we know, the linear momentum is the generator of translations. Denote by  $f_a = f_a(x) = f(x+a)$  the translated wave function, a test function say. We expand this into a Taylor series:

$$f(x+a) = f(x) + \frac{a}{1!}f'(x) + \frac{a^2}{2!}f''(x) + \dots \quad (2.86)$$

This may be rewritten into

$$f_a(x) = \left( f + \frac{ia}{1!}Kf + \frac{ia^2}{2!}K^2f + \dots \right) (x) \quad (2.87)$$

or

$$f_a = e^{iaK} f \text{ or } f_a = e^{\frac{i}{\hbar}aP} f. \quad (2.88)$$

The wave number operator  $K$  and the linear momentum  $P$  are

$$K = -i \nabla \text{ and } P = -i \hbar \nabla, \text{ respectively.} \quad (2.89)$$

$\nabla$  stands for ordinary differentiation.

Chapter 1 on Basics is about an arbitrary system described by an abstract Hilbert space. There we discussed spatial translations and its generator, the linear momentum. Now we talk about a specific system with its specific Hilbert space  $\mathcal{L}_2(\mathbb{R})$  of wave functions. No wonder why we now obtain a concrete representation of the momentum operator, an expression which operates on wave functions.

In which sense is the linear momentum operator self-adjoint? It is certainly not defined on the entire Hilbert space since not all square-integrable functions are differentiable.

A function  $f = f(x)$  is absolutely continuous if it can be written as an integral from  $-\infty$  to  $x$  over a square-integrable function  $g$ . We declare the derivative of it by  $f'(x) = g(x)$ . The largest domain of definition for the momentum operator therefore is

$$\mathcal{D}_P = \{f \in \mathcal{H} \mid f(x) = c + \int_{-\infty}^x dy g(y) \text{ where } g \in \mathcal{H}\}. \quad (2.90)$$

$\nabla$  is well defined on  $\mathcal{D}_P$ , and we show in the chapter on Mathematical Aspects that the momentum operator is self-adjoint with this domain of definition.

The momentum operator evidently maps test functions into test functions. It is a simple exercise to prove, by partial integration, that

$$(Pu, t) = (u, Pt) \text{ for } t, u \in \mathcal{S} \quad (2.91)$$

holds true. This is no proof that  $P$  is self-adjoint, however, rather close to it.

We summarize these domain considerations by  $P\mathcal{S} \subset \mathcal{S}$  and  $P\mathcal{D}_P \subset \mathcal{H}$ .

By the way, the commutation relation of location and momentum is calculated by

$$[X, P]f(x) = x \frac{\hbar}{i} f'(x) - \frac{\hbar}{i} (xf(x))' = -\frac{\hbar}{i} f(x), \quad (2.92)$$

i.e.

$$[X, P] = i\hbar I \text{ or } \{X, P\} = I. \quad (2.93)$$

The latter formula can be found in Sect. 1.2 on the Classical Framework as well as in Sect. 1.3 on the Quantum Framework in Chap. 1 on Basics.

### 2.4.4 Wave Packets

Formally, the eigenfunctions of the location operator are

$$\xi_a(x) = \delta(x - a), \quad (2.94)$$

because of  $X\xi_a(x) = x\delta(x - a) = a\delta(x - a) = a\xi_a(x)$ . The eigenvalue is  $a$ , a real number. The  $\delta$ -distribution, however, cannot be squared and integrated. It is not in the Hilbert space; and it is not a proper eigenfunction. In the following sense, however, it serves as such:

$$f(x) = \int da f_a \xi_a(x). \quad (2.95)$$

The integral replaces the sum over eigenvalues, and each quasi-eigenfunction  $\xi_a$  is multiplied by a coefficient  $f_a = f(a)$ . The decomposition (2.95) is of no use.

The situation is different for the momentum observable. The eigenvalue equation for  $\pi_q(x)$  reads

$$P\pi_q = q\pi_q \text{ or } \frac{\hbar}{i}\pi'_q(x) = q\pi_q(x). \quad (2.96)$$

The solution is

$$\pi_q(x) = e^{\frac{i}{\hbar}qx}, \quad (2.97)$$

it exists for all real eigenvalues  $q$ . These solutions, however, are not in the Hilbert space since  $|\pi_q(x)|^2 = 1$  cannot be integrated over  $x \in \mathbb{R}$ .

The decomposition of an arbitrary wave function into momentum quasi-eigenfunctions (2.97) is

$$f(x) = \int \frac{dq}{2\pi\hbar} \hat{f}(q) \pi_q(x) = \int \frac{dq}{2\pi\hbar} \hat{f}(q) e^{\frac{i}{\hbar}qx}. \quad (2.98)$$

This is nothing else but the Fourier transformation  $f \rightarrow \hat{f}$  of the wave function! The integral replaces the usual sum over eigenvalues. The exponentials are the quasi-eigenfunctions which get multiplied by the Fourier transform  $\hat{f}$ .

Because of

$$\int dx e^{\frac{i}{\hbar}(q'' - q')x} = 2\pi\hbar \delta(q'' - q') \quad (2.99)$$

one calculates

$$\int dx |f(x)|^2 = \int \frac{dq}{2\pi\hbar} |\hat{f}(q)|^2. \quad (2.100)$$

If  $f$  is square-integrable, then its Fourier transform  $\hat{f}$  is square-integrable as well.

Momentum quasi-eigenfunctions, or plain waves, are not admissible to represent a pure state, but packets (2.98) of plane waves are.

### 2.4.5 Motion of a Free Particle

For a free particle, the Hamiltonian depends on the momentum only, and not on location. This may be

$$H = \sqrt{m^2 c^4 + P^2 c^2} \quad (2.101)$$

for a relativistic particle of mass  $m$  or

$$H = mc^2 + \frac{1}{2m} P^2 \quad (2.102)$$

in non-relativistic approximation.

Recall that states  $f = f_t$  change with time according to the Schrödinger equations

$$\frac{d}{dt} f_t = -\frac{i}{\hbar} H f_t. \quad (2.103)$$

The average location of the particle at time  $t$  is

$$\langle X \rangle_t = \int dx f_t^*(x) X f_t(x). \quad (2.104)$$

We calculate

$$\frac{d}{dt} \langle X \rangle_t = \int dx f_t^*(x) \{X, H\} f_t(x). \quad (2.105)$$

In non-relativistic approximation (2.102) we have

$$\{X, P^2\} = P\{X, P\} + \{X, P\}P = 2P \quad (2.106)$$

and therefore

$$\frac{d}{dt} \langle X \rangle_t = \frac{1}{m} \langle P \rangle_t. \quad (2.107)$$

If we differentiate once more with respect to time, we will encounter the commutator of the momentum with the energy. It vanishes for a free particle since the energy is a function of momentum only. Thus,

$$\frac{d}{dt} \langle P \rangle_t = 0 \text{ and } \frac{d^2}{dt^2} \langle X \rangle_t = 0. \quad (2.108)$$

A free particle moves with constant velocity, unaccelerated.

### 2.4.6 Spreading of a Free Particle

How well can a particle be localized? We shall answer this question soon for a free particle.

The variance  $\sigma^2(X) = \langle X^2 \rangle - \langle X \rangle^2$  is a measure of localization. In order to simplify the calculation we choose an inertial system such that the particle—which moves with constant velocity—is at rest,  $\langle X \rangle_t = 0$ . Then the momentum expectation value  $\langle P \rangle_t$  vanishes as well, see (2.107). It follows that  $\langle X^2 \rangle$  and  $\langle P^2 \rangle$  are the respective variances. How do they depend on time?

The momentum variance does not change with time. For the location we calculate

$$\frac{d}{dt} \langle X^2 \rangle_t = \int dx f_t^*(x) \{X^2, H\} f_t(x), \quad (2.109)$$

in analogy with (2.105). The Poisson bracket gives  $(XP + PX)/m$ . The second derivative results in (2.109), and the bracket now reads  $\{XP + PX, P^2\}/2m^2 = 2P^2/m^2$ . Hence:

$$\frac{d^2}{dt^2} \langle X^2 \rangle_t = \frac{2}{m^2} \langle P^2 \rangle, \quad (2.110)$$

or

$$\sigma^2(X)_t = \sigma^2(X)_0 + \frac{\sigma^2(P)}{m^2} t^2. \quad (2.111)$$

This result requires interpretation.

Equation (2.110) says that the second derivative with respect to time is a positive constant, the solution therefore a convex parabola. Such a parabola has a minimum at a certain time which we chose to be  $t = 0$ . The precision with which the particle is localized grows quadratically with time. The minimal spread cannot be made to vanish since

$$\sigma(X) \sigma(P) \geq \frac{\hbar}{2} \quad (2.112)$$

holds true for any state  $f$ . This is Heisenberg's uncertainty relation which we discussed in the Introduction Sect. 1.1 and in the chapter on Mathematical Aspects.

Often the spread of an observable  $M$  is assessed by the standard deviation  $\sigma(M) = \sqrt{\langle M^2 \rangle - \langle M \rangle^2}$ . Heisenberg's uncertainty principle reads  $\sigma(X) \sigma(P) \geq \hbar/2$ . Equation (2.111) says that the spread of the wave packet ultimately grows linearly with time.

Also note that the spread growth rate is inversely proportional to the mass. The more massive a particle, the longer it behaves classically, i.e. it does not spread at all.

### 2.4.7 Summary

The probability amplitude  $f = f(x)$  for finding the particle at a certain location  $x$  is a wave function. Linear combinations of such wave functions span the Hilbert space of square-integrable functions of one real argument with its natural scalar product.

The location and the linear momentum operators have been discussed. The former multiplies the wave function by its argument, the latter amounts to differentiation. Both operators are unbounded and cannot be defined on the entire Hilbert space, and we have said a few words on their respective domains of definitions. We also introduce test functions which form a dense linear subspace. Location and momentum obey the canonical commutation relations.

Instead of discrete eigenvalues and their eigenvectors we encounter a continuum of quasi-eigenvalues and quasi-eigenfunctions which are not in the Hilbert space. Nevertheless, any wave function may be decomposed into such quasi-eigenfunctions, the sum being replaced by an integral. In the case of the momentum observable one has re-discovered the Fourier decomposition.

The energy of a free particle does not depend on location; it depends on momentum only. Therefore, the particle's average location moves with constant velocity. However, it tends to spread. The spread, as assessed by the root mean square deviation increases linearly with time. The more massive the particle, the longer one can ignore the deterioration of location.

As a consequence, although self-adjoint, both observables have eigenvectors which are not in the Hilbert space. Nevertheless, replacing the sum by an integral over the quasi-eigenvalues, any wave function may be expanded into quasi-eigenfunctions. We also re-derive the canonical commutation rules, now for a concrete representation and briefly discuss wave packets.

We then have focused on free particles: the Hamiltonian depends on momentum only, it is translationally invariant. We demonstrated that the particle's average location moves with constant speed, the classical result. In the course of time, however, the particle spreads out more and more. The more massive the particle, the longer this effect can be ignored.

## 2.5 Small Oscillations

The following situation is encountered rather often. There is a stable equilibrium configuration with  $X$  denoting the deviation from it. The potential energy, which has its minimum at the equilibrium configuration, may be expanded around  $X = 0$ . The linear term vanishes because we assume equilibrium. The quadratic term is positive because the equilibrium is stable. Close-by configurations have a larger potential energy. Higher powers of the deviation, so-called anharmonicities, are neglected. One speaks of an harmonic oscillator. To a good approximation, the vibrational degrees of freedom of molecules and of solids are small oscillations, the latter giving rise

to the concept of phonons. We shall present in this section an algebraic approach to diagonalizing the Hamiltonian of the harmonic oscillator. There is a ladder of eigenstates with operators for climbing up and down this ladder. The wave function representations of eigenstates, the eigenfunctions, are calculated as well.

In this book shall come across ladder operators several times, for instance when the irreducible representations of angular momentum are studied or when discussing the particle number as an observable.

### 2.5.1 The Hamiltonian

Let us write

$$H = \frac{1}{2m} P^2 + \frac{m\omega^2}{2} X^2 \quad (2.113)$$

for the Hamiltonian.  $m$  is a mass and  $m\omega^2$  the positive spring constant. The self-adjoint operators  $X$  and  $P$  shall satisfy the canonical commutation relations

$$[X, P] = i\hbar I. \quad (2.114)$$

In the Heisenberg picture we calculate

$$\dot{X} = \{X, H\} = \frac{1}{m} P \quad \text{and} \quad \ddot{X} = \{\dot{X}, H\} = -\omega^2 X, \quad (2.115)$$

as expected.

We define the linear operator

$$A = \sqrt{\frac{m\omega}{2\hbar}} X + i \sqrt{\frac{1}{2m\omega\hbar}} P. \quad (2.116)$$

The following commutation rule is basic for what follows

$$[A, A^\star] = I. \quad (2.117)$$

Here we just state that the energy can be written as

$$H = \hbar\omega \left( N + \frac{1}{2} I \right) \quad \text{where} \quad N = A^\star A. \quad (2.118)$$

$N$  is self-adjoint while  $A$  is not.

### 2.5.2 Ladder Operators

The self-adjoint operator  $N$  has real eigenvalues. Let  $z$  be one of them and  $e$  the corresponding normalized eigenfunction:

$$Ne = ze. \quad (2.119)$$

Because of

$$[A^\star, N] = [A^\star, A^\star A] = A^\star[A^\star, A] = A^\star \quad (2.120)$$

we conclude

$$NA^\star e = A^\star Ne + A^\star e = (z + 1)A^\star e. \quad (2.121)$$

This says that  $A^\star e$  is another eigenvector of  $N$  with eigenvalue  $z + 1$ . Likewise,  $Ae$  is an eigenvector of  $N$  with eigenvalue  $z - 1$ , because of

$$[N, A] = -A \quad (2.122)$$

and

$$NAe = ANe - Ae = (z - 1)Ae. \quad (2.123)$$

By repeating this procedure one might conclude that the eigenvalues of  $N$  are  $z, z \pm 1, z \pm 2$ , and so on.

However, this cannot be the case since  $N$  is non-negative, and consequently its eigenvalues must also be non-negative. How to resolve this dilemma?

Well, eigenvectors must be normalized or normalizable. When stepping down, one will encounter a vanishing vector which erroneously went for an eigenvector. There must be a normalized vector  $\Omega$  such that

$$A\Omega = 0, \quad (2.124)$$

the null vector.  $N\Omega = 0$  says that this vector  $e_0 = \Omega$  is an eigenvector of  $N$  with eigenvalue 0. Therefore, all eigenvectors are obtained by stepping up repeatedly,

$$e_n = \frac{(A^\star)^n}{\sqrt{n!}} \Omega \text{ for } n = 0, 1, 2, \dots \quad (2.125)$$

One can show by complete induction that the  $e_n$  are normalized and obey

$$Ne_n = ne_n. \quad (2.126)$$

$N$  is a number operator: its eigenvalues are the natural numbers.

Now we have solved the initial task, namely to diagonalize the energy:

$$H e_n = \left( n + \frac{1}{2} \right) \hbar \omega e_n. \quad (2.127)$$

The energy levels are equidistant.

### 2.5.3 Eigenstate Wave Functions

Up to now we did not have to specify the Hilbert space. The above spectrum of energy eigenvalues and the corresponding eigenstates have been obtained by purely algebraic means. We have employed the canonical commutation rules and nothing else. We now want to construct the wave functions.

We therefore specialize to the Hilbert space  $\mathcal{H} = \mathcal{L}_2(\mathbb{R})$ . Now the location operator  $X$  and the linear momentum are described by

$$(Xf)(x) = xf(x) \text{ and } (Pf)(x) = \frac{\hbar}{i} f'(x). \quad (2.128)$$

Stepping down with  $A$  is terminated by the condition  $A\Omega = 0$  which translates to

$$\Omega'(x) + \kappa^2 x \Omega(x) = 0 \text{ where } \kappa = \sqrt{\frac{m\omega}{\hbar}}. \quad (2.129)$$

Note that  $\kappa$  has the dimension of an inverse length. The solution is

$$e_0(x) = \Omega(x) \propto e^{-\kappa^2 x^2 / 2}. \quad (2.130)$$

This Gaussian is the ground state of the harmonic oscillator. It is an even function of  $x$ .

The first excited state is generated by applying  $A^*$  to the ground state. One obtains

$$e_1(x) = A^* \Omega(x) \propto x \Omega(x). \quad (2.131)$$

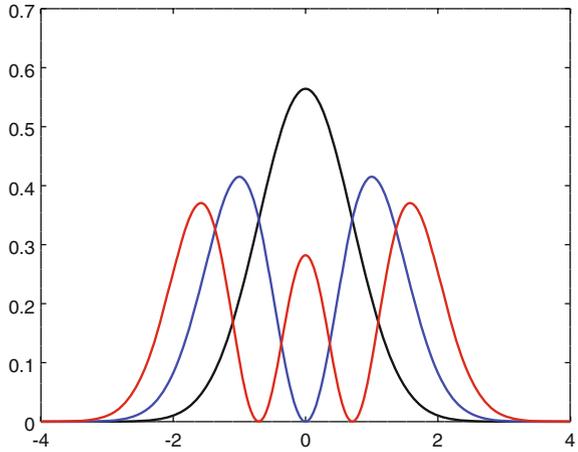
This is an odd function.

It should have become clear by how to proceed. There is a closed formula

$$e_n(x) \propto H_n(\kappa x) e^{-\kappa^2 x^2 / 2} \quad (2.132)$$

where the  $H_n$  are Hermite polynomials. Unfortunately, we must stop here.

**Fig. 2.6** Harmonic oscillator eigenfunctions. The probability densities  $|e_n(x)|^2$  are plotted versus  $\kappa x$  for the lowest three eigenstates. The ground state has one peak, the next two, and so on



Note that all harmonic oscillator eigenfunctions are test functions. They may serve as an orthogonal base for the linear subspace  $\mathcal{S}$ .

We have plotted the probability density  $|e_n(x)|^2$  for the lowest eigenstates  $n = 0, 1, 2$  in Fig. 2.6.

### 2.5.4 Summary

We have justified the harmonic oscillator model for small oscillations about a stable equilibrium. The Hamiltonian which is quadratic in both momentum  $P$  and deviation  $X$  may be re-written in  $\hbar\omega N$  where  $N = A^\star A$  is a number operator.

This was established by observing that  $A^\star$  climbs up and  $A$  steps down a ladder of eigenstates by one. Since the harmonic oscillator Hamiltonian is bounded from below, there must be a ground state  $\Omega$  to be annihilated by  $A$ . The energy eigenvalues are  $n\hbar\omega$  where  $n \in \mathbb{N}$  plus an irrelevant constant energy shift  $\hbar\omega/2$ .

By choosing a representation in terms of wave-functions, the ground state  $e_0 = \Omega(x)$  and all energetically higher excited states can be calculated. The harmonic oscillator eigenfunctions are test functions, they may serve as an orthogonal base.



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