Mössbauer spectroscopy is based on recoilless emission and resonant absorption of γ-radiation by atomic nuclei. The aim of this chapter is to familiarize the reader with the concepts of nuclear γ-resonance and the Mössbauer effect, before we describe the experiments and relevant electric and magnetic hyperfine interactions in Chaps. 3 and 4. We prefer doing this by collecting formulae without deriving them; comprehensive and instructive descriptions have already been given at length in a number of introductory books ([7–39] in Chap. 1). Readers who are primarily interested in understanding their Mössbauer spectra without too much physical ballast may skip this chapter at first reading and proceed directly to Chap. 4. However, for the understanding of some aspects of line broadening and the preparation of optimized samples discussed in Chap. 3, the principles described here might be necessary.

2.1 Nuclear γ-Resonance

Most readers are familiar with the phenomenon of resonant absorption of electromagnetic radiation from the observation of light-induced electronic transitions. Visible light from a white incident beam is absorbed at exactly the energies of the splitting of d-electrons in transition metal ions or at the energies corresponding to metal-to-ligand charge transfer transitions in coordination compounds. These are the most common causes of color in inorganic complexes. Only when the quantum energy of the light matches the energy gap between the electronic states involved does such resonant absorption occur.

An analogous process is possible for γ-radiation, for which nuclear states are involved as emitters and absorbers. In such experiments, the emission of the γ-rays is mostly triggered by a preceding decay of a radioactive precursor of the resonance nuclei with Z protons and N neutrons (Fig. 2.1). The nuclear reaction (α-, or β-decay, or K-capture) yields the isotope (Z, N) in the excited state (e) with energy $E_e$. The excited nucleus has a limited mean lifetime $\tau$ and will undergo a transition to its ground state (g) of energy $E_g$, according to the exponential law of decay. This leads,
with a certain probability, to the emission of a $\gamma$-photon, which has the quantum energy $E_0 = E_e - E_g$ if the process occurs without recoil. Under this, and certain other conditions which we shall discuss below, the $\gamma$-photon may be reabsorbed by a nucleus of the same kind in its ground state, whereby a transition to the excited state of energy $E_e$ takes place. The phenomenon, called nuclear resonance absorption of $\gamma$-rays, or Mössbauer effect, is described schematically in Fig. 2.1.

Resonant $\gamma$-ray absorption is directly connected with nuclear resonance fluorescence. This is the re-emission of a (second) $\gamma$-ray from the excited state of the absorber nucleus after resonance absorption. The transition back to the ground state occurs with the same mean lifetime $\tau$ by the emission of a $\gamma$-ray in an arbitrary direction, or by energy transfer from the nucleus to the K-shell via internal conversion and the ejection of conversion electrons (see footnote 1).

Nuclear resonance fluorescence was the basis for the experiments that finally led to R. L. Mössbauer’s discovery of nuclear $\gamma$-resonance in $^{199}$Ir ([1–3] in Chap. 1) and is the basis of Mössbauer experiments with synchrotron radiation which can be used instead of $\gamma$-radiation from classical sources (see Chap. 9).

In order to understand the Mössbauer effect and the importance of recoilless emission and absorption, one has to consider a few factors that are mainly related to the fact that the quantum energy of the $\gamma$-radiation used for Mössbauer spectroscopy ($E_0 \approx 10–100$ keV) is much higher than the typical energies encountered, for instance, in optical spectroscopy (1–10 eV). Although the absolute widths of the

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1Not all nuclear transitions of this kind produce a detectable $\gamma$-ray; for a certain portion, the energy is dissipated by internal conversion to an electron of the K-shell which is ejected as a so-called conversion electron. For some Mössbauer isotopes, the total internal conversion coefficient $\alpha_T$ is rather high, as for the 14.4 keV transition of $^{57}$Fe ($\alpha_T = 8.17$). $\alpha_T$ is defined as the ratio of the number of conversion electrons to the number of $\gamma$-photons.
energy levels involved in both spectroscopies are rather similar ([15] in Chap. 1), the relative widths of the nuclear levels are very small because of the high mean energies ($\Delta E/E_0 \approx 10^{-13}$ or less, see Fig. 2.2). Consequently, the recoil connected with any emission or absorption of a photon is a particular problem for nuclear transitions in gases and liquids, because the energy loss for the $\gamma$-quanta is so large that emission and absorption lines do not overlap and nuclear $\gamma$-resonance is virtually impossible. Thermal motion and the resulting Doppler broadening of the $\gamma$-lines are another important aspect. R. L. Mössbauer showed that, for nuclei fixed in solid material, a substantial fraction $f$ of photons, termed the Lamb–Mössbauer factor, are emitted and absorbed without measurable recoil. The corresponding $\gamma$-lines show natural line widths without thermal broadening.

### 2.2 Natural Line Width and Spectral Line Shape

The energy $E_0$ of a nuclear or electronic excited state of mean lifetime $\tau$ cannot be determined exactly because of the limited time interval $\Delta t$ available for the measurement. Instead, $E_0$ can only be established with an inherent uncertainty, $\Delta E$, which is given by the Heisenberg uncertainty relation in the form of the conjugate variables energy and time,

$$\Delta E \Delta t \geq h,$$  \hspace{1cm} (2.1)

where $h = 2\pi\hbar = $ Planck’s constant.
The relevant time interval is on the order of the mean lifetime, $\Delta t \approx \tau$. Consequently, ground states of infinite lifetime have zero uncertainty in energy.

As a result, the energy $E$ of photons emitted by an ensemble of identical nuclei, rigidly fixed in space, upon transition from their excited states (e) to their ground states (g), scatters around the mean energy $E_0 = E_e - E_g$. The intensity distribution of the radiation as a function of the energy $E$, the *emission line*, is a Lorentzian curve as given by the Breit–Wigner equation [1]:

$$I(E) = \frac{\Gamma/(2\pi)}{(E - E_0)^2 + (\Gamma/2)^2}. \quad (2.2)$$

The emission line is centered at the mean energy $E_0$ of the transition (Fig. 2.2). One can immediately see that $I(E) = 1/2 I(E_0)$ for $E = E_0 \pm \Gamma/2$, which renders $\Gamma$ the full width of the spectral line at half maximum. $\Gamma$ is called the *natural width* of the nuclear excited state. The emission line is normalized so that the integral is one: $\int I(E) dE = 1$. The probability distribution for the corresponding absorption process, the *absorption line*, has the same shape as the emission line for reasons of time-reversal invariance.

Weisskopf and Wigner [2] have shown that the natural width of the emission and the absorption line is readily determined by the mean lifetime $\tau$ of the excited state because of the relation (note the equal sign):

$$\Gamma \tau = \hbar. \quad (2.3)$$

The ratio $\Gamma/E_0$ of width $\Gamma$ and the mean energy of the transition $E_0$ defines the precision necessary in nuclear $\gamma$-absorption for “tuning” emission and absorption into resonance. Lifetimes of excited nuclear states suitable for Mössbauer spectroscopy range from $\sim 10^{-6}$ s to $\sim 10^{-11}$ s. Lifetimes longer than $10^{-6}$ s produce too narrow emission and absorption lines such that in a Mössbauer experiment they cannot overlap sufficiently because of experimental difficulties (extremely small Doppler velocities of $< \mu$m s$^{-1}$ are required). Lifetimes shorter than $10^{-11}$s are connected with transition lines which are too broad such that the resonance overlap between them becomes smeared and no longer distinguishable from the base line of a spectrum. The first excited state of $^{57}$Fe has a mean lifetime of $\tau = t_{1/2}/\ln 2 = 1.43 \cdot 10^{-7}$ s; and by substituting $\hbar = 6.5826 \cdot 10^{-16}$ eV s, the line width $\Gamma$ evaluates to $4.55 \cdot 10^{-9}$ eV.

### 2.3 Recoil Energy Loss in Free Atoms and Thermal Broadening of Transition Lines

In the description of nuclear $\gamma$-resonance, we assume that the photon emitted by a nucleus of mean energy $E_0 = E_e - E_g$ carries the entire energy, $E_\gamma = E_0$. This is not true for nuclei located in free atoms or molecules, because the photon has
momentum. When a photon is emitted from a nucleus of mass \( M \), recoil is imparted to the nucleus and consequently the nucleus moves with velocity \( u \) in a direction opposite to that of the \( \gamma \)-ray propagation vector (see Fig. 2.3).

Suppose the nucleus was at rest before the decay, it takes up the recoil energy

\[
E_R = \frac{1}{2} M u^2. \tag{2.4}
\]

Momentum conservation requires that

\[
p_n = -p_\gamma, \tag{2.5}
\]

where \( p_n (= M u) \) and \( p_\gamma \) are the linear momenta of the nucleus and the \( \gamma \)-photon, respectively, and \( c \) is the velocity of light. The momentum \( p_\gamma \) of the (mass-less) photon is given by its quantum energy:

\[
p_\gamma = -E_\gamma / c, \quad \text{with} \quad E_\gamma = E_0 - E_R. \tag{2.6}
\]

Because of the large mass of the nucleus and the low recoil velocity involved, we may use the nonrelativistic approximation

\[
E_R = \frac{1}{2} M u^2 = \frac{(Mu)^2}{2M} = \frac{p_n^2}{2M} = \frac{E_\gamma^2}{2Mc^2}. \tag{2.8}
\]

Since \( E_R \) is very small compared to \( E_0 \), it is reasonable to assume that \( E_\gamma \approx E_0 \), so that we may use the following elementary formula for the recoil energy of a nucleus in an isolated atom or molecule:

\[
E_R = \frac{E_0^2}{2Mc^2}. \tag{2.9}
\]
By substituting numerical values for $c$ and $M = m_{n/p} \cdot A$ one obtains

$$E_R = 5.37 \cdot 10^{-4} \frac{E_0^2}{A} \text{ eV}, \quad (2.10)$$

where $m_{n/p}$ is the mass of a nucleon (proton or neutron), $A$ is the mass number of the Mössbauer isotope, and $E_0$ is the transition energy in keV. For example, for the Mössbauer transition between the first excited state and the ground state of $^{57}\text{Fe}$ ($E_0 = E_c - E_g = 14.4 \text{ keV}$), $E_R$ is found to be $1.95 \cdot 10^{-3} \text{ eV}$. This value is about six orders of magnitude larger than the natural width of the transition under consideration ($\Gamma = 4.55 \cdot 10^{-9} \text{ eV}$).

The recoil effect causes an energy shift of the emission line from $E_0$ to smaller energies by an amount $E_R$, whereby the $\gamma$-photon carries an energy of only $E_\gamma = E_0 - E_R$. However, a recoil effect also occurs in the absorption process so that the photon, in order to be absorbed by a nucleus, requires the total energy $E_\gamma = E_0 + E_R$ to make up for the transition from the ground to the excited state and the recoil effect (for which $\vec{p}_n$ and $\vec{p}_\gamma$ will have the same direction).

Hence, nuclear resonance absorption of $\gamma$-photons (the Mössbauer effect) is not possible between free atoms (at rest) because of the energy loss by recoil. The deficiency in $\gamma$-energy is two times the recoil energy, $2E_R$, which in the case of $^{57}\text{Fe}$ is about $10^6$ times larger than the natural line width $\Gamma$ of the nuclear levels involved (Fig. 2.4).

In real gases and liquids, however, atoms are never at rest. If $\gamma$-emission takes place while the nucleus (or atom) is moving at velocity $v_n$ in the direction of the $\gamma$-ray propagation, the $\gamma$-photon of energy $E_\gamma$ is modulated by the Doppler energy $E_D$ [3]:

$$E_D = \frac{v_n}{c} E_\gamma, \quad (2.11)$$

which adds to $E_\gamma$:

$$E_\gamma = E_0 - E_R + E_D. \quad (2.12)$$

Fig. 2.4 Energy separation of $\gamma$-emission and absorption lines caused by recoil of resting free nuclei ($2E_R \approx 10^6 \Gamma$, note the three separate sections of the energy scale). Since there is virtually no overlap between emission and absorption line, resonant absorption is not possible.
Kinetic gas theory predicts a broad variation of velocities in gases, which for an ideal gas obeys the classical Maxwell distribution \([3]\). At normal temperature and pressure, the average time between collisions of the gas particles is so long \((10^{-9} - 10^{-10} \text{ s})\) that a typical Mössbauer isotope during its mean lifetime of about \(10^{-9} \text{ s}\) hardly experiences changes in motion. Relevant to the Doppler shift imparted to a certain \(\gamma\)-emission therefore is the component of the nuclear motion parallel or antiparallel to \(\vec{p}_\gamma\). The large variety of possible results, with \(E_D\) possibly being positive or negative, leads to a wide statistical scattering of \(\gamma\)-energies, the so-called \emph{Doppler broadening} of the transition line. The distribution has its maximum at \(E_D = 0\), which is plausible since all motions with a net velocity vector close to \(\vec{v}_n \perp \vec{p}_\gamma\) contribute virtually nothing to the energy of the photon, \(E_D \approx 0\). For sufficiently high \(\gamma\)-energies (large recoil energies) and fast kinetic motion, the shape of the recoil-shifted and Doppler-broadened emission and absorption lines for free atoms and molecules can be approximated by a Gaussian distribution. A derivation of the subject is given in (\([15]\) in Chap. 1). There it is also shown that the width of the Doppler broadening can be given in terms of the recoil shift \(E_R\) of the \(\gamma\)-energy and the average kinetic energy \(\frac{1}{2}kT\) of the gas particles at temperature \(T\):

\[
\Gamma_D = 2\sqrt{E_R \cdot kT}.
\]

The Doppler broadening \(\Gamma_D\) is of the order of \(E_R\) or larger. For \(^{57}\text{Fe}\) with \(E_0 = 14.4 \text{ keV}\) and \(E_R = 1.95 \cdot 10^{-3} \text{ eV}\), for instance, it exceeds \(E_R\) by a factor of 5: \(\Gamma_D \approx 10^{-2} \text{ eV}\) at 300 K. Thus, there must be a finite probability for nuclei in gases and liquids to compensate for the recoil loss \(E_R\) of the photon by the Doppler shift \(E_D\). The strength of the absorption and the shape of the absorption line are mathematically obtained from folding the overlapping emission and absorption lines. Since the line amplitudes are very small (the area of the broadened lines is the same as that of the sharp natural lines), the absorption probability is very small. Experimentally, it is difficult to detect nuclear \(\gamma\)-resonance in gases and liquids at all, except for very viscous fluids. For practical applications, it is more important that the usual Doppler modulation of the \(\gamma\)-radiation, as it is used as the “drive” system in classical Mössbauer spectroscopy (see Fig. 2.6), does not affect \(\gamma\)-absorption in gases and liquids. Motions with velocities of a few millimeters per second are negligible because of the extreme line broadening in nonsolid samples, which is more than \(10^6\) times the natural width \(\Gamma\).

### 2.4 Recoil-Free Emission and Absorption

The arguments seen in section 2.3 suggest that resonant \(\gamma\)-absorption should decrease at very low temperatures because the Doppler broadening of the \(\gamma\)-lines decreases and may even drop below the value of the recoil energy. In his experiments with solid sources and absorbers, however, R.L. Mössbauer (\([1]\) in Chap. 1) observed on the
contrary a dramatic increase in resonant absorption when the temperature approached that of liquid nitrogen. The correct explanation of this effect is found in the quantized nature of vibrations in solids ([1–3] in Chap. 1 [4]). In the following, we shall briefly illustrate the corresponding principles by means of a simple model. More information on this topic is found in Chap. 9 on Mössbauer spectroscopy with synchrotron radiation and nuclear inelastic scattering.

In the solid state, the Mössbauer active nucleus is more or less rigidly bound to its environment and not able to recoil freely, but it can vibrate within the framework of the chemical bonds of the Mössbauer atom. The effective vibration frequencies are of the order of $1/\tau_{\text{vib}} \approx 10^{13}\text{s}^{-1}$ ([15] in Chap. 1). Since, under this condition, the mean displacement of the nucleus essentially averages to zero during the time of the nuclear transitions, $\tau \approx 10^{-7}\text{s}$, there is, firstly, no Doppler broadening of the $\gamma$-energy and, secondly, the recoil momentum can only be taken up by the “crystal-lite” as a whole: $p = M_{\text{crystal}}v$. The induced velocity $v$ of the emitter in this case is vanishing because of the large mass of the system (even the finest “nano”-particles may contain $10^{14}$ atoms or molecules) and, hence, the corresponding recoil energy $E_R = 1/2M_{\text{crystal}}v^2$ of translational motion is negligible.

Instead, part of the energy $E_0$ of the nuclear transition can be transferred to the lattice vibrational system if the recoil excites a lattice vibration, a so-called phonon. Alternatively, a phonon can also be annihilated by the nuclear event. In either case, the corresponding energy deficit or excess of the emitted $\gamma$-quantum, $E_{\text{vib}}$, is again orders of magnitude larger than the natural line width $\Gamma$ of the nuclear levels. Nuclear $\gamma$-resonance absorption is therefore not possible if phonon excitation or annihilation is involved. However, a quantum mechanical description of the nucleus and its vibrational environment includes a certain finite probability $f$ for so-called zero-phonon processes. The factor $f$, also known as the Lamb–Mössbauer factor, denotes the fraction of $\gamma$-emissions or absorptions occurring without recoil, the recoil-free fraction. It is in fact equivalent to the Debye–Waller factor for Bragg X-ray scattering by periodic lattices. Characteristic $f$-values are, e.g., 0.91 for the 14.4 keV transition of $^{57}$Fe in metallic iron at room temperature, and 0.06 for the 129 keV transition of $^{191}$Ir in metallic iridium.

Independent of specific theoretical models for the phonon spectrum of a solid matrix, the recoil-free fraction can be given in terms of the $\gamma$-energy $E_\gamma$ and the mean local displacement of the nucleus from its equilibrium position ([2] in Chap. 1) [5]:

$$f = \exp \left[-\langle x^2 \rangle E_\gamma^2 / (\hbar c)^2 \right], \quad (2.14)$$

---

2The Bragg scattering of X-rays by a periodic lattice in contrast to a Mössbauer transition is a collective event which is short in time as compared to the typical lattice vibration frequencies. Therefore, the mean-square displacement $\langle x^2 \rangle$ in the Debye–Waller factor is obtained from the average over the ensemble, whereas $\langle x^2 \rangle$ in the Lamb–Mössbauer factor describes a time average. The results are equivalent.
where \( \langle x^2 \rangle \) is the expectation value of the squared vibrational amplitude in the direction of \( \gamma \)-propagation, known as the mean-square displacement. The \( f \) factor depends on the square of the \( \gamma \)-energy, similar to recoil in free atoms. This in fact limits the choice of isotopes for Mössbauer spectroscopy; nuclei with excited state energies beyond 0.2 MeV are found to be impracticable because of prohibitively small \( f \) factors for the transitions.

The recoil-free fraction is temperature-dependent, as one would expect from the introductory remarks. Higher temperatures yield larger mean-square displacements \( \langle x^2 \rangle \), and according to (2.14), lower values for the \( f \) factor. A thorough description of the temperature dependence would require a detailed and comprehensive description of the phonon spectrum of the solid matrix, which is virtually unavailable for most Mössbauer samples. Since the nucleus is a local probe of the lattice vibrations, sophisticated approaches are often not necessary. For most practical cases, the simple Debye model for the phonon spectrum of solids yields reasonable results, although in general it is not adequate for chemical compounds and other complex solids. This model is based on the assumption of a continuous distribution of phonon frequencies \( \omega \) ranging from zero to an upper limit \( \omega_D \), with the density of states being proportional to \( \omega^3 \) [3]. The highest phonon energy \( \hbar \omega_D \) at the Debye frequency limit \( \omega_D \) depends on the elastic properties of the particular material under study, and often it is given in terms of the corresponding Debye temperature \( \Theta_D = \hbar \omega_D / k \) representing a measure of the strength of the bonds between the Mössbauer atom and the lattice. The following expression is obtained for the temperature dependence of \( f(T) \):

\[
f(T) = \exp \left[ -\frac{3E^2_g}{k_B\Theta_DMc^2} \left\{ \frac{1}{4} + \left( \frac{T}{\Theta_D} \right)^2 \int_0^{\Theta/T} \frac{x}{e^x - 1} \, dx \right\} \right],
\]

where \( E^2_g / 2Mc^2 \) is the free-atom recoil energy \( E_R \), and \( k \) is the Boltzmann factor. Appropriate approximations of the integral yield a \( T^2 \) dependence for \( f(T) \) in the low temperature limit \( (T \ll \Theta_D) \):

\[
f(T) = \exp \left[ -\frac{E^2_g}{k_B\Theta_D2Mc^2} \left( \frac{3}{2} + \frac{\pi^2 T^2}{\Theta_D^2} \right) \right],
\]

whereas at high temperatures \( (T > \Theta_D) \), it approaches a linear regime

\[
f(T) = \exp \left[ -\frac{3E^2_g T}{k_B\Theta_D^2Mc^2} \right].
\]

The Debye temperature \( \Theta_D \) is usually high for metallic systems and low for metal–organic complexes. For metals with simple cubic lattices, for which the model was developed, \( \Theta_D \) is found in the range from 300 K to well above \( 10^3 \) K. The other extreme may be found for iron in proteins, which may yield \( \Theta_D \) as low as 100–200 K. Figure 2.5a demonstrates how sharply \( f(T) \) drops with temperature for such systems. Since the intensity of a Mössbauer spectrum is proportional to the
The recoil-free fraction and since the measuring time necessary to obtain a good signal-to-noise ratio depends on the square of the intensity (see Sect. 3.2), the performance of a corresponding experiment can be significantly improved by cooling the sample to liquid nitrogen or liquid helium temperature.

The recoil-free fraction $f$ is an important factor for determining the intensity of a Mössbauer spectrum. In summary, we notice from inspecting (2.14)–(2.17) and Fig. 2.5a that

1. $f$ increases with decreasing transition energy $E_{\gamma}$;
2. $f$ increases with decreasing temperature;
3. $f$ increases with increasing Debye temperature $\Theta_D$.

For a more detailed account of the recoil-free fraction and lattice dynamics, the reader is referred to relevant textbooks ([12–15] in Chap. 1).

The Lamb–Mössbauer factor as spectroscopic parameter

For practical applications of (2.15), i.e., the exploration of the elastic properties of materials, it is convenient to eliminate instrumental parameters by referring the measured intensities to a base intensity, usually measured at 4.2 K. The corresponding expression is then [6]:

$$\ln\left(\frac{f(T)}{f(4.2 \text{ K})}\right) = \frac{-3E_{\gamma}^2}{k_B \Theta_M M_{\text{eff}} c^2} \left( T^2 \int_0^{\Theta_M/T} \frac{x}{e^x - 1} \, dx - 29K^2 \right). \tag{2.18}$$

The logarithm expression can be obtained from measured Mössbauer intensities, or areas $A(T)$ of the spectra, $\ln(f(T)/f(4.2 \text{ K})) = \ln(A(T)/A(4.2 \text{ K}))$. The mass $M$ of the nucleus is replaced in (2.18) by a free adjustable effective mass, $M_{\text{eff}}$, to
take into account also collective motions of the Mössbauer atom together with its ligands. These may vibrate together as large entities, particularly in “soft” matter like proteins or inorganic compounds with large organic ligands. Similarly, the Debye temperature is replaced by the Mössbauer temperature \( \Theta_M \), which is also specific to the local environment sensed by the Mössbauer nucleus. These modifications are consequences of the limitations of the Debye model. The parameters \( \Theta_M \) and \( M_{\text{eff}} \) are not to be considered as universal quantities; they rather represent effective local variables that are specific to the detection method. Nevertheless, their values can be very helpful for the characterization of Mössbauer samples, particularly when series of related compounds are considered. A series of simulated traces for \( \ln(f(T)/f(4.2\text{K})) \), calculated within the Debye model as a function of different Mössbauer temperatures \( \Theta_M \) and for two effective masses \( M_{\text{eff}} \), is plotted in Fig. 2.5b.

The recoil-free fraction depends on the oxidation state, the spin state, and the elastic bonds of the Mössbauer atom. Therefore, a temperature-dependent transition of the valence state, a spin transition, or a phase change of a particular compound or material may be easily detected as a change in the slope, a kink, or a step in the temperature dependence of \( \ln f(T) \). However, in fits of experimental Mössbauer intensities, the values of \( \Theta_M \) and \( M_{\text{eff}} \) are often strongly covariant, as one may expect from a comparison of the traces shown in Fig. 2.5b. In this situation, valuable constraints can be obtained from corresponding fits of the temperature dependence of the second-order-Doppler shift of the Mössbauer spectra, which can be described by using a similar approach. The formalism is given in Sect. 4.2.3 on the temperature dependence of the isomer shift.

## 2.5 The Mössbauer Experiment

From Sect. 2.3 we learnt that the recoil effect in free or loosely bound atoms shifts the \( \gamma \)-transition line by \( E_R \), and thermal motion broadens the transition line by \( I_D \), the Doppler broadening (2.13). For nuclear resonance absorption of \( \gamma \)-rays to be successful, emission and absorption lines must be shifted toward each other to achieve at least partial overlap. Initially, compensation for the recoil-energy loss was attempted by using the Doppler effect. Moon, in 1950, succeeded by mounting the source to an ultracentrifuge and moving it with high velocities toward the absorber [7]. Subsequent experiments were also successful showing that the Doppler effect compensated for the energy loss of \( \gamma \)-quanta emitted with recoil.

The real breakthrough in nuclear resonance absorption of \( \gamma \)-rays, however, came with Mössbauer’s discovery of recoilless emission and absorption. By means of an experimental arrangement similar to the one described by Malmfors [8], he intended to measure the lifetime of the 129 keV state in \(^{191}\text{Ir} \). Nuclear resonance absorption was planned to be achieved by increasing overlap of emission and absorption lines via heating and increased thermal broadening. By lowering the temperature, it was expected that the transition lines would sharpen because of less effective Doppler broadening and consequently show a smaller degree of overlap.
However, in contrast, the resonance effect increased by cooling both the source and the absorber. Mössbauer not only observed this striking experimental effect that was not consistent with the prediction, but also presented an explanation that is based on zero-phonon processes associated with emission and absorption of $\gamma$-rays in solids. Such events occur with a certain probability $f$, the recoil-free fraction of the nuclear transition (Sect. 2.4). Thus, the factor $f$ is a measure of the recoilless nuclear absorption of $\gamma$-radiation – the Mössbauer effect.

In an actual Mössbauer transmission experiment, the radioactive source is periodically moved with controlled velocities, $+v$ toward and $-v$ away from the absorber (cf. Fig. 2.6). The motion modulates the energy of the $\gamma$-photons arriving at the absorber because of the Doppler effect: $E_\gamma = E_0(1 + v/c)$. Alternatively, the sample may be moved with the source remaining fixed. The transmitted $\gamma$-rays are detected with a $\gamma$-counter and recorded as a function of the Doppler velocity, which yields the Mössbauer spectrum, $T(v)$. The amount of resonant nuclear $\gamma$-absorption is determined by the overlap of the shifted emission line and the absorption line, such that greater overlap yields less transmission; maximum resonance occurs at complete overlap of emission and absorption lines.

### 2.6 The Mössbauer Transmission Spectrum

In the following, we consider the shape and the width of the Mössbauer velocity spectrum in more detail. We assume that the source is moving with velocity $v$, and the emission line is an unsplit Lorentzian according to (2.2) with natural width $\Gamma$. If we denote the total number of $\gamma$-quanta emitted by the source per time unit toward the detector by $N_0$, the number $N(E)dE$ of recoil-free emitted $\gamma$-rays with energy $E_\gamma$ in the range $E$ to $E + dE$ is given by ([1] in Chap. 1)

$$N(E, v) = f_s N_0 \frac{\Gamma/(2\pi)}{[E - E_0(1 + v/c)]^2 + (\Gamma/2)^2},$$

where $f_s$ is the recoil-free fraction of the source, $E_0$ is the mean energy of the nuclear transition, and $E_0(1 + v/c)$ is the Doppler-shifted center of the emission line.

In a Mössbauer transmission experiment, the absorber containing the stable Mössbauer isotope is placed between the source and the detector (cf. Fig. 2.6). For the absorber, we assume the same mean energy $E_0$ between nuclear excited and ground states as for the source, but with an additional intrinsic shift $\Delta E$ due to chemical influence. The absorption line, or resonant absorption cross-section $\sigma(E)$, has the same Lorentzian shape as the emission line; and if we assume also the same half width $\Gamma$, $\sigma(E)$ can be expressed as ([1] in Chap. 1)

$$\sigma(E) = \sigma_0 \frac{(\Gamma/2)^2}{(E - E_0 - \Delta E)^2 + (\Gamma/2)^2}.$$

2 Basic Physical Concepts
The absorption line is normalized to the maximum cross section \( \sigma_0 \) at resonance, \( E = E_0 + \Delta E \), which depends on the \( \gamma \)-energy \( E_\gamma \), the spins \( I_e \) and \( I_g \) of the

\[ \sigma_0(\text{cm}^2) = \frac{2.446 \times 10^{-15} 2I_e + 1 2I_g + 1}{(E_\gamma \text{keV})^{1/2} \Gamma^{1/2}}. \]

Fig. 2.6 Schematic illustration of a Mössbauer transmission experiment in five steps. The “Absorption” bars indicate the strength of recoilless nuclear resonant absorption as determined by the “overlap” of emission and absorption lines when the emission line is shifted by Doppler modulation (velocities \( v_1, \ldots, v_5 \)). The transmission spectrum \( T(v) \) is usually normalized to the transmission \( T(\infty) \) observed for \( v \to \infty \) by dividing \( T(v)/T(\infty) \). Experimental details are found in Chap. 3.
nuclear excited and ground states, and the internal conversion coefficient \(\alpha\) for the nuclear transition (footnote 1). In the case of \(^{57}\)Fe, for example, the maximum cross section is \(\sigma_0 = 2.56 \cdot 10^{-18}\,\text{cm}^2\).

We are interested in the transmission of \(\gamma\)-quanta through the absorber as a function of the Doppler velocity. The radiation is attenuated by resonant absorption, in as much as emission and absorption lines are overlapping, but also by mass absorption due to photo effect and Compton scattering. Therefore, the number \(T_M(E)\,dE\) of recoilless \(\gamma\)-quanta with energies \(E\) to \(E + dE\) traversing the absorber is given by

\[
T_M(E, v) = N(E, v) \exp\{ -\sigma(E)f_{\text{abs}}n_M + \mu_e t' \}, \tag{2.21}
\]

where \(t'\) is the absorber thickness (area density) in \(\text{g cm}^{-2}\), \(f_{\text{abs}}\) is the probability of recoilless absorption, \(n_M\) is the number of Mössbauer nuclei per gram of the absorber, and \(\mu_e\) is the mass absorption coefficient \(^4\) in \(\text{cm}^2\text{g}^{-1}\).

The total number of recoil-free photons arriving at the detector per time unit is then obtained by integration over energy

\[
T_M(v) = \int_{-\infty}^{+\infty} N(E, v) \exp\{ -\sigma(E)f_{\text{abs}}n_M + \mu_e t' \} \, dE. \tag{2.22}
\]

So far we have considered only the recoil-free fraction of photons emitted by the source. The other fraction \((1 - f_S)\), emitted with energy loss due to recoil, cannot be resonantly absorbed and contributes only as a nonresonant background to the transmitted radiation, which is attenuated by mass absorption in the absorber

\[
T_{NR} = (1 - f_S)N_0 \exp\{ -\mu_e t' \}, \tag{2.23}
\]

so that the total count rate arriving at the detector is \(^5\)

\[
C(v) = T_{NR} + T_M(v) \quad \text{or} \quad C(v) = N_0 e^{-\mu_e t'} \left[ (1 - f_S) + \int_{-\infty}^{+\infty} N(E, v) \cdot \exp\{ -f_{\text{abs}}n_M\sigma(E)t' \} \, dE \right]. \tag{2.24}
\]

\(^4\)Mass absorption is taken as independent of the velocity \(v\), because the Doppler shift is only about \(10^{-11}\) times the \(\gamma\)-energy, or less.

\(^5\)This expression holds only for an ideal detection system, which records only Mössbauer radiation. Practical problems with additional nonresonant background contributions from \(\gamma\)-ray scattering and X-ray fluorescence are treated in detail in Sects. 3.1 and 3.2.
The expression is known as the transmission integral in the actual formulation, which is valid for ideal thin sources without self-absorption and homogeneous absorbers assuming equal widths \( f \) for source and absorber [9]. The transmission integral describes the experimental Mössbauer spectrum as a convolution of the source emission line \( N(E,\nu) \) and the absorber response \( \exp\{ -\sigma(E)f_{\text{abs}}n_M t \} \). The substitution of \( N(E,\nu) \) and \( \sigma(E) \) from (2.19) and (2.20) yields in detail:

\[
C(\nu) = N_0 e^{-\mu_0 \nu} \left[ (1 - f_s) + \int_{-\infty}^{+\infty} \frac{f_s \Gamma/(2\pi)}{[E - E_0(1 + \nu/c)]^2 + (\Gamma/2)^2} \cdot \exp \left\{ \frac{-t(\Gamma/2)^2}{(E - E_0 - \Delta E)^2 + (\Gamma/2)^2} \right\} dE \right].
\]

(2.26)

by which we have introduced the effective absorber thickness \( t \). The dimensionless variable summarizes the absorber properties relevant to resonance absorption as

\[
t = f_{\text{abs}} n_M t_0 \quad \text{or} \quad t = f_{\text{abs}} N_M \sigma_0,
\]

(2.27)

where \( N_M = n_M t_0 \) is the number of Mössbauer nuclei per area unit of the absorber (in \( \text{cm}^{-2} \)). Note that the expressions hold only for single lines, which are actually rare in practical Mössbauer spectroscopy. For spectra with split lines see footnote.6

### 2.6.1 The Line Shape for Thin Absorbers

For thin absorbers with \( t \ll 1 \), the exponential function in the transmission integral can be developed in a series, the first two terms of which can be solved yielding the following expression for the count rate in the detector:

\[
C(\nu) = N_0 e^{-\mu_0 \nu} \left[ 1 - f_s \frac{t}{2} \frac{\Gamma^2}{[E_0(\nu/c) - \Delta E]^2 + \Gamma^2} \right],
\]

(2.28)

---

6Most Mössbauer spectra are split because of the hyperfine interaction of the absorber (or source) nuclei with their electron shell and chemical environment which lifts the degeneracy of the nuclear states. If the hyperfine interaction is static with respect to the nuclear lifetime, the Mössbauer spectrum is a superposition of separate lines \( (i) \), according to the number of possible transitions. Each line has its own effective thickness \( t(i) \), which is a fraction of the total thickness, determined by the relative intensity \( w_i \) of the lines, such that \( t(i) = w_i t \).
Since the resonance absorption vanishes for $v \to \infty$, the count rate off resonance is given entirely by mass absorption

$$C(\infty) = N_0 e^{-\mu_0 t},$$

so that the absorption spectrum for a thin absorber is

$$\frac{C(\infty) - C(v)}{C(\infty)} = f_s^2 \frac{t}{2} \frac{I^2}{[E_0(v/c) - \Delta E]^2 + I^2}.$$  \hspace{1cm} (2.30)

Thus, the experimental Mössbauer spectrum of a thin single-line absorber is a Lorentzian line, with full-width at half maximum twice the natural line width of the separate emission and absorption lines: $\Gamma_{\text{exp}} = 2\Gamma$.

**Broadening of Mössbauer lines due to saturation.**

Although Lorentzian line shapes should be strictly expected only for Mössbauer spectra of thin absorbers with effective thickness $t$ small compared to unity, Margulies and Ehrman have shown [9] that the approximation holds reasonably well for moderately thick absorbers also, albeit the line widths are increased, depending on the value of $t$ (Fig. 2.7). The line broadening is approximately

$$\Gamma_{\text{exp}}/2 = (1 + 0.135t)\Gamma_{\text{nat}} \quad \text{for } t \leq 4$$
$$\Gamma_{\text{exp}}/2 = (1.01 + 0.145t - 0.0025t^2)\Gamma_{\text{nat}} \quad \text{for } t > 4.$$  \hspace{1cm} (2.31)

Exact analyses of experimental spectra from thick absorbers, however, have to be based on the transmission integral (2.26). This can be numerically evaluated following the procedures described by Cranshaw [10], Shenoy et al. [11] and others.

In many cases, the actual width of a Mössbauer line has strong contributions from inhomogeneous broadening due to the distribution of unresolved hyperfine splitting in the source or absorber. Often a Gaussian distribution of Lorentzians,

---

7The experimental line width is $2\Gamma$ because an emission line of the same width scans the absorption line; see Fig. 2.6.
which approaches a true Gaussian envelope when the width of the distribution substantially exceeds the natural line width and thickness broadening, can give the shape of such Mössbauer lines. The problem has been discussed in detail by Rancourt and Ping [12]. They suggest a fit procedure, which is based on Voigt profiles. The depth of such inhomogeneously broadened lines with quasi-Gaussian shapes depends to some extent also on the effective thickness of the absorber; an example is shown in Fig. 2.7. Additional remarks on line broadening due to diffusion processes and line narrowing in coincidence measurements are found in the first edition of this book, Sect. 3.5, p. 38 (cf. CD-ROM).

2.6.2 Saturation for Thick Absorbers

The broadening of the experimental Mössbauer line for thick, saturating absorbers can be regarded as a consequence of line shape distortions: saturation is stronger for the center of the experimental line, for which the emission and absorption lines are completely overlapping, than for the wings, where the absorption probability is less. Thus, the detected spectral line appears to be gradually more compressed from base to tip. Consequently, there must also be a nonlinear dependence of the maximum absorption on the effective thickness $t$. An inspection of the transmission integral, (2.26), yields for the maximum fractional absorption of the resonant radiation the expression [13]

$$\varepsilon(t) = [1 - e^{-t/2}J_0(it/2)], \quad (2.32)$$

such that the depth of the Mössbauer line is $f_s\varepsilon(t)$ (cf. Fig. 2.8b). Here $J_0(it/2)$ is the zeroth-order Bessel function and $f_s$ is the recoil-free fraction of the source. From the

![Fig. 2.8](image_url) (a) Fractional absorption of a Mössbauer absorption line as function of the effective absorber thickness $t$. (b) The depth of the spectrum is determined by $f_s\varepsilon$. The width $\Gamma_{\text{exp}}$ for thin absorbers, $t \ll 1$, is twice the natural line width $\Gamma$ of the separate emission and absorption lines (see (2.30)). $\Delta E$ is the shift of the absorption line relative to the emission line due to chemical influence.
plot of $\varepsilon(t)$ shown in Fig. 2.8a, it is clear that the amplitude of the Mössbauer line is proportional to the effective absorber thickness only when $t \ll 1$, where an expansion of the fractional absorption yields $\varepsilon(t) \approx t/2$.

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